SYNTHESIS OF ALKYL ARYL ETHERS, THIOETHERS, AND SULFONES

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BY

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DEPARTMENT OF CHEMISTRY

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SYNTHESIS OF ALKYL ARYL ETHERS, THIOETHERS, AND SULFONES

BY

YUN LEI

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

MASTER OF SCIENCE

ABSTRACT

The development of a new method for the synthesis of diethers, disulfides, and disulfones with aliphatic and aromatic linkages is described.

In the presence of potassium salts, aromatic nucleophilic substitution reactions (S_NAr) of chloroarene cyclopentadienyliron complexes with bifunctional nucleophiles in a THF/DMF mixture led to the formation of diiron complexes. A series of diols and dithiols were used as nucleophiles. It was demonstrated that this reaction did not suffer from any steric hindrance when 2,6-dimethylchlorobenzene complex was used as starting material. The oxidative reactions of disulfides to disulfones by m-chloroperbenzoic acid (m-CPBA) were also carried out. The diiron arene complexes containing chlorine could also undergo S_NAr reactions. This allows the introduction of various groups to diiron arene complexes and/or polymerization.

By photolytic demetallation, the cyclopentadienyliron moiety is easily removed. A number of diethers, disulfides, and disulfones were synthesized.

ACKNOWLEDGEMENTS

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Chapter 1. Introduction

1.1. Usual Routes For the Synthesis of Diaryl Alkyl Diethers

1.1.1. Williamson Reaction

The foremost method for the synthesis of symmetric and unsymmetric ethers is the Williamson reaction (Scheme 1), first discovered in 1850 [1]. While halides were the groups of choice, sulfonate, sulfate ester, and carboxylate leaving groups can be also used. Due to the ready accessibility of alkyl halides, halides are the most common leaving groups.

$$R^1OH + NaOH \longrightarrow R^1O^-$$

$$R^1O^- + R^2X \longrightarrow R^1OR^2 + X^-$$

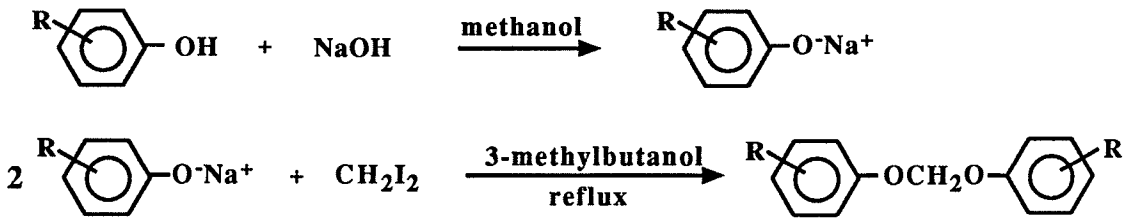
X = sulfonate, sulfate ester, carboxylate, or halide

Scheme 1: Williamson reaction

Because of the electron rich nature of aromatic rings, halides or other groups attached to an aromatic ring cannot be easily substituted by nucleophiles. Aromatic nucleophilic substitution reactions (S_NAr) may be achieved by the presence of strong electron withdrawing groups on the same benzene ring [2,3], or the presence of catalysts [4-6].

When the Williamson reaction is used for the preparation of alkyl

aryl ethers, phenols or phenoxide ions are used as nucleophiles and alkyl halides are the most common alkylating reagents. For the synthesis of diaryl alkyl diethers, the α,ω-dihaloalkanes were used as alkylating agents. For the synthesis of diaryl alkyl diethers, this method generally gave yields below 45%. Miron used a procedure to increase the yield to 75% [7]. In this procedure, a methanolic solution of sodium hydroxide was used to convert the phenol to its sodium salt. The solution was standardized prior to each synthesis with acid and the pure phenolic compound was neutralized with alkali. After removing the methanol under reduced pressure, the equivalent amount, or slightly less, of pure methylene iodide was introduced, together with enough solvent to keep the reactants in solution. This procedure is illustrated in Scheme 2.

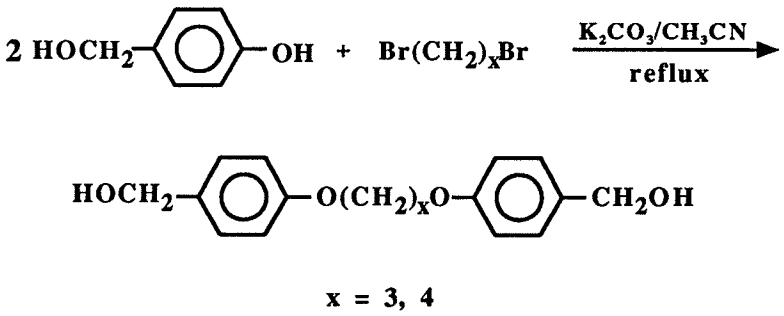


R = Ph, $PhCH_2$, Cl, Br, o-cyclohexyl, p-tert-amyl, p-formyl

Scheme 2: Two step Williamson reaction for
the synthesis of diaryl alkyl diethers

Phenols may also be used directly in the preparation of diaryl alkyl diethers by reacting a substituted phenol with a base and the appropriate alkylating agent as shown in Scheme 3. In this case, the generation of nucleophiles (phenoxides) and the alkylation of the phenoxides were carried out simultaneously [8]. When secondary or tertiary alkyl halides

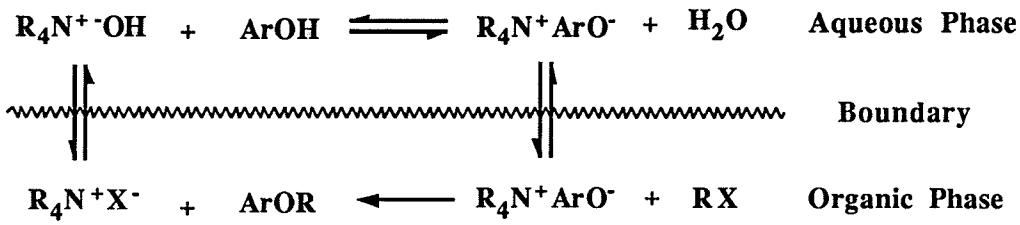
were used as the alkylating agents, the Williamson reaction is unsuccessful due to the elimination of the alkyl halides under basic conditions. This particular method has only been used to synthesize diaryl alkyl diethers with a short alkyl chain.



Scheme 3: One step Williamson reaction for the synthesis of diaryl alkyl diethers

1.1.2. Phase Transfer Catalysis of The Williamson Reaction

Phase transfer catalysis (PTC), which is a well developed method for the generation of reactive nucleophiles [9,10], has been adopted to improve the yield of the Williamson reaction [11,12]. In liquid-liquid PTC, whose principle [13,14] is shown in Scheme 4, there are two phases: the aqueous phase of the quaternary ammonium hydroxide ($R_4N^+OH^-$) and the organic phase of the alkyl halide. When the phenol, which is soluble in both the aqueous and the organic phase, is added to the two phase system, the phenol is converted into the corresponding quaternary ammonium phenoxide ($R_4N^+ArO^-$) in the aqueous phase.



Scheme 4 : The principle of liquid-liquid PTC

This salt ($R_4N^+ArO^-$) has a discrete solubility in the organic phase. In the two phase system, it is extracted into the organic phase and reacts irreversibly with the alkyl halide in the organic phase to produce the aryl alkyl ether (ArOR) and the quaternary ammonium halide ($R_4N^+X^-$). This quaternary ammonium halide is then converted to its hydroxide (the starting salt) in the aqueous phase. The important point of the PTC Williamson reactions is that the phase containing the alkyl halide is not basic. This protects the alkyl halides from being eliminated. A number of quaternary ammonium salts, such as tert-butyl ammonium bromide (TBAB) and cetyltrimethyl ammonium bromide (CTAB), have been used to carry out the PTC Williamson reaction. Jursic has prepared a series of alkyl phenyl ethers using CTAB as the PT catalyst [15]. However, the procedures were complicated. First, the nucleophiles were generated with 20% aqueous solution of sodium hydroxide (1000 mL), CTAB, and the phenols at 60°C. After cooling down, alkyl halides were added to the mixture and were re-heated to 80°C. Other reports dealing with the PTC Williamson reaction of diaryl alkyl diethers have also indicated that these reaction are carried out at about 80°C with complicated procedures [16-18].

1.1.3. Other Methods

The Williamson reaction and PTC are the primary and general methods for the preparation of diaryl alkyl diethers. Various other methods have also been used for the preparation of diaryl alkyl diethers. One of them is dimerization of free phenoxyalkyl radicals [19-21]. These reactions led to the formation of an alkyl chain instead of aryl alkyl etheric linkage. By the use of di-tert-butyl hyponitrite, di-tert-butyl peroxide, benzoyl peroxide, or acetyl peroxide as the source of the reactive radicals, the free phenoxymethyl radical was produced. The dimerization of the pheoxymethyl radical produced 1,2-phenoxyethane (Scheme 5) [19, 20].

$$\text{t-BuON=NOBu-t} \longrightarrow N_2 + 2\,\text{t-BuO}^{\cdot}$$

$$\text{t-BuO}^{\cdot} + \text{PhOCH}_3 \longrightarrow \text{BuOH} + \text{PhOCH}_2^{\cdot}$$

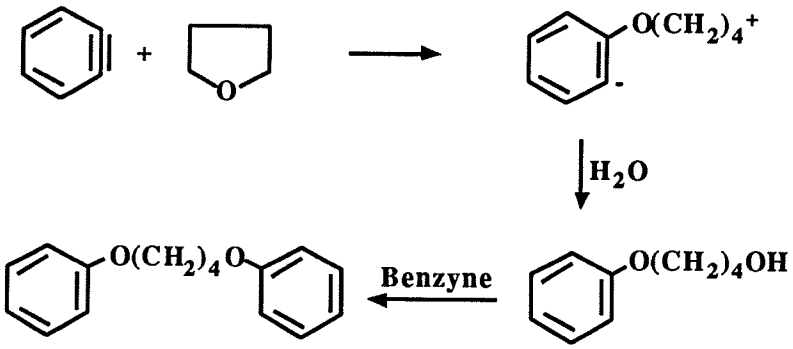
$$2\,\text{PhOCH}_2^{\cdot} \longrightarrow \text{PhOCH}_2\text{CH}_2\text{OPh}$$

Scheme 5. Dimerization of phenoxymethyl radicals

When 2-cyclohexenone cyclic ketals and N-bromosuccinimide (NBS) were reacted in a 1:1 ratio in carbon tetrachloride, and refluxed for 5 min., the α,ω-diphenoxyalkane was the major product. A much smaller amount of $PhO(CH_2)_xOH$ was also obtained [22].

Benzyne can react with a variety of ethers to produce phenyl alkyl ethers [23]. When tetrahydrofuran (THF) was used as the ether, under heat and with an equivalent amount of water, the cleavage of THF by benzyne led to the formation of 1,4-diphenoxybutane in only 8% yield as

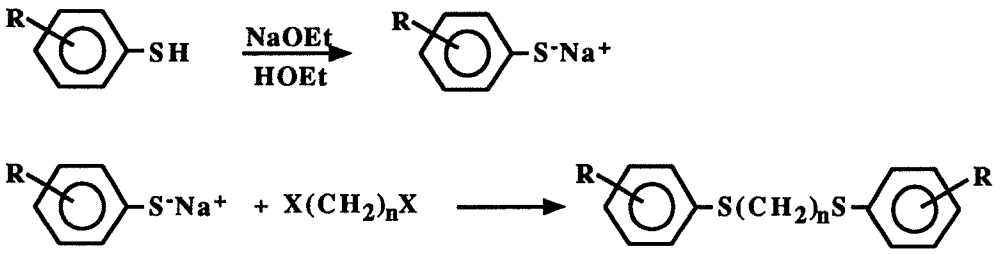
shown in Scheme 6 [24]. In the presence of triphenylbismuth diacetate and copper salt {$Cu(OAc)_2$}, the hydroxy group in diols were also converted to alkyl phenyl ethers [25,26].



Scheme 6: Formation of 1,4-diphenoxybutane by cleavage of THF

1.2. Usual Routes For the Synthesis of Diaryl Alkyl Disulfides

The most economical way to prepare sulfides is the reaction of alkyl halides with inorganic sulfides [27]. However, this method is only suitable for the preparation of symmetric sulfides. The most common and general reaction for the synthesis of unsymmetric aryl alkyl sulfides is the alkylation reaction analogous to the Williamson reaction. This reaction includes the generation of the thiophenoxide ions followed by alkylation reactions. Some procedures require refluxing [28-32], while others were achieved at room temperature with longer reaction times (48 hr) [33]. Scheme 7 illustrates the principle of this approach.

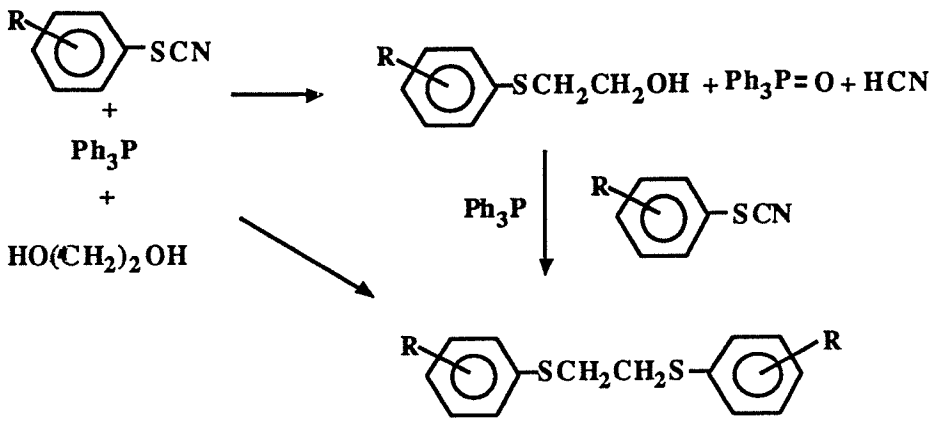


X = halide, R = H, 2-NH_2, 4-CH_3, n = 1-4,

Scheme 7: The synthesis of diaryl alkyl disulfides via alkylation of thiophenoxide

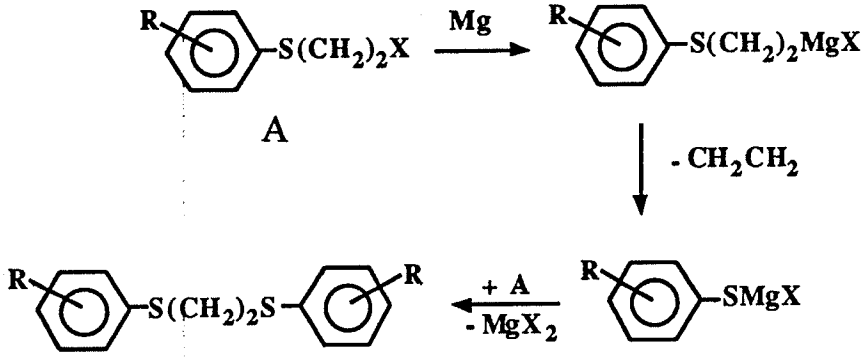
These reactions can also be carried out in the presence of water and small amounts of phase-transfer catalysts, such as hexadecyltributyl phosphonium bromide, and quaternary ammonium bromide [34,35]. These methods generally gave good yields (about 80%), but were conducted at reflux temperature with complicated procedures.

In the presence of triphenylphosphine, the interaction between aryl thiocyanate (ArSCN) and primary alcohols such as glycol under reflux in dry dioxan gave diaryl alkyl disulfides in 78% yield [36]. The diaryl alkyl disulfides were prepared in one or two steps as shown in Scheme 8.



Scheme 8: Interaction of aryl thiocyanates and glycol in the presence of triphenylphosphine

Another way to prepare diaryl alkyl disulfides is the rearrangement of aryl thioalkyl halides upon treatment with neutral alumina under heat (about 120°C), with magnesium (Scheme 9), or alkalicyanides [37,38].

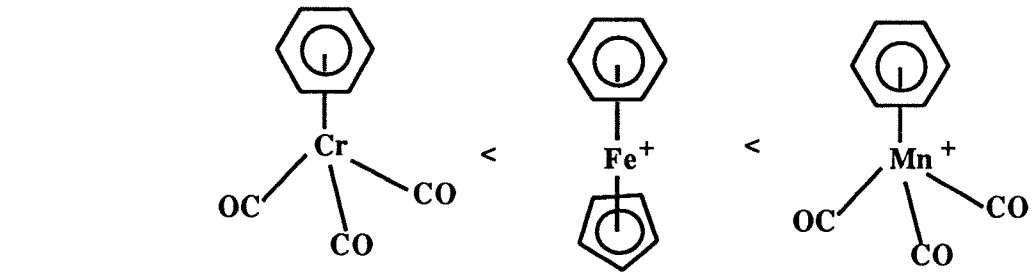


Scheme 9: Rearrangement of arylthio halides

1.3. Reactivity of Organometallic Arene Complexes

In 1951, the discovery of the first sandwich compound, bis(cyclopentadienyl)iron also known as "ferrocene" $(\eta^5\text{-}C_5H_5)_2Fe$, greatly stimulated organometallic chemistry [39,40]. In 1991, Janiak and Schumann [41] wrote a quite comprehensive review article about the complexes containing cyclopentadienyl ligand or its derivatives. They stated that more than 80% of all known transition metal complexes containing these ligands.

Some transition metal moieties act as strong electron-withdrawing groups when complexed to an aromatic compound. This complexation reverses the property of the arene from electrophilic to nucleophilic. A number of transition metal moieties have been studied. The common moieties include tricarbonylchromium $\{Cr(CO)_3\}$, tricarbonylmanganese $\{Mn(CO)_3^+\}$, and cyclopentadienyliron $\{FeCp^+\}$. These are arranged according to their electron withdrawing ability in Scheme 10 [42,43].

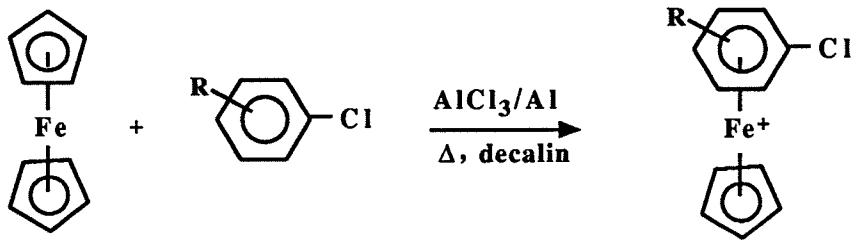


Scheme 10: The activation of arenes by π-coordination to transition metal groups

Among these transition metals, the iron moiety has advantages for synthetic strategies because it has good activation to arenes, low cost , ease of complexation and decomplexation, and low toxicity [43].

1.3.1. Synthesis of Diiron Complexes

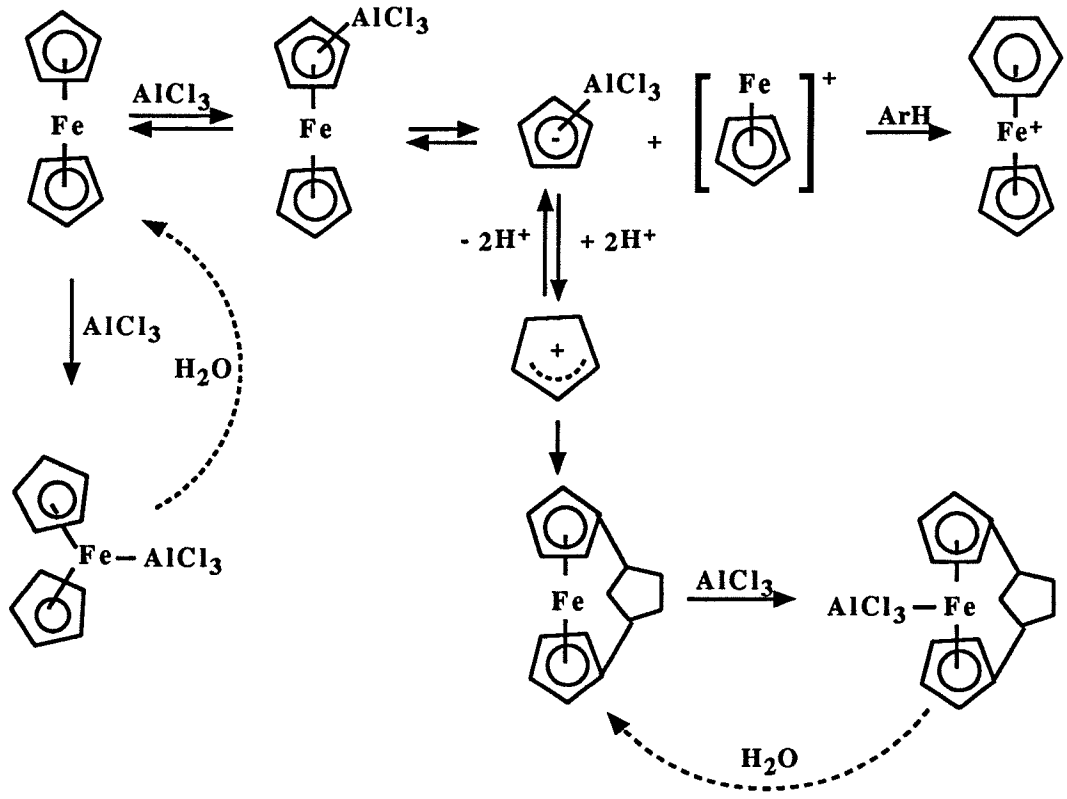
The most exploited synthetic route for the synthesis of η^6-arene-η^5-cyclopentadienyliron monocations is the ligand exchange process which was first established by Nesmeyanov [44]. The procedure for the ligand exchange is quite general. In the presence of a two or four fold excess of aluminum trichloride and an equimolar quantity of aluminum powder, the mixture of ferrocene and excess appropriate aromatic hydrocarbons is heated between 80 to 165°C in organic solvent or without solvent for a period of 4 to 24 hours. The reaction resulted in the replacement of one of the cyclopentadienyl rings by an aromatic arene ring (Scheme 11). The $AlCl_3$ acts as a catalyst while the aluminum powder prevents ferrocene from being oxidized to the ferricinium cation.



