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Magneto-structural correlations of Iron-salicylaldoxime clusters.

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ABSTRACT

The syntheses and characterisation of polynuclear metal clusters using a series of derivatised salicylaldoxime ligands are described in this thesis. The polynuclear iron clusters contain metallic cores consisting of oxo-centred triangles. It was found that slight modifications of the phenolic oxime ligands can lead to metal clusters with different nuclearities, thus producing a variety of magnetic properties within the materials. The predominant building block in the complexes is a triangular $[\text{Fe}_3\text{O}(\text{R-sao})_3]^+$ (R = alkyl derivative, sao = salicylaldoxime) unit which can self-assemble into more complicated arrays depending on reaction conditions.

A number of ligands containing a single phenolic oxime unit has been synthesised. These ligands have been used to form di-iron (**C1**), hexairon (**C2**), and heptairon (**C3**) complexes.

A second series of ligands containing two double-headed phenolic oxime units linked by diamine straps has been synthesised and fully characterised. Two copper complexes **C5** and **C7** were crystallised and pyridine also took part in coordination to the copper centres. Three of the iron complexes formed with double-headed oxime ligands are heptairon compounds. The heptairon compounds were all analogous in their iron coordination environment. The hexairon complex (**C8**) formed from a double-headed oxime was analogous to the complex **C2** formed from a single-headed oxime ligand in its iron coordination environment. The tri-iron complex (**C10**) also contains a metaborate ion. In each case of the heptairon complexes and the hexairon complex, the metallic skeleton of the cluster was based on a trigonal prism in which two $[\text{Fe}_3^{\text{III}}\text{O}]$ triangles are fastened together via three helically twisted double-headed oxime ligands. Each of these ligands is present as (**L-2H**) where the oximic and phenolic O-atoms are deprotonated and the amino N-atoms protonated, with the oxime moieties bridging across the edges of the metal triangles. The identity of the metal ion has a major impact on the nuclearity and topology of the resultant cluster.

The magnetic susceptibility measurements of these iron complexes suggest the presence of strong antiferromagnetic interactions between the metal centres and the Mössbauer analyses confirm the oxidation state of all the iron centres is 3+. The CHN analyses and

other general characterisation allowed verifying and / or modifying the formulae generated by the X-ray analyses.

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DECLARATION BY THE CANDIDATE

I do hereby declare that the work described in this thesis was carried out by me under the supervision of Associate Professor Paul Plieger and Professor David Harding and a report on this has not been submitted in whole or part to any university or any other institution for another Degree or Diploma. To the best of my knowledge it does not contain any material published or written by another person, except as acknowledged in the text.

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DECLARATION BY THE SUPERVISORS

This is to certify that this dissertation is based on the work carried by Ms D.N.T. De Silva under our supervision. The dissertation has been prepared according to the format stipulated and is of acceptable standard.

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ABBREVIATIONS

AF	Antiferromagnetic exchange
SMMs	Single molecule magnets
SCMs	Single chain magnets
ZFS	Zero field splitting parameter (<i>D</i>)
M	Magnetisation
H	External magnetic field
χ	Magnetic susceptibility
T _c	Curie temperature
T _N	Néel temperature
VT	Variable temperature
QTM	Quantum tunnelling of magnetisation
QPI	Quantum phase interference
MeOH	Methanol
EtOH	Ethanol
MeCN	Acetonitrile
EtOAc	Ethyl acetate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Et ₂ O	Diethylether
Et ₃ N	Triethylamine
Py	Pyridine
CDCl ₃	Deuterated chloroform
T	Temperature
RT	Room temperature
MP	Melting point
dc	Direct current
br	Broad
m	Medium
s	Strong
saoH ₂	Salicylaldoxime
Me-saoH ₂	Methyl salicylaldoxime
Et-saoH ₂	Ethyl salicylaldoxime

Ph-saoH ₂	Phenyl salicylaldoxime
MRI	Magnetic resonance imaging
XRD	X-ray diffraction
SQUID	Superconducting quantum interference device
TLC	Thin layer chromatography
NMR	Nuclear magnetic resonance
ESI-MS	Electrospray ionisation mass spectrometry
IR	Infra-red
UV-Vis	Ultraviolet-visible
TMS	Trimethylsilane

CHAPTER 1

INTRODUCTION

1.1 Objectives

This research study seeks to synthesise polynuclear iron and copper clusters with derivatised salicylaldoxime ligands. The basic characterisation techniques such as IR, UV and CHN, together with VT magnetic studies, as well as Mössbauer studies were performed on the metal complexes. The solid state structure of a number of the complexes was also determined using single crystal X-ray diffraction techniques. The salicylaldoxime ligands synthesised are all new and they were characterised with ^1H , ^{13}C , relevant 2D NMR, IR, ES-MS and CHN analyses.

This research was undertaken to explore, how simple salicylaldoxime functionalised ligands and ‘strapped’ or double-headed salicylaldoxime derivatives can vary the nuclearity and the structure of the metal clusters. There is significant interest in the magnetic properties of high nuclear iron clusters.

1.2 Magnetism

The origin of magnetism has its root in the arrangement of electron spin at the atomic level. There are several magnetic behaviours that have been identified in solids, the most common types being, dia-, para-, ferro-, ferri-, and antiferromagnetism.¹ Traditional magnetic materials are composed of transition or lanthanide metal-containing spin systems and they are usually arranged in one, two or three dimensional arrays of the inorganic atoms.

There are two fundamental types of magnetism on the atomic level: diamagnetism and paramagnetism and all the other complex magnetic behaviours evolve from these two basic types of magnetism. Diamagnetism emerges as a result of the interaction between the applied magnetic field and the orbital with paired electrons. Diamagnetic substances repel the applied magnetic field in the opposite direction. On the other hand, paramagnetic substances are attracted into the applied magnetic field. Paramagnetism

arises from the interaction between the applied magnetic field and the unpaired electrons in the atomic or molecular orbitals. The paramagnetic interactions depend on the temperature.

1.2.1 Magnetisation (M) / A m^{-1}

This can be defined as the *magnetic-dipole moment per unit volume* acquired by a substance in an applied magnetic field (H) and is proportional to the H (A m^{-1}).

Diamagnetic materials are where all the electrons are paired and the net spin is zero and these are weakly repelled by magnets. Both M and magnetic susceptibility χ_m are negative. The magnetic field within the material is reduced with the external magnetic field (H) (Figure 1.1).

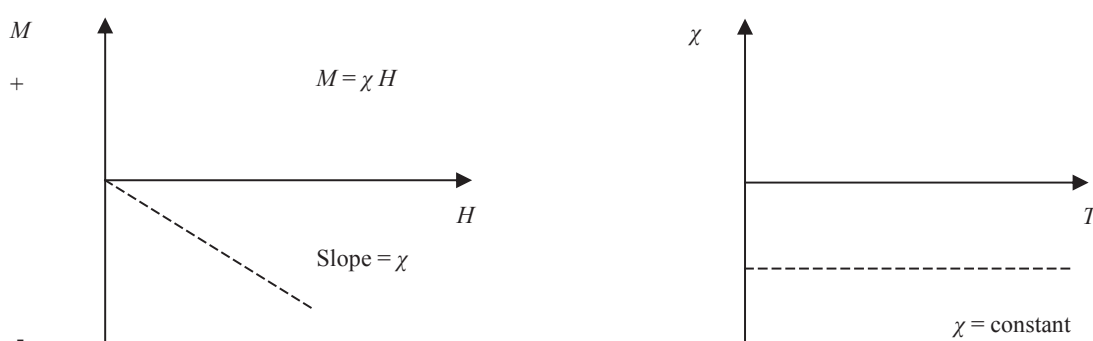


Figure 1.1: left: Variation of magnetisation (M) with external magnetic field (H), right: Variation of magnetic susceptibility (χ) with temperature (T) of diamagnets.

Paramagnetic materials have a net magnetic moment due to partially filled orbitals present and these are attracted by magnets. A net positive magnetisation results due to a partial alignment of the atomic magnetic moments in the direction of the applied magnetic field.

Magnetisation becomes zero when the external magnetic field is removed. The applied magnetic field orientates the magnetic dipole moments. But it is severely obstructed by thermal chaos in terms of rapid collisions of the molecules within the substance. This phenomenon leads to a randomisation of the orientation of the molecular dipole

moments. This results in a temperature dependent susceptibility, known as the Curie law discovered by P Curie in 1895 (see Figure 1.2).

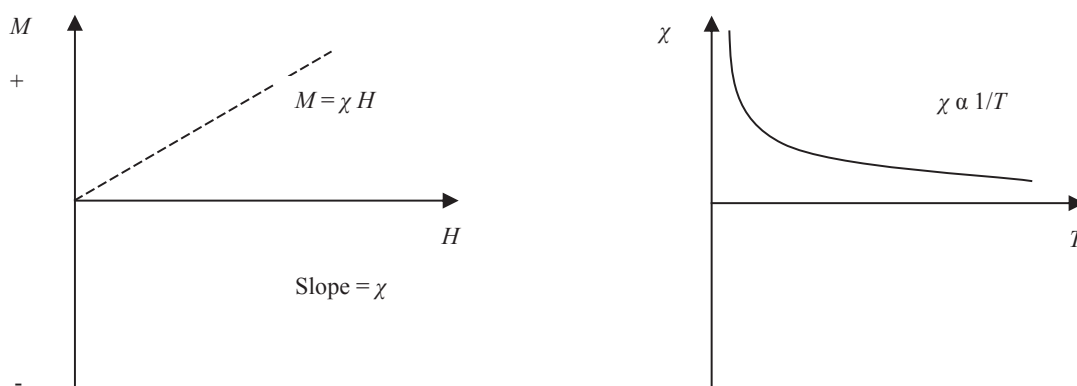


Figure 1.2: left: Variation of magnetisation (M) with external magnetic field (H), right: Variation of magnetic susceptibility (χ) with temperature (T) of paramagnets.

The relationship between magnetic susceptibility and temperature is given by; $\chi_m = C/T$, where C is the Curie constant (unit = K) and is unique for the atom or molecule concerned. χ_m is magnetic susceptibility which is dimensionless, and T is temperature in K.

Ferromagnetic materials are compounds where the unpaired electrons are held in an alignment by ferromagnetic coupling and these are strongly attracted by magnets. Ferromagnetism (it was originally seen in metallic Fe, so it is called ‘ferromagnetism’) is much less common. This is a form of cooperative magnetism at the atomic level between adjoining magnetic dipoles as a result of their parallel coupling. This parallel alignment of magnetic moments results in a large net magnetisation even in the absence of a magnetic field in *hard* magnets, i.e. they exhibit ‘*magnetic hysteresis*’. Therefore, spontaneous magnetisation and a magnetic ordering temperature are two main features of ferromagnetic materials. The magnitude of this spontaneous magnetisation at 0 K depends upon the spin magnetic moments of electrons (Figure 1.3).

The magnetisation in ferromagnetic materials is saturated in moderate magnetic fields and when T reaches 0 K or higher temperatures compared to paramagnetic materials. Paramagnetism switches to ferromagnetism when the temperature is lowered and χ_m can

reach up to $\sim 10^4$. This particular temperature is defined as the Curie temperature (T_c). Below the T_c , ferromagnets stay ordered but above this temperature they become disordered and saturation magnetization drops to zero at T_c (Figure 1.4).

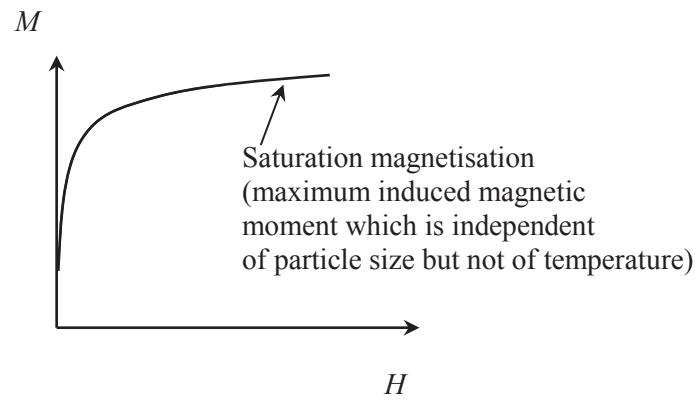


Figure 1.3: Applied magnetic field (H) vs magnetisation (M) in ferromagnetic materials.

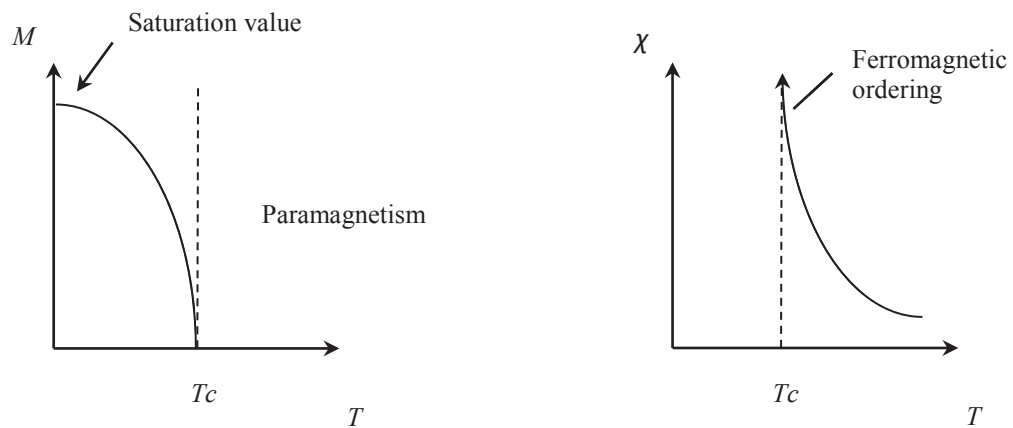


Figure 1.4: Switch from paramagnetism to ferromagnetism.²

Magnetic hysteresis is the ability of *hard* ferromagnets to retain a memory or retention of magnetisation (remanence or residual magnetisation) of an applied magnetic field once it has been removed and a hysteresis loop results from a plot of variation of magnetisation with applied magnetic field (Figure 1.5).

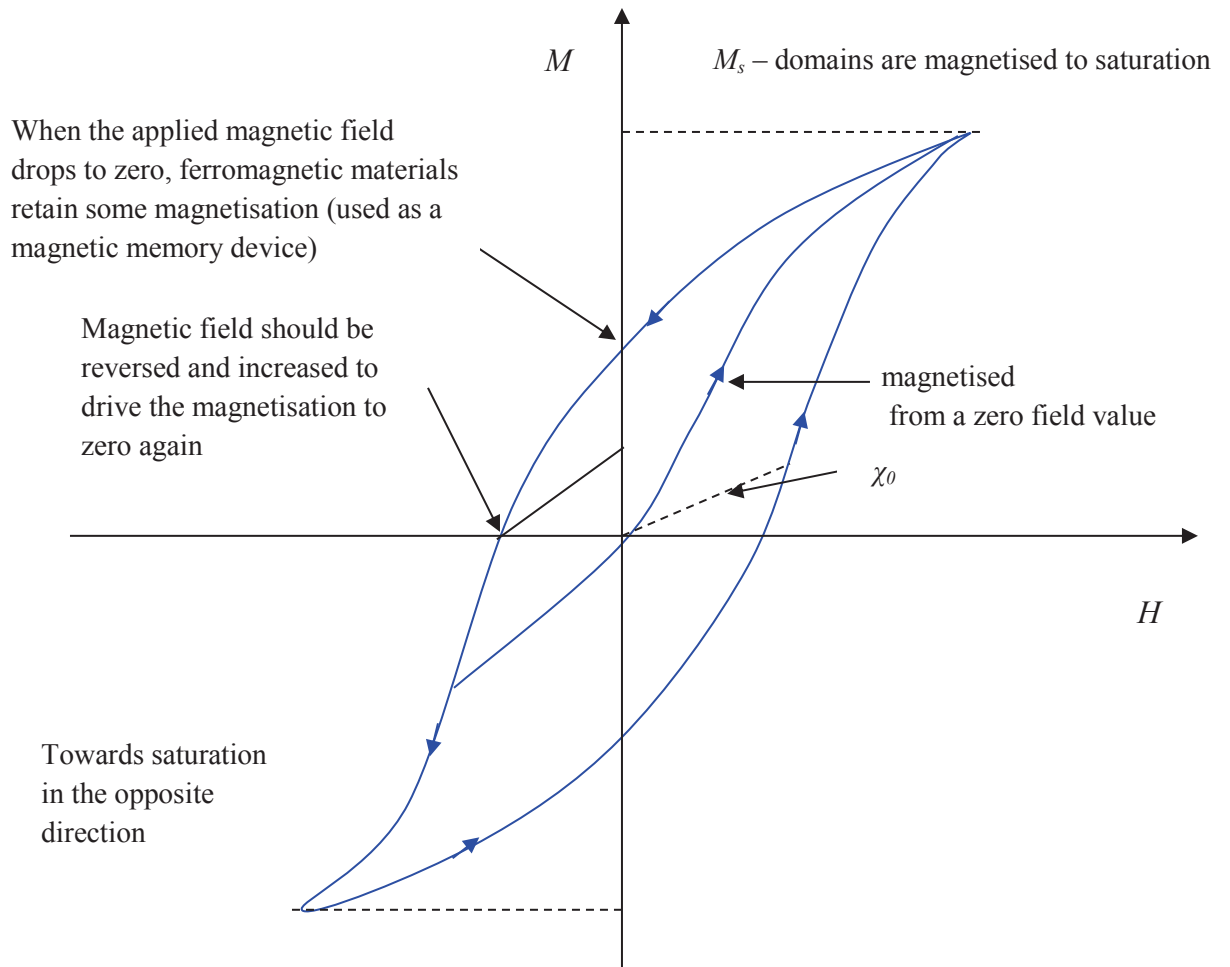


Figure 1.5: Hysteresis loop that exhibits the history dependent nature of magnetisation of ferromagnetic materials.

Magnetic domains - the sample consists of small regions called magnetic domains and within these domains the local magnetisation is saturated but not necessarily parallel. Local magnetisation vectors can be aligned by applying a magnetic field and these lead to the retainment of the cooperative magnetism within the sample once the field is switched off.

Ferrimagnetic materials are compounds where unpaired electrons present within a discrete molecule are held in a pattern with some spins up and some down, generally with more spins held in one direction. Therefore, these compounds are attracted by magnets. This phenomenon is seen in crystal structures. Magnetic crystal structures consist of sub lattices. As an example, two sub lattices (tetrahedral & octahedral) in magnetite are separated by oxygen. The exchange interactions are mediated by oxygen

anions. These interactions result in an anti-parallel alignment of the spins between two sub lattices which possess very different crystal sites. This difference leads to a complex form of exchange interactions between the iron atoms, between and within the two crystal sites. The ordering within sub-lattices is productively ferromagnetic. The net magnetisation within two sub-lattices is unequal in magnitude and they interact in opposite direction (or they *anti-ferromagnetically* interact) which ultimately results in a net magnetisation.

When antiferromagnetic materials are cooled to low T (below T_c), the unpaired electrons are aligned as each direction has an equal number of spins. These materials are strongly repelled by magnets. This anti-parallel configuration occurs as a result of a spontaneous magnetic ordering of adjacent dipoles and it is repeated all through the lattice. The majority of the magnetic dipoles tend to orientate with a moderately strong applied magnetic field while a few dipoles align in the opposite direction. In this case, the interaction between these two sets is stronger than the dipole in the field direction.

In the case of having crystallographically equivalent magnetic centres (Mn^{2+} in MnO), the dipoles within two sub-lattices are oppositely aligned which leads to a resultant net zero magnetisation as the temperature tends to absolute zero. As the temperature rises, anti-parallel alignment is disturbed by thermal chaos, which ultimately leads to an increase in the susceptibility. Then, the antiferromagnetism switches to paramagnetism at a certain temperature which is called the Néel temperature (T_N). T_N is characteristic of the material (see Figure 1.6).

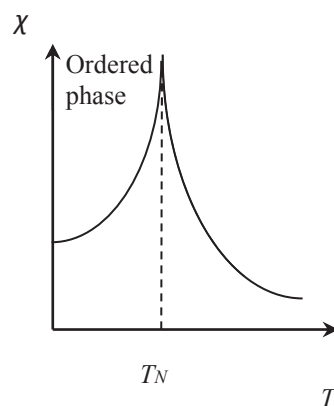


Figure 1.6: Paramagnetism-antiferromagnetism transition.²

For ferromagnetism, antiferromagnetism, and ferrimagnetism, the domain structure is disturbed due to the temperature as a result of vibrational motions, and therefore, the magnetic properties of these materials are strongest at low temperatures. At high temperatures, these materials become paramagnetic and the particular temperature at which this property is seen is called the *Curie temperature* (T_c) and for the antiferromagnetic materials, it is called the *Neel temperature* (T_N). Effective magnetic moment is unable to be used to describe the magnetic behaviour of these materials due to their dependence upon the temperature and the magnitude of the external magnetic field unlike in the case of paramagnets and diamagnets. A net magnetic moment may be given by the alignment of the magnetic moments even without an external field and this will result in a permanent magnet. A material can have a net magnetic moment retained only after being exposed to an external magnetic field. This property is used to store information in cassettes and video tapes and a strong memory is indicated by a wide hysteresis loop.

In paramagnetic compounds;

$$\chi = C / T,$$

where $C = (Ng^2\mu_B^2)S(S+1)/ 3k_B$, where χ = magnetic susceptibility, C = Curie constant, T = absolute temperature, N = Avogadro's number, g = electron g factor, μ_B = the Bohr magneton, k_B = the Boltzman constant. An inverse relationship between χ and T is observed in most paramagnetic compounds, but extrapolation of temperature to zero does not obey the Curie law. These compounds obey the Curie-Weiss law;

$$\chi = C / (T - \theta),$$

where, θ is the Weiss constant which can have values in the range -70 to 3000 K (see Figure 1.7).

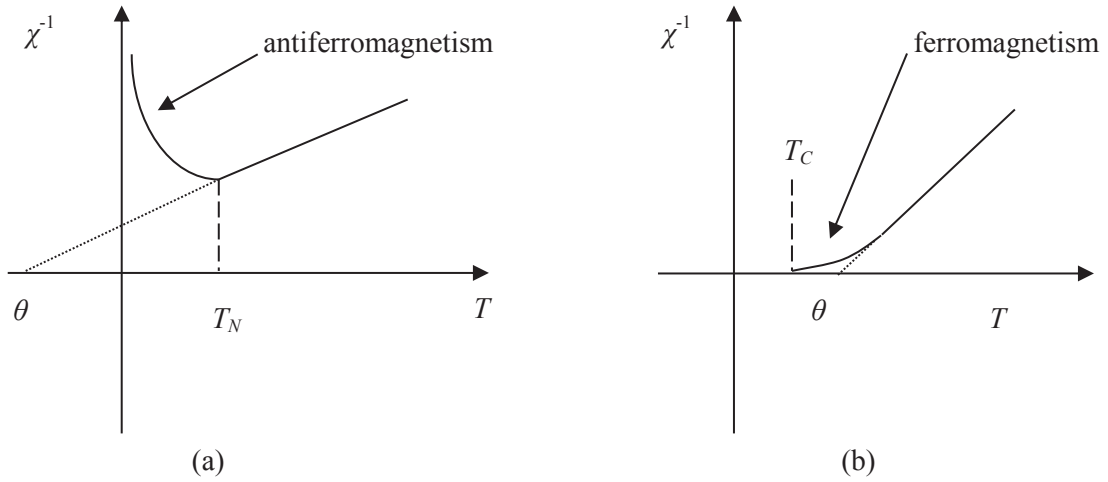


Figure 1.7: Illustration of the Curie-Weiss law in (a) antiferromagnetic and (b) ferromagnetic materials.²

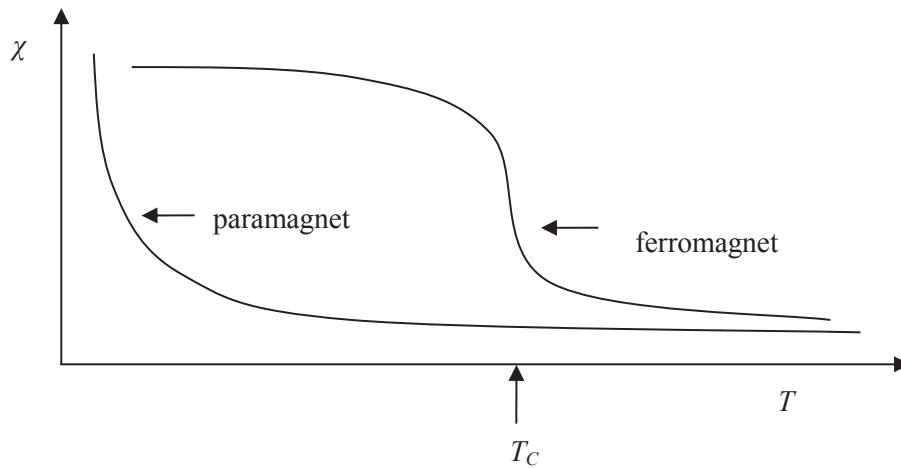


Figure 1.8: Curie temperatures.

In ferromagnetic and ferrimagnetic compounds, the curvature of the graph changes when the Curie temperature is reached (Figure 1.8) and at this temperature, these compounds become paramagnetic. Magnetic susceptibility of antiferromagnetic materials increases until its T_N and then they also become paramagnetic.¹

Mono or polynuclear clusters form 3D magnetic ordering at a finite temperature (T_c) which is known as long-range order and it may be ferro- or antiferromagnetic. This 3D order is dependent upon the interaction type that is present between the isolated units. In general, conversion of a paramagnetic state to an ordered magnetic state is a phase

transition and the molecular spin orientation is independent of nearby atoms. But, when T_c is reached, correlation begins to be finite and it will be infinite when $T = T_c$. All the total spin correlations occur below this temperature. When the correlations among ions are ferromagnetic, all spins will be parallel while the neighbour spins are anti-parallel when they are antiferromagnetic. Above the T_c , all spins align according to the external magnetic field and then go back to normal random positions when the field is removed. Nevertheless, long range order is observed below T_c where all spins will be aligned parallel if the order is ferromagnetic even in the absence of an external magnetic field. Molecular magnetism has been studied for many years with molecule-based magnets and these have shown the typical properties of a classical magnet such as magnetite (Fe_3O_4). They show an increase in magnetisation to saturation when the temperature is decreased and exhibit magnetic hysteresis where the opposite magnetic field has to be supplied to drop the magnetisation to zero which causes remnant magnetisation. A coercive field/opposite directed magnetic field should be supplied to avoid this remnant magnetisation.^{2,3}

1.2.2 Exchange interactions occur in polynuclear clusters

Direct exchange interactions occur as a result of the direct overlap between the half occupied orbitals of metal ions without intermediate ligand orbitals.

Superexchange interactions occur as a result of the overlap between the half occupied orbitals of metal ions via intermediate ligand orbitals. Superexchange can occur in polynuclear clusters in two ways; antiferromagnetic exchange (see Figure 1.9) can occur between the metal centres when the M-L-M bond angle is linear (180°) and when it is reduced to 90° ; the ferromagnetic exchange can occur between metal ions by aligning unpaired electrons on the metal ions with *different* p -orbitals on the ligand (see Figure 1.10).²

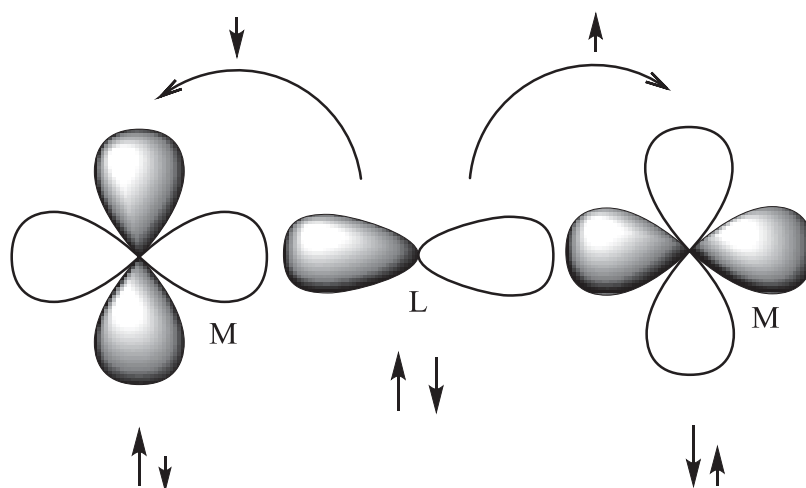


Figure 1.9: Antiferromagnetic superexchange.

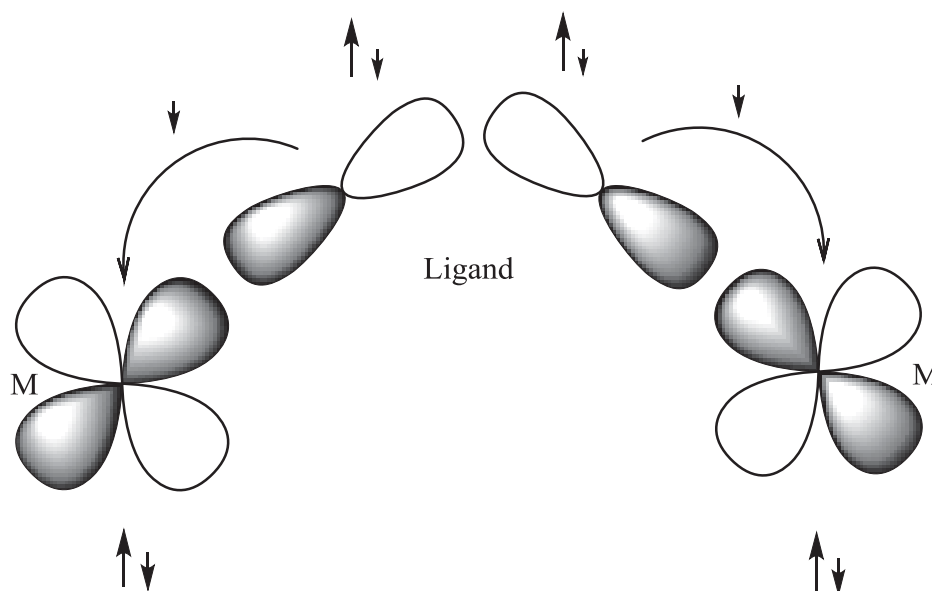


Figure 1.10: Ferromagnetic superexchange.

One of the fastest growing subfields in the area of molecular magnetism has been the exploration of the magnetic behaviour of polynuclear complexes. The studies in this field have led to the modelling and understanding of the behaviour of many bioinorganic processes³ and the synthesis of many novel molecules known as molecule-based magnets.⁴ In the early 1990's, it was discovered that certain molecular transition-metal clusters could be magnetised without long-range collective interactions and it was first observed in the coordination complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$ (**1**) or Mn_{12}OAc that consists of 12 oxide and acetate bridged manganese ions. This new series

of discrete molecules is called Single Molecule Magnets (SMMs).⁵ This cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (**I**) was reported to be obtained as the product of the reaction between MnO_4^- and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ by Lis *et. al.*⁶

Mn_{12}OAc has been abundantly used to synthesise carboxylate derivatives by substitution with other carboxylates. It has been determined that it is not a requirement to have high nuclearity for molecules to behave as SMMs. The second and the properly identified SMM is $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ (**II**) (tacn=1,4,7-triazacyclononane) and some other families of SMMs exist such as vanadium(III), cobalt(II), nickel(II), and mixed metal clusters.⁷ Construction of SMMs containing only a single metal ion centre has been led by the discovery of slow magnetic relaxation in lanthanide complexes such as $[\text{LnPc}_2]^-$ (Pc=dianion of phthalocyanine; Ln=Tb, Dy, Ho).⁸

The discovery of $[\text{Co}(\text{hfac})_2\{\text{NIT}(\text{C}_6\text{H}_4\text{OMe})\}]$ (**III**) (hfac=hexafluoroacetylacetonate, NIT=2-(4'-R)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) in 2001 has led to an expansion in the study of SMMs. This cluster shows hysteresis above 4 K without undergoing 3D magnetic ordering.⁹ A strong Ising (or easy axis) type of anisotropy (negative Zero Field Splitting/ZFS) and a very low ratio of interchain/intrachain interactions are necessary for the slow magnetization dynamics. These two requirements are very tricky to fulfil. A new dinuclear Mn^{3+} complex has been reported which has an intermediate behaviour between SMMs and SCMs (Single Chain Magnets).¹⁰

1.3 Single molecule magnets (SMMs)

SMMs exhibit magnetic hysteresis below a particular temperature (blocking temperature/ T_B).^{5,11} Usually, the metallic core of the molecules covered by organic ligands behaves as an individual nanomagnet. Large total ground state spin (S) favours the molecules to exhibit such properties. A large S will have $2S+1$ microstates which are denoted by M_S . M_S loses degeneracy in the absence of an applied magnetic field (zero field splitting/ZFS (D)) due to spin-orbit coupling interactions which in turn lead to an energy barrier (ΔE) to the reversal of the spin.

For example, consider the system with a ground state spin, $S = 10$ (see Figure 1.11) where the lowest energy state occurs at $M_S = \pm S$ and the highest energy state is at $M_S =$

0. The molecule must overcome the energy barrier (ΔE) to change from the $M_S = +10$ state level to $M_S = -10$ state. This energy barrier is calculated as,

$$\Delta E \propto S^2 |D| \text{ (for integer spins)}$$

$$\Delta E \propto (S^2 - 1/4) |D| \text{ (for half-integer spins)}^{12,13}$$

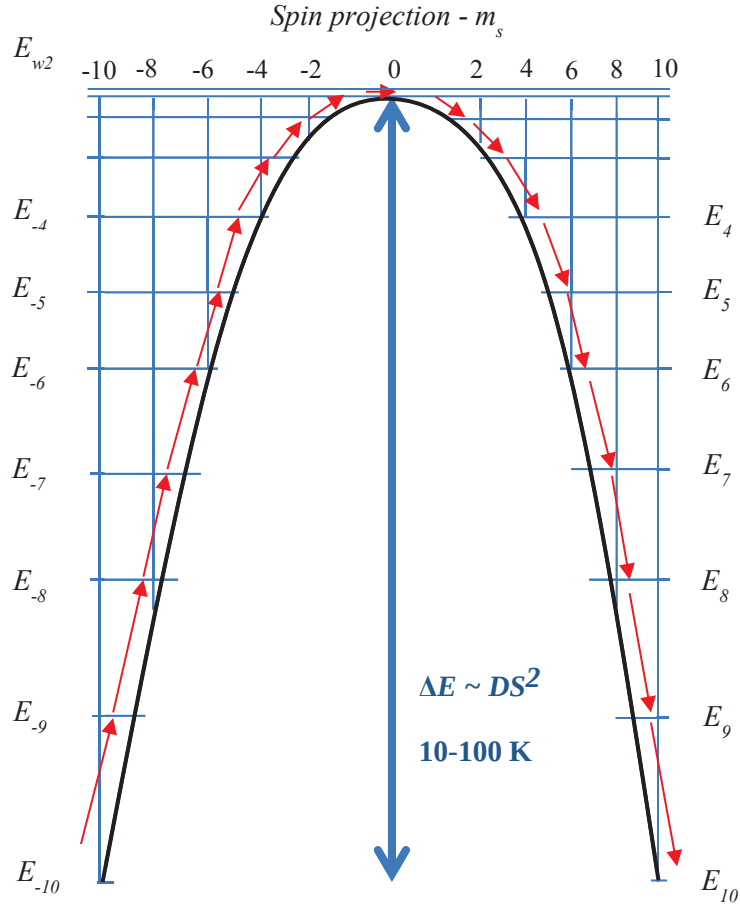


Figure 1.11: Energy diagram exhibiting the relative positions of the ZFS, M_S levels of an $S=10$ system (blue arrow indicates the energy barrier and the red arrows indicate the thermal pathway to reorientate from $-M_S$ to $+M_S$), and the barrier between the M_S+10 and -10 states).

When the magnetic field which is applied in order to populate a microstate energy well is removed, the molecule will retain its magnetisation. The time taken for the relaxation is given by the Arrhenius equation, $\Gamma = \Gamma_0 \exp(\frac{E_{eff}}{k_B T})$, where τ is the relaxation time, τ_0 is the pre-exponential factor, and k_B is the Boltzmann constant. Reversal can take years to occur for some cases. This barrier is only balanced by thermal activation. But, quantum phenomena such as quantum tunnelling of magnetisation (QTM) and quantum phase interference (QPI)¹⁵ occur due to the nanosize of the molecules. In the case of

QTM, the magnetisation can reverse through the barrier instead of needing to overcome the energy barrier. This can take place only when two M_S states at the same energy level are separated by the barrier. This easily can occur at the zero-field (see Figure 1.12) and it is also possible if an axial field is applied, so that $H = nD/g\mu_B$, where g is a fitting parameter and μ_B is Bohr magneton.¹⁶

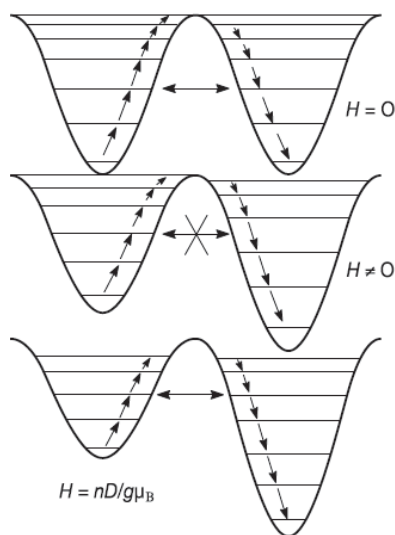


Figure 1.12: Change in potential-energy of an SMM as the magnetic field is changed from $H = 0$ to $H = nD/g\mu_B$.¹⁴

Mn_{12}Ac has been the first as well as the best example to date which has shown important quantum effects (Figure 1.13 and 1.14). The T_B of this molecule was found to be 3 K, $S = 10$ spin ground state¹⁷ and $D = -0.5 \text{ cm}^{-1}$ which results in an effective energy barrier of $E_{\text{eff}} = 60 \text{ K}$.¹⁷ SMMs are considered to be very important for further study because of their future applications in magnetic data storage or as qubits in quantum computers.^{5,19-23}

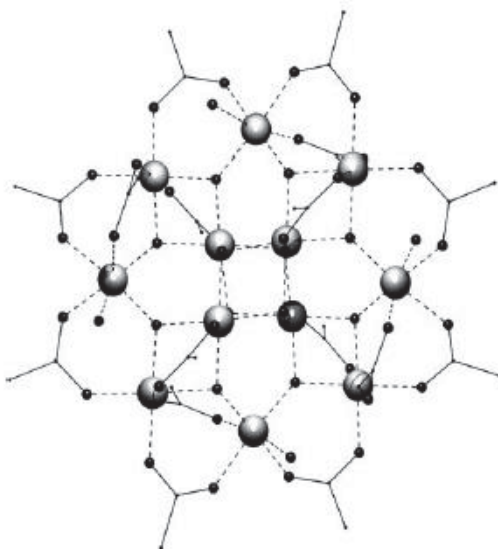


Figure 1.13: Structure of $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (**I**) (codes for atoms: large grey; Mn, medium black; O, rest; C, and H atoms are omitted for clarity).⁵

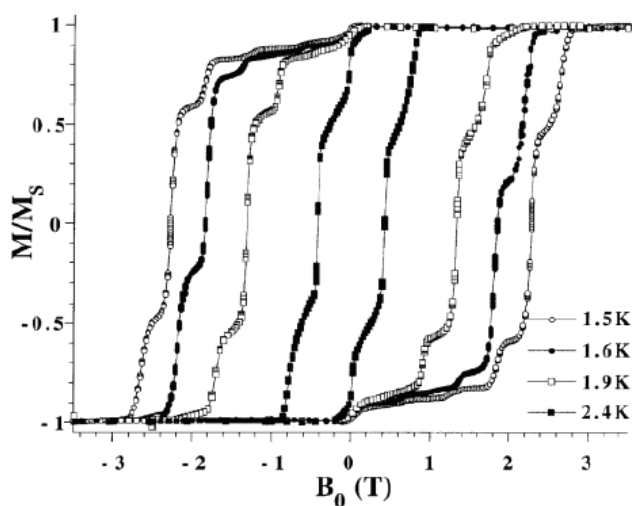


Figure 1.14: Hysteresis loop of magnetisation for Mn_{12}Ac .²²

1.3.1 Magnetic properties of iron

The highest ground state spin for Fe is $5/2$ and comes from the oxidation state of Fe(III). Mostly, the dominant exchange interactions between neighbouring Fe(III) are antiferromagnetic which make the synthesis of iron clusters with large spin ground states very difficult and subsequently the geometric shape of the complex can have a great effect on the exchange interactions that occur between the metal centres in the iron clusters. It is important to note that antiparallel alignment of the spins between interacting Fe(III) centres is much more common than parallel alignment.

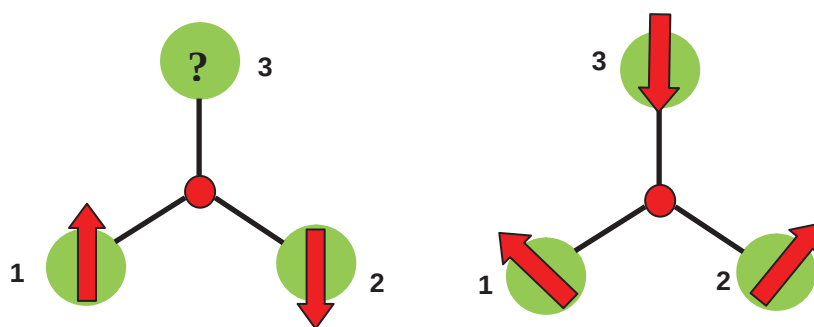


Figure 1.15: Schematic diagram of spin alignment of μ_3 -oxo bridge (Fe = light green; O = red).

As Figure 1.15 illustrates, the spin alignment between the metal ion 1 and 2 is antiparallel and the metal ion 3 should also have antiferromagnetic interactions both with metal ion 1 and 2. But, if the spin of the metal ion 3 aligns antiparallel to that of the metal ion 1, the spin of the metal ion 3 will align parallel to that of the metal ion 2 which makes the system energetically unfavourable. Therefore, this contradiction leads to a spin frustration generating a non-zero ground state spin.^{24,25}

1.4 Salicylaldoxime-metal clusters

1.4.1 Iron complexes

Ephraim first used salicylaldoxime as a ligand to complex with metal ions in 1930.²⁶ Shortly after 1935, X-ray structural reports²⁷ on the square planar metal complexes of Ni(II), Pd(II), and Pt(II) were published. But there were only a few structural reports²⁸⁻³⁹ on salicylaldoximate-complexes. The metal clusters of salicylaldoxime or derivatised salicylaldoximes have been widely investigated as some of them are biologically important and most of them are important as magnetic materials.^{40,41} The most synthesised and studied oxime-bridged metal clusters are Mn(III) containing complexes and oxime-bridged $[\text{Fe}_3\text{O}]$ structural analogues of the manganese complexes.⁴²

Polynuclear iron clusters are studied for diverse reasons.^{43,44} As an example, bioinorganic chemists are interested in synthesising iron cages for further understanding their role in the iron containing protein ferritin which keeps and regulates Fe within

living organisms.⁴⁵⁻⁴⁷ Additionally, the large spin of the Fe(III) ions also allows these clusters to possess a large spin ground state and / or interesting magnetic properties.⁴⁸

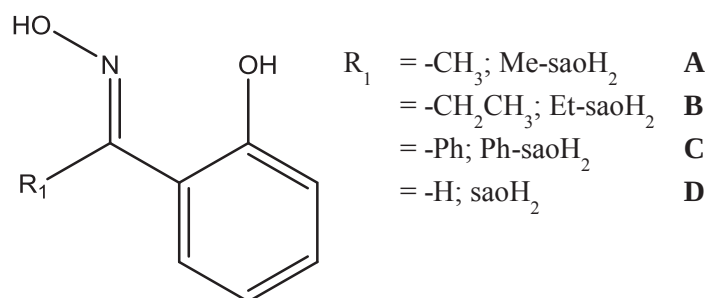


Figure 1.16: Structural formulae of salicylaldoxime ligands discussed in the text.

The first reported Fe(III)-salicylaldoxime complex $[\text{Fe}_4\text{O}(\text{saoH})_4(\text{sao})_4]$ (**IV**) was a tetranuclear species synthesised using the simplest salicylaldoxime (see D in Figure 1.16).⁴⁹ There are many examples of Fe(III)-salicylaldoxime-derivatised complexes that have been reported during the past two decades. The nuclearity of those complexes varies from two to up to ten.⁴⁹⁻⁵⁶ Particularly, a few trigonal prismatic assemblies including the hexanuclear Fe(III) complex $[\text{HNEt}_3]_2[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{Et-sao})_4(\text{O}_2\text{CPh}(\text{Me})_2)_6] \cdot 2\text{MeCN}$ (**V**) synthesised with a derivatised salicylaldoxime ligand (Figure 1.16, B) have been reported by Mason *et al.*⁵² An analogue of the trigonal prismatic core of the latter example has been observed by M. Hołyńska *et al.*⁵⁷ The presence of a central proton between the triangles, hypothesised by Mason *et al.*⁵² in the crystal structure, was later proved in the analogous Fe(III) complex published by Hołyńska *et al.*⁵⁷, who provided experimental evidence such as X-ray diffraction and IR to confirm the hydrogen atom location (see Figure 1.17, H2 between the triangles). The X-ray structure of the complex displays the distances between the Fe atoms between the two $[\text{Fe}^{\text{III}}_3\text{O}]$ triangles lie in the range of 3.145(2) - 3.165(2) Å and the distance between the central oxygen atoms is 2.537(7) Å. The shifts of the central oxygen atoms towards each other from the metal planes of the two triangles are 0.265(5) Å and 0.358(5) Å. They reported magnetic susceptibility measurements in an applied dc magnetic field of 0.1 T in the temperature range of 280 – 1.8 K. They observed a very low value of 8.3 $\text{cm}^3\text{Kmol}^{-1}$ for χT at RT which is very lower than the expected value (26.25 $\text{cm}^3\text{Kmol}^{-1}$) for six non non-interacting Fe(III) ions and it decreases up to 0.36 $\text{cm}^3\text{Kmol}^{-1}$ with the cooling to 1.8 K as expected due to the presence of dominant intra-complex

antiferromagnetic interactions. The analysis of Mössbauer spectroscopic results at 78 K indicate a single symmetric quadrupole doublet at an isomer shift (δ) of 0.49 mms^{-1} which subjects to symmetric quadrupole splitting of 0.45 mms^{-1} that reveal single iron species.⁵⁷

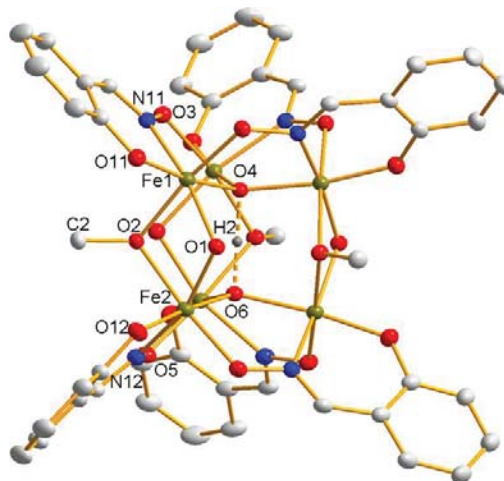


Figure 1.17: Metallic core of the complex $[\text{Fe}_6\text{O}_2\text{H}(\text{sao})_6(\text{CH}_3\text{O})_3(\text{OH})_3]^{3-}$ (**VI**) (all the H-atoms are omitted for clarity except the proton between the $[\text{Fe}_3\text{O}]$ triangles and the symmetry-independent part is labelled).⁵⁷

In 2008, Gass *et al*⁵⁸ published a series of Fe complexes with derivatised salicylaldoxime ligands. When the ligand Ph-saoH₂ with a bulky group -Ph at the R1 position (see Figure 1.16) is reacted with $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ in a methanoic solution in the presence of Et_3N a dinuclear cluster, $[\text{HEt}_3\text{N}][\text{Fe}_2(\text{OMe})(\text{Ph-sao})_2(\text{Ph-saoH})_2] \cdot 5\text{MeOH}$ (**VII**) is formed. As this formula indicates, it consists of two fully deprotonated ligands and two half deprotonated (at the phenolic positions) ligands.

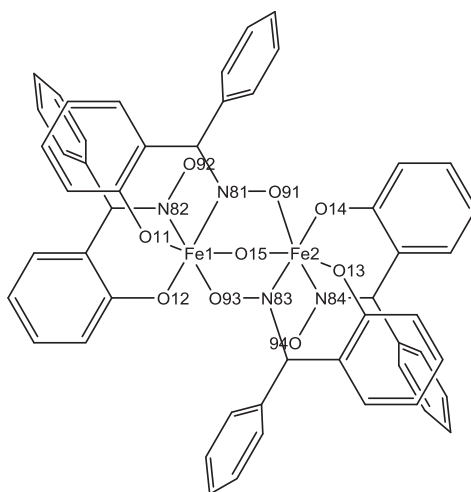


Figure 1.18: The molecular structure of the anion of $[\text{HEt}_3\text{N}][\text{Fe}_2(\text{OMe})(\text{Ph-sao})_2(\text{Ph-saoH})_2] \cdot 5\text{MeOH}$ (**VII**).

Both Fe ions lie in the distorted octahedral geometry where the coordination sphere of each Fe is occupied by a phenolate oxygen atom and an oximic nitrogen atom of a ligand molecule which is fully deprotonated, a phenolic oxygen atom and an oximic nitrogen atom of the adjacent half deprotonated ligand molecule as well as a central MeO⁻ and an oximic oxygen atom of a neighbouring fully deprotonated ligand molecule (see Figure 1.18).

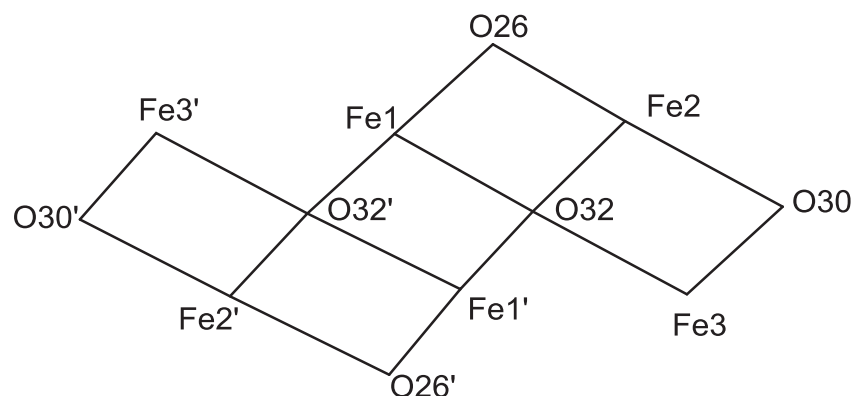


Figure 1.19: Fe-O core of $[\text{HEt}_3\text{N}]_2[\text{Fe}_6\text{O}_2(\text{Me-sao})_4(\text{SO}_4)_2(\text{OMe})_4(\text{MeOH})_2]$ (**VIII**).

The same reaction carried out with the less bulky ligand Me-saoH₂ forms a hexanuclear complex, $[\text{HEt}_3\text{N}]_2[\text{Fe}_6\text{O}_2(\text{Me-sao})_4(\text{SO}_4)_2(\text{OMe})_4(\text{MeOH})_2]$ (**VIII**). Therefore, the oxime ligand possessing a less bulky R1 group produces a larger cluster together with bridging SO_4^{2-} ions. The core of the complex illustrates that Fe ions are connected through two O^{2-} ions (O32 & O32') and four MeO⁻ ions (O26, O26', O30, & O30') forming a $[\text{Fe}_6\text{O}_2(\text{OMe})_4]^{10+}$ core (see Figure 1.19). It is interesting to note, when Et-saoH₂ is reacted with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a methanolic solution in the presence of NaOOCPh in a molar ratio of 1:1:1 and 0.5 of NEt_4OH , the nuclearity has increased to three together with a fully deprotonated salicylaldoxime, five carboxylate molecules, and two methanol molecules to form the complex $[\text{Fe}_3\text{O}(\text{Et-sao})(\text{O}_2\text{CPh})_5(\text{MeOH})_2] \cdot 3\text{MeOH}$ (**IX**). All the Fe(III) ions lie in a distorted octahedral geometry. The same reaction carried out with a molar ratio of 3:5:1 with Me-saoH₂ forms a tetranuclear complex $[\text{Fe}_4(\text{Me-sao})_4(\text{Me-saoH})_4] \cdot \text{MeOH}$ (**X**) with no carboxylates. It has also been reported that the reactions of Me-saoH₂, Et-saoH₂, and Ph-saoH₂ with $\text{Fe}(\text{O}_2\text{CMe})_2$ in the presence of triethanolamine (H_3tea) in methanolic solutions have yielded octanuclear isostructural complexes having the common formula $[\text{Fe}_8\text{O}_3(\text{R1-sao})_3(\text{tea})(\text{teaH})_3(\text{O}_2\text{CMe})_3] \cdot x\text{MeOH}$ (**XI**) (see Figure 1.20) where, x is the number of MeOH molecules. Therefore, incorporation of tripodal alcohol with oximes

has led to the formation of larger Fe clusters. The relatively large negative magnetic exchange interaction values (J) and the monotonic decrease of temperature dependence of magnetic susceptibility values ($\chi_M T$) upon cooling are suggestive of the presence of relatively strong antiferromagnetic interactions between the metal centres.

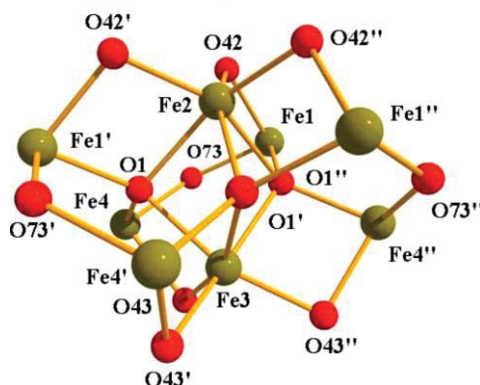


Figure 1.20: Fe-O core of $[\text{Fe}_8\text{O}_3(\text{R1-sao})_3(\text{tea})(\text{teaH})_3(\text{O}_2\text{CMe})_3] \cdot x\text{MeOH}$ (**XI**).⁵⁸ Atom O1 is the oxo group.

Several hexa- and octanuclear Fe complexes have been synthesised with derivatised salicylaldoximes (Me-saoH₂ and Et-saoH₂) and the resulting complexes subjected to a structural and magnetochemical analysis. The crystal structures and magnetic behaviour have been studied in 2011 by Mason *et al.*⁵⁴ An octanuclear complex $[\text{Fe}_8\text{O}_2(\text{OMe})_4(\text{Me-sao})_6\text{Br}_4(\text{py})_4]$ (**XII**) was produced by reacting FeBr₃ with Me-saoH₂ in a MeOH/pyridine solution. This complex consists of two tetrahedra $[\text{Fe}_4\text{O}]$ sharing two Fe(III) ions in the middle. Each tetrahedron is capped by another Fe(III) ion on either side of the core (see Figure 1.21). This is the first time that the μ_4 -coordination mode has been observed using oxime ligands. Bromide ions, pyridine molecules, and also MeO[−] ions have all contributed in completing the coordination spheres around the Fe(III) ions.

Modification of the complex could be achieved by anion exchange, for example, the terminal Br[−] ions were replaced with terminal azide ligands and $\mu\text{-OMe}^-$ bridge was partially replaced by a $\mu\text{-N}_3^{3-}$ bridge by introducing NaN₃ to the reaction mixture yielding the complex $[\text{Fe}_8\text{O}_2(\text{OMe})_{3.85}(\text{N}_3)_{4.15}(\text{Me-sao})_6(\text{py})_2]$ (**XIII**). The presence of bridging azides in Fe³⁺ cluster chemistry promotes ferromagnetic exchange interactions.^{59,60}

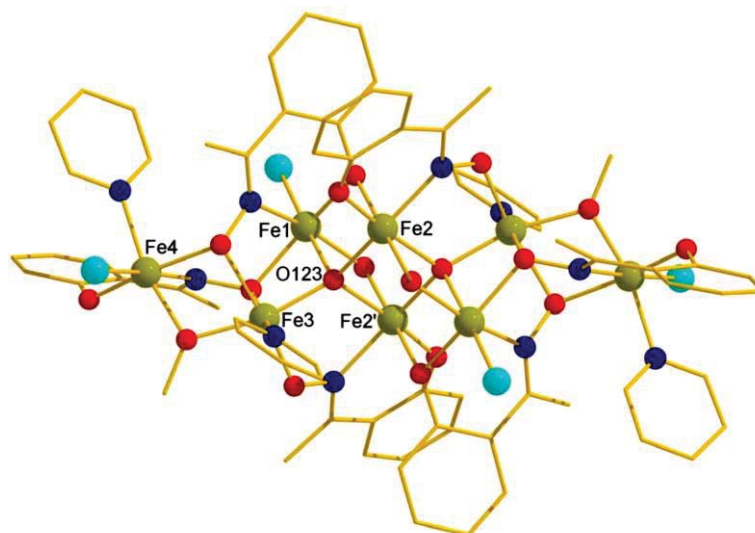


Figure 1.21: The molecular structure of $[\text{Fe}_6\text{O}_2(\text{OMe})_4(\text{Me-sao})_6\text{Br}_4(\text{py})_4]$ (**XII**) (Fe-olive green, O-red, N-dark blue, C-gold, Br-light blue).⁵⁴ Atom O123 is the oxo group.

Introduction of carboxylates in the form of $\text{NaO}_2\text{CPh-4-NO}_2$ to the reaction between $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Me-saoH_2 in a molar ratio of 1:1:1 in a MeOH/pyridine solution leads to the hexanuclear complex $[\text{Fe}_6\text{O}_2(\text{OMe})_4\text{Cl}_2(\text{O}_2\text{CPh-4-NO}_2)_4(\text{Me-sao})_2\text{Cl}_2(\text{py})_2]$ (**XIV**). A number of μ -bridging carboxylates have capped the Fe^{3+} ions at either end of the structure (see Figure 1.22). The analogue of the latter complex is produced when the reaction is repeated with the ligand Et-saoH_2 . The authors failed to isolate complexes using any other carboxylates, which they attributed to the steric effects by the $-\text{NO}_2$ group and / or the stable interactions between the neighbouring $-\text{NO}_2$ groups. It has been observed that introduction of carboxylates to the reactions and μ -coordination of the oximes appear to lead to smaller clusters. Again, hexanuclear clusters are formed when $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ is reacted in air with Me-saoH_2 in the presence of Et_3N in a methanolic solution⁵⁸ and its analogous structure is produced when the reaction is repeated with Et-saoH_2 . Moreover, all the complexes have been found to contain relatively strong antiferromagnetic exchange interactions.

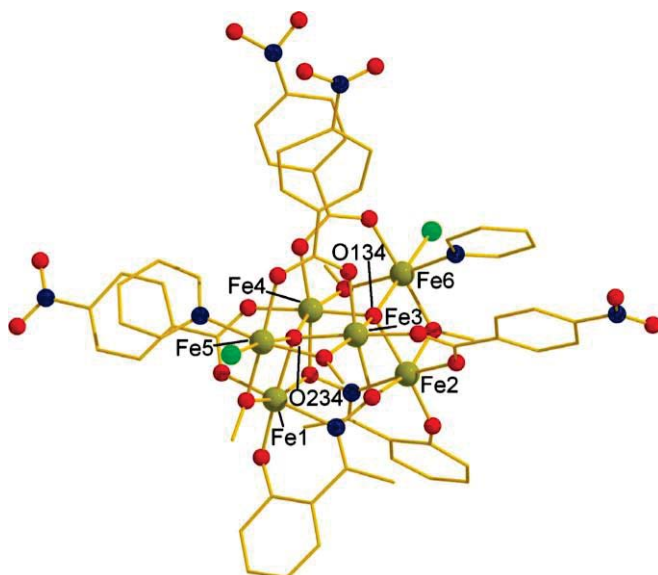
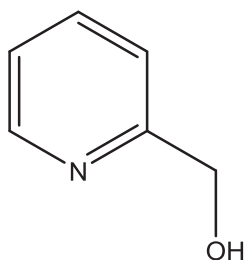
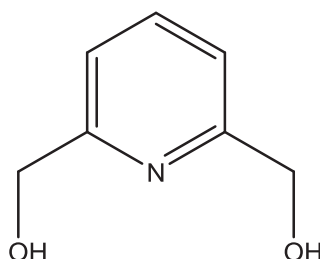


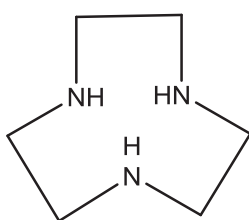
Figure 1.22: The molecular structure of $[\text{Fe}_6\text{O}_2(\text{OMe})_4\text{Cl}_2(\text{O}_2\text{CPh-4-NO}_2)_4(\text{Me-sao})_2\text{Cl}_2(\text{py})_2]$ (**XIV**) (Fe-olive green, O-red, N-dark blue, C-gold, Cl-bright green).⁵⁴ Atoms O134 and O234 are the oxo groups.



2-(hydroxymethyl)pyridine; hmpH



2,6-di(hydroxymethyl)pyridine; pdmH₂



1,4,7-triazacyclononane; tacn

Figure 1.23: Widely used co-ligands in the synthesis of Fe(III) clusters.

The synthesis of polynuclear iron clusters utilising derivatised salicylaldoximes in the presence of a number of co-ligands has been reported by Mason *et al* in 2013.⁶¹ The co-ligands play a role in completing the iron coordination sites (see Figure 1.23). The co-

ligands were chosen based on their previous success in synthesising Fe clusters.⁶²⁻⁸² The introduction of tacn as the co-ligand in the reaction of saoH_2 with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ with excess Et_3N has formed a tetrairon 'butterfly' complex from tetrametallic cubes formed purely with R-saoH₂ ($[\text{Fe}_4(\text{Me-sao})_4(\text{Me-saoH})_4] \cdot \text{MeOH}$ (**XV**) and $[\text{Fe}_4(\text{sao})_4(\text{saoH})_4] \cdot \text{saoH}_2 \cdot \text{C}_8\text{H}_{10}$ (**XVI**)).^{49,58} The replicate of the same reaction with Me-saoH₂ and Et-saoH₂ instead of purely saoH₂ in MeOH/MeCN has afforded analogous tetrairon complexes (**XVI**). In this case, the co-ligand tacn has dominated the structural formation in spite of the solvent or the ratio of the reactants employed. The reaction between $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and Et-saoH₂ in the presence of hmpH and NaOMe in MeCN has produced a nonametallic or nine metal complex in which a Na^+ ion present at the centre of the cluster might play an important role in determining the structure identity. This reaction is considered similar to the aforementioned reactions which were carried out in MeOH/MeCN that afforded the analogous structures of (**XVI**), except tacn has been replaced by hmpH. Therefore, the relatively flexible hmpH acts both as a chelating and bridging ligand providing numerous coordination sites. It has also been reported that repetition of the latter reaction produced a square Fe_4 cluster in the presence of $\text{Ca}(\text{OMe})_2$ instead of NaOMe. But the reaction with other R-saoH₂ family members has not produced any crystalline materials. When the phenyl derivatised oxime is substituted for the ethyl version under the same conditions as for the nonametallic complex, a square Fe_4 cluster is produced which suggests that the steric bulk present in the ligand has a direct influence on nuclearity.

Another nonametallic cage has been reported from the reaction of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and saoH_2 in the presence of pdmH_2 , saoH_2 , NaN_3 in MeOH/MeCN . The co-ligand, pdm^{2-} (Figure 1.23) present in this cage has been more dominant than hmp^- present in the previously mentioned nonametallic cage when the ratio of R-sao²⁻ : co-ligands present in the cages is considered. Further, the magnetic behaviour of all the 'butterfly' complexes discussed earlier has been found to have very strong antiferromagnetic exchange interactions and diamagnetic ground states.

