MODIFICATION OF ASPIRIN DERIVATIVES BY COORDINATION TO IRON AND MANGANESE

NDUMISO MSHICILELI

MODIFICATION OF ASPIRIN DERIVATIVES BY COORDINATION TO IRON AND MANGANESE

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by

NDUMISO MSHICILELI

BSc (Hons) (Cape Town)

Department of Chemistry

University of Cape Town

Rondebosch 7701

South Africa

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To my late father

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ABSTRACT

In this work new metal complexes of acetylsalicylic acid (aspirin) derivatives have been synthesised. Complexes that were studied were those of manganese (Mn) and iron (Fe). The sodium salt of metal anion reacts with an acyl chloride (the most reactive carboxylic acid derivative) to give the acyl metal complexes of the type $[ML_nC(O)C_6H_4OCH_2Ph]$ (M = Fe or Mn, L_n = Cp $(CO)_2$ or $(CO)_5$). This type of reaction is nucleophilic. It involves the displacement of chloride anion by the metal anion. The core organic ligand, 2-benzyl-oxybenzoic acid was first prepared then converted to the acyl chloride, alcohol and aldehyde compounds. These were useful in the synthesis of the above-mentioned metal complexes and ferrocene containing derivatives.

The metal complexes were isolated as crystalline solids and oils and were highly soluble in chlorinated organic solvents and fully characterised by infrared, ^1H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectrometry and elemental analysis. The metal complexes were found to be stable at room temperature. The acylmanganese complexes were less stable in solution than the acyliron derivatives. It was discovered that the acyl-manganese complex, $[Mn(COC_6H_4OCH_2C_6H_5)(CO)_5]$ decarbonylates to lose a CO group and form the corresponding arylmanganese complex. Aspirin derivatives containing the ferrocene moiety were also synthesised and characterised. These compounds contain a secondary amine nitrogen donor atom which is a potential binding site for other metal complexes.

X-Ray crystallography was used to obtain the crystal structure of the acyl iron complex, $[CpFe(CO)_2(COC_6H_4OCH_2C_6H_5)]$ (space group $P2_1/c$) . The structure of this complex is compared to structures of similar reported complexes. The thermal behaviour of the acyliron, $[CpFe(CO)_2(COC_6H_4OCH_2C_6H_5)]$ and the arylmanganese complex, $[Mn(C_6H_4-OCH_2C_6H_5)(CO)_5]$ were investigated by thermal gravimetric analysis and differential scanning calorimetry. Reactivity of the above-mentioned metal complexes with triphenyl-phoshine was investigated. Decarbonylation reactions were also carried out. The resulting complexes for these reactions were characterised.

ABBREVIATIONS

Å	=	angstrom
Ar	=	aromatic
Bn	=	benzyl
ca	=	approximately
COD	=	1,5-cyclooctadiene
Cp	=	cyclopentadienyl (η^5-C_5H_5-)
Cp^+	=	substituted cyclopentadienyl (η^5-C_5H_3-)
CQ	=	chloroquine
°	=	degree
DMF	=	*N, N*-Dimethlyformamide
DSC	=	differential scanning calorimetry
EI	=	electron impact
Et	=	ethyl (-CH_2CH_3)
FAB	=	fast atom bombardment
IR	=	infrared
lit.	=	literature
L_n	=	ligand
Me	=	methyl (-CH_3)
M	=	parent molecular ion
min.	=	minute
m.p	=	melting point
m/z	=	mass to charge ratio
NMR	=	nuclear magnetic resonance
Ph	=	phenyl, (-C_6H_5)
PPh_3	=	triphenylphosphine
ppm	=	parts per milliom
Pr	=	propyl
R	=	alkyl
r.t	=	room temperature

TEA = triethylamine

THF = tetrahydrofuran

TGA = thermal gravimetric analysis

TMS = tetramethylsilane

Note: References are valid with individual chapter only and compound numbers are valid only with Chapter 1

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CHAPTER 1

A REVIEW OF TRANSITION METAL COMPLEXES IN MEDICINE

1.1 Introduction

Metal ions or metal complexes have been used in medicine for centuries, rather than zerovalent metals.[1,2] Currently there is a growing interest in the use transition metal complexes as medicines and in other biological areas.[3,4] Bioinorganic/bioorganometallic chemistry is a rapidly growing field that is offering inorganic chemistry ideas for biomedical chemistry. This has led to potential applications in medicine and thus widening the scope for drugs, an area which has been dominated by organic chemistry. The use of metal complexes as chemotherapeutic agents is well established, particularly in the field of cancer.[1,5] The field has been revolutionised by the successful example of cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, the world's best selling anticancer drug and the application of other platinum complexes.[1,6-8] The first work on the antitumor activity of platinum compounds was reported by Rosenberg *et. al*, thirty years ago.[9]

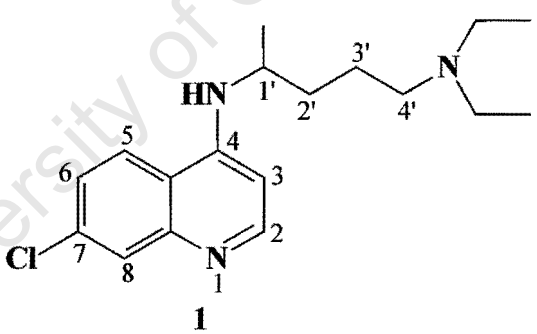
Many inorganic and biomedical research groups have carried out extensive work which has contributed to the success of metals in medicine. A recent review on metals in medicine by Sadler and Guo focuses on the recent developments of metal complexes as anticancer, antiarthritic and antiulcer agents and other wider applications involving metal complexes.[10] In this chapter, the work of various research groups on metal complexes and their biological activities is reviewed. The use of metal complexes as antiparasitic and antitumor drugs as well as in other biological areas is highlighted. An overview of some of the parasitic diseases, in which metal complexes (or research on metal complexes) have played a major role, is given in **section 1.2**.

1.2 Parasitic diseases

1.2.1 Malaria

The first example of a parasitic disease highlighted is malaria. Malaria is the most wide-spread parasitic illness affecting intertropical zones. At present an estimated 270 million people contract the parasite every year and the disease, claims up to 2 million deaths annually with at least 100 million cases of acute illness being observed.[11] Malaria is caused by four species of the genus *Plasmodium*. Of these the most lethal to humans is *Plasmodium falciparum*.[12]

The great majority of these deaths are occurring in Africa. Various drugs have been used for the treatment of this disease, *e.g.*, chloroquine (**1**) and fansidar [mixture of sulfadoxine (**2**) and pyrimethamine (**3**)].[13]



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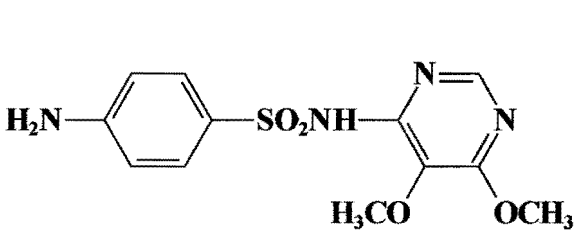

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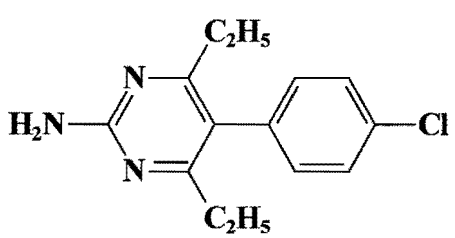

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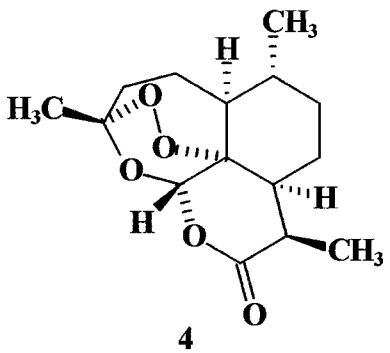


4

Another clinically used drug is artemisinin (qinghaosu, **4**), which is extracted from a herb known as qinghao.[14] This compound was isolated in 1972 and has been approximately equal in potency to chloroquine, with a good therapeutic index on the treatment of multi-drug resistant *P. falciparum* has received increasing attention in recent years.[15]

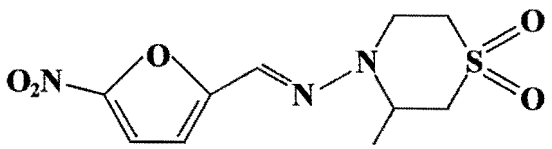
The spread of chloroquine-resistant strains of *Plasmodium falciparum* has become a major health problem.[11] An inexpensive and effective drug or insecticide is required.

The pharmaceutical companies are no longer investigating drugs to combat malaria since it affects many of the poorest countries in Africa, Asia and South America. Recently many research groups have shown great interest in the use of transition metal complexes towards development of the new antimalarial drug.[18-20]

1.2.2 Chagas disease

Another parasitic tropical disease of note is Chagas disease which affects millions of people in Central and South America. It is caused by the hemoflagellate protozoan *Trypanosoma cruzi* which is transmitted to the human body by Reduviid insects.[16] The parasite has been observed in three main morphological forms, namely the epimastigotes, trypomastigotes and amastigotes. The mode of transmission of this parasite is a cyclic process. Similarly, there is lack of interest from the pharmaceutical companies to carry out a serious research and development program because it is not commercially attractive.

Currently the drugs being used for treating Chagas disease are nifurtimox (4-[5-nitrofurfurylidene]-amino)-3-methylthimorpholine-1, 1-dioxide (**5**) and benznidazole, *N*-benzyl-2-nitro-1-imidazoleactamida (**6**).[16]



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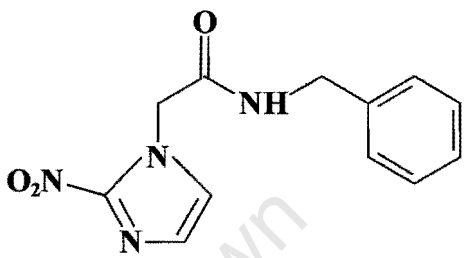


6

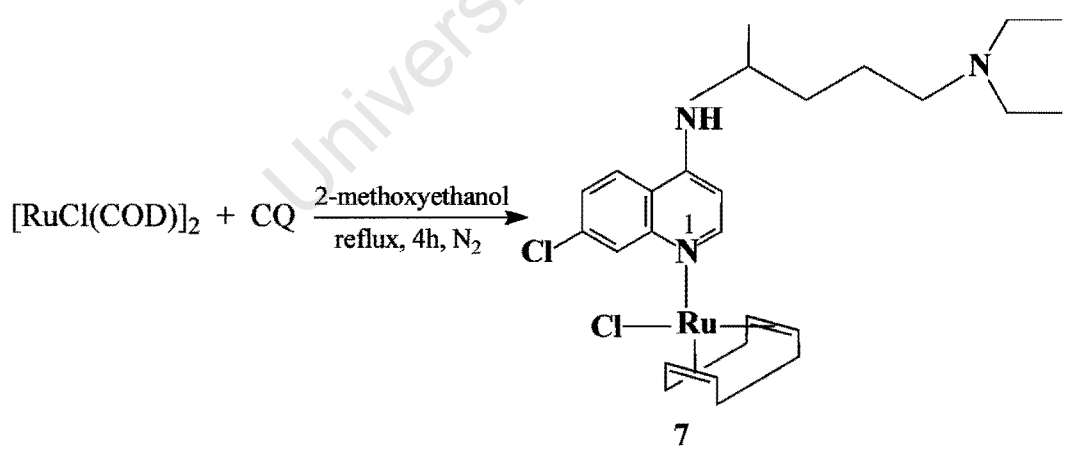
Sections 1.3 – 1.6 review recent research studies aimed at development of new antiparasitic, antibacterial and antitumor agents or any other biological activity.

1.3 Metal complexes as antiparasitic drugs

Since the 1940s, chemists have developed a wide variety of highly effective antibiotics (sulfa-drugs, penicillins and tetracyclines)[17] that are effective against bacterial infections but the progress with antiviral and antiprotozoal agents has been slower and more difficult. The problem is one of selectivity. Any drug must selectively kill pathogens in between the metabolisms of bacterial and mammalian cells to allow selectivity. Selective antibiotics have been developed.[17] Similarly, a selective antiparasitc or antitumor drug must be designed.

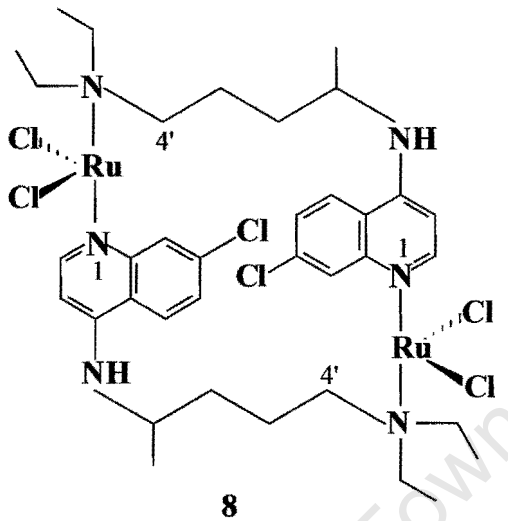
1.3.1 Metal complexes as antimalarial drugs

Sánchez-Delgado and co-workers[18] reported a new strategy for the development of alternative therapies against tropical parasitic diseases based on the modification of compounds with known potential antiparasitic activity through incorporation of a transition metal into the molecular structure. The new complexes resulting from the coordination of chloroquine (CQ) to rhodium (Rh) and ruthenium (Ru) to form Rh(COD)(CQ)Cl (**7**) and $[RuCl_2(CQ)]_2$ (**8**) respectively have been reported[18]. Complex **7** was synthesised by reacting $[RhCl(COD)]_2$ with 3 equivalents of CQ under mild conditions. Complex **8** was synthesised from interaction of $RuCl_3.3H_2O$ with 5 equivalents of CQ in the presence of Zn powder. This reaction was also carried out under mild conditions. The reactions are shown in the equations **1.1** and **1.2** below. These are highly active against a chloroquine-resistant strain of *Plasmodium falciparum in vitro*, as well as *in vivo*. These complexes were characterised by IR, NMR and elemental analysis. Chloroquine binds to the metal in **7** through the unsubstituted N(1) atom which is a good donor site for chloroquine. Rh(I) forms a square planar configuration.



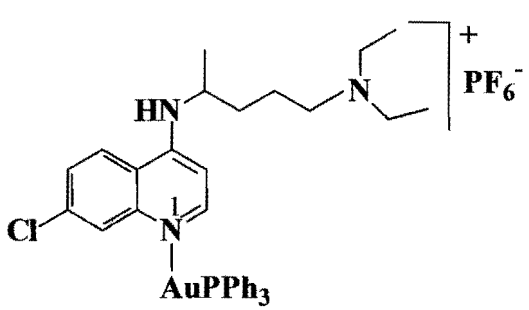
7 (1.1)

In complex **8**, chloroquine binds to the metal through both the N(1) and N(4′) atoms. This is suggested from the chemical shifts in the ^1H NMR spectra of the CQ molecule and the bonded CQ for H(8), NH and H(4′) and H(5′) atoms.

$RuCl_3.3H_2O + CQ \xrightarrow[\text{reflux, 6h, } N_2]{\text{Zn/MeOH}}$ 

8 (1.2)

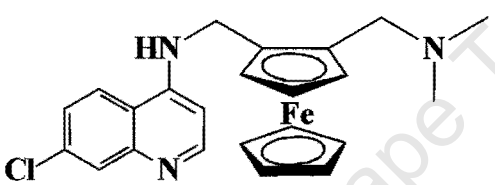
Sánchez-Delgado and co-workers[19] also reported the coordination of CQ to the $[Au(PPh_3)]^+$ fragement (**equation 1.3**). The reaction of $AuClPPh_3$ with CQ and KPF_6 in acetonitrile produced $[Au(PPh_3)(CQ)]PF_6$ (**9**). Complex **9** proved to be more active against *in vitro* cultures of chloroquine-resistant strains of *P. falciparum* and also against *P. berghei* (rodent malaria) *in vitro* and *in vivo*, compared to CQ.

$[AuClPPh_3] + CQ \xrightarrow[KPF_6, \text{ reflux, } N_2]{CH_3CN}$ 

9 (1.3)

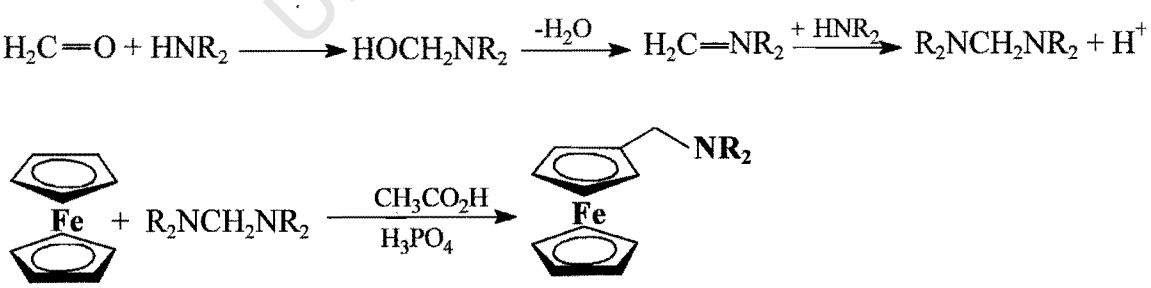
Au coordinated to the CQ moiety *via* the unsubstituted N(1) atom is probably bonded in linear coordination geometry, which has been previously associated with biological activity.[20]

The importance of transition metal complexes in the development of antimalarial drugs was further shown by a report on the modification of CQ side chain which improved the activity of CQ against *in vitro* chloroquine-resistant strains of *P.falciparum*.[21] The ferrocene-CQ complex (**10**) was synthesised with the CQ lateral side chain replaced by the hydrophobic ferrocenyl group.



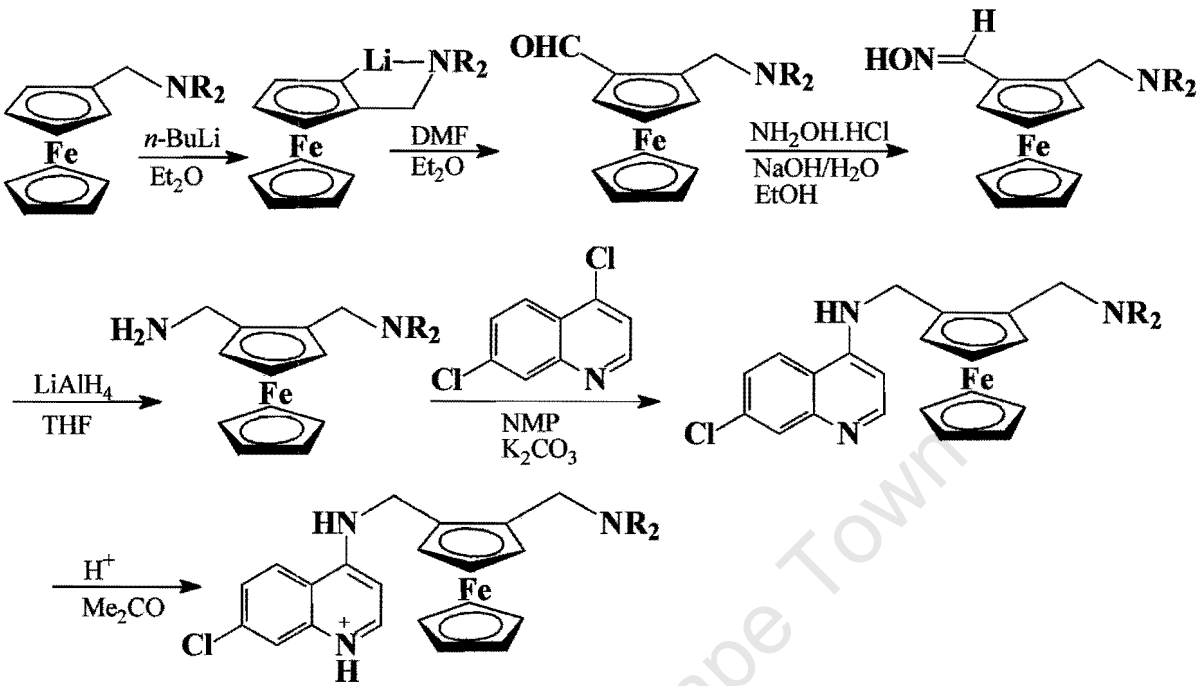
10

7-chloro-4-[[[2-[(*N, N*-Dimethylamino)methyl]ferrocenyl]methyl]amino]quinoline (**10**) was synthesised by first preparing [(dimethylamino)methyl)]ferrocene precursor (**Figure 1.1**). Condensation of 2-[(*N, N*-Dimethylamino)methyl]ferrocenylmethylamine with 4,7-dichloroquinoline in *N*-methyl-2-pyrrolidinone gave complex **10** (see **Figure 1.2**).



R = -Me

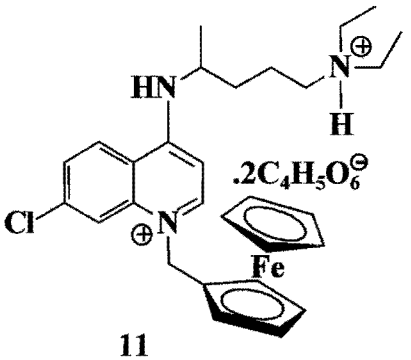
Figure 1.1 Synthesis of [*N, N*-dimethylamino)methyl]ferrocene[21]



H^+ = L-(+)-tartaric acid

Figure 1.2 Synthesis of 7-chloro-4-[[[2-[(*N,N*-dimethylamino)methyl]ferrocenyl]methyl] amino]quinoline (**10**)[21]

A recently published report by Brocard and co-workers on the synthesis, characterisation and antimalarial activity of new ferrocene-chloroquine compounds shows introduction of the ferrocenyl unit into another position of the CQ.[22] These compounds, **11** and **12** showed very promising antimalarial activity *in vivo* (in mice) against *Plasmodium berghei* N. and *in vitro* against *Plasmodium falciparum*.



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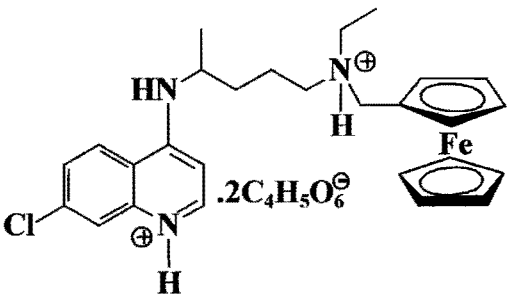
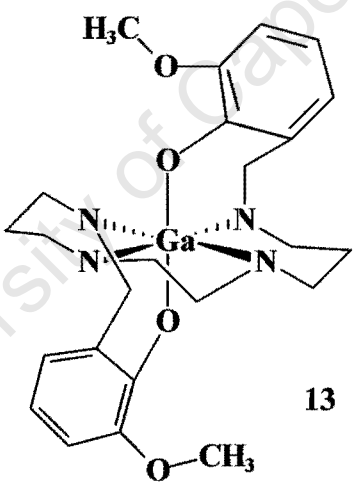


12

An amine phenol Ga(III) complex (**13**) with antimalarial activity, including its crystal structure has been reported.[23] This complex was reported to selectively target chloroquine-resistant *Plasmodium falciparum*.



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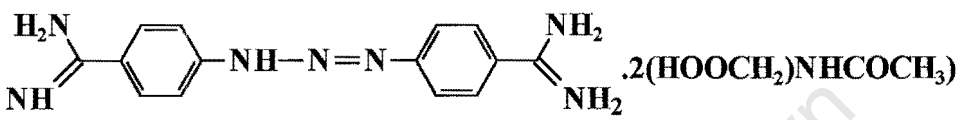
1.3.2 Metal complexes as antitrypanosomal agents

The similarities between rapidly dividing tumor cells and pathogenic trypanosomes, both in metabolism and drug behaviour stimulated Farrell and co-workers to study trypanosome cells in the presence of antitumor-type drugs. Some antitumor and related metal complexes are moderately active against African trypanosomes.[24,25]

In the studies by Farrell, ligands for metal drug complexes were selected according to their effect on the growth rate of trypanosomes and their capability for metal coordination. Compounds such as berenil, (4,4′-diazoaminodibenzamidine-bis(*N*-acetylglycinate) (**14**), ethidium bromide, (2,7-diamino-10-ethyl-9-phenyl-phenantridium bromide) (**15**) were used as ligands.



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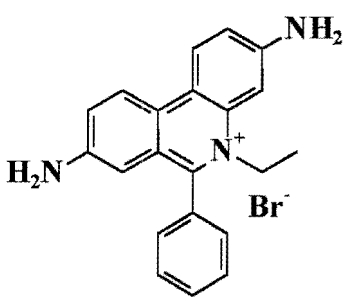

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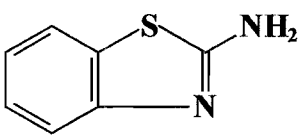
The metal complexes from compounds **14** and **15**, $[Rh_2(acetate)_4(berenil)_2]$ (**16**) and $[Rh_2(butyrate)_3(berenil)]$ (**17**), were shown to possess greater biological activity compared to the parent drug (ligand) as moderate antireplicative agents against *Trypanosoma rhodesiense*. The behaviour of these compounds was interestingly paving a way for further development of organometallic complexes for Chagas disease chemotherapy. Also several other rhodium and antimony complexes were reported[5] with ligands chosen for their antitrypanosomal properties and coordination aptitude.

The following compounds were among those that showed bioactivity: $[Rh(CO)_2L(Cl)]$ L = 2-aminobenzothiazole (**18**), L = 5-chloro-2-methylbenzothiazole (**19**); $[Rh(L)_nX_2]^+$ X^-, L_n = (1,4-diaminopiperazine)$_2$, X = Cl (**20**), L_n = (2-hydroxybenzothiazole)$_4$, X = Br (**21**); $[SbL_3]$, L = *N, N*-morpholinodithiocarbamate (**22**)] *etc.*[16]

Compounds **21** and **22** were shown to present antiproliferative activity against *T. cruzi* epimasigotes.



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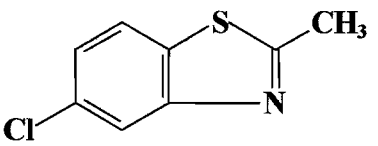

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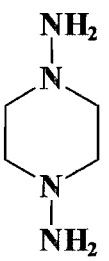

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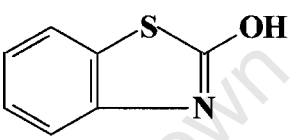

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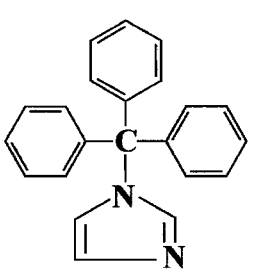
Figure 1.3 Ligands with antitrypanosomal activity

Sánchez-Delgado and co-workers[26] reported an approach towards development of chemo-therapy against Chagas disease. This was similar to the one reported for the antimalarial Ru-CQ complex.[18] An azole-type antifungal agent that has a marginal anti *T. cruzi* activity, clotrimazole (CTZ), (1-[(2-chlorophenyl)diphenylmethyl]-1*H*-imidazole



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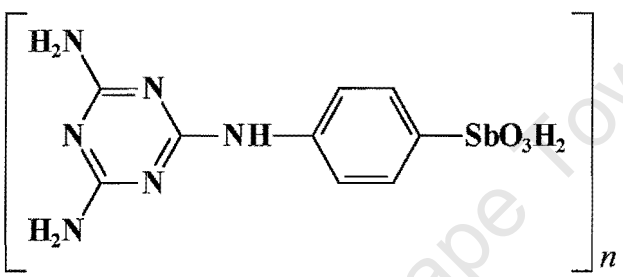
(**23**) was modified by forming, a ruthenium complex. The ligand binds to the metal through the unsubstituted N(3) atom, which is the best donor site of CTZ. The complex $[RuCl_2(CTZ)_2]$ (**24**) was found to have a high trypanocidal activity against *T.cruzi*, with low toxicity.

MSb which is polymerised *p*-melaminylphenylstilbonic acid containing 32.6 per cent pentavalent antimony (**25**), was been shown to provide long-lasting protection against trypanosomal infections.[31] Friedheim and co-workers reported the therapeutic possibilities offered by MSb and its derivative MSbB (**26**) in the short-term treatment of first- and second-stage African sleeping sickness caused by *Trypanosoma gambiense*.[32]



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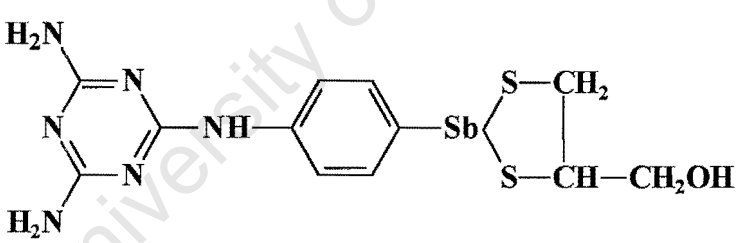

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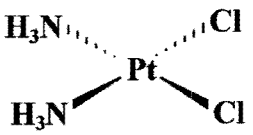
1.4 Metal complexes as antitumor agents

1.4.1 Platinum complexes

The use of metal complexes as antitumor agents has been known for many years, particularly with platinum complexes, cisplatin (**27**) being the most successful anticancer drug.[1,5,27-30] Second generation platinum drugs, such as carboplatin (**28**), spiroplatin (**29**) and iproplatin (**30**) have been clinically tested and show similar efficacy to cisplatin.



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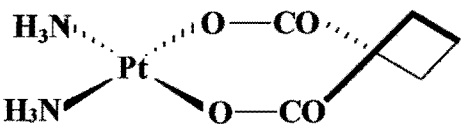

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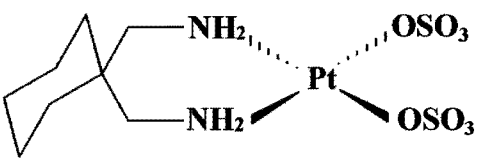

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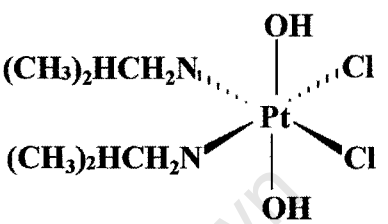

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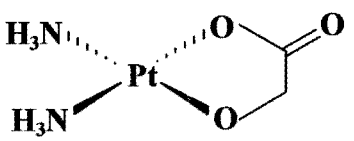

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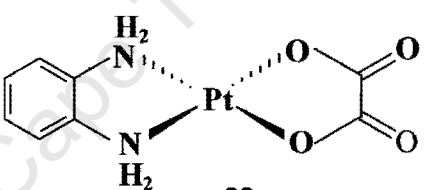

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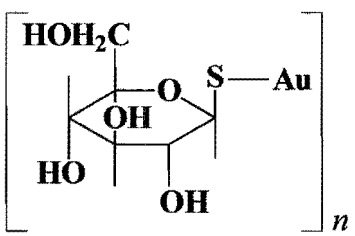
Some platinum complexes with improved characteristics compared with cisplatin are being brought into clinical use (*e.g.* nedaplatin (**31**) and oxaliplatin (**32**) in Japan and France respectively).[10] Most of the work on platinum anticancer complexes has been concentrated on *cis*-diam(m)ine complexes since it was discovered that *trans*-$[PtCl_2(NH_3)_2]$ is inactive.

1.4.2 Gold complexes

Gold has also been used in chemotherapy for many years. The modern use of gold in medicine was initiated in the early 19th century by Chrestien and Figuier.[33] In 1890, Robert Koch discovered that gold(I)cyanide, AuCN, inhibits the growth of bacteria that cause tuberculosis (TB) but it was found to be very toxic.[34] In 1924, a thiosulfato complex of gold(I) was used in an attempt to cure (TB).