R = H, CH_3, Cl

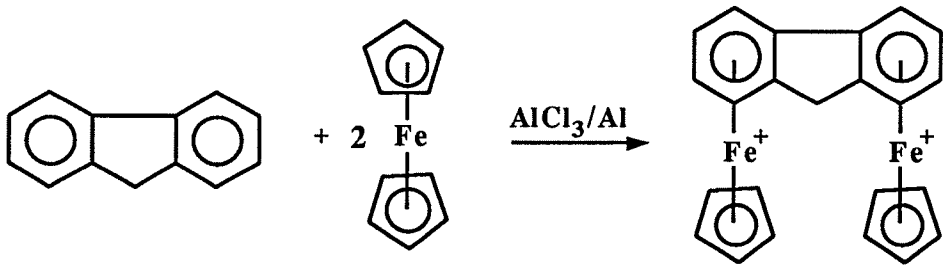
Scheme 11: Ligand exchange reaction

It was found that the ring substitution reaction of ferrocene in ligand exchange reactions was facilitated by the electron donating groups on either the arene ring or the cyclopentadienyl rings, and was hindered by electron withdrawing substituents [45]. The most likely reason is that the mechanism of ligand exchange is based on an electrophilic aromatic substitution as shown in Scheme 12 [46,47]. The decreasing of electron density on the cyclopentadienyl rings limited the attack of the $AlCl_3$ to the rings and/or the substituted cyclopentadienyl ring less reactive towards cleavage. The decreasing electron density on the arene ring decreases the nucleophilicity of the arene ring and prevented the ligand exchange from taking place.



Scheme 12: The mechanism of ligand exchange reaction

Due to their catalytic activity, electrochemical properties, and possible synthetic uses, bimetallic complexes have obtained a great deal of attention [48-53]. One of the most common routes [54-57] for the synthesis of bis(arene cyclopentadienyliron) complexes is the ligand exchange reaction. In this case, a polyaromatic compound was used as the ligand. In order to get pure dication complexes, an excess of ferrocene was used to react with the polyaromatic compounds. In the presence of $AlCl_3$ and Al powder, this reaction gave rise to a product which has two η^5-cyclopentadienyliron(II) moieties π-bonded to two arenes of the polyaromatic compounds (Scheme 13). However, this method suffers from low yield, generally 35-50%, and lack of ability to introduce some functional groups [58].

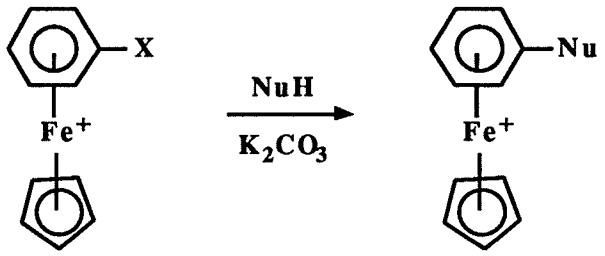


Scheme 13: Synthesis of bimetallics via ligand exchange reactions

1.3.2. Nucleophilic Substitution Reaction of Cyclopentadienyliron Arene Complexes

As was mentioned previously, the cyclopentadienyliron moiety ($FeCp^+$) is a significantly strong electron withdrawing group. It is roughly equivalent to two nitro groups in terms of activation [42]. Nesmeyanov and coworkers first demonstrated the displacement of the chlorine atom in the η^6-chlorobenzene-η^5-cyclopentadienyliron cation by a number of oxygen, sulfur, and nitrogen containing nucleophiles, such as the ethoxy, phenoxy, thiophenoxy, n-butylthio, or phthalimido group [42,59]. Since then, many such nucleophilic substitution reactions of the chloro as well as the nitro group in η^6-arene-η^5-cyclopentadienyliron complexes have been carried out [59-62]. Chloroarene or nitroarene $FeCp^+$ complexes can also undergo these kinds of S_NAr reactions with carbanion-enolate anion nucleophiles [59, 63-67]. These reactions have shown uses in synthetic organic chemistry. For example, diaryl ether and triaryl ether linkages, cinnoline ring system, alkanoic acid esters, and diethyl arylmalonates have been synthesized by these S_NAr reactions [63,68-71]. These compounds are of importance due to their biological activities.

The S_NAr reactions between nucleophiles and chloroarene or nitroarene $FeCp^+$ complexes involve combination of the η^6-arene-η^5-cyclopentadienyliron complexes, the appropriate nucleophiles, a suitable base (which in most cases was potassium carbonate) and an organic solvent (Scheme 14).



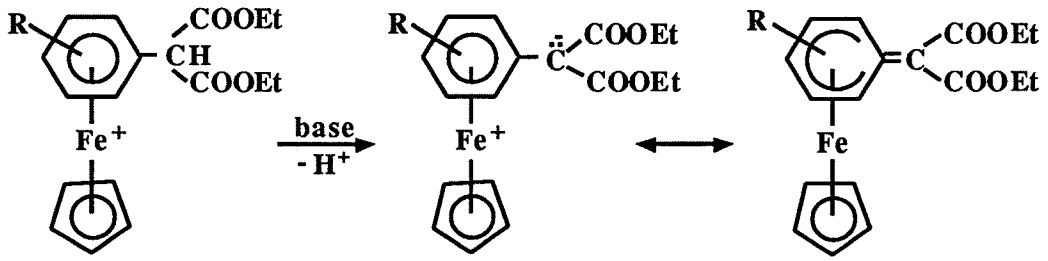
X = Cl, NO_2

NuH = O, S, N, and C-containing nucleophiles

Scheme 14: Nucleophilic substitution reactions of chloro- or nitroarene cyclopentadienyliron complexes

For nucleophilic substitution reactions of dichlorobenzene cyclopentadienyliron complexes, it is possible to control the degree of substitutes to mono- or disubstitution. After a nucleophile substituted one of the chloro or nitro groups, the second nucleophile (same or different) was introduced to the arene ring [63,69].

More rigorous studies have been conducted by Abd-El-Aziz *et al.* Under basic conditions, the proton on the α-position to an arene coordinated to $FeCp^+$ is lost easily to give a zwitterionic species which might form an electron rich cyclopentadienyl complex with an exocyclic double bond hindering further nucleophilic substitution (Scheme 15) [60, 72-75].

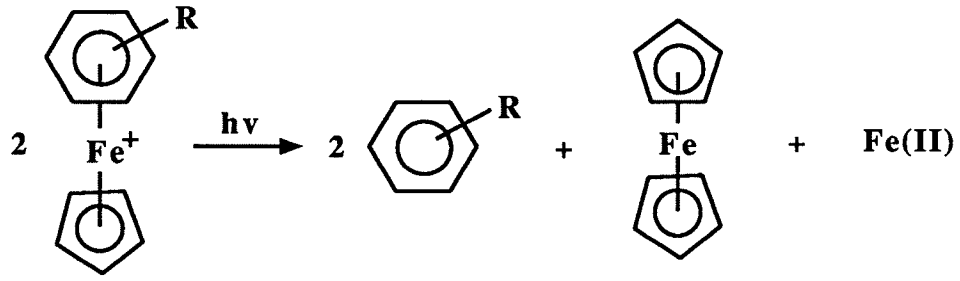


Scheme 15: Zwitterionic species

1.4. Demetallation of the η^6-arene-η^5-cyclopentadienyliron Complexes

There are a range of efficient ways of removing cyclopentadienyliron moiety from their corresponding complexes. Using typical electron donor reagent, an electron was transferred from the donor reagent to the η^6-arene-η^5-cyclopentadienyliron cation to form a 19 electron reduction product [76]. This reduction product is not stable and could decompose to give the free arene, ferrocene, and Fe(II) salt. This method has been used for the demetallation of cyclopentadienyliron complexes [69, 77].

Photolytic demetallation is the most commonly used method. When a solution of cyclopentadienyliron complex is irradiated under visible or ultra violet light, the free arene as well as ferrocene and iron(II) salt is liberated [65,78,79]. Scheme 16 illustrates the photolytic demetallation of cyclopentadienyliron monocations.



Scheme 16: Photolytic liberation of arene
from cyclopentadienyliron complexes

The mechanism of the photolytic demetallation may also involve a 19 electron intermediate which came from the electron transfer from solvent to complex forced by irradiation [80]. The solvent dependence of the photolysis of (arene)cyclopentadienyliron complexes was reinforced this mechanism. In the early 80s, Mann *et al.* [81-83] proposed that the photolytic demetallation of (arene)cyclopentadienyliron complexes was through arene replacement. The arene can be displaced by a six electron ligand or by three two-electron ligands.

Pyrolytic sublimation is another important decomplexation method. Under partial vacuum (about 0.5 Torr), the complex is heated at about 180-240°C to result in a similar decomplexation [64,84,85] as photolysis. This technique can only be used where the product arene is thermally stable. Electroreductive techniques have also been used with some studies [86], for example, in the case of recovery of nitrogen containing heterocycles from their complexes.

1.5. Objective of the Present Work

Aryl alkyl ether linkages widely exist in macrocyclic crown ethers and some other superstructures which were used in host guest systems or in crystal engineering [87-89]. A series of new thermal recording materials contain diaryl alkyl diethers, disulfides, and disulfones.

The objective of this work is to establish a new and useful route for the synthesis of diaryl alkyl diethers, thioethers, and sulfones via the use of the cyclopentadienyliron moiety.

This study started from the synthesis of cyclopentadienyliron bimetallic complexes. A number of nucleophilic aromatic substitution reactions between a variety of chloroarene cyclopentadienyliron complexes and a series of aliphatic diols have been carried out, and a series of such bimetallic complexes have been prepared by this method.

The oxidation of sulfides is a very important method for the synthesis of sulfones. We have oxidized a number of diaryl alkyl disulfide cyclopentadienyliron complexes to their corresponding diaryl alkyl sulfone complexes without effect on the $FeCp^+$ moiety.

Functionalization of chloroarene bimetallic complexes of cyclopentadienyliron with aliphatic thioether and sulfone bridges with oxygen, sulfur, and carbon nucleophiles are also presented in this work.

A number of diaryl alkyl ethers, disulfides, and disulfones were prepared by photolytic demetallation of the corresponding cyclopentadienyliron complexes.

Chapter 2. Results and Discussion

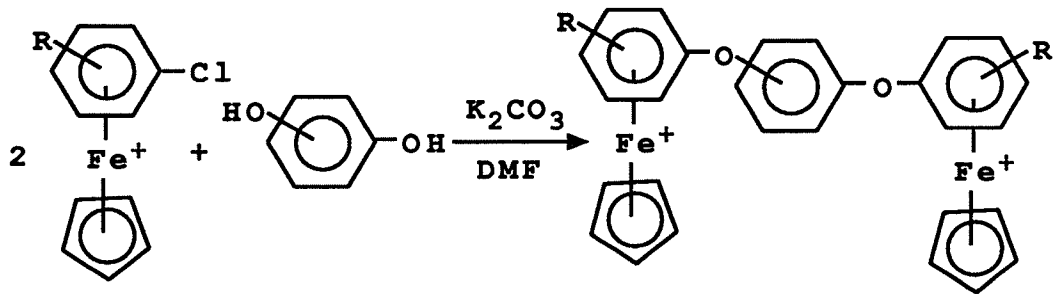
2.1. Synthesis of Diaryl Alkyl Diethers and Disulfides

As stated in 1.1 and 1.2, a number of methods have been used for the preparation of diaryl alkyl diethers and disulfides. However, those methods were carried out under harsh reaction conditions (reflux) and complicated procedures. On the other hand, aromatic ethers have been successfully synthesized by temporarily adopting cyclopentadienyliron moiety [58]. Our interest was to develop a new and useful synthetic method for synthesis of a new type of bis(cyclopentadienyliron) complexes with aliphatic ether and thioether linkages and the subsequent synthesis of diaryl alkyl diethers and disulfides.

2.1.1. Synthesis of Bis(η^6-phenoxy-η^5-cyclopentadienyliron) Alkane Hexafluorophosphates

The method for the synthesis of bis(η^6-arene-η^5-cyclopentadienyliron) complexes with aromatic ether linkages was developed by Abd-El-Aziz *et al.* [58]. The general procedure is that an appropriate η^6-chloroarene-η^5-cyclopentadienyiron complex, a dihydroxyaromatic compound and a weak base were dissolved in a polar aprotic solvent system (Scheme 17). Then the mixture was stirred at room temperature under a nitrogen atmosphere for 17 hours. The weak base was potassium carbonate and the polar aprotic solvent system was dimethylformamide (DMF) or a mixture of DMF and tetrahydrofuran

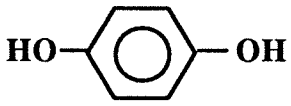
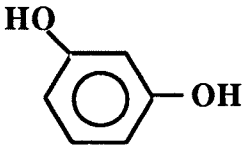
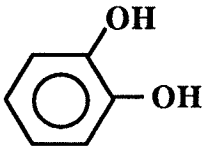
(THF).



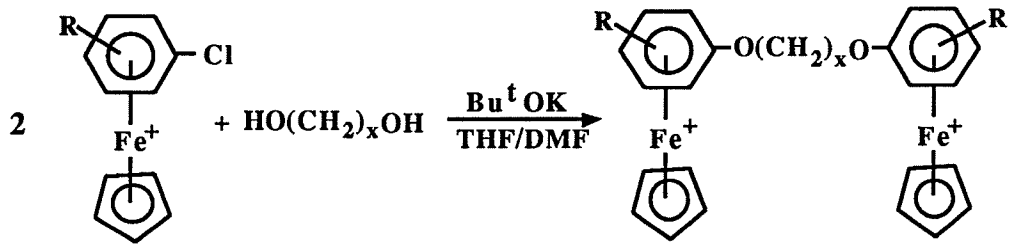
Scheme 17

The initial studies in the synthesis of bimetallic complexes containing aliphatic ether linkages were carried out by using the same synthetic strategy. However, when aliphatic diols were used as the starting materials and in the presence of potassium carbonate, this reaction failed to give either the desired diiron or monoiron complexes with aliphatic ether linkages. The starting material was the only thing recovered. This is due to the differences in the pKa values [90] of aromatic diols and aliphatic dithiols (Table 1). The pKa values indicate that the aliphatic diols have higher pKa values than aromatic diols. The reactivity of aliphatic diols in terms of acidity and nucleophilicity is lower than aromatic diols. A much stronger base is required to generate the nucleophiles. Potassium tert-butoxide was found to be the ideal base for generating aliphatic dialkoxo ions $^{-}O(CH_2)_nO^{-}$.

Table 1: The pKa of some hydroxo compounds [91,92]

Compound	pKa_1	pKa_2
$HO(CH_2)_2OH$	14.22	
	12.04	9.91
	12.32	9.44
	12.98	9.36
$HS(CH_2)_2SH$	10.43	8.85

Reaction of 2.0 mmol of the appropriate diols (2a-f) with 2.4 mmol of potassium tert-butoxide in dry THF for 45 min. led to the generation of the potassium salts $KO(CH_2)_nOK$. Then 2.0 mmol of the chloroarene cyclopentadienyliron complexes (1a-d) and 1 mL of DMF were added to the reaction mixture. The mixture solution was then stirred under a nitrogen atmosphere at room temperature for 20 hours (Scheme 18).



1a R=H **2a-f** **3a. R=H x=2**

1b R=4-Cl **x=2,4,6,8,10,12** **3b. R=H x=4**

1c R=4-CH_3 **3c. R=H x=6**

1d R=3-CH_3 **3d. R=H x=8**

1e R=2,6-$(CH_3)_2$ **3e. R=H x=10**

3f. R=H x=12

3g. R=4-Cl x=2

3h. R=4-CH_3 x=2

3i. R=3-CH_3 x=2

3j. R=2,6-$(CH_3)_2$ x=2

3k. R=2,6-$(CH_3)_2$ x=4

Scheme 18

The bis(η^6-arene-η^5-cyclopentadienyliron) complexes (3a-i) were isolated as their hexafluorophosphate salts in 45-86% yields. Similarly, reaction of 2,6-dimethylchlorobenzene cyclopentadienyliron complex (1e) with 1,2-ethanediol (2a) or 1,4-butanediol (2b) gave rise to the corresponding diiron complexes (3j-k) in 61% and 68% yield, respectively. These results show that there is no significant steric effect

in the S_NAr reaction for the disubstitution reaction of diols.

The ^1H and ^{13}C NMR data for 3a-k are listed in Tables 2 and 3. Due to the symmetry of these diiron complexes, the ^1H NMR spectra show a very distinctive single peak from the cyclopentadienyl (Cp) protons at 5.06-5.33 ppm. The ^{13}C NMR spectra in which the Cp carbons gave rise to a single resonance in the range of 76.01-79.74 ppm also proved this distinctiveness. Because of the strong electron withdrawing of cyclopentadienyliron moiety, the peaks of the complexed aromatic ring hydrogens and carbons are shifted upfield. As an example, the ^1H and ^{13}C NMR spectra of 1,2-bis(η^6-4-chlorophenoxy-η^5-cyclopentadienyliron) ethane hexafluorophosphate (3g) are presented in Figures 1 and 2.

Table 2: Yield and ^1H NMR data for diiron Complexes 3a-k and 4.

Complex No.	Yield (%)	δ (DMSO-d_6, ppm) Cp	Complexed Ar	Others
3a #	56	5.23	6.28 (m, 2H), 6.49 (m, 8H)	4.81 (s, 4H, CH_2)
3b	62	5.11	6.15 (m, 2H), 6.32 (m, 8H)	1.97 (br.s, 4H, CH_2), 4.28 (br.s, 4H, CH_2)
3c	81	5.07	6.08 (m, 2H) 6.27 (m, 8H)	1.52 (br.s, 4H, CH_2), 1.81 (br.s, 4H, CH_2) 4.19 (t, 4H, J = 6.0 Hz, CH_2)
3d	71	5.06	6.08 (m, 2H) 6.27 (m, 8H)	1.41 (m, 8H, CH_2), 1.76 (br.s, 4H, CH_2) 4.16 (t, 4H, J = 6.2 Hz, CH_2)
3e	75	5.06	6.08 (m, 2H) 6.27 (m, 8H)	1.30(m, 12H, CH_2), 1.72 (br.s, 4H, CH_2) 4.16 (t, 4H, J = 6.2 Hz, CH_2)
3f	86	5.06	6.07 (m, 2H) 6.27 (m, 8H)	1.27 (m, 16H, CH_2), 1.73 (br.s, 4H, CH_2) 4.15 (t, 4H, J = 5.6 Hz, CH_2)
3g #	51	5.33	6.56 (d, J = 6.5 HZ, 4H) 6.77 (d, J = 6.5 Hz, 4H)	4.76 (s, 4H, CH_2)
3h #	45	5.17	6.31 (d, J = 6.8 Hz, 4H) 6.40 (d, J = 6.6 Hz, 4H)	2.49 (s, 6H, CH_3), 4.47 (s, 4H, CH_2)
3i #	49	5.15	6.19 (m, 2H) 6.37 (m, 6H)	2.56 (s, 6H, CH_3) 4.76 (s, 4H, CH_2)
3j #	61	5.11	6.18 (t, J = 6.0 Hz, 4H) 6.40 (d, J = 6.2 Hz, 2H)	2.74 (s, 12H, CH_3) 4.74 (s, 4H, CH_2)
3k #	68	5.07	6.14 (t, J = 6.6 Hz, 4H) 6.35 (d, J = 6.5 Hz, 2H)	2.18 (br.s, 4H, CH_2), 2.64 (s, 12H, CH_3) 4.13 (t, 4H, J = 2.9 Hz, CH_2)
4	73	5.13 5.14	6.16 (m, 2H) 6.31 (m, 8H)	1.50 (d, J = 5.8 Hz, 3H, CH_3) 3.28 (br.s, 4H, CH_2) 4.42 (m, 1H, CH)

The solvent for the NMR study was $(CD_3)_2CO$ instead of DMSO-d_6

Table 3: ^{13}C NMR data for diiron complexes 3a-k and 4.