1.4.2 Manganese complexes

The interest in synthesising polynuclear Mn complexes was inspired by the discovery of the complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**I**)⁸³ which could preserve the magnetisation within the cluster below its blocking temperature (T_B) and exhibit superparamagnetic-like behaviour with the manifestation of hysteresis loops.⁸⁴ These properties were found to be due to the large ground state spin (S) along with a significant negative zero-field splitting parameter (ZFS) D , which results in a high cost to reverse the magnetisation (ΔE_{eff}). The molecules that possess such behaviour were later named as Single Molecule Magnets (SMMs). Since then, many attempts have been directed towards synthesising metal clusters containing many metal ions, particularly manganese, due to desirable properties that this metal ion possesses such as large S and D values. Several complexes have been pursued in the quest for new types of SMMs with a hope to synthesise materials that can be explored in an extensive range of potential applications such as information storage, molecular spintronics, quantum computation, magnetic refrigeration and MRI.¹¹

The first ferromagnetic Mn triangle $[\text{Mn}^{\text{III}}_3\text{O}(\text{bamen})_3]^+$ was reported in 2002 where $\text{bamenH}_2 = 1,2\text{-bis}(\text{biacetylmonoximeimino})\text{ethane}$. This triangular shaped complex is different from the basic Mn carboxylates because it contains six diatomic oxime bridges (Mn-N-O-Mn) rather than six triatomic bridges (Mn-O-C-O-Mn).^{83,85} Stamatatos *et al.* reported a second example, $[\text{Mn}^{\text{III}}_3\text{O}(\text{MeCO}_2)_3(\text{mpko})_3]^+$, (see Figure 1.24) where, $\text{mpkoH} = \text{methyl-2-pyridyl ketone oxime}$. The latter complex consists of three triatomic Mn-O-C-O-Mn carboxylate bridges and three diatomic Mn-N-O-Mn oximate bridges, each of which bridges two Mn atoms on the same edge of the triangle.⁸⁶ The Mn complexes consisting of monoatomic bridges (Mn-O-Mn) have always been found to possess dominant antiferromagnetic exchanging interactions.⁸⁷

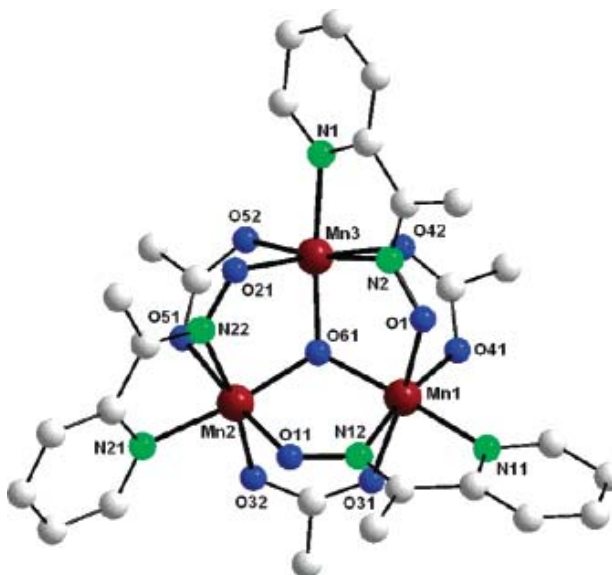


Figure 1.24: Crystal structure of the cation $[\text{Mn}^{\text{III}}_3\text{O}(\text{MeCO}_2)_3(\text{mpko})_3]^+$, Mn-brown, O-blue, N-green, C-gray.⁸⁶

The first salicylaldoxime-based manganese cluster $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{O}_2\text{CR})_2(\text{sao})_6(\text{EtOH})_4]$ where R = alkyl group (**XVI**) (see the structure type illustrated in Figure 1.25) was made in Patras, Greece in 2003, as a result of a simple reaction between $\text{Mn}(\text{O}_2\text{CR})_2 \cdot 2\text{H}_2\text{O}$ and salicylaldoxime (saoH_2) in EtOH. This metallic core has two equal stacked triangles, $[\text{Mn}^{\text{III}}_3(\mu\text{-O})(\text{sao})_3]^+$ which are common to this structural type. Each edge of the triangles are bridged by oximate groups ($-\text{N}-\text{O}-$) and these triangles are interconnected via two oxime groups which leads to a $[\text{Mn}^{\text{III}}_6(\mu\text{-O})_2(\text{NO}_{\text{oxime}})_6]$ magnetic core in the cluster. This cluster contains two μ -1,3-bridging carboxylates and four solvent molecules at the terminal bordering positions. The geometry of this metal cluster is distorted octahedral and all the Jahn-Teller axes are more or less perpendicular to the $[\text{Mn}_3]$ planes. There are two Mn ions in two triangles in the geometry of square pyramidal which is five coordinate and its axial bond length contact to the proximal phenolate O atom is $\sim 3.5 \text{ \AA}$ (see Figure 1.25). It has been found that the spin of the system was $S = 4$ with axial anisotropies, $D \approx -1.2 \text{ cm}^{-1}$ and $\Delta E_{\text{eff}} \approx 28 \text{ K}$.^{42(f),88,89}

It has been demonstrated that the total magnetic spin of the above system (**XVI**) can be halved to $S = 2$ by halving the cluster. This is achieved by capping it with two pyridine molecules and a water molecule which prevents dimerisation. This was easily achieved by dissolving the first complex $[\text{Mn}_6]$ into pyridine (see Figure 1.26). The axial anisotropy (D) of the cluster $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{O}_2\text{CR})_2(\text{sao})_6(\text{EtOH})_4]$ (**XVI**) is the largest among manganese complexes despite its small energy barrier. This $[\text{Mn}_6]$ complex has

been used as the starting material $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CR})_2(\text{R-sao})_6(\text{L})_{4-6}]$ ($\text{L}=\text{solvent}$; $\text{R}=\text{Me, Et, Ph}$) to synthesise various Mn clusters with improved SMM magnetic properties. A number of factors was identified that affect these properties such as differences in planarity of triangles in the cluster or steric concerns (torsion angle etc.) which have led to differences in magnetic exchange. As an example $[\text{Mn}_3\text{O}(\text{mpko})_3(\text{O}_2\text{CR})_3]^+$ ($\text{mpkoH} = \text{methyl 2-pyridyl ketone oxime}$) has been found to be ferromagnetic with $S = 6$. The location of central $\mu\text{-O}$ in the core is determined to be $\sim 0.27 \text{ \AA}$ out of the plane and ferromagnetic exchange has been dominant.⁸⁸

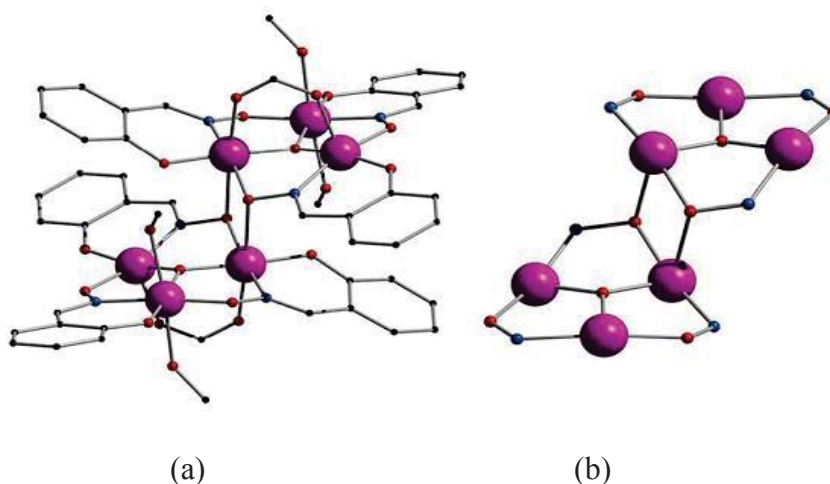


Figure 1.25: (a) The structure of $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{O}_2\text{CH}_3)_2(\text{sao})_6(\text{MeOH})_4]$. (b) its magnetic core (Mn^{III} = purple; O = red; N = blue; C = black. H-atoms are omitted for clarity).⁸⁸

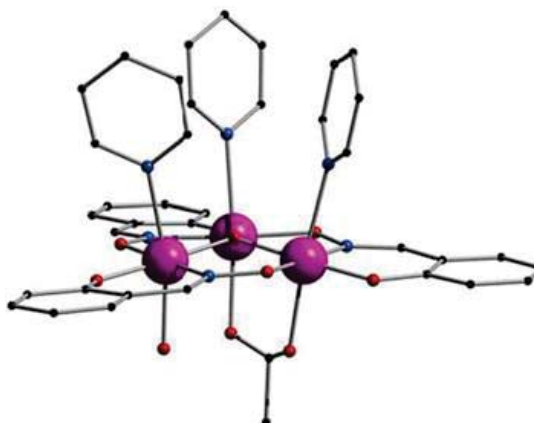


Figure 1.26: The structure of $[\text{Mn}_3\text{O}(\text{sao})_3(\text{O}_2\text{CCH}_3)(\text{py})_3(\text{H}_2\text{O})]$ cluster.⁸⁸

Salicylaldoximes such as 3,3'-[1,6-hexanediyl]bis[(methylimino) methylene]]bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde-1,1'-dioxime (**L**) have been utilised to synthesise some dinuclear complexes such as $[\text{Cu}_2(\text{L-2H})_2]$.⁹⁰⁻⁹² A major rearrangement of the said dinuclear complex was observed when it was treated with NaPF_6 in water. The resultant cluster, $[\text{Cu}_6(\text{L-2H})_3(\mu_3\text{-O})(\mu_3\text{-OH})](\text{PF}_6)_3$ was the first polynuclear (salicylaldoxime) copper(II) complex⁹³ and the two $\text{Cu}(\text{II})_3(\mu_3\text{-O})^{4+}$ units are arranged in the similar way to that of $[\text{Mn}_3(\text{salox}^{2-})_3(\mu_3\text{-O})]^+$ which are held together by doubly deprotonated salicylaldoxime ligands in Mn(III) complexes.^{42(c),94(a),95} The hexanuclear copper complex formed a helical structure which consists of three ligands (Figure 1.27). The ligand **L** since has been found to form two clusters, $[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{H}_2\text{L})_3(\text{py})_6](\text{BF}_4)_5 \cdot 6\text{H}_2\text{O} \cdot 14\text{MeOH}$ with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and pyridine in MeOH and $[\text{Mn}_6\text{O}_2(\text{OH})_2(\text{H}_2\text{L})_3(\text{py})_4(\text{MeCN})_2(\text{NO}_3)](\text{BF}_4)_5 \cdot 3\text{MeCN} \cdot \text{H}_2\text{O} \cdot 5\text{py}$ with **L**, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and NaBF_4 in MeCN. The complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{H}_2\text{L}')_3](\text{BF}_4)_3 \cdot 4\text{H}_2\text{O} \cdot 9\text{MeOH}$ was formed with the analogous ligand **L'** (where the spacer group or strap contains eight CH_2 groups), $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, and pyridine in MeOH, and each possesses the same structural architecture which is illustrated in Figure 1.27. The dominant exchange interactions between the metal ions in the clusters are strongly antiferromagnetic.⁹⁶

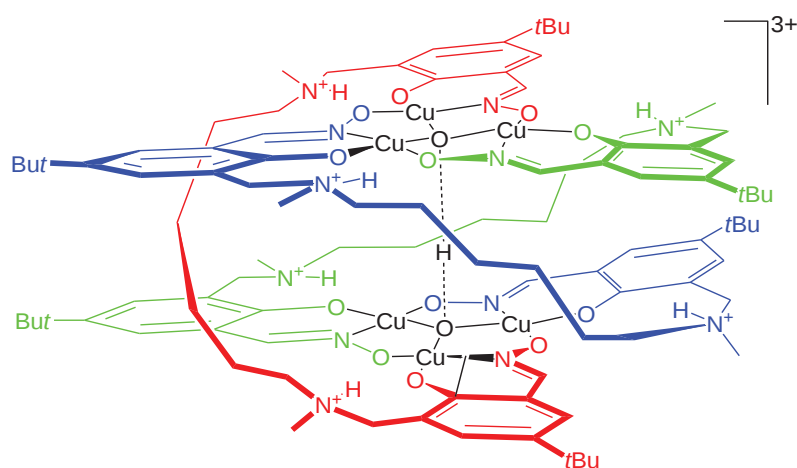


Figure 1.27: Schematic representation showing the three straps and the interplane $(\mu_3\text{-O}) \cdots \text{H} \cdots (\mu_3\text{-O})$ hydrogen bond.

A series of Mn complexes of salicylaldoxime based ligands with SMM magnetic properties has been produced by Milios *et al* in 2008⁹⁷, particularly hexanuclear SMMs having the general formula of $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{R-sao})_6(\text{RCO}_2)_2(\text{sol})_{4-6}](\text{R}=\text{H}, \text{Me}, \text{Et}; \text{R}'=$

various; sol = H₂O, MeOH, EtOH) for which a magneto-structural correlation could be built by deliberate structural modifications of the core such as twisting Mn-N-O-Mn moieties within each triangle, and an SMM with the largest effective energy barrier to magnetisation reversal.^{42(c),98,99} The exchange interactions of the hexanuclear SMMs between the two triangles, [Mn^{III}₃O(R-sao)₃]⁺ are found to be ferromagnetic and it was found that twisting and structurally distorting the core of the complex by substituting oximate and/carboxylate ligands can switch the exchange interactions within the triangles from antiferromagnetic to ferromagnetic. This substitution led to a change in the Mn–N–O–Mn torsion angle (α) and as a consequence, there is a change in the ground state spin of the complex due to an elevation or drop in the pairwise exchange coupling. It has been found that complexes with α angles below $\sim 30.4^\circ$ possess antiferromagnetic pairwise exchange whereas α angles above $\sim 31.3^\circ$ produced ferromagnetic pairwise exchange.^{42(c),99}

In 2008, Milios *et al* reported several R-saoH₂ based Mn complexes containing carboxylate bridges with the general formula of [Mn^{III}₃O(R-sao)₃(RCO₂)(sol)₃₋₄]^{87,94(a)} as well as complexes of general formula [Mn^{III}₃O(R-sao)(XO₄)(sol)₃]^{94(b),94(c)} (X = Cl, Re as ClO₄[−] and ReO₄[−] that act as ‘princer’ type tripodal ligands). They have also reported in 2010 two new Mn complexes, [Mn^{III}₃O(Et-sao)₃(HCO₂)(MeOH)₅] and [Mn^{III}₃O(Me-sao)₃(MeOH)₅]Cl (see Figure 1.28(a)) which do not contain any auxiliary bridging ligands other than oximes. The distance between Mn3 and Cl[−] counter ion is 3.107(2) Å and the Cl[−] ion weakly interacts with Mn3.¹⁰⁰ (see Figure 1.28(b)).

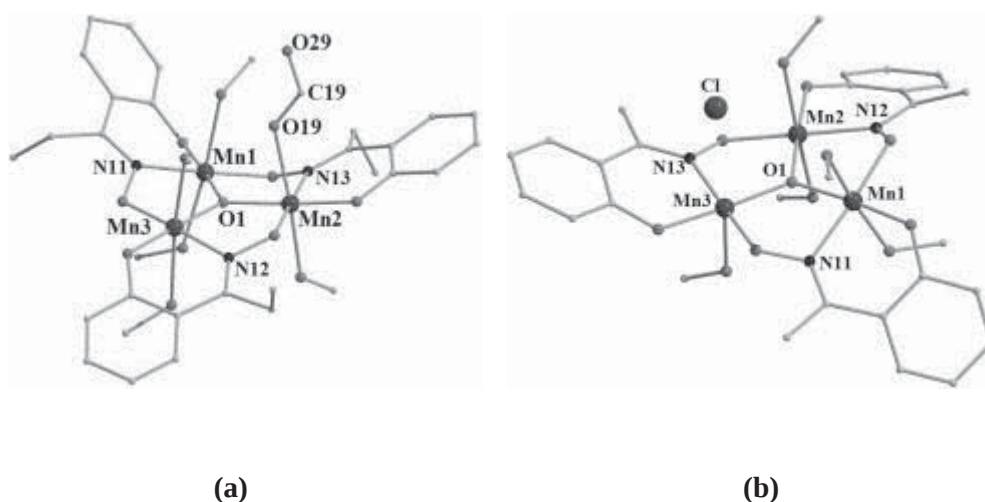


Figure 1.28: Molecular structures of (a) [Mn^{III}₃O(Et-sao)₃(HCO₂)(MeOH)₅] and (b) [Mn^{III}₃O(Me-sao)₃(MeOH)₅]Cl.¹⁰⁰

Perlepes found the first hexanuclear Mn complex with salicylaldoxime ligand in 2004^{45(f)} since when a series of oxime-based Mn₆ clusters have emerged.¹⁶⁻¹⁹ Particularly, Brechin and his collaborators were able to synthesise Mn₆ units with salicylaldoxime derivatives of which the total ground state spin (*S*) varied from 4 to 12 with effective energy barriers for magnetisation reversal.^{13,88,98,101,102}

As it has been established that metal complex aggregates are assembled by alkali and alkaline earth metals under particular circumstances Wu *et al.* have synthesised a 2D coordination polymer sheet by adding alkali metal ions into an oximate-bridged Mn(III) salicylaldoxime complex. X-ray crystallographic analysis of the resulting complexes revealed a complex where the Mn₆ units are bridged by sodium ions and 1,2,3,4-butane tetracarboxylate groups producing the complex, Na₂[Mn^{III}₆O₂(sao)₆(btca)(H₂O)₂·5H₂O which show dominant antiferromagnetic interactions (see Figure 1.29) where H₂sao = salicylaldoxime and H₄btca = 1,2,3,4-butane tetracarboxylate acid.¹⁰³

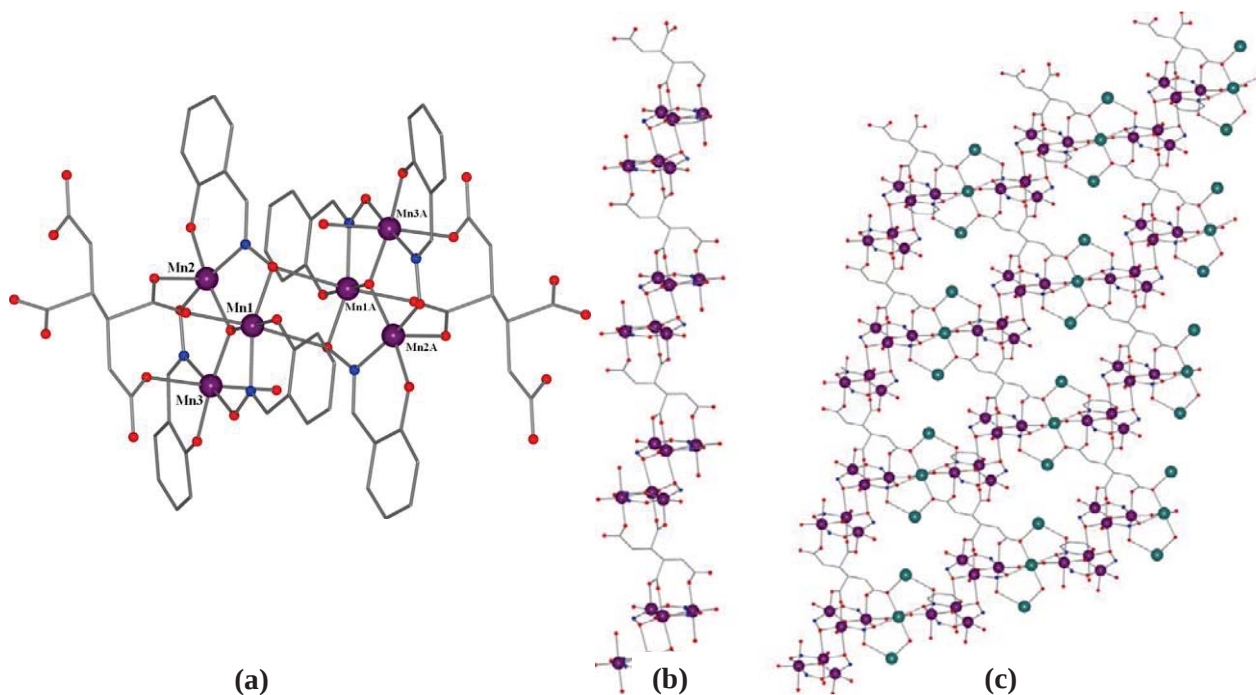


Figure 1.29: (a) Mn₆ cluster (b) coordination chain of Mn₆ (c) their assembly into 2D through coordination of Na⁺ ions by some of the carboxylic groups, phenyl ring of sao²⁻ ligands and hydrogen atoms have been omitted for clarity (Mn-purple, N-blue, O-red, Na-green, C-gray).¹⁰³

1.5 Phenolic oxime ligands

As is clear from the preceding section, phenolic oxime ligands are widely used as synthons for magnetic cluster formation. As these compounds contain both oximic and phenolic groups (see Figure 1.30) they can either be singly-deprotonated at the phenol or doubly deprotonated at both the phenolic and oximic oxygen.

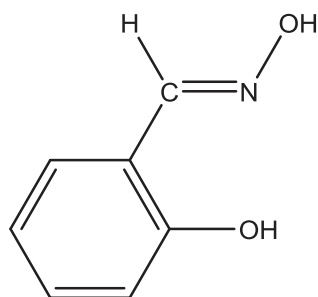


Figure 1.30: General molecular structure of salicylaldoxime.

Mono-deprotonation at the phenol group leads to a *pseudo*-macrocyclic arrangement (see Figure 1.31). The size of the cavity formed within this arrangement is ideal for the Cu(II) ion. Therefore, it is very selective for Cu(II) and Ni(II), especially over ions such as Fe(III), which has meant that phenolic oximes are extensively used in extractive hydrometallurgy to the point that 20-30% of the world copper production is now produced using this procedure.

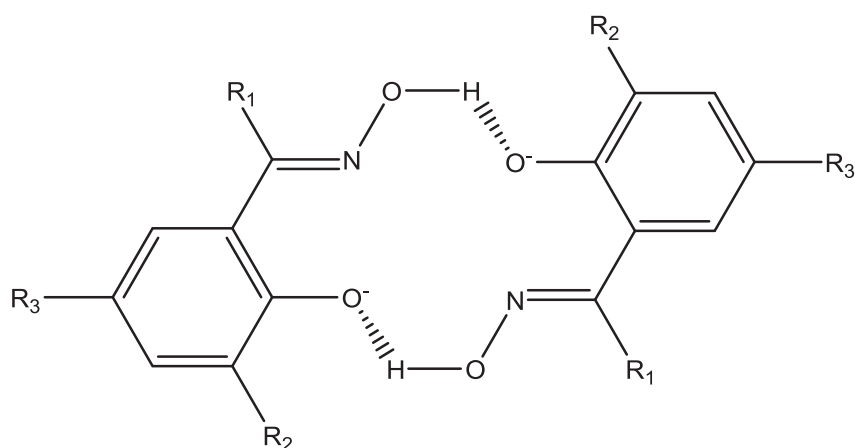


Figure 1.31: *pseudo*-Macrocyclic arrangement of singly deprotonated salicylaldoxime.

Similar complexes using singly deprotonated salicylaldoximes with metal ions such as Ni^{2+} , Zn^{2+} , Pd^{2+} , and Co^{2+} have been reported which also possess this *pseudo*-macrocyclic arrangement where there exist H bonds between the oximic group and phenolic group.¹⁰⁴ It has been shown that the strength of extraction of the metal ion can be increased by substituting at R2 (Figure 1.31) a H bond acceptor such as a halogen atom which reinforces the strength of the H bonding and enhances stability. On the other hand, bulkier groups have been shown to decrease binding strength.¹⁰⁵

Deprotonation at both the phenol and oxime groups open up the possibilities to form polynuclear complexes and the most common structural motif is the tri-metal unit connected through three salicylaldoximes each coordinating to two metal ions (see Figure 1.32).

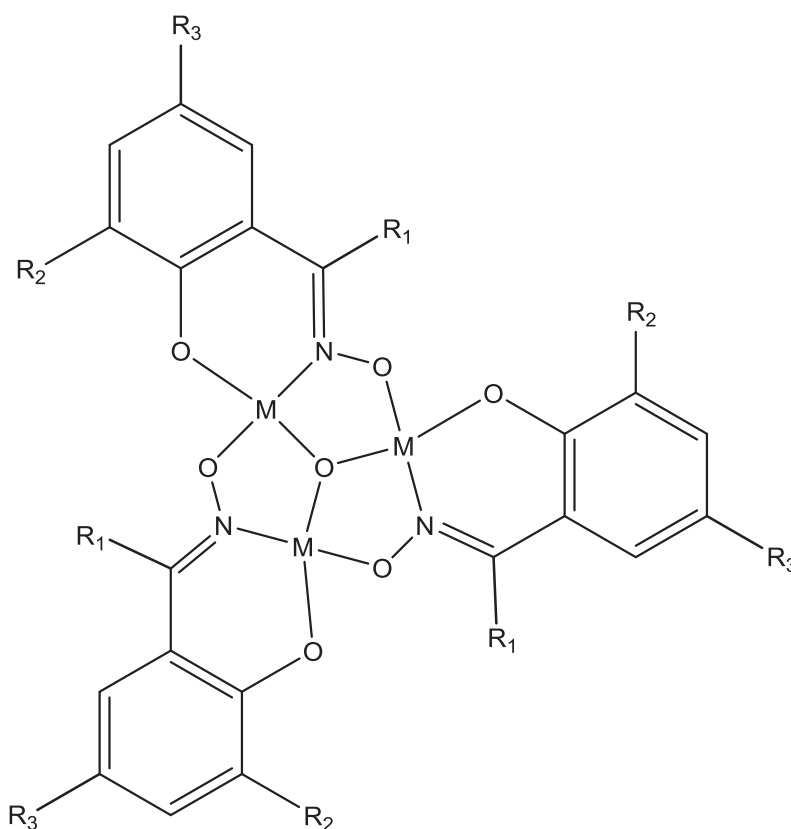


Figure 1.32: $[\text{M}_3^{\text{III}}\text{O}(\text{oximate})_3]^+$ moiety.

As described in the objectives, the purpose of this study is to design, synthesise, and explore the magneto-structural relationships present in a series of iron containing salicylaldoxime derivatives.

The discovery of the first hexacopper-derivatised salicylaldoxime complex which contains the same moiety as illustrated in the Figure 1.32, published by Plieger *et al.* in 2009 led to start this project.⁹³ It was hypothesised that analogous iron complexes would exhibit interesting magnetic properties. Therefore, salicylaldoxime was derivatised into the ligands consisting of ‘straps’ varied in the length, rigidity or flexibility, etc. (further discussed in 1.5.1). These ligands were then utilised to complex with various iron salts using numerous conditions.

Apart from the above major reason, salicylaldoximes have been employed in Mn and Fe cluster chemistry to great effect in terms of developing magnetic materials. Salicylaldoximes are polydentate compounds which can act as both chelating and bridging ligands and the number of the donor atoms present in the pure salicylaldoximes was increased by transforming them into ‘double-headed’ salicylaldoximes by introducing a ‘strap’ between two salicylaldoxime molecules (further discussed in 1.5.1) which can lead to stable, multi-iron clusters.

1.5.1 Derivatised salicylaldoximes

Salicylaldoximes can be derivatised into many ligands by substituting different R2 and R3 groups but keeping R1 the same (see Figure 1.32).

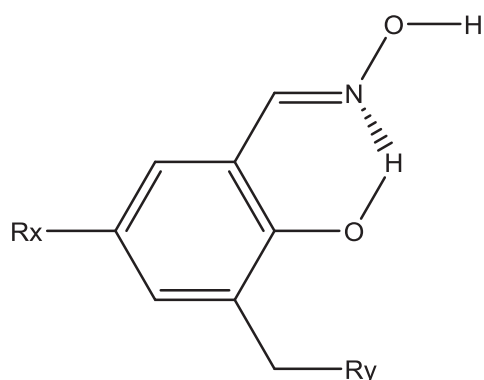


Figure 1.33: General structure of derivatised salicylaldoximes.

The ligands utilised in this project are shown in the Table 1.1. As indicated in the Table 1.1, the ligands **L1-L4** and **L11** consist of only one oxime group and a phenol group attached to one aromatic ring (‘one oxime head’). All the ligands **L5-L10** contain two

oxime groups and two phenol groups attached to two aromatic rings ('two oxime heads') on either side which are inter-connected through the Ry group (see Figure 1.33).

The ligands with one oxime head are henceforth called '**single-headed**' salicylaldoximes whereas the ligands with salicylaldoxime groups at either end of the strap are called '**double-headed**' salicylaldoximes.

Table 1.1: Derivatised salicylaldoximes utilised in this project.

ligand		Rx	Ry
3-Ry-5-Me-saoH ₂	L1	Me	-N(CH ₂ CH ₂) ₂ O
3-Ry-5- <i>t</i> -Bu-saoH ₂	L2	<i>t</i> -Bu	-N(CH ₂ CH ₂) ₂ O
3-Ry-5-Me-saoH ₂	L3	Me	-N(CH ₂ CH ₂) ₂ CO ₂ (CH ₂) ₂
3-Ry-5-Me-saoH ₂	L4	Me	-N(CH ₃)CH ₂ CH(OCH ₃) ₂
bis(3-Ry-5-Me-saoH ₂)	L5	Me	-N(CH ₂ CH ₂) ₂ N-
bis(3-Ry-5-Me-saoH ₂)	L6	Me	-N(CH ₃)CH ₂ (1,4-Ph)CH ₂ (CH ₃)N-
bis(3-Ry-5-Me-saoH ₂)	L7	Me	-N(CH ₃)(CH ₂ Ph)(CH ₂) ₅ (CH ₂ Ph)(CH ₃)N-
bis(3-Ry-5-Me-saoH ₂)	L8	Me	-N(CH ₂ Ph)(CH ₂) ₂ (CH ₂ Ph)N-
bis(3-Ry-5-Me-saoH ₂)	L9	Me	-N(CH ₃)(CH ₂ -1,3-Ph-CH ₂ (CH ₃)N-
bis(3-Ry-5-Me-saoH ₂)	L10	Me	-N(CH ₃)(CH ₂) ₆ (CH ₃)N-
3-Ry-5- <i>t</i> -Bu-saoH ₂	L11	<i>t</i> -Bu	-N(CH ₂ CH ₂) ₂ CH ₂

The trinuclear units (see Figure 1.32) are expected to assemble into complexes containing two parallel triangles that are mainly inter-connected through the Ry group on the double-headed salicylaldoximes. This assembly readily leads to the formation of high metal nuclearity clusters such as hexamers and heptamers. Flexibility of the Ry group ('strap') varies the distances between the metal centres on the triangles and may vary the torsion and bond angles with the ultimate intention of forming magnetically interesting polynuclear clusters with strong paramagnetic 3d transition metals such as Mn and Fe.

1.6 Basic techniques

Apart from the general characterisation such as IR spectroscopy, UV spectroscopy, CHN analyses, electro-spray ionisation mass spectrometry, the complexes have been subjected to X-ray diffraction analysis to elucidate the solid-state structures. Mössbauer spectrometry has also been used to determine the oxidation states of the Fe ions in the Fe clusters and magnetic susceptibility measurements were undertaken to look into the magnetic behaviour within the polynuclear Fe clusters.

1.6.1 X-ray diffraction (XRD)

The technique of XRD (see Figure 1.34) allows identification of the crystalline phases within materials (microcrystalline or powder). This is an experimental technique where X-rays are diffracted by the material when they are irradiated with X-rays. The X-rays (wavelength 10^{-10} m) are scattered by the electron cloud of an atom of corresponding size. The diffracted X-rays are then collected by a detector. Then the signals are processed to give an X-ray pattern or diffractogram.

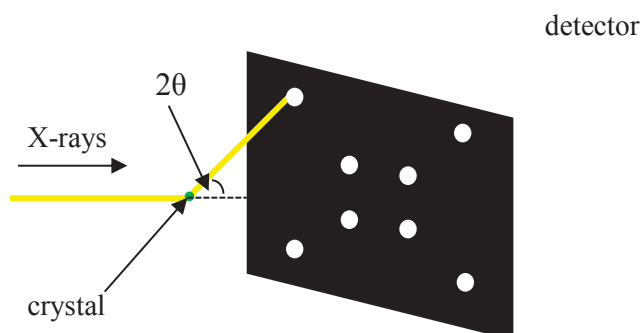


Figure 1.34: General X-ray experimental set up.

Diffracted X-rays are scattered by the crystal at a certain angle. The extent the X-ray is scattered determines how fine the information can be distinguished in the final model of the structure. Therefore, high resolution is desired. The resolution d can be calculated by knowing the wavelength (λ) and the angle of a reflection (θ).

$$d = \frac{\lambda}{2 \sin \theta}$$

$$\lambda = 2d \sin \theta$$

The diffractogram is a one dimensional graphical representation of a three dimensional reciprocal lattice of a material, where the diffraction intensities are plotted vs. the 2θ Bragg angle. X-ray diffraction patterns allow identification of the phases present in a sample and the gaining of information of its structural properties (cell parameters, lattice type, atomic parameters, crystallinity, particle size, strain, preferred orientation) by analysing the position, intensity, and shape of the peaks.^{106,107}

The Rietveld method is used to analyse the identified phases on the X-ray pattern quantitatively. The least-squares refinement is used to minimise the difference between the observed and calculated intensity profiles in the Rietveld Method. It requires reference structure files of the identified phases and does not need any internal or external standard. The phase weight fraction can be calculated using the values of scale factors, number of formula units per unit cell, molecular mass of the formula unit, and the unit cell volume during the refinement of the structures.^{107,108}

Here the full three dimensional diffraction patterns were used to determine the structures of compounds made. Structures were solved by standard direct methods and all non-hydrogen atoms were refined by full-matrix least-squares methods. Missing atoms were located in difference Fourier electron density maps. Hydrogen atoms and atoms in disordered parts of the structure were generally restrained to standard values for bond distances and angles.

1.6.2 Magnetic measurements

Quantitatively, a magnetisation (M) is induced with an applied magnetic field (H) and M is proportional to the magnetic susceptibility (χ) which is a function of the temperature.

$$\chi = \frac{M}{H} \dots \dots \dots (1)$$

The magnetic moment (μ) can be defined from the magnetic susceptibility (χ) by the following equation (2) using k_B = Boltzmann's constant, N = Avogadro's constant, and μ_B = Bohr magneton.

$$\mu = \sqrt{\frac{3k_B}{N\mu_B^2}} \cdot \sqrt{\chi T} \dots \dots \dots (2)$$

Magnetic susceptibility is the sum of diamagnetic and paramagnetic susceptibilities. Molar paramagnetic susceptibility or molar susceptibility is much stronger than diamagnetism and is independent of the magnetic field but is temperature (T) dependent.

Earlier it was discussed that for magnetically dilute systems, $\chi \propto 1/T$ which can be described by the Curie constant (C).

Magnetic data is usually reported as χT values which can be related to the total spin (S) by equation (3).

$$C = \chi T = \frac{N\mu_B^2}{3k_B} g^2 [S(S + 1)] \sim \frac{g^2}{8} S(S + 1) \dots \dots \dots (3)$$

Equation (3) can be developed for systems with 'n', non-interacting paramagnetic centres as follows;

$$\chi T \sim \frac{g^2}{8} \cdot n \cdot S(S + 1) \dots \dots \dots (4)$$

Only at high temperatures and low magnetic fields is the Curie law applicable. There are often deviations from the Curie law in magnetically dilute systems. (see equation 5).

$$\chi = \frac{C}{T - \theta} \dots \dots \dots (5)$$

where θ is the Weiss constant and is given by the intercept of the $1/\chi$ vs T plot. Ferromagnetic interactions give a positive θ and if negative the magnetic interaction is antiferromagnetic.

The magnetic measurements of all the polynuclear Fe complexes were carried out using the superconducting quantum interference device (SQUID), which is the most sensitive device available for measuring magnetic fields. The SQUID does not measure the magnetic moment of the sample directly. Instead, the sample is moved through a superconducting detection coil system which causes the magnetic moment within the sample to generate an electric current in the coils (see Figure 1.35). The superconducting coils are connected to the SQUID as any change in the current in the coils will cause corresponding variations in the output voltage of the SQUID which is strictly proportional to the magnetic moment within the sample. The measured magnetic moment is usually a function of the applied magnetic field or temperature.¹⁰⁹⁻¹¹¹ A typical output graph of output voltage versus sample position from the SQUID is illustrated in Figure 1.36.

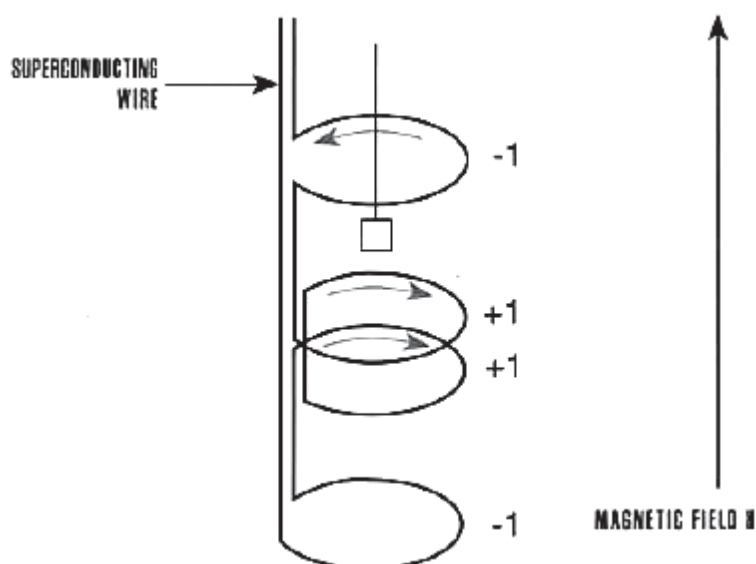


Figure 1.35: Superconducting detection coil.¹⁰⁹

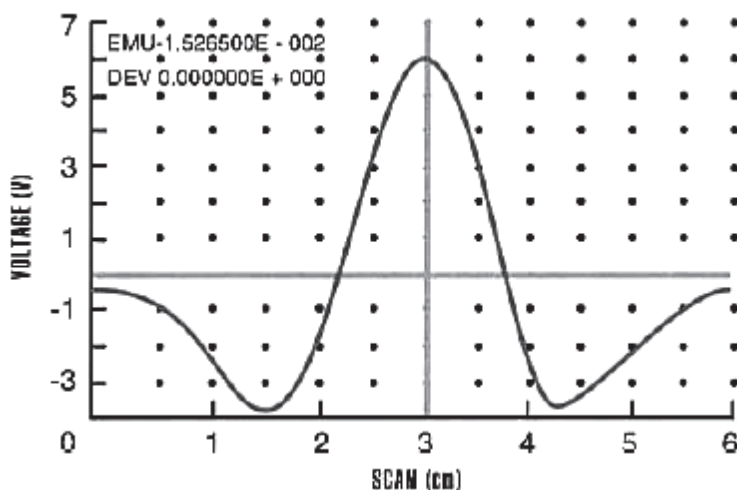


Figure 1.36: Typical output from the SQUID.¹⁰⁹

1.6.3 Mössbauer spectroscopy

The physical principle behind this technique is the “recoilless emission and resonant absorption of gamma radiation by atomic nuclei in solids”, which is known as the Mössbauer effect.¹⁰⁹ This technique is used to get distinctive measurements of electronic, magnetic, and structural properties within materials at different conditions such as room temperature, low and high temperature, and under magnetic field.

The emitted gamma radiation is modulated by the Doppler Effect by moving the gamma source (usually ^{57}Co in a rhodium matrix) forward and backward to a thin absorber. Then the gamma rays passing through the sample are detected by a scintillation detector, then amplified and analysed by a multichannel analyzer, and finally the Mössbauer spectrum is generated. The spectrum is essentially a graph of the count rate registered as a function of the source velocity in a multichannel analyzer. In order to obtain the Mössbauer parameters, isomer shift (IS), quadrupole splitting (QS), peak width-line (W), and hyperfine magnetic field (B_{hf}), two mirror spectra are recorded, folded and fitted. It is possible to obtain information about the iron oxidation state, nature of the chemical bond, electronic and crystallographic structure, symmetry of the iron site, and determine the presence or absence of magnetic ordering from the values of the Mössbauer parameters.¹¹²⁻¹¹⁴

1.6.3.1 Theory

An atomic nucleus is capable of absorbing gamma rays if the energy of the gamma ray is equal to the energy difference between two states of the nucleus. This is called resonant absorption. A nucleus can also emit gamma rays when an energy transition from an excited state to a lower energy state takes place. According to the conservation of momentum, the nucleus will recoil when it emits the gamma rays. Therefore, the total energy difference between the two states will be equal to the energy of the gamma ray and recoil energy. So there is a barrier for the continuity of this phenomenon due to the lack of the required energy in the gamma ray to be absorbed by another nucleus.

$$R = \frac{E^2}{2MC^2}$$

where R = recoil energy, M = nuclear mass, C = velocity of light, E = energy of the gamma ray.

Therefore, if a nucleus is to be excited by an energy E due to the absorption of radiation, the photon energy must be approximately $E + (\frac{E^2}{2MC^2})$ for momentum to be conserved. Thus the centres of the absorption and emission lines are displaced with respect to each other by an energy separation of $\frac{E^2}{2MC^2}$. Resonant absorption will not be observed if this is much greater than the line width.

In 1957, Rudolf Mössbauer showed that the recoil energy is reduced when the emitting and absorbing nuclei are strongly bound in lattices which in turn allows the observation of the resonant absorption.^{115,116} To apply the technique, gamma ray energy is changed over a small range applying Doppler motion in order to observe the resonance absorption. The spectrum of the gamma radiation undergoes a Doppler energy shift, ΔE when either the source or absorber is moving.

The change in energy is given by the equation, $\Delta E = \frac{V}{C}E$, where E is the energy of the emitted gamma ray, C is the velocity of light, and V is the relative velocity of the source and absorber. Relative velocities at which resonant absorption is observed are used to

measure very small shifts in the nuclear energy levels due to the environment of the nucleus.

The gamma source consists of ^{57}Co embedded in rubidium. Cobalt transforms to iron and the Mössbauer gamma ray is produced by a transition from the spin $3/2$ excited state to the spin $1/2$ ground state (see Figure 1.37).

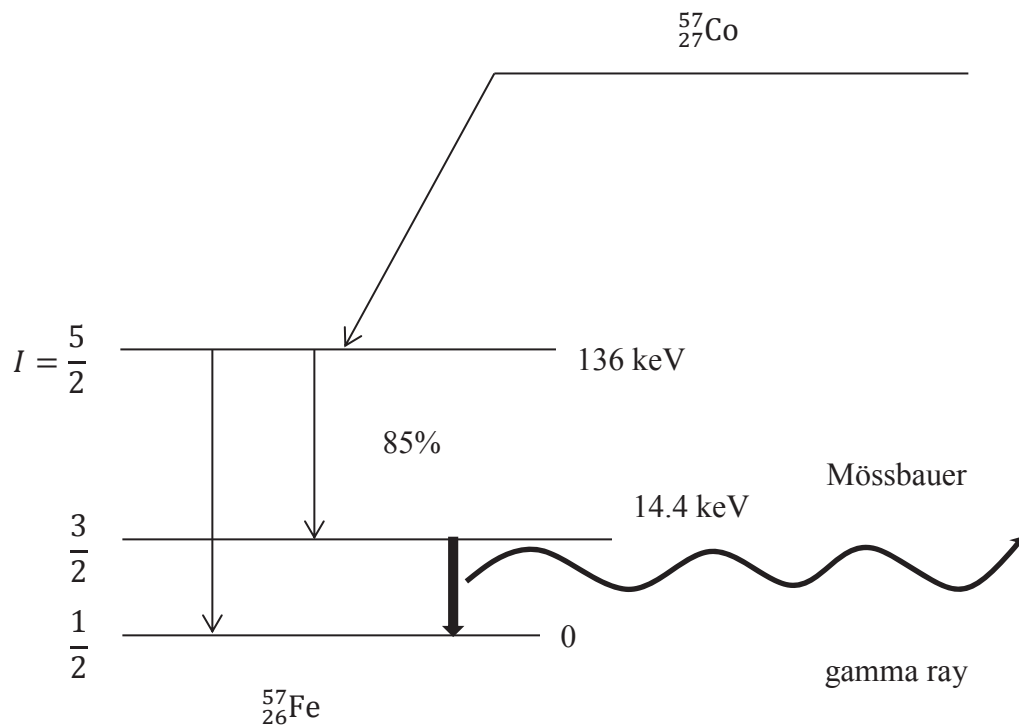


Figure 1.37: Nuclear decay scheme of ^{57}Co exhibiting the transition giving a 14.4 keV Mössbauer gamma ray.

These shifts are described by three parameters: isomer shift, quadrupole splitting, and magnetic splitting.

1. Chemical isomer shift / IS (δ)

The chemical isomer shift is created as a result of the interaction between the nucleus density and the surrounding 's' electron cloud. IS can give information about the bonding and shielding of iron atoms in the material (and most importantly the oxidation state).

2. Quadrupole splitting / QS (ΔE_Q)

A nuclear quadrupole moment arises with non-spherical charge distributions. Nuclear energy levels may be split in the presence of an electric field gradient or non-uniform electric field. The measurement of the splitting can give information about the electron configuration of iron in the material (see Figure 1.38).

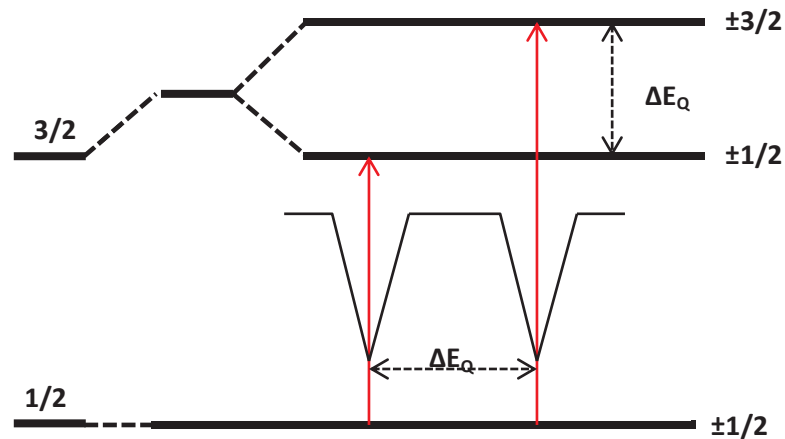


Figure 1.38: Energy level diagram showing the isomer shift (δ) and quadrupole splitting (ΔE_Q) for the $3/2$ to $1/2$ transition in ^{57}Fe .

3. Magnetic splitting

Interaction of the magnetic dipole moment of the nucleus and magnetic field causes magnetic splitting. This parameter provides information about the magnetic properties of the material (see Figure 1.39).

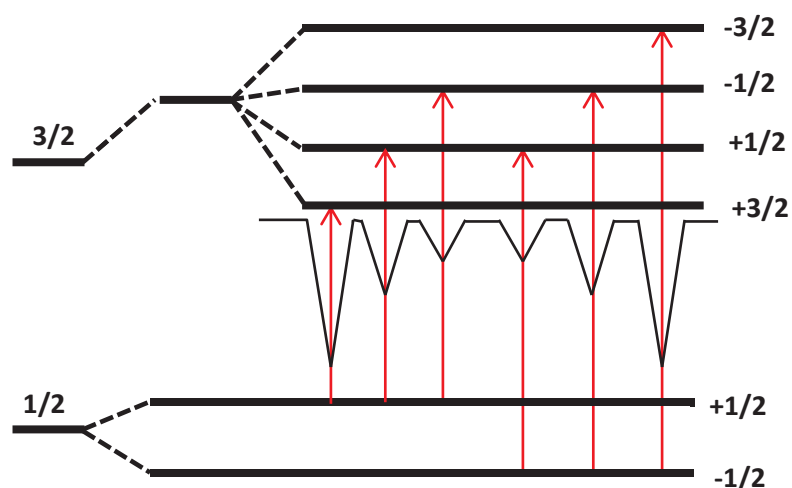


Figure 1.39: Energy level diagram illustrating magnetic splitting in ^{57}Fe .

References:

1. Hurd, C. M., *Contemp. Phys.*, **1982**, 23, 469.
2. Orchard, A. F., *Magnetochemistry*, New York: Oxford University Press, Inc., **2003**.
3. Morrish, A. H., *The Physical Principles of Magnetism*: John Wiley & Sons, New York, **1965**, p. 546.
4. Christou, G., *Polyhedron*, **2005**, 24, 2065.
5. Mingos, D. M. P., Winpenny, R., Aromi, G., Brechin, E. K., *Structure and Bonding: Single-Molecule Magnets and related phenomena*; Berlin Heidelberg: Springer-Verlag, **2006**, p3.
6. T. Lis, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, **1980**, 36, 2042.
7. Barra, A. L., Debrunner, P., Gatteschi, D., Schulz, C. E., Sessoli, R., *Europhys Lett.*, **1996**, 35, 133.
8. Aromí, G., Brechin, E. K., *Struc. Bond.*, **2006**, 122, 1.
9. Coulon, C., Miyasaka, H., Clérac, R., *Struc. Bond.*, **2006**, 122, 163.
10. Gispert, J. R., *Cooordination Chemistry*, Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, Inc., **2008**.
11. Gatteschi, D., Sessoli, R., Villain, J., *Molecular Nanomagnets*; Oxford University Press Inc., New York, **2006**, p106.
12. Andres, H., Basler, R., Güdel, H. U., Aromí, G., Christou, G., Buttner, H., Ruffle, B., *J. Am. Chem. Soc.*, **2000**, 122, 12469.
13. Milios, C. J., Piligkos, S., Brechin, E. K., *Dalton Trans.*, **2008**, 1809.
14. Christou, G., Gatteschi, D., Hendrickson, D. N., Sessoli, R., *Bull. MRS.*, **2000**, 66.
15. Powell, G. W., Lancashire, H. N., Brechin, E. K., Collison, D., Heath, S. L., Mallah, T., Wernsdorfer, W., *Angew. Chem. Int. Ed.*, **2004**, 43, 5772.
16. Gatteschi, D., Sessoli, R., Cornia, A., *Chem Commun.*, **2000**, 725.
17. Sessoli, R., Gatteschi, D., Caneschi, A., Novak, M. A., *Nature*, **1993**, 365, 141.
18. Caneschi, A., Gatteschi, D., Sessoli, R., Barra, A. L., Brunel, L. C., Guillot, M., *J. Am. Chem. Soc.*, **1991**, 113, 5873.
19. Kuroda-Sowa, T., Bian, G. Q., Hatano, M., Konaka, H., Fukuda, S., Miyoshi, S., Maekawa, M., Munakata, M., Miyasaka, H., Yamashita, M., *Polyhedron*, **2005**, 24, 2680.
20. Kim, J., Han, S., Lim, J. M., Choi, K. Y., Nojiri, H., Suh, B. J., *Inorg. Chim. Acta*, **2007**, 360, 2647.

21. Christou, G., Abboud, K. A., Wernsdorfer, W., Murugesu, M., *Polyhedron*, **2005**, 2894.
22. Leuenberger, M. N., Loss, D., *Nature*, **2001**, 410, 789.
23. Barbara, B., *Magn. Magn. Mater.*, **1999**, 200, 167.
24. Schnack, J., *Dalton Trans.*, **2010**, 39, 4677.
25. Kahn, O., *Chem. Phys. Lett.*, **1997**, 265, 109.
26. Ephraim, F., *Berichte*, 63, **1930**, 1928.
27. Cox, E. G., Pinkard, F. W., Wardlaw, W., Webster, K. C., *J. Chem. Soc.*, **1935**, 459.
28. Jarski, M. A., Lingafelter, E. C., *Acta Crystallogr.*, **1964**, 17, 1109.
29. Srivastava, R. C., Lingafelter, E. C., Jain, P. C., *Acta Crystallogr.*, **1967**, 22, 922.
30. Orioli, P. L., Lingafelter, E. C., Brown, B. W., *Acta Crystallogr.*, **1964**, 17, 1113.
31. Merritt, L. L., Gaure, C., Lessor, A. E., *Acta Crystallogr.*, **1956**, 9, 253.
32. Pfluger, C. E., Harlow, R. L., *Acta Crystallogr.*, **1970**, B26, 1631.
33. Grigg, J., Collison, D., Garner, C. D., Helliwell, M., Tasker, P. A., Thorpe, J. M., *J. Chem. Soc., Chem. Commun.*, **1993**, 1807.
34. Bielig, H.-J., Mollinger, H., *Liebigs Ann. Chem.*, **1957**, 605, 117.
35. Toyota, E., Umakoshi, K., Yamamoto, Y., *Bull. Chem. Soc. Jpn.*, **1995**, 68, 858.
36. Liu, S., Zhu, H., Jubieta, J., *Polyhedron*, **1989**, 8, 2473.
37. Zerbib, V., Robert, F., Gouzerh, P., *J. Chem. Soc., Chem. Commun.*, **1994**, 2179.
38. Potocnak, I., Heinemann, F. W., Rausch, M., Steinborn, D., *Acta Crystallogr.*, **1997**, C53, 54.
39. Rettig, S. J., Storr, A., Trotter, J., *Acta Crystallogr.*, **1992**, C48, 1587.
40. (a) Wieghardt, K., Pohl, K., Jibril, I., Huttner, G., *Angew. Chem., Int. Ed. Engl.* **23**, **1984**, 77; (b) Barra, A.-L., Debrunner, P., Gatteschi, D., Schulz, C. E., Sessoli, R., *Europhys. Lett.*, **35**, **1996**, 133; (c) Rodriguez, E., Gich, M., Roig, A., Molins, E., Nedelko, N., Slawska-Waniewska, A., Szewczyk, A., *Polyhedron*, **25**, **2006**, 113.
41. (a) Vincent, J. B., Olivier-Lilley, G. L., Averill, B. A., *Chem. Rev.*, **90**, **1990**, 1447; (b) Cohen, I. A., *Struct. Bonding*, **40**, **1980**, 1; (c) Jones, P. L., Jeffery, J. C., McCleverty, J. A., Ward, M. D., *Polyhedron*, **16**, **1997**, 1567; (d) Horn, A., Neves, A., Bortoluzzi, A. J., Drago, V., Ortiz, W. A., *Inorg. Chem. Commun.*, **4**, **2001**, 173; (e) Faiella, M., Andreati, C., Torres, R., de Rosales, M., Pavone, V.,

Maglio, O., Nastri, F., DeGrado, W. F., Lombardi, A., *Nature Chem. Biol.*, **5**, **2009**, 882.

42. (a) Milios, C. J., Vinslava, A., Wernsdorfer, W., Moggach, S., Parsons, S., Perlepes, S. P., Christou, G., Brechin, E. K., *J. Am. Chem. Soc.*, **129**, **2007**, 2754; (b) Milios, C. J., Inglis, R., Vinslava, A., Bagai, R., Wernsdorfer, W., Parsons, S., Perlepes, S. P., Christou, G., Brechin, E. K., *J. Am. Chem. Soc.*, **129**, **2007**, 12505; (c) Inglis, R., Jones, L. F., Milios, C. J., Datta, S., Collins, A., Parsons, S., Wernsdorfer, W., Hill, S., Perlepes, S. P., Piligkos, S., Brechin, E. K. *Dalton Trans.*, **2009**, 3403; (d) Jones, L. F., Cochrane, M. E., Koivisto, B. D., Leigh, D. A., Perlepes, S. P., Wernsdorfer, W., Brechin, E. K., *Inorg. Chim. Acta*, **361**, **2008**, 3420; (e) Prescimone, A., Milios, C. J., Sanchez-Benitez, J., Kamenev, K. V., Loose, C., Kortus, J., Moggach, S., Murrie, M., Warren, J. E., Lennie, A. R., Parsons, S., Brechin, E. K., *Dalton Trans.*, **2009**, 4858; (f) Milios, C. J., Raptopoulou, C. P., Terzis, A., Lloret, F., Vicente, R., Perlepes, S. P., Escuer, A., *Angew. Chem., Int. Ed.*, **43**, **2004**, 210; (g) Prescimone, A., Milios, C. J., Moggach, S., Warren, J. E., Lennie, A. R., Sanchez-Benitez, J., Kamenev, K., Bircher, R., Murrie, M., Parsons, S., Brechin, E. K., *Angew. Chem., Int. Ed.*, **47**, **2008**, 2828; (h) Yang, C.-I., Cheng, K.-H., Nakano, M., Lee, G.-H., Tsai, H.-L., *Polyhedron*, **28**, **2009**, 1842; (i) Moro, F., Corradini, V., Evangelisti, M., De Renzi, V., Biagi, R., del Pennino, U., Milios, C. J., Jones, L.F., Brechin, E. K., *J. Phys. Chem., B* **112**, **2008**, 9729; (j) Jones, L. F., Milios, C. J., Prescimone, A., Evangelisti, M., Brechin, E. K., *Chimie, C. R.*, **11**, **2008**, 1175; (k) Song, X., Liu, R., Zhang, S., Li, L., *Inorg. Chem. Commun.*, **13**, **2010**, 828; (l) Milios, C.J., Vinslava, A., Wernsdorfer, W., Prescimone, A., Wood, P. A., Parsons, S., Perlepes, S. P., Christou, G., Brechin, E. K., *J. Am. Chem. Soc.*, **129**, **2007**, 6547; (m) Milios, C. J., Inglis, R., Bagai, R., Wernsdorfer, W., Collins, A., Moggach, S., Parsons, S., Perlepes, S. P., Christou, G., Brechin, E. K., *Chem. Commun.*, **2007**, 3476; (n) Kotzabasaki, V., Inglis, R., Siczek, M., Lis, T., Brechin, E. K., Milios, C.J., *Dalton Trans.*, **40**, **2011**, 1693.
43. Khanra, S., Helliwell, M., Tuna, F., McInnes, E. J. L., Winpenny, *Dalton Trans.*, **2009**, 31, 6166.
44. Miao, Y. L., Liu, J. L., Lin, Z. J., Ou, Y. C., Leng, J. D., Tong, M. L., *Dalton Trans.*, **2010**, 39 (20), 4893.

45. Malone, S. A., Lewin, A., Kilic, M. A., Svistunenko, D. A., Cooper, C. E., Wilson, M. T., Le Brun, N. E., Spiro, S., Moore, G. R., *J. Am. Chem. Soc.*, **2004**, 126, 496.
46. Theil, E. C., *Annu. Rev. Biochem.*, **1986**, 56, 289.
47. Xu, B., Chasteen, N. D., *J. Biol. Chem.*, **1991**, 266, 19965.
48. Greedan, J. E., *J. Mater. Chem.*, **2001**, 11(1), 37.
49. Thorpe, J. M., Beddoes, R. L., Collison, D., Garner, C. D., Helliwell, M., Holmes, J. M., Tasker, P. A., *Angew. Chem. Int. Ed.*, 38, **1999**, 1119.
50. Raptopoulou, C. P., Sanakis, Y., Boudalis, A. K., Psycharis, V., *Polyhedron*, 24, **2005**, 711.
51. Verani, C. N., Bothe, E., Burdinski, D., Weyhermuller, T., Florke, U., Chaudhuri, P., *Eur. J. Inorg. Chem.*, **2001**, 2161.
52. Mason, K., Gass, I. A., Parsons, S., Collins, A., White, F. J., Slawin, A. M. Z., Brechin, E. K., Tasker, P. A., *Dalton Trans.*, 39, **2010**, 2727.
53. Bill, E., Krebs, C., Winter, M., Gerdan, M., Trautwein, A. X., Florke, U., Haupt, H.-J., Chaudhuri, P., *Chem. Eur. J.*, 3, **1997**, 193.
54. Mason, K., Gass, I. A., White, F. J., Papaefstathiou, G. S., Brechin, E. K., Tasker, P. A., *Dalton Trans.*, 40, **2011**, 2875.
55. (a) Lah, M. S., Kirk, M. L., Hatfield, W., Pecoraro, V. L., *Chem. Commun.*, **1989**, 1606; (b) Chaudhuri, P., Winter, M., Fleischhauer, P., Haase, W., Florke, U., Haupt, H.-J., *Inorg. Chim. Acta.*, 212, **1993**, 241.
56. Raptopoulou, C. P., Boudalis, A. K., Sanakis, Y., Psycharis, V., Clemente-Juan, J. M., Fardis, M., Diamantopoulos, G., Papavassiliou, G., *Inorg. Chem.*, 45, **2006**, 2317.
57. Hołyńska, M., Clérac, R., Langer, T., Pottgen, R., Dehnen, S., *Polyhedron*, 52, **2013**, 1425.
58. Gass, I. A., Milios, C. J., Collins, A., White, F. J., Budd, L., Parsons, S., Murrie, M., Perlepes, S. P., Brechin, E. K., *Dalton Trans.*, **2008**, 2043.
59. Reddy, K. R., Rajasekharan, M. V., Tuchagues, J. P., *Inorg. Chem.*, **1998**, 37, 5978.
60. De Munno, G., Poerio, T., Viau, G., Julve, M., Lloret, F., *Angew. Chem., Int. Ed. Engl.*, **1997**, 36, 1459.
61. Mason, K., Prescimone, A., Schau-Magnussen, M., Piligkos, S., Tasker, P. A., Brechin, E. K., *Current Inorganic Chemistry*, **2013**, 3(2), 76.

62. Brechin, E. K., Knapp, M.J., Huffman, J. C., Hendrickson, D. N., Christou, G., *Inorg. Chim. Acta.*, **2000**, 297(1-2), 389.
63. Christmas, C. A., Tsai, H. L., Pardi, L., Kesselman, J. M., Gantzel, P. K., Chadha, R. K., Gatteschi, D., Harvey, D. F., Hendrickson, D. N., *J. Am. Chem. Soc.*, **1993**, 115(26), 12483.
64. Clemente-Juan, J. M., Mackiewicz, C., Verelst, M., Dahan, F., Bousseksou, A., Sanakis, Y., Tuchagues, J. P., *Inorg. Chem.*, **2002**, 41(6), 1478.
65. Drüeke, S., Wiegardt, K., Nuber, B., Weiss, J., Bominaar, E. L., Sawaryn, A., Winkler, H., Trautwein, A. X., *Inorg. Chem.*, **1989**, 28(25), 4477.
66. Poganiuch, P., Liu, S., Papaefthymiou, G. C., Lippard, S. J., *J. Am. Chem. Soc.*, **1991**, 113(12), 4645.
67. Taguchi, T., Stamatatos, T. C., Abboud, K.A., Jones, C. M., Poole, K. M., O'Brien, T. A., Christou, G., *Inorg. Chem.*, **2008**, 47(10), 4095.
68. Taguchi, T., Thompson, M. S., Abboud, K. A., Christou, G., *Dalton Trans.*, **2010**, 39(38), 9131.
69. Wiegardt, K., Bossek, U., Gebert, W., *Angew. Chem. Int. Ed.*, **1983**, 22(4), 328.
70. Wiegardt, K., Pohl, K., Gebert, W., *Angew. Chem. Int. Ed.*, **1983**, 22(9), 727.
71. Barra, A. L., Caneschi, A., Cornia, A., Fabrizi de Biani, F., Gatteschi, D., Sangregorio, C., Sessoli, R., Sorace, L., *J. Am. Chem. Soc.*, **1999**, 121(22), 5302.
72. Barra, A. L., Bencini, F., Caneschi, A., Gatteschi, D., Paulsen, C., Sangregorio, C., Sessoli, R., Sorace, L., *Chem. Phys. Chem.*, **2001**, 2(8-9), 523.
73. Boskovic, C., Brechin, E. K., Streib, W. E., Folting, K., Bollinger, J.C., Hendrickson, D. N., Christou, G., *J. Am. Chem. Soc.*, **2002**, 124(14), 3725.
74. Boskovic, C., Wernsdorfer, W., Folting, K., Huffman, J. C., Hendrickson, D. N., Christou, G., *Inorg. Chem.*, **2002**, 41(20), 5107.
75. Harden, N.C., Bolcar, M. A., Wernsdorfer, W., Abboud, K. A., Streib, W. E., Christou, G., *Inorg. Chem.*, **2003**, 42(22), 7067.
76. Lecren, L., Roubeau, O., Coulon, C., Li, Y. G., Le Goff, X. F., Wernsdorfer, W., Miyasaka, H., Clérac, R., *J. Am. Chem. Soc.*, **2005**, 127(49), 17353.
77. Murugesu, M., Habrych, M., Wernsdorfer, W., Abboud, K. A., Christou, G., *J. Am. Chem. Soc.*, **2004**, 126(15), 4766.
78. Sañudo, E. C., Brechin, E. K., Boskovic, C., Wernsdorfer, W., Yoo, J., Yamaguchi, A., Concolino, T.R., Abboud, K.A., Rheingold, A.L., Ishimoto, H., Hendrickson, D. N., Christou, G., *Polyhedron*, **2003**, 22(14-17), 2267.

79. Stamatatos, T. C., Abboud, K. A., Wernsdorfer, W., Christou, G., *Angew. Chem. Int. Ed.*, **2006**, 45(25), 4134.
80. Stamatatos, T. C., Poole, K. M., Abboud, K. A., Wernsdorfer, W., O'Brien, T. A., Christou, G., *Inorg. Chem.*, **2008**, 47(11), 5006.
81. Stamatatos, T. C., Vlahopoulou, G. C., Raptopoulou, C. P., Terzis, A., Escuer, A., Perlepes, S.P., *Inorg. Chem.*, **2009**, 48(11), 4610.
82. Yang, E. C., Wernsdorfer, W., Zakharov, L. N., Karaki, Y., Yamaguchi, A., Isidro, R. M., Lu, G. D., Wilson, S. A., Rheingold, A. L., Ishimoto, H., Hendrickson, D. N., *Inorg. Chem.*, **2005**, 45(2), 529.
83. Lis, T., *Acta Crystallogr.*, Sect. B, **1980**, 36, 2042.
84. Sessoli, R., Gatteschi, D., Caneschi, A., Novak, M. A., *Nature*, **1993**, 365, 141.
85. Xu, H. B., Wang, B.-W., Pan, F., Wang, Z.-M., Gao, S., *Angew. Chem. Int. Ed.*, **2007**, 46, 7388.
86. Stamatatos, T. C., Foguet-Albiol, D., Stoumpos, C. C., Raptopoulou, C. P., Terzis, A., Wernsdorfer, W., Perlepes, S. P., Christou, G., *J. Am. Chem. Soc.*, **2005**, 127, 15380.
87. Cano, J., Cauchy, T., Ruiz, E., Milios, C. J., Stoumpos, C. C., Stamatatos, T. C., Perlepes, S. P., Christou, G., Brechin, E. K., *Dalton Trans.*, **2008**, 234.
88. R. Inglis, C. J. Milios, L. F. Jones, S. Piligkos, E. K. Brechin, *Chem. Commun.*, **2012**, 181.
89. Milios, C. J., Whittaker, G. A., Brechin, E. K., *Polyhedron*, **2007**, 26, 1927.
90. Wenzel, M., Jameson, G. B., Ferguson, L. A., Knapp, Q. W., Forgan, R. S., White, F. J., Parsons, S., Tasker, P. A., Plieger, P. G., *Chem. Commun.*, **2009**, 3606.
91. Wenzel, M., Knapp, Q. W., Plieger, P. G., *Chem. Commun.*, **2011**, 47, 499.
92. Chang, J. Y. C., Parsons, S., Plieger, P. G., Tasker, P. A., *J. Incl. Phenom. Macrocycl. Chem.*, **2011**, 71, 529.
93. Wenzel, M., Forgan, R. S., Faure, A., Mason, K., Tasker, P. A., Piligkos, S., Brechin, E. K., Plieger, P. G., *Eur. J. Inorg. Chem.*, **2009**, 4613.
94. (a) Inglis, R., Jones, L. F., Collins, A., Moggach, S. A., Parsons, S., Perlepes, S. P., Wernsdorfer, W., Brechin, E. K., *Chem. Eur. J.*, **2008**, 14, 9117; (b) Inglis, R., Taylor, S. M., Jones, L. F., Papaefstathiou, G. S., Perlepes, S. P., Datta, S., Hill, S., Wernsdorfer, W., Brechin, E. K., *Dalton Trans.*, **2009**, 9157. (c) Inglis, R.,

- Jones, Karotsis, G., Collins, A., Parsons, S., Perlepes, S. P., Wernsdorfer, W., Brechin, E. K., *Chem Commun.*, **2008**, 5924.
95. Smith, A. G., Tasker, P. A., White, D. J., *Coord. Chem. Rev.*, **2003**, 241, 61; b) Stoumpos, C. C., Inglis, R., Karotsis, G., Jones, L. F., Collins, A., Parsons, S., Milios, C. J., Papaefstathiou, G. S., Brechin, E. K., *Cryst. Growth Des.*, **2009**, 9, 24; c) Prescimone, A., Milios, C. J., Moggach, S., Warren, J. E., Lennie, A. R., Sanchez-Benitez, J., Kamenev, K., Bircher, R., Murrie, M., Parsons, S., Brechin, E. K., *Angew. Chem. Int. Ed.*, **2008**, 47, 2828; e) Jones, L. F., Inglis, R., Cochrane, M. E., Mason, K., Collins, A., Parsons, S., Perlepes, S. P., Brechin, E. K., *Dalton Trans.*, **2008**, 6205; f) Feng, P. L., Koo, C., Henderson, J. J., Nakano, M., Hill, S., del Barco, E., Hendrickson, D. N., *Inorg. Chem.*, **2008**, 47, 8610; g) Yang, C.-I., Wernsdorfer, W., Cheng, K. -H., Nakano, M., Lee, G. -H., Tsai, H. -L., *Inorg. Chem.*, **2008**, 47, 10184; h) Raptopoulou, C. P., Boudalis, A. K., Lazarou, K. N., Psycharis, V., Panopoulos, N., Fardis, M., Diamantopoulos, G., Tchuagues, J. -P., Mari, A., Papavassiliou, G., *Polyhedron* **2008**, 27, 3575; i) Milios, C. J., Inglis, R., Jones, L. F., Prescimone, A., Parsons, S., Wernsdorfer, W., Brechin, E. K., *Dalton Trans.*, **2009**, 2812; j) Bahr, S., Milios, C. J., Jones, L. F., Brechin, E. K., Mosser, V., Wernsdorfer, W., *New J. Chem.*, **2009**, 33, 1231.
96. Mason, K., Chang, J., Prescimone, A., Garlatti, E., Carretta, S., Tasker, P. A., Brechin, E. K., *Dalton Trans.*, **2012**, 41, 8777.
97. Milios, C. J., Vinslava, A., Moggach, S., Parsons, S., Wernsdorfer, W., Christou, G., Perlepes, S. P., Brechin, E. K., *J. Am. Chem. Soc.*, 129, **2007**, 2754.
98. C. J. Milios, A. Vinslava, S. Moggach, S. Parsons, W. Wernsdorfer, G. Christou, S. P. Perlepes, E. K. Brechin, *J. Am. Chem. Soc.*, **2007**, 129, 2754.
99. Milios, C. J., Inglis, R., Vinslava, A., Bagai, R., Wernsdorfer, W., Parsons, S., Perlepes, S. P., Christou, G., Brechin, E. K., *J. Am. Chem. Soc.*, **2007**, 129, 12505.
100. Milios, C. J., Manolopoulou, E., Stoumpos, C. C., Siczek, M., Lis, T., Brechin, E. K., *Eur. J. Inorg. Chem.*, **2010**, 483.
101. Prescimone, A., Milios, C. J., Sanchez-Benitez, J., Kamenev, K. V., Loose, C., Kortus, J., Moggach, S., Murrie, M., Warren, J. E., Lennie, A. R., Parsons, S., Brechin, E. K., *Dalton Trans.*, **2009**, 4858.
102. Inglis, R., Bendix, J., Brock-Nannestad, T., Weihe, H., Brechin, E. K., Piligkos, S., *Chem. Sci.*, 1, **2010**, 631.

103. Wu, L-F., Wang, Z- X., Geng, J- P., Xiao, H- P, Li, M- X., *Inorg. Chim. Acta.*, **412** , **2014**, 1.
104. Smith, A. G., Tasker, P. A., White, D. J., *Coord. Chem. Rev.*, **2003**, 241, 61.
105. Forgan, R. S., Wood, P. A., Campbell, J., Henderson, D. K., McAllister, F. E., Parsons, S., Pidcock, E., Swart, P. M., Tasker, P. A., *Chem. Commun.*, **2007**, 4940.
106. Brundle, C. R., Evans, C. A. J., Wilson, S., *Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films*, Manning Publications Co., Greenwich, **1992**, p. 751.
107. Pecharsky, V. K., Zavalij, P. Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, Second, Springer, New York, **2009**, p.744.
108. Young, R. A., *The Rietveld Method. IUCr Monographs on Crystallography 5*, Oxford University Press, New York, **1995**, p. 308.
109. McElfresh, M., *Fundamentals of Magnetism and Magnetic Measurements*, **1994**, Quantum Design.
110. Black, R. C., Wellstood, F. C., *The SQUID Handbook, Vol. 2*, edited by Clarke, J., Braginski, A. I., Willey-VCH Verlag GmbH & Co. KGaA, Weinheim (Germany), **2004**, p. 391.
111. Graham, C. D., *J. Mater. Sci. Technol.*, **2000**, 16, 97.
112. Amthauer, G., Grodzicki, M., Lottermoser, W., Redhammer, G., *EMU Notes in Mineralogy, Vol. 6: Spectroscopic Methods in Mineralogy*, edited by Beran, A., Libowitzky, E., Eotvos University Press, Budapest, **2004**, p. 345.
113. Dyar, M. D., Agresti, D. G., Schaefer, M. W., Grant, C. A., Sklute, E.C., *Annu. Rev. Earth Planet. Sci.*, **2006**, 34, 83.
114. Gutlich, P., Bill, E., Trautwein, A.X., *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications*, Springer-Verlag, Berlin, Heidelberg, **2011**, p. 620.
115. Megaw, H. D., *Acta Cryst.*, **1968**, B24, 153.
116. Khanra, S., Weyhermüller, T., Bill, E., Chaudhuri, P., *Inorg. Chem.*, **45**, **2006**, 5911.