More research was done on gold complexes and some were applied as antitumor agents. Aurothioglucose (**33**, Solganol) as well as sodium auro(I)thiomalate (**34**, Myocrisin) are applied in the therapy of rheumatoid arthritis.[35] Another gold antiarthritic compound in clinical use is auranofin, (**35**, 2,3,4,6-tetrakis-*O*-acetyl-1-thio-β-D-glucopyranosido)gold-(I)triethylphosphine).[34] Auranofin emerged in the late 1970s and is administered orally.[36]



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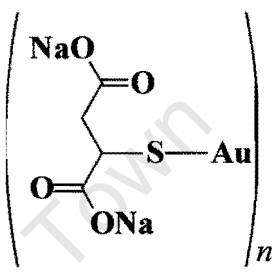

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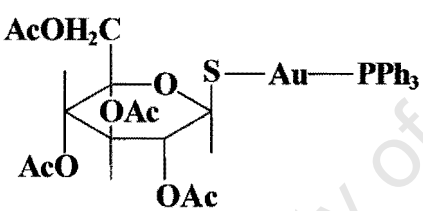

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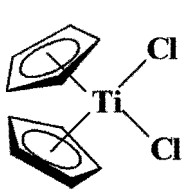
1.4.3 Other metal complexes

A variety of metallocene dihalides and pseudohalides Cp_2MX_2 ($Cp = \eta^5\text{-}C_5H_5$; M = Ti, V, Nb, Mo; X = F, Cl, Br, I, NCS, N_3) are known to be highly active anticancer agents against a number of tumor lines.[37-39] The antitumor activity of titanocene dichloride (**36**) was first recognised in 1979.[40,41]



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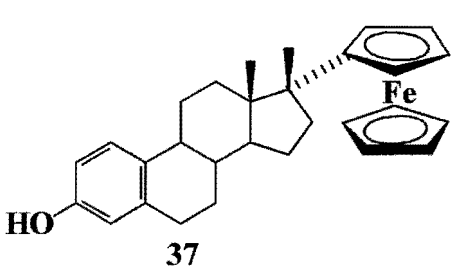
Other antitumor drugs reported in the literature are tin-based. Several organotin compounds have been found to exhibit very promising *in vitro* antitumor activities.[42] For example, di-*n*-butyltin-, di-*t*-butyltin- and diphenyltin-2, 6-pyridinecarboxylate were found to be more active than cisplatin against a mammary tumour and a colon carcinoma. New diorganotin(IV) complexes, which have shown antimicrobial and anti-inflammatory activities have also been reported.[43]

1.5 The use of metal complexes in other biological fields

The rapid growing interest in the use of transition metal complexes in the biological areas is also indicated by the work done by Jaouen.[4] A ferrocenyl moiety was introduced at the 17α-position of estradiol (as shown in compound **37**). This caused a change in the behaviour of the hormone at the binding site resulting in an irreversible binding, however the presence of the 17α-ferrocenyl group does not hinder the recognition properties of the hormone. Ferrocene derivatives are stable and nontoxic in many chemical media.

Jaouen later reported using organometallic compound markers as tracers in immunoassays[3]. For example different metal carbonyl markers were attached to three important antiepileptic drugs, *viz.* carbamazepine, phenobarbital and phenytoin.[44]



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Metal complexes have also found another important use as antibacterial drugs. Cobalt(III) complexes with heterochelate ligands are of interest because of their antibacterial properties. The toxicity of cobalt(III) amine complexes on *E.coli* B[45] and on repair-deficient

strains of *E. coli* K-12[46], as well as antibacterial activity of several cobalt(III) complexes have been reported.[47] Cobalt(III) diethylenetriaminemonoacetato complexes were shown to inhibit *Eschrichia coli* B.[48] Metal complexes of heterocyclic thiocarbazones have been reported to be biologically active. Copper(II) complexes of 2-formylpyridine[4]*N*-methyl-, [4] *N*-dimethyl-, [4]*N*-diethyl and [4]*N*-dipropylthiosemicarbazones show antifungal properties.[1,5]

Other metals that have played a vital role in medicine are bismuth and antimony. Bismuth(III) compounds have been used for treating gastrointestinal disorders for more than two centuries.[49] Antimony (Sb) has been used for medicinal purposes for many centuries, with Sb(III) complexes more toxic than Sb(V) complexes. Gallium salts are known to exhibit anticancer activity. Gallium(III) maltolate complex is being tested for the treatment of bone diseases.[10]

The review by Sadler[10] mentions four Gd(III) complexes that have been approved for clinical use and are widely used, for example, for the detection of abnormalities of the blood-brain barrier.

1.6 Conclusion

Clearly the use of transition metal complexes as drugs is a rapid growing field. The work of many research groups (including coordination, inorganic chemists and biomedical researchers), on metal-based drugs or metal complexes as potential drugs has been highlighted. The innovation of these research groups is shown on work done to improve the activity of the existing drugs *e.g.*

- coordination of platinum(II) to biologically important ligands, platinum(IV) complexes of bioactive ligands[50] and the renewed interest in *trans* complexes [*trans*-$[PtCl_2(py)_2]$ (py = pyridine)][51] since it was discovered early that *trans*-$[PtCl_2(NH_3)_2]$ is inactive.

- The new metal complexes formed by coordination of Ru, Rh and Au to CQ (an antimalarial drug) were reported to have biological activity against the CQ resistant strains of malaria.
- Also coordination of the Ru complex to clotrimazole (which has antifungal activity) led to improved activity against *Trypanosoma cruzi*.

These results illustrate the potential of the new metal complexes as future chemotherapeutic agents is certain. The success of these complexes depends on a better understanding of coordination chemistry as well as their structures and mechanisms of reaction. Inorganic and coordination chemistries have increased the scope for the synthesis of new metal complexes with a wide range of potential biological activities.

1.7 Project objectives

The primary objective of this work was to synthesise and fully characterise iron and manganese complexes of an acetylsalicylic acid (aspirin) derivative. Aspirin derivatives containing a ferrocene moiety were also synthesised. These contain a nitrogen donor site which can be useful for binding to form bimetallic complexes. The secondary objective was to carry out reactivity studies of the synthesised complexes.

The aspirin derivative, 2-benzyloxybenzoic acid was chosen as a biologically privileged scaffold since it is derived from a compound which has previously provided a drug (aspirin). The metal chosen iron and manganese have been studied but with less medicinal applications. For example, Mn- and Fe-based porphyrins and macrocylic complexes exhibit superoxide dismutase (SOD) mimic activity.[10] Another example is manganese 5,10,15,20-tetrakis(4-benzoic acid)-porphyrin is of potential interest for the treatment of the brain disease such as Parkinson's and Alzheimer's diseases. It would be of interest to explore these metals as potential therapeutics. These complexes could exhibit biological properties such antiparasitic, antitumor properties *etc*.

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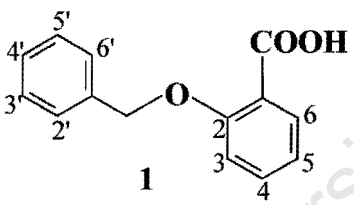
CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF LIGANDS

2.1 Introduction

2.1.1 Organic ligands

The aspirin derivative, 2-benzyloxybenzoic acid (**1**) was synthesised by Farkas *et. al.*[1] It is a benzyl protected salicylic acid whereas aspirin is an acetylated derivative of salicylic acid. 2-methoxybenzoic acid (**2**) is a methyl-protected salicylic acid. The acid functional group in compound **1** was altered for the synthesis of acid chloride (**3**), alcohol (**4**)[2], and aldehyde (**5**)[3] derivatives. Compound **5** was further used in the synthesis of compounds **9** and **10**.



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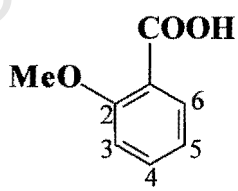

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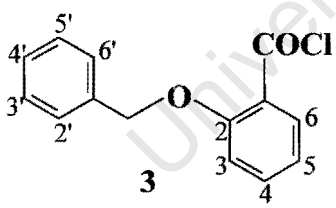

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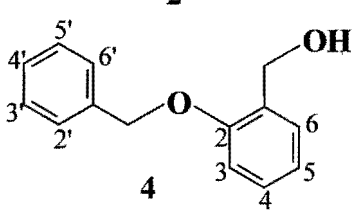

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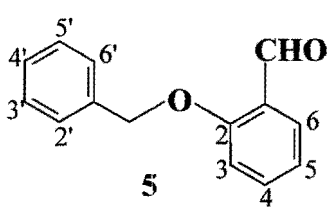
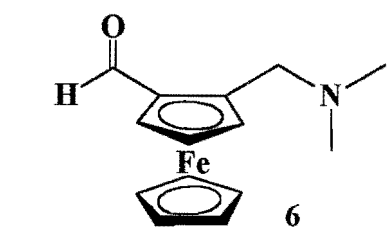


5

2.1.2 Organometallic ferrocene containing ligands

Compounds **6**, 7 and **8** were prepared by using the reported procedure[4], with **7** and **8** being prepared from **6** and 7 respectively. The reaction of 2-benzyloxybenzyl aldehyde (**5**) and salicylic acid with 2-[(*N*, *N*-Dimethylamino)methyl]ferrocenylamine (**8**) gave compounds **9** and **10** respectively. These ligands are ferrocene derivatives of 2-benzyloxybenzoic acid *i.e.* they contain both the aspirin derivative part and the ferrocenyl moiety. They contain a nitrogen donor site which can be of interest for the synthesis of bimetallic complexes.[5] These compounds were characterised by elemental analysis, infrared, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



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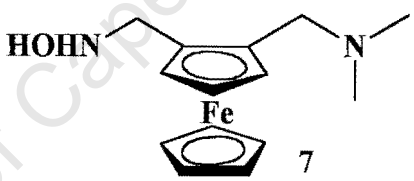

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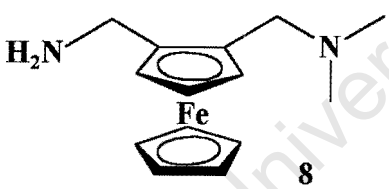

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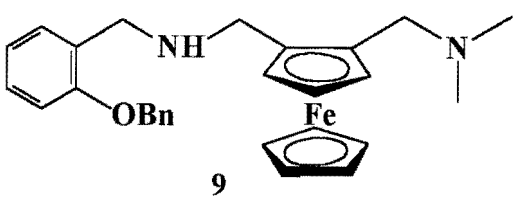

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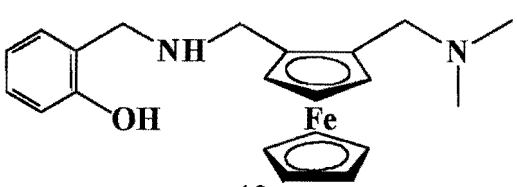

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The interest in synthesising these type of complexes was the stimulated by many reports on ferrocene derivatives having useful properties such as chemical stability and non-toxicity in many media.[4,6-18]

Ferrocene containing compounds have been widely studied owing to their potential in catalysis, material science *etc.*[6] Ferrocene has been employed as a marker for the electrochemical detection of amino acids in liquid chromatography[7,8] or in selective anion sensors.[9] Mitzel-Nolte and co-workers reported the synthesis of organometallic amines (*N*-substituted ferrocene-methylamines) and their coupling to the C-terminus of amino acids and peptides.[10]

The group of Jaouen has done extensive research on the use of organometallic compound markers in immunoassays.[11-14] They also reported the introduction of a ferrocenyl moiety at the 17α-position of estradiol as mentioned previously (Chapter 1).[15] The importance of ferrocene and a large number of ferrocene derivatives is their use as redox-active molecules.[16,17] Ferrocene derivatives have been obtained by suitable chemical attachment of organic ligands to Cp rings.

Functionalisation of ferrocene with molecules containing coordination sites have received considerable attention.[18] The chemistry of ferrocene has been explored extensively. Clearly, many useful properties can be derived from ferrocene-based complexes.

2.2 Synthesis and characterisation

2.2.1 2-benzyloxybenzoic acid (1)

The reaction scheme in **Figure 2.1** shows the steps taken in preparing compound **1**. This compound was isolated as a white precipitate and was recrystallised from methanol. The characterisation data are given in the experimental section. The melting point recorded (76°C – 78°C) was in good agreement with the reported value (lit. 76-78°C).[1] The spectroscopic results are discussed below.

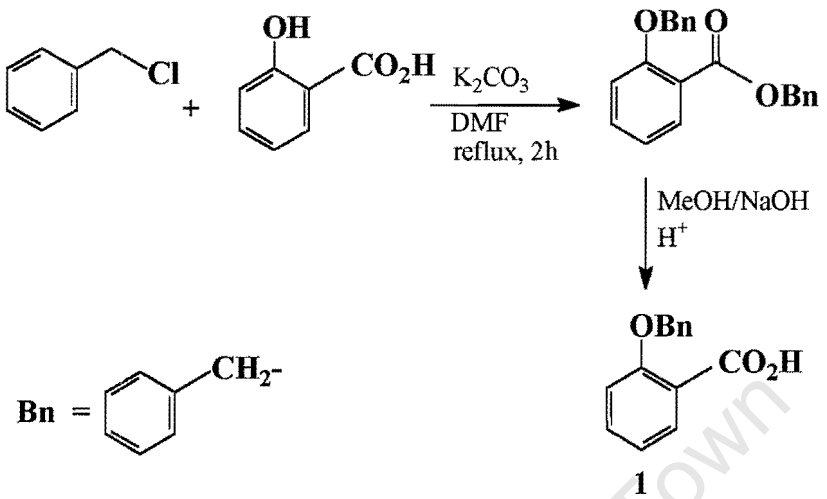


Figure 2.1 Reaction scheme for the synthesis of 2-benzyloxybenzoic acid (**1**)

Infrared spectroscopy

Infrared spectrum of compound **1** shows a broad peak with weak intensity at 3300cm^{-1}. This is due to O-H stretching frequency. A strong band at 1739cm^{-1} due to the CO group was observed.

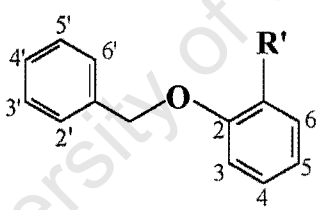
^{1}H NMR spectroscopy

The ^{1}H NMR spectrum for compound **1** shows a methylene proton resonance at δ5.29. The phenyl protons gave resonance peaks in the range δ7.11 – 8.20. The protons of the phenyl group with COOH group are deshielded due to electron-withdrawing effect of the acid group. An unsymmetrical doublet of doublets due to each proton H4 and H5 (see **Figure 2.2**) are observed at δ7.55 and δ8.20 respectively. **Table 2.1** shows the ^{1}H NMR data for 2-benzyloxybenzoic acid. The ^{1}H NMR spectrum is given in **Appendix 1**.

Table 2.1 ^{1}H NMR data for 2-benzyloxybenzoic acid[a] (**1**)

Chemical shift (ppm)	Multiplicity	Integration	Assignment
5.29	s	2H	O-CH_2
7.11-7.18	m	2H	H3, H6
7.40-7.46	m	4H	H3′,H5′,H2′,H6′
7.55	t	1H	H4′
7.55	udd, ^2J 1.60 Hz 2.00 Hz	1H	H4
8.20	udd, ^2J 1.60 Hz, 2.00 Hz	1H	H5

a : $CDCl_3$: s = singlet, m = multiplet, dd = doublet of doublets, udd = unsymmetrical doublet of doublets, t = triplet



R' = functional group

Figure 2.2 Numbering system used for assignment of aromatic protons and carbon atoms

2.2.2 2-methoxybenzoic acid (2)

The synthesis of 2-methoxybenzoic acid was also based on the procedure reported by Farkas[1] (as shown in **Figure 2.1**). Benzyl chloride was replaced by methyl iodide. It was isolated as a white crystalline solid. The melting point recorded, 100°C – 102°C, was in good agreement with the reported value (lit. 98°C-100°C).[19]

Infrared spectrum showed the O-H and CO stretching frequencies at the expected values, *viz.* 3296cm^{-1} and 1738cm^{-1} respectively.[20]

^{1}H NMR spectroscopy

The proton NMR spectrum for **2** recorded was similar to the reported spectrum of the 2-methoxybenzoic acid.[21] A singlet due to the methyl protons is observed at δ4.08, because of the electronegative oxygen atom. The –COOH proton peak was not observed for both compounds **1** and **2**.This could be due to high exchangeable rate of acid protons in the chloroform solution and far downfield absorption (δ10.5–12). The aromatic peaks appear in a similar manner as in compound **1**, except for the extra multiplet due to the phenyl protons (in spectrum of **1**) and a very slight upfield shift of the aromatic peaks (about δ0.01) in the spectrum of **2**. The latter change is due the effect of different protecting groups *i.e.* methyl and benzyl groups.

2.2.3 2-benzyloxybenzoyl chloride (3)

The acid chloride was prepared by reacting 2-benzyloxybenzoic acid with thionyl chloride. The reaction was monitored by infrared spectroscopy. The spectrum showed the disappearance of the CO band at 1739cm^{-1} and the re-appearance of the CO band at a higher frequency of 1779cm^{-1}. The absence of O-H stretching frequency (at 3300cm^{-1}) indicated the formation of compound **3**.

2.2.4 2-benzyloxybenzyl alcohol (4)

Compound **4** was synthesised by employing a modified procedure reported by Finne and co-workers.[2] Compound **1** was reduced with $LiAlH_4$ to form **4**. Infrared spectrum showed a stretching frequency at 3599cm^{-1} due to O-H. In the ^{1}H NMR spectrum two singlets due to the methylene protons, O-CH_2 and CH_2OH were observed at δ5.13 and δ4.75 respectively. An O-H proton resonates as a small broad singlet at δ2.28. This peak disappears under D_2O wash confirming the presence of an O-H proton.

2.2.5 2-benzyloxybenzyl aldehyde (5)

Swern oxidation[3] of 2-benzyloxybenzyl alcohol resulted in 2-benzyloxybenzyl aldehyde. Its ^{1}H NMR spectrum showed an aldehyde proton resonance at δ10.55.

A singlet due to methylene protons was observed at δ5.19. Aromatic protons resonate in the range δ6.90 – 7.88.

2.2.6 2-[(*N, N*-Dimethylamino)methyl]ferrocenecarboxyaldehyde (6)

Compound **6** was prepared by first lithiating [(dimethylamino)methyl]ferrocene with *n*-butyllithium in diethyl ether, followed by reacting the resulting solution with *N, N*-Dimethylformamide. After hydrolysis, a yellow/orange oil was isolated. The ^{1}H NMR spectrum showed an aldehyde proton resonance at δ10.09. Five protons of the unsubstituted Cp ring are presented at δ4.23. The substituted cyclopentadienyl ring protons show multiplets at δ4.81, δ4.65 and δ4.56. The methylene protons appear as two doublets at δ3.85 and 3.40 due to inequivalence of these two protons. The signal of the methyl protons is at δ2.23. This was in good agreement with the similar results previously reported.[22,23]

2.2.7 2-[(*N, N*-Dimethylamino)methyl]ferrocenecarboxyaldehyde Oxime (7)

This compound was formed by reacting the aldehyde (**6**) with a solution of sodium hydroxide and hydroxylamine hydrochloride (in ethanol) followed by neutralisation with carbon dioxide. The ^{1}H NMR spectrum shows a new singlet at δ8.05 and the disappearance of the aldeyhde proton signal at δ10.09. There is a slight upfield shift in the peaks due to protons of the substituted and unsubstituted cyclopentadienyl rings when compared to the spectrum of **6** above. This is due the electron donating effect of the nitrogen and the double bond. The singlet due to unsubstituted Cp ring protons is observed at δ4.14 (0.09ppm less compared to that of compound **6**). The two doublets due to methylene protons appear at δ3.81 and δ3.32.

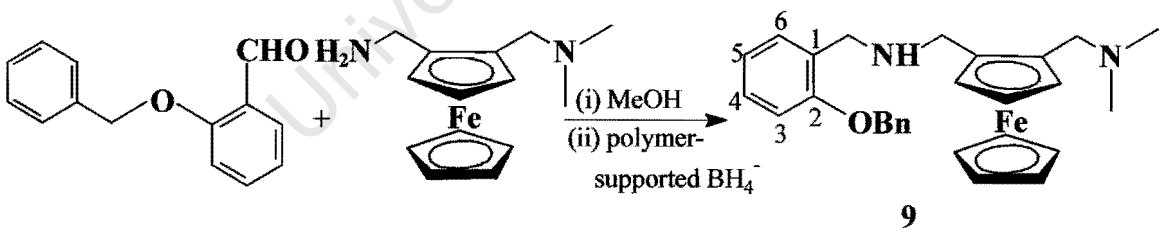
2.2.8 2–[(*N, N*-Dimethylamino)methyl]ferrocenylamine (8)

2-[(*N, N*-Dimethylamino)methyl]ferrocenylamine was synthesised by following the procedure reported by Brocard and co-workers.[4] The oxime was reduced with $LiAlH_4$ to the

amine in 89% yield. The proton spectrum shows a further decrease in the chemical shifts of the peaks. The unsubstituted cyclopentadienyl protons give a singlet at δ4.04. This is observed at 0.19ppm and 0.10ppm less than the Cp peaks of compounds **6** and **7** respectively. The methyl protons are also shielded and resonate at δ2.14. A new set of doublets due to the methylene protons adjacent to the amine group is observed at δ3.61 and δ2.87.

2.2.9. Reaction of 2–[(*N, N*-Dimethylamino)methyl]ferrocenylamine with 2-benzyloxybenzyl aldehyde to give compound 9

The reaction of 2-[(*N, N*-Dimethylamino)methyl]ferrocenylamine with 2-benzyloxybenzyl aldehyde in methanol at room temperature yielded a Schiff base which was subsequently reduced *in situ* using polymer-supported borohydride to give a yellow amine compound **9**. This was recrystallised from dichloromethane-hexane solvent system to give **9** as air and light stable yellow needles. The reaction is shown in the **equation 2.2** below. The formation of a Schiff base and the amine compound was followed by ^{1}H NMR spectroscopy by observing the disappearance of the aldehyde proton resonance at δ10.55.



9 (2.2)

Infrared spectroscopy

An infrared spectrum of **9** shows a weak band at *ca.* 3657cm^{-1} due to the stretching of the secondary amine (N-H) that formed. Another weak band at 1616cm^{-1} could be due to ν(C-N).

^{1}H NMR spectroscopy

The ^{1}H NMR data for compound **9** is given in **Table 2.2**. There is a further upfield shift in the peaks due to cyclopentadienyl protons compared to Cp protons of compound **8**. The spectrum shows a singlet due to the unsubstituted cyclopentadienyl protons at δ3.97 and three multiplets due to the protons of the substituted Cp ring. The expected new set of peaks in the aromatic region is observed. This confirmed the formation of compound **9**.

Table 2.2 ^{1}H NMR spectrum of compound **9**[a]

Chemical shift	Multiplicity	Integration	Assignment
2.06	s	6H	C*H*$_3$
2.26	brs	1H	N*H*
2.87	d, ^2J 12.90Hz	1H	Cp$^+$-C*H*$_2$-NMe$_2$
3.41	d, ^2J 12.90Hz	1H	Cp$^+$-C*H*$_2$-NMe$_2$
3.49	d, ^2J 12.60Hz	1H	NH-C*H*$_2$-Cp$^+$
3.72	d, ^2J 12.60 Hz	1H	NH-C*H*$_2$-Cp$^+$
3.90	d, ^2J 2.50Hz	2H	Ar-C*H*$_2$-NH
3.97	s	5H	Cp
4.08	m	1H	C$_5$*H*$_3$
4.16	m	1H	C$_5$*H*$_3$
4.20	m	1H	C$_5$*H*$_3$
5.10	s	2H	O-C*H*$_2$
6.89-7.00	m	2H	Ar*H*
7.22	d, J 1.50Hz	1H	Ar*H*
7.22	dd, ^2J 1.80Hz	1H	Ar*H*
7.30-7.50	m	5H	Ar*H*

a : $CDCl_3$: brs = broad singlet, s = singlet, m = multiplet, d = doublet, td = triplet of doublets
Cp$^+$ = substituted cyclopentadienyl ring

The benzyl methylene protons resonate as a singlet at δ5.10. The two pairs of methylene protons adjacent to the substituted cyclopentadienyl ring are diasterotopic, hence each proton gives a doublet (see **Table 2.2**). The coupling of the methylene protons (adjacent to the aromatic group) to N-H proton gives small doublet with a coupling constant of 2.50Hz at δ3.90. A broad singlet due to N-H proton is observed at δ2.26. **Figure 2.3** shows the ^{1}H NMR spectrum of **9**.

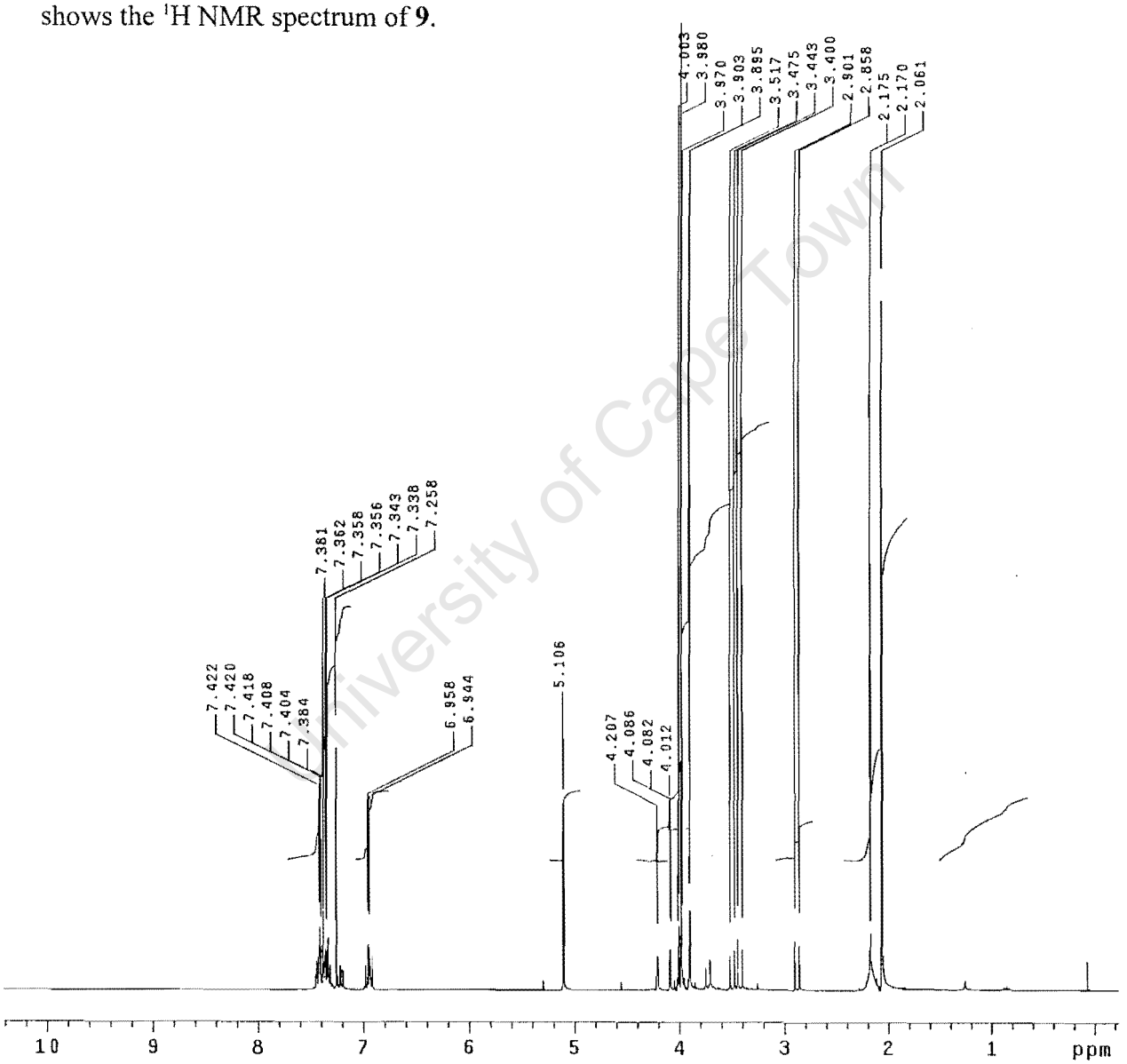


Figure 2.3 A 300MHz ^{1}H NMR spectrum of compound **9**

^{13}C NMR spectroscopy

The ^{13}C NMR spectrum (**appendix 3**) of **9** shows the single carbon peaks in the range δ111.7- δ156.6 which are due to aromatic carbons. The most deshielded peak at δ156.6 is due to C2 of the 2-benzyloxybenzyl group. This is influenced by the electronegativity of the oxygen atom bonded to C2. The chemical shifts of the ferrocenyl and other non-aromatic carbons are tabulated in **Table 2.3**. The two substituted carbons of the Cp^+ ring are in a very similar chemical environment. This could lead to an appearance of a single peak (low intensity) observed at δ48.1.

Table 2.3 ^{13}C NMR spectrum of **9**[a]

Chemical shift	Assignment
44.9	CH_3
47.1	C_5H_3
48.1	$2 \times C$ (C_5H_3)
57.8	Cp^+-CH_2-NMe_2
66.0	NH-CH_2-Cp^+
68.9	Cp
69.5	C_5H_3
69.9	Ar-CH_2-NH
70.6	O-CH_2
83.4	C_5H_3

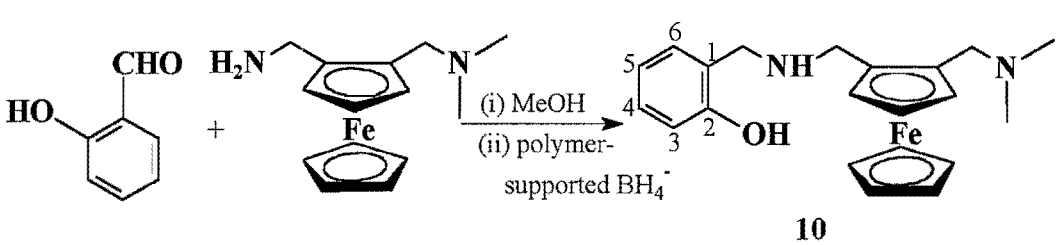
a : $CDCl_3$
Cp^+ = substituted cyclopentadienyl ring

Mass spectrometry

The FAB mass spectrum of **9** shows the parent molecular ion peak at *m/z* 467.85. The fragmentation pattern is observed for the organic ligand, which shows the following peaks that correspond to, $[PhCH_2O]^+$ (*m/z* 107)(5%), $[PhCH_2]^+$ (*m/z* 91)(100%) $[Ph]^+$ (*m/z* 77)(10%). Other observed peaks are $[CpFeC_5H_3CH_2NHCH_2]$(*m/z* 213)(73%), $[CpFeC_5H_3CH_2NH]$(*m/z* 199)(2%), $[CpFeCH]^+$(*m/z* 134)(20%) and $[CpFe]^+$ (*m/z* 121)(13 %). The mass spectrum recorded on the EI mass spectrometry confirms the presence of a parent molecular ion peak at *m/z* 468. Clear fragmentation peaks assigned from the spectrum are, *viz.* $[M\text{-}NMe_2]$ (*m/z* 423), $[PhCH_2OCCH]$(*m/z* 132), [CpFe](*m/z* 121), $[PhCH_2]^+$(*m/z* 91), $[Ph]^+$ (*m/z* 77), $[C_5H_5]^+$ (*m/z* 65) and $[Fe]^+$ (*m/z* 56). This clearly indicates that there is more than fragmentation pattern followed by the complex. EI and FAB mass spectra are shown in **Appendix 4**.

