The Design of Functionalized Organoiron and Organic Polymers Containing Azo Dyes and Calixarenes

by

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Abstract

Organic azo dye polymers are prepared from the ring-opening metathesis polymerization of azo dye functionalized norbornenes. These polymers are examined for their *trans-cis* isomeration, UV-visible properties, and their acid sensing capabilities. The organoiron polymers are prepared through polycondensation reactions between organoiron azo dye complexes and O-, S-, or N-containing dinucleophiles. These polymers are analyzed for their thermal and UV-visible properties.

Next, the synthesis and characterization of upper rim functionalized calix[4]arenes are described. Calix[4]arenes containing propanol groups on either the 5- or both the 5- and 11-positions were prepared. These calix[4]arenes also contained either: phenolic, propoxy, or *t*-butyl-dimethyl-siloxy groups on the lower rim. These calixarenes were reacted with chloro-terminated organoiron carboxylic acid complexes to prepare metallocalix[4]arenes containing one, two, or four metal centres on their upper rims. The metallocalix[4]arenes were used to prepare calix[4]arene containing azo dyes, or ferrocenes. These metallocalix[4]arenes were also used to prepare organoiron based polycalixarenes. Organic polymers were also prepared from the organic upper rim propanol functionalized calix[4]arenes. The metallocalix[4]arenes were additionally studied for their electrochemical properties. The azo dye containing metallocalix[4]arenes were studied for their UV-visible properties and acid sensing capabilities. The polycalix[4]arenes were additionally studied through gel permeation chromatography, thermal gravimetric analysis and differential scanning calorimetry.

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*`Cp	Non-functionalized cyclopentadienyl ring of ferrocene-1-carboxylic acid.
*Cp	Functionalized cyclopentadienyl ring of ferrocene-1-carboxylic acid
Conc.	Concentrated
°C	Degrees Celsius
^{13}C NMR	Carbon 13 nuclear magnetic resonance spectroscopy
^{1}H NMR	Proton nuclear magnetic resonance spectroscopy
2MeTHF	2-methyltetrahydrofuran
Ar	Aryl
bp	Boiling point
br	broad
calc.	calculated
Cp	cyclopentadienyl ring
d	Doublet
d_6	6 deuterium
DCC	Dicyclohexylcarbodiimide
DCM	Dichloromethane
DCU	Dicyclohexylurea

dd	doublet of doublets
ddd	doublet of doublets of doublets
DMAP	N,N'-dimethylaminopyridine
DMF	N,N'-dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
dt	Doublet of triplets
eq.	Equivalents
Et	Ethyl
gCOSY	Gradient correlation spectroscopy
gHMBC	Gradient heteronuclear correlation spectroscopy
gHSQC	Gradient heteronuclear single quantum correlation
GPC	Gel permeation chromatography
HMBC	Heteronuclear correlation spectroscopy
HPLC	High performance liquid chromatography
Hz	Hertz
IR	Infrared spectroscopy
J	J value

Kcal	kilocalorie
M	Molar
m	Multiplet
m	Meta
MeOH	Methanol
MHz	Mega hertz
min	Minute
mL	Millilitre
mom	Millimolar
mmol	Millimoles
mol	Moles
nm	Nanometer
NMR	Nuclear magnetic resonance spectroscopy
o	Ortho
p	Para
PDI	Polydispersity index
pK_a	-log of the Acid dissociation constant
ppm	parts per million

Pr	Propyl
q	Quartet
RBF	Round bottom flask
ROMP	Ring opening metathesis polymerization
s	Singlet
t	Triplet
t	tert
TBDMS	Tertbutyldimethylsilane
T_g	Glass transition temperature
THF	Tetrahydrofuran
UV	Ultraviolet
UV-vis	Ultraviolet visible
ws	weak shoulder
Δ	Heat
δ	Chemical shift
λ_{ex}	Excitation wavelength

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"I just want to say one word to you...just one word. Are you listening? Plastics."

--Mr. McGuire to Benjamin Braddock, The Graduate (1967)

Chapter 1 Introduction

1.1 Polymers

There have been many breakthroughs in chemistry from its birth as alchemy to the present day. However, none of these discoveries is perhaps greater than the discovery of polymers, or macromolecules. Polymer chemistry has its roots in the late 1700s. However, research into polymer synthesis didn't really begin until the early 1800s when Goodyear developed a vulcanized rubber by heating natural rubber with sulfur. Baekeland prepared the first truly synthetic polymer in the 1900s. However, it was not until the 1930s when research in polymer chemistry really exploded with the synthesis of Nylon 6,6 by Carothers (Figure 1-1).[1]

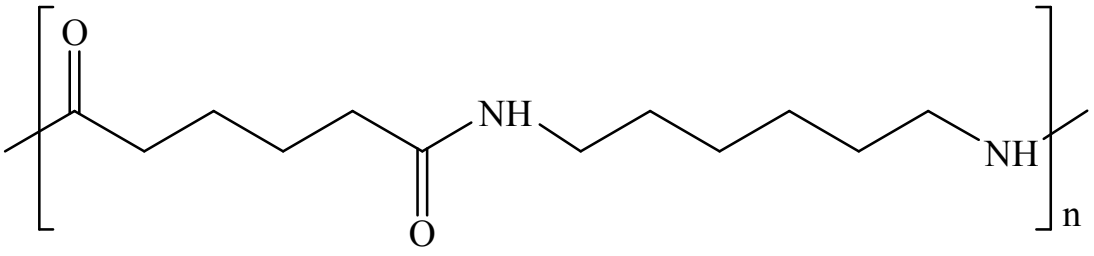


Figure 1-1: Structure of nylon 6,6.

There are millions of different polymers and methods to prepare them. Of the many families of polymers, this dissertation focuses on the preparation of linear polymers. This family of polymers may possess many different pendent groups, side chains, and functionalities, but they all possess the commonality of a single linear back bone (Figure 1-2).

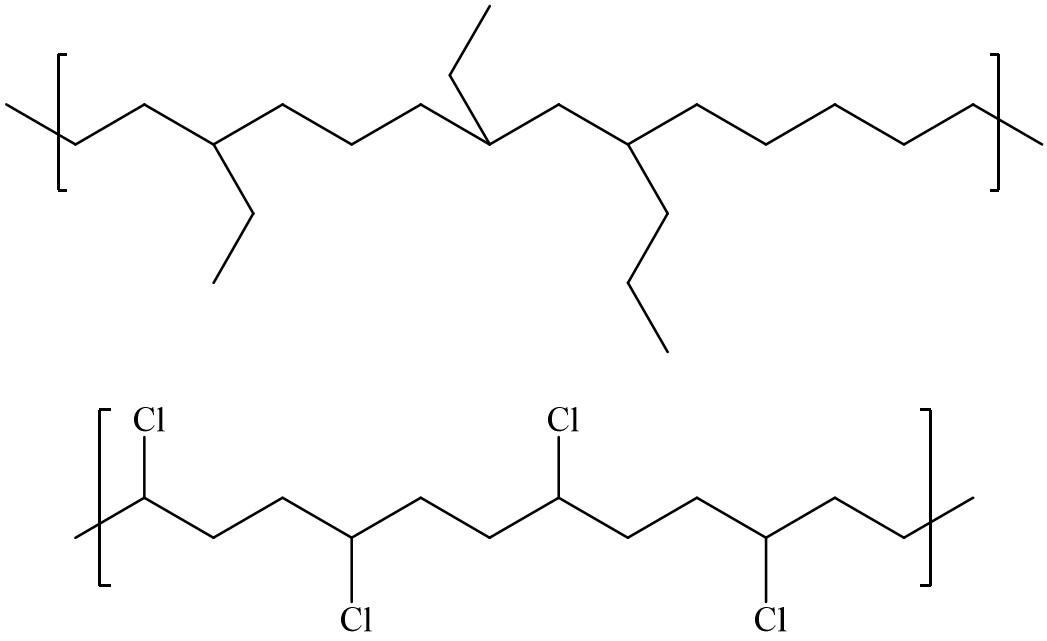


Figure 1-2: Linear polymers: polyethylene (top); polyvinylchloride (bottom).

There are several methods to prepare linear polymers such as: radical-, condensation-, ring opening metathesis-, and ring opening-polymerization. Two of these methods will be utilized in further chapters; these are condensation polymerization and ring-opening metathesis polymerization (ROMP).

1.1.1 Condensation polymerization

Condensation polymerization reacts two di-functional compounds to form long chains while eliminating a small molecule such as H_2O or HCl (Figure 1-3).

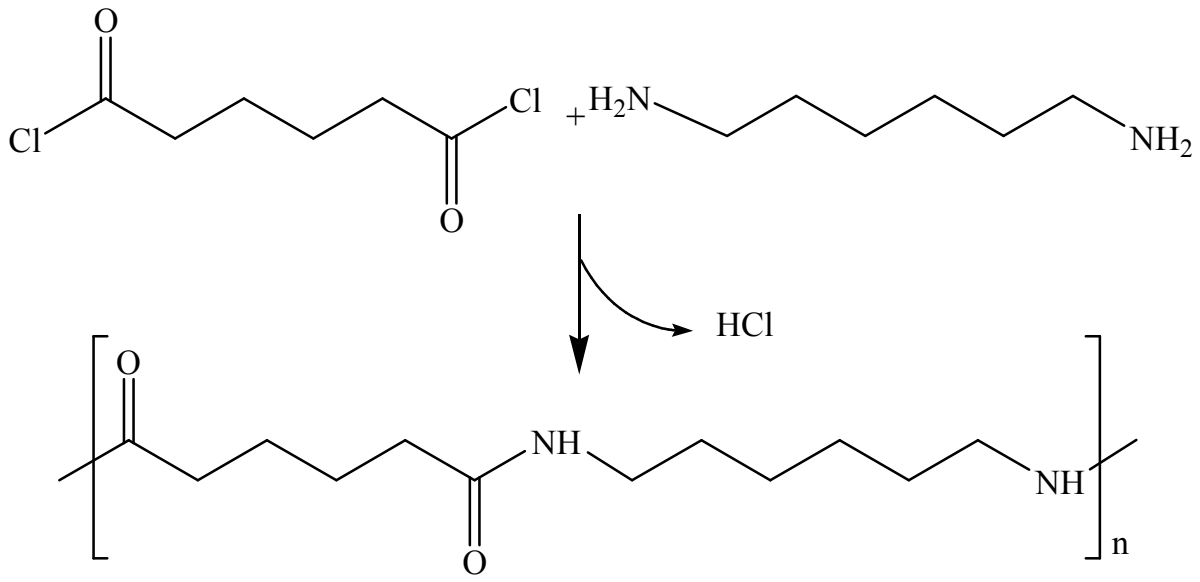


Figure 1-3: Polycondensation between adipoylchlroide and 1,6-hexane diamine.

In the early days of polymer chemistry, it was thought that polymers would possess lower reactivity,[2] since large molecules should be slow moving in solution and therefore the possibility of reactive collisions would be reduced. Fortunately, this is not the case. The reactive ends of large polymers, while attached to large slow moving molecules, are as active as their analogous small molecules. For example, studies on the reaction kinetics of ester formation of dicarboxylic large molecules and small mono carboxylic molecules showed that as the length of the spacer between the carboxylic acid groups increased, the reactivity of the functional site remained very similar to that of the analogous mono acid (**Table 1-1**).[2] Since, the reactive sites are on the termini, they behave independently of the length of spacer and are essentially separate reactive sites; therefore regardless of the length spacer the reactive sites maintain their reactivity.

Table 1-1: Reaction rates of mono- and di-carboxylic acid compounds

n* (length of spacer)	$H(CH_2)_nCOOH$ (gram equivalents/L)$^{-1}$sec^{-1})	$HOOC(CH_2)_nCOOH$ (gram equivalents/L)$^{-1}$sec^{-1})
3	7.5	8.7
4	7.4	8.4
5	7.4	7.8
6	7.4	7.3
7	7.4	7.3

Condensation polymerization is very susceptible to premature chain termination. Therefore, it is important to ensure that equimolar amounts of each di-functional reactant are used. If either of the reactants is used in excess it is possible to obtain low molecular weight polymers due to incorporation of the excess reactant which causes premature chain termination.[2] It is also necessary to perform polycondensation reaction at high concentrations. This is due to the fact that di-functional reactants can also form cyclic structures (Figure 1-4). By using very concentrated reaction mixtures the chances of producing the cyclic structures is greatly reduced because the likelihood of two adjacent molecules in solution is greater than that of an intramolecular reaction forming a ring.

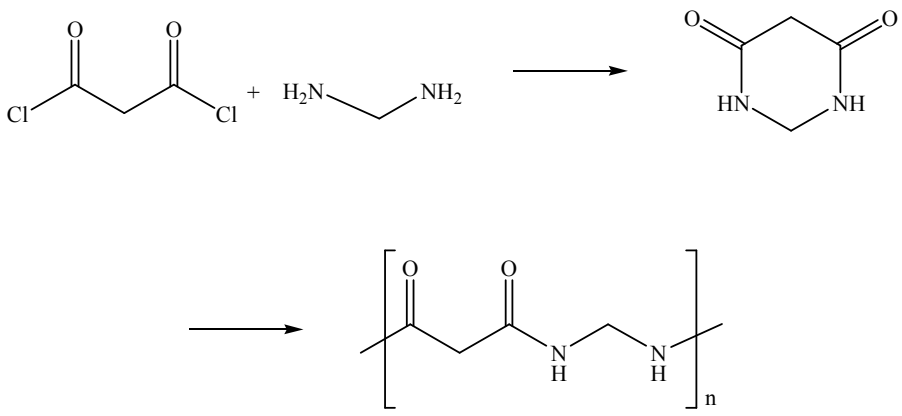


Figure 1-4: Linear and cyclic structures.

1.1.2 Ring-opening metathesis polymerization (ROMP)

The formation of a carbon-carbon backbone is an important process for the production of polymers and can proceed through various methods. Olefin metathesis is one method of carbon-carbon bond formation first reported in 1967 by Calderon and coworkers.[3] Olefin metathesis is a metal-catalyzed reaction where carbon-carbon double bonds are redistributed through a molecule (**Figure 1-5**).

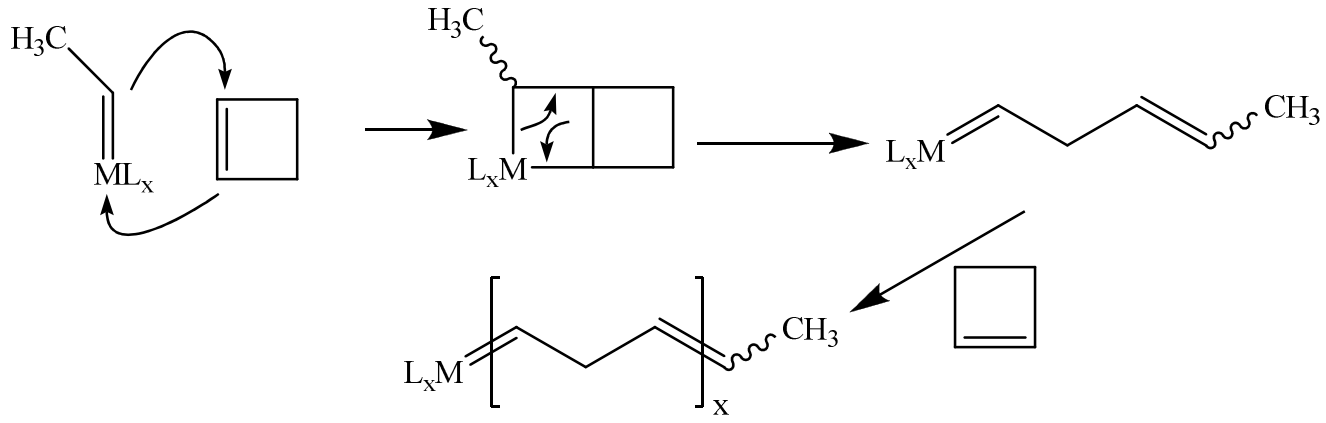


Figure 1-5: Olefin metathesis.

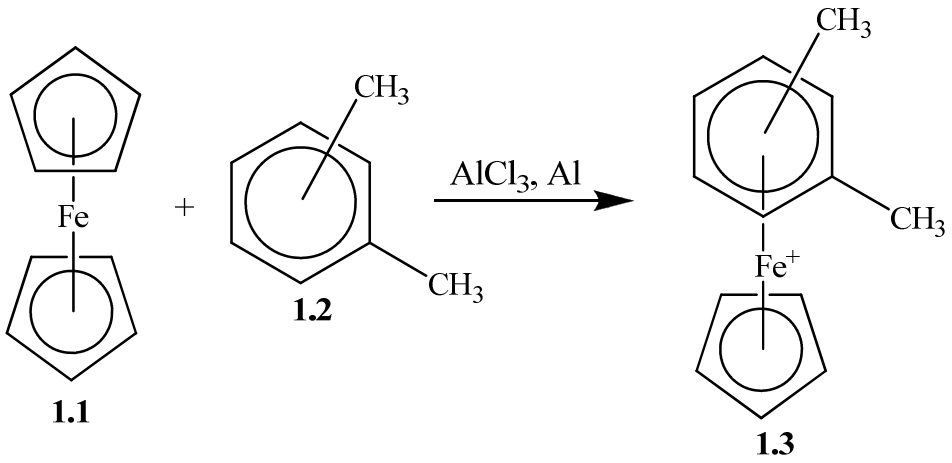
Ring-opening metathesis polymerization is a type of olefin metathesis, where cyclic olefins are opened and convert into linear polyalkenes. When a highly strained ring structure is used in olefin metathesis the reaction is irreversible.[4] This is a powerful method for the preparation of functionalized polymers with controlled structure, size, and bulk properties.[3-12]

Historically ROMP was catalyzed using basic inorganic salts of W, Re, and Mo.[4] More recently a new generation of ROMP catalysts based on W/Mo and Ru were developed by Schrock and Grubbs respectively. These catalysts are well-defined and based on alkylidene complexes that allow for living polymerizations with high control of the polydispersity index (PDI) and molecular weight.[3-12]

1.2 Organoiron complexes based on cyclopentadienyliron cations.

The synthesis of arene-coordinated organoiron complexes and materials containing arene-coordinated cyclopentadienyliron complex are interesting due to their unique properties and applications for catalysis, organic synthesis, and material chemistry.[13-16]

Arene-coordinated cyclopentadienyliron complexes were first reported in 1957 by Coffield *et al* .by the reaction of cyclopentadienyliron dicarbonylchloride with mesitylene in the presence of $AlCl_3$.[14] This synthesis, while useful for some ligands, gave poor yields. Nesmeyanov later reported the ligand exchange reaction between ferrocene and arenes in the presence of $AlCl_3$ (Scheme 1-1).[17, 18] Nesmeynov's synthesis proved to be an efficient method for the preparation of arene-coordinated cyclopentadienyliron complexes and is the most commonly used preparation today.



Scheme 1-1: Synthesis of arene-coordinated cyclopentadienyliron complexes via ligand exchange.

The proposed mechanism of the ferrocene ligand exchange (Figure 1-6) follows a "Friedel-Crafts type" mechanism. In this mechanism the $AlCl_3$ coordinates to one of the cyclopentadienyliron rings of the ferrocene molecule. The coordination of the $AlCl_3$ disrupts the

bond between the ring and the iron, cleaving the ring from the ferrocene, creating the cyclopentadienyliron cation. The cationic iron moiety then coordinates to the arene.[16, 19]

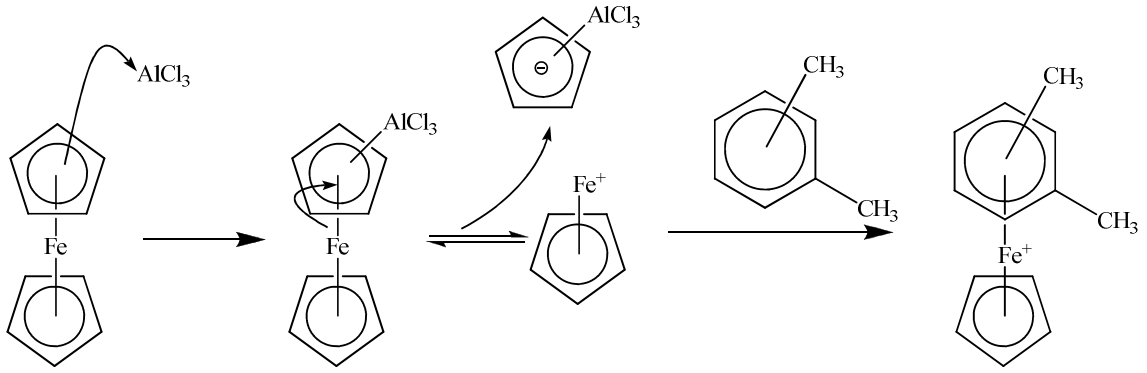


Figure 1-6: Mechanism of the ligand exchange reaction on ferrocene.

Coordination of the cyclopentadienyliron moiety to functionalized arenes imbues these cationic complexes with useful properties for synthetic chemists. Firstly, the coordination of the cationic cyclopentadienyliron moiety to mono- and di-halobenzene activates the arene group to nucleophilic aromatic substitution due to the electron withdrawing nature of the cyclopentadienyliron moiety.[13-16, 20-24] The activation of η^6–chlorosubstituted arene–η^5–cyclopentadienyliron complexes is so great that substitution of the chloro group by phenolic groups can occur at room temperature in the presence of weak bases such as K_2CO_3. Substitution of chlorobenzene with phenolic groups otherwise requires, long reaction times, high temperature, high pressure, or harsh catalysts. Secondly, the coordination of the iron centre to arenes provides an excellent method of analysis in ^{1}H NMR and ^{13}C NMR spectroscopy. In both methods of NMR spectroscopy the resonances due to the complexed arene appear at a significantly lower ppm range then non-complexed arene rings. For example, comparison of the ^{1}H NMR spectra of *p*-dichlorobenzene and η^6-dichlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate complex (Figure 1-7) demonstrates that the proton resonances due to *p*-dichlorobenzene appear around 7.42 ppm whereas the resonances due to the complexed arene

of η^6-dichlorobenzene-η^5-cyclopentadienyliron appear around 6.96 ppm. This upfield shift in the ^{1}H NMR is due to the destabilization of the anisotropy of the arene due to coordination of the π system to the iron centre. Since the resonances of the complexed arene appear at a unique chemical shift compared to other arenes, they can be used as diagnostic resonances to determine successful reactions.

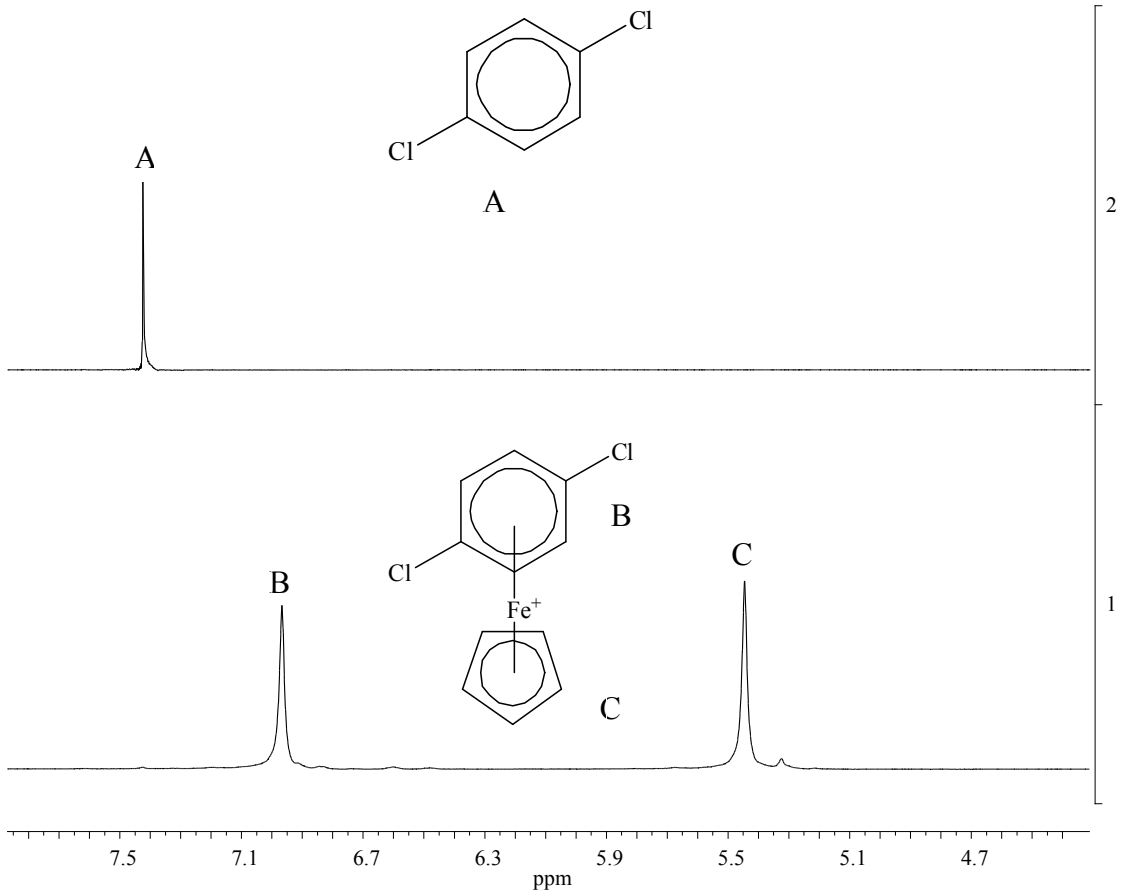


Figure 1-7: ^{1}H NMR spectra of *p*-dichlorobenzene (2) and η^6-dichlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate complex (1).

Cationic arene-coordinated cyclopentadienyliron complexes possess unique electrochemical properties. Unlike ferrocene, which undergoes a single electron reversible electrochemical oxidation, cationic cyclopentadienyliron complexes go through two, single

electron reductions. When electrochemically reduced, cationic cyclopentadienyliron complexes are first reduced to neutral 19 e^- complexes and then further reduced to anionic 20 e^- species.[20,24-26] The 19 e^- complex is fully reversible; however, the reversibility of the reduction to form the 20 e^- species greatly depends on the substituents of the arene ring and cyclopentadienyliron ring. Electron-withdrawing groups attached to the complexed arene will result in the complex undergoing reduction at more positive voltages than those with electron-donating groups due to the increased electron delocalization.[27-29]

Another useful property of arene-coordinated cyclopentadienyliron complexes is that the cyclopentadienyliron moiety can easily be removed, giving purely organic analogues of the iron complex. There are two main methods to remove the cationic iron moiety: pyrolysis and photolysis; however, electrolysis has also been used.[30, 31]

Cleavage of the cationic moiety using pyrolysis requires either extreme heating in a high temperature solvent (dimethylsulfoxide (DMSO) or diphenyl ether) or heating under vacuum in a pyroletic sublimator. To use pyrolysis the organic analogues must be thermally stable; otherwise, decomposition of the product may occur. Photolysis is a far less extreme method to remove the cationic group.

Photolytic cleavage of the cationic cyclopentadienyliron moiety is an effective, mild and convenient method to obtain organic analogues of the iron complex.[32] Photolysis of cationic groups requires the exposure of the arene-coordinated cyclopentadienyliron complex to ultraviolet light (300 nm) in highly coordinating solvents (e.g. acetonitrile).[32-36] This procedure gives ferrocene, iron salts, and the organic arene, which can be isolated and purified through extractions and column chromatography. The proposed mechanism of photolysis (Figure 1-8) excites the arene-coordinated cyclopentadienyliron complexes into their triplet states, which

causes "ring-slippage" from η^6 to η^4 and makes available a coordination site on the iron atom. The newly formed coordination site is quickly filled with either a highly coordinating solvent (acetonitrile) or the complex's counter ion, which forms a new intermediate complex that readily decomposes to give ferrocene, iron salts, and the organic compound (Figure 1-8).

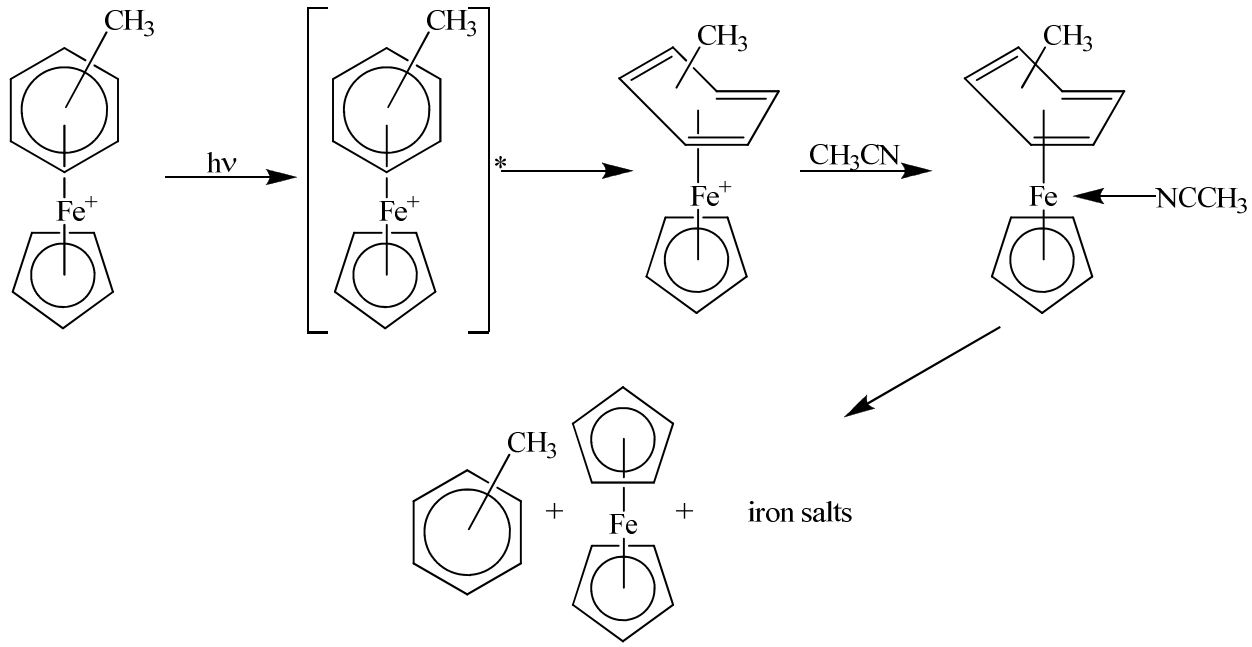


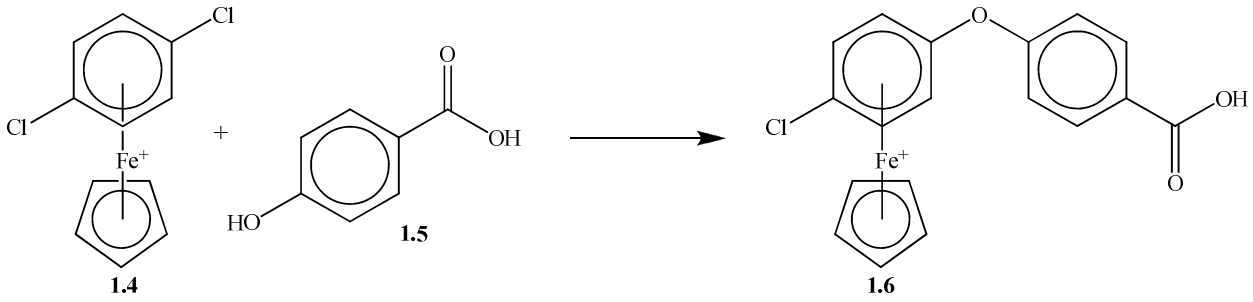
Figure 1-8: Mechanism of the photolytic cleavage of the cation cyclopentadienyliron moiety.

Arene-coordinated cyclopentadienyliron complexes are useful tools to prepare various types of organoiron complexes that can be further functionalized into larger complexes. This dissertation will discuss and describe a number of new organoiron complexes prepared from *p*-dichlorobenzene-cyclopentadienyliron complexes and its derivatives

1.2.1 Carboxylic acid containing organoiron complexes

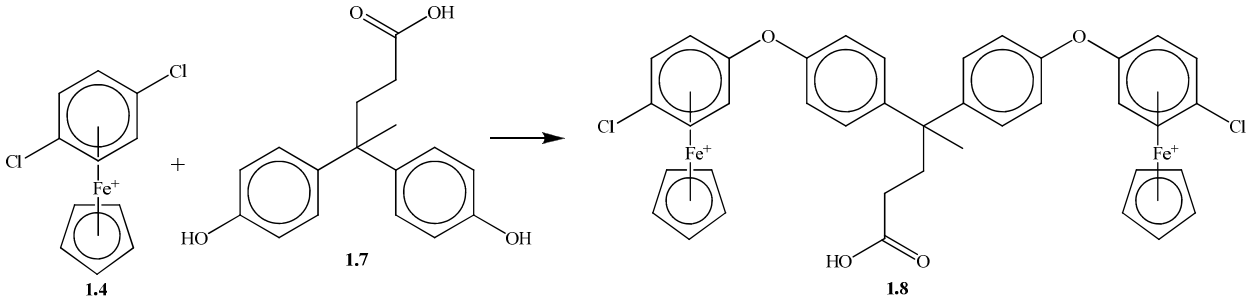
The presence of the cationic cyclopentadienyliron moiety of halogen-functionalized-arene-coordinated cyclopentadienyliron moieties increases the functionalized arene towards nucleophilic aromatic substitution. This property has been greatly utilized by the Abd-El-Aziz group to prepare a number of carboxylic acid functionalized organoiron complexes.[37] Two carboxylic acid containing cationic organoiron complexes will be utilized in subsequent chapters: a monometallic acid complex, and a bimetallic acid complex.

Mono-metallic acid complexes were reported from the reaction of *p*-dichlorobenze-cyclopentadienyliron hexafluorophosphate with 4-hydroxybenzoic acid. This reaction was carried out in a mixture of DMF and THF at 50 °C for 16 hours (Scheme 1-2)[37]. This synthesis was improved to a single solvent system at room temperature.



Scheme 1-2: Synthesis of mono-metallic acid complex.

A bimetallic acid complex is produced from the reaction between *p*-dichlorobenzene-cyclopentadienyliron hexafluorophosphate and 4,4-bis(4-hydroxyphenyl)valeric acid (Scheme 1-3)



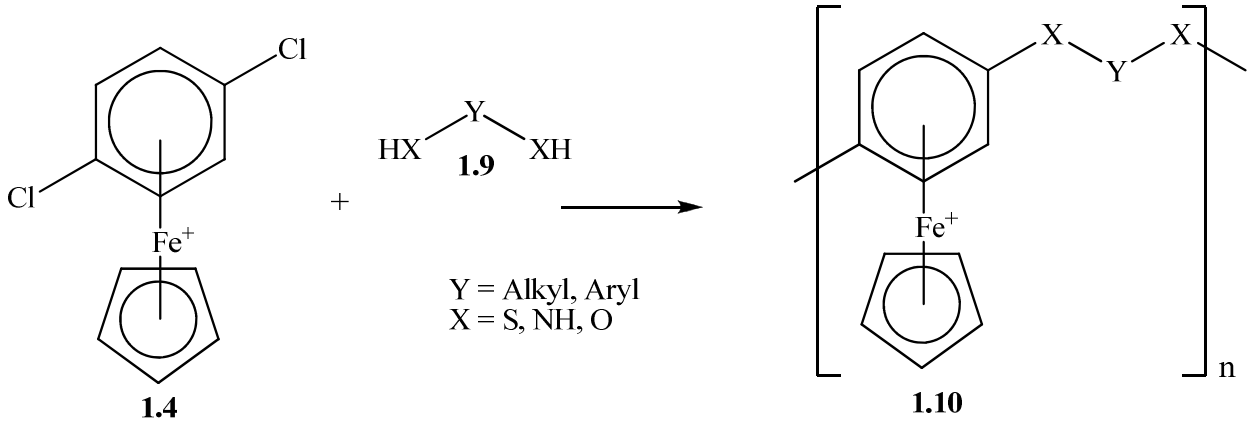
Scheme 1-3: Synthesis of a bimetallic carboxylic acid complex.

These two complexes (**1.6** and **1.8**) have been utilized to prepare a number of organoiron complexes containing a large variety of functional groups.[37-43] The terminal chloro groups on **1.6** and **1.7** allow for the subsequent polymerization through condensation reactions to generate different organoiron based polymers.

1.3 Organoiron based polymers

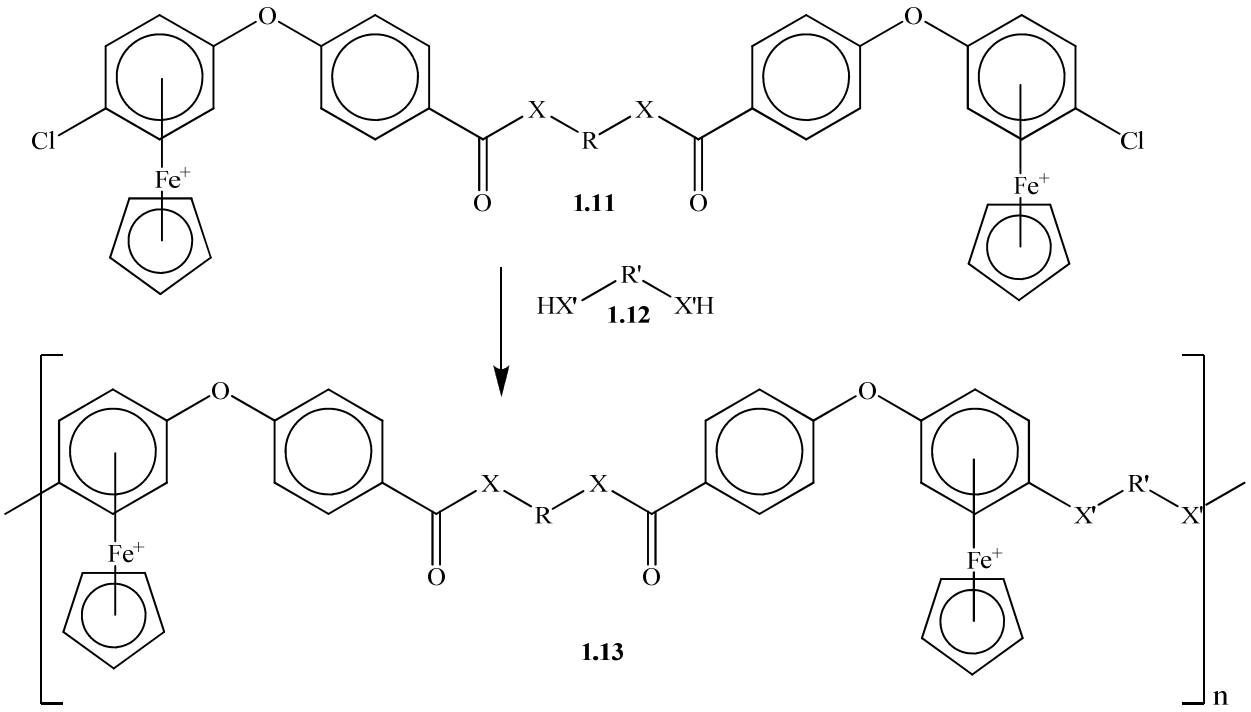
Polymers containing organometallic subunits are used as electrocatalysts, modified electrodes, chemical sensors, and molecular devices.[44, 45] The incorporation of organoiron moieties in particular is known to give materials with unique optical, magnetic, and electrochemical properties.[46]

The Abd-El-Aziz group has shown that the nucleophilic aromatic substitution of chloro-functionalized arene-cyclopentadienyliron complexes by O-, S-, or N-containing dinucleophiles can lead to the isolation of organoiron based oligomers and polymers (Scheme 1-4).[46]



Scheme 1-4: Synthesis of organoiron polymers through nucleophilic aromatic substitution.

The presence of two chloroarene-cyclopentadienyliron groups imbues the molecule with the potential for polymerization through polycondensation. For example, if two mono-carboxylic acid complexes are attached through a secondary linking group then polycondensation with dinucleophiles will give polymers containing the linker in the backbone (Scheme 1-5). This methodology has been utilized to prepare a large number of organoiron polymers based on cationic cyclopentadienyliron complexes.



Scheme 1-5: Synthesis of organoiron polymers containing different spacers in the backbone.

This dissertation will focus the synthesis and characterization of organic and organometallic polymers containing azo dyes or calixarenes. Organometallic polymers will be designed utilizing cationic cyclopentadienyliron moieties. Organic polymers will either be generated via ROMP of organic monomers or by the photolytic cleavage of analogous cationic organoiron polymers.

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Chapter 2 Synthesis of azo dye containing polymers

2.1 Introduction

Synthetic dye chemistry plays an important role in today's society. Many everyday items from clothes to DVDs contain synthetic dyes. Azo dyes are a large family of synthetic dyes characterized by the N=N (azo) group.[1] Azo chemistry dates back to the mid 1800s when Peter Griess discovered diazo compounds. Shortly after Griess' discovery, one of his compounds became the first commercially available azo dye called aniline yellow or 4-aminoazobenzene (Figure 2-1).[1]

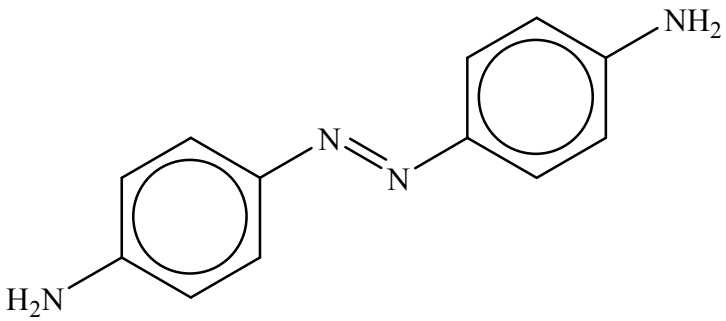


Figure 2-1: 4-Aminoazobenzene.

Azo dyes are prepared from the coupling of a diazotized amine with another aromatic compound either in solution or as a suspension. Diazotized amines are prepared from the reaction of primary aromatic amines with nitrous acid (Figure 2-2).[1, 2]

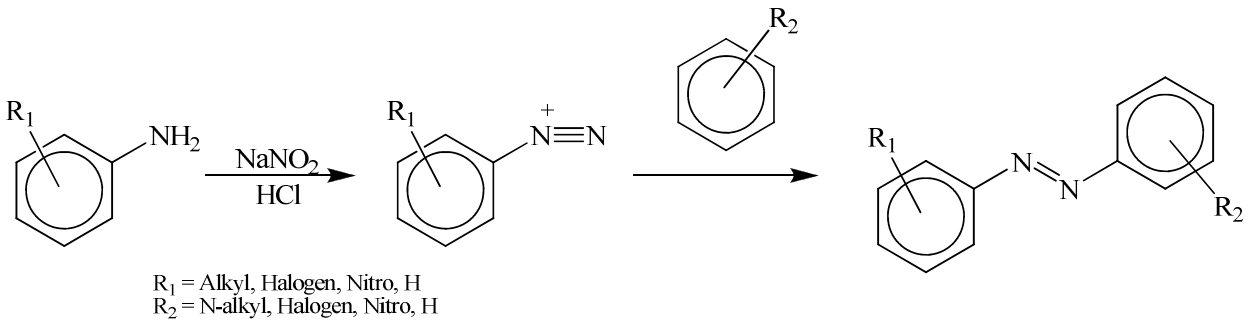


Figure 2-2: Preparation of azo dyes.

The diazotization reaction (Figure 2-3) generally occurs in an aqueous mineral acid solution, and the nitrous acid is generated *in situ* by the addition of sodium nitrate. The formation of the azo dye occurs in a second step where the diazonium ion attaches ("couples") to another arene. Depending on the nature of the coupling component, couplings can occur in acidic or basic solutions. Generally, if the coupler is phenolic or carboxylic in nature the coupling would occur in a basic medium; if the coupler is amino-phenyl in nature the coupling would occur in acid medium. It is important to use the appropriate amount of sodium nitrite as excess nitrous acid reacts with the coupling components. This is especially necessary when coupling in acid medium. Excess nitrous acid is easily detected by testing with starch-iodide paper, and the excess can be decomposed by adding sulfamic acid or urea.[1, 2]

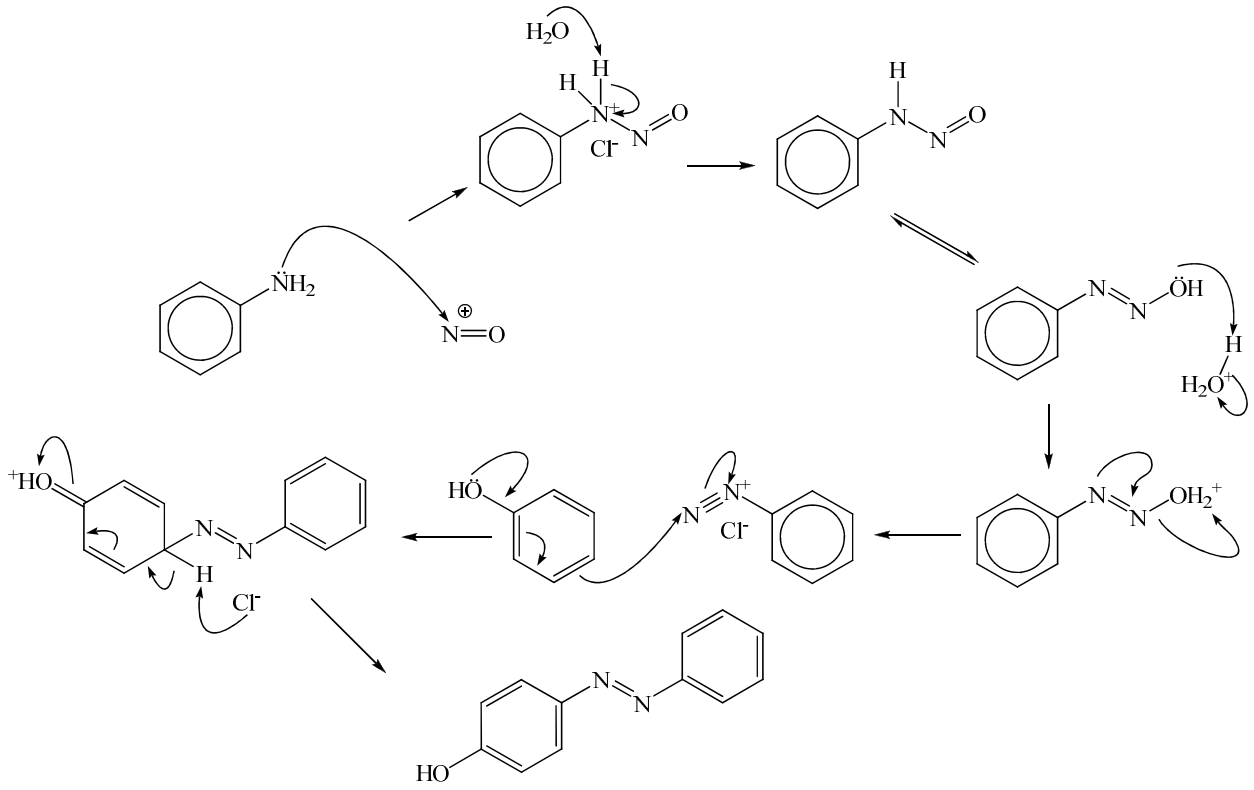


Figure 2-3: Mechanism of azo dye formation.

There are several classes of azo dye that fall within two families: aryl- and hetaryl-azo dyes. Aryl azo dyes are based on carbon based arenes. Both azobenzenes and aminoazobenzenes fall into this class of compounds.[1-7] Hetaryl azo dyes contain aromatic rings that possess a heteroatom such as sulfur or nitrogen, hetaryl azo dyes include both benzothiazole and thiophene based dyes.[8-11] Hetaryl azo dyes are rapidly becoming more prevalent due to their increased brightness and fastness, compared to aryl azo dyes.[10, 11]

Azo dyes can display the full spectrum of visible colour depending on their structure and substitutents.[1-4, 12-14] The colour of azo dyes is based on the conjugation of their π-systems. For example, aminoazobenzene dyes have a high level of conjugation and are generally red in colour (depending on substituents), whereas hetaryl azo dyes, based on pyridine and thiophene systems, generally range in colour from yellow to orange due to the poor delocalization of their π-

systems.[10] The substituents on the aromatic rings of azo dyes also play an important role in the colour and absorption of azo dyes. Electron withdrawing groups delocalize the π-system and cause a bathochromic shift in the absorption of the azo dye, while electron donating groups have the opposite effect and result in hypsochromic shifts.[1, 3, 4, 15]

Another important physical property of azo dyes is their *trans-cis* isomerization. Azo dyes generally exist in a *trans* conformation, but exposure to high intensity light can cause the azo dye to convert to its *cis* conformation. The *trans-cis* isomerization is completely reversible, so that if the excitation source is removed the azo dye will thermally revert back to the *trans* isomer. This property in particular is utilized in applications such as photo-optic switches, optical storage media and liquid crystals.[16-18] The acid-base chemistry of azo dyes is an interesting and useful property. Many azo dyes (Methyl Red, Congo Red, Alizarin Yellow) are utilized as acid-base indicators due to the protonation of the azo group and its effect on the absorbance of the azo dye. The azo group is easily protonated to form the azonium ion (Figure 2-4), which generally causes a dramatic bathochromic shift in its absorption.[2] The protonation of an azo dye is reversible and the azo form is regenerated by the addition of base.

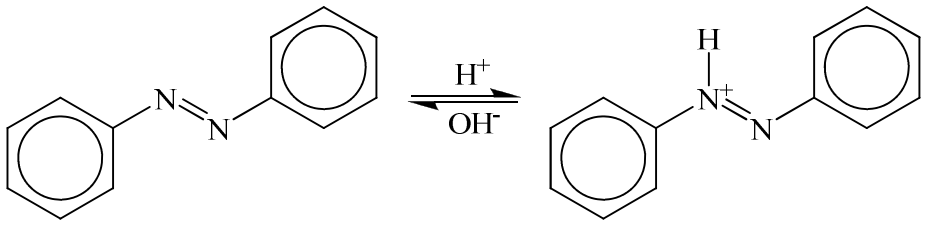


Figure 2-4: Generation of azonium dye.

The azo dye properties discussed above have led to important applications for these materials. The incorporation of these materials into polymeric systems can give processible materials for many different applications. The synthesis and properties of azo dye based

polymers has drawn a considerable amount of attention due to their applications as reversible optical storage media, chiroptical switches, electrooptic modulators and chemical sensors.[18-37]

Generally, azo dye-polymers are comprised of an azo dye suspended or doped in a polymeric material or spin coated onto a substrate.[38-40] While, this does give a material possessing some of the properties of azo dyes, the azo dye is not part of the polymer and can leach out of the polymer matrix. This disadvantage can be overcome if the azo dye is directly incorporated into a monomer and polymerized to give materials with the azo dye as an integral part of the polymer. This way the azo dye cannot be removed unless the polymer is destroyed. This strategy has been demonstrated using atom transfer radical polymerization (ATRP), radical polymerization and epoxide opening.[41-45] Since many azo dyes contain groups that are known to quench free radical polymerizations (such as nitrobenzene groups[46]) this method is not suitable for all azo dye monomers. Utilization of monomers that employ other polymerization methods can bypass the issue of radical quenching. For example, the use of norbornene monomers allows for fairly uniform high molecular weight polymers with defined structures using ring-opening metathesis polymerization (ROMP) with catalysts such as Grubbs' catalysts.

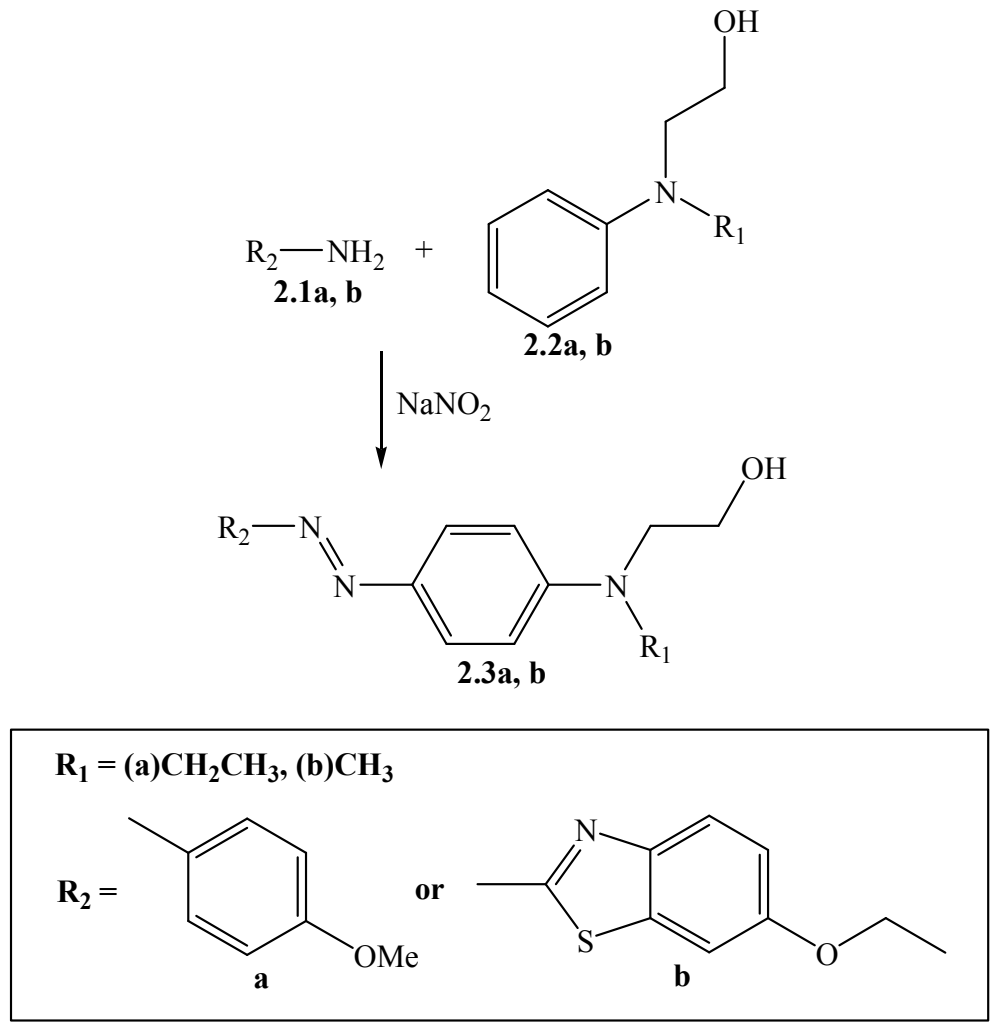
This chapter will discuss the synthesis and characterization of a number of different azo dye based polymers. First, the synthesis of organic homo- and co-polymers of aryl- and hetaryl-azo dye based norbornenes will be discussed. This will be followed by a discussion of the preparation of cationic organoiron polymers containing azo dyes and ferrocene in their backbones. The last section will discuss the preliminary results of the design of organometallic complexes containing three classes of azo dyes.

2.2 Results and discussion

2.2.1 Synthesis of azo dye-containing polynorbornenes

Azo dye polymers have many possibilities for industrial and commercial applications. However, these types of polymers generally do not have the "tune-ability" that is associated with other materials. It is the goal of this research to produce polymers possessing multiple types of azo dyes to give materials that can display different spectral properties.

The azo dyes used in this chapter were prepared by diazotization of primary aromatic amines through reaction of the amines with sodium nitrite (**Scheme 2-1**). Two different methods were used to prepare the dyes. The aryl azo dye was dissolved in a dilute aqueous solution of HCl and for the hetaryl azo dye the benzothiazole unit was suspended in 50% H_2SO_4. Low temperatures were required for the diazotization as diazonium salts decompose above 5 °C[1, 2]. The two different methods were used since a very strongly acidic pH <1 is required for diazotization of amino-benzothiazoles as these compounds are highly active.[47]



Scheme 2-1: Synthesis of azo dyes.

Figure 2-5 shows the NMR spectrum of azo dye **2.3a**. The aromatic resonances appear as 4 sets of doublets at 7.75 ppm, 7.71 ppm, 7.06 ppm, and 6.80 ppm. The methoxy group appears as a singlet at 3.83 ppm. The aliphatic methylenes appear as a triplet at 3.83 ppm for the CH_2 alpha to the alcohol group and a multiplet at 3.48 ppm integrating for 4H, two protons for each CH_2 attached to the nitrogen. The aliphatic CH_3 appears as a triplet at 1.13 ppm. The coupling of the diazonium ion to the coupling amine give para substituted compounds because the π–orbitals of the diazonium and the amine groups prevent the coupling from occurring at the ortho positions.

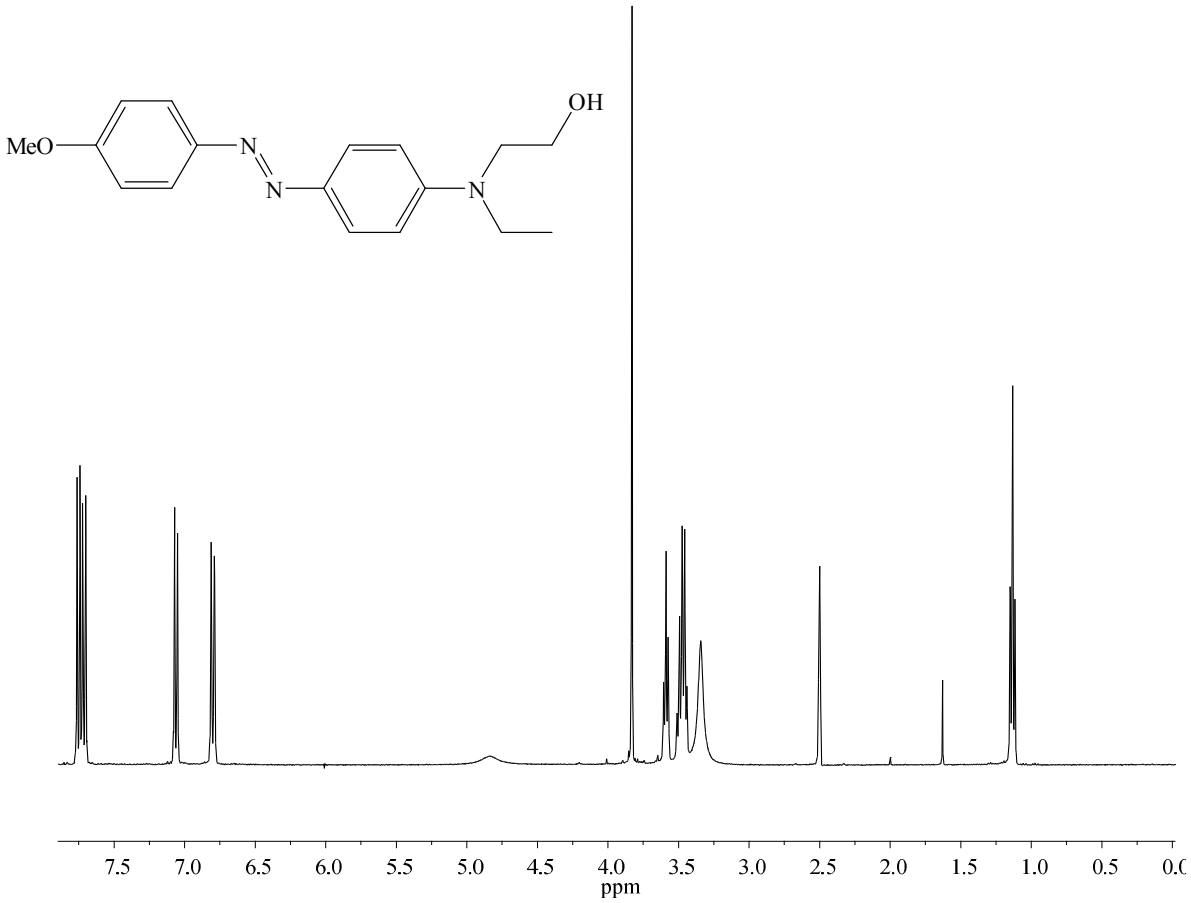
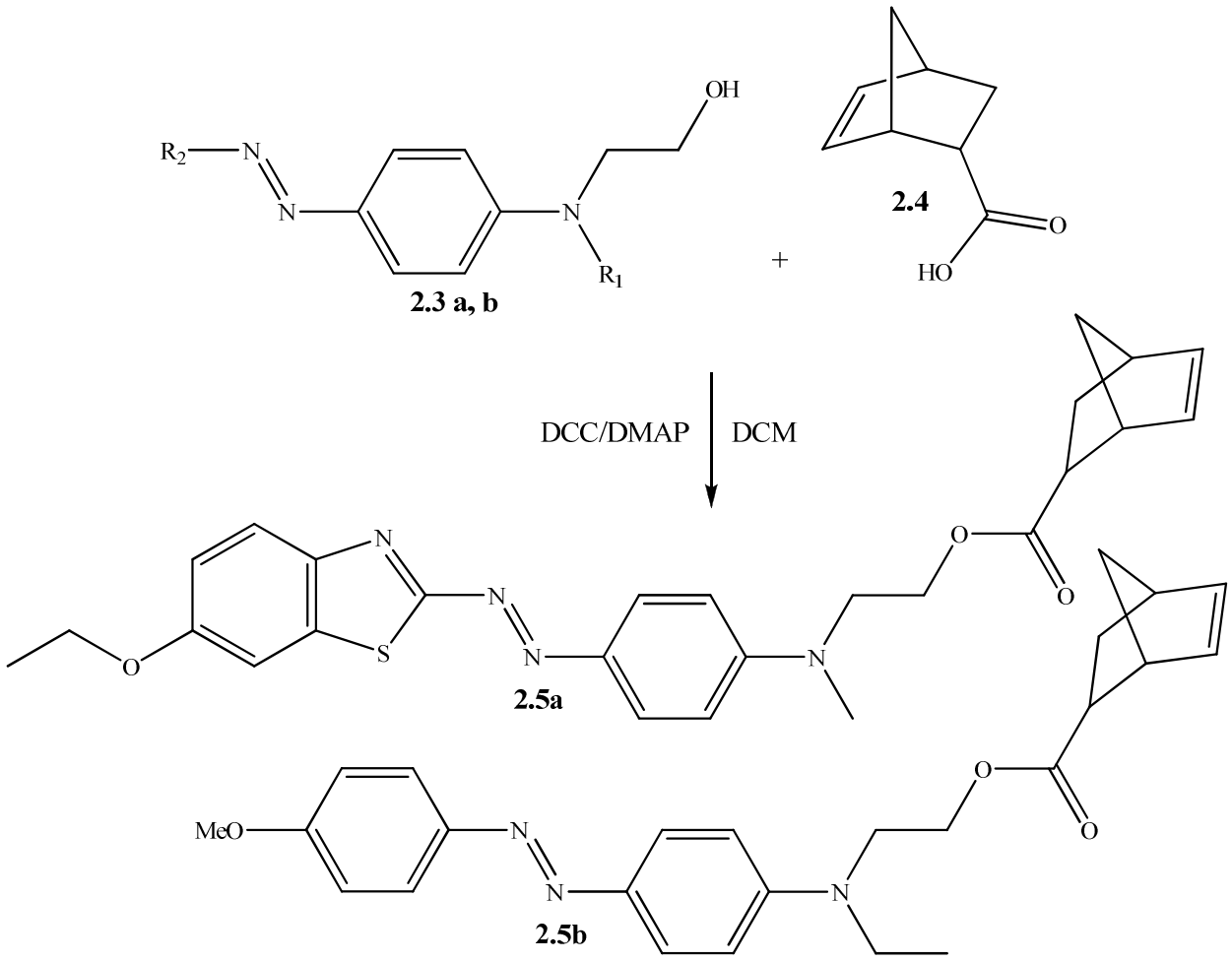


Figure 2-5: 400 MHz ^{1}H NMR spectrum of azo dye 2.3a.

These azo dyes were chosen due to their distinctly different absorptions. The aryl azo dye (**2.3a**) appears as an orange to yellow solid and displays a λ_{max} = 280 nm in DMF which shifts to 420 nm when acidified. The hetaryl azo dye (**2.3b**) is a purple to red solid and displayed a λ_{max} = 380 nm that shifts to 480 nm when acidified. These two azo dyes have λ_{max}s approximately 100 nm apart from each other which should provide a significant range of the visible spectrum.

The azo dyes were reacted through their terminal alcohol with 2-norbornene-5-carboxylic acid via a Steglich type esterification to yield azo dye containing norbornene monomers (Scheme 2-2). The success of the synthesis was determined from the shift in the ^{1}H-NMR resonance for

the CH_2 connected to the alcohol at 3.83 ppm (for azo dye **2.3a**) to 4.22 ppm indicating the presence of an ester as well as the appearance of the olefinic resonances between 6.17 ppm and 5.87 ppm (Figure 2-6).



Scheme 2-2: Synthesis of azo dye-norbornene monomers.

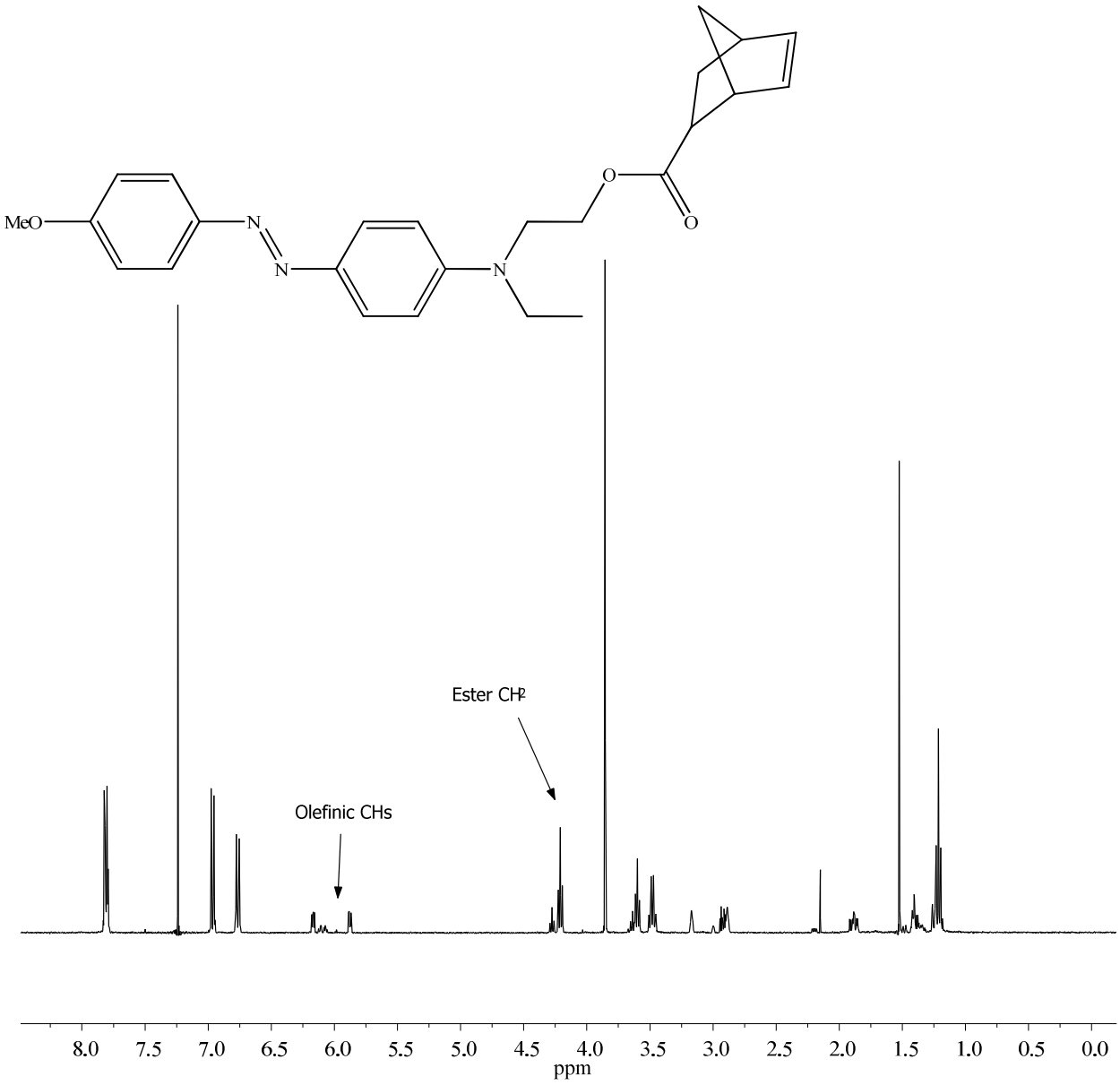


Figure 2-6: 400 MHz ^{1}H NMR spectrum of monomer 2.5b.

The formation of the ester is further confirmed in the COSY spectrum (Figure 2-7) where the resonance at 4.22 ppm exhibits coupling into the triplet at 3.58 ppm.

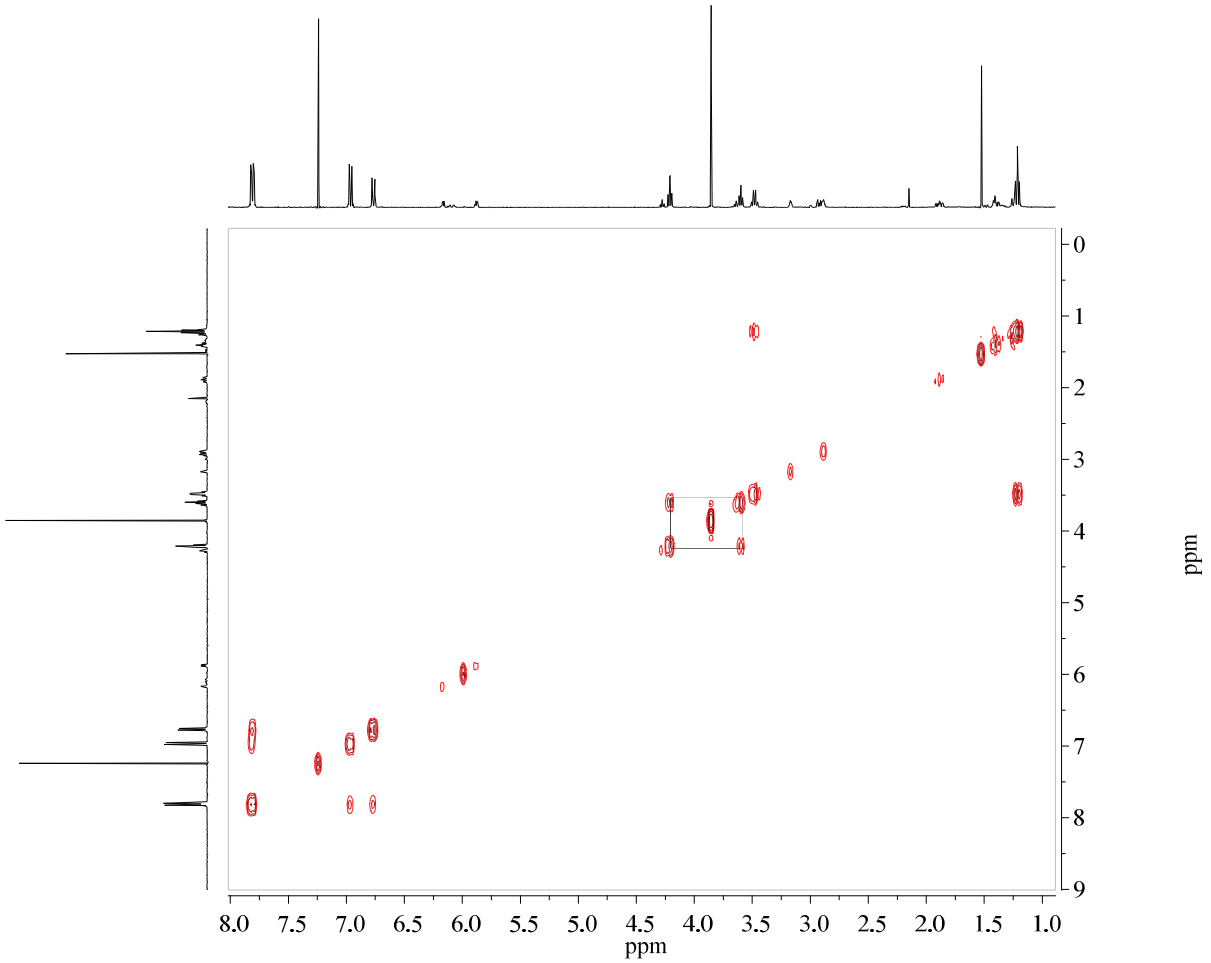


Figure 2-7: COSY spectrum of monomer 2.5b.

Since a mixture of endo/exo norbornene was used all the product peaks are doubled. The majority of the product is endo with the exo product being 25% of the total product based on NMR resonances (Figure 2-8).

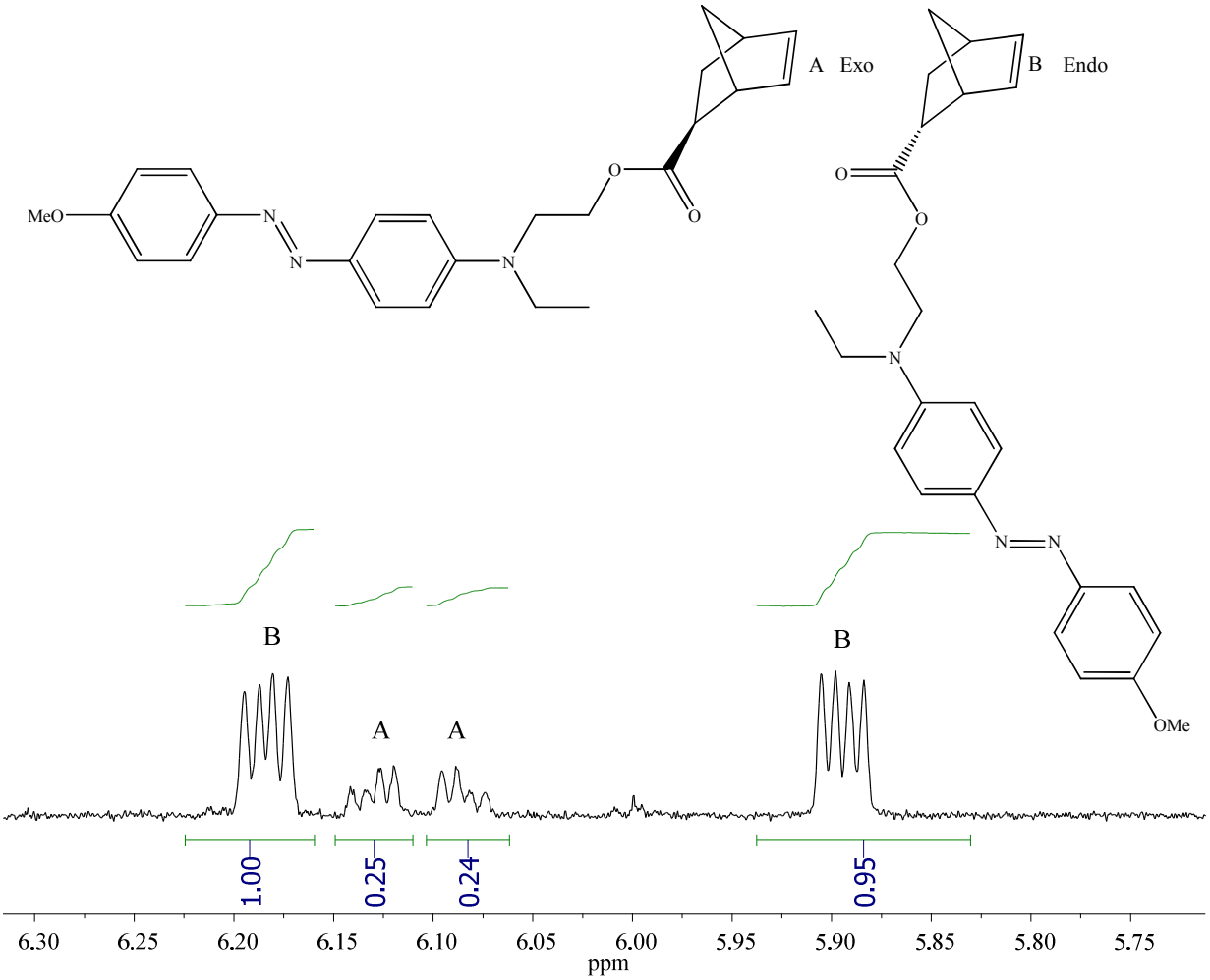
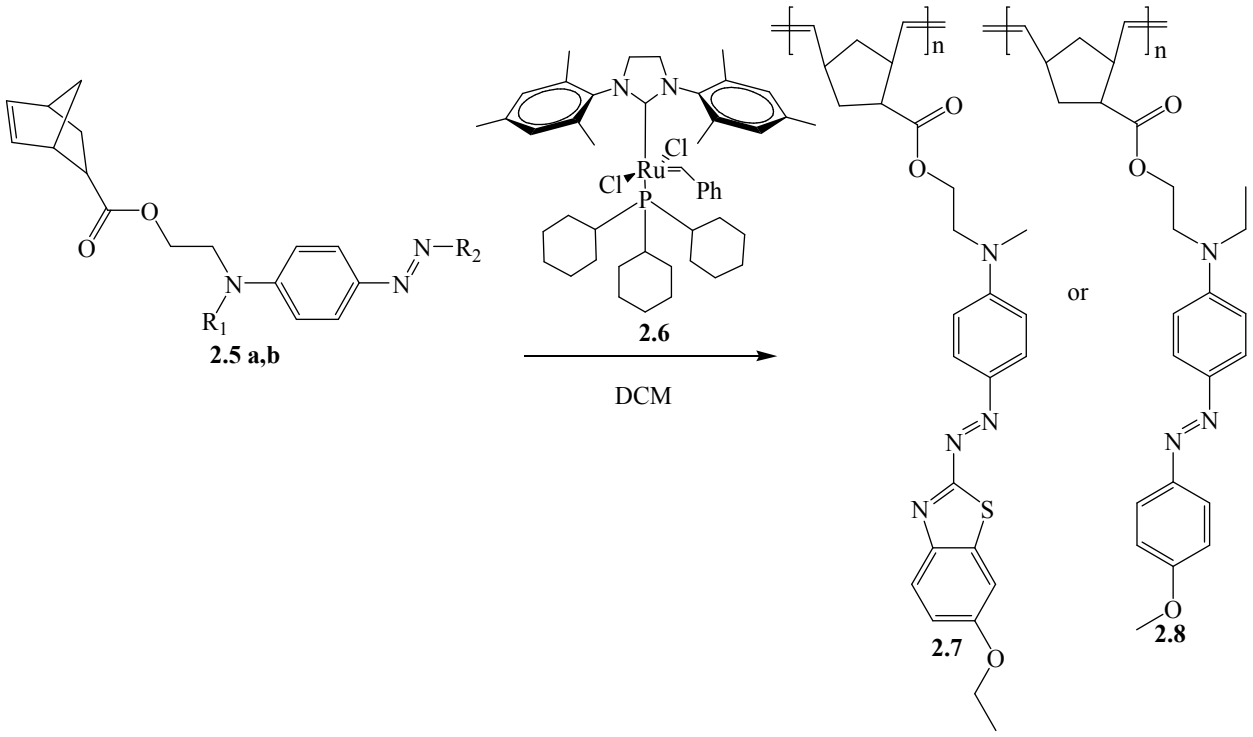


Figure 2-8: 400 MHz ^{1}H NMR resonances of the olefin resonances for the endo/exo mixture of monomer 2.5b.

The azo dye-containing norbornene monomers **2.5a** and **2.5b** were analyzed using UV-visible spectroscopy. The monomers were shown to possess λ_{max} at 417 nm (**2.5b**) and at 495 nm (**2.5a**). The λ_{max}s underwent bathochromic shifts when exposed to $HCl_{(aq)}$ due to the formation of the azonium form of the azo group.

Monomers **2.5a** and **2.5b** were reacted with Grubbs' catalyst 2nd generation to give polymers **2.7** and **2.8** through ring-opening metathesis polymerization (Scheme 2-3). The reaction time was determined through a timed ROMP reaction where aliquots of the

polymerization solution were removed every 30 min for 4 hours, the aliquots were tested on a GPC to determine their $\overline{M_w}$s. The reaction time that gave the greatest $\overline{M_w}$s was 90 min. ^{1}H NMR spectra of polymer **2.7** and its corresponding monomer **2.5a** are shown in Figure 2-9. The successful polymerization is indicated by the shift of the olefinic protons in the ring structure from between 6.20 ppm to 5.90 ppm for monomer (**2.5b**) to between 5.25 ppm and 5.15 ppm in the polymers for the linear olefins. Broadening of the ^{1}H NMR resonances also indicates polymer formation.



Scheme 2-3: Synthesis of polymers 2.7 and 2.8.

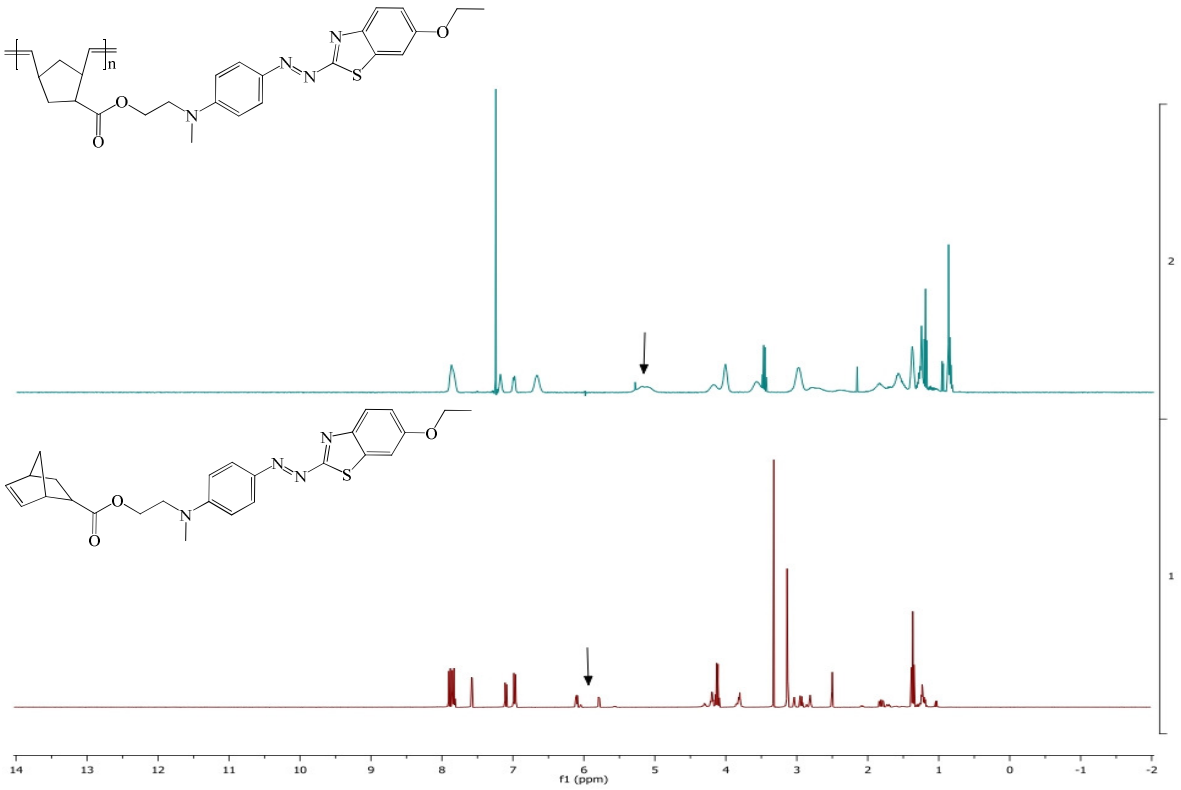
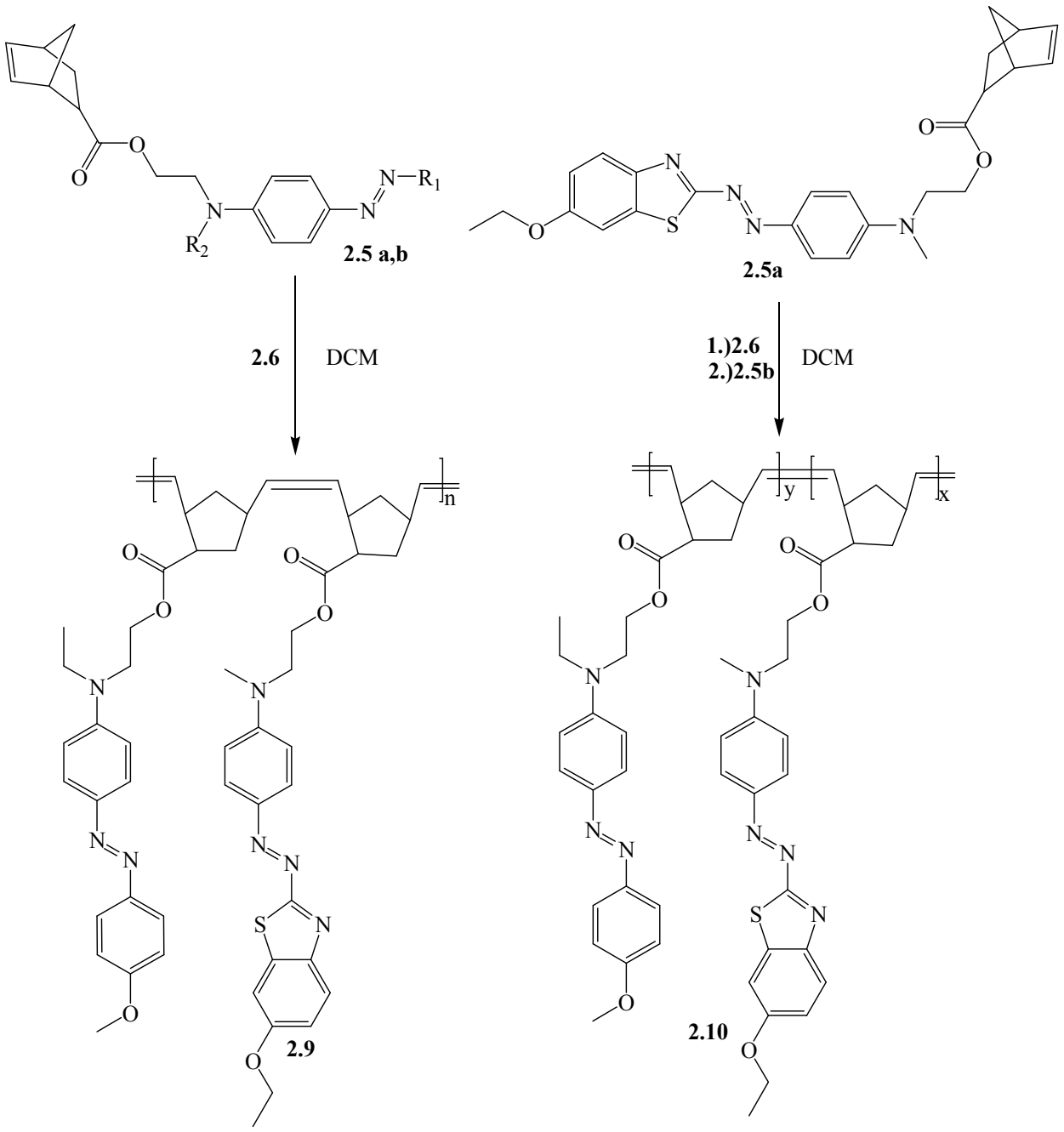


Figure 2-9: ^{1}H NMR spectrum of polymer 2.7 and corresponding monomer 2.5a.

Co-polymers (both random and block) were also prepared from these monomers (Scheme 2-4). They were generated via ROMP in two fashions: a) monomer **2.5a** and monomer **2.5b** were reacted together with Grubbs' catalyst for 90 min; b) monomer **2.5a** was reacted with Grubbs' catalyst for 30 min and the monomer **2.5b** was added and the reaction allowed to stir for an additional 90 min. These reactions gave copolymers with monomer ratios (monomer **2.5a**/monomer **2.5b**) of 1.00 to 1.00 and 1.08 to 1.00, respectively. The monomer ratios show that polymer **2.9** is a random copolymer and polymer **2.10** is block copolymer with small blocks of **2.5a** and **2.5b**.



Scheme 2-4: Synthesis of copolymers 2.9 and 2.10.

The ^{1}H NMR spectrum of copolymer **2.9** is shown in Figure 2-10 (3). As can be seen the copolymer displays a combination of the proton resonances of homo-polymers (Figure 2-10 (2), (1)). The resonances due to the aryl azo dye arenes appear at 7.76 ppm, 6.91 ppm and 6.66 ppm,

while the resonances due to the hetaryl azo dye aromatics appear at 7.88 ppm, 7.17 ppm, 6.98 ppm, and 6.66 ppm.

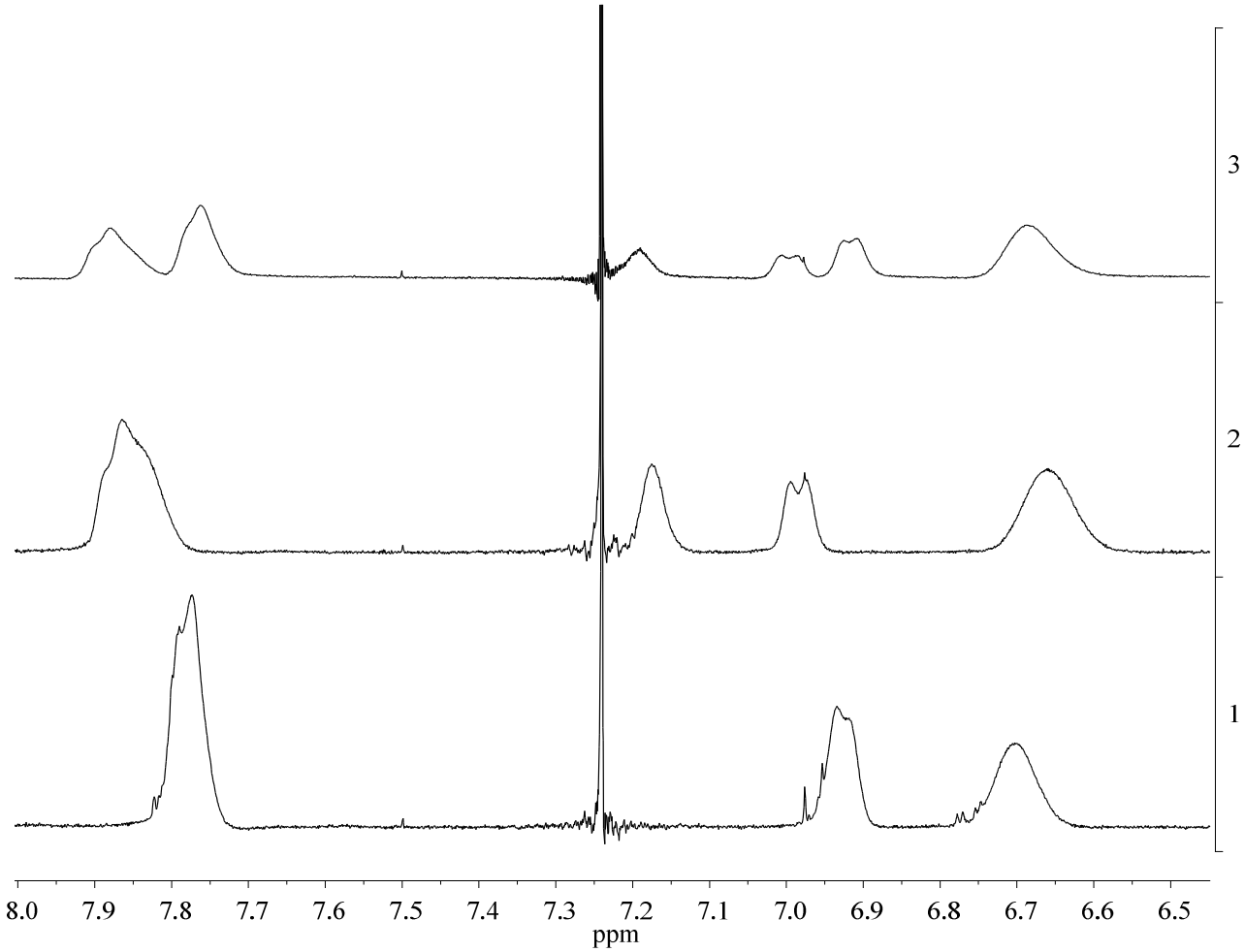


Figure 2-10: ^{1}H NMR spectra of copolymer 2.9 (3), homopolymers 2.7 (2), and homopolymers 2.8 (1).

The molecular weights of the polymers (Table 2-1) were determined using GPC. The homopolymers possessed molecular weights of 113 000 and 72600 with PDIs of 2.1 and 1.6 for polymers **2.7** and **2.8** respectively. The copolymers possessed molecular weights of 230 000 and 233 000 with PDIs of 1.7 and 1.6 for the random and block copolymer respectively.

Table 2-1: Molecular weight distributions of polymers 2.7 – 2.10

Polymer #	$\overline{Mn}$	$\overline{Mw}$	PDI
2.7	53000	113000	2.1
2.8	43500	72600	1.6
2.9	134000	230000	1.7
2.10	142000	233000	1.6

The UV-vis studies of the polymers were performed in THF solutions and are tabulated in Table 2-2. The UV-visible analysis showed that the *p*-methoxyanisole based azo dye-containing polymer displayed a λ_{max} at 417 nm with a weak shoulder at 443 nm. The absorption at 417 nm is due to the $\pi - \pi*$ transition of the azo dye.[48] The benzothiazole based polymer displayed a λ_{max} at 495 nm. When the polymer solutions were exposed to $HCl_{(aq)}$ their λ_{max} underwent bathochromic shifts to 540 nm and 560 nm due to the formation of the azonium ion (protonated form of the azo dye)(Figure 2-11). While one of the original goals of the project was to obtain materials that displayed two distinct absorptions in the UV-vis region, a blending of the absorption spectra of the two azo dyes was seen in the copolymers. While the azo dye monomers displayed a 100 nm separation, this was not large enough to give separate λ_{max}. The UV-vis of the copolymers displayed a combination of both the azo dyes. Copolymers **2.9** and **2.10** for displayed λ_{max}s between 430 nm and 550 nm. When acidified, the λ_{max} shifted to 560 nm and 570 nm with weak shoulders between at 650 nm and 660 nm (Figure 2-12).

Table 2-2: Photo-physical data of polymers 2.7 – 2.10 (ws = weak shoulder, s = shoulder).

Polymer	λ_{max} neutral (nm)	λ_{max} acidic (nm)
2.7	495	540, 650s
2.8	417, 443ws	560
2.9	430ws, 470s, 550	560, 650ws
2.10	430ws, 460ws, 504s	570, 660ws

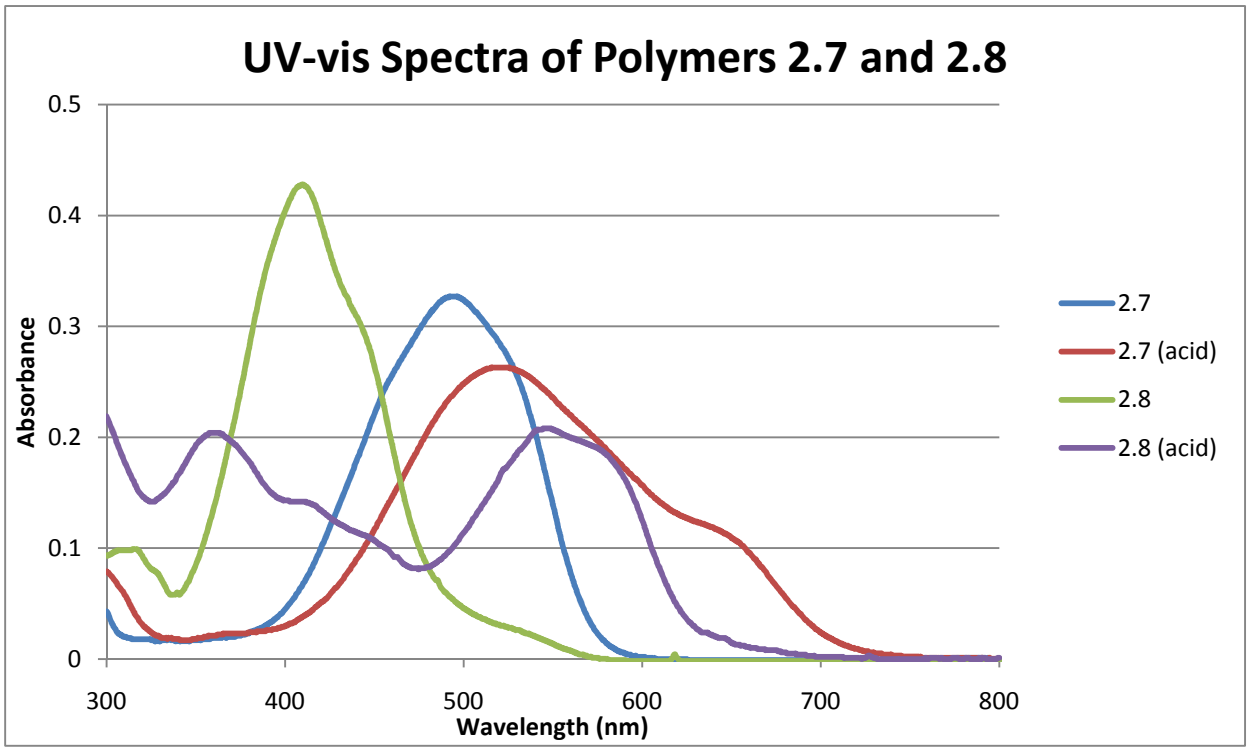


Figure 2-11: UV-visible spectrum of homopolymers 2.7 and 2.8.