CHAPTER 2

IRON COMPLEXES OF SINGLE-HEADED SALICYLALDOXIMES

2.1 Salicylaldoximes

Salicylaldoximes are defined as the oxime functionalised derivative of salicylaldehyde (Figure 2.1).

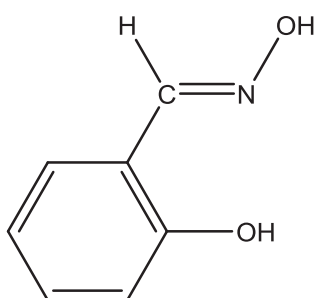


Figure 2.1: General structure of salicylaldoxime.

Our interest in phenolic oximes is driven by the ability of salicylaldoximes to bridge multiple metal centres (Figure 2.2). This chapter outlines attempts to synthesise polynuclear 3d metal clusters in a search for new molecule-based magnets using these phenolic oximes. Metal-oximates have been popular among inorganic chemists because they can be used as building blocks for the rational synthesis of polynuclear clusters.¹ Phenolic oximes have a natural tendency to form polynuclear complexes by using both the oxime and phenolate groups as chelating and/or bridging units in either a mono- or di-anionic form.²

Figure 2.2 illustrates the possible coordination and bridging modes of salicylaldoximes where M is the metal ion, μ displays the number of metal ions coordinated to the ligand and η exhibits different coordination sites of the ligand and the number of metal ions coordinated to each site. As an example, there is one metal ion coordinated to both oximic N-atom and phenolate O-atom of the salicylaldoxime and there are two metal ions coordinated to the oximic O-atom. Therefore, the coordination of the ligand can be written as $\mu_3: \eta^1: \eta^2: \eta^1$. Phenolic oximes can act as chelating agents via the phenolate

oxygen and oximate nitrogen atoms (see mode 1, Figure 2.2) in metal complexes.³⁻⁷ The phenolic oxygen can itself act as both a chelating and bridging agent (see mode 2, Figure 2.2).^{3,8}

Phenolic oximes as dianions usually use the phenolate oxygen and oximic nitrogen atoms to chelate to one metal and the oximate- oxygen atom (as a bridging unit) to bind to a second metal. This is the most common (μ_2) bridging mode (see mode 3, Figure 2.2). It has been reported that a variety of di-⁹⁻¹¹, tri-⁷⁻¹², and tetranuclear¹³⁻¹⁵ complexes consist of the $\mu: \eta^1: \eta^1: \eta^1$ coordination mode.

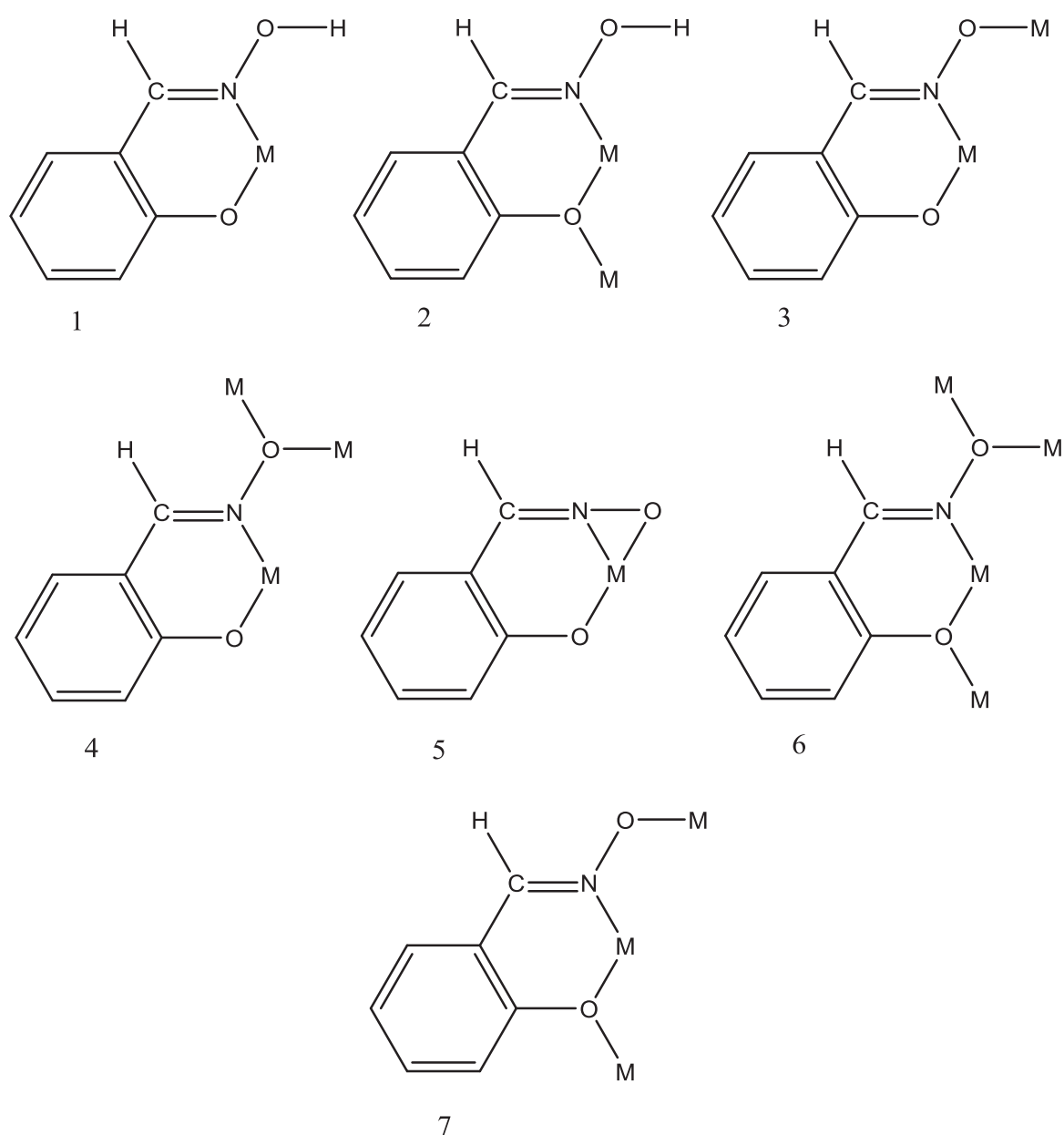


Figure 2.2: Coordination and bridging modes of salicylaldoximes.

The coordination mode $\mu_3: \eta^1: \eta^2: \eta^1$ is obtained by binding the oximic oxygen atoms to two metal ions leading to complexes with higher nuclearity, for example, a hexanuclear cluster (see mode 4)^{16,17} but has also been observed in tri-¹⁸ and tetranuclear⁴ complexes.

The di-anion can also act as a chelating tridentate ligand (see mode 5 in Figure 2.2). Modes 4 & 7 are the most common μ_3 binding modes and mode 6 has been reported as forming the largest polynucleating coordination complex to date.

In this project, almost exclusively, each of the complexes formed were of mode 3 (see Figure 2.2, 3).

2.2 Single-headed Salicylaldoximes

Doubly deprotonated salicylaldoximes open the possibility to form polynuclear metal complexes. The most common binding mode of these clusters is the trinuclear species depicted in Figure 2.3, which allows three metal ions to form in a triangle around a μ_3 -oxo atom (see Figure 2.4 for examples of ligands which contain just one of the salicylaldoxime units, the so called ‘single-headed’ oximes used in this project).

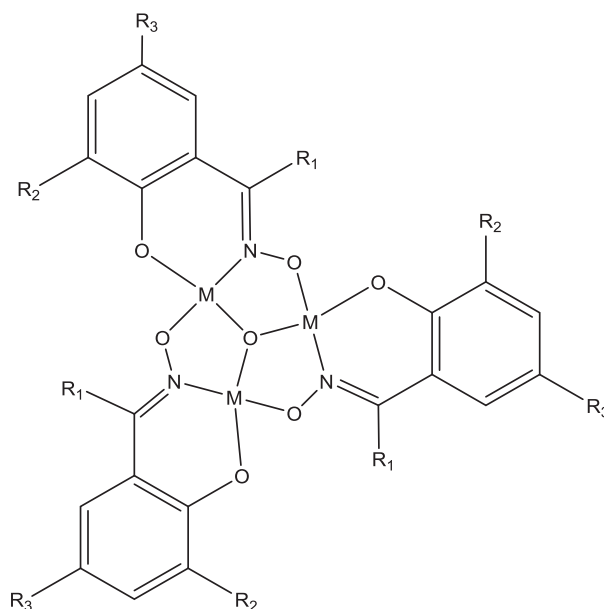


Figure 2.3: The most common building block for polynuclear complexes of salicylaldoximes, the $[M_3^{\text{III}}O(\text{oximate})_3]^+$ moiety, where $R_1 = \text{H}$, $R_2 = R_3 = \text{alkyl groups}$.

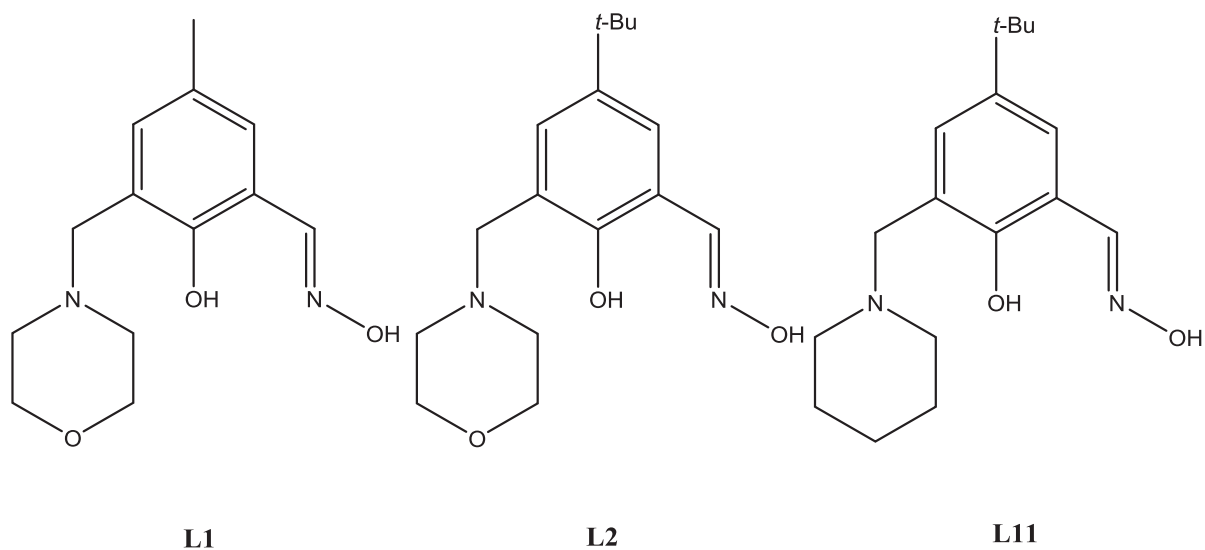


Figure 2.4: Examples of single-headed oximes utilised in this project.

2.2.1 Synthesis of the ligands

The ligand synthesis was started from the formylation reaction, which was carried out using the starting materials, 4-*t*-butyl-phenol for **L2** and **L11** and 4-methylphenol for all other ligands according to the experimental procedure as stated in Neilan *et al.*¹⁹ The resultant aldehydes were purified by column chromatography to give an average yield of 36 %. The aldehydes were then subjected to bromomethylation to produce 3-bromomethyl-2-hydroxy-5-methylbenzaldehyde (96%) and 3-bromomethyl-5-(1,1-dimethylethyl)-2-hydroxy-benzaldehyde (98%).²⁰ The coupling reactions between the bromo compounds and the secondary amines (compounds **2-5**, see experimental section for more details)²¹ to produce the precursors of the ligands were carried out using the experimental procedure stated in Plieger *et al.*²¹ The oximation, the last step of the ligand synthesis was carried out using the procedure published by Plieger *et al.*²¹

The precursor **L2a** of the ligand **L2** is a known compound which was previously synthesised and characterised by Tasker *et al* in 2000.²² The ligand **L11** was prepared in high yield and purity by oximation²³ of the precursor aldehyde, which had been synthesised previously²⁴ and every other ligand synthesised in this project was new.

2.2.2 NMR interpretation of the oximes and their precursors, aldehydes

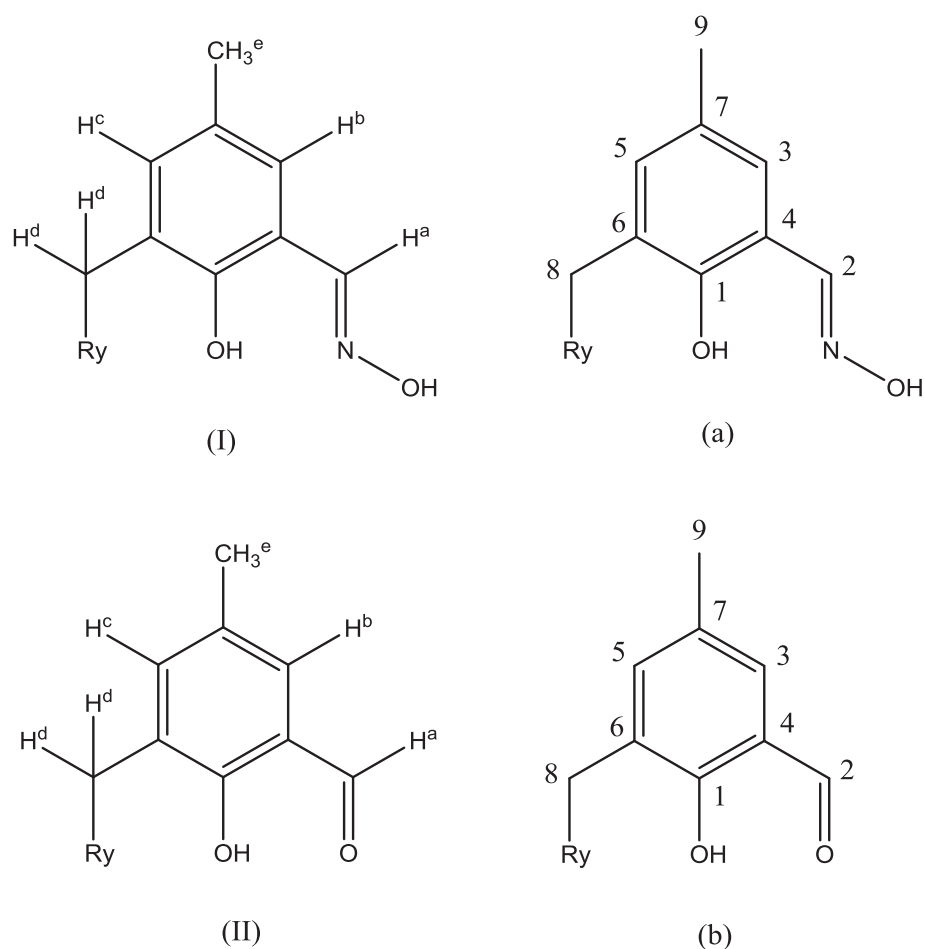


Figure 2.5: The common numbering for the aldehydes and the oximes, Ry = rest of the ligand.

A protocol of drying to constant weight under high vacuum was carried out for all the compounds. Even so, the NMR and CHN analyses indicate that there was some solvent remaining in the samples. It therefore appears that some solvent molecules are trapped within the compounds.

The chemical shifts in the ^1H NMR and ^{13}C NMR spectra for the common aromatic region and the functional groups on all the aldehydes and the oximes do not vary significantly. Therefore, the same numbering system has been used to interpret the spectra for the peaks that are common to all the aldehyde and oxime compounds (see Figure 2.5 and appropriate sections in the experimental).

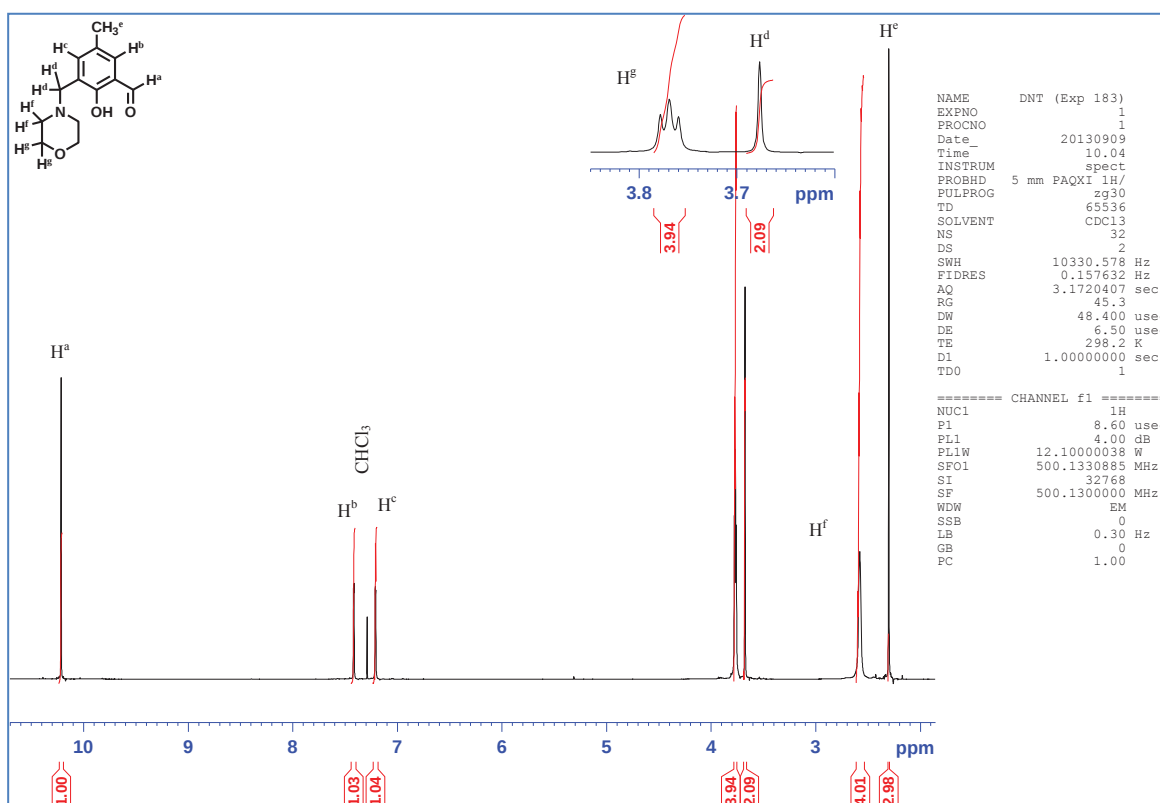


Figure 2.6: The ¹H NMR spectrum of L1a.

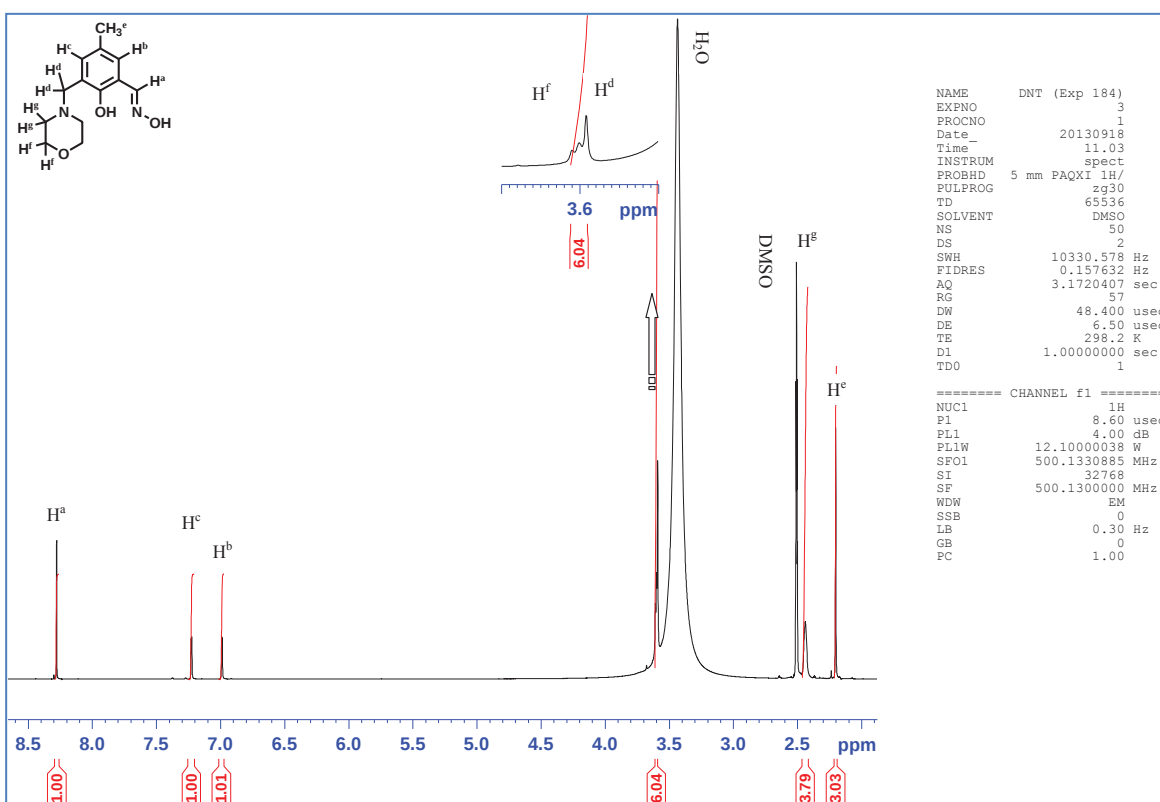


Figure 2.7: The ¹H NMR spectrum of L1.

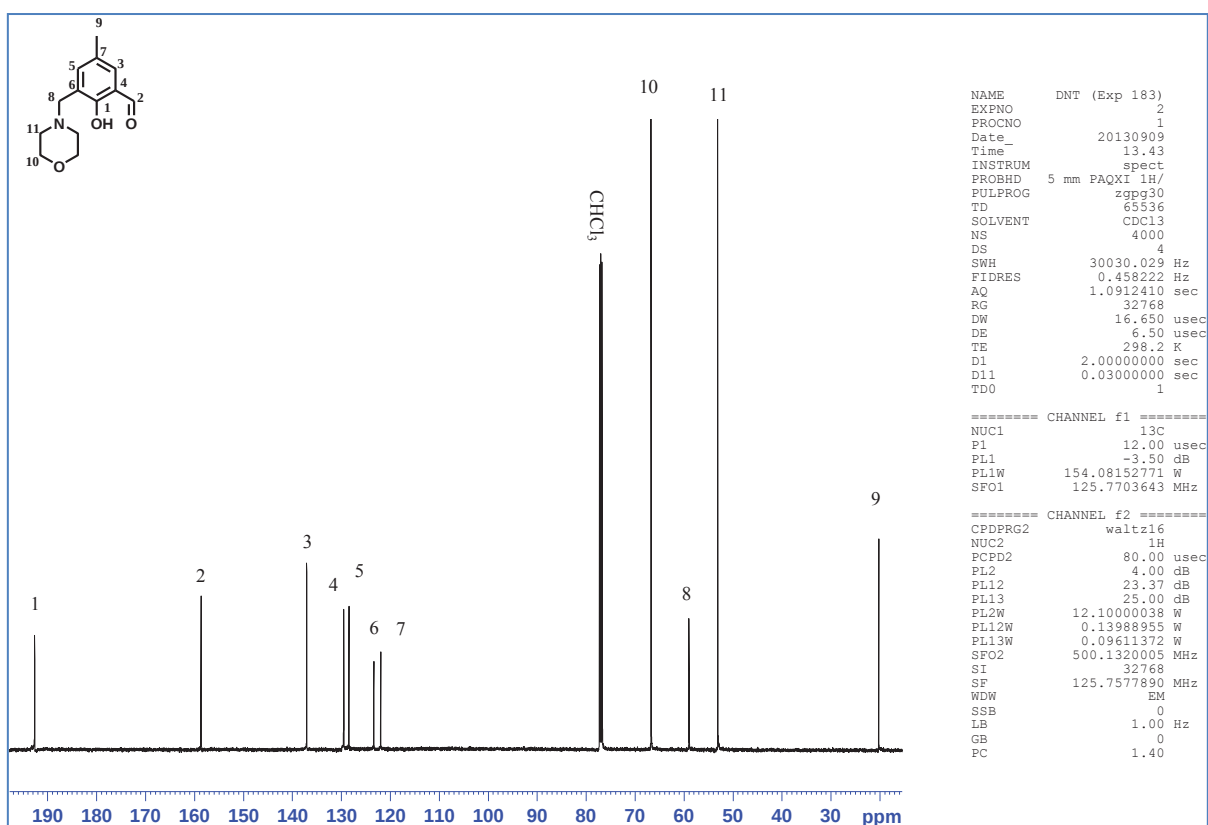


Figure 2.8: The ^{13}C NMR spectrum of **L1a**.

The carbon labelled C1 is located in the downfield and it is the most deshielded carbon atom of the compound as it is directly attached to the phenol O-atom. The carbon atom C2 is attached to the aldehyde oxygen atom in 2.5(b) and the oximic N-atom on the oxime (Figure 2.5, (a)). In both cases, the carbon atom C2 has the second highest chemical shift which was confirmed by the 2D NMR coupling between the proton H^a and C2. ^1H NMR spectral analyses on both oximes and aldehydes show that H^a , the proton which is attached to the O-atom either on the aldehyde group or oximic C-atom on the oxime has the highest chemical shift (see Figure 2.5, (I) and (II)). Representative spectra of the ligand **L1** and its precursor **L1a** are shown in Figures 2.6-2.10.

The quaternary aromatic carbon atoms 1 and 4 for all of the ligands are located with almost the same chemical shifts in the ^{13}C NMR spectrum. The carbon atom labelled C3 is located near the most electronegative regions such as the aldehyde group on the precursor and oximic group on the ligand.

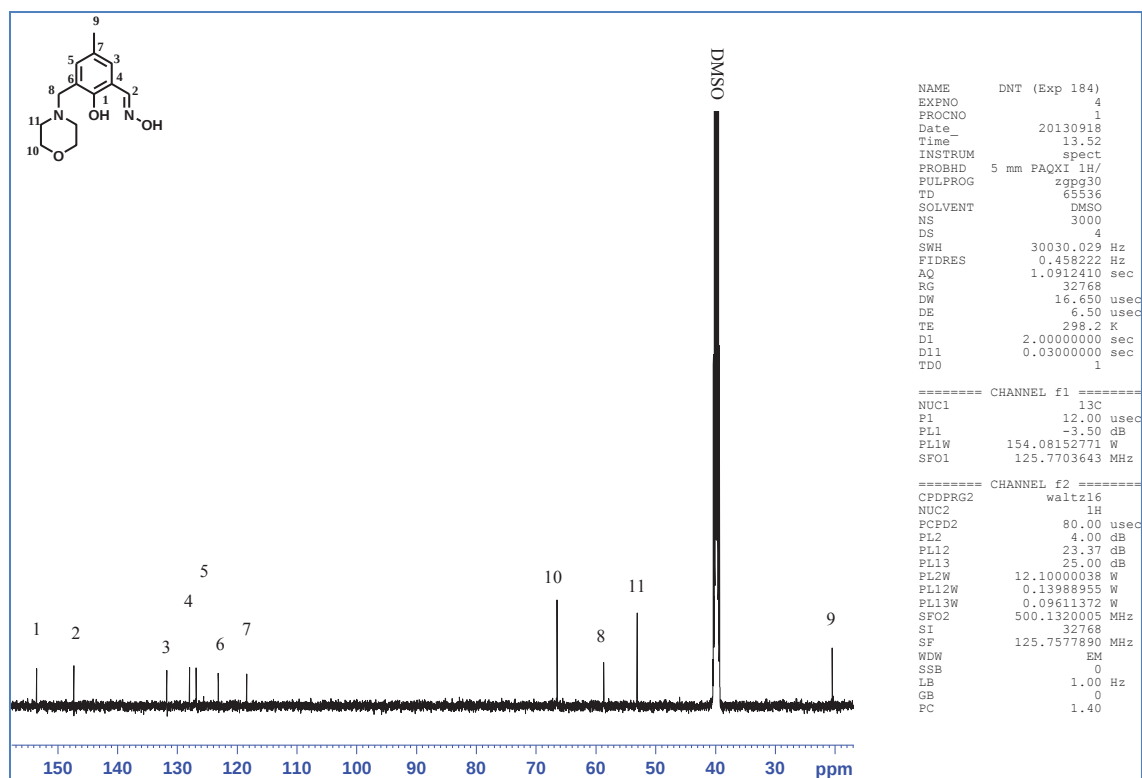


Figure 2.9: The ^{13}C NMR spectrum of L1.

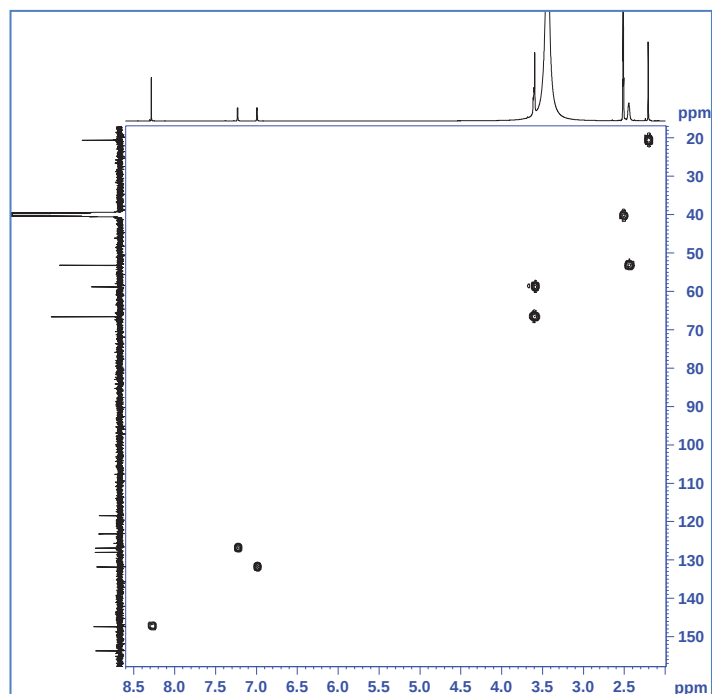


Figure 2.10: The HMQC spectrum of L1.

Therefore, the C3 carbon always has a higher chemical shift than that of C5. Correspondingly, the 2D correlation spectral analysis reveals that the hydrogen H^c always has a higher chemical shift than that of H^b in the ¹H NMR spectra for ligands containing both aldehydes and oximes. The protons labelled H^d, directly attached to the Ry (the rest of the ligand) and aromatic C6 carbon are always located around the chemical shift region of 3.5-3.8 ppm on all the the aldehyde and oxime in the ¹H NMR spectra and 55-60 ppm in the ¹³C NMR spectra. The protons labelled H^e on the C9 carbon which in turn is directly attached to the common aromatic ring on all the ligands and their precursors, are revealed as possessing the most upfield chemical shifts in both the ¹H NMR and ¹³C NMR spectra. The signal for this group H^e always comes around 2.2 ppm for all the ¹H NMR spectra of both the ligands and their precursors when there is only one methyl group attached to the common aromatic ring (see Figure 2.5, I and II). The C9 peak occurs around 20 ppm in all the ¹³C NMR spectra for all the aforementioned ligands and aldehydes. The exceptions are ligand **L2** and **L11**²⁵ and their precursors which due to the *p-t*-Bu group have signals at 1.2 ppm in the ¹H NMR spectrum and the carbon signal is found around 31 ppm in the ¹³C NMR spectrum.

The protons and C-atoms on the Ry arm (see Figure 2.11 and Table 2.1) of each ligand and its precursor were assigned according to the 2D correlations, chemical shifts of the atoms relating to their electronegativity, integration relating to the number of protons at the same chemical environment, and the symmetry of the molecule (see Appendix for the assignments).

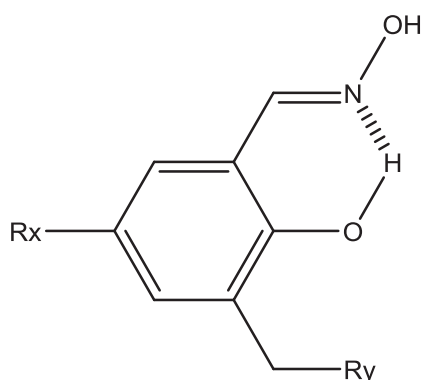


Figure 2.11: General structure of derivatised salicylaldoximes.

Table 2.1: Derivatised ‘single-headed’ salicylaldoximes utilised in the project.

Ligand		Rx	Ry
3-Ry-5-Me-saoH ₂	L1	Me	-N(CH ₂ CH ₂) ₂ O
3-Ry-5- <i>t</i> -Bu-saoH ₂	L2	<i>t</i> -Bu	-N(CH ₂ CH ₂) ₂ O
3-Ry-5-Me-saoH ₂	L3	Me	-N(CH ₂ CH ₂) ₂ CO ₂ (CH ₂) ₂
3-Ry-5-Me-saoH ₂	L4	Me	-N(CH ₃)CH ₂ CH(OCH ₃) ₂
3-Ry-5- <i>t</i> -Bu-saoH ₂	L11	<i>t</i> -Bu	-N(CH ₂ CH ₂) ₂ CH ₂

The OH group on benzene is a strong ortho-para director. Thus, blocking the *para*-position (Rx) is required before the bromination of the aldehyde. The bulkiness of the Rx position appears to affect the solubility of the ligands and thereby affects the solubility of the ultimate metal complex. The Ry position is occupied by various tertiary amine groups containing hetero-atoms (see Table 2.1). Therefore, parameters such as polarity, molecular weight, inter-molecular forces, and solubility of the resultant ligands are varied. The general synthetic scheme of the ligands is shown in the Figure 2.12 (see Appendix for descriptive synthesis and characterisation of each ligand).

Y = secondary amine

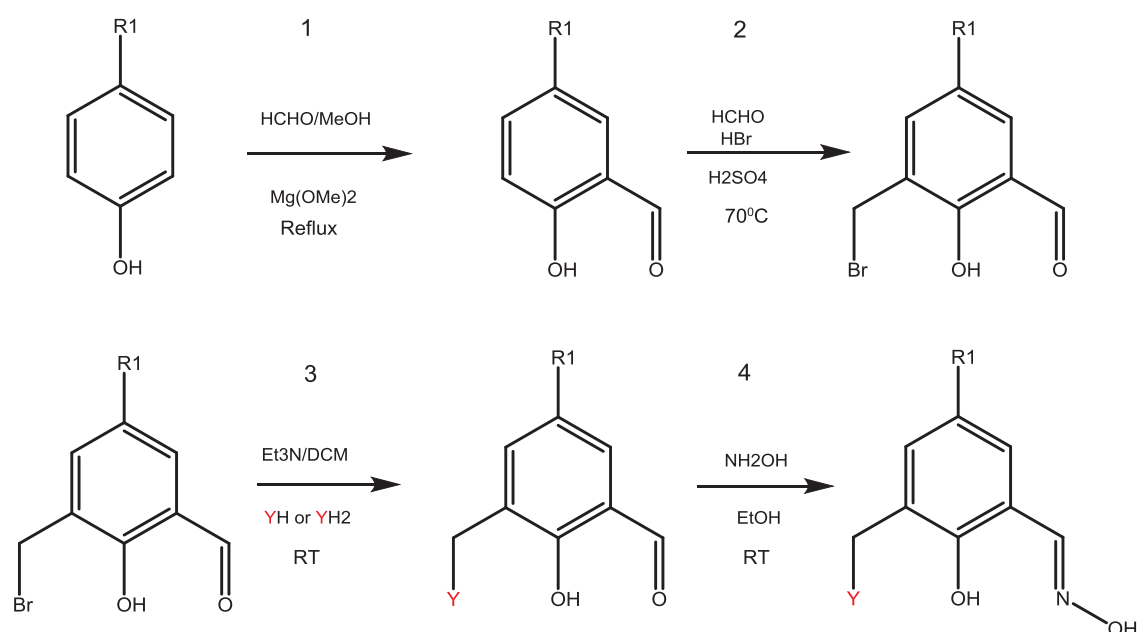


Figure 2.12: General synthetic scheme of the salicylaldoxime ligands.

2.3 Complexation reactions and crystallisation

The desired metal ions used for the complexation reactions were Fe^{2+} and Cu^{2+} (see Table 2.2 for the metal salts used in this project) and also a number of complexation attempts were made with Ni(II) salts with no success. Mixed oxidation states of manganese as well as iron in salicylaldoxime clusters are known to play a considerably important role in increasing the total ground state spin and also the energy barrier to magnetic reversal (see literature review for more information). Copper complexes of salicylaldoximes are abundantly studied due to the ease of crystallising the complexes, the diversity of resulting structures, as well as the exploration of host guest properties (see literature review and Chapter 3 for more information).

The di-anionic form of the single-headed oximes allows the metal ions to bind to the ligand (the modes of chelating and bridging of the metal ions are explained under heading 2.1) which ultimately should result in a multinuclear cluster.

Table 2.2: Metal salts utilised in the project.

Cu^{2+}	Fe^{2+}
$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$
$\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Fe}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
CuBr_2	

The deprotonation of the oximic functional group of the ligands was carried out using bases such as NaOMe, pyridine, 4-*t*-butyl pyridine, 2-pyridinemethanol, 4-dimethylaminopyridine in different ligand to base molar ratios. Most of the reactions were carried out in MeOH, EtOH, or MeCN at room temperature varying the metal salt to ligand molar ratios as well as the ligand to base ratio. High boiling point solvents such as DMF and DMSO were used, when the reactions were performed at very high temperatures such as $\sim 200^\circ\text{C}$ or higher in a sealed system. Solvothermal or hydrothermal synthesis of a number of complexes was also trialled in an effort to grow crystals of high temperature clusters but were ultimately not successful.

Several parameters were varied in the complexation attempts such as temperature, molar ratios of the reactants, solvent medium, and also the order in which the chemical reactants were added to the reaction. In addition to the very high temperature and room temperature reactions, moderate temperatures such as 30°C - 80°C were also used.

Colour change in every complexation reaction confirmed that complexation had occurred. Despite this, it was difficult to get full information on each complex that did not crystallise. The data sought included the nuclearity of the complex, the oxidation states of the metal ions that are coordinated, the anions and/or cations, and/or solvent molecules within the complex or lattice. It has also been difficult to predict the structure of the complexes formed in every reaction based just on the normal non-structural characterisation due to the numerous possibilities of assembly (see Figure 2.2).

The main goal of this project was to study the magnetic properties of the metal complexes. The crystal structure of the metal complex is therefore a must for magnetic measurements as the fitting of these data requires structural parameters such as bond lengths, bond angles, torsion angles, metal-ligand connectivity and the presence of lattice solvent. Therefore, forming X-ray quality crystals of the metal complexes was the major experimental task.

There were several techniques that were trialled in an effort to form quality crystals. Parallel crystallisation attempts had been made using different techniques for every complex. The abundantly used crystallisation techniques during this project were solvent evaporation, vapour diffusion, and solvothermal and hydrothermal synthesis. Although, numerous conditions were used, only the complexations of the oximes in MeOH with the salt $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of pyridine at room temperature followed by the slow solvent evaporation resulted in X-ray quality crystals of the iron-oxime clusters. The formulations of the metal complexes were assigned according to the analytical techniques such as Mössbauer, Infrared spectroscopy and microanalysis. There were large amounts of water present in some of the metal complexes which could have happened during weighing prior to CHN analysis and also there were some potential magnetic impurities present in some of the metal complexes (**C1**). Additionally, the crystal structure of the ligand **L2** was elucidated as a result of one of

the complexation attempts with $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in MeCN at room temperature followed by the diffusion of DEE into the complex in MeCN.

The copper complexes were formed as a result of the reactions between some of the ‘double-headed’ oximes (see Chapter 3) and $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ salt in MeOH/pyridine solution at room temperature. All the copper complexes for which the X-ray structures were obtained were crystallised by slow evaporation of the filtered reaction mixture.

2.3.1 Crystal structure of L2

As stated above, the **L2** ligand structure was elucidated after crystals were grown as a result of an attempt to complex **L2** with $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in MeCN at room temperature (see Figure 2.13). The analysed crystal was an irregular shape and green in colour. This ligand crystallises in the space group $P\bar{1}$ and the asymmetric unit contains the complete molecule with two molecules per unit cell. The ligand **L2** is present as a cation as the nitrogen atom N(612) on the morpholino part of the ligand is protonated (H612) and the NO_3^- ion is present within the lattice. The structure refined to a final $R1 = 6.31\%$; details of refinement can be found in Table 2.18.

There are several moderately strong H-bond interactions such as between the phenolic H-atom and oximic N-atom (1), O-atoms on NO_3^- ion and the H-atom on the morpholino N-atom (2) & (3) (see Table 2.3).

Each of the ionisable protons was found via the difference map and refined isotropically with the exception of H612 as this led to a long NH bond and subsequent alert.

Table 2.3: H-bond lengths for **L2**.

Atoms (D·····A)	Distance (Å)
O11-H11·····N212	2.635(3)
O213- H213·····O103'	2.751(3)
N612- H612·····O102	2.740(2)

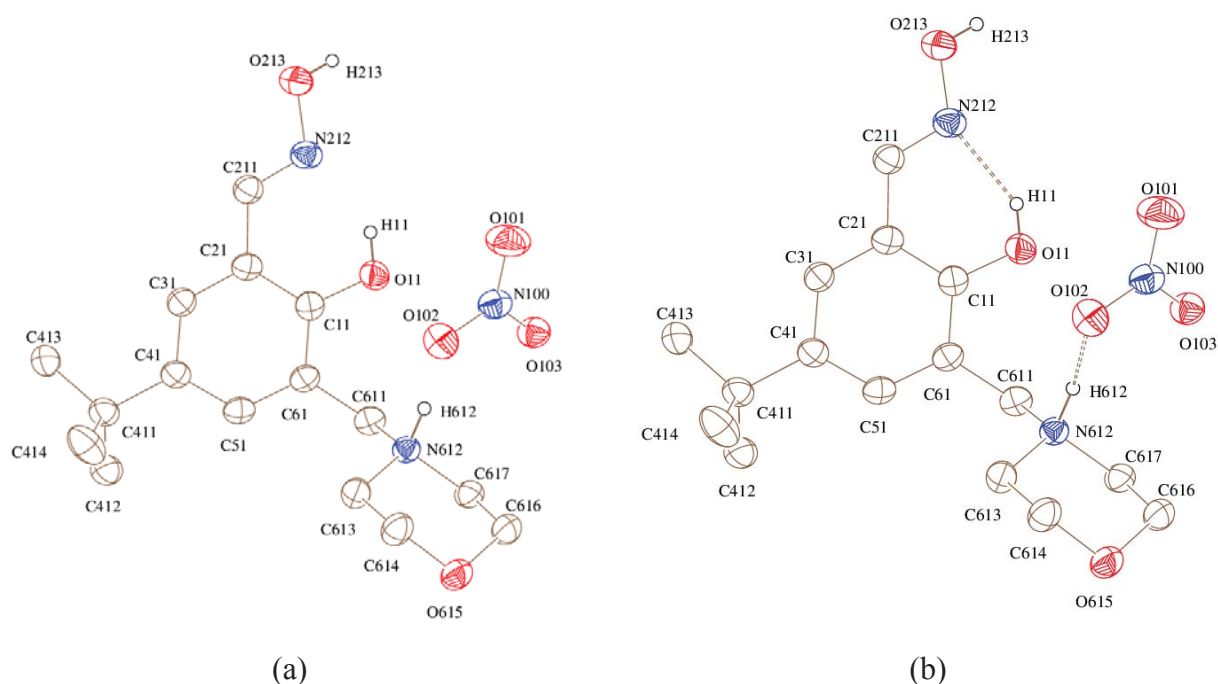


Figure 2.13: (a) Crystal structure of HL2⁺·NO₃⁻ (b) H-bonds present within the lattice (C-brown, N-blue, O-red, H-white, H-bonds are illustrated in brown dotted lines); ORTEP view at 30% probability level.

2.4 IR spectral analyses of the Fe complexes

The ligands and the complexes were characterised using general analytical techniques such as NMR (for organic compounds), CHN, IR and UV-Vis in addition to magnetic and Mössbauer techniques for the metal complexes.

Despite minor variations in the ligands, the coordination modes of all the iron complexes are more or less similar as all the ligands carry the same main functional groups which are involved in coordination to the metal ions. Therefore, we cannot expect significant variations of IR spectra of the metal complexes.

The medium absorption peak at 1610-1625 cm⁻¹ due to C=N stretching on the free ligand has shifted to lower or higher frequencies in the range 1-5 cm⁻¹ in all the Fe complexes to indicate the coordination of the N-atoms to Fe atoms in the complex.²⁶ The strong stretch of C-O at 1267-1288 cm⁻¹ on the free ligand has also shifted to slightly higher frequencies at 1300 cm⁻¹ in all the Fe complexes as the O-atoms are

coordinated to the Fe atoms in the complex.²⁷ A very strong N-O stretch on all the free oxime ligands at around 1000-1100 cm⁻¹ has shifted to higher frequencies of around 1125 cm⁻¹ in the Fe complexes due to the covalent bonding between N and Fe.²⁸ The very strong absorptions around 1450 cm⁻¹ and 730-860 cm⁻¹ on both the ligands and the metal complexes reveal the scissor vibrations on the aliphatic -CH₂ and aromatic C-H bending. Weak vibrations of Fe-N and Fe-O appear around 430 cm⁻¹ and 520 cm⁻¹ for all the Fe complexes. A strong intensity absorption at 480 cm⁻¹ is an indication of the presence of [Fe₃-μ₃O]⁷⁺ units.²⁸ Therefore, the complexes indicating the aforementioned band in the IR spectra are assigned to contain oxo groups as the central O-atoms within the metal triangles. The BF₄⁻ ions contained within the lattices indicate an absorption band at 1084 cm⁻¹.²⁹ The N⁺-H stretch around 3400 cm⁻¹ is an indication of the protonation of the amine N-atoms of the ligands in the complexes.³⁰

2.4.1 Complex [Fe₂B₂(L1-H)₄(F)₂(O)₂](BF₄)₂ (MeOH)₄,

C1·4MeOH

Reacting Fe(BF₄)₂·6H₂O with **L1** in a molar ratio of 1 : 1 in MeOH/pyridine solution and subsequent crystallisation yielded dark red rhombic shaped crystals of the complex [Fe₂B₂(L1-H)₄(F)₂(O)₂](BF₄)₂(MeOH)₄ (**C1**·4MeOH) which crystallises in the *P* $\bar{1}$ space group. The asymmetric unit consists of half the molecule (see Figure 2.14) with the other half generated by inversion symmetry.

The complex contains four molecules of the ligand **L1** is present as **L-H** in which the phenolic and oximic oxygen atoms are deprotonated and the amino nitrogen atom is protonated, two boron atoms, two hydroxo groups, and two oxo groups. Additionally, four solvent molecules (MeOH) and two BF₄⁻ ions are found within the lattice.

Each boron atom of the complex lies in a distorted tetrahedral geometry (see the bond lengths and angles in Tables 2.4 and 2.5) by coordinating to two oximic oxygen atoms from two of the ligands, an oxygen atom which is assumed to have come from water as hydrolysis products of the anion, and a F⁻ ion. These boron atoms and fluoride ions are also assumed to have come from hydrolysis of BF₄⁻ ions which ultimately resulted in two BO₃F parts within the structure (further explained at the end of the section 2.4.1).

Each oxo group (O13 and O13^a) is coordinated to an iron atom as well as to a boron atom which forms the bridge between the Fe and B atoms and each oximic N-O unit also forms a bridge between each Fe and B atoms. Both Fe(III) atoms and oxo groups (O13 and O13^a) sit in the same plane while boron atoms sit out of the plane on either side (see Figure 2.15 and 2.16). Each iron atom lies in a distorted octahedral geometry by coordinating to an oximic nitrogen atom (N212), a phenolate oxygen atom (O11), and to a bridging oxo group (either O13 or O13^a) in the asymmetric unit (see Figure 2.14 and 2.15). As the ligand L1 is a single headed oxime, all four ligands and boron atoms together with the bridging oxygen atoms provide the coordination donors to both Fe(III) atoms and therefore in contrast to the other iron complexes, no pyridine molecules are coordinated to the complex. The added pyridine presumably played a role in deprotonating all the phenolic and oximic groups of the ligands.

Table 2.4: Selected bond lengths of the complex **C1**·4MeOH

Bond	Distance (Å)	Bond	Distance (Å)
Fe1-O11	1.961(3)	Fe1-O13 ^a	2.011(3)
Fe1-O12	1.919(3)	F226-B224	1.406(5)
Fe1-O13	2.038(3)	B224-O13	1.440(6)
Fe1-N212	2.171(4)	B224-O223	1.495(5)
Fe1-N222	2.154(4)	B224-O225	1.490(6)

The bond distance between the boron centres and the oxo groups (O13 and O13^a) of the complex **C1**·4MeOH is 1.440(6) Å which is considerably higher than the B224-F226 bond length (1.406(5) Å) of the complex **C1**·4MeOH. The CHN results for the complex **C1**·4MeOH can be matched with eight water molecules which might have come from atmospheric moisture. Therefore, CHN analysis and the B224-F226 bond length confirm that it is not an oxygen atom but a fluorine atom bound to the boron atom in the complex **C1**·4MeOH.³¹

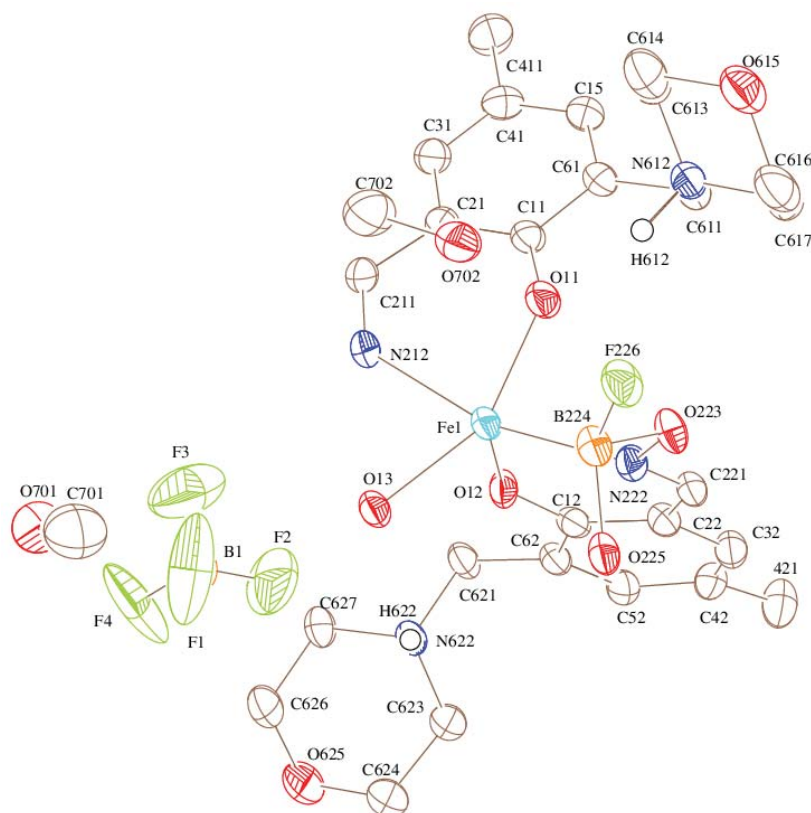


Figure 2.14: Asymmetric components of the crystal structure **C1·4MeOH**, [FeB(L1-H)₂F(O)](BF₄)(MeOH)₂ (Fe-cyan, B-orange, N-blue, O-red, F-green, C-brown, H-white and all H-atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms); ORTEP view at 50% probability level.

Table 2.5: Distorted tetrahedral angles of a boron atom and Fe(III) atom of the complex **C1·4MeOH**.

Atoms	Angle (°)	Atoms	Angle (°)
O11-Fe1-O12	106.31(13)	O13 ^a -Fe1-N222	76.54(13)
O11-Fe1-O13	151.99(13)	O13-Fe1-N222	122.45(13)
O11-Fe1-N212	80.99(13)	O13-Fe1-O13 ^a	78.24(11)
O11-Fe1-N222	81.89(13)	N212-Fe1-N222	160.85(12)
O11-Fe1-O13 ^a	96.42(13)	F226-B224-O13 ^a	113.0(4)
O12-Fe1-N212	93.77(14)	O13 ^a -B224-O223	111.6(4)
O12-Fe1-N222	82.87(13)	O13 ^a -B224-O225	111.7(3)
O12-Fe1-O13 ^a	146.73(13)	O223-B224-O225	105.6(4)
O13-Fe1-N212	76.36(12)	F226-B224-O223	105.8(3)
O13 ^a -Fe1-N212	113.89(13)	F226-B224-O225	108.8(4)

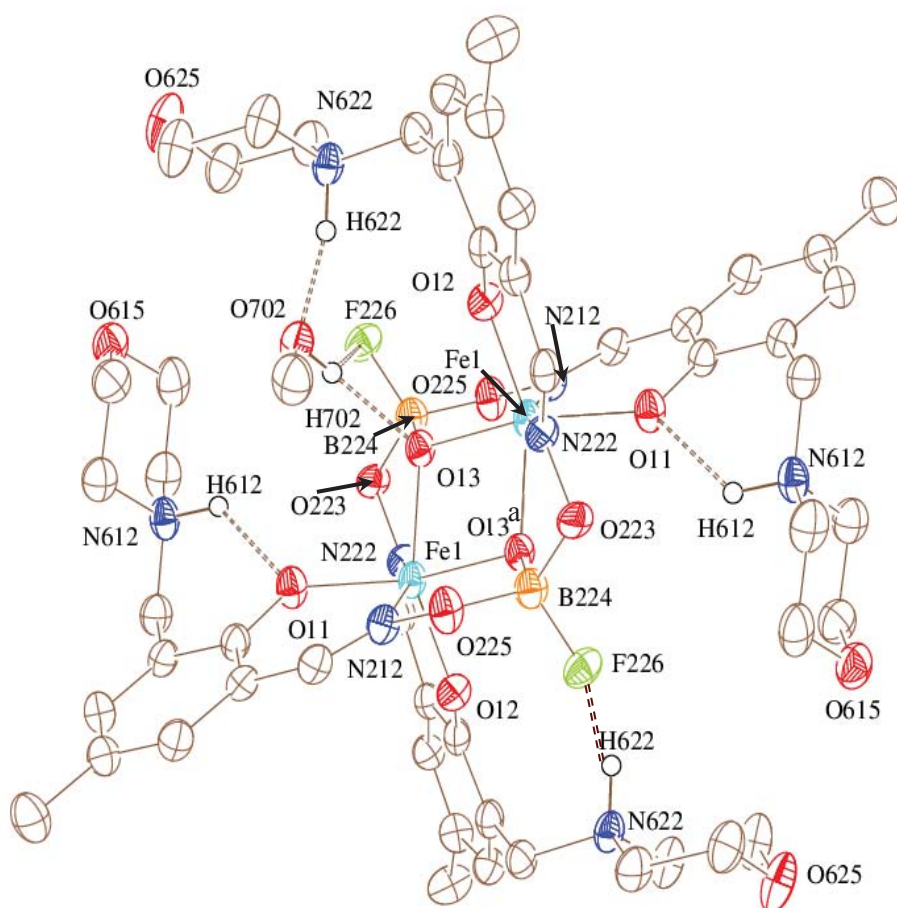


Figure 2.17: Selected H-bond contacts drawn in brown dotted lines within the complex, $[\text{Fe}_2\text{B}_2(\text{L1-H})_4\text{F}_2(\text{O})_2]^{2+}$ (Fe-cyan, F-green, N-blue, O-red, C-brown, B-orange, H-white, and all the non H-bonding H-atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms); ORTEP view at 50% probability level.

Table 2.6: Selected H-bond lengths of the complex **C1**·4MeOH.

Atoms (D·····A)	Distance (Å)
N622-H612·····O11	2.752 (4)
N622-H622·····O702	2.799 (4)
O702-H702·····F226	2.859(5)
O702-H702·····O13	2.798(4)

The hydrogen atoms on the amines are involved in forming numerous H-bonds. They form an intramolecular H-bond with the phenolate O-atom and a weak intermolecular H-bond with the hydroxyl oxygen atom of the solvent methanol molecule (see Figure 2.17 and Table 2.6). All H-bonds appear to be moderately strong as the bond lengths are

all greater than 3.2 Å.³² The oxidation states of Fe atoms were determined to be all 3+ using charge balance considerations (see Table 2.7) and were later confirmed by Mössbauer spectroscopy.

Table 2.7: Charge balance analysis of the complex **C1**.

2 Fe ³⁺	2 B ³⁺	4 (L1-H)	2 F ⁻	2 O ²⁻	2 BF ₄ ⁻
2 x 3+	2 x 3+	4 x 1-	2 x 1-	2 x 2-	2 x 1-
6+	6+	4-	2-	4-	2-

Both iron atoms in the complex **C1** are in the 3+ oxidation state as confirmed by the Mössbauer analysis. Each of four ligands possesses a 1- charge as both phenolate and oximic O-atoms are deprotonated and the amine N-atom is protonated. Thus, the four ligands contribute a total 4- charge to the complex. The two Fe-bridging O-atoms have a 4- charge, two boron atoms together give a 6+ charge, and two fluoride and BF₄⁻ ions together balance the remaining 4- charge of the complex.

In 1992, Rose *et al* reported three binuclear iron compounds featuring a similar dinuclear structure to **C1**·4MeOH.³³ The first compound (I) (see Figure 2.18(b)) has been isolated from a reaction of 2,6-diacetylpyridine dioxime (DAPDH₂) with ferric chloride hydrate in the presence of phenylboric acid in methanol and the second compound (II) has been obtained by dissolving the first compound (I) in pyridine followed by recrystallisation in a water/acetonitrile solution. Evaporation of the filtrate which was obtained from a mixture of phenylboric acid, DAPDH₂, ferric chloride, and sodium hydroxide in water produced the third di-iron compound (III) which was extracted with chloroform which was again recrystallised from tetrahydrofuran.

All three di-iron compounds contain the same core (see Figure 2.18(b)) similar to the core which is present in the complex **C1**·4MeOH (see Figure 2.18(a)). The iron atoms are bridged by two O-atoms from the phenylborate moiety in compound (I) (see Figure 2.18(b)). Each of the iron atoms are coordinated by three N-atoms from a dioxime, two bridging O-atoms from a phenylborate. The methoxide O-atom in the middle of the cage and the Cl atoms act as the axial coordination sites for the metal. The compound (II) contains a bridging OH- group instead of a methoxide and compound (III) has a

chloride ion in the middle to bridge the iron atoms. These Fe_2B_2 complexes contain a similar core as in the complex **C1**, as well as **C10** (see Chapter 3, section 3.3.1).

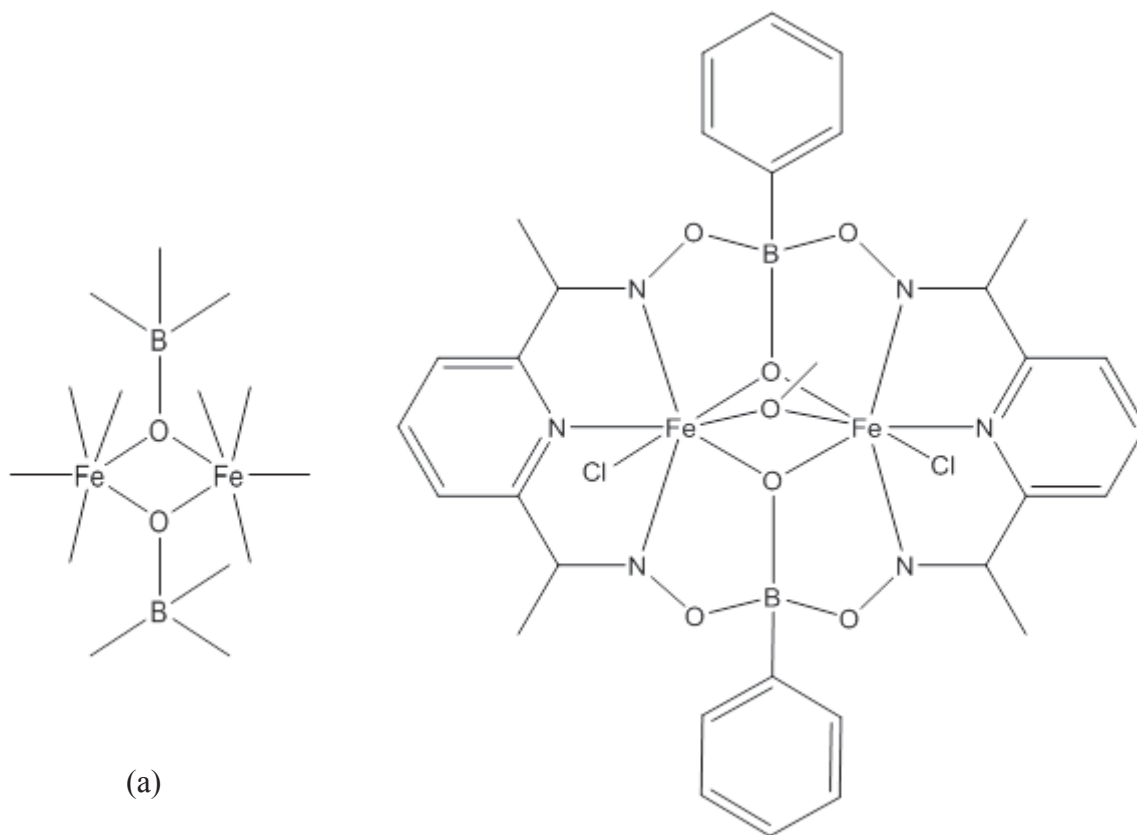


Figure 2.18: (a) The core of the complex **C1**·4MeOH, (b) Compound (I), $[\text{Fe}_2(\text{C}_{30}\text{H}_{29}\text{B}_2\text{N}_6\text{O}_6)\text{Cl}_2(\text{CH}_3\text{O})]$

In 2006, Chaudhuri and his coworkers synthesised a linear tetranuclear complex containing a $\text{B}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}\text{B}^{\text{III}}$ unit (see Figure 2.19(a) for the crystal structure). This was as a result of the reaction between the ligand, 2-6-diformyl-4-methylphenol oxime (H_3dfmp , see Figure 2.19(b)) and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 1.5 : 1 molar ratio in methanol in the presence of triethylamine to which methylboronic acid ($\text{CH}_3\text{B}(\text{OH})_2$) was added. The subsequent recrystallisation of the yellow precipitate from the reaction in DCM-EtOH mixture resulted in the crystal structure shown in Figure 2.19(a).³⁴

As illustrated in Figure 2.19, $[\text{Mn}_2(\text{dfmp})_3]^{5-}$ links two $\text{CH}_3\text{B}^{\text{III}}$ centres through the deprotonated oximato oxygen atoms. The phenolate oxygen atoms of all three ligands are μ_2 bridging that separate the Mn centres by 2.9091(6) Å. The Mn centres lie in a distorted octahedral geometry with each having a $\text{MnN}_3(\text{oximato})\text{O}_3(\text{phenolate})$ donor set

while boron centres are tetrahedrally coordinated by a carbon atom of the CH₃- group, and three adjacent phenolate oxygen atoms from three ligands.

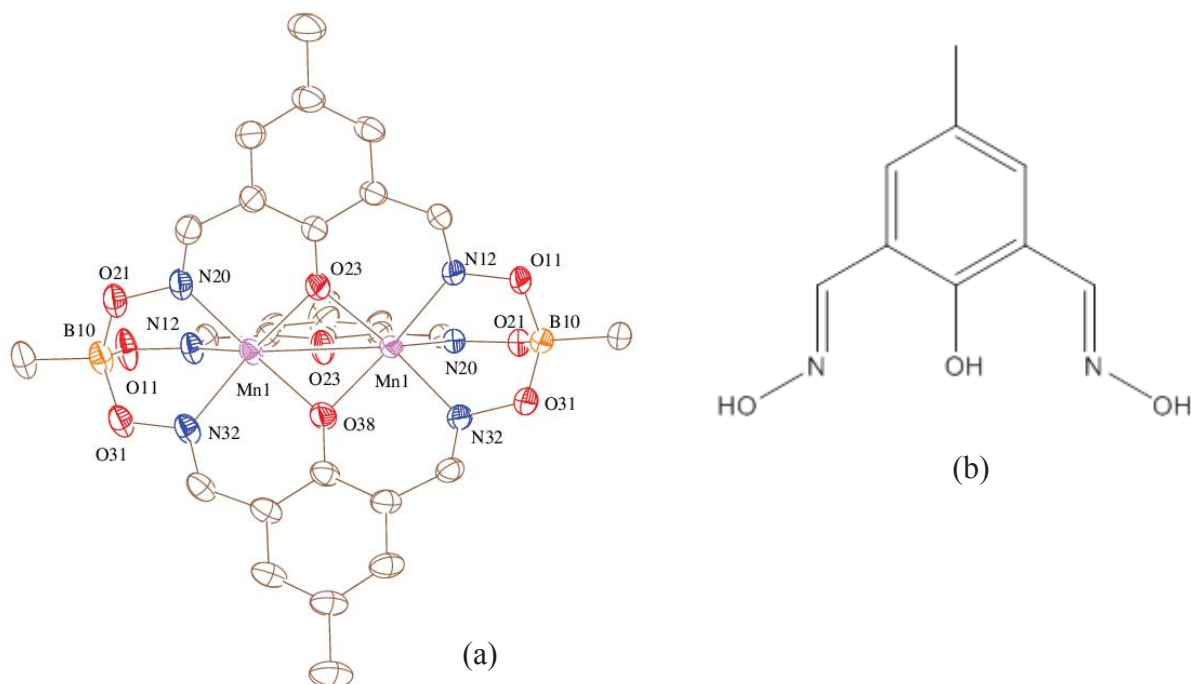


Figure 2.19: (a) Linear tetranuclear complex containing a B^{III}Mn^{II}Mn^{II}B^{III} unit²⁸, (b) 2-6-diformyl-4-methylphenol oxime (H₃dfmp).³⁴

The bond distances between the boron centres and oximato oxygen atoms lie in the range of 1.496(3)-1.506(3) Å, which is analogous with the two boron-oximato oxygen bond lengths (B224-O225 = 1.490(6) Å, B224-O223 = 1.495(5) Å) of the complex C1·4MeOH.

2.4.2 Complex [Fe₆O(OH)₇(L1-H)₅(L1-2H)](BF₄)₂(MeOH)₅, C2·5MeOH

The reaction of **L1** with Fe(BF₄)₂·6H₂O in a molar ratio 1 : 1 in a MeOH/pyridine solution followed by crystallisation, produces dark red rhombic shaped crystals of the complex [Fe₆O(OH)₇(L1-H)₅(L1-2H)](BF₄)₂·(MeOH)₅ (**C2**·5MeOH) that crystallises in the *P* $\bar{1}$ space group.

The complex contains two structures that are crystallographically independent. These two structures are similar as they both carry the same chemical environment. The asymmetric unit contains only half the overall molecule of both structures (see Figure 2.20). The full complex is generated by inversion symmetry. The asymmetric unit of

each molecule consists of three metal centres, three ligand molecules, two of the six hydroxo groups bridging the Fe atoms, a central oxo/hydroxo group, and a BF_4^- ion within the lattice. The ligands are present as either **L1-H** or **L1-2H** as **L1** is a “single-headed” oxime where both phenolate and oximic oxygen atoms are deprotonated and the amino nitrogen atom is protonated in the **L1-H** form and amine N-atom stays unprotonated in the **L1-2H** form. There are three ligand molecules which connect the three Fe^{3+} atoms through oximic and hydroxo- bridges to form a triangle.