2.2.10 Reaction of 2-[(*N, N*-dimethylamino)methyl]ferrocenylamine with salicylic aldehyde to give compound 10

The procedure used in **section 2.2.9** above was adapted to the synthesis of compound **10**, which was obtained as an orange/red oil. It is air and light stable and highly soluble in chlorinated solvents. The reaction followed is shown in **equation 2.3**.



(2.3)

10

^{1}H NMR spectroscopy

Table 2.4 shows the proton NMR assignment of **10**. A similar spectrum to that of compound **9** was obtained for **10**, except for the aromatic region. All the protons in the non-aromatic region were shielded compared to those of compound **9** in the same region with the exception of the Cp protons which differ by 0.05ppm. The shielding could be due to the difference in aromatic groups. A very broad peak due to the O-H proton is observed at about δ4.69. (See ^{1}H NMR spectrum in **Figure 2.4**)

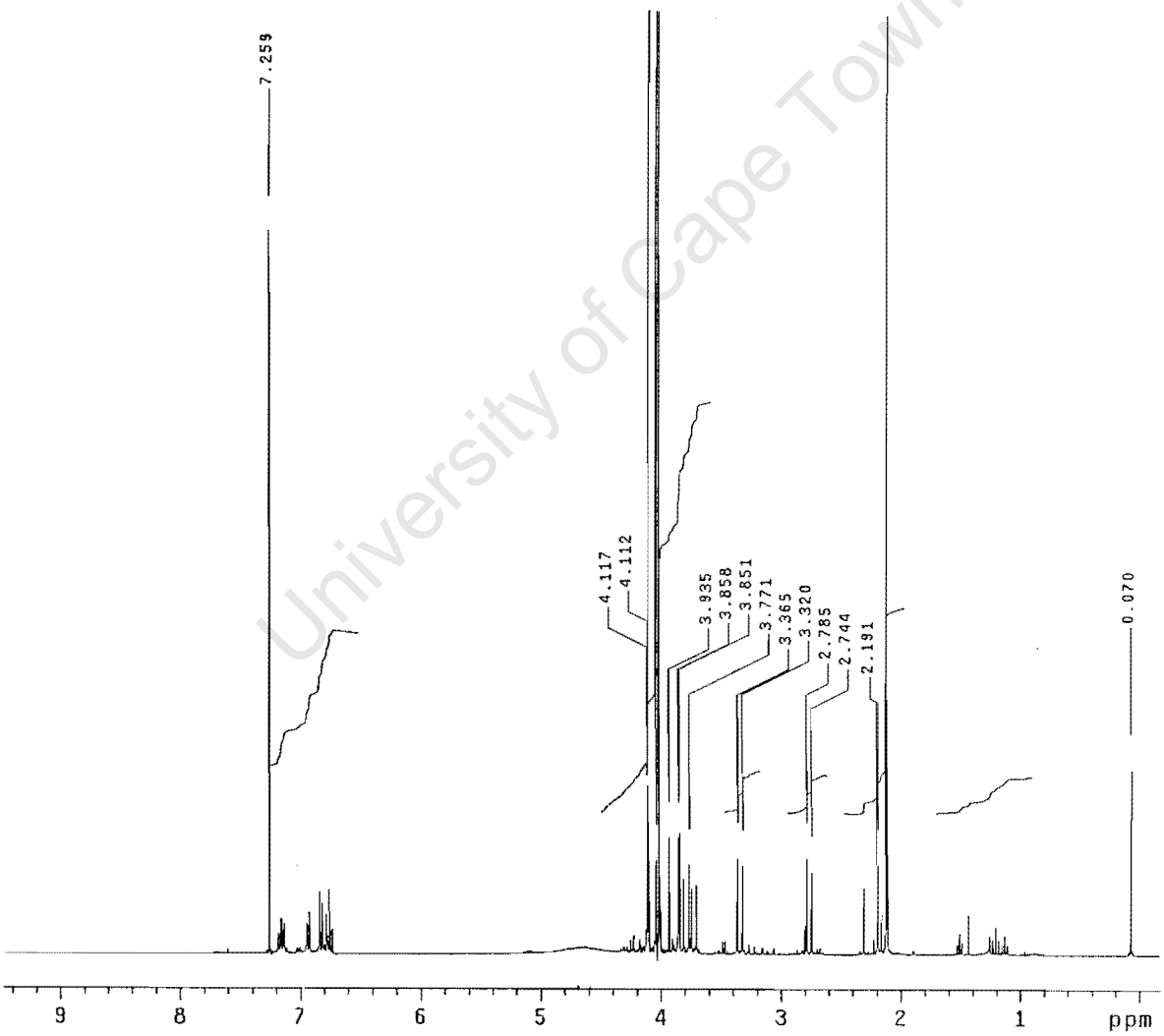


Figure 2.4 A 300MHz ^{1}H NMR spectrum of **10**

The N-H proton is not observed in the ^{1}H NMR spectrum, but it was detected by proton counting.[24]

Table 2.4 ^{1}H NMR data for compound **10**[a]

Chemical shift	Multiplicity	Integration	Assignment
2.12	s	6H	CH_3
2.76	d, ^2J 12.30Hz	1H	Cp^+-CH_2-NMe_2
3.34	d, ^2J 13.50Hz	1H	NH-CH_2-Cp^+
3.73	d, ^2J 12.60Hz	1H	Cp^+-CH_2-NMe_2
3.79	d, ^2J 13.50Hz	1H	NH-CH_2-Cp^+
3.85	d, ^2J 2.10Hz	2H	Ar-CH_2-NH
4.01	m	1H	C_5H_3
4.02	s	5H	Cp
4.05	m	1H	C_5H_3
4.11	m	1H	C_5H_3
6.71-7.22	m	4H	Ar*H*

a : $CDCl_3$: s = singlet, m = multiplet, d = doublet,

Cp^+ = substituted cyclopentadienyl ring

^{13}C NMR spectroscopy

In ^{13}C NMR spectrum of compound **10**, the aromatic carbon (C2) bonded to hydroxyl group resonates at δ158.9 as expected. A low intensity singlet due C1 is observed at δ122.5. Carbons C4 and C5 overlap because of a similar chemical shift hence a singlet at δ128.4 is observed. The other two aromatic carbons, C3 and C6 resonate at δ118.7 and δ116.4 respectively. **Table 2.5** gives the assignments of other carbons of compound **10**. The two peaks at δ83.9 and δ84.3 are associated to non-hydrogenated carbons of Cp^+ because of the low intensity of the peaks. The spectrum is shown in **Appendix 5**.

Table 2.5 ^{13}C NMR spectroscopy of compound 10[a]

Chemical shift	Assignment
44.8	CH_3
45.8	C_5H_3
50.7	C_5H_3
58.3	C_5H_3
65.9	Ar-CH_2-NH
69.0	Cp
70.6	NH-CH_2-Cp^+
71.2	Cp^+-CH_2-NMe_2
83.9	C-C_4H_3
84.4	C-C_4H_3

a : $CDCl_3$: s = singlet, m = multiplet, d = doublet,

Cp^+ = substituted cyclopentadienyl ring

Mass spectrometry

A parent molecular ion was observed for compound **10** at *m/z* 378 (40%) in the spectrum recorded using EI. More than one fragmentation pattern can be observed. Other observed peaks are $[CpFe]^+$ (*m/z* 121) (82%), $[C_6H_4CH_2(OH)]^+$ (*m/z* 107)(33%), $[PhCH_2]^+$ (*m/z* 91)(52%), $[Cp]^+$ (*m/z* 65)(6%) and $[Fe]^+$ (*m/z* 56)(31%). The spectrum is shown in **Appendix 6**.

2.3 Conclusion

2-methoxy- and 2-benzyloxybenzoic acids (**1** and **2** respectively) were synthesised and showed very similar spectroscopic data. New complexes **9** and **10** containing ferrocenyl moiety and aspirin derivative were synthesised and fully characterised. Parent molecular ions were observed for both compounds (**9** and **10**) in the mass spectra.

In future this work can be extended to the synthesis of bimetallic complexes by, for example, binding the metal complexes to the nitrogen atom of the alkyl chain bonded to the ferrocene moiety. In the view of the high affinity of gold for sulfur, gold complexes can be prepared from aspirin derivatives containing a sulfur atom. These complexes may have useful medicinal properties such as antiparasitic, antibacterial or antitumor properties. As such they can be tested for biological activity and compared to the activity of known drugs.

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CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF METAL COMPLEXES OF ACETYLSALICYLIC ACID DERIVATIVE (2-BENZYLOXYBENZOIC ACID)

3.1 Introduction

A short introduction about the synthesis of acyl iron and mangenese complexes is given in **sections 3.1.1** and **3.1.2** respectively.

3.1.1 Acyl iron complexes of the type [$CpFe(CO)_2C(O)R$]

Many complexes of the type [$CpFe(CO)_2C(O)R$] have been previously reported.[1-5] The first example of this kind was acetyl derivative [$CpFe(CO)_2COCH_3$] formed by the reaction of Na[$CpFe(CO)_2$] and acetyl chloride.[1] Acyl derivatives are also reported to be obtained in reaction of alkyldicarbonylcyclopentadienyliron complexes, [$CpFe(CO)_2R$] (R = Me, Et, or Pr^i) with carbon monoxide and phosphorus ligands (PPh_3, $PPhMe_2$, PPh_2Me, $P(OC_6H_5)_3$, $P(OC_4H_9)_3$ and $P(n\text{-}C_4H_9)_3$).[6,7] The diacyl derivatives of the general formula [$CpFe(CO)_2CO(CH_2)_nCO(CO)_2FeCp$] have also been prepared from sodium salt, Na[$CpFe(CO)_2$] and various diacyl chlorides.[1]

The [$CpFe(CO)_2C(O)R$] complexes have been less investigated compared to acyl derivatives of manganese and found to be much less useful because of their inability to decarbonylate for the syntheses of organometallic alkyl derivatives. Conditions for decarbonylation were later discovered[5,8,9] and are described in Chapter 4. The acyl complexes are of special interest because they can be involved in catalytic activities.[10]

3.1.2 Acyl manganese complexes

A number of acyl derivatives of manganese carbonyl of general formula $RCOMn(CO)_5$ have been prepared and extensively documented in the literature.[11-15] One of the earliest acyl manganese pentacarbonyl complexes to be reported was propionyl derivative, [$Mn(COC_2H_5)(CO)_5$].[11] In the more recent years, Moss and Andersen[16]

reported an extensive series of alkyl and acyl manganese pentacarbonyls. These were all prepared by reaction of the manganese pentacarbonyl anion with the appropriate alkyl or acyl halide. These complexes are of fundamental importance in many catalytic reactions. Binuclear complexes $[(CO)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ have also been reported.[17]

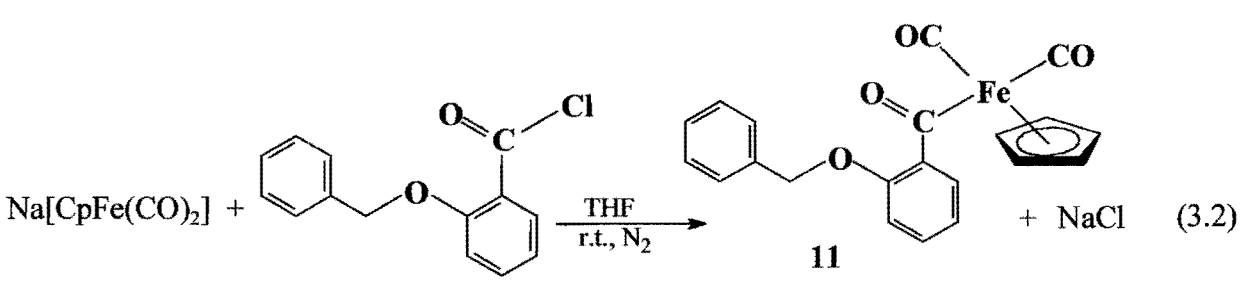
3.2 Synthesis and Characterisation

3.2.1 Synthesis of 2-benzyloxybenzoyl-η^5-cyclopentadienylirondicarbonyl $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (11)

This new complex was prepared by reaction of 2-benzyloxybenzoyl chloride with the sodium salt of cyclopentadienyliron dicarbonyl anion (**equations 3.1 and 3.2**). The method used is analogous to the method for the synthesis of acyl complexes $[CpFe(CO)_2\{C(O)R'\}]$ (R′ = Me[1], Et[2], Pr[3], R′ = *n*-C_5H_{11}, *n*-$C_{17}H_{35}$[4], R′ = $CPPh_3$, $CPPh_2Me$[5]).

The acyl iron complex **11** was isolated as a yellow oil after chromatography of the reaction mixture. This solidified and was recrystallised from dichloromethane-hexane to give the product as yellow crystals. The compound was found to be air and light stable in the solid state but decomposes in solution (photochemical decarbonylation). The iron dimer, $[CpFe(CO)_2]_2$ was also isolated from this due to decomposition. Infrared, elemental analysis, ^1H and ^{13}C NMR, mass spectrometry and X-Ray crystallography were used to characterise complex **11**. Characterisation data are presented in **Tables 3.1, 3.2 and 3.3**.

$$[CpFe(CO)_2]_2 \xrightarrow[THF]{Na/Hg} 2Na[CpFe(CO)_2] \qquad (3.1)$$



(3.2)

3.2.2 Characterisation of [$CpFe(CO)_2C(O)C_6H_4OCH_2Ph$] (11)

IR spectroscopy

Infrared absorptions in the ν(CO) region (2200-1600cm^{-1}) recorded in dichloromethane showed three carbonyl stretching bands which are characteristic of the compounds of the type [$CpFe(CO)_2C(O)R$].[1-3] These correspond to the symmetric and asymmetric stretches of the terminal Fe(CO) groups as well as the acyl carbonyl (see **Table 3.1**). The IR spectrum also showed two stretching frequencies at 2017s and 1961s cm^{-1} from the first fraction separated by chormatography. These suggest that cyclopentadienyliron dicarbonyl alkyl, [$CpFe(CO)_2C_6H_4OCH_2Ph$] could have formed from photochemical decarbonyl-ation in solution. The third fraction was confirmed to be the dimer, [$CpFe(CO)_2]_2$ with IR stretching frequencies at 1996w, 1954w and 1773w cm^{-1}. These were exactly same as for the [$CpFe(CO)_2]_2$ starting material.

Table 3.1 Infrared[a] data for [$CpFe(CO)_2C(O)C_6H_4OCH_2Ph$] (**11**)

ν(CO)cm^{-1}	
C ≡ O	C=O
2020s, 1963s	1621m

a : CH_2Cl_2, s = strong, m = medium

^{1}H NMR spectroscopy

The ^{1}H NMR data for complex **11** are shown in **Table 3.2**. The proton NMR spectrum shows a singlet due to the cyclopentadienyl protons at δ4.75 which is at the characteristic position for the compounds, [$CpFe(CO)_2C(O)R$][2,4] The methylene protons for **11** appear at δ5.06 (*i.e.* 0.23ppm less than that of methylene protons of the starting material, 2-benzyloxybenzoic acid). This is due to the effect of the iron which influences the environment of the organic ligand. The aromatic protons appear as a multiplet in the range δ6.64-7.47 for nine protons. **Figure 3.1** shows the ^{1}H NMR spectrum of **11**.

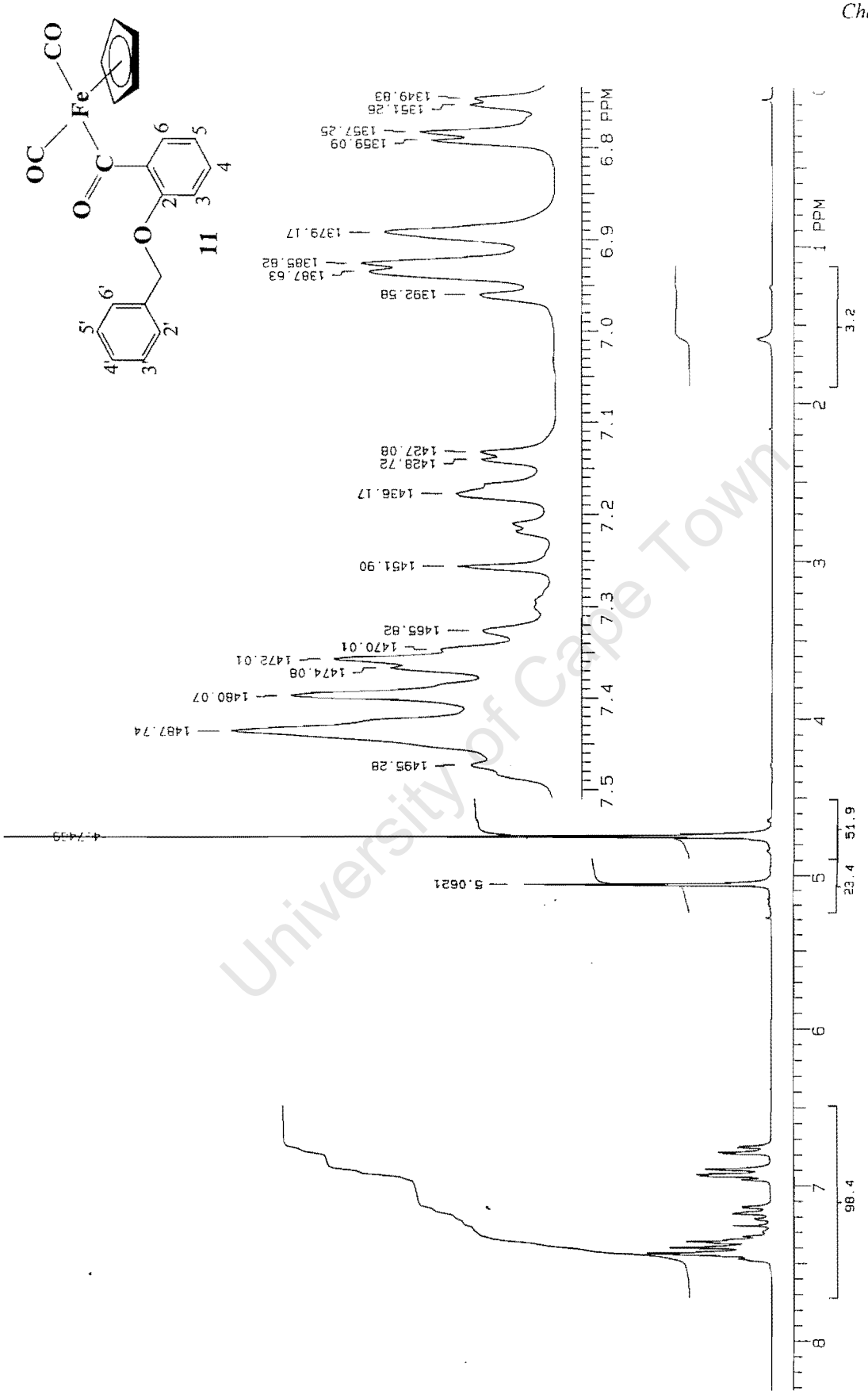


Figure 3.1 A 200MHz ^{1}H NMR spectrum of **11**

Table 3.2 ^{1}H NMR data for [$(CpFe(CO)_2C(O)C_6H_4OCH_2Ph]^a$ **(11)**

Chemical shift δ(ppm)	Multiplicity	Integration	Assignment
4.75	s	5H	Cp
5.06	s	2H	O-C*H*$_2$
6.64 – 7.47	m	9H	Ar*H*

a : $CDCl_3$: s = singlet, m = multiplet

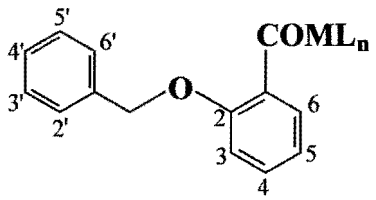
^{13}C NMR spectroscopy

The ^{13}C NMR data for compound **11** is given in **Table 3.3**. The resonances for the cyclopentadienyl carbons and the CO groups appear at the expected positions. The presence of the metal atom causes an upfield shift in the resonance of the aromatic carbons. In the ^{13}C NMR spectrum the two terminal carbonyls show a peak at δ213.9 (see **Appendix 7**). It has been reported previously that terminal carbonyls of these systems resonate in the range δ210-220.[4] The acyl carbon atom is more deshielded than the terminal carbonyl atoms. The acyl carbon peak was observed at δ 257 which is in agreement with the literature for similar compounds.[4]

Table 3.3 ^{13}C NMR data for [$CpFe(CO)_2C(O)C_6H_4OCH_2Ph]^a$ **(11)**

Chemical shift δ(ppm)	Assignment*
70.4	O-CH_2
86.8	Cp
112.5	C1′
120.7	C3′, C5′
121.5	C2′, C6′
127.9	C4′
128.1	C3
128.4	C5
128.5	C6
136.7	C4
146.4	C1
150.5	C2
213.9	terminal carbonyl (folded peak)
257.0	acyl CO

a : $CDCl_3$; *: see Figure 3.2 for atom numbering system



M = Fe, Mn, L_n = $Cp(CO)_2$, $(CO)_5$

Figure 3.2 Numbering system used for assignment of aromatic protons and carbon atoms in complexes **11**, **12** and **13**.

Mass spectrometry

The mass spectrum (EI) of compound **11** does not show the parent molecular ion peak at *m/z* 388, but the highest mass peaks at *m/z* 360 and *m/z* 304 are observed. This suggests a loss of one and two carbonyls consecutively. The most intense peaks observed correspond to $[PhCH_2]^+$ (*m/z* 91) and [M-3CO] (*m/z* 304). In the high-resolution mass spectrum (FAB), a molecular ion peak is observed. The main peaks observed with intensities are listed in **Table 3.4**. The main fragmentation patterns that occurred are shown in **Figure 3.3**. This type of pattern has also been observed for other acyl complexes.[4] The mass spectra for **11** appear in **Appendix 8**.

Table 3.4 Mass spectral data for $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (**11**)

Assignment	Relative peak intensities (%)
M	3
M-CO	15
M-2CO	6
M-3CO	100
M-3CO-Cp	19
$PhCH_2$	80
$CpFe(CO)_2$	16
CpFe	21
Cp	5
Fe	9

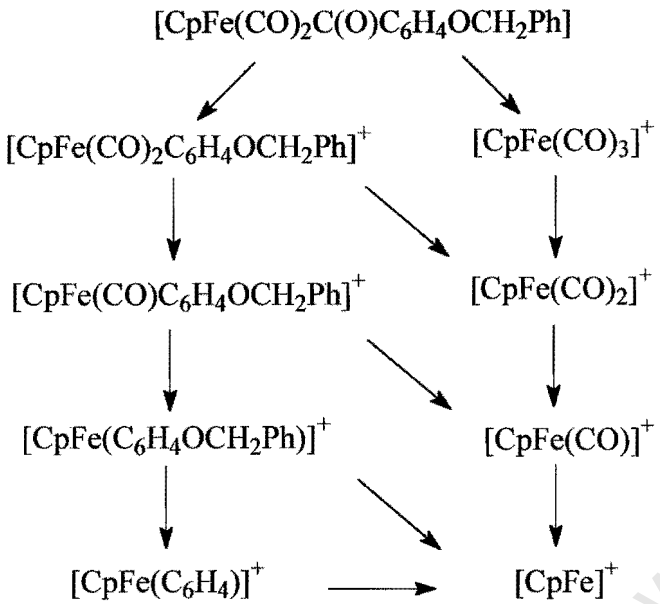


Figure 3.3 Main fragmentation pathways of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ **(11)**

X-ray crystallography

Crystal data collection, reduction and refinement for (11)

Suitable single yellow crystals of **11** were grown from dichloromethane-hexane solvent system by diffusion method at 15°C. Compound **11** was dissolved in a minimum amount of dichloromethane and hexane was layered on top. Crystals were formed after the solution was kept at about 4°C for a week.

A single crystal was glued on to a glass fibre. X-ray intensity data were collected at 298 K using a Nonius Kappa CCD with 1.5 kW graphite monochromated Mo radiation. The diffraction patterns could be indexed using a monoclinic cell. The strategy for the data collection was evaluated using the *Collect* Software[18]. The detector to crystal distance was 40 mm. Data were collected by a phi scan and several omega scans. The data were scaled and reduced using *Denzo-SMN*[19]. Unit cell dimensions were refined on all data. The space group P $2_1/c$ was chosen on inspecting the systematic absences and the symmetry of the diffraction patterns. The structure was solved and refined using *SHELX97*[21]. There is no disorder and the thermal ellipsoids for all atoms are reasonable. Hydrogen atoms were placed in calculated positions and included in the model during later stages of the refinement. Plots of the molecular structure were obtained with *ORTEP* [22] and *PLATON* [23].

A summary of the crystal data, experimental details and refinement results is listed in **Table 3.5**. The molecular structure together with the atom-numbering scheme and crystal packing diagram of **11** are shown in **Figures 3.4** and **3.5** respectively. The selected bond lengths and angles are shown in **Table 3.6**. The crystal structure confirms the formation of complex **11** based on analytical and spectroscopic data. It however shows no novel features.

Table 3.5 Crystal data and structure refinement for $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$

Empirical formula	$C_{21}H_{16}FeO_4$
Formula weight	388.19
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P $2_1/c$
Unit cell dimensions	a = 14.7377(3) Å $\alpha = 90°$.
	b = 7.46270(10) Å $\beta = 107.7340(10)°$.
	c = 17.2599(4) Å $\gamma = 90°$.
Volume	1808.09(6) $Å^3$
Z	4
Density (calculated)	1.426 Mg/m^3
Absorption coefficient	0.856 mm^{-1}
F(000)	800
Crystal size	0.33 x 0.30 x 0.22 mm^3
Theta range for data collection	3.23 to 27.48°.
Index ranges	-19<=h<=19,-8<=k<=9, -22<=l<=22
Reflections collected	13513
Independent reflections	4146 [R(int) = 0.0245]
Completeness to theta = 27.48°	99.7 %
Max. and min. transmission	0.8339 and 0.7653
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4146 / 0 / 236
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0788
R indices (all data)	R1 = 0.0424, wR2 = 0.0842
Extinction coefficient	0.0000(10)
Largest diff. peak and hole	0.256 and -0.209 $e.Å^{-3}$

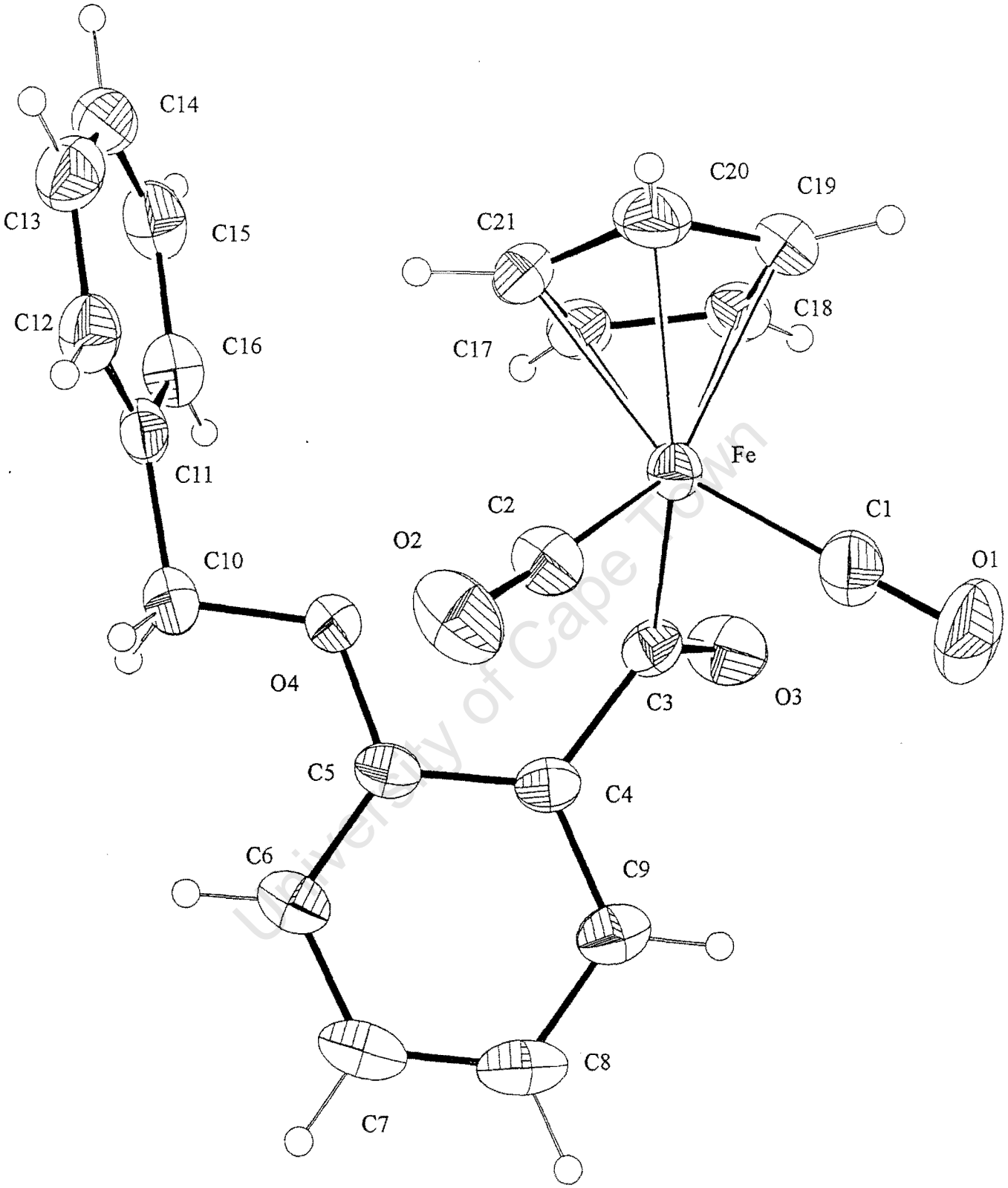


Figure 3.4 ORTEP drawing of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (**11**) showing atom labeling. Thermal ellipsoids are plotted at 30% probability level.