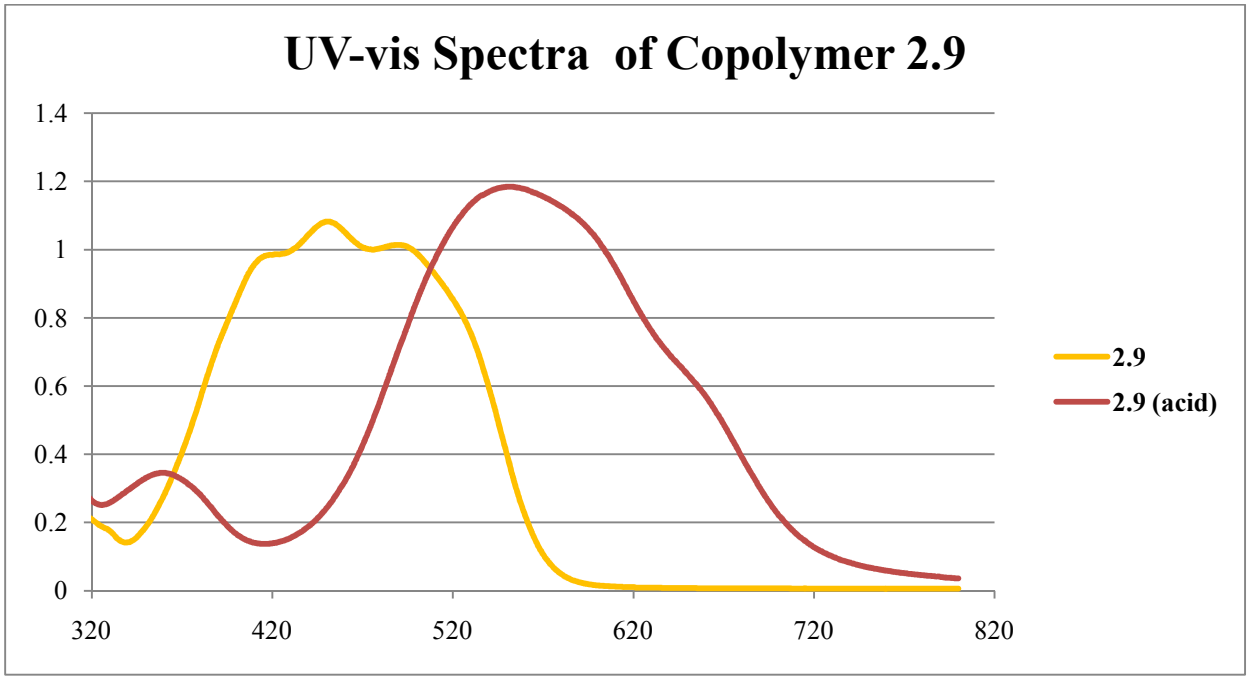


Figure 2-12: UV-visible spectra of copolymers 2.9.

The monomers and polymers displayed H^+ sensing capabilities in both solution and solid state, this indicated that these materials may be used as acid sensing devices. In DMF solutions monomers **2.5a** and **2.5b** reversibly changed colour when exposed to H^+. For example, monomer **2.5a** changed from purple in DMF to blue with increasing concentration of H^+. As the concentration increased further the monomer changed from blue to brown/red (Figure 2-13). The *p*-methoxyanisole based azo dye was yellow in DMF solution and changed to purple in the presence of H^+. The colour changing aspect of these materials shows that they can be used for the visual detection of acid.

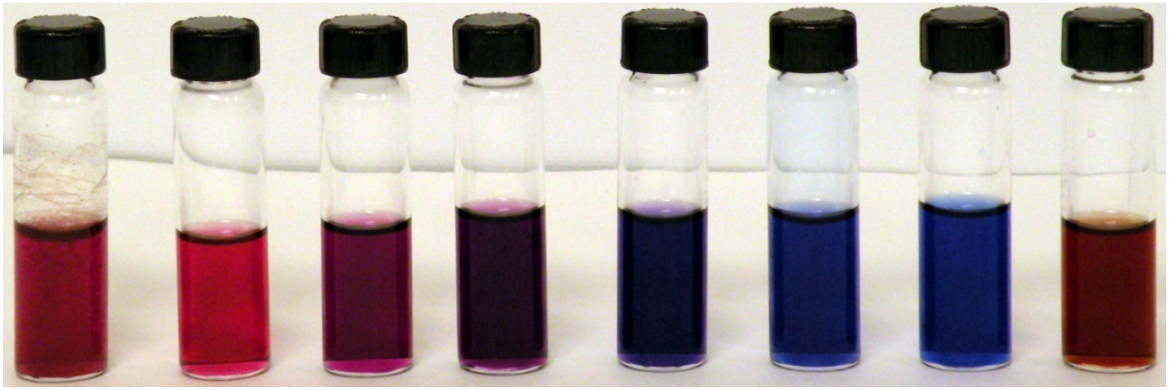


Figure 2-13: Colour change of monomer 5a in the presence of increasing [H+] in a DMF solution.

In THF solutions the homo- and co-polymers (**2.7 – 2.10**) displayed similar behaviour to the monomers. Polymer **2.8** changed from yellow to purple in the presence of H^+, and copolymer **2.10** changed from pink/orange to blue/purple and then precipitated (Figure 2-14).

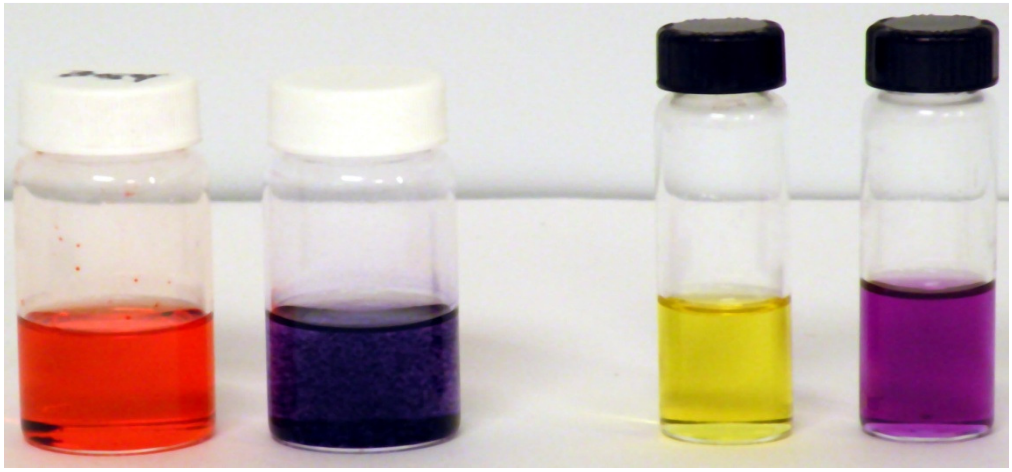


Figure 2-14: Change in colour of polymer 2.10 and 2.8 with addition of acid.

Thin films of the polymers were prepared by spin coating from THF solutions onto glass slides. When the thin films were exposed to either 1.2 M $HCl_{(aq)}$ or $HCl_{(g)}$, the polymer films turned from red or yellow to blue or purple (polymer **2.7, 2.9, 2.10** and polymer **2.8** respectively). This indicates that the azonium complex forms at the surface of the polymer film. When the acidified polymer film was exposed to 1M $NaOH_{(aq)}$ or $NH_{3(g)}$ the film reverted back

to its original non-protonated colour (Figure 2-15). This cycle was repeated five times with no sign of detrimental effects to the polymer films. This behaviour indicates that these polymers (**2.7-2.10**) show potential as reusable solid state H^+ sensors for both aqueous and gaseous sources of acid. For example, if these materials can be processed into a sheet or a rod, they can be dipped into solutions to test for acid, they can then be washed with a bicarbonate solution to return the plastic back to its original colour. This has advantages over litmus paper as it is reusable, and works in organic solvents.

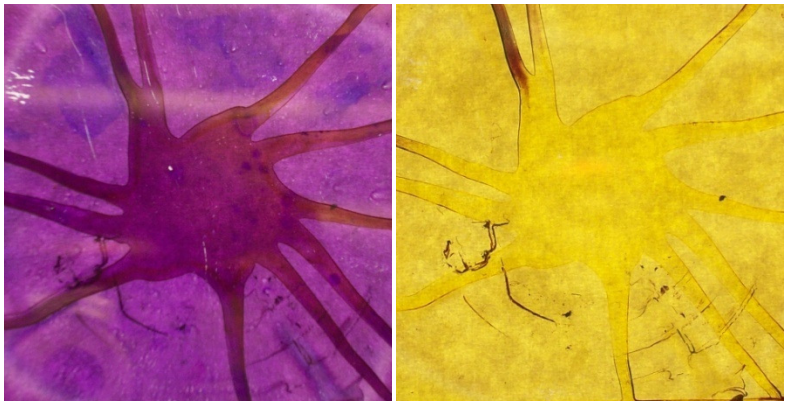


Figure 2-15: Thin film on glass of polymer (2.8) after exposure to HCl(g) (left). Thin film on glass of polymer (2.8) after exposure to NH_3(g) (right).

The *trans-cis* photoisomerization was investigated for the monomers (**2.5a** and **2.5b**) and the polymers (**2.7 – 2.10**). When monomer **2.5a** was excited with 410 nm light, the absorption due to the *trans* isomer (425 nm) of the azo dye slowly disappeared (53 min) and the absorption due to the *cis* form (375 nm and 500 nm) of the azo dye increased (Figure 2-16).[49] When the excitation source was removed the *cis* form of the azo dye thermally relaxed to regenerate the *trans* azo dye over 100 min (Figure 2-16).

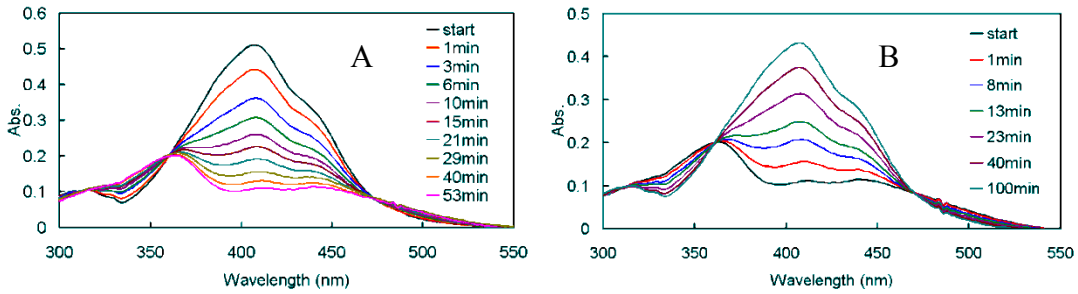


Figure 2-16: (A) *Trans-cis* photoisomeration of azo dye containing monomer 2.5a at 298K in 2MeTHF using 410 nm excitation source. (B) Thermal *cis-trans* isomeration of monomer 2.5a.

The analogous polymer (**2.7**) displayed similar *trans-cis* photoisomeration. As the polymer was exposed to an excitation source of 410 nm in 2MeTHF, the absorbance centred around 425 nm (*trans* form) decreased over 30 min and the absorbencies around 375 nm and 500 nm increased (*cis* form). When the excitation was removed the *cis* azo dye slowly converted back to the *trans* form of the azo dye (80 min) (Figure 2-17).

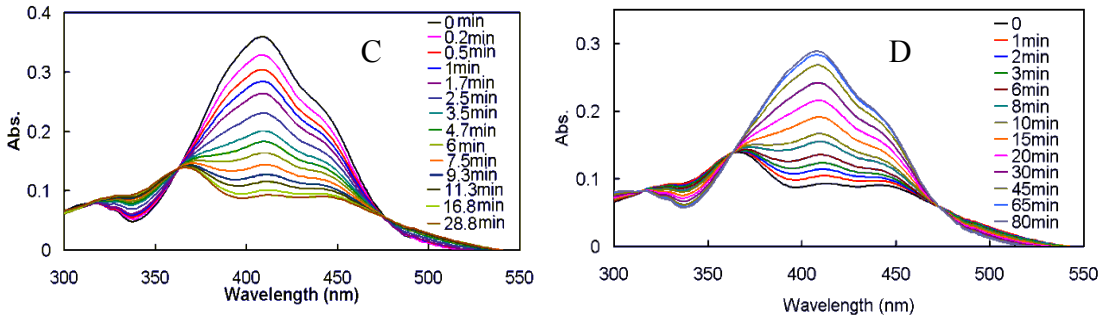


Figure 2-17: (C) *Trans-cis* photoisomeration of polymer 2.7 at 298K in 2MeTHF using 410 nm excitation source. (D) *Cis-trans* isomeration of polymer 2.7.

Copolymer **2.10** showed the *trans-cis* isomeration of both the hetaryl and aryl azo dyes (Figure 13). The gradual increase in the absorbance around 250 nm was due to the generation of the *cis* aryl azo dye and the band at 375 nm was due to the *cis* form of the hetaryl azo dye.[49]

Once the excitation source was removed the *cis* forms of the azo dyes thermally relaxed back to their *trans* isomers (Figure 2-18).

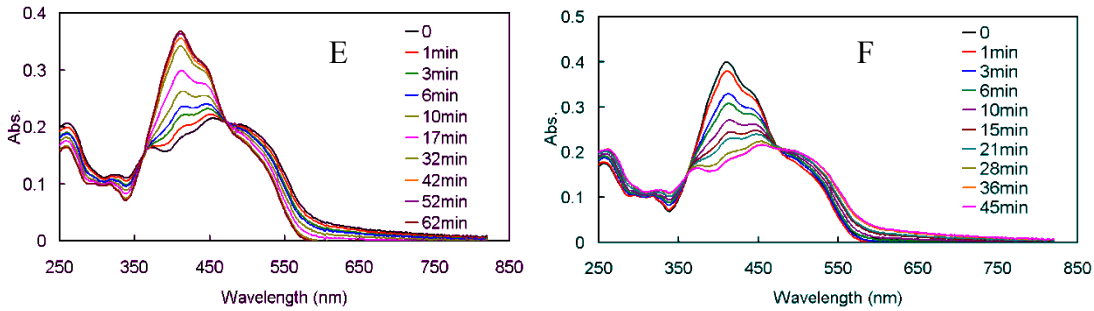


Figure 2-18:(E) *Trans-cis* photoisomeration of polymer 2.10 at 298K in 2MeTHF using 410 nm excitation source. (F) *Cis-trans* thermal isomeration of polymer 2.10.

The thermal properties of the polymers were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the resulting thermal data for polymers **2.7 – 2.10** are tabulated in Table 2-3. Thermal gravimetric analysis of the homo- and co-polymers showed that the polymers were relatively thermally stable. The thermogram of polymer **2.7** is shown in Figure 2-19. Polymer **2.7** displayed 3 degradations. The first decomposition occurred between 250 °C and 390 °C corresponds to the degradation of the azo group, which is consistent with previous results of azo dye containing polymers,[48] as well as with the degradation of the free azo dyes. The second decomposition occurred between 400 °C and 550 °C due to the decomposition of the polynorbornene backbone,[50, 51] and the third decomposition occurred between 600 °C and 1000 °C. Homopolymers **2.7** and **2.8** and copolymer **2.9** showed complete degradation at temperatures below 900 °C (850 °C, 700 °C, and 840 °C respectively) whereas copolymer **2.10** showed complete degradation above 950 °C.

Table 2-3:Thermal gravimetric analysis data of polymers 2.7 – 2.10

Polymer #	Segment 1 Temperature (onset/endset)	%weight loss	Segment 2 Temperature (onset/endset)	%weight loss	Segment 3 Temperature (onset/endset)	%weight loss
2.7	250 °C – 345 °C	28	350 °C – 500 °C	26	550 °C – 700 °C	43
2.8	250 °C – 400 °C	33	400 °C – 540 °C	33	540 °C – 850 °C	33
2.9	250 °C – 380 °C	30	390 °C – 520 °C	40	580 °C – 840 °C	30
2.10	250 °C – 375 °C	28	400 °C – 580 °C	32	600 °C – 950 °C	29

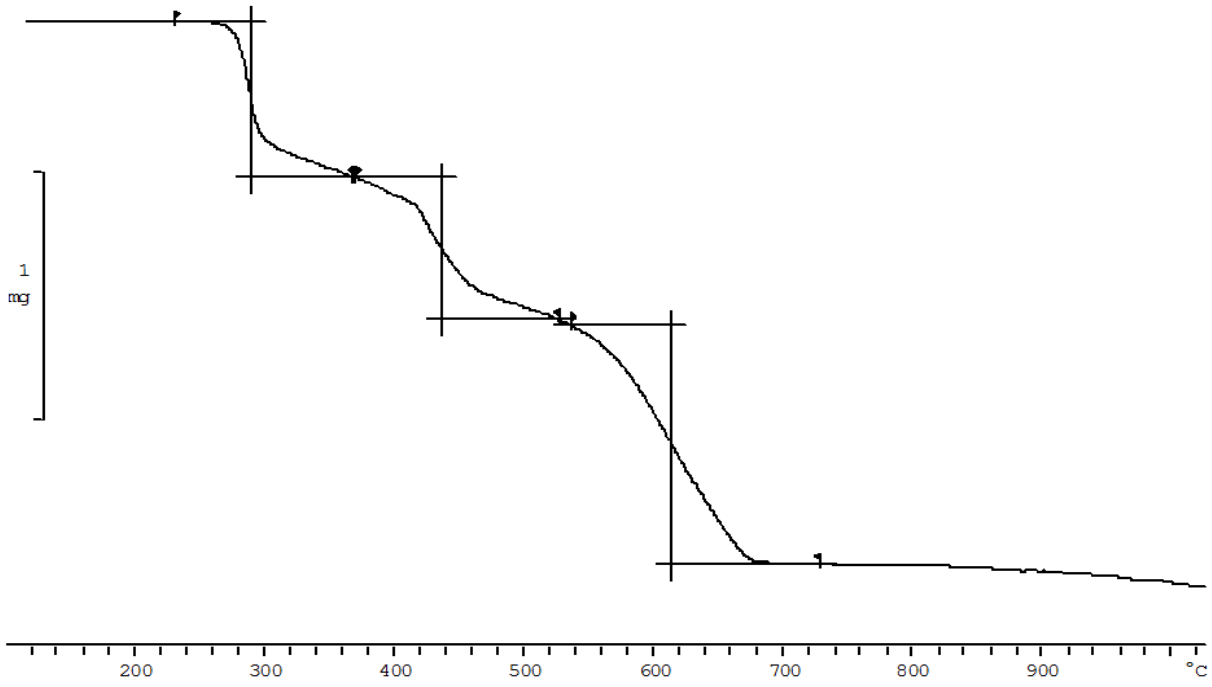


Figure 2-19: TGA thermogram of polymer 2.7 showing 3 decomposition steps.

The glass transition temperatures of the polymers were recorded between 93 °C and 133 °C (Table 2-4). Polymer **2.7,** with the bulkier benzothiazole based azo dye, possessed a higher T_g (132.5 °C) than polymer **2.8** comprised of the azoaniline dye (93.9 °C). The

copolymers possessed T_gs near the same values. Figure 2-20 shows the thermogram of polymer **2.10** as a representative sample.

Table 2-4: Glass transition temperatures of polymers 2.7 - 2.10

Polymer #	T_g (°C) at the midpoint
2.7	132.5
2.8	93.9
2.9	110.8
2.10	93.3

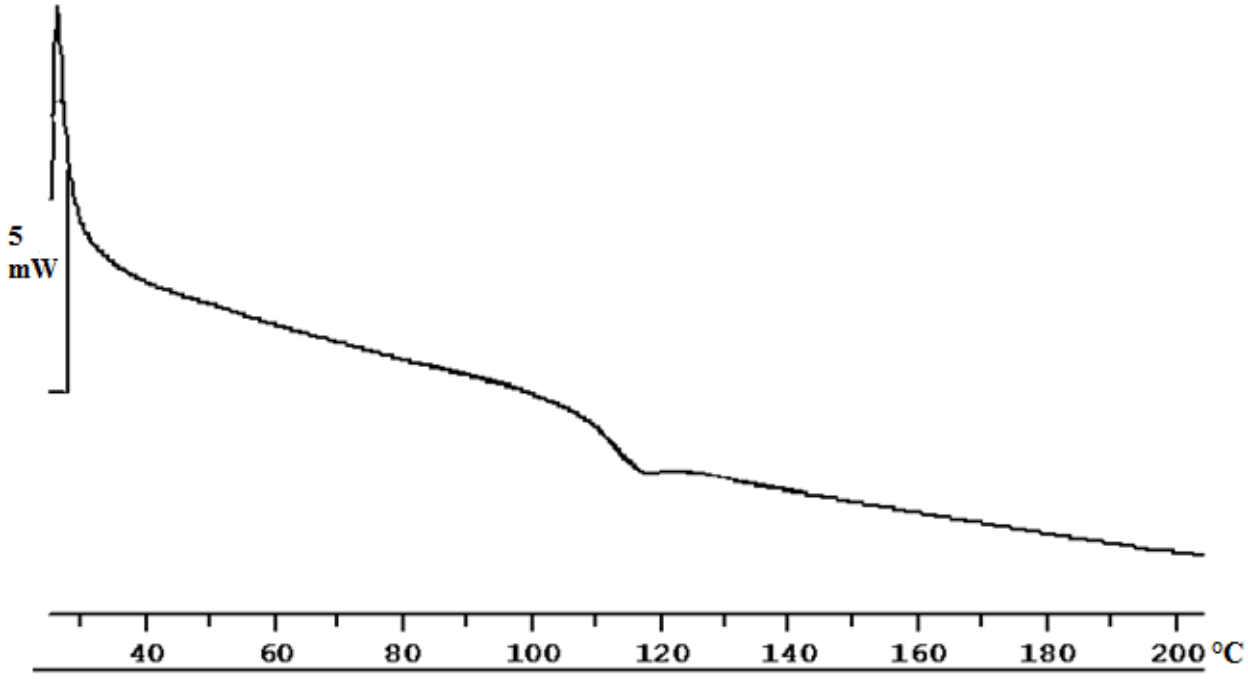


Figure 2-20: DSC Thermogram of polymer 2.10.

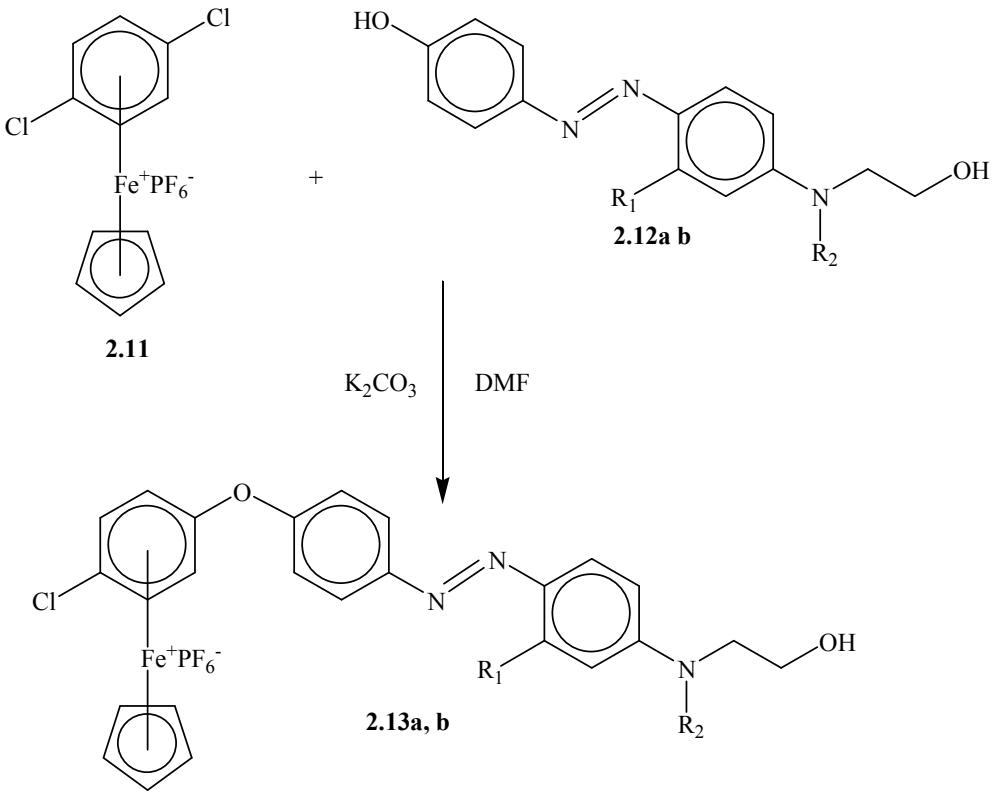
2.2.2 Preparation of cationic cyclopentadienyliron based polymers containing ferrocene and azo dyes in their backbones.

The preparation of polymers containing pendent cationic cyclopentadienyliron moieties, azo dyes, and ferrocene was performed in the attempts to develop materials that possess the

photophysical properties of azo dyes along with the redox properties of both ferrocene and cationic cyclopentadienyliron.

Azo functionalized cationic organoiron complexes were prepared utilizing the enhanced susceptibility of the chloro groups on the η^6–dichlorobenzene–η^5– cyclopentadienyliron to nucleophilic aromatic substitution. In this study azo dyes containing two different types of OH groups were utilized: phenolic and alcoholic. Both groups can be deprotonated and used for nucleophilic aromatic substitution. During this reaction, it is important to control the reaction conditions to force the azo dye to react with the chosen site. While the alcoholic group is more nucleophilic than the phenolic group, by controlling the pH of the reaction mixture it is possible to deprotonate only the phenolic group, therefore only allowing the phenoxide group to partake in the substitution reaction (pK_a of alcoholic groups: 16-18, pK_a of phenolic groups: 9.95). The reaction of η^6–dichlorobenzene–η^5– cyclopentadienyliron (**2.11**) with azo dyes **2.12a** or **2.12b** in the presence of K_2CO_3 resulted in the formation of the vibrantly coloured azo dye functionalized complexes **2.13a** and **2.13b** (Scheme 2-5).

The products were analyzed through ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **2.13a** is shown in Figure 2-21. The azo dye aromatic resonances appear as doublets centred at 7.96 ppm, 7.84 ppm and 7.48 ppm. There is one doublet due to the azo dye overlapping with the resonances due to the complexed aromatics (the azo dye should have four sets of doublets). The complexed aromatics appear as a multiplet between 6.93 ppm and 6.84 ppm (due to overlap with the azo dye resonance) and as a doublet at 6.59 ppm.



a = R_1 = H, R_2 = CH_2CH_3
b = R_1 = CH_3, R_2 = CH_2CH_2CN

Scheme 2-5: Synthesis of organoiron complexes containing azo dyes.

The sharp singlet at 5.42 ppm is due to the cyclopentadienyliron moiety and the multiplet at 3.91ppm (a) is from the CH_2-O of the azo dye aliphatics. The remaining azo dye aliphatics appear at 3.81 ppm (b), 3.65 ppm (c), and 1.16 ppm (d). The successful synthesis of **2.13a** can be concluded due to the single cyclopentadienyliron resonance, and that there are two doublets for the complexed aromatics.

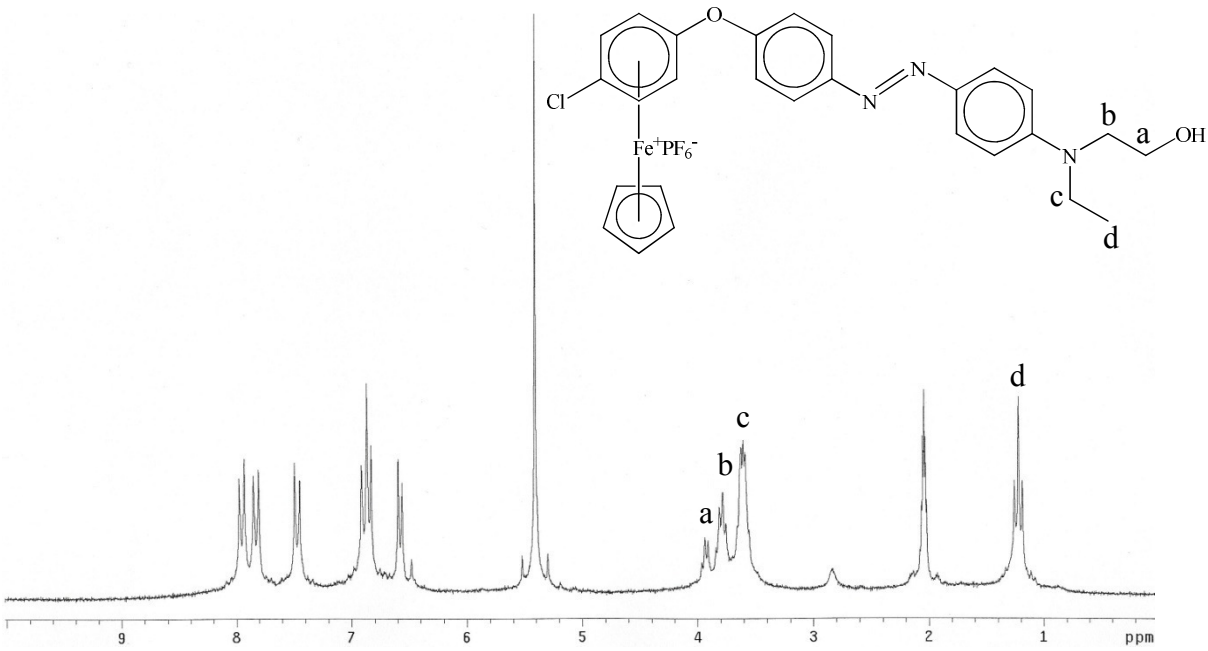


Figure 2-21: 200 MHz ^{1}H NMR spectrum of complex 2.13a.

The ^{13}C NMR spectrum of complex **2.13a** (Figure 2-22) further confirms the structure and successful synthesis of the product. The carbons of the azo dye aromatics appear at 126.10 ppm, 124.94 ppm, 122.11 ppm, and 112.12 ppm. The carbon resonances of the complexed aromatics appear at 87.81 ppm and 77.43 ppm and their quaternary signals appear at 133.45 and 105.01 ppm. These resonances are characteristic of arene-coordinated cyclopentadienyliron groups where the arene is substituted with one oxygen and one chlorine. The cyclopentadienyl ring's carbons appear as a sharp resonance at 80.49 ppm. The remaining aliphatic groups resonate at 60.03 ppm (a), 53.24 ppm (b), 46.24 ppm (c), and 12.34 ppm (d). These resonances are due to the methylene attached to the alcohol, the methylene between the alcohol and nitrogen, the methylene bound to the nitrogen and terminal CH_3, and the CH_3 respectively.

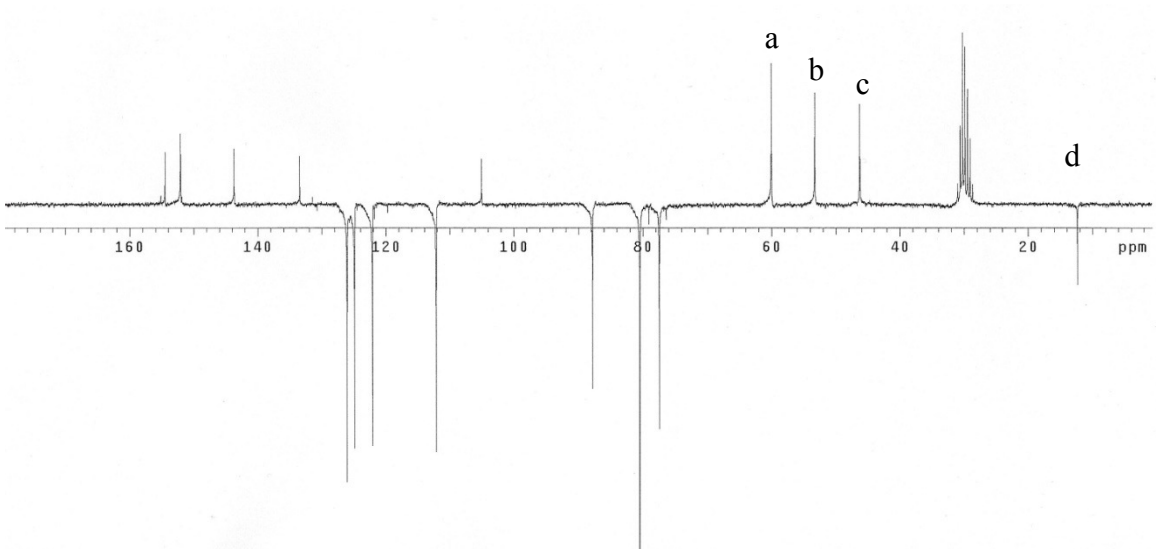
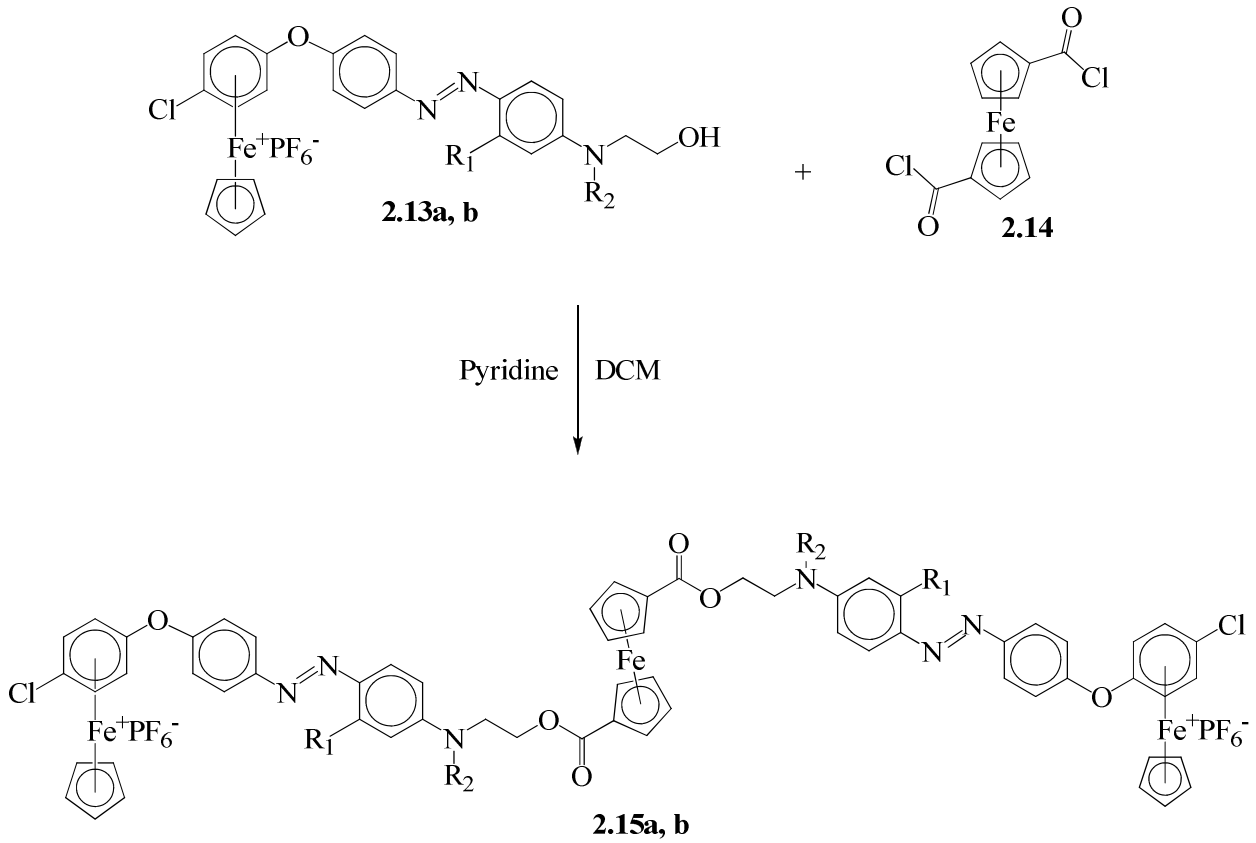


Figure 2-22: 50 MHz attached proton test (APT) ^{13}C-NMR spectrum of complex 2.13a.

Complexes **2.13a** and **2.13b** possess single chloro-groups; however, two terminal chloro-groups are required for polymerization. Therefore, it was necessary to prepare monomers possessing azo dyes in their backbone as well as two terminal chlorine groups on the complexed aromatic ring. The azo dyes in complexes **2.13a, b** each contain terminal aliphatic alcohol groups. Reacting these complexes with a dicarboxylic acid or dicarbonyl chloride would give a complex that possesses two organoiron complexes, each possessing a terminal chlorine group, which could be subsequently polymerized. Complexes with two pendent cationic cyclopentadienyliron moieties and two azo dye groups bridged by a ferrocene moiety were prepared through the reaction of complex **2.13a, b** with 1,1'-dicarbonylchloride ferrocene (**2.14**) (Scheme 2-6).



Scheme 2-6: Synthesis of azo dye containing organoiron monomers.

Figure 2-23 shows the ^{1}H NMR spectrum of monomer **2.15a**. The major difference between the spectrum of monomer **2.15a** and its corresponding starting materials complex **2.13a**, is that resonances due to the ferrocene moiety have appeared at 5.41 ppm and 4.46 ppm. Also, the resonance due to the alcoholic methylene of the azo dye has shifted from 3.91 ppm to overlap with the ferrocene signal at 4.46 ppm; this is due to the formation of the ester. As final confirmation of the product, the integrations of the resonances are consistent with the structure.

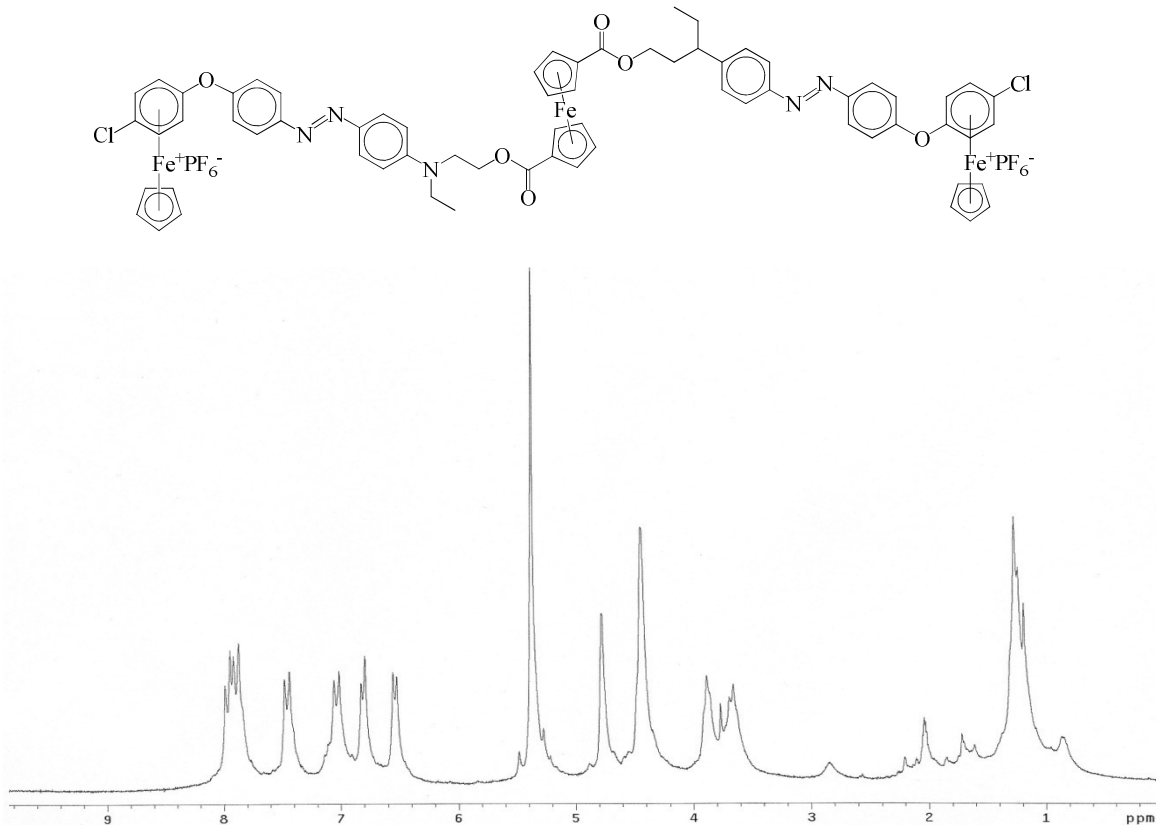


Figure 2-23: ^{1}H NMR spectrum of monomer 2.15a.

The ^{13}C NMR spectrum of monomer **2.15a** (Figure 2-24) also confirmed the formation of the product from the appearance of the resonances at 73.60 ppm, 72.42 ppm, and 170.39 ppm due to the ferrocene moiety. Also, an ester group was confirmed by with the ester methylene resonance, which shifted from 60.03 ppm to 62.51ppm.

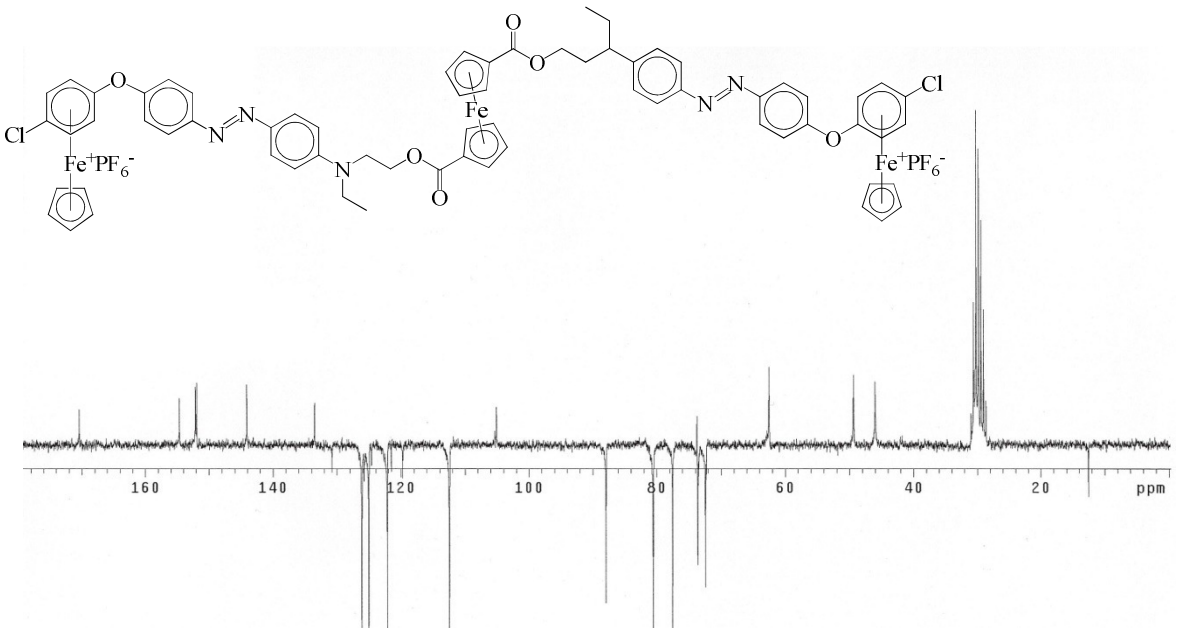
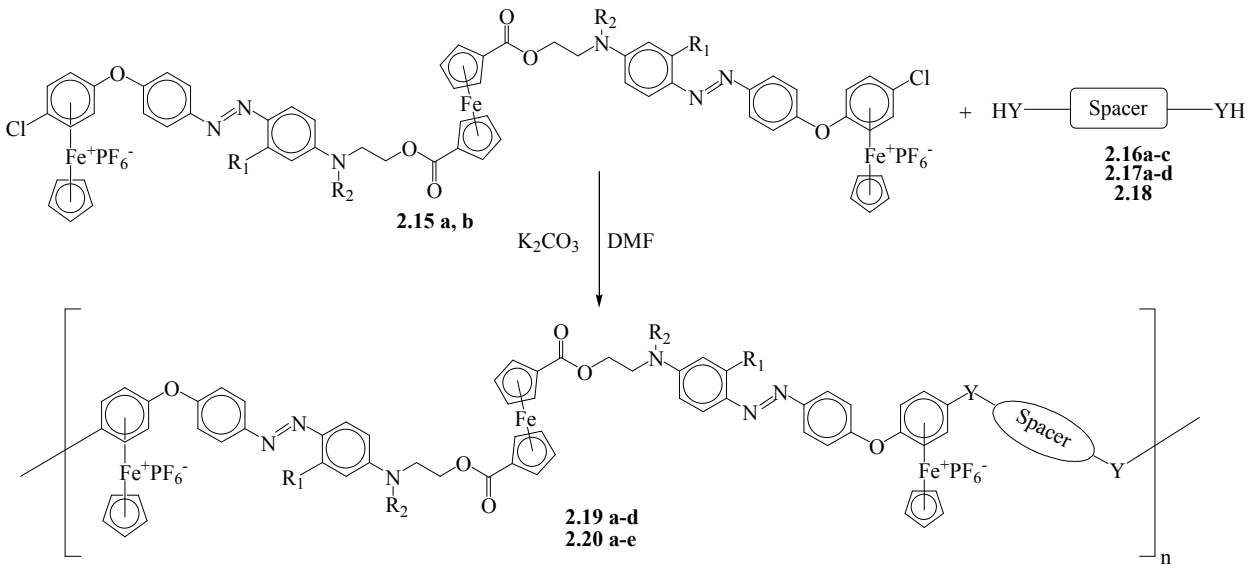


Figure 2-24: 50 MHz APT ^{13}C-NMR spectrum of monomer 2.15a.

The availability of the terminal chloro groups on monomers **2.15a, b** allows for polymerization through nucleophilic aromatic substitution. Chloro-substituted arene cationic cyclopentadienyliron complexes can be substituted using mild conditions using phenols, thiols or aliphatic amines to give: aromatic-ethers, -thioethers, and –amines. Dinucleophiles dissolved in a minimal amount of solvent will force the formation of polymers.

Monomers **2.15a** and **2.15b** were reacted with a number of dinucleophiles (**2.16 a – c, 2.17a – d,** and **2.18**) to give polymers containing pendent cyclopentadienyliron moieties and both ferrocene and azo dyes in their backbones. (Scheme 2-7).



2.19	Y	Spacer	2.20	Y	Spacer
a	NH	C_3H_6	**a**	S	C_2H_4
b		$C_{10}H_{20}$	**b**		C_4H_8
c		$C_{12}H_{24}$	**c**		C_6H_{12}
d	O	*p*-C_6H_4-$C(CH_3)_2$-*p*-C_6H_4	**d**		C_8H_{16}
			e	O	*p*-C_6H_4-$C(CH_3)_2$-*p*-C_6H_4

2.19: $R_1 = H$, $R_2 = CH_2CH_3$
2.20: $R_1 = CH_3$, $R_2 = CH_2CH_2CN$

Scheme 2-7: Synthesis of organoiron based azo dye polymers.

The success of the polymerization was determined through NMR spectrometry. Figure 2-25 shows the ^{1}H NMR spectrum of polymer **2.19d**. Clearly, the complexed aromatic protons have shifted from 6.68 ppm to 6.35 ppm. The resonances of the complexed aromatics are very close together since both sides of the arenes are now substituted with oxygen. The resonances due to the bisphenol A aromatics appear at 7.41 ppm and 7.24 ppm, and the terminal CH_3s appear at 1.72 ppm. There is also broadening of the proton resonances due to the increased size of the polymer as well as the polydispersity.

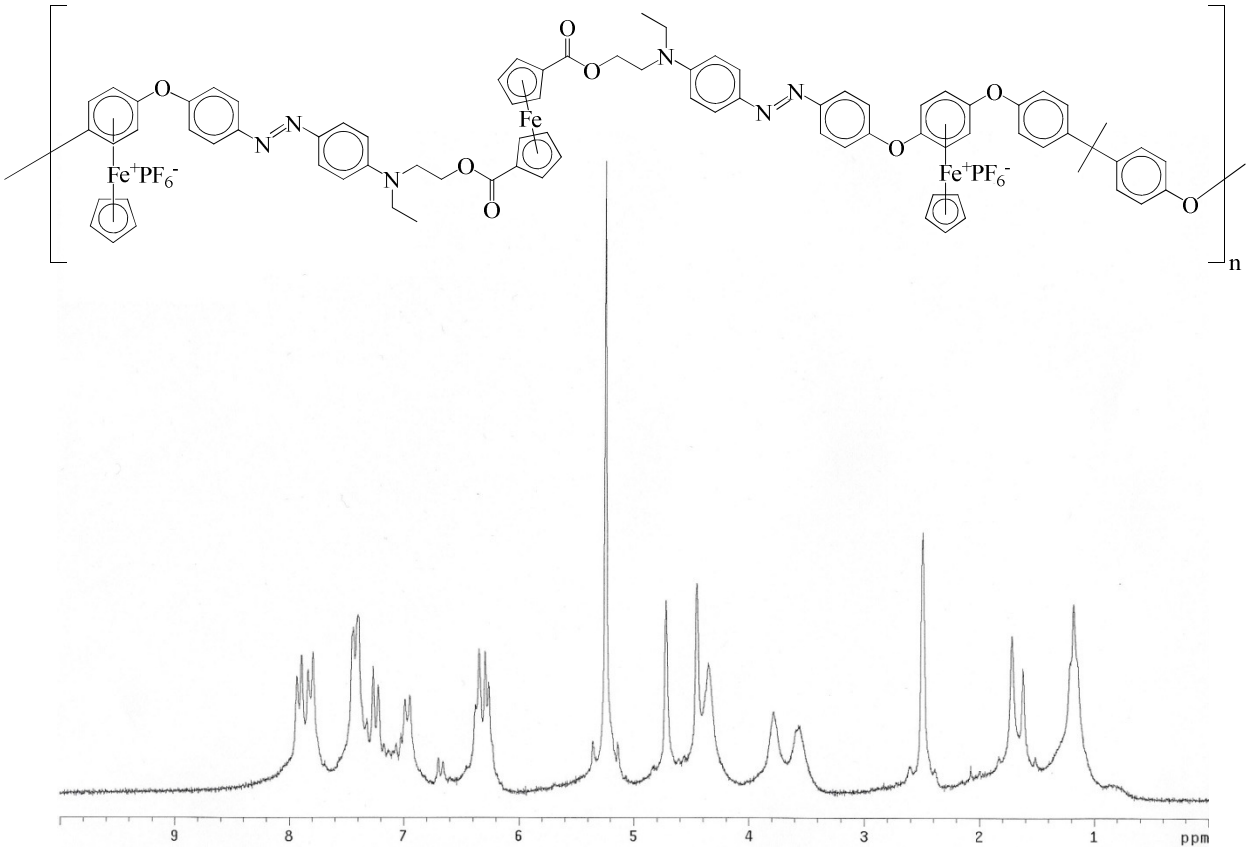


Figure 2-25: ^{1}H NMR spectrum of cationic polymer 2.19d.

The ^{13}C NMR spectrum **(**Figure 2-26**)** of polymer **2.19d** shows the resonances due to the methyl groups of the bisphenol A resonating at 30.55 ppm and the quaternary carbon at 42.09 ppm. The resonance of the complexed aromatic CHs next to the chlorine have shifted from 87.88 ppm to 75.43 ppm, and the quaternary carbon shifted from 105.09 ppm to 129.53 ppm due to the substitution with oxygen. There is also an upfield shift in the complexed aromatic ring from 87.88 ppm to 75.43 ppm due to the loss of the chlorine and formation of the ether linkage. The aromatic carbons of the bisphenol A unit resonate between 114 ppm and 125 ppm (CHs) and 142-155 ppm (Cs).

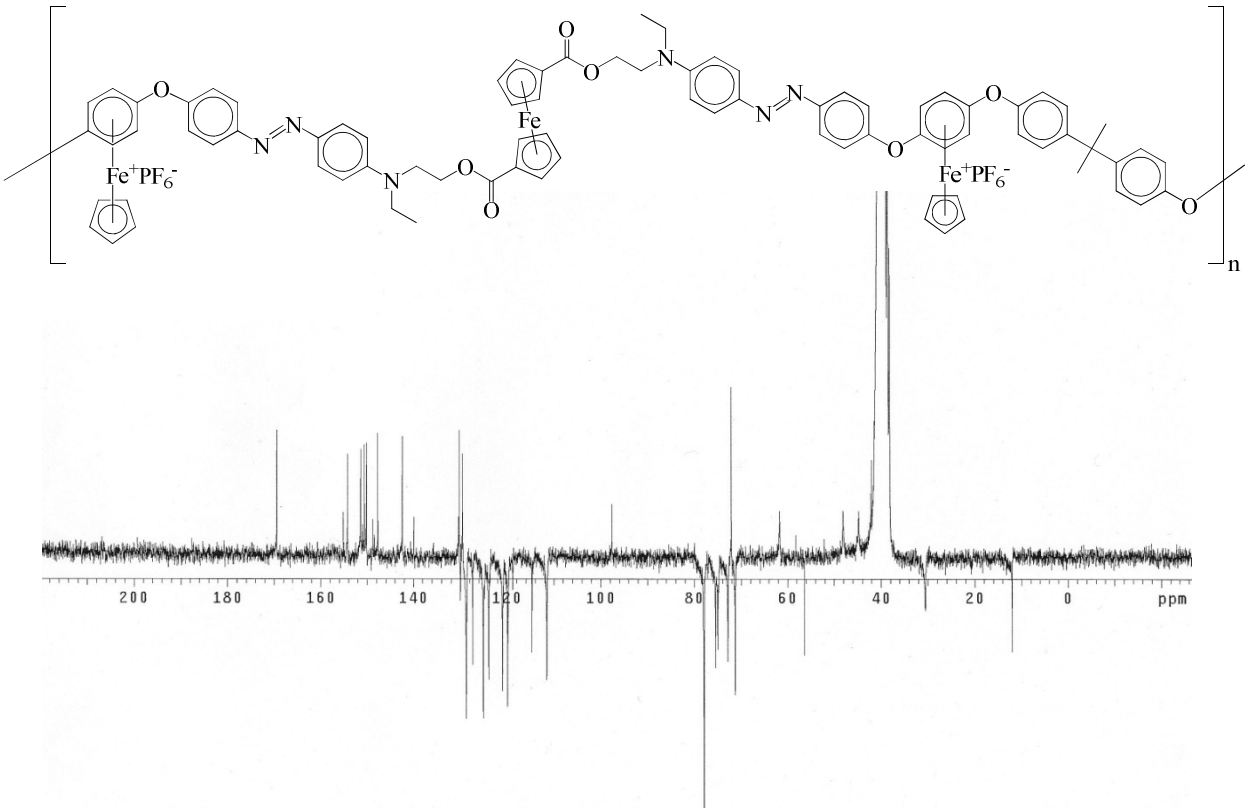


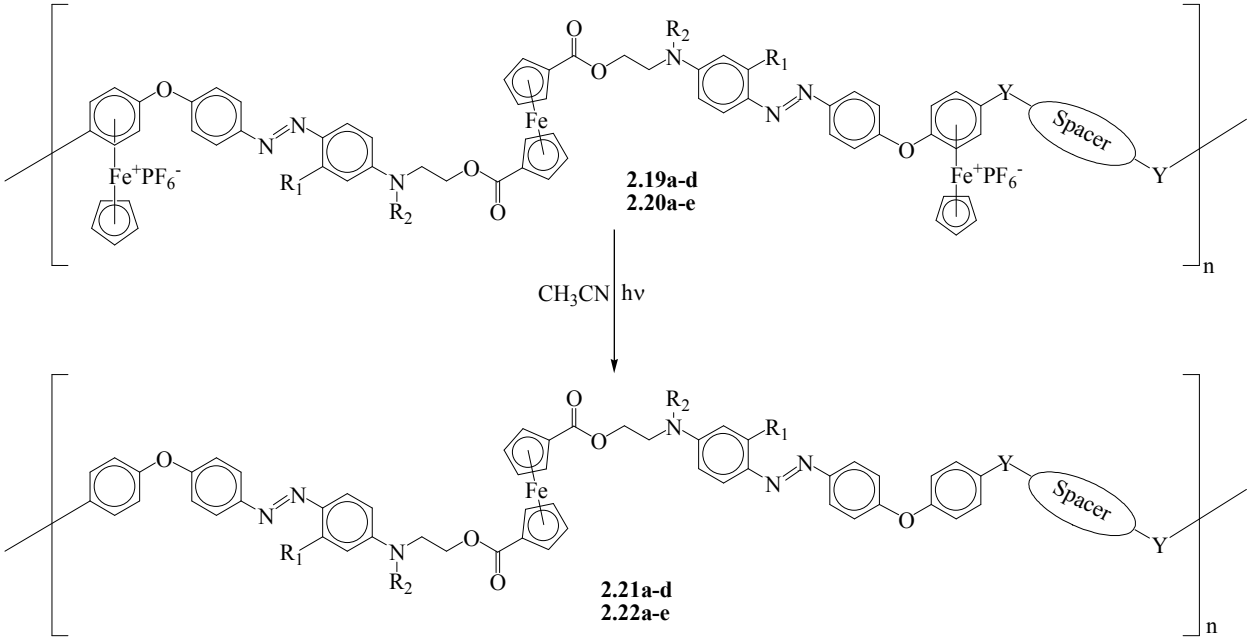
Figure 2-26: 50 MHz APT ^{13}C-NMR spectrum of cationic polymer 2.19d.

The coordination bonds between the cyclopentadienyliron and the arene ring in the cationic organoiron groups are relatively weak. The use of UV light (300 nm) in a strongly coordinating solvent such as acetonitrile can cleave the cyclopentadienyliron moiety from the arene. Ferrocene however, possess stronger coordination bonds between the iron and cyclopentadienyl rings and is therefore unharmed in this process.[52] Thus, photolysis cleaves the arene-bound Fe from **2.19** and **2.20** and leaves the polymer intact.

Gel permeation chromatography (GPC) is one of the most common methods to determine the molecular weight of polymers. Unfortunately, cationic cyclopentadienyliron moieties have unfavourable interactions with the gel permeation columns generally used.[52] To overcome this

problem, the neutral polyferrocene derivates of polymer **2.22a-d** and **2.23a-e** were prepared via photolysis.

Solutions of polymers **2.19a-d** and **2.20a-e** in DMF/CH_3CN were exposed to 300 nm light to give polyferrocenes **2.21a-d** and **2.22a-e** (Figure 2-27). After cleavage of the cationic cyclopentadienyliron moieties, the solubility of the polymers in polar organic solvents drastically decreased due to the loss of their polyelectrolyte behaviour. Also, due to the high aromaticity of the polymers they were highly insoluble in non-polar organic solvents as well. Therefore, spectroscopic characterization was limited to ^{1}H NMR spectroscopy in $CDCl_3$ or DMSO-d_6.



Scheme 2-8: Synthesis of azo dye containing polyferrocenes.

As can be seen in ^{1}H NMR spectrum of polyferrocene **2.21d** (Figure 2-27) the resonance at 5.24 ppm due to the cationic cyclopentadienyliron moiety is completely removed, and the resonances due to the complexed aromatics have shifted dramatically from 6.35 ppm to overlap with the resonances of other aromatic resonances as well as the resonance of $CDCl_3$ at 7.26 ppm.

These polymers are very poorly soluble as can be seen by the poor signal to noise in the ^{1}H NMR spectrum.

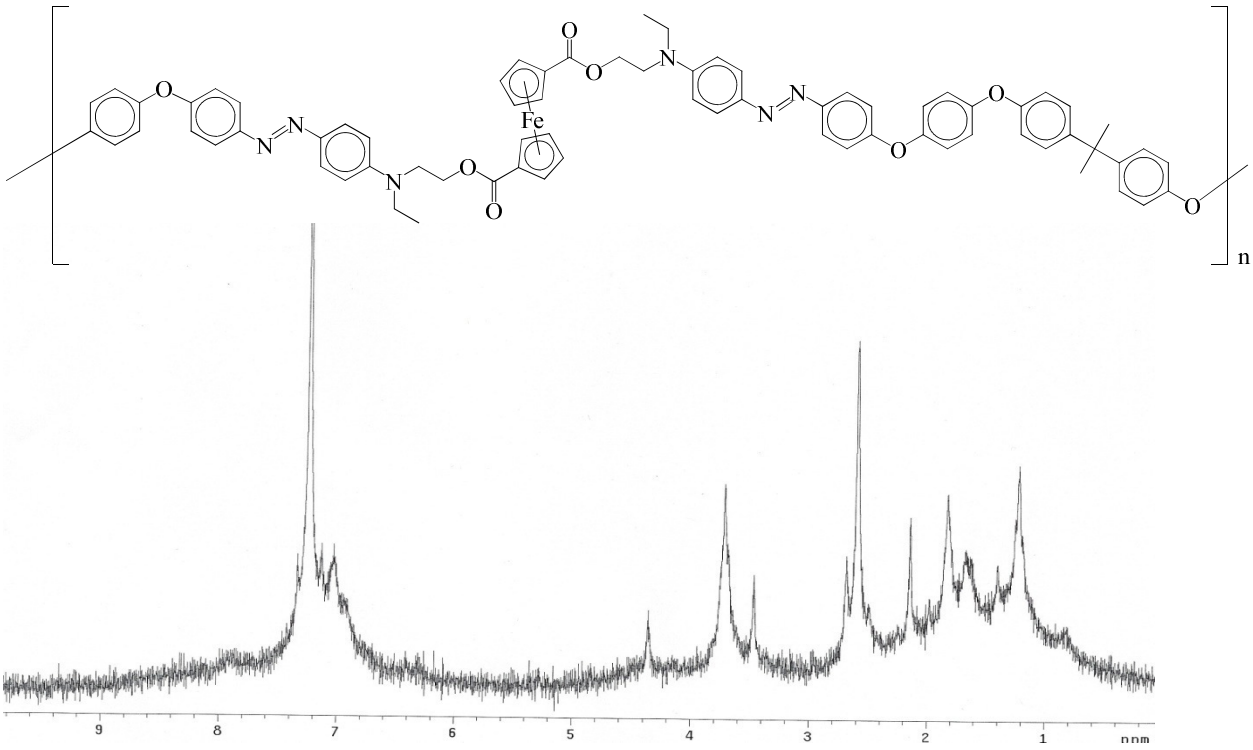


Figure 2-27: ^{1}H NMR spectrum of polyferrocene 2.22d

Polyferrocenes **2.22a-d** and **2.23a-e** were subjected to GPC analysis in order to determine their molecular weights and polydispersity indices (PDIs). Table 2-5 shows the $\overline{M_w s}$ of the soluble fractions of polymers **2.22a-d**. Unfortunately polyferrocenes **2.23a-e** were insoluble in THF and $\overline{M_w s}$ could not be obtained. Polyferrocenes **2.22a-d** were found to possess $\overline{M_w s}$ between 8600 and 11 500, which corresponded to $\overline{M_w s}$ between 10 000 and 13 000 for the cationic polymers **2.19a-d** (Table 2-6). The polymers also possessed PDIs between 1.5 and 2.5 indicating a large range of polymer chain lengths amongst individual polymer samples.

Table 2-5: Molecular weights of polyferrocenes 2.21a-d and 2.22a-e.

Polymer	$\overline{M_n}$	$\overline{M_w}$	PDI
2.21a	5000	11 500	2.3
2.21b	4736	9 000	1.9
2. 21c	7600	19 000	2.5
2. 21d	5733	8600	1.5
2.22a		Insol	
2. 22b		Insol	
2. 22c		Insol	
2. 22d		Insol	
2. 22e		Insol	

Table 2-6: Molecular weights of cationic polymers 2.19a-d and 2.20a-e.

Polymer	$\overline{M_n}$	$\overline{M_w}$	PDI
2.19a	5650	13 000	2.3
2.19b	5263	10 000	1.9
2.19c	8800	22 000	2.5
2.19d	6700	10 000	1.5
2.20a		Insol	
2.20b		Insol	
2.20c		Insol	
2.20d		Insol	
2.20e		Insol	

Differential scanning calorimetry was performed to determine the glass transition temperatures of the cationic polymers **2.20a-e.** The glass transition temperatures were found to range between 69 °C to 130 °C (Table 2-7). It can be seen that polymer **2.20 b-d** have similar T_gs, and polymer **2.20e** possesses a significantly higher T_g. This is to be expected since aliphatic polymers are known characteristically possess lower T_gs than aromatic polymers since less energy is required to initiate motion in aliphatic chains.

Table 2-7: Glass transition temperatures of polymers 2.20a-e.

Polymer #	T_g (°C)
2.20a	69
2.20b	96
2.20c	112
2.20d	98
2.20e	130

Thermal gravimetric analysis was performed on both the cationic organoiron polymers (Table 2-8) and the neutral polyferrocenes (Table 2-9). The thermal analysis showed that all the polymers were thermally stable. The cationic polymers began to decompose between 200 °C and 260 °C due to the pyrolysis of the cationic cyclopentadienyliron moiety and degradation of the azo group. The remaining ferrocene and aromatic groups decomposed between 300 °C to 550 °C.

Table 2-8: Thermal decomposition data for cationic polymers 2.19a-d and 2.20a-e.

Polymer	Onset (°C)	Endset (°C)	% Loss	Onset (°C)	Endset (°C)	% Loss
2.19a	200	278	19.0	290	480	23.8
2.19b	184	282	21.3	292	458	42.8
2.19c	200	310	13.8	330	534	34.6
2.19d	182	364	16.2	390	474	34.1
2.20a	190	260	15	310	520	52
2.20b	200	270	13	320	550	52
2.20c	200	240	12	300	500	40
2.20d	210	260	12	310	460	52
2.20e	230	280	15	380	520	48

The polyferrocenes **2.22a-d** and **2.23a-e** also showed decomposition beginning at 180 °C due to the decomposition of the azo group. In most cases there was a single decomposition which began between 180 °C and lasted until the polymer were completely decomposed (up to 800 °C).

Table 2-9: Thermal decomposition data for polyferrocenes 2.21a-d and 2.22a-e

Polymer	Onset (°C)	Endset (°C)	% Loss	Onset (°C)	Endset (°C)	% Loss
2.21a	180	322	31.1	362	498	36.1
2.21b	205	312	35.7	---	---	---
2. 21c	180	398	18.9	515	736	33.6
2. 21d	145	260	23.3	---	---	---
2.22a	210	780	85			
2. 22b	300	480	62			
2. 22c	220	460	78			
2. 22d	350	800	90			
2. 22e	210	500	70			

Upon analysis of the thermal data it is impossible to make any correlations between the polymer spacer and the thermal stability or T_g. In theory a correlation should be seen between length of aliphatic spacer and lower T_g since this is known to increase the flexibility of the polymer backbone. There should also be an increase in thermal stability of the polymers with aromatic spacer compared to those of the aliphatic spacers. One possible reason no correlation can be drawn is due to the dramatic differences in the molecular weights of the polymers, as polymer size would have an overpowering affect on the physical properties of the polymers. Since polymers **2.22a-d** and **2.23a-e** are not of the same general size the physical properties of these polymers cannot directly be correlated to each other and thus can only be reported as individual values.

UV-visible analysis of polymer **2.22a-d** and **2.23a-e** showed that in DMF solutions, the polymer displayed λ_{max}s between 415 nm and 430 nm due to $\pi-\pi*$ transition of the azo dye. When solutions were exposed to increasing amounts of $HCl_{(aq)}$ the λ_{max}s shifted to between 540 nm and 560 nm due to the formation of the azonium form of the azo group (Table 2-10).

Table 2-10: UV-visible data for polymer 2.19a-d.

Polymer	λ_{max} DMF (nm)	λ_{max} Acidified (nm)
2.19a	421.0	555.5
2.19b	418.5	551.0
2.19c	416.0	554.0
2.19d	427.5	549.5

As can be seen in Figure 2-28 as the amount of acid was increased, the absorbance due to the azo group gradually decreased and the absorbance due to the azonium group gradually increased through an isosbestic point.

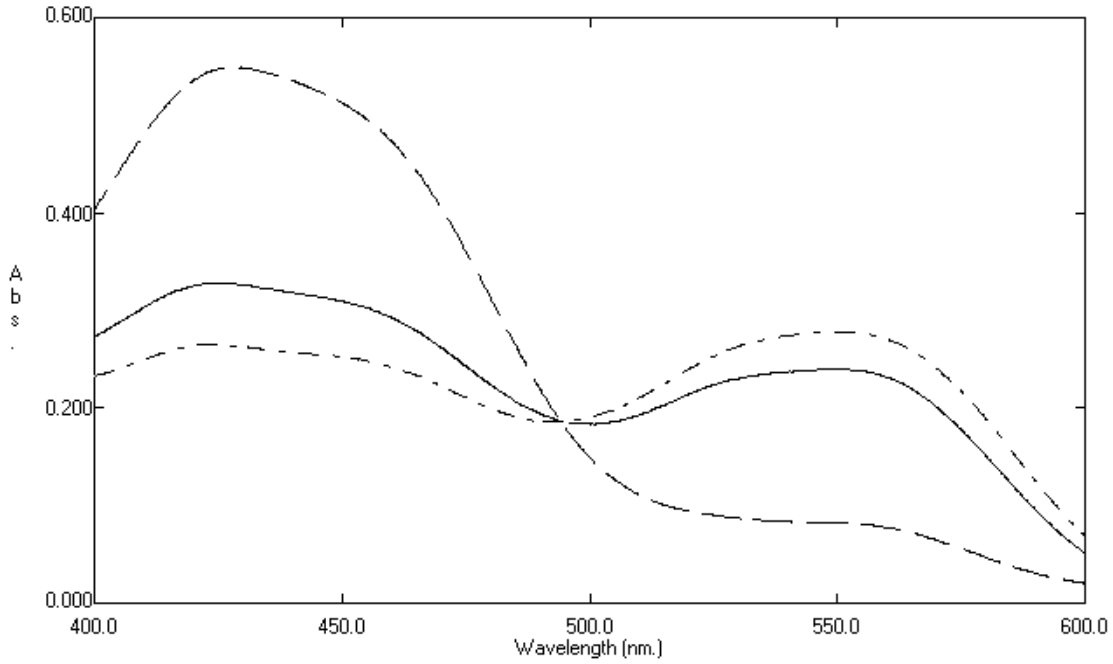


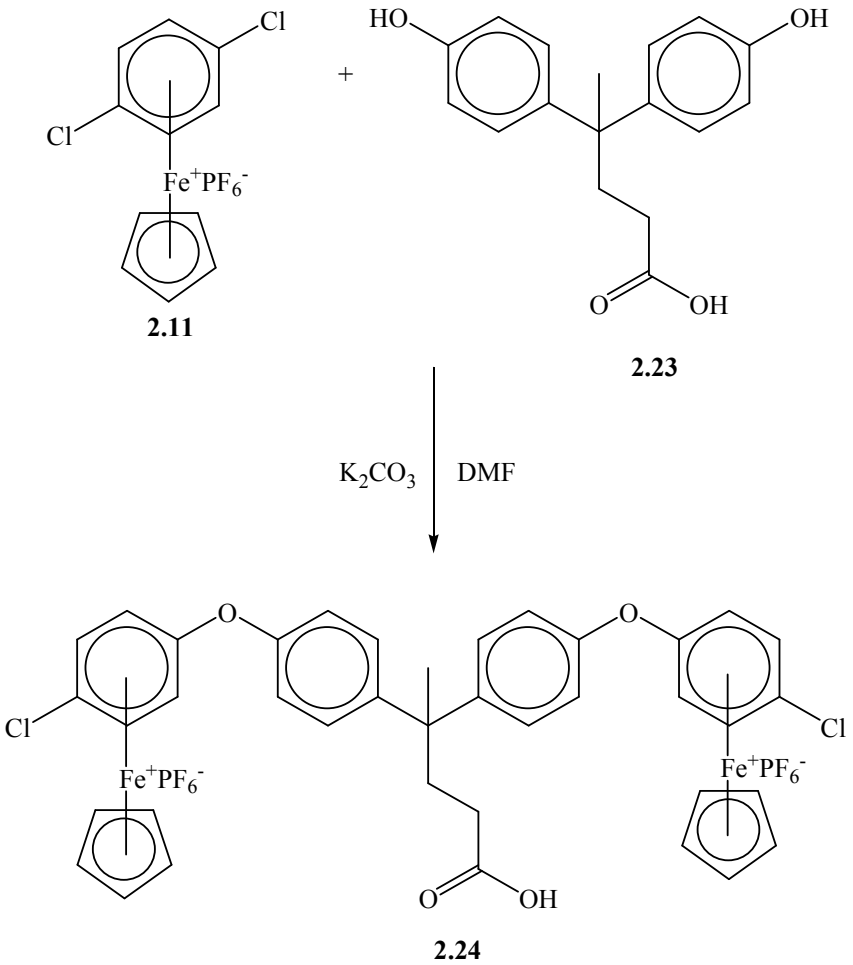
Figure 2-28: UV-visible spectrum of polymer 2.19d.

The photo-physical properties of complexes **2.19a-d** and **2.20a-e** and monomers **2.15a** and **2.15b** were analyzed to observe the *trans-cis* photo-isomeration of the azo group. However, no isomerization was observed for these materials. It is theorized that the *trans-cis* isomeration was not observed due to the metal centre. It is thought that the cationic metal centre acts as an "energy sink" and that it absorbs the energy that would otherwise cause the azo dye to isomerize.

2.2.3 Synthesis and analysis of organoiron complex containing multiple dyes

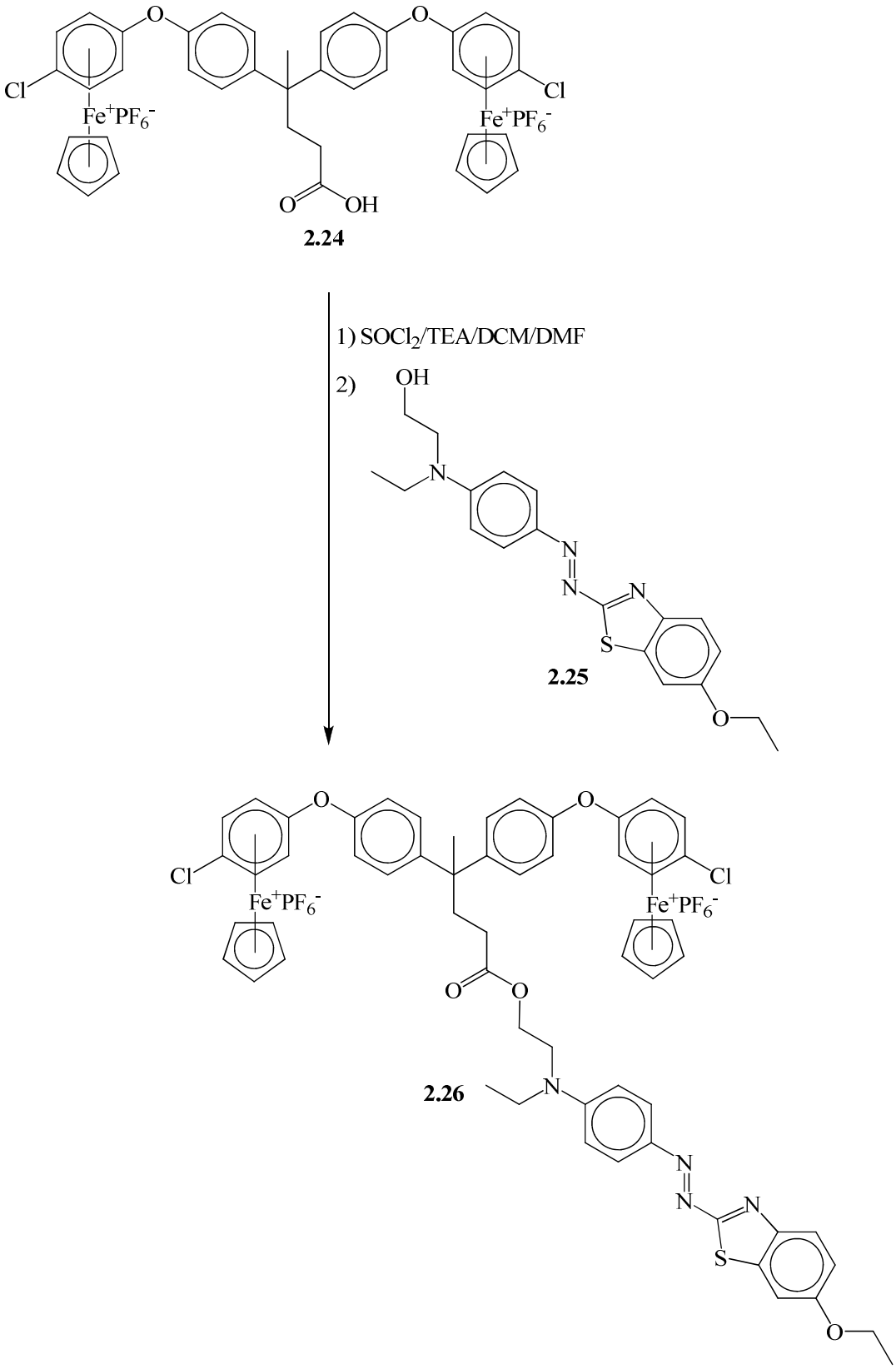
Designing compounds that contain several classes of azo dyes can result in multifunctional materials. Utilizing η^6–dichlorobenzene–η^5– cyclopentadienyliron mediated syntheses, it is possible to prepare complexes containing a wide variety of compounds. The use of η^6–dichlorobenzene–η^5– cyclopentadienyliron derivatives were utilized for the production of an organoiron complex containing multiple classes of azo dyes.

The reaction between η^6–dichlorobenzene–η^5– cyclopentadienyliron (**2.11**) and 4,4'-hydroxy-bisbenzene valeric acid resulted in the formation of the valeric bimetallic complex (**2.24**) (Scheme 2-9).



Scheme 2-9: Synthesis of organoiron complex 2.24 "valeric bimetallic".

Complex **2.24** possesses a carboxylic acid group, which can be condensed with various alcoholic groups to yield esters. Complex **2.24** was reacted with thionyl chloride to give the acid choride of complex **2.24**. This was then reacted with azo dye **2.25** to give a vibrantly coloured material containing one azo dye (**2.26**) in good yield (Scheme 2-10). Comparison between the IR spectra of complexes **2.24** and complex **2.26** showed a shift in the position of the carbonyl peak from 1709 cm^{-1} to 1732 cm^{-1} indicating formation of the ester.



Scheme 2-10: Synthesis of azo dye complex 2.26.

The synthesis of complex **2.26** was further indicated by the ^{1}H NMR spectrum (Figure 2-29). As can be seen the peaks at 1.75 ppm, 2.18 ppm and 2.53 ppm correspond to the methyl and methylenes of the iron complex respectively. The methyls of the azo dye appear at 1.25 ppm and 1.41 ppm. The triplets at 3.5 ppm and 4.0 ppm correspond to the amine CH_2 and ester CH_2 of the azo dye respectively. The quartet at 4.16 is due to the OCH_2 of the benzothiazole ring. The cyclopentadienyl ring resonates at 5.38 ppm and the complexed aromatic protons resonate at 6.4 ppm and 6.9 ppm. The benzothiazole aromatic protons appear between 6.9 and 7.2 ppm and the non-complexed aromatics appear at 7.2 and 7.6 ppm. The aromatics of the aniline group resonate between 7.8 and 7.95 ppm.

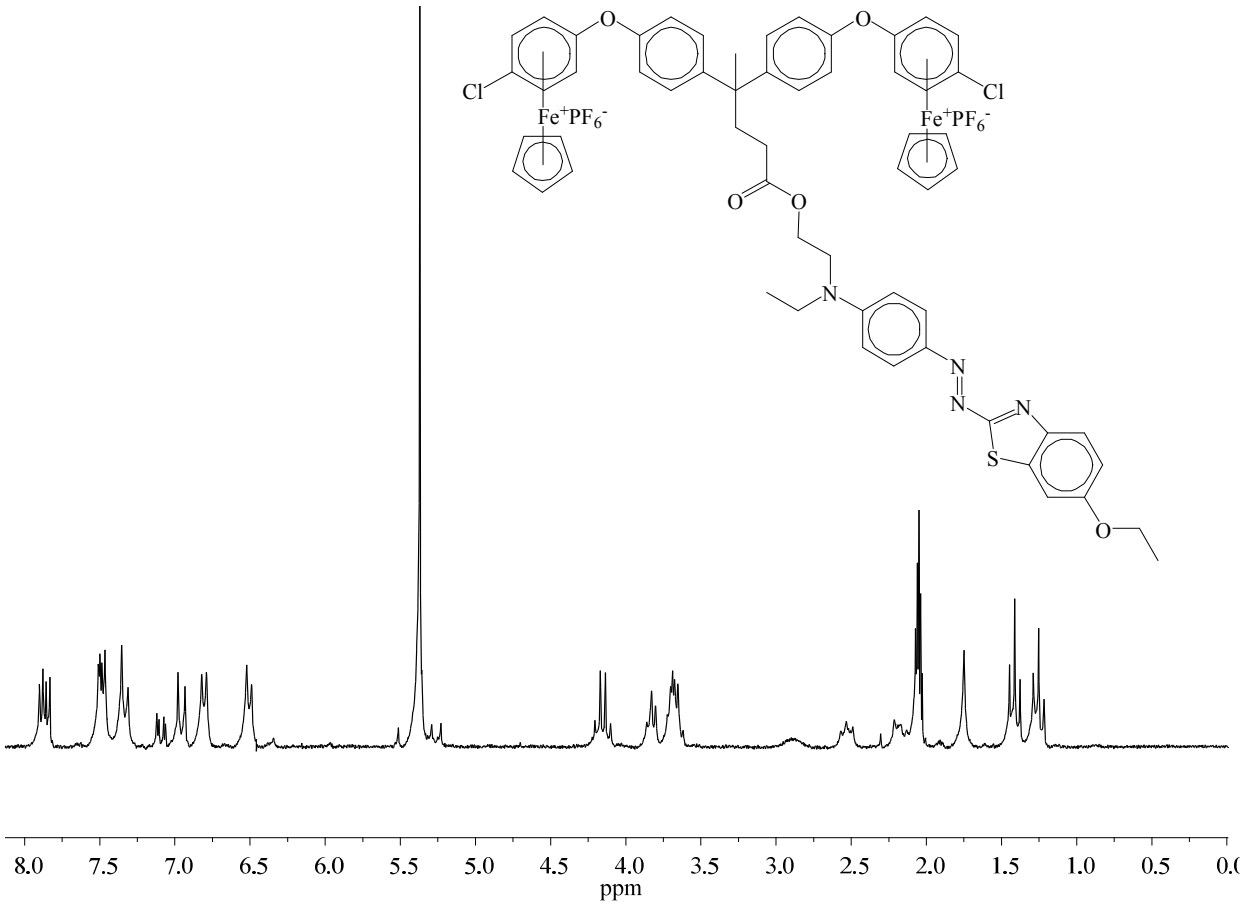


Figure 2-29: ^{1}H NMR spectrum of complex 2.26.

The ^{13}C NMR spectrum (Figure 2-30) further confirms the successful synthesis of the product. The resonances 64.80 ppm is characteristic of an ester CH_2 and the carboxyl carbon now appears at 174.63 ppm which is also characteristic of an aliphatic ester carbonyl.

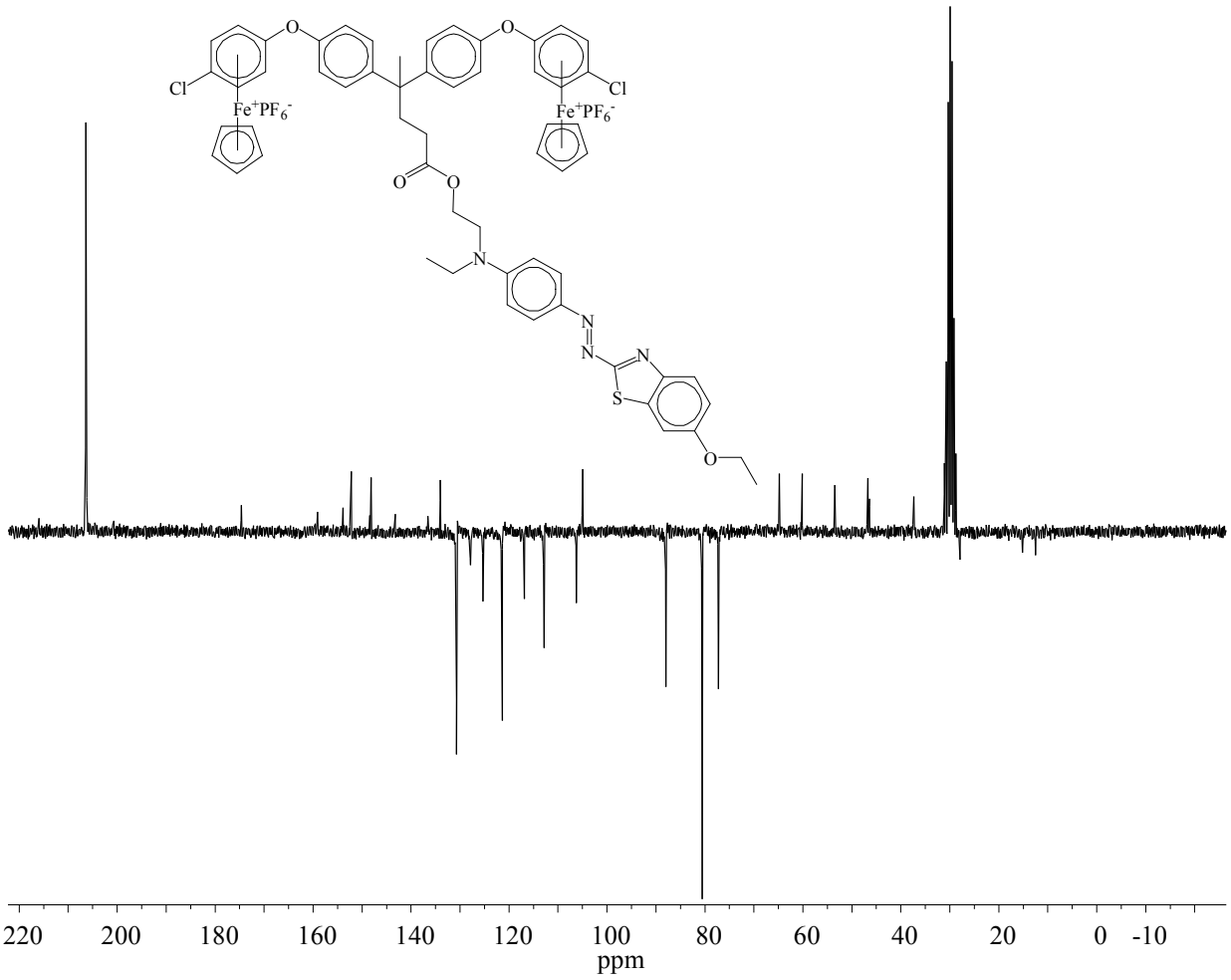
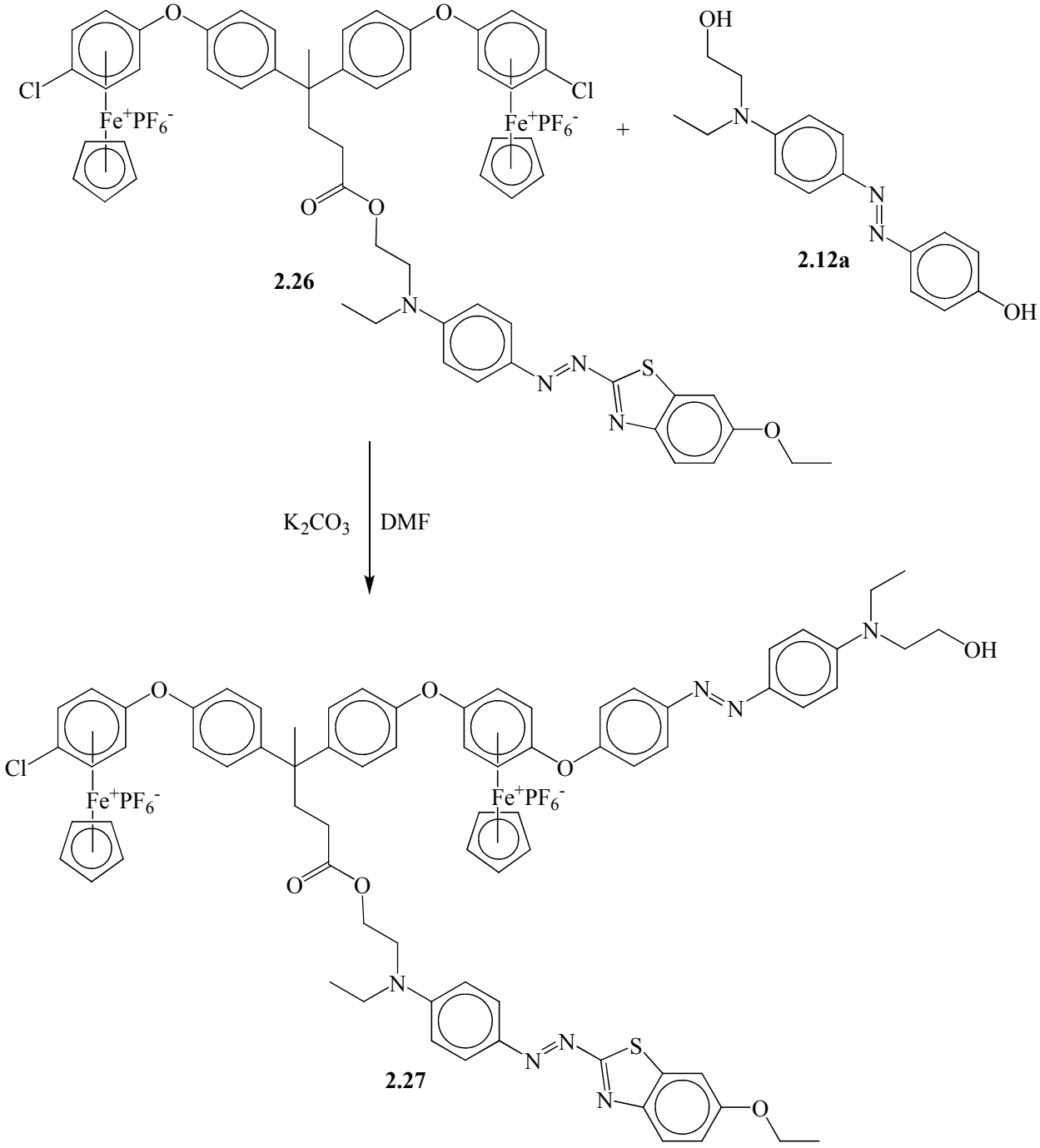


Figure 2-30: 50 MHz APT ^{13}C NMR spectrum of complex 2.26.

UV-vis analysis of complex **2.26** showed that in a solution of DMF the complex displayed a λ_{max} = 521 nm due to the $\pi-\pi*$ transition of the azo group. When exposed to $HCl_{(aq)}$ the λ_{max} shifted to 620 nm due to the formation of the azonium ion.

Utilizing the activation of the complexed arene towards nucleophilic aromatic substitution a second azo dye was incorporated into the molecule (Scheme 2-11). The second dye (**2.12a**) is aryl based which provided a separate λ_{max} from the hetaryl azo dye moiety.



Scheme 2-11: Synthesis of complex 2.27.

Figure 2-31 shows the ^{1}H NMR spectrum of complex **2.**27. The incorporation of the aryl azo dye is evident by the increased number of resonances in the aromatic region of the spectrum. Also, the triplet due to the terminal CH_3 of the aniline of the hetaryl dye now appears as a multiplet due to the overlap with the resonance due to the terminal CH_3 of the aniline for the aryl dye. This resonance also integrates for 6 Hs. Finally, there are two resonances for the different cyclopentadienyl rings, since one ring is disubstituted with oxygen and the other is substituted with a chlorine and an oxygen atom.

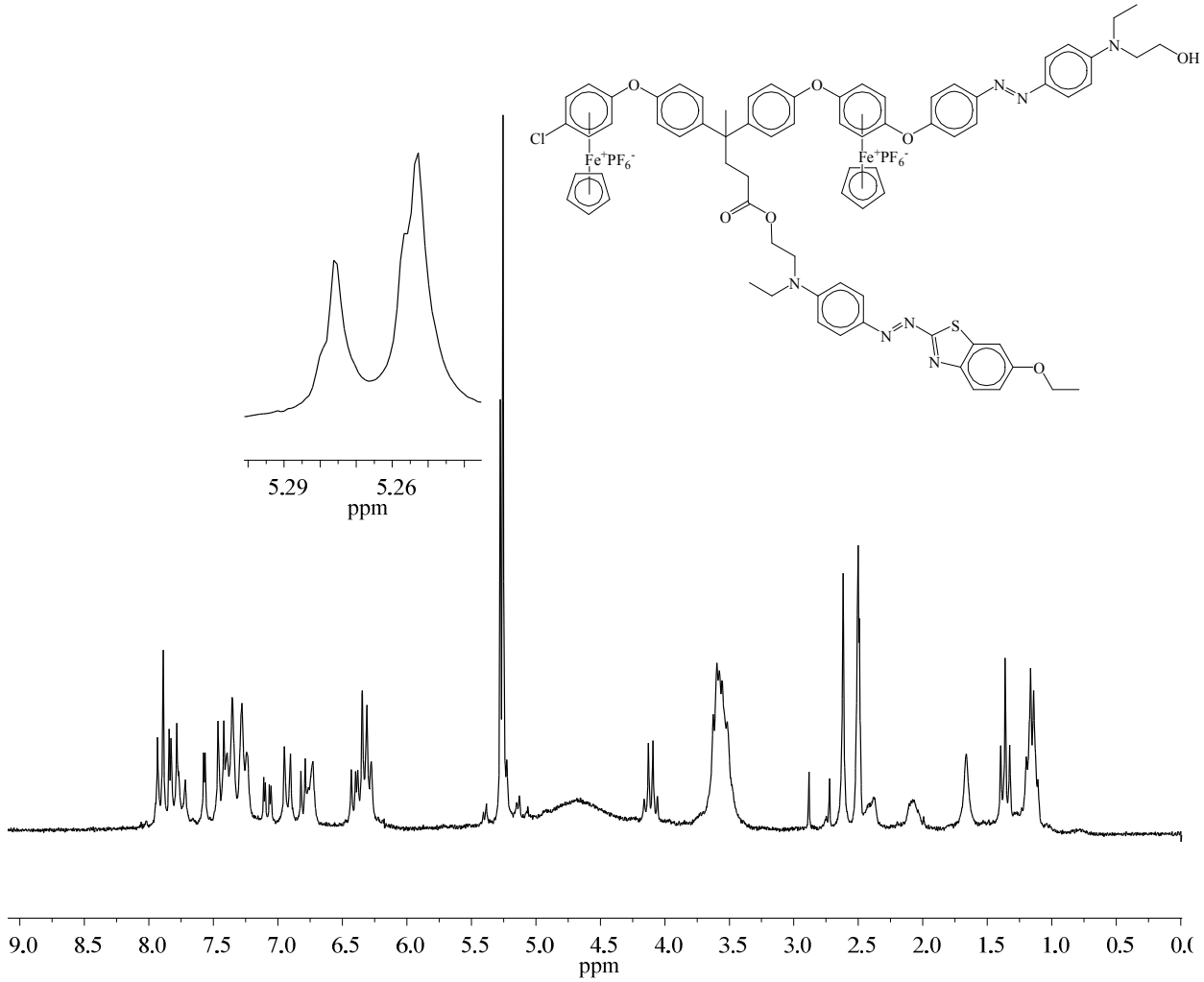


Figure 2-31: ^{1}H NMR spectrum of 2.27.

The ^{13}C NMR spectrum (Figure 2-32) of complex **2.27** further confirms the successful synthesis. The resonance due to the complexed aromatics have split from two resonances to three due to the presence of the arene disubstituted by oxygen. There is also the appearance of another methyl proton at 17.74 ppm for the introduction of a new polysubstituted aniline group.