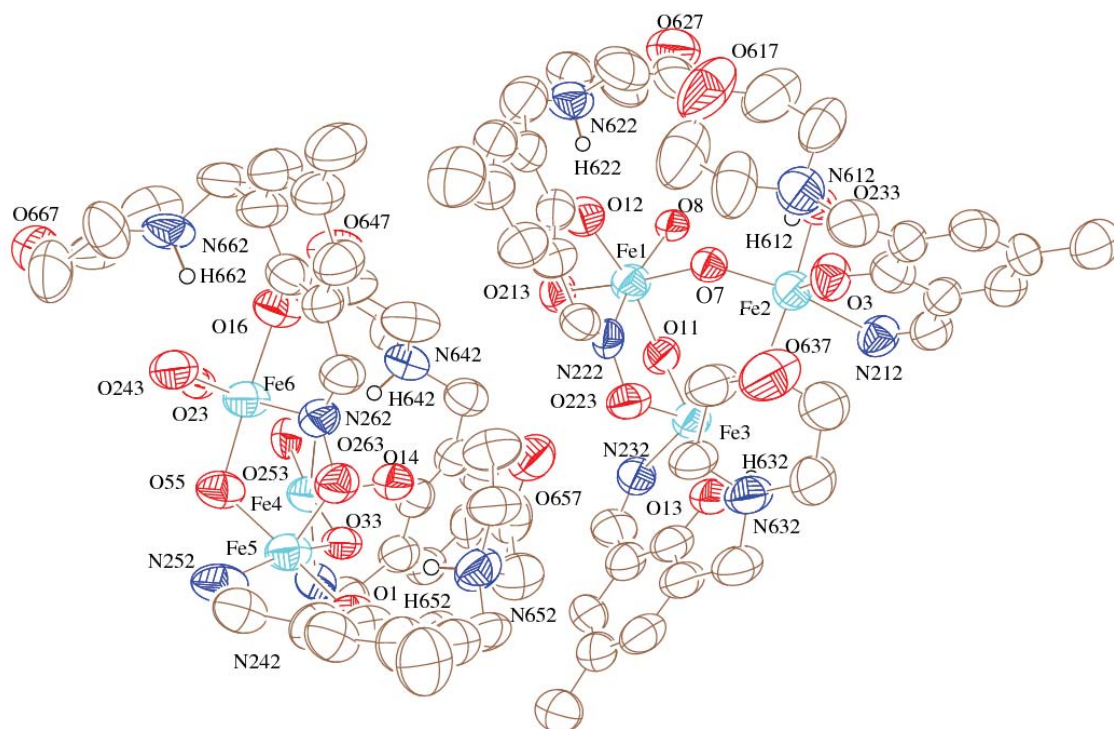


Figure 2.20: Asymmetric components of the crystal structure of $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms have been omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 50% probability level.

Every Fe atom of both structures lies in a distorted octahedral geometry. The equatorial positions are occupied by the oximic N-atom and phenolic O-atom of a ligand molecule, a hydroxo μ_2 group linking the triangles, and μ_3 O-atom (-oxo group). The axial positions are occupied by a second μ_2 -hydroxo group and an oximic oxygen atom of an adjacent ligand molecule. As an example, the equatorial positions of Fe1 are O12 (phenolic) and N222 (oximic) of the first ligand, O8 (μ_2 hydroxo-) and O11 (μ_3 central oxygen atom) while the axial positions for Fe1 are occupied by O7 (μ_2 -hydroxo) and O213 (oximic-oxygen atom) of a neighbouring ligand molecule (see Figure 2.21-2.23, Table 2.8, and Table 2.9).

The μ_3 central oxygen atoms connecting the iron triangles are displaced out of the metal plane towards each other by 0.155(5) Å and 0.134(5) for two independent molecules (see Figure 2.22 and Figure 2.24). Therefore, the displacements of the central oxygen atoms from the metal planes in the two structures appear to be considerably lower than the values previously reported of 0.31-0.35 Å, in analogous hexa- and heptairon salicylaldoxime clusters, where, respectively a proton links the pair of Fe_3O clusters and the $[\text{Fe}_3\text{O}]^{7+}$ clusters are separated by an $[\text{Fe}(\text{OH})_6]^{3-}$ group.^{35,36} It is clear from the X-ray analysis of the central oxygen atoms that there should be a hydrogen bond between them, based on the short distance of O11-O11 = 2.730(11) Å and O55-O55 = 2.628(8) Å, the fact they are displaced towards each other (see Figure 2.22 and Figure 2.24), although these distances are slightly higher than the reported distances observed in the analogous salicylaldoxime clusters in the literature^{35,36} (These structural parameters and IR data of the complex are further discussed in Chapter 4). It is therefore clear that one of the nitrogen atoms must be deprotonated if the elemental analysis and charge balance is to be consistent with this formulation. Examination of the nitrogen (amine) to oxygen (phenolate) bond lengths for each of the six amine nitrogen atoms present shows similar distances (2.596(11) - 2.856(12) Å). The only logical conclusion therefore is that the nitrogen bound hydrogen atoms are not isolated on just five of the amine nitrogen atoms but are instead averaged over the entire structure.

Table 2.8: Bond lengths around the Fe(III) atoms of the complex **C2**.

Bond	Distance (Å)	Bond	Distance (Å)
Fe1-O7	2.065(5)	Fe4-O33	2.030(5)
Fe1-O8	1.955(5)	Fe4-O5	1.990(5)
Fe1-N222	2.117(8)	Fe4-N242	2.140(8)
Fe1-O213	2.003(6)	Fe4-O253	2.003(6)
Fe1-O12	1.953(7)	Fe4-O14	1.912(7)
Fe1-O11	1.908(6)	Fe4-O55	1.872(6)
Fe2-O2	2.039(4)	Fe5-O23	2.031(5)
Fe2-O7	1.968(5)	Fe5-O33	1.955(5)
Fe2-N212	2.149(9)	Fe5-N252	2.149(9)
Fe2-O233	1.988(6)	Fe5-O263	1.986(6)
Fe2-O3	1.964(7)	Fe5-O1	1.922(7)
Fe2-O11	1.891(6)	Fe5-O55	1.899(7)
Fe3-O8	2.050(5)	Fe6-O5	2.008(5)
Fe3-O2	1.985(5)	Fe6-O23	1.968(5)
Fe3-N232	2.139(8)	Fe6-N262	2.129(7)
Fe3-O223	1.970(6)	Fe6-O243	1.962(7)
Fe3-O13	1.940(7)	Fe6-O16	1.955(6)
Fe3-O11	1.898(6)	Fe6-O55	1.917(6)

Table 2.9: Bond angles around Fe(III) atoms of the complex **C2**.

Atoms	Angle (°)	Atoms	Angle (°)
O7-Fe1-O12	92.4(2)	O5-Fe4-O14	92.9(2)
O7-Fe1-O8	80.3(2)	O5-Fe4-O33	80.0(2)
O8-Fe1-O11	97.2(2)	O5-Fe4-O55	98.3(2)
O8-Fe1-O12	92.4(2)	O5-Fe4-O253	93.6(2)
O8-Fe1-O213	95.5(2)	O33-Fe4-O253	172.3(2)
O8-Fe1-N222	161.5(3)	O5-Fe4-N242	166.3(3)
O11-Fe1-O12	168.3(3)	O14-Fe4-O55	167.8(3)
O11-Fe1-O213	87.6(2)	O55-Fe4-O253	90.8(3)
O11-Fe1-N222	86.6(3)	O55-Fe4-N242	86.3(3)
O12-Fe1-O213	85.0(3)	O14-Fe4-O253	83.6(3)
O12-Fe1-N222	86.3(3)	O14-Fe4-N242	84.0(3)
O213-Fe1-N222	102.8(3)	O253-Fe4-N242	99.3(3)
O7-Fe1-O213	174.9(2)	O14-Fe4-O33	92.4(3)
O7-Fe1-N222	81.4(2)	O33-Fe4-N242	86.7(3)
O7-Fe1-O11	95.6(2)	O33-Fe4-O55	94.4(2)
O2-Fe2-O233	173.5(3)	O23-Fe5-O263	174.7(2)
O2-Fe2-N212	87.0(3)	O23-Fe5-N252	87.4(3)
O2-Fe2-O3	88.1(2)	O1-Fe5-O33	90.6(2)
O2-Fe2-O7	81.1(2)	O23-Fe5-O33	80.53(19)
O7-Fe2-O233	93.1(2)	O33-Fe5-O263	95.8(2)
O7-Fe2-N212	167.7(3)	O33-Fe5-N252	167.6(3)
O7-Fe2-O11	99.6(2)	O23-Fe5-O55	94.6(2)
O11-Fe2-O233	90.6(3)	O55-Fe5-O263	89.8(2)
O11-Fe2-N212	83.9(3)	O55-Fe5-N252	82.9(3)
O3-Fe2-N212	83.8(3)	O1-Fe5-N252	86.9(3)
O3-Fe2-O11	167.5(3)	O1-Fe5-O55	168.2(3)
O3-Fe2-O7	92.9(3)	O1-Fe5-O23	90.9(2)
O3-Fe2-O233	89.5(3)	O1-Fe5-O263	85.4(2)
O2-Fe2-O11	93.1(2)	O33-Fe5-O55	100.7(2)
O233-Fe2-N212	98.7(3)	O263-Fe5-N252	96.1(3)
O8-Fe3-N232	88.4(3)	O5-Fe6-N262	86.0(2)
O11-Fe3-N232	84.2(3)	O55-Fe6-N262	85.4(3)
O11-Fe3-O223	90.8(3)	O55-Fe6-O243	90.1(3)
O8-Fe3-O11	95.1(2)	O23-Fe6-O55	98.0(2)
O11-Fe3-O13	169.0(3)	O16-Fe6-O55	168.4(3)
O2-Fe3-O8	78.5(2)	O5-Fe6-O23	82.9(2)
O2-Fe3-O223	94.9(2)	O23-Fe6-O243	93.7(3)
O2-Fe3-N232	166.6(3)	O23-Fe6-N262	168.5(2)
O2-Fe3-O11	99.5(2)	O5-Fe6-O55	94.1(2)
O2-Fe3-O13	91.5(2)	O16-Fe6-O23	92.9(2)
O13-Fe3-O223	88.0(3)	O16-Fe6-O243	85.2(3)
O13-Fe3-N232	85.1(3)	O16-Fe6-N262	84.6(3)
O8-Fe3-O13	87.3(2)	O5-Fe6-O16	91.2(2)
O223-Fe3-N232	98.0(3)	O243-Fe6-N262	97.3(3)
O8-Fe3-O223	171.8(2)	O5-Fe6-O243	174.9(3)

Table 2.10: Selected H-bond distances of the asymmetric unit of the complex **C2**.

Atoms (D·····A)	Distance (Å)
N612-H612·····O3	2.596(11)
N622-H622·····O12	2.597(11)
N652-H652·····O1	2.712(10)
N662-H662·····O16	2.700(1)
N662-H662·····O243	3.020(1)
O11-O11	2.730(11)
O55-O55	2.628(8)

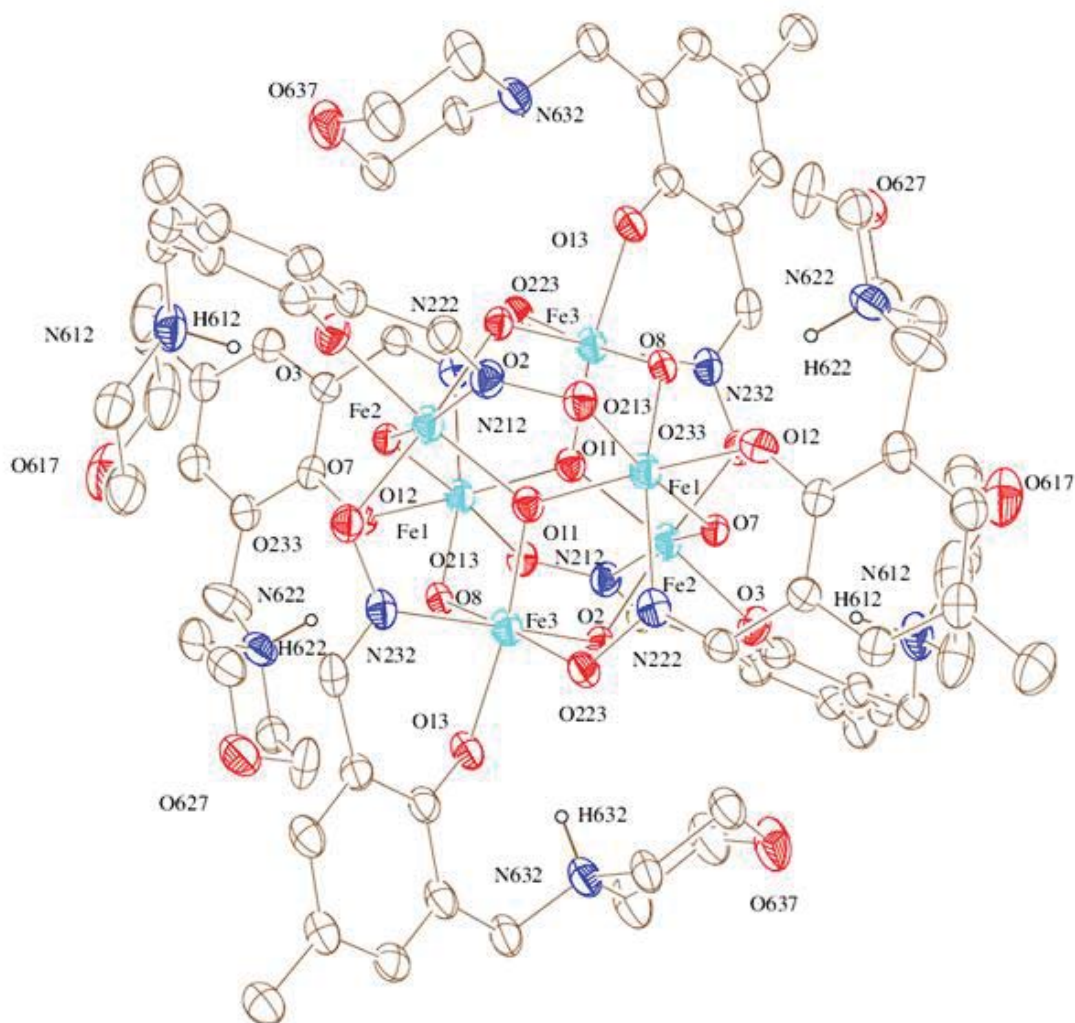


Figure 2.21: The crystal structure of the first independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms have been omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 15% probability level.

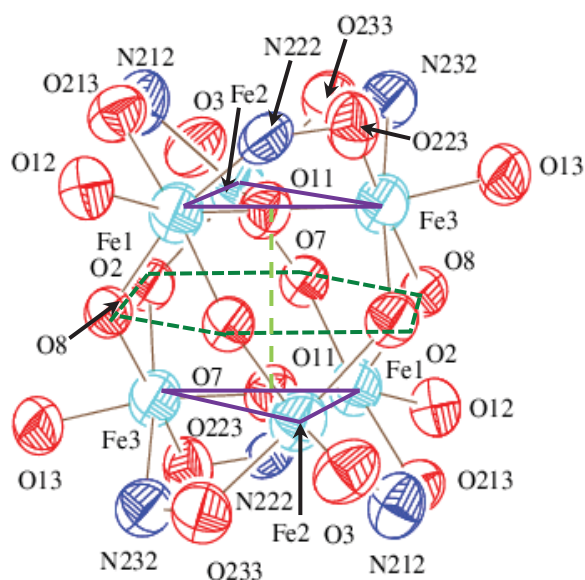


Figure 2.22: The metallic core of the crystal structure $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level. Displacement of O11 is 0.155(5) Å.

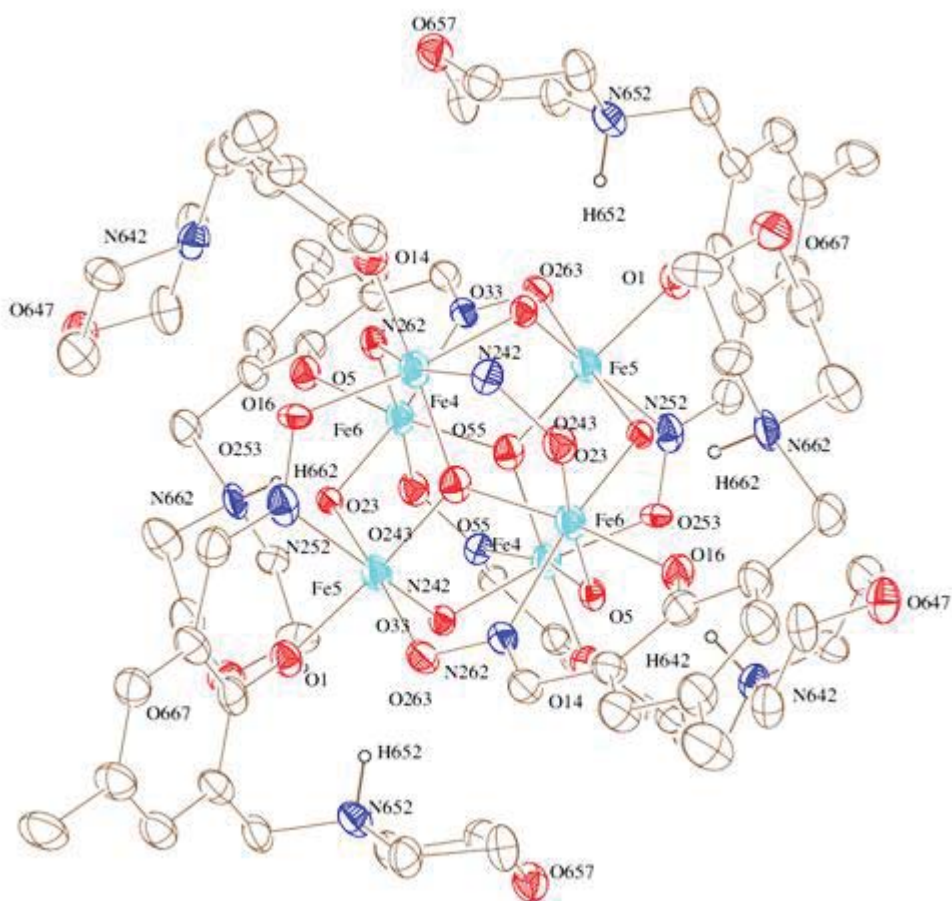


Figure 2.23: The crystal structure of the second independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms have been omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 15% probability level.

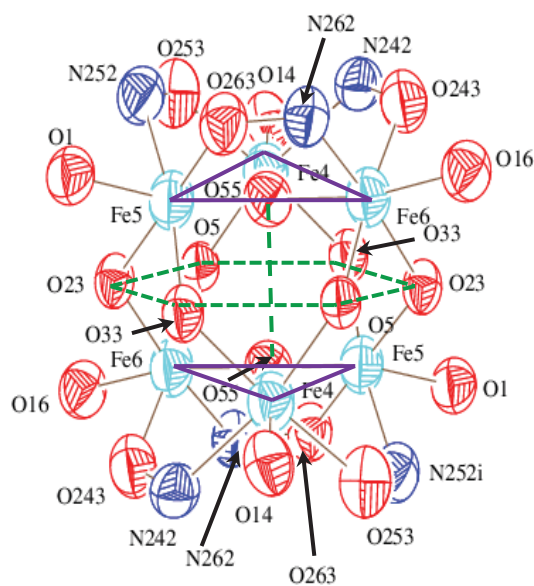


Figure 2.24: The metallic core of the crystal structure of the second independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level. Displacement of O55 is 0.134(5) Å.

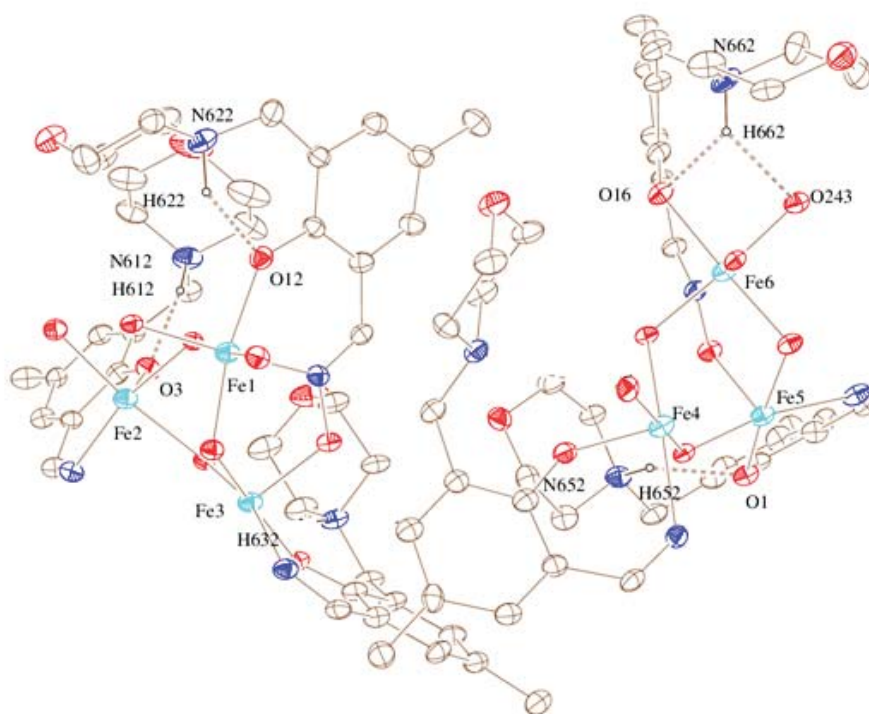


Figure 2.25: Selected H-bond contacts within the asymmetric unit of complex, **C2** drawn in brown dotted lines (Fe-cyan, N-blue, O-red, C-brown, all the H-atoms involved in forming H-bonds are illustrated in white); ORTEP view at 10% probability level.

Table 2.11: Torsion angles around Fe(III) atoms of the complex **C2**.

Atoms	Angle (°)
Fe1-O213-N212-Fe2	0.6(7)
Fe2-O233-N232-Fe3	6.9(8)
Fe3-O223-N222-Fe1	13.9(7)
Fe4-O253-N252-Fe5	12.8(8)
Fe5-O263-N262-Fe6	4.8(7)
Fe6-O243-N242-Fe4	5.2(8)

Both structures form a hexagon at the core of the structure where six O-atoms of the hydroxo groups connect the in-plane trimetallic clusters. These O-atoms sit on a plane which is located approximately parallel to the triangles on either side but bisecting them (see Figure 2.22 and Figure 2.24). The tertiary amine N-atoms on the ligands in both structures are involved in forming numerous H-bonds within the structural units further stabilising the structure. The hydrogen atoms on the amine nitrogen atoms form H-bond interactions with the phenolate oxygen atom within the same ligand and also it can form a weak H-bond with an oximic oxygen atom on the neighbouring ligand (N642-H662·····O243 = 3.072(9) Å). The ligand based H-bonds within the asymmetric unit are illustrated in Figure 2.25 (see Table 2.10 for the hydrogen bond distances).

Torsion angles between the metal ions about the oxime bridges seem to be playing an important role in terms of magnetism within the metal clusters. As described in the introduction (see Chapter 1), it has been found that increasing the average torsion Mn-N-O-Mn angle in metal clusters consisting of the $[\text{Mn}_3^{\text{III}}\text{O}]$ moiety favoured *ferromagnetic* interactions via the oximato bridge which in turn can enhance the nanomagnetic behaviour within these Mn_6 clusters. It may be applicable to Fe clusters as well in terms of improving magnetic properties. The values of the torsion angles between the Fe(III) atoms within the triangles are shown in Table 2.11. All the values of the torsion angles about the Fe-O-N-Fe units of the complex **C2** are less than 30°. It has been shown that polynuclear salicylaldoxime manganese clusters that are found to possess important magnetic properties have approximately 30° or greater values for the torsion angles about the Mn-N-O-Mn units.^{37,38}

The number of anions (2BF_4^-) found in the structural analysis was confirmed by the charge balance considerations (see Table 2.12) as well as by CHN analysis. The CHN

results indicate that there are no solvent molecules present because the drying of the complex **C2** *in vacuo* might have caused the solvent molecules (MeOH) present within the lattice to evaporate. The oxidation state of all the Fe atoms was determined to be +3 by the charge balance and later by the Mössbauer analysis.

Table 2.12: Charge balance analysis of the complex **C2**.

6 Fe ³⁺	O ²⁻	7 OH ⁻	5 (L1-H)	(L1-2H)	2 BF ₄ ⁻
6 x 3+	1 x 2-	7 x 1-	5 x 1-	1 x 2-	2 x 1-
18+	2-	7-	5-	2-	2-

The total positive charge, 18+ is obtained from six iron atoms each holding 3+ charge. The central O-atom from one of the triangles contributes a 2- charge, 7- from the hydroxo groups, and 2- from two BF₄⁻ ions. The remaining 7+ charge is balanced by the 5- charge created by five ligands of which amine N-atoms are protonated and oximic and phenolate O-atoms are deprotonated and 2- by a ligand of which the oximic and phenolate O-atoms are deprotonated and the amine N-atom stays unprotonated. The H-atoms on these amine N-atoms form H-bonds with the neighbouring O-atoms from hydroxo groups and also phenolate O-atoms.

A series of tri- and hexairon complexes that contain one and/or two [Fe₃(μ₃-O)]⁷⁺ triangle/s was synthesised by Mason *et al.* in 2009 using mixtures of salicylaldoximes and carboxylates with an iron salt and a base (see Table 2.12).³⁹ The complex **C2** also contains two oxo/hydroxo bridged trinuclear triangles at its core as do all the complexes stated in the Table 2.13 except the first two. Thus they all share the same core although different ligands, bases, metal salts and solvents were used. The complex **C2** is unique as it is the first hexairon complex synthesised with the ligand **L1**.

Table 2.13: Fe/R-sao²⁻ complexes with the [Fe₃(μ₃-O)]⁷⁺ core.³⁹

Molecule	Core
[Fe ₃ O(OMe)(Ph-sao) ₂ Cl ₂ (py) ₃].2MeOH	[Fe ₃ (μ ₃ -O)] ⁷⁺ triangle
[Fe ₃ O(OMe)(Ph-sao) ₂ Br ₂ (py) ₃].Et ₂ O	[Fe ₃ (μ ₃ -O)] ⁷⁺ triangle
[Fe ₆ O ₂ (OH) ₂ (O ₂ CPh) ₆ (Et-sao) ₂ (Et-saoH) ₂]	2 x [Fe ₃ (μ ₃ -O)] ⁷⁺ triangles
[HNet ₃] ₂ [Fe ₆ O ₂ (OH) ₂ (O ₂ CPh(Me) ₂) ₆ (Et-sao) ₄].2MeCN	2 x [Fe ₃ (μ ₃ -O)] ⁷⁺ triangles

$[\text{Fe}_6\text{Na}_3\text{O}(\text{OH})_4(\text{OMe})_3(\text{Me-sao})_6(\text{H}_2\text{O})_3(\text{MeOH})_6]\cdot\text{MeOH}$	$[\text{Fe}_3(\mu_3\text{-O})]^{7+}$ and $[\text{Fe}_3(\mu_3\text{-OH})]^{8+}$ triangles
$[\text{Fe}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(3\text{-}t\text{-Bu-5-NO}_2\text{-sao})_2(\text{H}_2\text{O})_2]\cdot 4\text{MeCN}$	2 x $[\text{Fe}_3(\mu_3\text{-O})]^{7+}$ triangles
$[\text{Fe}_6\text{O}_2(\text{O}_2\text{CCH}_2\text{Ph})_{10}(3\text{-}t\text{-Bu-sao})_2(\text{H}_2\text{O})_2]\cdot 5\text{MeCN}$	2 x $[\text{Fe}_3(\mu_3\text{-O})]^{7+}$ triangles

2.4.3 Complex $\text{Na}[\text{Fe}_7(\text{OH})_8(\text{L11-2H})_6(\text{Py})_6](\text{BF}_4)_2(\text{H}_2\text{O})_6(\text{Py})_3$, $\text{C3}\cdot 6\text{H}_2\text{O}\cdot 3\text{Py}$

The reaction of **L11** with $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ in a molar ratio 1 : 1 in a MeOH/pyridine solution followed by crystallisation, produces dark red rhombic shaped crystals of the complex $\text{Na}[\text{Fe}_7(\text{OH})_8(\text{L11-2H})_6\text{Py}_6](\text{BF}_4)_2(\text{H}_2\text{O})_6(\text{Py})_3$ (**C3** $\cdot 6\text{H}_2\text{O}\cdot 3\text{Py}$) that crystallises in the $R\bar{3}$ space group. The asymmetric unit contains one sixth of the molecule (see Figure 2.26) and the full complex is generated by a S_6 improper rotation.

The ligand **L11** is a “single-headed” oxime present as **L11-2H** in which the phenolic and oximic oxygen atoms are deprotonated and the amino nitrogen atom stays unprotonated, six ligand molecules, seven Fe atoms, eight hydroxo groups and six pyridine molecules are involved in the formation of this cluster. There are additional three pyridine molecules, six water molecules, two BF_4^- ions, and one Na^+ ion within the lattice.

Table 2.14: Distorted octahedral bond lengths around the Fe2(III) atom.

Bond	Distance (Å)
Fe2-O2 (μ_3 -hydroxo)	1.9337(13)
Fe2-O213 (oxime)	1.950(5)
Fe2-O1 (phenolato)	1.941(3)
Fe2-N212 (oxime)	2.122(5)
Fe2-N100 (pyridine)	2.198(5)
Fe2-O3 (μ_2 -hydroxo)	2.043(3)

Table 2.15: Distorted octahedral angles of Fe2(III) atoms on the plane for complex **C3**.

Atoms	Angle (°)	Atoms	Angle (°)
N100-Fe2-O2	94.3(2)	N100-Fe2-O3	174.2(2)
N100-Fe2-O213	90.1(2)	O1-Fe2-O2	173.0(2)
N100-Fe2-O1	87.8(2)	N213-Fe2-212	176.5(2)
N100-Fe2-N212	89.8(2)	O1-Fe2-N213	91.5(2)
O3-Fe2-O1	87.1(2)	O213-Fe2-O2	95.2(2)
O3-Fe2-O2	90.5(2)	O2-Fe2-N212	88.3(2)

O3-Fe2-N212	87.1(2)	N212-Fe2-O1	85.1(2)
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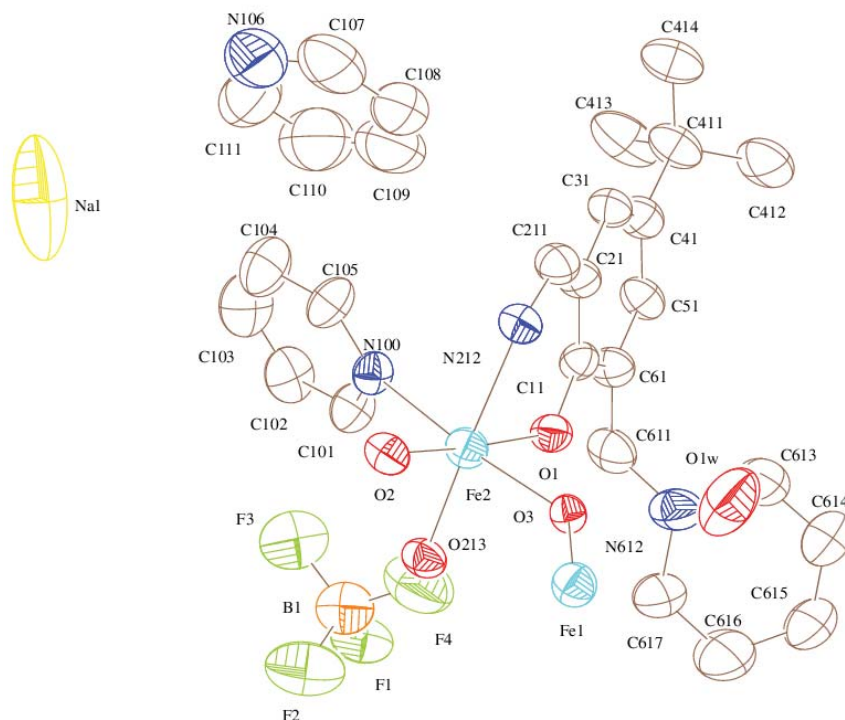


Figure 2.26: Asymmetric components of the crystal structure, **C3** {Na_{0.167}[Fe_{1.167}(OH)_{1.333}(**L11**-2H)Py](BF₄)_{0.333}(H₂O)Py_{0.500}} (Fe-cyan, B-orange, N-blue, O-red, F-green, C-brown, Na-yellow, and all the H atoms are omitted for clarity except the ones bound to the tertiary amine nitrogen atoms of the ligand); ORTEP view at 50% probability level.

The complex, **C3** is a trigonal antiprism consisting of two triangles of [Fe^{III}₃(μ₃-OH)]⁸⁺ sitting parallel to each other in which each oxime moiety bridges across each edge of the triangles in Fe-N-O-Fe sequence. The triangles [Fe₃(OH)]⁸⁺, are centrally connected through [Fe(OH)₆]³⁻, i.e. the upper and lower triangles are linked through a seventh Fe atom *via* six hydroxo bridges three of which connect to the Fe atoms on the upper plane while the other three connect to the Fe atoms on the lower plane. The iron atoms on each triangle are assigned as μ₃-hydroxo bridged. The Mössbauer results indicate that this heptairon complex is different from the other heptairon complexes as the quadrupole splitting parameter value is significantly smaller from the values obtained for the other heptairon complexes (see section 2.7 for more information). The bond distances of Fe₃^{III} μ-hydroxo/oxo do not provide enough information to prove whether the central oxygen atom is either hydroxo or oxo. However, the charge balance considerations and microanalytical CHN analyses agree with the assignment of the central oxygen atoms as hydroxo groups. Each Fe³⁺ on the triangles is coordinated to a

phenolate oxygen atom, an oximic nitrogen atom of one ligand, an oximic oxygen atom of another ligand, and a central oxygen atom of the relevant triangle sit on the same plane and other two axial sites are occupied by a pyridine molecule and an oxygen atom perpendicular to the plane (see Tables 2.14 and 2.15). It was observed that the torsion angle of the unit Fe2-O213-N212-Fe2 within the triangle is 17.1(5)°. The pyridine molecules coordinated to the Fe atoms sit slightly away from each other as the central oxygen atoms, O2 are displaced out of the plane pointing outward from the triangular planes (see Figures 2.27 and 2.28) by 0.318(6) Å, substantially larger than the values observed for the hexairon complex **C2** and **C8** (see below). The central Fe atom also has a distorted octahedral geometry created by the O₆ donor set where each angle is approximately 90° and the bond length around Fe2 is 1.933(2) Å. The distance between the metal planes is approximately 6.5 Å. The complex **C3** is an analogue of the complex **C4** described in section 3.2. The difference between the **C3** and **C4** is due to the single vs double oxime ligand that has been used and also the central O-atoms in the **C3** are originated from hydroxo groups whereas oxo groups in the **C4**.

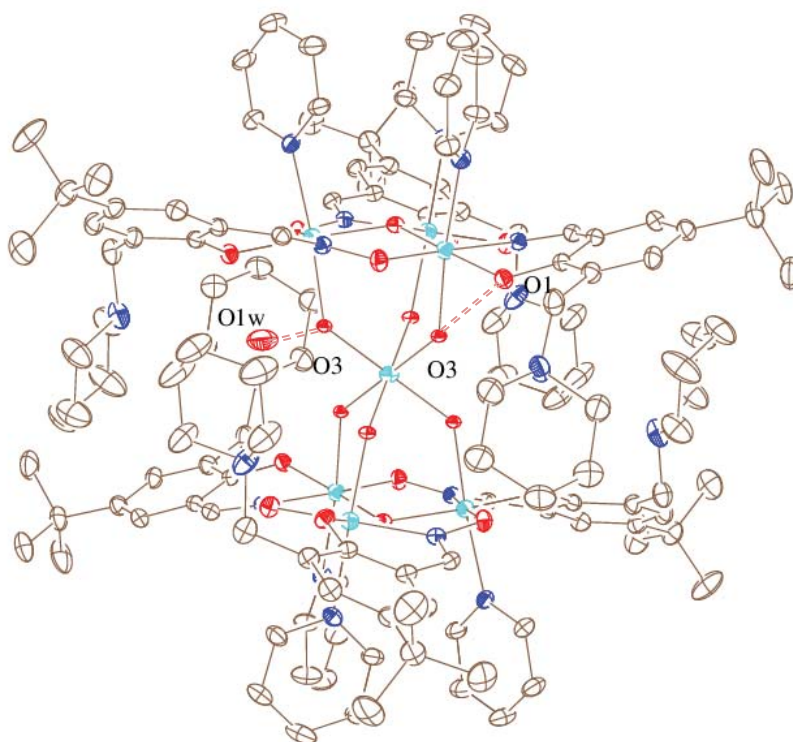


Figure 2.27: Parallel view of Na[Fe₇(OH)₈(L11-2H)₆Py₆]²⁺ (**C3**) (Fe-cyan, N-blue, O-red, C-brown and all the H atoms (white) are omitted for clarity. All the atoms involved in forming hydrogen bonding are labelled); ORTEP view at 25% probability level.

Table 2.16: Selected H-bond lengths of the complex **C3**·6H₂O·3Py.

Atoms (D·····A)	Distance (Å)
O3·····O1w	2.819(7)
O3·····O1	2.744(4)

A μ_2 -hydroxo group between the triangles can form a moderately strong hydrogen bond with a water molecule and also with a phenolate oxygen atom (see Figure 2.27 and Table 2.16). The distance between the amine N-atoms and the phenolate O-atoms (O1) of the same ligand is significantly long (3.014(7) Å), which supports the conclusion that the amine nitrogen atoms remain unprotonated. Therefore, according to the charge balance considerations and CHN analysis, all of the amine nitrogen atoms must remain unprotonated.

The oxidation states of the Fe atoms were determined to be all 3+ according to the charge balance considerations (see Table 2.17) and this was later confirmed by Mössbauer spectroscopy. The CHN results indicate the presence of an additional Na⁺ ion in the complex **C3**, which is compatible with the charge balance.

The central O-atoms of the complex **C3** are originated from two hydroxo groups which is a difference between the complex **C3** and the complex **C4** (discussed in Chapter 3). This information is further supported by the IR analysis. Comparison of structural parameters such as the Fe^{III} μ -oxo/hydroxo bond lengths, displacement of the central oxygen atoms from the metal planes and also IR data of the complexes with previously reported values of similar iron complexes are described in Chapter 4 (see Table 4.4).

The presence of a Na⁺ ion within the lattice of the complex, **C3** can be related to the addition of NaPF₆. This is also a major contrastive fact seen between the complexes **C3** and **C4** as addition of NaPF₆ provided a PF₆⁻ anion to the complex **C4**.

Table 2.17: Charge balance analysis of the complex **C3**.

7 Fe ³⁺	1 Na ⁺	8 OH ⁻	6 (L11-2H)	2 BF ₄ ⁻
7 x 3+	1 x 1+	8 x 1-	6 x 2-	2 x 1-
21+	1+	8-	12-	2-

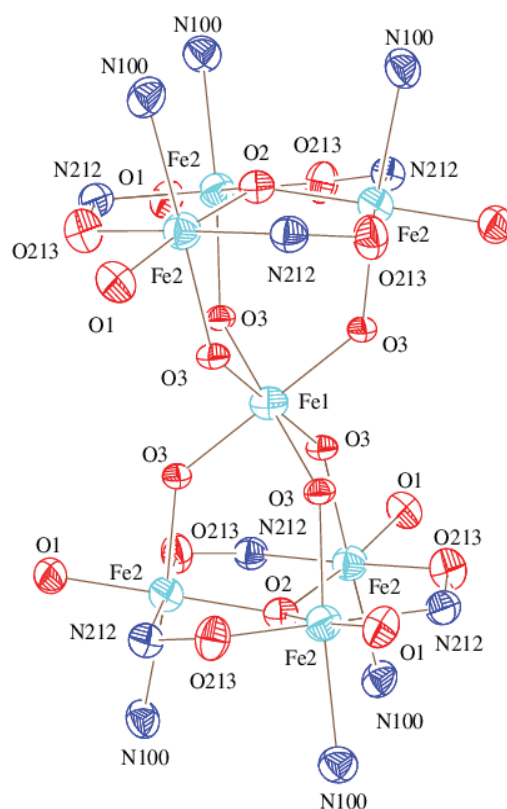


Figure 2.28: Magnetic core of $\text{Na}[\text{Fe}_7(\text{OH})_8(\text{L11-2H})_6\text{Py}_6]^{2+}$ (**C3**) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.

In 2008, Tasker and co-workers synthesised and characterised a series of copper and zinc complexes using the ligand **L11** and different metal salts such as chlorides, bromides, and nitrates. The ligand **L11**, 5-*tert*-butyl-2-hydroxy-3-piperidin-1-yl-methylbenzaldehyde oxime, consists of a pendant dialkylaminomethyl arm that can be protonated thus providing an electrostatic and H-bonding site for anions. All the copper and zinc complexes utilised a zwitterionic form of the ligand except the complex $[\text{Cu}(\text{L11-H})_2]$. These are all *trans*-complexes in which H-bonds exist between the H-atoms on the amine N-atoms and oximic O-atoms, H-bonds exist between the counter anions and the protons on the amine N-atoms and also there are intramolecular H-bonds between the protons on amine N-atoms and phenolate O-atoms buttress the complex structures.²⁵

2.5 Results and discussion

The $\text{Fe}^{3+}/\text{R-saoH}_2$ clusters reported in the literature vary in their nuclearity equal to or lower than $[\text{Fe}_{12}]$.^{4,9,10,12,13,16,39-43} The $[\text{Fe}_3(\mu\text{-O})]^{7+}$ trinuclear unit has been the most common building block and is structurally equivalent to $\text{Mn}^{3+}/\text{R-saoH}_2$ chemistry.³⁹ There are a number of factors that may affect the nuclearity as well as the magnetic properties of the complexes, such as bulkiness of the R- group(s), the introduction of co-ligands, inherent structural properties such as the torsion angle along the Fe-N-O-Fe unit of the complexes within the trinuclear units, and proximity of the metal ions to each other within the complexes.

A comparison between complexes **C1**, **C2**, and **C3** reveals that **C1** is different from **C2** and **C3** because **C1** does not contain the trinuclear units present in the others. Instead, the core of **C1** was formed from oxo-bridged Fe(III) and boron atoms. **C1** was formed as a result of the crystallisation of the filtered reaction mixture in the first attempt of making this complex and was not reproducible thereafter. It was assumed that the boron in this complex came from by the hydrolysis of BF_4^- ions in the metal salt. The purity needed for the magnetic measurements on this complex was not achieved. The repetition of the same reaction conditions formed the **C2** complex which has a completely different structure from that of the **C1** complex. Both the complexes **C2** and **C3** possess the expected Fe-only metallic core. The hexairon complex **C2** has two metal triangles and **C3** has a heptairon core but still retains the two metal triangles. The maximum torsion angle of the Fe-O-N-Fe unit observed was $14.1(7)^\circ$ and $17.1(5)^\circ$. The distances ($2.626(8) \text{ \AA}$ and $2.730(11) \text{ \AA}$) between the central oxygen atoms within the two triangles of the **C2** complex is relatively short and it confirmed the presence of a shared proton between them, whereas there is a Fe atom between the triangles of the complex **C3** which extends the triangle/triangle distance considerably ($2.626(8) \text{ \AA}$ vs $6.517(1) \text{ \AA}$). The crystallographic details of the complexes, **C1-C3** are shown in the Table 2.18.

Table 2.18: Crystallographic details of the complexes, **C1-C3** and **L2**.

	C1	C2	C3	L2
formula	C ₅₆ H ₈₄ B ₄ F ₈ Fe ₂ N ₈ O ₂₀	C ₇₈ H ₁₀₂ Fe ₆ N ₁₂ O ₂₆	C ₁₄₇ H ₂₀₇ B ₈ Fe ₇ N ₂₁ O ₂₆ Na	C ₁₆ H ₂₅ N ₃ O ₃ ·NO ₃
<i>M</i> , g mol ⁻¹	1502.25	4090.23	3271.88	355.39
crystal system	triclinic	triclinic	trigonal	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.292(5)	16.8193(10)	22.558(5)	8.2141(6)
<i>b</i> , Å	12.325(3)	17.3271(10)	22.558(5)	10.1302(7)
<i>c</i> , Å	15.431(5)	21.1897(15)	33.105(5)	12.3011(9)
<i>α</i> , deg (°)	73.437(5)	107.161(8)	90	69.894(5)
<i>β</i> , deg (°)	71.084(3)	99.537(7)	90	88.602(6)
<i>γ</i> , deg (°)	67.319(5)	100.103(7)	120	72.317(5)
<i>V</i> , Å ³	1679.5(11)	5651.6(7)	14589(8)	912.12(12)
<i>T</i> , K	152	293	153	153
<i>Z</i>	1	1	3	2
<i>ρ</i> _{calc} [g cm ⁻³]	1.485	1.202	1.117	1.294
crystal shape / colour	Rhomboïd / dark red	Rhomboïd / dark red	rhomboid / dark red	square / green
crystal size [mm]	0.35 x 0.44 x 1.01	0.25 x 0.38 x 0.75	0.17 x 0.20 x 0.20	0.30 x 0.30 x 0.30
<i>μ</i> , [mm ⁻¹]	4.352	6.621	0.577	0.833
restraints/parameters	54 / 465	187 / 1098	84 / 364	0 / 228
unique data	6255	18839	6222	3261
<i>R</i> _{int} / <i>R</i> _σ	0.0663 / 0.0608	0.1223 / 0.1346	0.0782 / 0.0528	0.0516 / 0.0524
<i>I</i> > 2σ(<i>I</i>)	6.40	12.54	10.75	6.38
unique data, (<i>I</i> > 2σ)	5719	9468	5176	2253
<i>R</i> ₁ ^a , w <i>R</i> ₂ ^b	0.0640, 0.2113	0.1259, 0.3793	0.1075, 0.3580	0.0638, 0.1949
goodness of fit	1.13	1.12	1.54	1.11

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$ for observed reflections. ^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)] / \sum[w(F_o^2)]\}^{1/2}$ for all data.

2.6 Magnetism

2.6.1 Magnetic measurements of the complex **C1**

There are factors, such as the metal ions, the chemical nature of the bridging ligands, and the bridging geometries that affect magnetic properties of exchanged coupled dinuclear complexes of transition metal ions.³¹ In addition, bridging angles and bridging distances play an important role in determining the magnetic properties of transition metal complexes.

The two Fe^{3+} ions of the **C1** complex are bridged with two oxo groups (see Figure 2.16). Therefore the exchange interactions between the two metal ions should take place through these bridges.

The magnetic properties of the complex **C1** were investigated by temperature-dependent magnetic susceptibility measurements. This resulted in a plot of the temperature dependence of the $\chi_{\text{M}}T$ product (Figure 2.29).

The $\chi_{\text{M}}T$ product of **C1** drops continuously almost linearly from the maximum value of *ca.* $3.50 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature to $0.67 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K (see Figure 2.29). The $\chi_{\text{M}}T$ value for two non-interacting Fe^{3+} ions at room temperature is $8.75 \text{ cm}^3 \text{ K mol}^{-1}$ ($S = 5/2$, $g = 2.00$)³⁹ which is suggestive of typical strong antiferromagnetically coupled Fe^{3+} ions in a dimeric unit where the observed $\chi_{\text{M}}T$ product is considerably lower than the expected value.

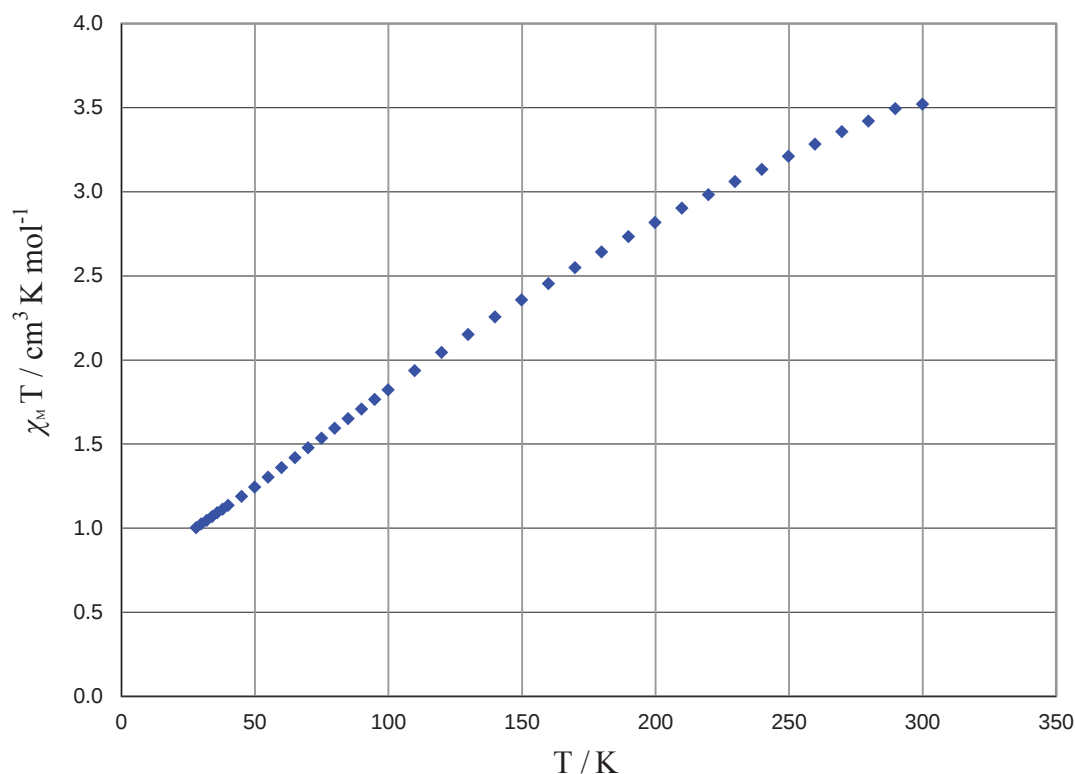


Figure 2.29: Plot of $\chi_M T$ vs T for the complex **C1**.

The sample sent for the magnetic susceptibility measurements was not in sufficient purity to fit the data on magnetisation variation with the applied magnetic field. Therefore, the data of temperature dependence of $\chi_M T$ was fitted with 15% impurity correction using the following appropriate simple isotropic ($g = 2.00$) spin Hamiltonian to treat this problem.

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2) + \sum_{i=1-2} \{\mu_B g \vec{B} \cdot \hat{S}_i\}$$

where J is the isotropic exchange interaction parameter, $\hat{S}$ is a spin operator and the last term accounts for the Zeeman interaction with the applied magnetic field and the Zeeman term includes the parameters, $i = 1, 2$, μ_B is the Bohr magneton, $\vec{B}$ is the applied magnetic field vector, and g is the g factor of the Fe^{III} ions. Coupling constants (J) or magnetic exchange interactions are a measure of energy as (cm^{-1}) and are positive for ferromagnetic and negative for antiferromagnetic interactions.

Fitting of the data affords a J value of -15.01 cm^{-1} . The fit of these data suggests that the total spin S of the system is equal to 0 (see Figure 2.30). The negative J value and the fit of the data are suggestive that the interaction between the Fe^{3+} cations is antiferromagnetic.

Variable-temperature-variable-field dc magnetisation experiments were performed in the temperature range of 2.0 - 7.0 K and in the magnetic field range of 0.5 T – 3 T respectively. These experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. μ_B/kBT , with N being Avogadro's number and k_B the Boltzmann constant) in Figure 2.31.

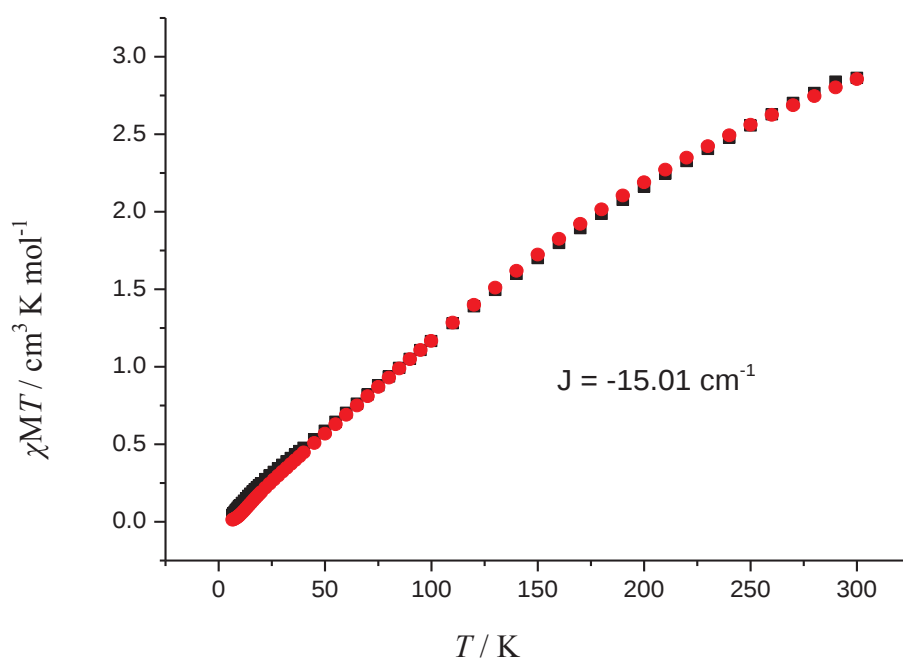


Figure 2.30: Plot of $\chi_M T$ vs T for the complex **C1** with fitted data with the 15% impurity removed from the raw data (fitted data best drawn as a line in red colour).

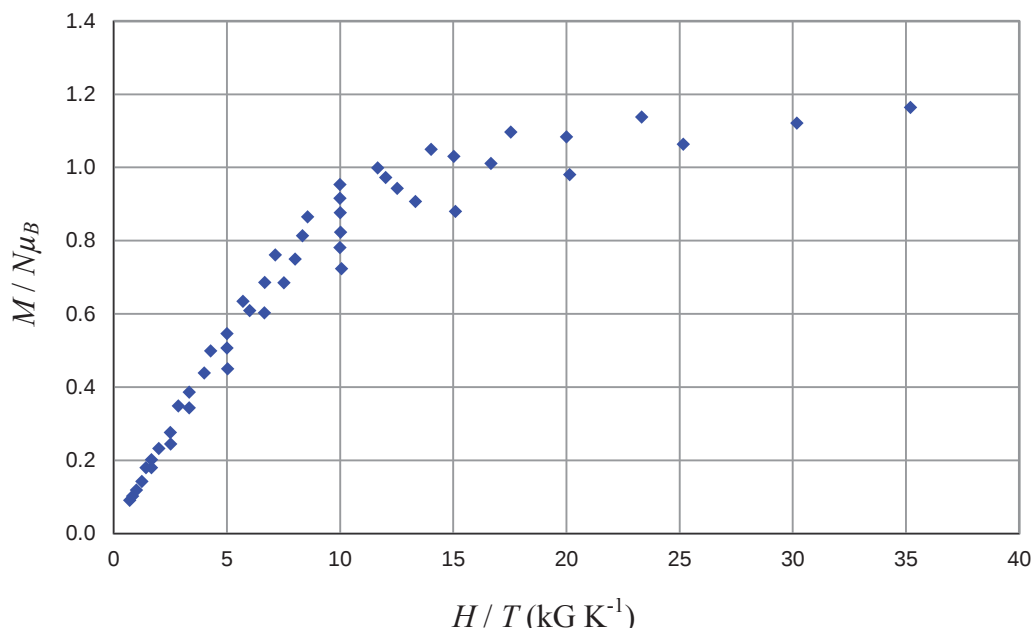


Figure 2.31: M vs. H / T plot for **C1**.

Due to the presence of a large amount of paramagnetic impurities in **C1**, the magnetisation data were unable to be fitted. Thus, a value for uniaxial anisotropy, D or an eigen plot which is used to determine the total ground state spin was unable to be generated.

2.6.2 Magnetic measurements of the complex C2

The experimental magnetic susceptibility data were interpreted from the temperature dependence of the $\chi_{\text{M}}T$ product (see Figure 2.32). As the Figure 2.32 indicates, the $\chi_{\text{M}}T$ product drops almost linearly and constantly from $6.526 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature to $0.0789 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K upon cooling. The experimental value at room temperature is lower than the expected value ($26.25 \text{ cm}^3 \text{ K mol}^{-1}$) of the $\chi_{\text{M}}T$ product for six non-interacting Fe^{3+} ions. Therefore, the magnetic behaviour of this complex is indicative of strongly antiferromagnetic exchange interactions between the metal centres.

Variable-temperature, variable-field dc magnetisation experiments were performed in the temperature range of 2.0 - 7.0 K and in the magnetic field range of 0.5 T – 3 T respectively. These experimental data are presented as reduced magnetisation ($M/N\mu_B$

vs. $\mu_B/k_B T$, with N being Avogadro's number and k_B the Boltzmann constant) in Figure 2.33.

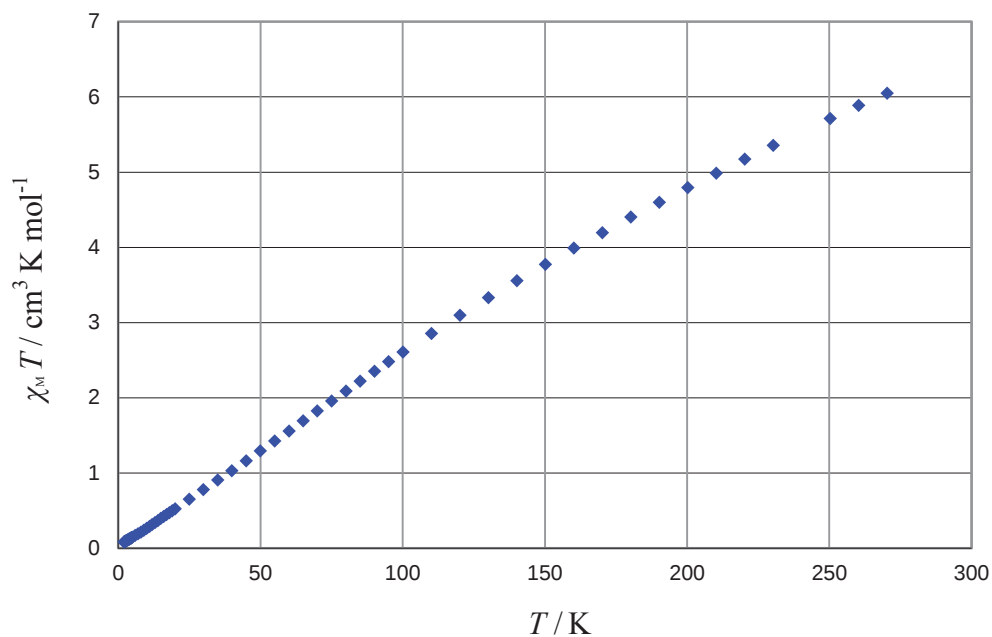


Figure 2.32: Plot of $\chi_M T$ vs T for the complex **C2**.

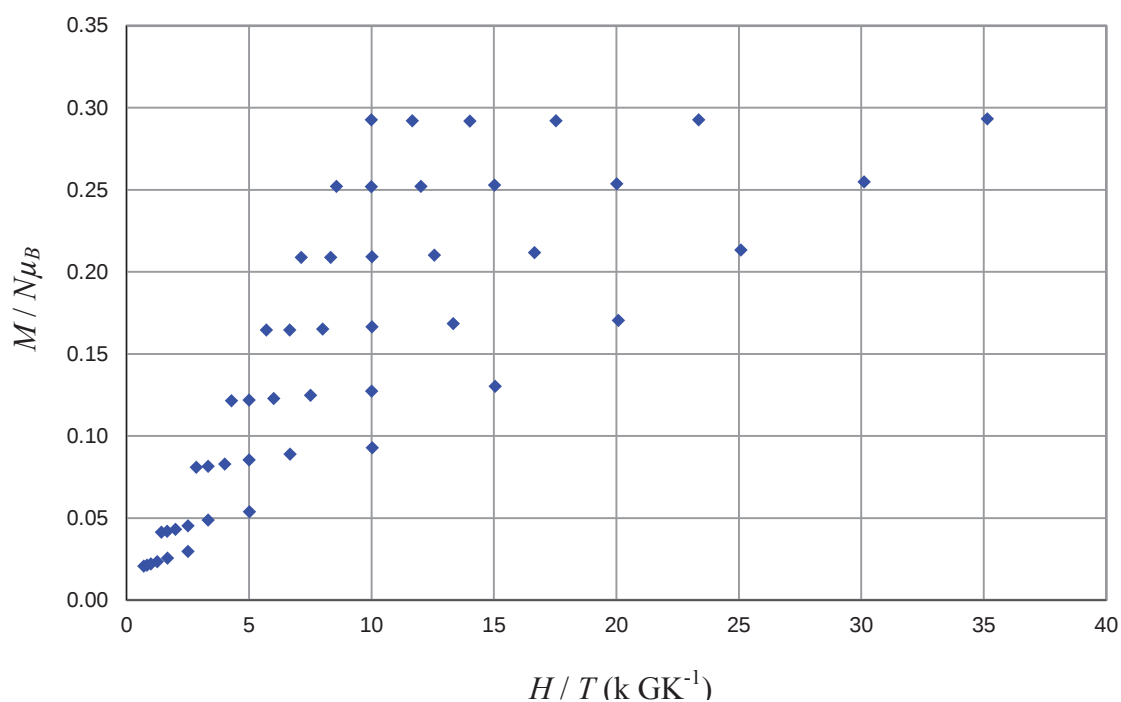


Figure 2.33: M vs. H / T plot for **C2**.

The complex **C2** is a large cluster containing two distinct molecules in the unit cell. Therefore, it is not possible to fit a set of parameters to a collection of

different molecules. Generation of eigenvalues would be meaningless, and the calculation of an averaged J value is not particularly helpful.

2.6.3 Magnetic measurements of the complex C3

The complex, **C3** is a heptanuclear iron cluster which consists of two hydroxo bridged units connected through one Fe^{3+} and six hydroxo bridges. The magnetic exchange interactions take place through these hydroxo and oximato bridges respectively within and between the triangles.

The magnetic measurements were performed on this complex in terms of temperature dependence of the $\chi_{\text{M}}T$ product and magnetisation. The $\chi_{\text{M}}T$ product continuously and almost linearly decreases from $13.17 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature to $3.96 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K (see Figure 2.34). The experimental value of the $\chi_{\text{M}}T$ product at room temperature is lower than the expected value of $30.63 \text{ cm}^3 \text{ K mol}^{-1}$ for seven non-interacting Fe^{3+} ions. The expected $\chi_{\text{M}}T$ value for a single iron species ($S = 5/2$) is $4.375 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K, which is also higher than the $\chi_{\text{M}}T$ value at 5 K observed for seven non-interacting Fe^{3+} atoms.

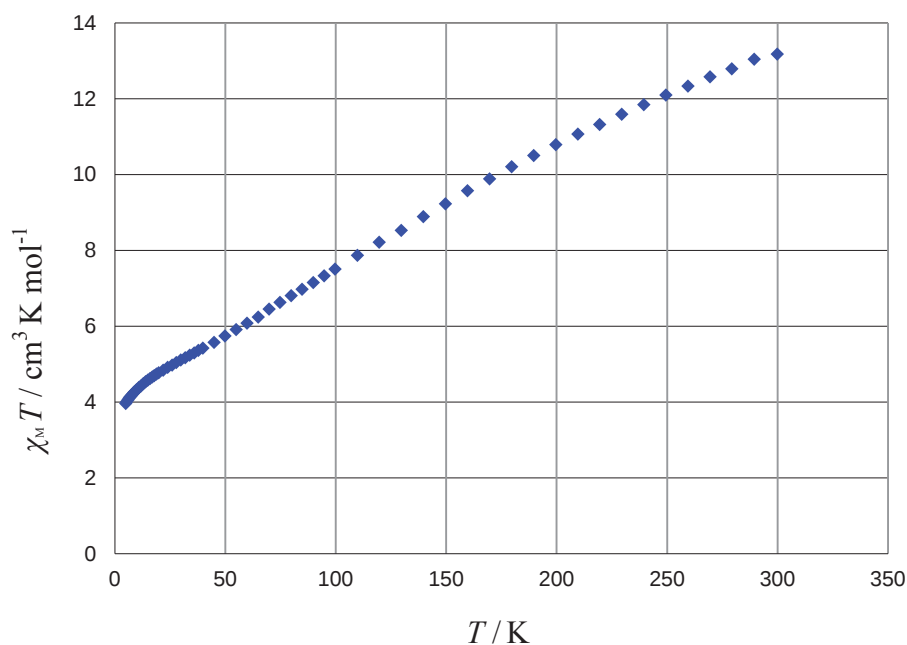


Figure 2.34: Plot of $\chi_{\text{M}}T$ vs T for the complex **C3**.

Variable-temperature, variable-field dc magnetisation experiments were performed in the temperature range of 2.0 - 7.0 K and in the magnetic field range of 0.5 T - 3 T respectively. These experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. μ_B/kT , with N being Avogadro's number and k_B the Boltzmann constant) in Figure 2.35. The J values, S , and also the uniaxial parameter (D) for the complex **C3** were not determined due to time constraints and lack of computational resources.

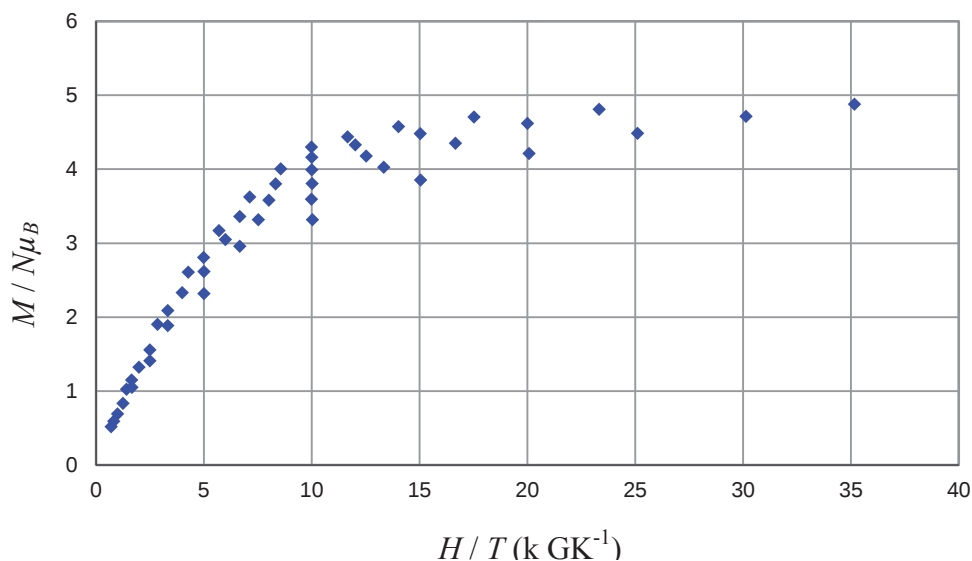


Figure 2.35: M vs. H / T plot for **C3**.

It is shown that all values of the $\chi_M T$ product at room temperature are smaller than the corresponding values of non-interacting Fe^{3+} ions for all three complexes, **C1**, **C2**, and **C3** and also it was found that their $\chi_M T$ values decrease with decreasing temperature which suggest the presence of sizeable antiferromagnetic exchange interactions.

The magnetic behaviour of related heptanuclear iron clusters of salicylaldoximes was previously reported by Brechin *et al.* in 2012.³⁵ The dominant magnetic interaction between the Fe atoms of this heptanuclear complex was also determined to be antiferromagnetic as the experimental $\chi_M T$ values constantly decrease with the decreasing temperature and also the considerably lower $\chi_M T$ value than that of the corresponding non-interacting metal ions reflects the presence of sizeable antiferromagnetic interactions.³⁵

2.7 Mössbauer spectroscopy

The Mössbauer spectroscopic technique is used to make precise measurements of shifts in nuclear energy levels. These measurements supply information about the chemical, structural, and magnetic properties of the material in which the nucleus resides. This technique has been used in a wide range of scientific investigations.⁴⁵

2.7.1 Results and discussion

The ⁵⁷Fe Mössbauer spectra of the complexes **C1**, **C2** and **C3** (see Figure 2.35 - 2.37) were recorded at high and low temperatures together with an integral fit of the transmission. The parameters of each of the samples are listed in Table 2.19.

Table 2.19: Fitting parameters of ⁵⁷Fe on **C1-C3** at low temperature and higher temperature (δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ_L = line width of the left peak, Γ_R = line width of the right peak, I = intensity).

[Fe₂B₂(L1-H)₄(F)₂(O)₂](BF₄)₂(MeOH)₄ C1·4MeOH					
T (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	I (%)
4.8	0.525	1.192	0.332	0.333	100
293	0.416	1.166	0.328	0.350	100
[Fe₆O(OH)₇(L1-H)₅(L1-2H)](BF₄)₂(MeOH)₅ C2·5MeOH					
T (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	I (%)
5.0	Not fitted*				
293	0.4	1.180	0.350	0.350	55
	0.4	0.570	0.400	0.400	45
Na[Fe₇(OH)₈(L11-2H)₆(Py)₆](BF₄)₂(H₂O)₆(Py)₃ C3·6H₂O·3Py					
T (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	I (%)
4.7	Not fitted*				
293	0.407	0.856	0.365	0.365	77.8
	0.398	0.498	0.206	0.206	28.9

* At high temperature the Fe^{3+} species collapses into a single quadrupole doublet with the same (when the second order Doppler effect is taken into account) isomer shift and quadrupole splitting as at low temperature. Therefore, fitting of the complicated slow relaxing Fe^{III} species at low temperature is not necessary.

The Mössbauer spectrum of the complex **C1** exhibits a single quadrupole doublet at an isomer shift of 0.42 mm s^{-1} with a quadrupole splitting of 1.17 mm s^{-1} at 293 K, which is indicative of the presence of a single Fe species in the sample (see Figure 2.36). The relatively larger ΔE_Q parameter of 1.17 mm s^{-1} at room temperature hints at the degree of asymmetry around the Fe atoms of the complex.²² Further, it is an indication of the presence of high spin Fe^{3+} ions in the octahedral geometry. This information is in agreement with the crystallographic results which revealed two chemically equivalent and crystallographically independent Fe atoms.