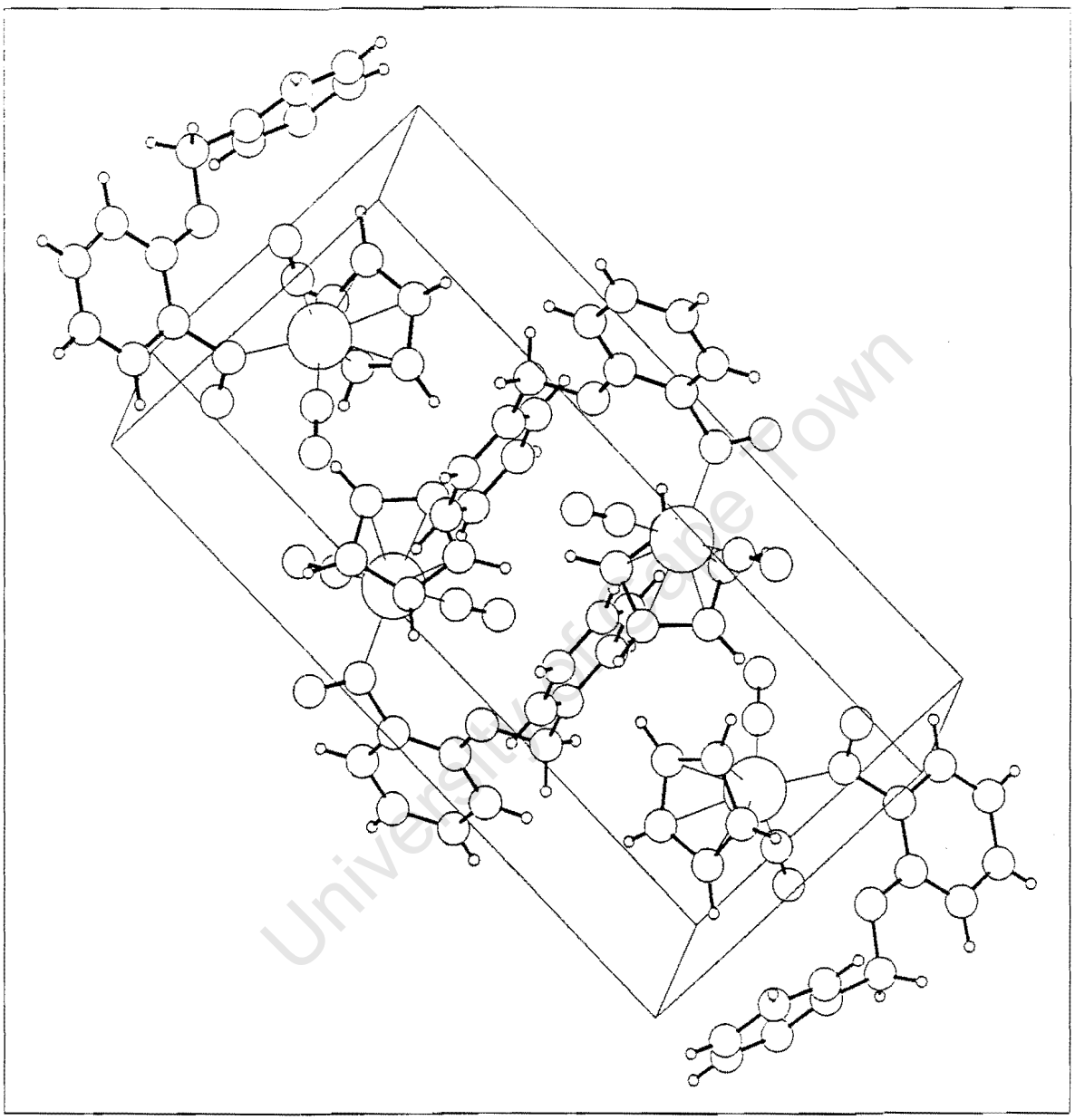


Figure 3.5 Crystal packing of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (**11**) along the *c*-axis

The two planes that contain the two aromatic and Cp rings are perpendicular to each other. This arrangement gives the lowest energy (most stable) conformation. The phenyl groups of each molecule in a unit cell are parallel to each other. The data are compared with the bond lengths and angles of the reported $[CpFe(CO)_2C(O)CHPMe_3]$.[24] The bond lengths and angles are within the expected range, and are very similar to those reported.

Table 3.6 Selected bond lengths [Å] and angles (°) for complex **11** with estimated standard deviations in parentheses

Fe(1)-C(1)	1.760(2)
Fe(1)-C(2)	1.764(2)
Fe(1)-C(3)	1.980(2)
Fe(1)-C(17)	2.094(2)
Fe(1)-C(18)	2.099(2)
Fe(1)-C(21)	2.107(2)
Fe(1)-C(19)	2.115(2)
Fe(1)-C(20)	2.138(2)
O(3)-C(3)	1.206(2)
C(1)-Fe(1)-C(2)	94.73(10)
C(1)-Fe(1)-C(3)	86.53(10)
C(2)-Fe-C(3)	94.14(8)

Fractional atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, torsion angles, hydrogen atomic co-ordinates and structure factors appear in **Appendix 9** (Tables 9a – 9f).

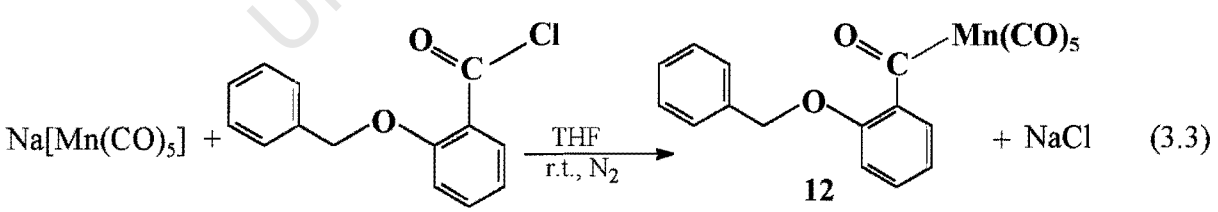
Thermal properties

The thermal properties of compound **11** were studied by Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA). The traces were recorded at a heating rate of 10°C/min. The DSC trace shows a sharp endothermic peak in the range 64°C-70°C, which is slightly lower than the melting point (70°C-73°C) determined using the hot-microscope. The exothermic peak at 205°C indicates the decomposition point of **11**. The TGA trace shows a mass loss of about 70% in the temperature range recorded. This could be due to decomposition. **Appendix 10** shows the DSC and TGA traces.

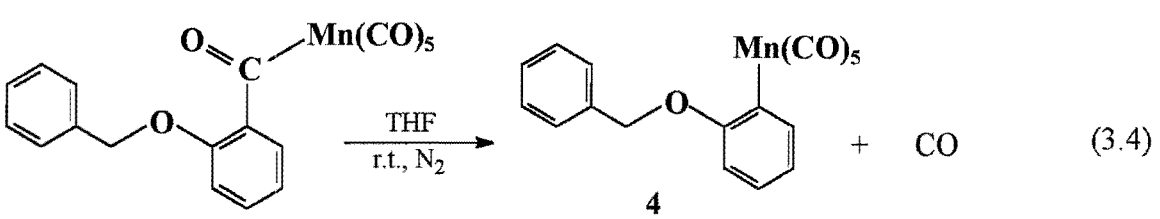
3.2.3 Synthesis of 2-benzyloxybenzoyl manganese pentacarbonyl $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (12)

The acylmanganese complex, **12** was prepared by reaction of the sodium salt of manganese pentacarbonyl anion with 2-benzyloxybenzoyl chloride (**equation 3.3**). This complex was isolated as a yellow solid and was found to be less stable than the iron complex. It is known that acylmanganese pentacarbonyls can readily be thermally decarbonylated, whereas cyclopentadienyliron dicarbonyl acyls do not undergo this reaction under similar conditions.[25]

It was discovered that the acylmanganese complex is unstable in solution and slowly decarbonylates at room temperature to form an arylmanganese complex, $[Mn(C_6H_4OCH_2Ph)(CO)_5]$, **13** (**equation 3.4**). Decomposition also takes place in solution. This was concluded from the interpretation of different techniques used to characterise the products *e.g.* elemental analysis, infrared, ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The formation (of complex **13**) was also confirmed when decarbonylation reaction was carried out on complex **12** (see **Chapter 4**). Complex **13** was recrystallised from methanol to give colourless crystals.



12 (3.3)



4 (3.4)

3.2.4 Characterisation of $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (12) and $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ (13)

Infrared spectroscopy

The IR spectra for complexes **12** and **13** were recorded in dichloromethane solution in the range of 2200-1600cm^{-1}. The data are given in **Table 3.7**. There is no significant variation in the carbonyl stretching frequencies of the two complexes except the acyl band for **12** and a strong band at 1992cm^{-1} for **13** (see **Appendix 11** and **12** respectively). The spectra show the expected number of peaks. These results are similar to those reported for related manganese pentacarbonyl complexes.

Table 3.7 Infrared data for $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (**12**) and $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ (**13**)

	ν(CO) cm^{-1}	
Compound	**C≡O**	**C=O**
12	2117m, 2056sh, 2019s	1616m
13	2116m, 2056sh, 2019s, 1991s	

a : CH_2Cl_2 , m = medium, sh = shoulder, s = strong, w = weak

^{1}H NMR spectroscopy

The ^{1}H NMR data for complexes **12** and **13** are given in **Tables 3.8** and **3.9** respectively. These were assigned according to the numbered structure in **Figure 3.2**. As with the acyl iron complex, the methylene protons resonate at a lower chemical shift (0.19ppm and 0.21ppm lower for complexes **12** and **13** respectively) compared to 2-benzyloxybenzoic acid. This shows that the metal has an influence on the chemical shift of the protons. Peaks due to aromatic protons overlap because of their similar chemical environment. **Figures 3.6** and **3.7** show the ^{1}H NMR spectra of **12** and **13** respectively.

Table 3.8 ^{1}H NMR[a] data for $[Mn(C(O)C_6H_4OCH_2Ph)(CO)_5]$ **(12)**

Chemical shift(ppm)	Multiplicity	Integration	Assignment*
5.10	s	2H	O-CH_2
6.80	dd, ^{2}J1.54Hz	1H	H6
6.84-6.88	m	2H	H3, H4
7.14-7.48	m	6H	H2′, H6′, H3′, H5′, H4′, H5

a : $CDCl_3$, s = singlet, dd = doublet of doublets, m = multiplet
see Figure 3.2 for atom numbering system

Table 3.9 ^{1}H NMR[a] data for $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ **(13)**

Chemical shift(ppm)	Multiplicity	Integration	Assignment*
5.08	s	2H	O-CH_2
6.80 – 6.95	m	2H	H5, H6
7.15	t, ^{2}J 7.45Hz	1H	H4′
7.34 – 7.47	m	5H	H3, H3′,H5′, H2′, H6′
7.55	d, ^{2}J 6.90Hz	1H	H4

a : $CDCl_3$, s =singlet, d= doublet, m = multiplet, t = triplet,*: Figure 3.2 for atom numbering system

^{13}C NMR spectroscopy

The methylene carbon (for **12** and **13**) resonates upfield compared to that of the free acid. This is because of the influence of the metal centre on the organic ligand. A peak due to terminal carbonyl was not well resolved and it was observed at the expected position[16] (at about δ210). The carbon resonance of the acyl carbon (C=O) of acetyl manganese pentacarbonyl complex was reported to appear at δ255[26]. However, this was not observed in the case of compound **12**. In the spectrum of **12,** a signal set of peaks due to compound **13** were observed, indicating its formation from complex **12** in solution *i.e.* the cross-marked peaks in spectrum of **12** (see **Figure 3.8**) are due complex **13**. The chemical shift values of the marked peaks were directly compared to the peaks in spectrum of **13** (**Figure 3.9**). The ^{13}C NMR data for **12** and **13** are given in **Tables 3.10** and **3.11** respectively.

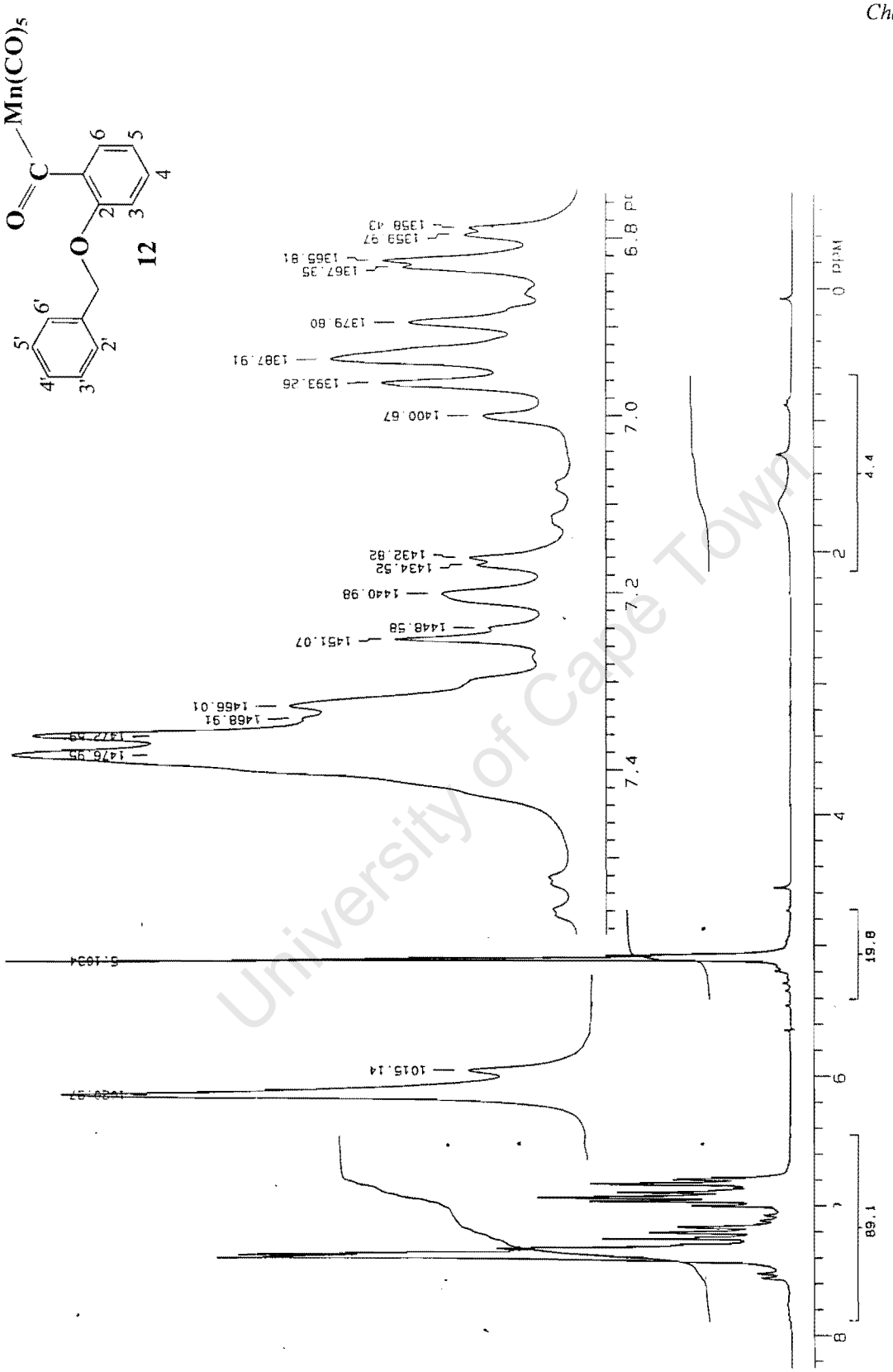


Figure 3.6 A 200MHz ^{1}H NMR spectrum of **12**

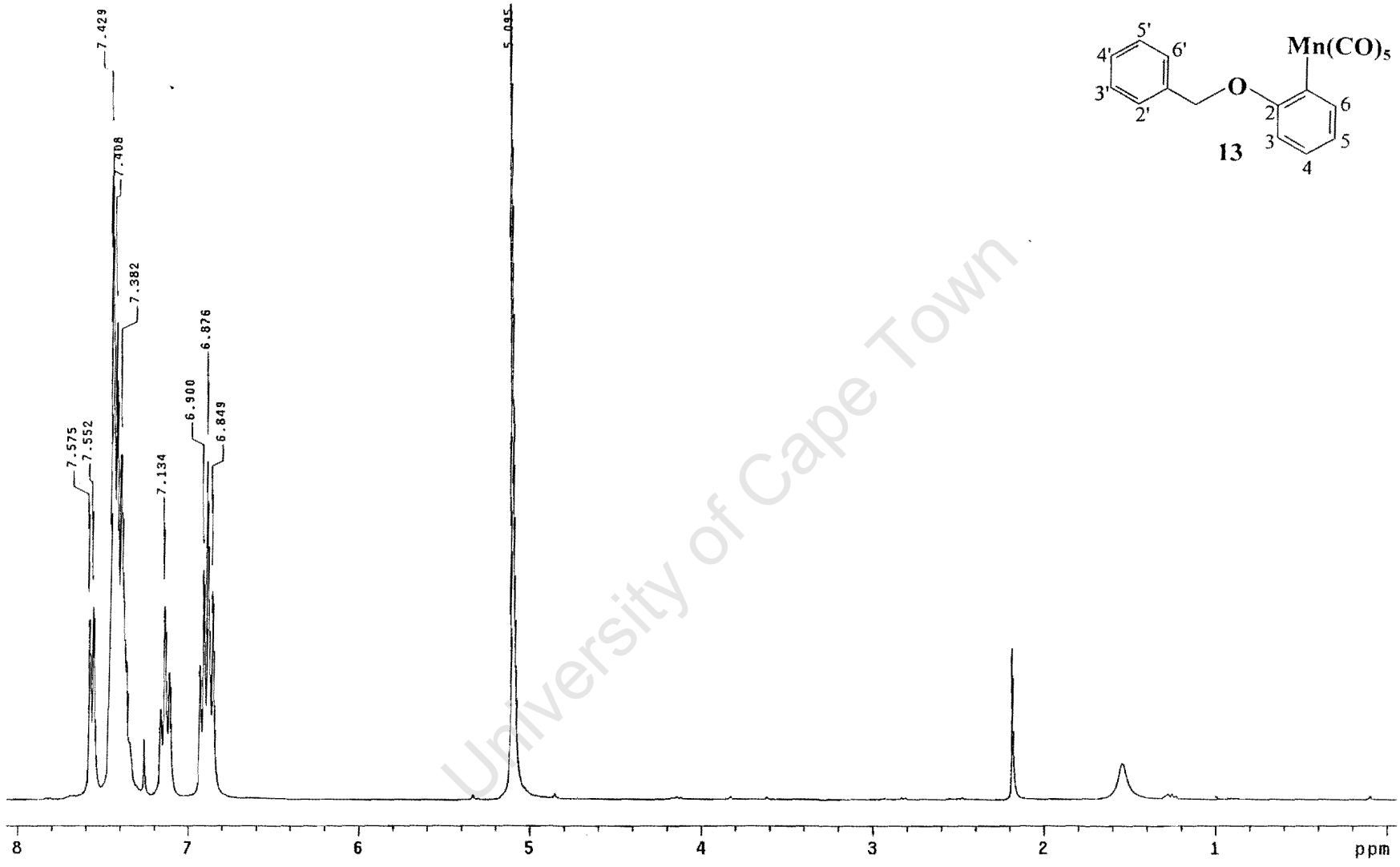


Figure 3.7 A 300MHz ^{1}H NMR spectrum of **13**

Table 3.10 ^{13}C NMR[a] data for $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (**12**)

Chemical shift (ppm)	Assignment*
70.4	O-CH_2
112.5	C1′
120.9	C3′, C5′
121.2	C2′, C6′
128.1	C4′
128.3	C3
128.5	C5
129.2	C6
136.2	C4
146.6	C1
151.1	C2
208.5	terminal carbonyls

a : $CDCl_3$, * : see Figure 3.2 for atom numbering system.

Table 3.11 ^{13}C NMR[a] data for $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ (**13**)

Chemical shift (ppm)	Assignment*
70.9	O-CH_2
110.7	C1′
121.9	C3′, C5′
126.2	C2′, C6′
127.9	C4′
128.1	C3
128.5	C5
132.7	C6
136.7	C4
145.8	C1
163.4	C2
210.7	terminal carbonyls

a : $CDCl_3$, *: Figure 3.2 for atom numbering system.

Mass spectrometry

Mass spectrum (for complex **13**) shows parent molecular ion (*m/z* 378). The suggested fragmentation pattern is the stepwise loss of terminal carbonyl groups followed by loss of Mn^{2+} from the aromatic group and fragmentation of the aromatic group. The most intense peaks observed corresponds to $[M-5CO]^+$, $[M-4CO]^+$. Other observed peaks are of the following ions, $[M-3CO]^+$ (*m/z* 294), $[M-4CO]^+$ (*m/z* 266), $[PhCH_2OC_6H_4]^+$ (*m/z* 183), $[PhCH_2]^+$ (*m/z* 91), $[Mn]^+$ (*m/z* 55), and $[CO]^+$ (*m/z* 28).

Figure 3.8 A 200MHz ^{13}C NMR spectrum of **12**

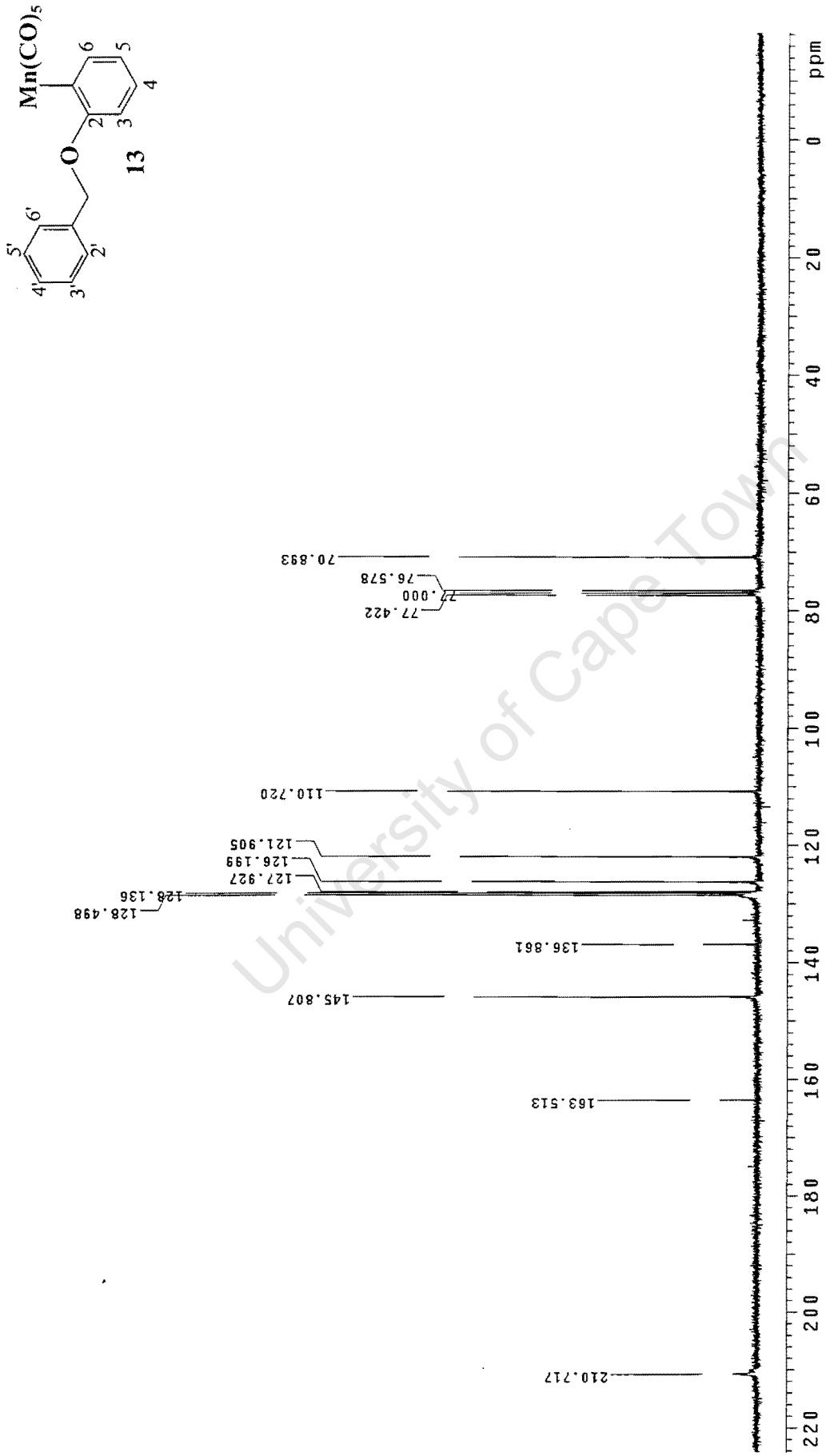


Figure 3.9 A 300MHz ^{13}C NMR spectrum of **13**

Thermal properties

The thermal properties of compound **13** were studied by Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA). The DSC and TGA traces at a heating rate of 10°C/min are shown in **appendix 14**. The DSC trace shows a sharp endothermic peak in the range 96°C - 104°C which could be assigned to melting. This corresponds well with the melting of the sample (100°C-102°C) determined using the hot-stage microscope. The exothermic peak at 190°C is due to the decomposition of the complex. The TGA trace shows a significant mass loss (*ca.* 62%) in the temperature range recorded. The decomposition point for **13** is estimated to be 190°C.

3.3 Conclusion

New complexes of aspirin derivative (2-benzyloxybenzoic acid) of transition metals (Fe and Mn) have been synthesised and successfully characterised. The crystal structure of the acyl iron complex **11** was determined.

The acyl manganese complex **12** was isolated in small yields because of its instability. It was discovered that complex **12** decarbonylates readily in solution to give complex **13**. Parent molecular ion and molecular ions due to the loss of carbonyl groups were observed in the mass spectra. Mass spectrometry for **12** was not recorded because it would easily decarbonylate to the corresponding aryl complex **13** and give the same fragmentation pattern as that of **13**.

The thermal behaviour of **11** and **13** were investigated by TGA and DSC. The DSC traces showed one endothermic peak which is within the determined melting point ranges.

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CHAPTER 4

REACTIVITY STUDIES – DECARBONYLATION AND SUBSTITUTION REACTIONS

4.1 Introduction

Many papers and reviews about decarbonylation of transition metal acyl complexes have been written.[1-5] The reaction equation 4.1 and the reverse reaction (*i.e.* carbonylation) have been used for the study of alkyl migration/CO insertion reaction mechanisms in general. A characteristic reaction of acyl derivatives is the facile decarbonylation to produce the corresponding alkyl derivatives (**equation 4.1**). The most common technique s for achieving decarbonylations are thermal and photochemical.

$$\mathbf{RCOM(CO)_n \longrightarrow RM(CO)_n + CO} \qquad (4.1)$$

Numerous acyl derivatives of manganese carbonyl of the general formula $RCOMn(CO)_5$ have been prepared.[6-10] The acylmanganese pentacarbonyls can be readily thermally decarbonylated. The corresponding acyl derivatives of various cyclopentadienyl metal carbonyls have been investigated in much less detail. This is because the cyclopentadienyliron acyls do not undergo a similar reaction under mild thermal conditions as, acylmanganese pentacarbonyls. For cyclopentadienyliron dicarbonyl acyls to undergo reaction analogous to the acylmanganese reactions more vigorous reaction conditions are required.[11,12]

Conditions for decarbonylation of complexes of the type $[CpFe(CO)_2(COR)]$ were discovered[14,15] (*i.e.* chemical and photochemical) and this led to new organometallic alkyl derivatives such as decarbonylated and ligand substituted iron complexes. Ford[13] and co-workers as well as Alexander[14] reported photochemical decarbonylation of the complexes of the type $[CpFe(CO)_2(COR)]$ (R = primary alkyl, aryl).

The disadvantages of this type of decarbonylation are that it results in low yields and decarbonylation of secondary alkyls results in decomposition.[14]

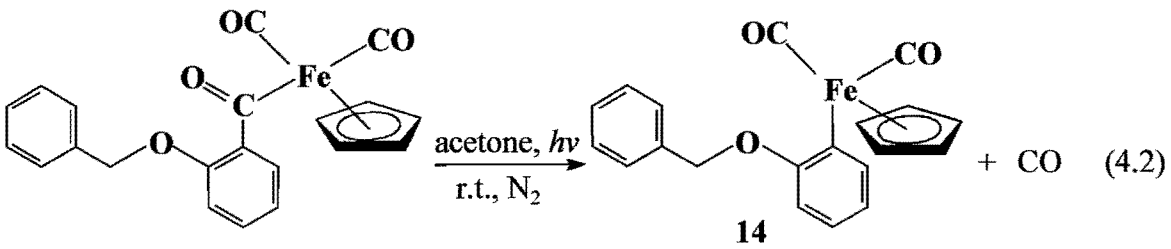
In the earlier work, Alexander reported the chemical decarbonylation of organometallic acyl complexes using chlorotris(triphenylphosphine)rhodium (I), $[Rh(PPh_3)_3Cl]$.[15]

The CO lost in the decarbonylation of $[(RCO)Mn(CO)_5]$derivatives has been demonstrated by radiochemical techniques[16] to arise from one of the carbonyl groups bonded to the metal atom rather than to the acyl carbonyl group. Thus the acyl carbonyl group rather being lost is converted into a terminal metal carbonyl group. Alexander[14] also confirmed a similar mechanism on photochemical decarbonylation of acetyl dicarbonyl- η^5-cyclopentadienyliron, $[CpFe(CO)_2C(O)CH_3]$. This mechanism suggests that the case of decarbonylation of acyl carbonyl group derivatives depends on the strength of the metal-carbon monoxide bond. It is therefore not surprising that the $[CpFe(CO)_2COR]$ derivatives fail to undergo decarbonylation on heating.[17] In this chapter the results for the photochemical and thermal decarbonylation of acyl dicarbonyl cyclopentadienyliron and acylmanganese pentacarbonyl complexes as well as their reactions with triphenylphosphine are investigated.

4.2 Results and Discussion

4.2.1 Photochemical decarbonylation of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$

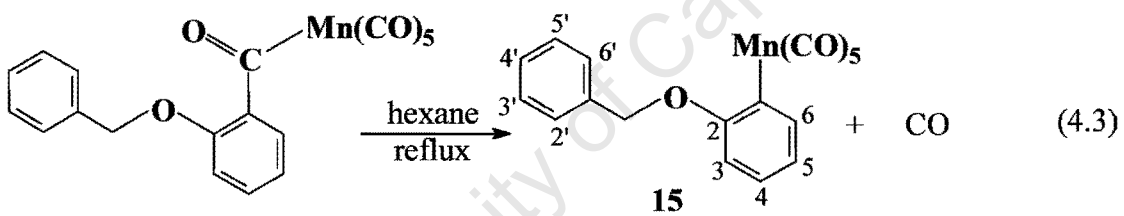
Since it has been reported that acyl derivatives of the type $[CpFe(CO)_2COR]$ are difficult to decarbonylate thermally, we employed photochemical method for the decarbonylation of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ in acetone to give **14** (**equation 4.2**). The reaction was monitored by infrared spectroscopy. Infrared spectra showed the disappearance of the acyl band and the two terminal carbonyl stretching frequencies appearing at lower frequencies (2017cm^{-1}, 1961cm^{-1}). This confirms that decarbonylation had taken place after 3h.



(4.2)

4.2.2 Thermal decarbonylation of $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (12)

The acyl manganese complex was decarbonylated by heating under reflux in hexane for 4h to give a pale yellow solid, **15** (**equation 4.3**). Infrared spectroscopy was used to monitor the reaction. Other methods used to characterise the product were elemental analysis, mass spectrometry and NMR.



(4.3)

Infrared spectroscopy

The infrared spectrum of **15** shows four carbon monoxide stretching frequencies, 2117 cm^{-1}, 2056cm^{-1}, 2018cm^{-1} and 1991cm^{-1}. There was no acyl band shown as expected.

^{1}H NMR spectroscopy

^{1}H NMR data for **15** is presented in **Table 4.2**. The spectrum recorded is identical to that of the decarbonylated by-product reported in **section 3.2.3**. The methylene protons appear at δ5.08 (*i.e.* 0.02ppm less than the methylene protons of 2-benzyloxybenzoic acid). There is also a change in the aromatic region, with the aromatic peaks being slightly deshielded.

Table 4.2 ^{1}H NMR data for $[Mn(C_6H_4OCH_2Ph)(CO)_5]^a$ **(15)**

Chemical shift(ppm)	Multiplicity	Integration	Assignment*
5.08	s	2H	O-CH_2
6.80 – 6.95	m	2H	H5, H6
7.15	t, ^2J 7.45Hz	1H	H4′
7.34 – 7.47	m	5H	H3, H3′,H5′, H2′, H6′
7.55	d, ^2J 6.90Hz	1H	H4

a : $CDCl_3$, s =singlet, d= doublet, m = multiplet, t = triplet

^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of **15** shows the expected number of peaks, when compared to compound **13** in **Chapter 3 - section 3.2.3**. All the carbon atoms were assigned as given in **Table 4.3**. The methylene carbon gives a singlet at δ70.9. The phenyl carbons are at a lower chemical shift values than those C1, C2, C3, C4, C5 and C6. This could be due to the effect of the oxygen and manganese atoms bonded to C1 and C2 respectvely.