Complex No.	δ (DMSO-d_6, ppm) Cp	Complexed Ar	Others
3a #	77.56	75.99 (4C), 85.26 (2C) 87.65 (4C), 134.46(2C, ipso)	68.76 (2C, CH_2)
3b	76.10	74.33 (4C), 83.82 (2C) 86.38 (4C), 133.40 (2C, ipso)	24.87 (2C, CH_2), 68.98 (2C, CH_2)
3c	76.07	74.31 (4C), 83.75 (2C) 86.38 (4C), 133.52 (2C, ipso)	24.95 (2C, CH_2), 28.20 (2C, CH_2) 69.30 (2C, CH_2)
3d	76.06	74.30 (4C), 83.73 (2C) 86.37 (4C), 133.54 (2C, ipso)	25.24 (2C, CH_2), 28.27 (2C, CH_2) 28.65 (2C, CH_2), 69.36 (2C, CH_2)
3e	76.01	74.24 (4C), 83.65 (2C) 86.30 (4C), 133.52 (2C, ipso)	25.17 (2C, CH_2), 28.22 (2C, CH_2) 28.62 (2C, CH_2), 28.86 (2C, CH_2) 69.32 (2C, CH_2)
3f	76.08	74.32 (4C), 83.72 (2C), 86.38 (4C), 133.60 (2C, ipso)	25.24 (2C, CH_2), 28.29 (2C, CH_2) 28.71 (2C, CH_2), 28.98 (4C, CH_2) 69.32 (2C, CH_2)
3g #	79.74	75.16 (4C), 87.45 (4C) 104.20 (2C, ipso) 133.53 (2C, ipso)	68.94 (2C, CH_2)
3h #	77.91	75.09 (4C), 87.65 (4C) 100.70 (2C, ipso) 133.27 (2C, ipso)	19.76 (2C, CH_3) 68.76 (2C, CH_2)

3i #	77.65	73.90 (2C), 76.89 (2C), 85.39 (2C), 86.50 (2C) 103.40 (2C, ipso) 133.97 (2C, ipso)	20.24 (2C, CH_3) 68.55 (2C, CH_2)
3j #	77.50	84.56 (2C), 87.24 (4C) 97,31 (4C, ipso) 129.04 (2C,ipso)	16.06 (4C, CH_3) 72.94 (2C, CH_2)
3k	77.30	84.23 (2C), 87.09 (4C) 96.96 (4C, ipso) 129.34 (2C, ipso)	15.86 (4C, CH_3) 26.08 (2C, CH_2) 73.71 (2C, CH_2)
4	76.29 76.38	74.58 (2C), 74.74 (2C) 83.91 (1C), 84.11(1C) 86.48 (2C), 86.58 (2C) 132.41(1C, ipso) 132.61 (1C, ipso)	15.66 (1C, CH_3), 71.35 (1C, CH_2) 73.92 (1C, CH)

The solvent for the NMR study was $(CD_3)_2CO$ instead of DMSO-d_6

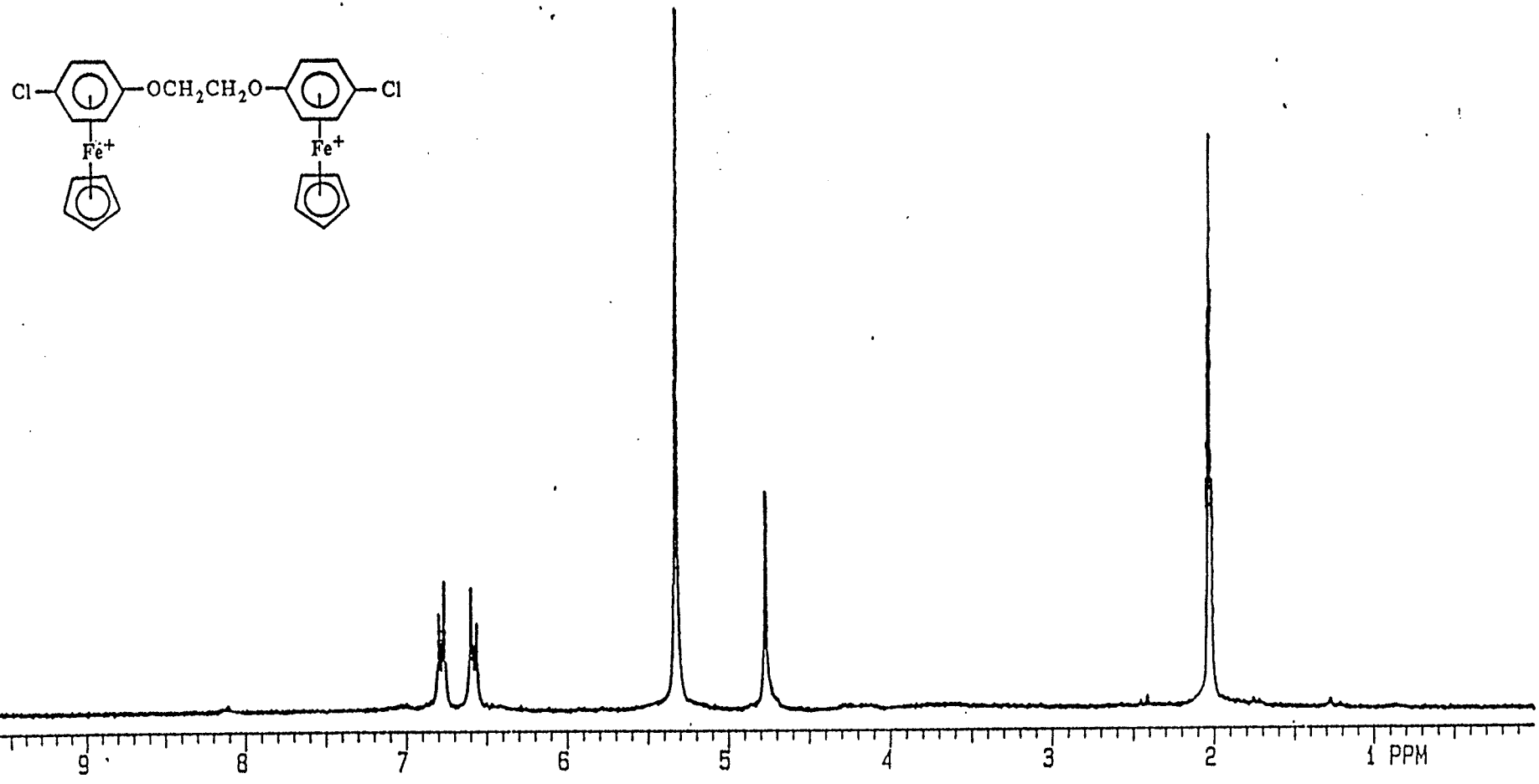


Figure 1: ^{1}H NMR spectrum of 1,2-bis(η^{6}-4-chlorophenoxy-η^{5}-cyclopentadienyliron) ethane hexafluorophosphate (3g) in acetone-d_6.

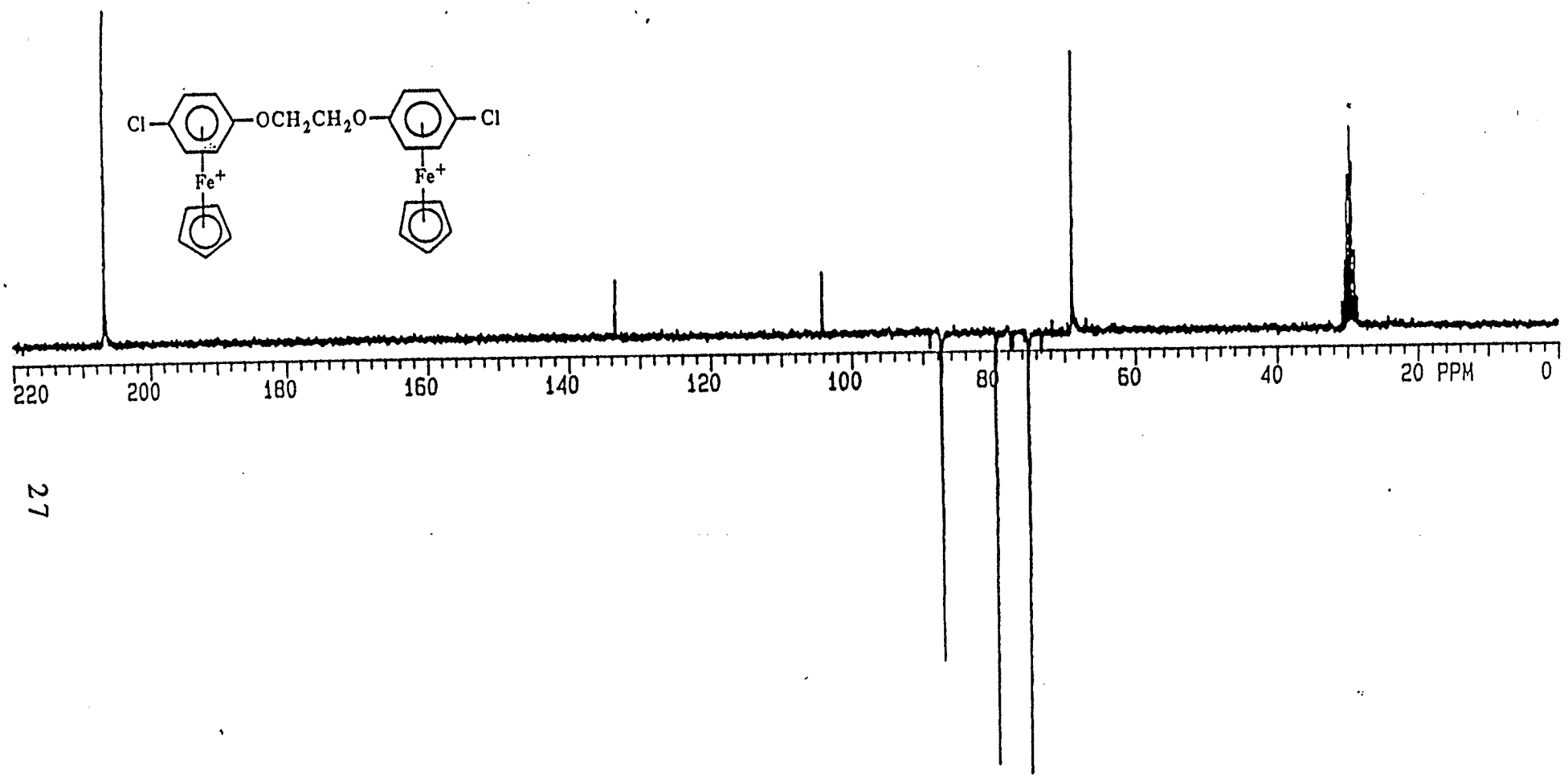
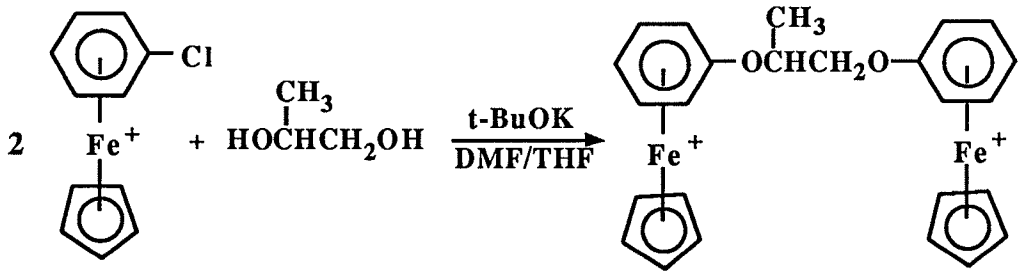


Figure 2: ^{13}C NMR spectrum of 1,2-bis(η^6-4-chlorophenoxy-η^5-cyclopentadienyliron) ethane hexafluorophosphate (3g) in acetone-d_6.

All of the above described reactions confirmed that this new method is successful for the synthesis of the symmetric arene diiron species with aliphatic ether linkages. It was also possible to prepare unsymmetrical bimetallic complexes by this method. As an example, reaction of chlorobenzene complex (1a) with 1,2-propanediol were carried out, as shown in Scheme 19. The result of the formation of the unsymmetrical diiron complex, 1,2-bis(η^6-phenoxy-η^5-cyclopentadienyliron) propane hexafluorophosphate (4), proved that this method was also useful in synthesis of unsymmetrical diiron complexes. Yield and ^1H and ^{13}C NMR data of the unsymmetrical bimetallic complex (4) are listed in Tables 2 and 3. The ^1H NMR spectrum shows two single peaks at 5.18 and 5.21 ppm for the protons of the two different Cp. The ^{13}C NMR spectrum gives rise to the two single peaks at 76.29 and 76.38 ppm for the carbons of the two Cps.



1a 4

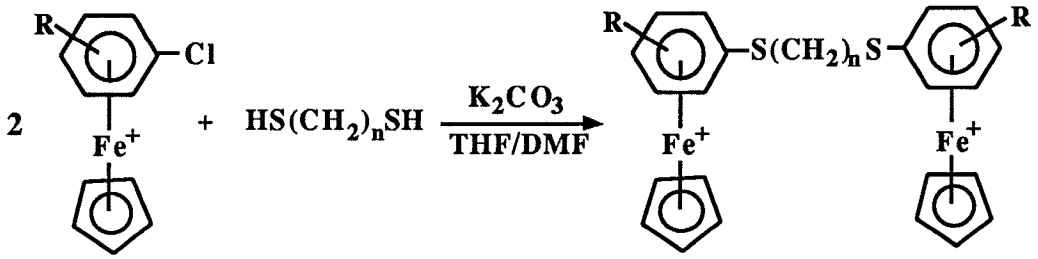
Scheme 19

It is important to point out that the logical use of a 2:1:2 molar ratio of the base: diol: complex resulted in a mixture of desired complex as well as the unreacted starting material. A slight excess of base to diol and

diol to complex, that was 2.4:2:2 molar ratio of the base: diol: complex, produced the dicationic complexes in a consistent manner.

2.1.2. Synthesis of Bis(η^6-thiophenoxy-η^5-cyclopentadienyl iron) Alkane Hexafluorophosphates

Sulfur compounds as nucleophiles are better than their oxygen analogous. The diaryl alkyl disulfides were prepared by previous method [61]. In the presence of potassium carbonate and mixture solvent THF/DMF (4/1), 2 mmol of chloroarene cyclopentadienyliron complexes reacted with 1 mmol of aliphatic dithiol and led to the formation of diaryl alkyl disulfides. The yields for these reactions were about 85%.

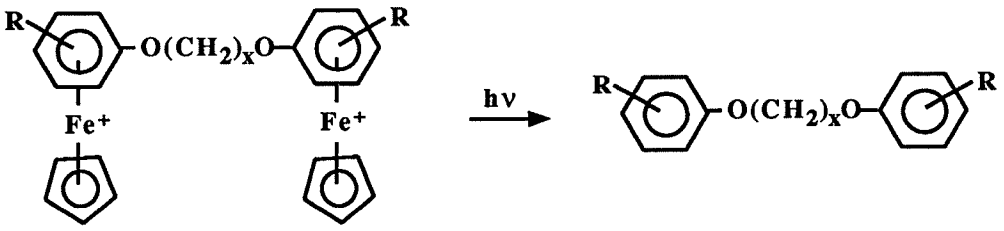


R = H, Cl, CH_3, 2,6-$(CH_3)_2$; n = 2, 4, 6

Scheme 20

2.1.3. Photolytic Demetallation of Diiron Complexes with Aliphatic Ether and Thioether Linkages

The ease of complexation and decomplexation is one of the characteristics of the cyclopentadienyliron complexes. There are a number of methods developed to remove the cyclopentadienyliron moiety [65,69,74-84]. We have investigated the possibility of liberation of diaryl alkyl diethers and disulfides from their corresponding diiron complexes with aliphatic ether and thioether linkages using photolysis. Liberation of diaryl alkyl diethers (5a-l) and diaryl alkyl disulfides (7a-j) from their corresponding diiron complexes are summarized in Schemes 21 and 22, respectively. The arene cyclopentadienyliron bimetallic complexes (6a-j) were synthesized with the method previously reported [61]. All of the demetallations were conducted by the same photolytic conditions which are fully outlined in the experimental chapter. The only exception for the photolytic conditions was the solvent ratio of CH_3CN/CH_2Cl_2 which was dependent on the solubility of the complexes.



31-k, 4

5a. R=H x=2

5b. R=H x=4

5c. R=H x=6

5d. R=H x=8

5e. R=H x=10

5f. R=H x=12

5g. R=4-Cl x=2

5h. R=4-CH_3 x=2

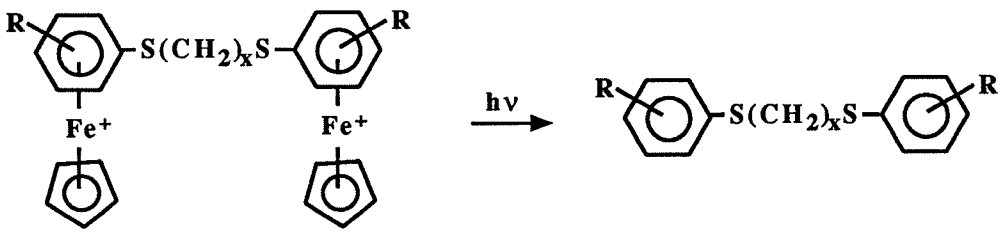
5i. R=3-CH_3 x=2

5j. R=2,6-$(CH_3)_2$ x=2

5k. R=2,6-$(CH_3)_2$ x=4

5l. R=H x=1 {$CH(CH_3)CH_2$}

Scheme 21



6 a - j

7a. R=H x=2

7b. R=2-CH_3 x=2

7c. R=3-CH_3 x=2

7d. R=4-CH_3 x=2

7e. R=2,6-$(CH_3)_2$ x=2

7f. R=4-Cl x=2

7g. R=H x=4

7h. R=2-CH_3 x=4

7i. R=4-CH_3 x=4

7j. R=4-Cl x=4

Scheme 22

The identification of these free arene compounds (5a-l and 7a-j) was carried out by ^1H and ^{13}C NMR, MS, and mp. The mp are uncorrected. While some of the compounds have been reported, the complete analytical data, the yield and the mp of these compounds (5a-l and 7a-j) are listed in Tables 4 and 5 and Tables 6 and 7, respectively. Figures 3 and 4 are the typical examples of the diaryl alky diethers and Figures 5 and 6 are representative of the diaryl alkyl disulfides. The major differences in the ^1H and ^{13}C NMR spectra of the complexes and the free arene compounds are the disappearance of the single Cp peaks and the shift of aromatic signals downfield.

Table 4: Yield, mp and ^{1}H NMR data for compounds 5a-l.

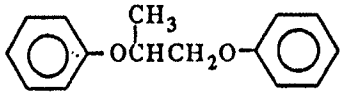
Compound No.	Yield (%)	mp (^oC)	δ ($CDCl_3$, ppm) Ar	Others
5a	85	93-94	6.96 (m, 6H) 7.29 (t, J = 7.3 Hz, 4H)	4.32 (s, 4H, CH_2)
5b	78	77-78	6.92 (m, 6H) 7.29 (t, J = 7.3 Hz, 4H)	1.99 (br.s, 4H, CH_2) 4.04 (br.s, 4H, CH_2)
5c	77	78-79.5	6.93 (m, 6H) 7.28 (t, J = 7.4 Hz, 4H)	1.56 (m, 4H, CH_2) 1.83 (t, 4H, J = 6.6 Hz, CH_2) 3.98 (t, 4H, J = 6.4 Hz, CH_2)
5d	92	76-77.5	6.94 (m, 6H) 7.29 (t, J = 7.3 Hz, 4H)	1.44 (m, 8H, CH_2) 1.80 (t, 4H, J = 6.6 Hz, CH_2) 3.98 (t, 4H, J = 6.3 Hz, CH_2)
5e	82	76.5-78	6.91 (m, 6H) 7.27 (t, J = 7.1 Hz, 4H)	1.32 (m, 12H, CH_2) 1.77 (m, 4H, CH_2) 3.94 (t, 4H, J = 6.5 Hz, CH_2)
5f	91	85-86	6.91 (m, 6H) 7.26 (t, J = 7.1 Hz, 4H)	1.29 (m, 16H, CH_2) 1.77 (m, 4H, CH_2) 3.94 (t, 4H, J = 6.5 Hz, CH_2)
5g	82	127-128	6.87 (d, J = 9.1 Hz, 4H) 7.25 (d, J = 8.9 Hz, 4H)	4.29 (s, 4H, CH_2)
5h	84	127-128.5	6.82 (d, J = 8.6 Hz, 4H) 7.07 (d, J = 8.1 Hz, 4H)	2.27 (s, 6H, CH_3) 4.26 (s, 4H, CH_2)
5i	87	oil	6.75 (m, 6H) 7.15 (t, J = 7.5 Hz, 2H)	2.31 (s, 6H, CH_3) 4.29 (s, 4H, CH_2)
5j	95	oil	6.97 (m, 2H) 7.03 (m, 4H)	2.36 (s, 12H, CH_3) 4.14 (s, 4H, CH_2)

5k	90	oil	6.95 (m, 6H)	2.05 (m, 4H, CH_2) 2.28 (s, 12H, CH_3) 3.84 (m, 4H, CH_2)
5l	79	oil	6.86 (m, 6H) 7.23 (m, 4H)	1.35 (d, 3H, J = 6.3 Hz, CH_3) 3.92 (dd, 1H, J = 9.8, 5.0 Hz, CH_2) 4.07 (dd, 1H, J = 9.7, 5.5 Hz, CH_2) 4.64 (sextet, 1H, J = 5.7 Hz, CH)

Table 5: Mass Spectral and ^{13}C NMR Data for Compounds 5a-l.