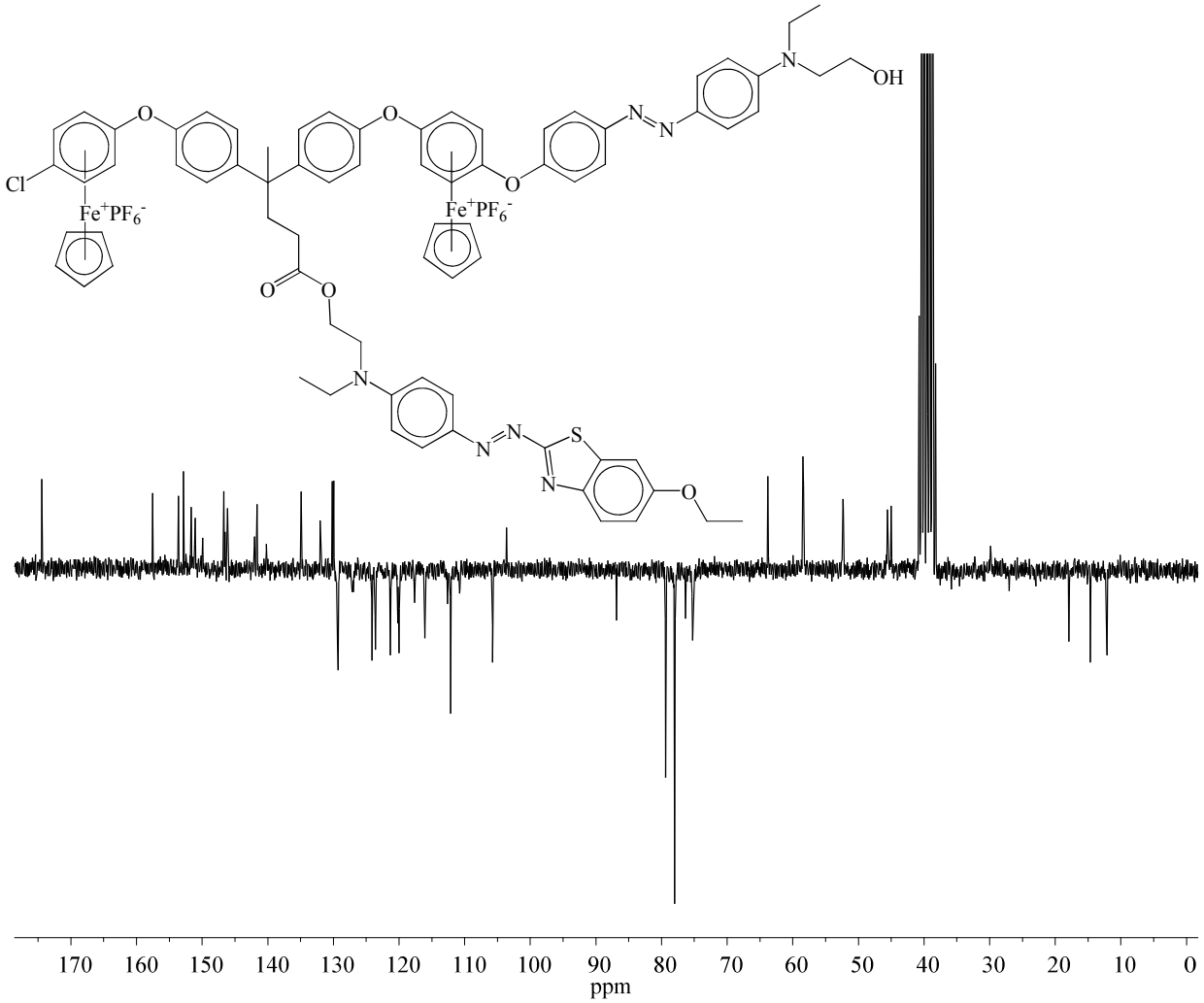
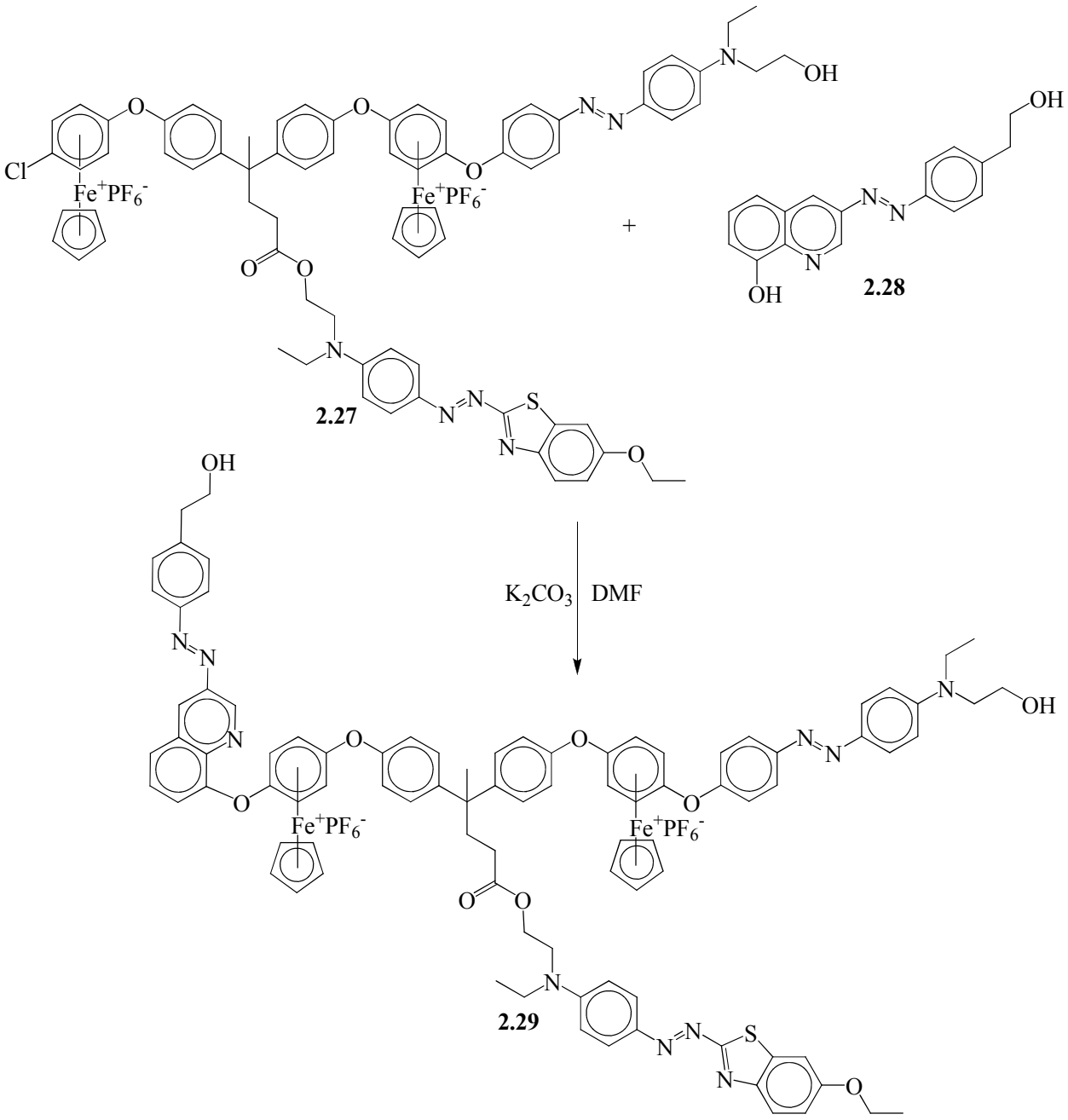


Figure 2-32: 50 MHz APT^{13}C NMR spectrum of complex 2.27.

The addition of a third azo dye (**2.29**) was prepared by reacting complex **2.27** with the quinoline based azo dye **2.28** (Scheme 2-12).



Scheme 2-12: Synthesis of complex 2.29.

The ^{1}H NMR spectrum of compound **2.29** (Figure 2-23) showed the incorporation of the third azo dye by the collapse of the complexed aromatics from two doublets into a broad singlet. Also, the resonance due to the cyclopentadienyliron moiety appear as two singlets since each

cyclopentadienyliron ring is electronically different. The new cyclopentadienyliron resonances appear at 5.24 ppm and 5.26 ppm.

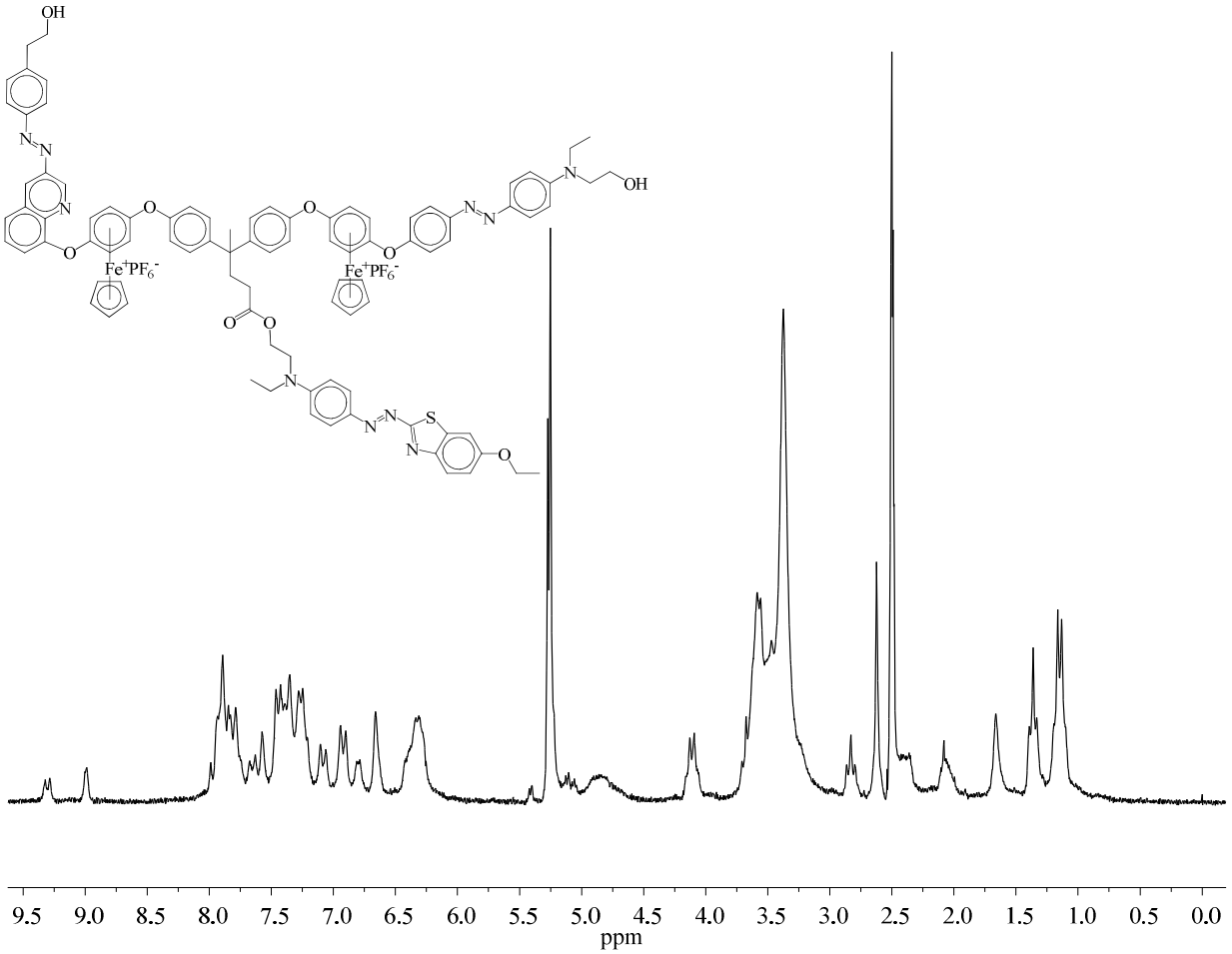


Figure 2-33: ^{1}H NMR spectrum of complex 2.29.

UV-visible analysis on complex **2.27** (2 dyes) (Figure 2-34) showed that in DMF solution complex **2.27** displayed a λ_{max} = 511 nm with a weak shoulder at 438 nm. The weak shoulder is due to the overlap of the λ_{max} of the $\pi-\pi*$ transition of azo dye (**2.15a**) with the $\pi-\pi*$ transition of azo dye (**2.25**). The λ_{max} at 511 nm is due to the $\pi-\pi*$ transition of azo dye (**2.25**). The addition of a solution of 40% HCl in DMF caused the λ_{max} to shift giving two maxima at 590 nm

and 615 nm. These maxima are due to the π–π* transitions of the azonium forms of azo dyes **2.15a** and **2.25** respectively.

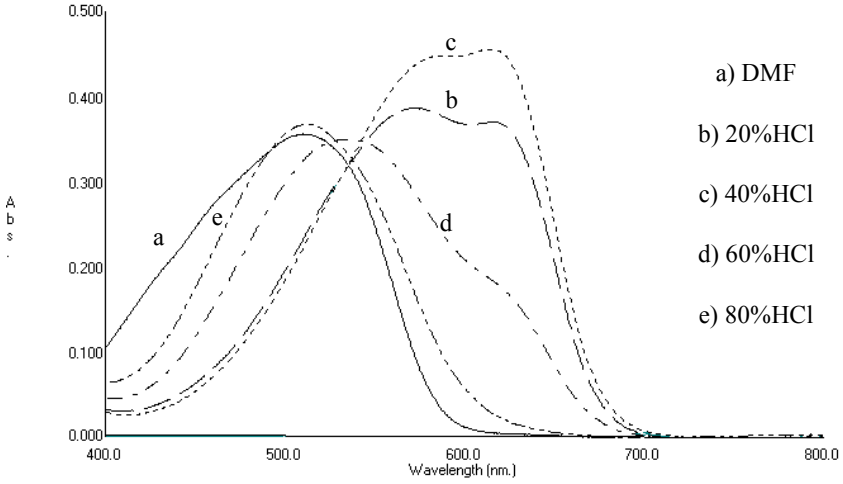


Figure 2-34: UV-visible spectrum of compound 2.27.

Figure 2-35 shows the UV-visible spectrum of complex **2.29** in various solutions of DMF and HCl/DMF. In DMF complex **2.29** showed a λ_{max} at 516 nm, when acidified the λ_{max} shifted to 618 nm with a shoulder at 588 nm. The λ_{max} at 516 nm is due to the combination of the λ_{max}s of all the combined azo dyes. When acidified the λ_{max} at 588 nm was a result of both the π–π* transitions of azo dye (**2.15a**) and (**2.25**) and the λ_{max} at 618 nm arose due to the combination of azo dye **2.25** and **2.28**.

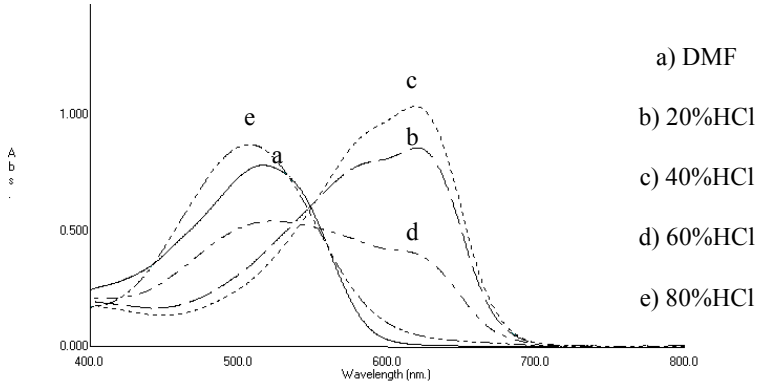


Figure 2-35: UV-visible spectrum of compound 2.28.

2.3 Conclusion

A number of organic compounds and organometallic complexes that contain azo dyes were prepared. The organic compounds were based on norbornene and contained either aryl or hetaryl based azo dyes. The azo dye functionalized norbornene monomers were polymerized through ROMP to give homo- and co-polymers containing aryl or hetaryl azo dyes. Thermal analysis of the polymers showed they were thermally stable with degradation of the azo group beginning at 250 °C and glass transition temperatures ranging from 93 °C to 133 °C. UV-vis studies showed that the polymers displayed λ_{max}= 417 nm (**2.8**) (homo-aryl), 495 nm (**2.7**) (homo-hetaryl) and that the copolymers displayed a λ_{max} that encompassed both the aryl and hetaryl azo dye range. Photo-physical analysis showed that the polymers underwent photo-induced *trans-cis* isomeration which is characteristic of azo dyes. Studies into the polymers abilities to detect acids showed that in both solution and the solid state, the polymers reversibly change colour in the presence of aqueous 1.2 M HCl and $HCl_{(g)}$. This behaviour indicates that these materials may be useful as reusable solid state sensors for acids.

Cationic organoiron polymers containing both azo dyes and ferrocene in their backbones were prepared. These polymers possess molecular weights between 22 000 and 10 000. Analogous polyferrocenes containing azo dyes in their backbones were prepared by the photolytic demetallation of the cationic polymers. Thermal analysis showed that both the cationic and neutral polymers showed thermal stability up to 180 °C, when the azo group and the cationic iron moiety decomposed. UV-vis analysis showed that the polymers possessed λ_{max}s between 415 nm and 430 nm in DMF solutions, and when exposed to $HCl_{(aq)}$ the λ_{max}s underwent a bathochromic shift to between 540 nm and 560 nm. Unfortunately, due to what is

believed to be drastic differences in the molecular weight distributions no correlations between the physical properties of the polymers and structures of the polymers could be drawn.

Finally, a preliminary study in organoiron complexes containing multiple azo dyes led to the preparation of a cationic cyclopentadienyliron complex containing three different azo dyes. The UV-visible analysis of this complex showed that the λ_{max} in DMF was due to the overlap of the $\pi-\pi*$ transitions of all three azo dyes. When exposed to $HCl_{(aq)}$ the λ_{max} partially resolved into two absorbencies: one at 588 ppm due to overlap of the aniline and benzothiazole based dyes and one at 618 ppm due to the overlap of the benzothiazole and quinoline base dyes.

2.4 Experimental

Materials:

All reagents were purchased from Sigma-Aldrich and used without further purification. All general solvents were HPLC grade and used without further purification except for the dichloromethane used for polymerization which was dried and degassed using established procedures and the 2-methyltetrahydrofuran (2MeTHF) which was distilled over calcium hydride under Ar.[53]

Characterizations:

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz respectively on a Varian Mercury Plus spectrometer equipped with a gradient field probe or ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Varian Gemini 200 NMR spectrometer, with chemical shifts referenced to residual solvent peaks and coupling constants reported in Hz. Infrared (IR) spectroscopy was recorded on a Nicolet IR200 FT-IR in KBr. Mass spectrometry was performed on a Micromass LCT Premier (ToF)MS manufactured by Waters Inc. using positive mode electrospray ionization (ESI+).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Mettler-Toledo TGA/SDTA851^{e} and DSC821^{e} instruments respectively, at heating rates of 20 °C/min under nitrogen atmospheres. Molecular weight determination was performed using a Waters' GPC2000 at 35°C with THF as the eluent or using aWaters 1525 HPLC pump and 2410 refractive-index detector with THF as the eluent. Molecular weights were calculated relative to polystyrene standards.

Photophysical measurements:

The spectroscopic and photophysical measurements were carried out in 2MeTHF. UV-visible spectra were recorded on either a UV-1800 UV spectrophotometer by Shimadzu, a

Hewlett Packard 8452 A diode array spectrophotometer using a standard 1cm^2 quartz cell or on a Shimadzu UV-250IPC recording spectrophotometer. For the photoisomerization, the excitation was achieved using the lamp of a Spex Fluorolog 2 instrument as the source of excitation, using λ_{ex} = 410 nm.

Electrochemical analysis:

Cyclic voltammetric experiments were performed using a conventional three-electrode cell. In these studies, the working electrode was a glassy carbon disk electrode (ca. 2 mm diam.), the auxiliary electrode was a Pt wire, and a Ag/AgCl reference electrode was utilized. The concentration of the complex was 2.0x10^{-3} M, while that of the supporting electrolyte (TBAP) was 0.1 M. The solutions were purged with nitrogen prior to use. An EG&G Princeton Applied Research model 263A potentiostat was used in all experiments.

Synthesis 2.3a[54]

p-Anisidine (6.158 g, 50 mmol) was dissolved in 25 mL HCl(conc.) and 30 mL H_2O. Ice was added to cool the solution to between 0 °C – 5 °C. Sodium nitrite (3.450 g, 50 mmol) was dissolved in 10 mL H_2O and added drop-wise to the amine solution maintaining the temperature between 0 °C – 5 °C. The diazonium solution was allowed to stir for 30 min and then tested using starch-iodide paper for the presence of nitrous acid, if acid was present sulfamic acid was added to decompose the nitrous acid. N-(ethylphenylethanol) (8.262 g, 50 mmol) was dissolved in 25 mL glacial acetic acid and 25 mL H_2O. The diazonium solution was then poured into the coupler solution and allowed to stir for 12 hours. Sodium acetate was added in portions to the azo dye solution until the azo dye precipitated. The precipitated azo dye was then filtered and washed with water and allowed to dry under reduced pressure. Yield: 17.83 g, 42.5 mmol, 85%. ^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.75 (d, *J* = 8.9, 2H, ArCH), 7.71 (d, *J* = 9.1, 2H, ArCH), 7.06 (d, *J* = 8.8, 2H, ArCH), 6.80 (d, *J* = 9.0, 2H, ArCH), 3.83 (s, 3H, CH_3), 3.59 (t, *J* = 6.3, 2H,

CH_2), 3.53 – 3.41 (m, 4H, CH_2), 1.13 (t, J = 6.9, 3H, CH_3). *consistent with previously reported structure, therefore ^{13}C NMR was not performed.

Synthesis of 2.3b

2-Amino-6-ethoxybenzothiazole (9.70 g, 50 mmol) and 50 mL 50% H_2SO_4 were combined and stirred for 20 min at room temperature. The reaction was cooled to 0 – 5 °C and $NaNO_2$ (3.45 g, 50 mmol) was added portion-wise to the amine while it was on ice. The reaction was stirred for 1 hour at 0 – 5 °C. 2-(methylphenylamino)ethanol (7.56 g, 50 mmol) was dissolved in 20 mL HCl (conc.) and 200 mL H_2O and cooled to 0 – 5 °C. The diazonium solution was poured into the coupler solution, and 300 mL H_2O added. The resulting mixture was stirred for 30 min. The crude precipitate was isolated by filtration and allowed to dry. The solid was suspended in 500 mL H_2O and NH_4OH added until the solution was basic. The product was collected by filtration and allowed to dry (Yield: 12.49 g, 35 mmol, 70%).

^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.88 (d, J = 8.9, 1H, ArCH), 7.82 (br d, J = 9.2, 2H, ArCH), 7.58 (d, J = 2.5, 1H, ArCH) 7.09 (dd, J = 8.9, 2.5, 1H, ArCH), 6.94 (br d, J = 9.2, 2H, ArCH), 4.84 (m, 2H, CH_2), 4.12 (q, J = 7.0, 2H, CH_2), 3.62 (m, 4H, CH_2), 3.16 (br s, 3H, CH_3), 1.37 (t, J = 7.0, 3H, CH_3).

^{13}C NMR (101MHz, DMSO-d_6) δ= 174.3, 157.6, 153.8, 146.8, 141.7, 135.0, 124.2, 116.1, 112.1, 105.7, 63.8, 58.3, 54.2, 39.3, 14.7.

Synthesis of 2.5a

To a 250 mL round bottom (RB) flask, 2-norbornene-5-carboxylic acid (0.613 mL, 5 mmol), azo dye **2.3b** (2.495 g, 7 mmol), dicyclocarbodiimide (DCC) (1.133 g, 5.5 mmol), N,N-dimethylaminopyridine (DMAP) (0.0610 g, 0.5 mmol), N,N-dimethylformamide (DMF) (100mL) and dichloromethane (DCM) (100 mL) were added. The reaction mixture was allowed to stir at room temperature overnight. The reaction was allowed to cool in a freezer for 2 hours,

after which the reaction was filtered to remove dicyclohexylurea (DCU). The reaction mixture was poured into water and extracted using ethyl acetate, dried over magnesium sulphate and the solvent removed *in vacuo*. The crude product was purified using flash chromatography with 80:20 hexane:ethyl acetate. To remove any further trace of DCU the product was recrystallized from hexane, (Yield 2.264 g, 4.75 mmol, 95%).

^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.89 (d, J = 8.9, 1H, ArCH), 7.84 (d, J = 9.4, 2H, ArCH), 7.10 (dd, J = 2.6, 8.9, 1H, ArCH), 6.97 (d, J = 9.4, 2H, ArCH), 6.10 (dd, J = 5.6, 2.9, 1H, CH=CH), 5.78 (dd, J = 5.7, 2.9, 1H, CH=CH), 4.19 (m, 2H, CH_2), 4.12 (q, J = 7.0, 2H, CH_2), 3.80 (m, 2H, CH_2), 3.14 (s, 3H, CH_3), 3.04 (br s, 1H, CH), 2.94 (dt, J = 3.8, 9.5, 1H, CH), 2.81 (br s, 1H, CH), 1.81 (ddd, J = 11.6, 9.3, 3.6, 1H, CH), 1.37 (t, J = 7.0, 3H, CH_3), 1.23 (m, 4H, CH_2, CH). Minor (exo) diastereomer has additionally 1.04 (d, J = 6.0, 1H), 1.72 (dt, J = 4.0, 11.6, 2H), 2.08 (ddd, J = 1.5, 4.3, 8.8, 1H), 2.86 (br s, 1H), 3.13 (s, 3H), 4.30 (m, 2H), 6.04 (dd, J = 5.6, 3.0). Endo:exo ratio was calculated to be 4:1 by integration.

^{13}C NMR (101MHz, DMSO-d_6) δ= 174.1, 173.7, 157.6, 153.5, 146.8, 142.0, 137.6, 135.0, 132.3, 126.6, 124.3, 116.1, 112.2, 105.7, 63.8, 61.3, 61.2, 50.1, 49.0, 45.9, 44.9, 42.6, 41.9, 39.8, 38.7, 28.7, 14.6.

Elemental analysis: %C: 65.18, %H: 5.90, %N: 11.40 (calc: %C: 65.55, %H: 5.87, %N: 11.76)

Synthesis of 2.5b

To a 250 mL round bottom (RB) flask, 2-norbornene-5-carboxylic acid (0.613 mL, 5 mmol), azo dye **2.3a** (2.094 g, 7 mmol), dicyclocarbodiimide (DCC) (1.133 g, 5.5 mmol), N,N-dimethylaminopyridine (DMAP) (0.0610 g, 0.5 mmol), and DCM (100 mL) were added. The reaction mixture was allowed to stir at room temperature overnight. The reaction was allowed to cool in a freezer for 2 hours, after which the reaction was filtered to remove DCU. The solvent was removed *in vacuo*. The crude product was purified using flash chromatography

using 80:20 hexane:ethyl acetate. To remove any further trace of DCU the product was recrystallized from hexane. (Yield: 1.993 g, 4.75 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.82 (d, *J* = 9.0, 2H, ArCH), 7.81 (d, *J* = 9.2, 2H, ArCH), 1.21 (t, *J* = 7.0, 3H, CH_3). 6.97 (d, *J* = 9.0, 2H, ArCH), 6.77 (d, *J* = 9.2, 2H, ArCH), 6.17 (dd, *J* = 5.7, 3.1, 1H, CH=CH), 5.88 (dd, *J* = 5.7, 2.8, 1H, CH=CH), 4.21 (t, *J* = 6.3, 2H, CH_2), 3.85 (s, 3H, CH_3), 3.60 (t, *J* = 6.3, 2H, CH_2), 3.48 (q, *J* = 7.4, 2H, CH_2), 3.17 (br s, 1H, CH), 2.92 (dt, *J* = 9.3, 3.9, 1H, CH), 2.89 (br s, 1H, CH), 1.89 (ddd, *J* = 13.1, 9.4, 3.7, 1H, CH), 1.54 (s, 1H, CH), 1.37 (m, 2H, CH_2), 1.25 (d, *J* = 8.5, 1H, CH), Minor (exo) diastereomer has additionally 1.21 (d, *J* = 7.0, 1H), 1.48 (d, *J* = 8.8, 1H), 2.20 (dd, *J* = 10.2, 4.5, 1H), 3.00 (br s, 1H), 3.64 (t, *J* = 6.4, 2H), 4.28 (t, *J* = 6.4, 2H), 6.07 (dd, *J* = 5.7, 3.0, 1H), 6.11 (dd, *J*=5.7, 3.0, 1H). Endo:exo ratio was calculated to be 4:1 by integration.

^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.1, 157.9, 149.8, 147.7, 144.0, 138.2, 132.5, 125.0, 124.1, 123.3, 114.3, 111.6, 61.6, 55.7, 49.9, 49.0, 45.9, 45.6, 43.5, 42.8, 29.5, 12.5. Exo (minor) diastereoisomer has additionally 46.6, 49.1, 61.8, 135.9, and 138.3.

Elemental analysis: %C: 71.68, %H: 7.05, %N: 9.97 (calc: %C: 71.61, %H: 6.91, %N: 10.02)

General procedure for ROMP (2.7, 2.8):

To a 50 mL RB flask the appropriate monomer (0.5 mmol) and dry, degassed DCM (10 mL) were added. Grubbs' 2nd generation catalyst ($5x10^{-4}$ mmol) was added as a 2 mL solution in DCM to the rapidly stirring monomer solution. The reaction was allowed to stir for 90 min and ethyl vinyl ether (10 mL) was added and the reaction was stirred for an additional 30 min. The reaction mixture was poured into hexane and the precipitate was allowed to settle. The hexane was decanted and the precipitate was triturated with methanol. The polymer(s) were then filtered from methanol and dried.

2.7: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.18 (br m, 3H, ArCH), 6.99 (br m, 1H, ArCH), 6.66 (br m, 1H, ArCH), 5.15 (br m, 2H, CH=CH), 4.17 (br m, 2H, CH_2), 4.01 (br m, 2H, CH_2), 3.57 (br m, 2H, CH_2), 2.98 (br m, 4H, CH_2), 2.72 (br m, 2H, CH_2), 2.39 (br m, 1H, CH), 1.84 (br m, 1H, CH), 1.54 (br m, 3H, CH_2, CH), 1.37 (br m, 3H, CH_3), 1.24 (br m, 3H, CH_2, CH), 1.07 (m, 1H, CH), 0.85 (m, 3H, CH_3). Yield 0.205 g, 0.43 mmol, 86%.

^{13}C NMR (101 MHz, $CDCl_3$) δ= Due to poor solubility this spectrum could not be obtained

2.8: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.77 (br m, 4H, ArCH), 6.93 (br m, 2H, ArCH), 6.70 (br m, 2H, ArCH), 5.25 (br m, 2H, CH=CH), 4.14 (br m, 2H, CH_2), 3.81 (br s, 3H, CH_2), 3.53 (br m, 2H, CH_2), 3.38 (br m, 2H, CH_2), 2.80 (br m, 2H, CH_2), 1.80 (br m, 6H, CH_2), 1.55 (s, 3H, CH), 1.25 (br m, 4H, CH_2), 1.13 (br m, 4H, CH_2, CH_2), 0.86 (m, 3H, CH_3). Yield 0.174 g, 0.41 mmol, 83%.

^{13}C NMR (101 MHz, $CDCl_3$) δ= Due to poor solubility this spectrum could not be obtained

Synthesis 2.9

To a 50 mL RB flask, monomers (**2.5a, b**) (0.5 mmol) and dry, degassed DCM (10 mL) were added. Grubbs' catalyst ($5x10^{-4}$ mmol) was added as a 2 mL solution in DCM to the rapidly stirring monomer solution. The reaction was allowed to stir for 90 min, ethyl vinyl ether (10 mL) was added and the reaction was stirred for an additional 30 min. The reaction mixture was poured into hexane and the precipitate was allowed to settle. The hexane was decanted and the precipitate was triturated with methanol. The polymer was filtered from methanol and dried. The ^{1}H NMR spectra of this and the other copolymers were consistent with the aryl and hetaryl polymers reported above. Yield 0.358 g, 0.4 mmol, 80%.

Synthesis of 2.10

To a 50 mL RB flask, monomer (**2.5a**) (0.5 mmol) and dry, degassed DCM (10 mL) were added. Grubbs' Catalyst ($5x10^{-4}$ mmol) was added as a 2 mL solution in DCM to the rapidly

stirring monomer solution. The reaction was allowed to stir for 30 min at which point, monomer (**2.5b**)(0.5 mmol) was added as a powder, and the reaction was purged with nitrogen and allowed to stir for an addition 60 min. Ethyl vinyl ether (10 mL) was added and the reaction was stirred for an additional 30 min. The reaction mixture was poured into hexane and the precipitate allowed settling. The hexane was decanted and the precipitate triturated with methanol. The polymer was filtered from methanol and dried. Yield 0.258 g, 0.3 mmol, 60%

Synthesis of 2.13 a, b

p-Dichlorobenzene cyclopentadienyliron complex (**2.11**) (4.0 mmol), azo dye (**2.12a, b**) (4.1 mmol), K_2CO_3 (5 mmol), and DMF (15 mL) were combined in a 50 mL RB flask with a magnetic stir bar. The reaction was allowed to stir for 24 hours at room temperature under N_2. The product was precipitated in 10% HCl with NH_4PF_6 yielding a deeply coloured precipitate. The precipitate was cooled at 10^{o}C for 1 hour and then collected in a Büchner funnel. The product was purified by an alumina column using acetone as the solvent.

2.13a: ^{1}H NMR (200 MHz, acetone-d_6) δ= 7.96 (d, J = 9.0, 2H, ArCH), 7.84 (d, J = 9.4, 2H, ArCH), 7.48 (d, J = 9.0, 2H, ArCH), 6.84-6.93 (m, 4H, *ArCH, ArCH), 6.59 (d, J =7.0, 2H, *ArCH), 5.42 (s, 5H, Cp), 3.91 (t, J = 5.1, 2H, CH_2), 3.81 (q, J = 5.5, 2H, CH_2), 3.65 (t, J = 5.7, 2H, CH_2), 1.28 (t, J = 6.4, 3H, CH_3).

^{13}C NMR (50 MHz, acetone-d_6) δ= 154.44, 152.07, 143.67, 133.45, 126.10, 124.94, 122.11, 112.12, 105.01, 87.81, 80.49, 77.43, 60.03, 53.24, 46.24, 12.34.

IR (KBr): 3104 cm^{-1} (OH). Yield 1.860 g, 3.6 mmol, 90%.

2.13b: ^{1}H NMR (200 MHz, DMSO-d_6) δ= 7.93 (d, J = 8.7, 2H, ArCH), 7.48 (d, J = 8.8, 2H, ArCH), 6.85 – 6.67 (m, 4H, *ArCH, ArCH), 6.50 (d, J = 6.8, 2H, *ArCH), 5.30 (s, 5H, Cp), 3.73

(dd, J = 18.6, 8.0, 11H, CH_2, contains H_2O), 3.59 (s, 4H, CH_2), 2.82 (t, J = 6.8, 2H, CH_2), 2.65 (s, 3H, CH_3).

^{13}C NMR (50 MHz, DMSO-d_6) δ= 153.13, 152.06, 148.65, 143.60, 140.00, 131.91, 123.49, 121.82, 119.31, 118.91, 113.45, 111.77, 103.80, 86.99, 79.59, 76.57, 58.40, 52.96, 46.88, 18.04, 15.76. Yield 2.528 g, 3.6 mmol, 90%.

Synthesis of 2.15a, b

Monometallic azo dye functionalized complexes (**2.13a, b**) (2.0 mmol), 1,1' ferrocenedicarbonyl chloride (**2.14**) (1.2 mmol), DCM (35 mL), and pyridine (35 drops) (2 mL of acetone could be added for solubility) were combined in a 50 mL RB flask with a stir bar and septum. The reaction was stirred under nitrogen for 24 hours. The solution was poured into 10% HCl with NH_4PF_6 (2.0 mmol) and extracted with DCM. The product was purified by a neutral alumina column with acetone as the mobile phase. The product was precipitated in 10% HCl with NH_4PF_6 (2.0 mmol) and collected.

2.15a: ^1H NMR (200 MHz, acetone-d_6) δ= 7.97 (d, J = 9.0, 4H, ArCH), 7.90 (d, J = 9.0, 4H, ArCH), 7.48 (d, J = 8.6, 4H, ArCH), 7.05 (d, J = 8.6, 4H, ArCH), 6.86 (d, J = 5.9, 6H, *ArCH), 6.59 (d, J = 5.9, 4H, *ArCH), 5.41 (s, 10H, Cp), 4.79 (s, 4H, *Cp), 4.46 (br s, 8H, CH_2, *Cp), 3.90 (t, J = 5.3, 4H, CH_2), 3.62-3.71 (m, 4H, CH_2),1.28 (t, J = 6.4, 6H, CH_3)**.**

^{13}C NMR (50 MHz, acetone-d_6) δ= 170.39, 154.62, 152.09, 151.88, 144.08, 133.50, 126.16 125.07, 122.17, 112.49, 105.09, 87.88, 80.55, 77.53, 73.73, 73.60, 72.42, 62.51, 49.38, 46.01, 12.54.

IR (KBr): 1716 cm^{-1} (C=O). Yield 2.251 g, 1.44 mmol, 72%.

2.15b: ^{1}H NMR (200 MHz, acetone-d_6) δ= 7.99 (d, J = 9.0, 4H, ArCH), 7.50 (d, J = 9.0, 4H, ArCH), 6.88 (dd, J = 7.2, 1.8, 6H, ArCH, *ArCH), 6.62 (d, J = 7.0, 4H, *ArCH), 5.44 (s, 10H, Cp), 5.13 – 5.06 (m, 4H, *Cp), 4.87 – 4.79 (m, 4H, *Cp), 4.19 – 3.65 (m, 16H, CH_2), 2.70 (s, 6H, CH_3).

^{13}C NMR (50 MHz, DMSO-d_6) δ= 153.13, 152.06, 148.65, 143.60, 140.00, 131.91, 123.49, 121.82, 119.31, 118.91, 113.45, 111.77, 103.80, 86.99, 79.59, 76.57, 72.46, 73.63, 62.40, 52.96, 46.88, 18.04, 15.76. Yield 2.465 g, 1.5 mmol, 75%.

Polymerization of trimetallic monomers (2.19a-d, 2.20a-e):

Trimetallic monomer (1 mmol), dinucleophile (1 mmol), K_2CO_3 (5 mmol), and DMF (1 mL) were combined in a 25 mL RB flask with a condenser, magnetic flea and septum. The reaction was heated at 50 ^{o}C for 4 hours with stirring under nitrogen, and then stirred at room temperature until solution became viscous. The polymer was precipitated in 10% HCl with NH_4PF_6 (2.0 mmol) and collected in a crucible.

2.19a : ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 8.0 - 7.2 (br, m, ArCH), 6.9 - 6.2 ppm (br, m ArCH, *ArCH), 5.1 (br, s, Cp), 4.5 (br, s, *Cp), 4.2 (br, s, *Cp), 4.1 – 2.7 (br, m, CH_2), 1.4 (br, s, CH_3, CH_2).

^{13}C NMR (50 MHz, DMSO-d_6) δ= Due to low solubility ^{13}C NMR data could not be obtained Yield 1.409 g, 90%.

2.19b: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 7.9 – 7.0 (br, m, ArCH), 6.7 – 6.3 (br, m, *ArCH), 5.1 (br, s, Cp), 4.8 - 4.1 (br, m, *CP), 3.1- 2.7 (br, m, CH_2), 1.4 (br, s, CH_3, CH_2).

^{13}C NMR (50 MHz, DMSO-d_6) δ= Due to low solubility ^{13}C NMR data could not be obtained Yield 1.463 g, 88%.

2.19b: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 8.1 – 7.0 (br, m, ArCH), 6.9 – 6.3 (br, m, *ArCH), 5.1 (br, s, Cp), 4.7 – 4.2 (br, m, *Cp), 3.1- 2.7 (br, m, CH_2), 1.4 (br, s, CH_3, CH_2).

^{13}C NMR (50 MHz, DMSO-d_6) δ= Due to low solubility ^{13}C NMR data could not be obtained Yield 1.268 g, 75%.

2.19d: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 7.91 (d, J = 8.6, 4H, ArCH), 7.81 (d, J = 8.6, 4H, ArCH), 7.41 (d, J = 8.6, 8H, ArCH), 7.24 (d, J = 8.6, 4H, ArCH), 6.97 (d, J = 8.2, 4H, ArCH), 6.35 (d, J = 6.3, 4H, *ArCH), 6.28 (d, J = 6.3, 4H, *ArCH), 5.24 (s, 10H, Cp), 4.72 (s, 4H, *Cp), 4.45 (s, 4H, *Cp), 4.35 (br s, 4H, CH_2), 3.78 (br s, 4H, CH_2), 3.57 (br s, 4H, CH_2), 1.72 (br s, 6H, CH_3), 1.18 (br s, 6H, CH_3).

^{13}C NMR (50 MHz, DMSO-d_6) δ 169.39, 154.18, 151.34, 150.53, 150.08, 147.66, 142.40, 130.23, 129.53, 128.69, 127.30, 125.05, 123.86, 120.93, 119.86, 114.70, 111.49, 77.88, 75.43, 74.94, 72.80, 72.13, 71.27, 61.73, 44.75, 48.10, 42.09, 30.55, 11.98.

IR (KBr): 1714 cm^{-1} (C=O). Yield 1.512 g, 88%.

2.20a : ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 7.93 (d, J=8.7, 2H, ArCH), 7.66 (d, J=9.1, 2H, ArCH), 7.48 (d, J=8.8, 4H, ArCH), 6.85 – 6.67 (m, 2H, *ArCH), 6.50 (d, J=6.8, 2H, *ArCH), 5.30 (s, 5H, Cp), 3.73 (dd, J=18.6, 8.0, 11H, CH_2), 3.59 (s, 4H, CH_2), 2.82 (t, J=6.8, 2H, CH_2), 2.65 (s, 3H, CH_3).

Due to low solubility ^{13}C NMR data could not be obtained Yield 1.508 g, 95%.

2.20b: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 7.90 – 7.73 (br s, ArCH), 7.72 – 7.33 (br s, ArCH), 7.20 – 6.97 (br s, ArCH), 6.97 – 6.60 (br s, ArCH), 6.43 – 6.21 (br s, *ArCH), 5.01 – 4.91 (br s, Cp), 4.78 – 4.71 (br s, *Cp), 4.72 – 4.66 (br s, *CP), 4.50 – 4.44 (br s, CH_2), 4.39 – 4.28 (br s,

CH_2), 3.86 (br s, CH_2), 3.18 (br s, CH_2), 2.98 (br s, CH_2), 2.92 – 2.73 (br s, CH_2), 2.62 (s, 19H, CH_2), 2.37 (s, 5H) , CH_2, 1.86 – 1.57 (br s, CH_2, CH_3).

^{13}C NMR (50 MHz, DMSO-d_6) δ= 170.72, 170.44, 169.09, 159.09, 148.15, 145.13, 140.85, 140.41, 139.67, 123.49, 119.58, 119.00, 118.41, 116.44, 115.48, 112.81, 110.22, 96.70, 82.63, 78.40, 77.54, 77.34, 74.13, 72.51, 72.32, 71.88, 71.01, 61.39, 26.93, 17.51, 15.31. Yield 0.969 g, 60%.

2.20c: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= 8.02 – 7.86 (br s), 7.87 – 7.74 (br s), 7.66 (br s), 7.54 – 7.32 (br s), 7.24 – 7.00 (br s), 6.90 (br s), 6.41 (br s), 5.15 (br s), 4.74 (br s), 4.69 (br s), 4.43 (br s), 4.34 (br s), 3.85 (br s), 1.87 – 1.51 (br s), 1.49 – 1.27 (br s).

^{13}C NMR (50 MHz, DMSO-d_6) δ= 171.07, 170.80, 169.44, 153.75, 150.59, 149.86, 141.31, 141.12, 130.81, 124.12, 121.42, 119.32, 116.76, 113.07, 110.46, 105.86, 82.75, 78.57, 77.58, 76.00, 73.77, 73.40, 73.35, 72.78, 72.60, 72.47, 72.20, 72.12, 71.46, 71.30, 71.17, 69.76, 61.65, 31.52, 27.96, 27.62, 17.76, 15.54. Yield 1.183 g, 72 %.

2.20d: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= Due to the low solubility of this complex, and presence of H_2O in the DMSO-d_6, ^{1}H NMR resonances of the compound was overshadowed by the resonance of H_2O.

^{13}C NMR (50 MHz, DMSO-d_6) δ= 170.88, 169.57, 159.49, 159.39, 150.60, 149.60, 148.40, 145.93, 141.49, 141.39, 141.21, 139.72, 132.10, 131.72, 130.81, 124.19, 123.97, 121.47, 119.59, 119.46, 116.81, 116.48, 115.80, 113.26, 110.58, 106.08, 83.69, 82.80, 78.63, 77.78, 77.64, 77.30, 76.07, 74.32, 74.03, 73.72, 73.42, 72.85, 72.54, 72.01, 71.53, 69.82, 68.12, 67.13, 61.68, 58.21, 48.91, 45.98, 40.78, 40.37, 39.96, 39.54, 39.12, 38.71, 38.28, 37.84, 36.45, 31.61, 28.50, 28.13, 19.13, 17.76, 15.82, 15.48. Yield 1.503g, 90%.

2.20e: ^{1}H-NMR (200 MHz, DMSO-d_6) δ= Due to the low solubility of this complex, and presence of H_2O in the DMSO-d_6, ^{1}H NMR resonances of the compound was overshadowed by the resonance of H_2O.

^{13}C NMR (50 MHz, $CDCl_3$) δ= 170.65, 169.31, 168.42, 155.10, 154.16, 154.03, 153.83, 151.46, 151.30, 150.87, 150.34, 150.24, 149.93, 149.46, 148.75, 148.17, 147.86, 147.61, 147.40, 147.15, 141.55, 141.13, 140.61, 139.81, 130.16, 129.90, 129.64, 129.48, 128.65, 127.24, 123.97, 123.74, 121.40, 121.08, 119.82, 119.82, 119.21, 117.10, 116.76, 114.69, 112.98, 112.64, 110.41, 77.84, 77.05, 75.22, 74.91, 73.82, 73.68, 72.47, 72.09, 71.57, 71.34, 71.18, 58.05, 52.47, 48.31, 46.46, 35.69, 30.37, 17.66, 15.66, 15.34.

Isolation of Ferrocene based polymers containing azo dyes (2.21a-d, 2.22a-e):

Polymers **(19a-d, 20a-e)** were placed in a 50 mL Pyrex tube and dissolved in a DMSO/acetonitrile solution or just acetonitrile. The Pyrex tubes were purged with nitrogen and placed in a photo-reactor using a Xe light source for 4 hours. The resulting solution was extracted in $CHCl_3$, washed with water, and dried under $MgSO_4$. The $CHCl_3$ was removed *in vacuo* and the neutral polymers collected.

Synthesis of complex 2.26:

2.24 (1.040 g, 1.0 mmol) and thionyl chloride (2 mL, 27.5 mmol) were heated to 50 °C under N_2 for 2 hours. The excess thionyl chloride was removed *in vacuo*, and the azo dye (**2.25**) (0.370 g, 1.0 mmol) and triethyl amine (1.1 mmol), DCM/DMF (15:3) (20 mL) were added and the reaction stirred under N_2 for 24 hours in the dark. The reaction was poured into 1.2 M HCl with NH_4PF_6 (0.326 g, 2.0 mmol) and extracted into dichloromethane, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue dissolved in minimal acetone and precipitated into ether. Yield 1.114 g, 0.8 mmol, 80%.

^{1}H NMR (200 MHz, acetone) δ 7.89 (d, *J* = 4.4, 2H, ArCH), 7.84 (d, *J* = 4.8, 2H, ArCH), 7.59 – 7.43 (m, 4H, ArCH), 7.33 (d, *J* = 8.7, 4H, ArCH), 7.10 (d, *J* = 9.0, 1H, ArCH), 6.96 (d, *J* = 9.3, 2H, ArCH), 6.81 (d, *J* = 6.5, 4H, 8ArCH), 6.51 (d, *J* = 6.6, 4H, *ArCH), 5.37 (s, 10H, Cp), 4.15 (q, *J* = 6.9, 2H, CH_2), 3.83 (t, *J* = 5.8, 2H, CH_2), 3.76 – 3.58 (m, 4H, CH_2), 2.53 (s, 2H, CH_2), 2.21 (s, 2H, CH_2), 1.75 (s, 3H, CH_3), 1.41 (t, *J* = 7.0, 3H, CH_3), 1.25 (t, *J* = 7.0, 3H, CH_3).

^{13}C NMR (50 MHz, Acetone) δ 174.63, 159.11, 153.89, 152.20, 148.14, 134.01, 130.71, 127.88, 125.32, 121.38, 116.88, 112.85, 106.22, 104.98, 87.95, 80.56, 77.24, 64.80, 60.15, 53.48, 46.75, 46.38, 37.36, 27.94, 15.15, 12.48.

IR (KBr): 1732cm^{-1} (CO).

Synthesis of complex 2.27:

Complex **2.26** (1.393 g, 1 mmol), azo dye **2.15a** (0.285 g, 1 mmol), and K_2CO_3 (0.276g, 2 mmol) were dissolved in 15 mL DMF and stirred under N_2 in the dark for 24 hours. The reaction mixture was precipitated into 1.2 M HCl with NH_4PF_6 (0.326 g, 2 mmol) and collected in a Büchner funnel. Yield 1.478 g, 0.9 mmol, 90%)

^{1}H NMR (200 MHz, DMSO) δ = 8.00 – 7.65 (m, 8H, ArCH), 7.62 – 7.19 (m, 9H, ArCH), 7.00 – 6.63 (m, 6H, ArCH), 6.33 (d, *J* = 7.1, 4H, *ArCH), 5.26 (d, *J* = 4.5, 10H, Cp), 4.11 (q, *J* = 7.0, 2H, CH_2), 3.69 – 3.40 (m, 10H, CH_2), 2.46 – 2.31 (m, 2H, CH_2), 2.18 – 1.93 (m, 2H, CH_2), 1.67 (s, 3H, CH_3), 1.36 (t, *J* = 6.9, 3H, CH_3), 1.15 (q, *J* = 6.9, 6H, CH_3).

^{13}C-NMR (50 MHz, DMSO-d_6) δ= 174.9, 157.7, 153.8, 152.7, 151.7, 151.0, 146.8, 146.1, 141.5, 134.9, 132.2, 130.0, 129.3, 124.0, 123.6, 121.5, 120.3, 116.2, 112.3, 106.0, 103.9, 87.1, 79.1, 78.0, 58.5, 52.3, 45.1, 17.8, 14.8, 12.3.

Synthesis of complex 2.29:

Complex **2.27** (1.642 g, 1 mmol), azo dye **2.28** (0.293 g, 1 mmol), and K_2CO_3 (0.276 g, 2 mmol) were dissolved in 15 mL DMF and stirred under N_2 in the dark for 36 hours. The reaction mixture was precipitated into 1.2 M HCl with NH_4PF_6 (0.326 g, 2 mmol) and collected in a Buchner funnel. (Yield 1.809 g, 0.95 mmol, 95%)

^{1}H NMR (200 MHz, DMSO) δ 9.47 – 9.21 (m, 1H, ArCH), 8.04 – 7.72 (m, 8H, ArCH), 7.74 – 7.51 (m, 1H, ArCH), 7.51 – 7.15 (m, 8H, ArCH), 7.15 – 7.01 (m, 1H) , ArCH, 7.01 – 6.84 (m, 2H, ArCH), 6.86 – 6.72 (m, 1H, ArCH), 6.73 – 6.49 (m, 2H, ArCH), 6.47 – 6.15 (m, 8H, *ArCH), 5.25 (s, 10H, Cp), 4.99 – 4.65 (m, 1H), 4.11 (d, *J* = 18.6, 2H), 3.63 (dd, *J* = 24.4, 5.8, 4H), 2.83 (t, *J* = 6.8, 1H), 2.62 (s, 3H), 1.77 – 1.58 (m, 2H), 1.36 (t, *J* = 6.3, 3H), 1.25 – 1.01 (m, 6H).

^{13}C-NMR (50 MHz, DMSO-d_6) δ= 157.6, 153.7, 152.9, 151.6, 146.9, 142.0, 141.2, 140.5, 135.2, 132.3, 130.5, 127.4, 140.6, 130.1, 129.3, 124.1, 122.7, 121.2, 120.4, 116.4, 112.0, 110.2, 106.1, 76.7, 75.5, 63.6, 62.1, 58.6, 52.5, 45.3, 18.0, 14.9, 12.5.

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Chapter 3 Calix[4]arenes

3.1 Introduction

3.1.1 Background

When Baeyer reacted formaldehyde with phenols[1-3] he obtained various resins that were not fully characterized due to the limited instrumentation of the day. Nevertheless, the field of phenol-formaldehyde chemistry was born. A few years later in 1894 Lederer and Manasse independently discovered the base catalyzed condensation reaction between phenol and formaldehyde.[4, 5] Lederer and Manasse isolated 2-hydroxybenzyl alcohol and 4-hydroxy benzylalcohol as crystalline materials, which were the first examples of well-defined materials from phenol-formaldehyde chemistry. The Lederer-Manasse reaction is highly dependent on mild and controlled reaction conditions. If these conditions are not adhered to the reaction leads to the same resinous material as the acid catalyzed reaction.[6] The potential of phenol-formaldehyde chemistry was not truly recognized until the beginning of the 20th century when Leo Baekeland filed a patent for the first synthetic plastic, Bakelite.[6, 7] Bakelite is a phenol-formaldehyde polymer made up of a number of different compounds such as resoles, dibenzyl ethers and novolaks. The formation of Bakelite required a curing process and during this phase a number of different chemical reactions and transformations occurred. The study of this phase resulted in a major breakthrough in this field of chemistry.

In 1942 Alois Zinke and Erich Ziegler began to study the condensation reaction between formaldehyde and *p*-substituted phenols.[6] This reaction simplified the phenol-formaldehyde reaction by preventing condensation at the *para*-position, which meant that the condensation could only occur at the *ortho*-positions to give linear materials. Zinke and Ziegler reported the synthesis of a crystalline material that decomposed above 300 °C.[8, 9] Elemental analysis of the

material indicated a molecular formula of $C_{11}H_{14}O$; however, unlike other compounds isolated from phenol-formaldehyde condensations, chemical tests indicated the lack of etheric bonds. The absence of etheric bonds led Zink and Ziegler to propose a cyclic tetramer structure for their compound. By 1948 Zinke had gone on to prepare a number of different cyclic *p*-substituted phenol tetramers,[10] and by 1952 Zinke provided proof through chemical means to support the cyclic tetramer structure.[11] Although it took until 1979 for the the crystal structure of Zinke's cyclic tetramer to be determined by Andreetti *et al.*, the field of "calix[4]arenes" was born.

Pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(26),9,11-13(27),15,17,19(28),21,23-dodecane-25,26,27,28-tetraol is one of a family of [1$_n$]metacyclophanes (n = # of benzene rings) called "calix[n]arenes".[6, 12, 13] Calix[n]arenes are made up of n number of phenol rings joined at the *ortho*-positions to form a ring (Figure 3-1).

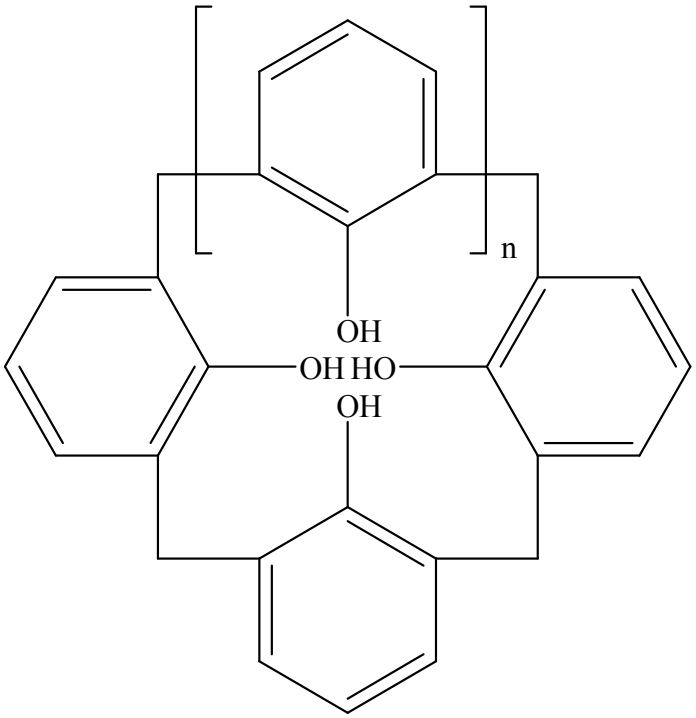


Figure 3-1: General structure of calix[n]arene.

Calix[n]arenes are primarily named according to the number of aryl rings incorporated into their structures. For example, a four aryl ring calix[n]arene is denoted calix[4]arene and an eight aryl ring calix[n]arene is a as calix[8]arene. When calixarenes are discussed in general they are denoted as calix[n]arenes (where n = # of aryl rings). When there are four identical functional groups in the *para* position calix[4]arenes are named with the functional group as a prefix for example, the calix[4]arene made with *tert*-butyl phenol is named *p-tert*-butylcalix[4]arene (Figure 3-2).

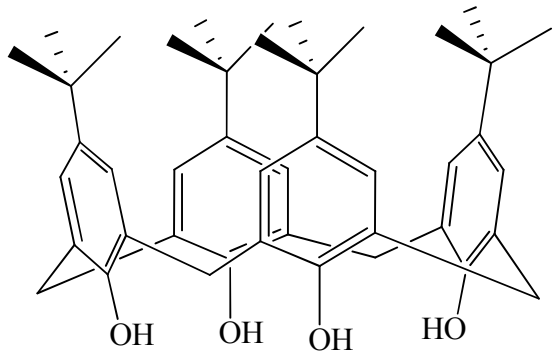


Figure 3-2: The structure of *p-tert*-butylcalix[4]arene.

When functional groups are incorporated into a calix[4]arene, the nomenclature follows the numbering system shown in Figure 3-3.With this nomenclature a calix[4]arene bearing 2 *p-tert*-butyl groups and 2 anisole groups would be named 5,17-di-*tert*-butyl-25,27-di-methoxy-26,28-dihydroxycalix[4]arene.

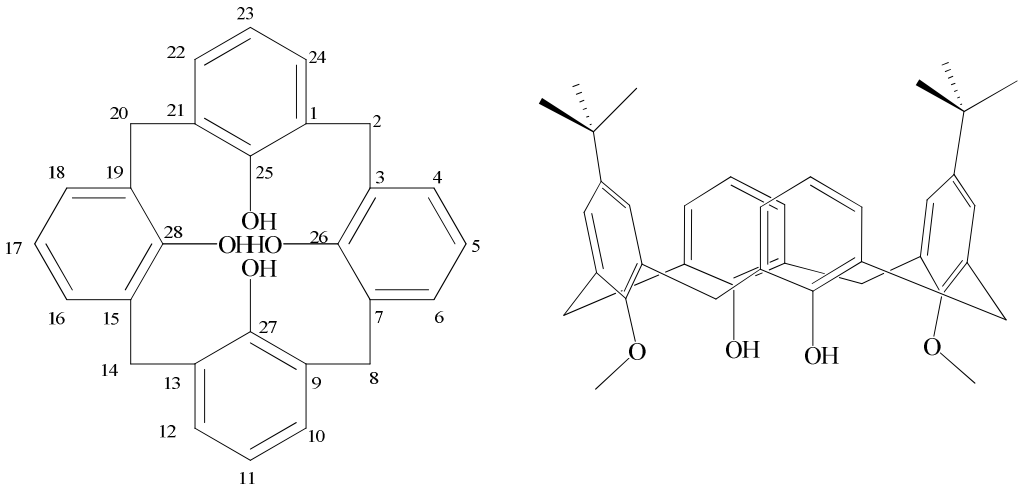


Figure 3-3: Numbering system for calix[4]arene (left); 5,17-di-*tert*-butyl-25,27-di-methoxy-26,28-dihydroxycalix[4]arene (right).

Intramolecular hydrogen bonding forces the calix[n]arene into a cone shape, where the phenolic groups are at the narrow rim (lower rim) and the *p*-positions of the arenes are at the wide rim (upper rim). Calix[4]arenes are named after the ancient Greek *calix* craters, which their shape resembles (Figure 3-4).[6, 13]

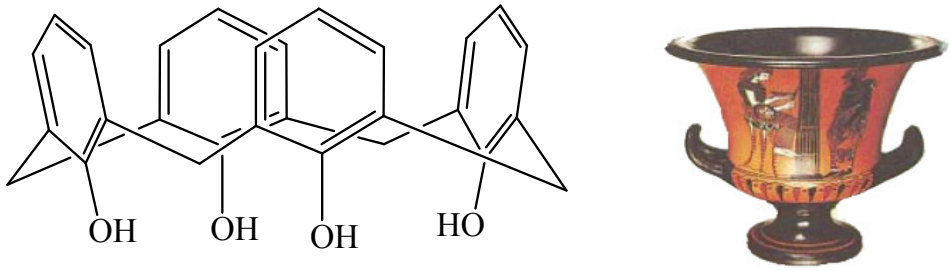
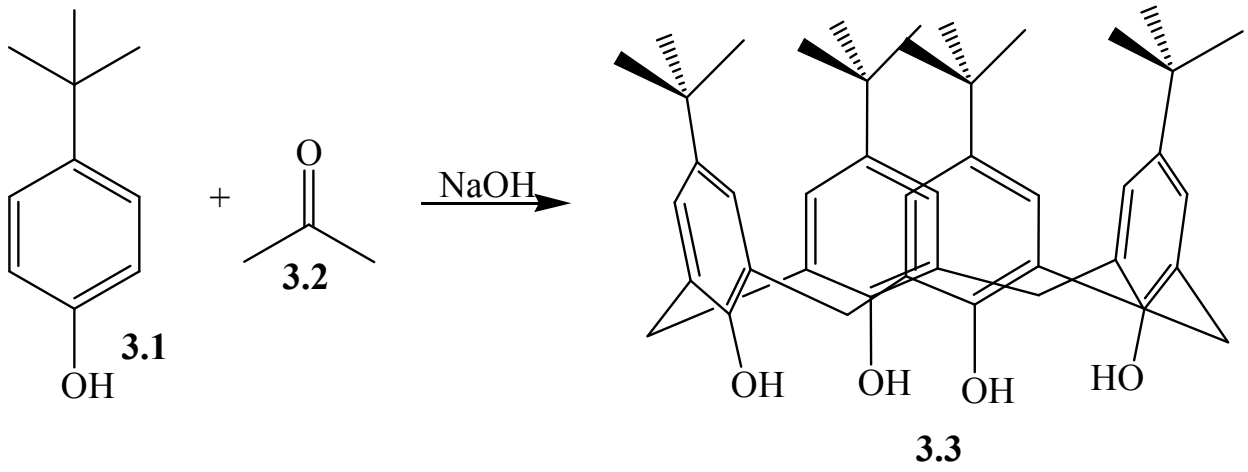


Figure 3-4: 25,26,27,28-tetrahydroxycalix[4]arene (left), Greek calix crater (right).

Calix[4]arenes are commonly prepared from the base catalyzed condensation between *p*-tert-butylphenol and formaldehyde (Scheme 3-1).[6, 13-15] Calix[4]arenes cannot be directly synthesized from phenol due to the *ortho/para*-directing nature of the OH group. Protecting the *para*-position allows the reaction to occur solely at the *ortho*-positions.



Scheme 3-1: Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrahydroxycalix[4]arene.

The proposed mechanism of calix[4]arene formation is considered to occur in two stages.[16-19] The first stage is the formation of hydroxymethyl phenols and the generation of mixtures of linear methoxymethylphenol oligomers (Figure 3-5).

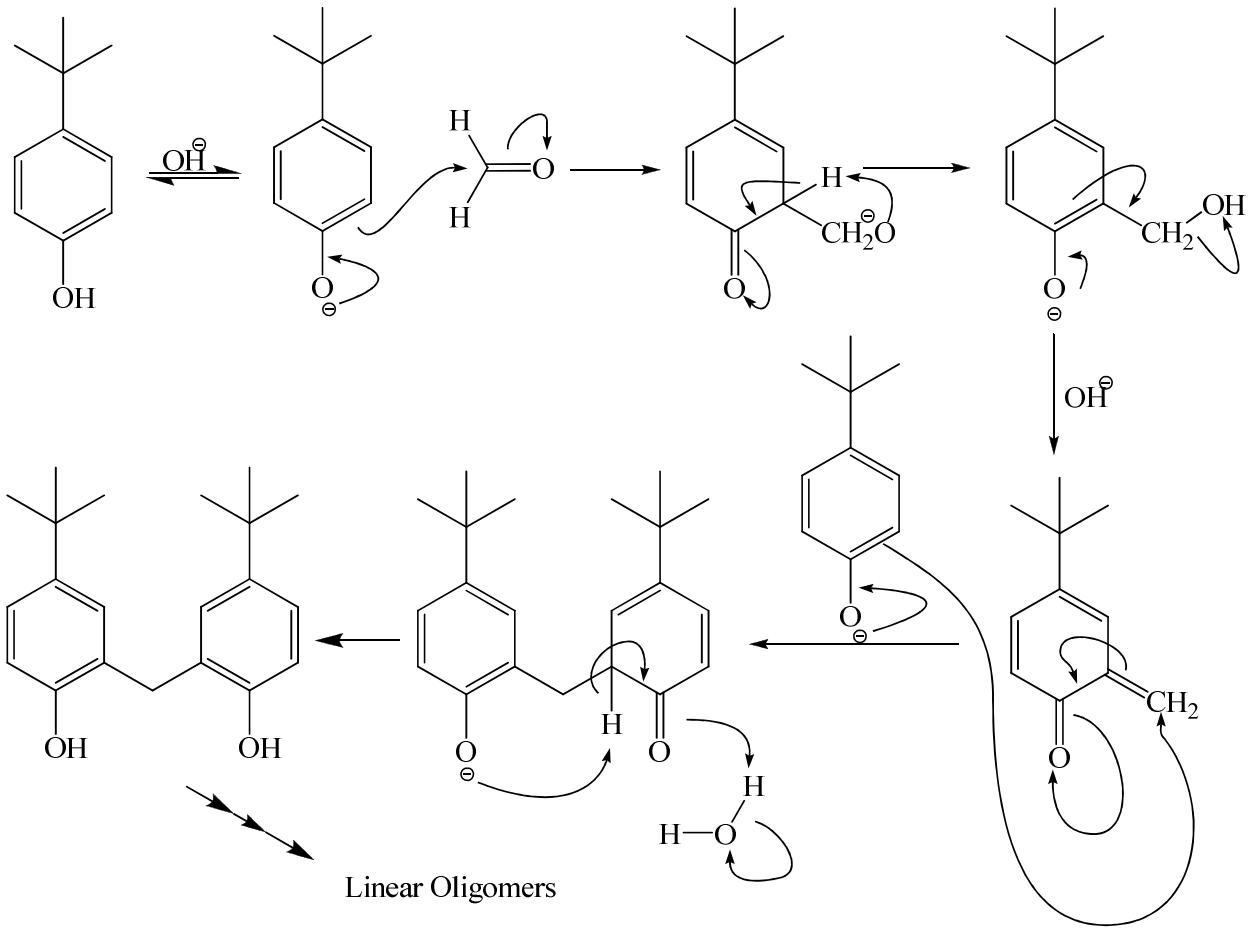


Figure 3-5: Mechanism of step 1 of calix[4]arene formation.

The second stage of the mechanism occurs at high temperature and results in the formation of the cyclic structure (Figure 3-6).

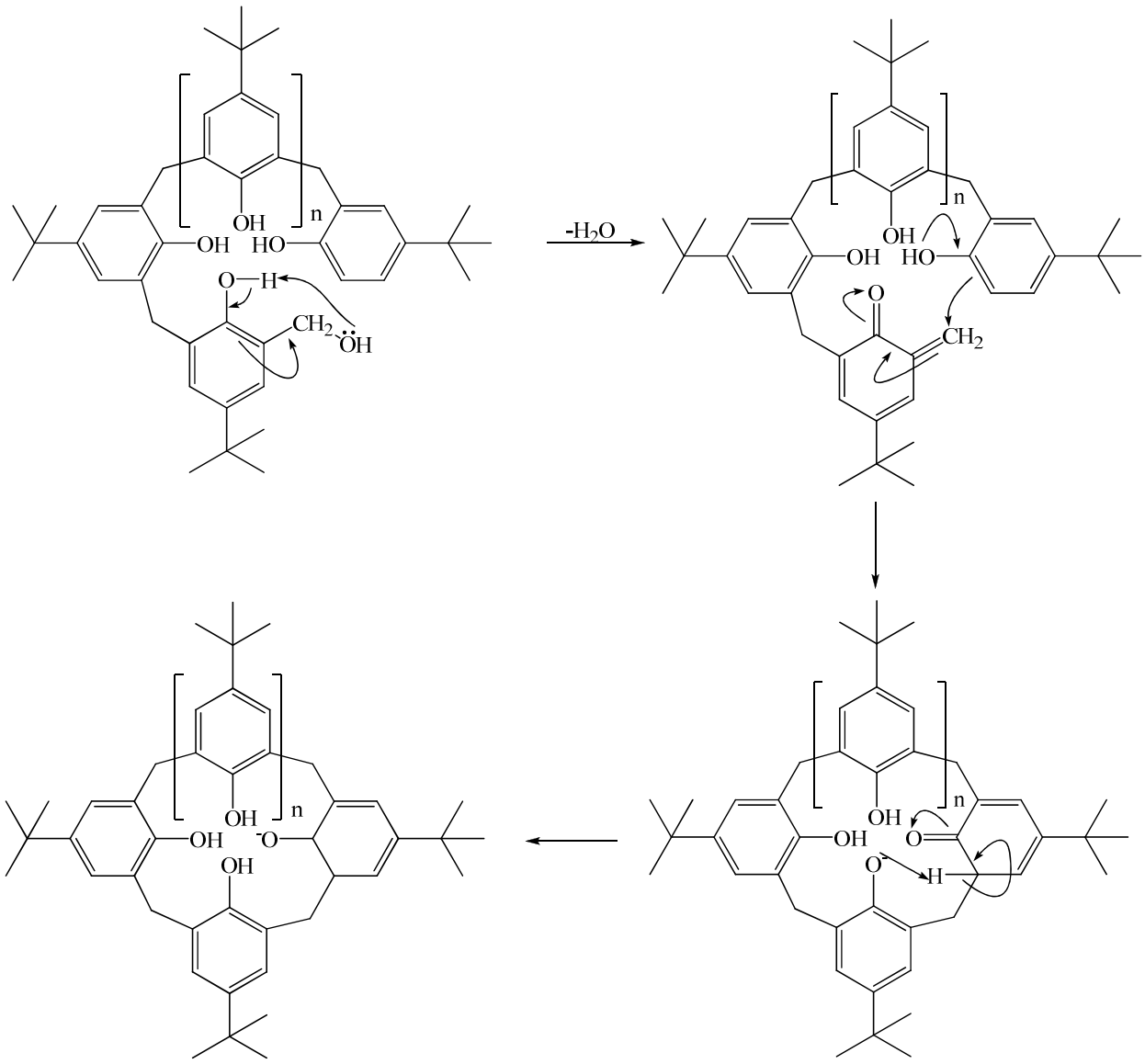


Figure 3-6: Mechanism of step 2 to prepare cyclic calix[n]arenes.

The synthesis of calix[4]arene undergoes a third step in the mechanism. It is prepared in refluxing diphenylether (bp = 260°C). Prior to reaching reflux calix[8]arene is formed, and at reflux the calix[8]arene is converted into calix[4]arene through a "molecular mitosis" (Figure 3-7).[16-19]

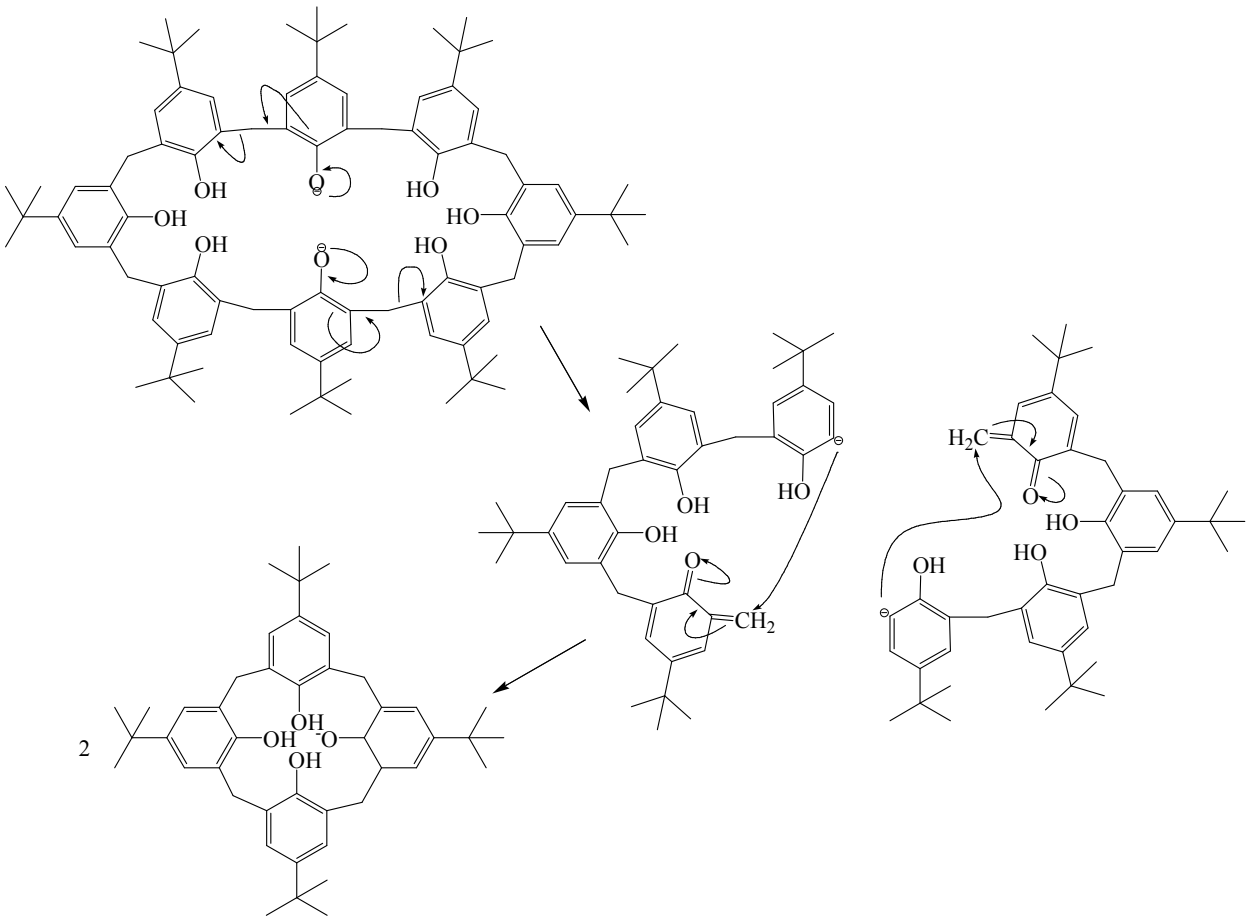


Figure 3-7: Mechanism of "molecular mitosis" to generate calix[4]arene.

Calix[4]arene is one of the more commonly used calix[4]arene species.[6, 12-15, 20-28] In the solid state it can exist in a cone conformation. However, in solution it can exist in four conformations: cone, partial cone, 1,3-alternate, and 1,2-alternate (Figure 3-8). [6, 12, 13]

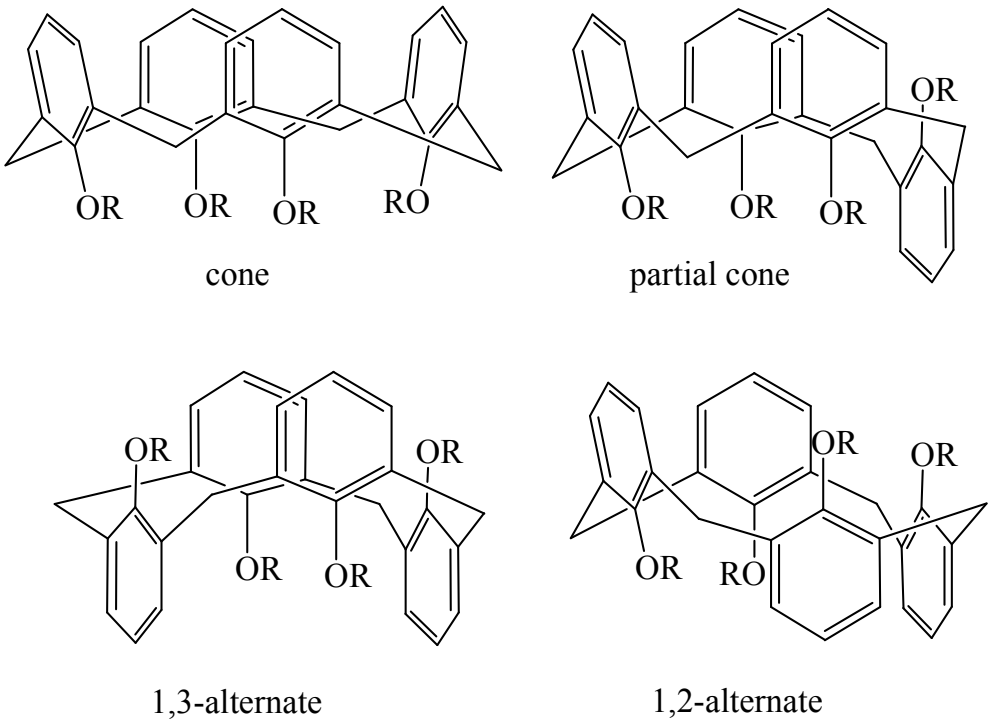


Figure 3-8: Conformers of calix[4]arene.

Rotation about the *meta-carbons* on the aryl rings gives rise to the different conformers. The rotation of the aryl groups is relatively fast, but can be measured using NMR spectroscopy.[29-33] The rate of interconversion of conformers varies with the substituents in the -*para* position, solvent polarity, and temperature.[32] In chloroform, the free energy of activation of *p-tert*-butylcalix[4]arene and *p-tert*-pentylcalix[4]arene are 15.7 kcal/mol and 14.5 kcal/mol, respectively.[32] The effect of solvent polarity is even stronger. In non-polar solvents such as chloroform and benzene the free energy of activation is much higher than in polar solvents, such as acetone and pyridine. For example, in chloroform the free energy of activation of *p-tert*-butylcalix[4]arene is 15.7 kcal/mol, whereas in pyridine the free energy of activation is 11.8 kcal/mol. The difference between non-polar and polar solvents is attributed to the disruption of intramolecular hydrogen bonding, which maintains the cone conformation.[32]

Each conformer can be easily identified based on the resonances observed with ^{1}H NMR for the bridging methylene protons. For example the methylene peaks for the cone conformation appear as one pair of doublets, whereas for the 1,3-alternate conformer the methylene peaks appear as one singlet. Table 3-1 shows the resonance pattern of the methylene protons for the 4 conformers of calix[4]arene.[34, 35]

Table 3-1: ^{1}H-NMR resonances for the bridging methylenes of the different conformers of calix[4]arene

Conformation	^{1}H NMR resonance
Cone	1 pair of doublets
Partial Cone	2 pairs of doublets (ratio 1:1) or a pair of doublets and a singlet (ratio 1:1)
1,3-alternate	1 singlet
1,2-alternate	1 singlet and 2 doublets (ratio 1:1)

As calix[4]arene is conformationally mobile, it is often necessary to "lock" the calix[4]arene into a particular conformation. Since the cone conformation is generally the most useful conformation, much effort is placed on generating functional calix[4]arenes in the cone conformation. The most common method to lock a calix[4]arene in a particular conformation is to alter the intramolecular hydrogen bonding by reacting the phenolic groups to form either ethers or esters.[6, 12] The Parma group[36] provided the first example of a locked calix[4]arene by replacing the OH groups with acetate groups. This calix[4]arene was locked in the partial cone conformation. In 1986, McKervey *et al*[37] isolated the first calix[4]arene in the cone conformation through etherification of the –OH groups with $–OCO_2Et$. It has since been determined that most calix[4]arene ethers adopt a cone conformation.[37-39] The smallest group known to lock a

calix[4]arene into the cone conformation is the propoxy group, this however will only occur if two propoxy groups are attached at directly opposite positions on the lower rim. Ethyoxy and methoxy groups do not impede rotation enough to prevent the formation of the different conformers.[40]

Locking calix[4]arenes into a particular conformation is just one of many steps to obtain materials for various applications. To generate a wide variety of calix[4]arenes, they must be functionalized with a variety of different groups. Functionalization of calix[4]arenes can occur on any of four areas: the upper-rim, the lower-rim, the outer-face, or the bridges (Figure 3-9).[6, 12-14]

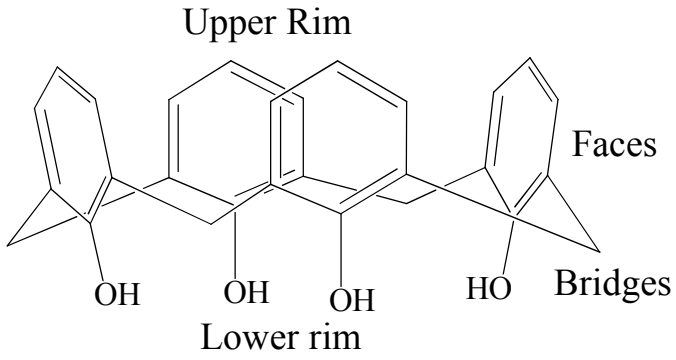
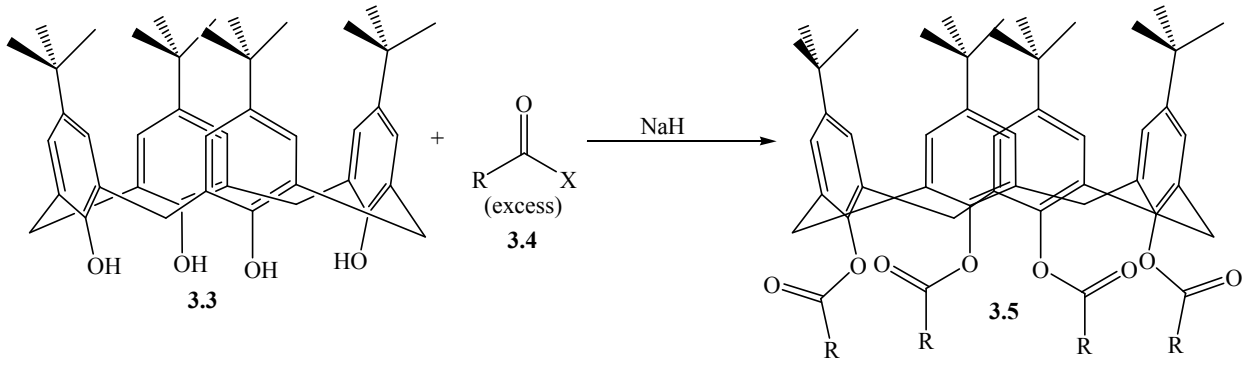


Figure 3-9: Calix[4]arene functionalization sites.

3.1.2 Functionalization of the lower rim

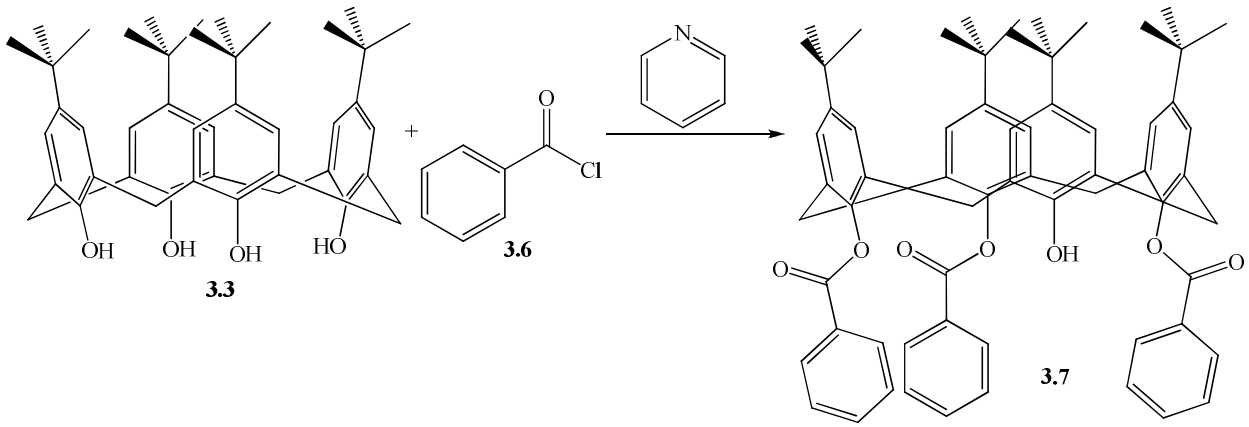
The lower rim of calix[4]arenes is easily functionalized due to the ease of substitution of the phenol –OH(s) using acid/base and nucleophilic substitution reactions, and has until recently been the main focus of calix[4]arene functionalization.[6, 13, 41] Esterification was the first method used to modify the lower rim.[6, 13] The benefit to obtaining ester-containing calix[4]arenes is that they are generally lower melting and have increased solubility. Most ester-containing calix[4]arenes are prepared by reaction of an acid halide and a strong base or Lewis acid such as NaH or $AlCl_3$ since, strong bases are required to fully deprotonate the lower rim. However, esterified calix[4]arenes can also be generated by reaction of an anhydride and H_2SO_4.[6, 13] In general, when an excess of the acid chloride or anhydride is used the product is completely functionalized (Scheme 3-2).[6, 13] No and coworkers[42] reported complete functionalization for the acetylation, propionylation, butyrylation and isobutyrylation of *p-tert*-butylcalix[4]arene and calix[4]arene. However, the conformation of the products varied.



Scheme 3-2: Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetra-esterifide calix[4]arene.

Partial functionalization of the lower rim allows for the introduction of multiple functionalities as well as for the creation of a platform for the functionalization of the upper rim. It is interesting to note that partially functionalized calix[4]arenes are generally more

conformationally locked than their fully functionalized analogues, since a partially substituted lower rim still maintains some hydrogen bonding capabilities. The use of weaker bases such as K_2CO_3, or pyridine and/or the stoichiometric control of the esterification agent allows for the partial substitution of the lower rim.[43-49] Gutsche reported the synthesis of 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene, one of the first examples of a partially functionalized calix[4]arene through the reaction of calix[4]arene with benzoyl chloride in pyridine (Scheme 3-3).[43]



Scheme 3-3: Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27-tribenzoyl-28-hydroxycalix[4]arene.

Partial functionalization is possible due to the nature of the intramolecular hydrogen bonding of the lower rim. Initially when there are four hydroxyl groups present on calix[4]arene, the pK_a values of the hydrogen atoms are approximately 0 (70:30 water:THF), indicating that the first proton is very easy to remove.[14] After removal of the first hydrogen atom, the pK_a values for the remaining hydrogen atoms increase dramatically: 10.3 to remove the 2nd hydrogen, 13 for the 3rd and >14 for the 4th. The increase in pK_a value is due to the destabilization of the hydrogen bonding. When the first proton is removed, the single negative charge is stabilized by the remaining hydrogen bonds hence affording higher pK_a values. However, the pK_a value of the last

proton to be removed is much higher, because that proton is held in a network of three anionic oxygen atoms.[14]

When preparing di-functionalized calix[4]arenes there are two possible isomers, the 1,3 isomer and the 1,2 isomer (Figure 3-10). For example, the $AlCl_3$ catalyzed reaction of calix[4]arene with 3,5-dinitrobenzoyl chloride gives the 1,3-diester.[50] While it is possible to obtain both the 1,3- and the 1,2-disubstituted calix[4]arenes, it is far more common to obtain the 1,3-disubstituted calix[4]arene since the protons at the 25 and 27 positions are the most acidic, due to resonance stabilization of the dianion by the intramolecular hydrogen bonding.[51]

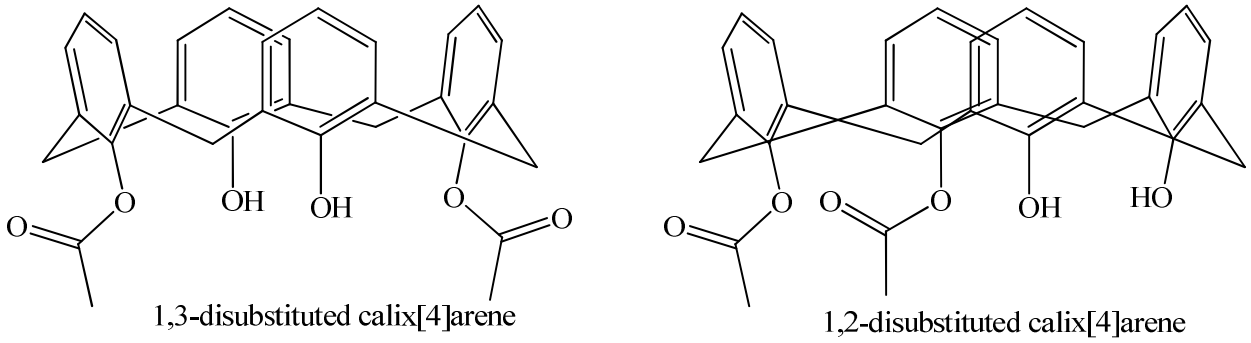
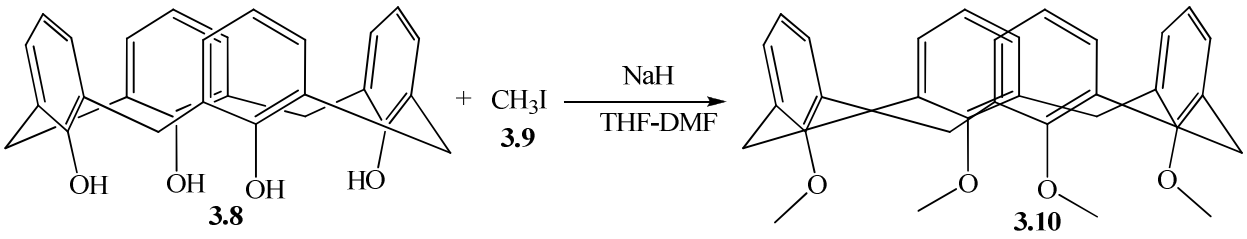


Figure 3-10: 1,3-Disubstituted calix[4]arene (left), 1,2-disubstituted calix[4]arene (right).

Etherification is the second most common reaction to functionalize the lower rim of the calix[4]arene. Much like the esterification reaction, etherification can result in both complete and partial functionalization of the lower rim. Etherification of calix[4]arenes is generally performed in a THF-DMF solution where the calix[4]arene is treated with NaH and then reacted with an alkyl halide (Scheme 3-4). This particular method of synthesis has provided methyl, ethyl, allyl, and benzyl ethers of calix[4]arenes.[34]



Scheme 3-4: Synthesis of 25,26,27,28-tetramethoxycalix[4]arene.

The functionalization of the lower rim of calix[4]arenes is not restricted to mono-functional groups. The use of reagents containing multiple functional groups allow for the production of calix[4]arenes containing bridges between phenolic groups. For example, the Parma group produced the bridged crown-5-diacetic acid calix[4]arene (Figure 3-11).[38]

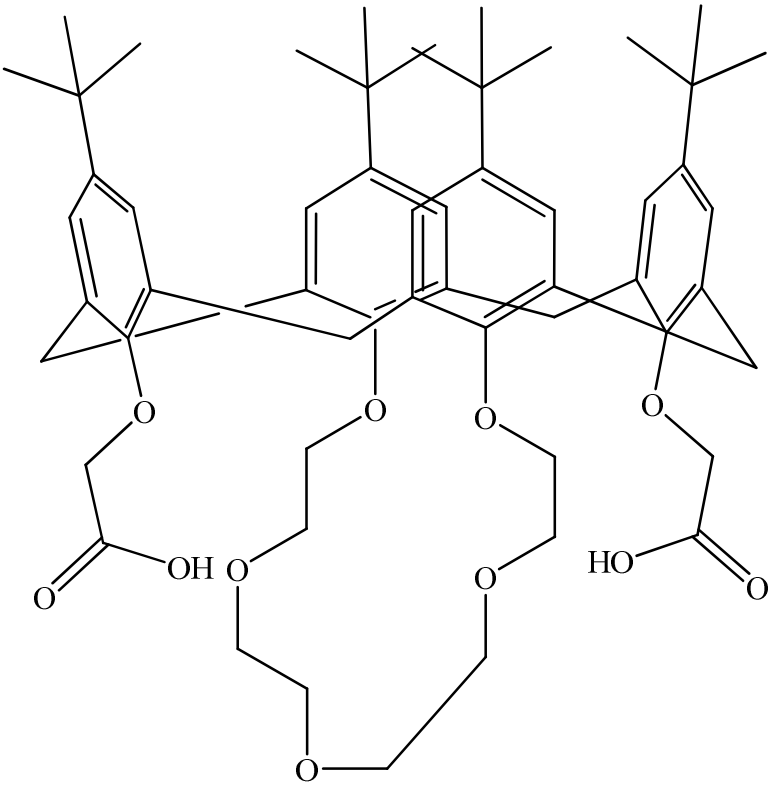
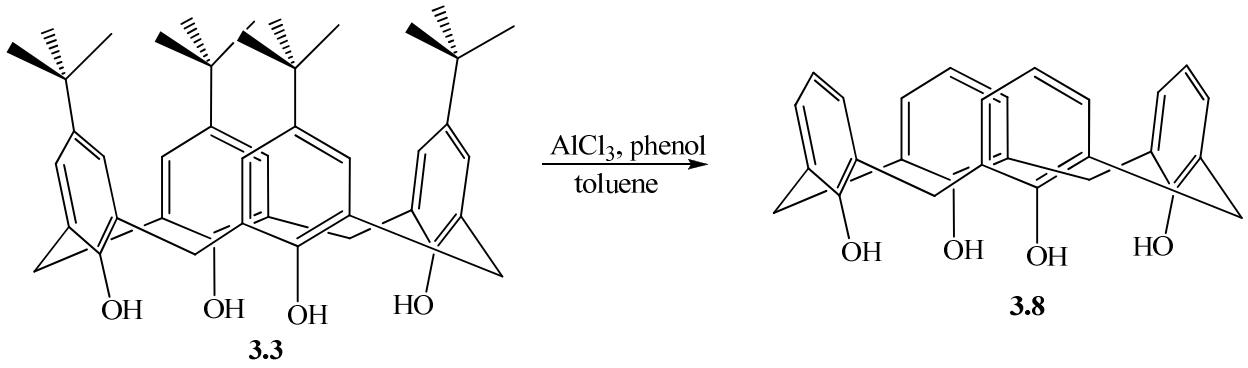


Figure 3-11: Struture of 25,27-crown 5-26,28-diacetic acid calix[4]arene.

One of the reasons to functionalize the lower rim of the calix[4]arene is to provide a portal to the functionalization of the upper rim of the calix[4]arene.

3.1.3 Functionalization at the upper rim

Upper rim functionalization of calix[4]arenes can occur through multiple pathways such as electrophilic addition, rearrangement and nucleophilic substitution. Since calix[4]arenes are prepared from *para*-*t*-butylphenol, they contain *tert*-butyl groups in the *para* positions, which prevent any functionalization at the upper rim. Fortunately, the *para*-*t*-butyl groups are easily removed through a reverse Friedel-Crafts acylation (Scheme 3-5).[52]



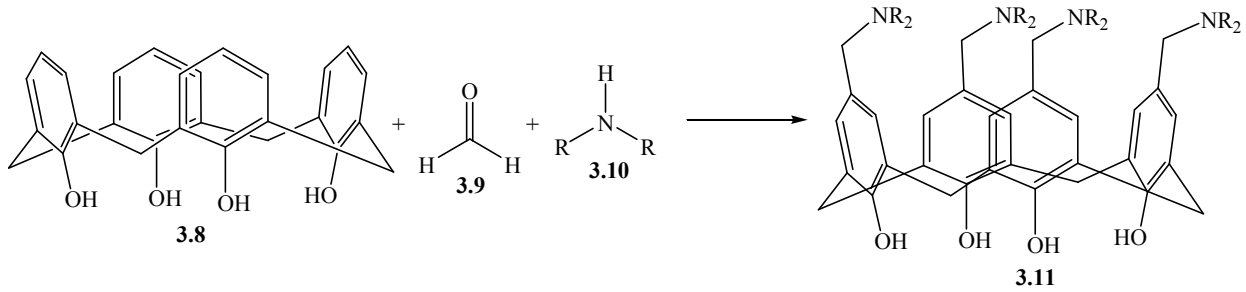
3.3 **3.8**

Scheme 3-5: Synthesis of 25,26,27,28-tetrahydroxycalix[4]arene.

This reaction gives calix[4]arenes that possess *para* sites available for functionalization. The reaction of calix[6]arene with H_2SO_4 was one of the first examples of electrophilic addition to the upper rim of a calix[4]arene.[36, 53] The reaction was quickly applied to calix[4]- and calix[8]-arene to provide sulfonato derivatives of both. Reacting calix[4]arenes with HNO_3 under similar conditions resulted in nitro derivatives.[54]

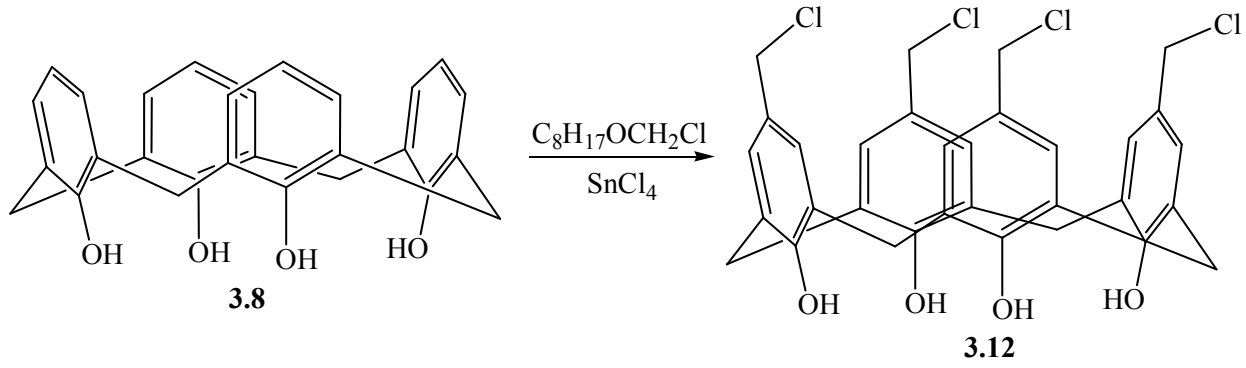
An alternative of direct electrophilic addition to the *para* position is the *p*-quinonemethide route,[55] which utilizes a Mannich-type reaction to prepare *p*-alkylaminomethylcalix[4]arenes from calix[4]arene, formaldehyde and secondary amines (Scheme 3-6). The alkylaminomethylcalix[4]arenes can then be substituted with various nucleophiles to provide a large variety of upper rim functionalized calix[4]arenes. However, this

route is not suitable for such nucleophiles as acetylides, or weakly basic nucleophiles like imidazole.



Scheme 3-6: *p*-Quinonemethide method for upper rim functionalization.

Another method of indirect electrophilic addition to the upper rim is the *p*-chloromethylation route (Scheme 3-7).[56] This method, introduced by the Parma group, reacts calix[4]arene with octyl chloromethyl ether and stannic chloride to yield *p*-chloromethylcalix[4]arene. Reaction with various nucleophiles allows for substitution of the chloro group to yield different upper rim functionalized calix[4]arenes.



Scheme 3-7: *p*-Chloromethylation method for upper rim functionalization.

Rearrangement is another method to functionalize calix[4]arenes on the upper rim, utilizing the *p*-Claisen rearrangement.[52] For this rearrangement to occur the lower rim of the calix[4]arene must first be substituted with one or several allylic groups, and then heated in a high boiling solvent such as N,N-diethylaniline. During this reaction the allylic group undergoes

two consecutive [3,3] sigmatropic rearrangements (Figure 3-12). The allylic group on the *para*-position provides a route to obtain other functionalities on the upper rim.