Table 4.3 ^{13}C NMR[a] data for $[Mn(C_6H_4OCH_2Ph)(CO)_5]^a$ **(15)**

Chemical shift (ppm)	Assignment
70.9	CH_2
110.7	C1′
121.9	C3′, C5′
126.2	C2′, C6′
127.9	C4′
128.1	C3
128.5	C5
132.7	C6
136.7	C4
145.8	C1
163.4	C2
210.7	terminal carbonyls

a : $CDCl_3$

Mass spectrometry

The mass spectrum of **15** shows the parent molecular ion at *m/z* 378 which corresponds to the molar mass of the expected product. The fragmentation pattern showed successive loss of terminal carbonyl groups followed by loss of Mn^{2+} from the aromatic group and fragmentation of the aromatic group. The most intense peaks observed correspond to $[M\text{-}5CO]^+$(*m/z* 238) and $[PhCH_2]^+$ (*m/z* 91). Other observed peaks are of the following ions, $[M\text{-}3CO]^+$ (*m/z* 294), $[M\text{-}4CO]^+$ (*m/z* 266), $[PhCH_2OC_6H_4]^+$ (*m/z* 183), $[PhCH_2OCCH]^+$ (*m/z* 132), $[Mn]^+$ (*m/z* 55), and $[CO]^+$ (*m/z* 28). The mass spectrum of **15** was identical to the mass spectrum of **13** (see **Appendix 13a**).

4.2.3 Reaction of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (11) with triphenylphosphine

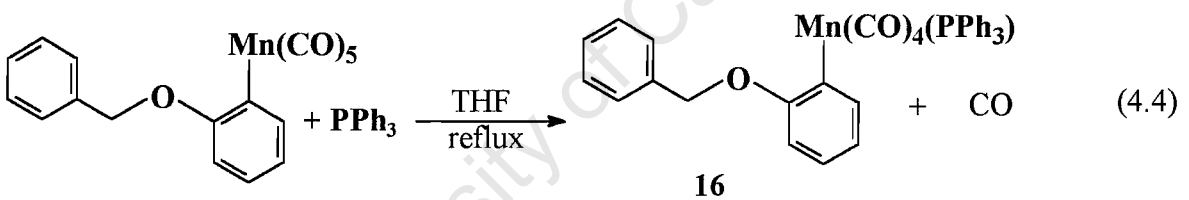
The reaction of the acyl iron complex with triphenylphosphine in acetonitrile and tetrahydrofuran did not show any substitution of CO with PPh_3 after heating under reflux for 72h. The expected product was the acyl cyclopentadienyl carbonyl phosphine complex $[CpFe(CO)(PPh_3)C(O)C_6H_4OCH_2Ph]$ (*i.e.* substitution of CO group with triphenylphosphine ligand). Monitoring the reaction by infrared spectroscopy showed that there was no reaction under the conditions used. The strength of the metal carbon bond could be the determining factor in this reaction. The stronger the bond the more difficult it is for the reaction to occur. The reaction conditions used are similar to those for the kinetic studies of reaction of benzyl iron system, $[CpFe\{(CH_2)_nPh\}(CO)_2]$ with PPh_3.[18] The reaction of methyl dicarbonyl cyclopentadienyliron with phosphorus ligands (*e.g.* PPh_3, $P(OC_6H_5)_3$, $P(OC_4H_9)_3$ and $P(n\text{-}C_4H_9)_3$) has been reported to give cyclopentadienyl(acetyl)iron carbonyl phoshine and phosphite complexes.[19]

4.2.4 Reaction of $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ (15) with triphenylphosphine

The reaction of alkyl/aryl manganese pentacarbonyl complexes with ligands such CO, PPh_3 *etc.* to form acyl species has been extensively studied.[18,20-24] This is because the intermediate step (alkyl/migration) of this reaction is important in the field of

catalysis. [25,26] The substitution reaction of CO with PPh_3 was carried out under reflux in THF. This procedure was based on the work reported by Andersen and Moss.[18]

The reaction was followed by infrared spectroscopy. After purifying the product by chromatography, yellow crystals of **16** were grown in a dichloromethane-hexane mixture. The carbon monoxide ligand in $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ was substituted with PPh_3 ligand to give *cis*-$[Mn(C_6H_4OCH_2Ph)(CO)_4(PPh_3)]$ (**16**). In our reaction it was observed that no acyl was formed. The acyl species could have formed but rapidly decarbonylated. This is possible because acylmanganese complex **12** (in **Chapter 3**) was discovered to easily decarbonylate at room temperature to form the corresponding arylmanganese complex. The product was characterised by elemental analysis, infrared and NMR spectroscopy. The melting point of the product was also recorded.



(4.4)

Infrared spectroscopy

In the infrared spectrum of **16**, three carbonyl stretching frequencies, 2066s cm^{-1}, 2019s cm^{-1}, 1974sh cm^{-1} are observed. This indicates that compound **16** has a *cis* geometry and low symmetry. For the *trans* isomer, only one band in the CO stretching region would be observed.[27] These stretching frequencies are lower when compared to those of the starting material. The decrease of the carbonyl frequencies confirms the substitution of the CO with triphenylphosphine ligand. PPh_3 is a good donor ligand and it increases electron density in the metal CO bond length hence the decrease in ν(CO) frequency.

^{1}H NMR spectroscopy

The ^{1}H NMR spectrum for **16** is given in **Figure 4.1**. It shows that all the proton peaks are shielded *e.g.* the methylene protons of the substituted product are at δ5.03 (0.04ppm less than that of the starting material). There is also a small peak observed at δ5.07 due to the methylene protons of the starting material, $[Mn(C_6H_4OCH_2Ph)(CO)_5]$. The peaks in the range δ6.40-7.45 (aromatic region) are due to triphenylphosphine and phenyl protons.

Table 4.4 ^{1}H NMR data for $[Mn(C_6H_4OCH_2Ph)(CO)_4(PPh_3)]$ (**16**)

Chemical Shift (ppm)	Multiplicity	Integration	Assignment
5.03	s	2H	O-C*H*$_2$
6.40	t, ^2J 1.14Hz	1H	Ar*H*
6.68	d, ^2J 7.96Hz	1H	Ar*H*
6.90	m	2H	Ar*H*
7.10-7.45	m	20H	Ar*H*

^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of **16** did not show any peak due to the acyl carbon at the expected region (δ250-260) (see **Appendix 15**). A methylene carbon (O-CH_2) gives a singlet at much lower chemical shift (at δ70.5) than methylene carbon of **16** (at 0.4ppm).

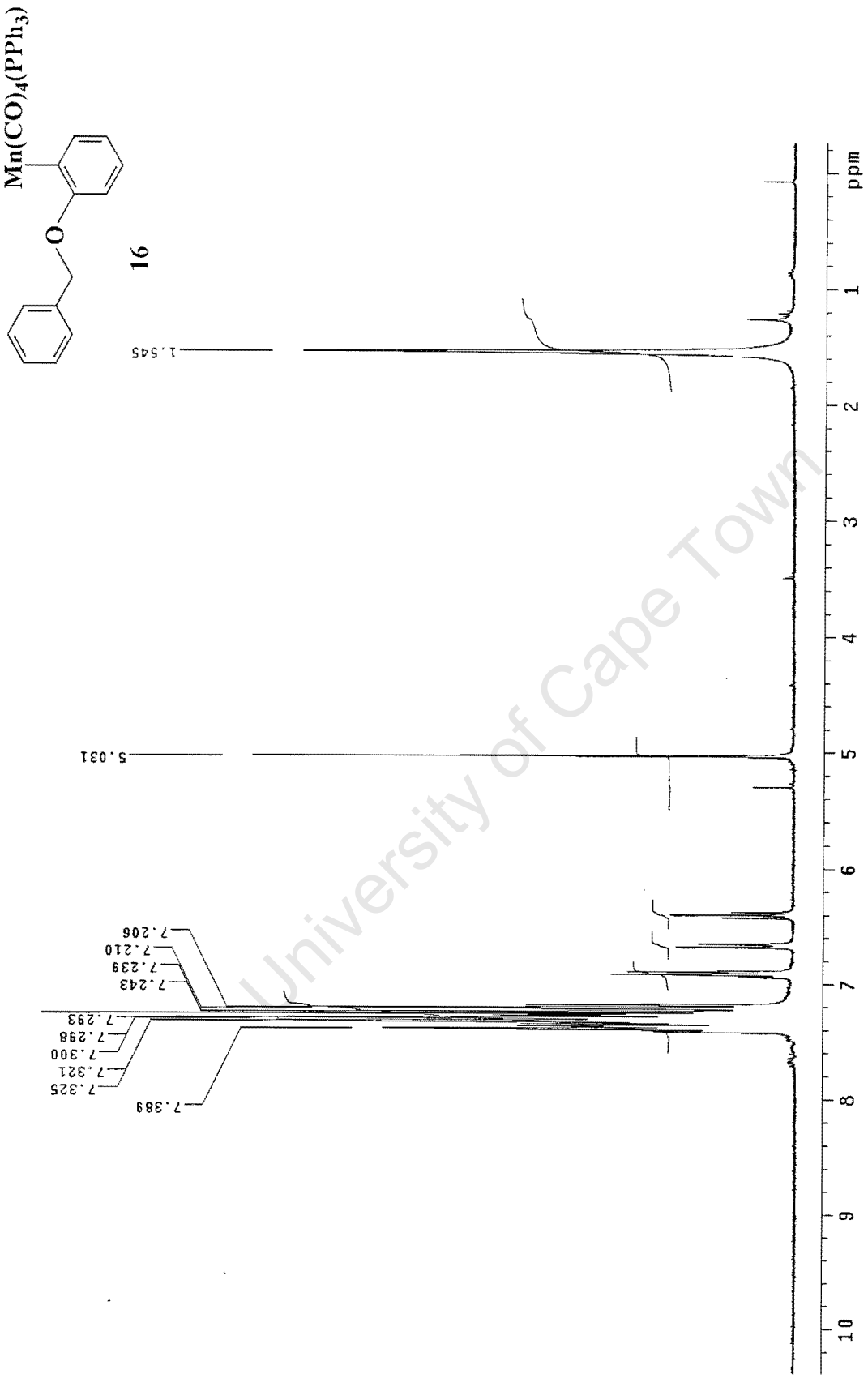


Figure 4.1 A 300MHz ^{1}H NMR spectrum of **16**

4.3 Conclusion

The acyl metal complexes [$CpFe(CO)_2C(O)C_6H_4OCH_2Ph$] (**11**) and [$MnC(O)C_6H_4OCH_2Ph(CO)_5$] (**12**) were successfully decarbonylated to the corresponding aryl metal complexes, [$CpFe(CO)_2C_6H_4OCH_2Ph$] (**14**) and [$Mn(C_6H_4OCH_2Ph)(CO)_5$] (**15**) respectively. The carbon monoxide ligand in [$Mn(C_6H_4OCH_2Ph)(CO)_5$] was substituted with PPh_3 ligand to give *cis*-[$Mn(C_6H_4OCH_2Ph)(CO)_4(PPh_3)$] (**16**), but there was no acyl species formation observed as it has been reported.[20-24] The acyl manganese complex could have formed but due to its instability, it immediately decarbonylated to form complex **16**. However, there was no substitution of carbon monoxide observed in the acyl iron complex, [$CpFe(CO)_2C(O)C_6H_4OCH_2Ph$].

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CHAPTER 5

EXPERIMENTAL

5.1 General experimental procedures

All the reactions were carried out under an atmosphere of nitrogen using standard Schlenk tube technique, unless stated otherwise.
Tetrahydrofuran and diethyl ether were dried over sodium wire and benzophenone ketyl and freshly distilled under nitrogen. Hexane was dried over sodium wire and distilled under nitrogen. Dichloromethane was dried over calcium hydride under nitrogen and distilled before use.

N, N-Dimethylformamide (Aldrich) and thionyl chloride (Riedel-de Haën) were used without further purification. *n*-BuLi obtained from Merck was used without further purification. Triphenylphosphine (Aldrich), $[Mn_2(CO)_{10}]$ and $[CpFe(CO)_2]_2$ (Strem Chemicals) were used without further purification .

Column chromatography was carried out using neutral aluminium oxide (BDH, active neutral, Brockman grade I) and silica gel 60 (70 – 230 mesh) (Merck). Polymer-supported borohydride was purchased from Aldrich. All other reagents were obtained commercially and used without further purification, unless otherwise stated.
Solvents were removed under reduced pressure and the resultant samples dried under vacuum (0.1 mmHg), unless otherwise stated.

Melting points were determined on a Kofler hot-stage microscope (Reichert-Thermovar). Differential scanning calorimetry and thermal gravimetric analysis were performed on a Perkin-Elmer PC Series 7 instrument under nitrogen atmosphere with heating rate of 10°C per minute. Microanalyses were carried out with Fisons EA 1108 CHNS analyser in the Microanalytical Laboratory at the University of Cape Town.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells with NaCl windows. The following abbreviations are used in the description of the infrared spectra: s = strong, m = medium and w = weak.

^{1}H and ^{13}C NMR spectra were recorded on a Varian XR200 MHz, XR300MHz or XR400 MHz spectrometers using tetramethylsilane as a standard (δ 0.00ppm). The deuterated solvent signals were used as references and chemical shifts adjusted accordingly. The following abbreviations are used in the description of NMR spectra: s = singlet, d = doublet, t = triplet, triplet of doublets, m = multiplet, dd = doublet of doublets, udd = unsymmetrical doublet of doublets and brs = broad singlet.

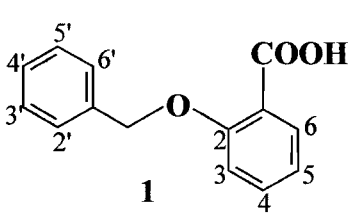
Low-resolution mass spectra (EI) were recorded with a VG Micromass 16F Electron Impact mass spectrometer. Fast Atomic Bombardment (FAB) mass spectra were obtained from the Cape Technikon.

Note: Compound numbers are valid with individual chapter only.

5.2 Experimental details pertaining to Chapter 2

5.2.1 Synthesis of 2-benzyloxybenzoic acid (1)

2-benzyloxybenzoic acid was synthesised by a modification of the method reported by Farkas *et.al.*[1] Salicylic acid (2.00 g, 14.50 mmol), anhydrous K_2CO_3 (6.67 g, 48.24 mmol), benzyl chloride (5 cm^3, 5.50 g, 43.48 mmol) and dimethylformamide (30 cm^3) were mixed and refluxed under nitrogen for 2h. When the reaction mixture was cooled to room temperature, water (50 cm^3) was added to the solution. The mixture was extracted with diethyl ether (3 × 50 cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resultant colourless oil was combined with a mixture of methanol (50 cm^3) and 40% aqueous sodium hydroxide (10 cm^3) and refluxed for 2h. The mixture was then cooled to room temperature, diluted with water (30 cm^3) and acidified with dilute HCl (1M) to pH 3. The white precipitate formed was filtered and

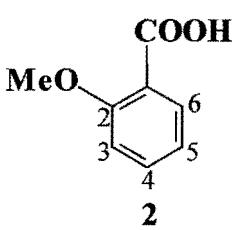


1

dried *in vacuo* to give **1** (2.24 g, 68%); m.p. 76-78°C (lit.[1], 76-78°C); (Found: C, 73.32; H, 5.02. Calc. For $C_{14}H_{12}O_3$: C, 73.68; H, 5.26%); ν_{max}/cm^{-1} 3300s (OH) and 1739s (CO) (CH_2Cl_2). δ_H ($CDCl_3$, 400MHz): 5.29 (s, 2H, O-C*H*$_2$), 7.11-7.18 (m, 2H, H3, H6), 7.40-7.46(m, 4H, H3′, H5′, H2′, H6′), 7.55(t, 1H, H4′), 7.55(udd, ^2J 1.60Hz, 2.00Hz 1H, H4) and 8.20(udd, ^2J 1.60Hz, 2.00Hz, 1H, H5); δ_C($CDCl_3$, 200MHz):72.2 (s, OCH_2)113.1(s, C1′), 118.1(s, C3′, C5′), 122.4(s, C2′, C6′), 127.9(s, C4′), 129.1(s, C4, C5), 157.4(s, C2) and 165.4(s, COOH). The NMR data was not reported in the reference mentioned above.

5.2.2 Synthesis of 2-methoxybenzoic acid (2)

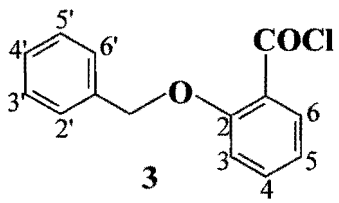
2-methoxybenzoic acid was synthesised by using modified literature method reported by Farkas *et.al.*[1] Salicylic acid (1.01 g, 7.25 mmol), anhydrous K_2CO_3 (4.51 g, 32.61 mmol), methyl iodide (1.4 cm^3, 3.09 g, 21.74 mmol) and dimethylformamide (30 cm^3) were mixed and refluxed under nitrogen for 5h. When the reaction mixture was cooled to room temperature, water (50 cm^3) was added to the solution. The mixture was extracted with diethyl ether (4 × 30 cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resultant colourless oil was combined with a mixture of methanol (50 cm^3) and 40% aqueous sodium hydroxide (10 cm^3) and refluxed for 2h. The mixture was then cooled to room temperature, diluted with water (30 cm^3) and acidified with dilute HCl (1M) to pH 2. The organic product was extracted with diethyl ether (3 × 30 cm^3). The solvent was removed under reduced pressure to give a white crystalline product, **2** (0.23 g, 44%), m.p = 100°C-102°C (lit.[2] 98°C-100°C); (Found: C, 63.08; H, 5.54. Calc. For $C_8H_8O_3$: C, 63.16; H 5.26%); ν_{max}/cm^{-1} 3296s(OH) and 1738s (CO) (CH_2Cl_2), δ_H ($CDCl_3$, 300MHz): 4.08(s, 3H, O-C*H*$_3$), 7.01-7.20(m, 2H, H3, H6), 7.58(dd, ^2J 1.86Hz, 1H, H4), 8.19(dd, ^2J 1.86Hz, 1H, H5).



2

5.2.3 Preparation of 2-benzyloxybenzoyl chloride (3)

A modified procedure reported by Roberts and co-workers[3] was employed.

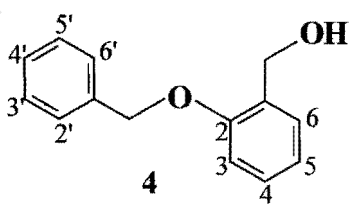


3

2-benzyloxybenzoic acid (1.00 g, 4.40 mmol) was dissolved in excess thionyl chloride (1.00 cm^3, 1.57 g, 13.18 mmol) under nitrogen. The solution was gently heated under reflux for 2h. The evolution of gas was initially observed (HCl and SO_2). Dichloromethane (5 cm^3) was added and excess thionyl chloride was distilled off to give **3** as a colourless oil (0.97 g, 89%), ν(CO)/cm^{-1} 1779s (dichloromethane).

5.2.4 Preparation of 2-benzyloxybenzyl alcohol (4)

A modified procedure reported by Finne and co-workers[4] was used.

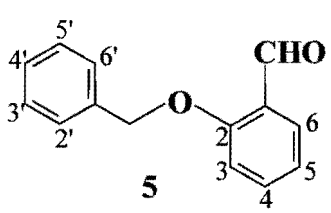


4

2-benzyloxybenzoic acid (1.24 g, 5.42 mmol) in ether (20 cm^3) was added slowly to a slurry of $LiAlH_4$ (1.05 g, 27.56 mmol) in ether (15 cm^3). The mixture was then refluxed for 24h. Methanol (6 cm^3) in ether (30 cm^3) was added slowly to quench the reaction. The mixture was then treated with 5% aqueous H_2SO_4 (50 cm^3). The mixture was decanted from the precipitated salts. The aqueous layer was extracted with ether (4 × 20cm^3), the combined organic phases were washed with 5% aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. After filtration the solvent was removed under reduced pressure to give **4** as a colourless oil (0.56 g, 48%).δ_H ($CDCl_3$, 400MHz): 2.28(brs, 1H, O-*H*), 4.75(s, 2H, CH_2OH), 5.13(s, 2H, O-CH_2), 6.96(s, 1H, H6), 6.98(dd, ^2J(H4H6), 1H, H5), 7.26(t, ^2J(H3H5) 1.83 Hz, 1.65 Hz, 1H, H4), 7.31 – 7.49(m, 6H, Ar*H*).

5.2.5 Preparation of 2-benzyloxybenzyl aldehyde (5)

Swern oxidation[5] was used to prepare this compound from 2-benzyloxybenzyl alcohol. A solution of oxalyl chloride (0.84 cm^3, 1.22 g, 9.63 mmol) in dichloromethane (20 cm^3) was mixed with DMSO (1.4 cm^3, 1.51 g, 19.26 mmol) in 5 cm^3 dichlorome-



5

thane at -60°C. The reaction mixture was stirred for 5 minutes and 2-benzyloxybenzyl alcohol (1.15 g, 5.39 mmol) in 5 cm^3 dichloromethane was added followed by triethylamine (TEA) (6 cm^3, 4.44 g, 43.83 mmol). The reaction was stirred for 10 minutes and then allowed to warm to room temperature. Water (30 cm^3) was added and the aqueous layer was extracted with dichloromethane (3 × 20 cm^3). The organic layers were combined, washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, after filtration, to give **5** as an orange oily product (0.97 g, 85%). δ_H($CDCl_3$, 200MHz): 5.19(s, 2H, O-C*H*$_2$), 6.98-7.10(m, 2H, H3, H6), 7.31-7.59(m, 6H, H3′, H5′, H2′, H6′, H4′, H5), 7.88(dd, 1H, H4), 10.55(s, 1H, C*H*O).

5.2.6 Synthesis of 2-[(*N,N*-Dimethylamino)methyl]ferrocene-carboxyaldehyde (6)

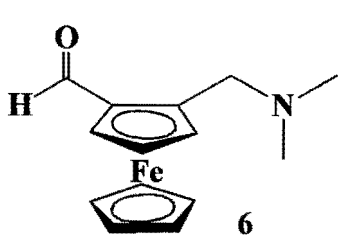
The procedures reported by Brocard and co-workers[6] were employed in the syntheses of compounds in **5.2.6 – 5.2.8.**

5.2.6.1 Lithiation of [(Dimethylamino)methyl]ferrocene

A magnetically stirred solution of [(dimethylamino)methyl]ferrocene (2 cm^3, 2.5 g, 10.10 mmol) in 20 cm^3 of Et_2O was treated with *n*-BuLi in hexane (5 cm^3, 12.5 mmol). Metalation was completed by stirring the dark red mixture for 24h at room temperature. The product was not isolated but directly used in the reaction below.

5.2.6.2 Condensation of the lithiated product (in 5.2.6.1)

A solution of lithio[(dimethylamino)-methyl]ferrocene formed above was treated with *N, N*-dimethlyformamide (0.8 cm^3, 12.5 mmol). The reaction was quenched after 4h by adding water (20 cm^3). The organic layer was separated, and the aqueous phase was washed with Et_2O (3 × 20 cm^3). The organic extracts were combined, dried over $MgSO_4$, filtered and evaporated to dryness to give

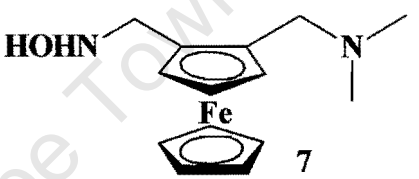


6

red oil. The crude product was purified through a silica gel chromatography. Elution with Et_2O/hexane/triethylamine (6:2:2) gave 2-[(*N, N*-Dimethylamino)methyl]ferrocenecarboxyaldehyde, **6** (2.46 g, 90 %). δ_H($CDCl_3$, 200MHz): 10.09 (s, 1H, C*H*O), 4.81(m, 1H), 4.65(m, 1H), 4.56(m, 1H), 4.23(s, 5H, Cp), 3.85(d, 1H, ^2J (HH) 13Hz), 3.40(d, 1H, ^2J (HH) 14Hz), 2.23(s, 6H, (CH_3)$_2$).

5.2.7 Synthesis of 2-[(*N, N*-Dimethylamino)methyl]ferrocenecarboxyaldehyde Oxime (7)

A solution of sodium hydroxide (0.67 g, 16.75 mmol) in water (4 cm^3) was added to a stirred mixture of 2-[(*N, N*-Dimethylamino)methyl]-ferrocenecarboxyaldehyde (1.38 g, 5.08 mmol) and hydroxylamine hydrochloride (0.58 g, 8.38 mmol) in EtOH (35 cm^3). The resulting solution was stirred and heated under reflux for 4h, quenched by addition of water (20 cm^3), neutralised by treatment with CO_2 gas (obtained by warming dry ice) and extracted with CH_2Cl_2 (3 × 20 cm^3). The combined extracts were dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. This was further dried *in vacuo* to give a red oil, **7** (1.21 g, 84%). δ_H($CDCl_3$, 200MHz): 8.05(s, 1H, NO*H*), 4.56(m, 1H), 4.36(m, 1H), 4.29(m, 1H), 4.14(s, 5H, Cp), 3.81(d, 1H, ^2J(HH) 13 Hz), 3.32(d, 1H, ^2J (HH)13 Hz), 2.22(s, 6H, (CH_3)$_2$).



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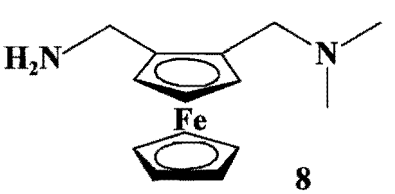
5.2.8 Synthesis of 2–[(*N, N*-Dimethylamino)methyl]ferrocenylamine (8)

$LiAlH_4$ (2.04 g, 53.73 mmol) and 2-[(*N, N*-Dimethylamino)methyl]ferrocenecarboxyaldehyde oxime (1.21 g, 4.46 mmol) were combined in THF (20 cm^3). The reaction mixture was then heated under reflux for 16h. The solution was cooled and diluted with Et_2O (50 cm^3), washed with brine and dried over K_2CO_3, filtered and evaporated to dryness to obtain the red oily product, **8** (1.08 g, 89%). δ_H($CDCl_3$, 200MHz): 4.13(m, 1H), 4.11(m, 1H), 4.04(s, 5H,



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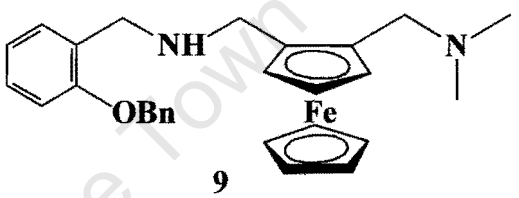
Cp), 4.01(m, 1H), 3.69(d, 1H, ^2J(HH) 2.46 Hz), 3.61(d, 1H, ^2J(HH) 2.06 Hz), 3.43(d, 1H, ^2J(HH) 14.47Hz), 2.87(d, 1H, ^2J(HH) 12.63 Hz), 2.14(s, 6H, (CH_3)$_2$). A broad peak due NH_2 protons is observed at 1.71ppm. This peak disappeared under D_2O wash.

5.2.9 Reaction of 2–[(*N, N*-Dimethylamino)methyl]ferrocenylamine with benzyloxybenzyl aldehyde to give compound 9

2-[(*N, N*-Dimethylamino)methyl]ferrocenylamine (0.28 g, 1.10 mmol) and 2-benzyloxybenzyl aldehyde (0.19 g, 0.89 mmol) were dissolved in methanol (20 cm^3). The reaction solution was stirred for 48h at room temperature. Polymer-supported borohydride (0.66 g, 1.65 mmol) was added to the solution and then shaken for further 16h at room temperature. The polymer was filtered off and the solvent removed under reduced pressure to give red oil. This was purified by chromatography on a silica-gel column. The desired product was eluted with dichloromethane/triethylamine mixture (7:3) and the solvent was removed in *vacuo* to give **9** as a yellow oil (0.17 g, 42%); m.p: 87°C - 89°C; (Found: C, 71.4; H 7.0; N, 5.9%; M$^+$469 $C_{28}H_{32}FeN_2O$ requires C, 71.8; H, 6.8; N, 5.9; M 468).



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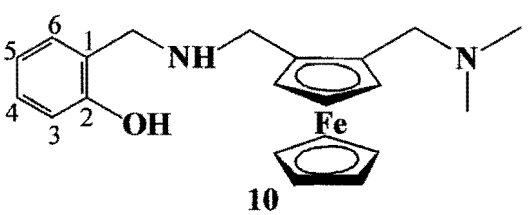
The NMR characterisation data are given in **Section 2.2.9.**

5.2.10 Reaction of 2-[(*N, N*-dimethylamino)methyl]ferrocenyamine with salicylic aldehyde to give compound 10

2-[(*N, N*-Dimethylamino)methyl]ferrocenylamine (0.56 g, 2.16 mmol) and salicylic aldehyde (0.23 g, 2.16 mmol) were dissolved in methanol (20 cm^3). The reaction solution was stirred for 24h at room temperature. Polymer-supported borohydride (1.00 g, 2.50 mmol) was added to the solution and then shaken for further 12h at room temperature. The polymer was then filtered off and the solvent removed under reduced pressure to give **10** as a yellow oil (0.57 g, 80%).



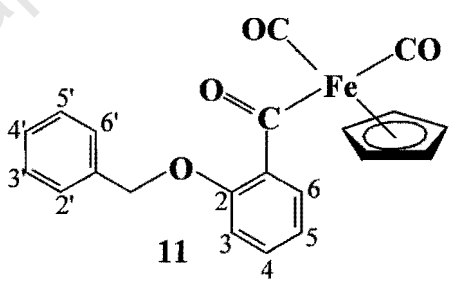
10

δ_H($CDCl_3$, 300MHz): 2.12(s, 6H, CH_3), 2.76(d, ^2J 12.30Hz, 1H, Cp^+-CH_2-NMe_2), 3.34(d, ^2J 13.50Hz, 1H, NH-CH_2-Cp^+), 3.73(d, ^2J 12.60Hz, 1H, Cp^+-CH_2-NMe_2), 3.79(d, ^2J 13.50Hz, 1H, NH-CH_2-Cp^+), 3.85(d, ^2J 2.10Hz, 2H, Ar-CH_2-NH), 4.01(m, 1H, C_5H_3), 4.02(s, 5H, Cp), 4.05(m, 1H, C_5H_3) and 4.11(m, 1H, C_5H_3), 6.72-7.19(m, Ar*H*). δ_C($CDCl_3$, 300MHz): 44.8(s, CH_3), 45.8(s, C_5H_3), 50.7(s, C_5H_3), 58.3(s, C_5H_3), 65.9(s, Ar-CH_2-NH), 69.0(s, Cp), 70.6(s, NH-CH_2-Cp^+), 71.2(s, Cp^+-CH_2-NMe_2), 83.9(s, *C*-C_4H_3), 84.4(s, *C*-C_4H_3), 116.4(s, C6), 118.7(s, C3), 122.5(s, C1), 128.4(s, C4, C5), 158.9(s, C2).