Compound No.	m/e (M^+, %)	δ ($CDCl_3$, ppm) Ar	Others
5a	214 (57%)	114.68 (4C), 121.08 (2C) 129.49 (4C), 158.61 (2C, ipso)	66.42 (2C, CH_2)
5b	242 (11%)	114.49 (4C), 120.61 (2C) 129.44 (4C), 158.98 (2C, ipso)	26.06 (2C, CH_2), 67.34 (2C, CH_2)
5c	270 (62%)	114.47 (4C), 120.48 (2C) 129.39 (4C), 159.04 (2C, ipso)	25.89 (2C, CH_2), 29.24 (2C, CH_2) 67.67 (2C, CH_2)
5d	298 (52%)	114.42 (4C), 120.39 (2C) 129.33 (4C), 159.04 (2C, ipso)	25.95 (2C, CH_2), 29.22 (2C, CH_2) 29.24 (2C, CH_2), 67.74 (2C, CH_2)
5e	326 (35%)	114.47 (4C), 120.42 (2C) 129.36 (4C), 159.10 (2C, ipso)	26.03 (2C, CH_2), 29.27 (2C, CH_2) 29.36 (2C, CH_2), 29.47 (2C, CH_2) 67.83 (2C, CH_2)
5f	354 (33%)	114.46 (4C), 120.40 (2C) 129.34 (4C), 159.08 (2C, ipso)	26.03 (2C, CH_2), 29.27 (2C, CH_2) 29.37 (2C, CH_2), 29.53 (4C, CH_2) 67.83 (2C, CH_2)
5g	282 (87%) 284 (58%)	115.97 (4C), 129.39 (4C) 126.10 (2C, ipso) 157.17 (2C, ipso)	66.78 (2C, CH_2)
5h	242 (100%)	114.57 (4C), 129.90 (4C) 130.29 (2C, ipso) 156.54 (2C, ipso)	20.47 (2C, CH_3), 66.67 (2C, CH_2)
5i	242 (71%)	111.50 (2C), 115.54 (2C) 121.85 (2C), 129.19 (2C) 139.51 (2C, ipso) 158.62 (2C, ipso)	21.50 (2C, CH_3), 66.35 (2C, CH_2)

5j	270 (74%)	123.88 (2C), 128.83 (4C) 131.01 (4C, ipso) 155.87 (2C, ipso)	16.36 (4C, CH_3), 71.35 (2C, CH_2)
5k	298 (4%)	123.70 (2C), 128.79 (4C) 131.01 (4C, ipso) 155.87 (2C, ipso)	16.26 (4C, CH_3), 27.25 (2C, CH_2) 71.83 (2C, CH_2)
5l	270 (53%)	114.36 (2C), 115.87 (2C) 120.70 (1C), 120.85 (1C) 129.17 (2C), 129.23 (2C) 157.47 (1C, ipso) 158.37 (1C, ipso)	16.88 (1C, CH_3), 70.50 (1C, CH) 72.15 (1C, CH_2)



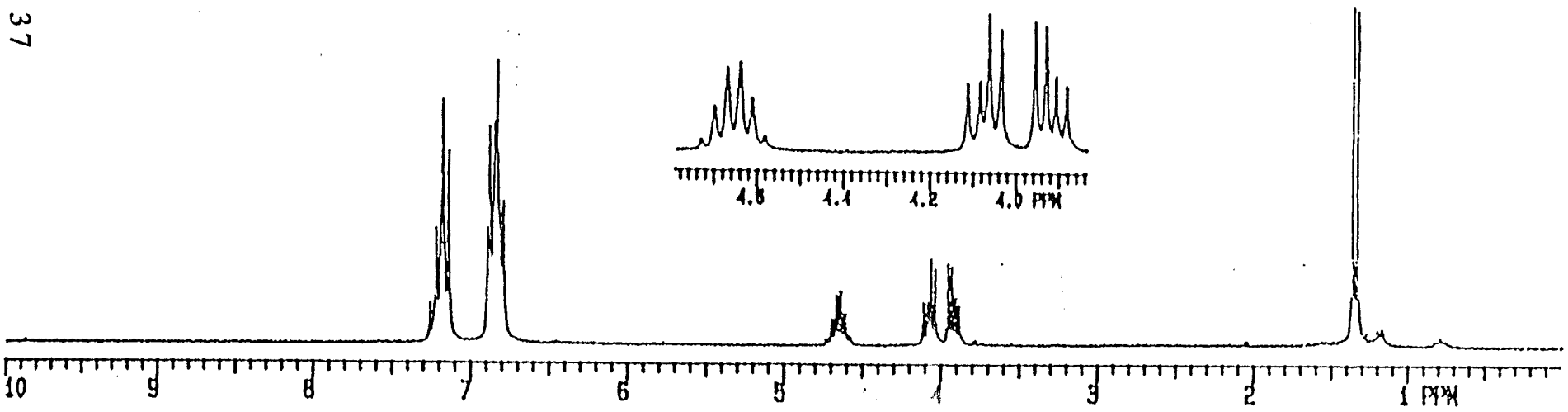


Figure 3: ^{1}H NMR spectrum of 1,2-bis(phenoxy) propane (51) in $CDCl_3$.

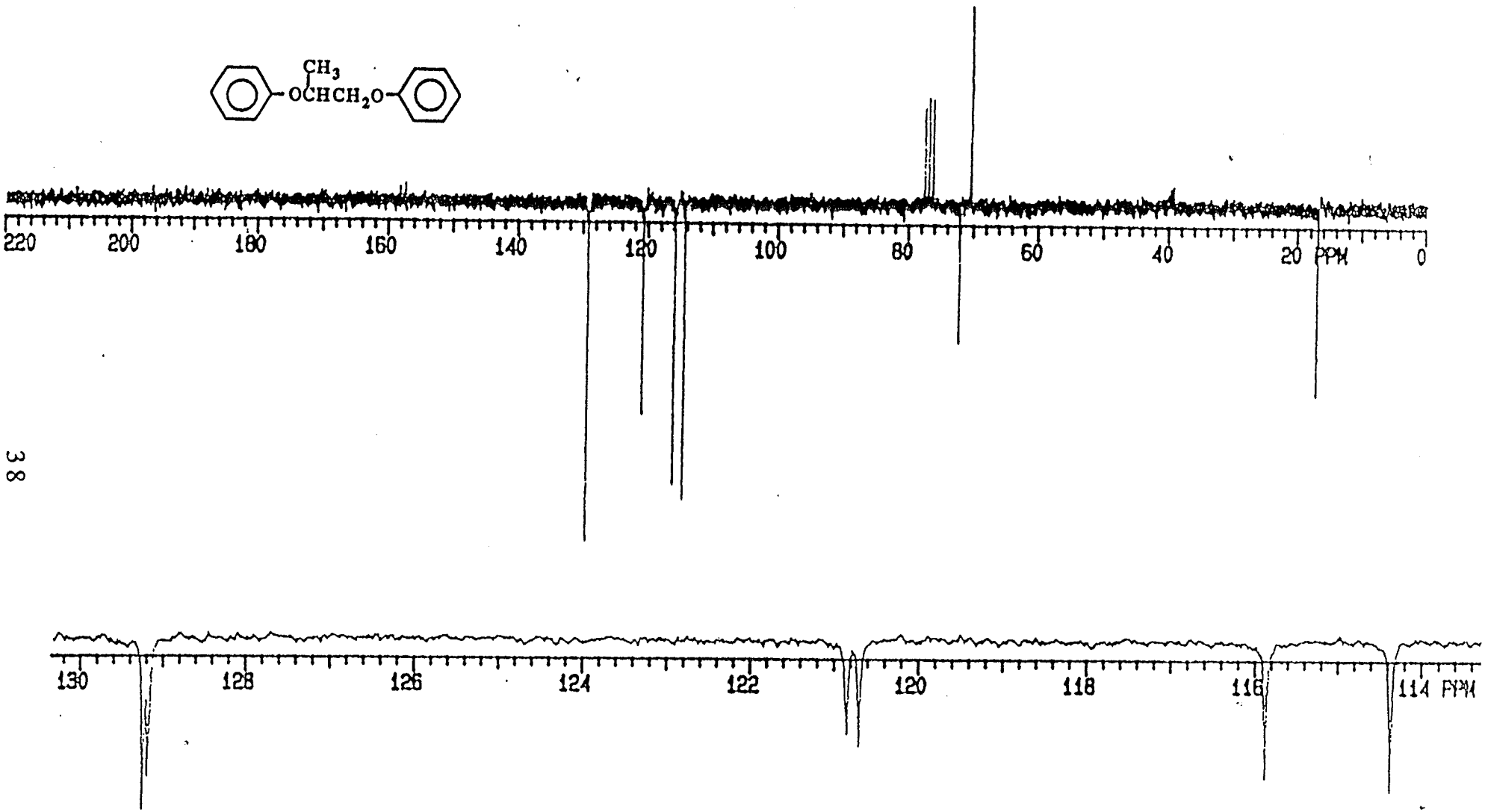


Figure 4: ^{13}C NMR spectrum of 1,2-bis(phenoxy) propane (51) in $CDCl_3$.

Table 6: Yield and ^1H NMR data for compounds 7a-j.

Compound No.	Yield (%)	δ ($CDCl_3$, ppm) Complexed Ar	Others
7a	37	7.15-7.27 (m, 10H)	3.05 (s, 4H, CH_2)
7b	70	7.19-7.31 (m, 8H)	2.47 (s, 6H, CH_3), 3.16 (s, 4H, CH_2)
7c	69	7.11-7.29 (m, 8H)	2.42 (s, 6H, CH_3), 3.19 (s, 4H, CH_2)
7d	95	7.12 (d, J = 3.3 Hz, 4H) 7.22 (d, J = 3.7 Hz, 4H)	2.35 (s, 6H, CH_3), 3.04 (s, 4H, CH_2)
7e	81	7.24 (m, 6H)	2.60 (s, 12H, CH_3), 2.88 (s, 4H, CH_2)
7f	89	7.24 (m, 8H)	3.03 (s, 4H, CH_2))
7g	87	7.10-7.24 (m, 10H)	1.72 (t, J = 6.9 Hz, 4H, CH_2), 2.85 (t, J = 6.6 Hz, 4H, CH_2)
7h	100	7.16-7.36 (m, 8H)	1.91 (t, J = 3.0 Hz, 4H, CH_2), 2.45 (s, 6H, CH_3), 2.98 (t, J = 3.4 Hz, 4H, CH_2)
7i	57	7.07 (d, J = 8.1 Hz, 4H), 7.22 (d, J = 7.6 Hz, 4H)	1.72 (d, J = 6.4 Hz, 4H, CH_2), 2.30 (s, 6H, CH_3), 2.84 (t, J = 6.4 Hz, 4H, CH_2)
7j	68	7.24 (m, 8H)	1.75 (br.s, 4H, CH_2), 2.89 (br.s, 4H, CH_2)

Table 7: Mp and ^{13}C NMR data for compounds 7a-j.

Compound No.	mp (°C)	δ ($CDCl_3$, ppm) Complexed Ar	Others
7a	61.5-62.5	126.56 (2C), 129.03 (4C) 130.01 (4C), 134.98 (2C, ipso)	33.34 (2C, CH_2)
7b	36.0-37.0	126.34 (2C), 126.36 (2C) 128.97 (2C), 130.31 (2C) 134.23 (2C, ipso), 138.38 (2C, ipso)	20.43 (2C, CH_3) 32.38 (2C, CH_2)
7c	48	126.87 (2C), 127.36 (2C) 128.81 (2C), 130.53 (2C) 134.71 (2C, ipso), 138.79 (2C, ipso)	21.27 (2C, CH_3) 33.29 (2C, CH_2)
7d	69.0-70.5	129.80 (4C), 130.76 (4C) 131.25 (2C, ipso), 136.77 (2C, ipso)	21.05 (2C, CH_3) 33.99 (2C, CH_2)
7e	123.0-124.0	128.12 (4C), 128.25 (2C) 132.40 (2C, ipso), 143.02 (4C, ipso)	22.04 (4C, CH_3) 34.44 (2C, CH_2)
7f	106.0	129.20 (4C), 131.52 (4C) 132.82 (2C, ipso), 133.37 (2C, ipso)	33.63 (2C, CH_2)
7g	78.0	127.61 (2C), 130.57 (4C) 130.93 (4C), 138.17 (2C, ipso)	29.81 (2C, CH_2) 34.92 (2C, CH_2)
7h	48.0	125.51 (2C), 126.32 (2C) 127.71 (2C), 130.04 (2C) 135.77 (2C, ipso), 137.42 (2C, ipso)	20.32 (2C, CH_3) 28.06 (2C, CH_2) 32.35 (2C, CH_2)
7i	oil	129.64 (4C), 130.13 (4C) 132.60 (2C, ipso), 136.12 (2C, ipso)	21.00 (2C, CH_3) 28.20 (2C, CH_2) 33.99 (2C, CH_2)
7j	oil	128.99 (4C), 130.59 (4C) 134.10 (2C, ipso), 134.84 (2C, ipso)	27.87 (2C, CH_2) 33.45 (2C, CH_2)

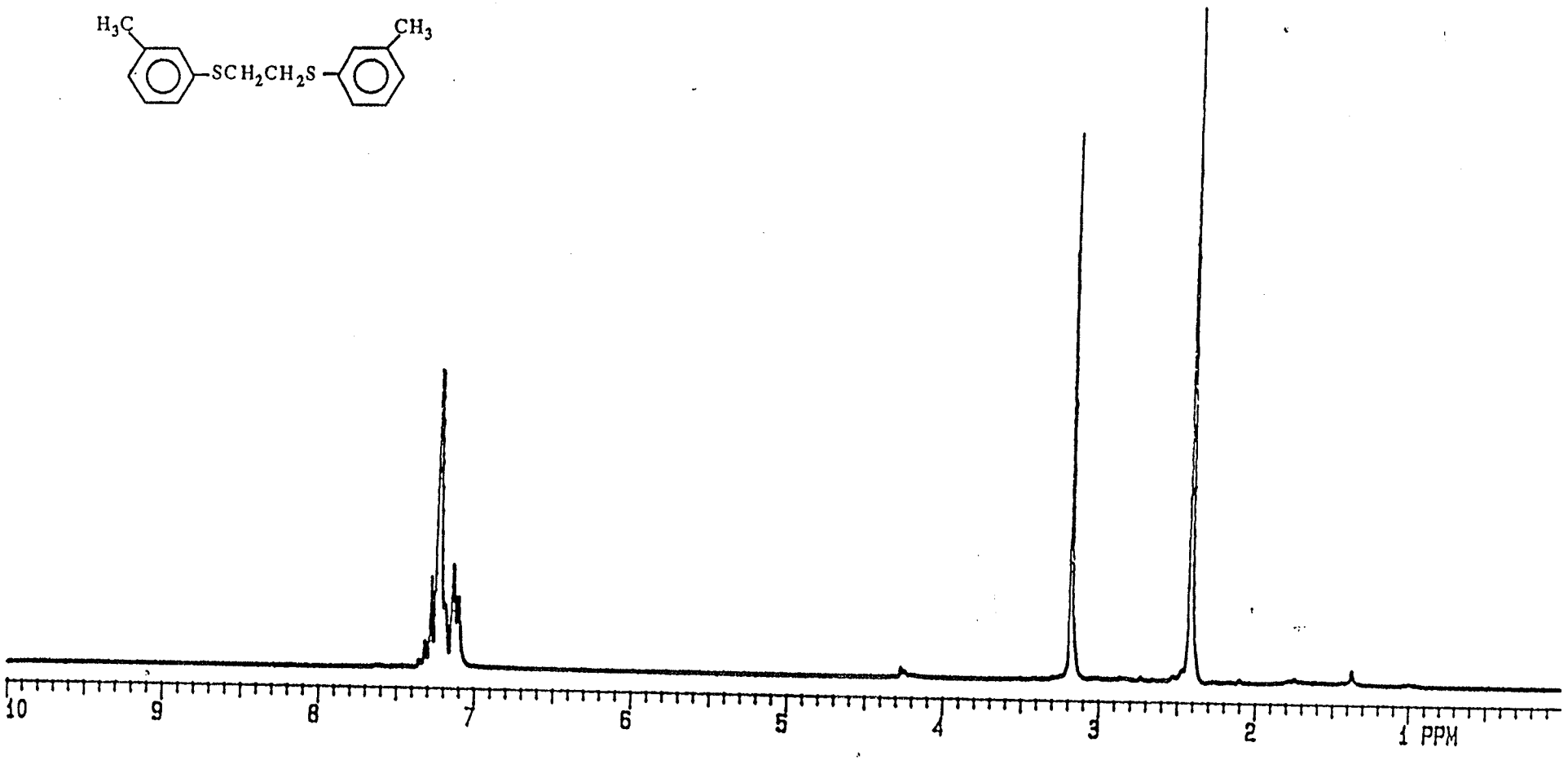


Figure 5: ^{1}H NMR spectrum of 1,2-bis(4-methylphenoxy) ethane (7c) in $CDCl_3$.

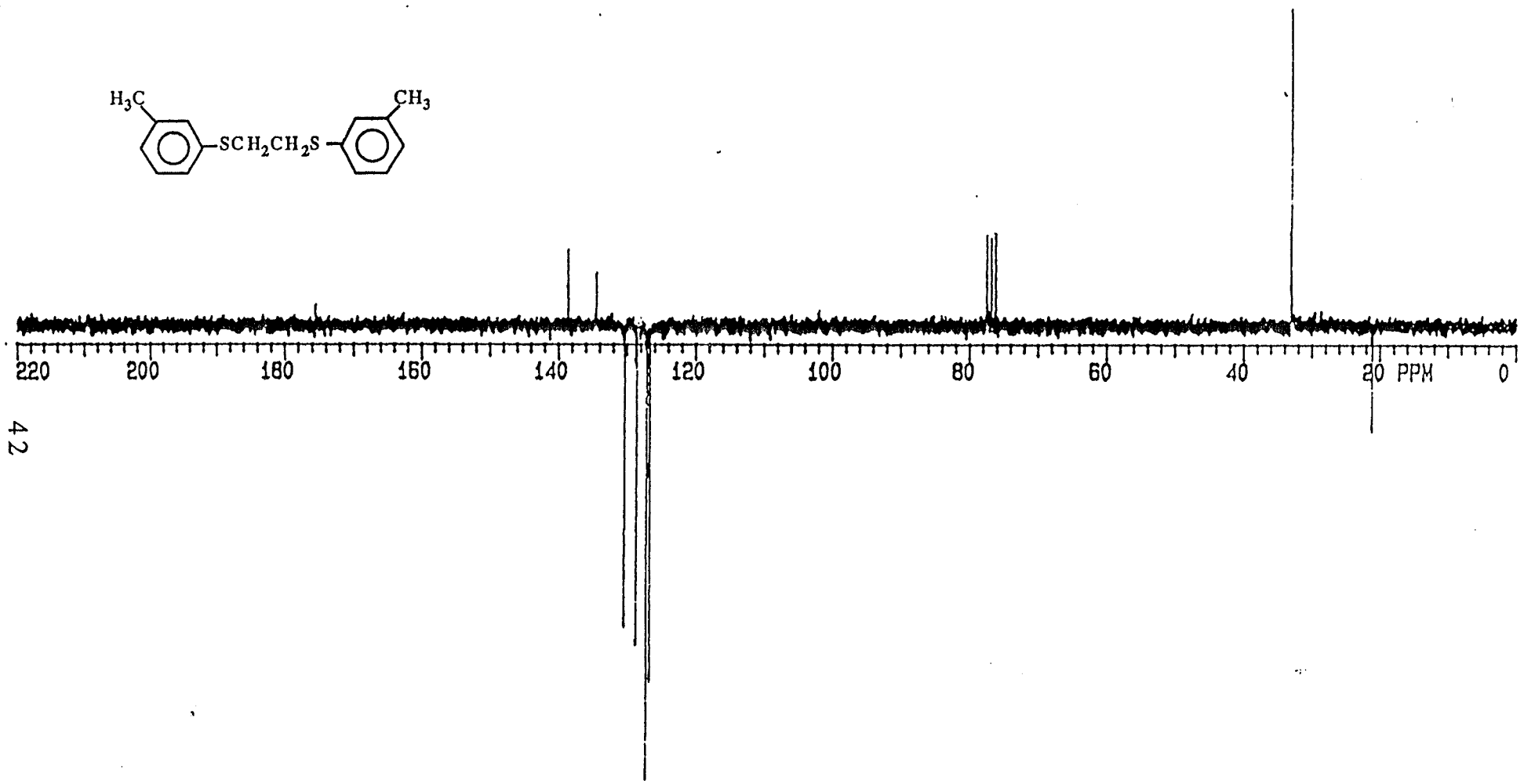


Figure 6: ^{13}C NMR spectrum of 1,2-bis(4-methylphenoxy) ethane (7c) in $CDCl_3$.