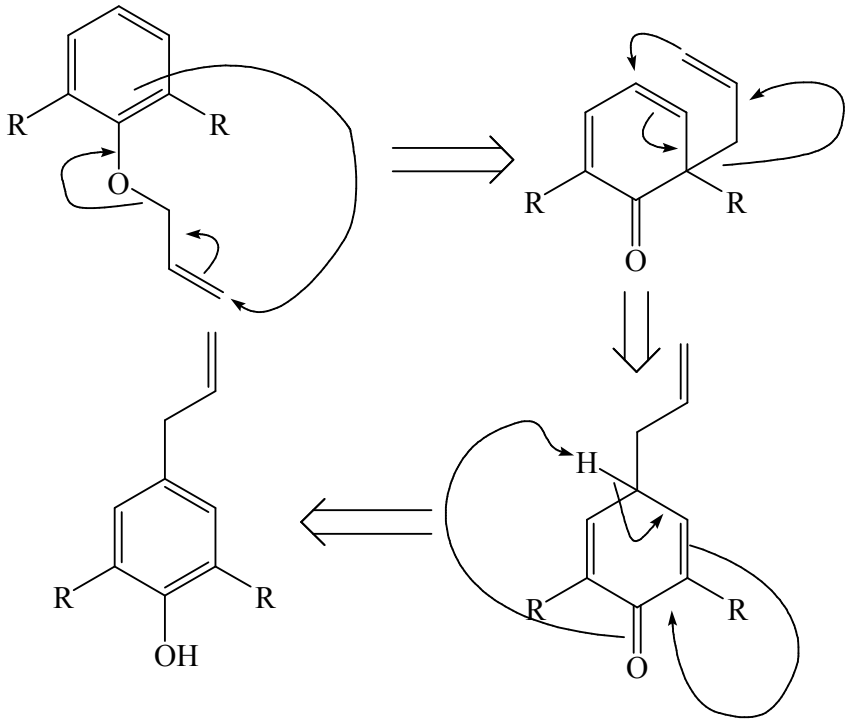


Figure 3-12: Mechanism for the *p*-Claisen rearrangement

3.1.4 Metal-containing calix[4]arenes

Functionalization of calix[4]arenes allows for the incorporation of many different types of groups to give new interesting properties. Metallic species are of particular interest due to the unique properties they impart. There are several ways to incorporate metallic moieties into calix[4]arenes, including coordination of free metallic ions either with the phenolic –OHs or through different ligands, or the incorporation of organometallic species.

Due to the nature of calix[n]arenes, they possess the ability to chelate metallic ions from solution. Generally, this occurs through the phenol groups on the lower rim. For example, calix[4]arene can coordinate to a transition metal using one to four of its phenolic groups (Figure 3-13).[57]

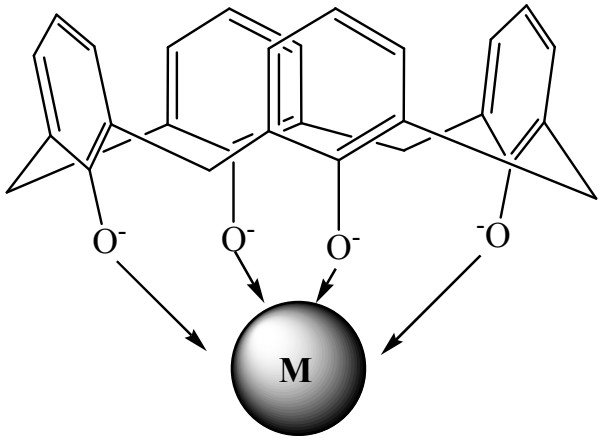


Figure 3-13: Complexation of a metal cation to calix[4]arene.

The complexation of metal ions by calix[4]arene can lead to several different structures. Mono-calix[4]arene complexes can occur where one metal is chelated by one calix[4]arene or the metal centre can act as a bridging unit to build calix[4]arene dimers and coordination polymers (Figure 3-14).[13] This method has resulted in a number of new complexes of Eu^{3+}, Lu^{3+}, La^{3+}, Tm^{3+}, Nb^{5+}, Ta^{5+}, Si^{4+}, Ti^{4+}, Al^{3+}, and Zn^{2+} including many others.[14, 58, 58-64] Early work in this type of complexation using alkali metals showed that a high pH was required, to maintain the negative charges on the lower rim of the calix[4]arene, for the complexation to succeed.[65, 66]

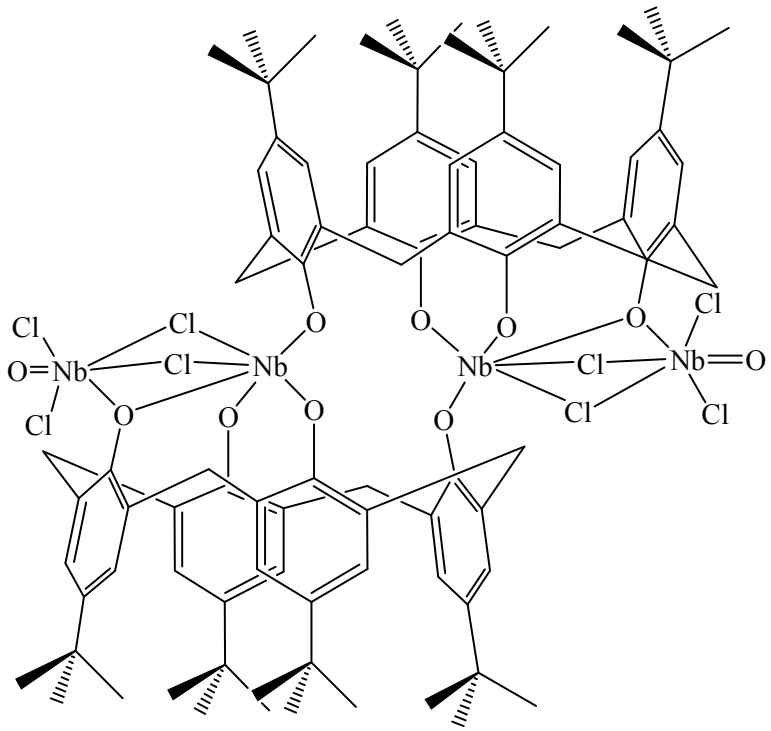


Figure 3-14: Niobium bridged dicalix[4]arene.

While coordination to the phenolic groups is one method for the complexation of metals to the lower rim of calix[n]arenes, modification of the lower rim with various functional groups allows a wider range of metals to be bound to the calix[n]arene. The increased range of complexable metals is due to the effects that the new functional groups can generate. For example, functionalization with crown ethers increases the size of the lower rim cavity, resulting in the ability to capture higher molecular weight metals, while functionalization with bipyridines can increase chelating ability (Figure 3-15).[13, 67]

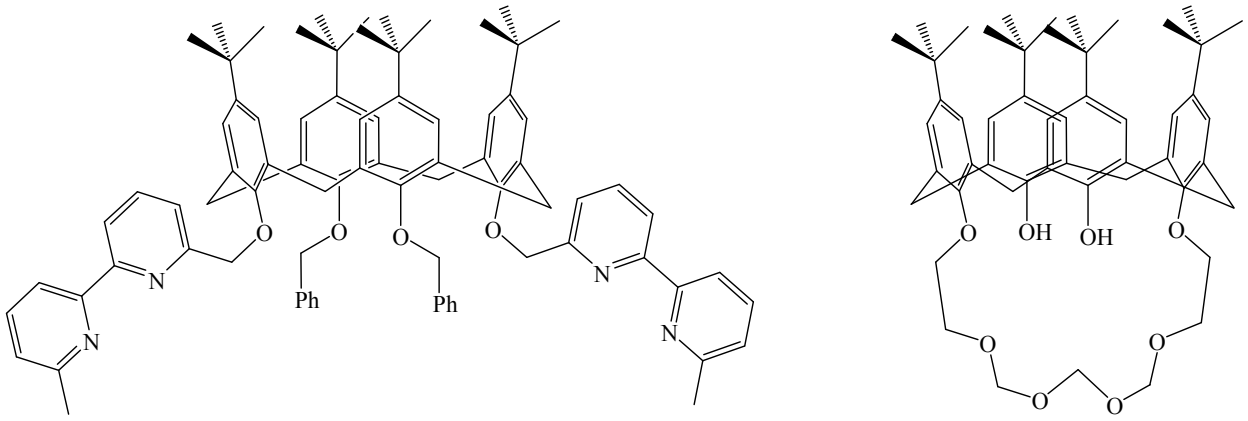


Figure 3-15: 25,27-Bis-bipyridine-26,28-dibenzylcalix[4]arene (left); 25,27-crown-6-26,28-dihydroxycalix[4]arene (right).

While incorporating chelating groups onto the lower rim of calix[n]arenes is one method for obtaining metallated calix[4]arenes, it is possible to incorporate metals via incorporation of organometallic units. The Beer group has prepared a number of calix[4]arenes functionalized with ferrocene derivatives on the lower rim.[68] Beer and coworkers prepared a number of *p-tert*-butylcalix[4]arene acid chlorides and reacted them with ferrocenemethylamine to give the ferrocene-containing calix[4]arenes. Due to steric interactions these reactions gave incomplete substitution of the lower rim.

3.1.5 Calix[4]arene polymers

A limited number of examples of polymers that contain calix[4]arenes have been reported, but they remain relatively rare. There are several methods for the incorporation of calix[4]arenes into polymers. These include: self assembly coordination, ring-opening metathesis polymerization, radical polymerization, and epoxide opening.[69-83]

Polymeric calix[4]arenes began to appear in the late 1980s when several patents for this kind of material were obtained. Some of the first examples of polymeric calix[4]arenes were prepared by polymerization of either upper rim or lower rim functional groups (Figure 3-16).[70]

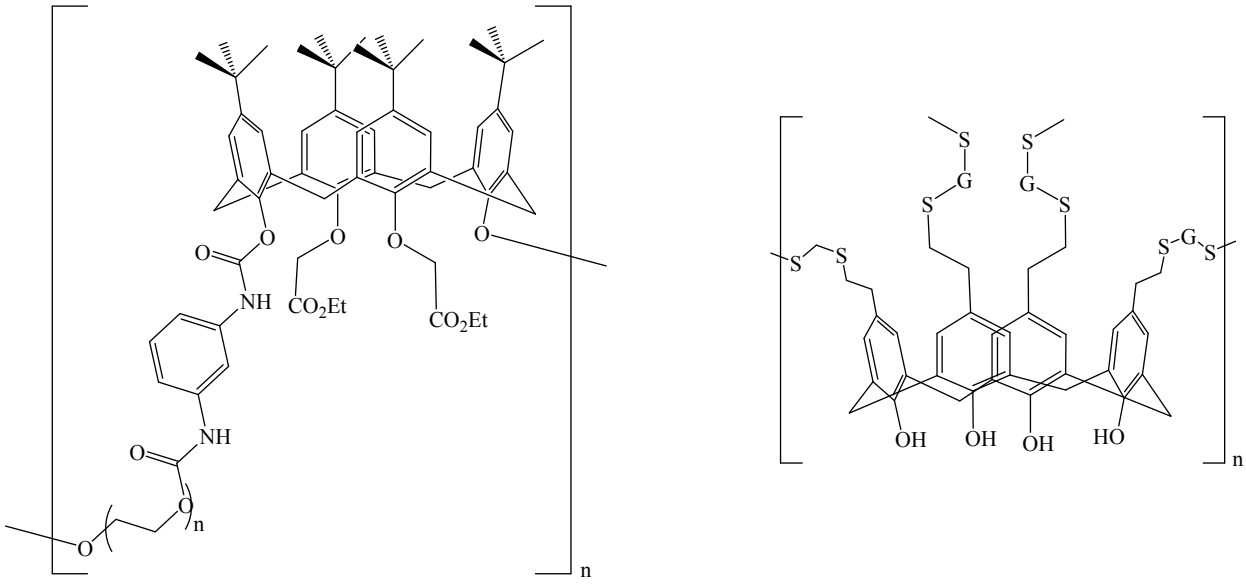


Figure 3-16: Lower (left) and upper (right) rim based polycalix[4]arenes.

Functionalization of the lower rim of calix[4]arene has also allowed for the production of polycalix[4]arenes via ROMP with norbornene and cyclooctene using Grubbs' 2nd generation catalyst (Figure 3-17).[79]

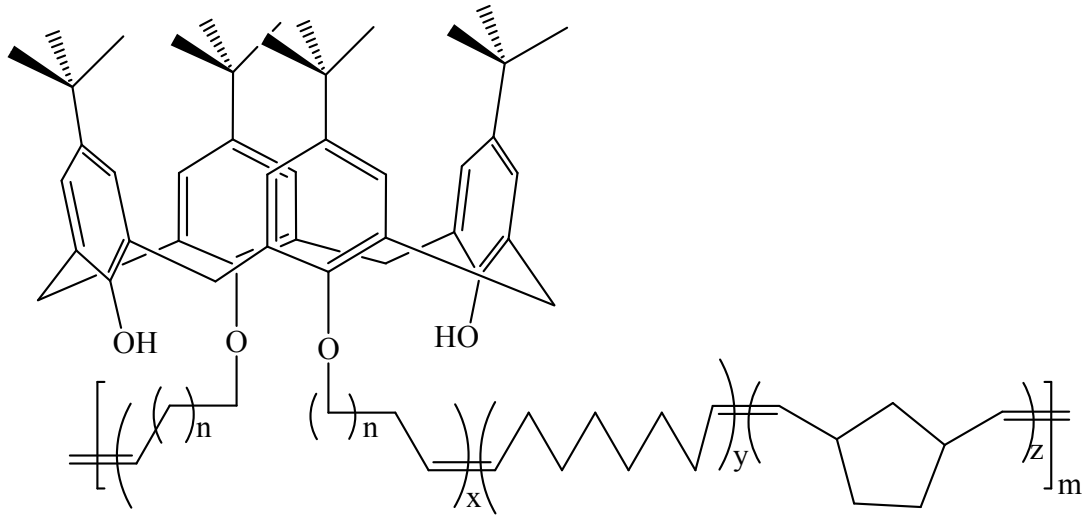


Figure 3-17: Polycalix[4]arene prepared through ROMP.

Reaction between calix[4]arenes and premade polymers have given polymer supported calix[4]arenes. For example, the reaction of *p*-tert-butylcalix[8]arene with a styrene-divinylbenzene copolymer containing an acid chloride gave a polymer supported calix[6]arene (Figure 3-18).[69]

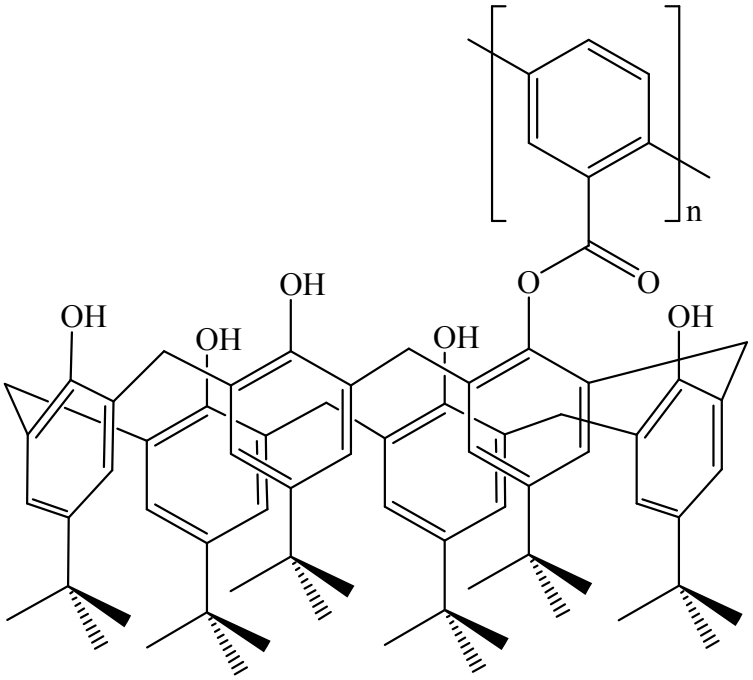


Figure 3-18: Polystyrene supported calix[6]arene.

Titanium functionalized cellulose has also been used as a polymer support for calix[4]arene (Figure 3-19).[82]

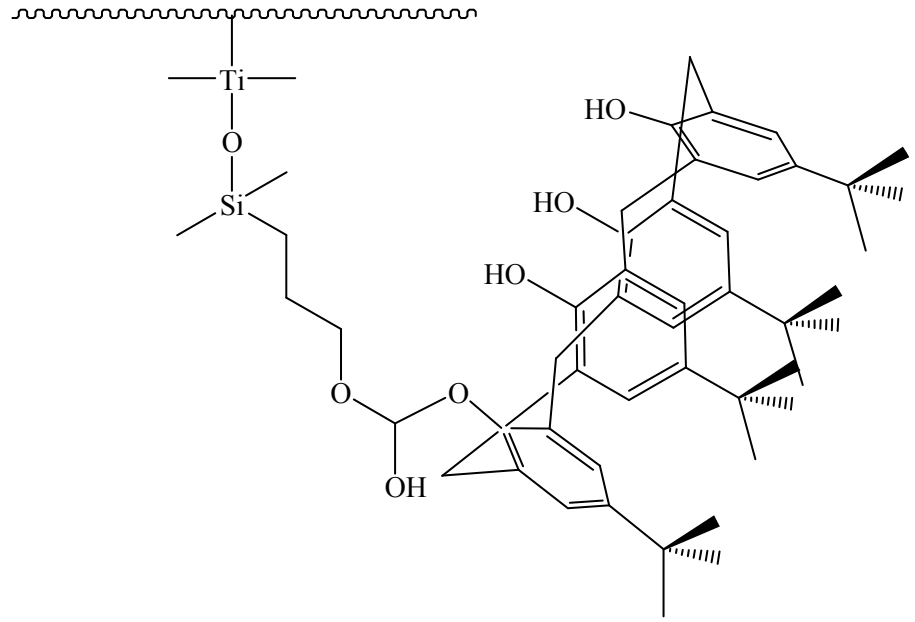


Figure 3-19: Cellulose supported calix[4]arene.

Monomeric calix[4]arenes have been prepared that contain vinyl or acrylate groups, which can be polymerized though radical polymerization. This can be done on either the upper

or lower rim of the calix[4]arene to give polycalix[4]arenes (Figure 3-20).[74, 75, 77]

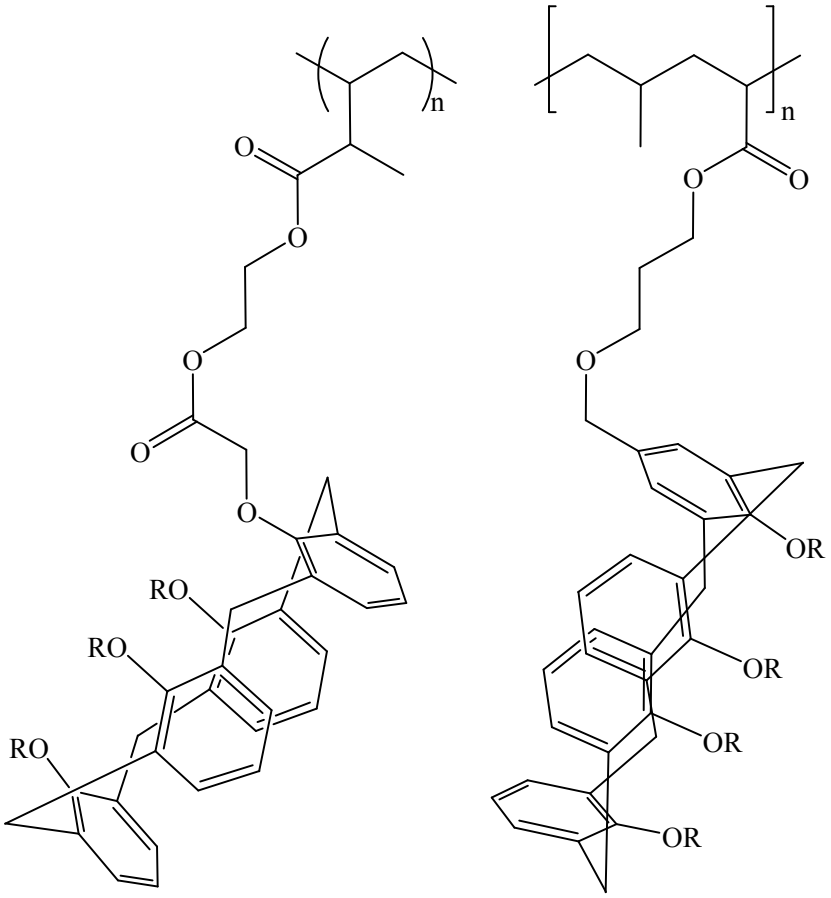


Figure 3-20: Lower (left) and upper (right) rim functionalized calix[4]arene containing polymetacrylates.

Difunctional calix[4]arene monomers can be condensed with various other difunctional materials to provide calix[4]arene containing polyesters or polyamides (Figure 3-21).[83]

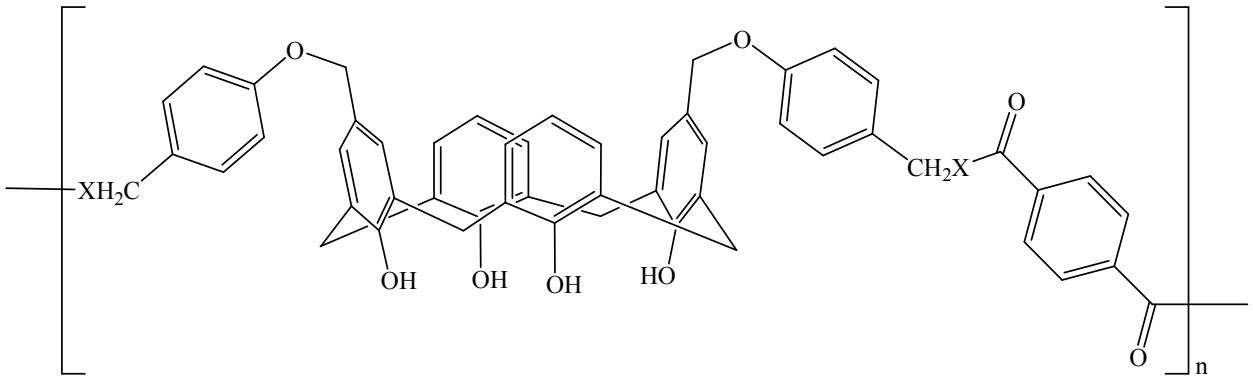


Figure 3-21: Calix[4]arene based polyesters and polyamides.

The following sections will detail the synthesis and characterization of number of new calix[4]arenes. The calix[4]arenes will be reacted with a number of organometallic groups to prepare new organoiron containing calix[4]arenes. These metallocalix[4]arenes will be further reacted to give azo dye containing metallocalix[4]arenes and organometallocalix[4]arene polymers. The organic calix[4]arenes will be functionalized with polymerizable groups and be used to prepare calix[4]arene polymers.

3.2 Results and discussion

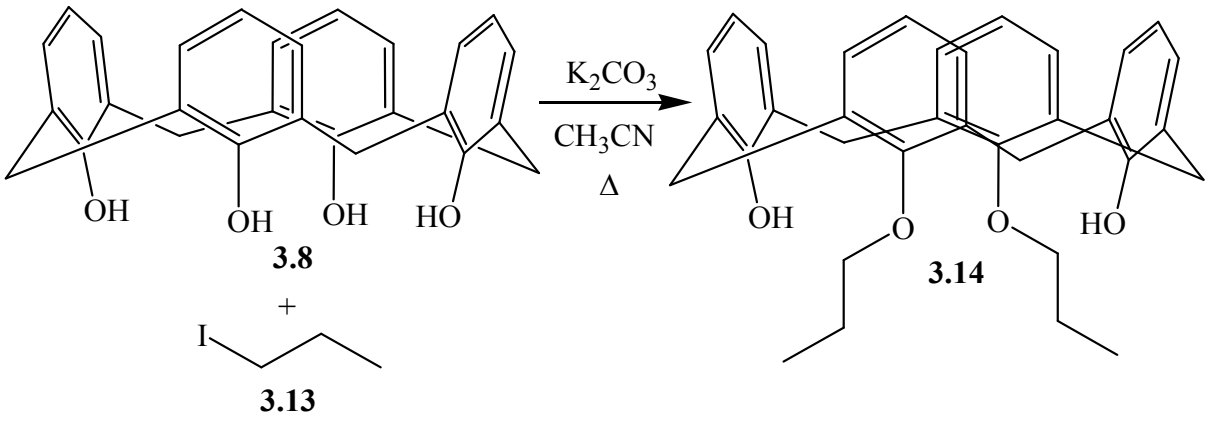
3.2.1 Synthesis of upper rim functionalized propanol containing calix[4]arenes

Upper rim functionalized calix[4]arenes are particularily interesting as they allow for the lower rim to maintain its functionality. Calix[4]arenes containing alcohol groups on the upper rim were prepared since the availability of the alcohol group would allow for further functionalization of the calix[4]arene with a number of organic and organometallic moieties. This section of this chapter will discuss the synthesis of mono- and di-upper rim alcohol functionalized calix[4]arenes.

3.2.1.1 Di-substituted calix[4]arenes

The syntheses of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrahydroxy-calix[4]arene (**3.3**), 25,26,27,28-tetrahydroxy-calix[4]arene (**3.8**), and 25,27-di-propoxy-26,27-di-hydroxy-calix[4]arene are well established (**3.14**).[84-86] Calix[4]arene (**3.8**) can easily be functionalized on either the upper or lower rim to allow for further functionalization.

The syntheses of calix[4]arene **3.18** and **3.23** have previously been reported.[86, 87] However, since the synthesis of these two compounds are extremely important to the discussion of the other calix[4]arenes prepared; a full discussion of the synthesis and characterization of these compounds is necessary. Two methods were employed to prepare a calix[4]arene containing two allylic groups on the upper rim. In the first method, two propoxy groups were first attached to calix[4]arene (**3.8**) by reaction with iodopropane in the presence of 1 molar equivalence of K_2CO_3 to give 25,27-dipropoxy-26,28-dihydroxycalix[4]arene (**3.14**) (Scheme 3-8). The reaction of (**3.8**) with 1 eq. of K_2CO_3 preferentially abstracts two protons from opposing sides of the calix[4]arene cone.



Scheme 3-8: Synthesis of calix[4]arene 3.14.

Figure 3-22 shows the ^{1}H NMR spectrum of **3.14**. As can be seen the phenolic groups appear at 8.28 ppm, and there are two sets of arene peaks: a doublet and triplet at 7.04 ppm and 6.73 ppm, and another doublet and triplet set at 6.91 ppm and 6.63 ppm. These are due to the phenol-containing and the propoxy-containing arenes respectively. The bridging methylenes appear at 4.31 ppm and 3.37 ppm both of which appear as doublets indicating the cone conformation of the calix[4]arene. The propoxy group appears as a triplet centered on 3.97 ppm, a sextet centered on 2.06 ppm, and a triplet at 1.30 ppm.

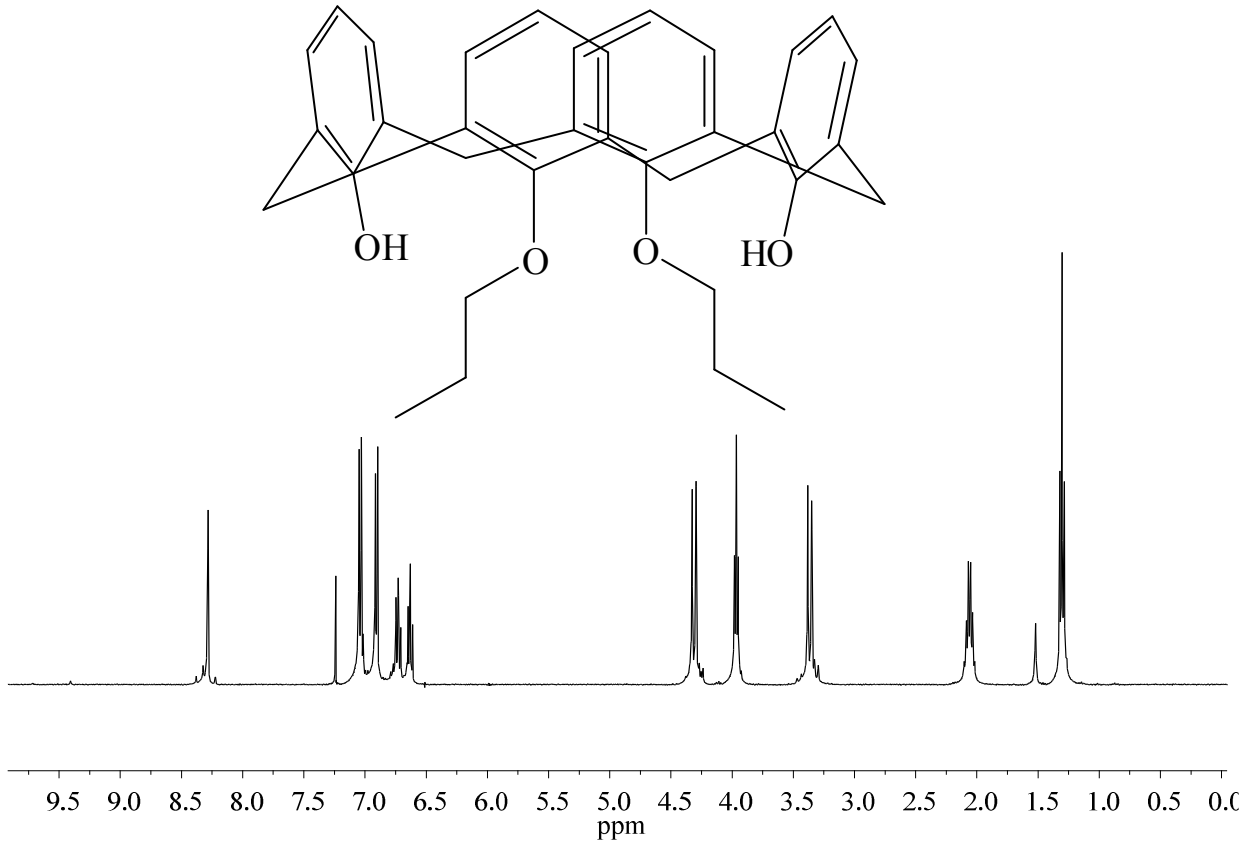
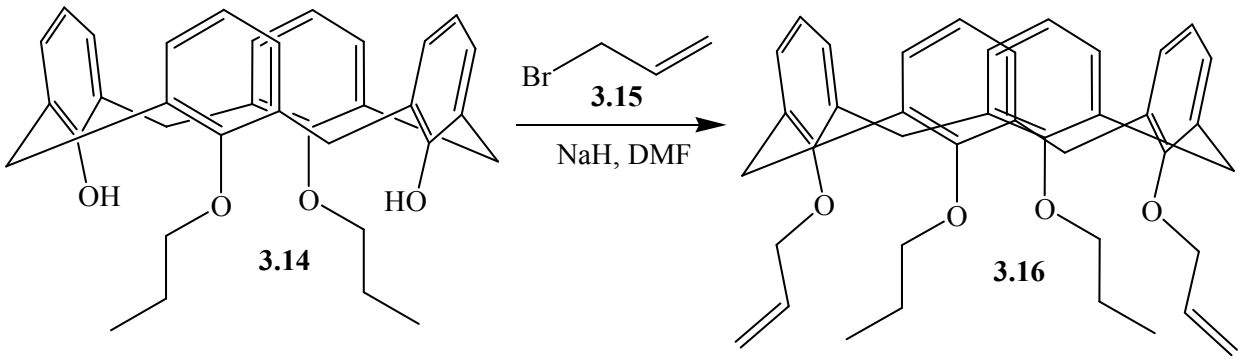


Figure 3-22: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.14.

Calix[4]arene **3.14** was then reacted with NaH and allyl bromide to give 25,27-diallyl-26,28-dipropoxycalix[4]arene (**3.16**) (Scheme 3-9).



Scheme 3-9: Synthesis of calix[4]arene 3.16.

Figure 3-23 shows the ^{1}H NMR spectrum of calix[4]arene **3.16**. The incorporation of the allylic groups is observed by the resonances centered at 6.44 ppm, 5.12 ppm and 4.61 ppm due to the CH and CH_2 of the allylic group and the OCH_2 group respectively. The original calix[4]arene resonances are centered on 6.98 ppm, 6.85 – 6.81 ppm, 4.40 ppm, 3.71 ppm, 3.14 ppm, 2.09 – 1.73 ppm, and 1.06 ppm.

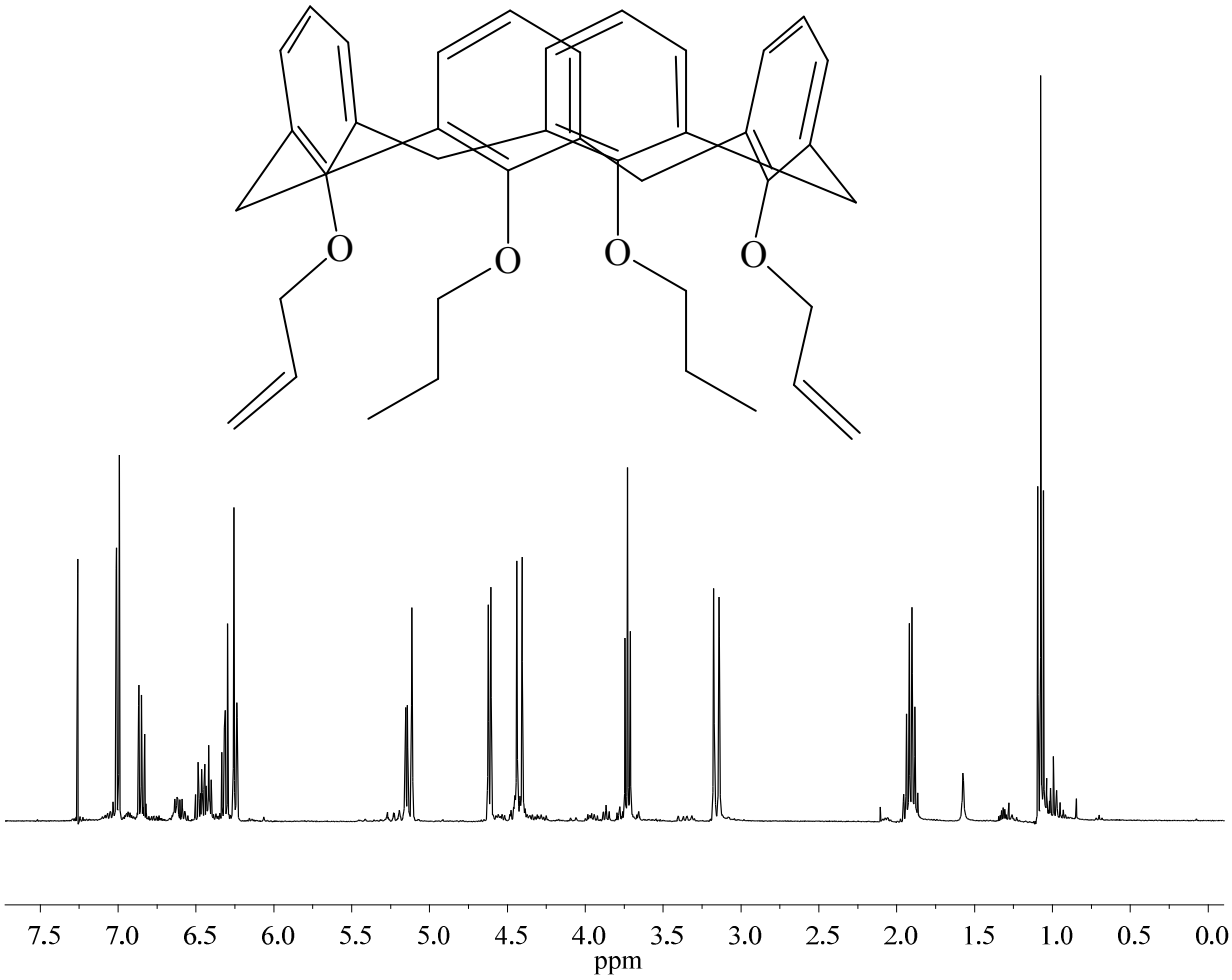
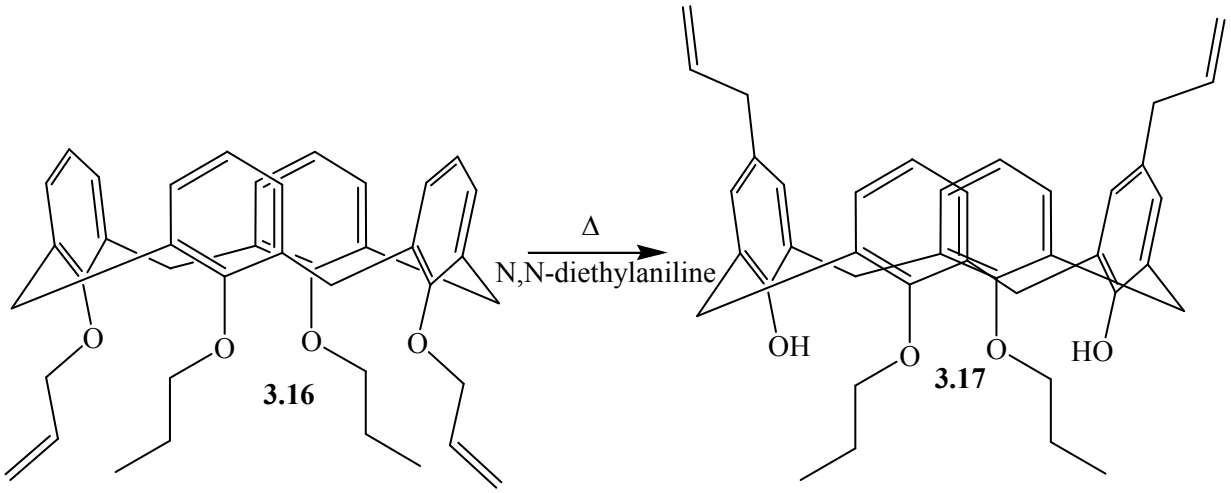


Figure 3-23: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.16.

Calix[4]arene **3.16** was refluxed in N,N-diethylaniline to rearrange the allylic group from the lower rim to the upper rim to give 5,11-diallyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**3.17**) (Scheme 3-10)



Scheme 3-10: Synthesis of calix[4]arene 3.17.

The ^{1}H NMR spectrum of calix[4]arene **3.17** is in Figure 3-24. As can be seen not only have the resonances due to the allylic group shifted from 6.44 ppm, 5.12 ppm and 4.61 ppm to 5.93 ppm, 5.03 ppm, and 3.24 ppm, respectively, but the calix[4]arene arene resonances now appear as a doublet, a singlet, and a triplet centered on 6.93 ppm, 6.85 ppm, and 6.75 ppm. Also, phenolic resonances are visible at 8.19 ppm.

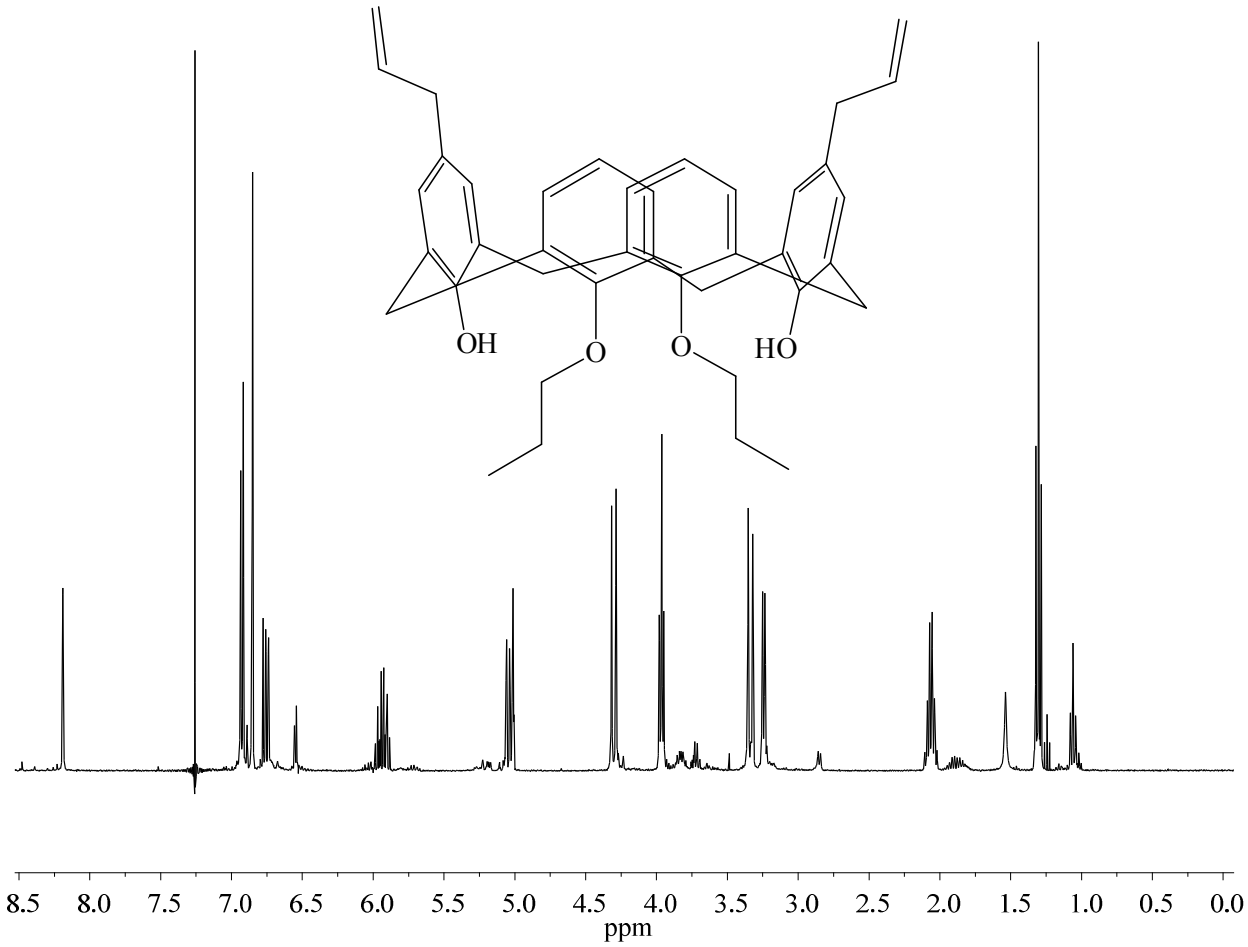
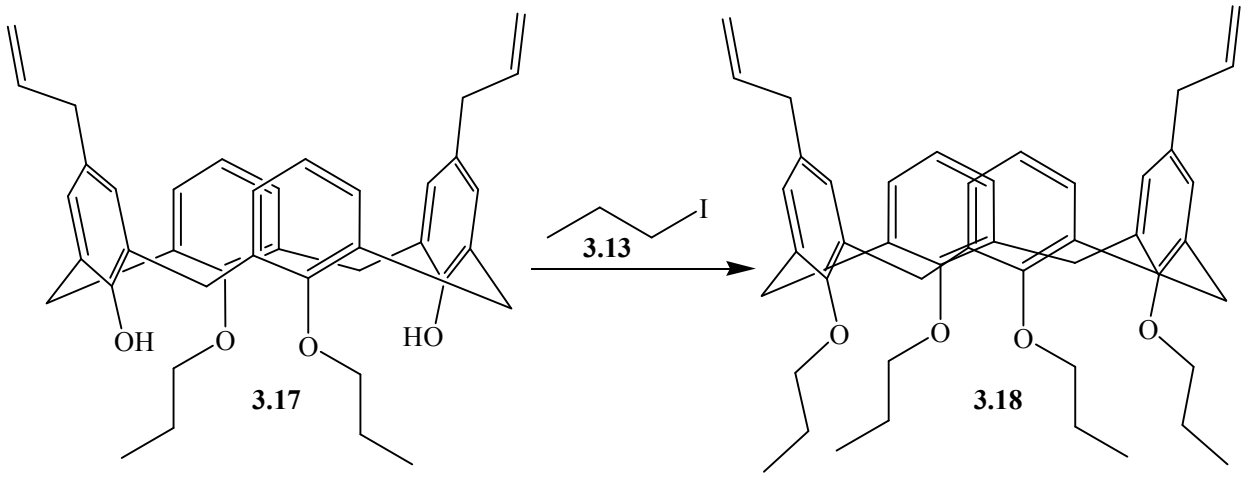


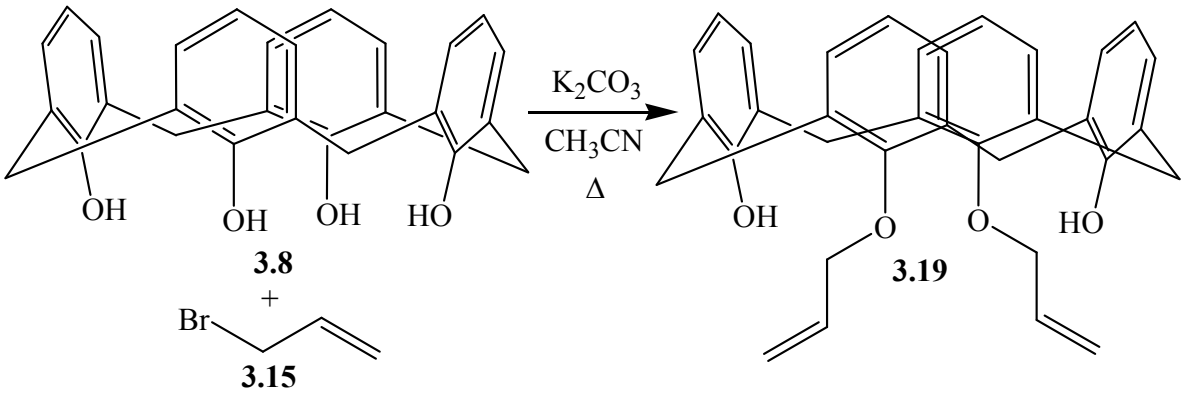
Figure 3-24: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.17.

Calix[4]arene **3.17** was then reacted with iodopropane and NaH to give 5,11-diallyl-25,26,27,28-tetrapropoxycalix[4]arene **3.18** (Scheme 3-11). The NMR analysis of this compound will be discussed later in this section.



Scheme 3-11: Synthesis of calix[4]arene 3.18.

This method to prepare 5,11-diallyl-25,26,27,28-tetrapropoxycalix[4]arene takes 5 steps, and suffers from a decreased yield in the final step. To obtain a greater yield of **3.18** a second method was used improve the synthesis. The second method prepares **3.18** in 3 steps and is performed by reacting calix[4]arene **3.8** with two equivalents of allyl bromide in acetonitrile to give 25,27-di-allyl-26,28-di-hydroxycalix[4]arene (**3.19**) in the cone conformation (Scheme 3-12). For this synthesis one molar equivalence of K_2CO_3 was used to selectively deprotonate the calix[4]arene. The ^{1}H NMR spectrum of **3.19** is shown in Figure 3-25. The aromatic peaks appear as two doublets and two overlapping triplets at 6.72 ppm, 6.92 ppm, and 7.11 ppm. The CH_2 of the double bond denoted (a) appears as two doublets of quartets centered at 5.83 ppm and 5.46 ppm. These resonances appear as two doublets of quartets due to the long range coupling to the benzylic CH_2. The CH of the double bond (b) resonates as a doublet of doublets of triplets centered at 6.30 ppm; the etheric CH_2 of the allylic group (c) resonates as a doublet of triplets at 4.59 ppm which is a characteristic chemical shift for phenolic ethers. The cone conformation of the calix[4]arene is confirmed presence of the doublets at 4.43 pm and 3.39 ppm for the bridging methylenes (d,e) (Figure 3-25). The presence of the allylic group at the end of the ether allows for the upper rim functionalization of the calix[4]arenes through the *p*-Claisen rearrangement.



Scheme 3-12: Synthesis of calix[4]arene 3.19.

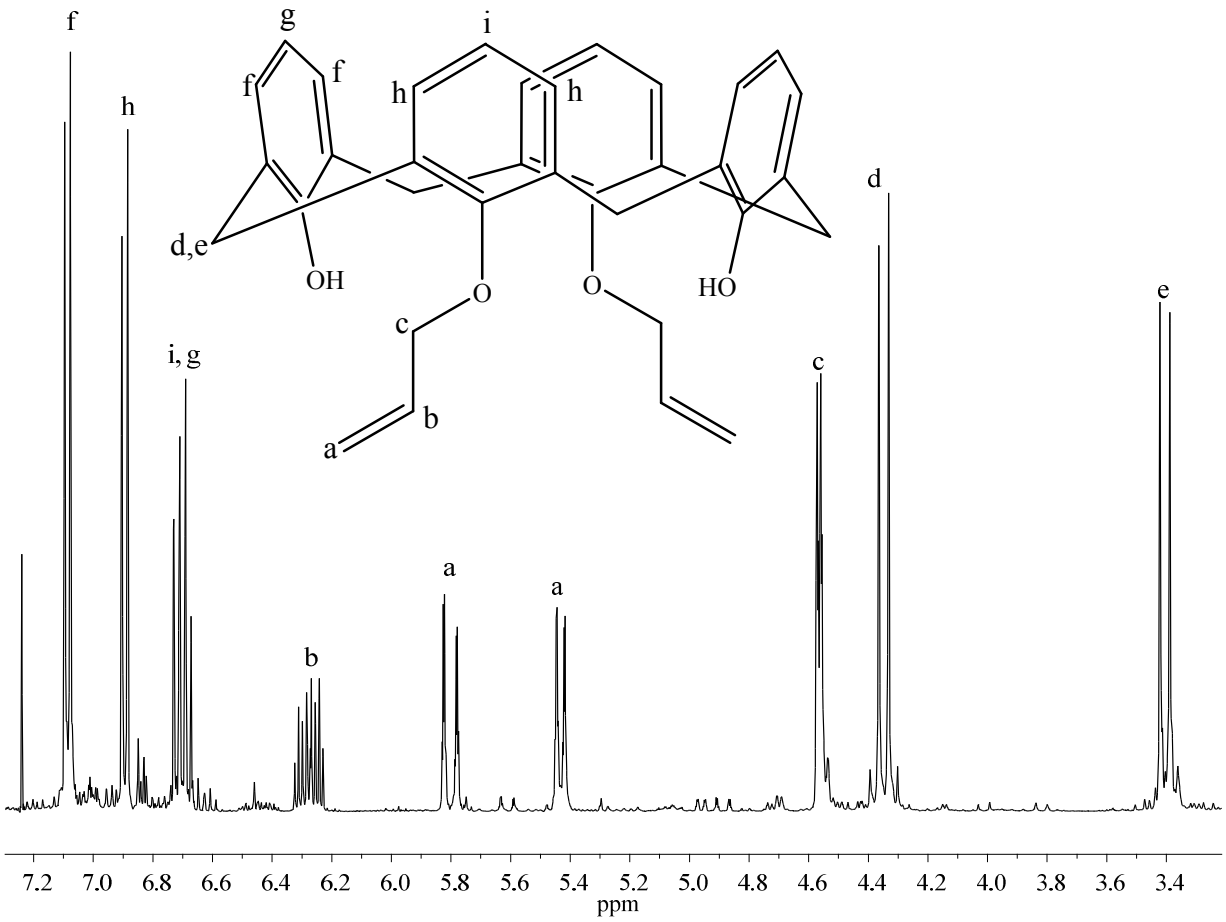
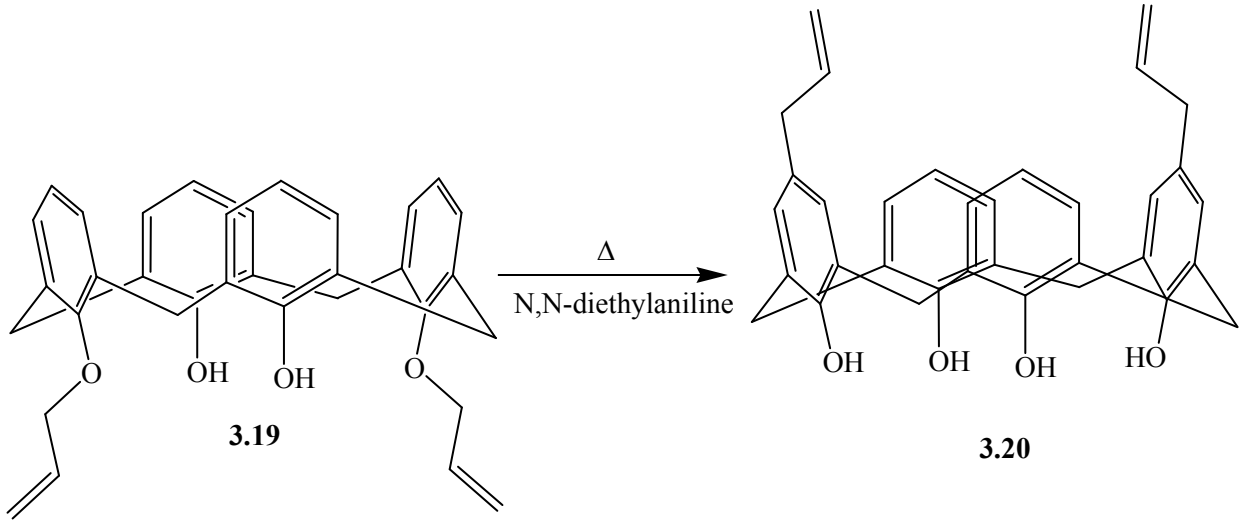


Figure 3-25: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.19.

Refluxing **3.19** in N,N-diethylaniline causes a *p*-Claisen rearrangement that "flips" the allylic groups from the 25 and 27 positions of the lower rim of the calix[4]arene to the 5 and 11 positions of the upper rim to yield **3.20** (Scheme 3-13). Figure 3-26 shows the ^{1}H NMR spectrum of calix[4]arene **3.20**. It can be seen that the rearrangement has successfully occurred as judged by the shift in the aromatic region to a doublet, a singlet and a triplet at 7.03 ppm, 6.84 ppm, and 6.72 ppm, which indicates that two of the *para* positions of the calix[4]arene have been functionalized. This is further substantiated by the shift in the resonances due to the allylic group. The resonance due to (a) has shifted from 5.83 ppm and 5.46 ppm to a multiplet centred on 5.03 ppm, while the resonance due to (b) has shifted from 6.30 ppm to 5.85 ppm and (c) has shifted from 4.59 ppm to 3.16 ppm characteristic of a benzylic position. The resonances due to the bridging methylenes have also become two broad singlets which is characteristic of a calix[4]arene possessing four phenolic groups on the lower rim.



3.19 **3.20**

Scheme 3-13: Synthesis of calix[4]arene 3.20.

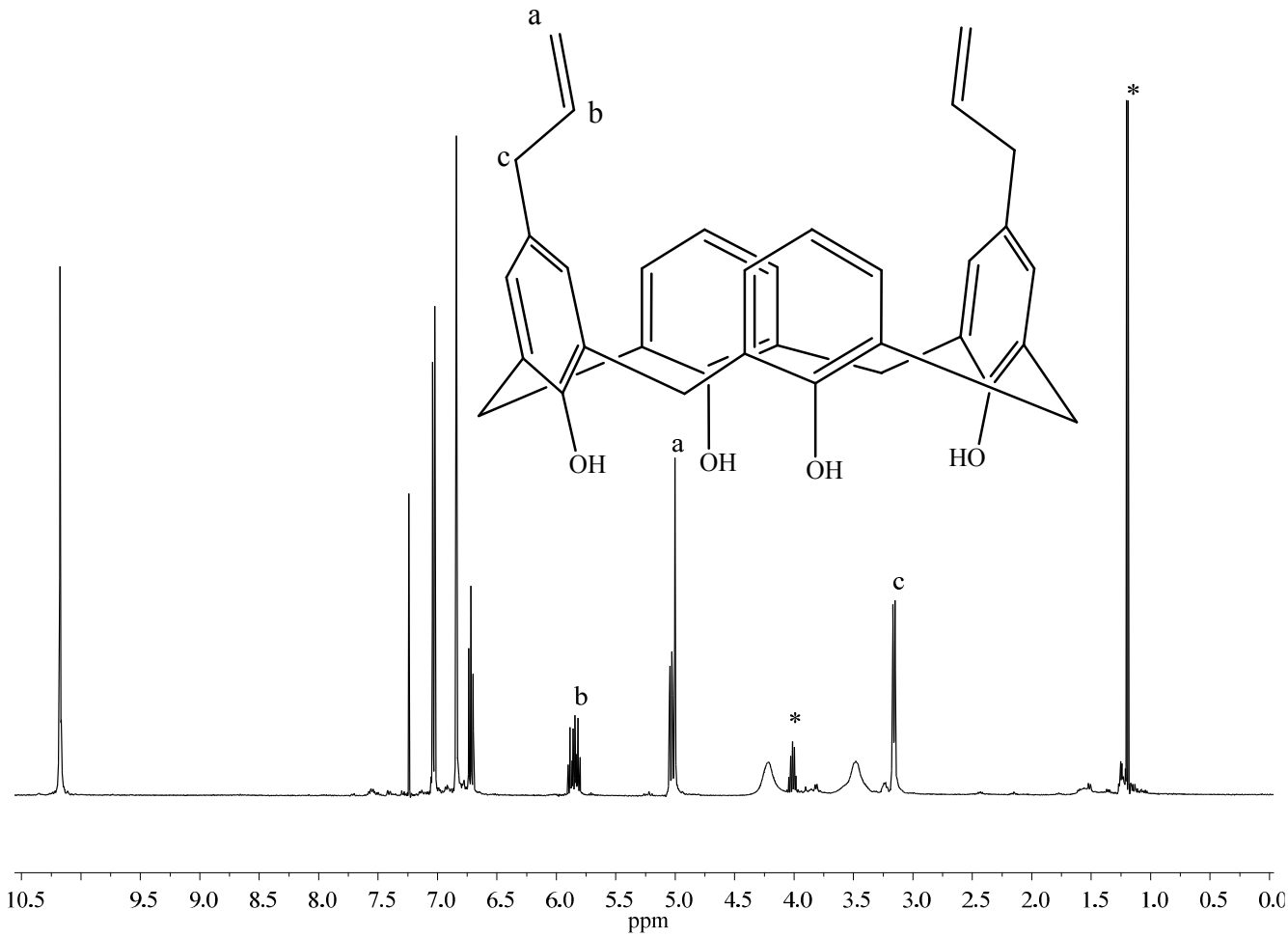
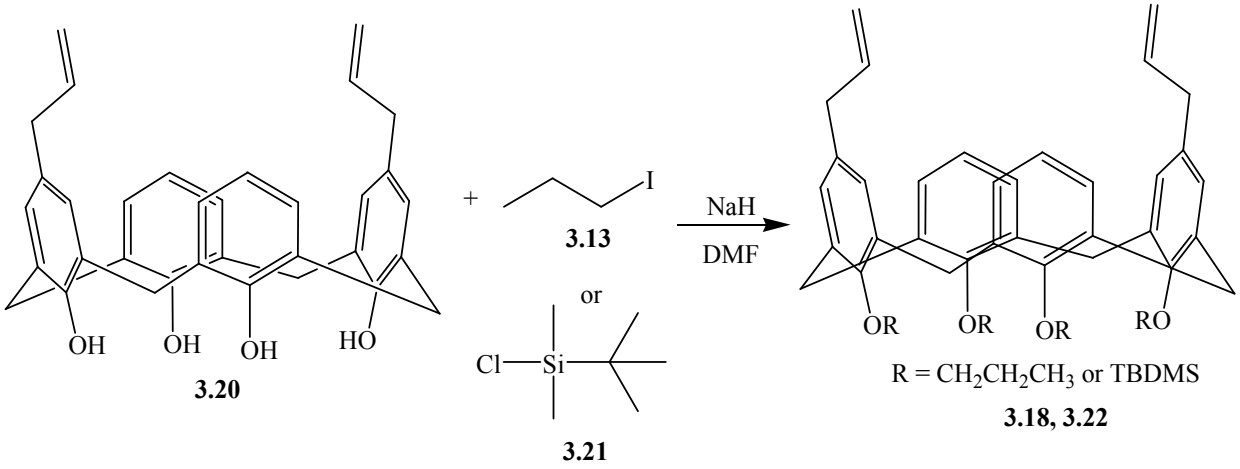


Figure 3-26: 400 MHz ^{1}H NMR spectrum of 3.20 *denote 2-propanol.

Since further reactions on the upper rim of the calix[4]arene will occur through reaction with alcohols it is necessary to protect the phenolic groups to prevent side reactions. Two methods for the protection of the lower rim were utilized: a) using iodopropane and b) using *t*-butyl dimethylchlorosilane (TBDMS) (Scheme 3-14). Figure 3-27 shows the ^{1}H NMR spectrum of the propane capped calix[4]arene (**3.18**); the incorporation of the propane groups is shown by the two triplets centred at 1.04 ppm and 0.95 ppm corresponding to the terminal methyl groups, the multiplet between 2.02 – 1.81 ppm corresponding to the centre methylene, and the two triplets at 3.90 ppm and 3.78 ppm for the etheric methylene. The difference in the proton resonances for the different propoxy groups is due to the electronic effects caused by the presence of the functionalization of the upper rim. Later in this chapter 2-dimensional NMR

(gCOSY, gHSQC, and gHMBC) will be used to determine which resonances are due to which propoxy group. This reaction gave **3.18** in the cone conformation as can be seen by the two doublets at 4.43 ppm and 3.12 ppm.



Scheme 3-14: Synthesis of calix[4]arenes 3.18 and 3.22.

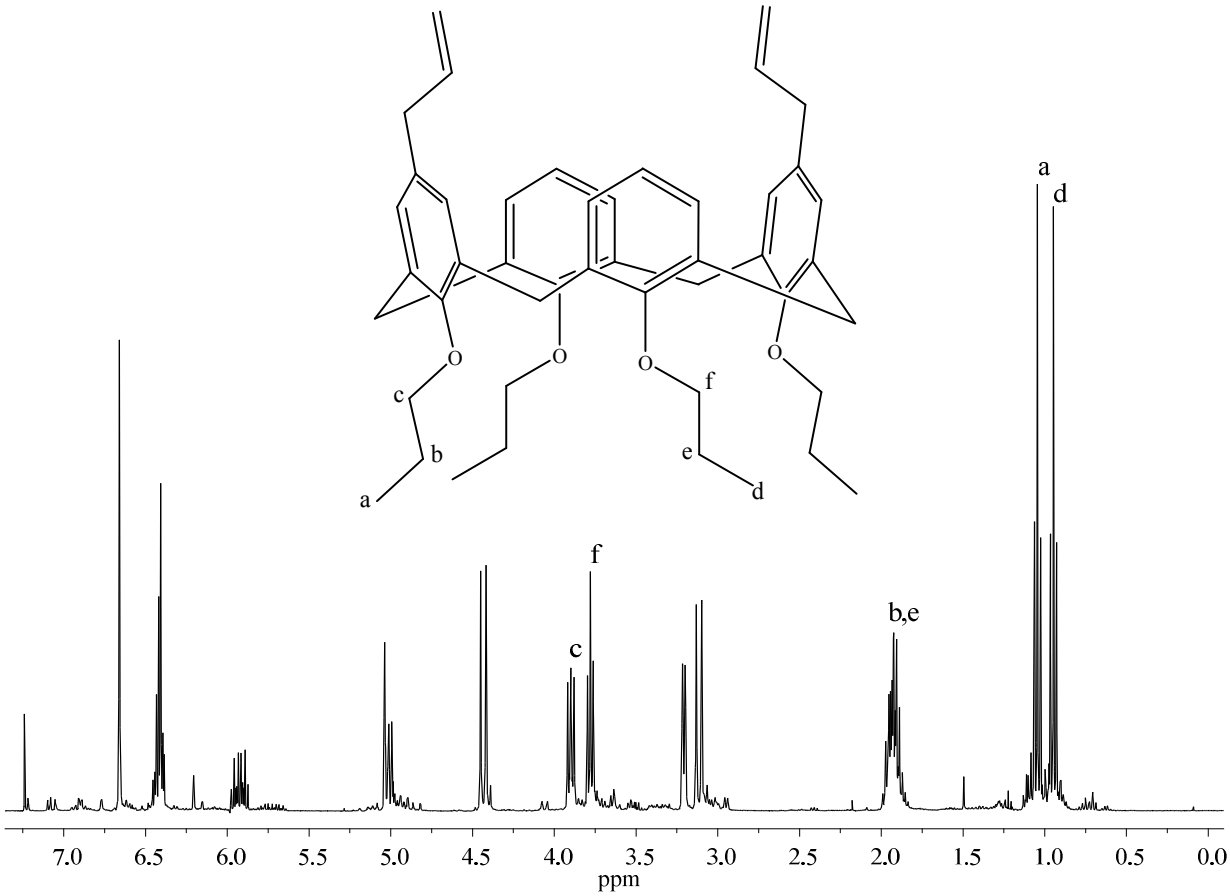
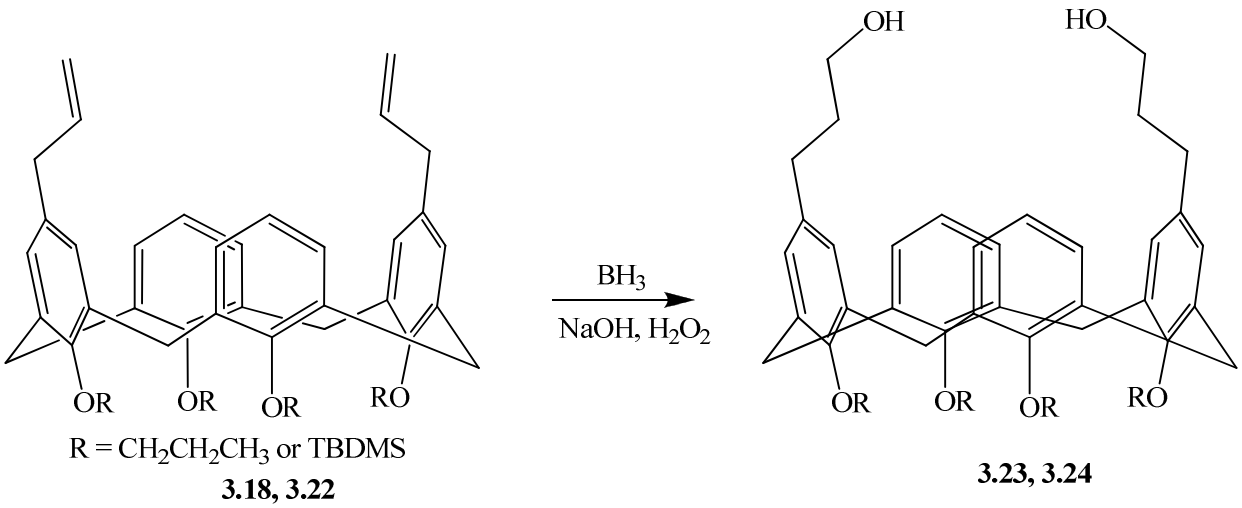


Figure 3-27: 400 MHz ^{1}H NMR spectrum of 3.18.

The silyl protected calix[4]arene (**3.22**) was also obtained. However, it was isolated in a mixture of conformers and as such the NMR analysis can only qualitatively indicate successful synthesis with the appearance of the TBDMS groups between 1 ppm and 0 ppm as well as the loss of the phenol signals above 10 ppm.

To further build on the upper rim of the calix[4]arenes the allylic group underwent hydroboration via reaction with BH_3 and $NaOH/H_2O_2$ to give calix[4]arene containing two propanol groups on their upper rims (**23** and **24**) (Scheme 3-15).



Scheme 3-15: Synthesis of calix[4]arenes 3.23 and 3.24.

The success of this reaction was determined through NMR spectroscopy. The ^{1}H NMR spectrum for the propoxy protected calix[4]arene (**3.23**) is shown in Figure 3-28. It can be seen that the resonances due to the allylic group have shifted from 5.93 – 5.76 ppm, 5.06 – 4.99 ppm, and 3.16 ppm to 3.57 ppm (a), 2.34 ppm (b), and 1.64 ppm (c). These resonances are characteristic of benzyl alkyl alcohols.

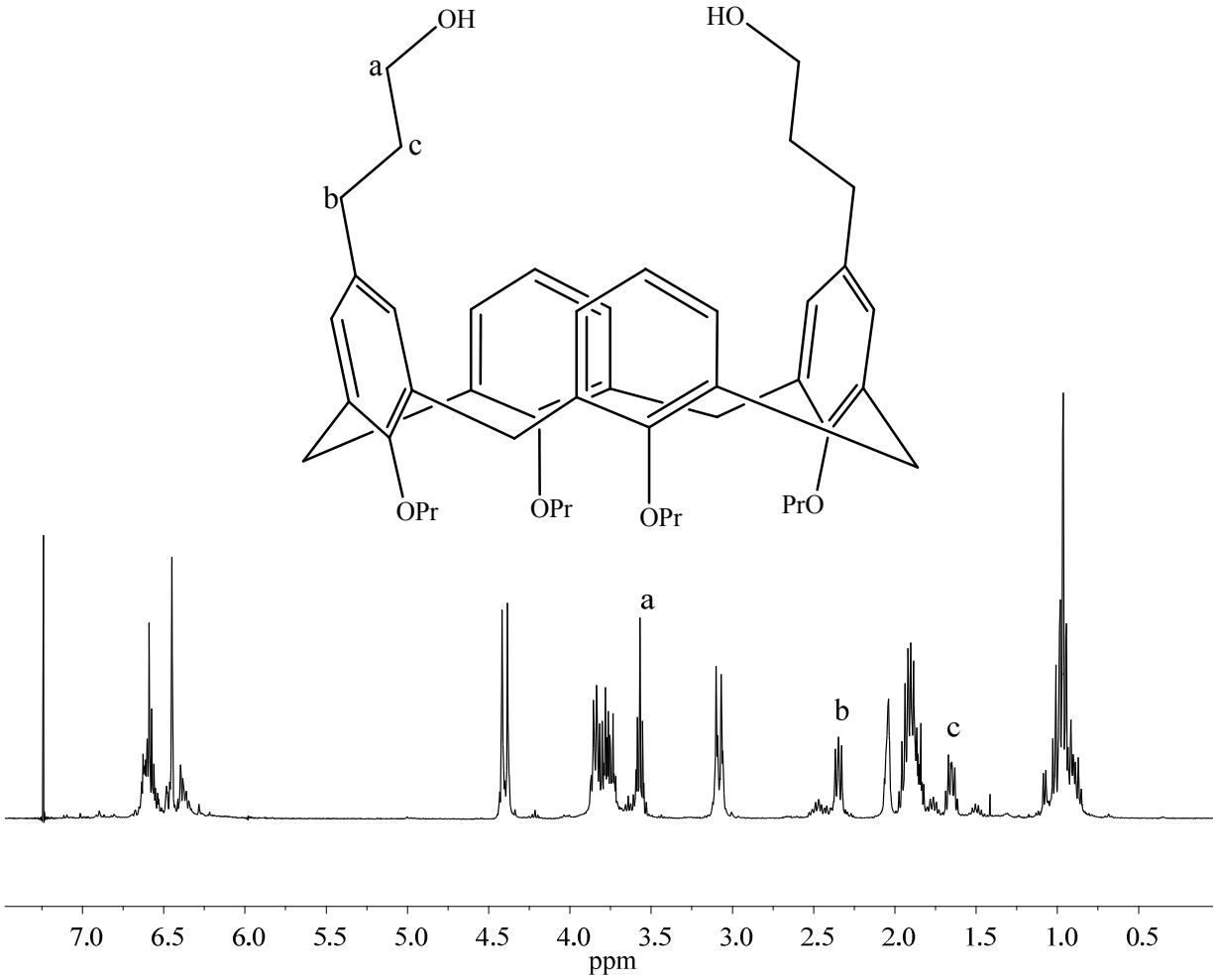


Figure 3-28: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.23.

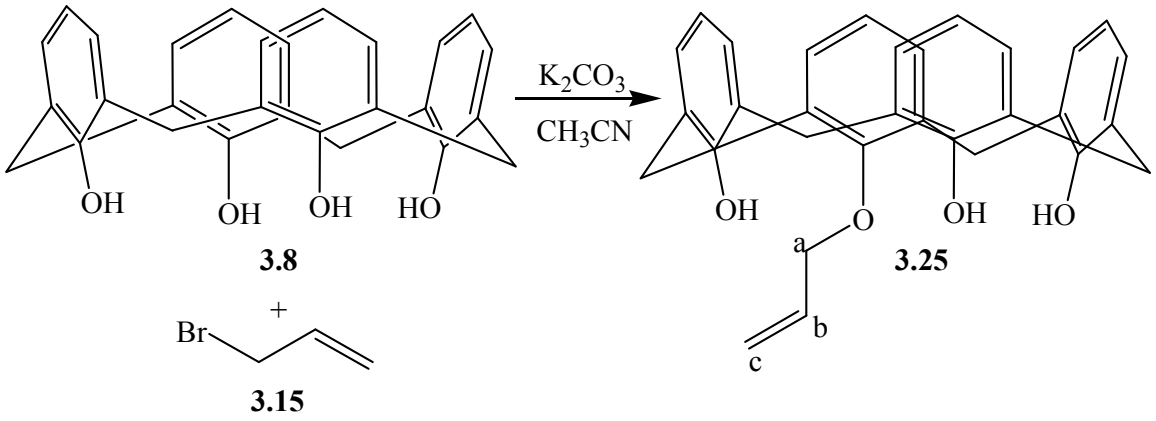
The TBDMS protected calix[4]arene (**3.24**) showed similar shifts from the alkyl to the propanol group.

Calix[4]arenes (**3.23** and **3.24**) possess terminal alcoholic groups on their upper rims that allow for further functionalization to prepare calix[4]arene containing materials. To prepare a large range of materials, calix[4]arenes containing only one upper rim functionalized phenyl ring were also prepared.

3.2.1.2 Mono-substituted calix[4]arenes

Calix[4]arenes **3.25** and **3.26** have previously been reported,[85] however these syntheses are three and five step reactions. Our synthesis prepares these calix[4]arenes in one

and two steps respectively, and is, to the best of our knowledge, the first time this method has been reported for these compounds. Similar to the synthesis of the upper rim disubstituted calix[4]arenes, the synthesis of mono-substituted calix[4]arenes is based on the initial control of pH during the substitution of the lower rim. When the molar equivalence of K_2CO_3 is reduced from 1 to 0.5 in the reaction between calix[4]arene **3.8** and allyl bromide results in the formation of 25-allyloxy-26,27,28-trihydroxy-calix[4]arene **3.25** (Scheme 3-16).



Scheme 3-16: Synthesis of calix[4]arene 3.25.

The incorporation of the allylic group was confirmed through ^{1}H NMR spectroscopy (Figure 3-29). In the ^{1}H NMR spectrum the methylene group (a) appears as a doublet of triplets centred at 4.68 ppm (major) and 4.54 ppm (minor). The CH of the allylic group (c) appears as 2 pairs of doublets of quartets centred at 5.67 ppm and 5.52 ppm (major) and 5.77 ppm and 5.41 ppm (minor). The CH_2 of the allylic group (b) appears as a multiplet centred at 6.43 ppm (major) and 6.25 ppm (minor). Integrations of all resonances confirmed mono-substitution.

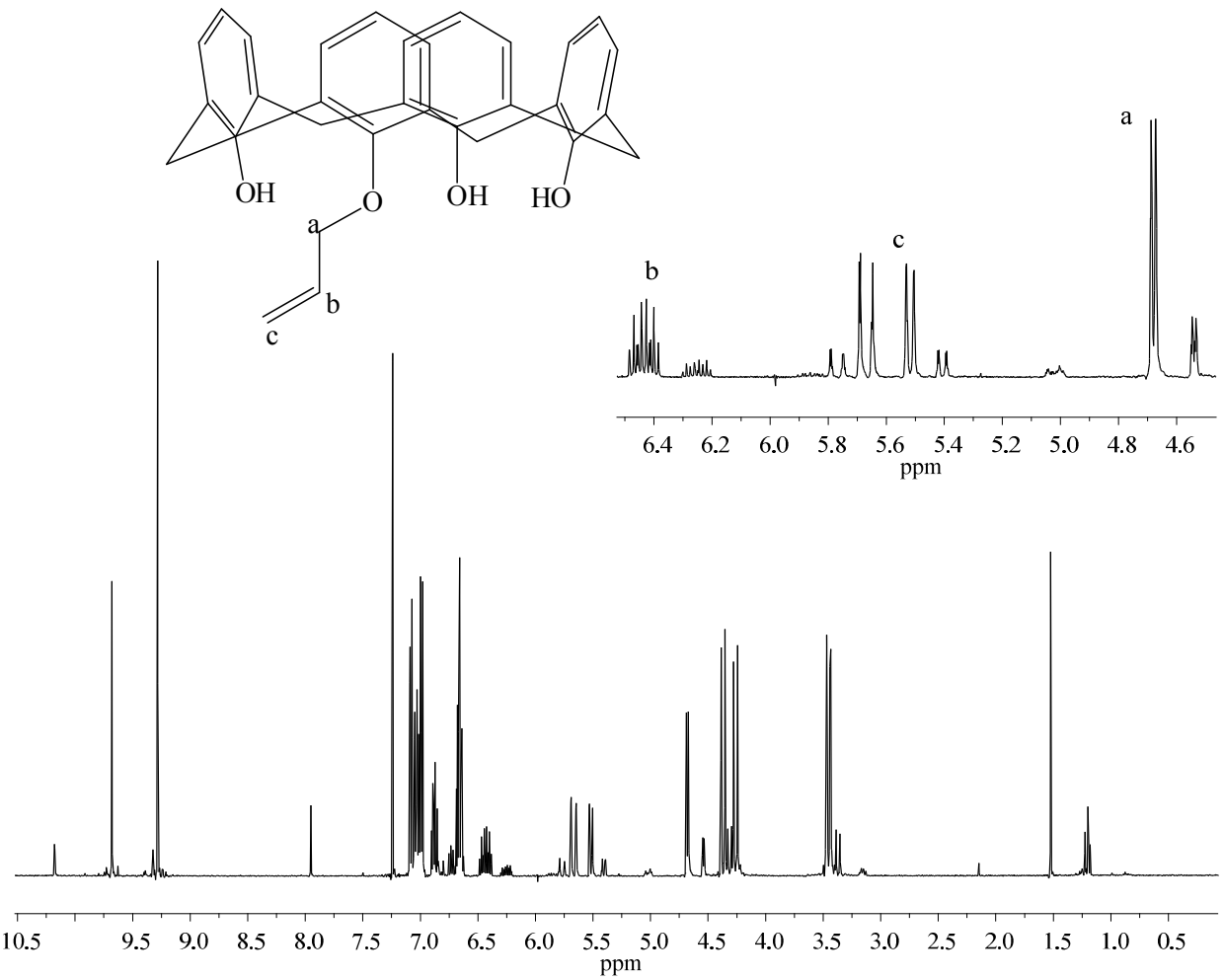
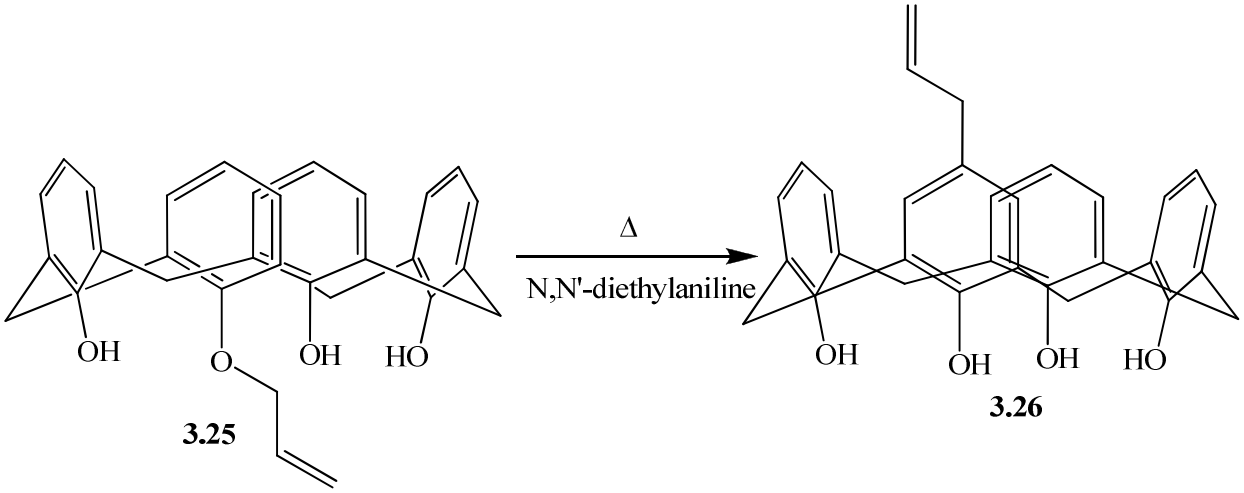


Figure 3-29: 400 MHz ^{1}H NMR spectrum of 3.25.

Unlike the di-allyl-substituted calix[4]arene (**3.19**), the monoallylic calix[4]arene (**3.25**) is not isolated exclusively in the cone conformation. This calix[4]arene (**3.25**) is isolated as a mixture of the partial cone (major) and cone (minor) conformations as determined by the two pairs of doublets (partial) of the bridging methylenes in the ^{1}H NMR spectrum at 4.37 ppm, 4.26 ppm and 3.47 ppm and 3.44 ppm and the pair of doublets for the cone conformation at 4.31 ppm and 3.37 ppm. While the partial cone is not optimal for applications of calix[4]arenes, we anticipated that the cone conformation would re-establish after the p-Claisen rearrangement due to the intramolecular hydrogen bonding of the lower rim.

Refluxing calix[4]arene (**3.25**) in N,N-diethylaniline afforded the upper rim functionalized calix[4]arene (**3.26**) (Scheme 3-17).



Scheme 3-17: Synthesis of calix[4]arene 3.26.

The success of the p-Claisen rearrangement is confirmed by the shift of the allylic group resonances in the ^{1}H NMR spectrum (Figure 3-30). The etheric methylene has shifted to a doublet centred at 3.16 ppm, the CH has shifted to between 5.93 – 5.77 ppm and the CH_2 has moved to between 5.06 – 4.98 ppm. As shown in Figure 3-30, calix[4]arene **3.26** was isolated in the cone conformation by the presence of the two broad resonances at 4.23 ppm and 3.49 ppm.

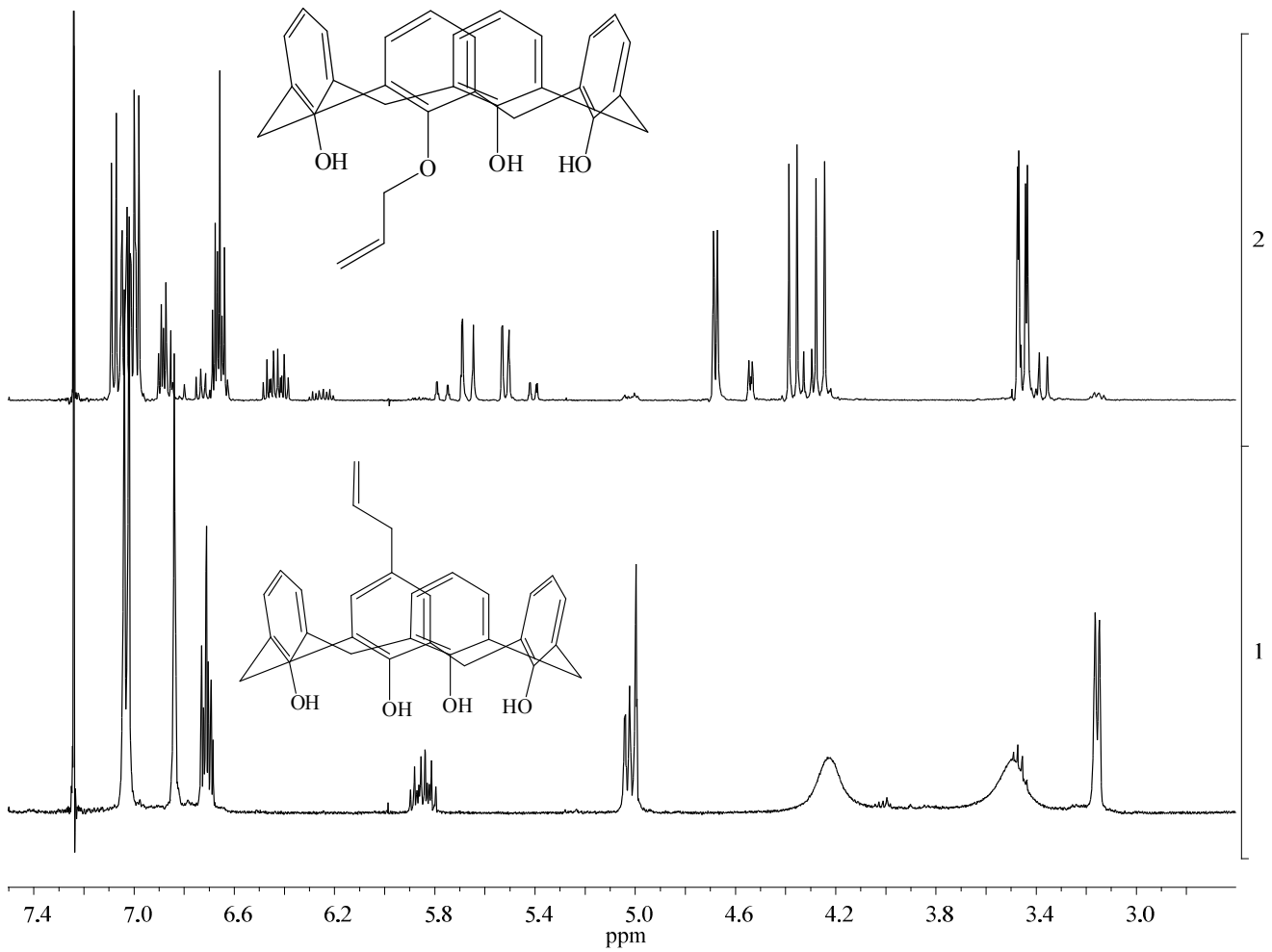
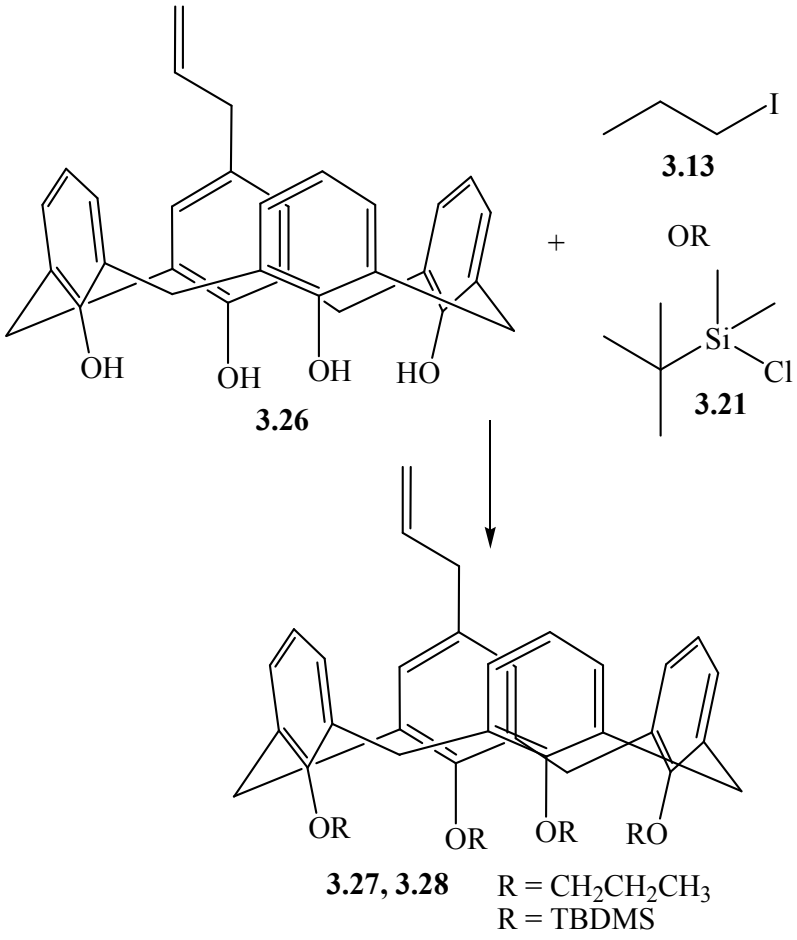


Figure 3-30: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.26 (1) and calix[4]arene 3.25 (2).

Calix[4]arene **3.26** was further reacted with iodo-propane or *tert*-butyl-dimethyl chlorosilane (TBDMS-Cl) to protect the lower rim of the calix[4]arene (Scheme 3-18). These reactions gave calix[4]arenes **3.27** and **3.28** as a mixture of conformers. The ^{1}H NMR spectrum of calix[4]arene **3.38** possessing four terminal TBDMS groups showed resonances similar to calix[4]arene (**3.26**) with the addition of the TBDMS resonances at 0.87 ppm for the *tert*-butyl group and 0.1 ppm for the methyl groups attached to the silicon.



Scheme 3-18: Synthesis of calix[4]arenes 3.27 and 3.28.

The propoxy protected calix[4]arene (**3.27**) was obtained as a mixture of partial cone and cone conformations as shown in the ^{1}H NMR spectrum (Figure 3-31) by the presence of the multiplets resonating between 4.46 – 4.39 ppm and 3.29 – 2.90 ppm. The incorporation of the propoxy groups are also confirmed by the peaks resonating between 4.00 – 3.70 ppm, 2.00 – 1.77 ppm, 1.38 – 1.12 ppm and 0.97 ppm for the OCH_2, CH_2 and CH_3 respectively. The extra resonances in the spectrum for compound (**3.27**) can be attributed to the different conformers.

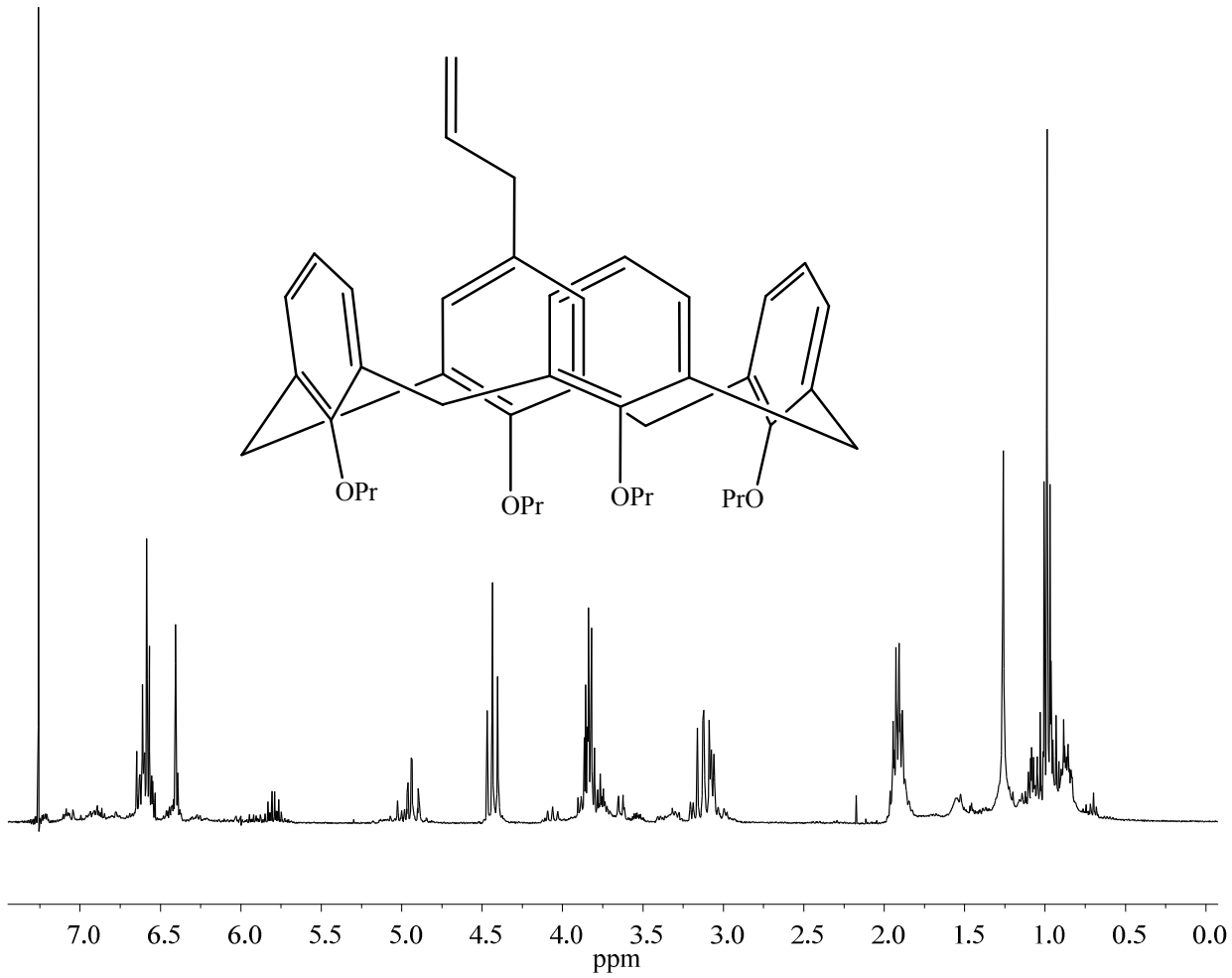
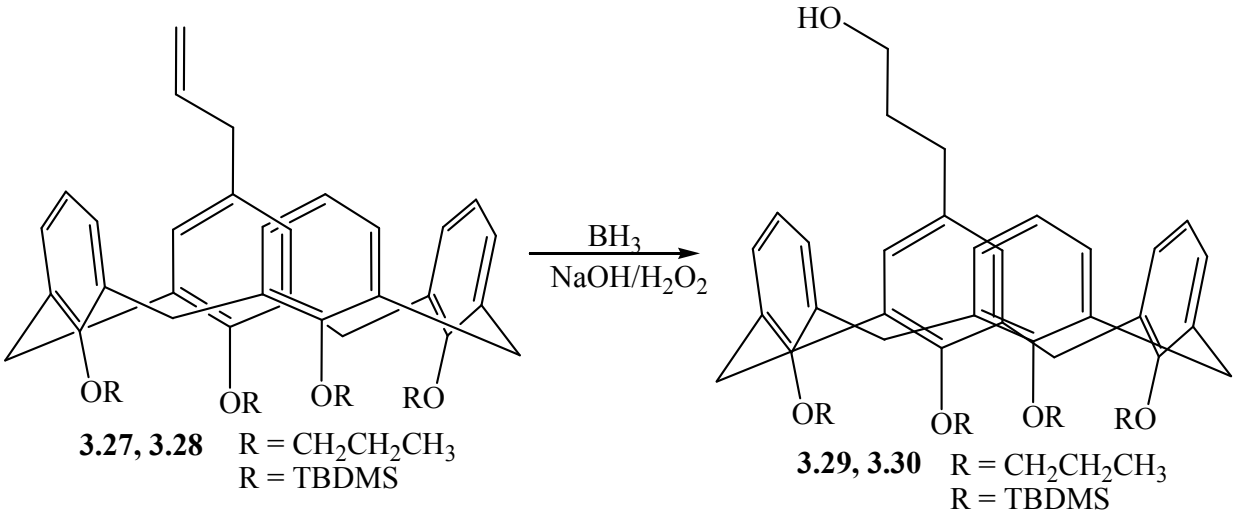


Figure 3-31: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.27.

Protection of the lower rim of the calix[4]arenes allows for the further functionalization of the upper rim. Calix[4]arenes **3.27** and **3.28** were reacted with a 1M THF solution of BH_3 followed by addition of NaOH and H_2O_2 to produce propanol containing calix[4]arenes **3.29** and **3.30** (Scheme 3-19).



Scheme 3-19: Synthesis of calix[4]arenes 3.29 and 3.30.

The ^{1}H NMR spectrum of the propoxy protected calix[4]arene **3.29** (Figure 3-32) indicated complete oxidation of the allylic group due to the disappearance of the resonances due to the allylic group and the appearance of the resonances due to the propanol group at 3.46 ppm, 2.37 – 2.32 ppm, and 1.66 - 157 ppm corresponding to the CH_2OH, benzyl CH_2, and the $–CH_2–$ respectively.

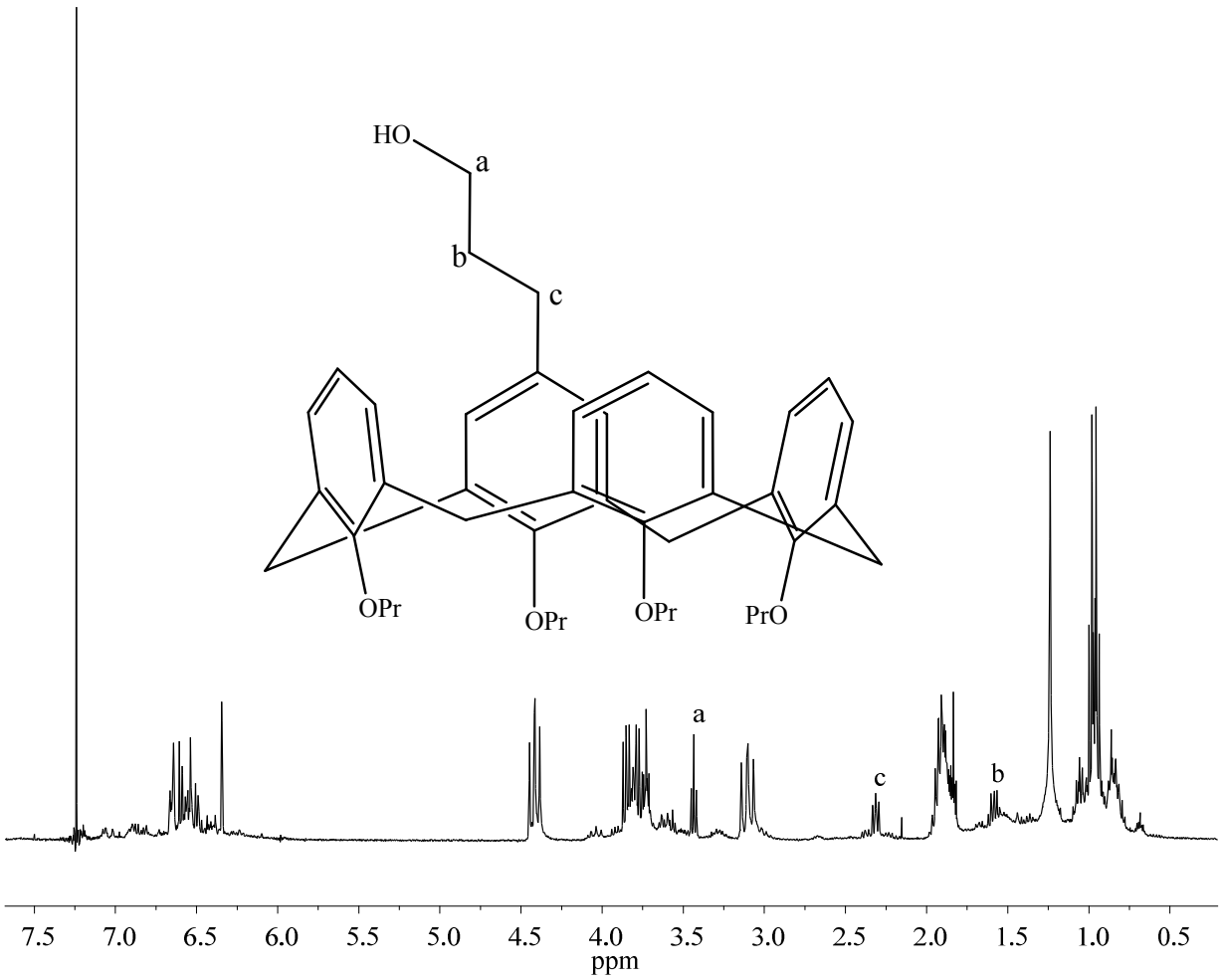


Figure 3-32: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.29.