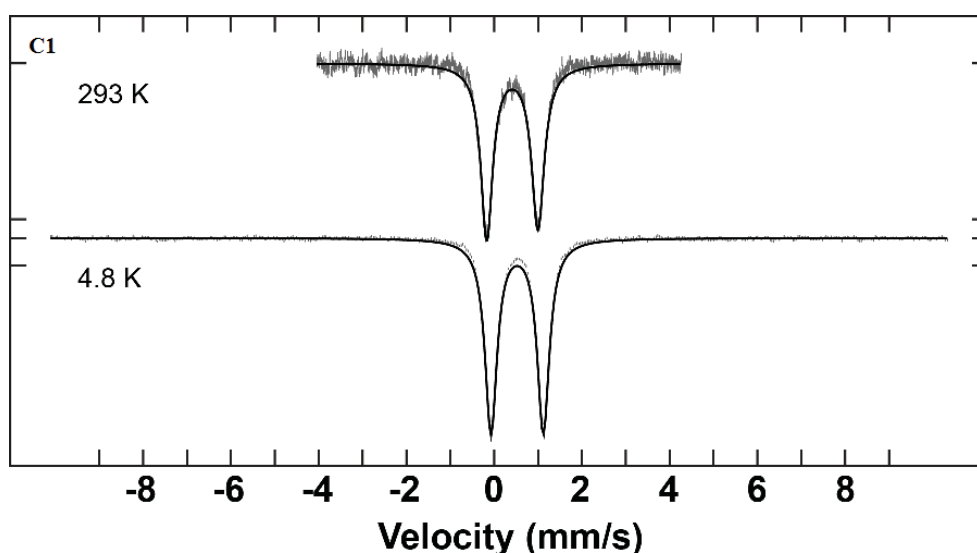


Figure 2.36: ^{57}Fe Mössbauer spectra of the complex **C1** (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature.

The Mössbauer spectrum of complex **C2** revealed a pair of quadrupole doublet at an isomer shift of 0.4 mm s^{-1} which was subjected to a quadrupole splitting of 1.18 mm s^{-1} and 0.57 mm s^{-1} . The fit indicates the presence of two species which is in line with the crystal structure of the complex (see Figure 2.37). The complex **C2** contains two crystallographically independent structures. Both structures of **C2** are highly symmetrical and are comprised of six equivalent Fe atoms. The two species may be indicative of the Fe atoms in the two complexes. The ratio of the two intensities is

almost equal to 1:1. The iron atoms within one of the two units of the complex has a relatively higher value of ΔE_Q , which indicates the geometry around the iron atoms within that unit is relatively distorted (the values of structural parameters of the two units vary slightly).

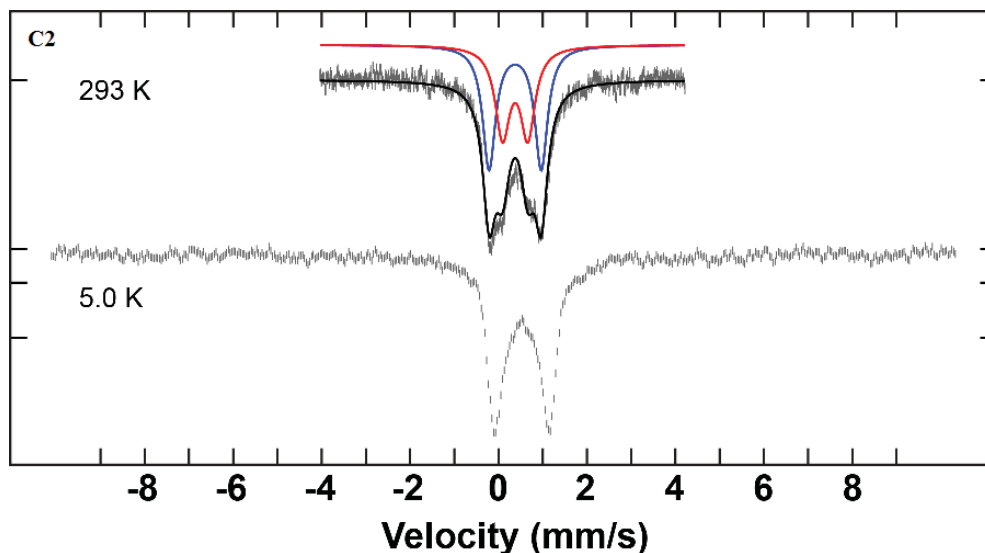


Figure 2.37: ^{57}Fe Mössbauer spectra of the complex **C2** [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit) at high and low temperature.

Crystallographically, the complex **C3** is a heptairon compound that consists of two chemically different iron environments namely, Fe2 the iron atoms within the triangles and between the triangles, Fe1. The spectrum at high temperature shows two species with isomer shift of 0.407 mm s^{-1} and 0.398 mm s^{-1} and quadrupole splitting of 0.856 mm s^{-1} and 0.498 mm s^{-1} , respectively (see Figure 2.38). This indicates the presence of the two chemically different Fe environments. The ratio of the intensities between the two species is approximately 7:3. Here we expect that value to be 1:6, as crystallographically there are six iron atoms present in the same octahedral coordination environment while the other iron atom is surrounded by six oxygen atoms. Nevertheless, the intensity ratio of the complex **C3** matches with that of the other heptairon complexes described in Chapter 3. At low temperature, hyperfine coupling is observed for this complex and also at 293 K quadrupole doublet with a slight quadrupole splitting is observed which were not observed for other heptairon complexes synthesised with double-headed salicylaldoxime ligands. The difference of the intensity ratio between the expected and experimental value may be due to the error originated from non resonant absorption.

The isomer shift and the quadrupole splitting values of the complexes **C1-C3** indicate that all the iron atoms are in the oxidation state of 3+ (see Figure 2.39).

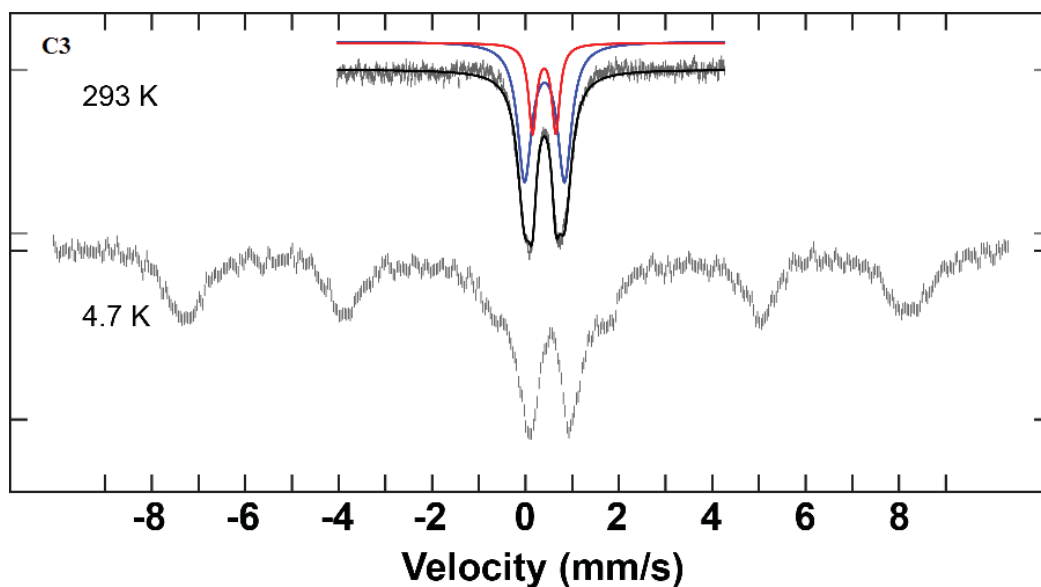


Figure 2.38: ^{57}Fe Mössbauer spectra of the complex **C3** [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit) at high and low temperature.

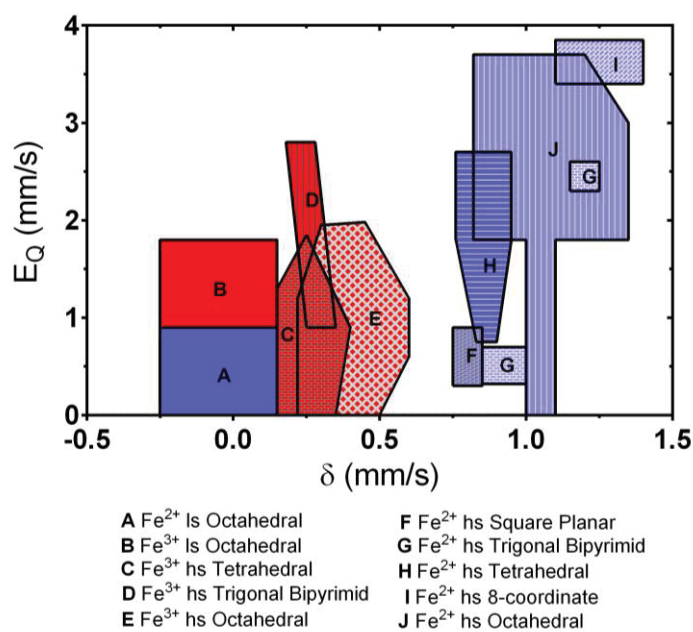


Figure 2.39: The relationship between the isomer shift and quadrupole splitting of the iron compounds (figure adapted from a presentation titled ' ^{57}Fe Mössbauer Spectroscopy: a Tool for the Remote Characterisation of Phyllosilicates' by Enver Murad.⁴⁴

2.8 Conclusion

Three new Fe(III) complexes with different nuclearity were synthesised with single-headed salicylaldoximes and the ligands employed to synthesise these iron complexes have only a few variations from each other. The ligand **L1** was utilised to produce two different complexes, **C1** and **C2** in the same conditions. The complex, **C1** was a diiron complex containing two boron atoms and the complex **C2** is a hexairon complex comprised of two crystallographically independent units. The ligand **L11** which is a slightly modified version of **L1**, formed a heptairon cluster **C3**. The magnetic susceptibility measurements reveal the presence of strong antiferromagnetic interactions within these complexes. Mössbauer spectra of the complexes **C1-C3** were recorded and to confirm the spin state and the oxidation states of the iron atoms in the complexes. The spin state of all three compounds was found to be high spin and the iron atoms are all in the oxidation state of 3+.

References:

1. Kahn, O., Molecular Magnetism, VCH-Verlagsgesellschaft, Weinheim, **1991**.
2. Chaudhuri, P., *Coord. Chem. Rev.*, **243**, **2003**, 143.
3. Smith, A. G., Tasker, P. A., White, D. J., *Coord. Chem. Rev.*, **241**, **2003**, 61.
4. Thorpe, J. M., Beddoes, R. L., Collison, D., Garner, C. D., Helliwell, M., Holmes, J. M., Tasker, P. A., *Angew. Chem. Int. Ed.*, **1999**, **38**, 1119.
5. Larkworthy, L. F., Povey, D. C., *J. Crystallogr. Spectrosc. Res.*, **1983**, **13**, 413.
6. Gallagher, M., Ladd, M. F. C., Larkworthy, L. F., Povey, D. C., Salib, K. A. R. *J. Crystallogr. Spectrosc. Res.*, **1986**, **16**, 967.
7. Chaudhuri, P., Hess, M., Weyhermüller, T., Bill, E., Haupt, H.-J., Flörke, U., *Inorg. Chem. Commun.*, **1**, **1998**, 39.
8. Willem, R., Bouhdid, A., Meddour, A., Gielen, C. C. F. M., Biesemans, M., Ribot, F., Sanchez, C., Tieknik, E.R.T., *Organometallics*, **1997**, **16**, 4377.
9. Chaudhuri, P., Winter, M., Fleischhauer, P., Haase, W., Flörke, U., Haupt, H.-J., *Inorg. Chim. Acta*, **1993**, 212, 241.
10. Verani, C. N., Bothe, E., Burdinski, D., Weyhermüller, T., Flörke, U., Chaudhuri, P., *Eur. J. Inorg. Chem.*, **2001**, 2161.
11. Liu, S., Zhu, H., Zubieta, J., *Polyhedron*, **8**, **1989**, 2473.
12. Bill, E., Krebs, G., Winter, M., Gerdan, M., Trautwein, A. X., Flörke, U., Haupt, H.-J., Chaudhuri, P., *Chem. Eur. J.*, **1997**, **3**, 193.
13. Chaudhuri, P., Rentschler, E., Birkelbach, F., Krebs, C., Bill, E., Weyhermüller, T., Flörke, U., *Eur. J. Inorg. Chem.*, **2003**, 541.
14. Chaudhuri, P., Winter, M., Fleischhauer, P., Haase, W., Flörke, U., Haupt, H.-J., *J. Chem. Soc., Chem. Commun.*, **1993**, 566.
15. Chaudhuri, P., Birkelbach, F., Winter, M., Staemmlar, V., Fleischhauer, P., Haase, W., Flörke, U., Haupt, H.-J., *J. Chem. Soc., Dalton Trans.*, **1994**, 2313.
16. Chaudhuri, P., Hess, M., Rentschler, E., Weyhermüller, T., Flörke, U., *New J. Chem.*, **1998**, 553.
17. Milios, C. J., Raptopoulou, C. P., Terzis, A., Lloret, F., Vicente, R., Perlepes, S. P., Escuer, A., *Angew. Chem. Int. Ed.*, **2004**, **43**, 210.
18. Zerbib, V., Robert, F., Gouzerh, P., *J. Chem. Soc., Chem. Commun.*, **1994**, 2179.
19. (a) Aldered, R., Johnston, R., Levin, D., Neilan, J., *J. Chem. Soc. Perkin Trans.*, **1994**, **1**, 1823; (b) Balali, E., Shameli, A., Naeimi, H., Ghanbari, M. M., *Orient. J. Chem.*, **2013**, **29**(4), 1611.

20. Wang, Q., Wilson, C., Blake, A. J., Collinson, S. R., Tasker, P. A., Schröder, M., *Tetrahedron Lett.*, **2006**, 47, 8983.
21. Stevens, J. R., Plieger, P. G., *Dalton Trans.*, **2011**, 40, 12235.
22. Hamish, A. Miller, N. L., Parsons, S., Parkin, A., Tasker, P. A., White, D. J., *J. Chem. Soc., Dalton Trans.*, **2000**, 3773.
23. Stepniak-Biniakiewicz, D., *Pol. J. Chem.*, **1980**, 54, 1567.
24. Coxall, R. A., Lindoy, L. F., Miller, H. A., Parkin, A., Parsons, S., Tasker, P. A., White, D. J., *Dalton Trans.*, **2003**, 55.
25. Forgan, R. S., Davidson, J. E., Galbraith, S. G., Henderson, D. K., Parsons, S., Tasker, P., White, F. J., *Chem. Commun.*, **2008**, 4049.
26. Houton, E., Meally, S. T., Sanz, S., Brechin, E. K., Jones, L. F., *Inorg Chim Acta.*, 421, **2014**, 416.
27. Lalia-Kantouri, M., Papadopoulos, C. D., Hatzidimitriou, A. G., Bakas, T., Pachini, S., *Z. Anorg. Allg. Chem.*, 636, **2010**, 531.
28. Raptopoulou, C. P., Sanakis, Y., Boudalis, A. K., Psycharis, V., *Polyhedron*, **2005**, 24, 711.
29. Hunt, R. L., Ault, B. S., *Spectrochim. Acta.*, **1981**, 37A, 63.
30. Silverstein, R. M., Bassler, G. C., Morrill, T. C., Spectrometric identification of organic compounds-5th ed. ; John Wiley & Sons, Inc., Singapore & Canada, **1991**, p125.
31. Megaw, H. D., *Acta Cryst.*, **1968**, B24, 153.
32. Steiner, T., *Angew. Chem. Int. Ed.*, **2002**, 41, 48.
33. Vasilevsky, I., Rose, N. J., *Acta Cryst.*, **1992**, B48, 444.
34. Khanra, S., Weyhermüller, T., Bill, E., Chaudhuri, P., *Inorg. Chem.*, 45, **2006**, 5911.
35. Mason, K., Chang, J., Prescimone, A., Garlatti, E., Carretta, S., Tasker, P. A., Brechin, E. K., *Dalton Trans.*, **2012**, 41, 8777.
36. Hołyńska, M., Clérac, R., Langer, T., Pottgen, R., Dehnen, S., *Polyhedron*, 52, **2013**, 1425.
37. Dey, S. K., Abedin, T. S. M., Dawe, Tandon, L. M., Collins, S. S., Thompson, L. K., Postnikov, A. V., Alam, M. S., Müller, P., *Inorg. Chem.*, **2007**, 46, 7767.
38. Abu-Nawwas, A. H., *Int. J. Eng. Res. Appl.*, **2014**, 4(2), 124.
39. Mason, K., Gass, I. A., Parsons, S., Collins, A., White, F. J., Slawin, A. M. Z., Brechin, E. K., Tasker, P. A., *Dalton Trans.*, **2010**, 39, 2727.

40. Gass, I., Milios, C. J., Collins, A., White, F. J., Budd, L., Parsons, S., Murrie, M., Perlepes, S. P., Brechin, E. K., *Dalton Trans.*, **2008**, 15, 2043.
41. Gass, I. A., Milios, C. J., Whittaker, A. G., Fabiani, F. P. A., Parson, S., Murrie, M., Perlepes, S. P., Brechin, E. K., *Inorg. Chem.*, **2006**, 45, 5281.
42. Raptopoulou, C. P., Boudalis, A. K., Sanakis, Y., Psycharis, V., Clemente-Juan, J. M., Fardis, M., Diamantopoulos, G., Papavassiliou, G., *Inorg. Chem.*, **2006**, 45, 2317.
43. Mason, K., Gass, I. A., White, F. J., Papaefstathiou, G. S., Brechin, E. K., Tasker, P. A., *Dalton Trans.*, **2011**, 40, 2875.
44. Murad, E., Cashion, J., *Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilisation*, Boston: Kluwer Academic Publishers, **2004**.
45. Murad, E., Oral Presentation entitled '⁵⁷Fe Mössbauer Spectroscopy: A Tool for the Remote Characterization of Phyllosilicates', the workshop on Martian Phyllosilicates, **2008**, Germany.

CHAPTER 3

METAL COMPLEXES OF DOUBLE-HEADED SALICYLALDOXIMES

3.1 Double-headed Salicylaldoximes

The simple singly functionalised phenolic oxime ligands described in Chapter 2 can be extended to bisubstituted oximic ligands, the so called ‘double-headed’ phenolic oximes. This can be done by connecting two phenolic oximes *via* aliphatic or aromatic diamino linkers (straps). These ligands therefore have an oxime group and a phenol group at either end to form double-headed salicylaldoximes (see Figure 3.1(a)). These ligands are expected to form multinuclear clusters having more than three metal centres uniting two planar units as illustrated in Figure 3.1(b).

3.2 Copper Complexes of Double-headed Salicylaldoximes

The first multinuclear salicylaldoxime-copper complex consisting of the same triangular motif illustrated in Figure 3.1(b) was synthesised by Plieger *et al.* in 2009 (see Figure 1.27 in Chapter 1).¹ Since then Brechin and his coworkers utilised the same oxime ligand **L**, (*N,N'*-dimethyl-*N,N'*-hexamethylenedi(3-hydroxyiminomethyl-2-hydroxy-5-*tert*-butylbenzylamine)), to produce large polynuclear manganese and iron clusters.²

Complexation with copper(II) resulted in tri and tetra copper complexes with the piperazinyl and ethylene linked oxime ligands **L5** and **L8** respectively (see Figure 3.2). The complexes contain different coordination environments around the copper ions despite the use of the same ligand coordination donor set. The piperazinyl and ethylene straps of these ligands are much shorter and thus are less flexible than the ligand **L**.

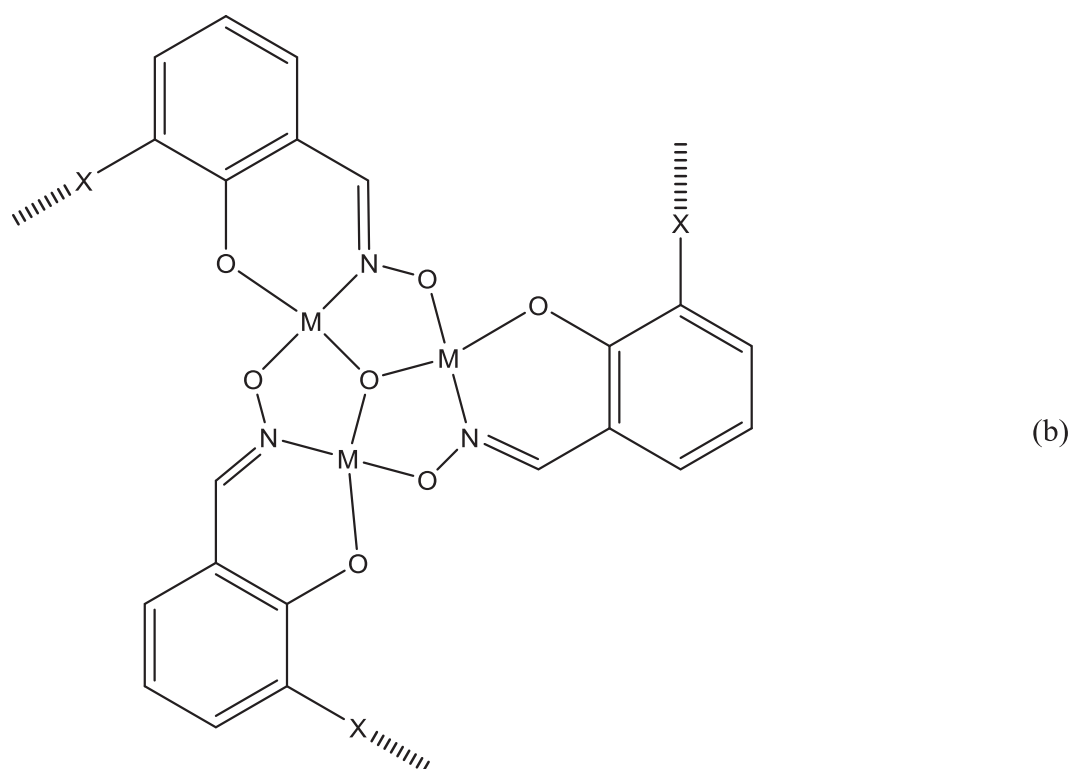
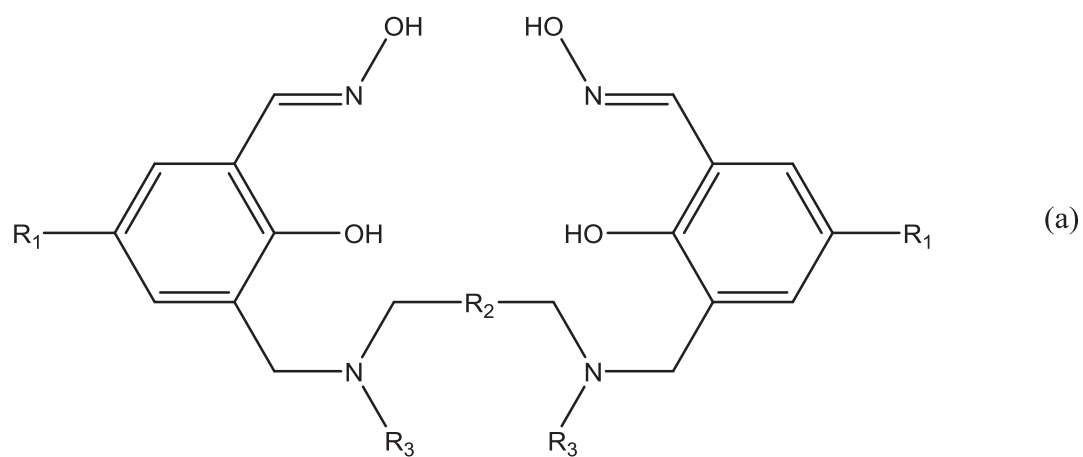


Figure 3.1: (a) Double-headed oxime, where $R_1 = \text{-}tert\text{-Bu}$, -CH_3 , $R_2 = \text{linkers}$ (see Figure 3.2), and $R_3 = \text{-CH}_3$, $\text{-CH}_2\text{-Ar}$ (see Figure 3.2). (b) The planar $[\text{M}_3\text{O}(\text{oximate})_3]^+$ with 3-fold symmetry, where X = rest of the ligand.

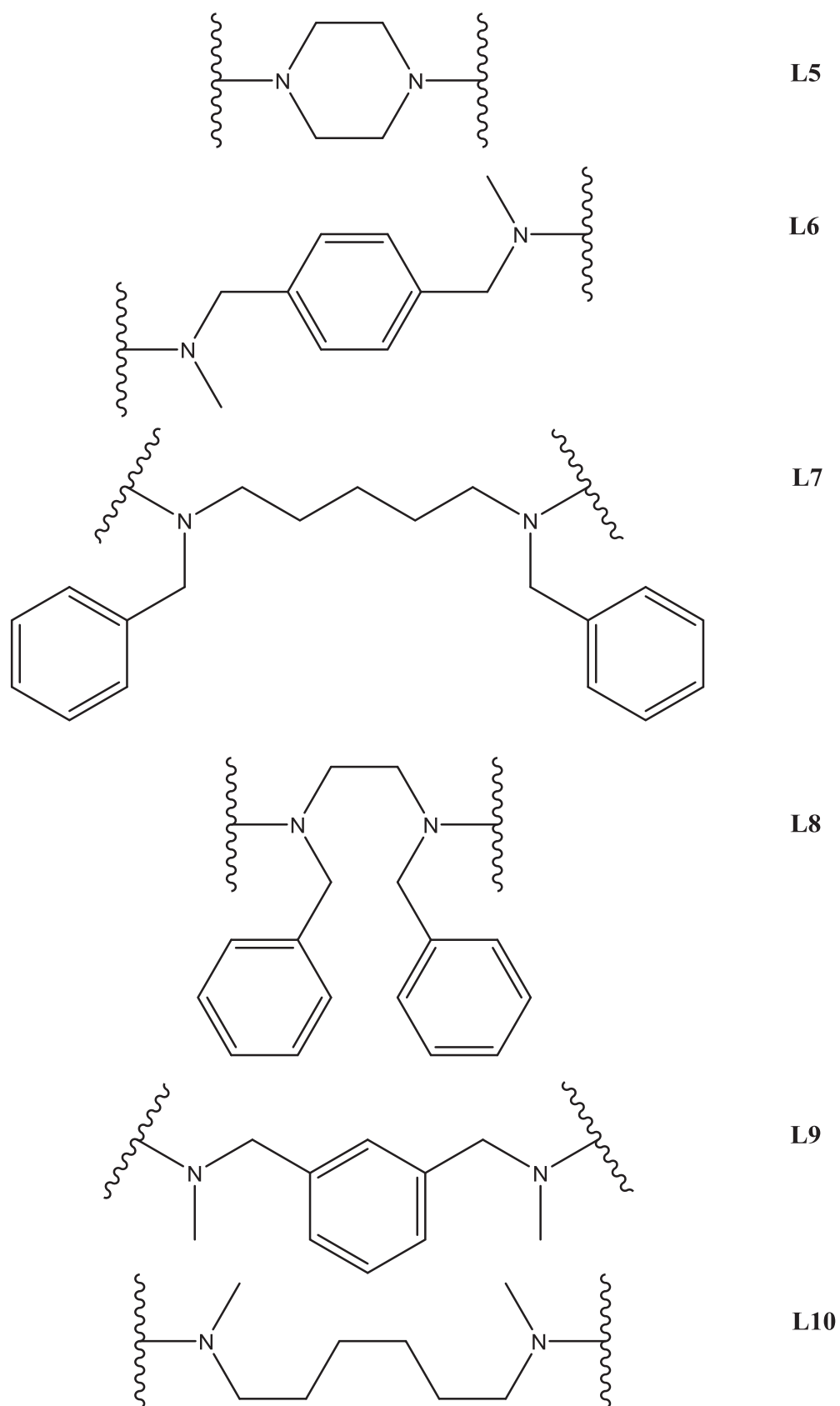


Figure 3.2: The R_2 linkers used in this chapter with R_3 modes ($R_3 = -CH_3, -CH_2-Ar$) shown.

3.2.1 Complex $[\text{Cu}_3(\text{L5-H})_3(\text{Py}_3)](\text{BF}_4)_2\text{PF}_6(\text{H}_2\text{O})_3(\text{MeOH})_3$, $\text{C5}\cdot 3\text{H}_2\text{O}\cdot 3\text{MeOH}$

The reaction of $\text{Cu}(\text{BF}_4)_2\cdot\text{H}_2\text{O}$ with **L5** in a 2 : 1 molar ratio in a MeOH/pyridine solution treated with NaPF_6 followed by crystallisation yields square shaped green crystals of the trinuclear complex, $[\text{Cu}_3(\text{L5-H})_3(\text{Py}_3)](\text{BF}_4)_2\text{PF}_6\cdot 3\text{H}_2\text{O}\cdot 3\text{MeOH}$ (**C5** $\cdot 3\text{H}_2\text{O}\cdot 3\text{MeOH}$). The complex contains three copper cations held together with three molecules of the ligand and three pyridine molecules. Additionally, three water molecules, three solvent molecules, two BF_4^- ions and a PF_6^- ion are present within the lattice. The anions balance the charge and sit outside the complex.

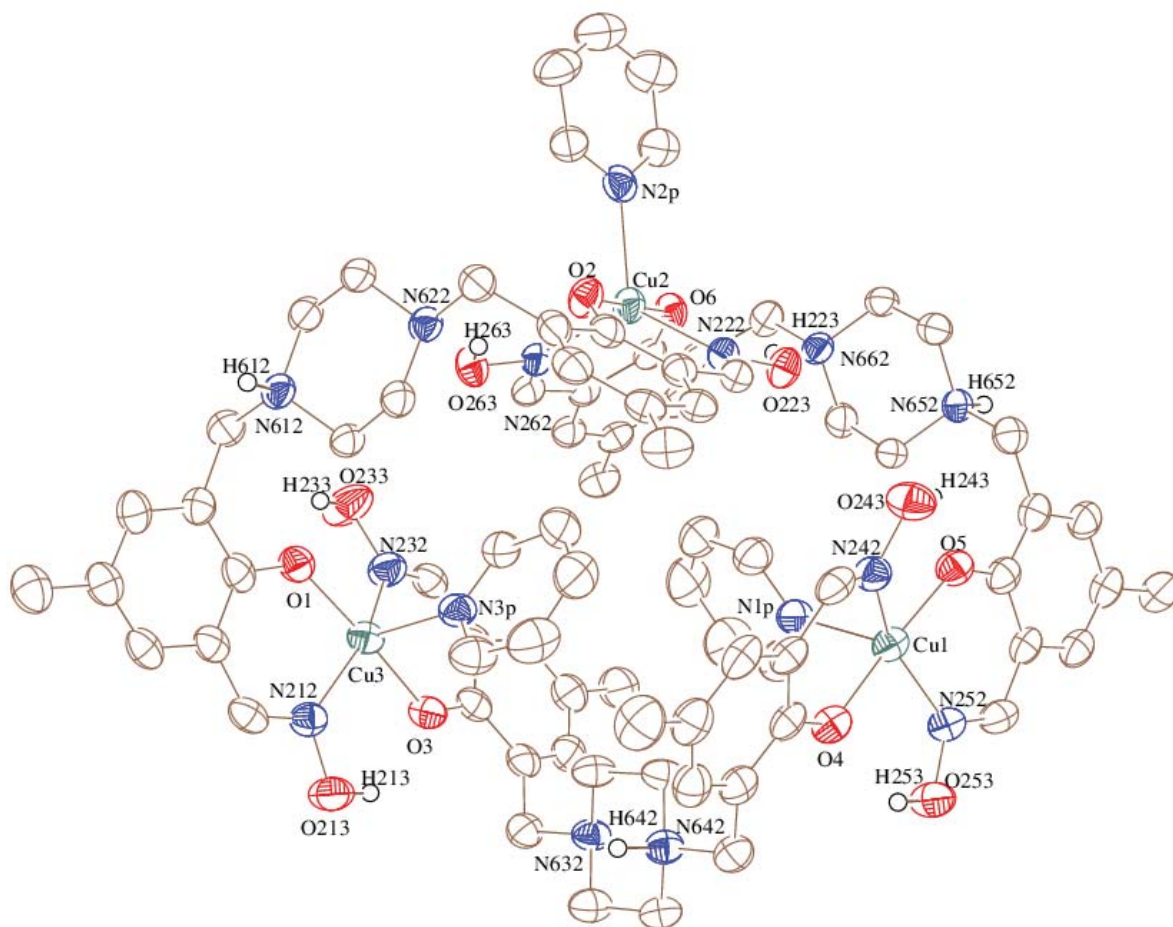


Figure 3.3: Crystal structure of the cation $[\text{Cu}_3(\text{L5-H})_3(\text{Py}_3)]^{3+}$ (Cu-dark green, N-blue, O-red, C-brown, and H atoms except the ones on the straps are omitted for clarity); ORTEP view at 50% probability level.

The complex **C5** crystallises in the $P2_1/n$ space group with four molecules per unit cell and the asymmetric unit contains the full complex. The ligand is a piperazine-linked

double-headed salicylaldoxime and is present in **C5** as H_3L^{5-} in which both phenolic O-atoms (see for example O1 and O2 in Figure 3.3) are deprotonated and one of the amino nitrogen atoms is protonated (see H612 on N612 in Figure 3.3). Each copper cation is bound to two ligands forming a 3+3 metal to ligand complex which adopts a tubular structure. The coordination sphere around each Cu atom is comprised of two phenolate O-atoms and two oximic N-atoms (one set from each ligand) and the fifth coordination site is occupied by a pyridine molecule in all cases. (see Figure 3.3, Tables 3.1 and 3.2 for bond distances and angles around the copper centres).

The pyridine molecule which is coordinated to Cu2 (see N2p in Figure 3.3) is pointing outwards away from the complex sphere while the other two pyridine molecules that are coordinated to Cu1 and Cu3 (see N1p and N3p in Figure 3.3), are contained within the sphere. The Cu(II)-O(phenolate) bond distances are in the range of 1.897(4)-1.947(4) Å, while the Cu(II)-N(oxime) bond distances lie in the range of 1.960(5)-2.027(5) Å. Due to the difference in coordination environment around the copper centres, one axial position on Cu1 or Cu3 is taken up by a pyridine molecule whereas both axial positions on Cu2 are occupied by phenolate O-atoms (O2 and O6, Figure 3.3) from two of the neighbouring ligands. Thus, the geometries of Cu1 and Cu3 are square pyramidal while Cu2 is located in a trigonal bipyramidal environment. This is despite the fact that all three metal centres share the same five atom donor set. The cause of this change in coordination geometry for Cu2 may be due to a number of factors. For instance, the cage complex is not capable of accommodating a third pyridine molecule within it. This, in addition to the hydrogen bond mediated preorganised coordination site [see Figure 3.4 for N-OH...N(amine) hydrogen bonds around Cu2], has given rise to a change in coordination geometry. The transformation from square pyramidal geometry to trigonal bipyramidal geometry has elongated the Cu2(II)-N(oxime) bond length with respect to the corresponding distances of the Cu1 and Cu3, and it is observed that the metal centres, Cu1 and Cu3 sit a similar distance from Cu2 (Cu2-Cu1 = 7.268(1) Å, Cu2-Cu3 = 7.597(1) Å, whereas Cu1-Cu3 = 9.448(2) Å). The inclusion of coordinated pyridine molecules within the structure prevents any anion encapsulation from occurring within the cavity.

Table 3.1: Selected bond distances for complex C5·3H₂O·3MeOH.

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Cu1-O4	1.947(4)	Cu2-O2	1.897(4)	Cu3-O1	1.925(4)
Cu1-O5	1.930(4)	Cu2-O6	1.903(4)	Cu3-O3	1.936(4)
Cu1-N1P	2.279(5)	Cu2-N2P	2.184(5)	Cu3-N3P	2.292(5)
Cu1-N242	1.964(5)	Cu2-N222	2.019(5)	Cu3-N212	1.975(5)
Cu1-N252	1.960(5)	Cu2-N262	2.027(5)	Cu3-N232	1.982(5)

Table 3.2: Selected bond angles for complex C5·3H₂O·3MeOH.

Atoms	Angle (°)	Atoms	Angle (°)		
O4-Cu1-O5	174.58(16)	O1-Cu3-O3	175.46(16)	O2-Cu2-O6	179.41(18)
O4-Cu1-N1P	93.20(17)	O1-Cu3-N3P	93.18(17)	O2-Cu2-N2P	88.67(19)
O4-Cu1-N242	90.03(19)	O1-Cu3-N212	90.33(19)	O2-Cu2-N222	90.31(17)
O4-Cu1-N252	88.02(19)	O1-Cu3-N232	88.37(19)	O2-Cu2-N262	89.41(17)
O5-Cu1-N1P	92.19(17)	O3-Cu3-N3P	91.36(17)	O6-Cu2-N2P	90.75(19)
O5-Cu1-N242	88.15(19)	O3-Cu3-N212	88.59(19)	O6-Cu2-N222	89.88(17)
O5-Cu1-N252	91.22(19)	O3-Cu3-N232	90.71(19)	O6-Cu2-N262	90.93(17)
N1P-Cu1-N242	103.7(2)	N3P-Cu3-N212	101.8(2)	N2P-Cu2-N222	120.97(19)
N1P-Cu1-N252	104.1(2)	N3P-Cu3-N232	103.8(2)	N2P-Cu2-N262	112.68(19)
N242-Cu1-N252	152.2(2)	N212-Cu3-N232	154.5(2)	N222-Cu2-N262	126.33(18)

Table 3.3: Selected H-bond distances for complex C5·3H₂O·3MeOH.

Atoms (D····A)	Distance (Å)
O213- H213····O3	2.670(5)
O223- H223····O6	2.807(5)
O223- H223····N662	2.851(6)
O233- H233····O1	2.687(7)
O243- H243····O5	2.636(6)
O253- H253····O4	2.660(5)
O263-H263····O2	2.833(5)
O263-H263····N622	2.856(6)

There are numerous H-bond interactions between the ligands, the BF₄⁻ ion and the ligands, as well as the PF₆⁻ ion and the ligands. Some of the important intermolecular hydrogen bonds between oximic hydrogen atoms and phenolate oxygen atoms as well as non-protonated amine nitrogen atoms and oximic hydrogen atoms are illustrated in Figure 3.4. (see Table 3.3 for H-bond distances). Similar H-bond interactions within copper dimers of oxime based ligands were reported in 2010 by Tasker *et al.*³

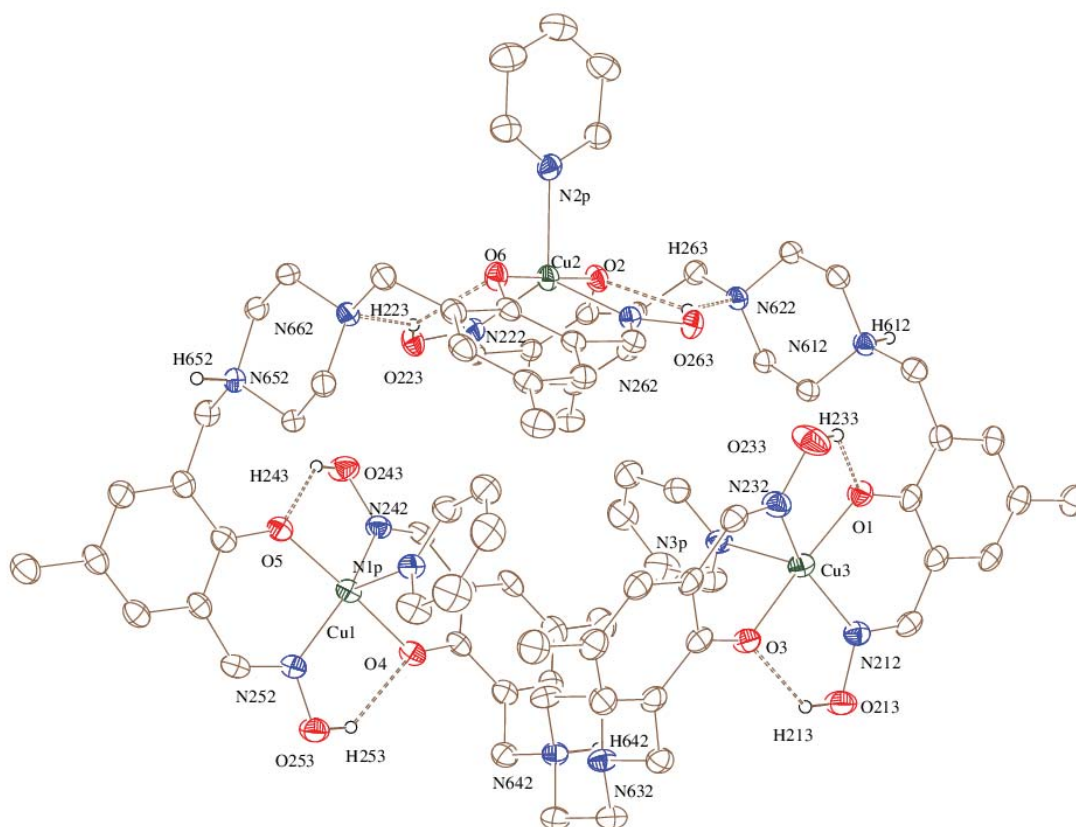


Figure 3.4: Selected H-bond contacts drawn in brown dotted lines (Cu-dark green, N-blue, O-red, C-brown, H-white, and all the H-atoms are omitted for clarity except the ones involved in forming H-bonds and the ones on amine N-atoms); ORTEP view at 30% probability level.

The complex was further purified by dissolving in DMF and precipitated with Et₂O. The CHN analysis for the complex **C5** agrees with the addition of one DMF molecule. The charge balance analysis is given in Table 3.4.

Table 3.4: Charge balance analysis of the complex **C5**.

3 Cu ²⁺	3 (L5-H)	2 BF ₄ ⁻	1 PF ₆ ⁻
3 x 2+	3 x 1-	2 x 1-	1 x 1-
6+	3-	2-	1-

All three copper ions exist in their most stable oxidation state 2+ in the liquid state. Thus the charge created by three copper ions is 6+. Each ligand carries -1 charge, because all the phenolate O-atoms are deprotonated and one of the amine N-atoms is protonated while all the oximic O-atoms remain protonated. These oximic H-atoms form intermolecular H-bond interactions with phenolate O-atoms from adjacent ligands

(see Table 3.3) and also the H-atoms on the protonated amine N-atoms form H-bond interactions with fluorine atoms from the anions (BF_4^- and PF_6^-) present within the lattice (N642-H642 $\cdots$ F10 from a BF_4^- = 2.869(8) Å and N612-H612 $\cdots$ F6 from the PF_6^- = 2.899(6) Å). The 3- charge created by three ligands and the 3- charge from the anions present within the lattice together balance the 6+ charge of copper ions.

In 2002, Kandaswamy and co-workers reported the synthesis of binuclear copper and nickel complexes of **L5**. These complexes exhibited a different metal coordination donor set from that observed in the complex **C5**.⁴ In their report, a monocopper complex was synthesised by reacting equimolar amounts of copper(II) acetate and **L5a** (the aldehyde precursor of **L5**). The Cu(II) in the mononuclear complex is coordinated by the two phenolate O-atoms and the tertiary amine N-atoms of the ligand. A series of binuclear copper compounds was then obtained by treating one equivalent of the aforementioned monocopper compound with an equal amount of the copper(II) salt (ClO_4^- , Cl^- , and NO_3^-) followed by the same amount of hydroxylamine and triethylamine in methanol. One of the Cu(II) ions is coordinated by the two tertiary amine N-atoms and the two phenolate O-atoms while the other Cu(II) is coordinated by the two oximic N-atoms and the same two phenolate O-atoms, creating two oxygen bridges between the copper ions. Thus the ligand is present as $[\text{HL}]^{3-}$ where both phenol oxygen atoms and one of the oximic oxygen atoms are deprotonated. This form of the ligand is accompanied by two Cu(II) ions and the corresponding counter anion. It was reported that the anions, Cl^- and NO_3^- , in the dicopper complexes, $[\text{Cu}_2\text{L}(\text{Cl})]\text{H}_2\text{O}$ and $[\text{Cu}_2\text{L}(\text{NO}_3)]\text{H}_2\text{O}$ are coordinated, while in the $[\text{Cu}_2\text{L}]\text{ClO}_4\cdot\text{CH}_3\text{OH}$ complex, the ClO_4^- ion remains uncoordinated⁴ and any coordinated or uncoordinated pyridine molecules are absent in these complexes which is in contrast to **C5**. No other complexes are known that have been synthesized with this ligand.

3.2.2 Complex $[\text{Cu}_4(\text{L8-3H})_2\text{Py}_2](\text{BF}_4)_2(\text{MeOH})(\text{Py})$,

C7·MeOH·Py

The reaction of $\text{Cu}(\text{BF}_4)_2\cdot\text{H}_2\text{O}$ with **L8** in a 2 : 1 molar ratio in a MeOH/pyridine solution followed by crystallisation yields green crystals of the tetracopper complex $[\text{Cu}_4(\text{L8-3H})_2\text{Py}_2](\text{BF}_4)_2(\text{MeOH})\text{Py}$ (**C7·MeOH·Py**). The complex **C7·MeOH·Py** consists of four Cu-atoms, two ligand molecules (which are present as **L8-3H** where both phenolic O-atoms but only one oximic O-atom are deprotonated), two pyridine

molecules and two oxo groups together with two BF_4^- ions are contained within the lattice. The complex crystallises in the $P\bar{1}$ space group with one half of the molecule represented in the asymmetric unit and the other half is generated by a centre of symmetry (see Figure 3.5).

There are two different copper ions in the complex in terms of their coordination environments. Both copper ions lie in a distorted square pyramidal geometry. The coordination donor set around Cu1 consists of two oximic N-atoms and two phenolic O-atoms from the same ligand while the remaining axial site is occupied by the N-atom (N1) of a pyridine molecule (see Figure 3.5).

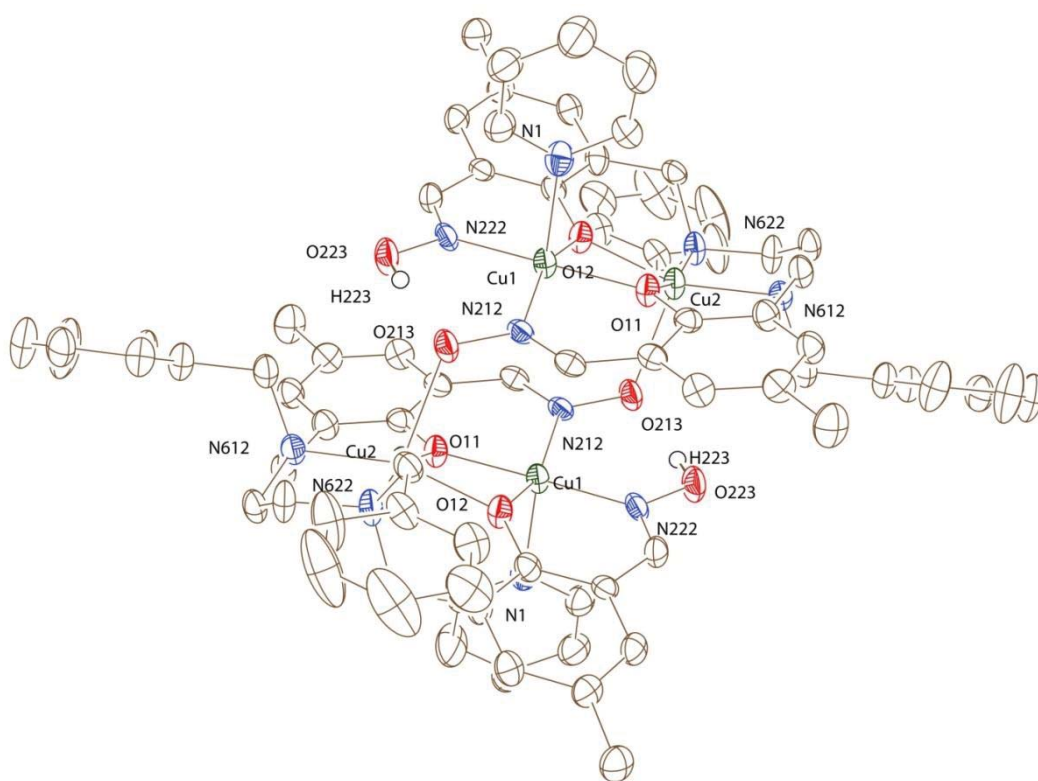


Figure 3.5: Cation, $[\text{Cu}_4(\text{L8-3H})_2\text{Py}_2]^{2+}$ of the complex $[\text{Cu}_4(\text{L8-3H})_2\text{Py}_2](\text{BF}_4)_2(\text{MeOH})\text{Py}$ ($\text{C7} \cdot \text{MeOH} \cdot \text{Py}$) [Cu-green, N-blue, O-red, C-brown, (C-atoms of the pyridine molecules are omitted for clarity) and H atoms are omitted for clarity except the oximic H-atoms]; ORTEP view at 50% probability level.

The pyridine molecule sits perpendicular to the metal plane created by the other donor atoms (O11, O12, N212, N222). Coordination environment for Cu2 consists of two phenolic O-atoms and two amino N-atoms on the same ligand while the remaining axial site is occupied by the deprotonated oximic O-atom (O213) on the second ligand molecule. Both copper metal centres share the same phenolate donors, which bridge

between them. The metal complex contains two planes which are approximately parallel to each other. Each plane contains a ligand molecule and a metal ion (see Tables 3.5 and 3.6 for bond distances and bond angles around the copper centres).

Table 3.5: Selected bond lengths around Cu ions of complex **C7**·MeOH·Py.

Bond	Distance (Å)	Bond	Distance (Å)
Cu1-O11	1.935(2)	Cu2-O11	1.945(2)
Cu1-O12	1.965(3)	Cu2-O12	1.957(2)
Cu1-O213	2.895(3)	Cu2-O213_a	2.278(3)
Cu1-O223	2.881(3)	Cu1-N222	1.958(3)
Cu1-N1	2.257(4)	Cu2-N622	2.008(4)
Cu1-N212	1.971(3)	Cu2-N612	2.015(3)

Table 3.6: Selected bond angles around the Cu(II) ions of complex **C7**·MeOH·Py.

Atoms	Angle (°)	Atoms	Angle (°)
O11-Cu1-O12	76.61(10)	O223-Cu1-N212	75.67(11)
O11-Cu1-O213	115.47(10)	N1-Cu1-N212	96.83(13)
O11-Cu1-O223	165.96(11)	N1-Cu1-N222	93.95(12)
O11-Cu1-N1	94.66(11)	N212-Cu1-N222	100.22(12)
O11-Cu1-N212	91.38(12)	O11-Cu2-O12	76.56(10)
O11-Cu1-N222	164.63(12)	O11-Cu2-N612	94.42(11)
O12-Cu1-O213	152.62(10)	O11-Cu2-N622	163.74(15)
O12-Cu1-O223	113.26(10)	O11-Cu2-O213_a	89.72(11)
O12-Cu1-N1	105.12(13)	O12-Cu2-N612	157.01(12)
O12-Cu1-N212	155.63(12)	O12-Cu2-N622	93.42(12)
O12-Cu1-N222	88.85(11)	O12-Cu2-O213_a	95.30(11)
O213-Cu1-N1	98.48(11)	N612-Cu2-N622	90.01(12)
O213-Cu1-N222	75.70(11)	O213_a-Cu2-N612	105.89(11)
O223-Cu1-N1	92.28(10)	O213_a-Cu2-N622	104.11(14)

Table 3.7: Selected H-bond distances for **C7**·MeOH·Py.

Atoms (D····A)	Distance
O223-H223····O213	2.498(4)
O223-H223····N212	3.062(4)

The strong intramolecular H-bond between the oximic H-atom and deprotonated oximic O-atom as well as weaker intramolecular H-bond between the oximic H-atom and the oximic N-atom stabilise the complex **C7** (see Table 3.7 for H-bond lengths). The CHN results of the complex **C7** match with the addition of 8.5 water molecules which may have come from the atmospheric moisture (see Table 3.8 for charge balance analysis of

the complex **C7**). The crystallographic data of the copper complexes are shown in Table 3.9.

Table 3.8: Charge balance analysis of the complex **C7**.

4 Cu ²⁺	2 (L8 -3H)	2 BF ₄ ⁻
4 x 2+	2 x 3-	2 x 1-
8+	6-	2-

An 8+ charge is possessed by the copper ions each possessing its most stable 2+ oxidation state. The total 6- charge to balance the charge is contributed by two ligands each possessing 3- from deprotonated two phenolate O-atoms and an oximic O-atom. These oximic H-atoms and deprotonated oximic O-atoms form intramolecular H-bonds. In addition, these oximic H-atoms form intramolecular H-bonds with adjacent amine N-atoms. The remaining 2+ charge is balanced by two BF₄⁻ ions within the lattice.

Table 3.9: Crystallographic details of the complexes **C5** and **C7**.

	C5·3H₂O·3MeOH	C7·MeOH·Py
formula	C ₈₄ H ₁₁₄ B ₂ Cu ₃ F ₁₄ N ₁₅ O ₁₂ P	C ₈₄ H ₈₉ B ₂ Cu ₄ F ₈ N ₁₁ O ₉
<i>M</i> , g mol ⁻¹	2113.47	1824.44
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	17.433(5)	10.7083(4)
<i>b</i> , Å	28.692(4)	14.5196(8)
<i>c</i> , Å	18.949(3)	14.9141(11)
α , deg (°)	90	67.471(5)
β , deg (°)	90.051(5)	83.531(6)
γ , deg (°)	90	75.146(5)
<i>V</i> , Å ³	9478(3)	2070.0(2)
<i>T</i> , K	140	143
<i>Z</i>	4	1
ρ , calc [g cm ⁻³]	1.481	1.464
crystal shape / colour	rhomboid / dark green	rhomboid / dark green
crystal size [mm]	0.16 x 0.16 x 0.20	0.15 x 0.20 x 0.20
μ , [mm ⁻¹]	1.816	1.845
restraints / parameters	191 / 1154	110 / 602
unique data	11508	6950
<i>R</i> _{int} / <i>R</i> _{σ}	0.0790/0.0671	0.0670/0.0514
<i>I</i> > 2 σ (<i>I</i>)	8.63	5.23

unique data, ($I > 2\theta$)	9579	6142
R_1^a , wR_2^b	0.0857, 0.2508	0.0523, 0.1683
goodness of fit	1.04	1.15

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$ for observed reflections. ^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)_2] / \sum[w(F_o^2)_2]\}^{1/2}$ for all data.

3.3 Iron complexes of double-headed salicylaldoximes

All the iron complexes synthesised that incorporated double-headed salicylaldoximes were as a result of a reaction between $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and a ligand (2:1) in a MeOH/pyridine solution at RT followed by crystallisation. By connecting two salicylaldoxime units together with alkyl and xylyl amino straps (Figure 3.1(a)), the formation of polynuclear complexes was possible. In the majority of cases, the complexes formed the stable trinuclear plane of metal atoms as depicted in Figure 3.1(b). The bridging mode of the oxime moiety for all the hexa- and hepta-iron complexes are described as an $\eta^1:\eta^1:\eta^2:\mu$ -mode (see Chapter 2) which is totally analogous to the bridging mode seen for the earlier reported salicylaldoxime $[\text{Mn}^{\text{III}}_3]$ and $[\text{Mn}^{\text{III}}_6]$ clusters.⁵⁻⁸ The control of the nuclearity and magnetic features of these iron complexes were investigated by altering the length and hence flexibility of the amino straps in the ligands.

All the complexes were analysed by Mössbauer, CHN, X-ray, IR, UV, VT magnetic, and ESI-MS techniques. Unless otherwise stated, ESI-MS analysis of the complexes was inconclusive.

3.3.1 Complex $[\text{Fe}_3\text{BO}_2(\text{L9-2H})_2(\text{OH})_2(\text{Py})_2](\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{MeOH})(\text{Py})$, $\text{C}_{10} \cdot 2\text{H}_2\text{O} \cdot \text{MeOH} \cdot \text{Py}$

The reaction of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with **L9**, in a molar ratio of 2 : 1 in MeOH/pyridine solution followed by crystallisation yields dark red, rhombic shaped crystals of the complex $[\text{Fe}_3\text{BO}_2(\text{L9-2H})_2(\text{OH})_2(\text{Py})_2](\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{MeOH})(\text{Py})$. The complex $\text{C}_{10} \cdot 2\text{H}_2\text{O} \cdot \text{MeOH} \cdot \text{Py}$ crystallises in the $P\bar{c}cn$ space group and there are two clusters per unit cell. The asymmetric unit contains one half of the molecule with the other half generated by reflection.

The complex consists of two ligands which are deprotonated at the phenol and oxime, but protonated at the amine sites. In addition, there are three Fe(III) atoms, and a metaborate ion (see Figure 3.6). Additionally, two BF_4^- ions, two water molecules, one methanol molecule, and one pyridine molecule are present within the lattice.

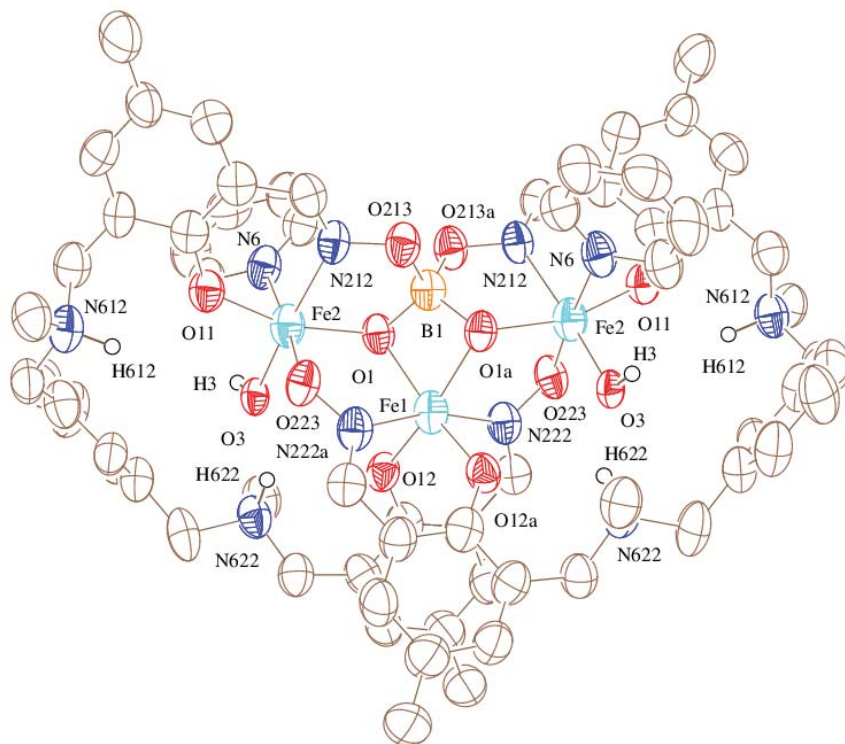


Figure 3.6: Crystal structure of the cation $[\text{Fe}_3\text{BO}_2(\text{L9-2H})_2(\text{OH})_2(\text{Py})_2]^{2+}$ of the complex C10 (Fe-cyan, B-orange, N-blue, O-red, C-brown) H atoms are omitted for clarity except the protons on the tertiary amines, counterions and solvent molecules have also been removed for clarity; ORTEP view at 50% probability level.

The metaborate ion BO_2^- is assumed to come from the hydrolysis of the tetrafluoroborate. It shares two oximic oxygen atoms and coordinates in a μ_3 fashion through O213 and O213a to each iron atom. The boron atom lies in a distorted tetrahedral geometry (see Tables 3.10 and 3.11). All the Fe(III) ions lie in a distorted octahedral geometry (see Table 3.10 and 3.11). The donor set around the Fe2(III) cation consists of four oxygen donors and two nitrogen donors. Based on bond lengths, the axial donors consist of the oximic oxygen (O223) atom and a pyridine nitrogen atom (N6). The equatorial donors are made up of an oximic nitrogen atom (N212) and a phenolate oxygen (O11), one from each ligand, a μ_2 oxo-group (O1), and a hydroxyl oxygen atom (O3) from water.

Table 3.10: Selected bond lengths around the metal ions for the complex **C10**·2H₂O·MeOH·Py.

Bond	Distance (Å)	Fe2-O1	1.942(4)
B1-O1	1.445(6)	Fe2-O3	1.873(3)
B1-O213	1.489(7)	Fe2-O11	1.934(4)
Fe1-O1	1.990(4)	Fe2-O223	1.992(4)
Fe1-O12	1.925(4)	Fe2-N6	2.202(5)
Fe1-N222	2.167(4)	Fe2-N212	2.159(5)

Table 3.11: Selected bond angles for the complex **C10**·2H₂O·MeOH·Py.

Atoms	Angle (°)	O1a-Fe1-O222a	106.97(18)
O1-B1-O213	112.4(2)	O12a-Fe1-N222a	83.80(17)
O1-B1-O1a	106.5(6)	O1-Fe2-O3	97.44(15)
O1-B1-O213a	109.50(19)	O1-Fe2-O11	161.18(16)
O1a-B1-O213	109.50(19)	O1-Fe2-O223	91.64(14)
O1-Fe1-O12	95.54(14)	O1-Fe2-N6	91.95(18)
O1-Fe1-N222	106.97(18)	O1-Fe2-N212	77.98(15)
O1-Fe1-N222a	85.35(18)	O3-Fe2-O11	101.28(15)
O1-Fe1-O1a	71.15(14)	O3-Fe2-O223	91.55(15)
O1-Fe1-O12a	159.51(15)	O3-Fe2-N6	86.36(17)
O1a-Fe1-O12	159.51(15)	O3-Fe2-N212	175.26(15)
O12-Fe1-O12a	101.13(16)	O11-Fe2-O223	89.90(15)
O12-Fe1-O222a	86.76(17)	O11-Fe2-N6	87.23(18)
O1a-Fe1-O222	85.35(18)	O11-Fe2-N212	83.27(16)
O12a-Fe1-N222	86.76(17)	O223-Fe2-N6	176.06(17)
N222-Fe1-N222a	165.1(2)	O223-Fe2-N212	89.79(17)
O1a-Fe1-O12a	95.54(14)	N6-Fe2-N212	92.56(18)

The donors around the Fe1(III) again make an N₂O₄ coordination set. This time there is no pyridine coordinated; instead both nitrogen donors originate from the oximic groups of each ligand, two phenolate-O atoms and two μ_2 -oxo atoms. The axial coordination sites are taken up by the two oximic nitrogen atoms from each ligand and the equatorial sites are taken up by the two phenolate oxygen atoms and two μ_2 -oxo atoms.

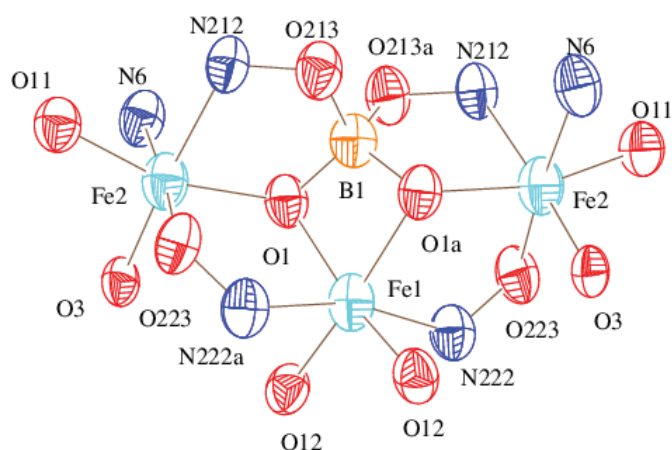


Figure 3.7: Metallic core of the structure, **C10**; ORTEP view at 50% probability level.

There are only two ligands per cluster. Therefore, some additional chelators such as pyridine molecules are required to complete the coordination sphere of two of the Fe(III) atoms. So, in this complex pyridine acts in a dual role both to coordinate vacant coordination sites and as the base to deprotonate the oxime moieties of the ligands.

There are some hydrogen bonding interactions present between water molecules and oximic oxygen atoms (O1w·····O223), water and protonated nitrogen atoms (N612·····O1w) and also a hydroxide and a protonated nitrogen atom (N622·····O3) (see Figure 3.8 and Table 3.12 for hydrogen bond lengths).

The oxidation states of the iron atoms were assigned according to charge balance considerations and later confirmed by VT magnetic measurements and Mössbauer analysis.

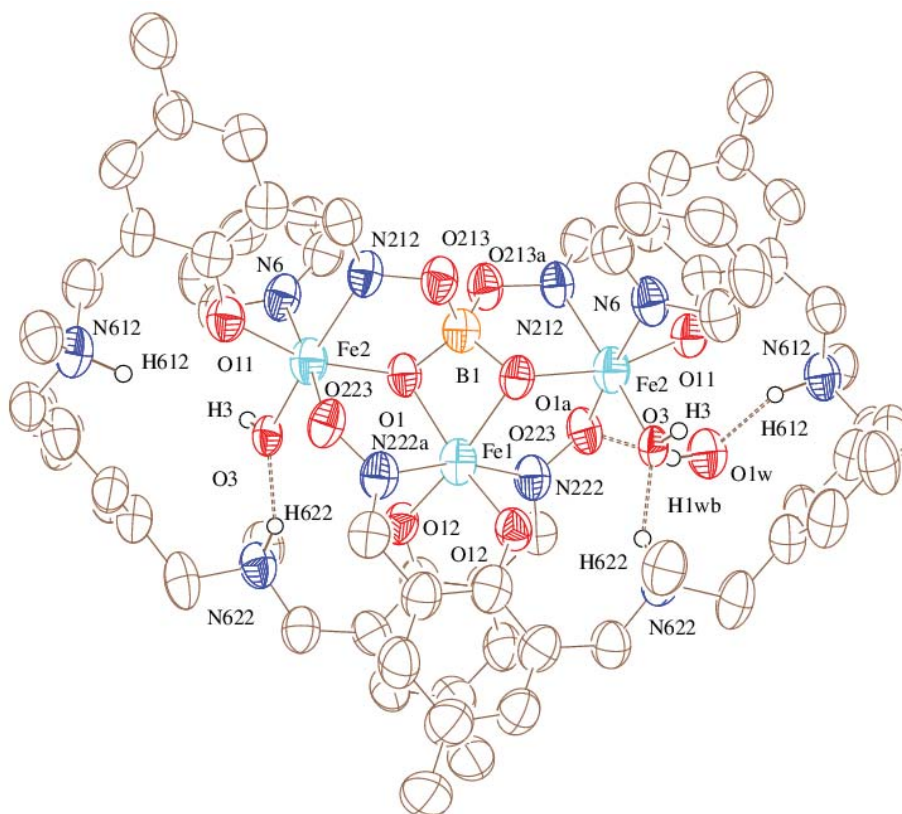


Figure 3.8: Hydrogen bonding present within the cation of the complex **C10**; ORTEP view at 50% probability level.

Table 3.12: Selected H-bonds for the complex **C10**·2H₂O·MeOH·Py.

Atoms (D·····A)	Distance (Å)
N622-H622·····O3	2.645(6)
N612-H612·····O1w	2.796(7)
O1w-H1wb·····O223	2.838(5)

The CHN analysis agrees with the addition of two water molecules contained within the complex **C10**. The charge balance analysis is shown in Table 3.13 and confirms (along with the Mössbauer, see later) that each ligand amine group is protonated.

Table 3.13: Charge balance analysis of the complex **C10**.

3 Fe ³⁺	1 B ³⁺	2 O ²⁻	2 (L7-2H)	2 OH ⁻	2 BF ₄ ⁻
3 x 3+	1 x 3+	2 x 2-	2 x 2-	2 x 1-	2 x 1-
9+	3+	4-	4-	2-	2-

3.3.1.1 Magnetic measurements of the complex C10

Magnetic susceptibility measurements were carried out on the complex **C10** and the results are reported as temperature dependence of the $\chi_M T$ product (see Figure 3.9).

The value of the $\chi_M T$ product at room temperature is $4.624 \text{ cm}^3 \text{ K mol}^{-1}$, lower than the calculated value for three non-interacting Fe^{3+} ions ($13.125 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.0$). The value of the $\chi_M T$ product decreases almost linearly and constantly to $3.674 \text{ cm}^3 \text{ K mol}^{-1}$ upon cooling to 80 K. On further cooling to 15 K, the value rises to $3.779 \text{ cm}^3 \text{ K mol}^{-1}$ where again it slightly declines to a value of $3.726 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K (see Figure 3.9). This behaviour is consistent with the presence of dominant antiferromagnetic interactions between the Fe^{3+} ions.