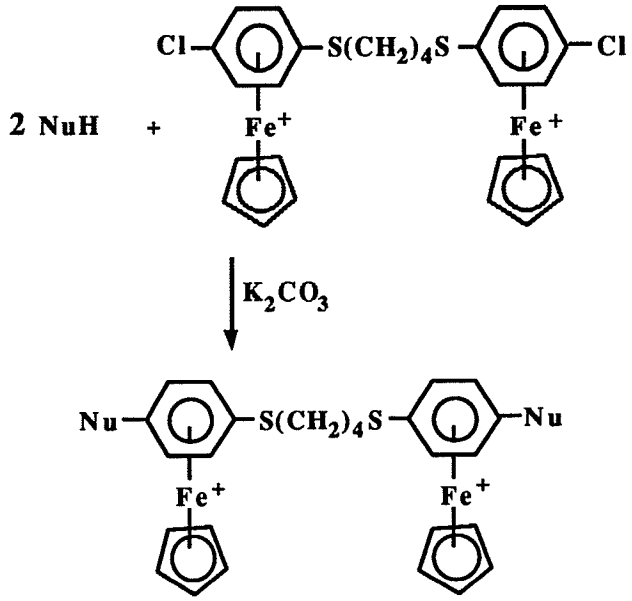
2.2. Reactivitives of the Disulfide Complexes

2.2.1. Reactions of Disulfide Complexes With Oxygen, Sulfur, and Carbon Containing Nucleophiles

The ligand exchange reaction is the most common method for the preparation of arene bis(η^6-arene-η^5-cyclopentadienyliron) bimetallic complexes. This method suffers from the lack of introducing arenes with some functional groups. On the other hand, the aromatic nucleophilic substitution reactions of chloroarene cyclopentadienyl monocation with various nucleophiles have been well studied and have been used to synthesize a wide range of organic compounds. The complexes with terminal chloro groups could react with various nucleophiles. In order to demonstrate the capability of introducing various groups to the cyclopentadienyliron bimetallics and the capability of liberation of the functionalized diaryl alkyl disulfides, the 1,4-bis(η^6-4-chlorothiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (6j) was selected to react with oxygen, sulfur and carbon containing nucleophiles. The reactions were carried out by following the similar procedure of the nucleophilic aromatic substitution of chlorobenzene cyclopentadienyliron monocation with appropriate nucleophiles [58,61,].

The reaction of 0.5 mmol of (6j) with 1.2 mmol of thiophenol in the presence of 4.0 mmol of potassium carbonate in THF and DMF (2:1) mixture gave 1,4-bis(η^6-4-thiophenoxy thiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (8a) in 87% yield. With the same ratio as (6j) to thiophenol, the mixed reactants of (6j) and

phenol in DMF were stirred for 17 hours and led to the formation of 1,4-bis(η^6-4-phenoxy thiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (8b) in 92% yield. The reaction of chloroarene cyclopentadienyliron complexes with diethyl malonate was also successfully carried out. When 0.4 mmol of complex (6j) was mixed with 0.88 mmol of diethyl malonate and 0.4 mmol of potassium carbonate in DMF, a cherry red color appeared after refluxing for 10 minutes. The reaction was completed in 5 hours at reflux temperature and resulted in the formation of a disubstituted complex (8c). Scheme 23 summarizes these reactions.



8a. Nu = SPh

8b. Nu = OPh

8c. Nu = $CH(COOEt)_2$

Scheme 23

^1H and ^{13}C NMR spectra were used to determine the structures of the products 8a-c. The NMR data are summarized in Tables 8 and 9. They are in full agreement with their structures. As an example, the spectra of 8b are shown in Figures 7 and 8. The single peak from the Cp supports the symmetrical structures.

Table 8: Yield and ^1H NMR data for complexes 8a-c.

Compound No.	Yield (%)	δ (acetone-d_6, ppm) ArH	Cp	Complexed ArH	Others
8a	87	7.60 (m, 6H) 7.71 (m, 4H)	5.14	6.30 (d, J = 5.2 Hz, 4H) 6.53 (d, J = 5.2 Hz, 4H)	1.95 (br.s, 4H, CH_2) 3.29 (br.s, 4H, CH_2)
8b	91	7.37 (m, 6H) 7.56 (t, J = 6.7 Hz, 4H)	5.22	6.37 (d, J = 5.9 Hz, 4H) 6.52 (d, J = 6.1 Hz, 4H)	1.97 (br.s, 4H, CH_2) 3.31 (br.s, 4H, CH_2)
8c	87		5.14	6.63 (d, J = 6.9 Hz, 4H) 6.55 (d, J = 5.3 Hz, 4H)	1.30 (t, J = 7.1 Hz, 12H, CH 2.04 (m, 4H, CH_2) 3.39 (m, 4H, CH_2) 4.32 (q, J = 7.0 Hz, 8H, CH 5.16 (s, 2H, CH)

Table 9: ^{13}C NMR data for complexes 8a-c.

Compound No.	δ (acetone-d_6,ppm) ArC	Cp	Complexed ArC	Others
8a	129.00 (2C, ipso)	80.18	84.22 (4C)	28.18 (2C, CH_2)
	131.15 (4C)		85.03 (4C)	31.50 (2C, CH_2)
	131.20 (2C)		107.73 (2C, ipso)	
	135.63 (4C)		108.76 (2C, ipso)	
8b	121.46 (4C)	79.62	76.77 (4C)	28.51 (2C, CH_2)
	127.25 (2C)		84.18 (4C)	32.48 (2C, CH_2)
	131.56 (4C)		106.67 (2C, ipso)	
	153.97 (2C, ipso)		132.71 (2C, ipso)	
8c		79.76	84.38 (4C)	14.08 (4C, CH_3)
			87.78 (4C)	28.28 (2C, CH_2)
			96.10 (2C, ipso)	31.39 (2C, CH_2)
			111.09 (2C, ipso)	55.59 (2C, CH)
				63.27 (4C, CH_2)
				166.58 (4C, CO)

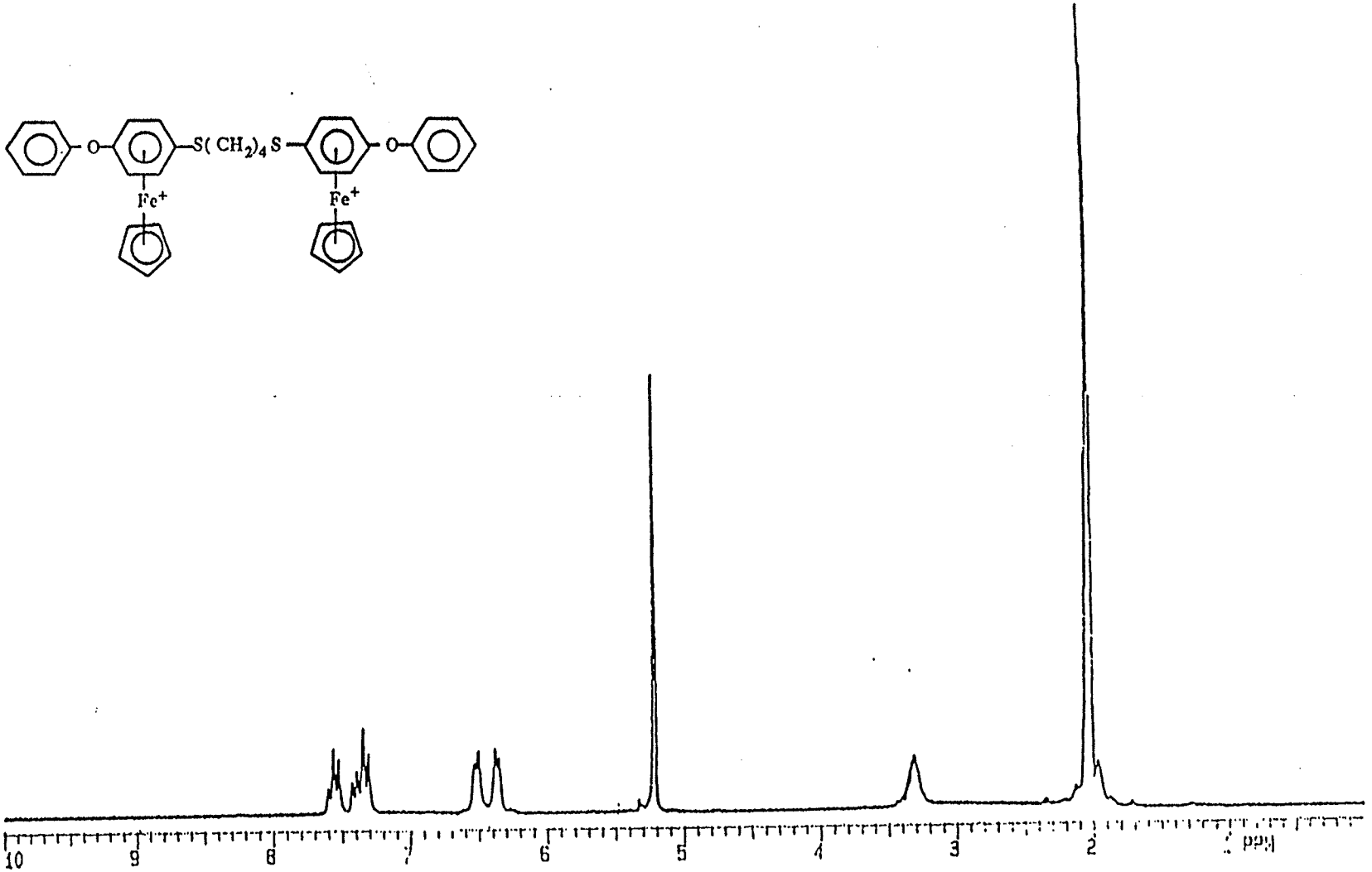


Figure 7: ^{1}H NMR spectrum of 1,4-bis(η^{6}-4-phenoxy thiophenoxy-η^{5}-cyclopentadienyliron) butane hexafluorophosphate (8a) in acetone-d_6.

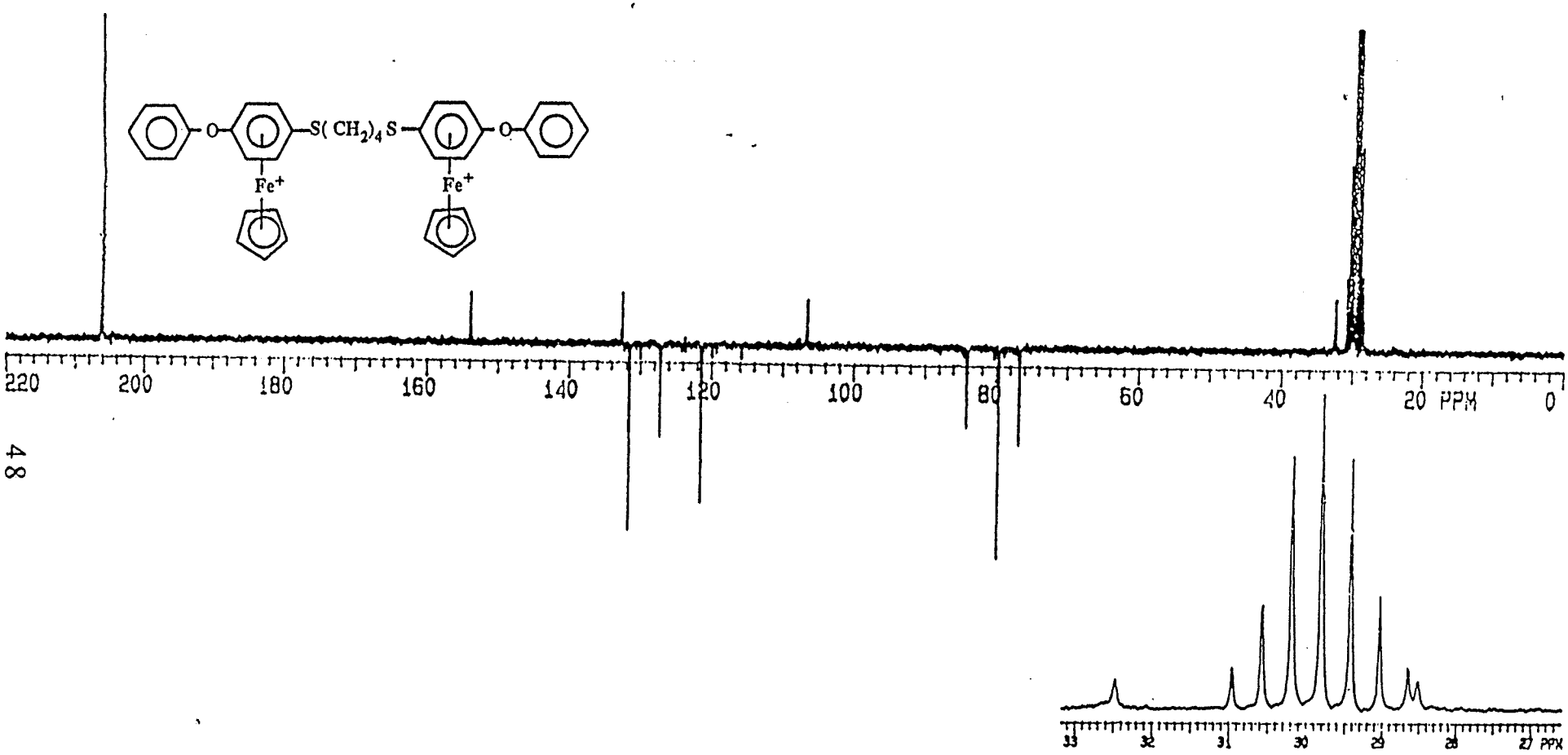
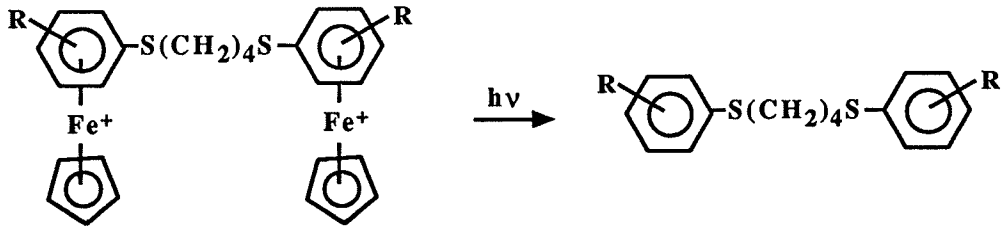


Figure 8: ^{13}C NMR spectrum of 1,4-bis(η^6-4-phenoxy thiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (8a) in acetone-d_6.

Photolytic demetallation of 8a-c under Xenon lamp gave the free functionalized phenyl alkyl disulfides 9a-c as shown in Scheme 24. While the products 9a and 9b were eluted with chloroform, the product 9c was eluted with the more polar solvent ethyl acetate.



8a-c

9a. R = SPh

9b. R = OPh

9c. R = $CH(COOEt)_2$

Scheme 24

The structure of the photolytic products, 9a-c were confirmed by ^{1}H and ^{13}C NMR. The major differences between the free arene compounds 9a-c and the complexes 8a-c are the disappearance of the Cp peaks and the down field shift of the complexed arene. The typical NMR spectra are shown in Figures 9 and 10 and the spectral data for 9a-c are listed in Tables 10 and 11.

Table 10: Yield and ^1H NMR data for compounds 9a-c.

Compound No.	Yield (%)	δ ($CDCl_3$, ppm) ArH	Others
9a	94	7.21-7.33 (m, 18H)	1.78 (br.s, 4H, CH_2), 2.91 (br.s, 4H, CH_2)
9b	77	6.97 (m, 8H), 7.12 (m, 2H) 7.31 (m, 8H)	1.76 (br.s, 4H, CH_2), 2.88 (br.s, 4H, CH_2)
9c	98	7.30 (m, 8H)	1.26 (t, J = 7.1 Hz, 12H, CH_3), 1.79 (t, J = 1.8 Hz, 4H, CH_2) 2.29 (t, J = 1.8 Hz, 4H, CH_2) 4.21 (m, 8H, CH_2), 4.56 (s, 2H, CH)

Table 11: ^{13}C NMR for compounds 9a-c.

Compound No.	δ ($CDCl_3$, ppm) ArC	Others
9a	126.99 (4C), 129.16 (2C), 129.57 (4C), 130.71 (4C), 131.64 (4C), 132.99 (2C, ipso) 135.75 (4C, ipso)	27.89 (2C, CH_2), 33.02 (2C, CH_2)
9b	118.93 (4C), 119.28 (4C), 123.44 (2C) 129.77 (4C), 132.21 (4C), 156.22 (4C, ipso) 156.92 (2C, ipso)	28.10 (2C, CH_2), 34.61 (2C, CH_2)
9c	128.76 (4C), 129.72 (4C), 130.25 (2C, ipso) 136.82 (2C, ipso)	13.95 (4C, CH_3), 27.98 (2C, CH_2) 32.79 (2C, CH_2), 57.38 (2C, CH) 61.79 (4C, CH_2), 167.97 (4C, CO)

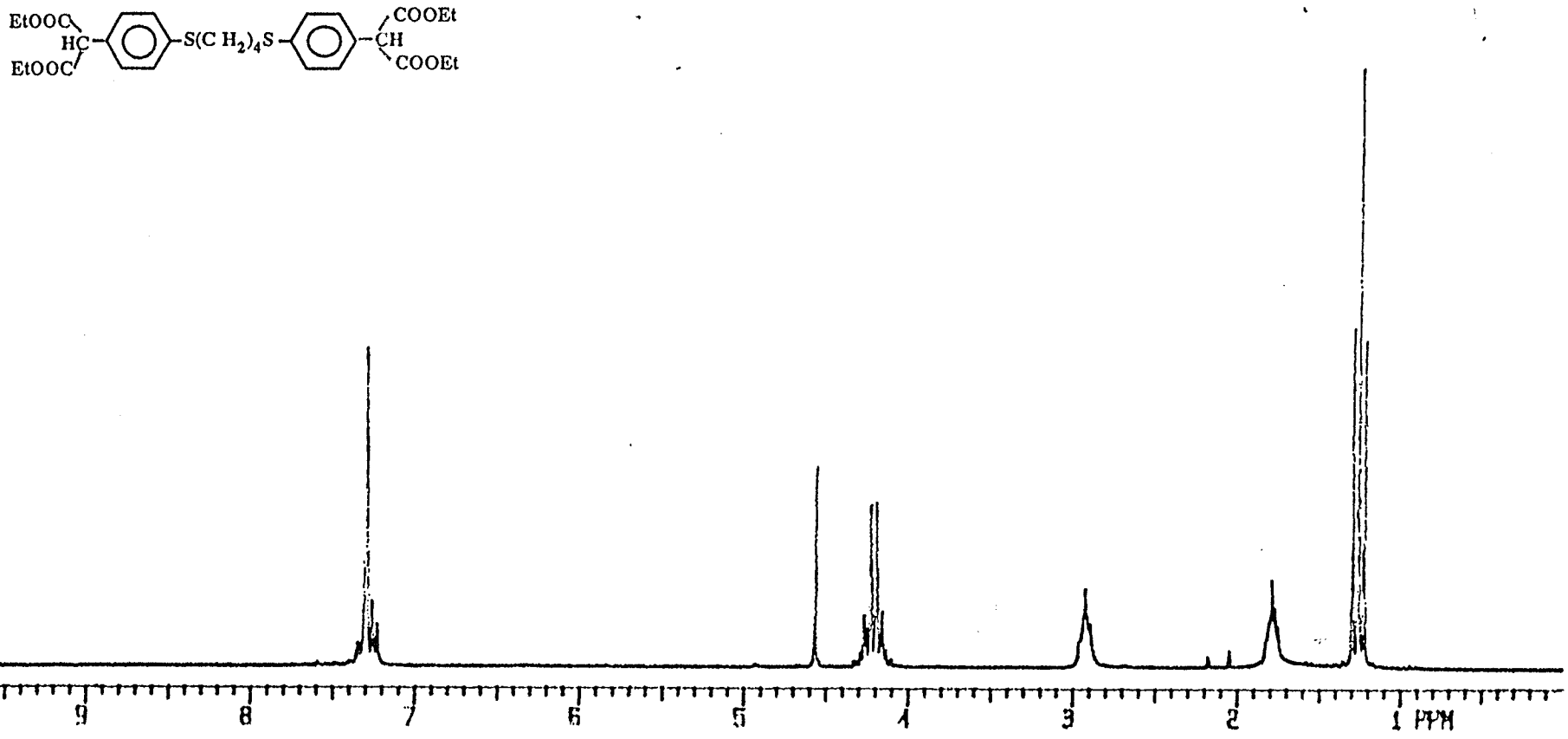


Figure 9: ^{1}H NMR spectrum of 1,4-bis(4-diethyl malonate thiophenoxy) butane (9c) in $CDCl_3$.