The TBDMS protected calix[4]arene (**3.30**) also showed successful synthesis by the loss of the peaks due to the allylic group and the appearance of the peaks due to the propanol group. The full assignment of all the resonances of the TBDMS protected calix[4]arene is difficult due to the presence of many conformers. It can be seen that in the ^{1}H NMR spectrum of calix[4]arene (**3. 30**) (Figure 3-33) there are several resonances due to each proton in the propanol chain due to the different conformers.

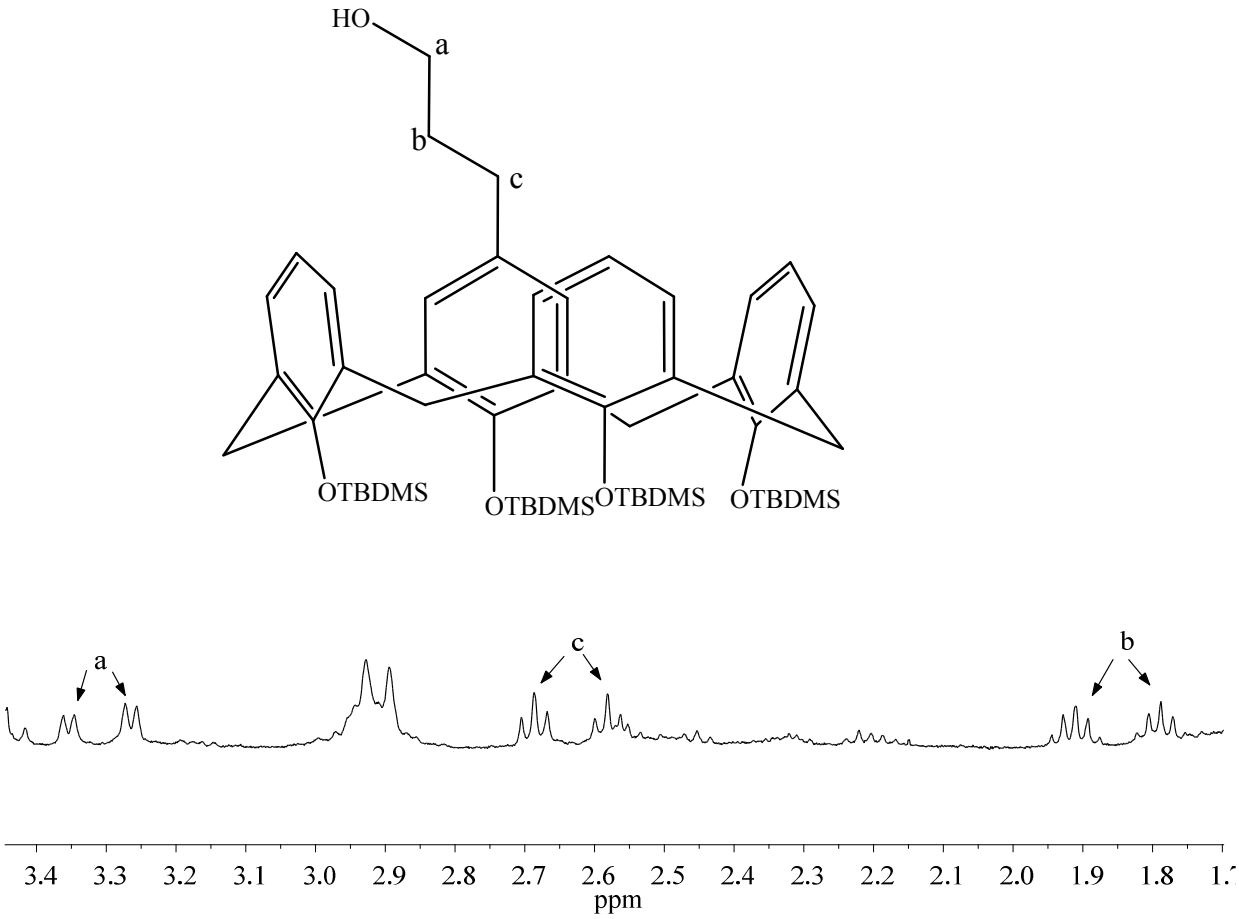


Figure 3-33: Expansion of the 400 MHz ^{1}H NMR resonances of the propanol group resonances on calix[4]arene 3.30.

The presence of the alcohol on the upper rim of calix[4]arenes **3.29** and **3.30** allowed the further functionalization of the calix[4]arene. These functionalizations as well as the functionalization of the disubstituted calix[4]arenes (**3.23** and **3.24**) will be the focus of the rest of this chapter. The functionalization of these calix[4]arenes will provide new organic and organometallic compounds and complexes and new polymeric materials.

*NOTE: 5-propanol-25,26,27,28-tetrahydroxycalix[4]arene (**3.31**) was prepared directly from reacting 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene. As will be discussed later in this chapter, the further functionalization of this complex did not work due to side

reactions with the lower rim of the calix[4]arene.

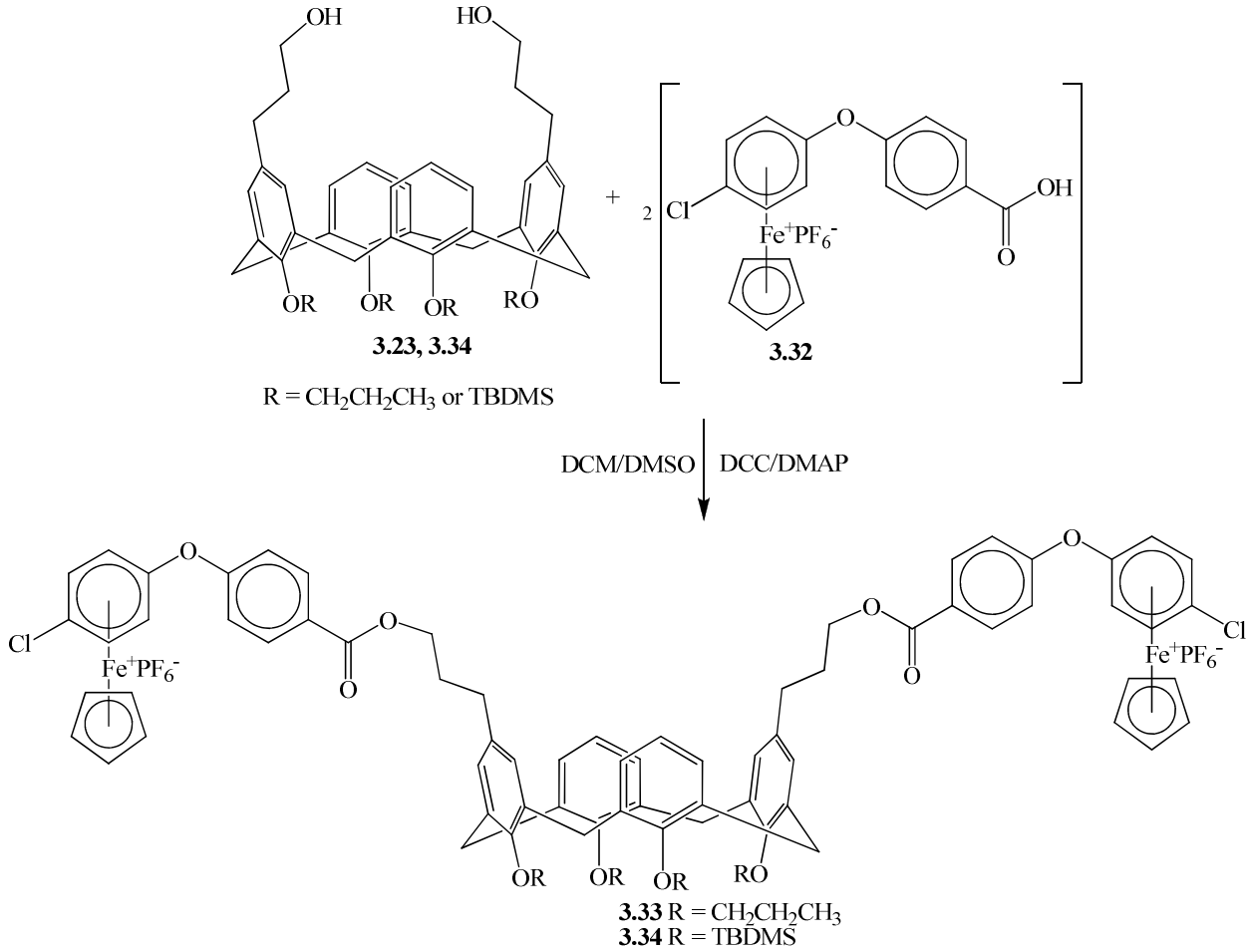
3.2.2 Cationic organoiron containing calix[4]arenes

Arene-coordinated cyclopentadienyliron complexes readily undergo nucleophilic aromatic substitution reactions under mild conditions. The incorporation of these types of organoiron complexes into calix[4]arene frameworks should allow for a versatile method for producing functionalized metallocalix[4]arenes. This section will discuss the synthesis and characterization of organoiron metallocalix[4]arenes.

The preparation of metallocalix[4]arenes based on η^6–dichlorobenzene–η^5–cyclopentadienyliron is interesting as the presence of the terminal chloro groups on the organoiron complex should allow for nucleophilic aromatic substitution reaction to further functionalize the prepared calix[4]arenes. The availability of the alcohol groups on previously discussed calix[4]arenes (**3.23 – 3.30**) allows for the addition of cationic organoiron groups to the calix[4]arene.

3.2.2.1 Metallocalix[4]arenes based on di-upper rim functionalized calix[4]arenes

The reaction of the carboxylic acid-containing organoiron acid complex (**3.32**) with calix[4]arenes (**3.23** and **3.24**) in the presence of DCC/DMAP gives the organoiron calix[4]arene complexes (**3.33 – 3.34**) possessing two metal moieties (Scheme 3-20).



Scheme 3-20: Synthesis of calix[4]arenes 3.33 and 3.34.

The ^{1}H NMR, ^{13}C NMR, COSY and HMBC spectra of complex **3.33** are shown in figures 3-32 – 3-36. The ^{1}H NMR spectrum of complex 3.33 shows the incorporation of the organoiron complex by the two doublets at 8.20 ppm and 7.47 ppm due to the non-complexed aromatics, the two doublets at 6.87 ppm and 6.63 ppm due to the complexed aromatics as well as the singlet due to the cyclopentadienyliron moiety at 5.37 ppm. The calix[4]arene aromatics resonate at 6.72 ppm, 6.47 ppm, and 6.40 ppm. The upper rim propanoate groups resonate at 4.29 ppm, 2.60 ppm and 1.96 ppm. The lower rim propoxy groups appear as two sets of peaks due to the same reason as the aromatics, they resonate at 3.91 ppm, 1.98 ppm and 0.99 ppm which are due to the propoxy groups attached to the arenes without propanoate groups; and 3.21

ppm, 1.98 ppm, and 1.06 ppm which are due to the propoxy groups attached to the arenes with propanoate. The formation of the ester is further indicated by the shift of the alcoholic CH_2 from 3.44 ppm to 4.29 ppm.

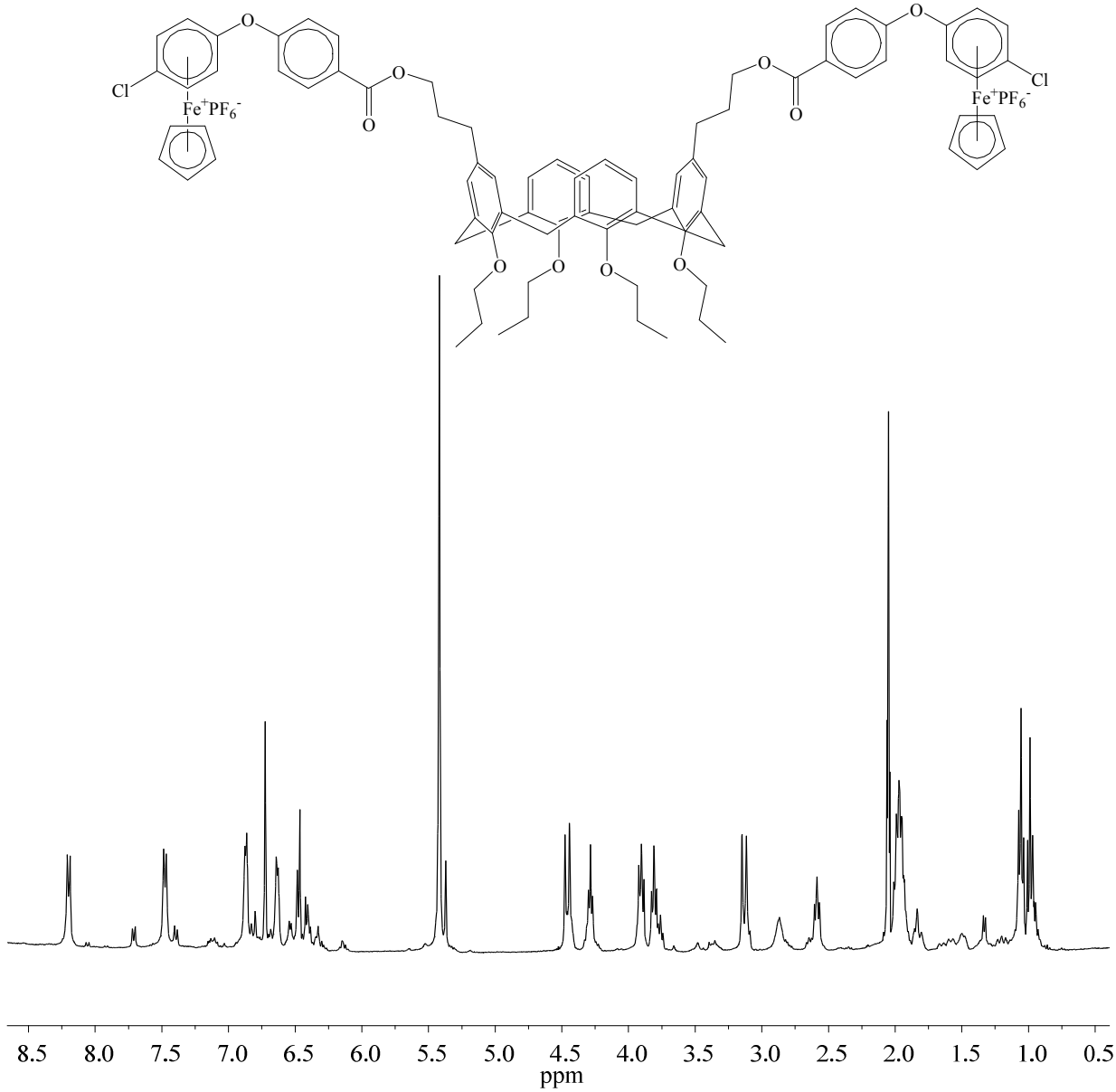


Figure 3-34: 400 MHz ^{1}H NMR spectrum of 3.33.

The proton assignments are supported by the COSY spectra (Figure 3-35). The proton resonances at 8.20 ppm and 7.47 ppm couple indicating they are within a ^{3}J relationship. The resonances at 6.87 ppm and 6.63 ppm also couple as an independent system with no coupling to

the downfield resonances indicating that they are independent systems. The bridging methylene peaks at 4.47 ppm and 3.14 ppm are also coupled. The resonance due to the upper rim propanate CH_2 at 4.29 ppm shows a coupling to the peak at 1.98 ppm which then couples into 2.60 ppm; and the lower rim propoxy groups show coupling between 0.99 ppm (1.06 ppm) and 1.98 ppm (1.96 ppm) which then couples to 3.91 ppm (3.82 ppm).

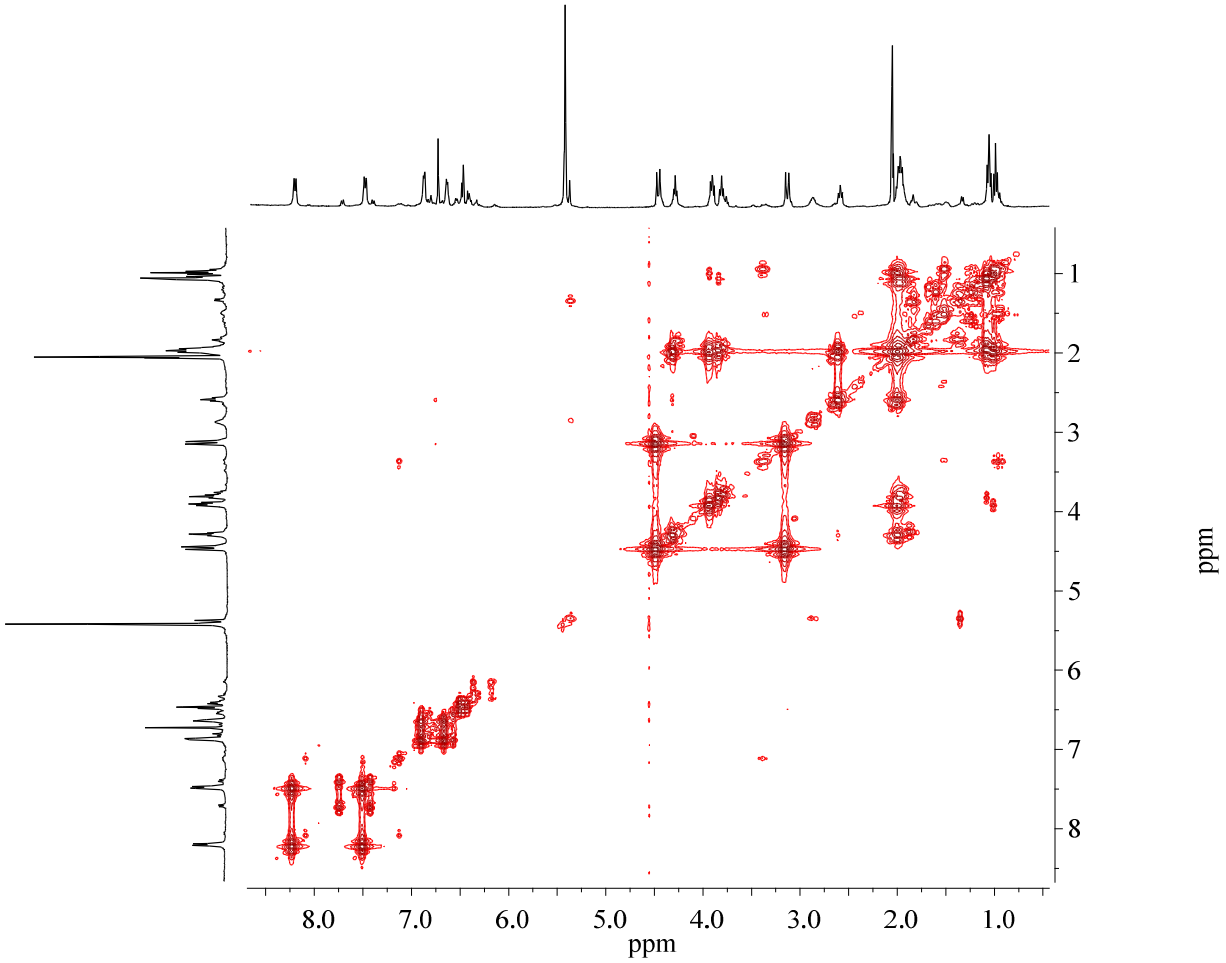


Figure 3-35: COSY spectrum of calix[4]arene 3.33.

The ^{13}C NMR spectrum (Figure 3-36) and the HSQC spectrum (Figure 3-37) further confirm the structure. The resonances in the ^{1}H NMR spectrum at 8.20 ppm and 7.47 ppm correlate to the ^{13}C NMR resonances at 133.15 ppm and 121.34 ppm, respectively. The complexed aromatics which appeared at 6.87 ppm and 6.63 ppm correlate to 88.19 ppm and

78.53 ppm in the ^{13}C NMR spectrum. The cyclopentadienyliron moiety at 5.42 ppm appears at 80.90 ppm. The calix[4]arene protons correlate to 129.34 ppm, 128.77 ppm, and 122.78 ppm. The bridging methylenes correlate to 31.43 and 31.41 ppm. The upper rim propanate groups appear at 65.26 ppm (4.29 ppm), 32.26 ppm (2.60 ppm), and 31.55 ppm (1.98 ppm). The lower rim propoxy groups which resonate (upper rim functionalized) appear at 77.57 ppm (3.82 ppm), 23.87 ppm (1.96 ppm), and 10.92 ppm (1.06 ppm); and other propoxy groups appear at 77.47 ppm (3.91 ppm), 23.75 ppm (1.98 ppm) and 10.6 (0.99 ppm).

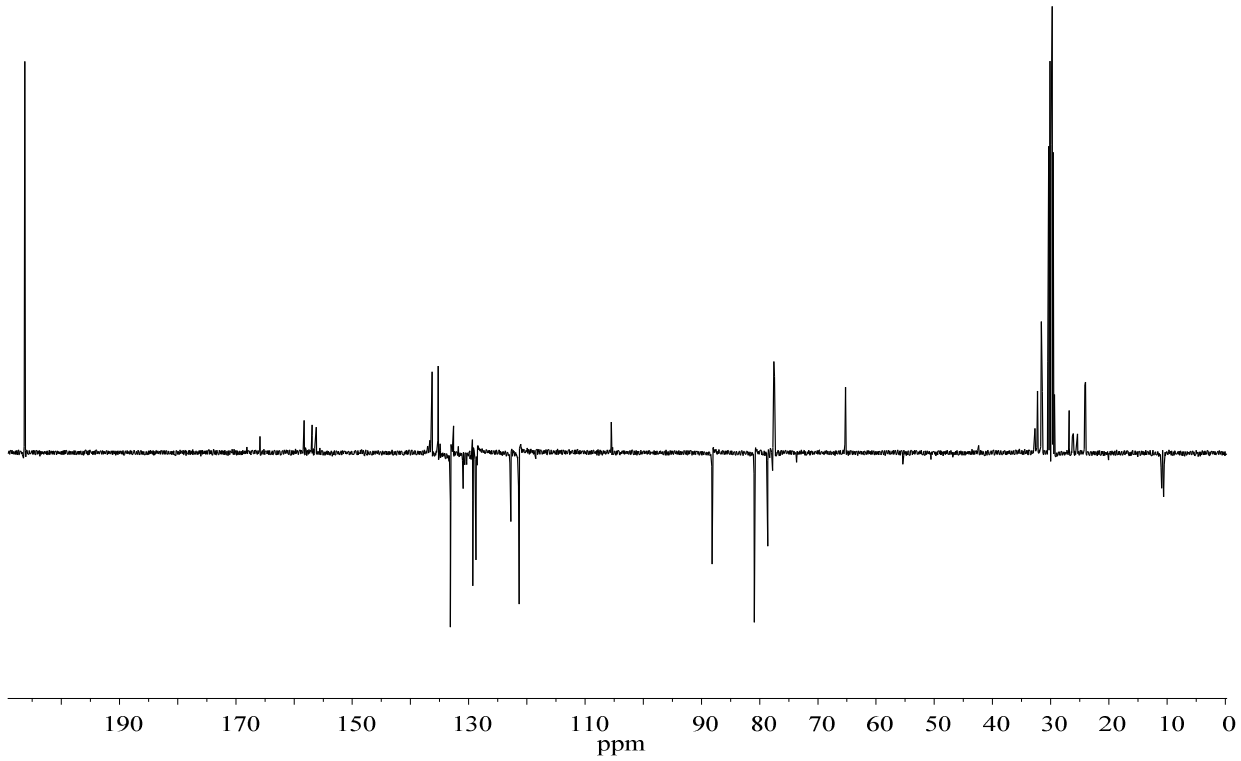


Figure 3-36: 101 MHz (APT) ^{13}C NMR spectrum of 3.33.

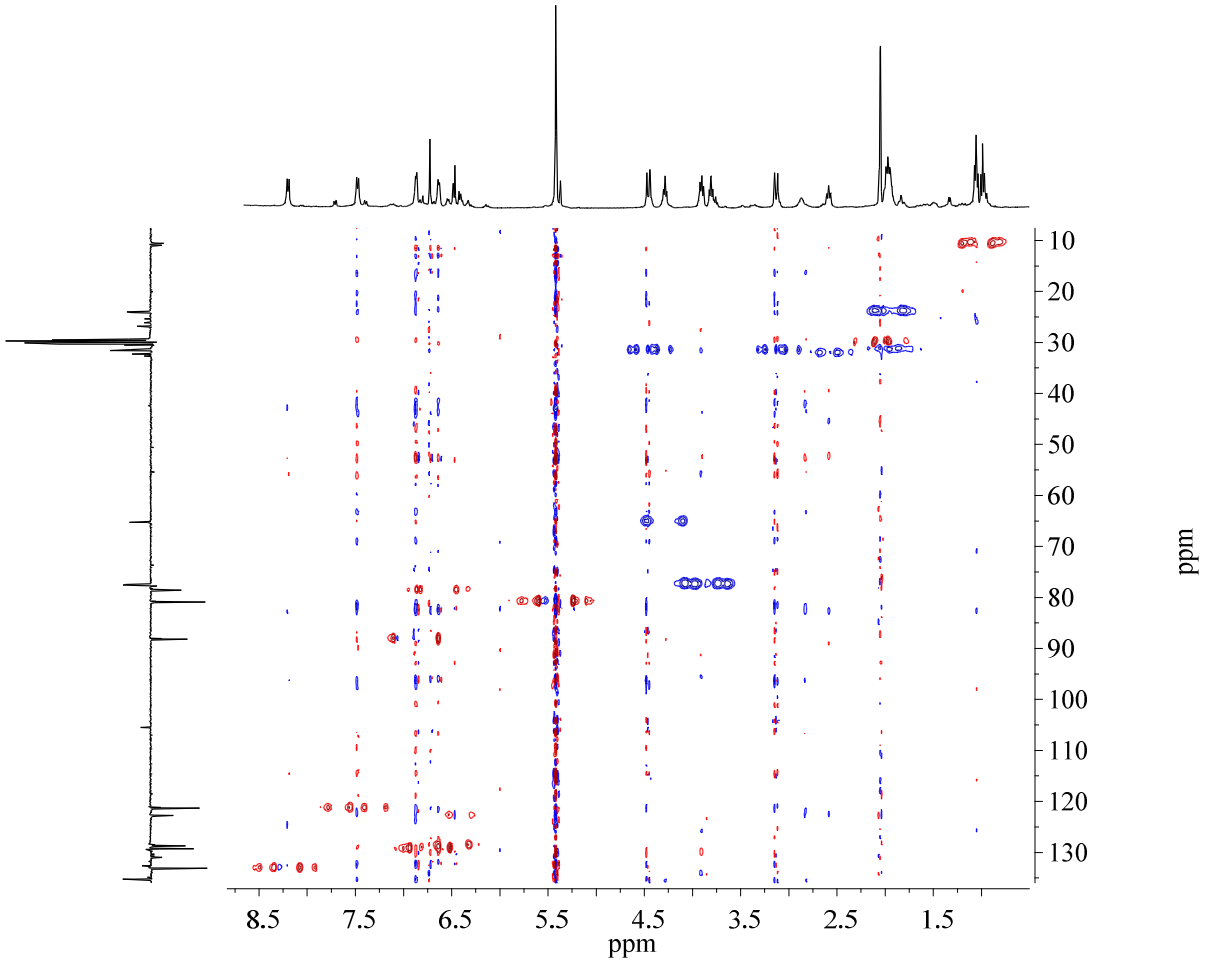


Figure 3-37: HSQC spectrum of calix[4]arene 3.33.

The HMBC spectrum (Figure 3-38) completely confirms the structure by showing connectively between the quaternary carbon resonance at 165.85 ppm due to the carbonyl and both the proton resonances at 8.20 ppm and 4.29 ppm. This proves that the non-complexed aromatic ring of the organometallic moiety and the upper rim CH_2 of the calix[4]arene are bound to the same carbonyl.

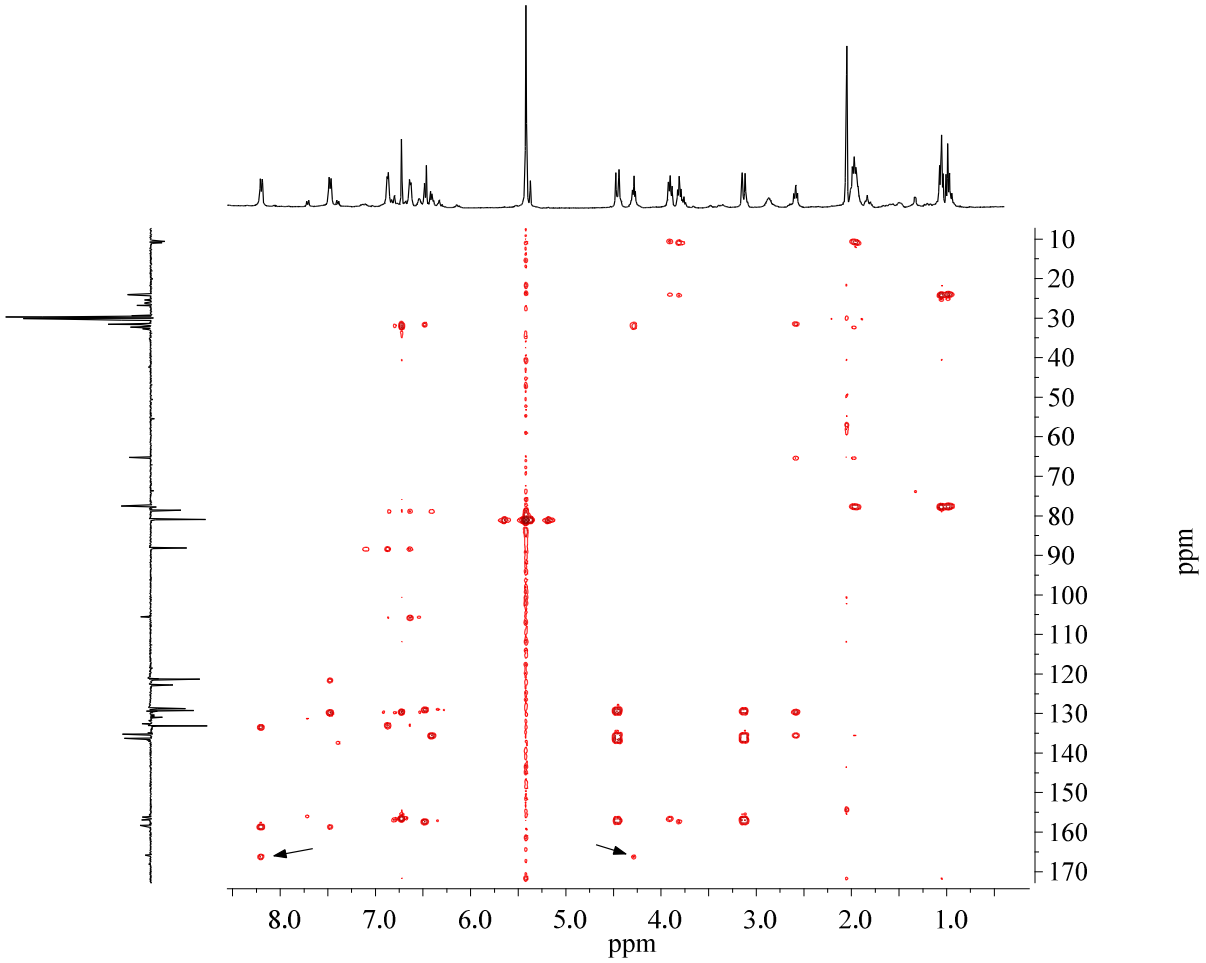
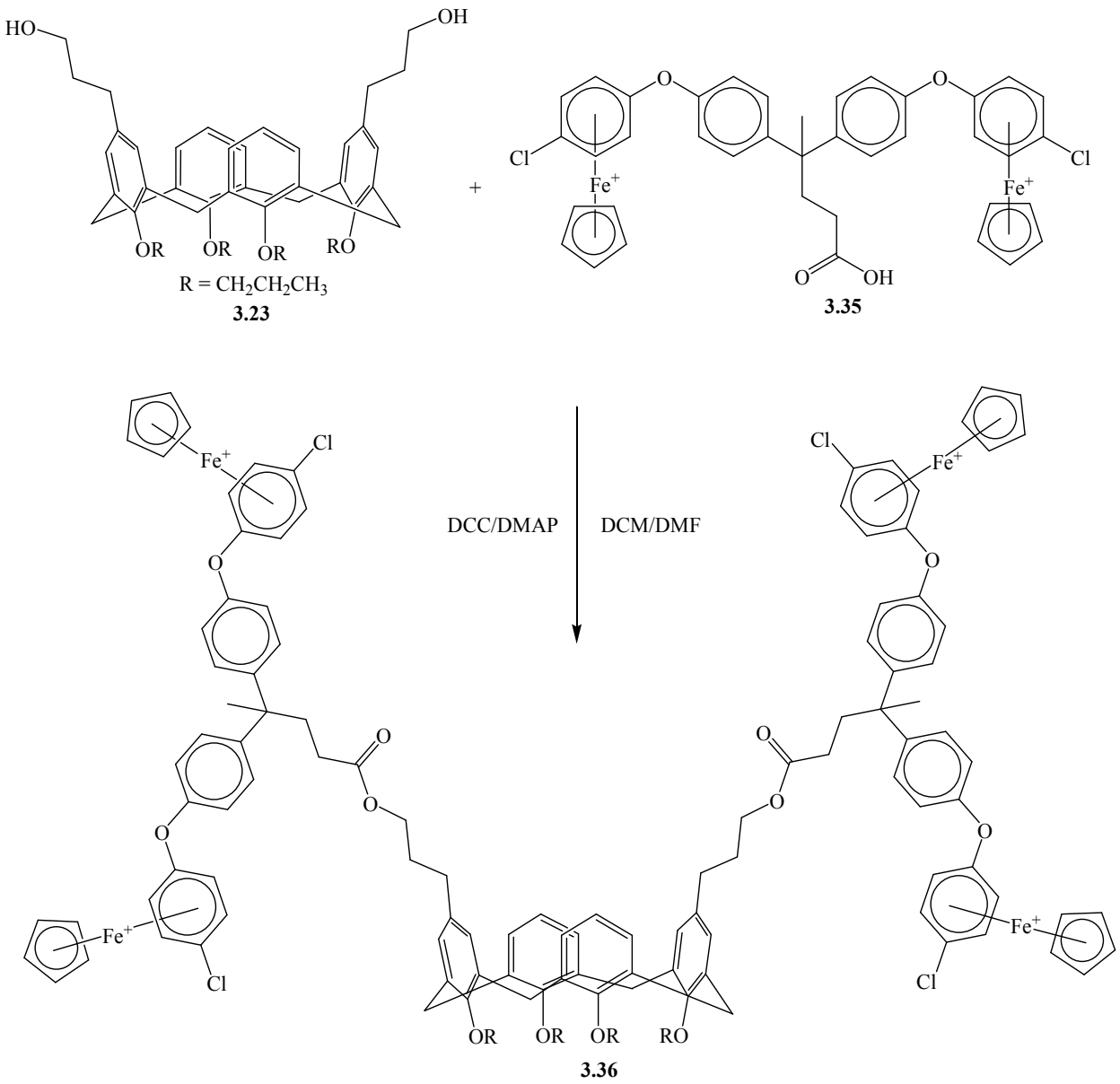


Figure 3-38: HMBC spectrum of calix[4]arene 3.33.

The reaction between the organoiron complex (**3.32**) with the TBDMS protected calix[4]arene also resulted in the formation of calix[4]arene **3.34** but to the large number of conformers made the analysis of the spectra very difficult.

The reaction of calix[4]arene **3.23** with the valeric bimetallic organoiron complex resulted in the formation of a tetra-metallic metallocalix[4]arene **3.36** (Scheme 3-21).



Scheme 3-21: Synthesis of calix[4]arene 3.36 .

Similarly to metallocalix[4]arene **3.33** and **3.34,** metallocalix[4]arene **3.36** was confirmed by the connectivity between the proton resonances of the organometallic moiety and the calix[4]arene moiety to the same quaternary carbon of the carboxylic acid carbonyl. In the HMBC spectrum of complex **3.36** (Figure 3-39), the success of the reaction was confirmed by the correlation between the resonances at 2.23 ppm and 4.01 ppm in the ^{1}H NMR and 174.11 ppm in the ^{13}C NMR spectrum which indicates the formation of the ester

group.

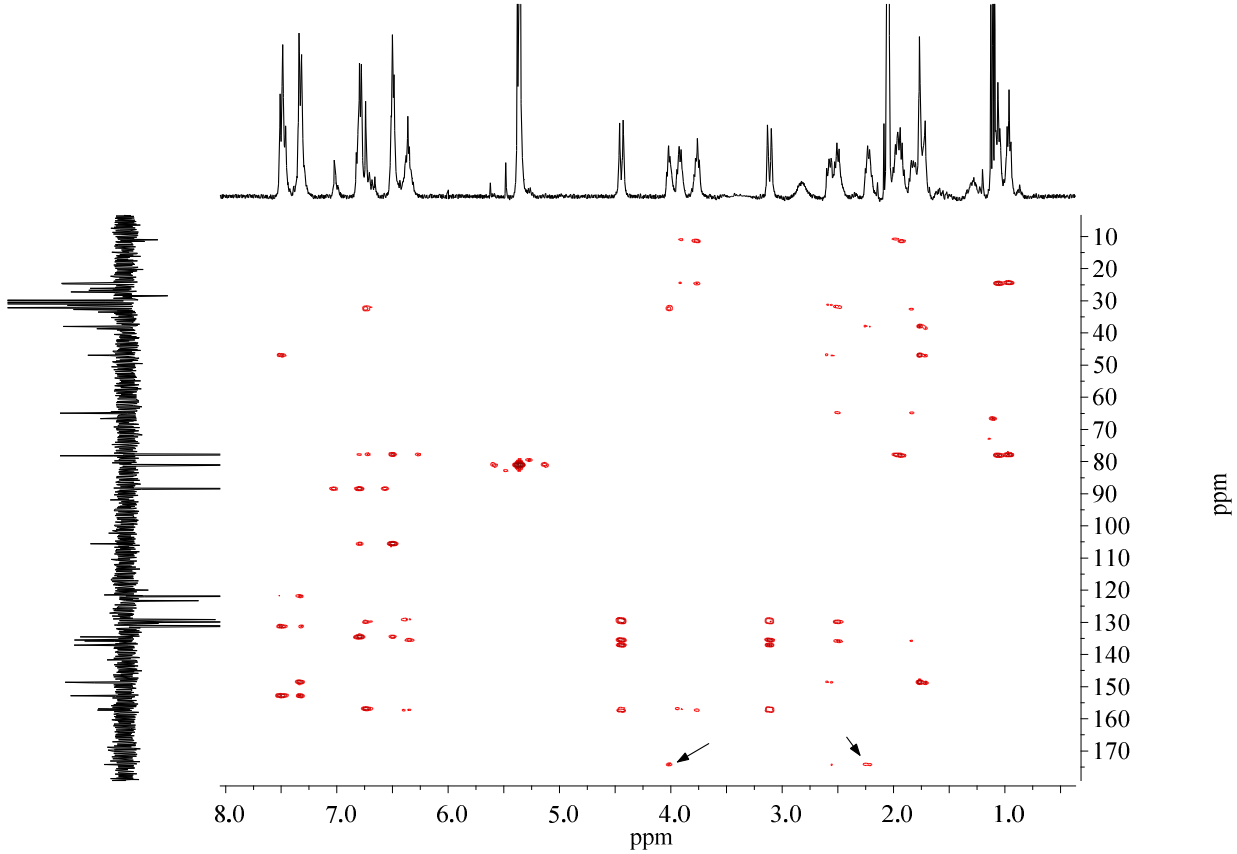
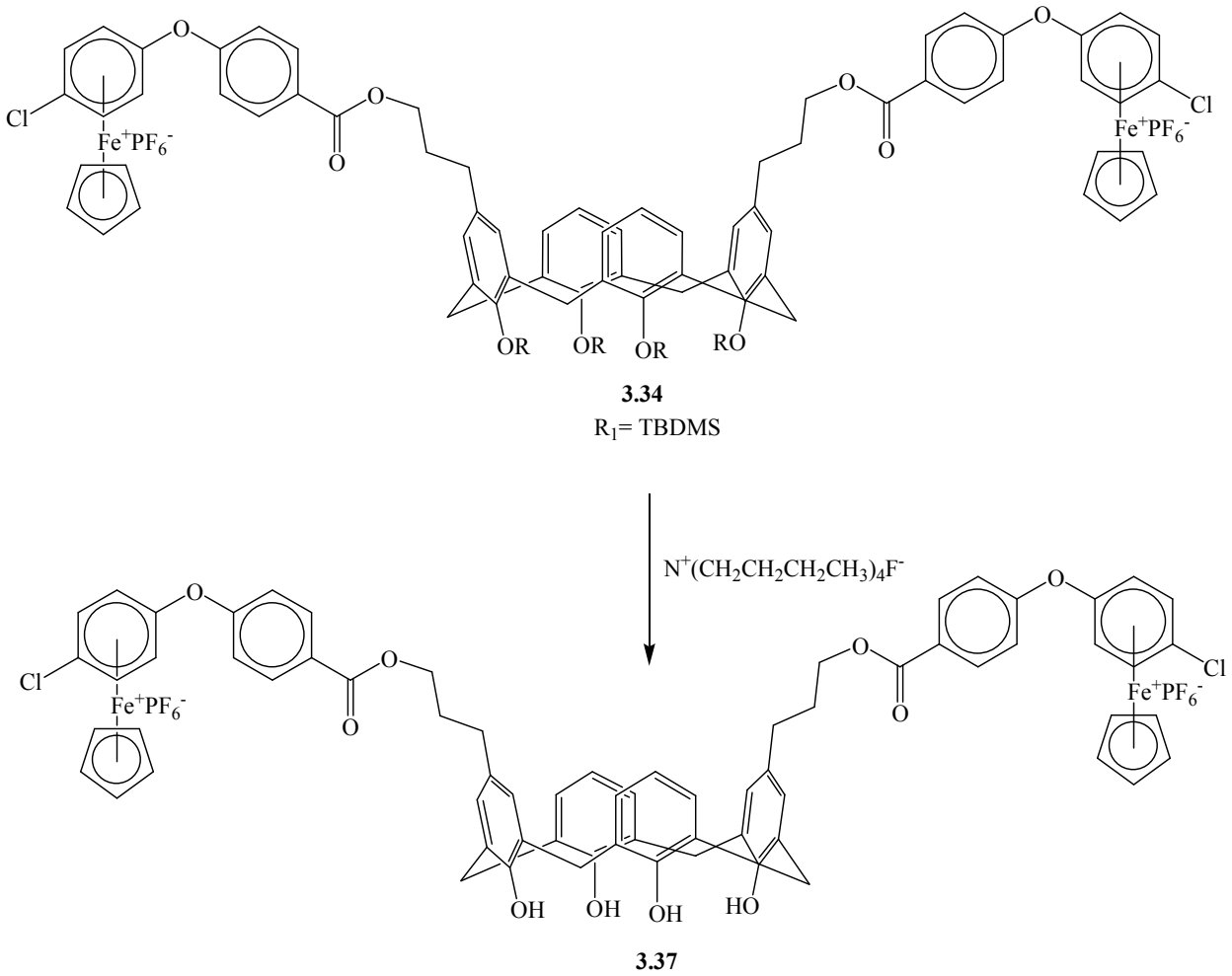


Figure 3-39: HMBC spectrum of calix[4]arene 3.36.

Calix[4]arene **3.34** possesses the TBDMS protecting group. This calix[4]arene was used to prepare metallocalix[4]arene **3.3.7** that possess OH groups on the lower rim. This was achieved by reacting calix[4]arene **3.34** with tetra-butylammonium fluoride (Scheme 3-22). The isolated calix[4]arene **3.37** was analyzed by ^{1}H NMR spectroscopy and shown to possess terminal phenolic groups by the resonance at 9.97 ppm. In addition, the calix[4]arene was obtained as one conformer in the cone conformation as determined by the appearance of defined peaks in the ^{1}H NMR spectrum. Unlike, the previously described calix[4]arenes containing four phenolic groups, the bridging methylenes in complex **3.37** overlapped to the point to become one

large broad signal at 3.90 ppm. However COSY NMR spectroscopy showed that there were in fact two distinct proton resonances under this signal, and the HSQC spectrum confirmed that these peaks were consistent with the carbon resonances of other calix[4]arene bridging methylenes. Figures 3-40 – 3.43 show the relevant spectra of complex **3.37**.



Scheme 3-22: Synthesis of calix[4]arene 3.37.

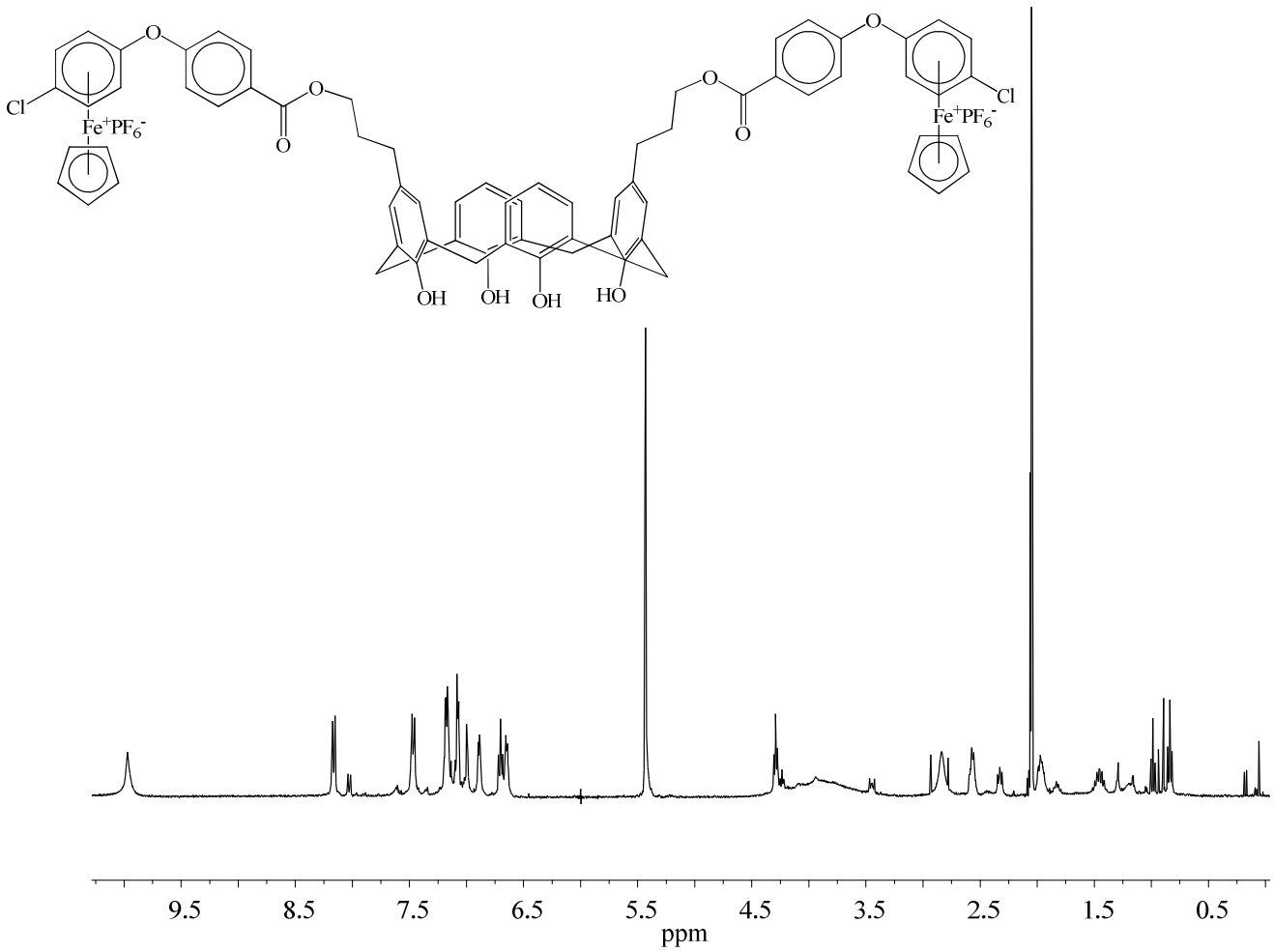


Figure 3-40: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.37.

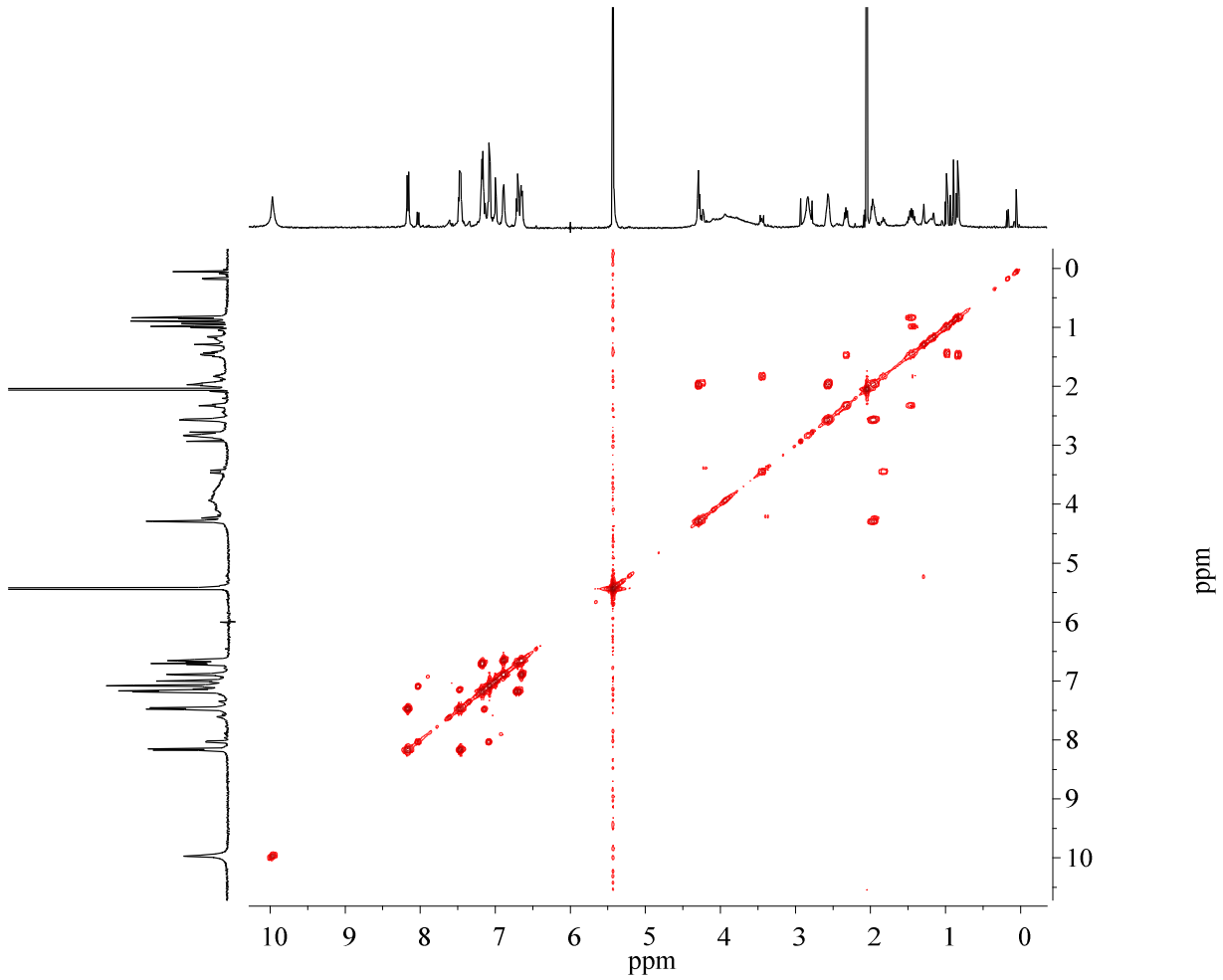


Figure 3-41: COSY spectrum of calix[4]arene 3.37.

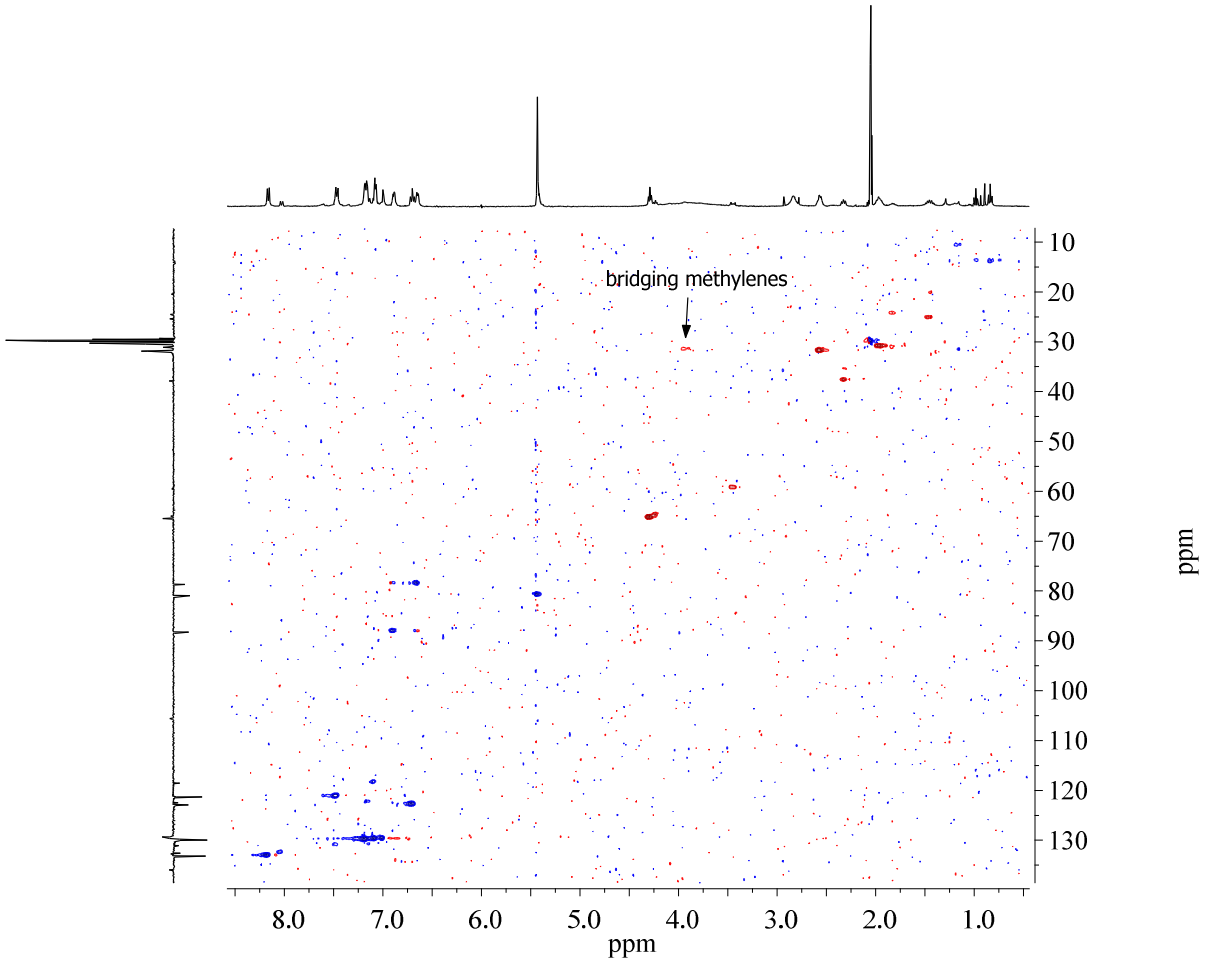


Figure 3-42 : HSQC spectrum of calix[4]arene 3.37.

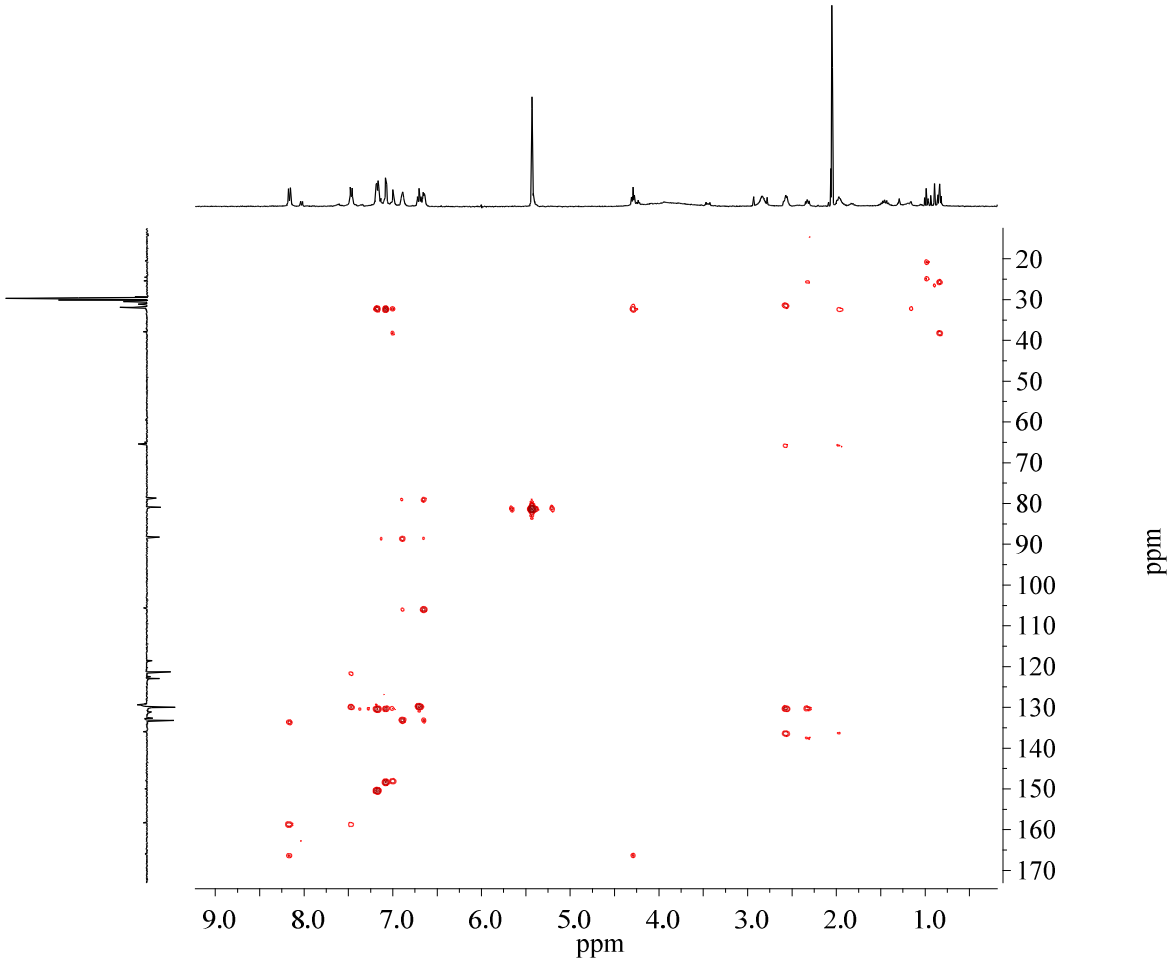
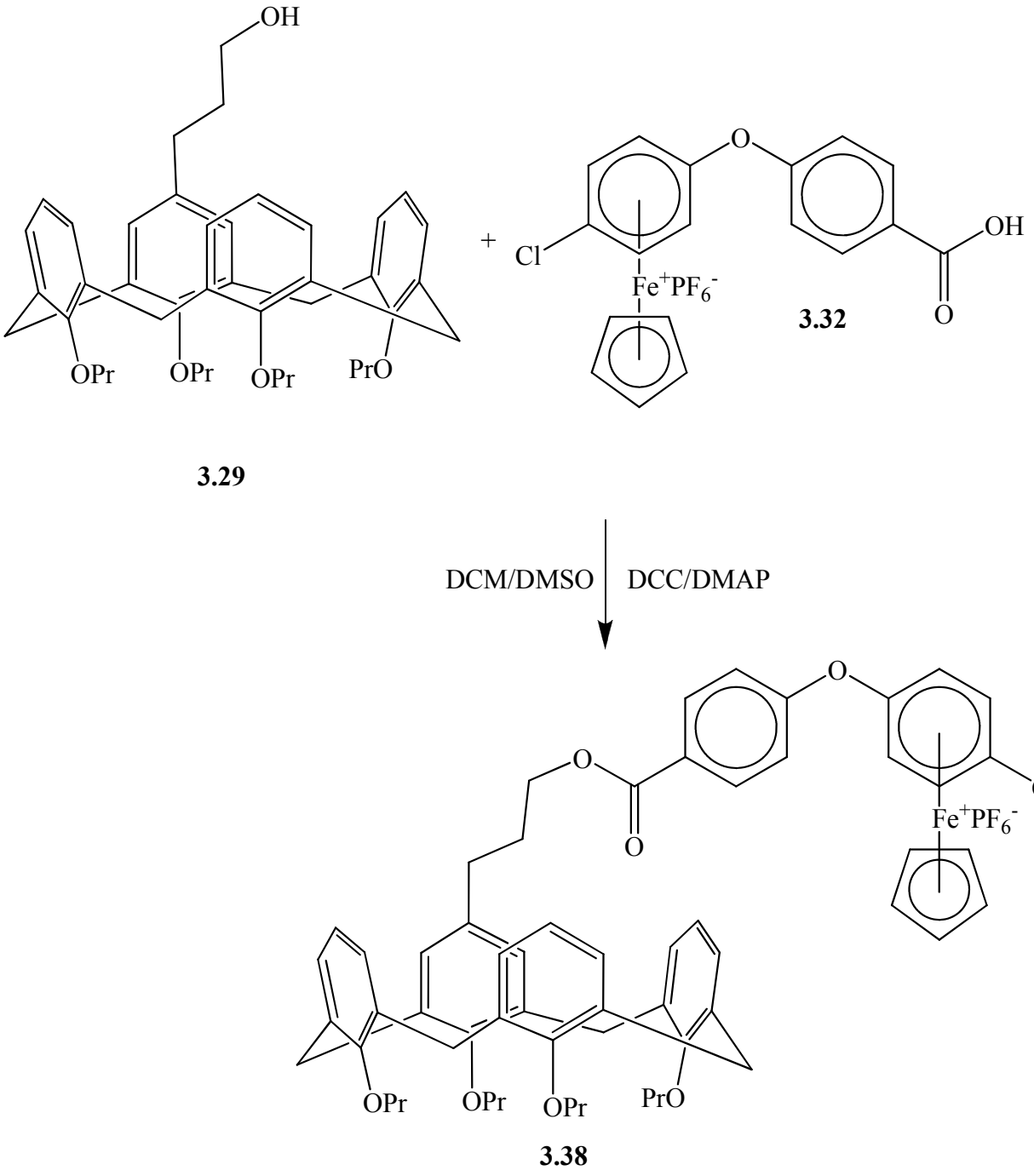


Figure 3-43: HMBC spectrum of calix[4]arene 3.37.

3.2.2.2 Metallocalix[4]arenes based on mono-functionalized calix[4]arenes

Calix[4]arene **3.29** was reacted with the organometallic acid complex **3.32** to give monometallic calix[4]arene **3.38** (Scheme 3-23). Figure 3-44 shows the ^{1}H NMR spectrum of complex **3.38.** It can be seen that the metallic moiety is incorporated into the calix[4]arene by the presence of the cyclopentadienyliron moiety resonating between 5.52 ppm and 5.33 ppm. Similarly to the previously discussed calix[4]arenes (**3.33 – 3.37**), the presence of the ester is confirmed by the shift in the ^{1}H NMR resonance due to the alcoholic CH_2 from 3.44 ppm to 4.15 ppm for the ester CH_2. Also, it can be seen that many of the proton resonances

are doubled (eg. cyclopentadienyliron resonance), this is due to the presence of the two conformers of the calix[4]arene (cone and partial cone).



Scheme 3-23: Synthesis of calix[4]arene 3.38.

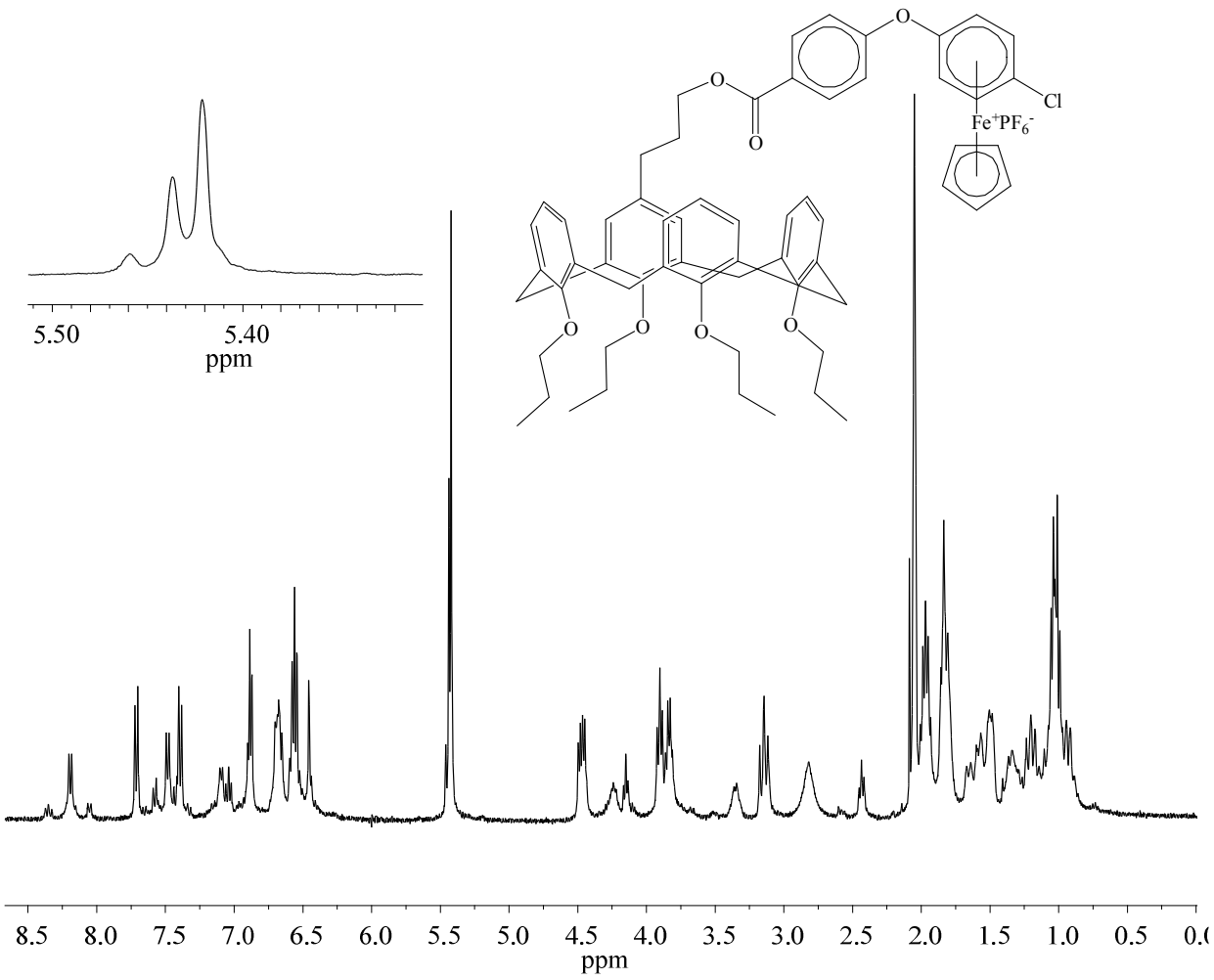
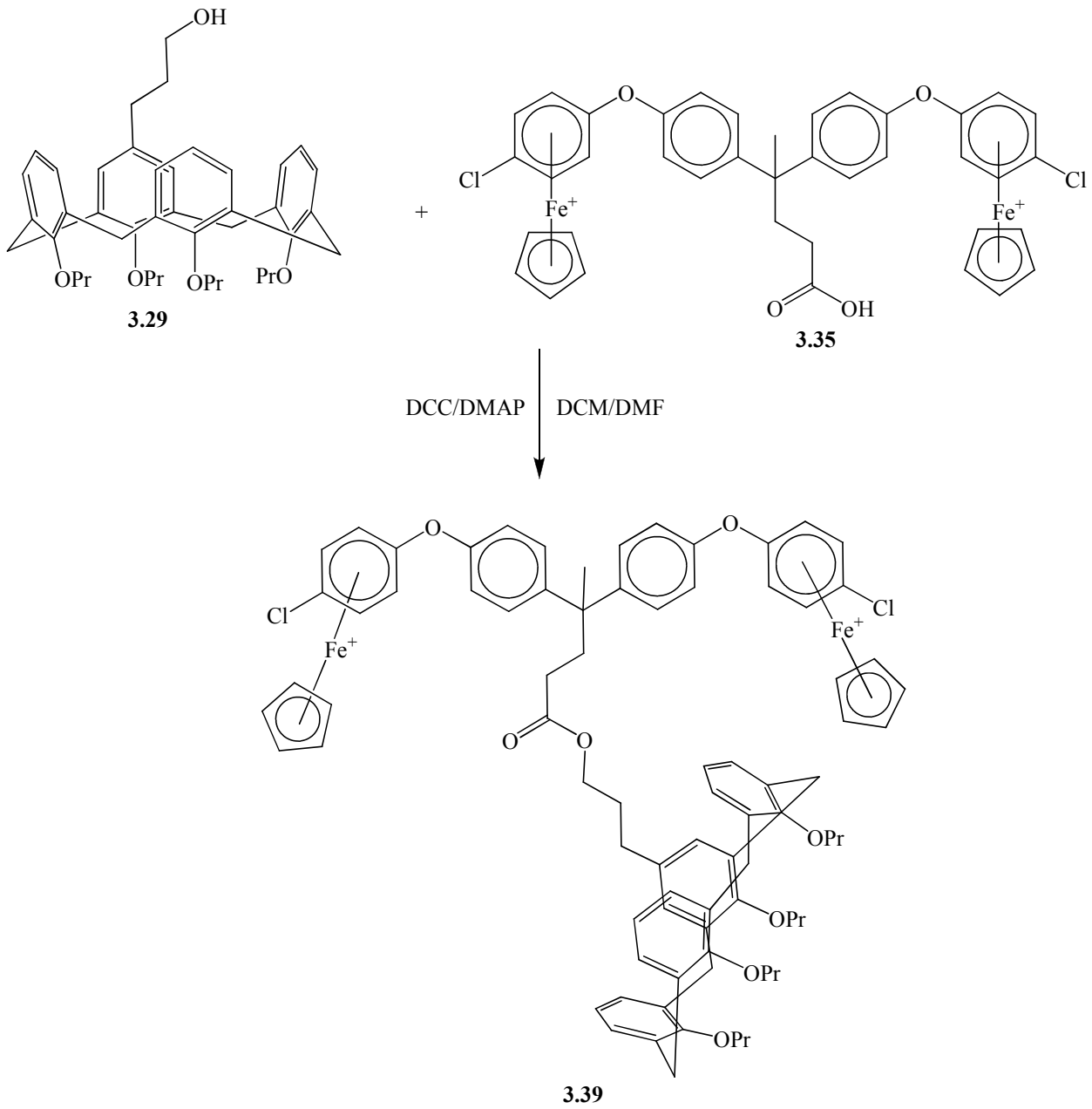


Figure 3-44: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.38.

Dimetallic calix[4]arene **3.39** was prepared from the reaction between calix[4]arene **3.29** and the valeric acid based organoiron complex **3.35** (Scheme 3-24).



Scheme 3-24: Synthesis of calix[4]arene of 3.39.

The ^{1}H and ^{13}C NMR spectra of **3.39** are shown in Figure 3-45 and Figure 3-46. As can be seen in ^{1}H NMR spectrum, the organoiron unit was successfully incorporated due to the appearance of the resonance due to the cyclopentadienyliron moiety at 5.27 ppm. The remaining iron complex peaks appear at 7.44 ppm and 7.28 ppm (non-complexed aromatics), 6.70 ppm and

6.39 ppm (complexed aromatics), 2.35 – 2.24 ppm and 2.24 – 2.12 ppm (aliphatic CH_2s) and 1.71 ppm (CH_3).

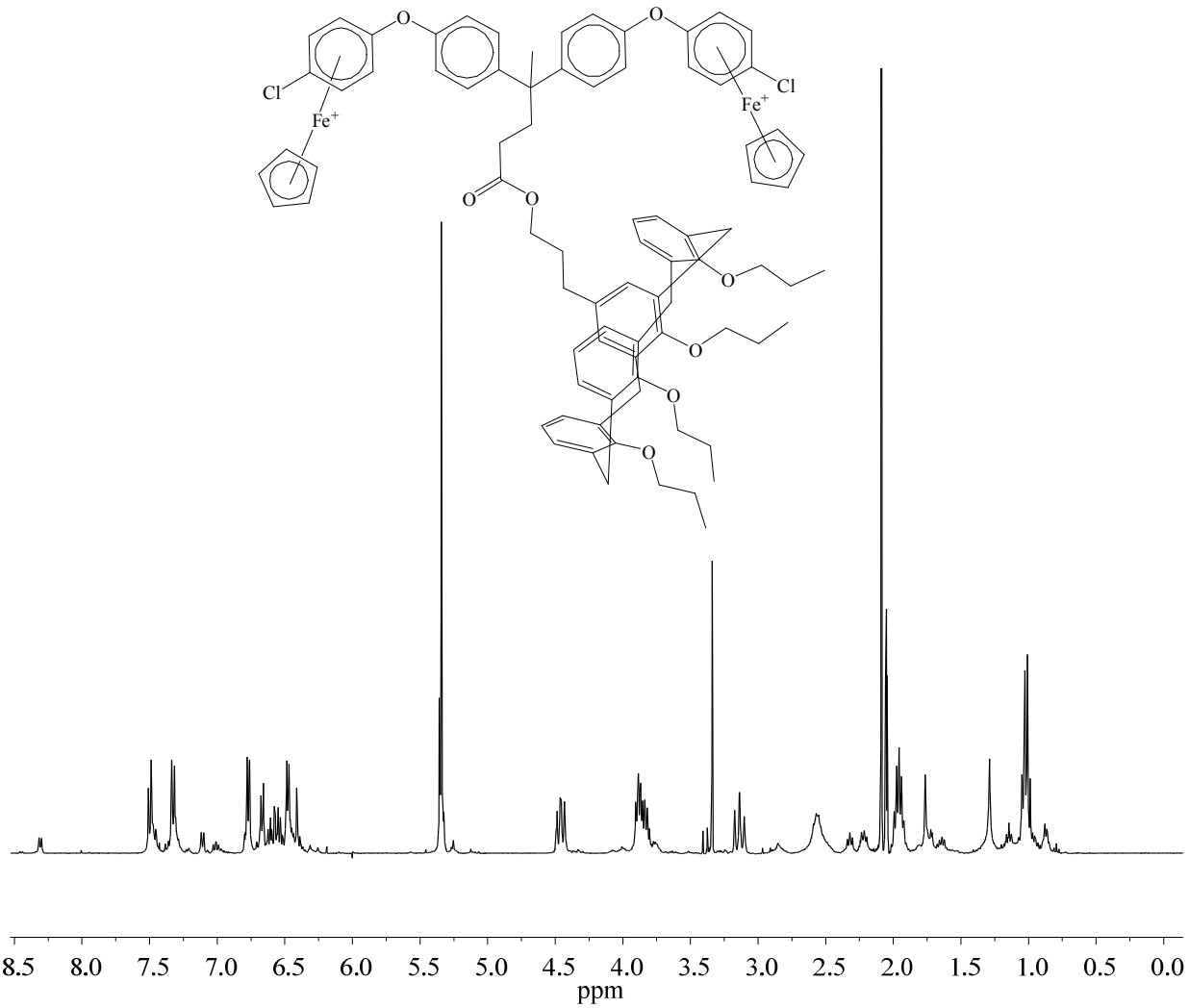


Figure 3-45: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.39.

The ^{13}C NMR spectrum (Figure 3-46) also showed the incorporation of the organoiron complex. The cyclopentadienyliron resonated at 79.85 ppm and the complexed aromatics at 87.24 ppm and 76.56 ppm. The ^{13}C NMR spectrum also confirms the formation of the ester from the shift in the calix[4]arene's CH_2-OH from 63.79 ppm to 63.59 ppm.

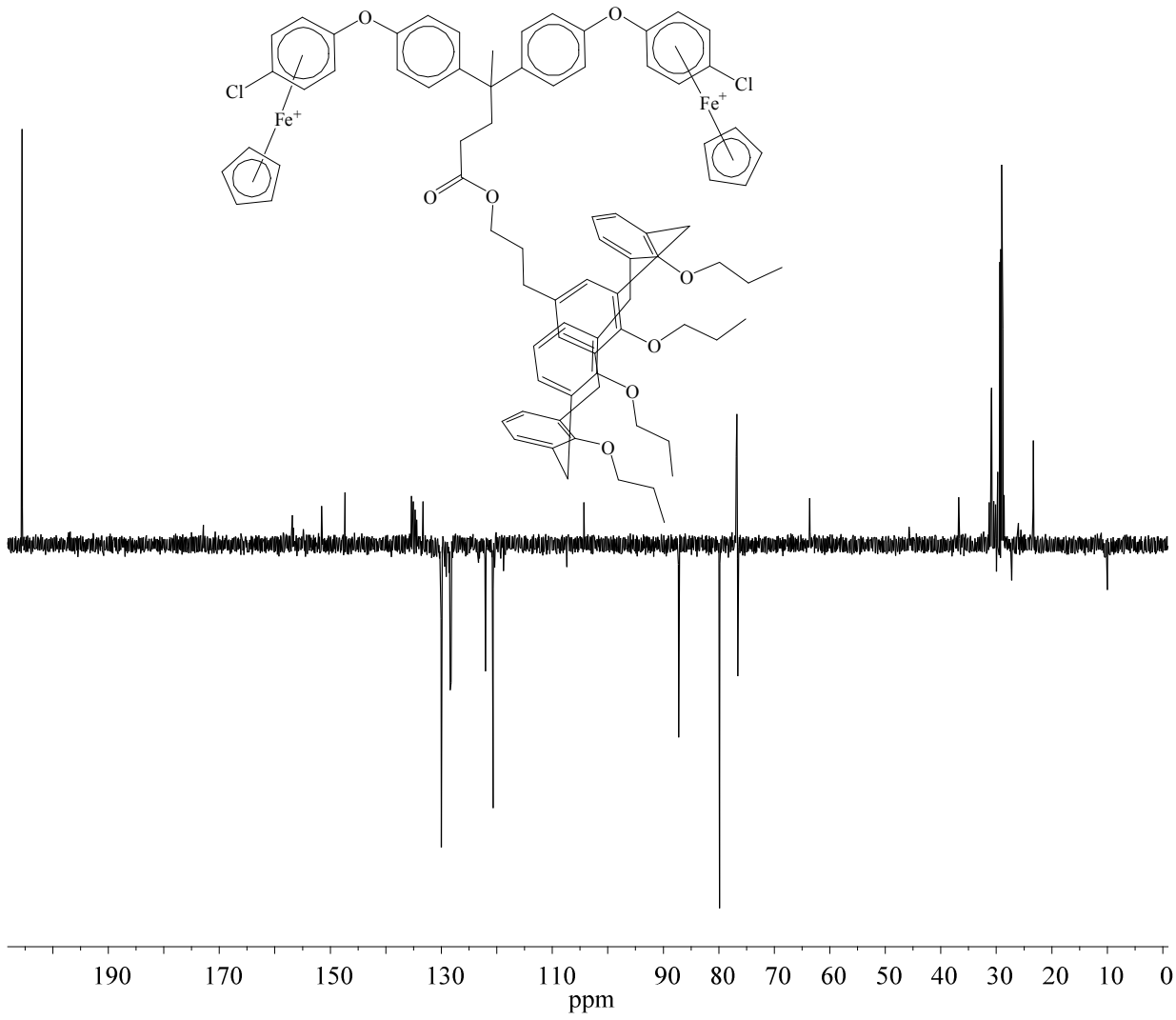


Figure 3-46: 101 MHz (APT) ^{13}C NMR spectrum of calix[4]arene 3.39.

Due to the presence of multiple conformers many of the peaks in both the ^{1}H and ^{13}C NMR spectra are doubled.

*Note: metallocalix[4]arene **3.37** was also attempted by the reaction of calix[4]arene **3.31** with the organoiron complex **3.32**. However, due to reactions with the lower rim this reaction was unsuccessful.

3.2.2.3 Cyclic voltammetry studies

Cyclopentadienyliron complexes are known to possess electrochemical properties and accordingly the calix[4]arenes **3.33, 3.34, 3.36 – 3.39** were analyzed using cyclic voltammetry to study the electrochemical properties of these complexes.

Cyclic voltammetry of **3.33, 3.34, 3.36, 3.37, 3.38, 3.39** showed that the iron centres displayed redox couples between -1.200 V and -1.740 V (Table 3-2). This redox couple was due to the reduction of the cationic iron moiety to the neutral 19 e^- species. A comparison between the propoxy protected calix[4]arene (**3.33**) and the TBDMS protected calix[4]arene (**3.34**) showed that there was no significant difference in the redox couple of the cationic iron. We hypothesize that the lower rim protecting groups are of sufficient distance from the iron centers to not affect redox potentials. Figure 3-47 shows the cyclic voltammogram of **3.33** as a representative example.

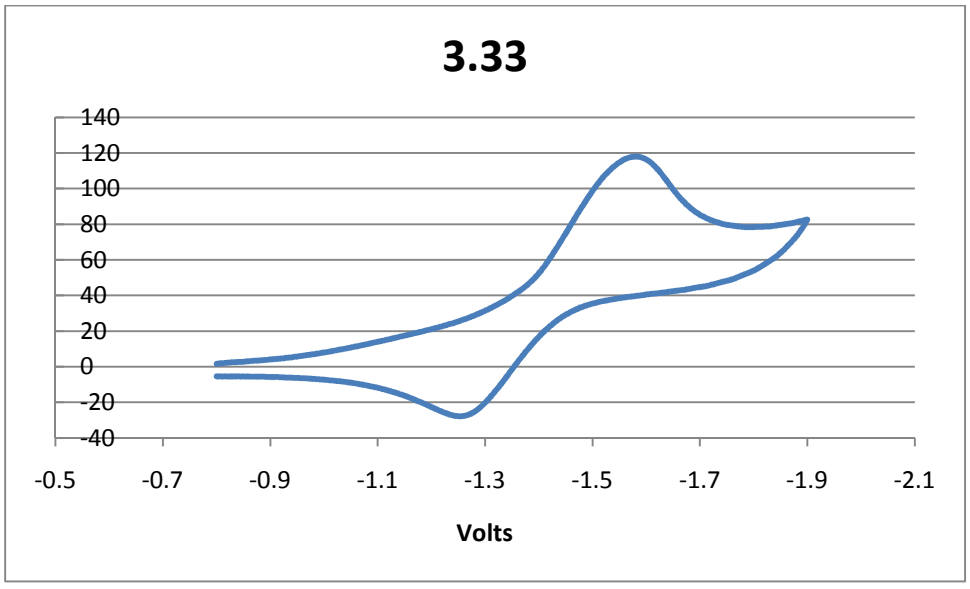


Figure 3-47: Cyclic voltammogram of calix[4]arene 3.33.

Table 3-2: Redox couple potentials for metallocalix[4]arenes 3.33 – 3.39

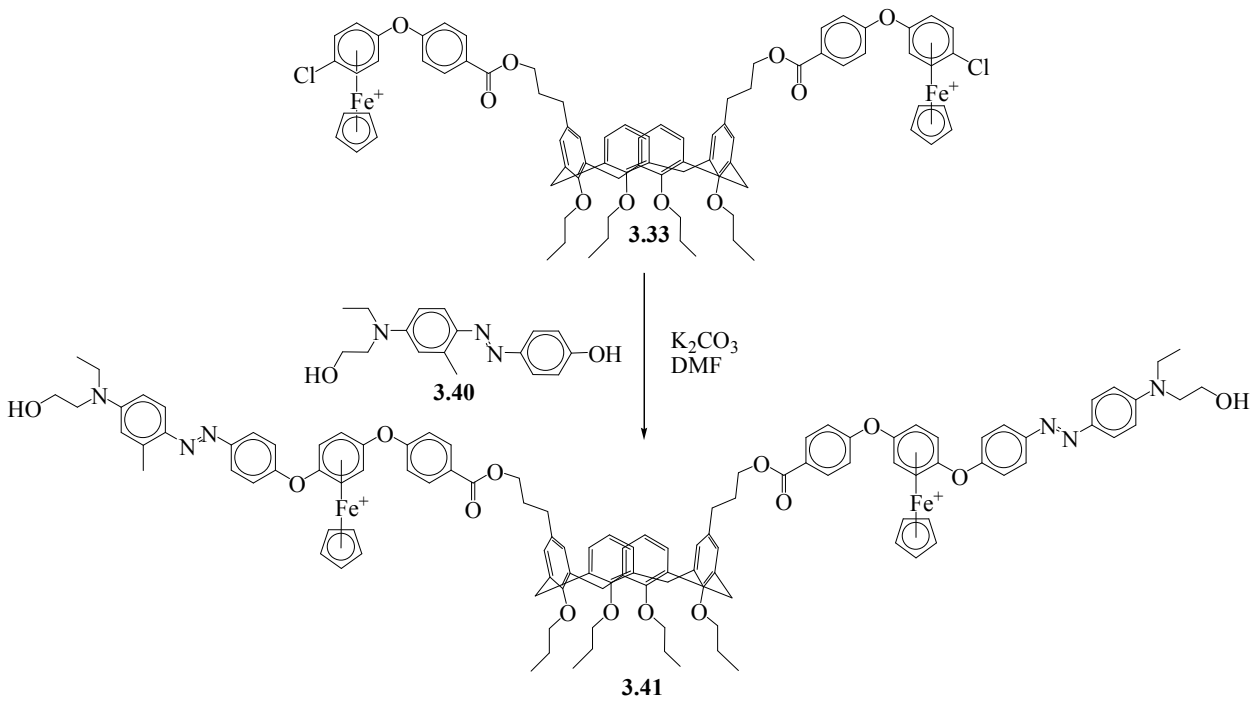
Compound	Reduction potential (V)	Oxidation Potential (V)	$E_{1/2}$
3.33	-1.550	-1.284	-1.417
3.34	-1.552	-1.302	-1.427
3.36	-1.790	-1.686	-1.738
3.37	-1.768	-1.538	-1.653
3.38	-1.386	-1.134	-1.260
3.39	-1.288	-1.116	-1.200

3.2.3 Azo dye-containing organometallocalix[4]arenes

Due to the presence of the cyclopentadienyliron moiety on the complexed arene, the chlorine group can readily undergo nucleophilic aromatic substitution reactions in relatively mild conditions. This reaction works very well with nucleophiles such as oxygen, nitrogen and sulfur. The incorporation of azo groups into calix[4]arenes can allow for potential multifunctional materials since azo dyes are well known for applications as optical storage media and sensors. The combination of properties of azo dyes with the properties of calix[4]arene (ion trapping, host-guest) may provide new multifunctional materials. This section will describe the synthesis and characterization of azo dye containing organometallocalix[4]arenes.

Previously, it was shown that azo dyes possessing a phenolic group can be utilized to prepare azo dye functionalized organoiron complexes. This methodology was used to prepare azo dye containing metallocalix[4]arenes.

The chloro-terminated metallocalix[4]arene **3.33** was reacted with azo dye **3.40**, which contains both phenolic and alcoholic groups (Scheme 3-25) to give the metallocalix[4]arene containing two azo dye moieties (**3.41**). Controlling the pH of the reaction mixture allowed only the phenolic group to substitute the complexed arene of the metallocalix[4]arene. Potassium carbonate was the chosen as a weak base as to avoid side reactions and allow for substitution only with phenolic groups. This reaction gave a vibrantly coloured purple material.



Scheme 3-25: Synthesis of calix[4]arene 3.41.

The incorporation of the azo dye into the calix[4]arene was clearly demonstrated by the appearance of resonances at 4.12 ppm, 3.58 ppm, and 1.16 ppm. These resonances were due to the aliphatic protons on the azo dye (a, b, c respectively (Figure 3-48)). There was also a shift in the complexed arene of the organoiron moiety, the resonances due to the CHs have shifted to 6.29 ppm and 6.43 ppm, Figure 3-48 shows the ^{1}H NMR spectrum for calix[4]arene **3.41**.

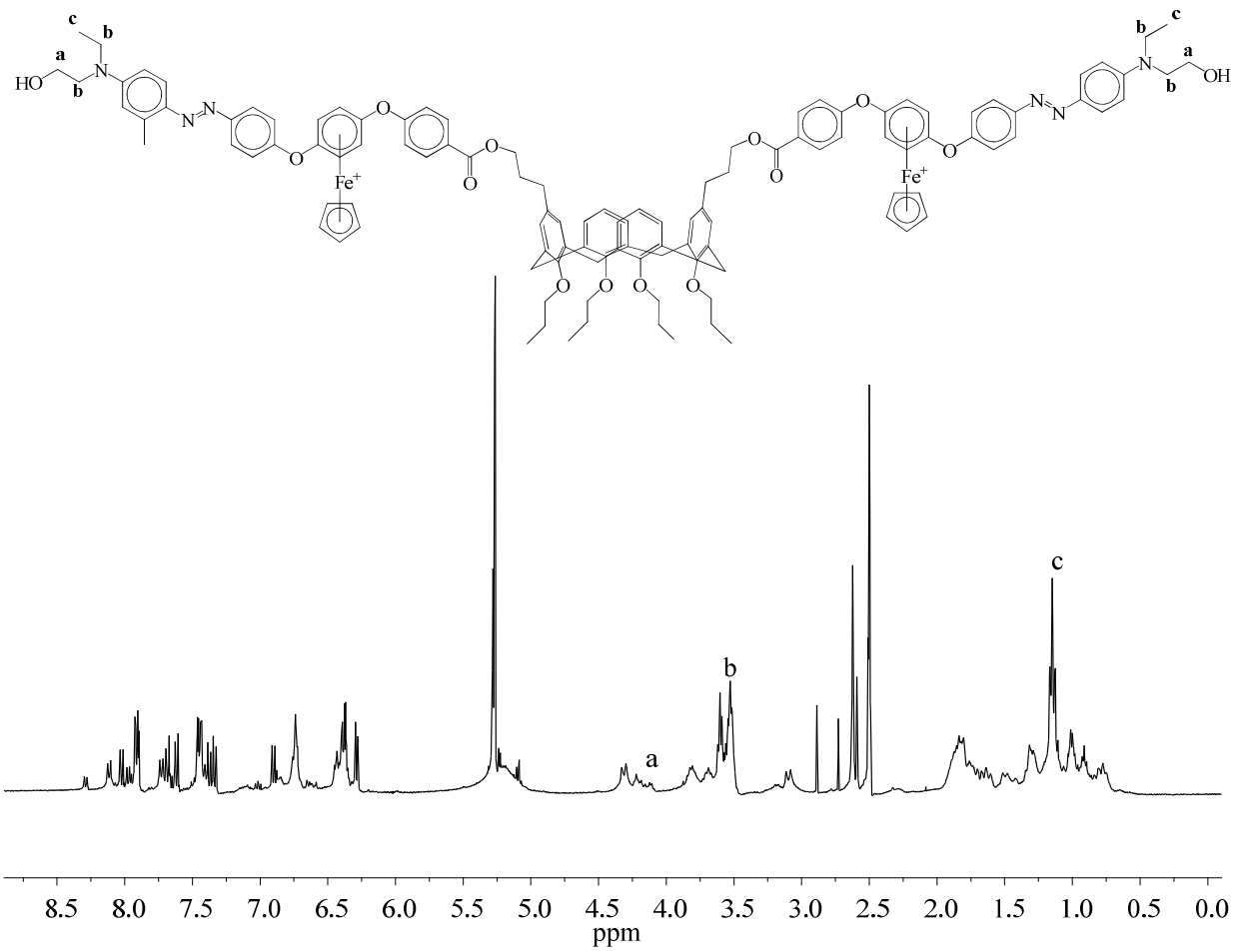


Figure 3-48: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.41.

The COSY spectrum of **3.41** (Figure 3-49) further confirms the incorporation of the azo since proton a couples to proton b, and proton b also couples with proton c. The fact that resonance "b" couples into both "a" and "c" indicates that this resonance is for both of the aniline N-methylene groups.

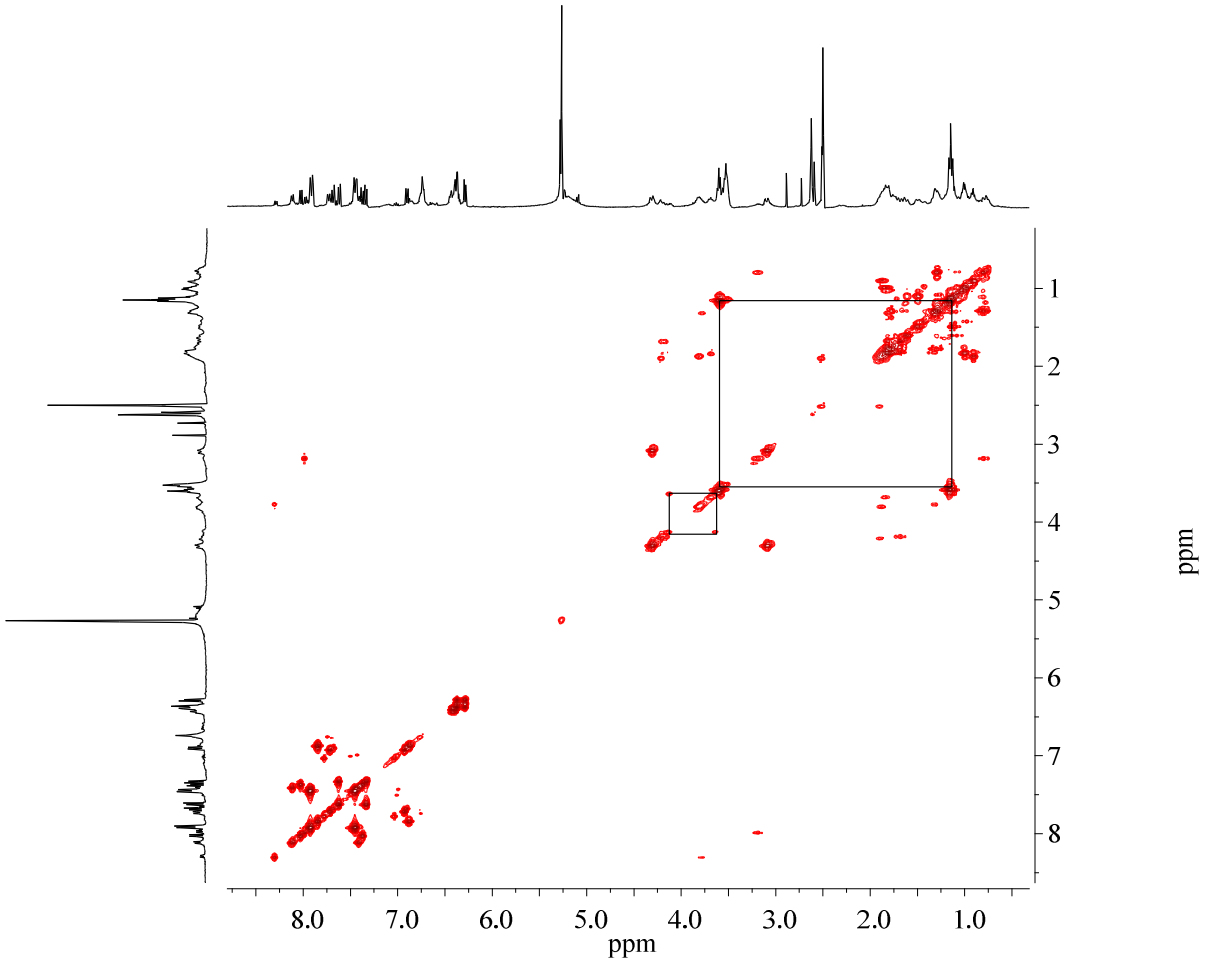


Figure 3-49: COSY spectrum of calix[4]arene 3.41.