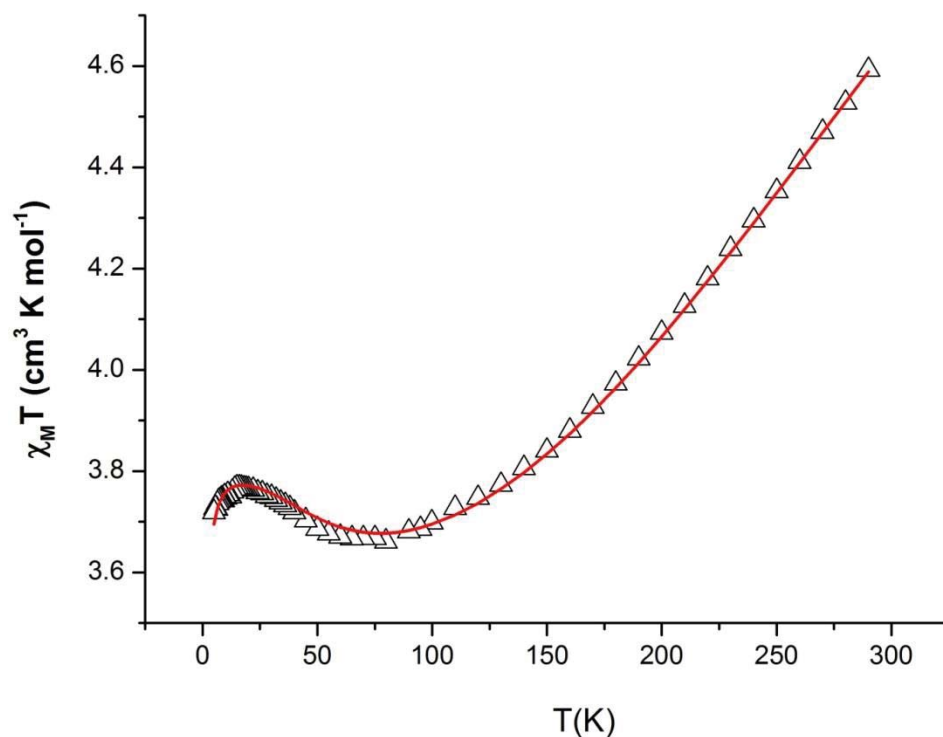


Figure 3.9: Plot of $\chi_M T$ vs T for the complex **C10** with fitted data (fitted data illustrated in red colour).

Figure 3.10 indicates the exchange coupling model containing two unique magnetic exchange-interaction parameters employed to fit the susceptibility data for the complex **C10**. The best-fit parameters were determined as $J_{1,2} = -23.83 \text{ cm}^{-1}$ and $J_{2,2} = +0.21 \text{ cm}^{-1}$ by fitting the $\chi_M T$ product that explains the presence of sizable antiferromagnetic interactions between the Fe1 and Fe2 whereas comparatively weak ferromagnetic interactions between Fe2 and Fe2 (see Figure 3.9).

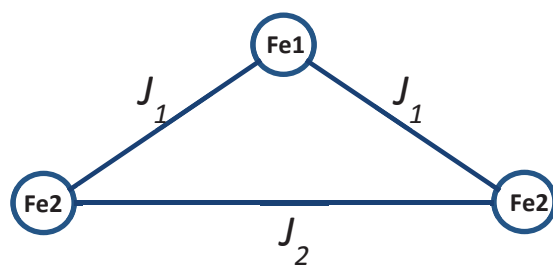


Figure 3.10: Schematic J model for the complex, C10.

The data were fitted to the following spin Hamiltonian:

$$\hat{H} = -2[J_1\{(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3)\} + J_2(\hat{S}_1 \cdot \hat{S}_3)] + \sum_{i=1,2,3} \{\mu_B g \vec{B} \cdot \hat{S}_i\}$$

where J_1 and J_2 are the isotropic exchange interaction parameters, $\hat{S}$ is a spin operator, $i = 1, 2, 3$, μ_B is the Bohr magneton, $\vec{B}$ is the applied magnetic field vector, and $g = 1.98$ is the g-factor of the Fe^{III} ions.

The plot of energy versus total spin shows the total spin state at the well isolated ground state (at the level where energy is equal to 0) of the system as 5/2 (see Figure 3.11) with the first excited state ($S = 3/2$) lying approximately 121 cm^{-1} higher in energy.

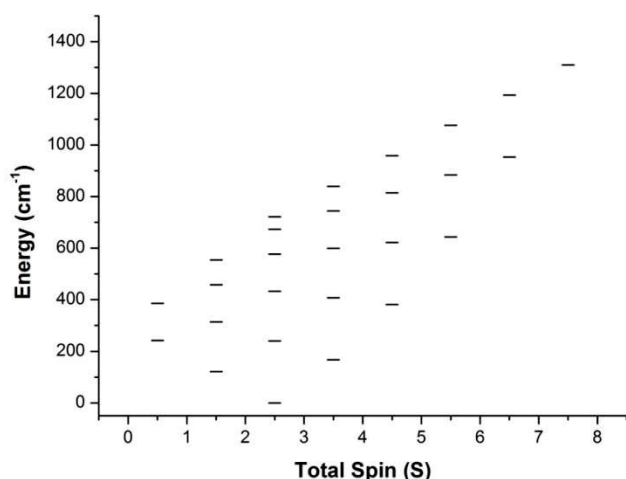


Figure 3.11: Plot of energy vs total spin of the complex C10.

Variable-temperature, variable-field dc magnetisation experiments were performed in the 2.0 K - 7.0 K and 0.5 T - 3 T temperature and magnetic field ranges respectively, in order to determine the single-ion axial anisotropy parameter for the Fe^{3+} centres. These

experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. $\mu_B/k_B T$, with N being Avogadro's number and k_B the Boltzmann constant) in Figure 3.12. They were fitted numerically by using the simplex algorithm to the axially anisotropic spin Hamiltonian below, by numerical diagonalisation of the full spin-Hamiltonian matrix:

$$\hat{H} = -2[J_1\{(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3)\} + J_2(\hat{S}_1 \cdot \hat{S}_3)] \\ + \sum_{i=1,2,3} \{ \mu_B g \vec{B} \cdot \hat{S}_i + D[\hat{S}_{z,i}^2 - S_i(S_i + 1)/3] \}$$

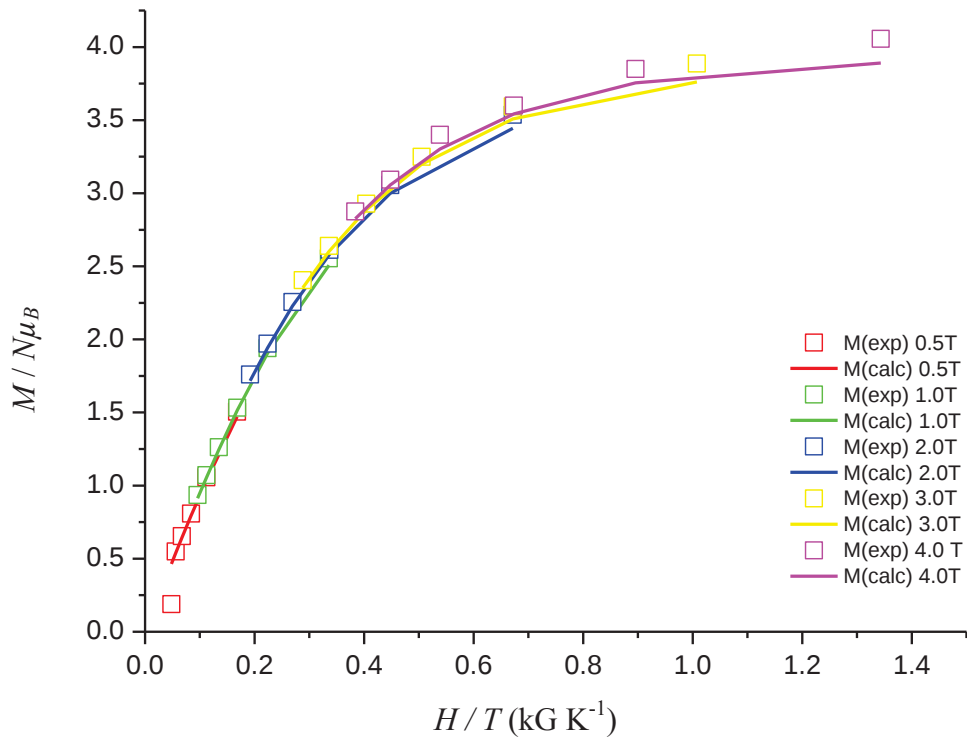


Figure 3.12: M vs. H / T plot for **C10**.

The uniaxial anisotropy D was determined to be $-2.441 \times 10^{-4} \text{ cm}^{-1}$ using the J values (J_1 and J_2 fixed to -23.8 cm^{-1} and $+0.21 \text{ cm}^{-1}$ respectively) and the total ground state spin ($S = 5/2$ which is the total spin of the Fe(III) ions). The value for D is very small and thus is negligible, which is a further indicator that the dominant exchange interaction is antiferromagnetic.

3.3.2 Complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3](\text{BF}_4)_3(\text{H}_2\text{O})_7\text{Py}$,

$\text{C8}\cdot 7\text{H}_2\text{O}\cdot \text{Py}$

The reaction of **L7** with $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ in the molar ratio of 1 : 2 in a MeOH/pyridine solution followed by crystallisation produces rhombic shaped dark red crystals of the complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3](\text{BF}_4)_3(\text{H}_2\text{O})_7\text{Py}$ (**C8** $\cdot 7\text{H}_2\text{O}\cdot \text{Py}$). The complex **C8** $\cdot 7\text{H}_2\text{O}\cdot \text{Py}$ is a hexairon cluster containing three **L7** ligands, which are present as **L7-2H** in the complex and held together with oxo/hydroxo bridging groups. Within the crystal lattice there exist seven water molecules, three BF_4^- ions, and a pyridine molecule.

The complex crystallises in the space group $P2_1/c$ and the asymmetric unit contains one complete molecule with four molecules per unit cell. The complex is comprised of a $[\text{Fe}^{\text{III}}_3]_2$ trigonal prism where each Fe atom lies in a distorted octahedral geometry and is coordinated to a phenolate oxygen atom and an oximic nitrogen atom of one ligand, the central oxygen atom (O10 or O11) of the relevant trinuclear unit, and an oxygen atom of a hydroxo interplane bridge. The two axial sites are occupied by another oxygen atom of a hydroxo bridge between the trinuclear units and an oximic oxygen of the neighbouring ligand molecule (see Figure 3.13, Table 3.14 and 3.15 for bond lengths and angles around the metal centres). The atomic sequence of the oximic bridges across each edge on both triangles is ‘anti-clockwise’ (Fe-O-N-Fe).

The ligand **L7** consists of a five carbon atom chain between the linker amines. This makes the ligand quite flexible, which in turn has produced a small cluster that consists of six iron atoms. The oxygen atom of the central hydroxo group within the triangle forms a hydrogen bond between two metal triangles, with the remaining central oxo-group. The hydrogen atom expected in this hydrogen bond could not be located via the Fourier difference map but it is suggested by the considerably short distance between the central oxygen atoms within the two triangles. The distance between the central oxygen atoms O10 and O11 is 2.453(9) Å, and also the central oxygen atoms O10 and O11 of the two triangles are displaced out of the $[\text{Fe}_3]$ planes pointing inwards towards each other by 0.290(6) Å and 0.220(4) Å, respectively, values somewhat larger than those observed for complex **C2** (0.155(5) and 0.134(5) Å). The metal triangle planes are linked to each other through six hydroxo bridges (Fe-O-Fe, 126-132°) as two of them are on each Fe atom and the straps of the three helical **L7** molecules. The oxygen atoms

of the hydroxo bridges are located in the shape of a hexagon between the metal triangles (see Figure 3.14). The distance between two neighbouring O-atoms of the hexagon, O-O, is in the range 2.529(8) - 2.636(8) Å.

Strong hydrogen bonds are formed between protonated nitrogen atoms in the straps and neighbouring phenolate oxygen atoms as well as with some water molecules within the lattice further stabilising the complex (see Table 3.16). The CHN analysis of the complex **C8** agrees with the addition of four water molecules and the oxidation states of the iron atoms were determined by the charge balance considerations (see Table 3.17 for the charge balance analysis), VT magnetic measurements and were later confirmed by Mössbauer spectroscopy.

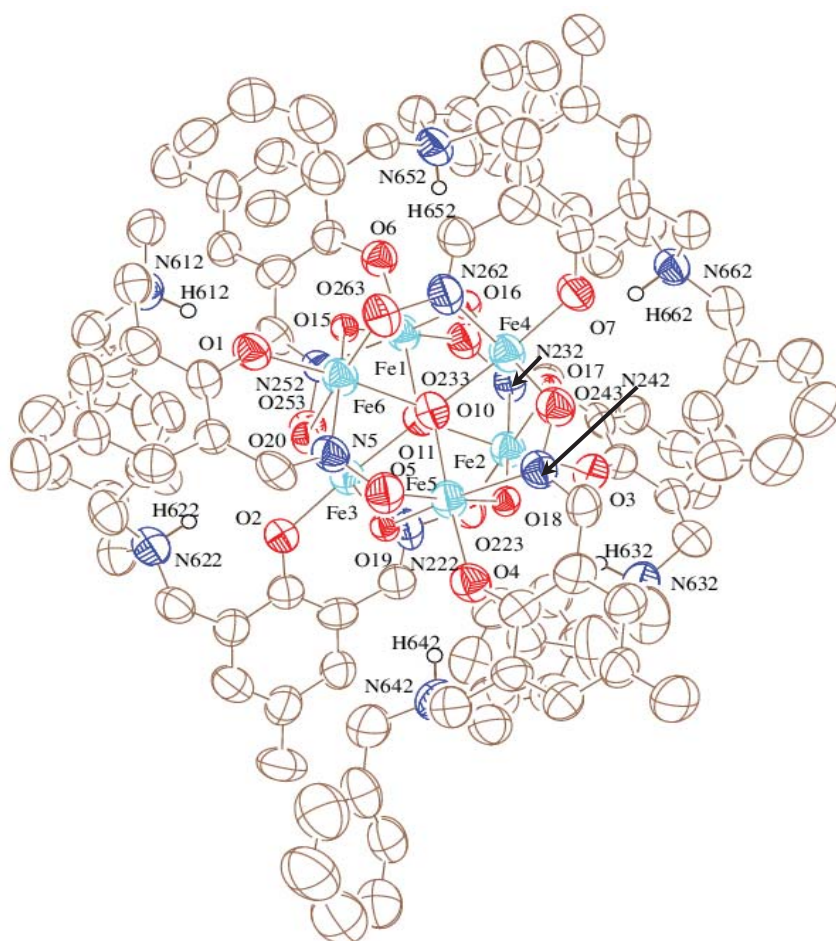


Figure 3.13: Crystal structure of the cation of the complex **C8** $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3]^{3+}$ (Fe-cyan, N-blue, O-red, C-brown). The H atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms; ORTEP view at 50% probability level.

Table 3.14: Selected bond lengths around metal ions of the complex **C8**·7H₂O·Py.

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Fe1-O11	2.021(6)	Fe2-O11	1.996(6)	Fe3-O11	1.981(6)
Fe1-O16	1.963(6)	Fe2-O17	2.039(7)	Fe3-O19	2.066(5)
Fe1-O233	1.969(7)	Fe2-O223	1.980(8)	Fe3-O253	1.943(6)
Fe1-O6	1.903(7)	Fe2-O3	1.928(7)	Fe3-O2	1.930(8)
Fe1-N252	2.141(9)	Fe2-N232	2.120(9)	Fe3-N222	2.114(10)
Fe1-O15	2.035(5)	Fe2-O18	1.959(5)	Fe3-O20	1.966(7)
Fe4-O10	1.961(8)	Fe5-O10	1.994(7)	Fe6-O10	2.026(6)
Fe4-O17	1.982(6)	Fe5-O19	1.965(6)	Fe6-O15	1.956(5)
Fe4-O243	1.949(7)	Fe5-O5	1.952(8)	Fe6-O263	1.940(7)
Fe4-O7	1.928(8)	Fe5-O4	1.915(7)	Fe6-O1	1.927(7)
Fe4-N262	2.126(10)	Fe5-N242	2.113(9)	Fe6-N5	2.129(9)
Fe4-O16	2.058(5)	Fe5-O18	2.038(6)	Fe6-O20	2.032(6)

Table 3.15: Selected bond angles around the metal centres of the complex **C8**·7H₂O·Py.

Atoms	Angle (°)		
		O233-Fe1-O16	96.1(3)
O15-Fe1-O233	174.7(3)	O233-Fe1-O11	88.4(3)
O6-Fe1-O11	169.0(3)	O233-Fe1-N252	100.7(3)
O16-Fe1-N232	87.0(2)	O233-Fe1-O6	87.9(3)
O16-Fe1-O11	92.1(2)	O16-Fe1-O15	79.8(2)
O11-Fe1-N252	84.2(3)	O15-Fe1-O11	88.4(2)
N252-Fe1-O6	86.3(3)	O15-Fe1-N252	83.2(3)
O6-Fe1-O16	98.6(3)	O15-Fe1-O6	96.0(3)

Table 3.16: Selected H-bond lengths of the complex **C8**·7H₂O·Py.

D·····A	length (Å)
N612-H612·····O1	2.823(10)
N622-H622·····O2	2.722(11)
N632-H632·····O3	2.748(12)
N642-H642·····O4	2.720(14)
N662-H662·····O7	2.666(12)
N652-H652·····O1W ^a	2.782(13)
O10-O11	2.453(9)

^a N652 does not H-bond to phenolate O6, in contrast to other amine moieties.

Table 3.17: Charge balance analysis of the complex **C8**.

6 Fe ³⁺	1 O ²⁻	7 OH ⁻	3 (L7-2H)	3 BF ₄ ⁻
6 x 3+	1 x 2-	7 x 1-	3 x 2-	3 x 1-
18+	2-	7-	6-	3-

The oxidation state of all the iron atoms was analysed to be 3+ by Mössbauer data. Thus three iron atoms give 18+ charge to the complex. Each ligand provides a charge of 2- as both amine N-atoms of each ligand are protonated while oximic and phenolate O-atoms are deprotonated. The H-atoms on the amine N-atoms form intramolecular H-bonds with the neighbouring phenolate O-atoms and also one of these six H-atoms forms a H-bond with a water molecule (see Table 3.16). Therefore, the total charge contribution from the ligands is 6-. As was discussed earlier, the short distance between the central O-atoms (O10 and O11) indicates the presence of a H-atom between them, which confirms that one of them is a OH group. Thus, the central O-atoms provide a 3- charge to the complex. The six hydroxyl bridges and three BF₄⁻ ions balance the remaining 6+.

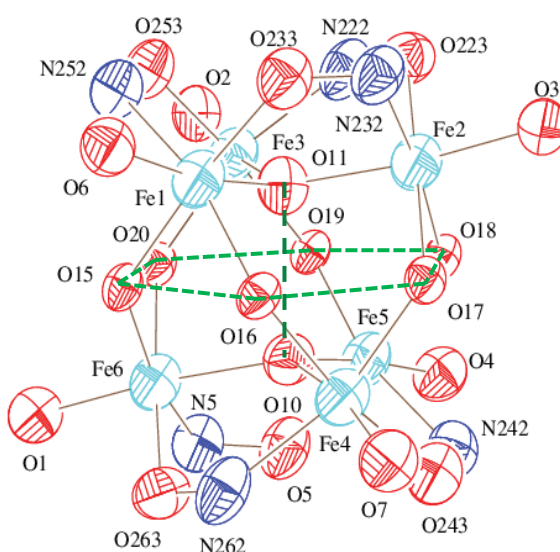


Figure 3.14: Metallic core [Fe₆O(OH)₇(L5-2H)₃]³⁺ of the complex **C8** emphasising the hydrogen bond contact (dark green dotted line) between the central oxygen atoms (O10 and O11) of the lower and upper triangles and the internal hexagon (O15 through O20, shown in dotted light green line) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.

3.3.2.1 Magnetic measurements of the complex $\text{C8}\cdot 7\text{H}_2\text{O}\cdot \text{Py}$

The magnetic susceptibility measurements performed on the complex, $\text{C8}\cdot 7\text{H}_2\text{O}\cdot \text{Py}$ were reported as $\chi_{\text{M}}T$ product against temperature (see Figure 3.15). The $\chi_{\text{M}}T$ values were calculated over the temperature range of 5-300 K. They continuously increase almost linearly over the temperature from $0.323 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K to $8.389 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature.

The calculated $\chi_{\text{M}}T$ value for six non-interacting Fe^{3+} ions is $26.25 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.0$. Thus the experimental $\chi_{\text{M}}T$ value at room temperature is considerably lower than the calculated value. This behaviour indicates the presence of strong antiferromagnetic interactions between the metal centres.

The total ground state spin is found to be zero as illustrated in the energy versus total spin graph in the Figure 3.16.

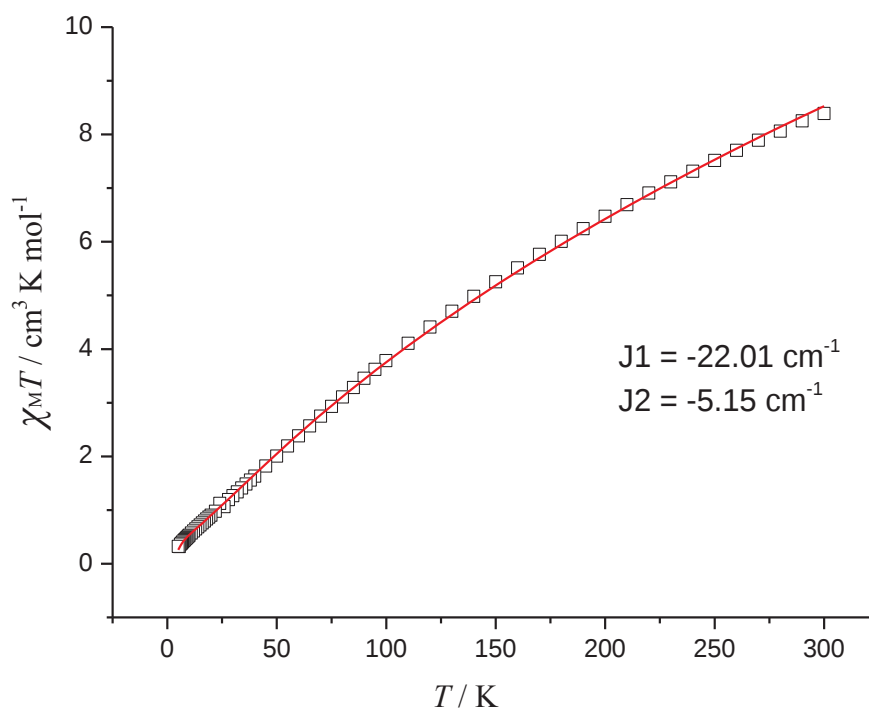


Figure 3.15: Plot of $\chi_{\text{M}}T$ product vs T for the complex $\text{C8}\cdot 7\text{H}_2\text{O}\cdot \text{Py}$ with fitted data (fitted data illustrated in red colour).

The data of temperature dependence of $\chi_{\text{M}}T$ was fitted using the following appropriate simple isotropic ($g = 2.00$) spin Hamiltonian (see Figure 3.15), where J is the isotropic exchange interaction parameter, $\hat{S}$ is a spin operator and the last term accounts for the Zeeman interaction with the applied magnetic field and the Zeeman term includes the

parameters, $i = 1-6$, μ_B is the Bohr magneton, $\vec{B}$ is the applied magnetic field vector, and g is the g factor of the Fe^{III} ions. Coupling constants (J) or magnetic exchange interactions are a measure of energy (cm^{-1}) and are positive for ferromagnetic and negative for antiferromagnetic interactions.

The coupling constants, $J1$ and $J2$ were found to be -22.02 cm^{-1} and -5.15 cm^{-1} respectively. The negative values are indicative of the presence of dominant antiferromagnetic interactions between the metal centres. The J model for the metal centres is shown in the Figure 3.17.

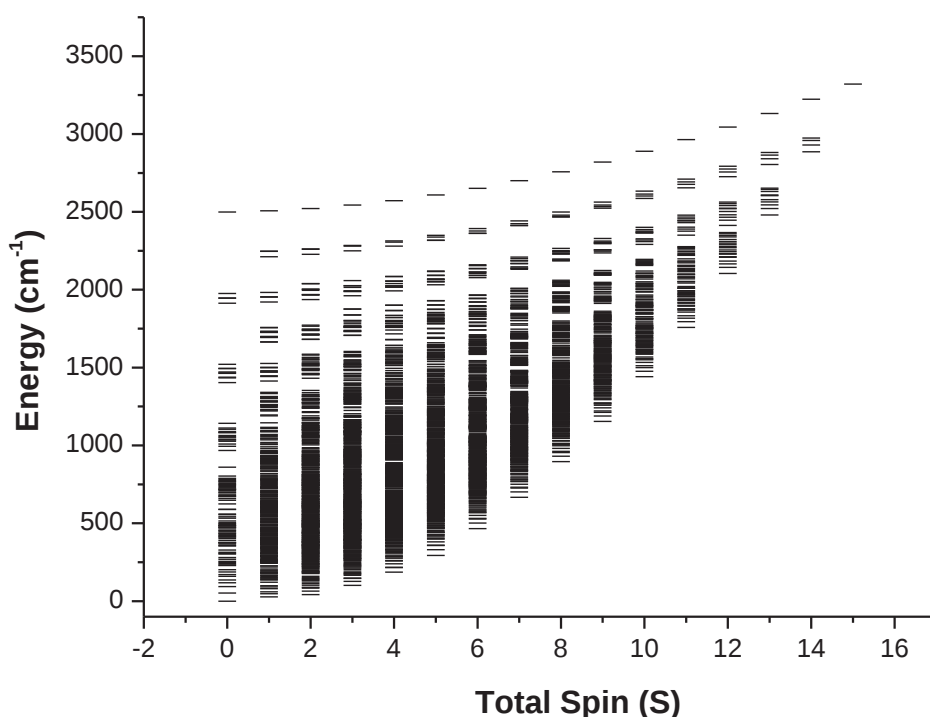


Figure 3.16: Plot of energy vs total spin for the complex $\text{C8} \cdot 7\text{H}_2\text{O} \cdot \text{Py}$.

$$\begin{aligned} \hat{H} = & -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_4 \cdot \hat{S}_6 + \hat{S}_5 \cdot \hat{S}_6) \\ & - 2J_2(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_1 \cdot \hat{S}_6 + \hat{S}_2 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_5 + \hat{S}_3 \cdot \hat{S}_5 + \hat{S}_3 \cdot \hat{S}_6) \\ & + \sum_{i=1-6} \{ \mu_B g \vec{B} \cdot \hat{S}_i \} \end{aligned}$$

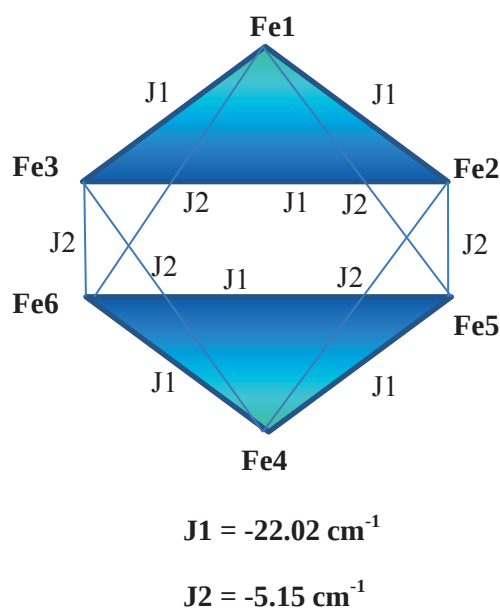


Figure 3.17: Schematic J model for the complex **C8**·7H₂O·Py.

3.3.3 Complex [Fe₇O₂(OH)₆(L5-2H)₃(Py)₆](BF₄)₄(PF₆)(H₂O)₇(Py)₃ **C4**·7H₂O·3Py

The reaction of ligand **L5** with Fe(BF₄)₂·6H₂O in a molar ratio of 1 : 2 in a MeOH/pyridine solution, followed by crystallisation, forms dark red rhombic shaped crystals of the formulation [Fe₇O₂(L5-2H)₃(OH)₆(Py)₆](BF₄)₄PF₆(H₂O)₇(Py)₃ **C4**·7H₂O·3Py. The complex contains seven Fe-atoms coordinated to three ligands and six pyridine molecules, held together with oxo/hydroxo groups. Also contained within the lattice are seven water molecules, three pyridine molecules, four BF₄⁻ ions and a PF₆⁻ ion.

The complex **C4** crystallises in the $P\bar{1}$ space group. The asymmetric unit contains the full complex and there are two molecules in the unit cell. The ligand on **C4** is present as the zwitterion **L5-2H** in which oximic oxygen atoms and phenolate oxygen atoms are deprotonated and the amine nitrogen atoms are protonated. This complex contains two parallel [Fe^{III}₃(μ₃-O)]⁷⁺, triangles which are connected centrally through a [Fe(OH)₆]³⁻ moiety (Fe_{triangle}-OH-Fe_{central} = 131.8(3) – 135.1(3)°) and by three straps between the oxime “heads” of the **L5** molecules (see Figure 3.18). The arrangement allows the Fe atoms of the complex to be antiprismatic with the two planes of [Fe^{III}₃(μ₃-O)]⁷⁺, which

sit parallel to each other. The distance between the complementary Fe(III) ions between the two triangles varies between 6.345(2) and 6.358(3) Å (see Table 3.18 for important distances and Table 3.19 for important bond angles). The central Fe atom, Fe7, situated between the Fe atoms on the upper triangle and lower triangle of the complex has a distorted octahedral symmetry created by a donor set comprised of six oxygen atoms of OH⁻ groups bridging between the two metal triangle planes. Each Fe atom contained within the triangles is coordinated by a phenolate oxygen atom, an oximic nitrogen atom from one ligand and an oximic nitrogen atom from an adjacent ligand together with a hydroxo group, a pyridine molecule, and the complementary central oxygen atom within the triangles. The central oxygen atoms O7 and O8 on **C4** are displaced out of the complementary metal planes by 0.335(5) Å and 0.254(4) Å respectively pointing away from the centre of the molecule. Hence the pyridine molecules coordinated to Fe atoms of the two units do not exactly sit vertically and tilt away from each other (Figure 3.19). The atomic sequence of the oximic bridges on the upper triangle of this iron complex with linked salicylaldoximes is clockwise, Fe-N-O-Fe whereas it is anti-clockwise, Fe-O-N-Fe, on the lower triangle (see Figure 3.18).

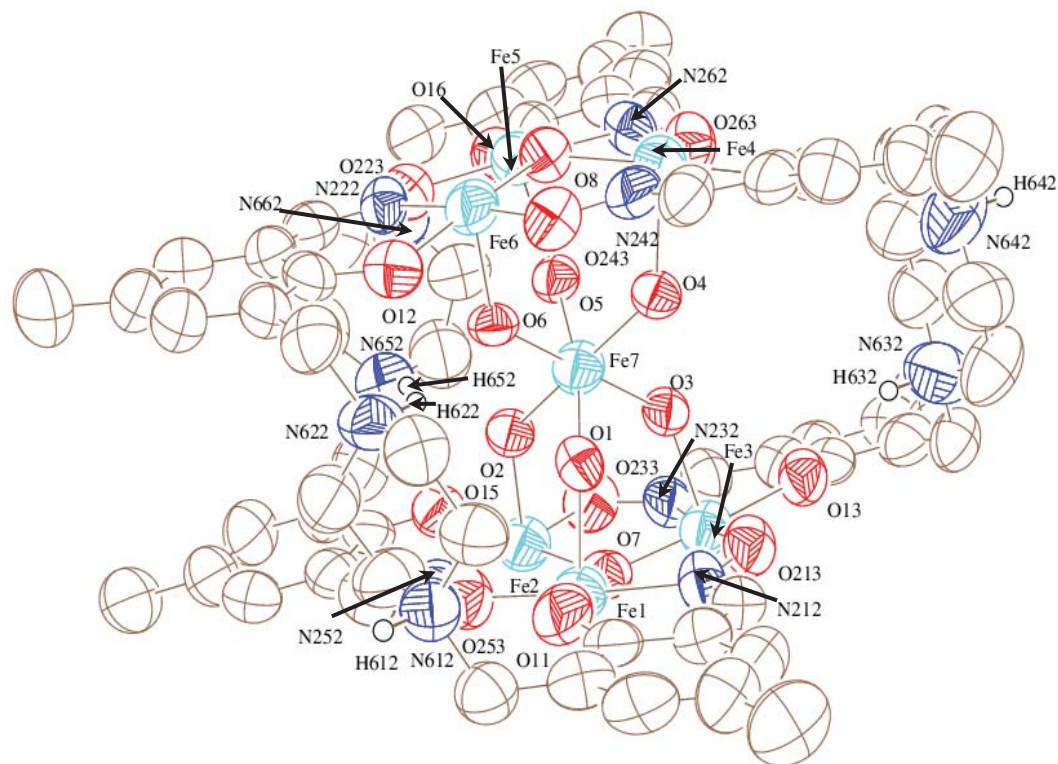


Figure 3.18: Crystal structure of the cation of the complex **C4** [Fe₇O₂(OH)₆(**L5-2H**)₃]⁵⁺ (Fe-cyan, N-blue, O-red, C-brown, all the H atoms except the ones bound to tertiary nitrogen atoms and all the axial pyridine molecules are omitted for clarity); ORTEP view at 50% probability level.

Table 3.18: Selected bond lengths around the metal centres of the complex **C4·7H₂O·3Py**.

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Fe1-O1	2.054(6)	Fe2-O2	2.050(6)	Fe3-O3	2.050(5)
Fe1-O7	1.921(7)	Fe2-O7	1.937(6)	Fe3-O7	1.935(8)
Fe1-O11	1.939(7)	Fe2-O15	1.950(7)	Fe3-O13	1.963(8)
Fe1-O253	1.943(9)	Fe2-O233	1.946(9)	Fe3-O213	1.947(6)
Fe1-N212	2.087(10)	Fe2-N252	2.118(11)	Fe3-N232	2.123(9)
Fe4-O4	2.060(6)	Fe5-O5	2.064(6)	Fe6-O6	2.051(5)
Fe4-O8	1.950(6)	Fe5-O8	1.919(5)	Fe6-O8	1.937(7)
Fe4-O14	1.946(7)	Fe5-O16	1.958(6)	Fe6-O12	1.923(9)
Fe4-O263	1.917(8)	Fe5-O223	1.973(8)	Fe6-O243	1.936(7)
Fe4-N242	2.110(10)	Fe5-N262	2.095(11)	Fe6-N222	2.104(8)
Fe7-O1	1.966(6)	Fe7-O4	1.956(7)	Fe2-Fe5	6.358(3)
Fe7-O2	1.960(7)	Fe7-O5	1.926(7)	Fe3-Fe4	6.356(2)
Fe7-O3	1.914(6)	Fe7-O6	1.942(6)	Fe1-Fe6	6.345(2)
				O7-O8	6.946(9)

Table 3.19: Selected bond angles around the metal centres of the complex **C4·7H₂O·3Py**.

Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
O1-Fe1-O7	89.8(3)	O2-Fe2-O7	90.5(3)	O3-Fe3-O7	90.4(3)
O1-Fe1-O11	90.0(3)	O2-Fe2-O15	85.9(3)	O3-Fe3-O13	87.0(3)
O1-Fe1-O253	93.5(3)	O2-Fe2-O233	94.9(3)	O3-Fe3-O213	94.3(2)
O1-Fe1-N212	83.1(3)	O2-Fe2-N252	84.4(3)	O3-Fe3-N232	83.0(3)
O7-Fe1-O11	174.8(4)	O7-Fe2-O15	174.5(3)	O7-Fe3-O13	176.6(3)
O7-Fe1-O253	93.7(3)	O7-Fe2-O233	95.5(3)	O7-Fe3-O213	93.2(3)
O7-Fe1-N212	88.7(3)	O7-Fe2-N252	88.7(3)	O7-Fe3-N232	91.6(4)
O11-Fe1-O253	91.5(3)	O15-Fe2-O233	89.1(3)	O13-Fe3-O213	89.3(3)
O11-Fe1-N212	86.2(4)	O15-Fe2-N252	86.8(4)	O13-Fe3-N232	85.9(4)
O253-Fe1-N212	175.8(3)	O233-Fe2-N252	175.8(3)	O213-Fe3-N232	174.6(4)
O4-Fe4-O8	91.4(3)	O5-Fe5-O8	89.1(2)	O6-Fe6-O8	90.0(3)
O4-Fe4-O14	87.6(3)	O5-Fe5-O16	92.1(2)	O6-Fe6-O12	85.2(3)
O4-Fe4-O263	94.2(3)	O5-Fe5-O223	93.5(3)	O6-Fe6-O243	96.4(2)
O4-Fe4-N242	83.5(3)	O5-Fe5-N262	84.1(3)	O6-Fe6-N222	80.7(2)
O8-Fe4-O14	176.0(3)	O8-Fe5-O16	174.6(4)	O8-Fe6-O12	174.3(3)
O8-Fe4-O263	94.5(3)	O8-Fe5-O223	94.4(3)	O8-Fe6-O243	95.2(3)
O8-Fe4-N242	89.5(3)	O8-Fe5-N262	88.5(3)	O8-Fe6-N222	89.0(3)
O14-Fe4-O263	89.5(3)	O16-Fe5-O223	90.9(3)	O12-Fe6-O243	88.4(3)
O14-Fe4-N242	86.5(3)	O16-Fe5-N262	86.4(4)	O12-Fe6-N222	87.2(3)
O263-Fe4-N242	175.4(4)	O223-Fe5-N262	176.3(3)	O243-Fe6-N222	174.9(4)
O1-Fe7-O6	83.7(3)	O3-Fe7-O4	85.8(3)	O5-Fe7-O6	88.0(2)
O2-Fe7-O3	88.8(3)	O3-Fe7-O5	97.1(3)	O1-Fe7-O2	88.7(3)
O2-Fe7-O4	171.5(3)	O3-Fe7-O6	173.7(2)	O1-Fe7-O3	91.8(2)
O2-Fe7-O5	84.8(3)	O4-Fe7-O5	89.4(3)	O1-Fe7-O4	98.0(3)
O2-Fe7-O6	95.5(3)	O4-Fe7-O6	90.6(3)	O1-Fe7-O5	168.9(3)
Fe1-O1-Fe7	133.6(3)	Fe3-O1-Fe7	133.2(4)	Fe5-O1-Fe7	135.1(3)
Fe2-O1-Fe7	132.2(3)	Fe4-O1-Fe7	131.8(3)	Fe6-O1-Fe7	133.6(4)

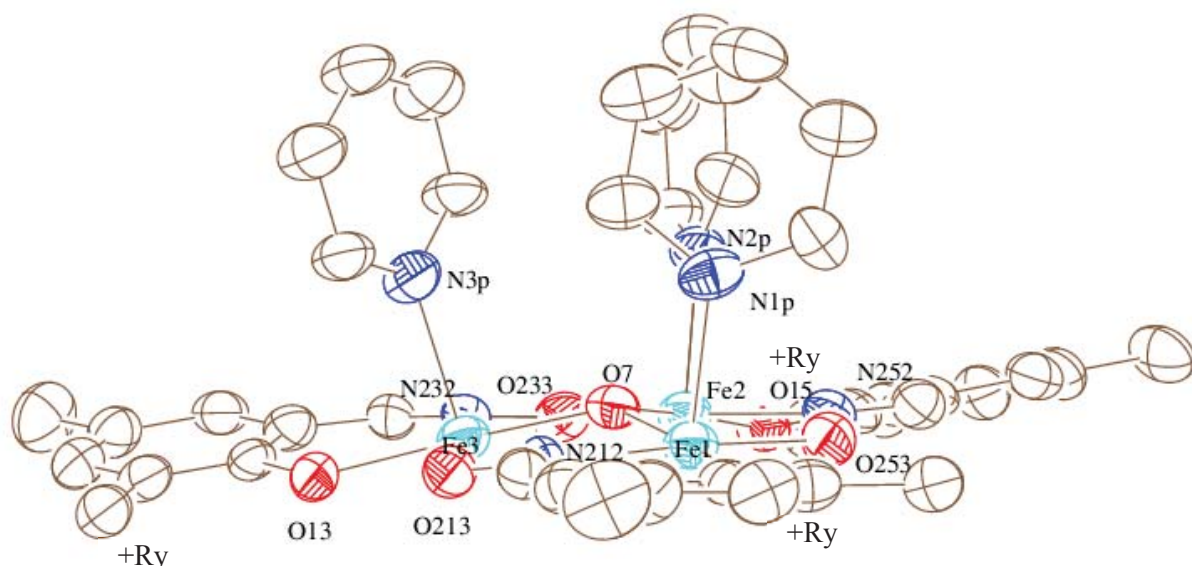


Figure 3.19: Partial structure of the complex **C4** that emphasises the displacement of the central oxygen atom O7 by 0.335(5) Å and the coordination by the pyridines (Ry = the rest of the ligand that connects to the second triangular unit, Fe-cyan, N-blue, O-red, C-brown, all the H are omitted for clarity); ORTEP view at 25% probability level.

The complex **C4** is supported by a number of internal hydrogen bonds within the structure. Some of the phenolate oxygen atoms form intramolecular hydrogen bonds with the hydrogen atoms on the amine nitrogen atoms (N622-H622 $\cdots$ O12). Some of the water molecules within the lattice form hydrogen bonds with the hydrogen atoms on the amine nitrogen atoms, oximic oxygen atoms, as well as oxygen atoms of the hydroxo- groups between the triangles. (see Figure 3.20 for the important hydrogen bonds and Table 3.20 for the distances).

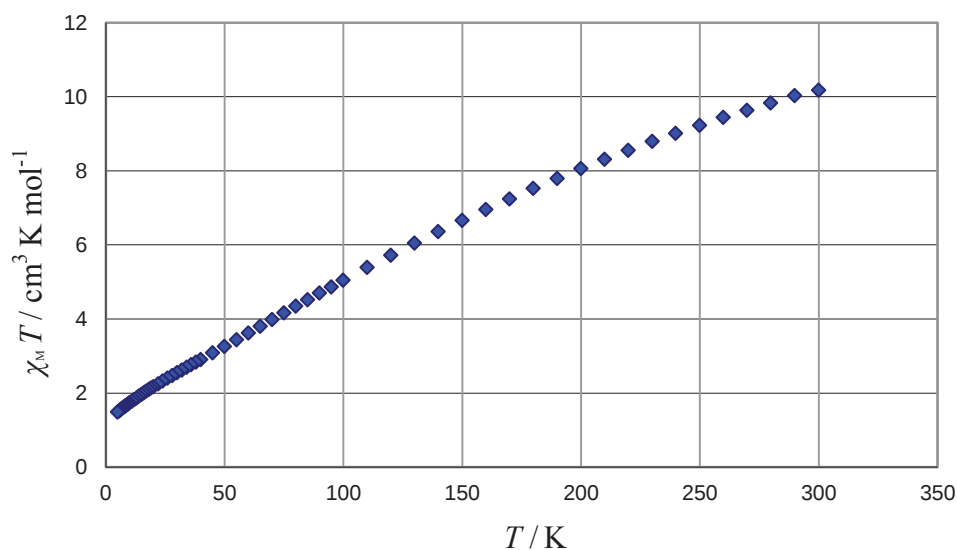
Crystallographically, the total anion count for the complex **C4** is 5 created with four fully occupied BF_4^- ions and one PF_6^- ion. The SQUEEZE procedure was used to treat the solvent region as implemented in Olex2.⁹ This resulted in 104 e^- per asymmetric unit which equates to 4 pyridine and 2 MeOH molecules per cell. According to the Mössbauer analysis of this complex, all the Fe atoms are in the oxidation state of 3+. Thus the charge balance agrees with the total anion charge being 5-. The CHN analysis of this complex is in agreement with this assessment. The CHN results for the complex agree with the addition of seven water molecules contained within the complex but also with the loss of non-coordinated pyridine.

Table 3.21: Charge balance analysis of the complex **C4**.

7 Fe ³⁺	2 O ²⁻	6 OH ⁻	3 (L5-2H)	4 BF ₄ ⁻	1 PF ₆ ⁻
7 x 3+	2 x 2-	6 x 1-	3 x 2-	4 x 1-	1 x 1-
21+	4-	6-	6-	4-	1-

3.3.3.1 Magnetic measurements of the complex, C4

The magnetic susceptibility measurements were performed on the complex **C4** over the temperature range of 5 – 300 K and the results were plotted as $\chi_M T$ against temperature (see Figure 3.21). The value of $\chi_M T$ continuously increases almost linearly from 1.49 cm³ K mol⁻¹ at 5 K to 10.18 cm³ K mol⁻¹ at 300 K. The calculated $\chi_M T$ value for seven non-interacting Fe³⁺ ions is 30.62 cm³ K mol⁻¹ with $g = 2.00$. Thus, the experimental $\chi_M T$ value at room temperature is considerably lower than the calculated value. This behaviour indicates the presence of strong antiferromagnetic interactions between the metal centres.

**Figure 3.21:** Plot of $\chi_M T$ product vs T for the complex **C4**.

Variable-temperature-variable-field dc magnetisation experiments were performed in the 2.0 - 7.0 K and 0.5 - 3 T temperature and magnetic field ranges respectively. The experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. μ_B/kT , with N being Avogadro's number and k_B the Boltzmann constant) in Figure 3.22. The data fitting was not done due to time constraints and lack of computational resources, as **C4**

is also a large iron cluster with seven Fe(III) ions. Thus, the values for S , D , or J were not determined.

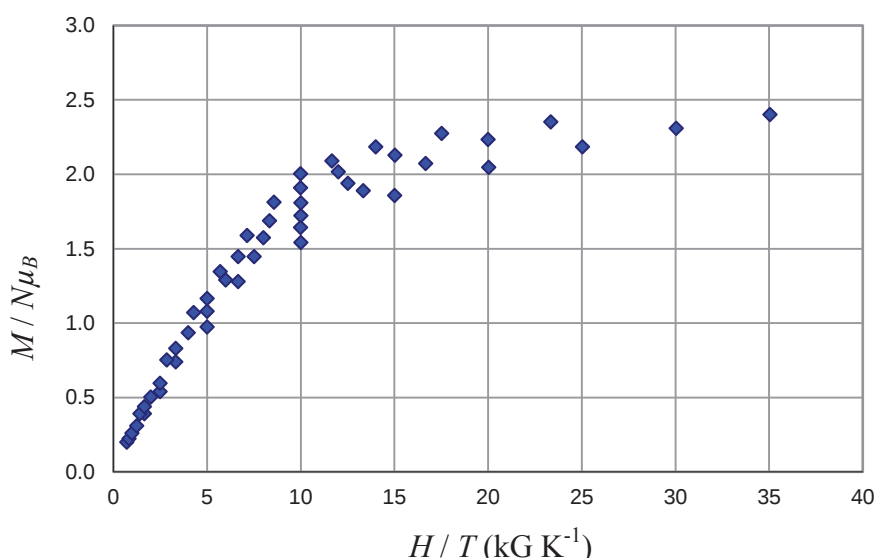


Figure 3.22: M vs. H / T plot for **C4**.

3.3.4 Complex $[\text{Fe}_7\text{O}_2(\text{L6-2H})_3(\text{OH})_6(\text{Py})_6](\text{PF}_6)_5(\text{H}_2\text{O})_2$, **C6**·5PF₆[−]·2H₂O

The reaction of ligand **L6** with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in a molar ratio of 1 : 2 in a MeOH/pyridine solution followed by crystallisation produces dark red rhombic shaped crystals of the complex, **C6**·2H₂O with the formulation, $[\text{Fe}_7\text{O}_2(\text{L6-2H})_3(\text{OH})_6(\text{Py})_6] 5\text{PF}_6 \cdot 2\text{H}_2\text{O}$ the crystals were solved and refined in the monoclinic space group $P 2_1/n$. The asymmetric unit contains half the molecule with the other half generated by inversion symmetry and there is one complex per unit cell (see Figure 3.20). This X-ray data collection was kindly performed by Heather Jameson at the Australian Synchrotron (for further details, see experimental section).

Similar to the complex **C4** (see 3.2.1.5), the complex **C6** is a heptairon complex with a similar coordination environment around the Fe(III) atoms. This pattern was also seen for the complex **C3** (see Chapter 2, 2.4.2). The seven Fe(III) ions are linked by three **L6** ligand molecules where all the phenolate and oximic oxygen atoms are deprotonated. The distances between the amine N-atoms and the phenolate O-atoms within the same ligands lie in the range of 2.611 Å - 2.696 Å. Therefore, these short distances suggest

that all of these amine N-atoms are likely to be protonated. Therefore, each ligand is present as **L6**-2H and all the Fe(III) ions lie in a slightly distorted octahedral geometry (see Figure 3.23).

Six of the Fe(III) ions form two triangles of the motif, $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ which are parallel to each other. The triangles are linked centrally through the presence of a $[\text{Fe}(\text{OH})_6]^{3-}$ moiety and peripherally by the three helically twisted phenolic oxime ligands, in which the arms of the molecule are positionally disordered equally over two sites. Each triangle consists of three Fe(III) ions, each of which is connected to a central oxygen atom. The central oxygen atoms (O4 and O4_a) are displaced out of the corresponding metal planes pointing away from the centre of the molecule by 0.326(4) Å, a value somewhat larger than seen in single-headed heptairon complex complex **C3**. The seventh Fe(III) ion is located between the triangles linked by six hydroxo groups each of which is connected to the Fe(III) ions within the triangles. Thus each of the Fe(III) ions within the triangles is coordinated by a phenolate oxygen atom and an oximic nitrogen atom from one ligand, an oximic oxygen atom from an adjacent ligand molecule, an oxygen atom from a hydroxo group, the central oxygen atom of the corresponding triangle, and a pyridine molecule. Due to the displacement of the central oxygen atoms, the axial pyridine molecules on the Fe(III) ions within the triangles are tilted away from each other. The atom sequence of the oximic bridges on both triangles of this iron complex with linked salicylaldoximes is anti-clockwise, Fe-O-N-Fe. The important bond lengths and bond angles around the metal centres are given in Tables 3.22 and 3.23 and the torsion angles observed about the Fe-O-N-Fe, varies in a very low range of 2.7 - 6.7° (see Table 3.24).

The complex **C6**·5PF₆⁻·2H₂O is stabilised by forming a number of hydrogen bonds between the adjacent phenolate oxygen atoms and hydrogen atoms on amine nitrogen atoms within the ligands (N612- H612···O11, D·····A distance 2.739(14) Å).

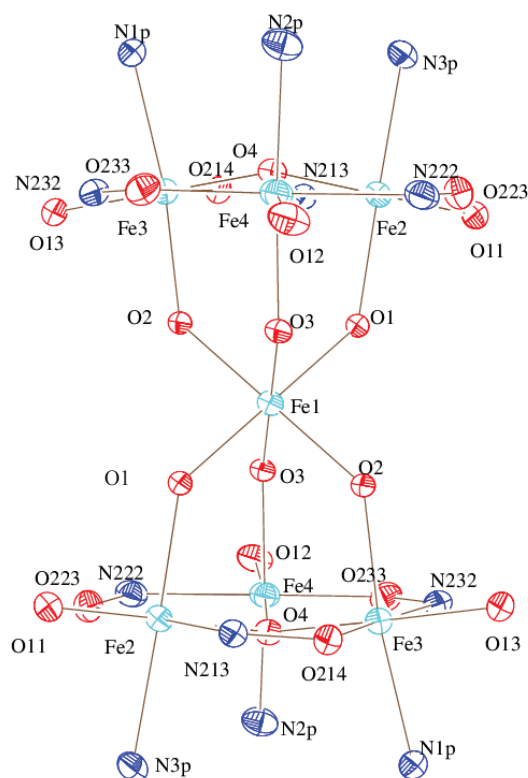


Figure 3.23: The metallic core of the complex **C6** (Fe-cyan, N-blue, O-red); ORTEP view at 10% probability level.

Table 3.22: Selected bond lengths around the metal centres of the complex **C6**·5PF₆⁻·2H₂O.

Atoms	Bond	Atoms	Bond length
Fe1-O1	1.968(3)	Fe3-O2	2.042(3)
Fe1-O2	1.968(3)	Fe3-O4	1.912(4)
Fe1-O3	1.956(3)	Fe3-O13	1.953(4)
Fe1-O1_a	1.968(3)	Fe3-N1P	2.206(5)
Fe1-O2_a	1.968(3)	Fe3-N232	2.141(5)
Fe1-O3_a	1.956(3)	Fe3-O214_a	1.933(4)
Fe2-O1	2.050(4)	Fe4-O3	2.039(3)
Fe2-O4_a	1.931(4)	Fe4-O4	1.924(4)
Fe2-O11	1.967(4)	Fe4-O12	1.951(5)
Fe2-N3P	2.230(6)	Fe4-N2P	2.190(7)
Fe2-N213	2.129(5)	Fe4-N222	2.112(7)
Fe2-O223_a	1.948(5)	Fe4-O233	1.940(5)

Table 3.23: Selected bond angles around the metal centres of the complex $\text{C6} \cdot 5\text{PF}_6^- \cdot 2\text{H}_2\text{O}$.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O1-Fe1-O2	91.82(14)	O2-Fe3-O13	88.69(17)
O1-Fe1-O3	91.68(14)	O2-Fe3-N1P	173.07(16)
O1-Fe1-O1 _a	180.00	O2-Fe3-N232	87.64(17)
O1-Fe1-O2 _a	88.18(14)	O2-Fe3-O214 _a	93.15(14)
O1-Fe1-O3 _a	88.32(14)	O2-Fe3-O4	90.61(15)
O2-Fe1-O3	88.99(14)	O13-Fe3-N1P	85.17(19)
O1 _a -Fe1-O2	88.18(14)	O13-Fe3-N232	86.63(18)
O2-Fe1-O2 _a	180.00	O4-Fe3-O13	175.04(16)
O2-Fe1-O3 _a	91.01(14)	O13-Fe3-O214 _a	90.30(16)
O1 _a -Fe1-O3	88.32(14)	N1P-Fe3-N232	88.79(19)
O2 _a -Fe1-O3	91.01(14)	O4-Fe3-N1P	95.23(17)
O3-Fe1-O3 _a	180.00	O214 _a -Fe3-N1P	90.10(17)
O1 _a -Fe1-O2 _a	91.82(14)	O4-Fe3-N232	88.44(18)
O1 _a -Fe1-O3 _a	91.68(14)	O214 _a -Fe3-N232	176.81(18)
O2 _a -Fe1-O3 _a	88.99(14)	O4-Fe3-O214 _a	94.64(16)
O1-Fe2-O11	89.36(18)	O3-Fe4-O12	88.28(18)
O1-Fe2-N3P	173.78(19)	O3-Fe4-N2P	174.0(2)
O1-Fe2-N213	87.07(17)	O3-Fe4-N222	88.36(18)
O1-Fe2-O4 _a	91.08(14)	O3-Fe4-O233	93.51(18)
O1-Fe2-O223 _a	93.34(19)	O3-Fe4-O4	90.99(15)
O11-Fe2-N3P	86.1(2)	O12-Fe4-N2P	86.3(2)
O11-Fe2-N213	86.1(2)	O12-Fe4-N222	85.8(2)
O4 _a -Fe2-O11	175.2(2)	O4-Fe4-O12	176.8(2)
O11-Fe2-O223 _a	89.8(2)	O12-Fe4-O233	89.3(2)
N3P-Fe2-N213	88.4(2)	N2P-Fe4-N222	88.7(2)
O4 _a -Fe2-N3P	93.11(17)	O4-Fe4-N2P	94.3(2)
O223 _a -Fe2-N3P	90.9(2)	O233-Fe4-N2P	89.0(3)
O4 _a -Fe2-N213	89.17(16)	O4-Fe4-N222	91.0(2)
O223 _a -Fe2-N213	175.8(2)	O233-Fe4-N222	174.8(2)
O4 _a -Fe2-O223 _a	95.01(19)	O4-Fe4-O233	93.9(2)

Table 3.24: Selected torsion angles of the complex $\text{C6} \cdot 5\text{PF}_6^- \cdot 2\text{H}_2\text{O}$.

Atoms	Torsion angle (°)
Fe4-O233-N232-Fe3	4.5(5)
Fe3-O214-N213-Fe2	6.7(5)
Fe2-O223-N222-Fe4	2.7(6)

The PF_6^- ions could not be located in the crystal structure, but CHN microanalytical data (repeated twice, Table 3.25) were best fit with 5 PF_6^- ions, as well as several water molecules. The structure was subjected to the SQUEEZE procedure, as implemented in OLEX2, indicating a total of 95 electrons per unit cell, and a void volume of 928 Å³. The void volume is consistent with the formulation, but the electron count is very low

due to elimination of low-resolution data (cutoff 7.5 Å resolution) in least-squares refinements.

Table 3.25: CHN results for the complex **C6**·5PF₆.

Batch No.	C (%)	H (%)	N (%)
1	42.84	4.24	7.92
2	42.87	4.22	7.88

The CHN results obtained for the vacuum-dried complex **C6**·5PF₆ is consistent with the presence of five PF₆[−] ions no water molecules. It is obvious that all the Fe atoms are in the 3+ oxidation state by Mössbauer analyses and VT magnetic measurements. The central O-atoms (μ₃-O) are oxo groups which were confirmed by the Mössbauer (discussed in section 3.5), IR analysis as [Fe₃-μO]⁷⁺ units in the complexes allow a strong absorption at 480 cm^{−1} (see section 2.4 in Chapter 2, Chapter 4 and Appendix for more information). Therefore, the anion count (5PF₆[−]) is in agreement with both the CHN and charge balance analyses (see Table 3.26 for charge balance analysis).

Table 3.26: Charge balance analysis of the complex **C6**·5PF₆[−].

7 Fe ³⁺	2 O ^{2−}	6 OH [−]	3 (L6 -2H)	5 PF ₆ [−]
7 x 3+	2 x 2−	6 x 1−	3 x 2−	5 x 1−
21+	4−	6−	6−	5−

3.3.4.1 Magnetic measurements of the complex **C6**

The solid-state dc magnetic susceptibility measurements were performed on the complex **C6** in the 2 - 300 K temperature range in the applied magnetic field of 0.1 T and the results were plotted as temperature dependence versus of $\chi_M T$. The value of $\chi_M T$ from 2.146 cm³ K mol^{−1} at 2 K to an approximate value of 3.228 cm³ K mol^{−1} at 15 K and then increases slowly and constantly in a linear fashion to a value of 11.817 cm³ K mol^{−1} at 300 K (see Figure 3.24).

The calculated $\chi_M T$ value for seven non-interacting Fe³⁺ ions is 30.62 cm³ K mol^{−1} with $g = 2.0$. Thus the experimental $\chi_M T$ value at room temperature is considerably lower

than the calculated value. This behaviour indicates the presence of strong antiferromagnetic interactions between the metal centres.

In order to determine the uniaxial anisotropy parameter for the Fe^{3+} centres, variable-temperature-variable-field dc magnetisation experiments were performed in the ranges of 2.0 - 7.0 K and 0.5 T - 3 T for temperature and magnetic field respectively. These experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. $\mu_B/k_B T$, with N being Avogadro's number and k_B the Boltzmann constant) in Figure 3.25.

Due to time constraints and lack of computational resources, the fitting of neither magnetisation nor magnetic susceptibility measurements was performed on the large heptairon clusters. Thus, the values for J or uniaxial anisotropy could not be determined.

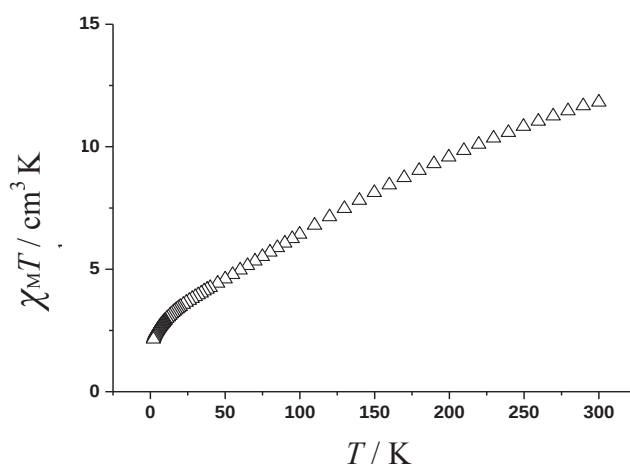


Figure 3.24: Plot of $\chi_M T$ product vs T for the complex $\text{C6} \cdot 5\text{PF}_2^-$.

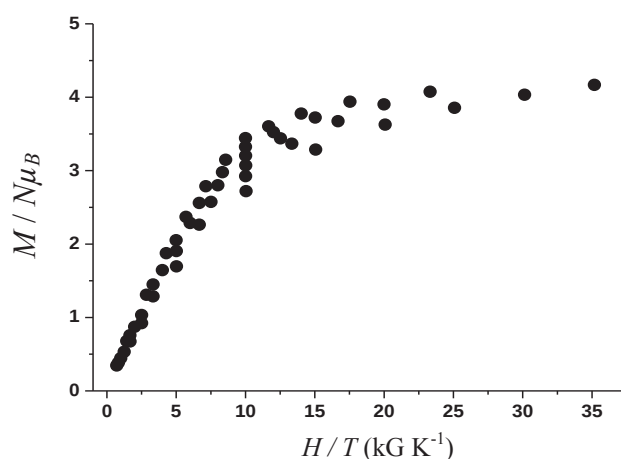


Figure 3.25: M vs. H/T plot for $\text{C6} \cdot 5\text{PF}_6^-$.

3.3.5 Complex $[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{L10-2H})_3(\text{Py})_6](\text{BF}_4)_3(\text{PF}_6)_2(\text{H}_2\text{O})_3(\text{Py})_2$ $\text{C9}\cdot 3\text{BF}_4\cdot 2\text{PF}_6\cdot 3\text{H}_2\text{O}\cdot 2\text{Py}$

The reaction of ligand **L10** with $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ in a molar ratio of 1 : 2 in a MeOH/pyridine solution followed by crystallisation, produces dark red rhombic shaped crystals of the complex $\text{C9}\cdot 3\text{BF}_4\cdot 3\text{H}_2\text{O}\cdot 2\text{Py}$ with formula $[\text{Fe}_7\text{O}_2(\text{L10-2H})_3(\text{OH})_6(\text{Py})_6]\cdot 3\text{BF}_4\cdot 2\text{PF}_6\cdot 3\text{H}_2\text{O}\cdot 2\text{Py}$. The structural data were kindly collected by Jason Price at the Australian synchrotron (for further details, see experimental section). The structure was solved and refined in the monoclinic space group, $P2_1/n$. The asymmetric unit contains the full molecular cation with three BF_4^- ions, three water molecules, and two pyridine molecules present within the lattice. The complex is a heptairon molecule linked with three ligands all of which are present as **L10-2H** where all the phenolate and the oximic oxygen atoms are deprotonated and all the amine nitrogen atoms are protonated. The metallic skeleton of the complex can be described as a $[\text{Fe}^{\text{III}}_3]_2$ trigonal prism containing two $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ triangles, linked by the $[\text{Fe}(\text{OH})_6]^{3-}$ anion which is located between the metal triangle planes. The rotation of the top triangle with respect to the bottom triangle is 64.3° . The three ligands are helically twisted around the core.

All the Fe(III) ions lie in a slightly distorted octahedral geometry (see Table 3.27 and 3.28 for bond lengths and angles around the metal centres). Each of the metal centres within the triangles is coordinated by an oximic nitrogen atom and a phenolate oxygen atom from one ligand, an oximic oxygen atom from a neighbouring ligand, the central oxo group within the triangle, a hydroxo group, and a terminal pyridine molecule. The Fe(III) of the $[\text{Fe}(\text{OH})_6]^{3-}$ moiety between the triangles is bridged by six hydroxo-groups which link to the two triangles on either side of it. These triangles are located exactly parallel to each other (the angle between the triangles is 1°). Both in the upper and lower triangles, the atoms bridging across each edge follows the clockwise sequence Fe-O-N-Fe. Additionally, the central oxygen atoms ($\mu_3\text{-OH}$) are displaced outwardly from the metal planes pointing away from the complex centre by $0.321(6)$ Å (O8) and $0.369(6)$ Å (O1), values very similar to those for complex **C6**. Each protonated nitrogen atom in the ligand strap is hydrogen bonded to either a water molecule of crystallisation or a phenolate O-atom in its close proximity (see Figure 3.26 for important H-bonds and Table 3.29 for H- bond distances).

Table 3.27: Selected bond lengths around the metal centres of the complex $\text{C9}\cdot 3\text{BF}_4\cdot 3\text{H}_2\text{O}\cdot 2\text{Py}$.

Atoms	Bond length (Å)	Atoms	Bond length (Å)	Atoms	Bond length (Å)
Fe2-N6P	2.216(5)	Fe4-N5P	2.219(5)	Fe6-N3P	2.204(5)
Fe2-O1	1.911(4)	Fe4-O1	1.938(4)	Fe6-O8	1.917(4)
Fe2-O4	2.053(4)	Fe4-O3	2.058(4)	Fe6-O5	2.034(4)
Fe2-O11	1.953(4)	Fe4-O15	1.950(5)	Fe6-O14	1.911(5)
Fe2-O233	1.923(4)	Fe4-O213	1.967(4)	Fe6-O263	1.993(4)
Fe2-N212	2.155(5)	Fe4-N252	2.132(5)	Fe6-N242	2.105(5)
Fe3-N4P	2.195(5)	Fe5-N1P	2.180(5)	Fe7-N2P	2.205(5)
Fe3-O1	1.956(4)	Fe5-O8	1.926(4)	Fe7-O8	1.934(5)
Fe3-O2	2.042(4)	Fe5-O6	2.010(5)	Fe7-O7	2.025(4)
Fe3-O13	1.897(4)	Fe5-O12	1.945(4)	Fe7-O16	1.972(4)
Fe3-O253	1.952(5)	Fe5-O243	1.958(4)	Fe7-O223	1.963(4)
Fe3-N232	2.126(5)	Fe5-N222	2.128(5)	Fe7-N262	2.134(5)
Fe1-O2	1.929(4)				
Fe1-O3	1.931(4)				
Fe1-O4	1.931(4)				
Fe1-O5	1.928(4)				
Fe1-O6	1.941(4)				
Fe1-O7	1.921(4)				

Table 3.28: Selected bond angles around the metal centres of the complex $\text{C9}\cdot 3\text{BF}_4\cdot 3\text{H}_2\text{O}\cdot 2\text{Py}$.

Atoms	Bond angle (°)	Atoms	Bond angle	Atoms	Bond angle (°)
O11-Fe2-N212	84.85(19)	O13-Fe3-N232	87.32(17)	O15-Fe4-N252	84.8(2)
O1-Fe2-O4	89.99(16)	O1-Fe3-O2	90.49(17)	O1-Fe4-O3	89.29(16)
O1-Fe2-O11	171.7(2)	O1-Fe3-O13	173.52(16)	O1-Fe4-O15	171.7(2)
O1-Fe2-O233	95.32(17)	O1-Fe3-O253	94.82(17)	O1-Fe4-O213	93.05(18)
O1-Fe2-N6P	95.02(18)	O1-Fe3-N4P	93.58(18)	O1-Fe4-N5P	97.16(18)
O1-Fe2-N212	87.80(19)	O1-Fe3-N232	87.32(17)	O1-Fe4-N252	88.84(18)
O4-Fe2-O11	86.13(15)	O2-Fe3-O13	85.98(17)	O3-Fe4-O15	85.29(19)
O4-Fe2-O233	95.33(17)	O2-Fe3-O253	94.28(18)	O3-Fe4-O213	96.22(18)
O4-Fe2-N6P	172.34(19)	O2-Fe3-N4P	175.53(19)	O3-Fe4-N5P	171.71(18)
O4-Fe2-N212	89.70(19)	O2-Fe3-N232	91.02(17)	O3-Fe4-N252	88.83(18)
O11-Fe2-O233	92.35(17)	O13-Fe3-O253	90.86(17)	O15-Fe4-O213	93.8(2)
O11-Fe2-N6P	88.14(18)	O13-Fe3-N4P	89.80(19)	O15-Fe4-N5P	87.7(2)
O233-Fe2-N6P	89.98(18)	O253-Fe3-N4P	87.24(19)	O213-Fe4-N5P	88.7(2)
O233-Fe2-N212	174.08(19)	O253-Fe3-	174.3(2)	O213-Fe4-N252	174.6(2)
N6P-Fe2-N212	84.7(2)	N4P-Fe3-N232	87.32(19)	N5P-Fe4-N252	86.1(2)
O12-Fe5-N222	85.7(2)	O14-Fe6-N242	87.6(2)	O16-Fe7-N262	85.30(16)
O8-Fe5-O6	92.00(18)	O8-Fe6-O5	91.39(18)	O8-Fe7-O7	91.24(17)
O8-Fe5-O12	174.28(18)	O5-Fe6-O14	89.94(16)	O7-Fe7-O16	89.07(16)

O8-Fe5-O243	95.08(19)	O8-Fe6-O263	89.2(2)	O8-Fe7-O223	96.64(18)
O8-Fe5-N1P	92.1(2)	O8-Fe6-N3P	93.1(2)	O8-Fe7-N2P	94.05(19)
O8-Fe5-N222	89.0(2)	O8-Fe6-N242	89.2(2)	O8-Fe7-N262	89.72(17)
O6-Fe5-O12	89.82(18)	O5-Fe6-O14	89.94(16)	O7-Fe7-O16	89.07(16)
O6-Fe5-O243	91.46(19)	O5-Fe6-O263	92.86(17)	O7-Fe7-O223	92.28(16)
O6-Fe5-N1P	174.38(19)	O5-Fe6-N3P	173.61(19)	O7-Fe7-N2P	173.44(18)
O6-Fe5-N222	86.4(2)	O5-Fe6-N242	84.68(19)	O7-Fe7-N262	87.01(17)
O12-Fe5-N1P	85.70(19)	O14-Fe6-N3P	85.34(19)	O16-Fe7-N2P	85.32(18)
O12-Fe5-O243	90.30(19)	O14-Fe6-O263	88.85(17)	O16-Fe7-O223	88.34(16)
O243-Fe5-N1P	91.96(19)	O263-Fe6-N3P	91.36(18)	O223-Fe7-N2P	90.96(18)
O243-Fe5-N222	175.47(19)	O263-Fe6-	175.66(19)	O223-Fe7-N262	173.61(17)
N1P-Fe5-N222	89.9(2)	N3P-Fe6-N242	90.8(2)	N2P-Fe7-N262	89.14(19)
O3-Fe1-O4	89.77(16)	O5-Fe1-O7	89.88(17)	Fe1-O5-Fe6	134.0(2)
O3-Fe1-O5	88.57(16)	O6-Fe1-O7	89.33(17)	Fe1-O6-Fe5	133.8(2)
O3-Fe1-O6	177.51(19)	Fe2-O1-Fe3	116.5(2)	Fe1-O7-Fe7	134.6(2)
O3-Fe1-O7	92.37(17)	Fe2-O1-Fe4	119.4(2)	Fe5-O8-Fe7	116.3(2)
O4-Fe1-O5	178.34(16)	Fe3-O1-Fe4	116.08(18)	Fe6-O8-Fe7	116.9(2)
O4-Fe1-O6	92.06(19)	Fe1-O2-Fe3	134.6(2)	Fe5-O8-Fe6	116.3(2)
O4-Fe1-O7	90.20(18)	Fe1-O3-Fe4	135.7(2)		
O5-Fe1-O6	89.61(19)	Fe1-O4-Fe2	135.2(2)		

Table 3.29: Important H-bond distances within the complex $\text{C9} \cdot 3\text{BF}_4 \cdot 3\text{H}_2\text{O} \cdot 2\text{Py}$.