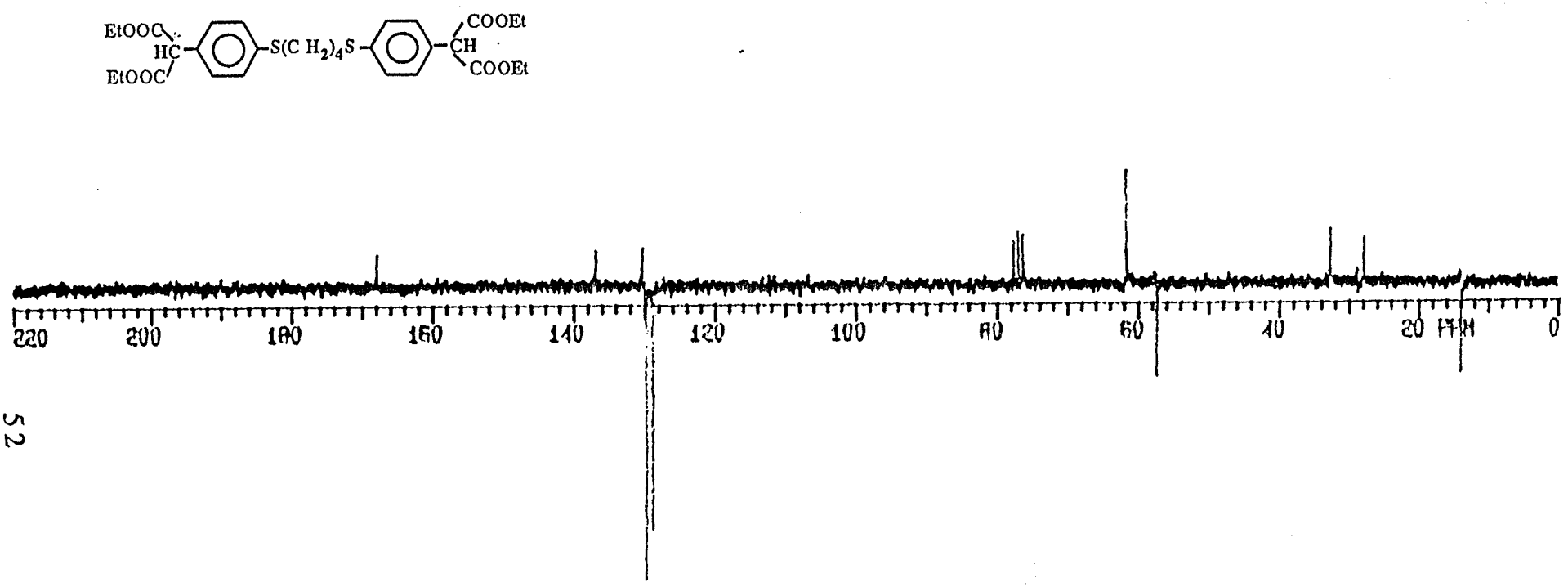


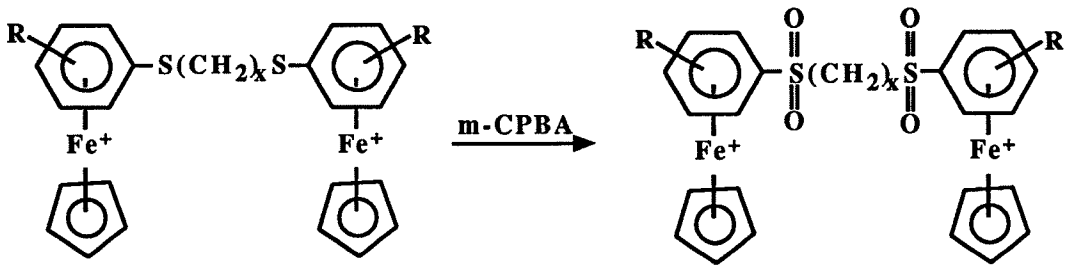
Figure 10: ^{13}C NMR spectrum of 1,4-bis(4-diethyl malonate thiophenoxy) butane (9c) in $CDCl_3$.

2.2.2. Oxidation of Cyclopentadienyliron Bimetallics With Aliphatic Thioether Linkages

One of the most common methods for the synthesis of sulfones is the oxidation of sulfides. A great variety of oxidants, such as hydrogen peroxide in glacial acetic acid [33,36], potassium permanganate and m-chloroperbenzoic acid (m-CPBA) in a variety of organic solvents [93], have been used to achieve the oxidation. The sulfides in arene cyclopentadienyliron complexes have been oxidized by hydrogen peroxide ($H_2O_2/TiCl_3$) [94] and by m-CPBA in CH_2Cl_2 [95]. The oxidation reaction with m-CPBA as the oxidant gave purer sulfone products. In this study, the arene cyclopentadienyliron bimetallic complexes containing aliphatic thioether linkages were used as starting materials.

The reaction of the complexes (6a-c, 6f, 6i, and 10a-c) with excess m-CPBA under reflux in a DMF/CH_2Cl_2 mixure for 5 hours led to the oxidation of sulfides to sulfones with the yields in the range of 72% to 94%. The 1,2-bis(η^6-2,6-dimethylchlorobenzene-η^5-cyclopentadienyliron) ethane hexafluorophosphate (6e) was also oxidized to its corresponding disulfone by m-CPBA. This demonstrated that the steric hindrance did not affect the oxidation reaction. Scheme 25 illustrates these oxidation reactions. ^1H and ^{13}C NMR and IR spectra were used to characterize the structure of the resulting complexes (11a-i). The typical ^1H and ^{13}C NMR spectra of 11c are shown in Figures 11 and 12. The ^1H and ^{13}C NMR data of the complexes 11a-i are

summarized in Tables 12 and 13. The yield and IR data of these complexes are listed in Table 14.



6a **11a. R=H x=2**

6b **11b. R=3-CH_3 x=2**

6c **11c. R=4-CH_3 x=2**

6d **11d. R=2,6-$(CH_3)_2$ x=2**

6f **11e. R=4-Cl x=4**

6i **11f. R=4-CH_3 x=4**

10a **11g. R=3-CH_3 x=4**

10b **11h. R=2-CH_3 x=4**

10c **11i. R=3-Cl x=4**

Scheme 25

Table 12: ^1H NMR data for complexes 11a-i.

Complex No.	δ ($(CD_3)_2CO$, ppm) Cp	Complexed Ar	Others
11a	5.40	6.82 (m, 6H), 7.02 (m, 4H)	4.16 (s, 4H, CH_2)
11b	5.34	6.72 (br.s, 4H), 6.90 (br.s, 4H)	2.65 (s, 6H, CH_3) 4.09 (s, 4H, CH_2)
11c	5.35	6.71 (d, J = 6.6 Hz, 4H) 6.94 (d, J = 6.6 Hz, 4H)	2.66 (s, 6H, CH_3) 4.11 (s, 4H, CH_2)
11d	5.36	6.62 (d, J = 5.9 Hz, 4H) 6.75 (t, J = 5.8 Hz, 2H)	2.83 (s, 12H, CH_3) 4.25 (s, 4H, CH_2)
11e #	5.39	6.95 (d, J = 6.0 Hz, 4H) 7.11 (d, J = 6.0 Hz, 4H)	1.72 (br.s, 4H, CH_2) 3.63 (br.s, 4H, CH_2)
11f	5.36	6.88 (d, J = 7.3 Hz, 4H) 6.70 (d, J = 7.3 Hz, 4H)	1.97 (br.s, 4H, CH_2) 2.67 (s, 6H, CH_3) 3.59 (br.s, 4H, CH_2)
11g	5.36	6.74 (br.s, 4H), 6.86 (br.s, 4H)	1.98 (br.s, 4H, CH_2) 2.68 (s, 6H, CH_3) 3.59 (br.s, 4H, CH_2)
11h	5.36	6.63 (d, J = 5.9 Hz, 2H) 6.73 (m, 4H) 6.93 (d, J = 6.2 Hz, 2H)	2.04 (br.s, 4H, CH_2) 2.87 (s, 6H, CH_3) 3.64 (br.s, 4H, CH_2)
11i	5.52	6.94 (m, 4H), 7.11 (m, 2H) 7.26 (m, 2H)	2.04 (br.s, 4H, CH_2) 3.67 (br.s, 4H, CH_2)

The solvent for the NMR study was DMSO-d_6 instead of $(CD_3)_2CO$.

Table 13: ^{13}C NMR data for complexes 11a-i.

Complex No.	δ (DMSO-d_6, ppm) Cp	Complexed Ar	Others
11a	78.89	88.19 (4C), 88.49 (4C) 90.64 (2C), 100.91 (2C, ipso)	47.64 (2C, CH_2)
11b #	80.47	87.79 (2C), 88.88 (2C) 89.30 (2C), 92.12 (2C) 102.29 (2C, ipso), 105.87 (2C, ipso)	20.57 (2C, CH_3) 49.29 (2C, CH_2)
11c	79.12	87.81 (4C), 88.26 (4C) 99.43 (2C, ipso), 106.62 (2C, ipso)	20.17 (2C, CH_3) 47.74 (2C, CH_2)
11d	79.28	89.48 (2C), 90.40 (4C) 103.97 (4C, ipso), 107.04 (2C, ipso)	20.72 (4C, CH_3) 47.76 (2C, CH_2)
11e	81.02	87.91 (4C), 88.34 (4C) 101.09 (2C, ipso), 108.63 (2C, ipso)	20.42 (2C, CH_2) 53.15 (2C, CH_2)
11f	79.05	87.24 (4C), 88.34 (4C) 100.51 (2C, ipso) 106.46 (2C, ipso)	20.15 (2C, CH_3) 20.59 (2C, CH_2) 53.26 (2C, CH_2)
11g	79.03	85.99 (2C), 87.52 (2C), 87.57 (2C) 90.70 (2C), 101.42 (2C, ipso) 104.09 (2C, ipso)	19.84 (2C, CH_3) 20.50 (2C, CH_2) 53.23 (2C, CH_2)
11h	78.92	87.14 (2C), 88.40(2C), 90.27 (4C) 101.09 (2C, ipso) 103.45 (2C, ipso)	18.31 (2C, CH_3) 20.37 (2C, CH_2) 53.24 (2C, CH_2)
11i #	82.38	88.38 (2C), 89.00 (2C) 89.36 (2C), 92.00 (2C) 103.94 (2C, ipso), 108.44 (2C, ipso)	21.82 (2C, CH_2) 54.98 (2C, CH_2)

The solvent for the NMR study was $(CD_3)_2CO$ instead of DMSO-d_6.

Table 14. Yield and IR data for compounds 11a-i.

Complex No.	Yield (%)	IR (cm^{-1}) (ν_{SO_2})
11a	83	1158, 1329
11b	89	1158, 1340
11c	93	1159, 1342
11d	85	1161, 1334
11e	94	1160, 1324
11f	84	1155, 1324
11g	87	1148, 1321
11h	86	1150, 1323
11i	72	1161, 1328

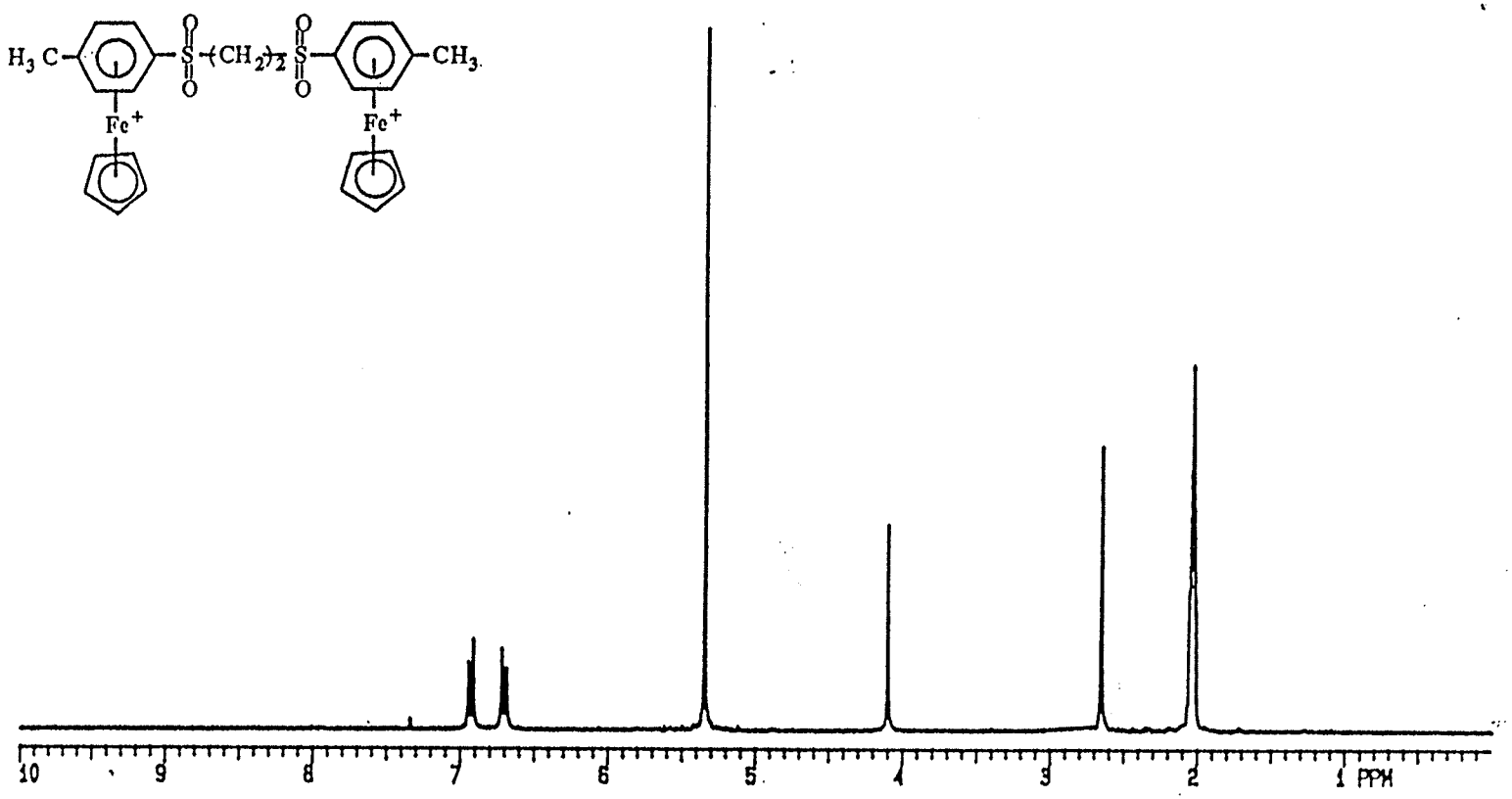


Figure 11: ^{1}H NMR spectrum of 1,4-bis(η^{6}-4-methyl phenylsulfonyl-η^{5}-cyclopentadienyliron) butane hexafluorophosphate (11c) in acetone-d_6.

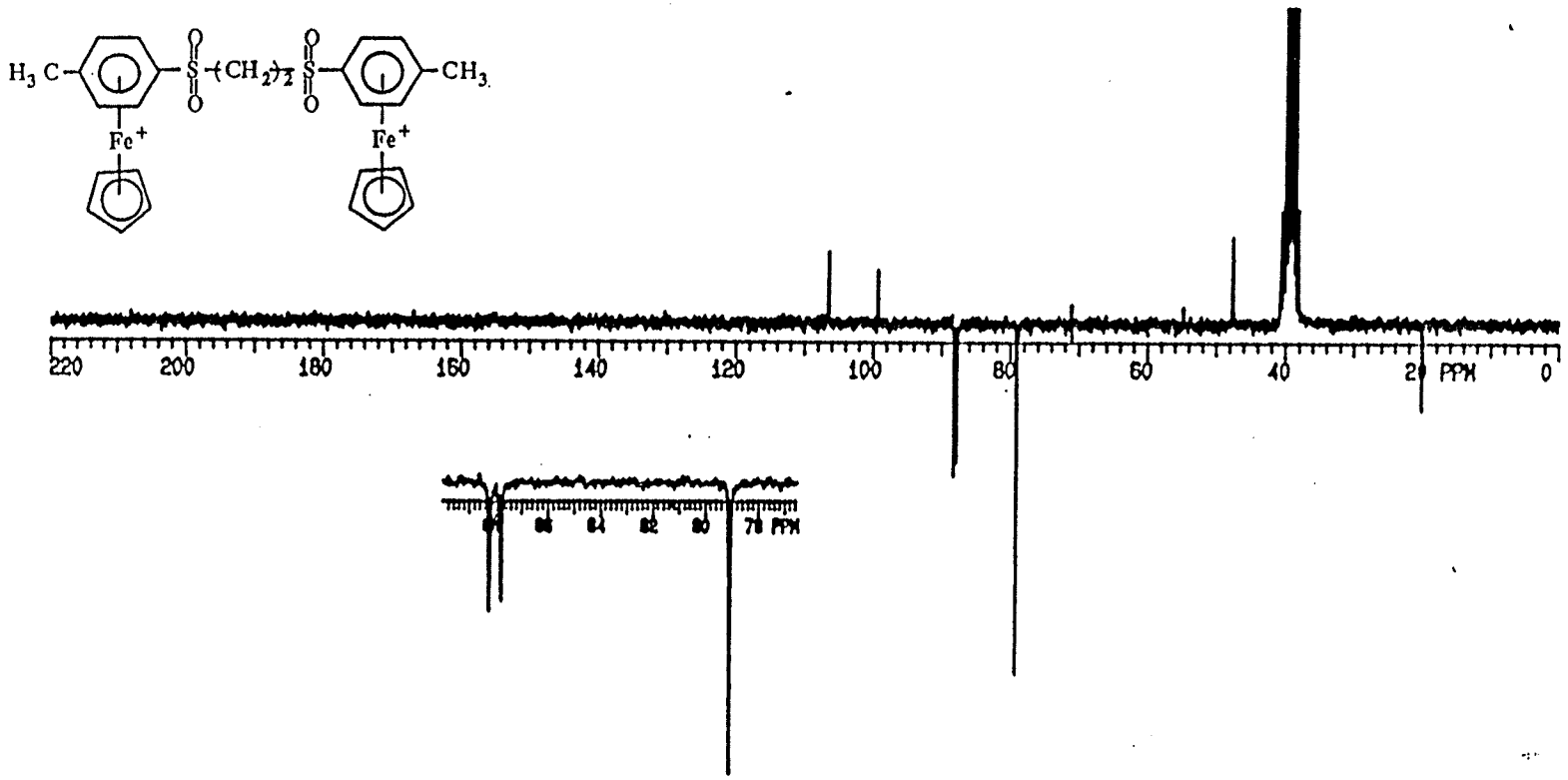
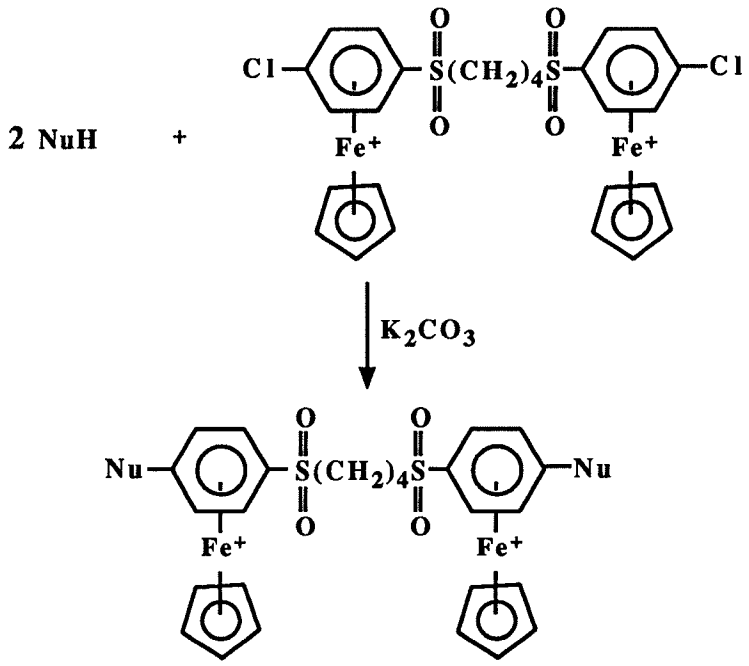


Figure 12: ^{13}C NMR spectrum of 1,4-bis(η^6-4-methyl phenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (11c) in DMSO-d_6.