The ^{13}C NMR spectrum of **3.41** (Figure 3-50) further confirms the substitution of the iron complex with the azo dye. The complexed aromatics of the iron complex have shifted from 88.18 ppm and 78.63 ppm to 76.66 ppm and 75.40 ppm. This shift is a good indication that the complexed arene is substituted by two oxygen atoms.

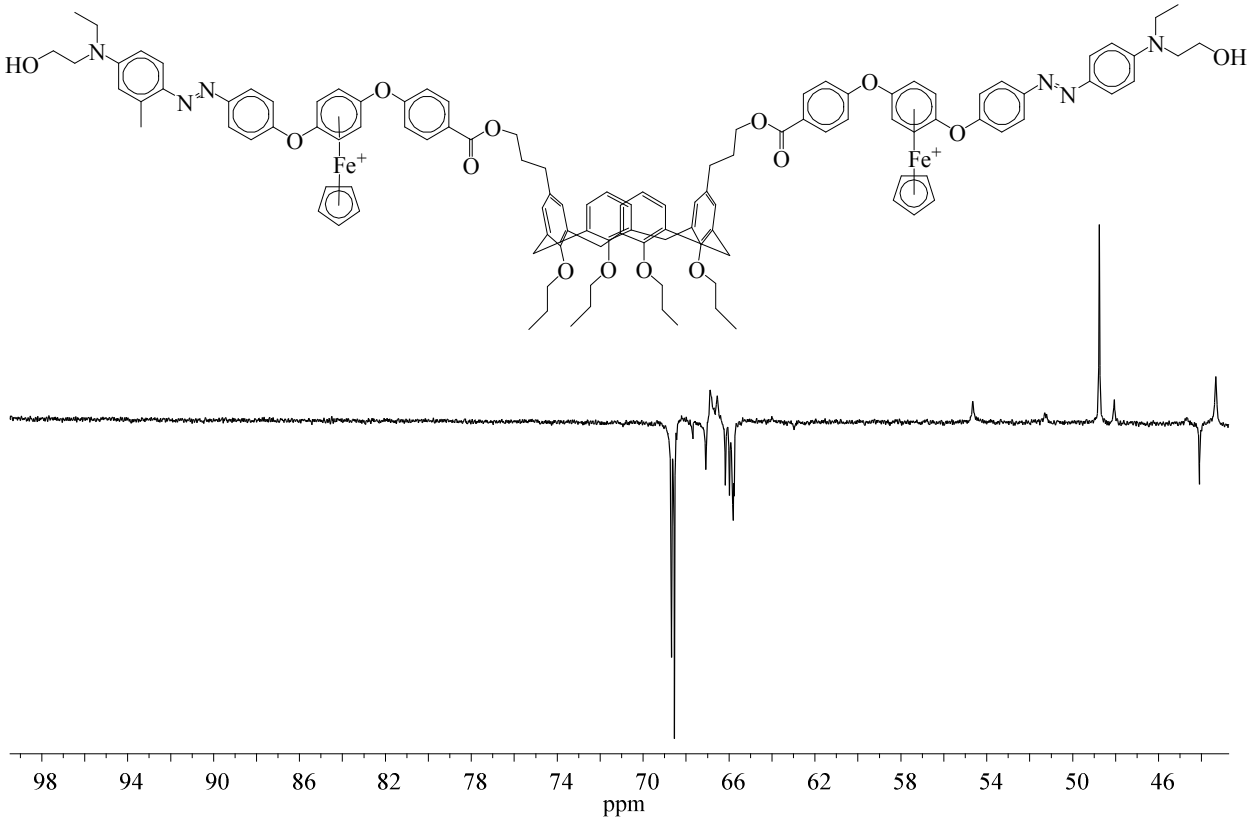
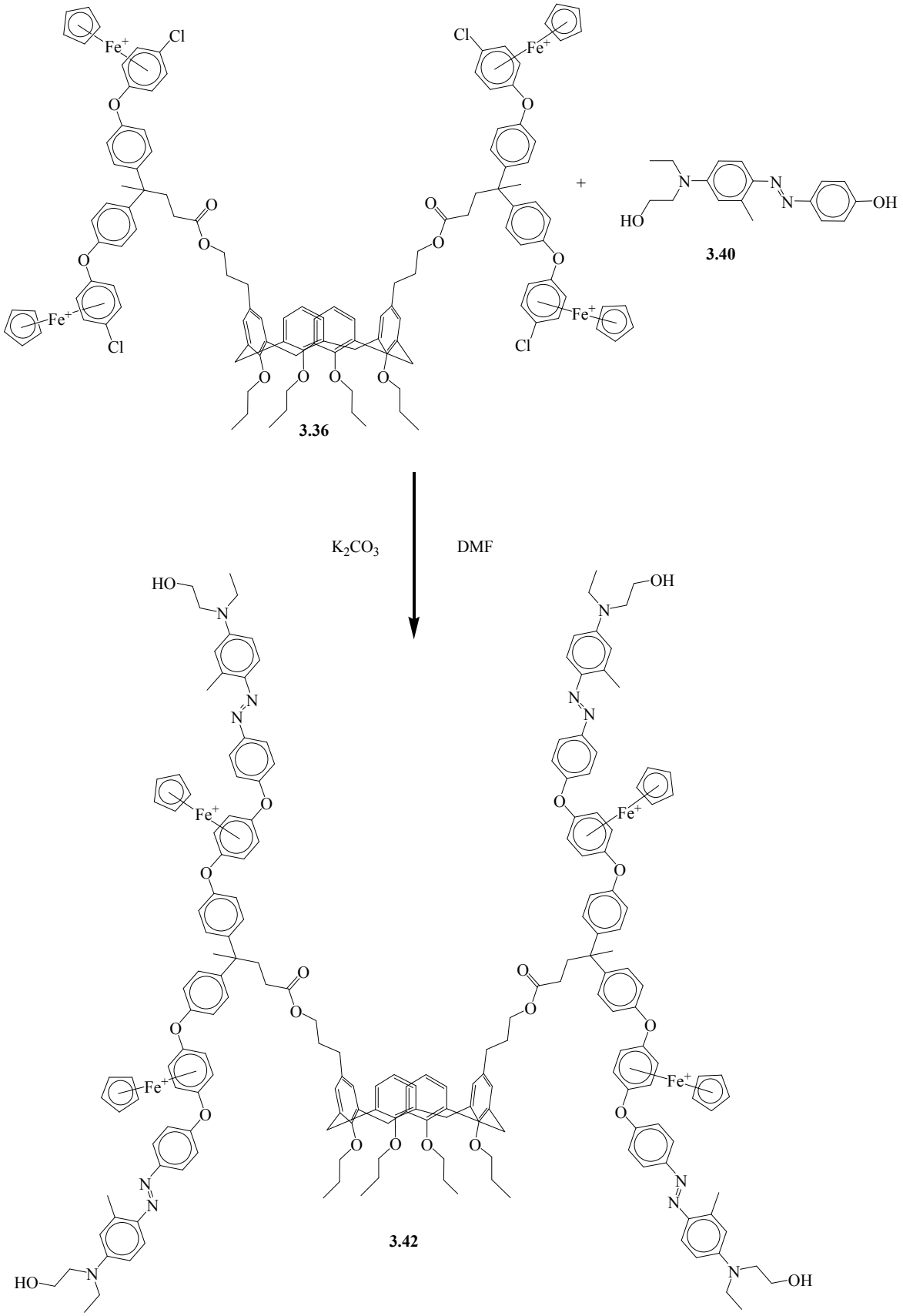


Figure 3-50: 101 MHz (APT) ^{13}C NMR spectrum of 3.41.

A metallocalix[4]arene containing four azo groups (**3.42**) was prepared from the reaction between calix[4]arene **3.36** and azo dye **3.40** (Scheme 3-25). This reaction gave the azo dye containing metallocalix[4]arene **3.42** as a brightly coloured reddish/purple powder.



Scheme 3-26: Synthesis of calix[4]arene 3.42.

As seen in the ^{1}H NMR spectrum (Figure 3-51), the azo dye was successfully incorporated by the appearance of proton resonances at 3.58 ppm and 1.11 ppm due to the aliphatic groups on the azo dye. Unlike complex **3.41**, the aniline CH_2s of **3.42** overlap with each other making them difficult to identify. This was also shown in the COSY spectrum (Figure 3-52) as there is only one coupling between 3.58 ppm and 1.11 ppm. However, when examining the HSQC spectrum (Figure 3-53), there are three clear ^{13}C resonances under the proton resonance at 3.58 ppm, these resonances appear at 57.69 ppm, 52.84 ppm, and 45.71 ppm.

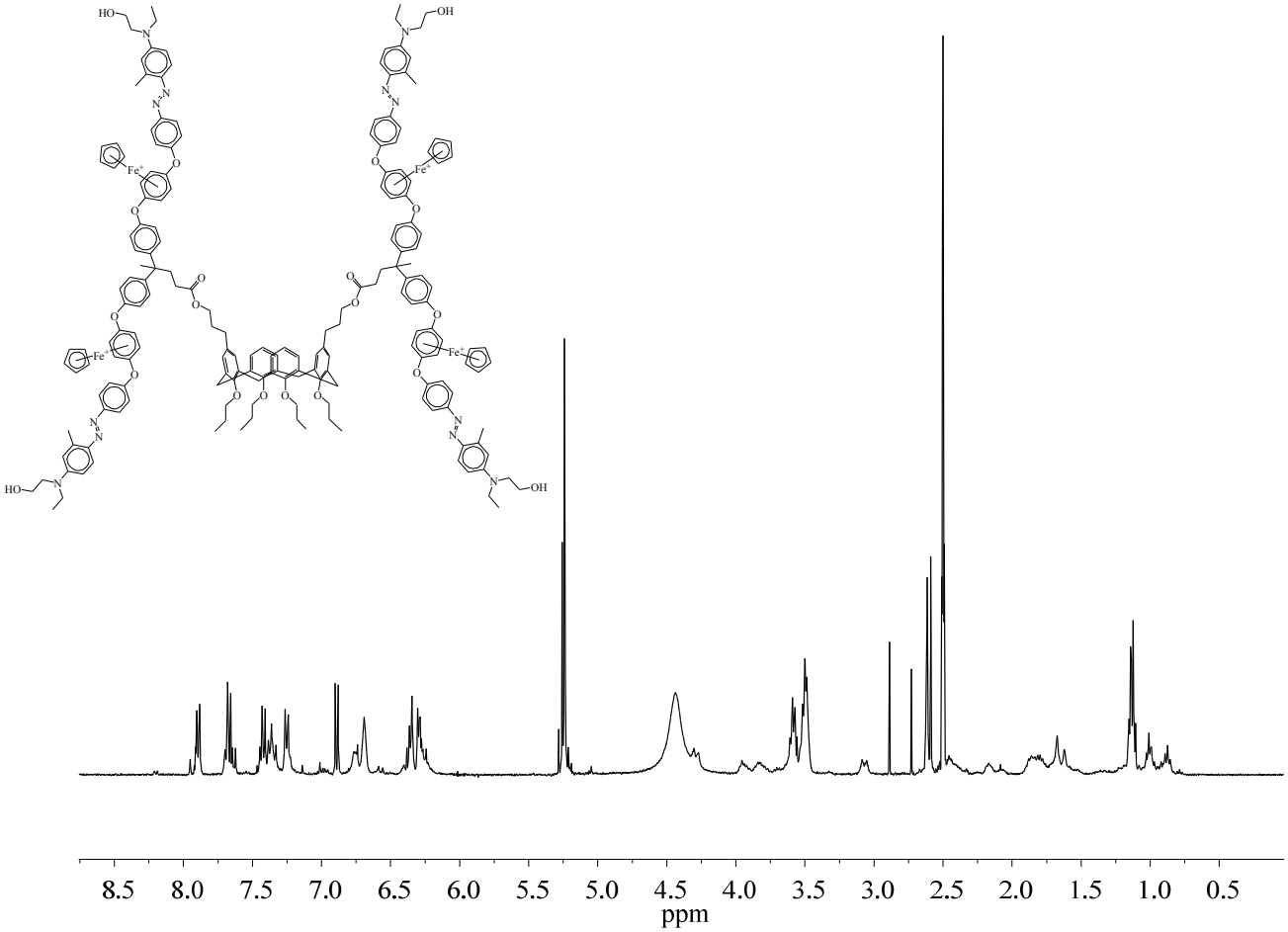


Figure 3-51: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.42.

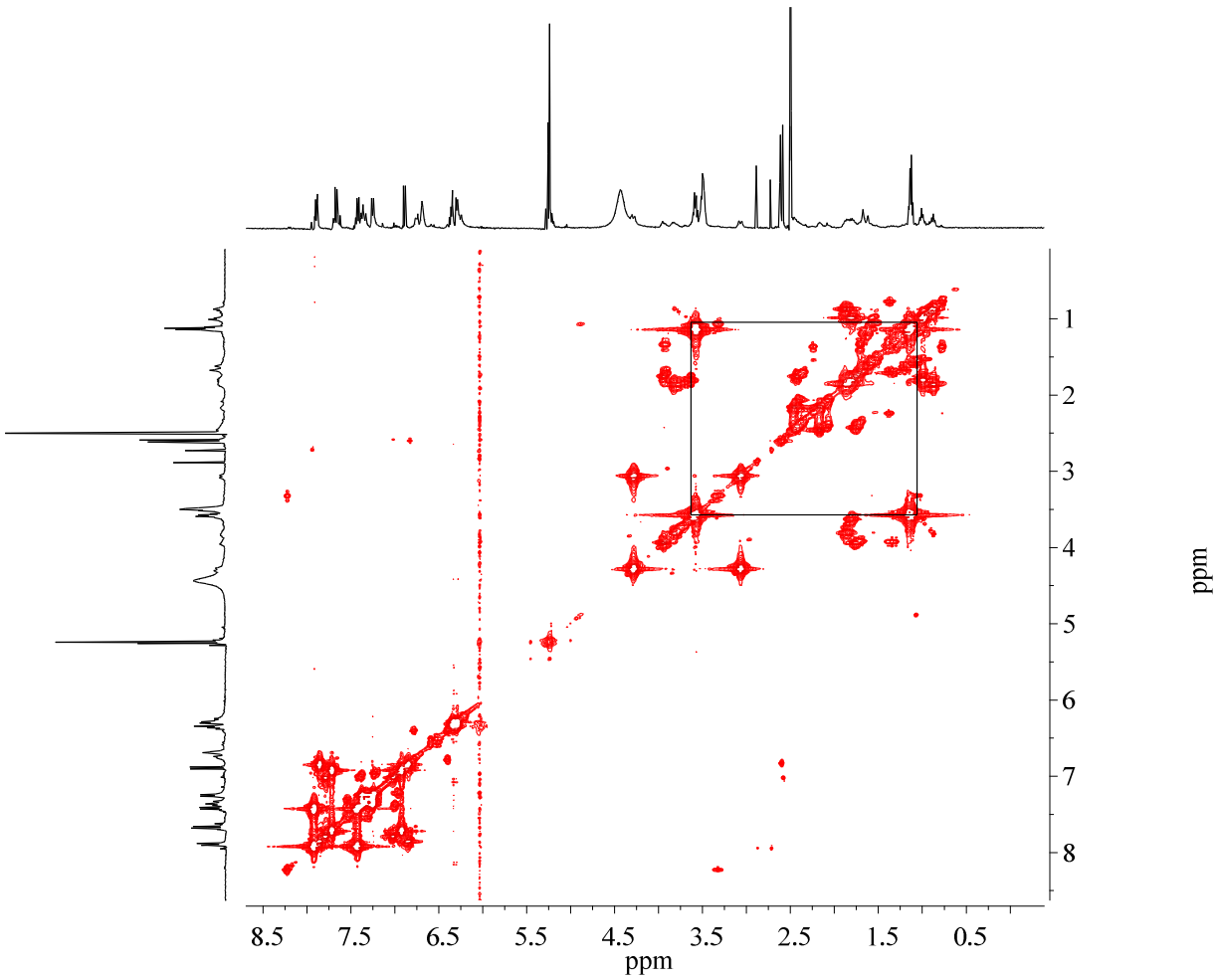


Figure 3-52: COSY spectrum of calix[4]arene 3.42.

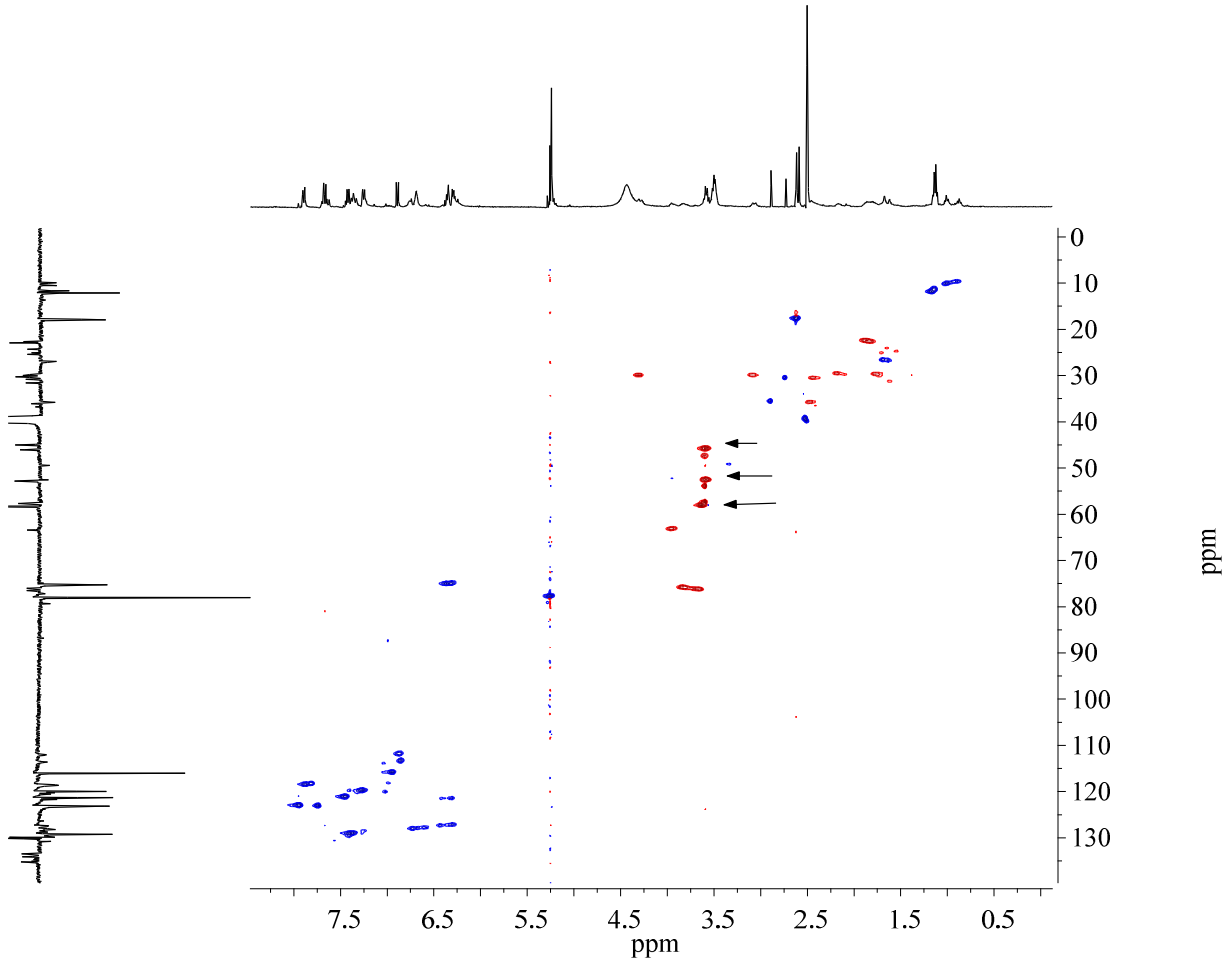
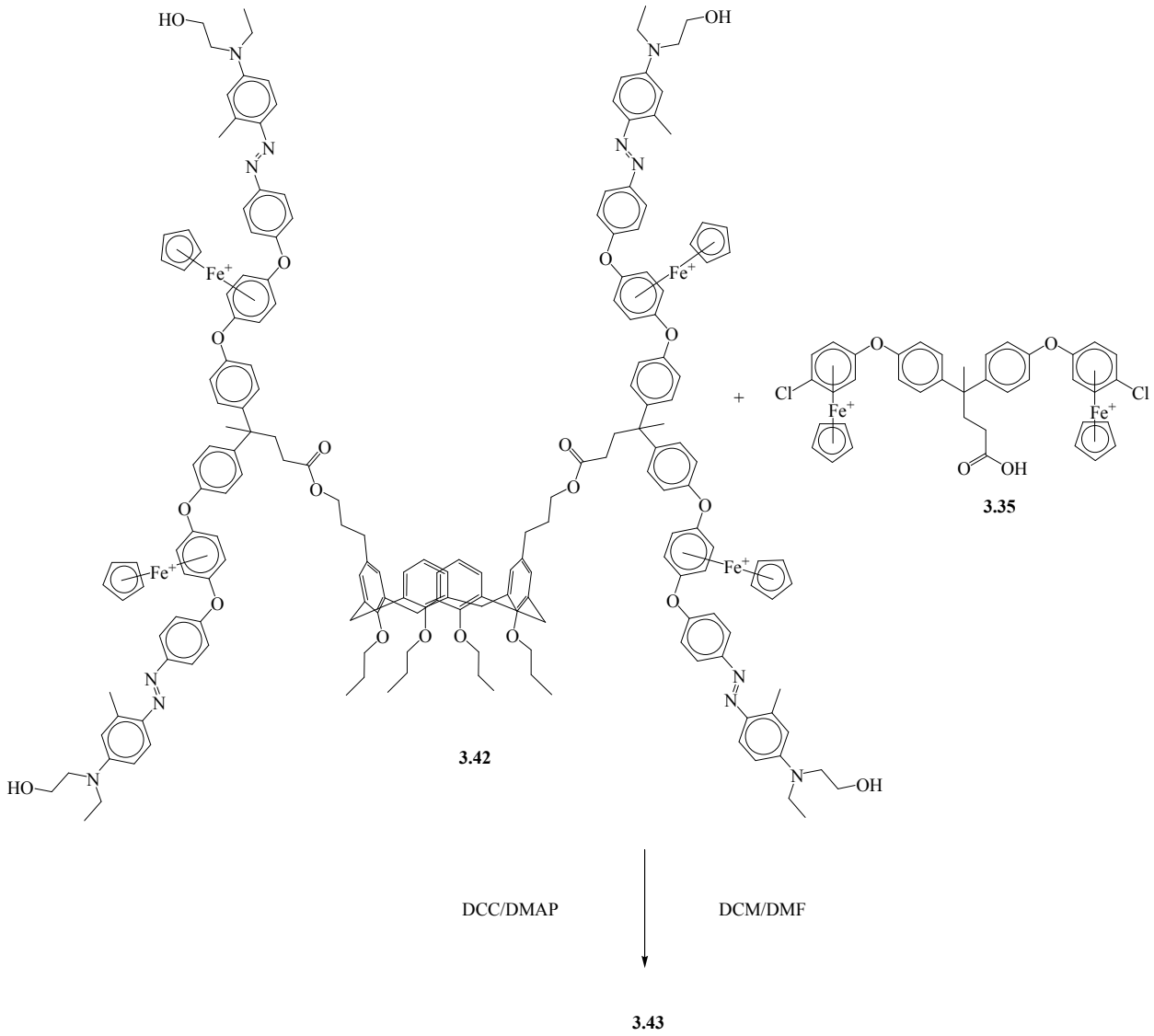


Figure 3-53: HSQC spectrum of calix[4]arene 3.42.

UV-vis spectroscopy studies on the azo dye containing metallocalix[4]arenes **3.41** and **3.42** showed that in a DMF/H_2O (1:1) solution, the calix[4]arenes displayed λ_{max}s due to the $\pi \rightarrow \pi^*$ transition at 447 nm (**3.41**) and 456 nm (**3.42**). When exposed to hydrochloric acid the λ_{max} shifted to 513 nm and 531 nm due to the formation of the azonium ion.

The azo dye-containing metallocalix[4]arene **3.42** possess multiple symmetrical branching sites, as such this calix[4]arene was used in the attempt to prepare azo dye containing metallocalix[4]arene dendritic molecules. Calix[4]arene **3.42** was reacted with four equivalents of the valeric bimetallic complex (**3.35**) to give calix[4]arene **3.43** with four azo dye and twelve metallic moieties (Scheme 3-27).



Scheme 3-27: Synthesis of calix[4]arene 3.43 (structure displayed on the following page).

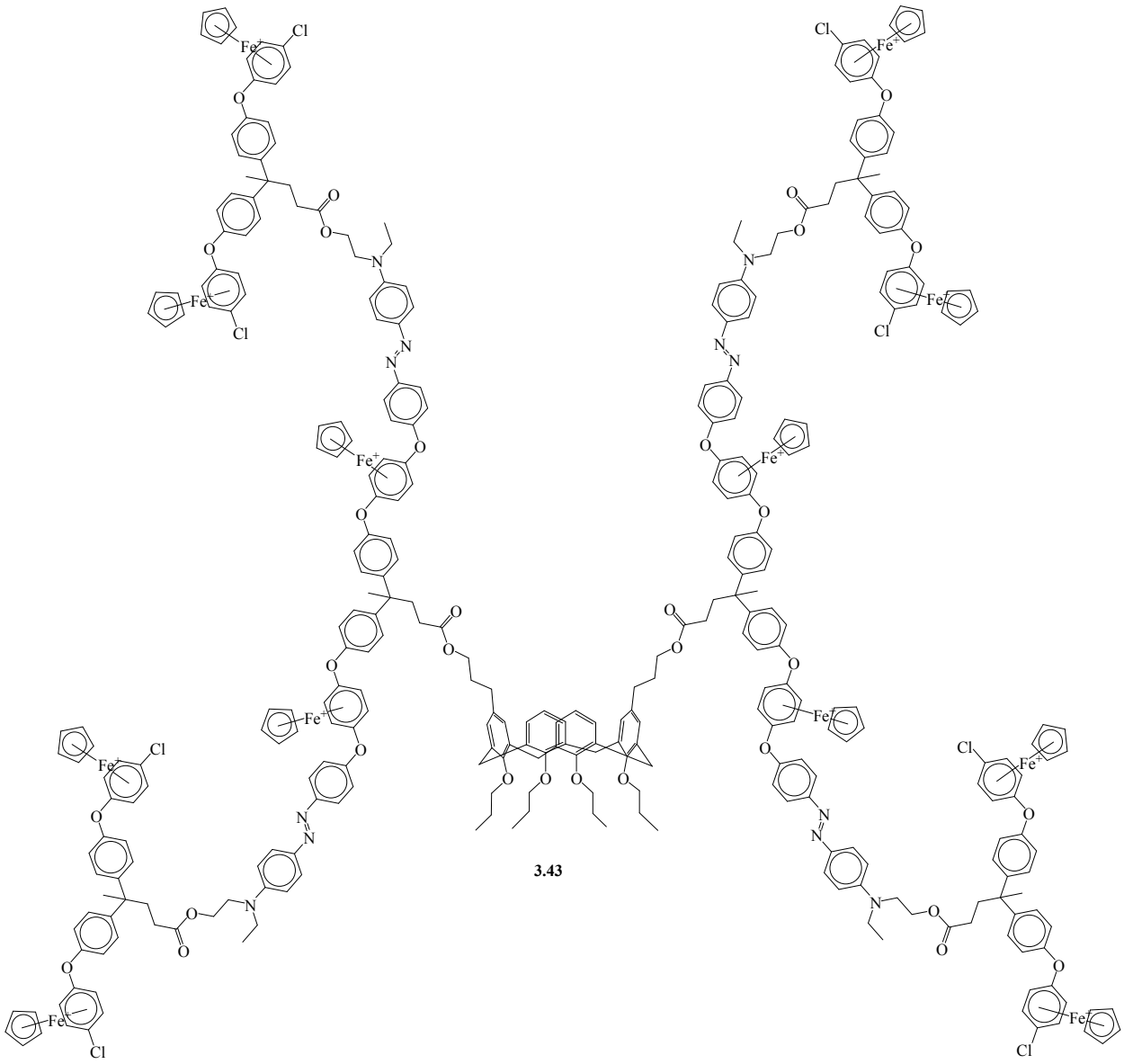


Figure 3-54: Structure of 3.43.

The ^{1}H NMR spectrum of calix[4]arene **3.43** is shown in Figure 3-55. The incorporation of the new metallic unit is shown from a number of new resonances. For example, the resonance due to the hydroxymethyl (CH_2OH) of the starting material has shifted from 3.58 ppm to 4.32 ppm, this is of course due to the formation of the ester. There are also two different cyclopentadienyliron resonances which, when integrated, show a 2:1 ratio since there are twenty

cyclopentadienyliron protons in one electronic environment and forty cyclopentadienyliron protons in a different electronic environment.

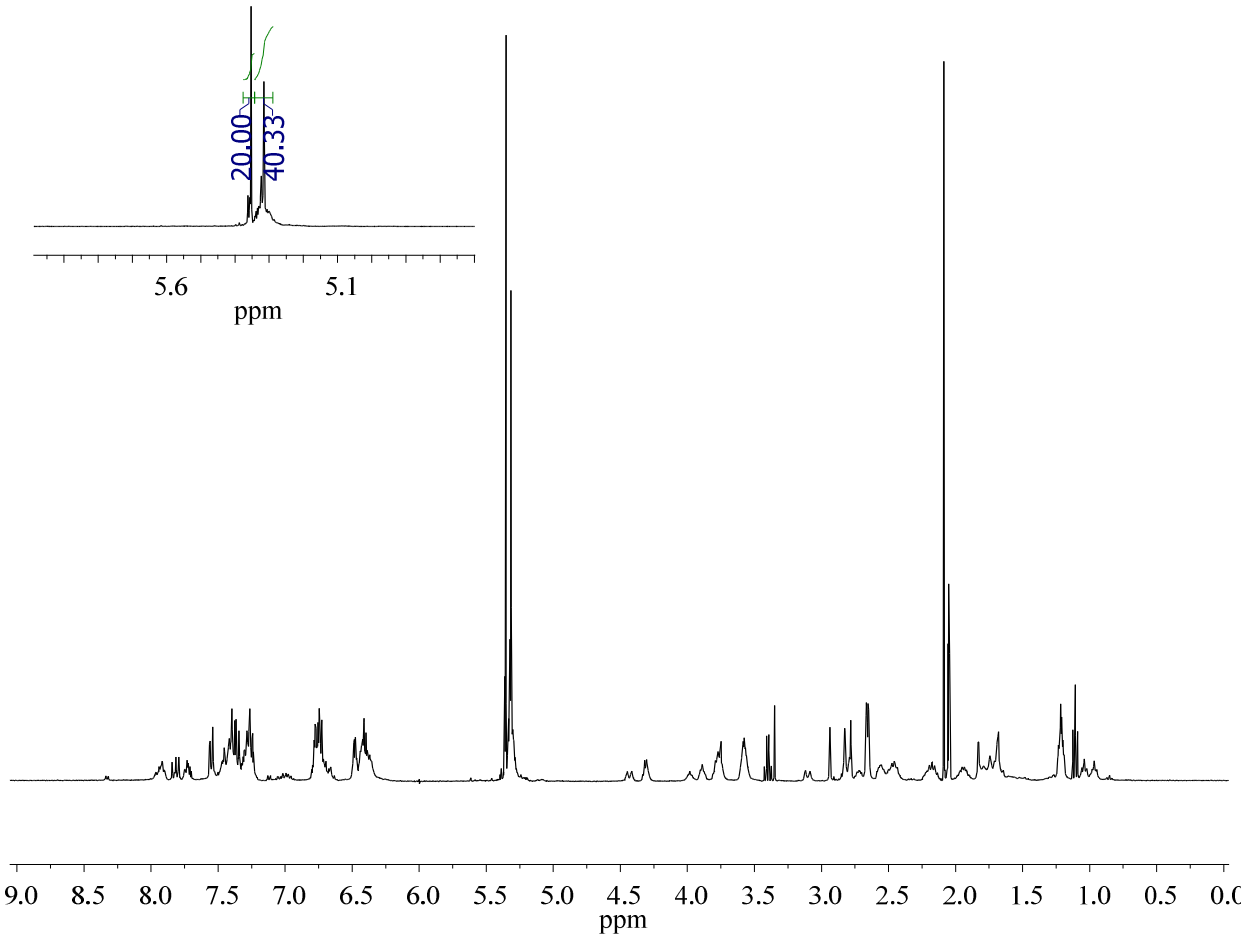


Figure 3-55: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.43.

The COSY spectrum of **3.43** (Figure 3-56) shows that the coupling between the N-alkyl groups of the azo dye has changed dramatically, instead of one coupling between the resonance at 2.58 ppm there are now two distinct couplings; one between the CH_2 of the ester (4.32 ppm) and the N-alkyl CH_2 (3.75) and a second between the N-alkyl CH_2 (3.59 ppm) and the terminal CH_3 (1.20 ppm).

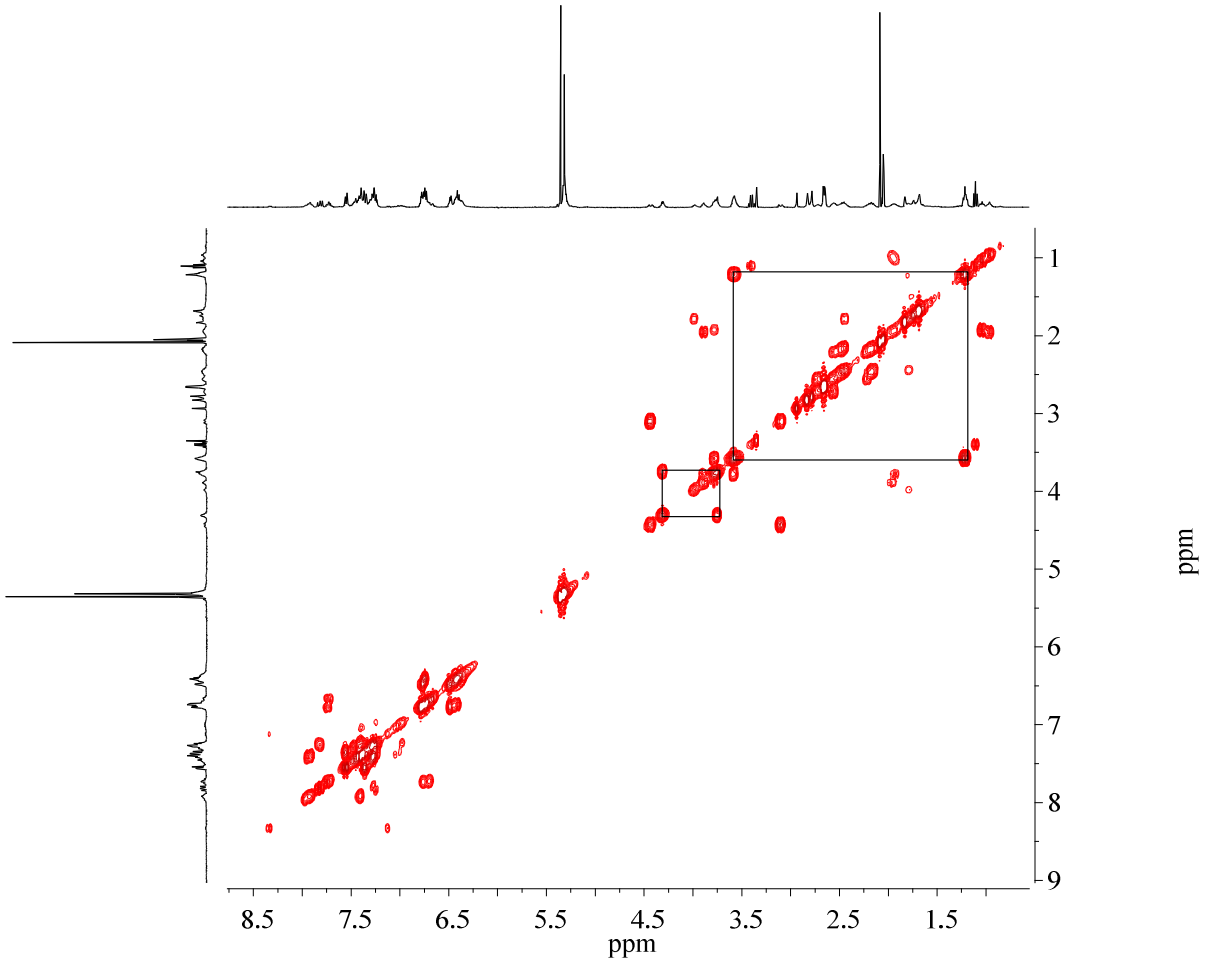


Figure 3-56: COSY spectrum of calix[4]arene 3.43.

The HSQC spectrum (Figure 3-57) confirms that there are two different organoiron species as it shows complex aromatics at 87.96 ppm, 77.28 ppm, and 77.18 ppm in the ^{13}C NMR spectrum which correlate to 6.76 ppm, 6.48 ppm, and 6.41 ppm in the ^{1}H NMR spectrum. The resonance at 87.96 ppm in the ^{13}C NMR spectrum is due to the chloro-substituted complexed arene.

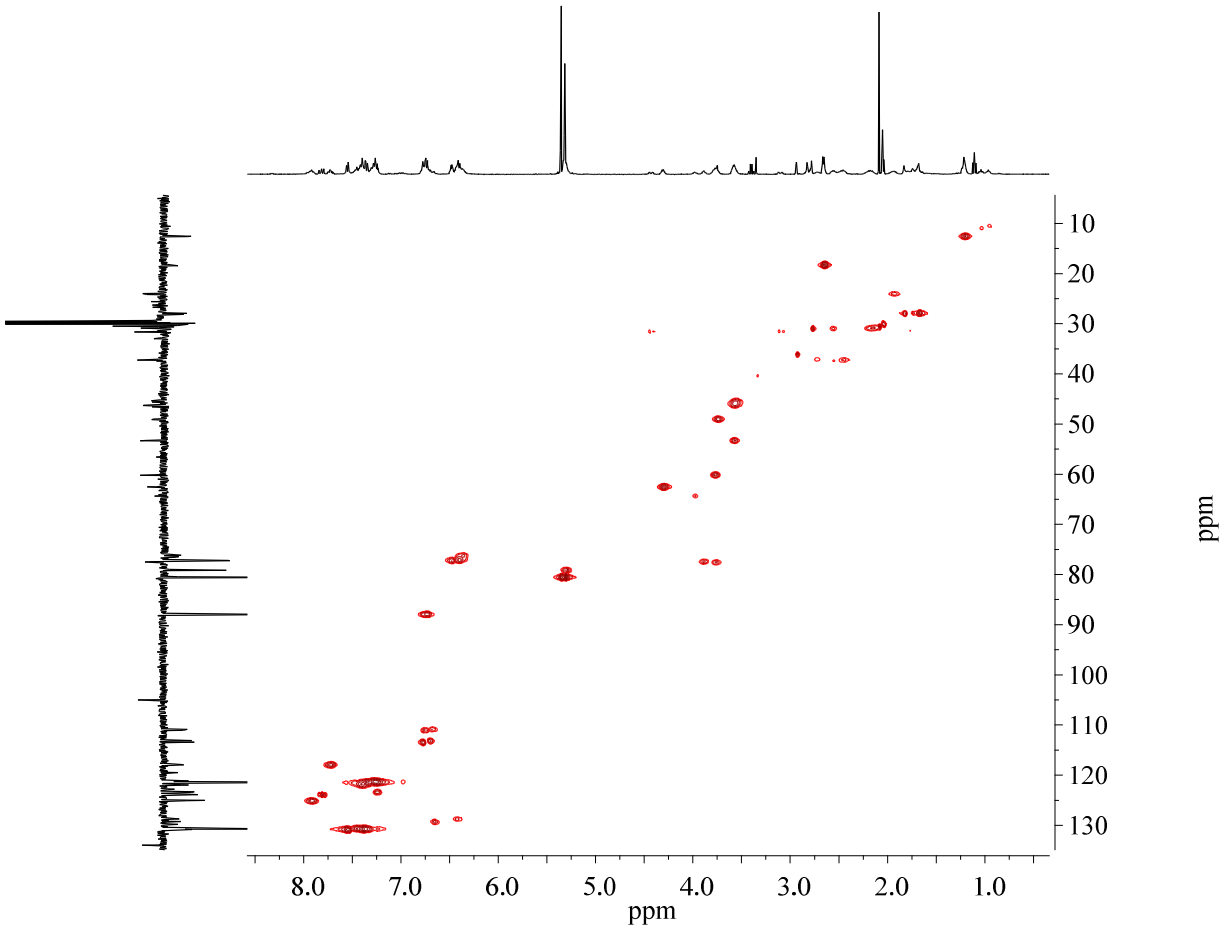


Figure 3-57: HSQC spectrum of calix[4]arene 3.43.

3.2.3.1 Acid sensing capabilities

Since azo dye materials are known to possess acid sensing abilities, the azo dye containing metallocalix[4]arenes were tested to determine if they could detect the presence of either aqueous HCl or gaseous HCl.

All the azo dye-containing metallocalix[4]arenes were coloured in solution, with colours ranging from yellow to orange in neutral or basic solutions and red to purple for all compounds in acidified solutions. The UV-vis spectrum for complex **3.43** in DCM is shown in Figure 3-58.

In solution (left) complex **3.43** appeared yellow and displayed a λ_{max} at 431 nm. When $HCl_{(g)}$ was passed over the surface of the solution (right) the colour instantly changed to red and the λ_{max} shifted to 535 nm. The red colour reverted to yellow when ammonia was passed over the surface of the solution. This class of material not only detected traditional solution-phase protonic acids, but also detected gaseous acids such as HCl and Lewis acids such as $AlCl_3$. A solid sample of complex **3.43** was also exposed to $HCl_{(g)}$ and was observed to change to a deep purple colour; when exposed to gaseous ammonia the purple colour changed back to orange. The colour change property allows for the visual identification of the presence of acids, indicating that these materials can be useful as both solid state acid sensors and acid sensors for organic and organic/aqueous solutions.

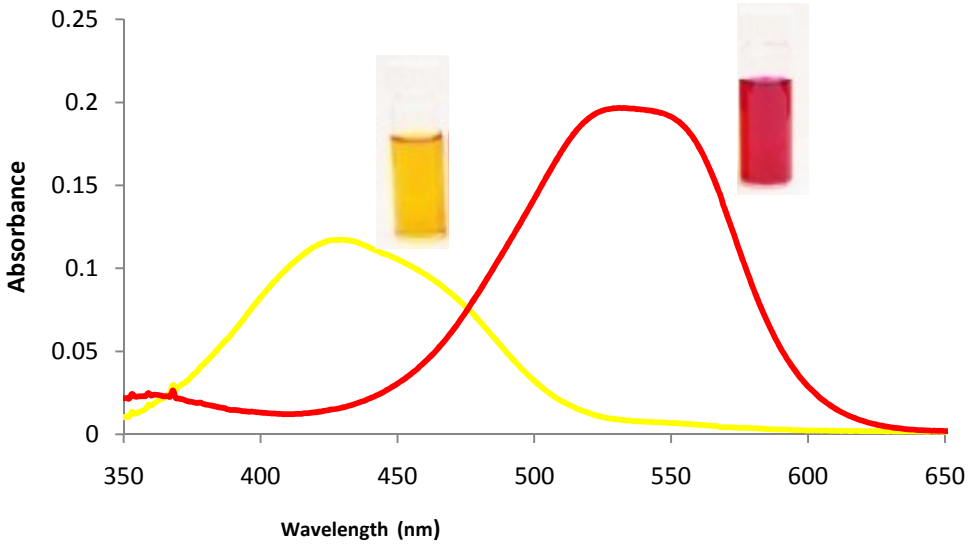


Figure 3-58: Absorption spectrum of complex 3.43 in DCM (yellow). Absorption spectrum of complex 3.47 in DCM after $HCl_{(g)}$ was passed over the surface (red).

3.2.3.2 Cyclic voltammetry studies

Cyclic voltammetric studies on the azo dye **3.42** metallocalix[4]arene **3.42** and the azo dye-containing metallocalix[4]arene **3.42** are shown in Figure 3-59 (all potentials referenced to Ag/AgCl). The free azo dye displayed two redox couples: one at $E_{1/2}$ = 0.269 V and another at $E_{1/2}$ = 0.888 V, corresponding to the oxidation of the aniline and the azo group, respectively.[88, 89] The metallocalix[4]arenes displayed an $E_{1/2}$ = -1.49 V for the reversible reduction of the cationic iron moieties. Complex **3.42** displayed two redox couples: one at $E_{1/2}$ = 0.696 V for the oxidation of the azo dye, and one at $E_{1/2}$ = -1.36 V for the reduction of the cationic iron moiety.

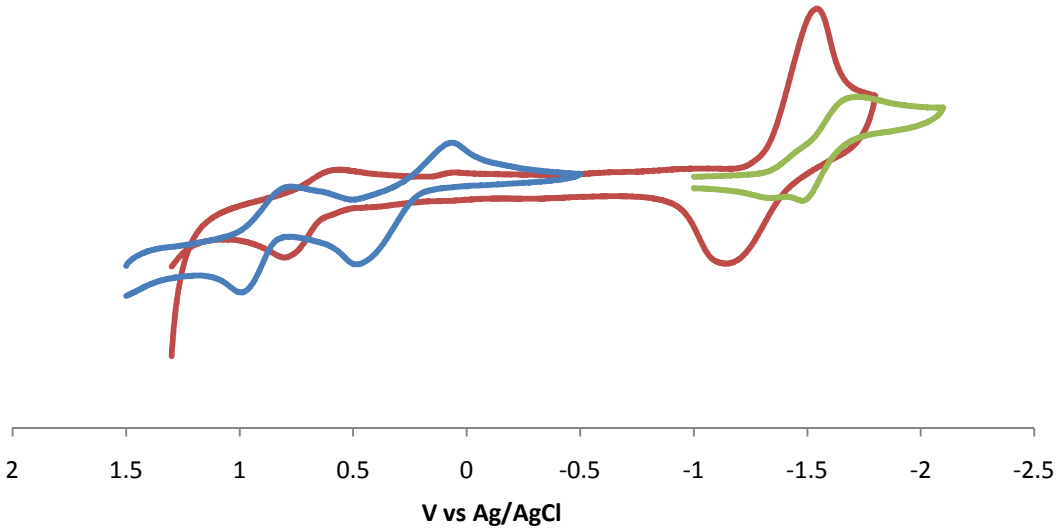


Figure 3-59: Cyclic voltammogram of phenolic azo dye 3.40 (blue), metallocalix[4]arene 3.33 (green), and azo dye-containing metallocalix[4]arene 3.43 (red).

Table 3-3: Electrochemical data of azo dye containing metallocalix[4]arenes

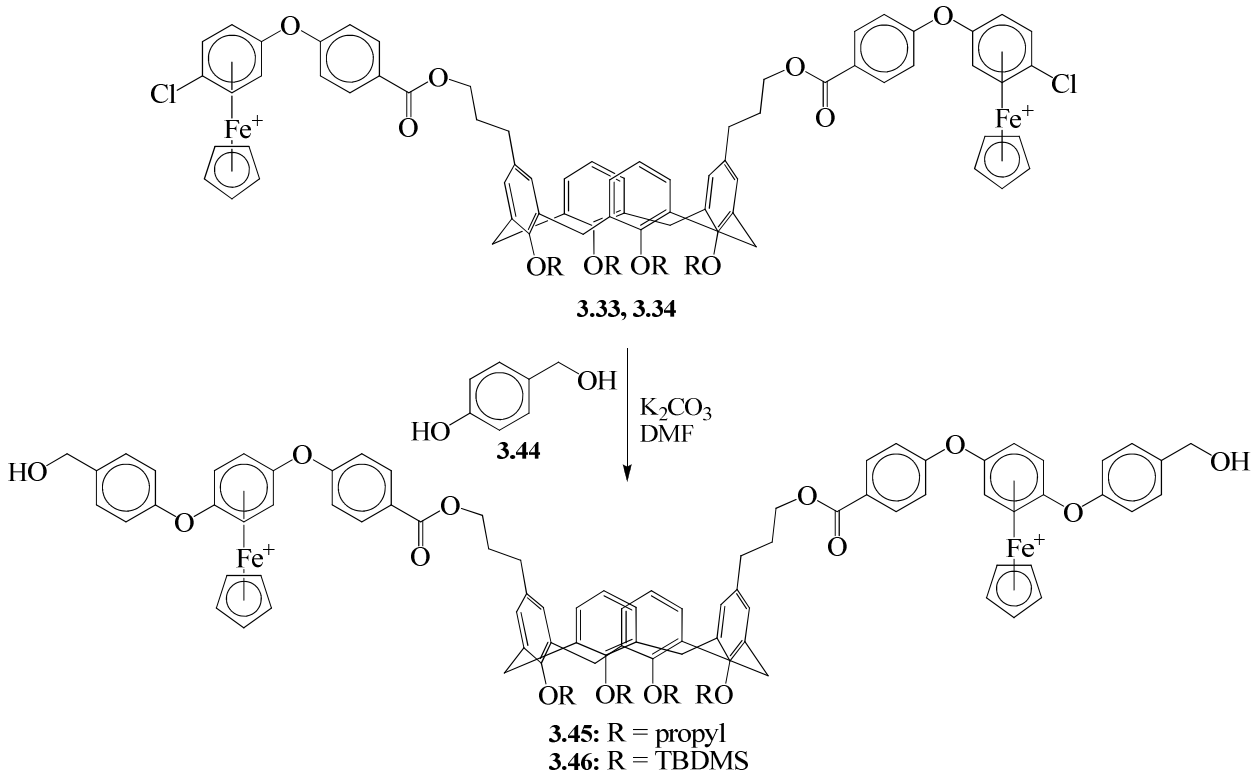
Compound	Reduction Potential (V)	Oxidation Potential (V)	$E_{1/2}$ (V)
3.41	-1.764	-1.618	-1.691
3.42	-1.49	-1.17	-1.33
3.43	-1.51	-1.19	-1.35

3.2.4 Organometallocalix[4]arenes-containing neutral and cationic organoiron species

Incorporation of different organoiron groups into the same complex can give unique electrochemical properties. The incorporation of both ferrocene and arene complexed cyclopentadienyliron complexes into the same compound may provide materials that possess the properties of both cationic and neutral organoiron species. The incorporation of both cationic and neutral ferrocene may lead to new electrochemical behaviour due to communication between the metal centres.

3.2.4.1 Di-Upper Rim Functionalized Calix[4]arene containing Neutral and Cationic Organoiron Species

The reaction of bimetallic upper rim functionalized calix[4]arenes **3.33** and **3.34** with 4-hydroxybenzyl alcohol (**3.49**) gave metallocalix[4]arenes that possess terminal primary aliphatic alcohols (Scheme 3-28). The ^{1}H NMR spectrum clearly shows the incorporation of the benzylic group due to the presence of a singlet centered around 4.70 ppm. This singlet is due to the benzyl methylene group. Figure 3-60 shows the ^{1}H NMR spectrum of complex **3.45** as a representative sample.



Scheme 3-28: Synthesis of calix[4]arenes 3.45 and 3.46.

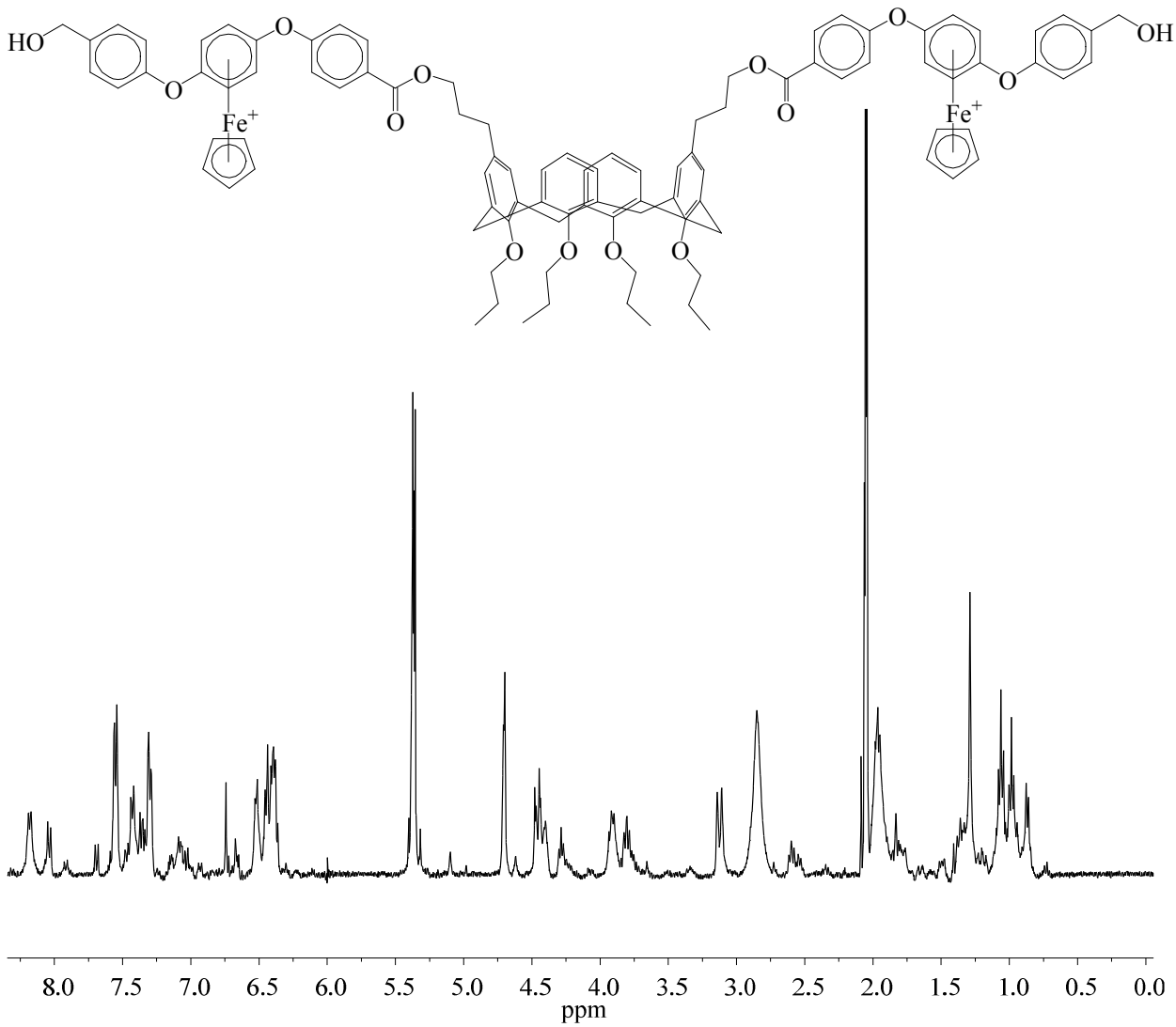


Figure 3-60: 400 MHz ^{1}H NMR spectrum of 3.45.

The ^{13}C NMR spectrum of **3.45** (Figure 3-61) shows that the metal complex was successfully substituted due to the shift in the resonance of the complexed CH next to the chloro group from 80.90 ppm to 76.77 ppm caused by replacing the chlorine with a phenolic group.

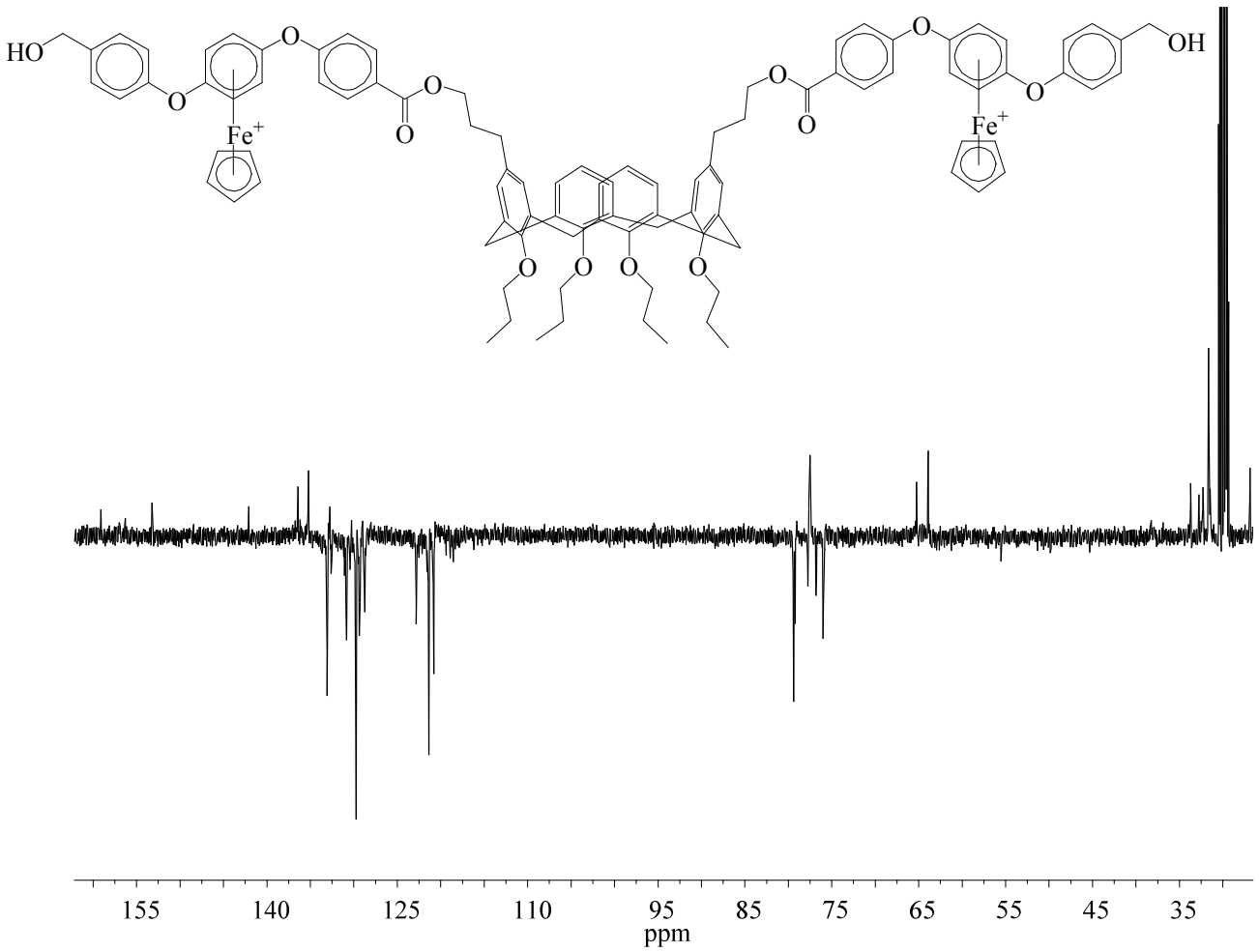
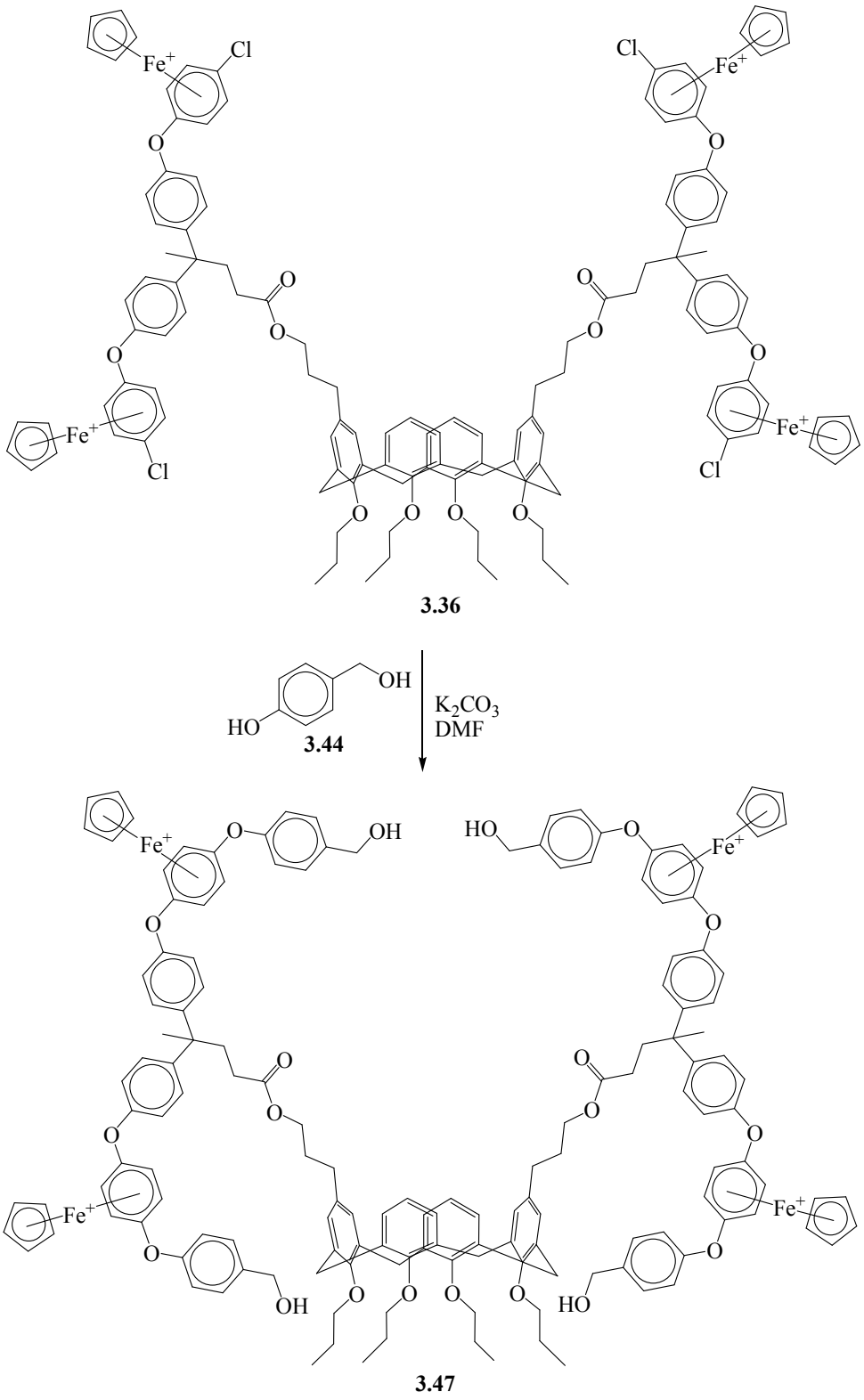


Figure 3-61: ^{13}C NMR spectrum of 3.45.

Using the tetrametallic calix[4]arene (**3.36**) and increasing the amount of 4-hydroxbenzylalcohol four-fold it was possible to prepare the tetra-hydroxy functionalized metallocalix[4]arene **3.47** (Scheme 3-29). Figure 3-62 shows the ^{1}H NMR spectrum of calix[4]arene **3.47**.



Scheme 3-29: Synthesis of calix[4]arenes 3.47.

The ^{1}H NMR spectrum of **3.47** (Figure 3-62) shows the incorporation of the benzyl alcohol group from the resonance at 4.67 ppm due to the benzylic CH_2. Also, the complexed aromatic resonances have collapsed from two doublets to a broad singlet at 6.31 ppm that overlaps some of the calix[4]arene aromatic resonances. This complex is also clearly isolated in the cone conformation due to the doublets caused by the bridging methylenes at 4.44 ppm and 3.11 ppm.

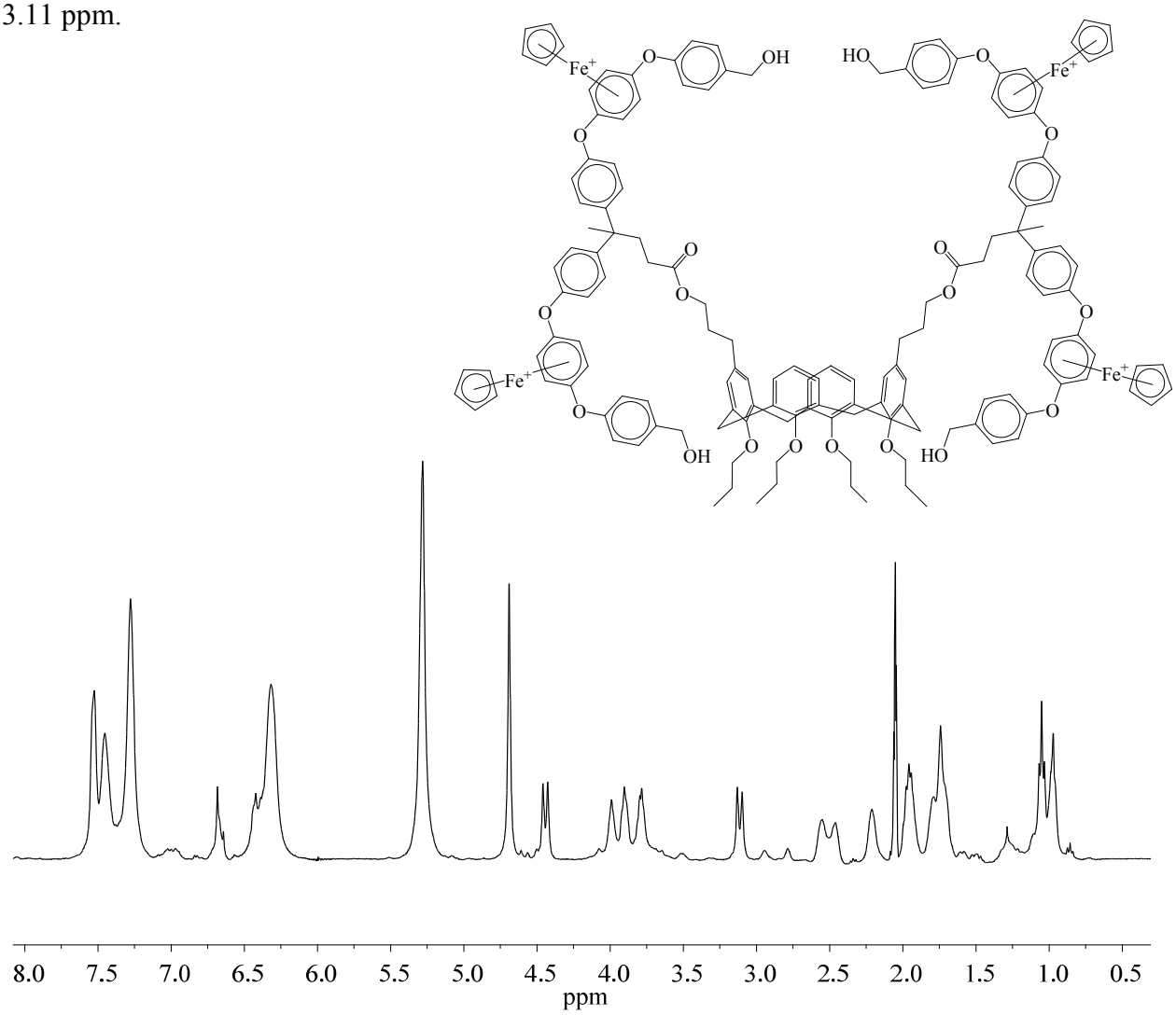


Figure 3-62: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.47.

The HSQC spectrum (Figure 3-63) confirms that the broad singlet at 6.31 ppm is due to two sets of CHs on the complexed arene, as this resonance shows correlation to two different carbons at 75.87 ppm and 76.14 ppm, which are in the characteristic range of oxygen substituted

complexed arenes. The benzylic CH_2 proton resonance correlates to a carbon resonance at 63.90 ppm, which is again consistent with the structure of metallocalix[4]arene **3.47**.

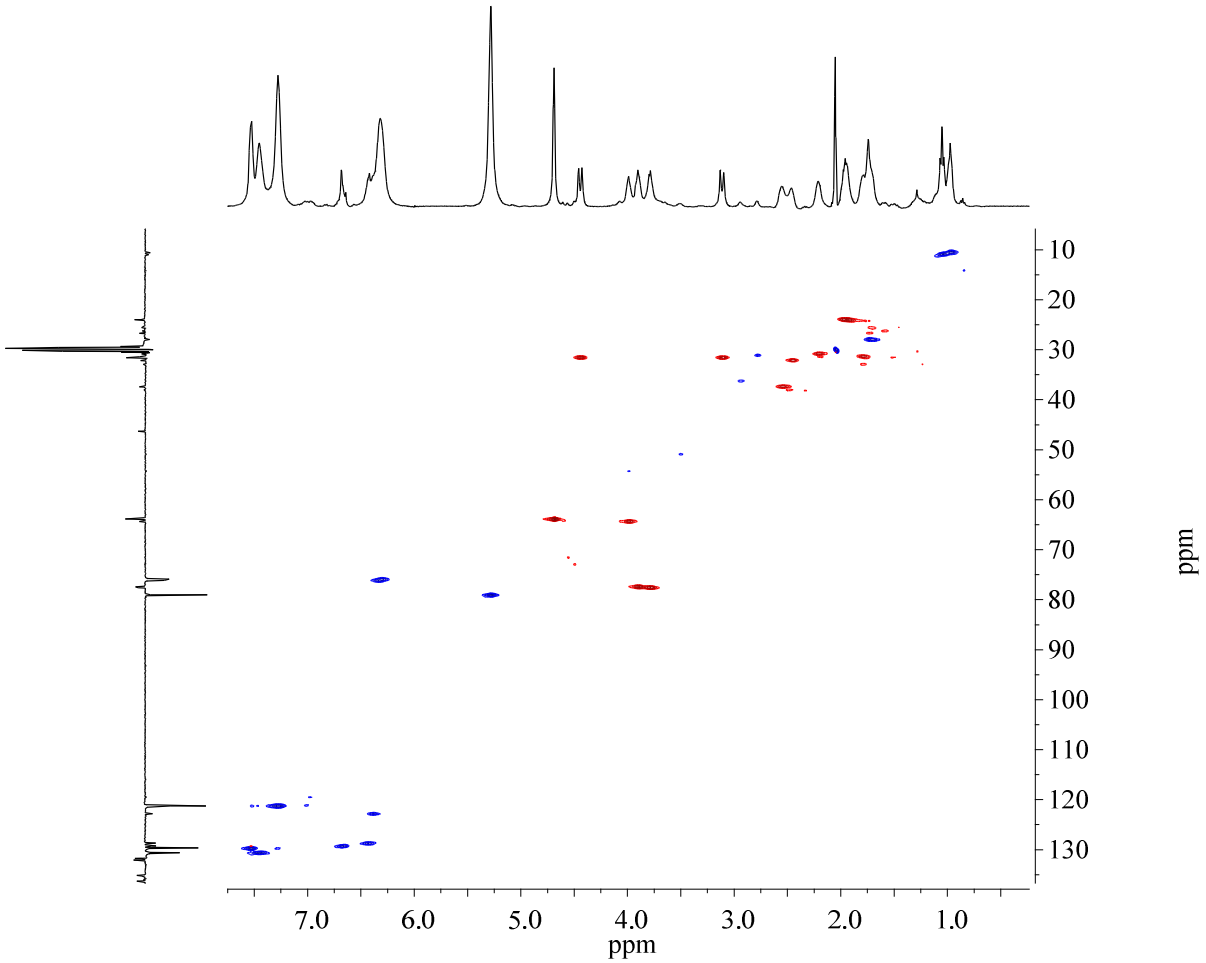
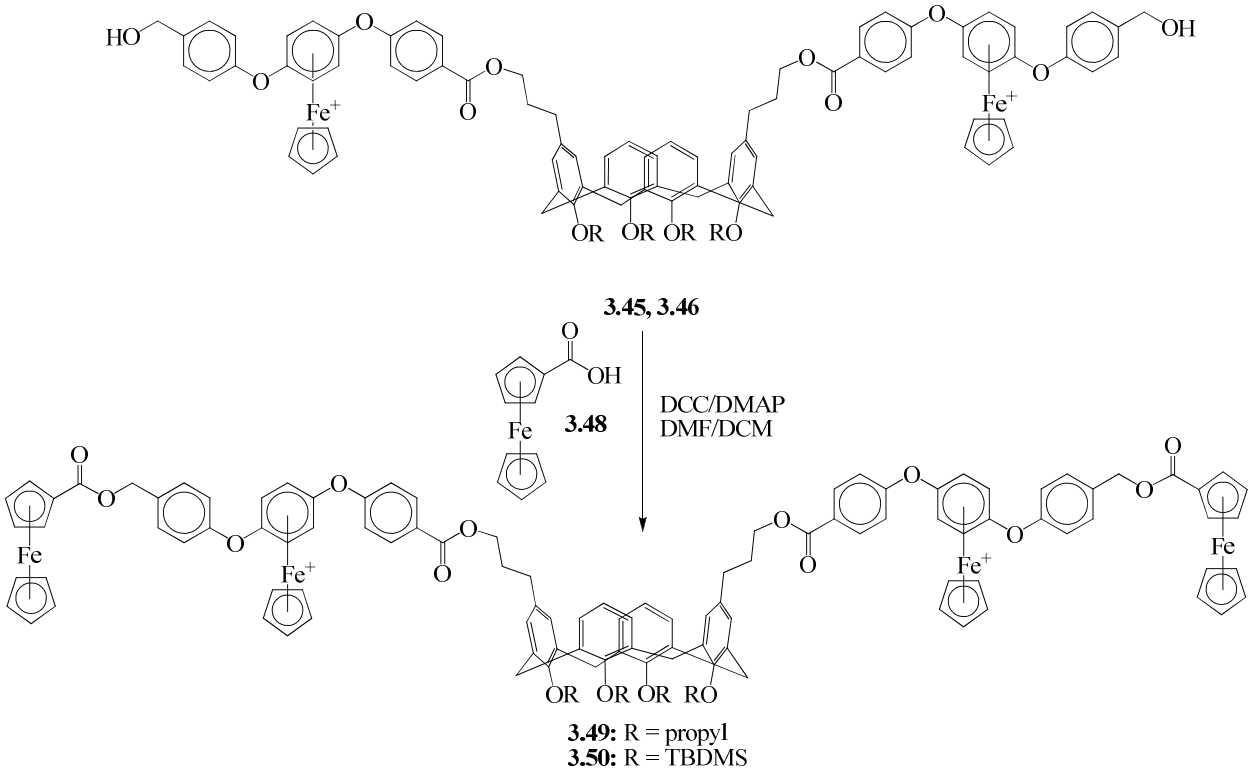


Figure 3-63: HSQC spectrum of calix[4]arene 3.47.

The alcohol groups of metallocalix[4]arenes **3.45 - 3.47** were esterified with ferrocene carboxylic acid. Carboxylic acid ferrocene is readily synthesized by Friedel-Crafts acetylation followed by oxidation with iodine. The ease of synthesis and affordability make it a valuable compound to incorporate ferrocene into the metallocalix[4]arenes. The reaction of alcohol containing metallocalix[4]arenes **3.45** and **3.46** with ferrocene carboxylic acid (**3.48**) in the presence of DCC/DMAP gave the ferrocene capped metallocalix[4]arene **3.49** and **3.50** (Scheme

3-30). These metallocalix[4]arenes were orange in colour rather than yellow due to the incorporation of the ferrocene moiety.



Scheme 3-30: Synthesis of calix[4]arene 3.49 and 3.50.

The ^{1}H NMR spectrum of **3.49** (Figure 3-64) confirmed complete synthesis due to the presence of a new Cp resonance at 4.15 ppm due to the non-functionalized Cp ring of the ferrocene as well as by the two resonances due to the functionalized Cp ring at 4.81 ppm and 4.48 ppm. The benzylic CH_2 resonance has also shifted to overlap with the cationic iron Cp at 5.33 ppm, this is confirmed using HSQC spectroscopy (Figure 3-65), which showed two carbon resonances correlating to the proton resonance at 5.33 ppm.

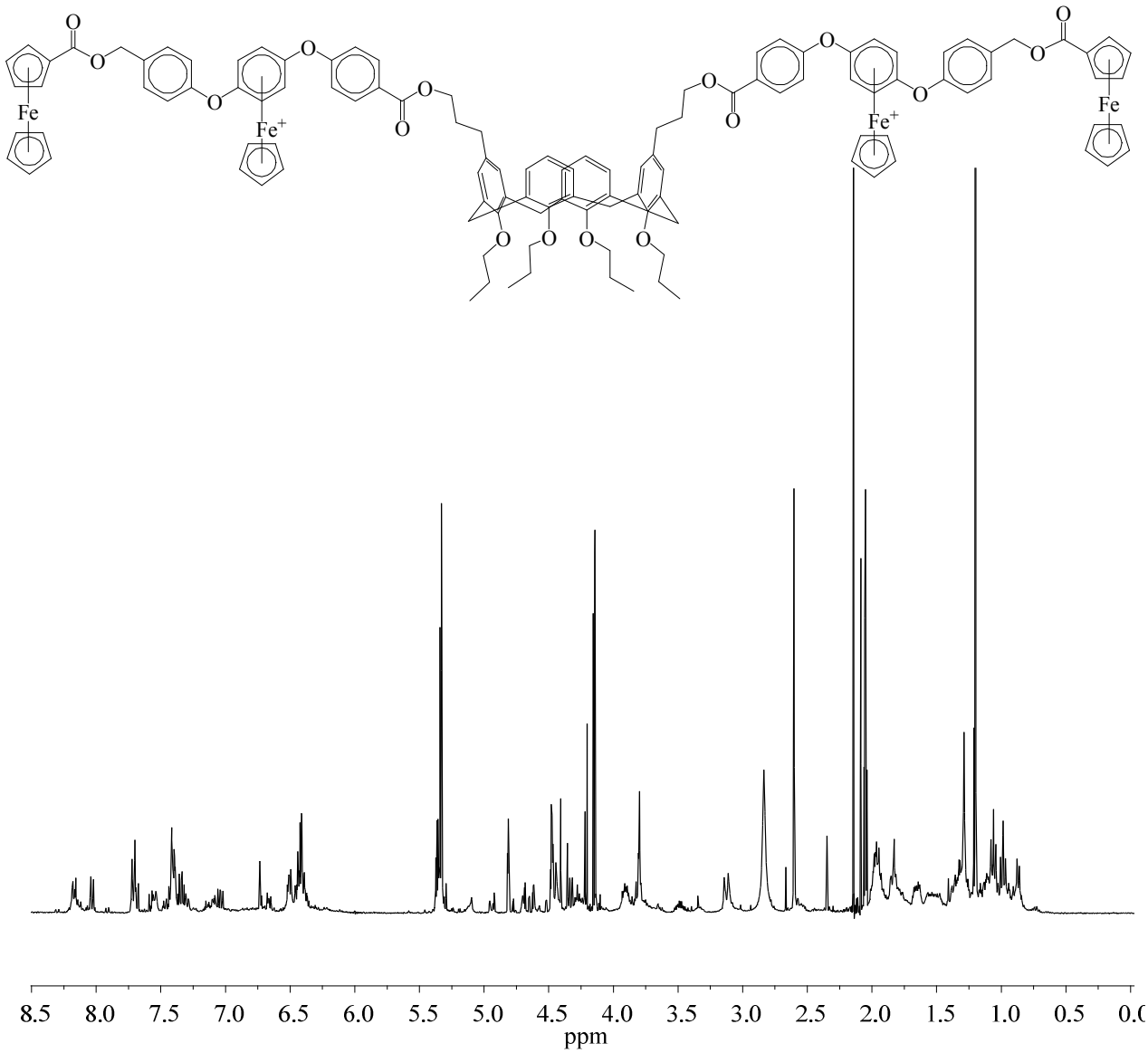


Figure 3-64: 400 MHz ^{1}H NMR spectrum of complex 3.49.

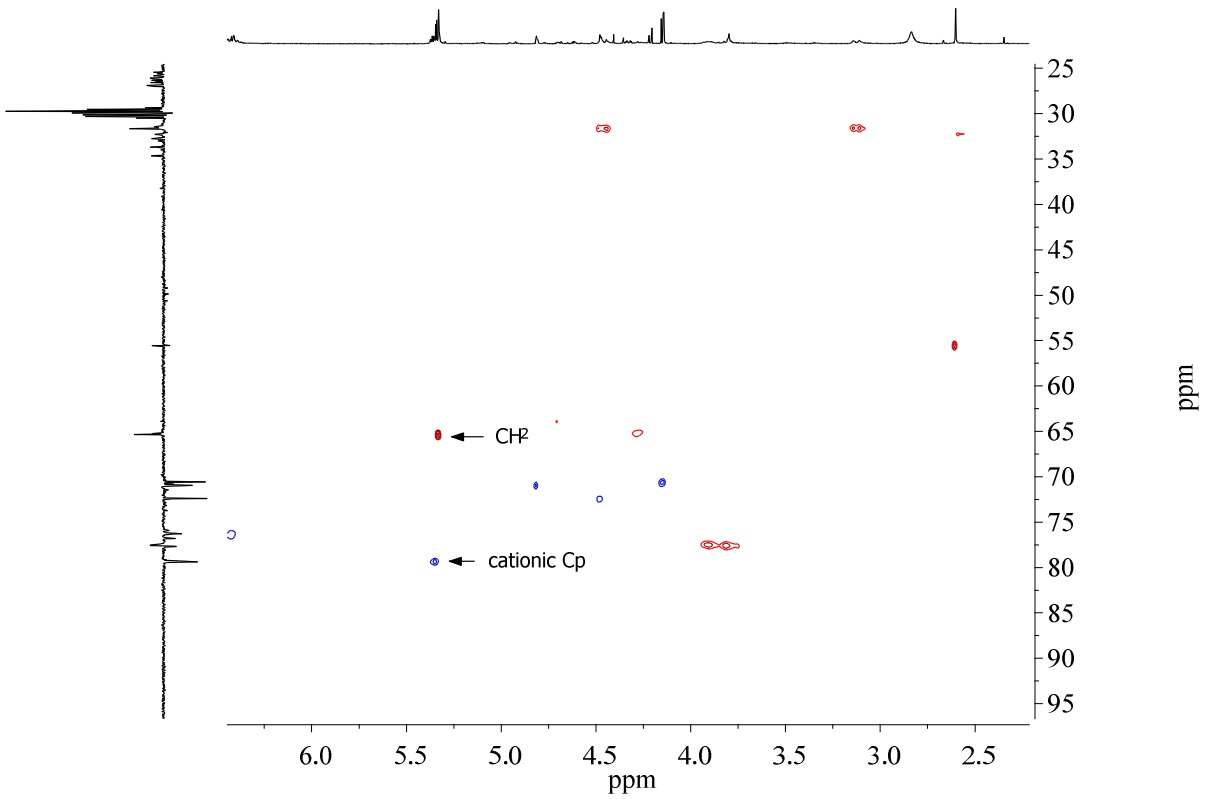
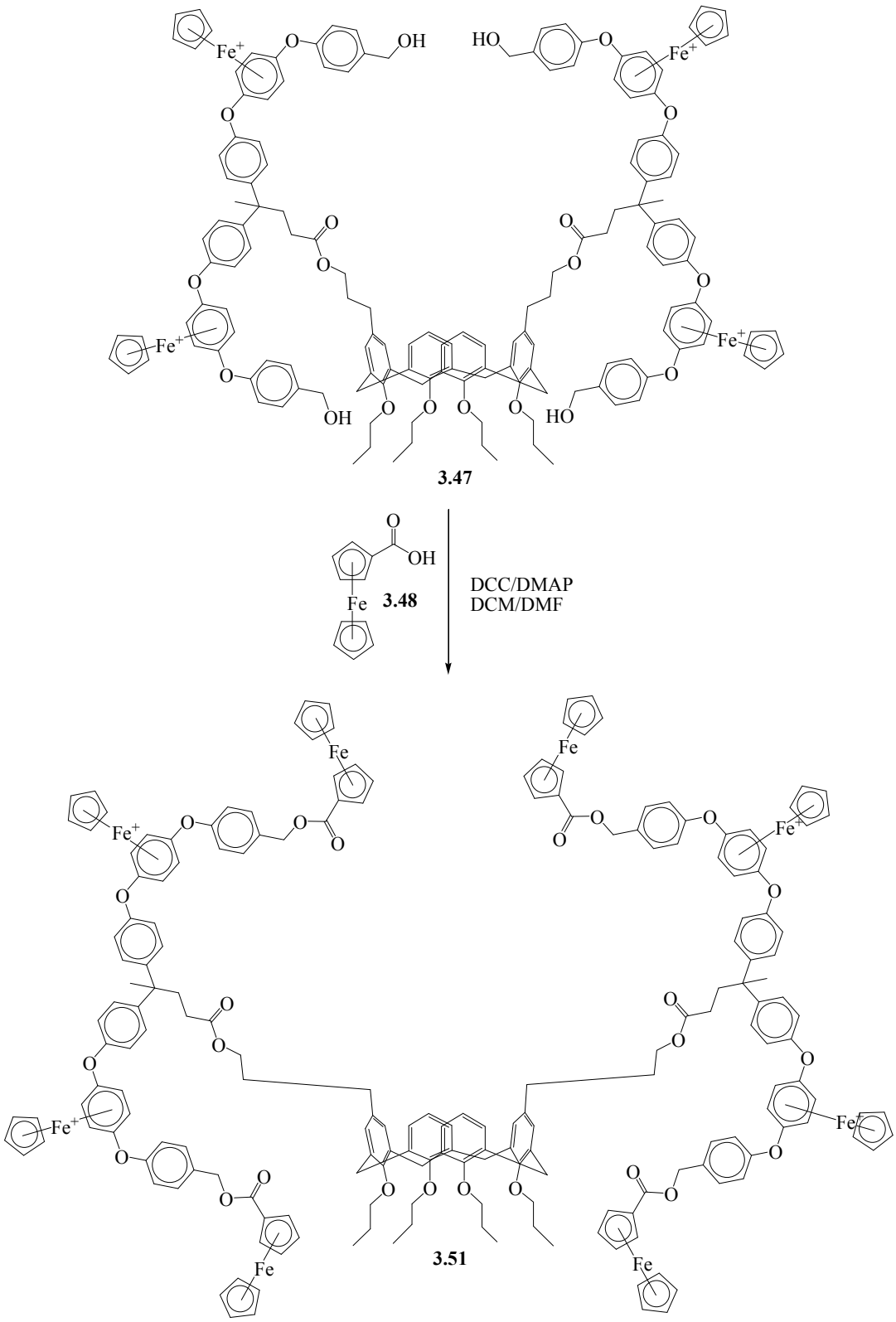


Figure 3-65: Expanded HSQC spectrum of 3.49.

The ^{13}C NMR spectrum of **3.49** and the ^{1}H NMR spectrum corroborated the proposed structure of **3.49**. The new ferrocene Cps appear at 72.43 ppm and 70.96 ppm (functionalized Cp) and 70.56 ppm (non-functionalized Cp). The ester CH_2 appears at 65.38 ppm which is a large shift from its analogous alcohol at 63.96 ppm. This shift is clearly due to the increased electron withdrawing nature of the ester.

Similarly the octa-metallic species containing four arene-cyclopentadienyliron moieties and four ferrocene moieties was prepared by reacting metallocalix[4]arene **3.47** with carboxylic ferrocene (Scheme 3-31). These compounds were also orange in colour and were highly soluble in organic solvents. The ^{1}H NMR spectrum of calix[4]arene **3.51** is shown in Figure 3-66.



Scheme 3-31: Synthesis of calix[4]arene 3.51.

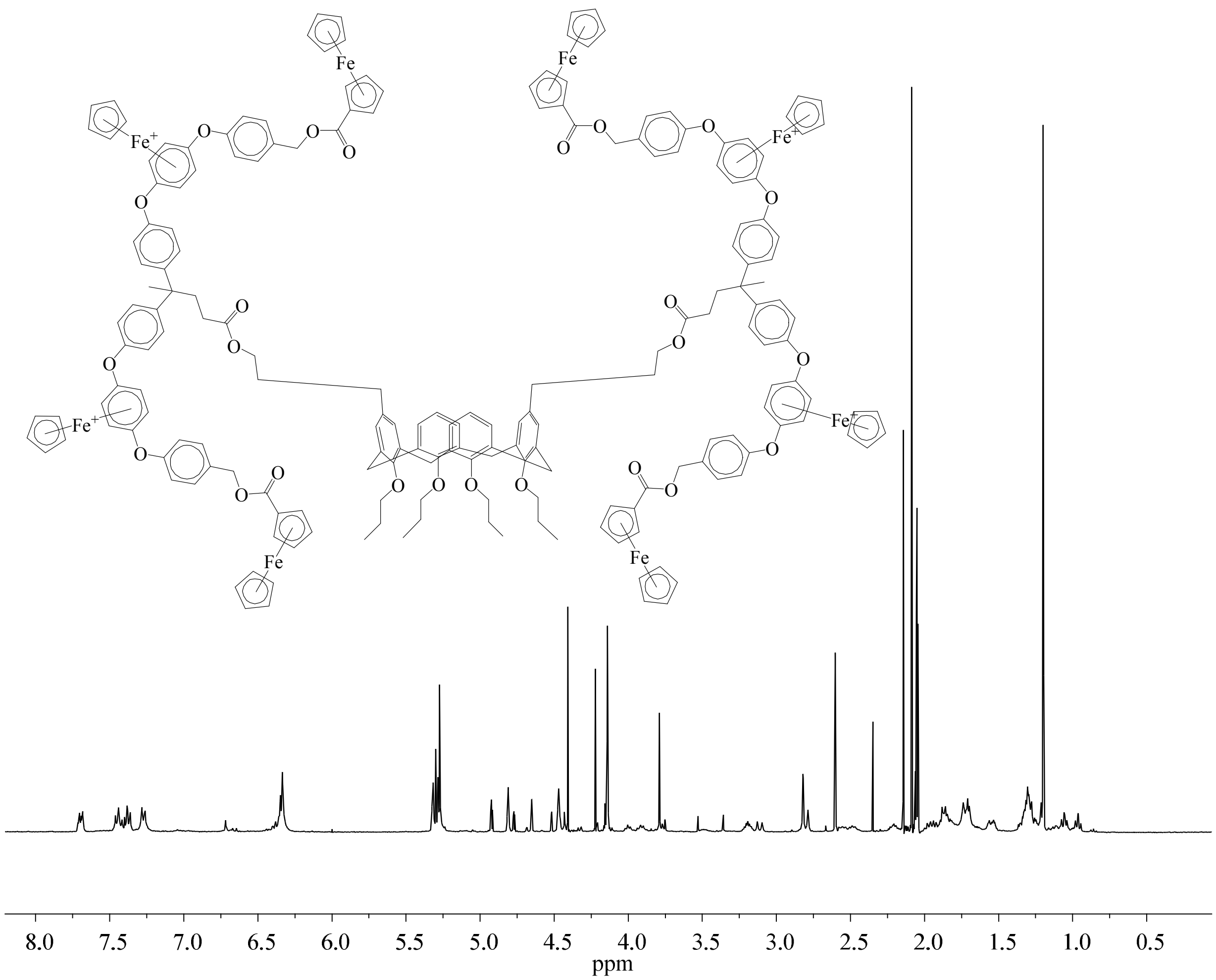
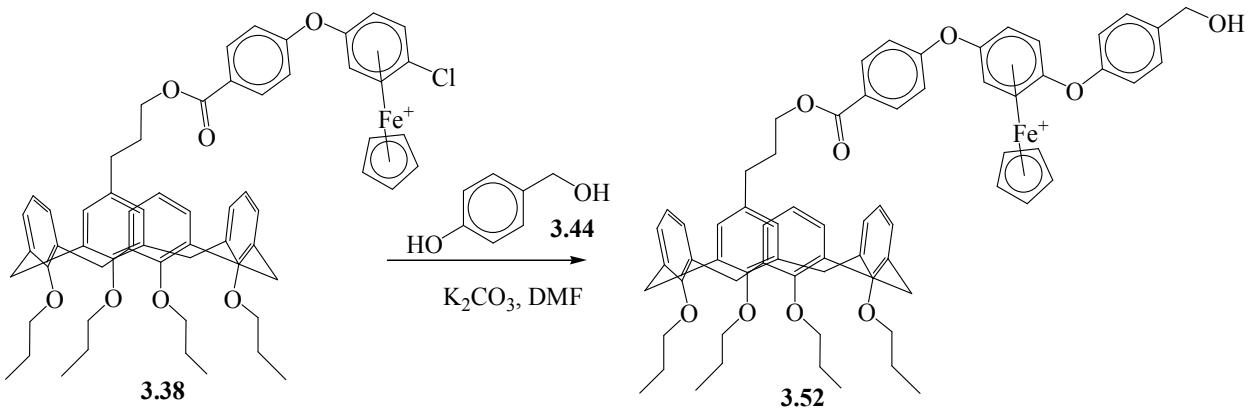


Figure 3-66: 400 MHz ^{1}H NMR spectrum of metallocalix[4]arene 3.51.

3.2.4.2 Mono and upper rim functionalized calix[4]arenes containing cationic and neutral organoiron species

Using the metallocalix[4]arene containing a single cationic iron centre (**3.38**) it was possible to prepare a metallocalix[4]arene containing a single terminal alcohol group. This was achieved by reacting calix[4]arene **3.38** with 4-hydroxybenzyl alcohol (**3.44**) (Scheme 3-32). This produced the alcohol terminated calix[4]arene (**3.52**) in high yields.



3.38 3.52

Scheme 3-32: Synthesis of calix[4]arene 3.52.

The ^{1}H NMR spectrum (Figure 3-67) shows the presence of the benzyl alcohol group from the resonance at 4.70 ppm. There are however two calix[4]arene conformers in this product (discussed previously for the mono-functionalized calix[4]arene), as shown by the two different benzyl alcohol resonances (second resonance at 4.715 ppm). Based on the integration ratios of the benzyl alcohol peaks there is a 2:1 ratio of conformers. Also, there is a shift in the complexed aromatics between the benzyl alcohol terminated and chlorine terminated calix[4]arenes. The complex aromatics have shifted from 6.91 ppm and 6.69 ppm in the chloro terminated to 6.51 ppm and 6.39 ppm for the alcohol terminated calix[4]arene.

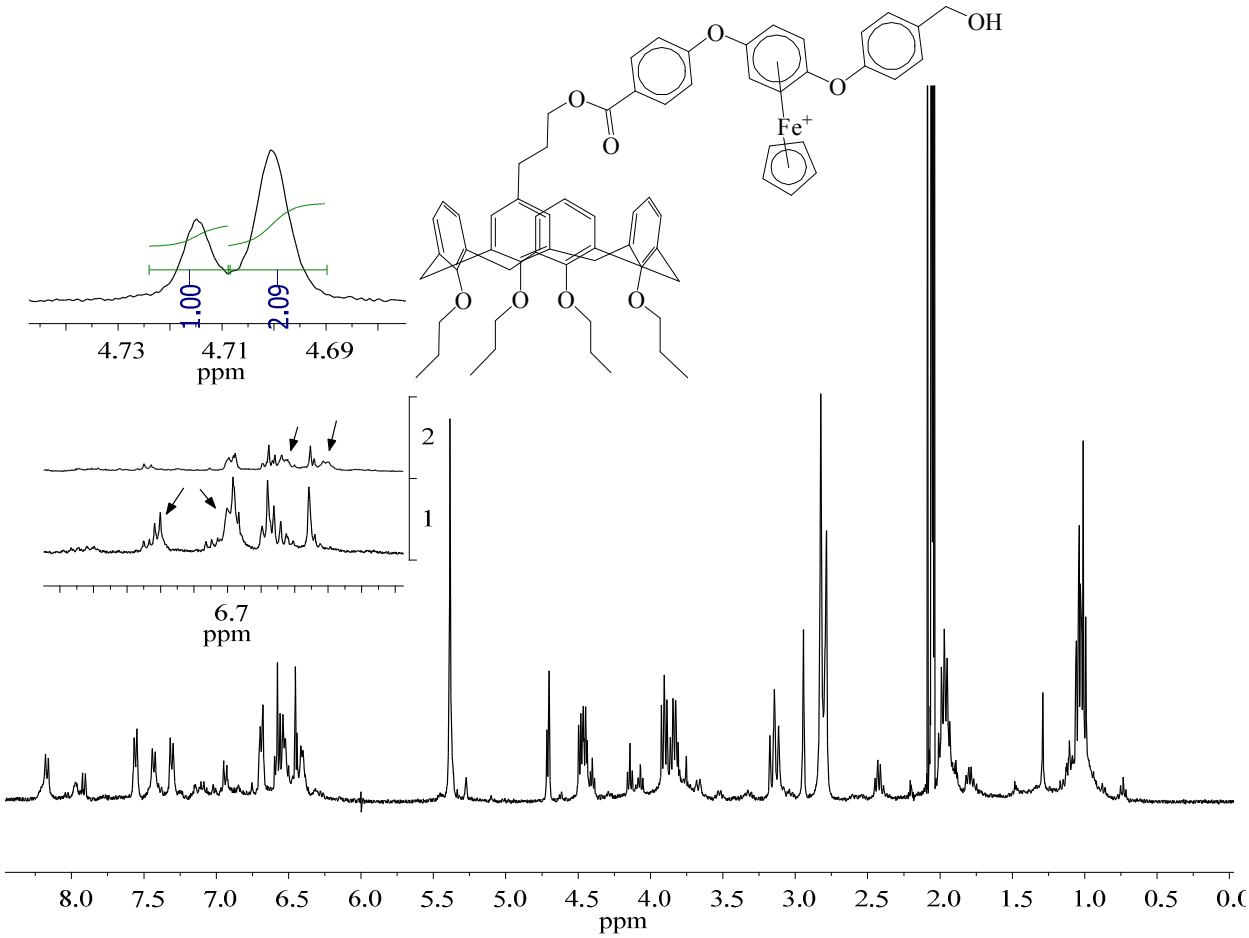


Figure 3-67: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.52.

The HSQC spectrum (Figure 3-68) confirms the formation of the product with the appearance of the benzyl alcohol peak at 63.92 ppm, also the complexed aromatics shifted from 88.26 ppm and 77.92 ppm to 77.75 ppm and 76.06 ppm which is characteristic when chlorine is replaced with oxygen on the complexed arene.