Atoms (D·····A)	Distance (Å)
N622- H622···O12	2.759(7)
N612 ···O3W ^a	2.838(9)
N632 ···O1W ^a	2.888(8)
N632- H632···O13	3.070(6)
N642- H642···O14	2.730(9)
N652 ···O2W ^a	2.862(8)

^a These amine groups are only partly protonated, so the proton for the hydrogen bond may be supplied by the water.

Table 3.30: Charge balance analysis of the complex $\text{C9} \cdot 3\text{BF}_4^- \cdot 2\text{PF}_6^-$.

7 Fe ³⁺	3 (L10-2H)	2 O ²⁻	6 OH ⁻	3 BF ₄ ⁻	2 PF ₆ ⁻
7 x 3+	3 x 2-	2 x 2-	6 x 1-	3 x 1-	2 x 1-
21+	6-	4-	6-	3-	2-

The oxidation state of all the metal centres was found to be 3+ by Mossbauer analyses. The central O-atoms are oxo groups (further discussed in Chapter 4) and all the amine

3.3.5.1 Magnetic measurements of the complex **C9**

The magnetic susceptibility measurements for the complex **C9** were carried out in the temperature range of 4.5 – 300 K in an applied magnetic field of 0.1 T. The results were plotted as temperature dependence versus $\chi_M T$ product. The value of $\chi_M T$ continuously increases from 2.40 cm³ K mol⁻¹ at 4.5 K to 12.53 cm³ K mol⁻¹ at 300 K in a constant linear fashion (see Figure 3.27). The theoretical value of $\chi_M T$ at room temperature for non-interacting seven Fe³⁺ ions is 30.62 cm³ K mol⁻¹ with $g = 2.0$. The considerably lower value of 12.53 cm³ K mol⁻¹ at room temperature indicates the presence of dominant antiferromagnetic interactions between the iron centres.

Variable-temperature, variable-field dc magnetisation experiments were performed over a temperature range of 2.0 - 7.0 K and a magnetic field range of 0.5 T – 3 T. These experimental data are presented as reduced magnetisation ($M/N\mu_B$ vs. $\mu_B/k_B T$, with N being Avogadro's number and k_B the Boltzmann constant) in Figure 3.28. Again, due to the time constraints and lack of computational resources, the fitting of data could not be performed on this complex, as this is a large heptairon cluster. Therefore, the values for J , S , and uniaxial parameter (D) have not been calculated for this complex.

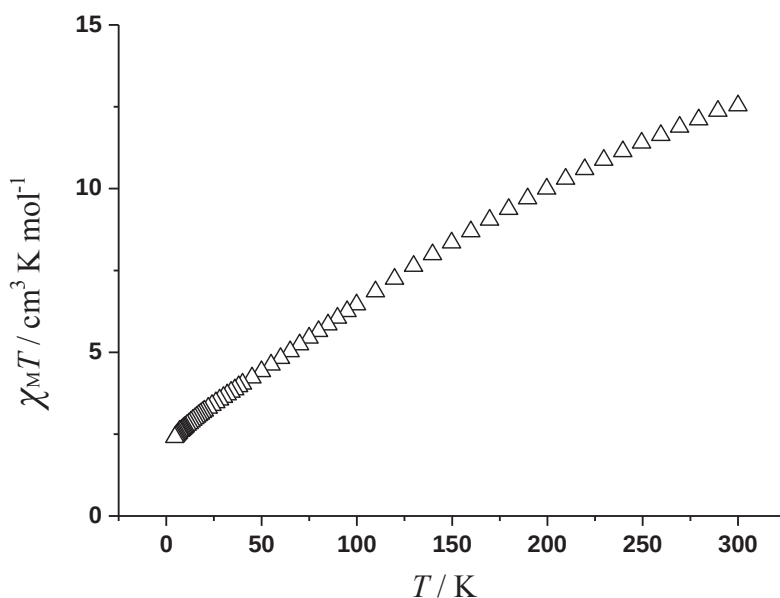


Figure 3.27: Plot of $\chi_M T$ product vs T for the complex **C9**·3BF₄·2PF₆·3H₂O.

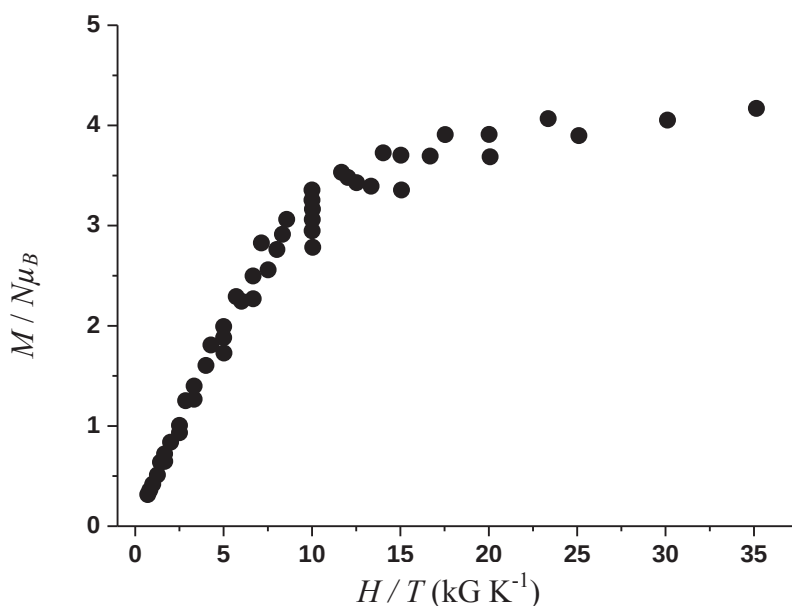


Figure 3.28: M vs. H / T plot for $\text{C9} \cdot 3\text{BF}_4 \cdot 2\text{PF}_6 \cdot 3\text{H}_2\text{O}$.

3.4 Results and discussion of the crystal structures

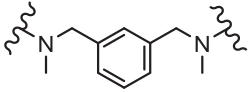
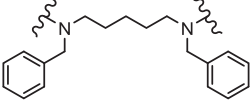
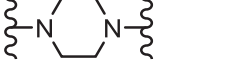
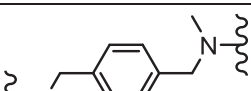
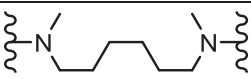
A clear relationship between the nuclearity of metal clusters and the flexibility of the amine straps utilised in the double-headed oximes cannot be distinguished. The degree of flexibility of the double-headed oximes can vary depending on the amine strap in the oxime ligand. The ligand **L5** contains a piperazine linker which has just two carbon atoms between the amine nitrogen atoms and this has resulted in the formation of a heptanuclear complex with the iron salt and a trinuclear complex with the copper salt. This ligand is expected to be less flexible than the longer carbon chains contained within the ligands **L7** and **L10** with five and six carbon amine straps respectively. Both **L5** and **L10** resulted in heptairon complexes despite the differences in the length and/or the flexibility of the amine straps of the ligands. In 2009, Plieger *et al.* published an analogous hexacopper complex using a slight modification of the ligand **L10**. Essentially, the methyl group was replaced with a *tert*-butyl group at the R1 position.¹ This complex also contained a pair of metal triangles $\text{Cu}^{\text{II}}_3(\mu_3\text{-O})^{4+}$, similar to that found in Mn(III) and Fe(III) complexes.^{2,5,12} In 2012, Brechin and his coworkers produced an analogous hexamanganese complex as well as a heptairon complex using the same ligand (**L**).² They produced a hexairon complex using a longer amine strap containing an eight carbon aliphatic chain, **L'** (again with a *tert*-butyl group at the R1

position, see Figure 3.1(a)). Thus, they reported that when the flexibility of the ligand increased, nuclearity of the resulting metal cluster decreased. This was attributed to the space reduction in between the two metal-containing triangles due to an ability of the ligand to bring the metal triangles close to each other, which led to a restriction in the complexes ability to accommodate an extra metal ion between the metal triangles.² The ligand **L10** has resulted in metal clusters of different nuclearity depending upon the metal ion used (eg: Cu₆, Mn₆, Fe₇).¹⁻² Use of the ligand **L7** resulted in a hexairon complex with the same moiety. The ligand **L6** incorporated a 1,4-xylyl linker in the amino strap while it was also six carbons long it resulted in the ligand being more rigid than **L10** and **L5**.¹³ It is clear that the nuclearity of the resulting complexes is more a function of the reaction conditions to make/crystallise them than the ligand used.

Almost all the hexanuclear clusters currently published are reported to contain a H-bond between the central oxygen atoms, (μ_3 -O) present within the metal triangles.¹⁻² It was suggested the presence of a shared proton between the central oxygen atoms of the two triangles because the distance between those atoms was short at 2.526 Å. It was observed that the analogous distances of the complex **C2** are 2.730(11) Å (O11-O11) and 2.628(8) Å (O55-O55) in the two independent units and 2.453(9) Å in the complex **C8**, which is also suggestive of a hydrogen bond between the central oxygen atoms.¹⁻² Further evidence can be seen as the O-atoms (μ_3 -O) are displaced towards each other.² This short distance between the μ_3 -O $\cdots\mu_3$ -O atoms brings the Fe atoms from each triangle close enough together that additional μ_2 -OH bridges have been established between each plane.

Complexation of the ligand, **L9** resulted in a triiron complex which is supported by a metaborate ion (BO₂⁻) and two extra hydroxyl ions from water (see Table 3.32). All the heptairon complexes, **C4**, **C6**, and **C9** follow the same coordination pattern of the iron centres observed in the heptairon cluster by Brechin *et al.*² They all carry six axial pyridines on each iron centre within the [Fe^{III}₃] triangles and the seventh iron centre is located between the triangles coordinated by a donor set comprised of six hydroxo groups.

Table 3.32: Iron clusters of double-headed salicylaldoxime derivatives.

Crystal Structure	Core	Nuclearity	Strap
[Fe ₃ BO ₂ (L9 -2H) ₂ (OH) ₂ (Py) ₂] (BF ₄) ₂ (H ₂ O) ₂ (MeOH)(Py) C10 ·2H ₂ O·MeOH·Py	[(Fe-μ ₃ -O)] ²⁺ and [Fe(μ ₃ -O)] ⁻	3	
[Fe ₆ O(OH) ₇ (L7 -2H) ₃](BF ₄) ₃ (H ₂ O) ₇ Py C8 ·7H ₂ O·Py	[Fe ₃ (μ ₃ -O)] ⁷⁺ and [Fe ₃ (μ ₃ -OH)] ⁸⁺ triangles	6	
[Fe ₇ O ₂ (OH) ₆ (L5 -2H) ₃ (Py) ₆] (BF ₄) ₄ PF ₆ (H ₂ O) ₇ (Py) ₃ C4 ·7H ₂ O·3Py	2 x [Fe ₃ (μ ₃ -O)] ⁷⁺ triangles	7	
[Fe ₇ O ₂ (OH) ₆ (L6 -2H) ₃ (Py) ₆](PF ₆) ₅ (H ₂ O) ₂ C6 ·5PF ₆ ·2H ₂ O	2 x [Fe ₃ (μ ₃ -O)] ⁷⁺ triangles	7	
[Fe ₇ O ₂ (OH) ₆ (L10 -2H) ₃ (Py) ₆] (BF ₄) ₃ (PF ₆) ₂ (H ₂ O) ₃ (Py) ₂ C9 ·3BF ₄ ·2PF ₆ ·3H ₂ O·2Py	2 x [Fe ₃ (μ ₃ -O)] ⁷⁺ triangles	7	

The complexes, **C4**, **C6** and **C9** are very similar to the heptairon cluster published by Brechin *et al.*² They both contain two units of [Fe₃O]⁷⁺ connected through a [Fe(OH)₆]³⁻ unit and the charge balance of both complexes is achieved by the total anion count of 5, except the types of the anions present in the complexes **C4**, **C6** and **C9** by the X-ray structures and microanalytical CHN analyses.

The distance between the central oxygen atoms, μ₃-O... μ₃-O in the heptairon complexes **C4**, **C6**, and **C9** are 6.946(9), 7.012(5), and 6.946(6) Å respectively, which are comparable to the distance that is observed in the heptairon complex (6.920 Å) reported by Brechin *et al.*² The long distances between the μ₃-O... μ₃-O in these clusters allow them to accommodate a Fe(OH)₆³⁻ ion between the metal triangles. The crystallographic data of these iron complexes is shown in the Table 3.33.

Table 3.33: Crystallographic details of the complexes, **C10**, **C8**, **C4**, **C6** and **C9**.

	C10-4H₂O-4Py	C8-7H₂O-Py	C4-7H₂O-3Py (squeezed)	C6-2H₂O (squeezed)	C9-3BF₄·3H₂O-2Py
formula	C ₈₆ H ₁₀₄ B ₃ F ₈ Fe ₃ N ₁₄ O ₁₆	C ₁₁₆ H ₁₄₅ B ₃ F ₁₂ Fe ₃ N ₁₃ O ₂₇	C ₁₁₁ H ₁₃₇ B ₄ F ₂₂ Fe ₇ N ₂₁ O ₂₇ P	C ₁₁₄ H ₁₃₀ Fe ₇ N ₁₈ O ₂₂	C ₁₁₈ H ₁₅₄ B ₃ F ₁₂ Fe ₇ N ₂₀ O ₂₃
<i>M</i> , g mol ⁻¹	1941.83	2748.98	3080.53	2495.31	2871.97
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> <i>c</i> <i>c</i> <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	15.408(4)	17.9936(4)	17.1685(11)	15.949(3)	16.949(3)
<i>b</i> , Å	19.133(5)	37.0613(7)	17.3485(11)	25.627(5)	17.795(4)
<i>c</i> , Å	30.848(4)	20.4370(14)	29.534(2)	18.611(4)	25.795(5)
<i>a</i> , deg (°)	90.00	90	86.396(6)	90	84.21(3)
<i>β</i> , deg (°)	90.00	113.409(8)	76.716(5)	107.11(3)	88.84(3)
<i>γ</i> , deg (°)	90.00	90	60.913(4)	90	78.94(3)
<i>V</i> , Å ³	9094(4)	12507.0(12)	7469.2(9)	7270(3)	7597(3)
<i>T</i> , K	143	163	163	100	100
<i>Z</i>	2	4	2	1	1
<i>ρ</i> _{calc} [g cm ⁻³]	1.230	1.458	1.360	1.134	1.186
crystal shape / colour	rhomboid / dark red	rhomboid / dark red	Rhomboid / dark red	Rhomboid / dark red	rhomboid / dark red
crystal size [mm]	0.17 x 0.70 x 0.77	0.16 x 0.19 x 0.45	0.41 x 0.43 x 0.82	0.07 x 0.08 x 0.04	0.11 x 0.10 x 0.06
<i>μ</i> _s [mm ⁻¹]	0.543	6.239	6.236	0.740	0.724
restraints / parameters	186 / 542	1144 / 1660	1110 / 1631	924 / 861	114 / 1694
unique data	7676	17912	21048	12210	32813
<i>R</i> _{int} / <i>R</i> _σ	0.1273 / 0.0952	0.1914 / 0.1850	0.0817 / 0.1269	0.0505 / 0.0437	0.0398 / 0.0313
<i>I</i> > 2σ (<i>I</i>)	10.23	12.54	12.63	9.67	11.08
unique data, (<i>I</i> > 2σ)	4954	8111	9463	9035	23385
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	0.1131, 0.3452	0.1098, 0.3317	0.1263, 0.3606	0.0967, 0.3273	0.1164, 0.3702
goodness of fit	1.19	1.00	1.07	1.34	1.50

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$ for observed reflections. ^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)_2] / \sum[w(F_o^2)_2]\}^{1/2}$ for all data.

3.5 Mössbauer results and discussion of the iron complexes

Mössbauer spectroscopy is an important technique for chemical structure analysis because it provides unique measurements of electronic, magnetic, and structural properties within materials. A Mössbauer spectrum gives quantitative measurement of intensity of γ -ray absorption versus energy for a specific resonant nucleus such as ^{57}Fe or ^{119}Sn . Absorbing γ -rays by a second nucleus with an efficiency which is emitted by another nucleus when both nuclei are embedded in solids is known as the “Mössbauer effect”.

Mössbauer spectra provide quantitative information on “hyperfine interactions,” which are small energies that result from the interaction between the nucleus and its neighbouring/surrounding electrons. There are three important hyperfine interactions that emerge from the electron density at the nucleus (the isomer shift), the gradient of the electric field (the nuclear quadrupole splitting), and the unpaired electron density at the nucleus (the hyperfine magnetic field). Methods have been developed for many years for the use of these three hyperfine interactions to determine valence and spin at the resonant atom. The hyperfine interactions can often be used as authentic “fingerprints” to identify the different local chemical environments of the resonant atom, even when these interactions are not easily interpreted. This technique is useful for quantitative phase analyses or determinations of the concentrations of resonant element in different phases, even when the phases are nanostructured or amorphous.¹⁴

Table 3.34: Fitting parameters of ^{57}Fe on **C8**, **C4**, **C9**, **C10**, and **C6** at low temperature and higher temperature (δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ_L = line width of the left peak, Γ_R = line width of the right peak, I = intensity).

[Fe ₆ O(OH) ₇ (L7-2H) ₃](BF ₄) ₃ (H ₂ O) ₇ Py C8·7H ₂ O·Py					
<i>T</i> (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	<i>I</i> (%)
5.0	0.542	0.789	0.315	0.322	100
293	0.428	0.771	0.273	0.313	100
[Fe ₇ O ₂ (OH) ₆ (L5-2H) ₃ (Py) ₆] (BF ₄) ₄ PF ₆ (H ₂ O) ₇ (Py) ₃ C4·7H ₂ O·3Py					
<i>T</i> (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	<i>I</i> (%)
293	0.40	1.50	0.35	0.35	70
	0.40	0.55	0.35 ± 0.15	0.35 ± 0.15	30
[Fe ₇ O ₂ (OH) ₆ (L10-2H) ₃ (Py) ₆] (BF ₄) ₃ (PF ₆) ₂ (H ₂ O) ₃ (Py) ₂ C9·3BF ₄ ·2PF ₆ ·3H ₂ O·2Py					
<i>T</i> (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	<i>I</i> (%)
293	0.274	0.549	0.779	0.513	28.1
	0.402	1.522	0.324	0.324	74.2
[Fe ₇ O ₂ (L6-2H) ₃ (OH) ₆ (Py) ₆](PF ₆) ₅ (H ₂ O) ₂ C6·5PF ₆ ·2H ₂ O					
<i>T</i> (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	<i>I</i> (%)
293	0.40	1.55	0.30	0.30	75
	0.35	0.45	0.35	0.35	26
[Fe ₃ BO ₂ (L9-2H) ₂ (OH) ₂ (Py) ₂] (BF ₄) ₂ (H ₂ O) ₂ (MeOH)(Py) C10·2H ₂ O·MeOH·Py					
<i>T</i> (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ_L (mm/s)	Γ_R (mm/s)	<i>I</i> (%)
290	0.39	0.805	0.398	0.508	100

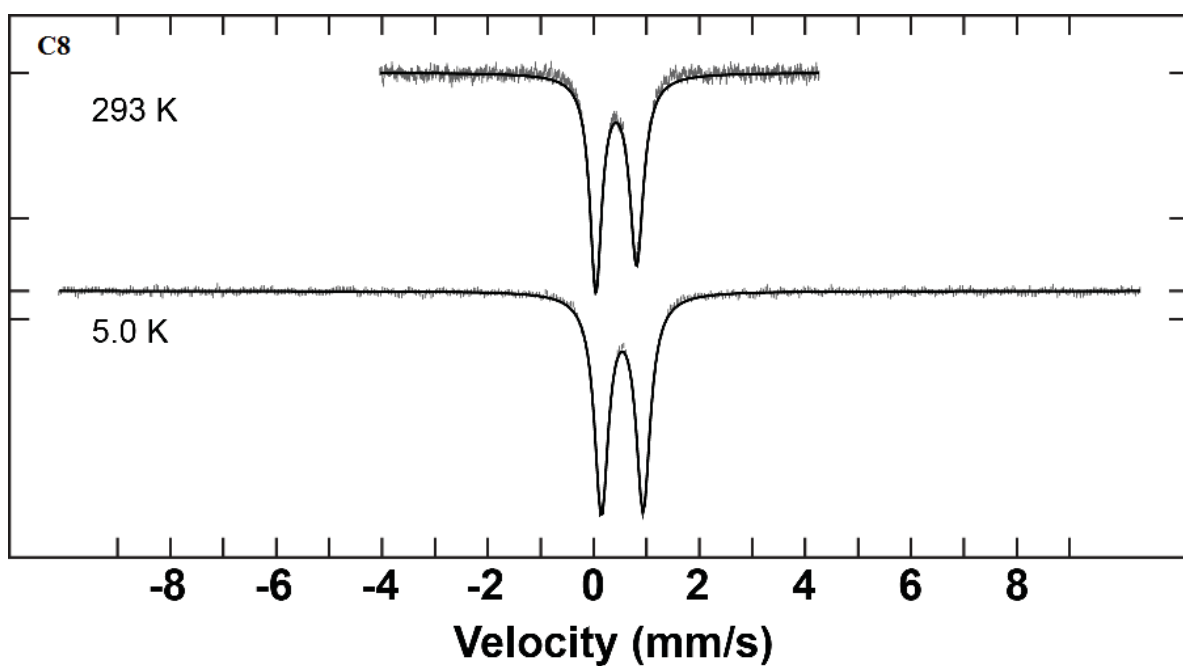


Figure 3.29: ^{57}Fe Mössbauer spectra of the complex **C8** (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature.

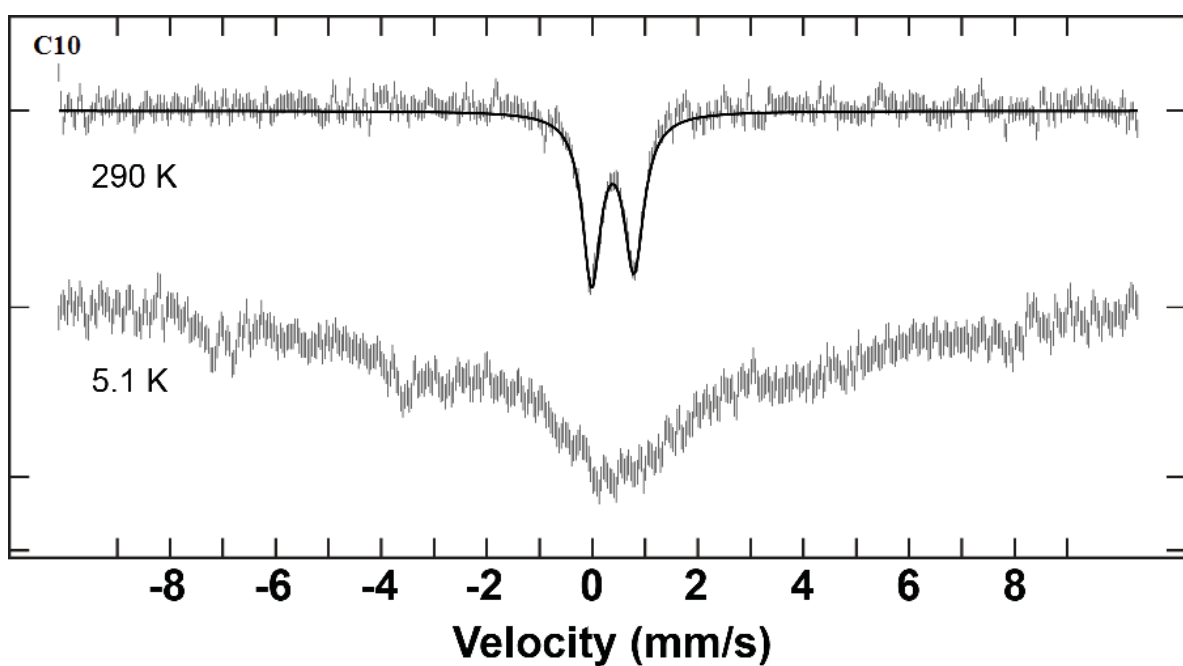


Figure 3.30: ^{57}Fe Mössbauer spectra of the complex **C10** (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature.

The complex **C10** is a tri-iron compound coordinated by a BO_2^- ion and **C8** is a hexairon compound. The complex **C8** is highly symmetric (see the crystal structures explained above). Symmetric quadrupole doublets were obtained for both compounds **C10** and **C8** at 293 K (see Table 3.34 and Figures 3.29 and 3.30).

All other complexes **C4**, **C9**, and **C6** in this chapter are heptairon clusters and have the same coordination architecture around the metal centres. That is, they all contain two Fe types in different chemical environments, i.e. $[\text{Fe}(\text{OH})_6]$ and $6 \times \text{Fe}^{3+}$ in similar coordination environments located within the two metal triangles and located between the metal planes. The metal ions within the triangles vary from the metal ion between the triangles in terms of the degree of asymmetry as well as in bond distances around the metal centre. The spectra recorded at 293 K illustrate two distinctive fitting lines (red and blue) for the experimental spectrum (see Figures 3.31-3.33). These two lines can be unambiguously attributed to the metal ions within and the metal ion between the triangles in each compound. The intensity of the blue peaks on the Mössbauer spectra of the complexes, **C4**, **C9**, and **C6** is much higher than that of the red peaks (see Figures 3.31-3.33). The intensity ratio between the two species of all of these heptairon compounds is approximately 7:3. This intensity ratio was observed for all the double-headed oxime containing heptairon complexes in this chapter, and was also observed in the heptairon single-headed oxime complex, **C3** (see Chapter 2, section 2.7.3). According to the crystallographic results, the intensity ratio between the two species is expected to be 6:1. However, the value of the ratio for all the heptairon complexes is more or less constant. The values of the isomer shift together with the quadrupole splitting support the ferric high spin state for all the iron sites present in the compounds (see Table 3.34 and see Figure 2.34 in Chapter 2,). There is no significant variation of the isomer shifts and quadrupole splitting values of these heptairon compounds synthesised with double-headed oximes at 293 K (see Table 3.34). On the other hand, the quadrupole splitting value of the complex **C3**, which was produced with a single-headed oxime (see chapter 2), is considerably different from that of the compounds **C4**, **C9**, and **C6**. It is on this basis that complex **C3** is assigned as an $[\text{Fe}_3(\text{OH})]^{8+}$ species, whereas complexes **C4**, **C6** and **C9** were assigned as $[\text{Fe}_3\text{O}]^{7+}$ species.

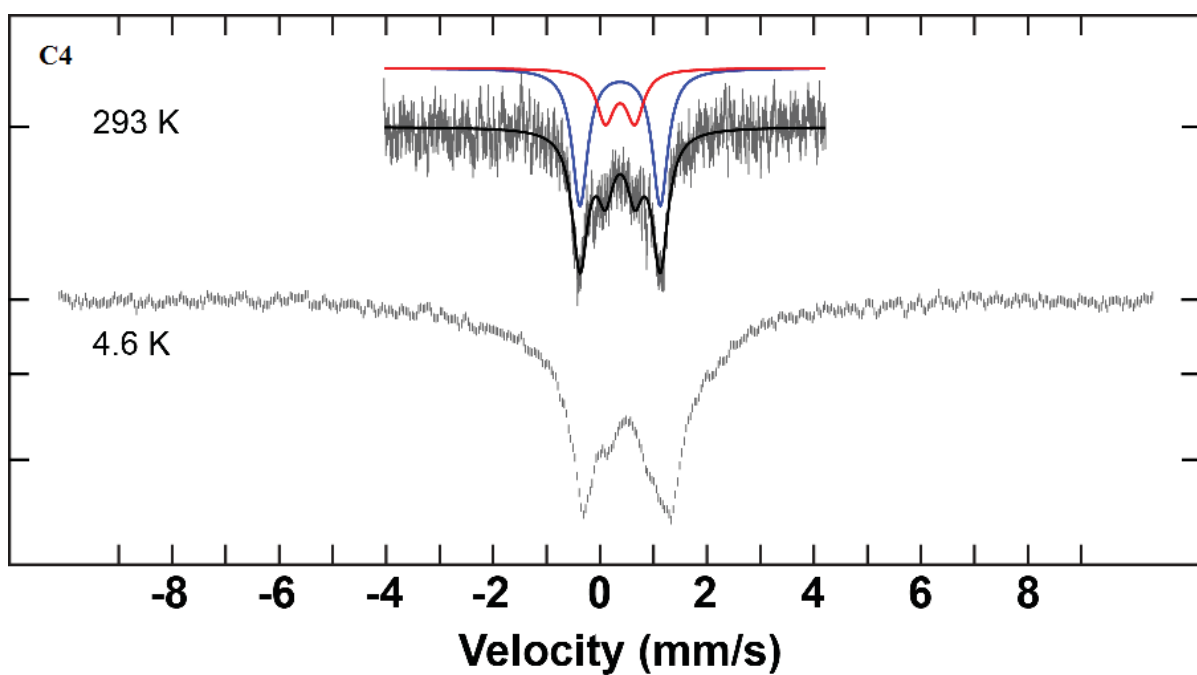


Figure 3.31: ^{57}Fe Mössbauer spectra of the complex **C4** [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit) at high and low temperature.

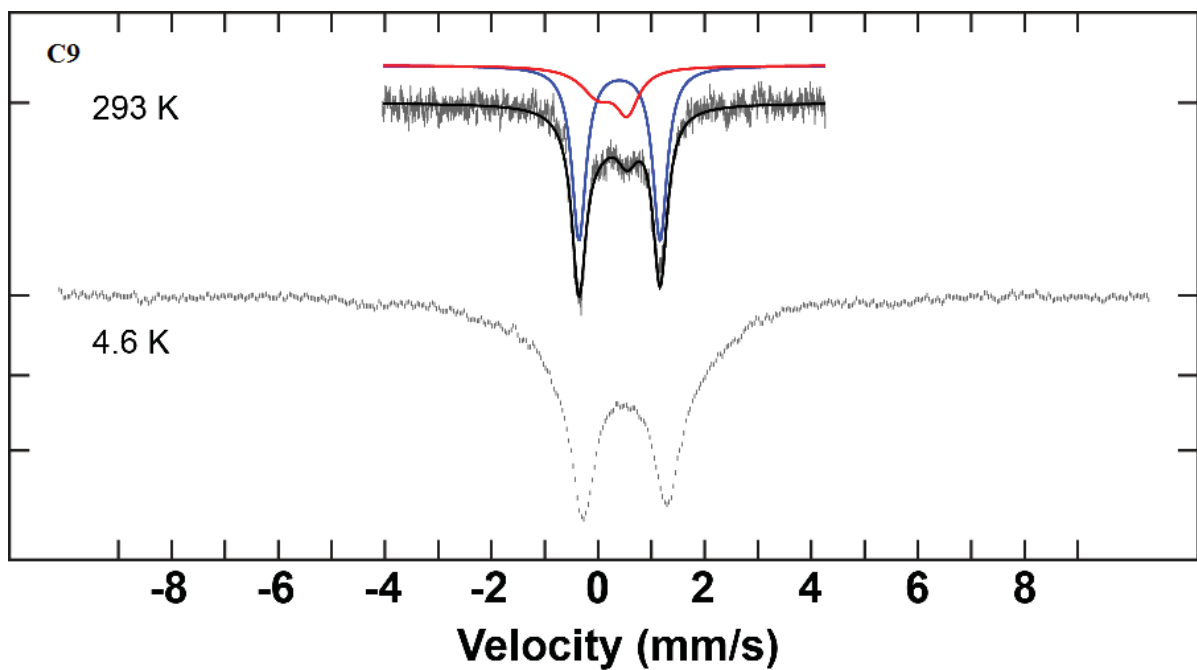


Figure 3.32: ^{57}Fe Mössbauer spectra of the complex **C9** [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit) at high and low temperature.

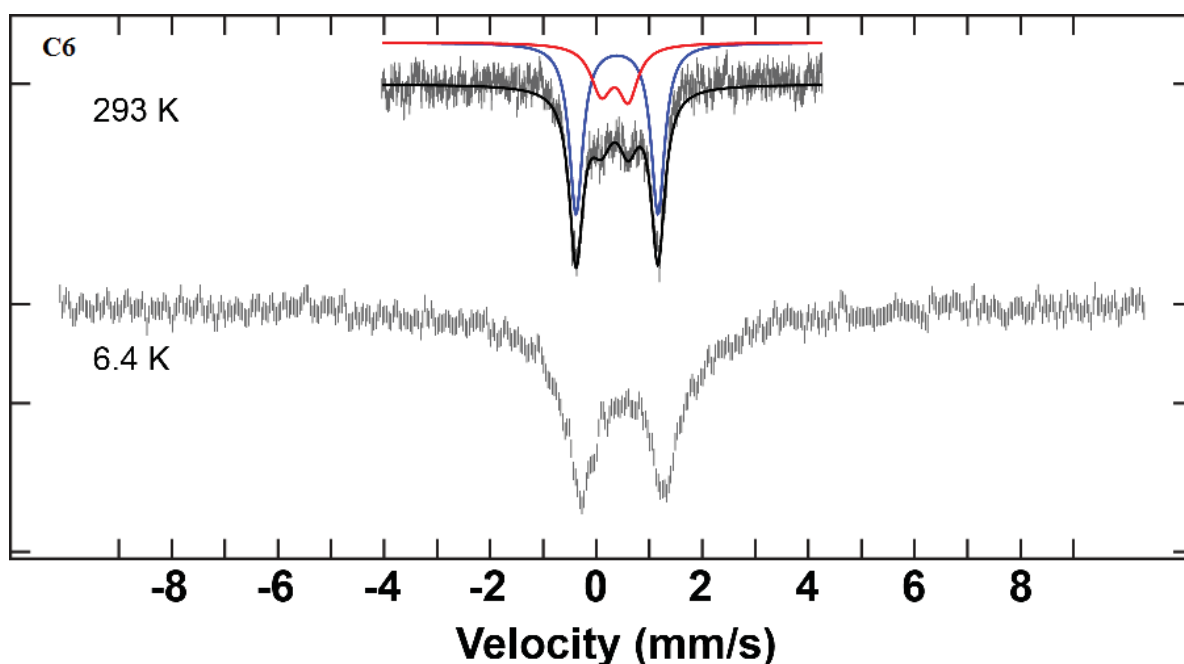


Figure 3.33: ^{57}Fe Mössbauer spectra of the complex C6 [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit) at high and low temperature.

3.6 Conclusion

Two new copper complexes and five iron complexes were synthesised using double-headed derivatised salicylaldoximes. Modification of the ligands by varying the amine strap resulted in the formation of metal-salicylaldoxime complexes with different nuclearities. A direct relationship between the nuclearity of the complexes and the type of the amine strap used in the double-headed oximes cannot be identified. The magnetic measurements indicate the presence of dominant antiferromagnetic interactions between the iron centres within the complexes C8 and C10. The magnetic results of the rest of the iron complexes have not been completed as it requires a lot of time and resources (supercomputers) for fitting magnetic data. Mössbauer spectra of the iron complexes were recorded and used to confirm the spin state and the oxidation states of the iron atoms in the complexes. The spin state of all three compounds was found to be high spin and the iron atoms are all in the oxidation state of 3+.

References:

1. Wenzel, M., Forgan, R. S., Faure, A., Mason, K., Tasker, P. A., Piligkos, S., Brechin, E. K., Plieger, P. G., *Eur. J. Inorg. Chem.*, **2009**, 4613.
2. Mason, K., Chang, J., Prescimone, A., Garlatti, E., Carretta, S., Tasker, P. A., Brechin, E. K., *Dalton Trans.*, **2012**, 41, 8777.
3. Forgan, R. S., Davidson, J. E., Fabbiani, F. P. A., Galbraith, S. G., Henderson, D. K., Moggach, S. A., Parsons, S., Tasker, P. A., White, F. J., *Dalton Trans.*, **2010**, 39, 1763.
4. Sengottuvelan, N., Manonmani, J., Kandaswamy, M., *Polyhedron*, **2002**, 21, 2767-2772; Karunakaran, S., Kandaswamy, M., *J. Chem. Soc., Dalton Trans.*, **1995**, 1851.
5. Inglis, R., Jones, L. F., Milios, C. J., Datta, S., Collins, A., Parsons, S., Wernsdorfer, W., Hill, S., Perlepes, S. P., Piligkos, S., Brechin, E. K., *Dalton Trans.*, **2009**, 18, 3403.
6. Inglis, R., Milios, C. J., Jones, L. F., Piligkos, S., Brechin, E. K., *Chem Commun.*, **2012**, 48, 181.
7. Inglis, R., Taylor, S. M., Jones, L. F., Papaefstathiou, G. S., Perlepes, S. P., Datta, S., Hill, S., Wernsdorfer, W., Brechin, E. K., *Dalton Trans.*, **2009**, 42, 9157.
8. Milios, C. J., Piligkos, S., Brechin, E. K., *Dalton Trans.*, **2008**, 1809.
9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H., *J. Appl. Cryst.*, **2009**, 42, 339.
10. a) Corbett, M. C., Latimer, M. J., Poulos, T. L., Sevrioukova, I. F., Hodgson, K. O., Hedman, B., *Acta Cryst.*, **2007**, D63, 951. b) Sommerhalter, M., Lieberman, R. L., Rosenzweig, A. C., *Inorg Chem.*, **2005**, 44, 770. c) Champloy, F., Gruber, K., Jogl, G., Kratky, C., *J Synchrotron Radiat.*, **2000**, 7(4), 267. d) Chance, B., Angiolillo, P., Yang, E. K., Powers, L., *FEBS lett.*, **1980**, 112(2), 178. e) Wilmot, C. M., Sjoegren, T., Carlsson, G. H., Berglund, G. I., Hajdu, J., *Methods in Enzymology*, **2002**, 353, *Redox Cell Biology and Genetics*, Part B, 301.
11. Symons, M. C. R., Taiwo, F. A., *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1413.
12. a) Smith, A. G., Tasker, P. A., White, D. J., *Coord. Chem. Rev.*, **2003**, 241, 61; b) Stoumpos, C. C., Inglis, R., Karotsis, G., Jones, L. F., Collins, A., Parsons, S., Milios, C. J., Papaefstathiou, G. S., Brechin, E. K., *Cryst. Growth Des.*, **2009**, 9, 24; c) Prescimone, A., Milios, C. J., Moggach, S., Warren, J. E., Lennie, A. R., Sanchez-Benitez, J., Kamenev, K., Bircher, R., Murrie, M., Parsons, S., Brechin,

- E. K., *Angew. Chem. Int. Ed.*, **2008**, 47, 2828; d) Jones, L. F., Cochrane, M. E., Koivisto, B. D., Leigh, D. A., Perlepes, S. P., Wernsdorfer, W., Brechin, E. K., *Inorg. Chim. Acta*, **2008**, 361, 3420; e) Inglis, R., Jones, L. F., Mason, K., Collins, A., Moggach, S. A., Parsons, S., Perlepes, S. P., Wernsdorfer, W., Brechin, E. K., *Chem. Eur. J.*, **2008**, 14, 9117; f) Jones, L. F., Inglis, R., Cochrane, M. E., Mason, K., Collins, A., Parsons, S., Perlepes, S. P., Brechin, E. K., *Dalton Trans.*, **2008**, 6205; g) Feng, P. L., Koo, C., Henderson, J. J., Nakano, M., Hill, S., del Barco, E., Hendrickson, D. N., *Inorg. Chem.*, **2008**, 47, 8610; h) Yang, C.-I., Wernsdorfer, W., Cheng, K.-H., Nakano, M., Lee, G.-H., Tsai, H.-L., *Inorg. Chem.*, **2008**, 47, 10184; i) Raptopoulou, C. P., Boudalis, A. K., Lazarou, K. N., Psycharis, V., Panopoulos, N., Fardis, M., Diamantopoulos, G., Tuchagues, J.-P., Mari, A., Papavassiliou, G., *Polyhedron*, **2008**, 27, 3575; j) Milios, C. J., Inglis, R., Jones, L. F., Prescimone, A., Parsons, S., Wernsdorfer, W., Brechin, E. K., *Dalton Trans.*, **2009**, 2812; k) Bahr, S., Milios, C. J., Jones, L. F., Brechin, E. K., Mosser, V., Wernsdorfer, W., *New J. Chem.*, **2009**, 33, 1231.
13. Plieger, P. G., Stevens, J., *Dalton Trans.*, **2011**, 40, 12235.
14. Fultz, B., "Mössbauer Spectrometry", in *Characterization of Materials*. Kaufmann, E., Editor, John Wiley, New York, **2011**.

CHAPTER 4

CONCLUSIONS AND FUTURE APPROACH

4.1 Single- and Double-headed Derivatised Salicylaldoximes

An original series of single-headed and double-headed derivatised salicylaldoxime ligands was used to generate a number of iron and copper clusters (see Appendix for characterisation). Despite whether the ligand is linked (double-headed) or non-linked (single-headed), the complexation reactions followed by crystallisation led to complexes of both high and low nuclearity.

The tricopper and tetracopper complexes were both formed with double-headed oximes. The ligand **L5** was used to produce both a copper and a large heptairon complex. The complex **C10** was formed with a BO_2^- moiety coordinated to three iron atoms, which makes it different from the usual hexa- and heptairon species. The heptairon complexes **C4**, **C6**, and **C9** are very similar to each other despite the minor structural variations (see Table 4.1 for a summary of the crystal structures).

Table 4.1: Crystallographical formulae of the complexes.

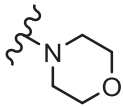
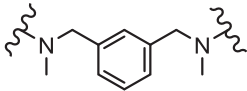
Crystal Structure	Core	Nuclearity
$[\text{Fe}_2\text{B}_2(\text{L1-H})_4(\text{F})_2(\text{O})_2](\text{BF}_4)_2(\text{MeOH})_4$ C1 ·4MeOH	$[(\text{Fe}-\mu_2-\text{O})_2]^{2+}$ and $[(\text{B}-\mu_3-\text{O})_2]^{2+}$	2
$[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})](\text{BF}_4)_2(\text{MeOH})_5$ C2 ·5MeOH	$[\text{Fe}_3(\mu_3-\text{O})]^{7+}$ and $[\text{Fe}_3(\mu_3-\text{OH})]^{8+}$	6
$\text{Na}[\text{Fe}_7(\text{OH})_8(\text{L11-2H})_6(\text{Py})_6](\text{BF}_4)_2(\text{H}_2\text{O})_6(\text{Py})_3$ C3 ·6H ₂ O·3Py	2 x $[\text{Fe}_3(\mu_3-\text{OH})]^{8+}$ triangles	7
$[\text{Fe}_3\text{BO}_2(\text{L9-2H})_2(\text{OH})_2(\text{Py})_2](\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{MeOH})(\text{Py})$ C10 ·2H ₂ O·MeOH·Py	$[(\text{Fe}-\mu_3-\text{O})_2]^{2+}$ and $[\text{Fe}(\mu_3\text{O})_2]^-$	3
$[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3](\text{BF}_4)_3(\text{H}_2\text{O})_7\text{Py}$ C8 ·7H ₂ O·Py	$[\text{Fe}_3(\mu_3-\text{O})]^{7+}$ and $[\text{Fe}_3(\mu_3-\text{OH})]^{8+}$ triangles	6
$[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{L5-2H})_3(\text{Py})_6](\text{BF}_4)_4\text{PF}_6(\text{H}_2\text{O})_7(\text{Py})_3$ C4 ·7H ₂ O·3Py	2 x $[\text{Fe}_3(\mu_3-\text{O})]^{7+}$ triangles	7
$[\text{Fe}_7\text{O}_2(\text{L6-2H})_3(\text{OH})_6(\text{Py})_6](\text{PF}_6)_5(\text{H}_2\text{O})_2$ C6 ·5PF ₆ ·2H ₂ O	2 x $[\text{Fe}_3(\mu_3-\text{O})]^{7+}$ triangles	7
$[\text{Fe}_7\text{O}_2(\text{L10-2H})_3(\text{OH})_6(\text{Py})_6](\text{BF}_4)_3(\text{PF}_6)_2(\text{H}_2\text{O})_3(\text{Py})_2$	2 x $[\text{Fe}_3(\mu_3-\text{O})]^{7+}$	7

C9 ·3BF ₄ ·2PF ₆ ·3H ₂ O·2Py	triangles	
[Cu ₃ (L5 -H) ₃ (Py) ₃](BF ₄) ₂ PF ₆ (H ₂ O) ₃ (MeOH) ₃ C5 ·3H ₂ O·3MeOH	Cu ₃	3
[Cu ₄ (L8 -3H) ₂ Py ₂](BF ₄) ₂ (MeOH)(Py) C7 ·MeOH·Py	2 x [(Cu-μ ₃ -O) ₂]	4

4.2 Dinuclear and Trinuclear iron complexes

Iron complexes of low nuclearity (see Table 4.2) synthesised using both linked and non-linked ligands were found to contain borate species (presumably by hydrolysis of the tetra-fluoroborate counter anion) coordinated to the iron centres through oxo- and oximato-oxygen atoms (see Figures 4.1 and 4.2). It appears the inclusion of the borate species inhibits larger cluster formation. The remaining coordination site of each boron atom of the diiron compound is taken by a fluorine atom which was confirmed by a comparison with similar bond lengths in literature^{1,2} and by elemental composition analysis. A similar core was reported by Rose *et al.* in 1992.²

Table 4.2: Complexes with low nuclearity.

Complex	Nuclearity	Number of links	Strap
C1	2	1	
C10	3	2	

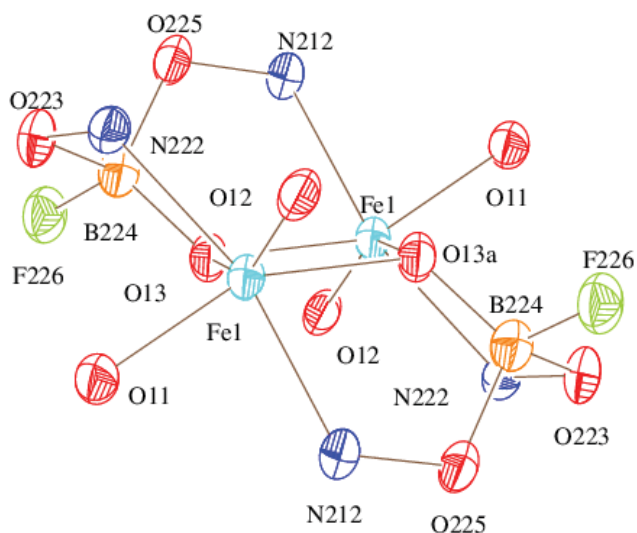


Figure 4.1: Structural representation of the dimetallic core of the complex **C1**; ORTEP view at 50% probability level.

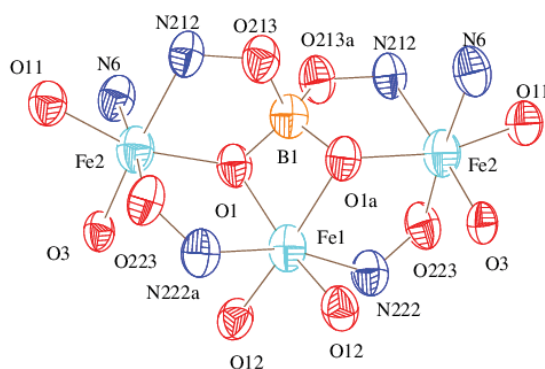
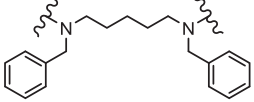
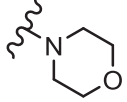
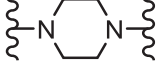
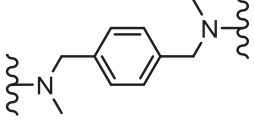
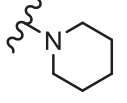


Figure 4.2: Metallic core of the structure **C10**; ORTEP view at 50% probability level.

The $\chi_M T$ values assuming non-interacting magnetic centres at room temperature for both complexes are higher than the experimental values at RT which is suggestive of the presence of sizable antiferromagnetic interactions. The ground state spin of the **C10** complex was found to be $S = 3/2$. The iron centres of both complexes are 3+ which was confirmed by Mössbauer analysis and charge balance considerations.

4.3 High nuclearity complexes.

Table 4.3: Complexes with high nuclearity.

Complex	Nuclearity	Number of links	Strap
C8	6	2	
C2	6	1	
C4	7	2	
C6	7	2	
C9	7	2	
C3	7	1	

4.3.1 The hexairon complexes

The two hexairon complexes (**C8** and **C2**, Figures 4.3 and 4.4) synthesised using respectively, linked and singular salicylaldoxime ligands. Both complexes have antiprismatically arranged $[\text{Fe}_3\text{-OH}_{0.5}]$ metallic cores. However, there is a pronounced difference in the arrangement of the oximato ligands between the two complexes. In complex **C2**, where there is a crystallographic inversion centre, the N-O groups of the oximato ligands run in opposite directions, one clockwise and one anticlockwise (see Figure 4.4). However, in complex **C8**, where there is no imposed crystallographic symmetry, the two N-O groups of the oximato ligands both run around the $[\text{Fe}_3\text{-OH}_{0.5}]$ in the same direction. This is easily seen when viewing the molecules along the central O-O axis and observing whether the O-N direction is the same or opposite at each metal plane. The previously reported hexairon complex reported by Brechin *et al* in 2012 has different directions of this bond at either metal plane and is therefore, like complex **C2**,

has perfect antiprismatic symmetry.³ Each complex contains a shared proton between the central O-atoms within the metal coordination core (see Figures 4.3 and 4.4). While this hydrogen atom was not able to be detected directly, the presence was confirmed by the short distance⁴ between the central oxygen atoms: O10...O11 distance is 2.453(9) Å for **C8** and O11...O11 = 2.730(11) and O55...O55 = 2.628(8) Å for the two independent molecules respectively in the structure determination of **C2**. The very short O...O distance for **C8** likely indicates symmetrical placement of the proton between the two oxygens, whereas for the **C2**, the proton is likely asymmetrically located, and because of crystallographic inversion centres disordered. The fact that the central O-atoms are also displaced towards each other by 0.155(5) and 0.134(5) Å for the two crystallographically independent half molecules of **C2** and by 0.290(6) and 0.220(4) Å for the two triangles of the complex **C8** is another indicator that there exists a hydrogen bond positioned between the metal planes (Figure 4.3). This structural information was further corroborated by the infra-red spectroscopy analysis. The distances above bookend the value of the confirmed H-bond of the hexairon complex (2.526 Å) of Brechin *et al*³ (see Table 4.4).

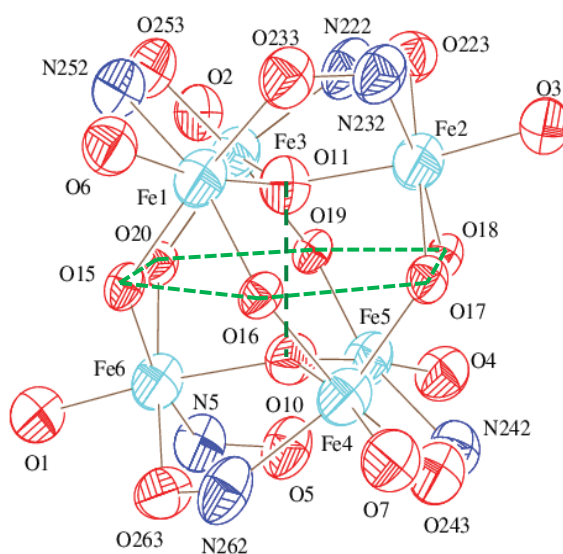


Figure 4.3: Metallic core, $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L5-2H})_3]^{3+}$ of the complex, **C8** emphasising the hydrogen bond contact (dark green dotted line) between the central oxygen atoms (O10 and O11) of the lower and upper triangles and the internal hexagon (O15 through O20, shown in dotted light green line) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.

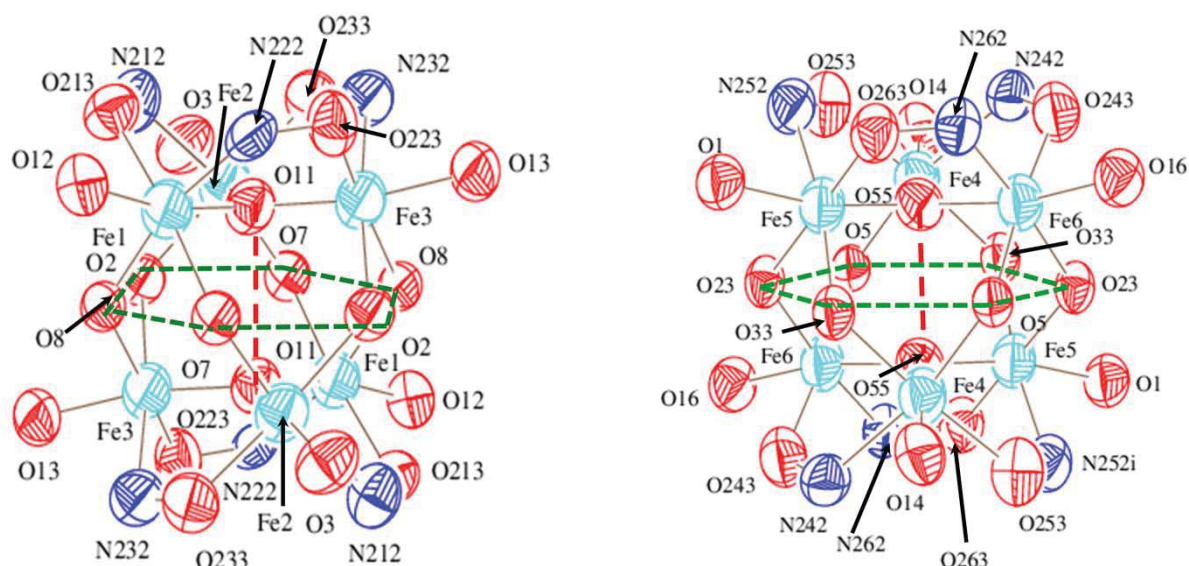


Figure 4.4: The metallic cores of the two crystallographic independent molecules of $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ **C2** (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.

The magnetic measurement analyses suggest the total ground state spin for the complex **C8** is equivalent to that observed for the hexairon complex reported by Brechin *et al.* The magnetic fitting was not performed on the complex **C2** due to the two independent structures present.

4.3.2 The heptairon complexes

Both non-linked and linked salicylaldoxime ligands appear to be able to form heptairon clusters with the Fe(II) tetrafluoroborate metal salt in air. These largely prismatic structures are comprised of two oxo-bridged iron(III) triangles that are connected *via* a central iron(III) hexa-hydroxide moiety. All of the heptairon complexes, despite the ligand used, form a very similar metallic core. The oximato bridging sequence on both triangles for complexes **C3**, **C6** and **C9** are the same and are thus very similar to the heptairon complex reported by Brechin *et al.*³ The exception to this is complex **C4**, which has an exact anti-prismatic arrangement of the N-O moieties of the oximato bridges on the upper and lower metal triangles as a result of the crystallographically imposed S_6 ($3\text{-}\bar{6}$) symmetry (Figure 4.5).

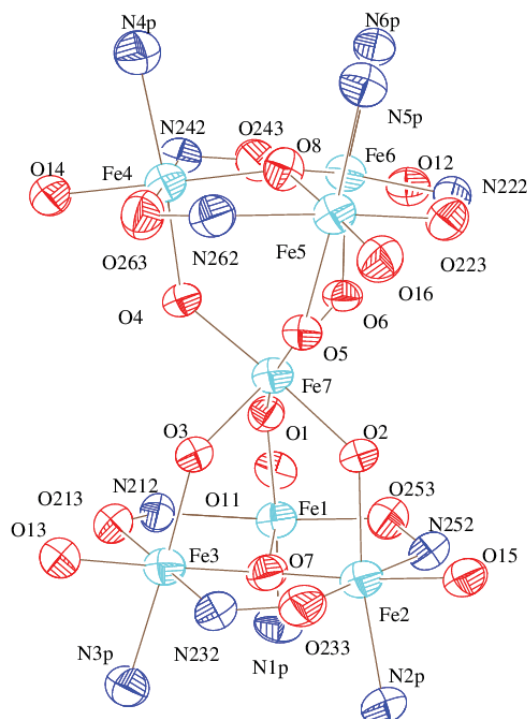


Figure 4.5: Metallic core, $[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{L5-2H})_3]^{5+}$ of the complex, **C4** emphasising anti-prismatic arrangement of the N-O bridging oximic bonds (Fe-cyan, N-blue, O-red); ORTEP view at 30% probability level.

In all cases, the Mössbauer spectra indicate the two distinctive iron environments with a consistent ratio of intensity (7:3) between them, a slightly reduced ratio then the expected 6:1. The quadrupole splitting ΔE_Q (mm s^{-1}) for all the heptairon complexes at 293 K is approximately 0.5 and 1.5 mm s^{-1} , except for the complex **C3**, for which it is approximately 0.5 and 0.9 mm s^{-1} . It was on this basis, due to the variation of the symmetry of the complex, that the central oxygens in complex **C3** were assigned as hydroxo groups, whereas in complexes **C4**, **C6** and **C9** these atoms were assigned as oxo groups. The quadrupole splitting for the hexairon complex **C8** at 293 K is 0.771 mm s^{-1} , whereas it is 0.570 mm s^{-1} and 1.180 mm s^{-1} for the complex **C2**, which is significantly different from the value for the complex **C8**. This can be due to the presence of two similar crystallographically independent hexairon units in the complex **C2**. The magnetic results are suggestive of the presence of dominant antiferromagnetic interactions.

Table 4.4: Comparison of IR data, ^a Fe^{III}μ-oxo/hydroxo bond lengths and displacements of the central oxygen atoms from the metal planes with each other and literature.

Complex	Fe ^{III} μ ₃ - oxo/hydroxo bond lengths (Å)	IR absorption (cm ⁻¹)	Displacement of the central oxygen atoms (Å)	O _{central} ...O _{central}
[Fe ₆ O(OH) ₇ (L1-H) ₅ (L1-2H)] (BF ₄) ₂ (MeOH) ₅ C2·5MeOH	1.908(6) 1.891(6) 1.898(6) 1.872(6) 1.899(7) 1.917(6)	454(w)	0.155(5) 0.134(5)	2.628(8) 2.730(11)
[Fe ₆ O(OH) ₇ (L7-2H) ₃] (BF ₄) ₃ (H ₂ O) ₇ Py C8·7H ₂ O·Py	2.021(6) 1.996(6) 1.981(6) 1.961(8) 1.994(7) 2.026(6)	522(m)	0.290(6) 0.220(4)	2.453(9)
Na[Fe ₇ (OH) ₈ (L11-2H) ₆ (Py) ₆] (BF ₄) ₂ (H ₂ O) ₆ (Py) ₃ C3·6H ₂ O·3Py	1.9337(13)	534(s), 437(m)	0.318(6)	6.917
[Fe ₇ O ₂ (OH) ₆ (L5-2H) ₃ (Py) ₆] (BF ₄) ₄ (PF ₆) ₃ (H ₂ O) ₇ (Py) ₃ C4·7H ₂ O·3Py	1.921(7) 1.937(6) 1.935(8) 1.950(6) 1.919(5) 1.937(7)	483(s)	0.335(5) 0.254(4)	6.946(9)
[Fe ₇ O ₂ (L6-2H) ₃ (OH) ₆ (Py) ₆] (PF ₆) ₅ (H ₂ O) ₂ C6·5PF ₆ ·2H ₂ O	1.931(4) 1.912(4) 1.924(4)	440(w) 522(m)	0.326(4)	7.012(5)
[Fe ₇ O ₂ (L10-2H) ₃ (OH) ₆ (Py) ₆] (BF ₄) ₃ (PF ₆) ₂ (H ₂ O) ₃ (Py) ₂ C9·3BF ₄ ·2PF ₆ ·3H ₂ O·2Py	1.911(4) 1.938(4) 1.956(4) 1.914(4) 1.934(5) 1.926(4)	467(w) 521(m)	0.369(6) 0.321(6)	6.946(6)
[Fe ₃ (μ ₃ -O)(O ₂ CPh) ₅ (salO) (MeOH) ₂]·1.25MeOH ·1.05H ₂ O (1)	1.944(8) 1.882(9) 1.855(8)	480(s)	0.075 0.054	-

Fe ₃ (μ ₃ -O)(O ₂ CPh) ₅ (salO)(EtOH)(H ₂ O)]·EtOH (2) ⁵	1.932(9) 1.877(9) 1.868(9) 1.835 - 1.923			
Na ₃ [Fe ₆ O ₂ H(sao) ₆ (CH ₃ O) ₃ (OH) ₃] ·8.14CH ₃ OH ⁶	1.970(4) - 1.975(4) 2.048(5) - 2.081(5)	439(vs) 609(s)	0.265(5) 0.358(5)	2.537(7)
[Fe ₇ O ₂ (OH) ₆ (L-2H) ₃ (py) ₆] (BF ₄) ₅ ·6H ₂ O·14MeOH	Not available	-	0.352 0.318	6.920
[Fe ₆ O(OH) ₇ (L'-2H) ₃](BF ₄) ₃ ·4H ₂ O·9MeOH ³	2.014(6) 1.978(6) 2.019(6) 1.978(5) 2.019(6) 2.014(6)	-	0.317	2.526(7)

^a Peak nearest 480 cm⁻¹ which has been assigned as diagnostic of a [Fe₃O]⁷⁺ moiety for related salicylaldehyde complexes.⁵

4.4 Conclusions

The salicylaldehyde ligands synthesised in this study centred around modifications to the amine connected strap between the salicylaldehyde units in the linked salicylaldehyde ligands for the double-headed oxime variants and amine appended derivatives for the single-headed oxime containing ligands. For the doubled-headed oximes, structural features of the ligands such as helicity and flexibility were investigated for changes in the magnetic properties based upon variations in the structural parameters of the complexes such as iron nuclearity, bond lengths and angles, torsion angles, formation of H-bonds and proximity of the iron centres that could all lead to differences in magnetic properties. The high nuclearity of iron centres in the larger clusters lead to dominant antiferromagnetic interactions in all the complexes synthesised. A suitable future modification and one that has been employed with some success in the literature would be to modify the simple salicylaldehyde head by

replacing the hydrogen on the oximic carbon with a more bulky substituent (see Figure 4.6). This has been shown to impart structural changes in the complexes, notably the torsion angle of the Metal-N-O-Metal units, which in turn has drastically influenced the magnetic properties of the resulting complex clusters. Further, mixed metal ions such as transition metal ions with lanthanides complexed with aforementioned simple salicylaldoxime ligands could lead to magnetically interesting complexes.

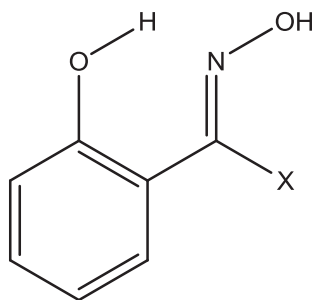


Figure 4.6: A representative simple salicylaldoxime where X is a more bulky group.

References

1. Vasilevsky, I., Rose, N. J., *Acta Cryst.*, **1992**, B48, 444.
2. Khanra, S., Weyhermüller, T., Bill, E., Chaudhuri, P., *Inorg. Chem.*, 45, **2006**, 5911.
3. Mason, K., Chang, J., Prescimone, A., Garlatti, E., Carretta, S., Tasker, P. A., Brechin E. K., *Dalton Trans.*, **2012**, 41, 8777.
4. Steiner, T., *Angew. Chem. Int. Ed.*, **2002**, 41, 48.
5. Raptopoulou, C. P., Sanakis, Y., Boudalis, A. K., Psycharis, V., *Polyhedron*, **2005**, 24, 711.
6. Hołyńska, M., Clérac, R., Langer, T., Pottgen, R., Dehnen, S., *Polyhedron*, 52, **2013**, 1425.

Appendix A: Experimental

A.1 General Experimental

A.1.1 Reagents and Solvents

All starting materials obtained from commercial sources were used without purification. Hydroxylamine·HCl was dried *in vacuo* prior to use. All solvents used in the reactions were analytical grade and used directly. If stated as dry, they were subject to further purification as follows: Tetrahydrofuran, dichloromethane, and toluene were passed through an alumina column on an in-house solvent purification system. Methanol was distilled from Mg turnings and I₂ and stored over 4 Å molecular sieves.

A.1.2 Synthetic Methods

All reactions were carried out in acetone-washed, oven-dried glassware under atmospheric pressure with magnetic stirring. For the crystallisation attempts, glassware was washed with concentrated nitric acid, rinsed with distilled water, and oven dried prior to use. All organic extracts were dried over magnesium sulfate and then filtered. The solvents were removed under reduced pressure on a rotary evaporator. The residue solvent was removed *in vacuo* prior to analysis.

A.1.3 Chromatography

Reactions were followed by TLC on aluminium-backed silica gel 60 F₂₅₄ sheets from E-Merck and visualised by UV light.

Flash column chromatography was performed using Scharlau silica gel 60, 0.04 – 0.06 mm, 230 – 400 mesh. The length of silica was typically 20 cm and the diameter was varied according to reaction scale. The silica gel slurry was compacted with the specified solvent system of hexane / EtOAc. The compound was then loaded onto the column and eluted with the specified solvent under positive pressure with air.

A.1.4 Synthesis and Characterisation

All the new organic compounds were characterised by NMR, ESI-MS, IR, CHN, and MPs. The Fe complexes were subjected to CHN, UV-Visible, IR, and ESI-MS analyses for the purposes of determining purity and characterisation. In addition, the Fe complexes were subjected to magnetic and Mössbauer measurements. In the case of the Cu complexes, the aforementioned general characterisation was also carried out.

5-*t*-Butylsalicylaldehyde and 5-methylsalicylaldehyde were synthesised according to the procedure published by Levin and Neilan¹ and confirmed by ¹H NMR analysis. The synthesis of 3-(bromomethyl)-2-hydroxy-5-methylbenzaldehyde (**1**) and 3-(bromomethyl)-2-hydroxy-5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde was carried out by the procedure of Tasker and Schröder.² The secondary amines (**2**) - (**5**) were prepared using the procedure of Plieger *et al.*³ and confirmed by ¹H NMR analysis. The ligand **L10** was synthesised according to the procedure published by Plieger *et al.*⁴ and **L11** by the procedure published by Tasker *et al.*⁵ All the aldehydes (precursors of oximes) were synthesised using the protocol in Schröder *et al.*¹ and all the oximations were carried out according to the procedure in Plieger *et al.*³

NMR spectra were collected on Bruker Avance 400 and 500 MHz spectrometers; the particular instrument is specified for each compound. In CDCl₃, all chemical shifts are reported relative to TMS (¹H) and residual solvent (¹³C). In all other deuterated solvents, the chemical shifts are reported relative to residual solvent (¹H, ¹³C). Full NMR assignments were made using ¹H, ¹³C.