5.3 Experimental details pertaining to Chapter 3

5.3.1 Synthesis of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (11)

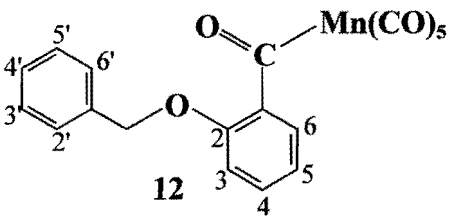
This complex was prepared according to the modified literature method.[7] Sodium metal (0.10 g) was combined with mercury (2 cm^3) to form a sodium amalgam. $[CpFe(CO)_2]_2$ (0.52 g, 1.48 mmol) was added to the amalgam in THF (10 cm^3) and stirred for 3h at room temperature. The resulting solution of $Na[CpFe(CO)_2]$ (6 cm^3, 1.92 mmol) was transferred *via* a syringe to 2-benzyloxy-benzoyl chloride (0.38 g, 1.52 mmol) at -78°C in THF (10 cm^3). The reaction mixture was stirred and allowed to warm to room temperature. THF was removed under reduced pressure to give a dark red residue which was extracted with dichloromethane (3 × 20 cm^3). The extracts were combined and filtered. Dichloromethane was removed *in vacuo* to give the crude product as a red solid. This crude product was purified by column chromatograph on silica gel made up with hexane. Three fractions were eluted with 20% CH_2Cl_2/hexane, 50% CH_2Cl_2/hexane and 100% CH_2Cl_2 respectively. The solvent was removed under reduced pressure from each fraction. The second dark red fraction contained the iron dimer, $[CpFe(CO)_2]_2$. The third fraction gave a yellow oil which was dried under vacuum. This later recrystallised from dichloromethane-hexane solvent system to give yellow crystals of **11** (0.39 g, 66%), mp 70–73°C, (Found: C, 64.8; H 4.3%; M^+ 388 $C_{21}H_{16}FeO_4$ requires C, 65.0; H, 4.1%; M 388). Spectroscopic data are given in **Tables 3.1 – 3.3** (see Chapter 3).



11

5.3.2 Synthesis of $[Mn(CO)_5(COC_6H_4OCH_2Ph)]$ (12)

The acyl complex $[Mn(CO)_5(COC_6H_4OCH_2Ph)]$ was prepared by adaptation of the literature method.[8] Sodium metal (0.23 g) was dissolved in mercury (2 cm^3) to form an amalgam. Manganese carbonyl (1.01 g, 2.68 mmol) in THF (10 cm^3) was added to the amalgam and stirred for 2h at room temperature. The resulting greyish green solution of $Na[Mn(CO)_5]$ (8 cm^3, 4.27 mmol) was added to a solution of 2-benzyloxybenzoyl chloride (1.05 g, 4.27 mmol) in THF (10 cm^3). The reaction mixture was stirred for 16h at room temperature. The solvent was removed under reduced pressure to give a red oily product. This was extracted with dichloromethane (3 × 20 cm^3). The combined extracts were evaporated under reduced pressure to give a yellow oil. Chromatography on a silica gel column gave two fractions which were eluted with 20%CH_2Cl_2/hexane and 40% CH_2Cl_2/hexane. The solvent was removed from both fractions under reduced pressure. The first fraction gave **13**, $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ as a yellow solid (0.35 g, 22%); mp.100-102°C; (Found: C, 57.0; H, 2.7 %;M^+ 377.94 $C_{18}H_{11}MnO_6$ requires C, 57.2; H, 2.9%; M 377.94). The second fraction gave a pale yellow solid **12**, $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (0.21 g, 12%)(Found: C, 56.2; H, 2.8%; M^+ 405.94 $C_{19}H_{11}MnO_7$ requires C, 56.2; H, 2.7%; M 405.94). The spectroscopic data are given in **Tables 3.5 – 3.9**.

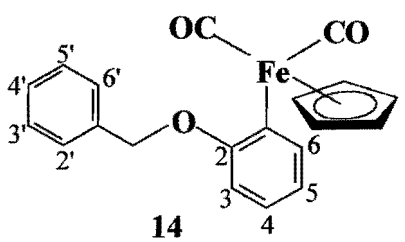


12

5.4 Experimental details pertaining to Chapter 4

5.4.1 Photochemical decarbonylation of $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (11)

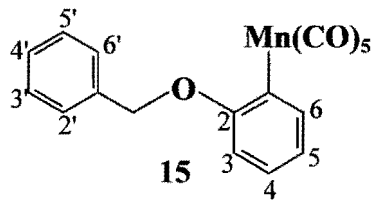
A yellow solution of the acyliron complex, $[CpFe(CO)_2C(O)C_6H_4OCH_2Ph]$ (0.05 g, 0.13 mmol) in 30 cm^3 of acetone was irradiated for 3h. A dark brown solution was obtained. The solvent was removed under reduced pressure to give a brown residue. The residue was extracted with dichloromethane to give a red solution. Removal of dichloromethane in *vacuo* gave **14** as a red solid (0.01 g, 23%), ν_{max}/cm^{-1} (CO) 2017s and 1961s (dichloromethane).



14

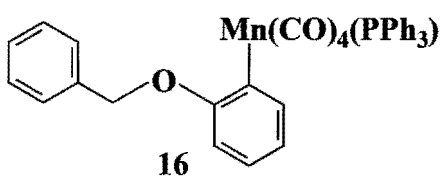
5.4.2 Thermal decarbonylation of $[Mn(C(O)C_6H_4OCH_2Ph)(CO)_5]$ (12)

A method reported by Andersen and Moss[8] was followed. The acylmanganese complex $[MnC(O)C_6H_4OCH_2Ph(CO)_5]$ (0.21 g, 0.52 mmol) was dissolved in hexane (10 cm^3) by stirring under inert atmosphere. The solution was heated under reflux for 2h. The solvent was removed under reduced pressure to give pale yellow compound **15** (0.18 g, 89%) (Found: C, 57.8; H, 3.2%; M^+ 377.94 $C_{18}H_{11}MnO_6$ requires C, 57.2; H, 2.9%; M 377.94). The ^1H and ^{13}C NMR spectrum recorded gave exactly the same results as for compound **13** (in Chapter 3, **section 3.2.3**).



5.4.3 Reaction of $[Mn(C_6H_4OCH_2Ph)(CO)_5]$ with PPh_3

The manganese complex, $[MnC_6H_4OCH_2Ph(CO)_5]$ (0.21 g, 0.55 mmol) and triphenylphosphine (0.14 g, 0.55 mmol) were dissolved in THF (20 cm^3). The solution was heated under reflux for 24h. The solvent was removed under reduced pressure to give a yellow residue. This was purified by column chromatograph on silica gel. The desired product (second fraction) was eluted with ethyl acetate/hexane mixture (1:9) as a yellow solid. It was further purified by recrystallisation (in dichloromethane-hexane system) to give yellow crystals of **16** (0.078 g, 23%), m.p 141-144°C, (Found: C, 68.7; H 4.2%; $C_{35}H_{26}MnO_5P$ requires C, 68.5; H, 4.2%).



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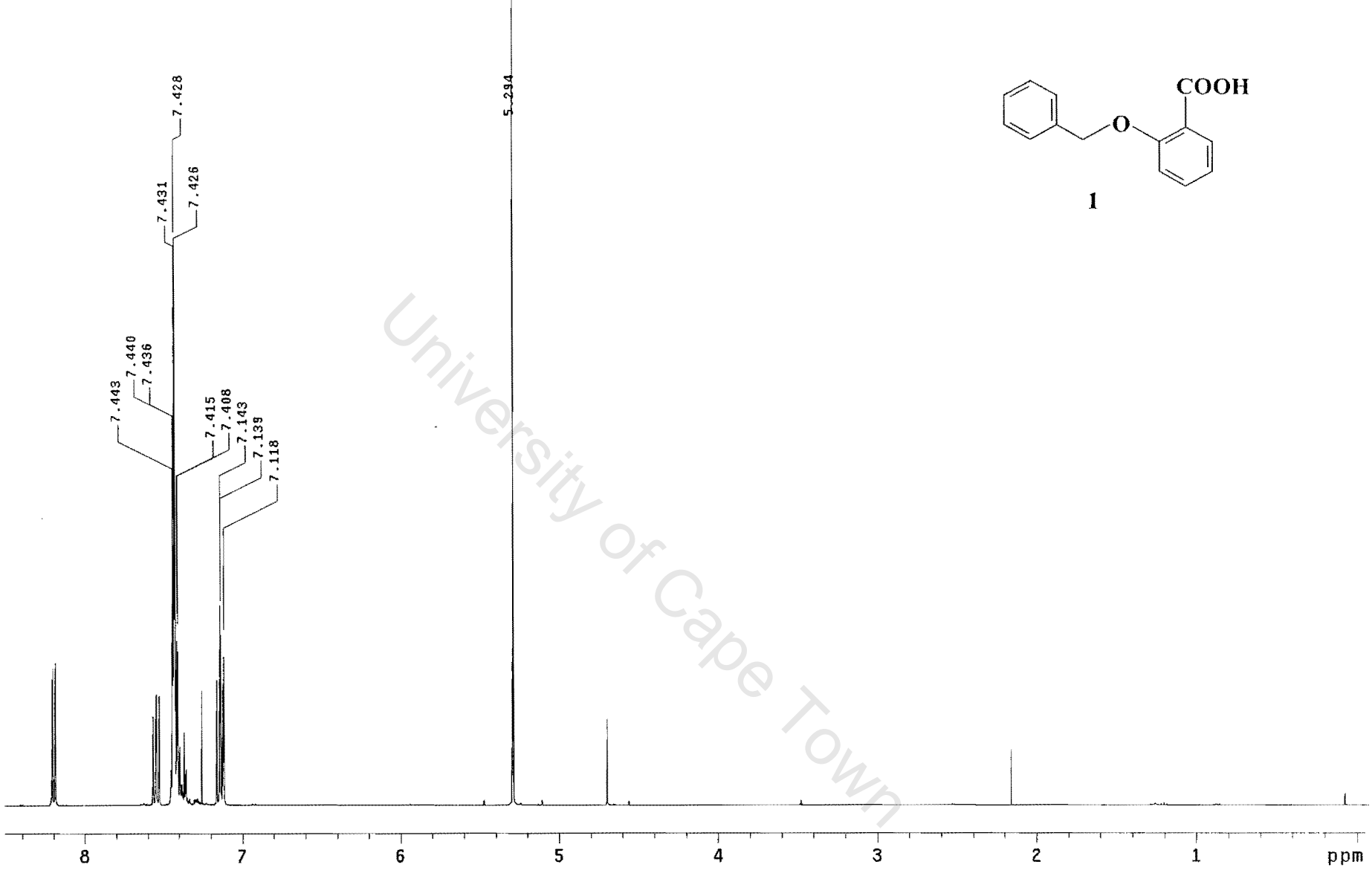
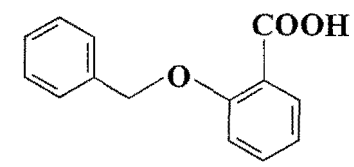
8. J.M. Andersen and J.R. Moss, *Organometallics*, **1994**, *13*, 5013.

APPENDICES



Appendix 1 A 400MHz ^{1}H NMR spectrum of **1**



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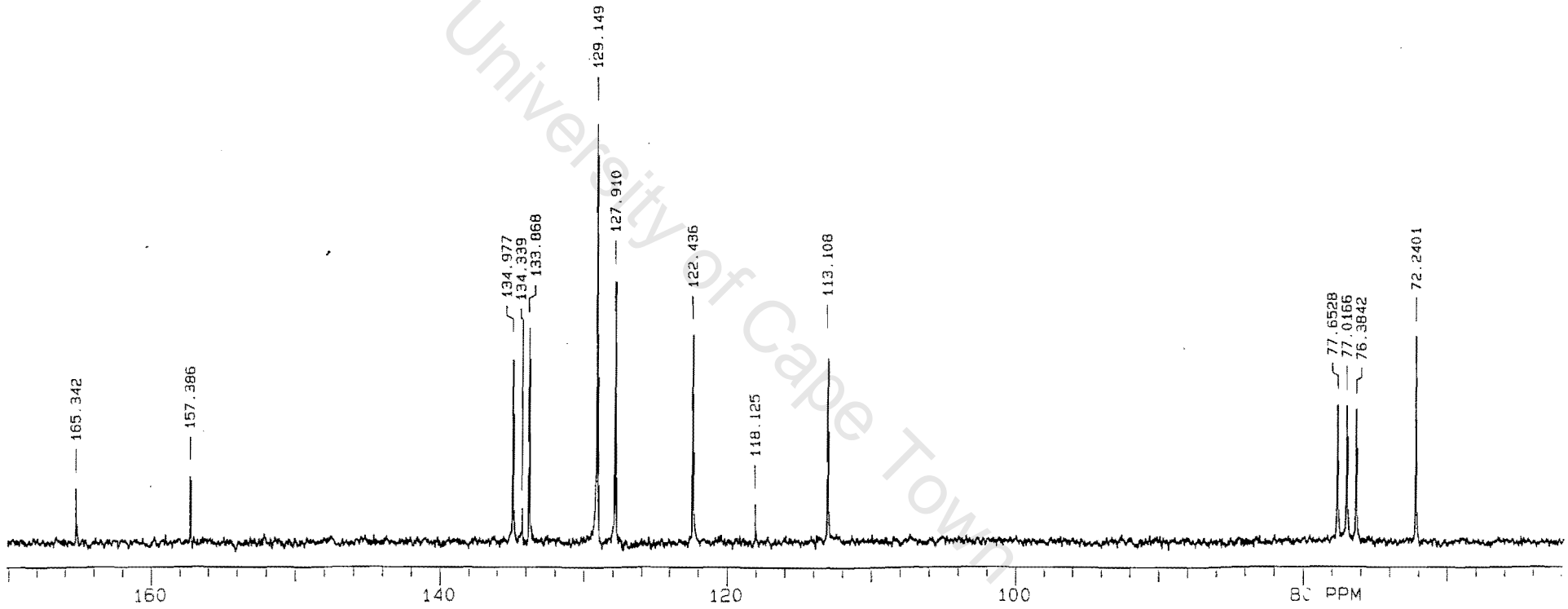
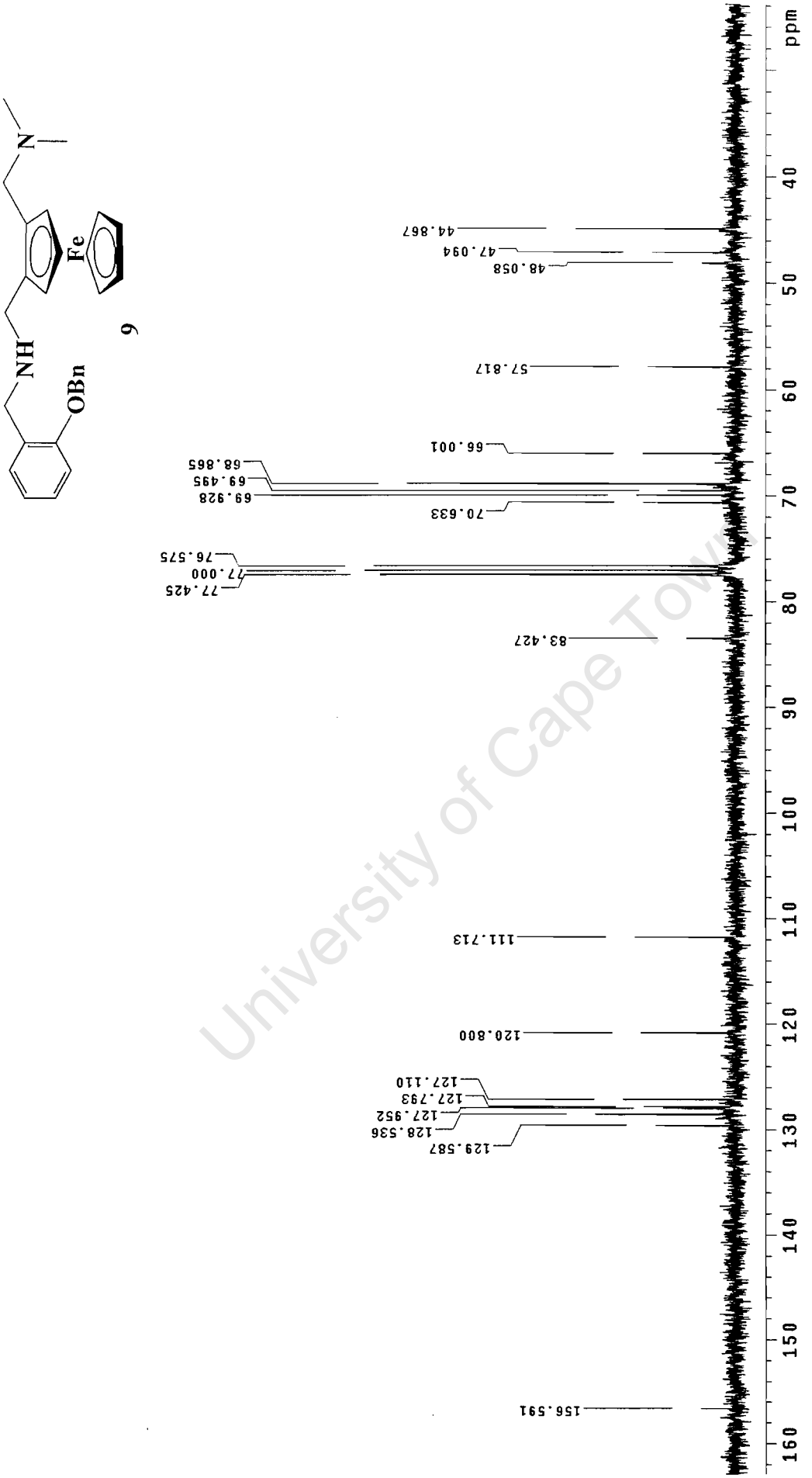
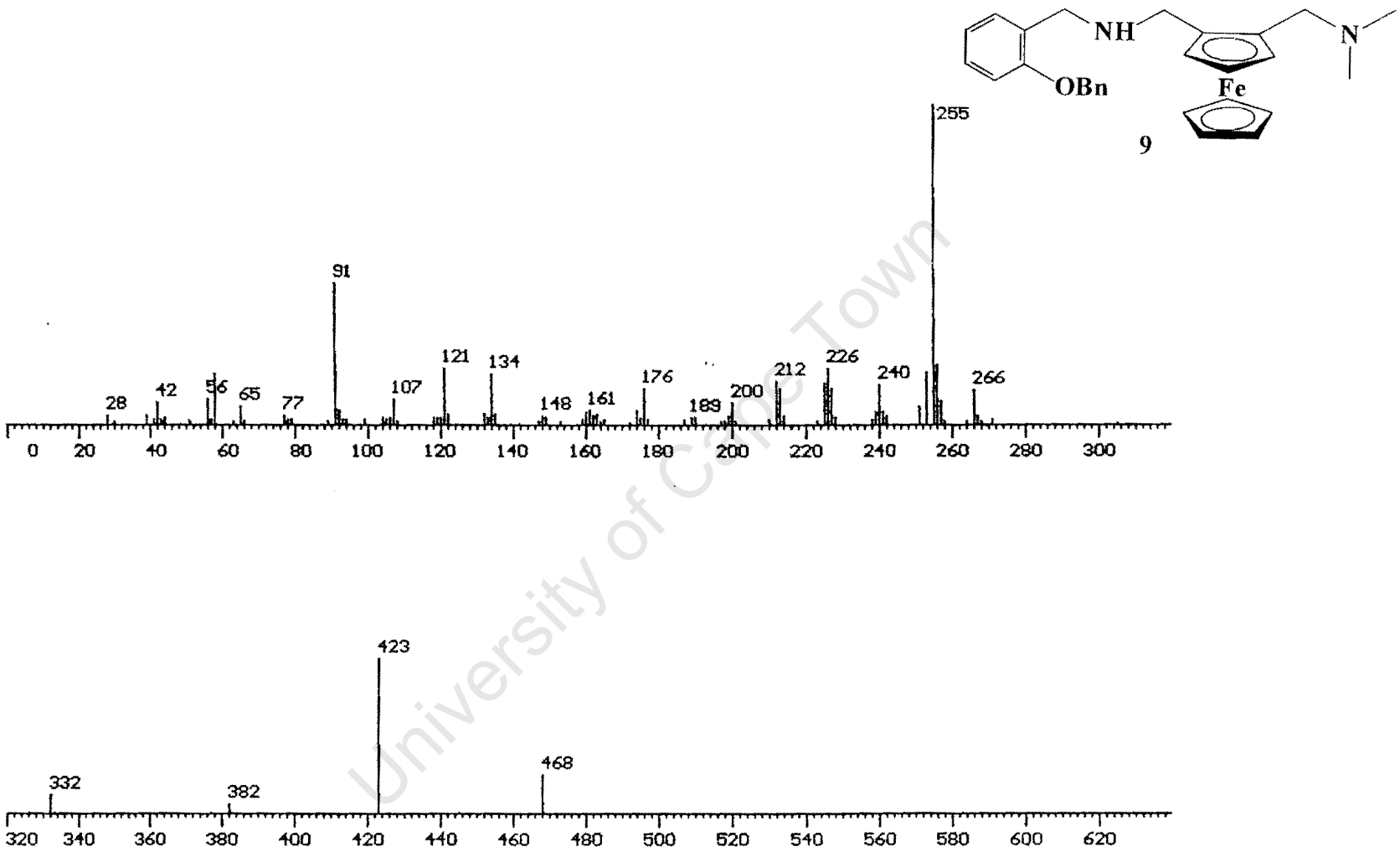


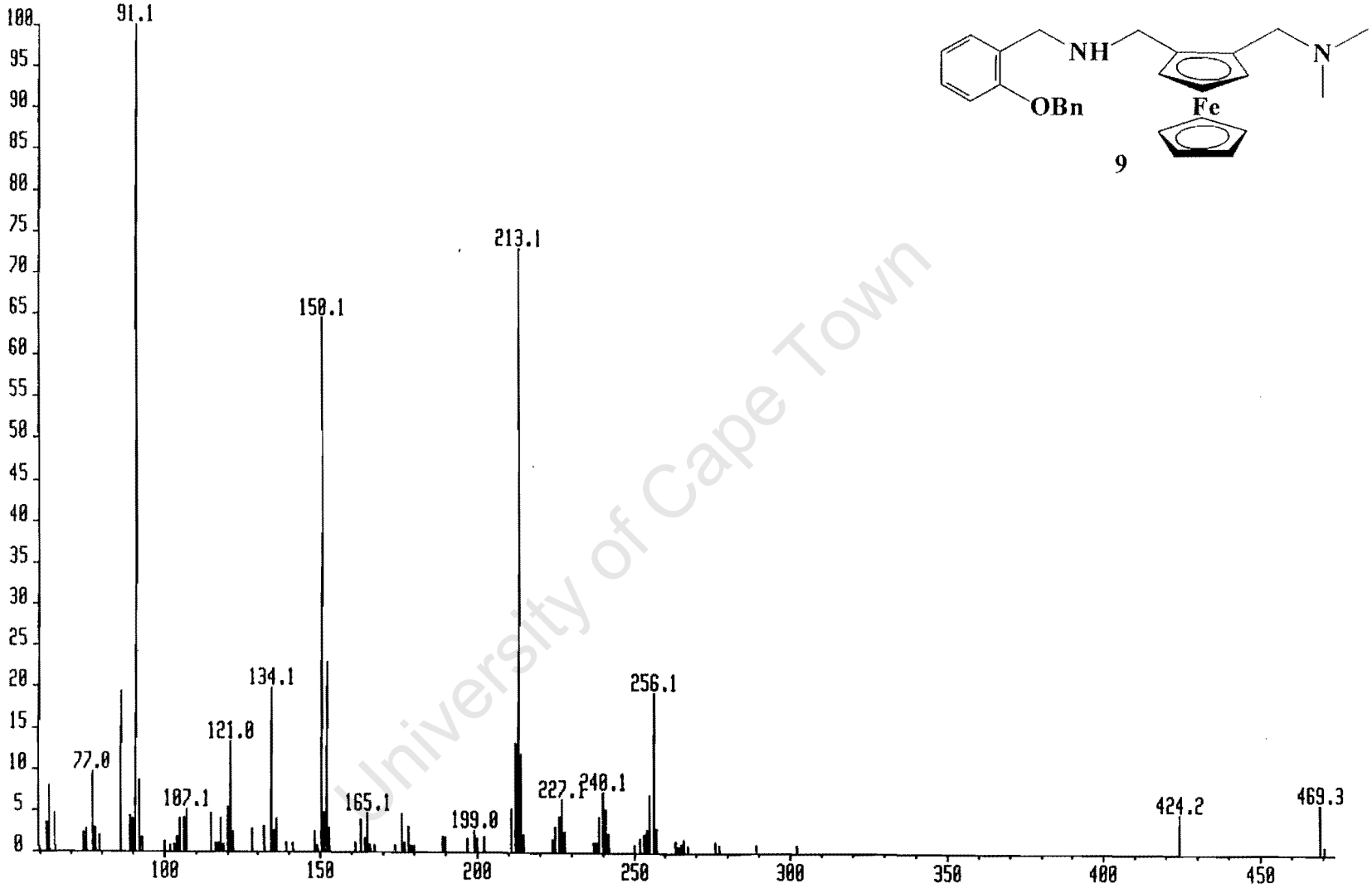
Appendix 2 A 200MHz ^{13}C NMR spectrum of **1**



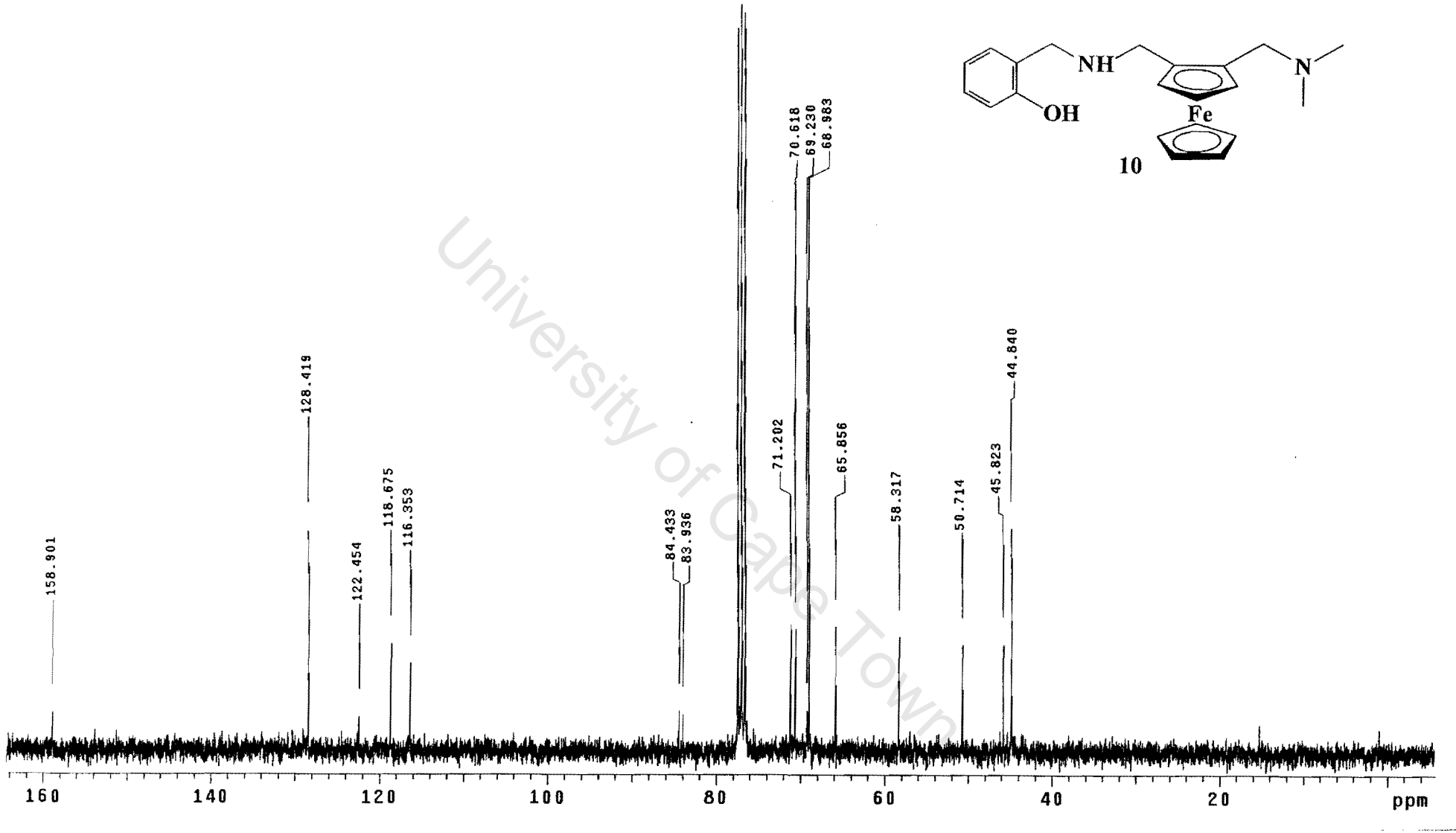
Appendix 3 A 300MHz ^{13}C NMR spectrum of **9**