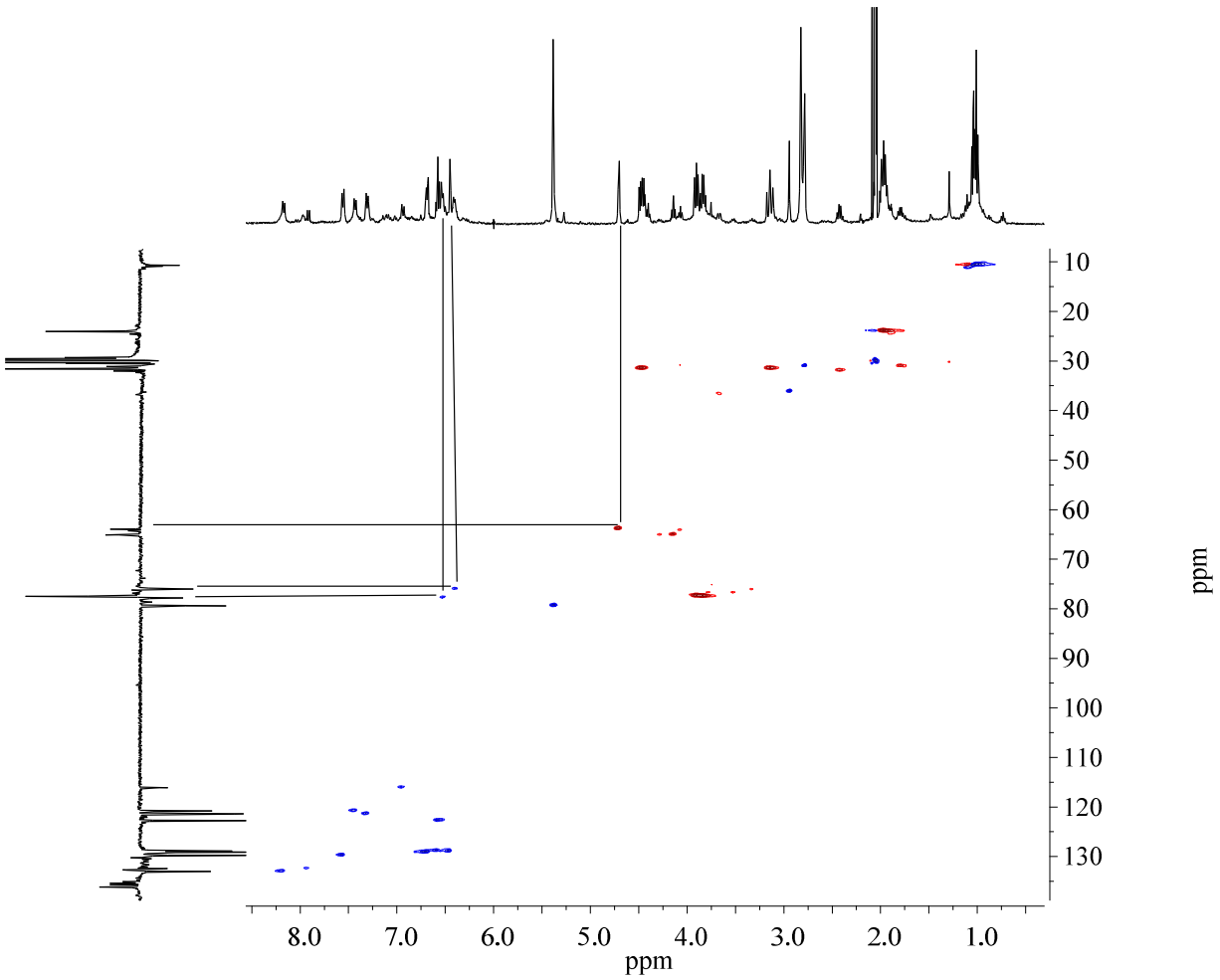
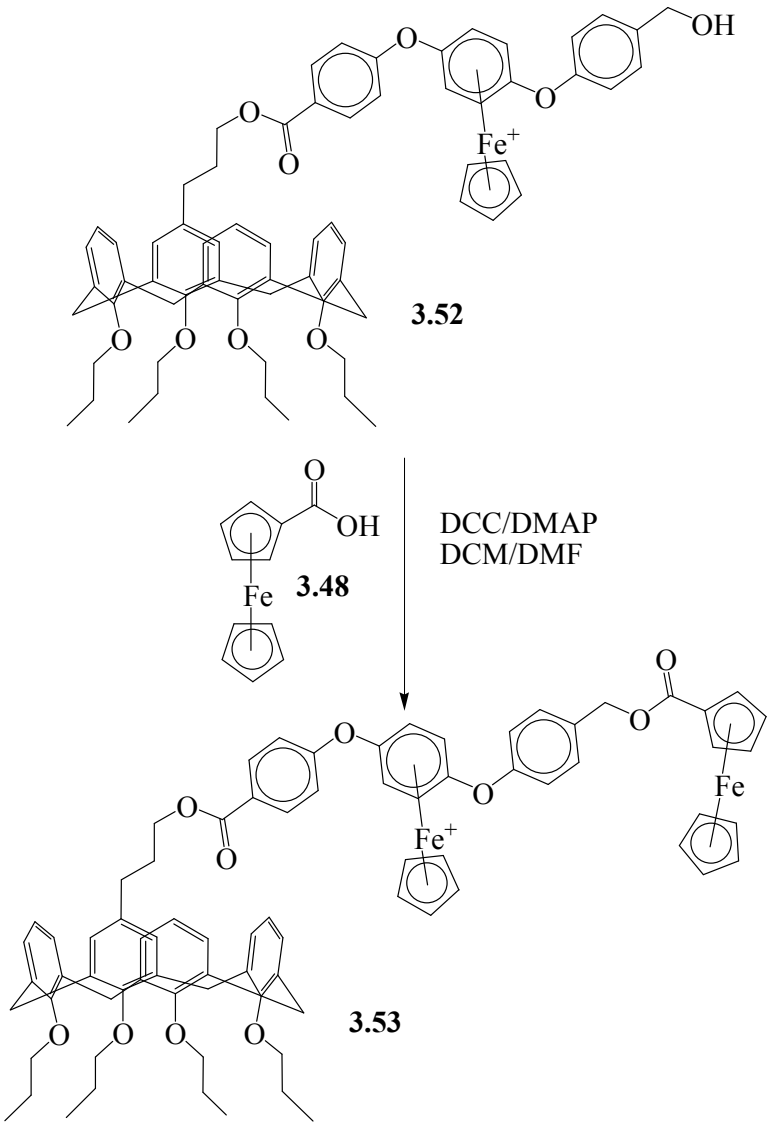


Figure 3-68: HSQC spectrum of calix[4]arene 3.52.

Calix[4]arene (**3.52**) can be "end-capped" with ferrocene to afford the bimetallic calix[4]arene possessing neutral and cationic iron moieties (Scheme 3-33). The ^{1}H NMR spectrum (Figure 3-69) shows the incorporation of the ferrocene moiety by the appearance of resonances at 4.81 ppm, 4.47 ppm, and 4.12 ppm due to the functionalized and non-functionalized cyclopentadienyl rings of the ferrocene carboxylic acid. There is also a dramatic shift in the resonance of the benzyl alcohol CH_2 from 4.70 ppm to 5.33 ppm.



Scheme 3-33: Synthesis of calix[4]arene of 3.53.

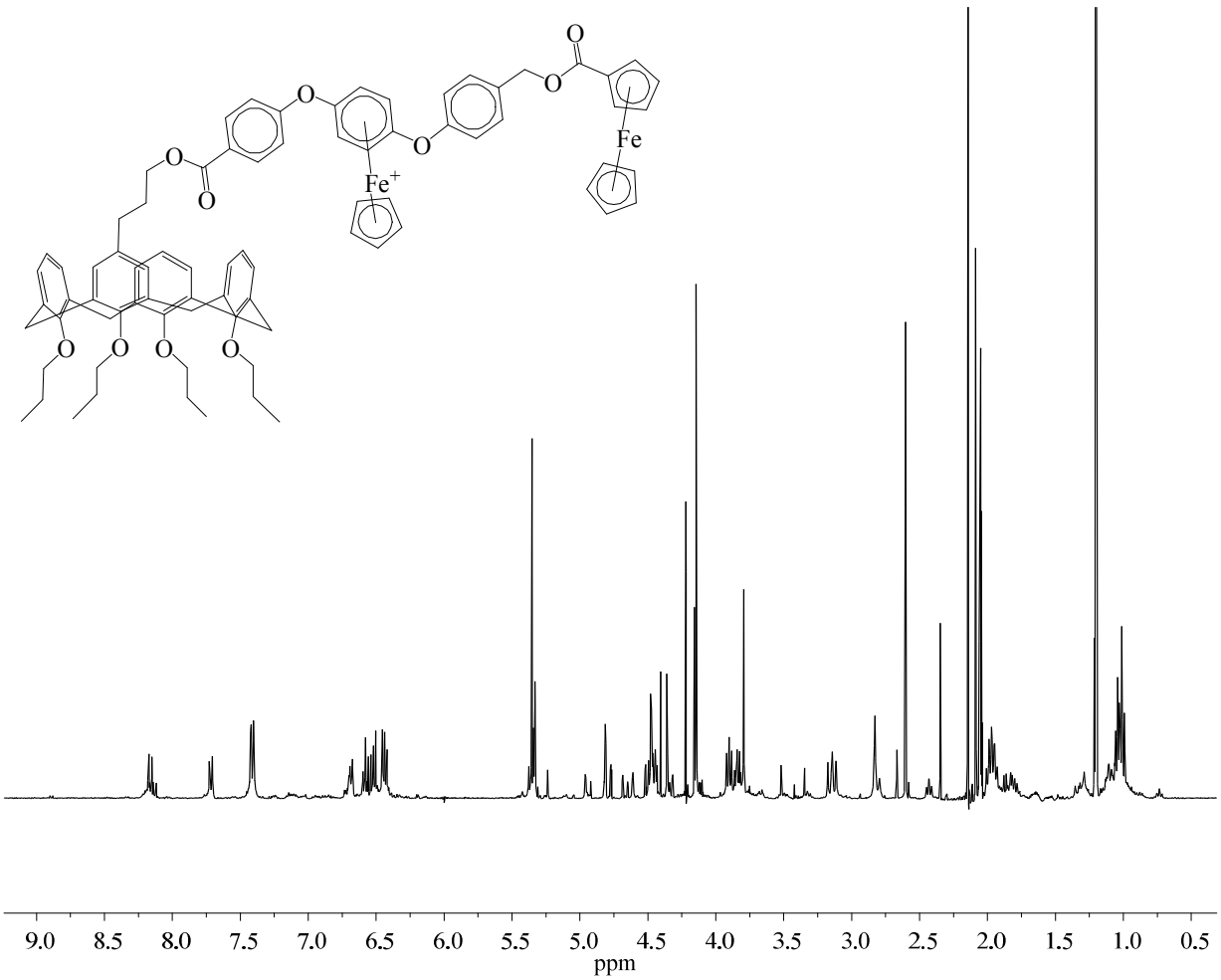
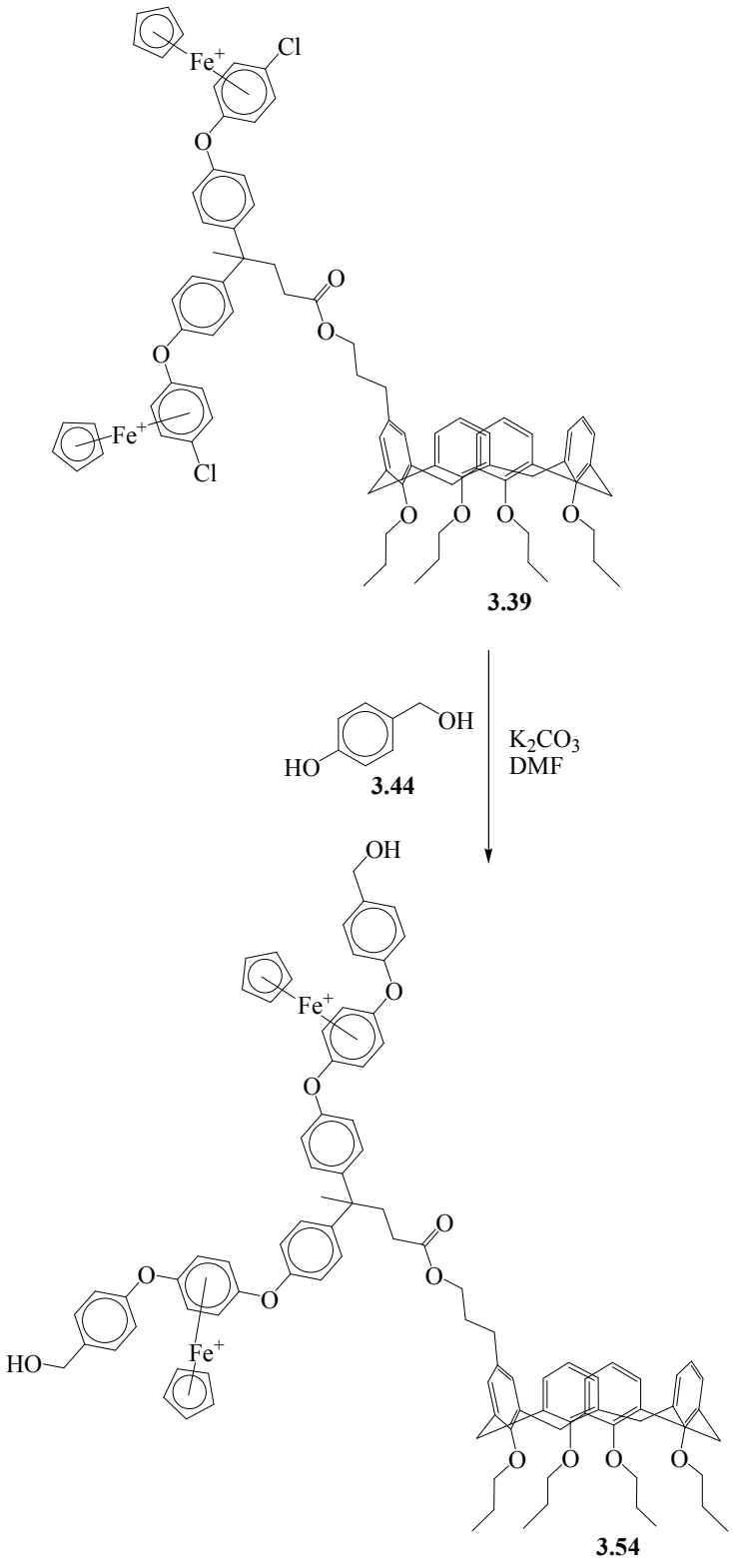


Figure 3-69: 400 MHz ^{1}H NMR spectrum of metallocalix[4]arene 3.53.

Mono-functionalized upper rim calix[4]arenes containing two terminal alcohol groups (**3.54**) were also prepared from the reaction of calix[4]arene **3.39** with 4-hydroxybenzyl alcohol (Scheme 3-34).



Scheme 3-34: Synthesis of calix[4]arene 3.54.

As seen in the ^{1}H NMR spectrum of metallocalix[4]arene **3.54** (Figure 3-70) the CH_2 of the benzyl alcohol group appears at 4.68 ppm. Also the complexed aromatic resonances have

collapsed from two doublets at 6.77 ppm and 6.47 ppm (Figure 3-70 (2)) to a broad singlet at 6.32 ppm (Figure 3-70 (1)).

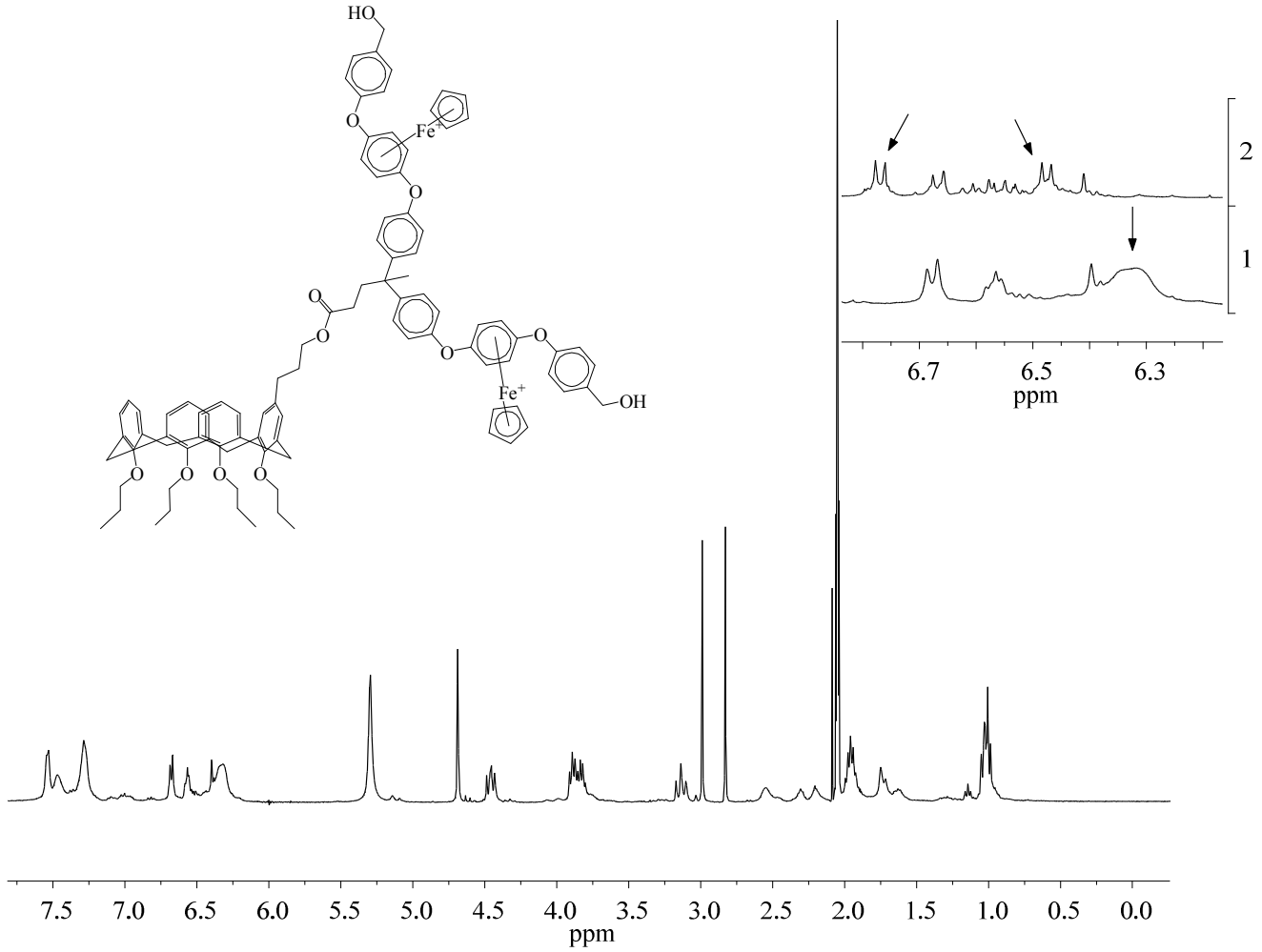


Figure 3-70: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.54.

The HSQC spectrum (Figure 3-71) corroborates the ^{1}H NMR spectrum. The resonance assigned to the benzyl alcohol CH_2 correlates to the peak at 63.82 ppm in the ^{13}C NMR spectrum which is characteristic for this type of group. The broad singlet at 6.32 ppm correlates to two resonances in the ^{13}C NMR spectrum at 76.07 ppm and 76.43 ppm, which are normal resonances for di-oxygen substituted complexed aromatics.

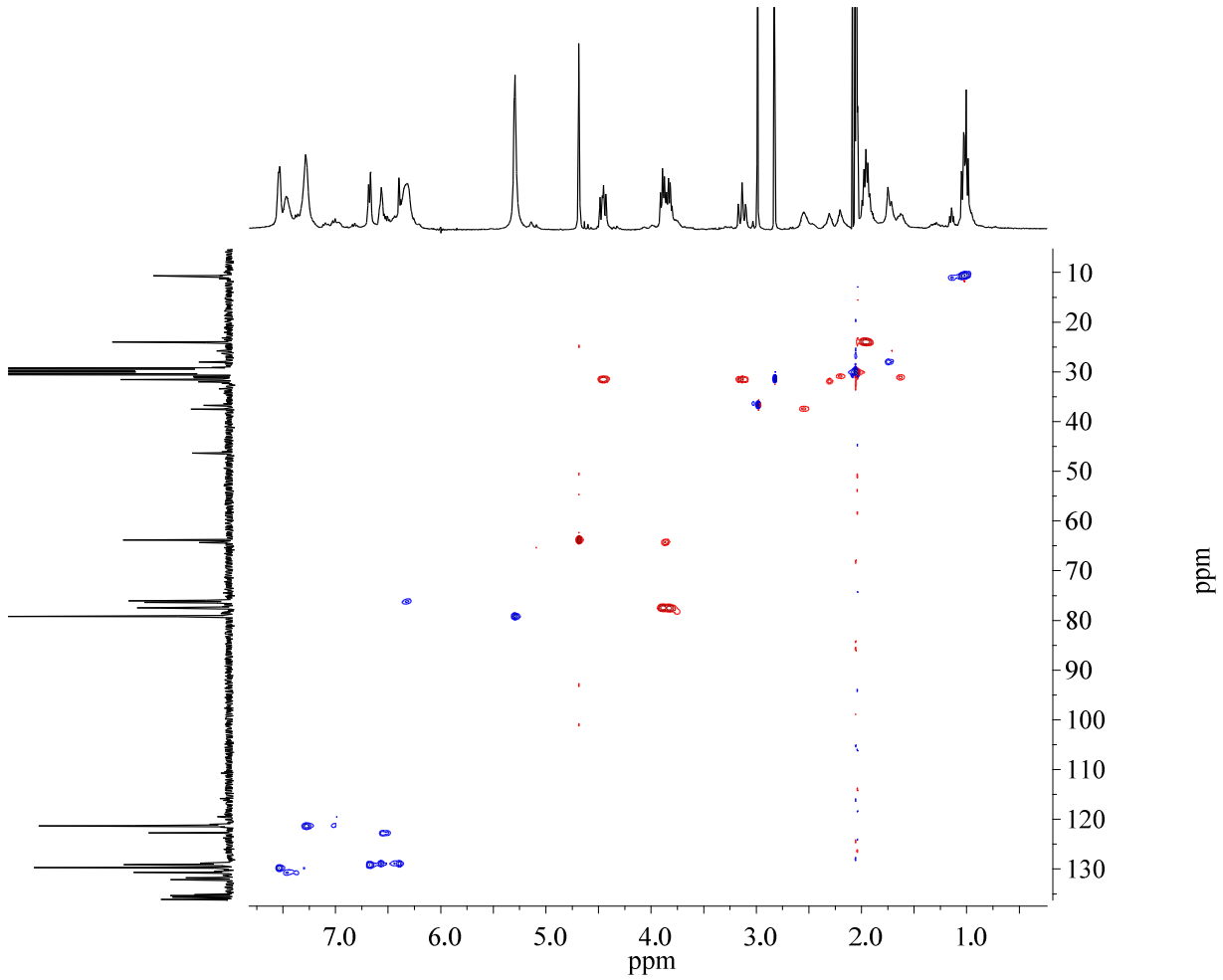
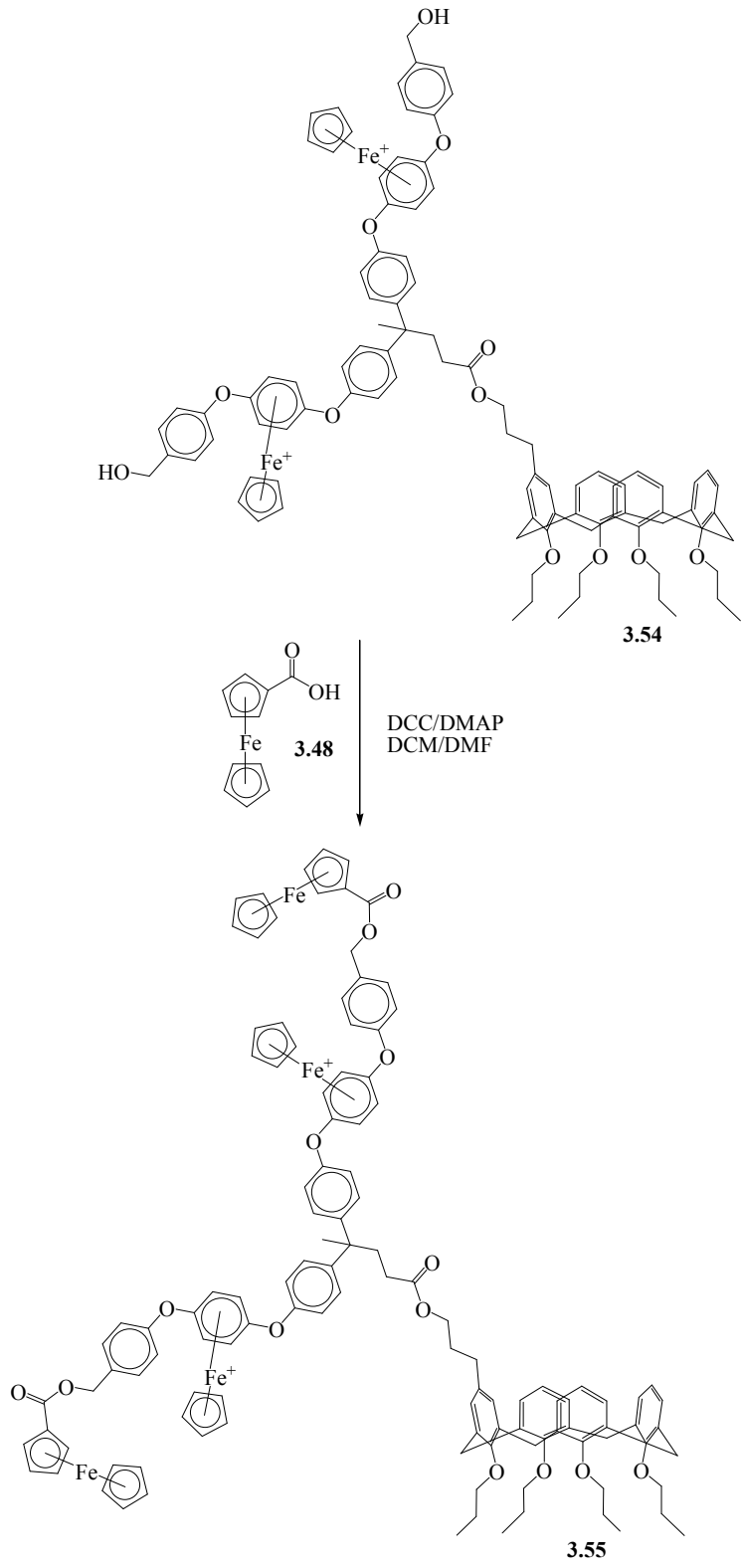


Figure 3-71: HSQC spectrum of calix[4]arene 3.54.

The reaction between calix[4]arene **3.54** and ferrocene carboxylic acid (**3.48**) resulted in the formation of the mono-upper rim functionalized tetra-metallic calix[4]arene containing neutral and cationic iron moieties (**3.55**) (Scheme 3-35).



Scheme 3-35: Synthesis of calix[4]arene 3.55.

The ^{1}H NMR spectrum (Figure 3-72) of calix[4]arene **3.55** shows the incorporation of the neutral ferrocene moiety. The ^{1}H resonances due to the ferrocene appear at 4.81 ppm, 4.47 ppm, and 4.14 ppm. As can be seen, the resonance at 4.47 ppm due to the ferrocene moiety overlaps with the resonance due to one of the bridging methylenes of the calix[4]arene. The incorporation of the ferrocene moiety is further indicated by the shift in the benzyl CH_2 from 4.32 ppm (Figure 3-72(2)) to 5.32 ppm (Figure 3-72(1)) due to the formation of the ester linkage.

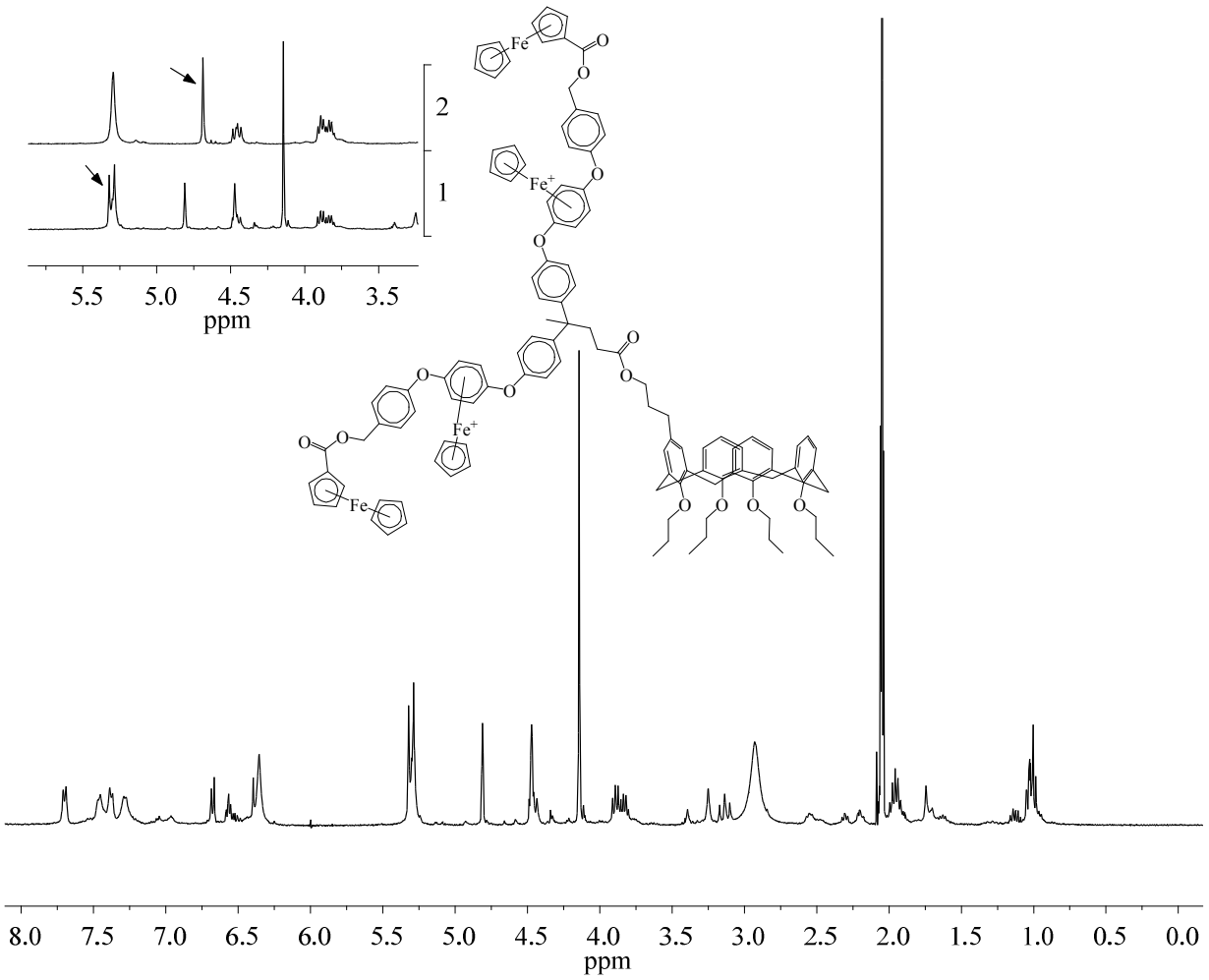


Figure 3-72: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.55.

The HSQC spectrum of calix[4]arene **3.55** (Figure 3-73) allowed for the analysis of the overlapping peaks. The overlapping resonances in the ^{1}H NMR spectrum at 5.30 ppm clearly belong to two different sets of protons on different carbons. This resonance shows correlation to

an evenly protonated carbon at 65.34 ppm (ester carbon) and an oddly protonated carbon at 79.16 ppm (cp of cationic iron complex). The overlapping proton resonance at 4.47 ppm also resolves into two separate correlations in the HSQC spectrum at 31.58 ppm (bridging methylene) and 72.37 ppm (substituted ferrocene Cp).

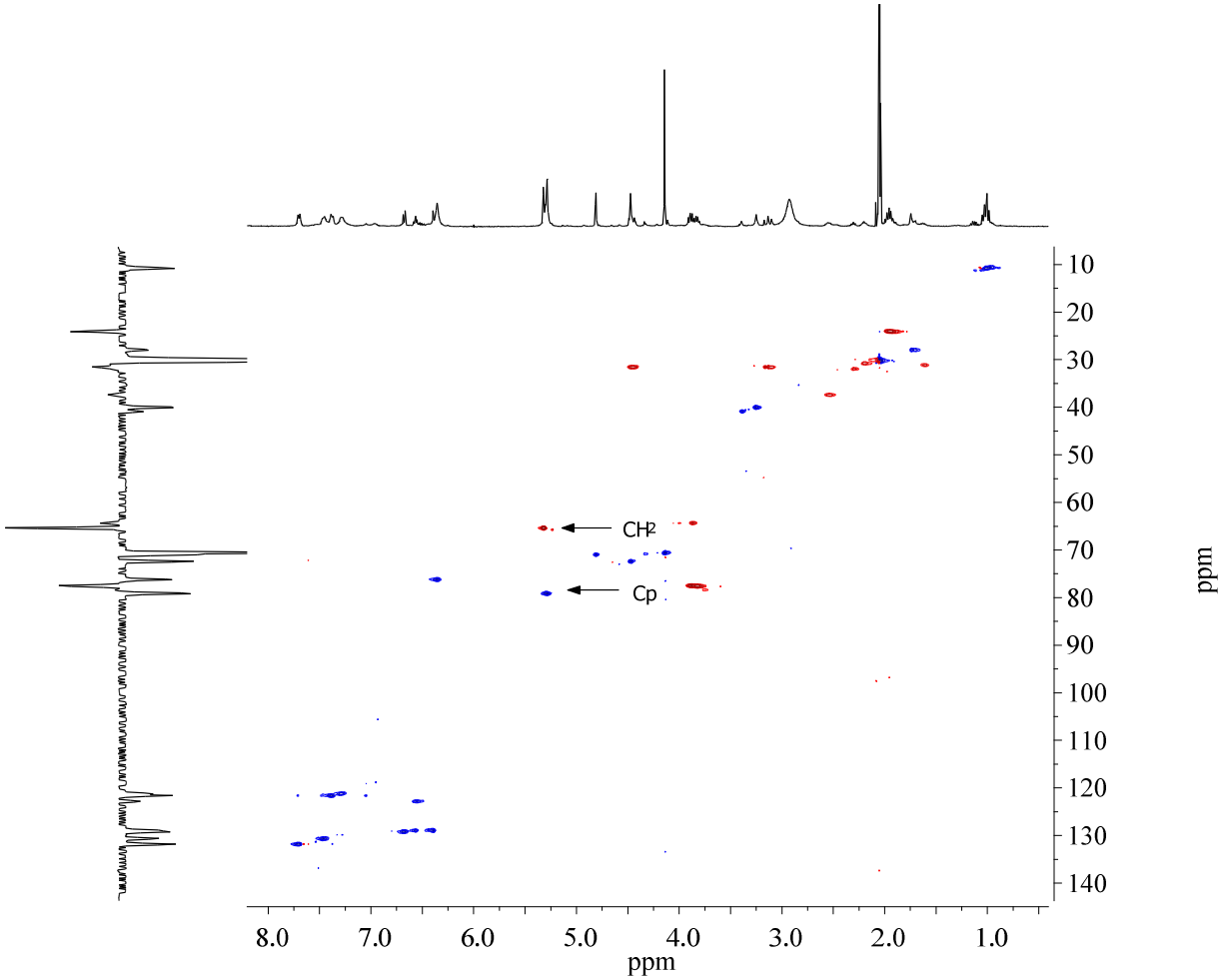


Figure 3-73: HSQC spectrum of calix[4]arene 3.55.

The HMBC spectrum (Figure 3-74) of calix[4]arene **3.55** showed the correlation between the resonances at 5.32 ppm in the ^{1}H NMR spectrum and 171.84 ppm in the ^{13}C NMR spectrum. This correlation indicated connectivity between the CH_2 of the benzyl alcohol and the carbonyl of the ferrocene carboxylic acid.

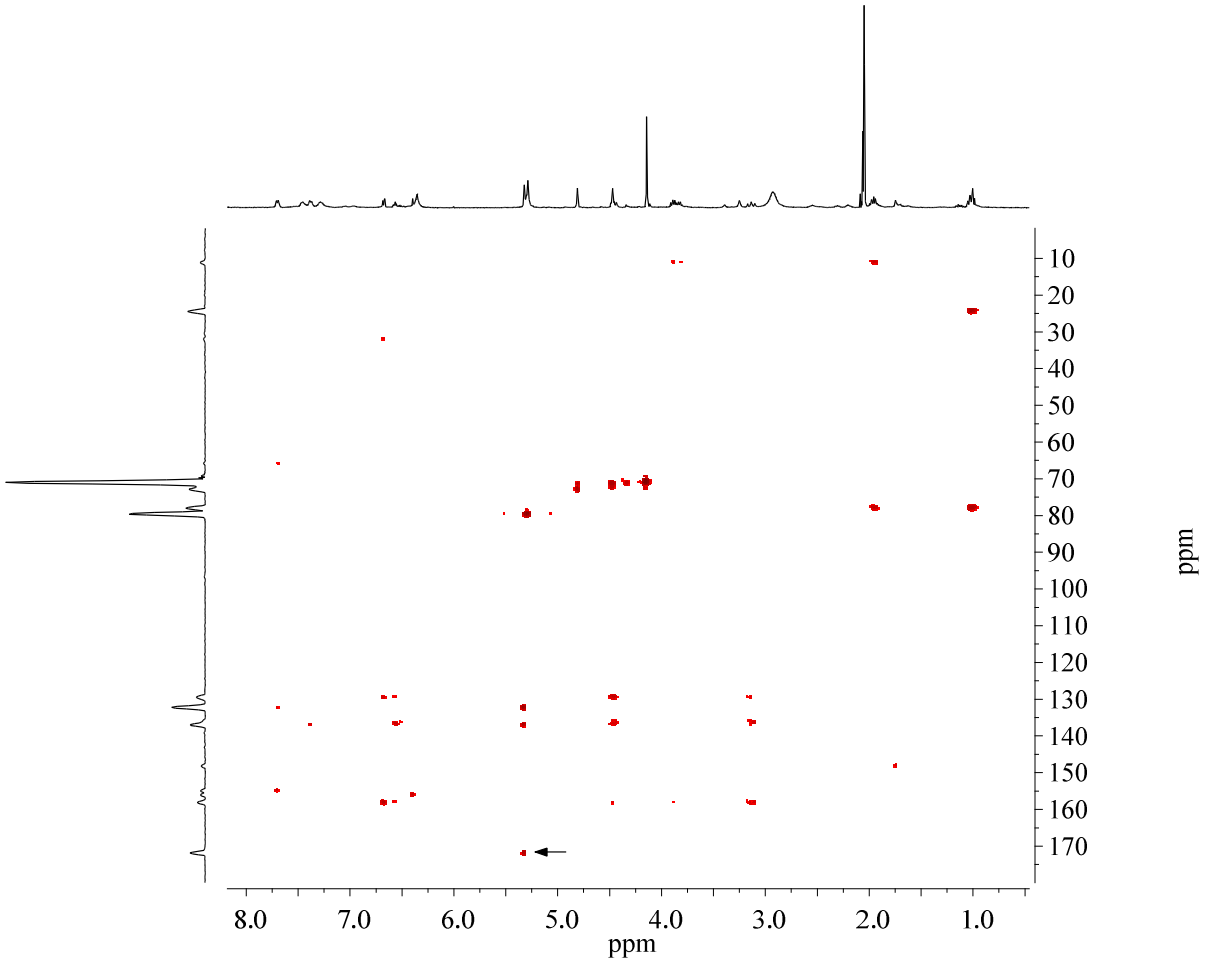


Figure 3-74: HMBC spectrum of calix[4]arene 3.55.

3.2.4.3 Electrochemical Analysis

Cyclic voltammetry was performed on all the benzyl alcohol and ferrocene terminated calix[4]arenes. The redox potentials for compounds **3.45 – 3.55** are tabulated in Table 3-4, the benzyl alcohol terminated calix[4]arenes showed one redox couple for the reduction of the cationic cyclopentadienyliron complex between -1.360 V and -1.560 V. The ferrocene terminated calix[4]arenes show two redox couples, one for the oxidation of ferrocene to ferrocinium and a second for the reduction of the cationic cyclopentadienyliron moiety. The oxidation of the ferrocene moiety occurred between 0.150 V and 0.275 V and the reduction of the cationic cyclopentadienyliron moiety occurred between -1.700 V and -1.835. Comparing the

reduction $E_{1/2}$ potentials between the benzyl alcohol terminated and ferrocene terminated calix[4]arenes, ferrocene terminated calix[4]arene's cationic cyclopentadienyliron moieties were reduced and had a more negative potential. This may indicate some long range influence on the reduction of the cationic group by the ferrocene.

Table 3-4: Redox potentials of calix[4]arene 3.45 - 3.55.

Compound	Reduction Potential (V)	Oxidation Potential (V)	$E_{1/2}$ (V)	Reduction Potential (V)	Oxidation Potential (V)	$E_{1/2}$ (V)
3.45	n/a	n/a	n/a	-1.544	-1.360	-1.542
3.46	n/a	n/a	n/a	-1.688	-1.438	-1.560
3.47	n/a	n/a	n/a	-1.438	-1.284	-1.360
3.49	0.318	0.522	0.420	-1.66	-1.356	-1.508
3.50	0.030	0.306	0.168	-1.920	-1.722	-1.821
3.51	0.150	0.362	0.256	-1.844	-1.649	-1.742
3.52	n/a	n/a	n/a	-1.616	-1.380	-1.498
3.53	0.110	0.194	0.152	-1.880	-1.782	-1.831
3.54	n/a	n/a	n/a	-1.646	-1.414	-1.530
3.55	0.208	0.342	0.275	-1.788	-1.638	-1.713

3.2.5 Calix[4]arene containing polymers

The incorporation of calix[4]arenes into polymeric materials has the potential to create new materials with many unique properties. Polycalix[4]arenes may be useful as solid filtering materials, or find use in metal ion abstraction.

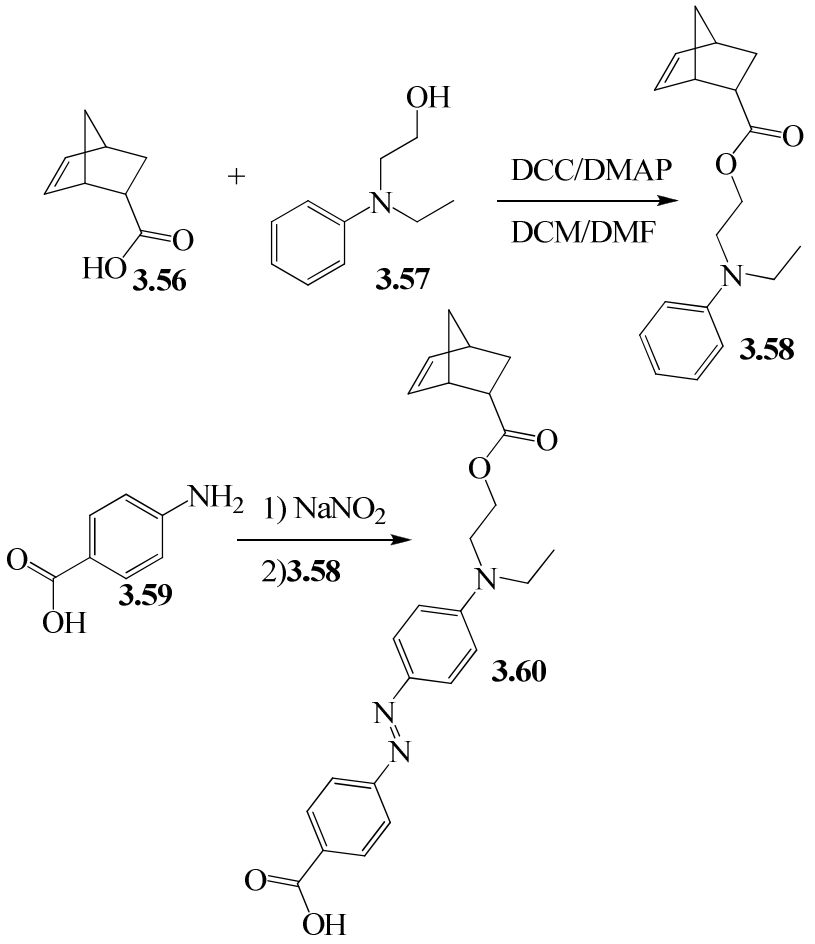
3.2.5.1 Polynorbornene containing calix[4]arenes

Calix[4]arenes **3.30, 3.31** and **3.52** possess terminal alcohol groups, which can undergo further reaction with carboxylic acids. If these groups also contain a polymerizable group, they can then be used to prepare polymers. Functionalized norbornenes were chosen to prepare calix[4]arene monomers as they can be polymerized through ROMP to provide polynorbornenes containing calix[4]arenes in their side chains.

Two types of functionalized norbornene were used to prepare the norbornene containing calix[4]arenes: 5-carboxylic-2-norbornene and an azo dye functionalized norbornene (**3.60**). The azo dye was prepared by first synthesizing a norbornene functionalized N-substituted aniline (**3.58**) by reacting **3.56** with N-ethyl-anilinoethanol (**3.57**) (Scheme 3-36). This reaction yielded compound **3.58**, which was subsequently used to couple to the diazonium salt of 4-aminobenzoic acid (Scheme 3-36).

The ^{1}H NMR spectrum of compound **3.60** (Figure 3-75) showed the resonances of the aryl groups as doublets centered on 8.20 ppm, 7.89 ppm, 7.88 ppm, and 6.79 ppm. The olefin resonances of the norbornene unit appear as two sets of doublets of doublets, however, since a mixture of exo:endo norbornene was used there are four sets of doublets of doublets. These appear at 6.17 ppm and 5.88 ppm (endo) and 6.12 ppm and 6.07 ppm (exo), the resonances due to the aliphatics of the aniline appear at 4.29 ppm (exo), 4.23 ppm (endo), 3.67 ppm (exo), 3.63 (endo), 3.51 ppm and 1.24 ppm. The exo:endo resonances for the non-functionalized aliphatics

of the aniline overlap so only one chemical shift could be determined. This azo dye displayed a λ_{max} at 438 nm in DMF, which shifted to 548 ppm in the presence of acid.



Scheme 3-36: Synthesis of norbornene containing azo dye 3.60.

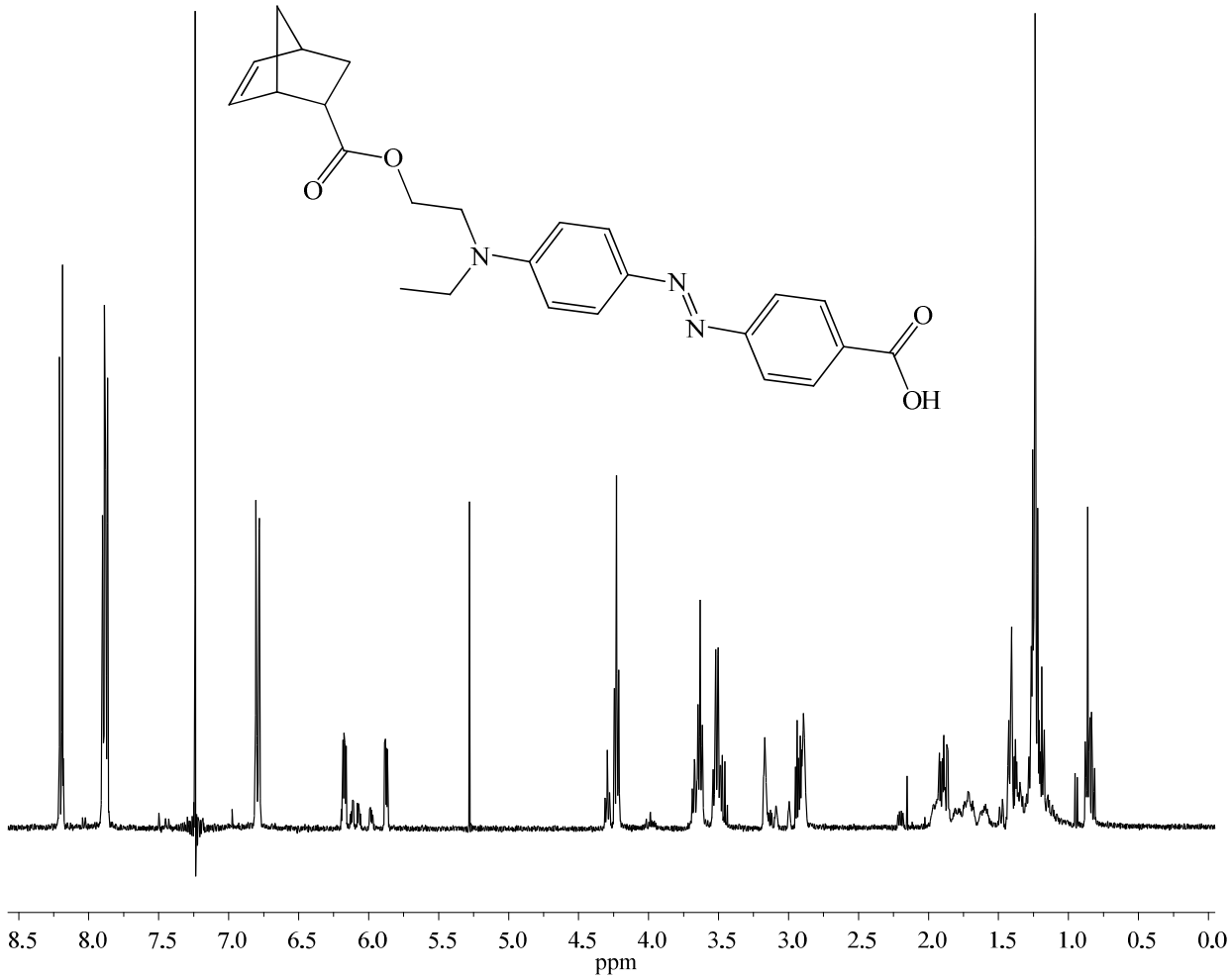
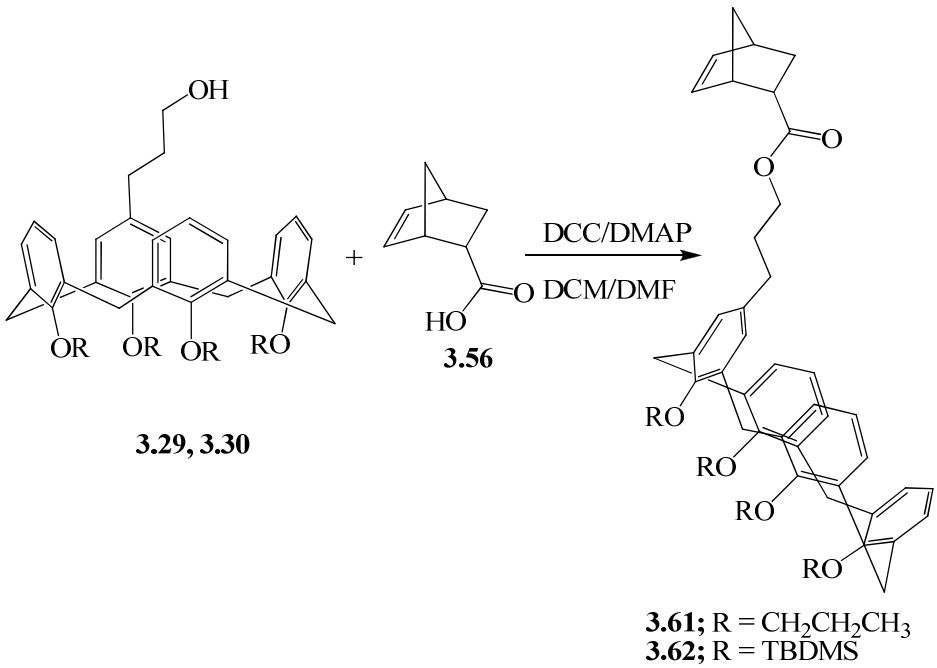


Figure 3-75: 400 MHz ^{1}H NMR spectrum of azo dye 3.60.

Calix[4]arene **3.29** and **3.30** were reacted with 5-carboxylic-2-norbornene to afford calix[4]arenes **3.61** and **3.62** with the norbornene attached through an ester to the upper rim of the calix[4]arene (Scheme 3-37). These compounds were obtained as mixtures of calix[4]arene conformers as well as mixtures of norbornene isomers since endo/exo norbornene was used.



Scheme 3-37: Synthesis of calix[4]arene 3.61 and 3.62.

The ^{1}H NMR spectrum of calix[4]arene **3.61** is shown in Figure 3-76. It can be seen that the norbornene was successfully incorporated from the resonances due to the olefinic peaks at 6.19 ppm and 5.98 ppm (endo) and 5.92 ppm (exo).

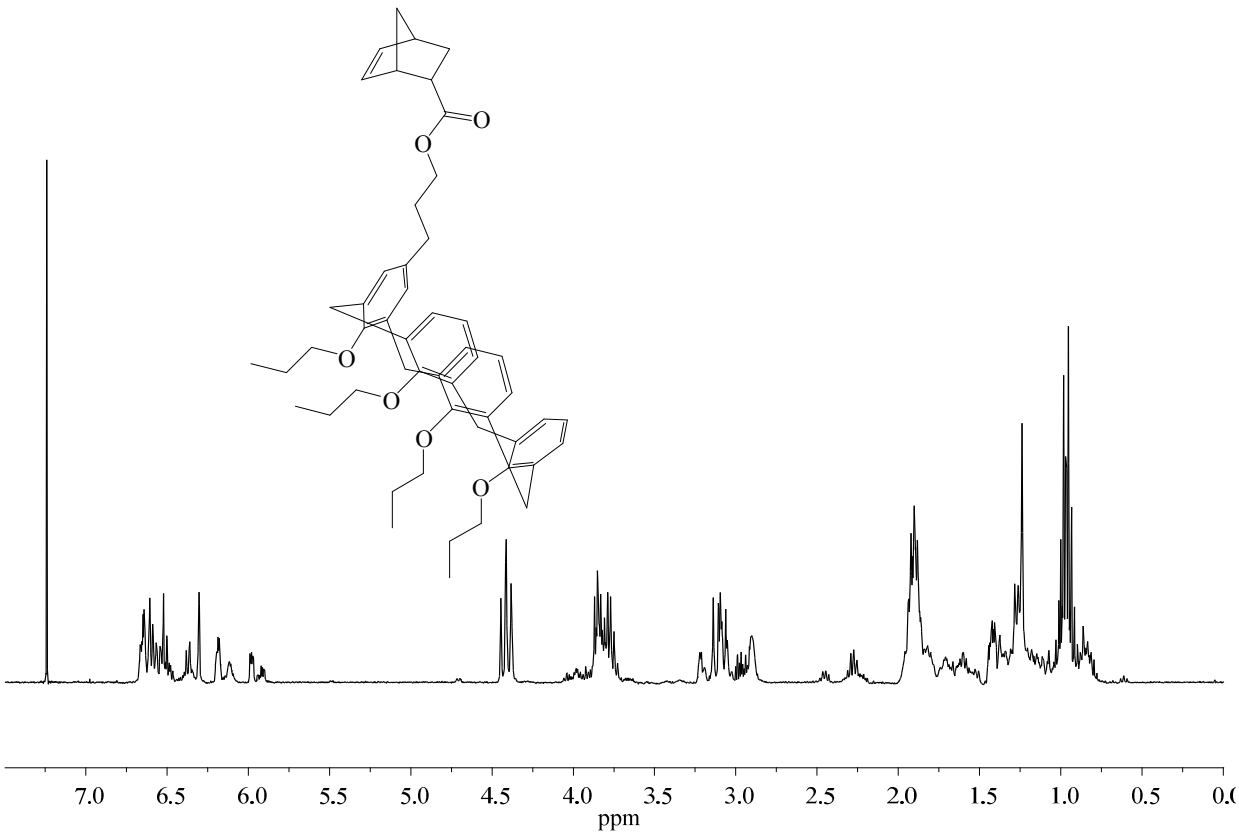
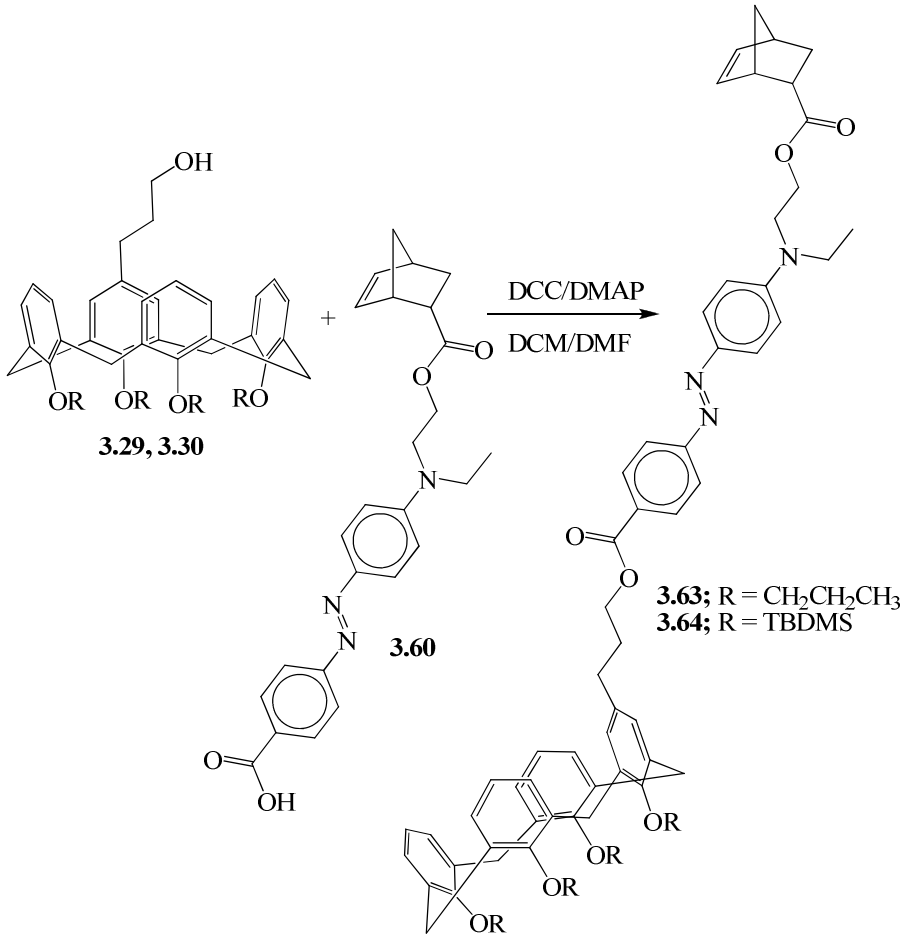


Figure 3-76: 400 MHz ^{1}H NMR spectrum of calix[4]arene monomer 3.61.

Azo dye based norbornene monomers containing calix[4]arene were prepared through reaction of calix[4]arenes **3.29** and **3.30** and azo dye **3.60** to give calix[4]arenes **3.63** and **3.64** as vibrantly coloured orange powders (Scheme 3-38) The ^{1}H NMR spectrum of calixarene **3.63** is shown in Figure 3-77. The incorporation of the azo dye is shown from the appearance of the olefinic groups at 6.16 ppm and 5.98 ppm (endo) as well as aromatics due to the azo dye at 8.12 ppm, 7.87 ppm, and 6.87 ppm.



Scheme 3-38: Synthesis of calix[4]arene monomers 3.63 and 3.64.

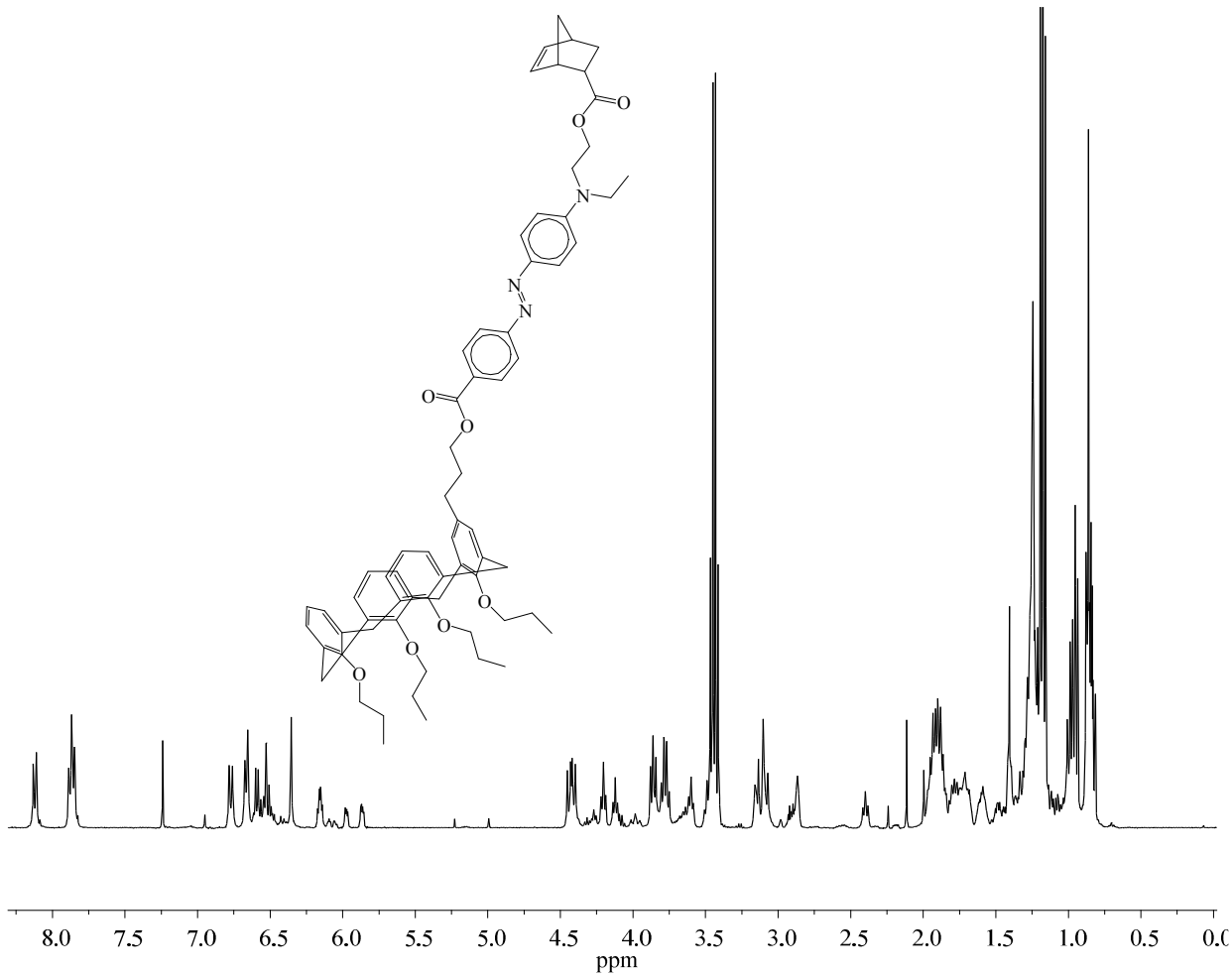
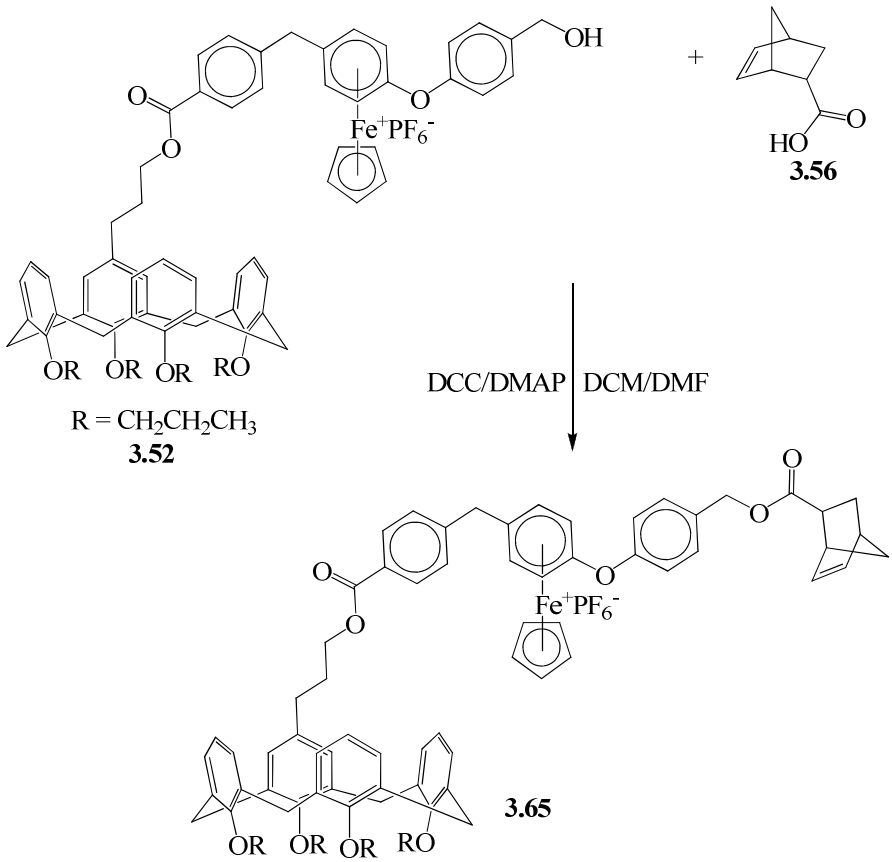


Figure 3-77: 400 MHz ^{1}H NMR spectrum of calix[4]arene 3.63.

Norbornene monomers containing metallocalix[4]arenes were also prepared from the reaction of the alcohol terminated calix[4]arenes **3.52** with 5-carboxylic-2-norbornene (**3.56**) (Scheme 3-39).



Scheme 3-39: Synthesis of norbornene containing calix[4]arene 3.65.

The ^{1} H NMR spectrum of (Figure 3-78) shows that the norbornene unit was successfully incorporated from the appearance of the resonances between 6.16 ppm and 5.86 ppm, due to the olefinic protons of the norbornene also the CH_2 of the benzyl group has shifted from 4.70 ppm to 5.65 ppm. The azo dye containing monomers were analyzed through UV-vis spectroscopy. The monomers were determined to display a λ_{max} = 435 nm in THF, which shifted to 550 nm when acidified with $HCl_{(g)}$.

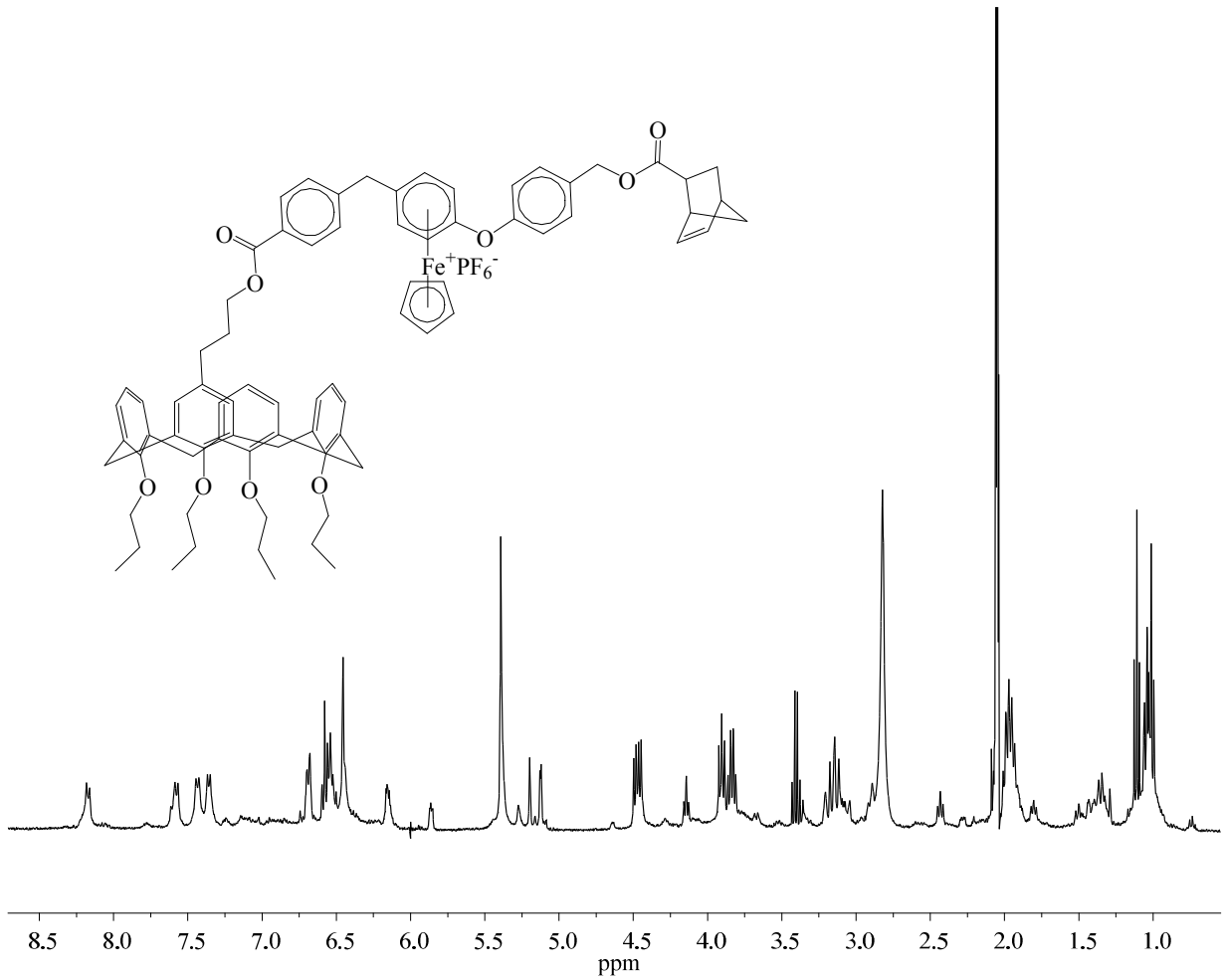
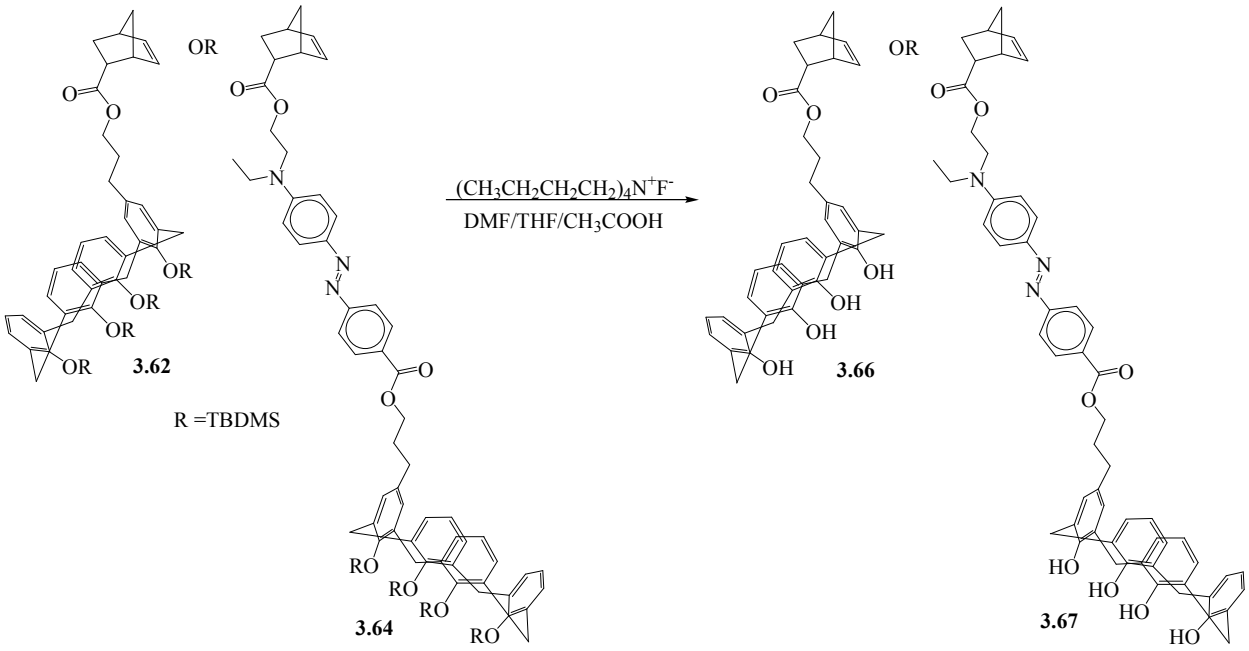


Figure 3-78: 400 MHz ^{1}H NMR spectrum of metallocalix[4]arene 3.65.

Since the cone conformation of calix[4]arene is the most useful for potential application such as ion trapping and guest-host chemistry, the silyl protected calix[4]arenes **3.62** and **3.64** were deprotected in the hopes that the cone conformation would be restored with the intramolecular hydrogen bonding on the lower rim. Calix[4]arenes **3.62** and **3.64** were reacted with tetra-butylammonium fluoride to remove the TBDMS (Scheme 3-40). This reaction gave the 25,26,27,28-tetrahydroxcalix[4]arene derivates **3.66** and **3.67** in good yield and NMR spectroscopies (Figure 3-79 Figure 3-81) indicated that the calix[4]arenes were isolated in the cone conformations from the presence of the broad resonances at 4.17 ppm and 3.44 ppm.



Scheme 3-40: Synthesis of calix[4]arene monomers 3.66 and 3.67.

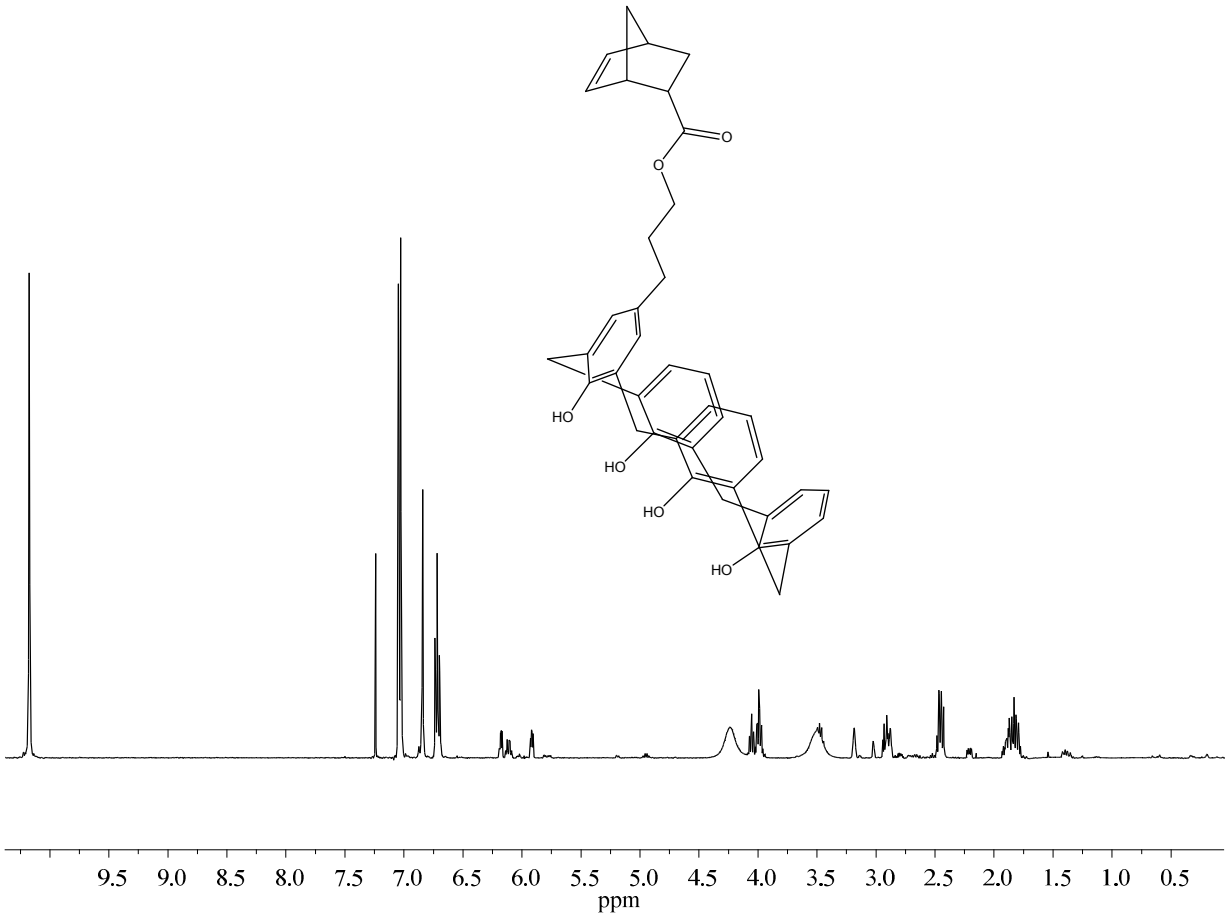


Figure 3-79: 400 MHz ^{1}H NMR spectrum of norbornene containing calix[4]arene 3.66.

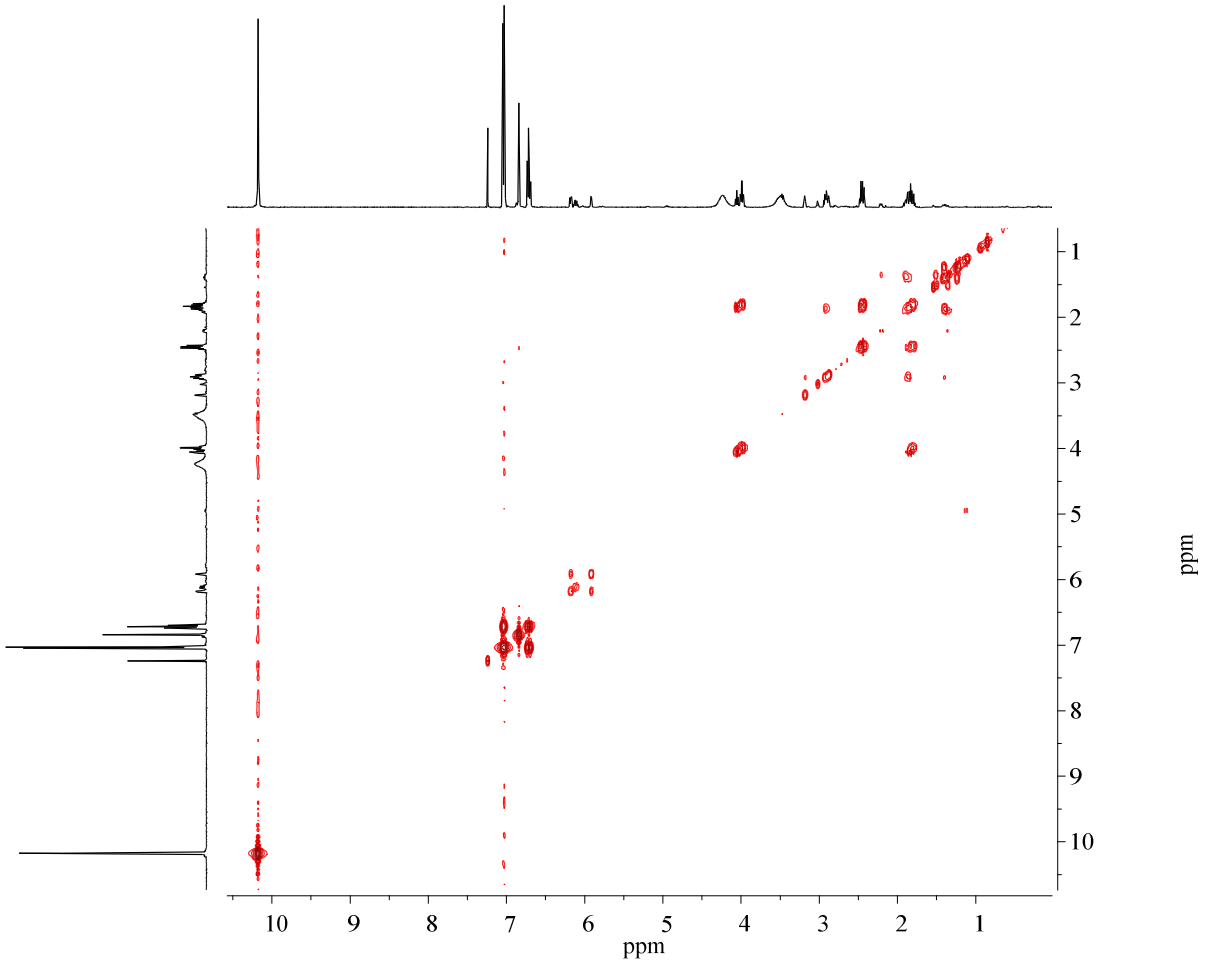


Figure 3-80: COSY spectrum of 3.66.

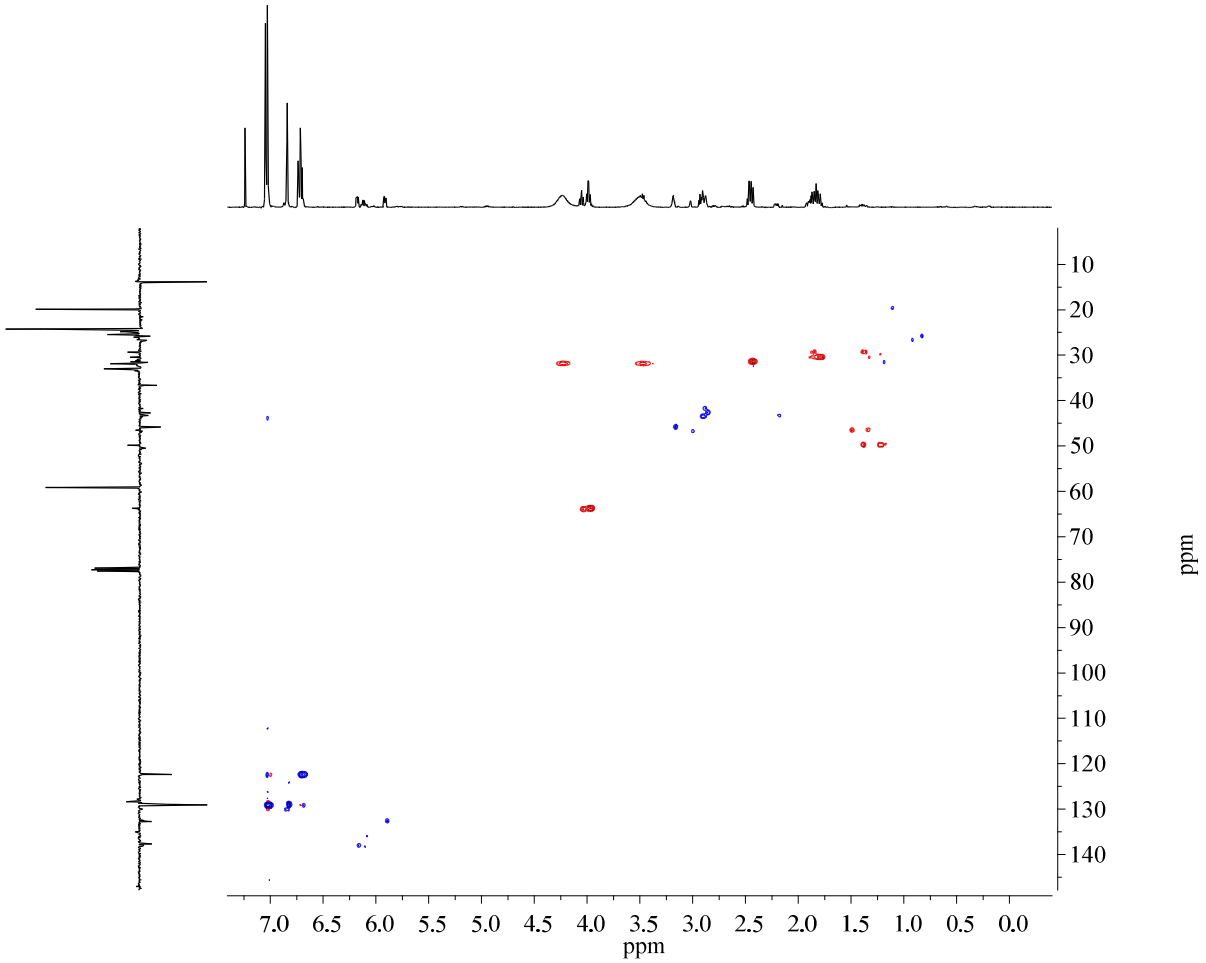
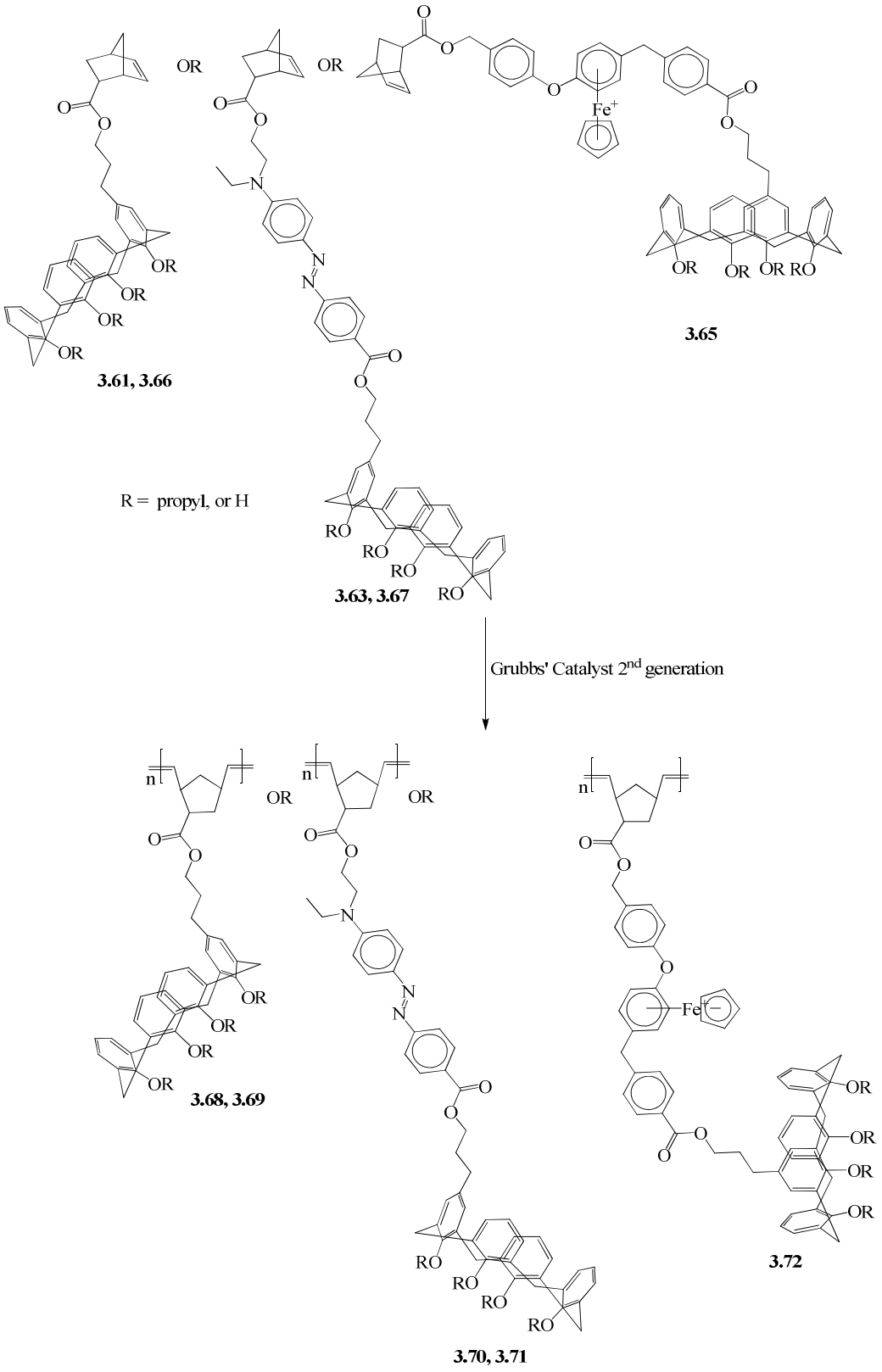


Figure 3-81: HSQC spectrum of 3.66.

Norbornene-containing calix[4]arenes **3.61, 3.63, 3.65, 3.66** and **3.67** were polymerized through ROMP with Grubbs' 2nd generation catalyst (Scheme 3-41). This afforded polynorbornenes containing calix[4]arenes in their side chains **3.68 – 3.72**.



Scheme 3-41: Synthesis of calix[4]arene polymers 3.68 – 3.72.

The polymers were obtained with weight average molecular weight ranging between 45 000 and 116 200 with polydispersity indices (PDIs) between 1.40 and 1.9. Table 3-5 shows the $\overline{M_n}$ and $\overline{M_w}$ of polymers **3.68 – 3.72**.

Table 3-5: Molecular weights of polymers 3.68 - 3.72

Polymer #	$\overline{M_n}$	$\overline{M_w}$	PDI
3.68	40 300	76 600	1.9
3.69	70 300	116 200	1.7
3.70	31 900	61 200	1.9
3.71	32 200	45 100	1.4

Thermal analysis of polymer **3.68 – 3.72** showed that polymers **3.68** and **3.69** were stable above 300 °C whereas, polymers **3.70** and **3.71** began to decompose just above 200 °C (Table 3-6). The difference in thermal stability is due to the presence of the azo dye in polymers **3.78** and **3.79**, since the azo group has been found to decompose at temperatures around 200 °C. Differential scanning calorimetry showed that the polymers possessed glass transition temperatures between 30 °C and 155 °C (Table 3-6). As can be seen, the phenol containing polymers **3.69** and **3.71** possess higher T_gs than polymer **3.68** and **3.70**. This result is not unexpected since since, polymers **3.6** and **3.70** contain aliphatic groups on the lower rim of the calixarenes; the aliphatic groups are known to decrease glass transition temperatures.

Table 3-6: Thermal data for polymer 3.68-3.72 reported in °C

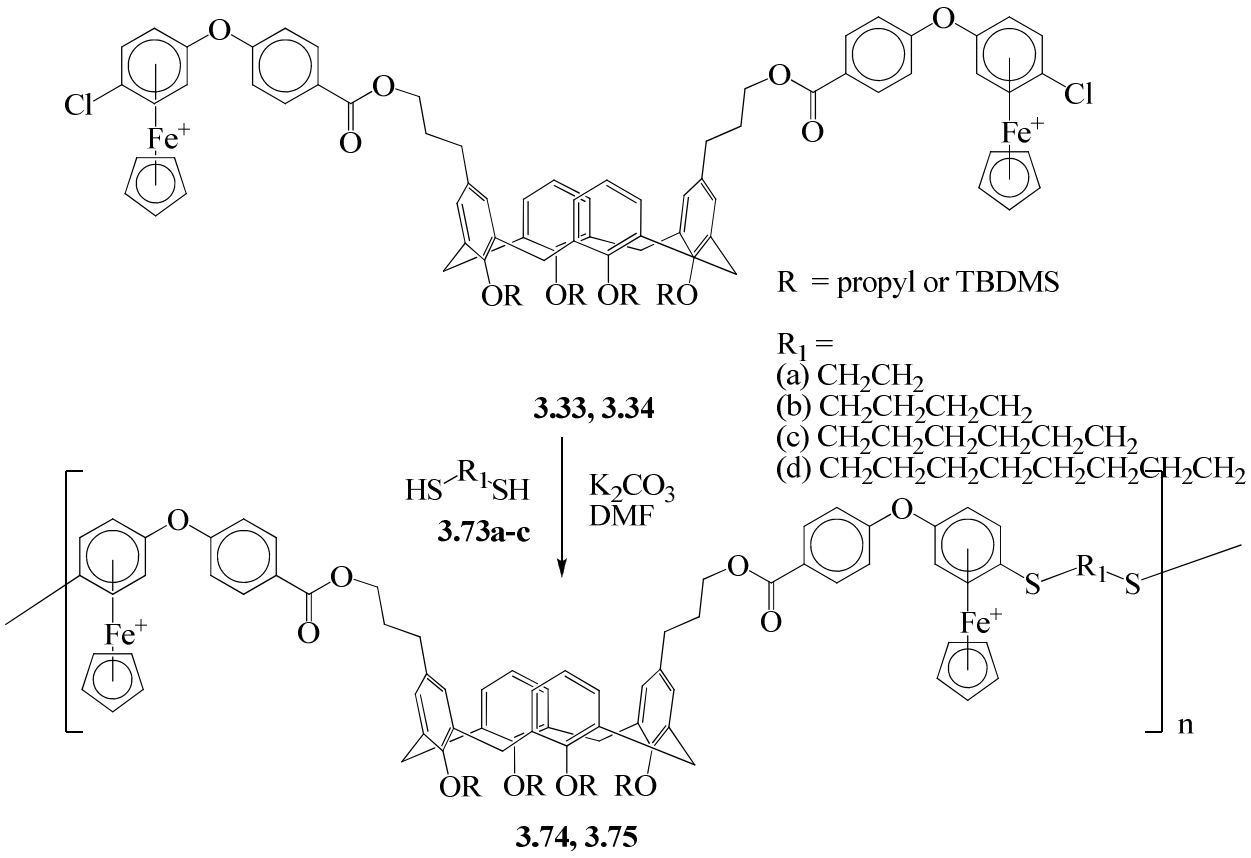
Polymer #	Step 1 °C	%	Step 2 °C	%	Step 3 °C	%	T_g
3.68	395-460	60	538-580	40			34 °C
3.69	409-450	40	538-580	48			103 °C
3.70	140-210	15	300-325	8	410-460	52	125 °C
3.71	270-290	11	405-450	32	550-680	42	154 °C

Polymers **3.70** and **3.71** were studied for their UV-vis properties. It was found that the polymers displayed λ_{max} at 430 nm in THF solutions and when acidified with $HCl_{(g)}$ the λ_{max} shifted to 520 nm, due to the formation of the azonium ion. Polymers **3.70** and **3.71** were poorly soluble in organic solvents so they were tested for visual identification of acid in the solid state. As solids, polymers **3.70** and **3.71** appear as orange to reddish orange materials, but when exposed to $HCl_{(g)}$ the materials become purple in colour. However, when these acidified materials are exposed to $NH_{3(g)}$ they revert to their original colour. This colour change indicates that the protonated form of the azo dye is reversibly produced in the solid state.

3.2.5.2 Metallocalix[4]arene containing polymers prepared through polycondensation

As described previously in this chapter, the terminal chloro groups on an arene complexed to cyclopentadienyliron are quite susceptible to nucleophilic aromatic substitution. The substitution of chloro-terminated metallocalix[4]arenes has been described using oxygen nucleophiles and sulfur dinucleophiles. Since calix[4]arenes **3.33, 3.34,** and **3.39** possess two terminal chloro groups the use of dinucleophiles can result in the formation of dimers, trimers, oligomers, and even polymers prepared through polycondensation. The use of strong nucleophiles such as oxygen, sulfur or nitrogen and minimal amounts of solvent can cause the formation of polymetallocalix[4]arenes.

The reaction of calix[4]arenes **3.33** or **3.34** with various aliphatic dithiols (**3.73**) gave polymers **3.74** containing calix[4]arenes in their backbones (Scheme 3-42). As can be seen by the ^{1}H NMR spectrum of **3.33a** (Figure 3-82) there is significant broadening of the ^{1}H resonances which is characteristic of polymers.



Scheme 3-42: Synthesis of calix[4]arene polymers 3.74a-d and 3.75a-d.

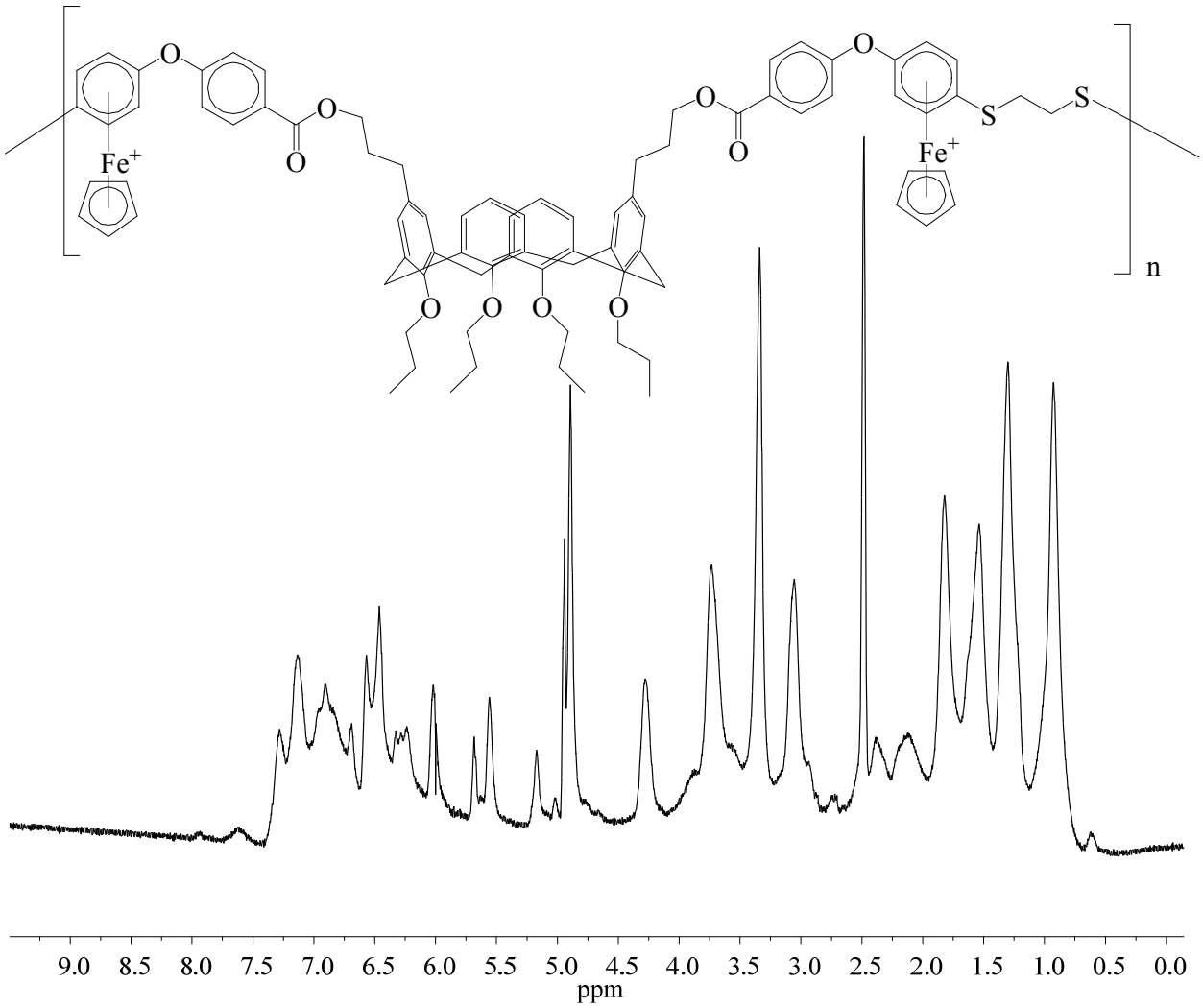


Figure 3-82: 400 MHz ^{1}H NMR spectrum of polymer 3.74a.