2.2.2.1. Functionalization of 1,4-Bis(η^6-4-chloro phenylsulfonyl-η^5-cyclopentadienyliron) Butane Hexafluorophosphate

1,4-Bis(η^6-p-chlorophenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (11e) was selected as the representative of these cyclopentadienyliron bimetallic complexes containing sulfonyl functional groups to react with oxygen, sulfur and carbon containing nucleophiles. The reactions of (11e) with thiophenol and phenol were carried out using the methods discussed in section 2.2.1. The reaction of (11e) with thiophenol (Scheme 26) in the presence of potassium carbonate produced the pure desired product, 1,4-bis(η^6-4-thiophenoxy phenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (13a) in a yield of 99%. ^{1}H and ^{13}C NMR and IR were used to confirm the structure. In its ^{1}H NMR spectrum (Figure 13), a very distinctive single appeared at 5.26 ppm which is characteristic of the complexation with the cyclopentadienyliron moiety. Other characteristics of (12a) are that the uncomplexed arene proton appeared in the normal range at 7.63-7.80 ppm and the complexed arene hydrogen appeared upfield at 6.41 and 6.79 ppm. The ^{13}C NMR spectrum (Figure 14) also showed similar characteristics, the uncomplexed arene carbon peaks appeared in normal range (130.85, 131.30 and 135.77 ppm) and the complexed arene carbon peaks appear upfield at 83.45 and 87.06 ppm. However, the reaction of (11e) with phenol in the presence of potassium carbonate in DMF failed to give a clean product (12b), and a mixture was obtained.

The reaction of (12e) with diethyl malonate was carried out in the presence of weak base, K_2CO_3, and under reflux in DMF for 5 hours. This reaction led to the formation of (12c). Once again, ^1H and ^{13}C NMR as well as IR were used to determine the structure of (12c). The spectroscopic results are summarized in Tables 15 and 16.



12a. Nu = SPh

12b. Nu = OPh

12c. Nu = $CH(COOEt)_2$

Scheme 26

Table 15. Yield and ^1H NMR for complexes 12a and 12c.

Comp. No.	Yield (%)	δ (DMSO-d_6, ppm) ArH	Cp	Complexed ArH	Others
12a	99	7.65 (m, 6H)	5.26	6.41 (d, J = 6.7 Hz, 4H)	1.68 (br.s, 4H, CH_2)
		7.75 (m, 4H)		6.79 (d, J = 6.7 Hz, 4H)	3.57 (br.s, 4H, CH_2)
12c #	70		5.38	6.85 (d, J = 5.1 Hz, 4H)	1.31 (t, J = 5.9 Hz, 12H, CH_3)
				7.02 (d, J = 5.1 Hz, 4H)	2.04 (br.s, 4H, CH_2)
					3.68 (br.s, 4H, CH_2)
					4.36 (m, 8H, CH_2)
					5.34 (s, 2H, CH)

The solvent for the NMR study was $(CD_3)_2CO$ instead of DMSO-d_6.

Table 16: IR and ^{13}C NMR for complexes 12a and 12c.

Comp. No.	IR (cm^{-1})	δ (DMSO-d_6, ppm) ArC	Cp	Complexed ArC	Others
12a	1156 (SO_2)	126.60 (2C, ipso)	80.10	83.45 (4C)	20.48 (2C, CH_2)
	1338 (SO_2)	130.85 (4C)		87.06 (4C)	53.24 (2C, CH_2)
		131.30 (2C)		99.73 (2C, ipso)	
		135.77 (4C)		113.71 (2C, ipso)	
12c #	1154 (SO_2)		80.98	89.01 (4C)	14.13 (4C, CH_3)
	1317 (SO_2)			89.19 (4C)	21.70 (2C, CH_2)
	1740 (CO)			101.50 (2C, ipso)	54.80 (2C, CH_2)
				103.38 (2C, ipso)	56.06 (2C, CH)
					63.64 (4C, CH_2)
					166.66 (4C, CO)

The solvent for the NMR study was $(CD_3)_2CO$ instead of DMSO-d_6.

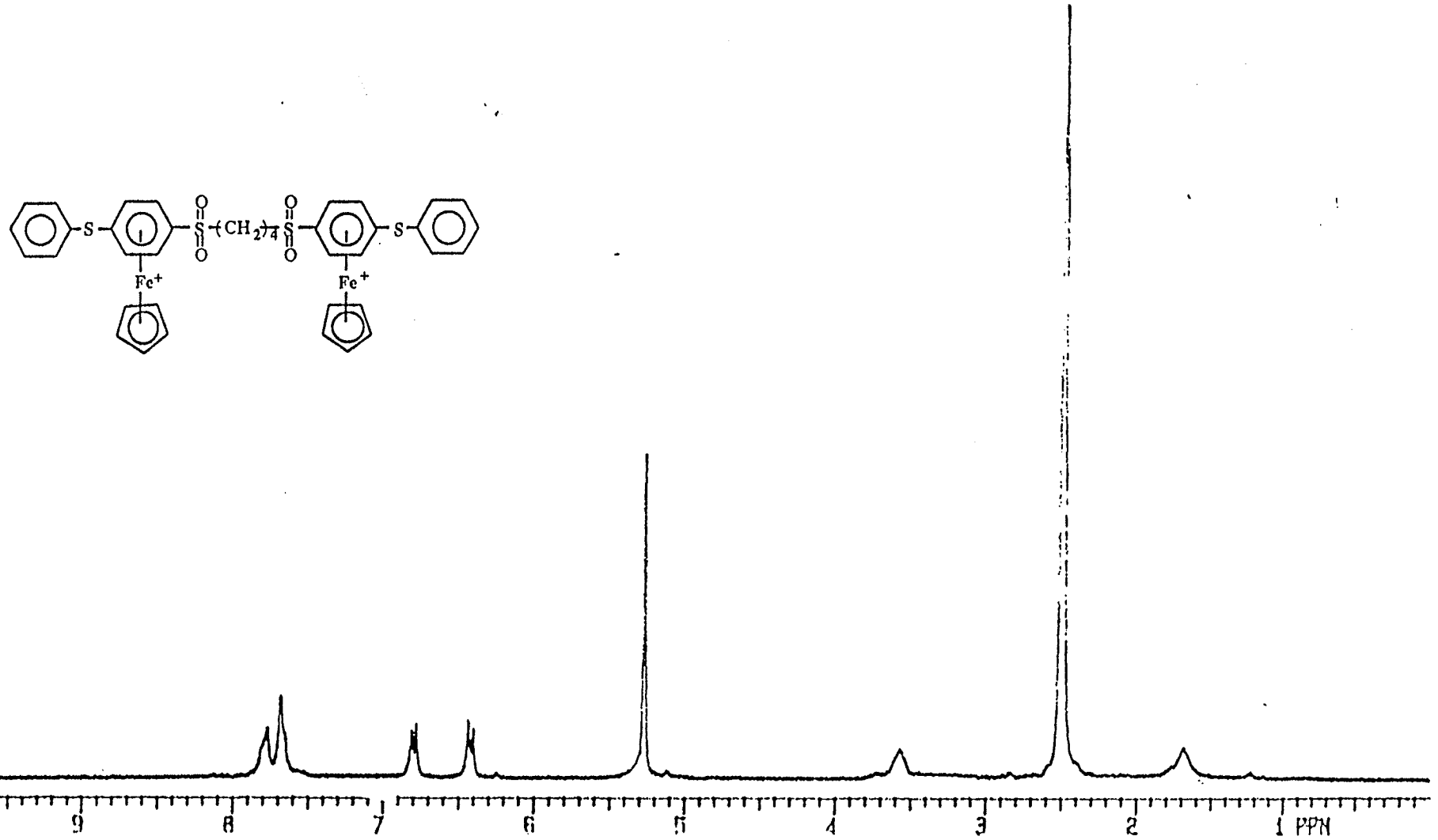


Figure 13: ^1H NMR spectrum of 1,4-bis(η^6-4-thiophenoxy phenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (12a) in DMSO-d_6.

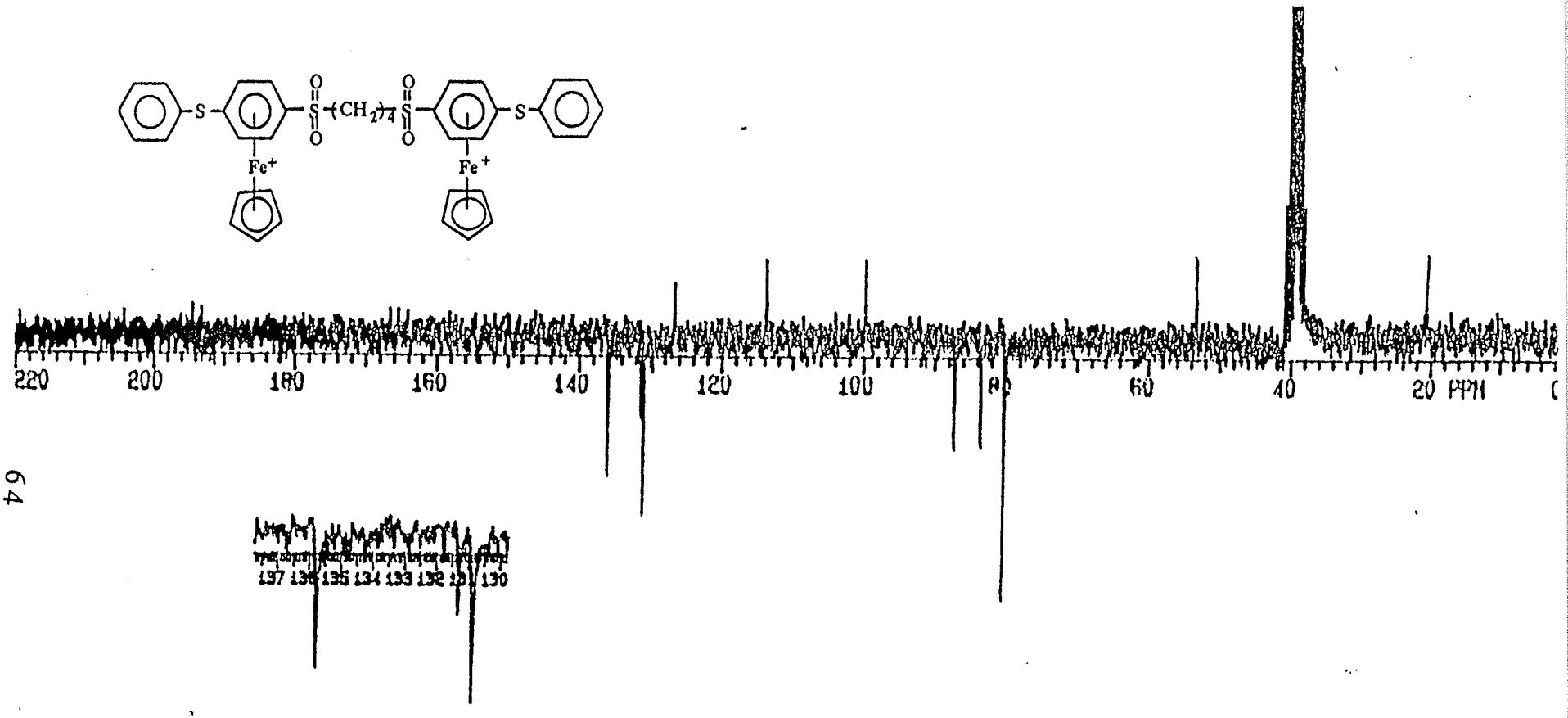
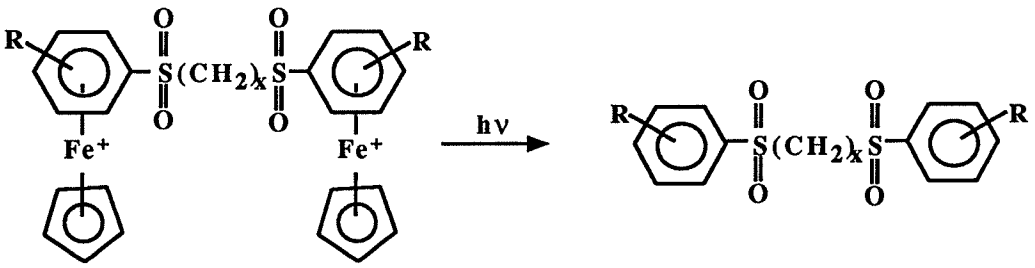


Figure 14: ^{13}C NMR spectrum of 1,4-bis(η^6-4-thiophenoxy phenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (12a) in DMSO-d_6.

2.2.2.2. Photolytic Demetallation of Cyclopentadienyliron Bimetallic Sulfone Complexes

The free diaryl alkyl sulfones were obtained by photolytic cleavage of cyclopentadienyliron moiety from the appropriate complexes as illustrated in Scheme 27.



11a-i

12a, 12c

13a. R=H x=2

13b. R=3-CH_3 x=2

13c. R=4-CH_3 x=2

13d. R=2,6-$(CH_3)_2$ x=2

13e. R=4-Cl x=4

13f. R=2-CH_3 x=4

13g. R=3-CH_3 x=4

13h. R=4-CH_3 x=4

13i. R=3-Cl x=4

13j. R=4-SPh x=4

13k. R=$CH(COOEt)_2$ x=4

Scheme 27

After purification by column chromatography, the products (13a-k) were isolated as white solids, with one exception of a light yellow oil (13g). Identification of these free diaryl alkyl sulfones were carried out by ^{1}H and ^{13}C NMR, MS and IR spectroscopies. The molecular ion peaks as shown in Table 17 prove that the products are sulfones. The major difference between the complexes and the free diaryl alkyl disulfones was the removal of the single Cp peak on the free arenes. The difference between the complex (12a) and the compound (13j) was also shown at the downfield movement of arene proton and carbon peaks. The analytic data are summarized in Tables 17-19. As an example, the NMR spectra of compound (13k) are shown in Figures 15 and 16.

Table 17: MS and ^{1}H NMR data for compounds 13a-k.

Compound No.	m/e (M^+, %)	δ ($CDCl_3$, ppm) Ar	Others
13a	366 (100)	7.52-7.71 (m, 6H) 7.86 (d, J = 7.2 Hz, 4H)	3.42 (s, 4H, CH_2)
13b	338 (46)	7.46 (m, 4H), 7.64 (m, 4H)	2.44 (s, 6H, CH_3), 3.40 (s, 4H, CH_2)
13c	338 (42)	7.36 (d, J = 7.9 Hz, 4H) 7.72 (d, J = 8.5 Hz, 4H)	2.45 (s, 6H, CH_3), 3.38 (s, 4H, CH_2)
13d	366 (24)	7.16(d, J = 7.3 Hz, 4H) 7.36 (t, J =7.7 Hz, 2H)	2.63 (s, 12H, CH_3), 3.50 (s, 4H, CH_2)
13e	407 (21) 409 (14) 411 (2)	7.53 (d, J = 8.7 Hz, 4H) 7.80 (d, J = 8.7 Hz, 4H)	1.84 (m, 4H, CH_2), 3.04 (m, 4H, CH_2)
13f	366 (38.4)	7.32 (t, J = 7.4 Hz, 4H) 7.49 (t, J = 6.7 Hz, 2H) 7.90 (d, J = 7.9 Hz, 2H)	1.81 (br.s, 4H, CH_2), 2.64 (s, 6H, CH_3) 3.07 (br.s, 4H, CH_2)
13g	366 (51)	7.24 (br.s, 4H) 7.45 (br.s, 4H)	1.60 (br.s, 4H, CH_2), 2.22 (s, 6H, CH_3) 2.84 (br.s, 4H, CH_2)
13h		7.33 (d, J = 8.3 Hz, 4H) 7.72 (d, J = 8.3 Hz, 4H)	1.78 (t, J = 7.3 Hz, 4H, CH_2) 2.43 (s, 6H, CH_3) 2.98 (t, J = 7.3 Hz, 4H, CH_2)
13i	407 (18) 409 (12) 411 (2)	7.52 (t, J = 7.7 Hz, 2H) 7.62 (d, J = 8.0 Hz, 2H) 7.75 (d, J = 7.5 Hz, 2H) 7.84 (s, 2H)	1.85 (br.s, 4H, CH_2), 3.06 (br.s, 4H, CH_2)

13j	554 (38)	7.22 (m, 4H), 7.49 (m, 10H) 7.67 (m, 4H)	1.80 (br.s, 4H, CH_2), 3.02 (br.s, 4H, CH_2)
13k	654 (12)	7.61 (d, J = 8.4 Hz, 4H) 7.85 (d, J = 8.4 Hz, 4H)	1.25 (t, J = 7.1 Hz, 12H, CH_3) 1.82 (t, J = 3.4 Hz, 4H, CH_2) 3.05 (t, J = 3.4 Hz, 4H, CH_2) 4.21 (m, 8H, CH_2) 4.68 (s, 2H, CH)

Table 18: ^{13}C NMR data for compounds 13a-k.

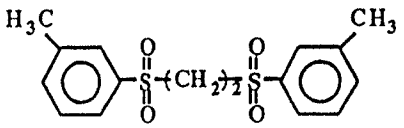
Compound No.	δ ($CDCl_3$, ppm) Ar	Others
13a	128.04 (4C), 129.69 (4C) 134.54 (2C), 138.00 (2C, ipso)	49.48 (2C, CH2)
13b	125.16 (2C), 128.28 (2C) 129.50 (2C), 135.31 (2C) 137.84 (2C, ipso), 140.14 (2C, ipso)	21.33 (2C, CH_3), 49.53 (2C, CH_2)
13c	128.09 (4C), 130.30 (4C) 135.03 (2C, ipso), 145.75 (2C, ipso)	21.71 (2C, CH_3), 49.73 (2C, CH_2)
13d	131.86 (4C), 133.42 (2C) 134.96 (2C, ipso), 140.18 (4C, ipso)	22.93 (4C, CH_3), 48.31 (2C, CH_2)
13e	129.51 (4C), 129.79 (4C) 137.26 (2C, ipso), 140.78 (2C, ipso)	21.54 (2C, CH_2), 55.47 (2C, CH_2)
13f	126.64 (2C), 130.09 (2C) 132.82 (2C), 133.81 (2C) 136.82 (2C, ipso), 137.85 (2C, ipso)	20.32 (2C, CH_3), 21.33 (2C, CH_2) 51.45 (2C, CH_2)
13g	124.78 (2C), 127.92 (2C) 128.98 (2C), 134.42 (2C) 138.34 (2C, ipso), 139.45 (2C, ipso)	21.05 (2C, CH_3), 21.25 (2C, CH_2) 55.07 (2C, CH_2)
13h	127.98 (4C), 129.96 (4C) 135.83 (2C, ipso), 144.89 (2C, ipso)	21.60 (2C, CH_3), 21.60 (2C, CH_2) 55.50 (2C, CH_2)

13i	126.11 (2C), 128.09 (2C) 130.74 (2C), 134.11 (2C) 135.73 (2C, ipso), 140.53 (2C, ipso)	21.39 (2C, CH_2), 55.34 (2C, CH_2)
13j	127.16 (4C), 128.36 (4C) 129.44 (2C), 129.91 (4C) 134.54 (4C), 130.58 (2C, ipso) 135.21 (2C, ipso), 147.14 (2C, ipso)	21.52 (2C, CH_2), 55.44 (2C, CH_2)
13k	128.17 (4C), 128.60 (4C) 138.62 (2C, ipso), 138.87 (2C, ipso)	13.91 (4C, CH_3), 21.39 (2C, CH_2) 55.31 (2C, CH_2), 57.58 (2C, CH) 62.26 (4C, CH_2), 167.07 (4C, CO)

Table 19: Yield and IR data for compounds 13a-k

Compound No.	Yield (%)	d.p. (°C)	IR (cm^{-1}) (ν_{SO2})
13a	93	73.5-75	1152, 1310
13b	88	99.5-101	1141, 1320
13c	95	201-202	1153, 1321
13d	70	233-237	1154, 1315
13e	80	184-186	1151, 1309
13f	62	157-159 *	1149, 1319
13g	89	oil	1140, 1312
13h	97	112-114.5	1151, 1320
13i	64	148-151.5	1157, 1328
13j	71	109.5-111.5	1153, 1290
13k	85	92-95.5 *	1152, 1310 1735 (CO)

* These are mp instead of d.p.