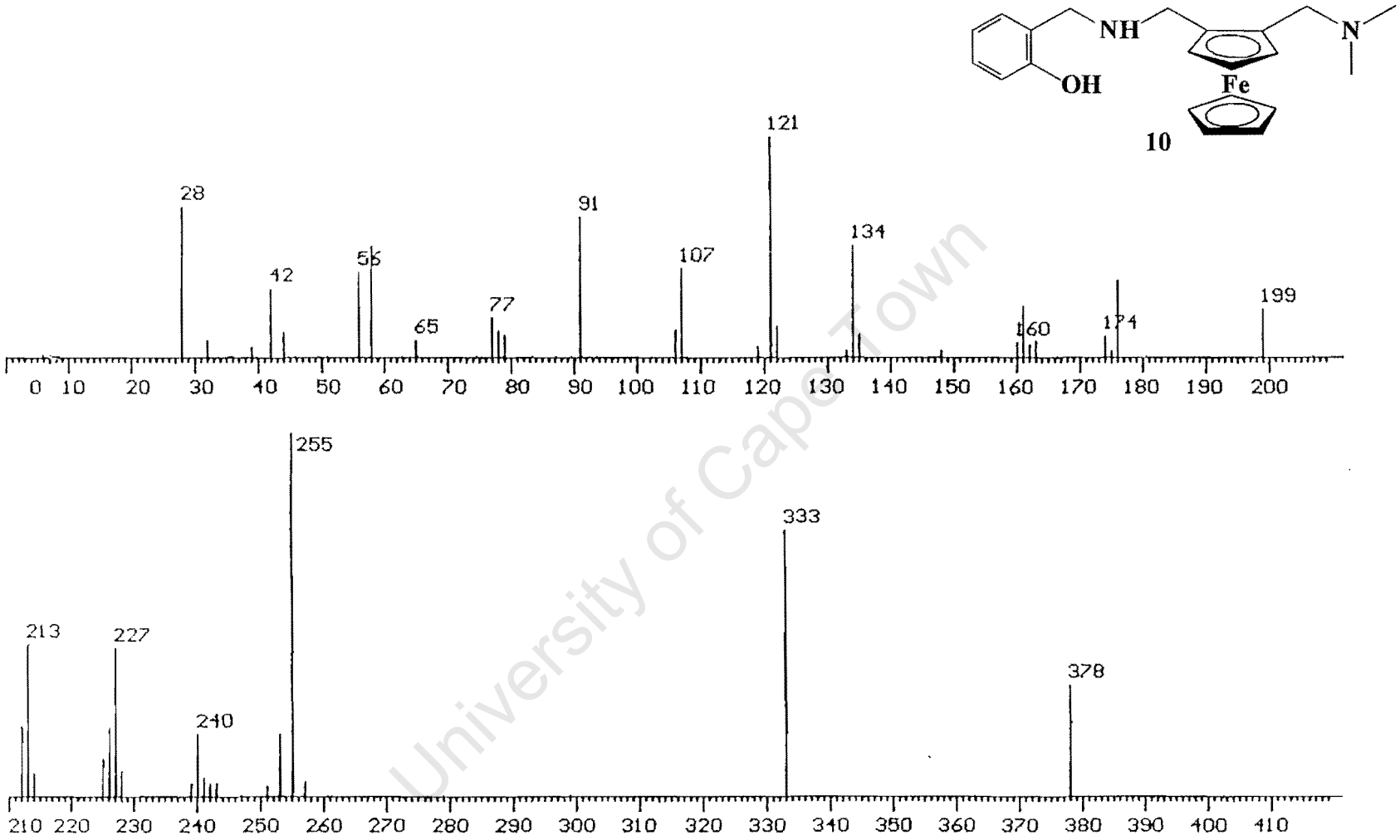
Appendix 4a EI mass spectrum of **9**



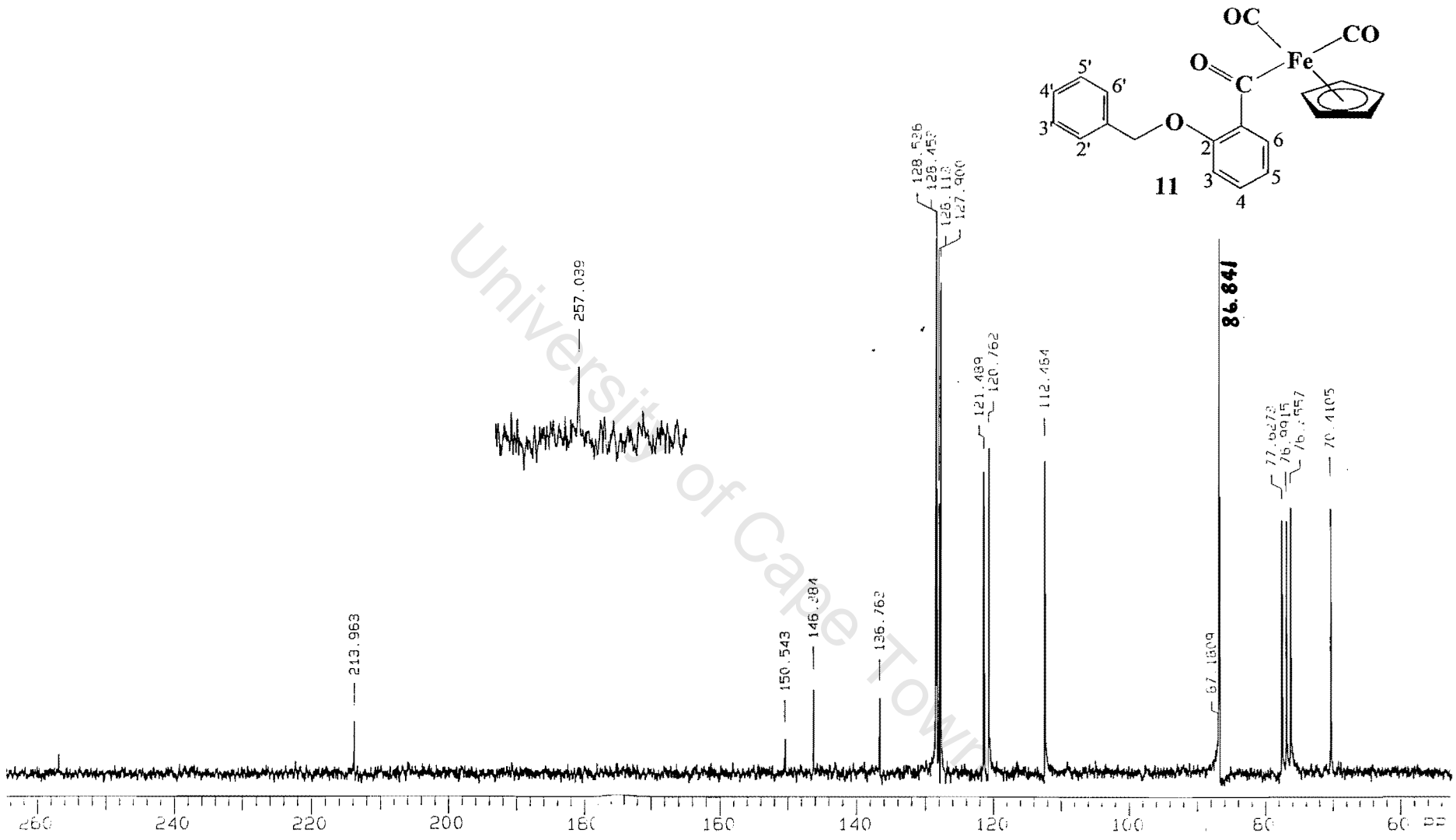
Appendix 4b FAB mass spectrum of **9**



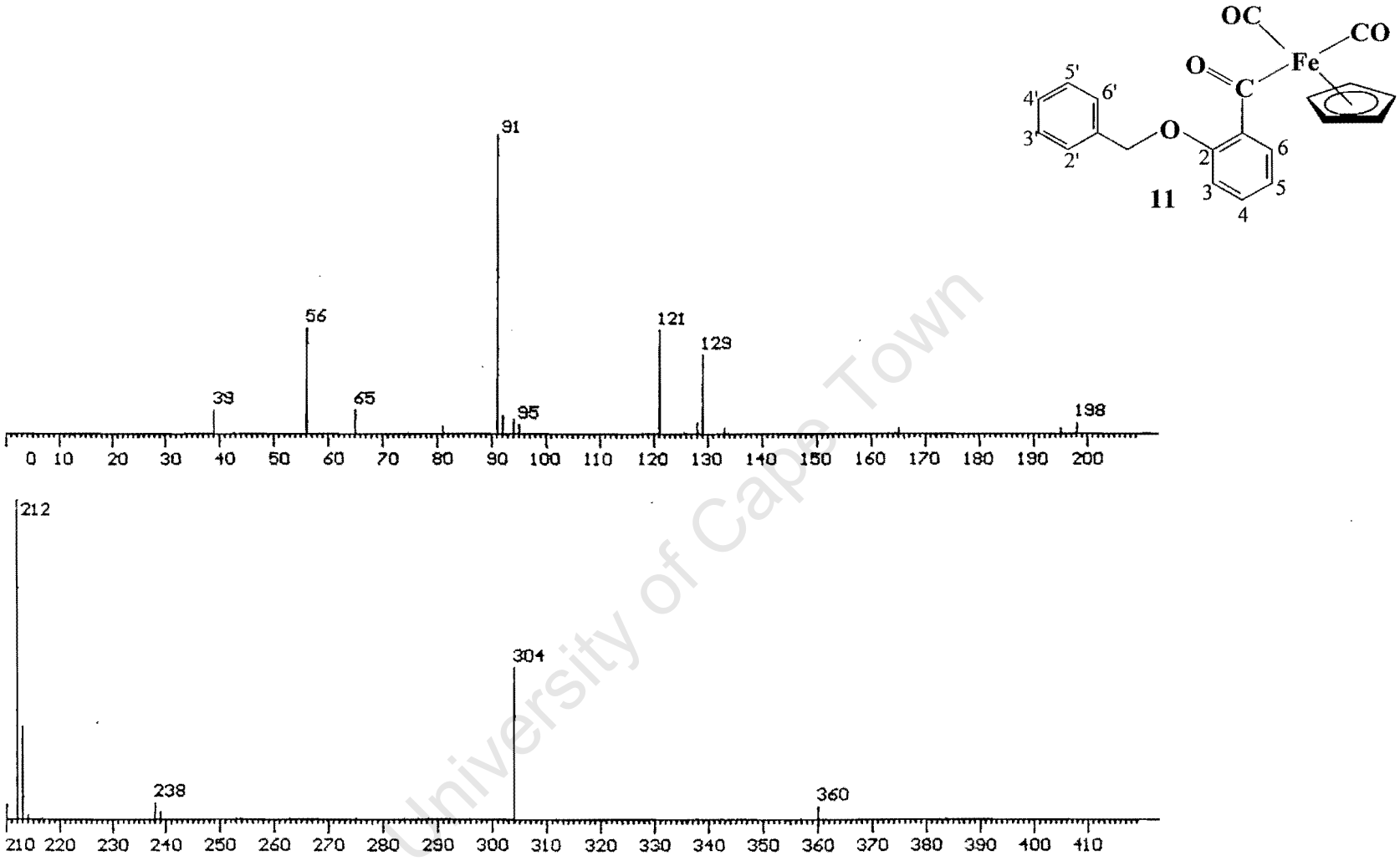
Appendix 5 A 300MHz ^{13}C NMR spectrum of **10**



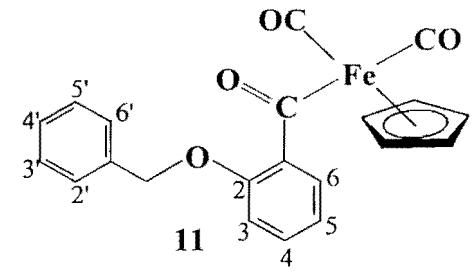
Appendix 6 EI mass spectrum of **10**

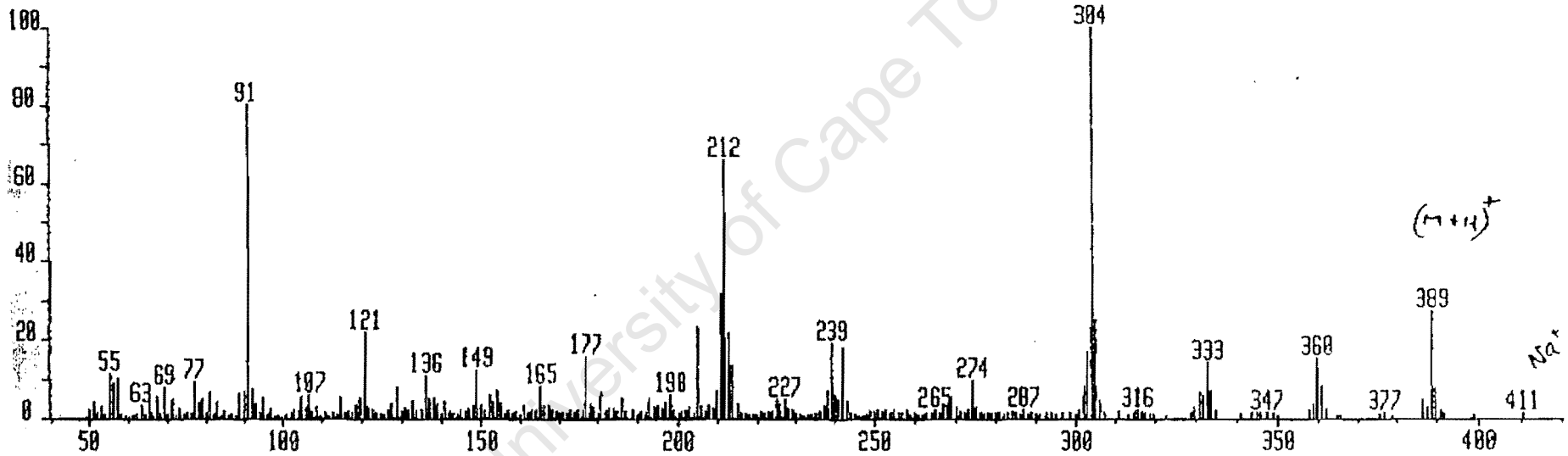


Appendix 7 A 200MHz ^{13}C NMR spectrum of **11**



Appendix 8a EI mass spectrum of **11**





Appendix 8b FAB mass spectrum of **11**

Appendix 9 Crystal structure data for $[CpFe(CO)_2(COC_6H_4OCH_2Ph)]$ (**11**)

Table 9a Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalised U^{ij} tensor

	x	y	z	U(eq)
Fe(1)	1703(1)	4186(1)	4154(1)	39(1)
O(4)	3074(1)	4710(2)	6145(1)	53(1)
C(5)	2429(1)	5965(2)	6220(1)	46(1)
C(2)	1200(1)	3419(2)	4899(1)	52(1)
C(3)	2118(1)	6508(2)	4704(1)	45(1)
C(21)	2682(1)	4267(3)	3490(1)	54(1)
O(1)	14(1)	6053(3)	3198(1)	101(1)
O(2)	885(1)	2860(2)	5375(1)	81(1)
C(6)	2231(2)	6333(3)	6940(1)	60(1)
C(4)	1968(1)	6900(2)	5511(1)	44(1)
C(8)	1109(2)	8582(3)	6259(2)	72(1)
C(9)	1322(1)	8236(3)	5543(1)	59(1)
C(17)	3137(1)	3650(3)	4287(1)	60(1)
C(20)	1960(2)	3040(3)	3120(1)	58(1)
C(18)	2690(2)	2062(3)	4396(1)	66(1)
C(1)	670(1)	5316(3)	3579(1)	59(1)
C(19)	1964(2)	1673(3)	3669(1)	66(1)
C(7)	1559(2)	7627(3)	6943(2)	70(1)
C(11)	4137(1)	2291(3)	6592(1)	52(1)
C(12)	4950(2)	2748(3)	6399(1)	62(1)
C(16)	3848(1)	526(3)	6527(1)	61(1)
C(10)	3564(2)	3693(3)	6852(1)	71(1)
C(13)	5451(2)	1467(4)	6127(1)	71(1)
C(15)	4355(2)	-755(3)	6258(1)	69(1)
C(14)	5150(2)	-281(4)	6057(1)	70(1)
O(3)	2434(1)	7673(2)	4375(1)	74(1)

Table 9b Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi[h^2 a^{*2} U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	42(1)	39(1)	38(1)	2(1)	14(1)	0(1)
O(4)	60(1)	59(1)	41(1)	3(1)	17(1)	14(1)
C(5)	47(1)	45(1)	50(1)	-11(1)	19(1)	-5(1)
C(2)	60(1)	45(1)	55(1)	-4(1)	22(1)	-14(1)
C(3)	46(1)	36(1)	54(1)	4(1)	19(1)	2(1)
C(21)	56(1)	59(1)	54(1)	1(1)	30(1)	5(1)
O(1)	59(1)	150(2)	91(1)	42(1)	18(1)	38(1)
O(2)	103(1)	82(1)	72(1)	-1(1)	49(1)	-34(1)
C(6)	68(1)	63(1)	54(1)	-13(1)	26(1)	-6(1)
C(4)	43(1)	36(1)	54(1)	-8(1)	18(1)	-5(1)
C(8)	64(1)	65(1)	94(2)	-28(1)	35(1)	5(1)
C(9)	55(1)	48(1)	74(1)	-9(1)	21(1)	4(1)
C(17)	46(1)	75(1)	56(1)	-7(1)	14(1)	17(1)
C(20)	69(1)	63(1)	43(1)	-6(1)	18(1)	7(1)
C(18)	89(2)	57(1)	57(1)	13(1)	28(1)	31(1)
C(1)	49(1)	77(1)	53(1)	9(1)	19(1)	6(1)
C(19)	96(2)	43(1)	66(1)	-9(1)	34(1)	0(1)
C(7)	74(1)	73(1)	73(1)	-28(1)	40(1)	-9(1)
C(11)	53(1)	66(1)	34(1)	10(1)	10(1)	11(1)
C(12)	61(1)	68(1)	56(1)	6(1)	14(1)	-6(1)
C(16)	51(1)	73(1)	57(1)	13(1)	15(1)	1(1)
C(10)	87(2)	84(2)	44(1)	12(1)	21(1)	29(1)
C(13)	50(1)	106(2)	59(1)	12(1)	21(1)	6(1)
C(15)	67(1)	62(1)	70(1)	1(1)	8(1)	3(1)
C(14)	64(1)	84(2)	56(1)	-3(1)	12(1)	23(1)
O(3)	111(1)	42(1)	86(1)	4(1)	56(1)	-16(1)

Table 9c Bond lengths [Å] and angles [°]

Fe(1)-C(1)	1.759(2)
Fe(1)-C(2)	1.7628(19)
Fe(1)-C(3)	1.9802(17)
Fe(1)-C(17)	2.0935(19)
Fe(1)-C(21)	2.0988(18)
Fe(1)-C(18)	2.1058(19)
Fe(1)-C(20)	2.1151(18)
Fe(1)-C(19)	2.137(2)
O(4)-C(5)	1.369(2)
O(4)-C(10)	1.432(2)
C(5)-C(6)	1.387(3)
C(5)-C(4)	1.393(3)
C(2)-O(2)	1.139(2)
C(3)-O(3)	1.206(2)
C(3)-C(4)	1.505(2)
C(21)-C(20)	1.401(3)
C(21)-C(17)	1.410(3)
O(1)-C(1)	1.132(2)
C(6)-C(7)	1.384(3)
C(4)-C(9)	1.392(2)
C(8)-C(7)	1.365(3)
C(8)-C(9)	1.388(3)
C(17)-C(18)	1.396(3)
C(20)-C(19)	1.391(3)
C(18)-C(19)	1.409(3)
C(11)-C(16)	1.378(3)
C(11)-C(12)	1.381(3)
C(11)-C(10)	1.497(3)
C(12)-C(13)	1.375(3)
C(16)-C(15)	1.377(3)
C(13)-C(14)	1.371(4)
C(15)-C(14)	1.367(3)
C(1)-Fe(1)-C(2)	94.77(9)

C(1)-Fe(1)-C(3)	86.52(9)
C(2)-Fe(1)-C(3)	94.16(8)
C(1)-Fe(1)-C(17)	145.56(9)
C(2)-Fe(1)-C(17)	119.52(9)
C(3)-Fe(1)-C(17)	87.74(8)
C(1)-Fe(1)-C(21)	107.40(8)
C(2)-Fe(1)-C(21)	156.73(8)
C(3)-Fe(1)-C(21)	94.16(7)
C(17)-Fe(1)-C(21)	39.31(8)
C(1)-Fe(1)-C(18)	154.10(10)
C(2)-Fe(1)-C(18)	91.71(9)
C(3)-Fe(1)-C(18)	118.02(9)
C(17)-Fe(1)-C(18)	38.82(9)
C(21)-Fe(1)-C(18)	65.24(8)
C(1)-Fe(1)-C(20)	93.69(9)
C(2)-Fe(1)-C(20)	134.98(9)
C(3)-Fe(1)-C(20)	130.47(8)
C(17)-Fe(1)-C(20)	65.18(8)
C(21)-Fe(1)-C(20)	38.84(8)
C(18)-Fe(1)-C(20)	64.65(8)
C(1)-Fe(1)-C(19)	115.33(10)
C(2)-Fe(1)-C(19)	99.59(9)
C(3)-Fe(1)-C(19)	152.80(8)
C(17)-Fe(1)-C(19)	65.06(9)
C(21)-Fe(1)-C(19)	64.86(8)
C(18)-Fe(1)-C(19)	38.77(9)
C(20)-Fe(1)-C(19)	38.19(8)
C(5)-O(4)-C(10)	117.81(14)
O(4)-C(5)-C(6)	124.21(17)
O(4)-C(5)-C(4)	115.22(15)
C(6)-C(5)-C(4)	120.57(17)
O(2)-C(2)-Fe(1)	177.46(19)
O(3)-C(3)-C(4)	118.80(16)
O(3)-C(3)-Fe(1)	120.85(14)
C(4)-C(3)-Fe(1)	120.16(12)
C(20)-C(21)-C(17)	107.49(18)

C(20)-C(21)-Fe(1)	71.21(11)
C(17)-C(21)-Fe(1)	70.14(11)
C(7)-C(6)-C(5)	119.2(2)
C(9)-C(4)-C(5)	118.70(17)
C(9)-C(4)-C(3)	118.17(17)
C(5)-C(4)-C(3)	123.12(15)
C(7)-C(8)-C(9)	119.4(2)
C(8)-C(9)-C(4)	120.8(2)
C(18)-C(17)-C(21)	107.76(19)
C(18)-C(17)-Fe(1)	71.07(12)
C(21)-C(17)-Fe(1)	70.55(10)
C(19)-C(20)-C(21)	108.88(18)
C(19)-C(20)-Fe(1)	71.76(11)
C(21)-C(20)-Fe(1)	69.95(10)
C(17)-C(18)-C(19)	108.45(18)
C(17)-C(18)-Fe(1)	70.11(11)
C(19)-C(18)-Fe(1)	71.81(12)
O(1)-C(1)-Fe(1)	178.57(19)
C(20)-C(19)-C(18)	107.4(2)
C(20)-C(19)-Fe(1)	70.05(11)
C(18)-C(19)-Fe(1)	69.42(11)
C(8)-C(7)-C(6)	121.4(2)
C(16)-C(11)-C(12)	119.05(19)
C(16)-C(11)-C(10)	120.3(2)
C(12)-C(11)-C(10)	120.6(2)
C(13)-C(12)-C(11)	120.4(2)
C(15)-C(16)-C(11)	120.4(2)
O(4)-C(10)-C(11)	107.40(15)
C(14)-C(13)-C(12)	119.9(2)
C(14)-C(15)-C(16)	120.1(2)
C(15)-C(14)-C(13)	120.2(2)

Table 9d Torsion angles [°]

C(10)-O(4)-C(5)-C(6)	1.1(3)
C(10)-O(4)-C(5)-C(4)	-179.42(18)
C(1)-Fe(1)-C(2)-O(2)	127(4)
C(3)-Fe(1)-C(2)-O(2)	-146(4)
C(17)-Fe(1)-C(2)-O(2)	-56(4)
C(21)-Fe(1)-C(2)-O(2)	-35(4)
C(18)-Fe(1)-C(2)-O(2)	-28(4)
C(20)-Fe(1)-C(2)-O(2)	27(4)
C(19)-Fe(1)-C(2)-O(2)	11(4)
C(1)-Fe(1)-C(3)-O(3)	-77.32(17)
C(2)-Fe(1)-C(3)-O(3)	-171.85(17)
C(17)-Fe(1)-C(3)-O(3)	68.71(17)
C(21)-Fe(1)-C(3)-O(3)	29.90(17)
C(18)-Fe(1)-C(3)-O(3)	93.99(17)
C(20)-Fe(1)-C(3)-O(3)	14.6(2)
C(19)-Fe(1)-C(3)-O(3)	67.7(2)
C(1)-Fe(1)-C(3)-C(4)	97.55(14)
C(2)-Fe(1)-C(3)-C(4)	3.02(15)
C(17)-Fe(1)-C(3)-C(4)	-116.43(14)
C(21)-Fe(1)-C(3)-C(4)	-155.23(14)
C(18)-Fe(1)-C(3)-C(4)	-91.15(14)
C(20)-Fe(1)-C(3)-C(4)	-170.56(12)
C(19)-Fe(1)-C(3)-C(4)	-117.44(18)
C(1)-Fe(1)-C(21)-C(20)	-73.64(14)
C(2)-Fe(1)-C(21)-C(20)	88.0(2)
C(3)-Fe(1)-C(21)-C(20)	-161.30(12)
C(17)-Fe(1)-C(21)-C(20)	117.41(17)
C(18)-Fe(1)-C(21)-C(20)	79.68(13)
C(19)-Fe(1)-C(21)-C(20)	36.73(12)
C(1)-Fe(1)-C(21)-C(17)	168.95(14)
C(2)-Fe(1)-C(21)-C(17)	-29.4(3)
C(3)-Fe(1)-C(21)-C(17)	81.29(13)
C(18)-Fe(1)-C(21)-C(17)	-37.73(13)
C(20)-Fe(1)-C(21)-C(17)	-117.41(17)

C(19)-Fe(1)-C(21)-C(17)	-80.68(14)
O(4)-C(5)-C(6)-C(7)	-179.66(18)
C(4)-C(5)-C(6)-C(7)	0.9(3)
O(4)-C(5)-C(4)-C(9)	-178.12(15)
C(6)-C(5)-C(4)-C(9)	1.4(3)
O(4)-C(5)-C(4)-C(3)	3.3(2)
C(6)-C(5)-C(4)-C(3)	-177.20(16)
O(3)-C(3)-C(4)-C(9)	62.4(2)
Fe(1)-C(3)-C(4)-C(9)	-112.62(16)
O(3)-C(3)-C(4)-C(5)	-119.1(2)
Fe(1)-C(3)-C(4)-C(5)	65.9(2)
C(7)-C(8)-C(9)-C(4)	1.7(3)
C(5)-C(4)-C(9)-C(8)	-2.7(3)
C(3)-C(4)-C(9)-C(8)	175.95(18)
C(20)-C(21)-C(17)-C(18)	-0.1(2)
Fe(1)-C(21)-C(17)-C(18)	61.68(13)
C(20)-C(21)-C(17)-Fe(1)	-61.78(13)
C(1)-Fe(1)-C(17)-C(18)	-136.46(18)
C(2)-Fe(1)-C(17)-C(18)	49.53(15)
C(3)-Fe(1)-C(17)-C(18)	143.03(13)
C(21)-Fe(1)-C(17)-C(18)	-117.59(18)
C(20)-Fe(1)-C(17)-C(18)	-79.75(13)
C(19)-Fe(1)-C(17)-C(18)	-37.48(12)
C(1)-Fe(1)-C(17)-C(21)	-18.9(2)
C(2)-Fe(1)-C(17)-C(21)	167.12(12)
C(3)-Fe(1)-C(17)-C(21)	-99.38(13)
C(18)-Fe(1)-C(17)-C(21)	117.59(18)
C(20)-Fe(1)-C(17)-C(21)	37.84(12)
C(19)-Fe(1)-C(17)-C(21)	80.11(13)
C(17)-C(21)-C(20)-C(19)	-0.4(2)
Fe(1)-C(21)-C(20)-C(19)	-61.51(14)
C(17)-C(21)-C(20)-Fe(1)	61.09(13)
C(1)-Fe(1)-C(20)-C(19)	-127.69(15)
C(2)-Fe(1)-C(20)-C(19)	-27.19(19)
C(3)-Fe(1)-C(20)-C(19)	143.74(14)
C(17)-Fe(1)-C(20)-C(19)	80.59(15)

C(21)-Fe(1)-C(20)-C(19)	118.88(18)
C(18)-Fe(1)-C(20)-C(19)	37.54(14)
C(1)-Fe(1)-C(20)-C(21)	113.43(13)
C(2)-Fe(1)-C(20)-C(21)	-146.07(13)
C(3)-Fe(1)-C(20)-C(21)	24.86(15)
C(17)-Fe(1)-C(20)-C(21)	-38.29(12)
C(18)-Fe(1)-C(20)-C(21)	-81.34(13)
C(19)-Fe(1)-C(20)-C(21)	-118.88(18)
C(21)-C(17)-C(18)-C(19)	0.6(2)
Fe(1)-C(17)-C(18)-C(19)	61.92(15)
C(21)-C(17)-C(18)-Fe(1)	-61.34(13)
C(1)-Fe(1)-C(18)-C(17)	116.9(2)
C(2)-Fe(1)-C(18)-C(17)	-138.53(13)
C(3)-Fe(1)-C(18)-C(17)	-42.90(14)
C(21)-Fe(1)-C(18)-C(17)	38.19(12)
C(20)-Fe(1)-C(18)-C(17)	81.26(13)
C(19)-Fe(1)-C(18)-C(17)	118.24(18)
C(1)-Fe(1)-C(18)-C(19)	-1.3(3)
C(2)-Fe(1)-C(18)-C(19)	103.24(14)
C(3)-Fe(1)-C(18)-C(19)	-161.13(12)
C(17)-Fe(1)-C(18)-C(19)	-118.24(18)
C(21)-Fe(1)-C(18)-C(19)	-80.04(14)
C(20)-Fe(1)-C(18)-C(19)	-36.98(13)
C(2)-Fe(1)-C(1)-O(1)	180(100)
C(3)-Fe(1)-C(1)-O(1)	86(10)
C(17)-Fe(1)-C(1)-O(1)	5(10)
C(21)-Fe(1)-C(1)-O(1)	-7(10)
C(18)-Fe(1)-C(1)-O(1)	-76(10)
C(20)-Fe(1)-C(1)-O(1)	-45(10)
C(19)-Fe(1)-C(1)-O(1)	-77(10)
C(21)-C(20)-C(19)-C(18)	0.8(2)
Fe(1)-C(20)-C(19)-C(18)	-59.61(14)
C(21)-C(20)-C(19)-Fe(1)	60.38(14)
C(17)-C(18)-C(19)-C(20)	-0.8(2)
Fe(1)-C(18)-C(19)-C(20)	60.01(15)
C(17)-C(18)-C(19)-Fe(1)	-60.85(14)

C(1)-Fe(1)-C(19)-C(20)	60.89(16)
C(2)-Fe(1)-C(19)-C(20)	160.87(13)
C(3)-Fe(1)-C(19)-C(20)	-79.8(2)
C(17)-Fe(1)-C(19)-C(20)	-80.93(14)
C(21)-Fe(1)-C(19)-C(20)	-37.35(12)
C(18)-Fe(1)-C(19)-C(20)	-118.5(2)
C(1)-Fe(1)-C(19)-C(18)	179.35(13)
C(2)-Fe(1)-C(19)-C(18)	-80.67(15)
C(3)-Fe(1)-C(19)-C(18)	38.6(2)
C(17)-Fe(1)-C(19)-C(18)	37.53(13)
C(21)-Fe(1)-C(19)-C(18)	81.11(14)
C(20)-Fe(1)-C(19)-C(18)	118.5(2)
C(9)-C(8)-C(7)-C(6)	0.6(3)
C(5)-C(6)-C(7)-C(8)	-1.9(3)
C(16)-C(11)-C(12)-C(13)	1.6(3)
C(10)-C(11)-C(12)-C(13)	-177.22(18)
C(12)-C(11)-C(16)-C(15)	-1.3(3)
C(10)-C(11)-C(16)-C(15)	177.55(19)
C(5)-O(4)-C(10)-C(11)	173.69(16)
C(16)-C(11)-C(10)-O(4)	-105.7(2)
C(12)-C(11)-C(10)-O(4)	73.1(2)
C(11)-C(12)-C(13)-C(14)	-0.9(3)
C(11)-C(16)-C(15)-C(14)	0.3(3)
C(16)-C(15)-C(14)-C(13)	0.4(3)
C(12)-C(13)-C(14)-C(15)	-0.1(3)

Table 9e Hydrogen co-ordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U(eq)
H(21)	2833	5300	3254	64
H(6)	2546	5719	7414	72
H(8)	664	9455	6272	86
H(9)	1029	8906	5080	71
H(17)	3643	4202	4670	72
H(20)	1546	3127	2594	70
H(18)	2846	1377	4868	80
H(19)	1562	683	3573	80
H(7)	1412	7851	7421	83
H(12)	5160	3930	6453	75
H(16)	3309	198	6665	73
H(10A)	3111	3136	7083	85
H(10B)	3979	4467	7260	85
H(13)	5993	1785	5991	85
H(15)	4155	-1943	6213	83
H(14)	5489	-1147	5872	84