The ^{13}C NMR spectrum of **3.74** is shown in Figure 3-83

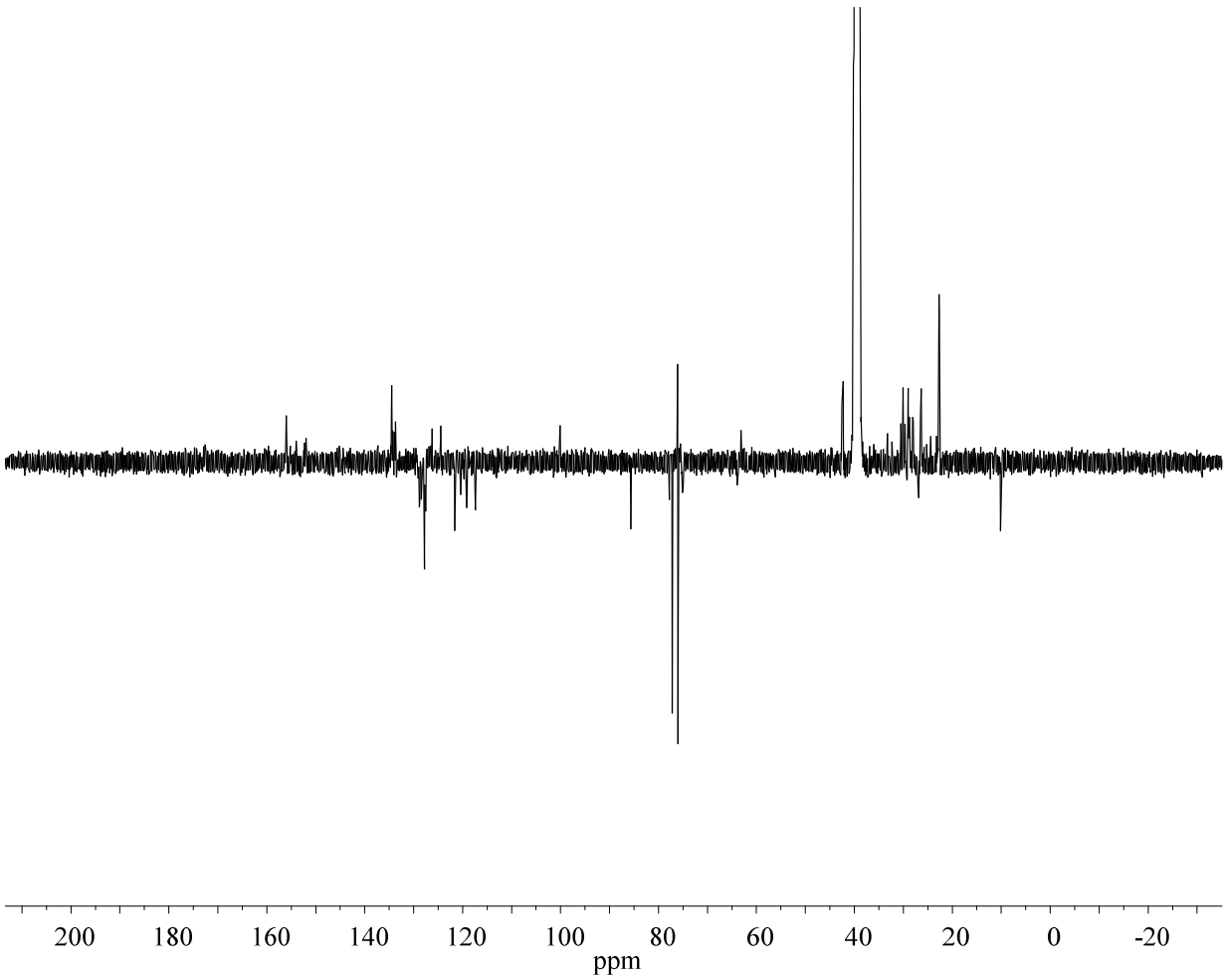
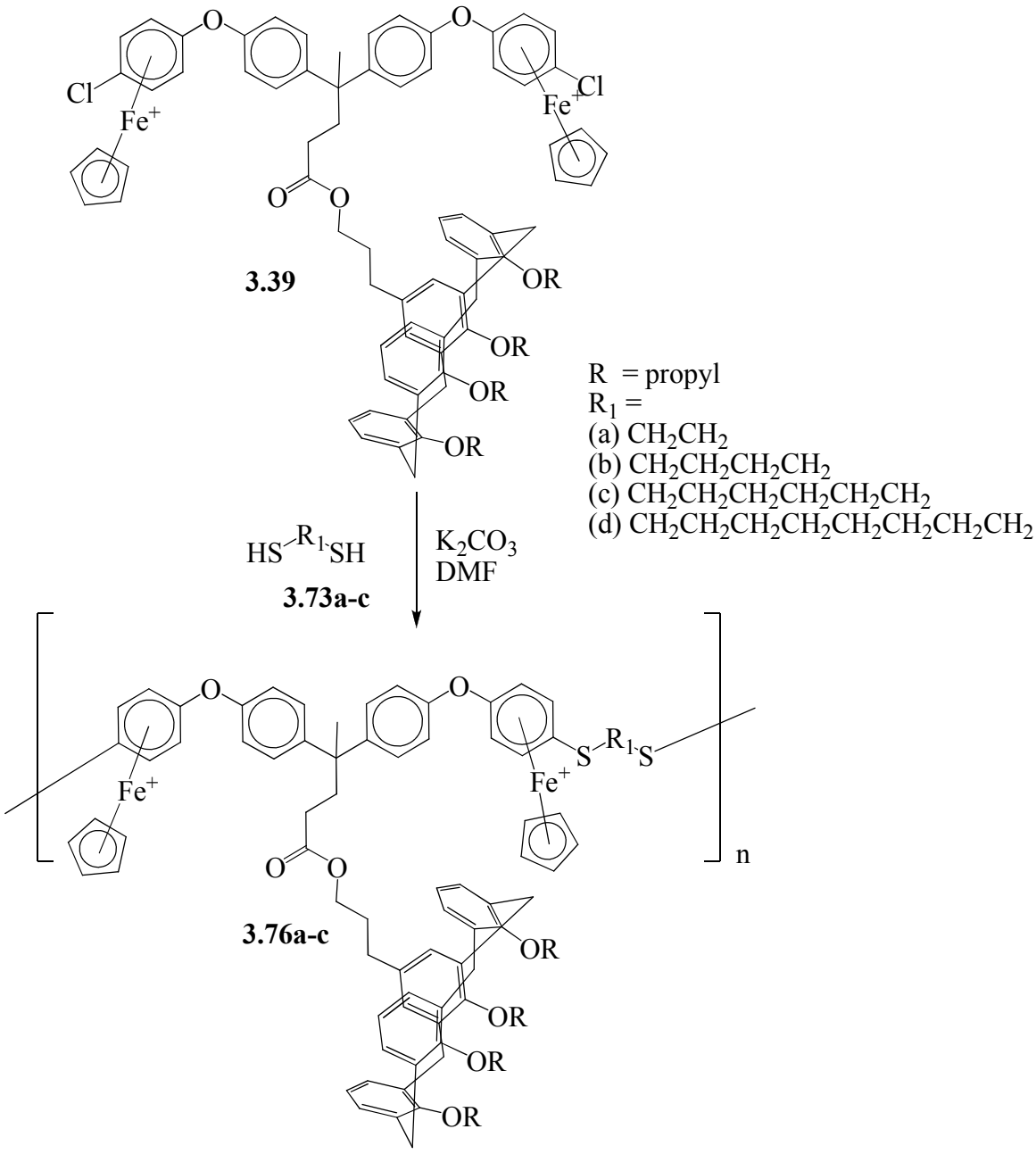


Figure 3-83: 101 MHz (APT) ^{13}C NMR spectrum of polymer 3.74a.

Polymetallocalix[4]arenes containing calix[4]arenes in the side chains were prepared by reacting calix[4]arenes **3.39** with various aliphatic dithiols (**3.73**) (Scheme 3-43).



Scheme 3-43: Synthesis of calix[4]arene polymers 3.75a-d.

The molecular weights of polymetallocalix[4]arene **3.74a-d** and **3.75a-d** were estimated from their analogous demetallated polymers using gel permeation chromatography and are tabulated in Table 3-7. The $\overline{M_w}$s were found to range between 4 300 and 53 000 with PDI between 1.07 and 1.22. As can be seen in Table 3-7, the polymers prepared with 1,2-ethane

dithiol gave only diols or tetraols whereas 1,6 hexane dithiol gave much higher molecular weights.

Table 3-7: Molecular weights of polymers 3.74a-d, 3.75a-d, and 3.76a-d

Polymer #	$\overline{M_n}$	$\overline{M_w}$	PDI
3.74a	3000	4800	1.57
3.74a	1400	1590	1.14
3.74c	35,000	19,400	1.80
3.74d	8000	10 800	1.35
3.75a	1310	1790	1.35
3.75b	3200	5600	1.75
3.75c	32,900	40,500	1.22
3.75d	8300	9100	1.10
3.76a	2900	3200	1.1
3.76b	5400	7000	1.30
3.76c	49,500	53,000	1.07
3.76d	4300	4350	1.02

The polymers were further analyzed through thermal gravimetric analysis and differential scanning calorimetry to study their thermal properties. TGA analysis (Table 3-8) showed that the polymers underwent two to three main decompositions; the cyclopentadienyliron moiety thermally degraded between 170 °C and 250 °C. The second degradation between 300 °C and 450 °C corresponded to the loss of the ester bond; the final degradations did not have a defined onset or endset temperatures and was a steady decomposition corresponding to the breakdown of

the polymer backbone. The glass transition temperatures for all polymers ranged between 80 °C and 100 °C.

Table 3-8: Thermal gravimetric analysis data of polymers 3.74a-d, 3.75a-d, and 3.76a-d

Polymer #	Onset (°C)	Endset (°C)	Onset (°C)	Endset (°C)	Onset (°C)	Endset (°C)
3.74a	200	250	320	450	580	800
3.74b	200	230	360	415	600	700
3.74c	200	250	390	460	580	750
3.74d	213	250	390	410	---	---
3.75a	215	250	380	450	580	800
3.75b	200	250	300	575	580	800
3.75c	172	214	381	305	310	800
3.75d	225	250	410	440	580	600
3.76a	205	246	390	455	580	730
3.76b	200	250	380	470	590	740
3.76c	200	245	383	434	440	800
3.76d	225	250	413	446	579	746

3.3 Conclusion

This chapter described the synthesis and characterization of a number calix[4]arenes possessing mono- or di-functionalized upper rims. These calix[4]arenes were reacted with different chloro-containing organoiron based carboxylic acids to give metallocalix[4]arenes possessing terminal chloro groups attached to the organoiron moiety. Electrochemical studies on these metallocalix[4]arenes showed that the iron moiety was reversibly reduced at $E_{1/2}$s between -1.200 V and -1.740 V.

Azo dye containing calix[4]arenes were prepared from the reaction of metallocalix[4]arenes with azo dyes containing phenols and alcohols. These compounds contained either two or four azo groups. The metallocalix[4]arenes possessing four azo groups and therefore four terminal alcohols were used to prepare early generation azo dye-containing metallocalix[4]arene dendrimers. Cyclic voltammetry showed that the azo dye based metallocalix[4]arenes showed a reversible oxidation of the azo group at 0.69 V and a reversible reduction of the cationic organoiron moiety at -1.36 V. Studies on the acid sensing behaviour showed that the calix[4]arene compounds can detect the presence of both Lewis and protic acids in both the solid state and in solution.

Metallocalix[4]arenes containing both cationic and neutral organoiron moieties were prepared. These calix[4]arenes were prepared by reaction the cationic alcohol terminated metallocalix[4]arenes with carboxylic ferrocene. Both the alcohol terminated- and ferrocene-containing metallocalix[4]arenes electrochemical properties were studied. Cyclic voltammetry indicated that the alcohol terminated metallocalix[4]arenes possessed one redox couple for the reduction of the cationic cyclopentadienyliron moiety between $E_{1/2}$s –1.36 V and – 1.56 V. Once the ferrocene was added to the metallocalix[4]arene two redox couples were apparent, one for the reversible oxidation of the ferrocene between $E_{1/2}$ 0.15 V and 0.28 V, and one for the

reversible reduction of the cationic moiety between $E_{1/2}$ –1.71 V and –1.83 V. The addition of the ferrocene moiety caused a shift in the cationic iron's redox couple potential; this potentially indicates some communication between the cationic and neutral iron groups.

Both the organic calix[4]arene and chloro-terminated metallocalix[4]arenes were used to prepare polycalix[4]arenes. Organic monomers were prepared by reaction of the mono-upper rim functionalized organic calix[4]arene with either 5-carboxylic-2-norbornene or an azo dye functionalized norbornene compound. These monomers were reacted with Grubbs' catalyst 2nd generation to give polynorbornenes containing calix[4]arenes. These polymers possessed weight averaged molecular weights between 32 700 and 81 700 with PDIs between 1.4 and 2.02. Thermal analysis showed that the azo dye containing polymers were stable up to 200 °C where the azo group decomposed; the other polymers were stable up to 400 °C.

Cationic organoiron polycalix[4]arenes were prepared through two methods. In the first method a metallocalix[4]arene possessing a single terminal alcoholic group was reacted with norbornene to give a norbornene based metallocalix[4]arene monomer. This monomer then underwent ROMP to give a cationic organoiron polynorbornene containing calix[4]arenes. The second method utilized the cationic organoiron complex's ability to undergo nucleophilic aromatic substitution reactions. Using dithiols and metallocalix[4]arenes containing two terminal chloro groups, polymetallocalix[4]arenes were prepared through polycondensation. These polymer possessed weight averaged molecular weights between 4350 and 53 000. Thermal analysis showed that the polymetallocalix[4]arenes were stable up to 175 °C where the cationic cyclopentadienyliron moiety decomposed.

3.4 Experimental

Materials: All reagents were purchased from Sigma-Aldrich and used without further purification. All general solvents were HPLC grade and used without further purification. The dichloromethane used for polymerization was HPLC grade and dried and degassed using established procedures.[90] Compounds **3.8, 3.14, 3.19,** and **3.20** were prepared using established procedures. [86, 87, 91] **3.18** and **3.23** were previously report however the syntheses reported herein are new.

Characterizations: ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz respectively on a Varian Mercury Plus spectrometer equipped with a gradient field probe, with chemical shifts referenced to residual solvent peaks and reported in ppm, the coupling constants reported in Hz. Thermogravimetric analysis and differential scanning calorimetry were performed on Mettler-Toledo TGA/SDTA851^{e} and DSC821^{e} instruments respectively, at heating rates of 20 °C/min under nitrogen atmospheres. GPC was performed on a Polymer Labs PL-GPC 50 plus with a PL-AS RT autosampler and PL-RI detector. The eluent was THF flowing at 1 ml/min at 30 °C. Two PLgel mixC columns were setup in series. The molecular weights were calculated against PS-H polystyrene standards. Cyclic voltammetric experiments were performed using a conventional three-electrode cell. In these studies the working electrode was a glassy carbon disk electrode (ca. 2 mm diameter), the auxiliary electrode was a Pt wire, and a (Ag/AgCl) reference electrode was utilized. Temperatures ranging from 293 to 243 K were obtained using a dry ice−acetone mixture. The concentration of the complex was 2.0 mM, while that of the supporting electrolyte (TBAH or TBAP) was 0.1 M. The solutions were deaerated

with nitrogen prior to use. An EG&G Princeton Applied Research model 263A potentiostat was used in all experiments.

Synthetic Methodology:

Synthesis of 3.14[91]

In a 250 mL RBF calix[4]arene (**3.8**) (6.106 g, 14.4 mmol), K_2CO_3 (1.990 g, 14.4 mmol), iodo-propane (2.9 mL, 28.8 mmol) and freshly distilled acetonitrile (600 mL) were refluxed under nitrogen for 15 hours. The solvent was removed *in vacuo* to leave a white residue. The residue was dissolved into $CHCl_3$ and 1.2 M HCl. The mixture was transferred into a separator funnel and the $HCl_{(aq)}$ removed. The product was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The crude product was purified on silica using a mixture of chloroform:hexanes (60:40) to yield the pure product. Yield 6.949 g, 13.68 mmol, 95%

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.28 (s, 2H, OH), 7.04 (d, *J* = 7.5, 4H, Ar-CH), 6.91 (d, *J* = 7.5, 4H, Ar-CH), 6.73 – 6.69 (m, 2H, Ar-CH), 6.63 (t, *J* = 7.5, 2H, Ar-CH), 4.31 (d, *J* = 12.9, 4H, CH_2), 3.97 (t, *J* = 6.3, 4H, CH_2), 3.37 (d, *J* = 12.9, 4H, CH_2), 2.12 – 2.00 (m, 4H, CH_2), 1.30 (t, *J* = 7.4, 6H, CH_3). Conforms to published spectra

Synthesis of 3.16

In a 100 mL RBF, **3.14** (.508 g, 1 mmol), NaH (0.120 g, 5.0 mmol), allyl bromide (**3.15**, 0.35 mL, 4.0 mmol) and 40 mL DMF were stirred under N_2 for 24 hours at room temperature. The solution was poured into 300 mL of 1.2 M HCl and the white precipitate was extracted into $CHCl_3$. The product was dried with $MgSO_4$, gravity filtered and the solvent was removed

through evapouration. The residue was recrystallized using $CHCl_3$/MeOH. Yield: 0.422 g, 0.91 mmol, 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.98 (d, *J* = 7.4, 8H, Ar-CH), 6.85 – 6.81 (m, 4H Ar-CH), 6.65 – 6.35 (m, 2H, CH=), 5.17 – 5.05 (m, 4H, CH_2=), 4.60 (dt, *J* = 6.6, 1.0, 4H, CH_2), 4.40 (d, *J* = 13.4, 4H, CH_2), 3.71 (t, *J* = 7.0, 4H, CH_2), 3.14 (d, *J* = 13.4, 4H, CH_2), 2.09 – 1.73 (m, 4H, CH_2), 1.06 (t, *J* = 7.4, 6H, CH_3). Conforms to published spectra[86]

Synthesis of 3.17

In a 50 mL RBF, **3.16** (0.588 g, 1.0 mmol) and 25 mL of N,N-diethylaniline was refluxed for 2 hours. The solution was then poured into 300 mL concentrated HCl and stirred for 15 min. The beige precipitate was filtered through a sintered glass crucible and dried under reduced pressure. The precipitate was recrystallized from 2-propanol. Yield: 0.445 g, 0.96 mmol, 96%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.19 (s, 2H, OH), 6.93 (d, *J* = 7.5, 4H, Ar-CH), 6.85 (s, 4H, Ar-CH), 6.79 – 6.71 (m, 2H, Ar-CH), 5.93 (ddt, *J* = 16.8, 10.1, 6.6, 2H, CH=), 5.08 – 4.97 (m, 4H, CH_2=), 4.30 (d, *J* = 12.9, 4H), 3.96 (t, *J* = 6.3, 4H, CH_2), 3.34 (d, *J* = 12.9, 4H, CH_2), 3.24 (dt, *J* = 6.7, 1.5, 4H, CH_2), 2.12 – 2.00 (m, 4H, CH_2), 1.30 (t, *J* = 7.4, 6H, CH_3).

^{13}C-NMR (50 MHz, $CDCl_3$) δ = 10.90, 23.25, 31.41, 39.38, 78.26, 115.06, 125.25, 128.40, 128.84, 128.02, 130.05, 133.61, 138.33, 151.51, 151.56.

Synthesis of 3.18

Method 1: In a 100 mL RBF, **3.17** (0.589 g, 1.0 mmol), NaH (0.072 g, 3.0 mmol), iodopropane (0.3 mL, 3.0 mmol) and 40 mL DMF were stirred under N_2 for 24 hours at room temperature. The solution was poured into 300 mL of 1.2 M HCl and the white precipitate was extracted into $CHCl_3$. The product was dried with $MgSO_4$, gravity filtered and the solvent was removed

through evapouration. The residue was recrystallized using $CHCl_3$/MeOH. Yield: 0.369 g, 0.73 mmol, 73%.

Method 2[91]: In a 100 mL RBF, **3.19** (0.484 g, 1 mmol), NaH (0.120 g, 5 mmol), iodopropane (**3.15**, 0.5mL, 5 mmol) 40 mL DMF and 10 mL THF were stirred under N_2 for 24 hours at room temperature. The solution was poured into 300 mL of 1.2 M HCl and the white precipitate was extracted into $CHCl_3$. The product was dried with $MgSO_4$, gravity filtered and the solvent was removed through evapouration. The residue was dissolved into 2-propanol and precipitated into 1.2M. Yield 0.455 g, 0.90 mmol, 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.66 (s, 4H, Ar-CH), 6.45 – 6.36 (m, 6H, Ar-CH), 5.98 – 5.86 (m, 2H, CH=), 5.08 – 4.97 (m, 2H, CH_2=), 4.43 (d, *J* = 13.3, 2H), 3.92 – 3.87 (m, 4H, CH_2), 3.78 (t, *J* = 7.2, 4H, CH_2), 3.21 (dt, *J* = 6.6, 1.4, 4H, CH_2), 3.12 (d, *J* = 13.3, 4H, CH_2), 2.01 – 1.81 (m, 8H, CH_2), 1.04 (t, *J* = 7.5, 6H, CH_3), 0.95 (t, *J* = 7.5, 6H, CH_3).

^{13}C-NMR (50 MHz, $CDCl_3$) δ = 10.97, 11.23, 21.97, 22.22, 31.41, 40.74, 78.52, 115.36, 121.81, 128.56, 129.36, 132.75, 135.13, 136.56, 139.15, 156.42, 156.75.

Synthesis of 3.19[87]

In a 250 mL RBF calix[4]arene (**3.8**) (6.105 g, 14.4 mmol), K_2CO_3 (1.990 g, 14.4 mmol), allyl bromide (2.49 mL, 28.8 mmol) and freshly distilled acetonitrile (100 mL) were refluxed under nitrogen for 15 hours. The solvent was removed *in vacuo* to leave a white residue. The residue was dissolved into $CHCl_3$ and 1.2 M HCl. The mixture was transferred into a seperatory funnel and the $HCl_{(aq)}$ removed. The product was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The crude product was purified on silica using a mixture of chloroform: hexanes (60:40) to yield the pure product. Yield: 6.621g, 13.68 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.00 (s, 2H, OH), 7.09 (d, *J* = 7.5, 4H, Ar-CH_2), 6.89 (d, *J* = 7.6, 4H, Ar-CH_2), 6.74 – 6.66 (m, 4H, Ar-CH), 6.28 (ddt, *J* = 17.1, 10.4, 5.1, 2H, CH=), 5.62 (ddq, *J* = 144.3, 10.6, 1.5, 4H, CH_2=), 4.57 (dt, *J* = 5.1, 1.6, 4H, CH2), 4.35 (d, *J* = 13.1, 4H, CH_2), 3.40 (d, *J* = 13.1, 4H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 153.42, 151.88, 133.52, 132.94, 129.13, 128.65, 128.26, 125.60, 119.21, 118.08, 77.02, 31.62.

Synthesis of 3.20[87]

In a 50 mL RBF, **3.19** (0.484 g, 1.0 mmol) and 25 mL of N,N-diethylaniline was refluxed for 2 hours. The solution was then poured into 300 mL concentrated HCl and stirred for 15 min. The beige precipitate was filtered through a sintered glass crucible and dried under reduced pressure. The precipitate was recrystallized from 2-propanol. Yield: 0.445 g, 0.96 mmol, 96%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 4H, OH), 7.03 (d, *J* = 7.6, 4H, Ar-CH), 6.84 (s, 4H, Ar-CH), 6.72 (t, *J* = 7.5, 2H, Ar-CH), 5.93 – 5.76 (m, 2H, CH=), 5.06 – 4.99 (m, 4H, CH_2=), 4.21 (s, 4H, CH_2), 3.48 (s, 4H, CH_2), 3.16 (dt, *J* = 6.8, 1.4, 4H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.33, 149.08, 147.20, 137.73, 133.77, 129.20, 129.17, 128.49, 128.36, 122.36, 115.87, 98.29, 77.55, 77.23, 76.91, 39.58, 31.99.

Synthesis of 3.22

In a 50 mL RBF **3.21** (0.464 g, 1.0 mmol) and NaH (0.120 g, 5.0 mmol), were combined under N_2. DMF (50 mL) and THF (5 mL) were added and the mixture allowed to stir for 30 min to generate the anion. *tert-B*utyldimethylchlorosilane (0.754 g, 5.0 mmol) was then injected into the reaction mixture and the mixture stirred for an additional 12 hours. The mixture was poured into 200 mL of HCl (1.2 M) and extracted into $CHCl_3$. The product was washed with water and dried

over $MgSO_4$. After filtration and removal of solvent the crude product was purified on silica using $CHCl_3$:hexanes (60:40). Yield: 0.831 g, 0.90 mmol, 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 3H), 7.09 – 6.90 (m, 7H), 6.91 – 6.72 (m, 5H), 6.70 – 6.56 (m, 1H), 6.46 (t, *J* = 7.3, 1H), 6.30 – 6.19 (m, 3H), 5.84 – 5.73 (m, 3H), 5.66 (s, 1H), 4.07 – 3.92 (m, 4H), 3.77 – 3.34 (m, 15H), 3.02 – 2.83 (m, 4H), 2.71 – 2.10 (m, 2H), 1.95 – 1.54 (m, 4H), 1.44 – 1.24 (m, 1H), 1.20 – 1.05 (m, 30H), 0.96 – 0.76 (m, 77H), 0.67 – 0.56 (m, 18H), 0.35 – 0.04 (m, 60H), 0.02 – -0.05 (m, 19H).

Synthesis of 3.23[87]

In a 100 mL 3-necked RBF affixed with an addition funnel, nitrogen inlet, and thermometer, **3.18** (2.846 g, 4.23 mmol) was dissolved in 40 mL dry THF under nitrogen and cooled to -10°C in a saltwater-ice bath. Borane 1M solution (10 mL, 10 mmol) was added dropwise while maintaining the temperature of the reaction below 0°C. After addition of borane the reaction was allowed to stir at or below 0°C for 30 min, after which, the reaction was warmed to room temperature and stirred for an additional 2 hours. After the 2 hours elapsed 8 mL of 1M NaOH (8 mmol) was added dropwise followed by H_2O_2(30% solution, 32 mmol) and the solution was stirred for 30 min. The solution was poured into 100 mL of H_2O and extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and gravity filtered, the solvent was then evaporated and the residue was recrystallized from $CHCl_3$/MeOH. Yield: 2.385 g, 3.75 mmol, 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.59 (t, *J* = 5.7, 4H, Ar-CH), 6.45 (s, 4H, Ar-CH), 6.42 – 6.33 (m, 2H, Ar-CH), 4.40 (d, *J* = 13.2, 4H, CH_2), 3.91 – 3.68 (m, 8H, CH_2), 3.57 (t, *J* = 6.3, 4H, CH_2), 3.08 (d, *J* = 13.2, 4H, CH_2), 2.39 – 2.29 (m, 4H, CH_2), 1.98 – 1.80 (m, 8H, CH_2), 1.70 – 1.60 (m, 4H, CH_2), 1.00 – 0.92 (m, 12H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 156.62, 154.79, 135.29, 134.88, 131.46, 128.19, 128.02, 122.11, 76.79, 62.62, 34.19, 31.65, 31.11, 24.95, 23.40, 23.34, 10.49, 10.45.

Synthesis of 3.24

In a 100 mL 3-necked RBF affixed with an addition funnel, nitrogen inlet, and thermometer, **3.21** (4.075 g, 4.23 mmol) was dissolved in 40 mL dry THF under nitrogen and cooled to -10°C in a saltwater-ice bath. Borane 1M solution (10 mL, 10 mmol) was added drop-wise while maintaining the temperature of the reaction below 0°C. After addition of borane the reaction was allowed to stir at or below 0°C for 30 min, after which, the reaction was warmed to room temperature and stirred for an additional 2 hours. After the 2 hours elapsed 8 mL of 1M NaOH (8 mmol) was added dropwise followed by H_2O_2(30% solution, 32 mmol) and the solution was stirred for 30 min. The solution was poured into 100 mL of H_2O and extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and gravity filtered, the solvent was then evaporated. Yield: 3.944 g, 4.019 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 6.61 (m, 7H), 6.28 (t, *J* = 7.6, 1H), 5.88 – 5.72 (m, 1H), 4.08 – 3.92 (m, 2H), 3.78 – 3.39 (m, 8H), 2.93 (dd, *J* = 13.3, 6.5, 2H), 2.76 – 2.53 (m, 1H), 1.98 – 1.71 (m, 2H), 1.63 – 1.31 (m, 2H), 1.25 – 1.06 (m, 10H), 1.02 – 0.84 (m, 20H), 0.65 (d, *J* = 36.5, 7H), 0.37 – 0.05 (m, 25H), 0.04 – -0.07 (m, 1H).

Synthesis of 3.25

In a 250 mL RBF calix[4]arene (**3.8**) (6.105 g, 14.4 mmol), K_2CO_3 (0.995 g, 7.2 mmol), allyl bromide (1.25 mL, 14.4 mmol) and freshly distilled acetonitrile (100 mL) were refluxed under nitrogen for 15 hours. The solvent was removed *in vacuo* to leave a white residue. The residue was dissolved into $CHCl_3$ and 1.2 M HCl. The mixture was transferred into a seperatory funnel and the $HCl_{(aq)}$ removed. The product was washed with water and dried over $MgSO_4$. The

product was filtered and the solvent removed *in vacuo*. The crude product was purified on silica using a chloroform:hexanes (60:40) mixture to yield the pure product. Yield: 6.347 g, 13.68 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.18, 9.60, 9.28 (s, 3H, OH), 7.12 – 6.93 (m, 6H, Ar-CH), 6.93 – 6.83 (m, 2H, Ar-CH), 6.66 (td, *J* = 7.5, 4.1, 3H, Ar-CH), 6.43 (ddt, *J* = 16.5, 10.4, 6.2, 1H, CH=), 5.59 (ddd, *J* = 13.7, 11.5, 1.3, 2H, CH_2=), 4.68 (dt, *J* = 6.2, 1.1, 2H, CH_2), 4.32 (dd, *J* = 43.6, 13.4, 4H, CH_2), 3.46 (dd, *J* = 13.4, 2.6, 4H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 153.12, 150.63, 134.20, 133.28, 132.14, 128.33, 128.31, 127.99, 120.85, 120.21, 117.82, 77.62, 31.49.

Synthesis of 3.26

In a 50 mL RBF **3.26** (1.160 g, 2.5 mmol) and N,N-diethylaniline were refluxed under N_2 for two hours. The mixture was allowed to cool and poured into 200 mL of H_2O. HCl conc. was added to the product mixture to precipitate the product. The precipitate was collected via vacuum filtration and allowed to dry. The crude product was dissolved in hot isopropanol and HCl (1.2M) was added to cause precipitation to give the pure product. The precipitate was collected and allowed to dry under reduced pressure. Yield: 1.102 g, 2.38 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.17 (s, 4H, OH), 7.03 (d, *J* = 7.6, 6H, Ar-CH), 6.84 (s, 2H, Ar-CH), 6.78 – 6.63 (m, 3H, Ar-CH), 5.93 – 5.77 (m, 1H, CH=), 5.06 – 4.98 (m, 2H, CH_2=), 4.23 (s, 4H, CH_2), 3.49 (s, 4H, CH_2), 3.16 (d, *J* = 6.8, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 149.00, 147.16, 137.70, 133.76, 133.75, 130.60, 129.18, 128.45, 128.33, 122.39, 115.85, 53.82, 31.95, 31.90.

Synthesis of 3.27

In a 50 mL RBF **3.26** (0.464 g, 1.0 mmol) and NaH (0.120 g, 5.0 mmol), were combined under N_2. DMF (50 mL) and THF (5 mL) were added and the mixture allowed to stir for 30 min to generate the anion. Iodopropane (0.850 g, 5.0 mmol) was then injected into the reaction mixture and the mixture stirred for an additional 12 hours. The mixture was poured into 200 mL of HCl (1.2 M) and extracted into $CHCl_3$. The product was washed with water and dried over $MgSO_4$. After filtration and removal of solvent the crude product was purified on silica using $CHCl_3$:hexanes (60:40). Yield: 0.593 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.78 – 6.49 (m, 9H, Ar-CH), 6.39 (d, J = 5.3, 2H, Ar-CH), 6.00 – 5.56 (m, 1H, CH=), 5.20 – 4.71 (m, 2H, CH_2=), 4.46 – 4.39 (m, 4H, CH_2), 4.00 – 3.70 (m, 8H, CH_2), 3.29 – 2.90 (m, 6H, CH_2, CH_2,), 2.00 – 1.77 (m, 8H, CH_2), 1.38 – 1.12 (m, 3H, CH_3), 0.97 (t, J = 7.5, 9H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 156.74, 155.16, 138.35, 135.85, 135.37, 135.30, 135.22, 135.08, 134.45, 133.14, 128.33, 122.06, 115.09, 76.86, 39.71, 31.19, 23.45, 10.55.

Synthesis of 3.28

In a 50 mL RBF **3.26** (0.464 g, 1.0 mmol) and NaH (0.120 g, 5.0 mmol), were combined under N_2. DMF (50 mL) and THF (5 mL) were added and the mixture allowed to stir for 30 min to generate the anion. *Tert*butyldimethylchlorosilane (0.754 g, 5.0 mmol) was then injected into the reaction mixture and the mixture stirred for an additional 12 hours. The mixture was poured into 200 mL of HCl (1.2 M) and extracted into $CHCl_3$. The product was washed with water and dried over $MgSO_4$. After filtration and removal of solvent the crude product was purified on silica using $CHCl_3$:hexanes (60:40). Yield: 0.876 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.29 – 6.57 (m, 45H), 6.47 (q, *J* = 7.4, 1H), 6.33 – 6.20 (m, 6H), 6.11 – 5.72 (m, 9H), 5.14 – 4.82 (m, 7H), 4.09 – 3.91 (m, 8H), 3.75 – 3.19 (m, 27H), 3.13 – 2.85 (m, 10H), 1.56 – 1.46 (m, 1H), 1.29 – 0.54 (m, 314H), 0.38 – -0.19 (m, 205H).

Synthesis of 3.29

In a 100 mL 3-necked RBF affixed with an addition funnel, nitrogen inlet, and thermometer, **3.27** (3.440 g, 5 mmol) was dissolved in 40 mL dry THF under nitrogen and cooled to -10°C in a saltwater-ice bath. Borane 1M solution (5 mL, 5 mmol) was added dropwise while maintaining the temperature of the reaction below 0°C. After addition of borane the reaction was allowed to stir at or below 0°C for 30 min, after which, the reaction was warmed to room temperature and stirred for an additional 2 hours. After the 2 hours elapsed 8 mL of 1M NaOH (8 mmol) was added dropwise followed by H_2O_2(30% solution, 32 mmol) and the solution was stirred for 30 min. The solution was poured into 100 mL of H_2O and extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and gravity filtered, the solvent was then removed *in vacuo*. The product residue was dissolved in hot isopropanol and precipitated into HCl (1.2 M) and collect though vacuum filtration. Yield: 3.365 g, 4.75 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.22 – 6.14 (m, 11H Ar-CH), 4.45 (dd, *J* = 13.2, 11.6, 4H, CH_2), 3.96 – 3.68 (m, 8H, CH_2), 3.46 (t, *J* = 6.4, 2H, CH_2), 3.14 (dd, *J* = 16.2, 13.2, 4H, CH_2), 2.37 – 2.32 (m, 2H, CH_2), 2.04 – 1.79 (m, 8H, CH_2), 1.66 – 1.57 (m, 2H, CH_2), 1.26 (d, *J* = 12.9, 3H, CH_3), 1.05 – 0.93 (m, 9H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 156.91, 154.76, 135.60, 135.53, 135.33, 135.06, 134.86, 134.70, 128.40, 128.36, 128.18, 128.16, 122.06, 121.95, 76.99, 76.84, 62.79, 62.58, 34.42, 34.27, 31.44, 31.18, 23.49, 23.40, 10.60, 10.46.

Synthesis of 3.30

In a 100 mL 3-necked RBF affixed with an addition funnel, nitrogen inlet, and thermometer, **3.28** (4.614 g, 5 mmol) was dissolved in 40 mL dry THF under nitrogen and cooled to -10°C in a saltwater-ice bath. Borane 1M solution (5 mL, 5 mmol) was added dropwise while maintaining the temperature of the reaction below 0°C. After addition of borane the reaction was allowed to stir at or below 0°C for 30 min, after which, the reaction was warmed to room temperature and stirred for an additional 2 hours. After the 2 hours elapsed 8 mL of 1M NaOH (8 mmol) was added dropwise followed by H_2O_2(30% solution, 32 mmol) and the solution was stirred for 30 min. The solution was poured into 100 mL of H_2O and extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and gravity filtered, the solvent was then removed *in vacuo*. The product residue was dissolved in hot isopropanol and precipitated into HCl (1.2 M) and collected though vacuum filtation. Yield: 4.470 g, 4.75 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 3H), 7.09 – 6.90 (m, 7H), 6.91 – 6.72 (m, 5H), 6.70 – 6.56 (m, 1H), 6.46 (t, J = 7.3, 1H), 6.30 – 6.19 (m, 3H), 5.84 – 5.73 (m, 3H), 5.66 (s, 1H), 4.07 – 3.92 (m, 4H), 3.77 – 3.34 (m, 15H), 3.02 – 2.83 (m, 4H), 2.71 – 2.10 (m, 2H), 1.95 – 1.54 (m, 4H), 1.44 – 1.24 (m, 1H), 1.20 – 1.05 (m, 30H), 0.96 – 0.76 (m, 77H), 0.67 – 0.56 (m, 18H), 0.35 – 0.04 (m, 60H), 0.02 – -0.05 (m, 19H).

Synthesis of 3.31

In a 100 mL 3-necked RBF affixed with an addition funnel, nitrogen inlet, and thermometer, **3.26** (2.320 g, 5 mmol) was dissolved in 40 mL dry THF under nitrogen and cooled to -10°C in a saltwater-ice bath. Borane 1M solution (5 ml, 5 mmol) was added dropwise while maintaining the temperature of the reaction below 0°C. After addition of borane the reaction was allowed to stir at or below 0°C for 30 min, after which, the reaction was warmed to room temperature and

stirred for an additional 2 hours. After the 2 hours elapsed 8 mL of 1M NaOH (8 mmol) was added dropwise followed by H_2O_2(30% solution, 32 mmol) and the solution was stirred for 30 min. The solution was poured into 100 mL of H_2O and extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and gravity filtered, the solvent was then removed *in vacuo*. The product residue was dissolved in hot isopropanol and precipitated into HCl (1.2 M) and collect though vacuum filtration. Yield: 2.30 g, 4.75 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.17 (s, 4H, ArOH), 7.04 (d, *J* = 7.6, 6H, ArCH), 6.86 (s, 2H, ArCH), 6.71 (t, *J* = 7.5, 3H, ArCH), 4.24 (s, 4H, $ArCH_2Ar$), 3.73 (t, *J* = 6.7, 1H, OH), 3.61 (t, *J* = 6.4, 2H, CH_2), 3.50 (s, 4H, $ArCH_2Ar$), 2.52 – 2.44 (m, 2H, CH_2), 1.81 – 1.73 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 149.03, 147.00, 135.60, 129.17, 129.15, 129.09, 128.50, 128.42, 128.32, 122.51, 122.42, 62.51, 34.44, 32.00, 31.95, 31.40, 25.83.

Synthesis of 3.32:

η^6-Dichlorobenzene-η^5-cyclopentadienyliron hexaphluorophosphate (1.652 g, 4.0 mmol), 4-hydroxybenzoic acid (2.21 g, 16 mmol), K_2CO_3 (5.52o g, 40 mmol) and DMF (80 mL) were stirred under Nitrogen in the dark at room temperature for 16 hours. The reaction was poured into 200 ml of 1.2 M HCl with NH_4PF_6 (4.0 mmol). The product was extracted into DCM, dried over $MgSO_4$, gravity filtered and the organic layer concentrated *en vacuo*. The product solution was poured into ether and stirred until a precipitate formed. The precipitate was collected and dried under reduced pressure. Yield: 1.854 g, 3.6 mmol, 90%.

Spectral analysis showed that the product conforms to published spectra.

Synthesis of 3.33 and 3.34

Propoxy- or TBDMS-protected calix[4]arene (**3.23** or **3.24**) (1.0 mmol), organoiron acid complex (**3.32**) (2.3 mmol), DCC (2.5 mmol), DMAP (2.5 mmol) and 15 mL DCM and 10 mL DMF were combined in a RBF and stirred for 5 hours under N_2 at room temperature in the dark. The reaction mixture was placed in a freezer for 1 hour to precipitate dicyclohexylurea (DCU). The reaction mixture was filtered into a seperatory funnel containing 100 mL HCl and NH_4PF_6 (2.3 mmol) to remove the DCU. The product was extracted into DCM and reaction mixture was washed with 1.2M HCl to remove DMAP and DMF. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed en vacuo to give a yellow/beige residue. The residue was dissolved in acetone and passed through a neutral alumina column to remove any unreacted acid complex. The product was precipitated into water with NH_4PF_6 (2.3 mmol) to give a yellow powder.

3.33: ^{1}H NMR (400 MHz, acetone-d_6) δ= 8.20 (d, J = 8.4, 4H, ArCH), 7.47 (d, J = 8.4, 4H, ArCH), 6.87 (d, J = 5.8, 4H, *ArCH), 6.72 (s, 4H, ArCH), 6.63 (d, J = 5.8, 4H, *ArCH), 6.47 (m, 4H, ArCH), 6.41 (m, 2H, ArCH), 5.37 (s, 10H, Cp), 4.47 (d, J = 13, 4H, $ArCH_2Ar$), 4.29 (t, J = 6.2, 4H, CH_2), 3.91 (t, J = 7.6, 4H, CH_2), 3.82 (t, J = 7.2, 4H, CH_2), 3.14 (d, J = 13, 4H, $ArCH_2Ar$), 2.60 (t, J = 7.5, 4H, CH_2), 1.98 (m, 4H, CH_2), 1.98 (m, 4H, CH_2), 1.96 (m, 4H, CH_2), 1.06 (t, J = 7.5, 6H, CH_3), 0.99 (t, J = 7.5, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 168.1, 158.3, 157.0, 156.2, 136.3, 135.2, 135.2, 133.1, 132.6, 129.4, 129.3, 128.7, 122.8, 121.3, 105.5, 88.2, 80.9, 78.6, 77.6, 77.5, 65.3, 32.3, 31.6, 31.5, 23.9, 23.8, 10.9, 10.6. Yield: 1.617 g, 0.95 mmol, 95%.

3.34: ^{1}H NMR (400 MHz, Acetone) δ 8.23 (s, 3H), 7.54 (t, *J* = 63.6, 5H), 6.87 (dt, *J* = 130.3, 39.8, 14H), 6.34 (s, 1H), 5.88 (s, 2H), 5.44 (s, 10H), 4.09 (s, 6H), 3.75 (s, 5H), 2.92 (d, *J* = 85.5, 6H), 2.19 (s, 0H), 1.40 – -0.31 (m, 86H). Yield: 1.876 g, 0.95 mmol, 95%.

Synthesis of 3.36

Calix[4]arene **3.23** (0.708 g, 1.0 mmol), valeric bimetallic organoiron complex (**3.35**) (2.390 g, 2.3 mmol), DCC (0.515 g, 2.5 mmol), DMAP (0.305 g, 2.5 mmol) and 15 mL DCM and 10 mL DMF were combined in a RBF and stirred for 5 hours under N_2 at room temperature in the dark. The reaction mixture was placed in a freezer for 1 hour to precipitate dicyclohexylurea (DCU). The reaction mixture was filtered into a seperatory funnel containing 100 mL HCl and NH_4PF_6 (0.750 g, 4.6 mmol) to remove the DCU. The product was extracted into DCM and reaction mixture was washed with 1.2M HCl to remove DMAP and DMF. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed *en vacuo* to give a yellow/beige residue. The residue was dissolved in acetone and passed through a neutral alumina column to remove any unreacted valeric bimetallic. The product was precipitated into water with NH_4PF_6 (0.750 g, 4.6 mmol) to give a yellow powder. Yield: 2.613 g, 0.95 mmol, 95%.

3.36: ^{1}H NMR (400 MHz, acetone-d_6) δ= 7.49 (m, 8H, ArCH), 7.32 (m, 8H, ArCH), 6.79 (m, 8H, *ArCH), 6.73 (s, 2H, ArCH), 6.50 (m, 8H, *ArCH), 6.37 (m, 4H, ArCH), 6.35 (m, 2H, ArCH), 5.36 (s, 20H, Cp), 4.45 (d, *J* = 13.1, 4H, $ArCH_2Ar$), 4.01 (m, 4H, CH_2), 3.91 (m, 4H, CH_2), 3.76 (m, 4H, CH_2), 3.13 (d, *J* = 13.1, 4H, $ArCH_2Ar$), 2.57 (m, 4H, CH_2), 2.50 (m, 4H, CH_2), 2.23 (m, 4H, CH_2), 1.97 (m, 4H, CH_2), 1.93 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 1.76 (s, 6H, CH_3), 1.05 (t, *J* = 7.4, 6H, CH_3), 0.96 (t, *J* = 7.4, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 174.2, 157.3, 156.9, 152.8, 148.6, 137.1, 135.5, 134.5, 131.2, 129.9, 129.1, 123.3, 121.9, 105.6, 88.5, 81.1, 78.2, 78.0, 64.9, 47.0, 38.0, 32.7, 32.1, 32.0, 31.4, 28.4, 24.7, 24.5, 11.5, 11.0.

Synthesis of 3.37

TBDMS-protected calix[4]arene **3.34** (0.9100 g, 0.5 mmol), $N(Bu)_4F$ (2.3 mmol, 1M solution in THF), DMF (7 mL), and glacial acetic acid (2.3 mmol) were stirred under N_2 for 24 hours. The reaction was poured into 1.2 M HCl and NH_4PF_6 (1 mmol) was added. The product was filtered into a crucible and dried under reduced pressure. Yield: 0.3602 g, 0.24 mmol, 48%.

^{1}H NMR (400 MHz, acetone) δ= 9.97 (s, 4H, ArOH), 8.16 (d, J = 8.4, 4H, ArCH), 7.47 (d, J = 8.6, 4H, ArCH), 7.21 – 7.14 (m, 4H, ArCH), 7.12 – 7.05 (m, 3H, ArCH), 6.99 (d, J = 4.3, 1H, ArCH), 6.89 (dd, J = 6.7, 2.9, 4H, *ArCH), 6.70 (s, 4H, *ArCH), 6.69 – 6.58 (m, 1H, ArCH), 5.43 (s, 9H, Cp), 4.26 (dt, J = 13.8, 6.5, 4H, CH_2), 4.18 – 3.54 (m, 8H, $ArCH_2Ar$), 2.66 – 2.48 (m, 4H, CH_2), 2.02 – 1.91 (m, 4H, CH_2).

^{13}C NMR (101 MHz, acetone-d_6) δ= 165.78, 158.28, 149.98, 147.92, 147.69, 133.18, 132.72, 129.97, 129.94, 129.92, 129.49, 129.36, 122.93, 121.29, 105.55, 88.23, 80.94, 78.65, 65.43, 32.05, 31.88, 31.88.

Synthesis of 3.38

Calix[4]arene **3.29** (0.652 g, 1.0 mmol), organoiron acid complex (**3.32**) (0.670 g, 1.3 mmol), DCC (0.309 g, 1.5 mmol), and DMAP (0.183 g, 1.5 mmol) and 15 mL DCM and 10 mL DMF were combined in a RBF and stirred for 5 hours under N_2 at room temperature in the dark. The reaction mixture was placed in a freezer for 1 hour to precipitate dicyclohexylurea (DCU). The reaction mixture was filtered into a seperatory funnel containing 100 mL HCl and NH_4PF_6 (0.212 g, 1.3 mmol) to remove the DCU. The product was extracted into DCM and reaction

mixture was washed with 1.2M HCl to remove DMAP and DMF. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed en vacuo to give a yellow/beige residue. The residue was dissolved in acetone and passed through a neutral alumina column to remove any unreacted acid complex. The product was precipitated into water with NH_4PF_6 (0.212 g, 1.3 mmol) to give a yellow powder. Yield: 1.034 g, 0.9 mmol, 90%.

^{1}H NMR (400 MHz, acetone) δ= 8.20 (d, *J* = 8.6, 2H, ArCH), 7.49 (d, *J* = 8.6, 2H, ArCH), 6.90 (d, *J* = 6.6, 2H, *ArCH), 6.75 – 6.39 (m, 13H, ArCH, *ArCH), 5.52 – 5.33 (m, 5H, Cp), 4.47 (dd, *J* = 13.1, 6.4, 4H, $ArCH_2Ar$), 4.15 (t, *J* = 6.5, 2H, CH_2), 3.96 – 3.77 (m, 8H, CH_2), 3.20 – 3.07 (m, 4H, $ArCH_2Ar$), 2.49 – 2.38 (m, 2H, CH_2), 2.03 – 1.92 (m, 8H, CH_2), 1.85 – 1.76 (m, 2H, CH_2), 1.16 – 0.91 (m, 12H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 133.08, 128.97, 128.72, 122.59, 121.25, 88.16, 80.83, 77.86, 77.54, 64.96, 31.72, 31.48, 31.11, 24.06, 10.68.

Synthesis 3.39

Calix[4]arene (**3.29**) (0.642 g, 1.0 mmol), valeric bimetallic organoiron complex (**3.35**) (2.390 g, 2.3 mmol), DCC (0.515 g, 2.5 mmol), DMAP (0.305 g, 2.5 mmol) and 15 mL DCM and 10 mL DMF were combined in a RBF and stirred for 5 hours under N_2 at room temperature in the dark. The reaction mixture was placed in a freezer for 1 hour to precipitate dicyclohexylurea (DCU). The reaction mixture was filtered into a seperatory funnel containing 100 mL HCl and NH_4PF_6 (0.750 g, 4.6 mmol) to remove the DCU. The product was extracted into DCM and reaction mixture was washed with 1.2M HCl to remove DMAP and DMF. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed en vacuo to give a yellow/beige residue. The residue was dissolved in acetone and passed through a neutral alumina column to remove any unreacted valeric bimetallic complex. The product was precipitated into

water with NH_4PF_6 (0.750 g, 4.6 mmol) to give a yellow powder. Yield: 1.580 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.44 (s, 4H, ArCH), 7.28 (s, 4H, ArCH), 6.70 (s, 4H, *ArCH), 6.61 (s, 4H, ArCH), 6.39 (s, 9H, ArCH, *ArCH), 6.28 – 6.16 (m, 2H, ArCH), 5.27 (s, 10H, Cp), 4.40 (s, 4H, $ArCH_2Ar$), 4.14 – 3.90 (m, 2H, CH_2), 3.83 (s, 8H, CH_2), 3.09 (s, 4H, $ArCH_2Ar$), 2.52 (s, 2H, CH_2), 2.35 – 2.24 (m, 2H, CH_2), 2.24 – 2.12 (m, 2H, CH_2), 1.91 (s, 8H, CH_2), 1.71 (s, 3H, CH_3), 1.64 – 1.54 (m, 2H, CH_2), 0.98 (s, 12H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 173.57, 157.43, 157.25, 155.47, 152.08, 147.99, 135.98, 135.94, 135.67, 135.34, 135.08, 133.87, 130.63, 129.01, 128.86, 128.82, 122.69, 121.31, 104.86, 87.81, 80.45, 77.44, 77.38, 77.08, 64.26, 46.36, 37.35, 31.51, 31.49, 27.90, 24.01, 23.95, 10.68.

Synthesis of azo dye containing complex 3.41:

Complex **3.33** (1.702 g, 1.0 mmol) was reacted with the azo dye (**3.40**) (0.748 g, 2.5 mmol) and K_2CO_3 (1.58 g, 10 mmol) in DMF (15 mL) at room temperature, under N_2, for 24 hours. The reaction mixture was poured into 10% HCl (300 mL) and NH_4PF_6 (0.326 g, 2.0 mmol) was added. The precipitate was filtered washed with water and dried under reduced pressure. Yield 2.151: g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 8.03 (d, J = 8.7, 4H, ArCH), 7.92 (d, J = 8.7, 4H, ArCH), 7.84 (d, J = 9.5, 2H, ArCH), 7.45 (d, J = 8.7, 4H, ArCH), 7.37 (m, 2H, ArCH), 7.33 (d, J = 8.7, 4H, ArCH), 6.87 (m, 2H, ArCH), 6.85 (s, 2H, ArCH), 6.70 (br s, 4H, *ArCH), 6.37 (m, 4H, *ArCH), 6.28, (m, 4H, ArCH), 5.25 (s, 10H, Cp), 4.29 (m, 4H, $ArCH_2Ar$), 4.21 (m, 4H, CH_2), 3.80 (m, 4H, CH_2), 3.68 (m, 4H, CH_2), 3.61 (m, 4H, CH_2), 3.58 (m, 4H, CH_2), 3.57 (m, 4H, CH_2), 3.08 (m, 4H, $ArCH_2Ar$), 2.60 (s, 6H, CH_2), 2.51 (m, 4H, CH_2), 1.90 (m, 4H, CH_2), 1.85 (m, 8H, CH_2), 1.15 (m, 6H, CH_2), 0.99 (m, 6H, CH_3), 0.90 (m, 6H, CH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ= 167.1, 155.5, 154.9, 153.6, 151.7, 148.5, 143.2, 140.1, 135.2, 135.0, 134.8, 133.7, 130.1, 130.0, 129. 7, 129.6, 128.2, 123.2, 121.4, 120.4, 119.8, ,118.8, 113.8, 112.3, 78.1, 76.5, 76.1, 75.6, 75.4, 64.2, 58.4, 52.9, 46.2, 30.9, 30.3, 30.0, 23.0, 22.7, 18.0, 12.2, 10.5, 10.0.

Synthesis of 3.42

Complex **3.36** (1.747 g, 1.0 mmol) was reacted with the azo dye (**3.40**) (0.748 g, 2.5 mmol) and K_2CO_3 (1.38 g, 10 mmol) in DMF (15 mL) at room temperature, under N_2, for 24 hours. The reaction mixture was poured into 10% HCl (300 mL) and NH_4PF_6 (0.652 g, 4.0 mmol) was added. The precipitate was filtered washed with water and dried under reduced pressure. Yield: 3.614 g, .90 mmol, 90%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.91 (d, J = 8.5, 8H, ArCH), 7.86 (d, J = 8.6, 4H, ArCH), 7.72 (d, J = 8.7, 4H, ArCH), 7.43 (m, 8H, ArCH), 7.37 (m, 8H, ArCH), 7.25 (m, 8H, ArCH), 6.92 (d, J = 8.7, 4H, ArCH), 6.85 (m, 2H, ArCH), 6.83 (m, 4H, ArCH), 6.35 (m, 8H, *ArCH), 6.30 (m, 8H, *ArCH), 6.29 (m, 4H, ArCH), 5,24 (s, 20H, Cp), 4.29 (d, J = 13.1, 4H, $ArCH_2Ar$), 3.94 (m, 4H, CH_2), 3.81 (m, 4H, CH_2), 3.57 (m, 28H, CH_2), 3.07 (d, 13.1 Hz, 4H, $ArCH_2Ar$), 2.61 (s, 12H, CH_2), 2.59 (s, 6H, CH_2), 2.46 (m, 4H, CH_2), 2.42 (m, 4H, CH_2), 2.16 (m, 4H, CH_2), 1.80 (s, 6H, CH_3), 1.74 (m, 4H, CH_2), 1.12 (m, 12H, CH_2), 0.99 (m, 6H, CH_3), 0.88 (m, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 172.9, 159.5, 155.3, 153.5, 153.5, 151.7, 151.7, 148.7, 146.0, 143.0, 140.0, 134.1, 133.5, 130.2, 129.2, 127.4, 123.2, 123.2, 121.3, 120.0, 118.7, 116.0, 113.6, 112.0, 78.0, 76.0, 75.3, 75.3, 63.5, 58.3, 57.7, 52.8, 46.1, 45.1, 36.1, 30.8, 30.2, 30.0.

Synthesis of 3.43

Calix[4]arene **3.42** (3.804 g, 1.0 mmol), **3.35** (4.365 g, 4.2 mmol) and DMAP (0.549 g, 4.5 mmol) were dissolved in 15 mL DMF and 10 mL DCM. DCC (0.927 g, 4.5 mmol) was added and the reaction mixture was placed under N_2 and allowed to stir for 5 hours at room temperature. The reaction was placed into a freezer for 30 min, after which the mixture was filtered to remove precipitated DCU. The reaction was extracted into DCM, washed with H_2O, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was dissolved in a minimal amount of DCM and placed in a freezer to crystallize the remaining DCU. The DCU was filtered off and the product passed through a neutral alumina column using acetone as the eluent to remove any remaining starting material. Yield: 4.734 g, 0.60 mmol, 60%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.92 (m, 6H, ArCH), 7.82 (m, 4H, ArCH), 7.73 (m, 4H, ArCH), 7.55 (m, 8H, ArCH), 7.40 (m, 28H, ArCH), 7.27 (m, 24H, ArCH), 6.73 (m, 28H, ArCH), 6.48 (m, 8H, ArCH), 6.40 (m, 24H, ArCH, *ArCH), 5.3 (m, 60H, Cp), 4.46 (d, J = 13.4, 4H, $ArCH_2Ar$), 4.31 (m, 8H, CH_2), 3.89 (m, 4H, CH_2), 3.78 (m, 8H, CH_2), 3.76 (m, 12H, CH_2), 3.58 (m, 16H, CH_2), 3.13 (d, J = 13.4, 4H, $ArCH_2Ar$), 2.73 (m, 6H, CH_2), 2.66 (s, 12H, CH_2), 2.57 (m, 8H, CH_2), 2.47 (m, 12H, CH_2), 2.18 (m, 12H, CH_2), 1.94 (m, 8H, CH_2), 1.83 (s, 6H, CH_3), 1.78 (m, 8H, CH_2), 1.69 (s, 12H, CH_2), 1.22 (m, 12H, CH_2), 1.04 (m, 6H, CH_3), 0.97 (m, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 173.7, 172.5, 152.5, 152.3, 152.1, 148.0, 142.4, 142.2, 136.3, 135.3, 135.2, 134.0, 130.8, 130.7, 125.1, 125.0, 123.8, 123.4, 121.9, 121.4, 121.3, 117.9, 113.5, 113.13, 111.1, 110.9, 105.0, 88.0, 80.6, 79.2, 77.6, 77.5, 77.3, 77.2, 76.6, 76.4, 76.2, 62.6, 60.2, 60.1, 53.3, 49.0, 46.6, 46.4, 46.3, 45.6, 45.4, 37.2, 31.6, 31.0, 30.9, 28.1, 27.9, 26.8, 26.3, 26.3, 25.6, 24.2, 24.0, 18.5, 12.6, 11.1, 10.6.

Synthesis of 3.45 or 3.46

Calix[4]arene **3.35** or **3.36** (1.0 mmol) and 4-hydroxybenzyl alcohol (**3.44**) (2.3 mmol) and K_2CO_3 (7.0 mmol) were stirred in 15 mL DMF for 24 hours under N_2 at room temperature in the dark for 24 hours. The reaction mixture was poured in to 1.2 M HCl with NH_4PF_6 (2.0 mmol) to precipitate the product. The precipitate was collected and dried under reduced pressure.

3.45: ^{1}H NMR (400 MHz, acetone) δ= 8.18 (d, *J* = 8.0, 4H, ArCH), 8.04 (d, *J* = 7.7, 4H, ArCH), 7.55 (d, *J* = 7.6, 4H, ArCH), 7.47 – 7.25 (m, 2H, ArCH), 7.22 – 6.89 (m, 5H, ArCH), 6.51 (s, 2H, ArCH), 6.48 – 6.29 (m, 12H, ArCH, *ArCH), 5.37 (s, 10H, Cp), 4.70 (s, 4H, CH_2), 4.50 – 4.34 (m, 6H, CH_2, $ArCH_2Ar$), 3.98 – 3.71 (m, 8H, CH_2), 3.12 (d, *J* = 13.2, 4H, $ArCH_2Ar$), 2.63 – 2.56 (m, 2H, CH_2), 2.02 – 1.89 (m, 8H, CH_2), 1.83 (t, *J* = 6.3, 2H, CH_2), 1.06 (t, *J* = 7.3, 3H, CH_3), 0.98 (t, *J* = 7.4, 3H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 159.10, 153.19, 142.04, 136.42, 135.23, 133.07, 130.89, 130.83, 129.74, 129.36, 128.73, 122.81, 121.38, 120.80, 79.31, 77.62, 77.56, 76.83, 76.03, 65.19, 63.88, 32.30, 31.65, 31.52, 29.70, 10.98, 10.61. Yield: 1.698 g, 0.90 mmol, 90%.

3. 46: ^{1}H NMR (400 MHz, acetone) δ 8.21 (s, 5H), 7.79 – 6.78 (m, 30H), 6.67 – 6.16 (m, 7H), 5.39 (s, 10H), 4.71 (s, 4H), 4.62 – 3.70 (m, 0H), 1.44 – -0.21 (m, 125H).

^{13}C NMR (101 MHz, Acetone) δ 165.91, 159.15, 159.05, 153.19, 152.63, 150.54, 142.04, 136.00, 135.68, 134.10, 133.08, 132.96, 132.76, 132.70, 132.61, 132.49, 132.34, 132.05, 131.75, 131.53, 131.09, 130.82, 130.20, 129.74, 129.54, 129.41, 129.06, 128.98, 128.88, 128.20, 124.50, 123.05, 122.45, 121.85, 121.40, 120.83, 120.50, 118.53, 116.11, 79.44, 79.41, 78.67, 77.83, 77.74, 76.92, 76.04, 75.84, 73.85, 65.32, 65.16, 64.46, 63.92, 38.83, 35.47, 35.03, 33.01, 32.56, 32.43, 32.06, 31.77, 31.67, 31.45, 29.73, 27.30, 27.06, 27.02, 26.62, 26.14, 26.07, 25.38, 20.51,

19.79, 19.45, -0.25, -0.65, -2.66, -2.82, -2.96, -3.11, -3.59, -15.33. Yield: 2.00 g, 0.90 mmol, 90%.

Synthesis of 3.47

Calix[4]arene **3.36** (2.751 g, 1.0 mmol) 4-hydroxy benzylalcohol (0.5570 g, 4.5 mmol) and K_2CO_3 (2.760 g, 20 mmol) were stirred in 25 mL DMF for 16 hours under N_2 in the dark. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.652 g, 4.0 mmol). The precipitate was collected and dried under reduced pressure. Yield: 2.667 g, 0.90 mmol, 90%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.53 (d, J = 7.3, 8H, ArCH), 7.46 (s, 8H, ArCH), 7.28 (s, 16H, ArCH), 6.70 (s, 3H, ArCH), 6.37 (d, J = 26.0, 23H, ArCH, *ArCH), 5.29 (s, 20H, Cp), 4.69 (s, 8H, CH_2), 4.44 (d, J = 13.0, 4H, $ArCH_2Ar$), 4.00 (t, J = 5.9, 4H, CH_2), 3.95 – 3.86 (m, 4H, CH_2), 3.83 – 3.75 ($ArCH_2Ar$), 2.62 – 2.52 (m, 4H, CH_2), 2.52 – 2.41 (m, 4H, CH_2), 2.27 – 2.14 (m, 4H, CH_2), 2.00 – 1.91 (m, 8H, CH_2), 1.85 (s, 4H, CH_2), 1.75 (s, 6H, CH_3), 1.05 (t, J = 7.4, 6H, CH_3), 0.97 (t, J = 7.4, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 173.69, 156.85, 156.19, 153.28, 152.87, 147.94, 147.64, 141.81, 136.33, 135.27, 135.13, 132.07, 131.76, 130.59, 129.66, 129.26, 128.69, 122.78, 121.26, 121.15, 79.04, 77.59, 77.43, 76.15, 75.87, 64.35, 63.87, 46.32, 37.41, 32.15, 31.37, 30.82, 27.96, 24.12, 23.96, 10.97, 10.57.

Synthesis of 3.49 or 3.50

Calix[4]arene **3.45** and **3.46** (1.0 mmol), carboxylic ferrocene (2.5 mmol), DCC (3.0 mmol), and DMAP (3.0 mmol) were stirred with 15 mL DCM under N_2 for 5 hours. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (2.0 mmol) and extracted into DCM. The organic layer was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The product

residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated into basic water to remove any excess carboxylic ferrocene. The precipitate was collected and dried under reduced pressure.

3.49: ^{1}H NMR (400 MHz, acetone) δ 8.17 (d, *J* = 9.0, 4H, ArCH), 8.03 (d, *J* = 8.9, 4H, ArCH), 7.71 (d, *J* = 8.7, 4H, ArCH), 7.63 – 7.51 (m, 2H, ArCH), 7.44 – 7.38 (m, 5H, ArCH), 7.36 – 7.26 (m, 2H, ArCH), 7.18 – 6.99 (m, 3H, ArCH), 6.56 – 6.47 (m, 2H, ArCH), 6.47 – 6.33 (m, 8H, ArCH, *ArCH), 5.41 – 5.31 (m, 14H, Cp, CH_2), 4.85 – 4.79 (m, 4H, *Cp), 4.49 – 4.41 (m, 8H, $ArCH_2Ar$, *Cp), 4.37 – 4.22 (m, 2H, CH_2), 4.17 – 4.13(m, 10H, *`Cp), 3.97 – 3.74 (m, 8H, CH_2), 3.13 (d, *J* = 13.1, 4H, $ArCH_2Ar$), 2.56 (t, *J* = 4.9, 2H, CH_2), 2.03 – 1.87 (m, 8H, CH_2), 1.83 (s, 2H, CH_2), 1.06 (t, *J* = 7.4, 6H, CH_3), 0.99 (t, *J* = 7.4, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 171.38, 165.98, 159.31, 157.19, 156.38, 154.47, 136.75, 133.07, 131.81, 129.31, 128.75, 122.27, 121.67, 120.87, 79.44, 77.65, 77.63, 77.60, 77.51, 77.50, 76.27, 72.43, 70.98, 70.61, 65.40, 65.23, 32.27, 31.62, 31.26, 23.86, 10.98, 10.62. Yield: 2.041 g, 0.95 mmol, 95%.

3.50: ^{1}H NMR (400 MHz, acetone) δ 8.26 (d, *J* = 56.7, 1H), 7.72 (d, *J* = 8.3, 1H), 7.41 (d, *J* = 8.4, 1H), 7.12 (d, *J* = 7.5, 1H), 7.07 – 6.63 (m, 1H), 6.42 (t, *J* = 34.3, 1H), 6.22 – 5.81 (m, 0H), 5.40 – 5.20 (m, 2H), 4.98 – 4.29 (m, 4H), 3.78 (s, 1H), 3.47 (d, *J* = 40.3, 1H), 3.19 (s, 1H), 1.95 – -0.05 (m, 39H). Yield: 2.210 g, 0.90 mmol, 90%.

Synthesis of 3.51

Calix[4]arene **3.47** (2.963 g, 1.0 mmol), carboxylic ferrocene (1.26 g, 4.5 mmol), DCC (1.030 g, 5.0 mmol), and DMAP (0.610 g, 5.0 mmol) were stirred with 15 mL DCM under N_2 for 5 hours. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.652 g, 4.0 mmol) and extracted into DCM. The organic

layer was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The product residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated into basic water to remove any excess carboxylic ferrocene. The precipitate was collected and dried under reduced pressure. Yield: 2.741 g, 0.85 mmol, 85%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.69 (d, J = 8.3, 8H, ArCH), 7.50 – 7.32 (m, 16H, ArCH), 7.27 (d, J = 8.3, 8H, ArCH), 6.33 (s, 26H, ArCH, *ArCH), 5.32 – 5.27 (m, 28H, Cp, CH_2), 4.81 (s, 8H, *Cp), 4.45 (d, J = 17.0, 12H, $ArCH_2Ar$, *Cp), 4.17 – 4.12 (m, 20H*`Cp), 4.00 (t, J = 6.4, 4H, CH_2), 3.94 – 3.85 (m, 4H, CH_2), 3.78 (t, J = 7.3, 4H, CH_2), 3.11 (d, J = 12.8, 4H, $ArCH_2Ar$), 2.62 – 2.51 (m, 2H, CH_2), 2.51 – 2.43 (m, 2H, CH_2), 2.25 – 2.16 (m, 4H, CH_2), 1.99 – 1.91 (m, J = 14.0, 6.3, 8H, CH_2), 1.85 (s, 4H, CH_2), 1.74 (s, 6H, CH_3), 1.05 (t, J = 7.5, 6H, CH_3), 0.97 (t, J = 7.3, 6H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 173.72, 171.40, 154.50, 152.91, 147.71, 136.45, 131.74, 131.68, 130.59, 129.33, 128.70, 122.82, 121.53, 121.14, 79.10, 77.47, 76.22, 76.12, 73.73, 72.41, 70.98, 70.58, 65.40, 64.41, 37.44, 34.62, 32.99, 32.20, 31.64, 29.73, 27.94, 24.18, 24.01.

Synthesis of 3.52

Calix[4]arene **3.38** (1.0 mmol) 4-hydroxy benzylalcohol (1.5 mmol) and K_2CO_3 (10 mmol) were stirred in 25 mL DMF for 16 hours under N_2 in the dark. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.163 g, 1mmol). The precipitate was collected and dried under reduced pressure. Yield: 1.120g, 0.90 mmol, 90%.

^{1}H NMR (400 MHz, acetone-d_6) δ 8.17 (d, J = 8.1, 2H, ArCH), 7.56 (d, J = 8.0, 2H, ArCH), 7.43 (d, J = 8.6, 2H, ArCH), 7.30 (d, J = 15.1, 2H, ArCH), 6.94 (d, J = 8.3, 6H, ArCH), 6.69 (d, J = 7.6, 3H, ArCH), 6.62 – 6.35 (m, 6H, ArCH, *ArCH), 5.39 (s, 5H, Cp), 4.70 (s, 2H, CH_2), 4.53 –

4.37 (m, 4H, $ArCH_2Ar$), 4.14 (t, J = 6.5, 2H, CH_2), 3.86 (dt, J = 19.0, 8.5, 8H, CH_2), 3.15 (dd, J = 13.0, 11.4, 4H, $ArCH_2Ar$), 2.42 (dd, J = 15.0, 8.0, 2H, CH_2), 1.97 (dt, J = 15.1, 7.6, 8H, CH_2), 1.79 (dd, J = 13.8, 7.2, 2H, CH_2), 1.03 (dd, J = 18.1, 7.5, 12H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 165.79, 159.05, 157.57, 153.18, 142.04, 136.14, 135.69, 135.41, 135.03, 133.01, 132.70, 132.43, 129.74, 129.12, 129.00, 128.87, 122.76, 121.40, 120.81, 116.11, 79.42, 77.79, 77.57, 77.47, 76.05, 65.11, 64.27, 63.92, 32.00, 31.60, 31.12, 24.12, 24.03, 10.87, 10.69.

Synthesis of 3.53

Calix[4]arene **3.52** (1.245 g, 1.0 mmol), carboxylic ferrocene (0.336 g, 1.2 mmol), DCC (0.309 g, 1.5 mmol), and DMAP (0.183 g, 1.5 mmol) were stirred with 15 mL DCM under N_2 for 5 hours. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.163 g, 1.0 mmol) and extracted into DCM. The organic layer was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The product residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated into basic water to remove any excess carboxylic ferrocene. The precipitate was collected and dried under reduced pressure. Yield: 1.429 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, acetone) δ 8.16 (d, J = 8.7, 2H, ArCH), 7.72 (d, J = 8.2, 2H, ArCH), 7.42 (dd, J = 8.7, 2.1, 2H, ArCH), 6.69 (dd, J = 8.4, 2.1, 2H, ArCH), 6.62 – 6.48 (m, 8H, ArCH), 6.45 (s, 7H, ArCH, *ArCH), 5.37 (s, 5H, Cp), 5.33 (s, 2H, CH_2), 4.95 – 4.89 (m, 2H, *Cp), 4.68 – 4.64 (m, 2H, *Cp), 4.52 – 4.42 (m, 6H, $ArCH_2Ar$, CH_2), 4.42 (s, 5H, *`Cp), 3.96 – 3.77 (m, 8H, CH_2), 3.18 – 3.10 (m, 4H, $ArCH_2Ar$), 2.49 – 2.38 (m, 2H), 2.03 – 1.91 (m, 8H, CH_2), 1.74 – 1.69 (m, 2H, CH_2), 1.14 – 0.95 (m, 12H, CH_3).

^{13}C NMR (101 MHz, Acetone) δ 177.31, 168.65, 137.84, 136.65, 136.12, 135.66, 135.39, 132.95, 131.76, 129.06, 128.95, 128.82, 122.70, 121.59, 120.72, 79.37, 77.54, 77.44, 77.42, 76.26, 72.36, 70.91, 70.51, 65.30, 65.09, 31.95, 31.56, 31.09, 29.65, 23.99, 10.63.

Synthesis of 3.54

Calix[4]arene **3.39** (1.663 g, 1.0 mmol) 4-hydroxy benzylalcohol (0.310 g, 2.5 mmol) and K_2CO_3 (1.38 g, 10 mmol) were stirred in 25 mL DMF for 16 hours under N_2 in the dark. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.326 g, 2.0 mmol). The precipitate was collected and dried under reduced pressure. Yield: 1.544 g, 0.84 mmol, 84%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.53 (s, 4H, ArCH), 7.46 (s, 4H, ArCH), 7.28 (s, 8H, ArCH), 6.68 (d, J = 7.2, 6H, ArCH), 6.57 (t, J = 5.0, 3H, ArCH), 6.40 (s, 2H, ArCH), 6.33 (s, 8H, *ArCH), 5.30 (s, 10H, Cp), 4.69 (s, 4H, CH_2), 4.46 (dd, J = 12.9, 8.9, 4H, $ArCH_2Ar$), 3.96 – 3.77 (m, 8H, CH_2), 3.17 – 3.10 (m, 4H, $ArCH_2Ar$), 2.61 – 2.48 (m, 2H, CH_2), 2.36 – 2.26 (m, 2H, CH_2), 2.21 (s, 2H, CH_2), 1.99 – 19.6 (m, 8H, CH_2), 1.75 (s, 3H, CH_3), 1.67 – 1.57 (m, 2H, CH_2), 1.12 – 0.89 (m, 12H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 173.53, 163.22, 157.56, 157.30, 155.52, 153.28, 152.92, 147.66, 141.85, 136.12, 135.69, 135.37, 135.12, 132.14, 131.79, 130.70, 129.70, 129.11, 128.92, 128.86, 122.75, 122.68, 121.34, 121.25, 79.20, 79.13, 77.54, 77.47, 76.41, 76.06, 64.31, 63.82, 46.36, 37.49, 36.71, 31.56, 30.89, 30.50, 24.10, 24.02, 10.86, 10.82, 10.69.

Synthesis of 3.55

Calix[4]arene **3.54** (1.839 g, 1.0 mmol), carboxylic ferrocene (1.12 g, 4.0 mmol), DCC (0.309 g, 1.5 mmol), and DMAP (0.183 g, 1.5 mmol) were stirred with 15 mL DCM under N_2 for 5 hours. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was poured into 1.2 M HCl with NH_4PF_6 (0.326 g, 2.0 mmol) and extracted into DCM. The organic

layer was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The product residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated into basic water to remove any excess carboxylic ferrocene. The precipitate was collected and dried under reduced pressure. Yield: 1.891 g, 0.90 mmol, 90%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.70 (d, J = 8.0, 4H, ArCH), 7.46 (d, J = 8.3, 4H, ArCH), 7.38 (d, J = 7.8, 4H, ArCH), 7.28 (d, J = 8.0, 4H, ArCH), 6.68 (d, J = 7.4, 6H, ArCH), 6.57 (t, J = 5.9, 3H, ArCH), 6.37 (d, J = 18.9, 12H, ArCH, *ArCH), 5.30 (dd, J = 9.9, 6.0, 14H, Cp, CH_2), 4.81 (s, 4H, *Cp), 4.45 (d, J = 14.5, 8H, $ArCH_2Ar$, *Cp), 4.14 (s, 10H,*`Cp), 3.95 – 3.77 (m, 8H, CH_2), 3.25 – 3.08 (m, 4H, $ArCH_2Ar$), 2.59 – 2.50 (m, 2H, CH_2), 2.34 – 2.27 (m, 2H, CH_2), 2.24 – 2.17 (m, 2H, CH_2), 2.00 – 1.92 (m, 8H, CH_2), 1.86 (s, 2H, CH_2), 1.75 (s, 3H, CH_3), 1.07 – 0.93 (m, 12H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 172.83, 170.64, 156.88, 153.74, 152.21, 146.96, 135.76, 135.43, 135.02, 134.70, 131.17, 131.01, 129.84, 129.09, 128.38, 128.20, 128.16, 122.03, 120.79, 120.36, 78.36, 76.84, 76.77, 75.46, 75.41, 71.66, 71.32, 70.23, 69.82, 64.64, 63.60, 45.65, 36.73, 33.88, 33.22, 31.54, 30.89, 27.20, 24.86, 23.39, 23.32, 9.97.

Synthesis of 3.58

N-ethyl-anilino-ethanol (**3.57**) (1.65 g, 1.0 mmol), 5-carboxylic-2-norbornene (**3.56**) (1.22 mL, 1.0 mmol), dicyclohexylcarbodiimide (0.309 g, 1.5 mmol) and N,N'-dimethylaminopyridine (0.183 g, 1.5 mmol) was dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed

with water and dried over $MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. Yield: 0.215 g, 0.75 mmol, 75%.

^{1}H NMR (400 MHz, acetone-d_6) δ= 7.82 – 6.90 (m, 5H, ArCH), 6.09 (dd, J = 5.6, 3.0, 1H, CH=CH), 5.82 (dd, J = 5.6, 2.8, 1H, CH=CH), 4.48 – 4.16 (m, 2H, CH_2), 3.76 (dt, J = 10.7, 5.1, 2H, CH_2), 3.58 (q, J = 7.0, 2H, CH_2), 3.15 – 2.72 (m, 2H, CH_2), 1.90 (ddd, J = 20.9, 8.1, 2.9, 1H, CH), 1.47 – 1.20 (m, 3H, CH_2, CH), 1.17 (t, J = 7.1, 3H, CH_3).

^{13}C NMR (101 MHz, acetone-d_6) δ= 174.28, 138.63, 138.19, 136.42, 133.23, 130.54, 60.53, 50.01, 47.10, 46.77, 46.19, 43.62, 43.41, 43.18, 42.25, 29.53, 11.24.

Synthesis of 3.60

4-Amino benzoic acid (**3.59**) (3.43 g, 25 mmol) and 4.5M HCl (40 mL) were combined and cooled to 0 – 5 °C. $NaNO_2$ (1.725 g, 25 mmol was added portion-wise to the amine solution while it was on ice. The reaction was stirred for 1 hour at 0 – 5 °C. Functionalized aniline (**3.58**) (1.85 g, 6.5 mmol) was dissolved in 20 mL DMF:Ethanol (1:1) and cooled to 0 – 5 °C. The diazonium solution was poured into the coupler solution and stirred for 24 hours. The product was collected by filtration and dried under reduced pressure. Yield: 2.257g, 5.2 mmol, 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.25 – 8.17 (m, 2H, ArCH), 7.88 (ddd, J = 7.2, 4.8, 2.8, 4H, ArCH), 6.79 (d, J = 9.4, 2H, ArCH), 6.23 – 5.82 (m, 2H, CH=CH), 4.26 (dt, J = 26.5, 6.3, 2H, CH_2), 3.65 (dt, J = 12.7, 6.3, 2H, CH_2), 3.49 (dq, J = 15.0, 7.1, 2H, CH_2), 3.19 – 2.83 (m, 3H, CH_2, CH), 1.99 – 1.83 (m, 2H, CH_2), 1.48 – 1.36 (m, 2H, CH_2), 1.27 – 1.18 (m, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.99, 156.74, 151.02, 144.06, 138.23, 132.41, 131.44, 130.73, 126.06, 125.94, 122.32, 111.64, 61.63, 61.50, 49.91, 49.01, 46.61, 45.93, 45.73, 43.54, 42.75, 30.54, 29.51, 12.51.

Synthesis of 3.61

Calix[4]arene **(3.29)** (0.642 g, 1.0 mmol), 5-carboxylic-2-norbornene (0.18 mL, 1.5 mmol) (**3.56**), dicyclohexylcarbodiimide (0.309 g, 1.5 mmol) and N,N'-dimethylaminopyridine (0.189g, 1.5 mmol) was dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed with water and dried over $MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. The product was dissolved into hot isopropanol and precipitated into water. Yield: 0.725 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.78 – 6.35 (m, 11H, ArCH), 6.26 (dd, *J* = 5.7, 3.0, 0.5H, CH=CH), 6.18 (dd, *J* = 7.3, 4.3, 1H, CH=CH), 6.00 (dd, *J* = 5.8, 3.0, 0.5H, CH=CH), 4.51 (dd, *J* = 13.2, 10.4, 4H, $ArCH_2Ar$), 3.99 – 3.81 (m, 10H, CH_2), 3.27 (s, 1H, CH), 3.19 (dd, *J* = 15.5, 13.2, 4H, $ArCH_2Ar$), 3.11 (s, 1H, CH), 3.05 – 2.88 (m, 2H, CH_2), 2.36 (dd, *J* = 15.2, 7.5, 1H, CH), 2.32 – 2.25 (m, 2H, CH_2), 2.08 – 1.90 (m, 10H, CH_2), 1.80 – 1.56 (m, 2H, CH_2), 1.55 – 1.39 (m, 2H, CH_2), 1.06 (dt, *J* = 14.8, 7.5, 12H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 176.19, 174.69, 156.87, 156.49, 154.74, 138.12, 137.79, 135.92, 135.48, 134.92, 134.62, 134.37, 134.32, 132.58, 128.34, 128.07, 122.04, 121.92, 76.90, 76.88, 76.76, 63.92, 63.71, 49.78, 46.77, 46.55, 45.89, 43.53, 43.37, 42.71, 41.81, 31.49, 31.45, 31.13, 30.49, 30.45, 29.86, 23.45, 23.34, 10.57, 10.40.

Synthesis of 3.62

Calix[4]arene (**3.30**) (0.940 g, 1.0 mmol), 5-carboxylic-2-norbornene (**3.56**) (0.18 mL, 1.5 mmol), dicyclohexylcarbodiimide (0.309 g,1.5 mmol) and N,N'-dimethylaminopyridine (0.189 g, 1.5 mmol) was dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed with water and dried over

$MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. The product was dissolved into hot isopropanol and precipitated into water. Yield: 1.00 g, 0.95 mmol, 95%.

NMR: Due to the number of conformers structural determination cannot be reported

Synthesis of 3.63

Calix[4]arene (**3.29**) (0.642 g, 1.0 mmol), azo dye (**3.60**) (0.651 g, 1.5 mmol), dicyclohexylcarbodiimide (0.309 g, 1.5 mmol) and N,N'-dimethylaminopyridine (0.189 g, 1.5 mmol) was dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed with water and dried over $MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. The product was dissolved into hot isopropanol and precipitated into water. Yield: 1.211 g, 0.95 mmol, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.12 (d, *J* = 8.6, 2H, ArCH), 7.87 (d, *J* = 8.8, 2H, ArCH), 7.87 (d, 7.5, 2H, ArCH), 6.77 (d, *J* = 9.2, 2H, ArCH), 6.66 (d, *J* = 7.2, 3H, ArCH), 6.63 – 6.47 (m, 6H, ArCH), 6.35 (s, 2H, ArCH), 6.16 (dd, *J* = 8.2, 5.2, 1H, CH=CH), 5.98 (dd, *J* = 5.8, 2.7, 0.5H, CH=CH), 5.87 (dd, *J* = 5.5, 2.7, 0.5H, CH=CH), 4.42 (dd, *J* = 13.1, 8.9, 4H, $ArCH_2Ar$), 4.20 (t, *J* = 6.2, 2H, CH_2), 4.12 (t, *J* = 6.4, 2H, CH_2), 3.90 – 3.82 (m, 4H, CH_2), 3.82 – 3.72 (m, 6H, CH_2), 3.65 – 3.57 (m, 2H, CH_2), 3.16 (s, 1H, CH), 3.10 (t, *J* = 13.1, 4H, $ArCH_2Ar$), 2.87 (s, 1H, CH), 2.40 (t, *J* = 7.4, 2H, CH_2), 1.98 – 1.84 (m, 8H, CH_2), 1.44 – 1.37 (m, 6H, CH_2), 0.91 – 0.79 (m, 15H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.67, 166.22, 156.80, 156.43, 155.98, 154.71, 154.49, 150.73, 143.94, 138.14, 137.97, 136.84, 135.47, 135.41, 134.84, 134.57, 134.14, 132.60, 132.27, 130.69, 130.52, 128.32, 128.29, 128.10, 128.03, 125.81, 122.03, 111.46, 76.86, 76.84, 76.70,

64.42, 61.45, 61.32, 49.74, 48.85, 46.44, 45.77, 45.55, 43.38, 42.61, 41.70, 32.93, 32.87, 31.68, 31.08, 31.06, 30.37, 29.34, 23.39, 23.28, 12.33, 10.48, 10.29.

Synthesis of 3.64

Calix[4]arene (**3.30**) (0.940 g, 1.0 mmol), azo dye (**3.60**) (0.651 g, 1.5 mmol), dicyclohexylcarbodiimide (0.309 g, 1.5 mmol) and DMAP (0.183 g, 1.5 mmol) were dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed with water and dried over $MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. The product was dissolved into hot isopropanol and precipitated into water. Yield: 1.290 g, 0.95 mmol, 95%.

NMR: Due to the number of conformers structural determination cannot be reported

Synthesis of 3.65

Calix[4]arene **3.52** (1.245g, 1.0 mmol), **3.56** (0.18 mL, 1.5 mmol), DCC (0.413g, 2.0 mmol), and DMAP (0.244 g, 2.0 mmol) were dissolved in 25 mL DCM and stirred for 5 hours at room temperature. The reaction mixture was placed in a freezer to precipitate DCU. The DCU was removed and the reaction mixture poured into 1.2M HCl, extracted into DCM washed with water and dried over $MgSO_4$. The $MgSO_4$ was removed and the solvent removed *in vacuo*. The product was dissolved into acetone and precipitated into 1.2 M HCl with NH_4PF_6 (1.0 mmol). Yield: 1.092g, 0.80 mmol, 80%.

^{1}H NMR (400 MHz, acetone) δ 8.17 (d, J = 8.0, 2H, ArCH), 7.58 (d, J = 8.1, 2H, ArCH), 7.44 (d, J = 8.1, 2H, ArCH), 7.36 (d, J = 7.3, 2H, ArCH), 6.71 – 6.65 (m, 2H, ArCH), 6.55 (dt, J = 15.0, 7.8, 4H, *ArCH), 6.45 (s, 3H, ArCH), 6.21 – 6.07 (m, 1.5H, CH=CH), 5.86 (dd, J = 5.7, 3.0, 0.5H, CH=CH), 5.39 - 5.12 (m, 6H, Cp, CH_2), 4.47 (dd, J = 13.1, 6.6, 4H, $ArCH_2Ar$), 4.14

(t, J = 6.4, 2H, CH_2), 3.97 – 3.77 (m, 8H, CH_2), 3.25 – 3.02 (m, 6H, CH_2, $ArCH_2Ar$), 2.43 (t, J = 7.5, 1H, CH), 2.28 (d, J = 4.7, 2H, CH_2), 1.97 (dt, J = 15.6, 7.8, 10H, CH_2), 1.85 – 1.76 (m, 1H, CH), 1.55 – 1.21 (m, 6H, CH_2, CH_3), 1.09 – 0.90 (m, 6H, CH_3).

Synthesis of 3.66

Calix[4]arene (**3.62**) (1.061g, 1.0 mmol), tetrabutylammonium fluoride 1M solution in THF (4.4 mL, 4.4 mmol), acetic acid (0.25 mL, 4.4 mmol) were dissolved in 7.2 mL DMF. The reaction was stirred at room temperature for 3 hours. The reaction mixture was poured into 1.2M HCl and extracted into $CHCl_3$. The product was washed with water, dried over $MgSO_4$ and filtered. The solvent was removed *en vacuo* and the crude product was purified by chromatography on silica with $CHCl_3$:hexanes (60:40) as eluent to give the pure product, Yield: 0.1344 g, 0.22 mmol, 22%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.18 (s, 4H, ArOH), 7.04 (d, J = 7.4, 6H, ArCH), 6.84 (s, 2H, ArCH), 6.71 (t, J = 7.6, 3H, ArCH), 6.18 (dd, J = 5.6, 3.1, 1H, CH=CH), 5.92 (dd, J = 5.7, 2.8, 1H, CH=CH), 4.24 (s, 4H, $ArCH_2Ar$), 4.10 – 3.93 (m, 2H, CH_2), 3.48 (s, 4H, $ArCH_2Ar$), 3.18 (s, 1H, CH), 2.88 (s, 1H, CH), 2.48 – 2.41 (m, 2H, CH_2), 1.88 – 1.78 (m, 2H, CH_2), 1.45 – 1.33 (m, 3H, CH_2, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.95, 149.02, 147.11, 138.27, 137.98, 135.96, 135.09, 132.58, 130.07, 129.17, 129.05, 128.48, 128.36, 122.43, 64.05, 63.82, 49.85, 46.86, 46.59, 45.95, 43.58, 42.75, 41.86, 32.00, 31.94, 31.57, 30.53, 29.42.

Synthesis of 3.67

Calix[4]arene (**3.64**) (1.355 g, 1.0 mmol), tetrabutylammonium fluoride 1M solution in THF (4.4 mL, 4.4 mmol), acetic acid (0.25 mL, 4.4 mmol) were dissolved in 7.2 mL DMF. The reaction was stirred at room temperature for 3 hours. The reaction mixture was poured into 1.2M

HCl and extracted into $CHCl_3$. The product was washed with water, dried over $MgSO_4$ and filtered. The solvent was removed *en vacuo* and the crude product was purified by chromatography on silica with $CHCl_3$:hexanes (60:40) as eluent to give the pure product, Yield: 0.540 g, 0.60 mmol, 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.16 (s, 4H, ArOH), 8.15 – 8.09 (m, 2H, ArCH), 7.94 – 7.77 (m, 4H, ArCH), 7.03 (d, *J* = 7.8, 6H, ArCH), 6.88 (s, 2H, ArCH), 6.79 (d, *J* = 9.2, 2H, ArCH), 6.74 – 6.66 (m, 3H, ArCH), 6.26 – 6.14 (m, 1H, CH=CH), 5.91 – 5.83 (m, 1H, CH=CH), 4.38 – 4.12 (m, 6H, $ArCH_2Ar$, CH_2), 3.75 – 3.37 (m, 8H, CH_2), 3.22 – 2.82 (m, 6H, $ArCH_2Ar$, CH_2), 2.64 – 2.51 (m, 1H, CH), 2.09 – 1.82 (m, 3H, CH_2, CH), 1.61 (s, 1H, CH), 1.42 (d, *J* = 5.3, 1H, CH), 1.32 – 1.17 (m, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.96, 166.66, 156.30, 150.98, 147.20, 143.93, 132.47, 138.24, 130.72, 129.93, 129.15, 128.99, 128.23, 122.47, 122.20, 111.62, 65.16, 64.67, 61.59, 61.49, 49.96, 49.89, 48.98, 46.96, 46.59, 46.49, 45.91, 45.70, 33.04, 31.91, 31.65, 31.53, 30.30, 29.52, 12.37.

Synthesis of 3.68 – 3.72

To a 50 mL RBF the appropriate monomer (0.5 mmol) and dry, degassed DCM (10 mL) were added. Grubbs' 2nd generation catalyst (25 mM solution in DCM) ($5x10^{-4}$ mmol) was added 2 mL solution in DCM to the rapidly stirring monomer solution. The reaction was allowed to stir for 45 min and then pour into methanol. The product was dissolved into $CHCl_3$ and reprecipitated into hexanes.

3.68: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.46 (d, *J* = 92.0, 11H, ArCH), 5.29 (d, *J* = 50.1, 2H, CH=CH), 4.42 (t, *J* = 13.0, 4H, $ArCH_2Ar$), 3.81 (s, 10H, CH_2), 3.18 – 2.99 (m, 4H, $ArCH_2Ar$), 2.28 (s, 2H, CH_2), 1.90 (s, 8H, CH_2), 1.25 (s, 2H, CH_2), 1.04 – 0.76 (m, 19H, CH_3, CH_2, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.54, 156.70, 154.88, 135.11, 134.38, 128.20, 128.00, 122.01, 76.77, 63.84, 50.34, 48.53, 43.40, 42.82, 40.32, 36.42, 31.42, 30.88, 30.31, 29.61, 10.56, 10.28. Yield: 0.336 g, 95%

3.69: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.16 (s, 4H, ArOH), 7.00 (s, 6H, ArCH), 6.81 (s, 2H, ArCH), 6.68 (s, 3H, ArCH), 5.54 – 5.06 (m, 2H, CH=CH), 4.21 (s, 4H, $ArCH_2Ar$), 4.07 – 3.80 (m, 2H, CH_2), 3.46 (s, 4H, $ArCH_2Ar$), 3.27 – 2.99 (m, 1H, CH), 2.97 – 2.62 (m, 1H, CH), 2.39 (s, 2H, CH_2), 2.11 – 1.88 (m, 1H, CH), 1.77 (s, 2H, CH_2), 1.50 – 1.31 (m, 1H, CH), 1.16 – 0.98 (m, 1H, CH). Yield: 0.286 g, 95%

^{13}C NMR (101 MHz, $CDCl_3$) δ= 174.54, 149.05, 148.19, 134.49, 130.62, 129.11, 128.84, 122.17, 63.74, 48.35, 37.59, 36.26, 31.75, 31.36, 30.30.

3.70: Insoluble Yield: 0.506 g, 95%

3.71: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 10.16 (s, 4H, ArOH), 8.18 – 8.01 (m, 2H, ArCH), 7.89 – 7.73 (m, 4H, ArCH), 7.02 (s, 6H, ArCH), 6.88 – 6.83 (m, 2H, ArCH), 6.76 – 6.64 (m, 4H, ArCH), 4.41 – 4.07 (m, 8H, $ArCH_2Ar$, CH_2), 3.62 – 3.34 (m, 8H, $ArCH_2Ar$). Norbornene peaks too broad to determine.

^{13}C NMR (101 MHz, $CDCl_3$) δ= Due to low solubility the ^{13}C NMR spectrum could not be obtained. Yield: 0.426 g, 95%

3.72: Insoluble Yield: 0.648 g, 95%

Synthesis of 3.74a-d, 3.75a-d, 3.76a-d

Calix[4]arenes (**3.33**, **3.34**, and **3.39**) (0.05 mmol) and dinucleophiles (**3.73a-d**) (0.05 mmol) were stirred in 1 mL DMF with K_2CO_3 (0.5 mmol) for 24 hours at room temperature under nitrogen, protected from the dark. The reaction mixture was then heated to between 40 °C

and 50 °C and stirred for an additional 24 hours or until viscous. The polymer solution was poured into 1.2 M HCl with NH_4PF_6 and the precipitate collected and dried under reduced pressure.

3.74a: ^{1}H NMR (400 MHz, DMSO) δ 7.02 (br s, 22H), 6.26 (br s, 24.7, 15H), 5.62 (br s, *J* = 49.4, 4H), 4.92 (br s, 8H), 4.28 (br s, 4H), 3.73 (br s, 10H), 3.06 (br s, 6H), 2.38 (br s, 1H), 2.12 (br s, 2H), 1.82 (br s, 8H), 1.54 (br s, 8H), 1.30 (br s, 15H), 0.93 (br s, 17H). ^{13}C NMR was impossible due to solubility. Yield 0.078 g, 90%

3.74b: NMR: **Insoluble** Yield: 0.076 g, 87%

3.74c: NMR: **Insoluble** Yield: 0.082 g, 92%

3.74d: NMR: **Insoluble** Yield: 0.077 g, 85%

3.75a: NMR: **Insoluble** Yield: 0.093 g, 93%

3.75b: NMR: **Insoluble** Yield: 0.081 g, 80%

3.75c: NMR: **Insoluble** Yield: 0.097 g, 95%

3.75d: NMR: **Insoluble** Yield: 0.078 g, 75%

3.76a: NMR: **Insoluble** Yield: 0.033 g, 60%

3.76b: NMR: **Insoluble** Yield: 0.050 g, 90%

3.76c: NMR: **Insoluble** Yield: 0.053 g, 92%

3.76d: NMR: **Insoluble** Yield: 0.048 g, 83%

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