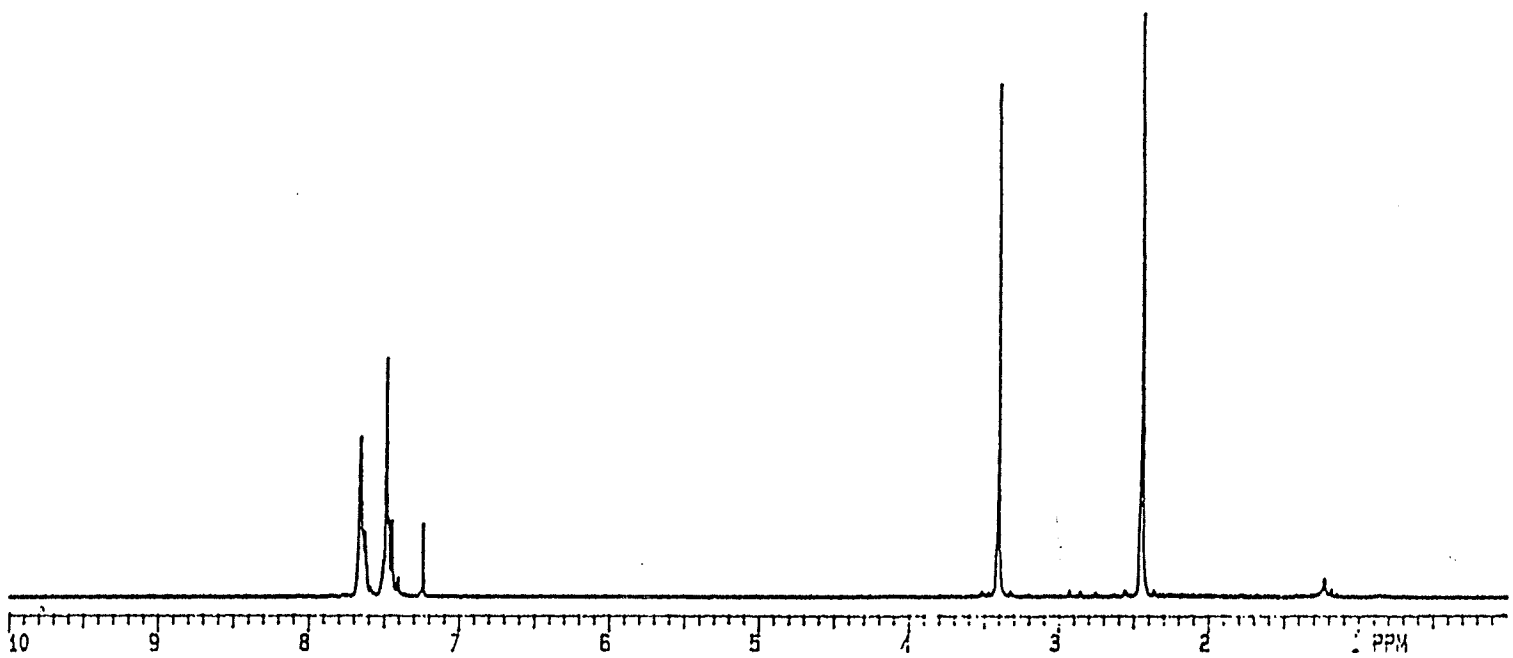


Figure 15: ^{1}H NMR spectrum of 1,2-bis(3-methyl phenoxysulfonyl) ethane (13b) in $CDCl_3$.

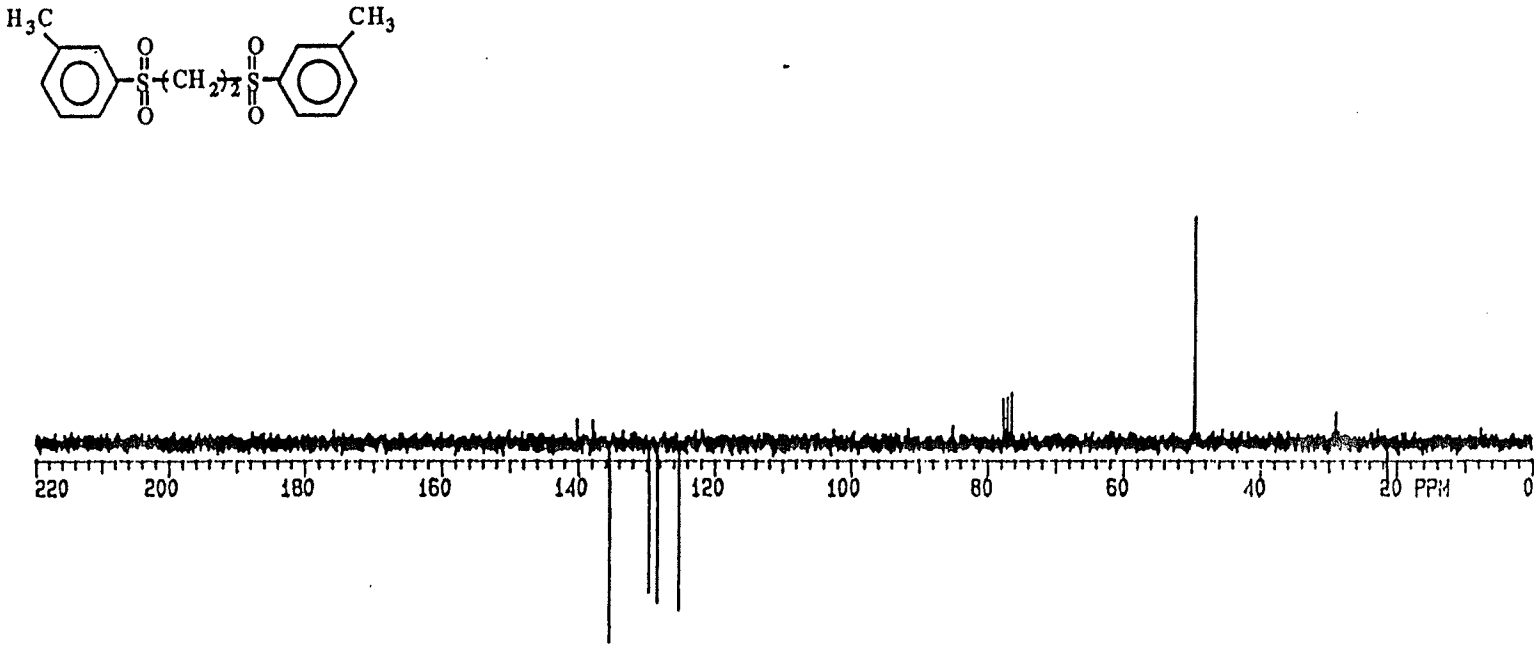


Figure 16: ^{13}C NMR spectrum of 1,2-bis(3-methyl phenoxysulfonyl) ethane (13b) in $CDCl_3$.

Chapter 3: Experimental

3.1. Chemicals and Instruments

Aluminum powder, anhydrous aluminum chloride, ferrocene, chloroarenes, aliphatic diols and dithiols, phenol, thiophenol, diethyl malonate, potassium tert-butoxide, potassium carbonate, ammonium hexafluorophosphate, magnesium sulfate, and m-chloroperbenzoic acid (m-CPBA) are commercially available and were used without further purification. All solvents, dimethylformamide (DMF), acetonitrile, chloroform, dichloromethane, hexane, diethyl ether, diethyl acetate and decalin, were reagent grade and were used without further purification, with the exception of freshly distilled tetrahydrofuran (THF). 60-100 mesh of silica gel was used in the column chromatographic purification of the free arenes demetallated from the corresponding bimetallic iron complexes.

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz on a Varian Gemini 200 NMR Spectrometer with chemical shifts (ppm) being calculated from the solvent signals. Deuteroacetone ($(CD_3)_2CO$) or deuterodimethylsulfoxide (DMSO-d_6) and deuterochloroform ($CDCl_3$) were used as solvents for the complexes and free arenes. IR spectra were recorded on a Perkin-Elmer 781 Spectrophotometer. MS were obtained on a Hewlett-Packard 5970 Series Mass Selective Detector, by electron impact (70ev) with signals given in m/z units. Melting points were measured in a capillary using a Mel-TempII and are uncorrected.

3.2. Experimental Details

3.2.1. Preparation of Diaryl Alkyl Diethers and Disulfides

3.2.1.1. Preparation of Bis(η^6-phenoxy-η^5-cyclopentadienyl iron) Alkane Hexafluorophosphates

In a 25 mL round bottom flask were placed 0.2693g (2.4 mmol) of potassium tert-butoxide, 4 mL of freshly distilled THF, and 2.0 mmol of the appropriate aliphatic diol (2a-f). This white cloudy mixture was stirred under a nitrogen atmosphere for 40 minutes, then 1.0 mL of DMF and 3.0 mL of THF were added to the reaction flask and the mixture was stirred for 20 minutes. To this reaction mixture, 2.0 mmol of the appropriate chloroarene cyclopentadienyliron(II) complex (1a-e) was added, and the reaction mixture was stirred at room temperature, under a nitrogen atmosphere for 17 hours.

The red reaction mixture was filtered into 20 mL of 10% HCl. The reaction flask was washed with acetone and the wash was also filtered into the filtrate. The acetone was removed under reduced pressure using a rotary evaporator (Buchi RE-111). Next a concentrated aqueous ammonium hexafluorophosphate (NH_4PF_6) solution was added to the filtrate. The product was extracted with CH_2Cl_2 (2x30 mL), and washed with distilled water (5x50 mL). After drying over $MgSO_4$, the solution was filtered and concentrated by rotary evaporation. The product was precipitated as yellow powder on addition of diethyl ether. Then the

yellow precipitate was filtered and dried over vacuum to yield the final products (3a-k and 4). The yield and NMR data for these products are summarized in Tables 2 and 3.

3.2.1.2. Preparation of Bis(η^6-thiophenoxy-η^5-cyclopentadienyliron) Alkane Hexafluorophosphates

In a 50 mL round bottom flask equipped with a magnetic stir bar were placed 0.4838g (3.5 mmol) of potassium carbonate, 2.0 mmol chloroarene cyclopentadienyliron(II) complexes, and 1 mmol of the appropriate aliphatic dithiol and 10 mL of mixted solvent of THF and DMF (4:1). This mixture was then stirred under a nitrogen atmosphere at room temperature for 17 hours. The yellow reaction solution was filtered into 15 mL of 10% HCl. The reaction flask was washed with acetone and the wash was filtered to the filtrate. After the removal of acetone by a rotary evaporator, concentrated aqueous ammonium hexafluorophosphate was added to the mixture. The addition of distilled water resulted in a yellow precipitate which was filtered, washed with distilled water (3x20 mL) and diethyl ether (3x20 mL), and dried under vacuum overnight to give rise to the final products (6a-j and 10a-c).

3.2.1.3 Photolytic Demetallation of Bis(η^6-arene-η^5-cyclopentadienyliron) Complexes With Aliphatic Ether and Thioether Linkages

The bis(η^6-arene-η^5-cyclopentadienyliron) complexes (3l-k, 4, and 6a-j) were dissolved separately with a small amount of CH_3CN in 50 mL of Pyrex photolytic tubes in which CH_2Cl_2 was added to a volume of 40 mL. The solution was deoxygenated for half an hour before the photolytic tube was irradiated with a Xenon lamp at room temperature for 4 hours. The solvent was concentrated to a volume of 1-2 mL using a rotary evaporator. The residue was purified through a silica gel column. The ferrocene was washed out with hexane and the products (5a-l and 6a-j) were eluted with chloroform. Removal of the solvent from the eluate gave the expected liberated arenes. Once dried under vacuum, the yield, m.p. and ^1H and ^{13}C NMR were determined and are listed in Tables 5-8.

3.2.2. Functionalization of 1,4-bis(η^6-p-chlorothiophenoxy-η^5-cyclopentadienyliron) Butane Hexafluorophosphate

3.2.2.1. Reaction With Thiophenol

To a 50 mL round bottom flask equipped with a stir bar, 0.4365 g (0.5 mmol) of 1,4-bis(η^6-4-chlorothiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (6j), 0.5529 g (4.0 mmol) of potassium carbonate, 0.13 mL (1.2 mmol) of thiophenol and 12 mL of a solvent

mixture of THF and DMF (2:1) were added. This mixture was then stirred under a nitrogen atmosphere at room temperature for 17 hours. The red reaction mixture was filtered into 20 mL of 10% HCl. The flask was washed with 4 mL of DMF and then acetone, and the wash was also added to the reaction mixture. The acetone was removed under reduced pressure using a rotary evaporator. Concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture. The product was extracted with CH_2Cl_2 and then washed with distilled water (5x50 mL). After drying over $MgSO_4$, the solution was concentrated by rotary evaporation. Addition of diethyl ether resulted in a yellow precipitate which was filtered, washed with diethyl ether and dried under vacuum. The yield of 1,4-bis(η^6-4-thiophenoxythiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (8a) was 87% and the NMR data are given in Tables 8 and 9.

3.2.2.2. Reaction With Phenol

0.4202 g (0.48 mmol) of 1,4-bis(η^6-4-chlorothiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (6j), 0.1192 g (1.15 mmol) of phenol, 0.5529 g (4.0 mmol) of potassium carbonate and 5 mL of DMF were placed in a 50 mL round bottom flask. The mixture was then stirred under nitrogen at room temperature for 16 hours. The reaction mixture was filtered into 20 mL of 10% HCl, the reaction flask was washed with acetone, and the wash was added to the reaction mixture. After removal of acetone by rotary evaporation, a concentrated aqueous ammonium hexafluorophosphate was added to the concentrated

reaction mixture. The product was extracted with CH_2Cl_2, then washed with water (3x50 mL). The reaction mixture was dried over $MgSO_4$, concentrated by a rotary evaporator. The product (8b) was then precipitated by diethyl ether, filtered and dried under vacuum before analysis. The yield of 1.4-bis(η^6-4-phenoxythiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate was 92%. The ^1H and ^{13}C NMR are listed in Tables 8 and 9.

3.2.2.3. Reaction With Diethyl Malonate

0.3518 g (0.4 mmol) of 1,4-bis(η^6-4-chlorothiophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (6j), 0.4146 g (3.0 mmol) of potassium carbonate, 0.1569 g (0.88 mmol) of diethyl malonate and 3 mL of DMF were placed in a 25 mL round bottom flask equipped with a magnetic stir bar. The brown reaction mixture was stirred under nitrogen and under refluxing. The reaction mixture changed to cherry red in 10 minutes. After stirring for 5 hours, the cherry red mixture was filtered into 15 mL of 10% HCl and washed with acetone and the wash was added to the reaction mixture. The acetone was removed by rotary evaporation. Concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture. The product was extracted with CH_2Cl_2 and washed with distilled water (5x50 mL). After drying over $MgSO_4$, the reaction mixture was concentrated by rotary evaporation. Addition of diethyl ether resulted in the precipitate which was filtered, washed with diethyl ether and dried over vacuum. The product (8c) was obtained in 87% yield. The yield,

and the NMR data are listed in Tables 8 and 9.

3.2.2.4. Photolytic Demetallation of 1,4-Bis(η^6-4-thiophenoxythiophenoxy-η^5-cyclopentadienyliron) Butane Hexafluorophosphate (8a), 1.4-Bis(η^6-4-phenoxy thiophenoxy-η^5-cyclopentadienyliron) Butane Hexafluorophosphate (8b), and 1,4-Bis(η^6-4-diethyl malonate-η^5-cyclopentadienyliron) Butane Hexafluorophosphate (8c)

In 50 mL Pyrex tubes were dissolved the 0.2293 g (0.22 mmol) of (8a), 0.3151 g (0.32 mmol) of (8b), or 0.2786 g (0.25 mmol) of (8c), separately, with acetonitrile. The CH_2Cl_2 was added to these Pyrex tubes until the total volume was 40 mL. These solutions were deoxygenated by bubbling nitrogen through them for half an hour, then these tubes were placed in a photochemical apparatus equipped with Xenon lamp and irradiated at room temperature for 4 hours. The solvent was concentrated to 1-2 mL using rotary evaporation. The residues were purified through a silica gel column. The ferrocene was washed out with hexane and the products (9a) and (9b) were eluted with chloroform and product (9c) was eluted with ethyl acetate. Removal of the solvent from the eluates gave the expected free arenes. Their yields and NMR data are summarized in Tables 10 and 11.

3.2.3. Synthesis of Bis(phenylsulfonyl) Alkanes

3.2.3.1. Preparation of Bis(η^6-arylsulfonyl-η^5-cyclopentadienyliron) Alkane Hexafluorophosphates

In a 50 mL round bottom flask was dissolved 0.5 mmol of the appropriate bis(η^6-thiophenoxy-η^5-cyclopentadienyliron) alkane hexafluorophosphate (6a-c, 6e-f, 6i and 10a-c) with about 2 mL DMF. A mixture of 0.6902 g (4 mmol) of m-chloroperbenzoic acid, 2 mL of DMF and 3 mL of CH_2Cl_2 was slowly added to this flask. The mixture was stirred and refluxed at 70°C for 5 hours. After the removal of CH_2Cl_2 by rotary evaporation, addition of diethyl ether resulted in precipitate which was filtered and washed with a solvent mixture of chloroform and diethyl ether (3:2) (5x20 mL) and with diethyl ether (2x20 mL). By drying over vacuum, the final products (11a-i) were obtained in 72% to 93% yield and were analyzed by ^1H and ^{13}C NMR, yield and IR which are given in Tables 12-14.

3.2.3.2. Reaction of 1,4-Bis(η^6-chlorophenylsulfonyl-η^5-cyclopentadienyliron) Butane Hexafluorophosphate With Diethyl Malonate

The similar procedure applied in the synthesis of (8c) was used in this study. In a 25 mL round bottom was placed 0.3358 g (0.35 mmol) of 1,4-bis(η^6-p-chlorophenylsulphonyl-η^5-cycleopentadienyliron) butane hexafluorophosphate, 0.1260 g (0.787 mmol) of diethyl malonate,

0.3507 g (2.5 mmol) of potassium carbonate and 3 mL of DMF. This mixture was stirred under a nitrogen atmosphere and under refluxing (50-55°C) for 5 hours. A cherry red solution was observed after 10 minutes. The cherry red reaction mixture was filtered into 20 mL of 10% HCl to give a yellow mixture. The reaction flask was washed with acetone and the wash was also added to the yellow reaction mixture. Addition of concentrated aqueous ammonium hexafluorophosphate gave rise to a precipitate which was filtered. The filtrate was extracted with CH_2Cl_2 and washed with distilled water. After drying over $MgSO_4$, the filtrate was concentrated. The product was precipitated by adding diethyl ether. The two portions of product were added together, washed with diethyl ether and then dried over vacuum before analysis. The yield of 1,4-bis(η^6-4-diethyl malonate-η^5-cyclopentadienyliron) butane hexafluorophosphate (12c) is 70%. The analytical results are summarized in Tables 15 and 16.

3.2.3.3. Reaction of 1,4-Bis(η^6-4-chlorophenylsulfonyl-η^5-cyclopentadienyliron) Butane Hexafluorophosphate With Thiophenol

The procedure used here is similar to the procedure for the synthesis of (8a). The reagents, 0.4658 g (0.5 mmol) of 1,4-bis(η^6-4-chloro phenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate, 0.125 mL (1.2 mmol) of thiophenol, 0.5594 g (4.0 mmol) of potassium carbonate, 6 mL of THF and 4 mL of DMF, were placed in a 50 mL round bottom flask and stirred at room temperature

under nitrogen for 17 hours. The red-drown reaction mixture was filtered into 20 mL of 10% HCl and the reaction flask was washed with acetone. Concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture. Addition of distilled water resulted in the precipitation of the product which was filtered, washed with distilled water (3x30 mL) and diethyl ether (3x30 mL), and dried over vacuum. The yield of 1,4-bis(η^6-4-thiophenoxyphenylsulfonyl-η^5-cyclopentadienyliron) butane hexafluorophosphate (12a) was 99%. The ^1H and ^{13}C NMR results are given in Tables 15 and 16.

3.2.3.4. Photolytic Demetallation of Bis(η^6-arylsulfonyl-η^5-cyclopentadienyliron) Alkane Hexafluorophosphates

The general photolytic procedure was used in this study. The bimetallic complexes of (11a-i, 12a and 12c) were separately dissolved in 50 mL of Pyrex tubes with CH_3CN and CH_2Cl_2. The solutions were deoxygenated by bubbling nitrogen through for half an hour. Then the Pyrex tubes were equipped in a photochemical apparatus and irradiated under Xenon lamp at room temperature for 4 hours. The solvents were removed by a rotary evaporation to a volume of 1-2 mL. The residues were purified separately through a silica gel column. The impurities were washed out with hexane and the products were eluted with ethyl acetate. The removal of the solvent from the eluate gave the expected pure free arenes (13a-k).

Conclusion

Double aromatic nucleophilic substitution reaction (S_NAr) of chloroarenes activated by cyclopentadienyliron moiety with diols and dithiols and subsequent photolytic demetallation is a useful and successful route for the synthesis of diaryl alkyl ethers and thioethers. This methodology was applied to various diols or dithiols, from 1,2-ethanediol, having short alkyl chain, to 1,12-dodecanediol, having a long alkyl chain, and to branched 1,2-propanediol. The chloroarene used in this method included nonsteric hindrance, chlorobenzene, and steric hindrance, 2,6-dimethylchlorobenzene. It was found that there is no significant steric hindrance on either the arene ring or the alkyl chain.

The diiron complexes with chloro groups on the arene rings allows for the introduction of other functional groups or for polymerization. The phenoxyl, thiophenoxyl, and diethyl malonate were introduced to a diiron complex by nucleophilic substitution of 1,4-bis(η^6-4-chlorophenoxy-η^5-cyclopentadienyliron) butane hexafluorophosphate (6j) with phenol, thiophenol, and diethyl malonate in the presence of potassium carbonate.

This technique has advantages over the other methods due to the mild reaction conditions.

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