Table 9f Observed and calculated structure factors

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s						
3	0	0	1342	1633	44	3	5	0	37	36	1	16	1	1	0	10	1
-2	4	1	142	124	1	-4	7	1	74	76	2						
4	0	0	66	63	3	4	5	0	243	247	1	17	1	1	35	38	9
-1	4	1	563	564	2	-3	7	1	237	241	2						
5	0	0	366	357	3	5	5	0	130	133	1	-18	2	1	71	68	5
0	4	1	224	227	1	-2	7	1	83	77	1						
6	0	0	505	507	4	6	5	0	4	2	4	-17	2	1	42	27	8
1	4	1	265	265	1	-1	7	1	17	23	8						
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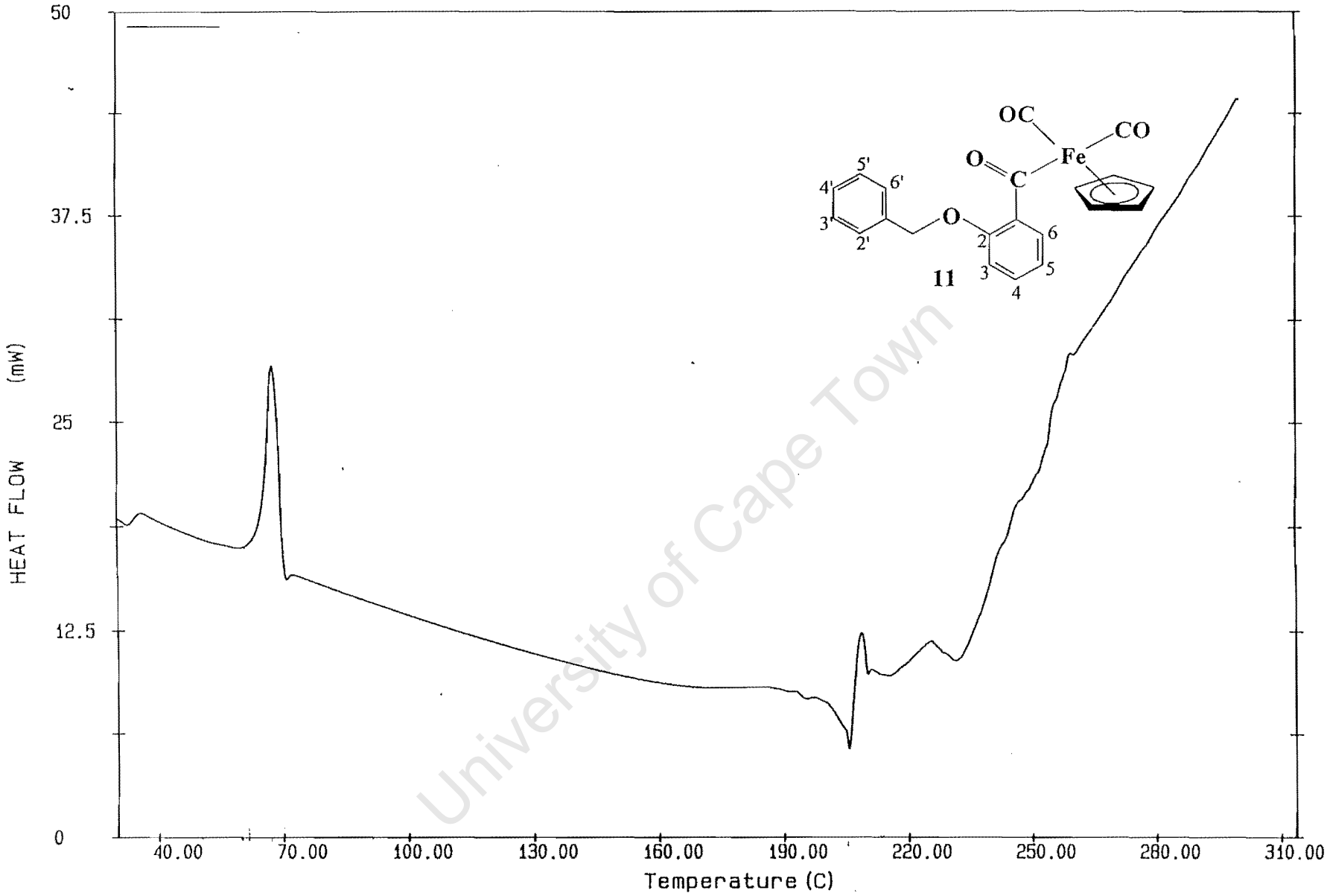
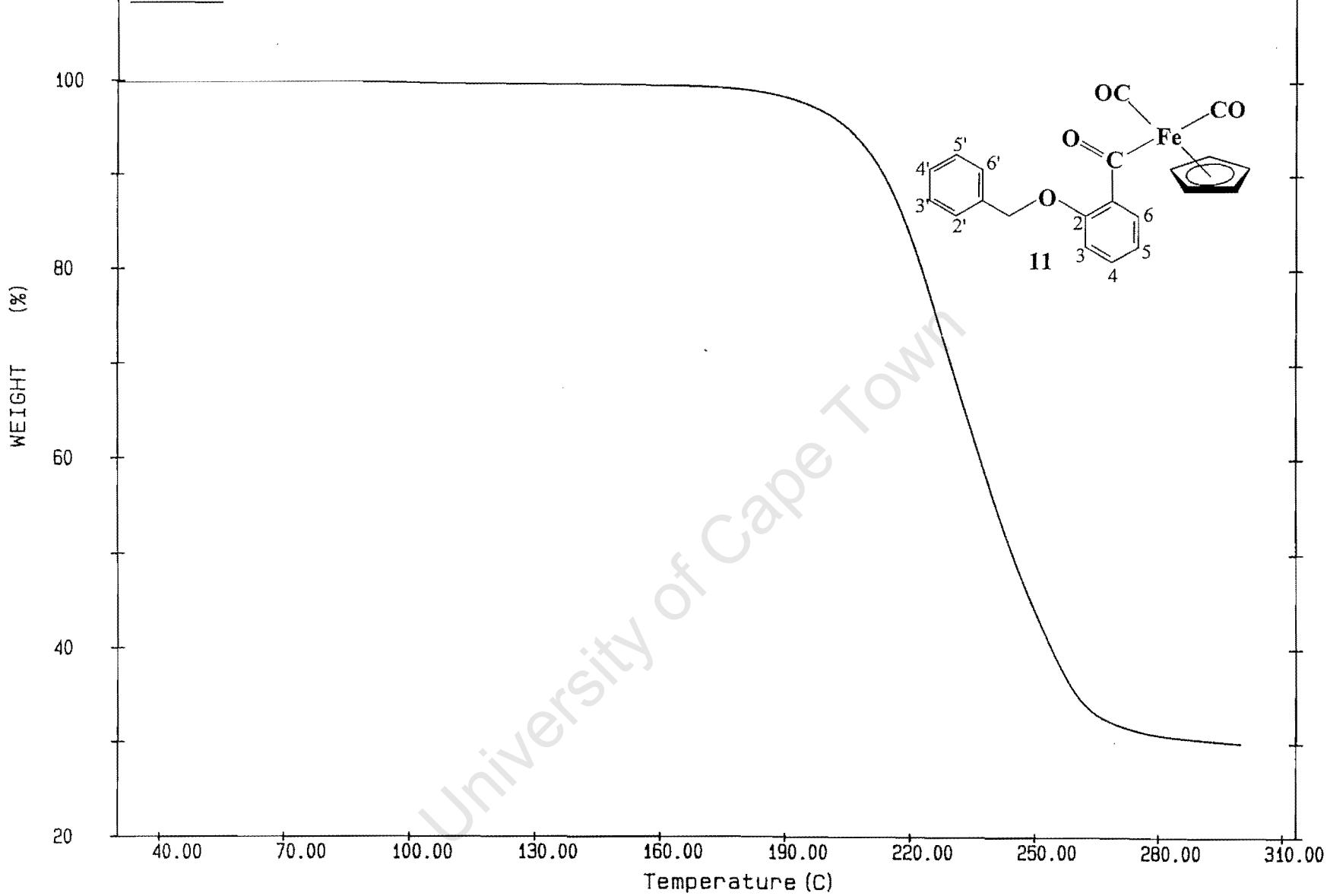
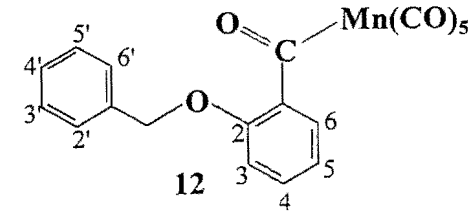
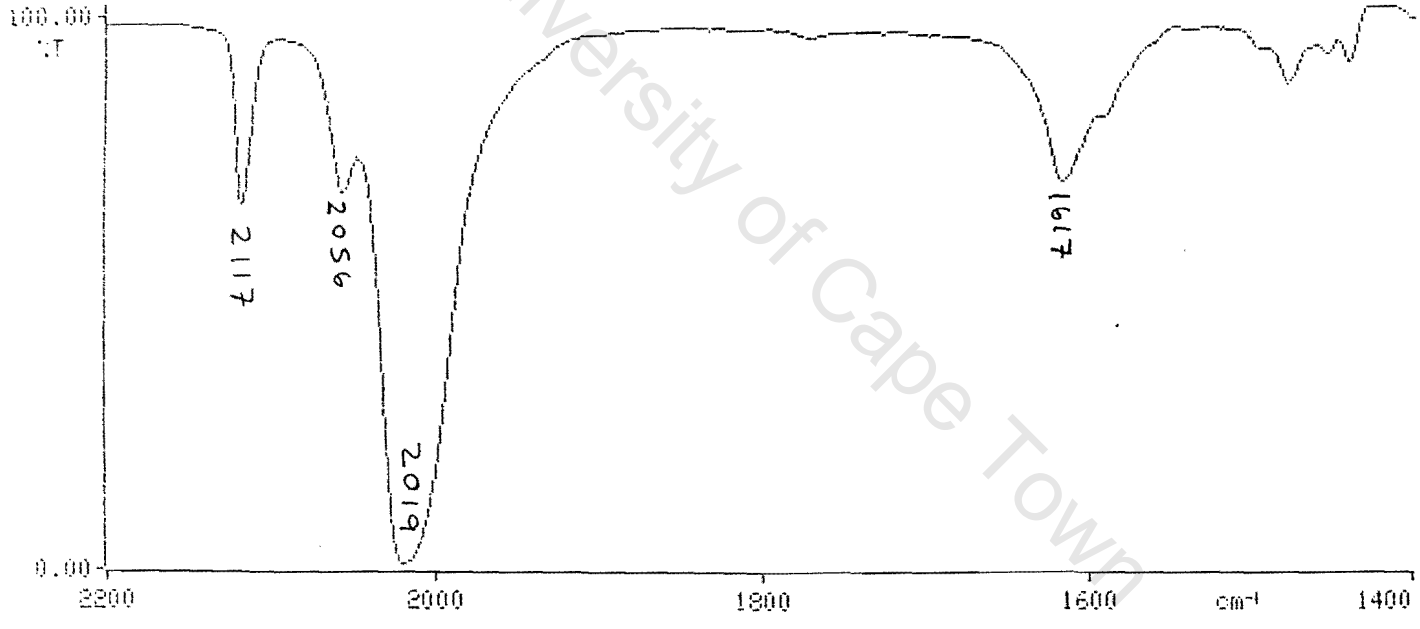


Appendix 10a DSC trace of **11** (Scanning rate = 10°C/min)

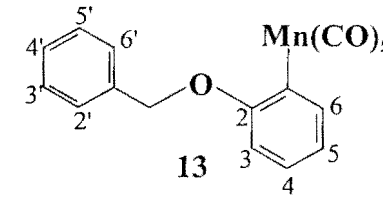


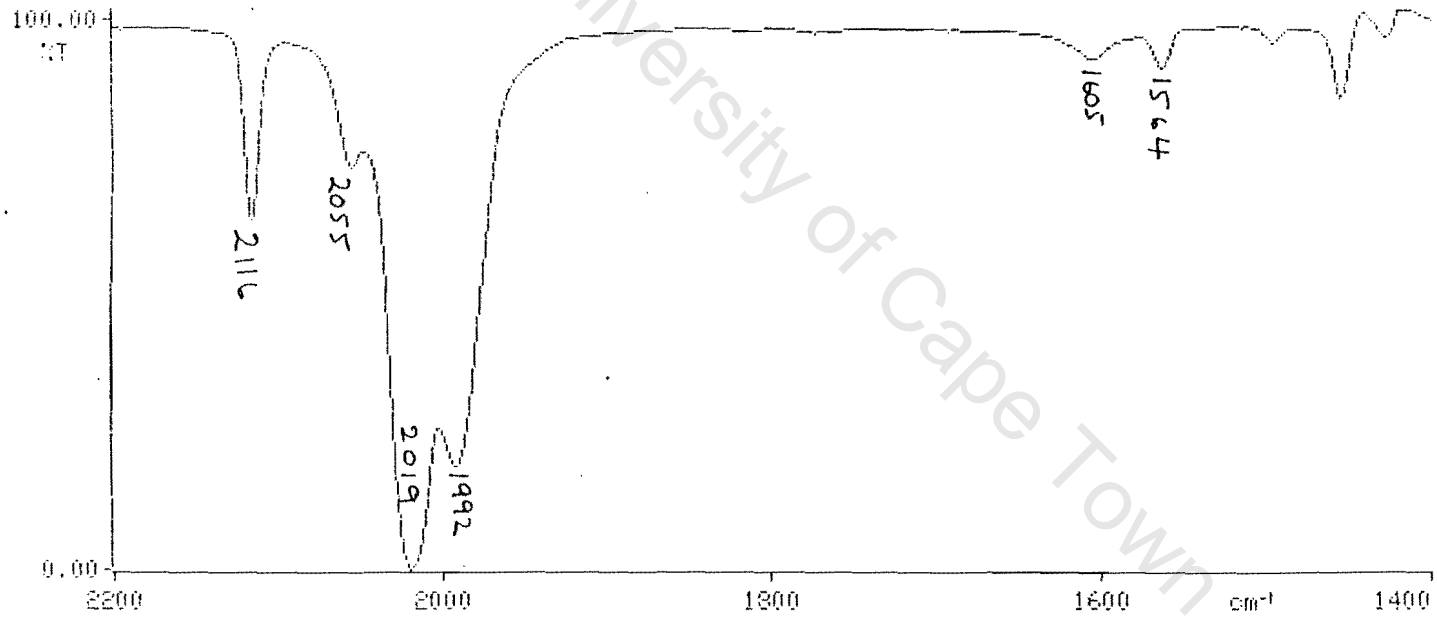
Appendix 10b TGA trace of **11** (Scanning rate = 10°C/min)



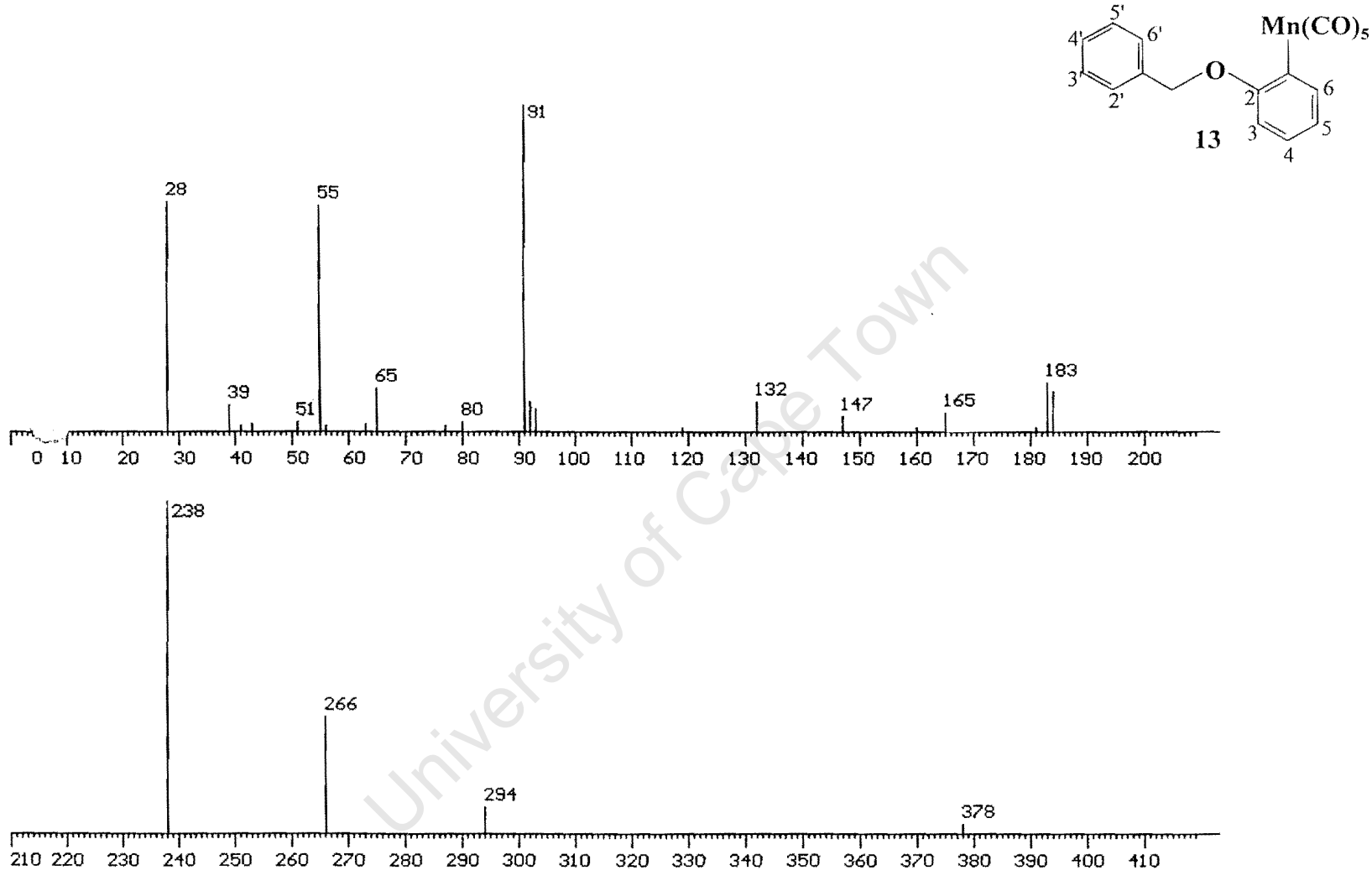


Appendix 11 An infrared spectrum of **12**

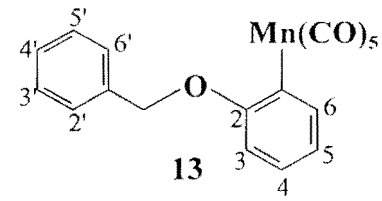




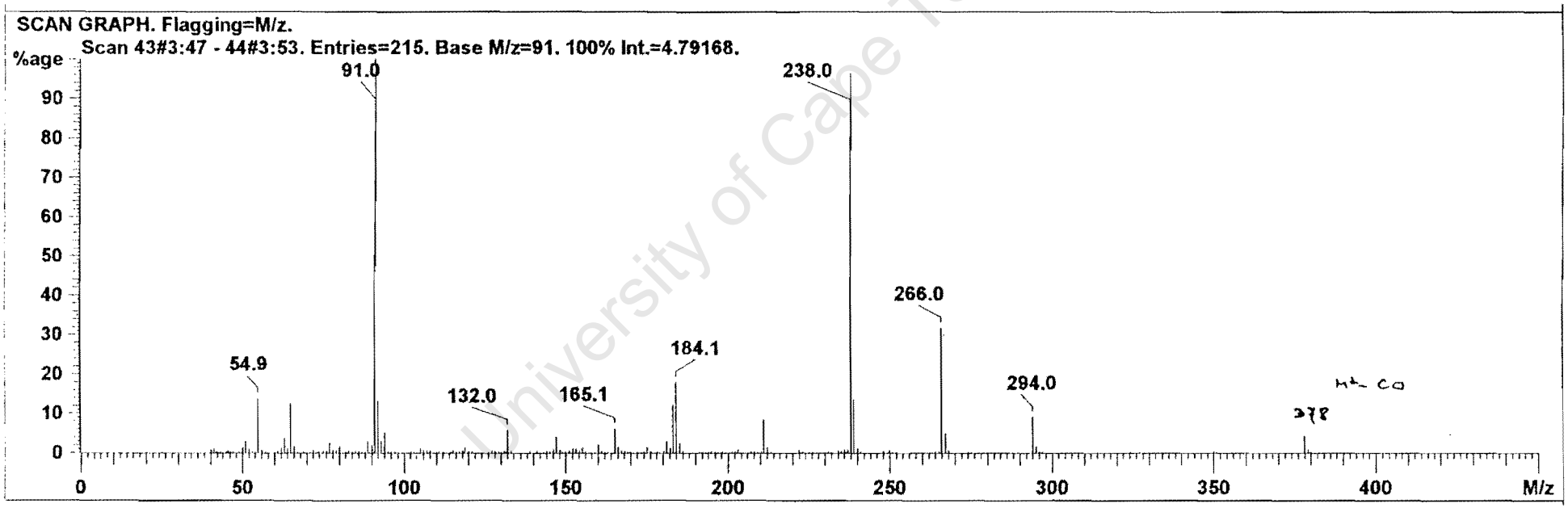
Appendix 12 An infrared spectrum of **13**



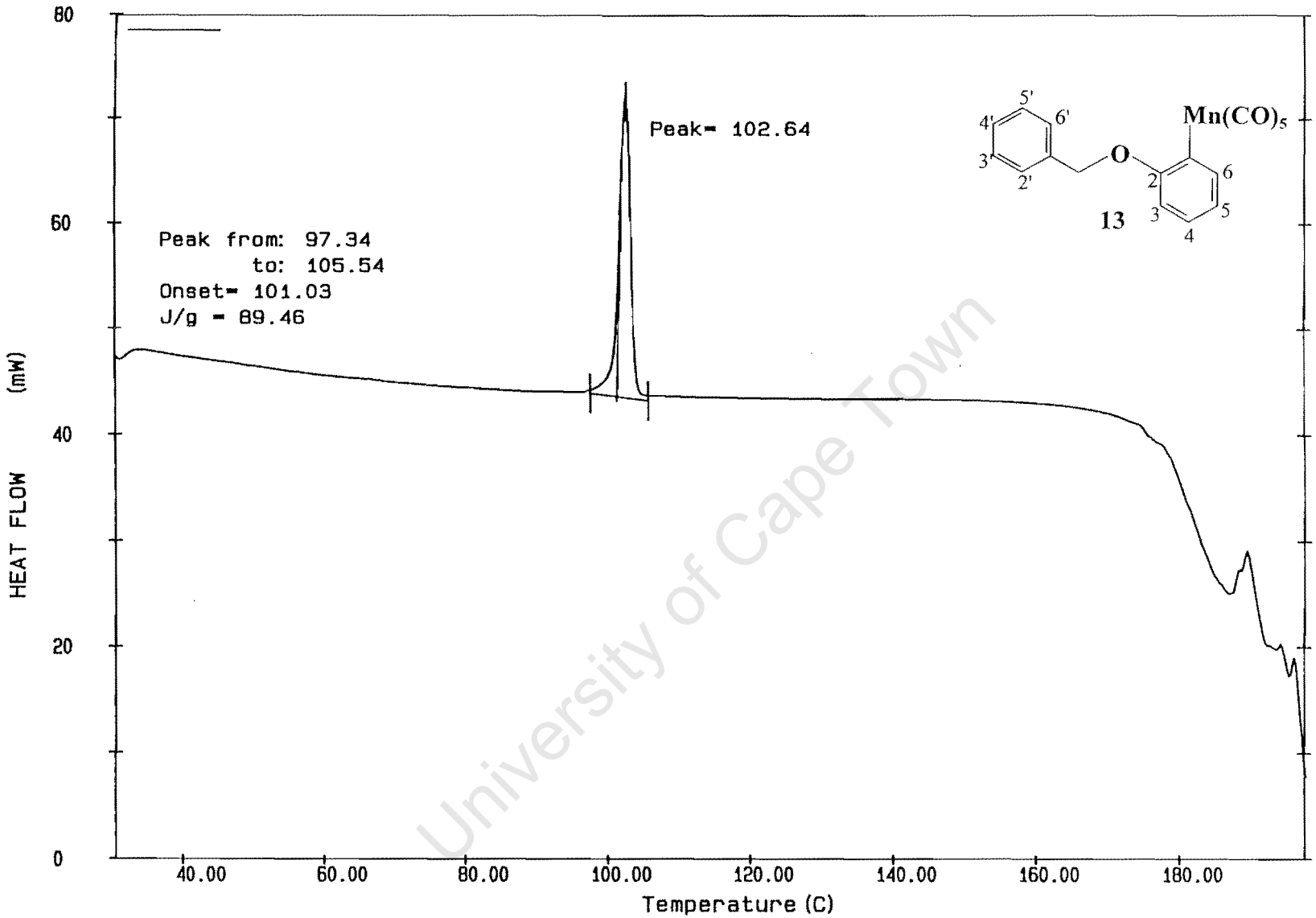
Appendix 13a EI mass spectrum of **13**



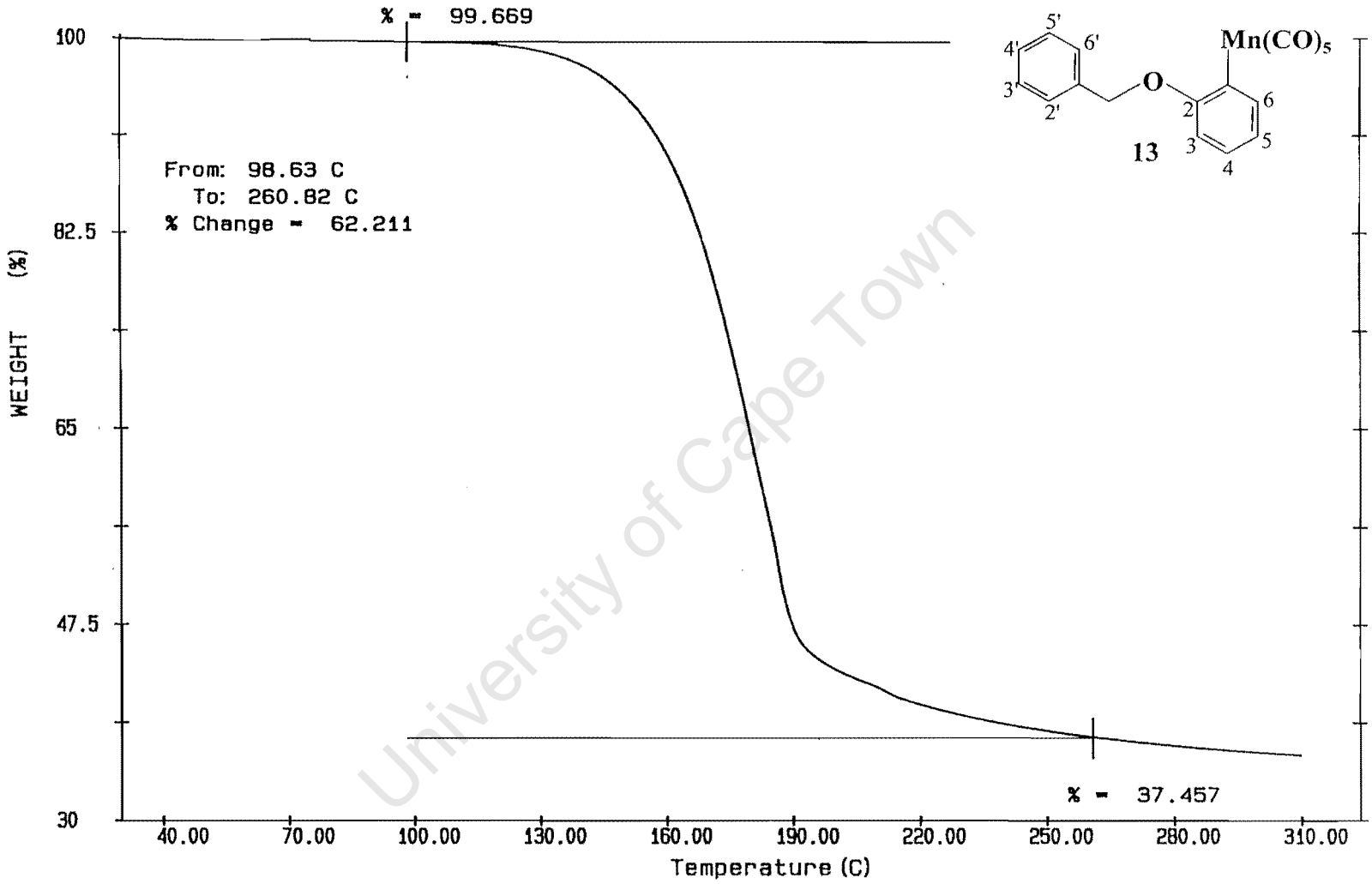
13



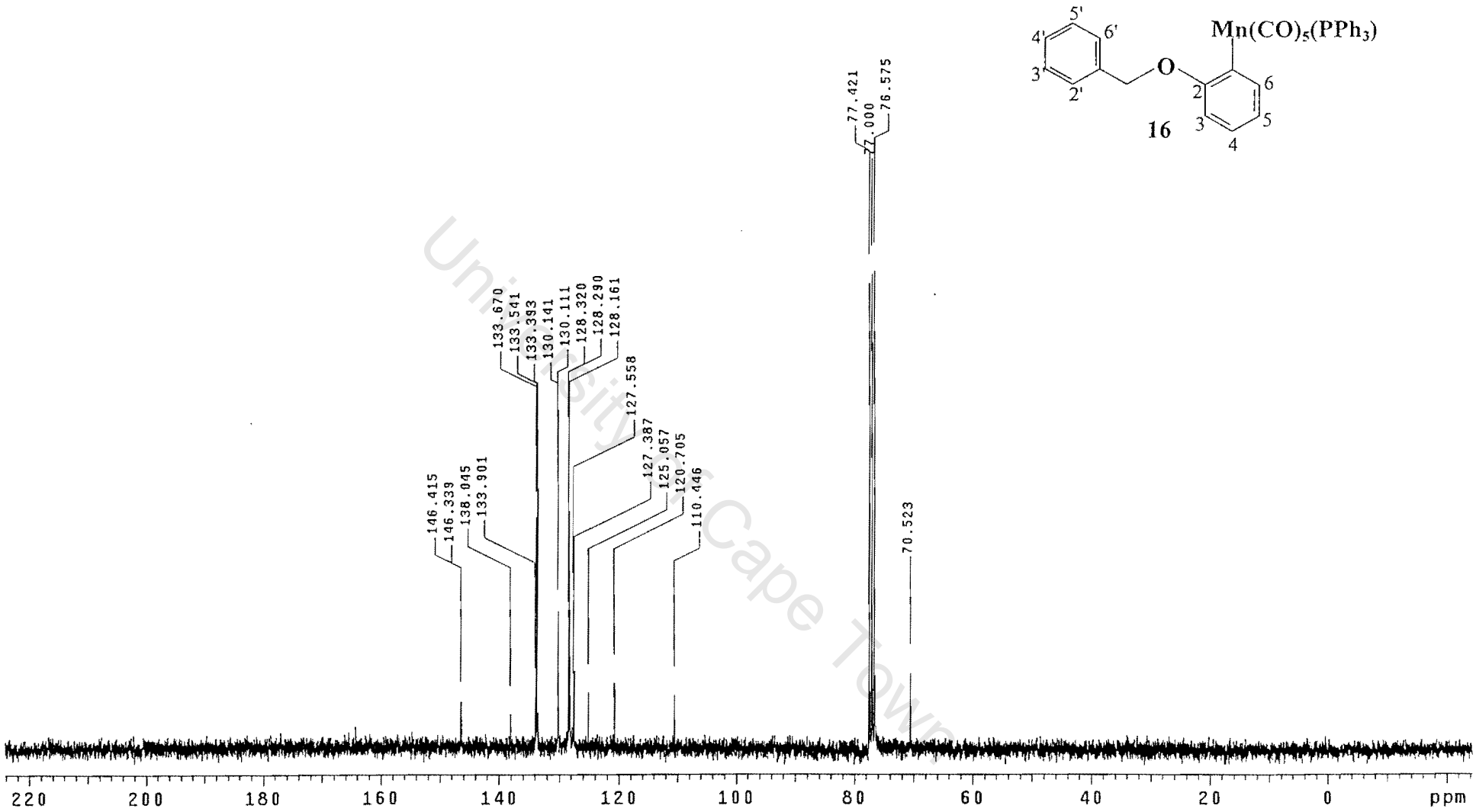
Appendix 13b FAB mass spectrum of **13**



Appendix 14a DSC trace of **13** (Scanning rate = 10°C/min)



Appendix 14b TGA trace of **13** (Scanning rate = 10°C/min)



Appendix 15 A 300MHz ^{13}C NMR spectrum of **16**