Electrospray mass spectra were recorded on a Mircomass ZMD spectrometer run in positive ion mode. High resolution mass spectra were recorded on a micrOTOF mass spectrometer, operating at a nominal voltage of 4500 V. This service was provided by The University of Waikato.

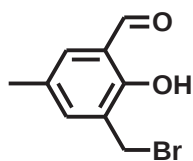
Elemental analyses were provided by the Campbell Microanalytical Laboratory, University of Otago.

UV-Vis spectra were recorded on a Shimadzu UV-3101PC spectrophotometer using UV Probe v1.1.

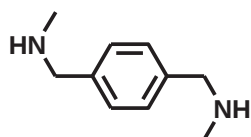
The X-ray data were collected at reduced temperature on a Rigaku Spider diffractometer equipped with a copper rotating anode X-ray source and a curved image plate detector. The crystals were mounted in an inert oil, transferred into the cold gas stream of the detector and irradiated with graphite monochromated Cu K α ($\lambda = 1.54178$ Å) X-rays. The data were collected by the CrystalClear program (v.1.4.0) and processed with FS-PROCESS to apply the Lorentz and polarisation corrections to the diffraction spots (integrated 3 dimensionally). The structures were solved by direct methods SHELXS-13 and refined using the SHELXL-13 as implemented in the OLEX2 program.⁶ Absorption data scalings corrections were carried out using multiscan. Hydrogens were calculated at their ideal positions unless otherwise stated.

For the X-ray data collection of the complexes, C6·H₂O and C9;

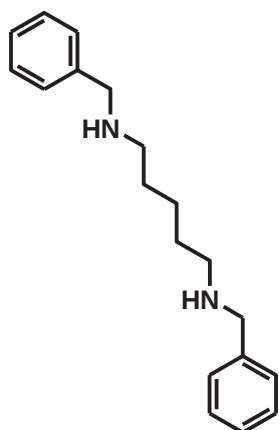
The crystals were harvested with a 0.20-mm nylon loop and flash-cooled in liquid nitrogen. Diffraction data were collected at 110 K on the MX2 beamline at the Australian Synchrotron, Victoria, Australia, at a wavelength of 0.7093 Å. The dataset was processed and evaluated using *XDS*.⁷ The resulting reflections were scaled using *AIMLESS*⁸ from the *CCP4* program suite.⁹



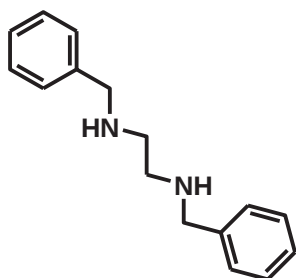
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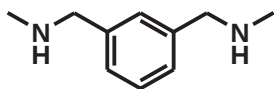
2 *N,N'*-Dimethyl-*p*-xylylenediamine



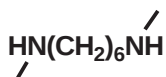
3 *N,N'*-Dibenzyl-1,5-pentanediamine



4 *N,N'*-Dibenzyl-ethylenediamine



5 *N,N'*-Dimethyl-*m*-xylylenediamine



6 *N,N'*-Dimethyl-1,6-hexanediamine

Magnetic measurements

Variable temperature, solid state, direct current (dc), magnetic susceptibility measurements of the microcrystalline samples of all the complexes suitable for SQUID magnetometry were performed at the University of Edinburgh by Prof. Euan Brechin and his student Jamie Frost. The measurements were carried out on the samples using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants and the susceptibility measurements were performed in the 2-290 K temperature range in the applied magnetic field of 0.1 T. The data were plotted as the $\chi_M T$ product versus T .

Mössbauer measurements

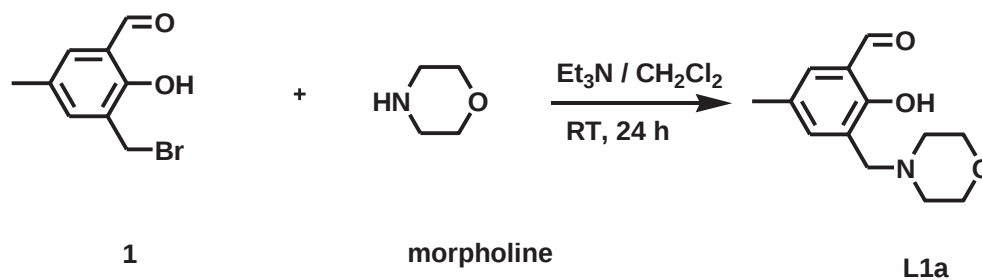
Samples were run and fitted by Dr Guy N. L. Jameson and Casey G. Davies from the Department of Chemistry and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago. The following instrumental set up was used; the Mössbauer spectrometer was obtained from the SEE Company (Science Engineering and Education Co., MN). It is equipped with a closed-cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.) and a temperature controller from Lakeshore Cryotronics, Inc. Data were collected in the constant acceleration mode in transmission geometry with an applied field of 47 mT parallel to the γ -rays. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 μ m metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co., Edina, MN).

A.2 Experimental

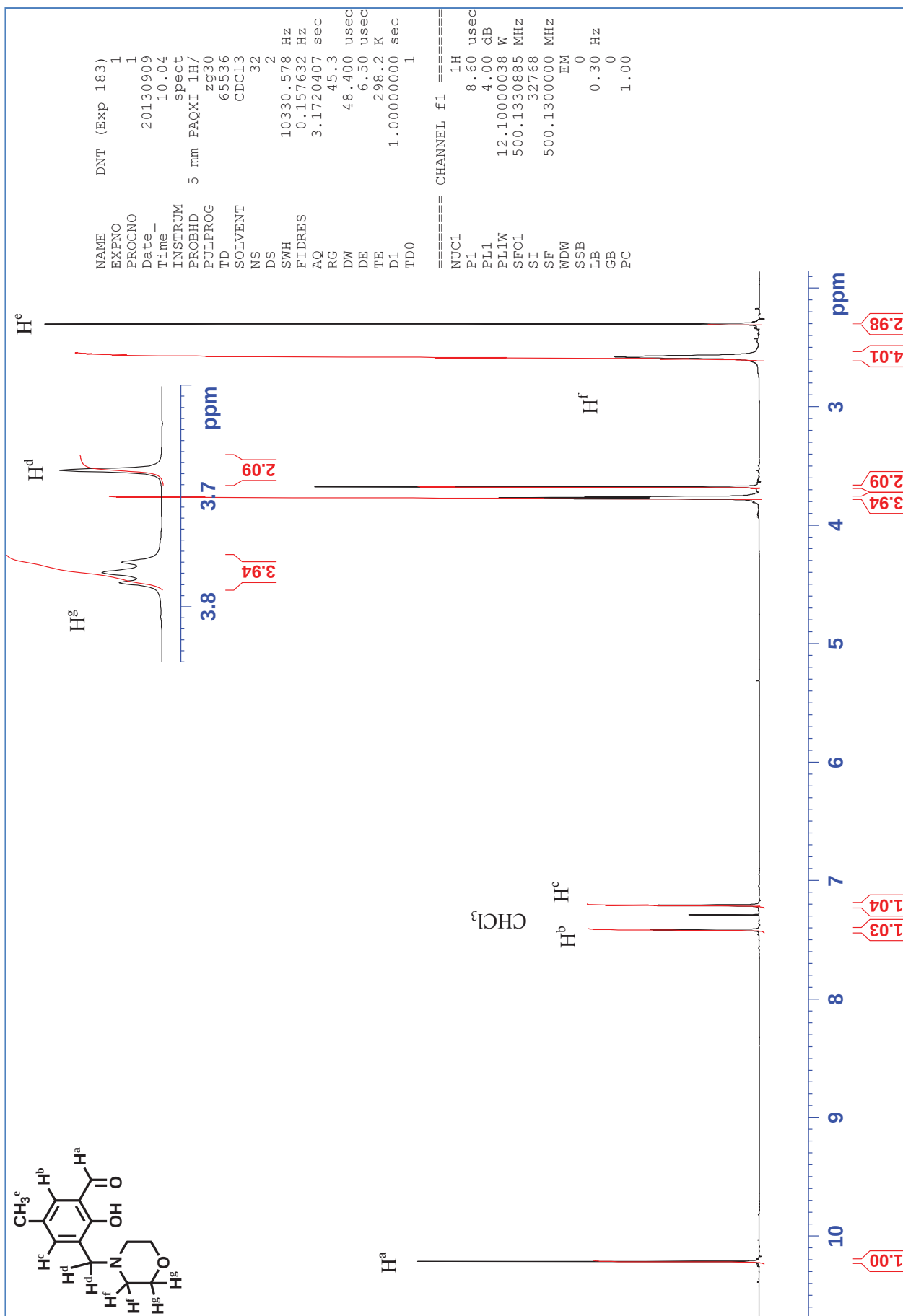
A.2.1 Synthesis of single-headed oxime ligands

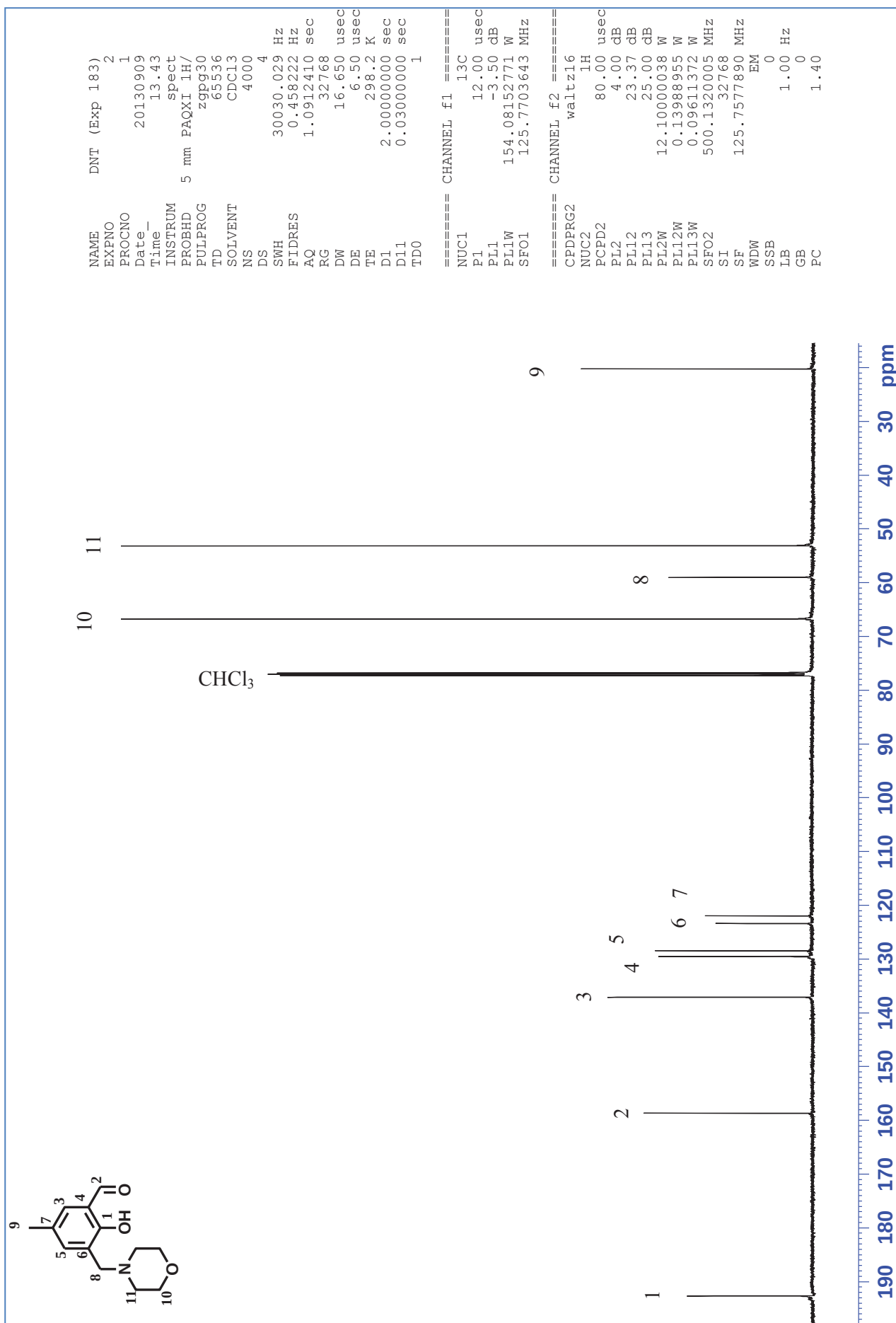
L1a

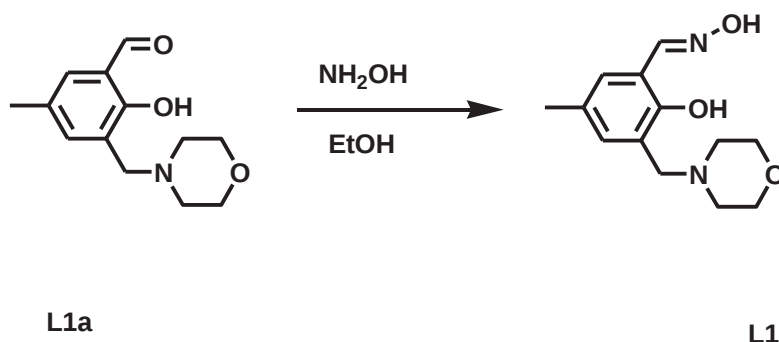
2-hydroxy-5-methyl-3-(4-morpholinylmethyl)-benzaldehyde



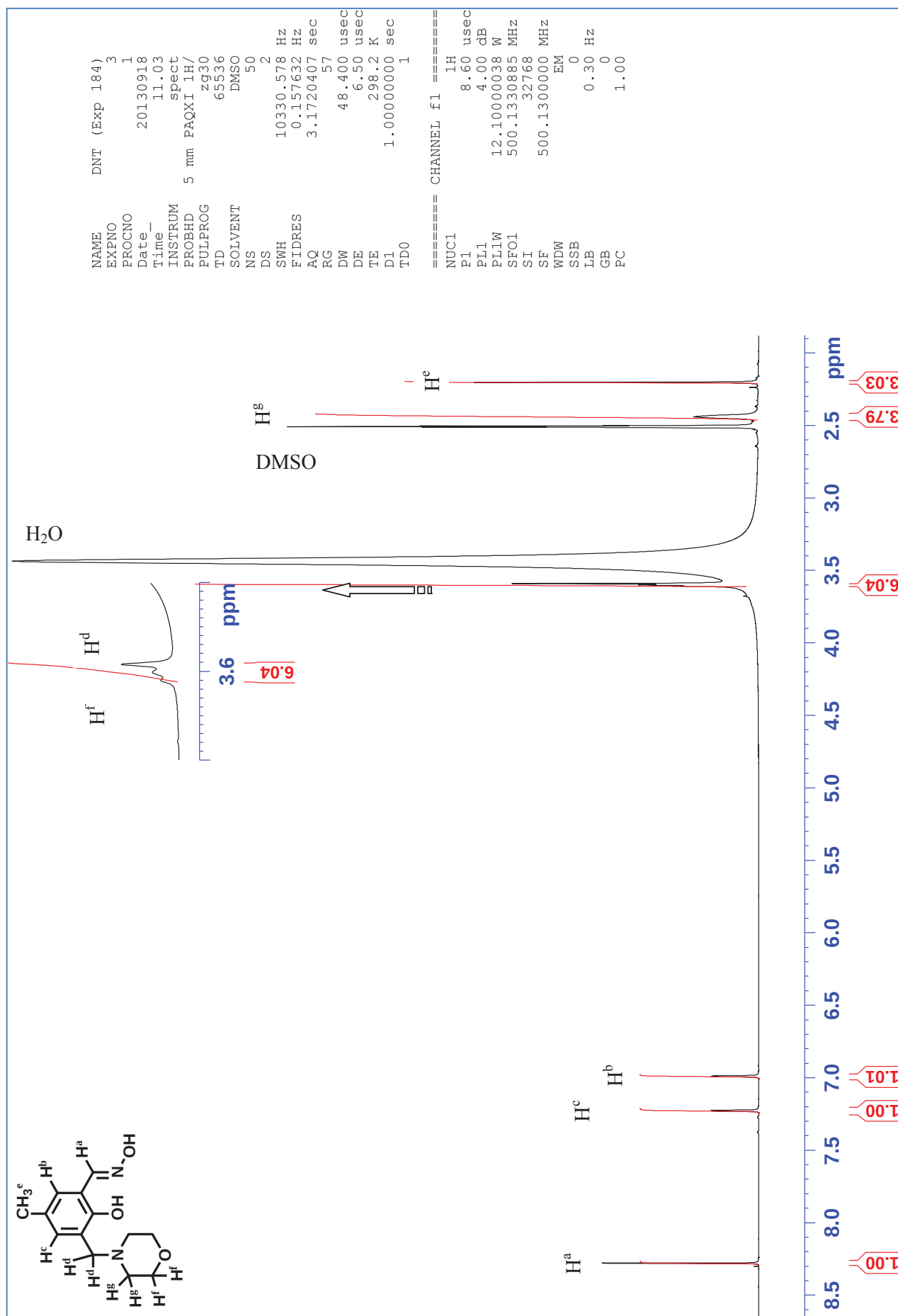
To a solution of Et_3N (3.40 g, 14.8 mmol) in CH_2Cl_2 (80 ml) were added simultaneously over 30 minutes solutions of **1** (1.27 g, 5.54 mmol) and morpholine (1.31 g, 14.8 mmol) each dissolved in dry CH_2Cl_2 (60 ml). The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 100 ml) and the organic phase dried over anhydrous Na_2SO_4 . Removal of the solvent afforded a yellow oil, which was dried *in vacuo* for 24 h. Yield (2.99 g, 86%). IR (KBr pellet): 1674 (s, C=O), 1115 (s, C-O), 1233 (m, C-N) cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.20; H, 7.42; N, 6.12. ^1H NMR (CDCl_3 , 500 MHz): δ 2.30 (s, 3H, CH_3), 2.57 (br, 4H, NCH_2), 3.67 (s, 2H, $\text{Ar-CH}_2\text{N}$), 3.76 (t, 4H, OCH_2), 7.20 (d, $J = 1.72$ Hz, 1H, Ar-H), 7.41 (d, $J = 1.72$ Hz, 1H, Ar-H), 10.21 (s, 1H, CHO). ^{13}C NMR (CDCl_3 , 500 MHz): δ 192.7, 158.7, 137.1, 129.5, 128.5, 123.4, 122.0, 66.7, 59.0, 53.1, 20.2 ppm. ES^+ -MS (m/z) 235 $[\text{M}+\text{H}]^+$.

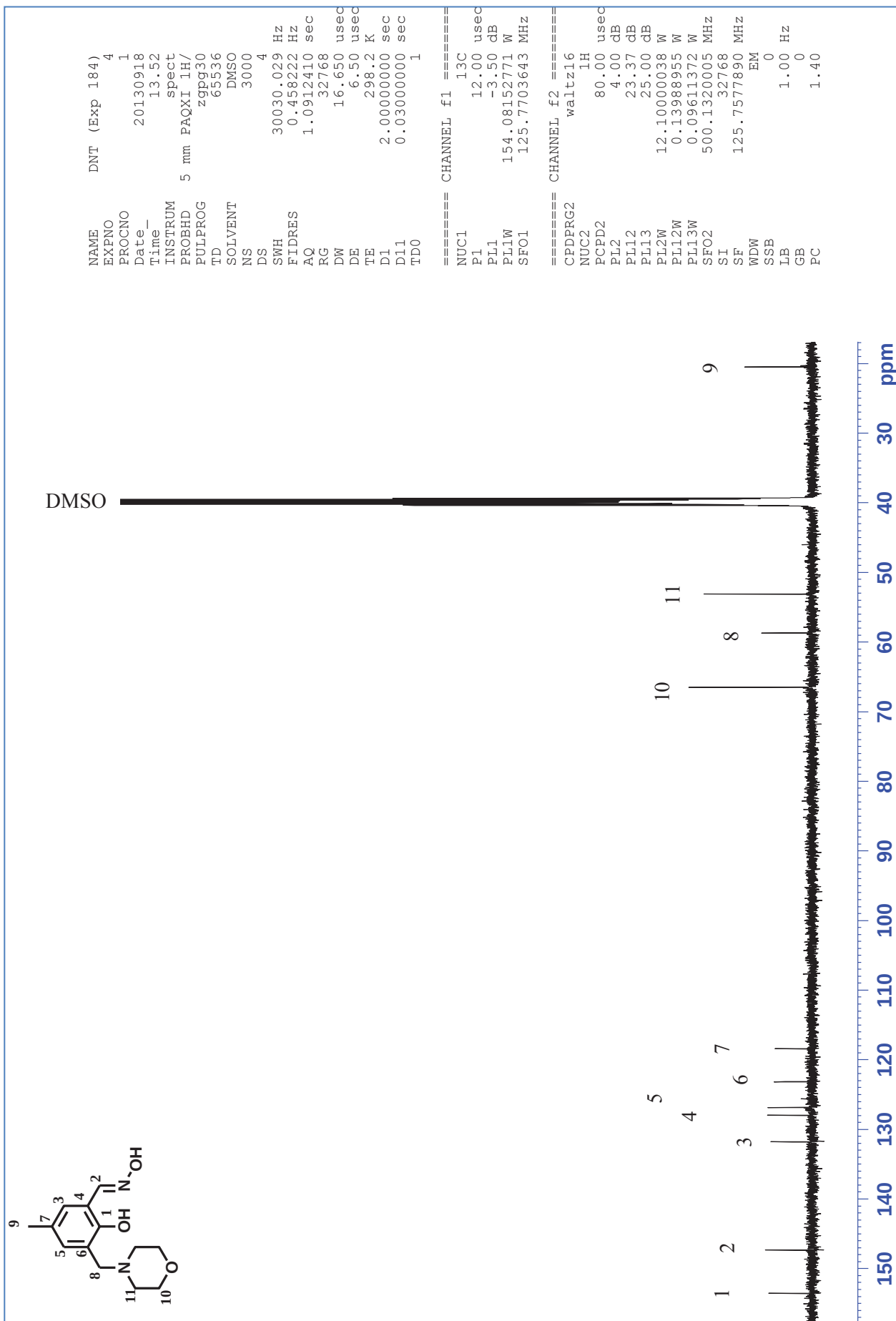


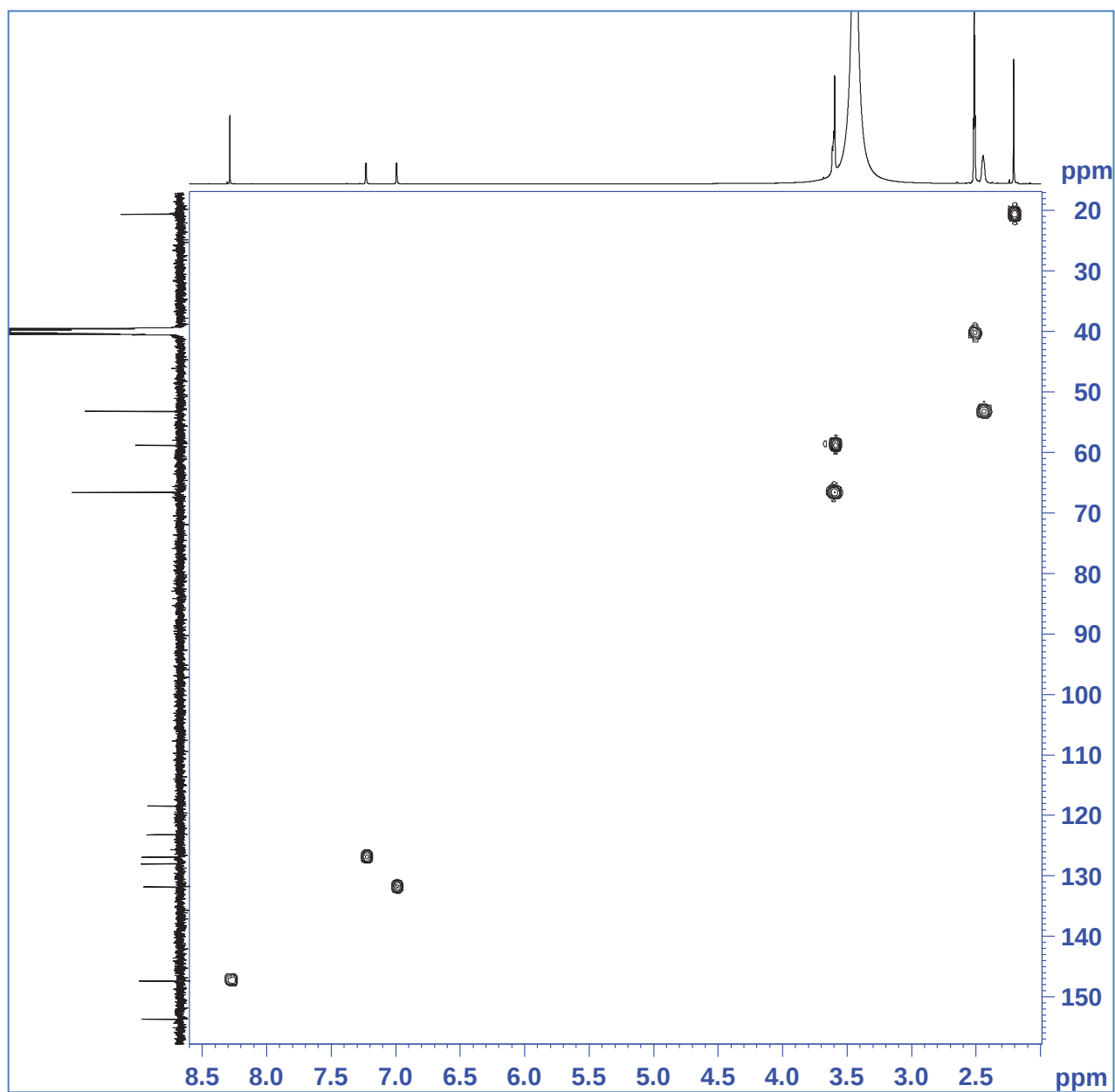


2-hydroxy-5-methyl-3-(4-morpholinylmethyl)-benzaldehydeoxime

A solution of potassium hydroxide (0.662 g, 11.80 mmol) in dry ethanol (100 ml) was added to a solution of hydroxylamine hydrochloride (2.784 g, 11.80 mmol) in dry ethanol (100 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L1a** (2.784 g, 11.80 mmol) in dry ethanol (200 ml) over 30 min. The pale yellow solution was stirred for a further 24 h at RT. The solution was washed with water (3 x 100 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a yellow solid, which was washed with cold ethanol (70 ml). The resulting white powder was dried *in vacuo* for 24 h. Yield (1.250 g, 42%). Mp 194.5–196.5 °C. IR (KBr pellet): 1618 (s, C=N), 2964 (m, C-H), 1471 (s, C-H), 1267 (m, C-O), 1111 (s, N-O) cm⁻¹. Anal. Calcd for C₁₃H₁₈N₂O₃: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.34; H, 7.34; N, 10.95. ¹H NMR (DMSO, 500 MHz): δ 2.03 (s, 3H, CH₃), 2.44 (br, 4H, NCH₂), 3.59 (s, 2H, Ar-CH₂N), 3.59 (t, 4H, OCH₂), 6.98 (d, *J* = 1.82 Hz, 1H, Ar-H), 7.22 (d, *J* = 1.87 Hz, 1H, Ar-H), 8.28 (s, 1H, CHN). ¹³C NMR (DMSO, 500 MHz): δ 153.5, 147.2, 131.7, 127.9, 126.8, 123.1, 118.4, 66.5, 58.7, 53.1, 20.5 ppm. ES⁺-MS (*m/z*) 251 [M+H]⁺.



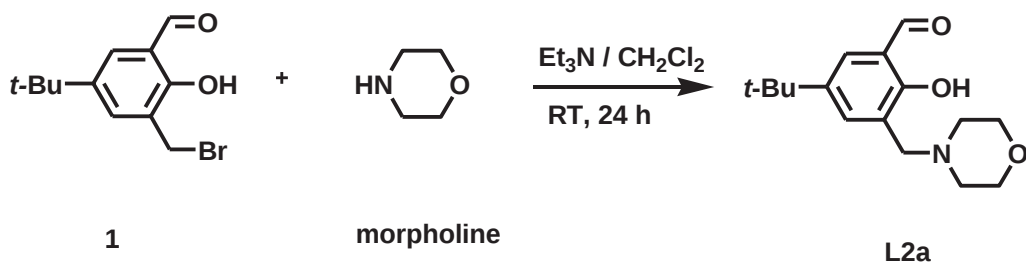




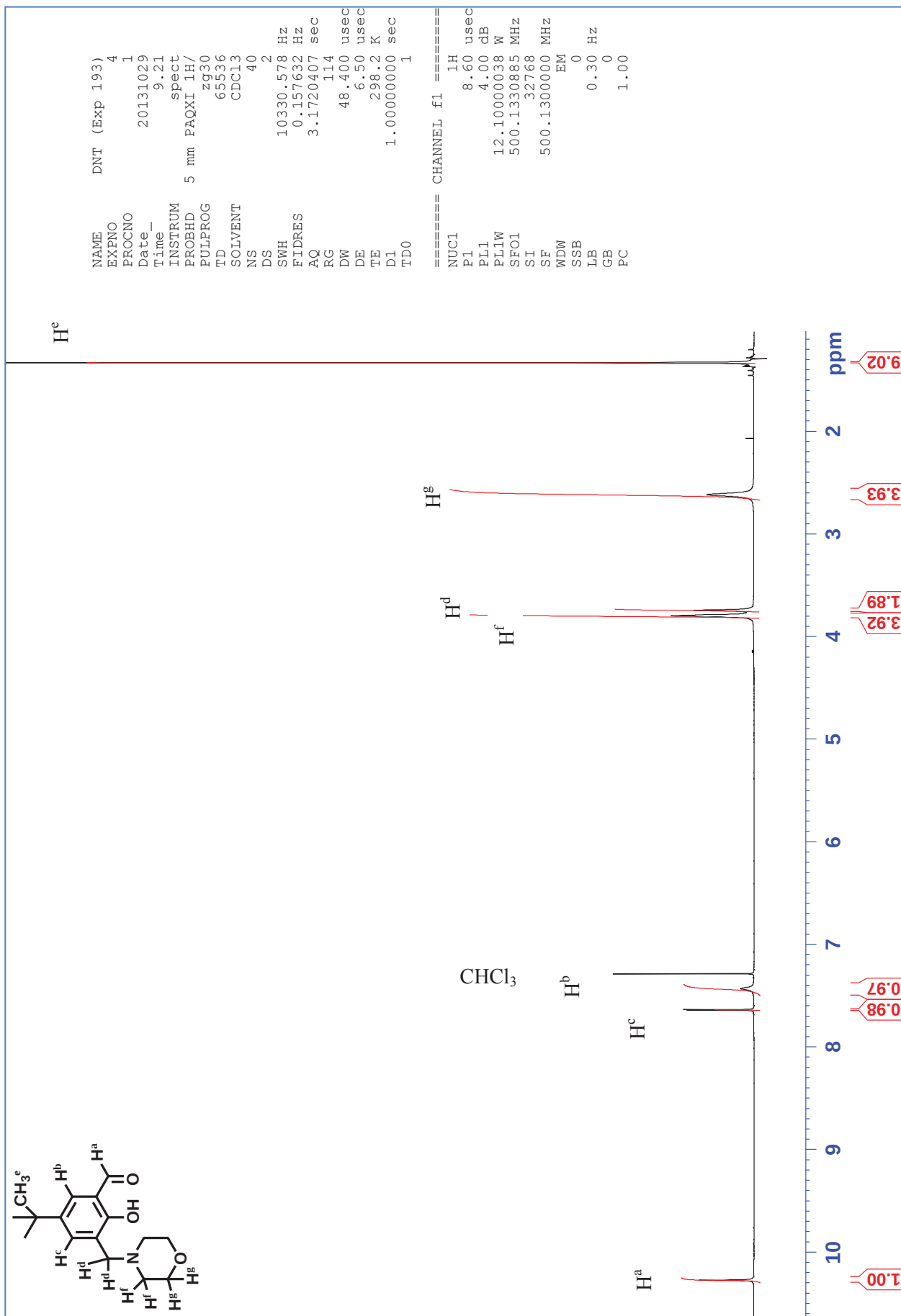
HMQC experiment of **L1**

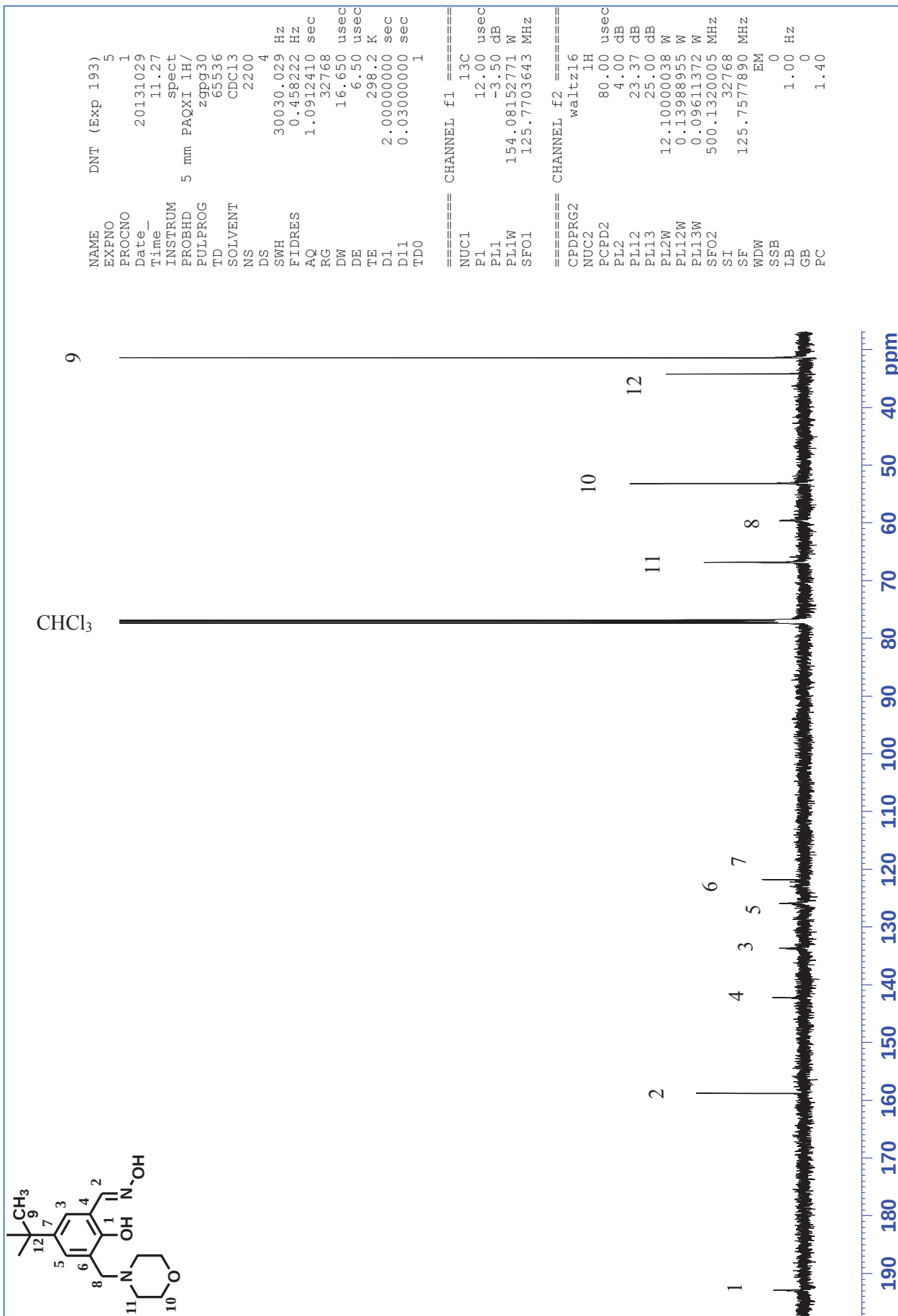
L2a

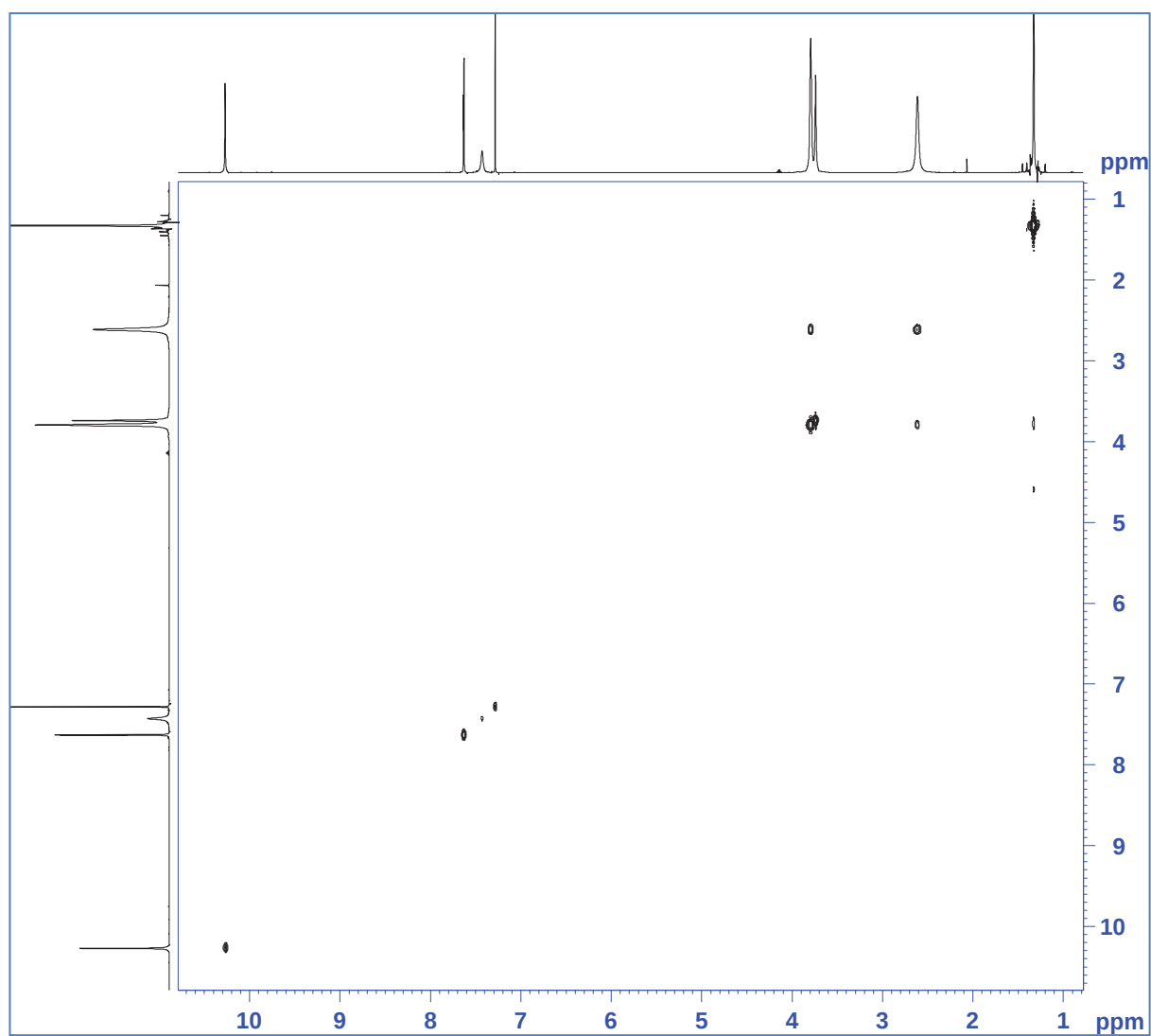
5-(1,1-dimethylethyl)-2-hydroxy-3-(4-morpholinylmethyl)-benzaldehyde



To a solution of Et₃N (1.13 g, 11.0 mmol) in CH₂Cl₂ (80 ml) were added simultaneously over 30 minutes solutions of **1** (3.00 g, 11.0 mmol) and morpholine (0.98 g, 11.0 mmol) each dissolved in dry CH₂Cl₂ (60 ml). The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 200 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a yellow oil, which was column purified (Hexane : EtOAc / 7:3, *R_f* = 0.36) and dried *in vacuo* for 24 h to afford a yellow solid. Yield (2.74 g, 89%). Mp 94.5-96.5 °C. IR (KBr pellet): 1670 (s, C=O), 1118 (s, C-O), 1235 (m, C-N) cm⁻¹. Anal. Calcd for C₁₆H₂₃NO₃: C, 69.26; H, 8.36; N, 5.05. Found: C, 69.50; H, 8.43; N, 5.10. ¹H NMR (CDCl₃, 500 MHz): δ 1.32 (s, 9H, C(CH₃)₃), 2.61 (br, 4H, O(CH₂)₂), 3.74 (s, 2H, Ar-CH₂N), 3.76 (t, 4H, CH₂N(CH₂)₂), 7.43 (br, 1H, Ar-H), 7.63 (d, *J* = 2.55 Hz, 1H, Ar-H), 10.26 (s, 1H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 192.7, 158.7, 142.1, 133.5, 125.8, 121.7, 77.2, 66.7, 59.5, 53.1, 34.1, 31.3 ppm. ES⁺-MS (*m/z*) 278 [M+H]⁺.



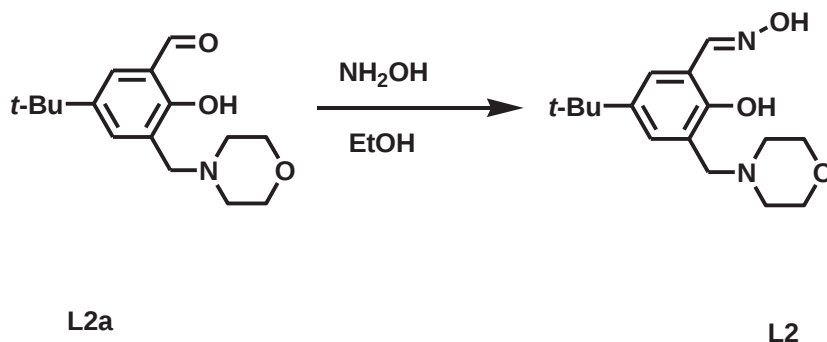




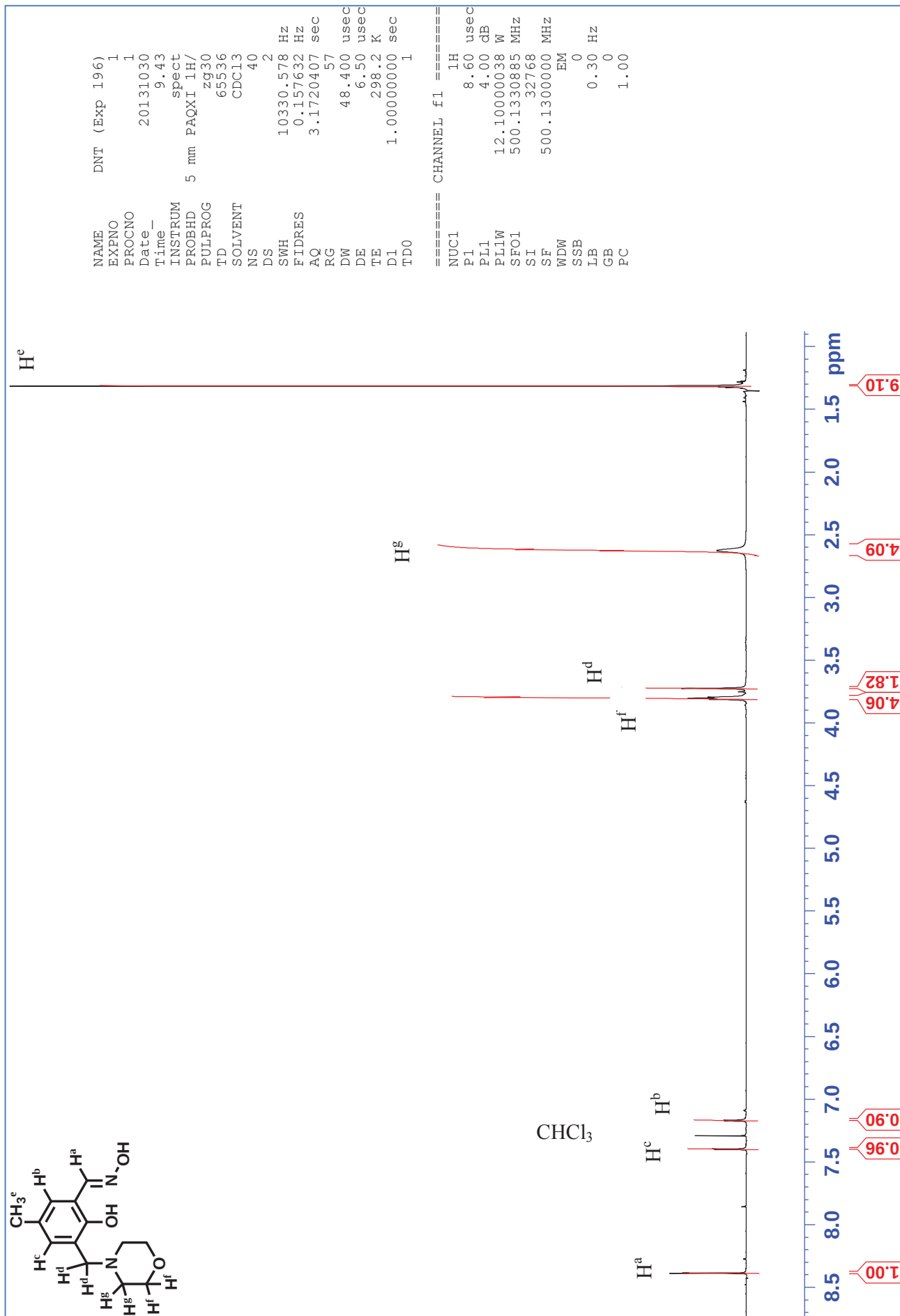
COSY experiment of **L2a**

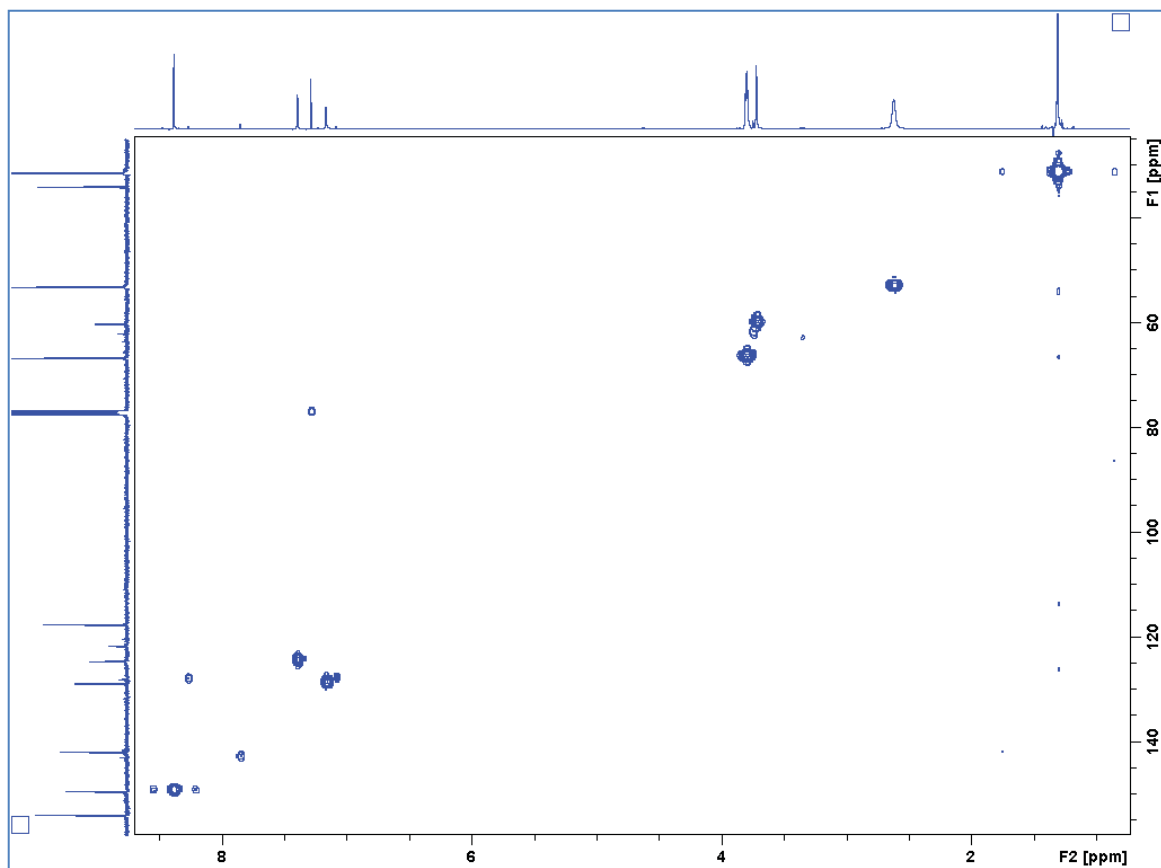
L2

5-(1,1-dimethylethyl)-2-hydroxy-3-(4-morpholinylmethyl)-benzaldehydeoxime

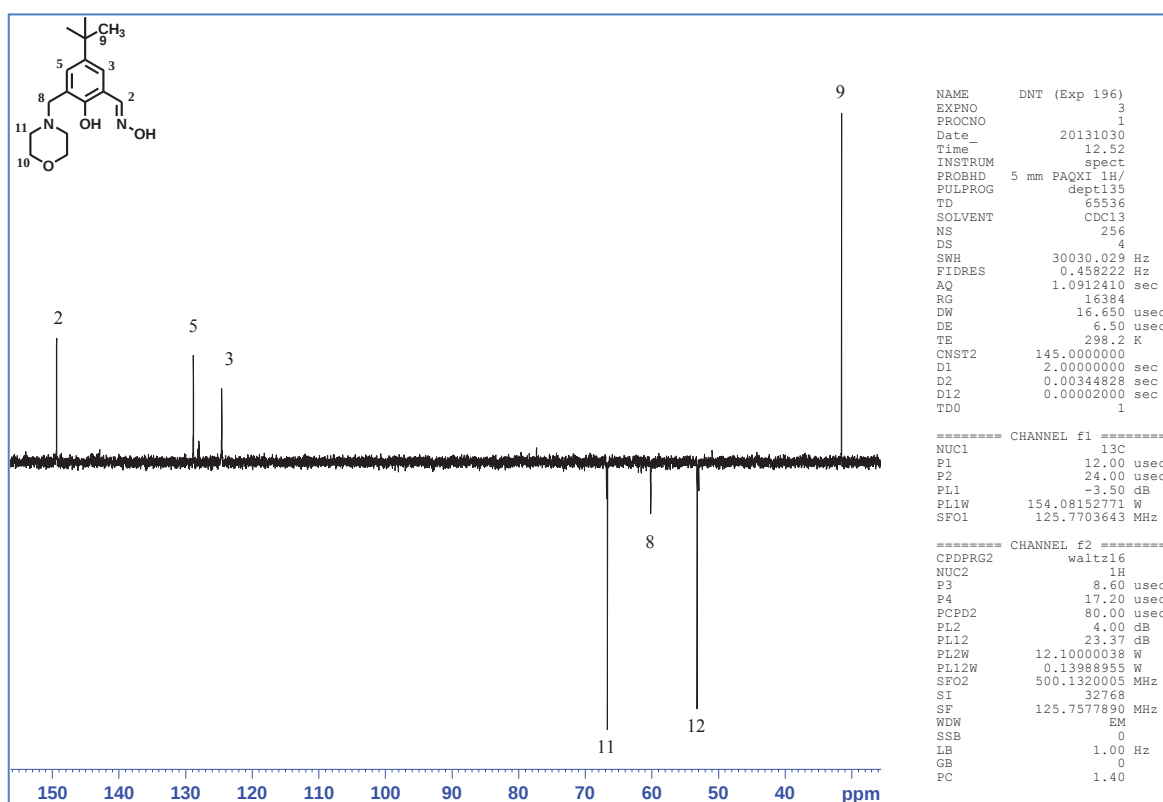


A solution of potassium hydroxide (0.364 g, 6.49 mmol) in dry ethanol (100 ml) was added to a solution of hydroxylamine hydrochloride (0.451 g, 6.49 mmol) in dry ethanol (100 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L2a** (1.800 g, 6.49 mmol) in dry ethanol (150 ml) over 30 min. The pale yellow solution was stirred for a further 24 h at RT. The solution was washed with water (3 x 100 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a yellow solid, which was dried *in vacuo* for 24 h. Yield (1.430 g, 76%). Mp 154.7-157.2 °C. IR (KBr pellet): 1617 (s, C=N), 2962 (m, C-H), 1476 (s, C-H), 1115 (s, C-O) cm⁻¹. Anal. Calcd for C₁₆H₂₄N₂O₃·0.5H₂O: C, 63.76; H, 8.36; N, 9.30. Found: C, 63.51; H, 8.05; N, 9.14. ¹H NMR (CDCl₃, 500 MHz): δ 1.30 (s, 9H, C(CH₃)₃), 2.62 (br, 4H, CH₂N(CH₂)₂), 3.72 (s, 2H, Ar-CH₂N), 3.59 (t, *J* = 4.47 Hz, 4H, O(CH₂)₂), 7.16 (d, *J* = 2.17 Hz, 1H, Ar-H), 7.39 (d, *J* = 2.44 Hz, 1H, Ar-H), 8.38 (s, 1H, CHN). ¹³C NMR (CDCl₃, 500 MHz): δ 153.9, 149.3, 141.8, 128.7, 124.5, 121.5, 117.4, 66.7, 60.1, 53.1, 34.0, 31.4 ppm. ES⁺-MS (*m/z*) 293 [M+H]⁺.

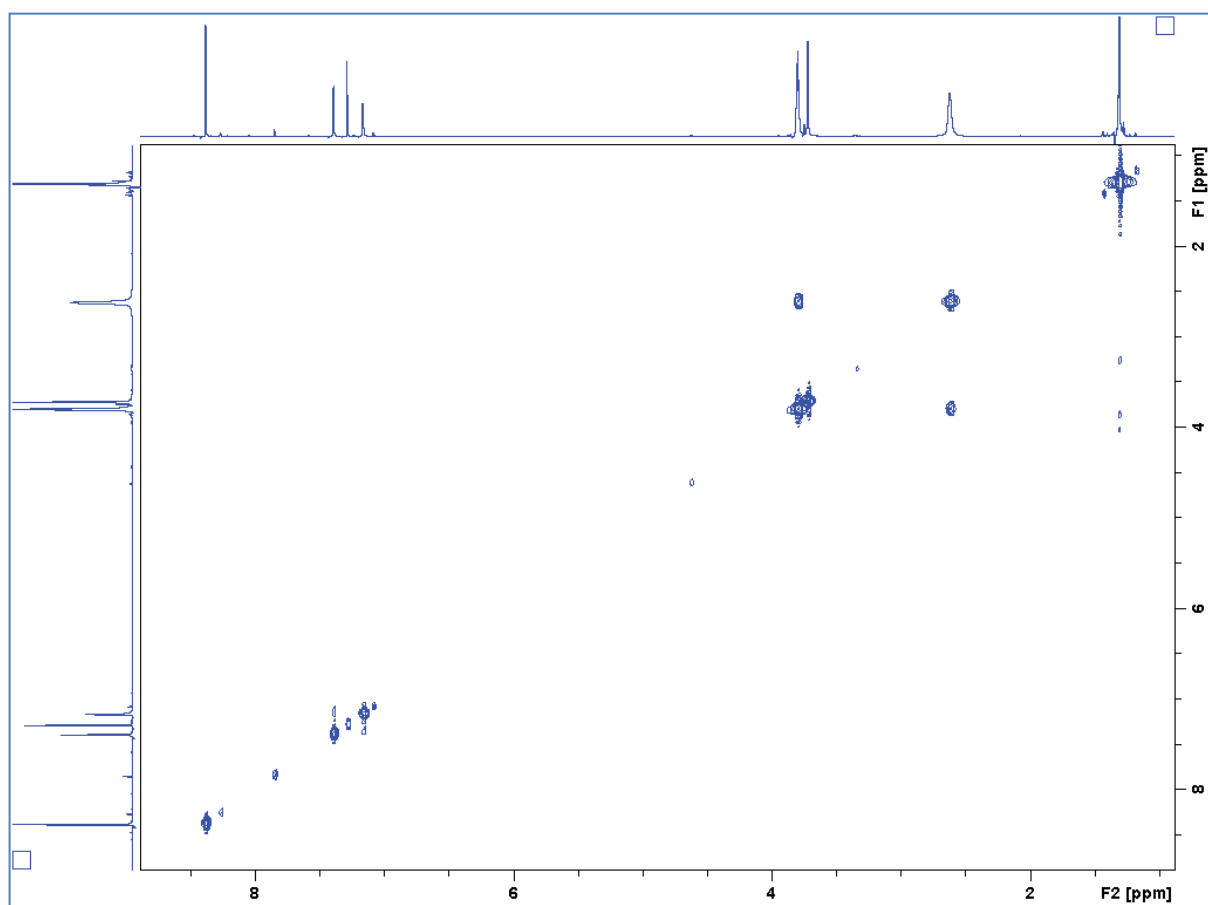




HMQC experiment of L2



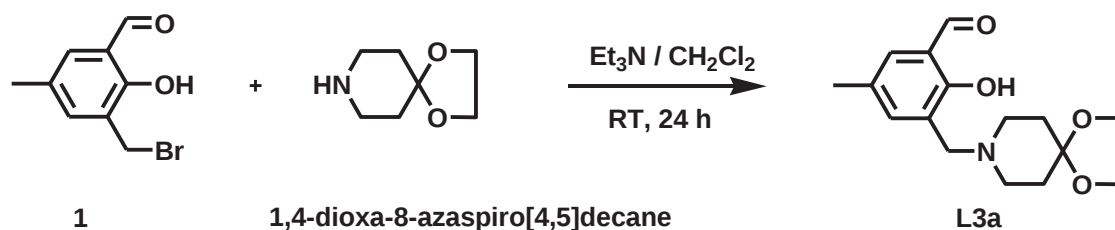
DEPT 135 experiment of L2



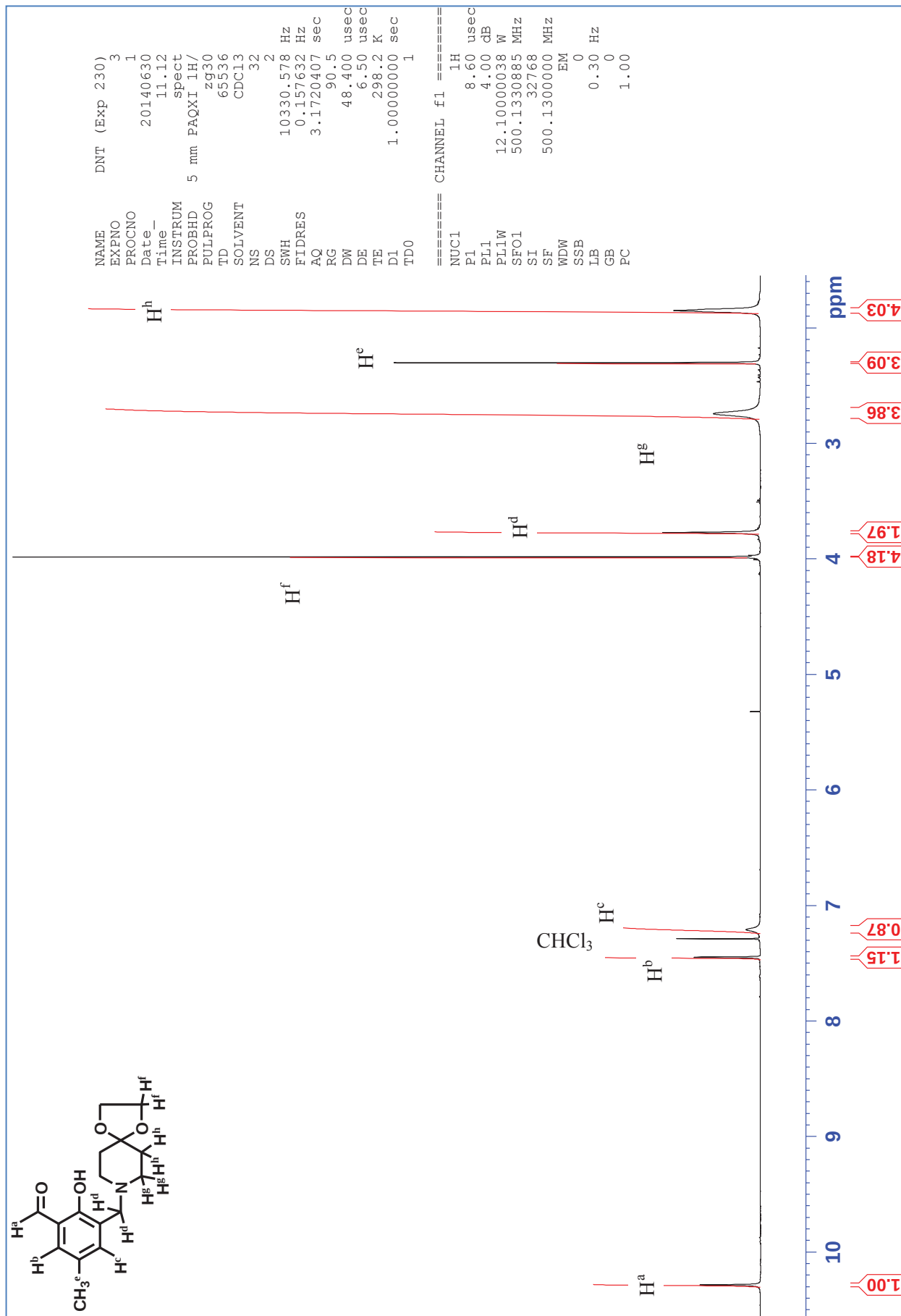
COSY experiment of **L2**

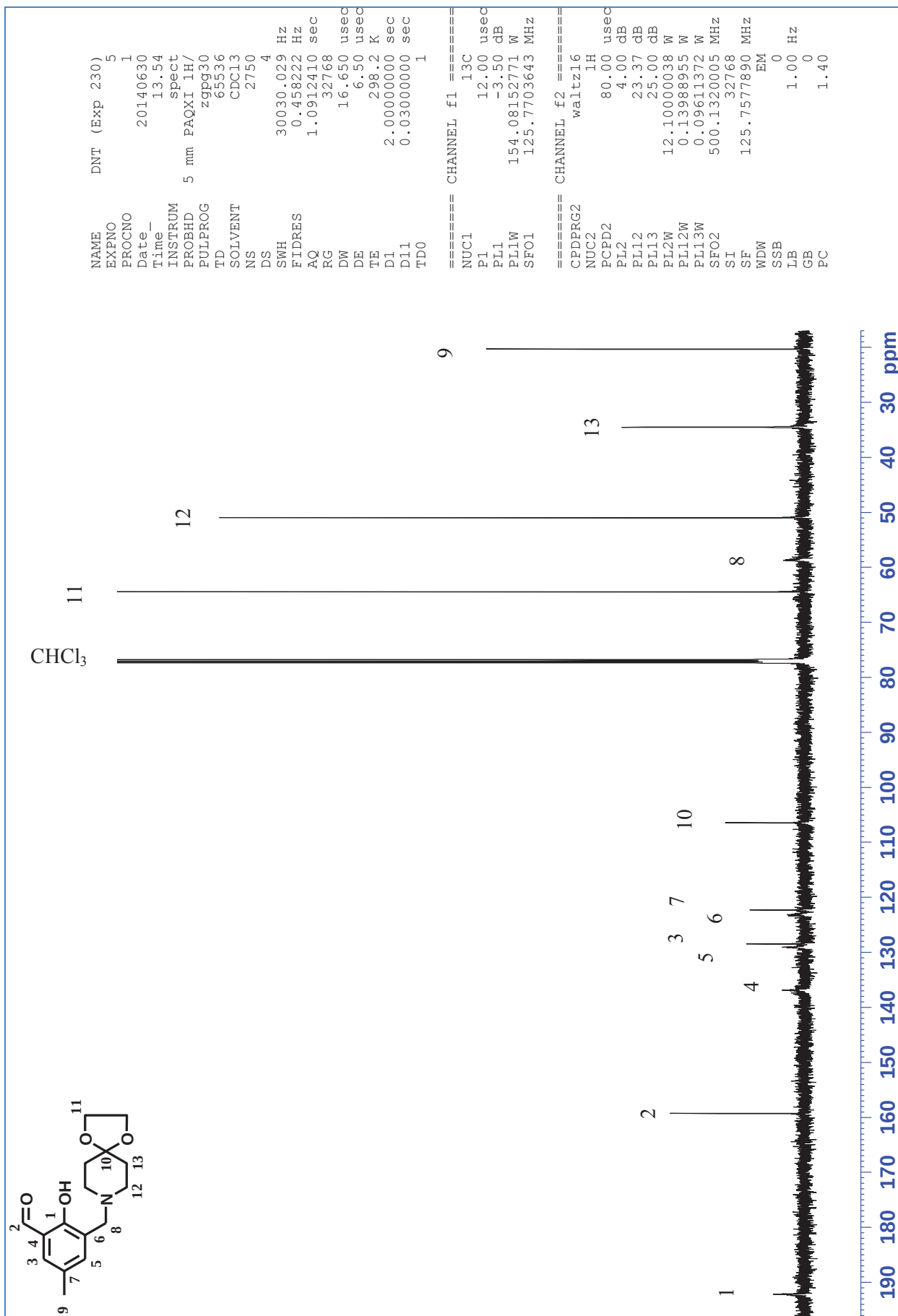
L3a

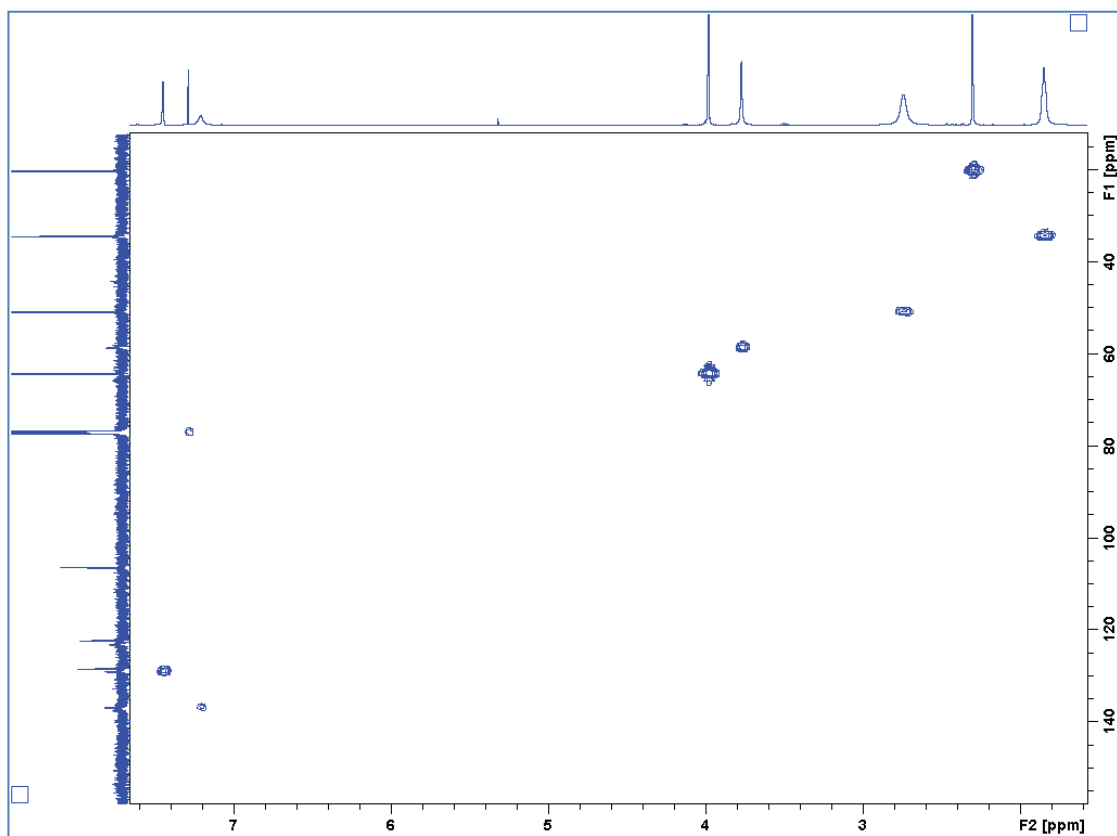
2-hydroxy-5-methyl-3-(4-(1,4-dioxo-8-azaspiro[4,5]dec-8-ylmethyl))-benzaldehyde



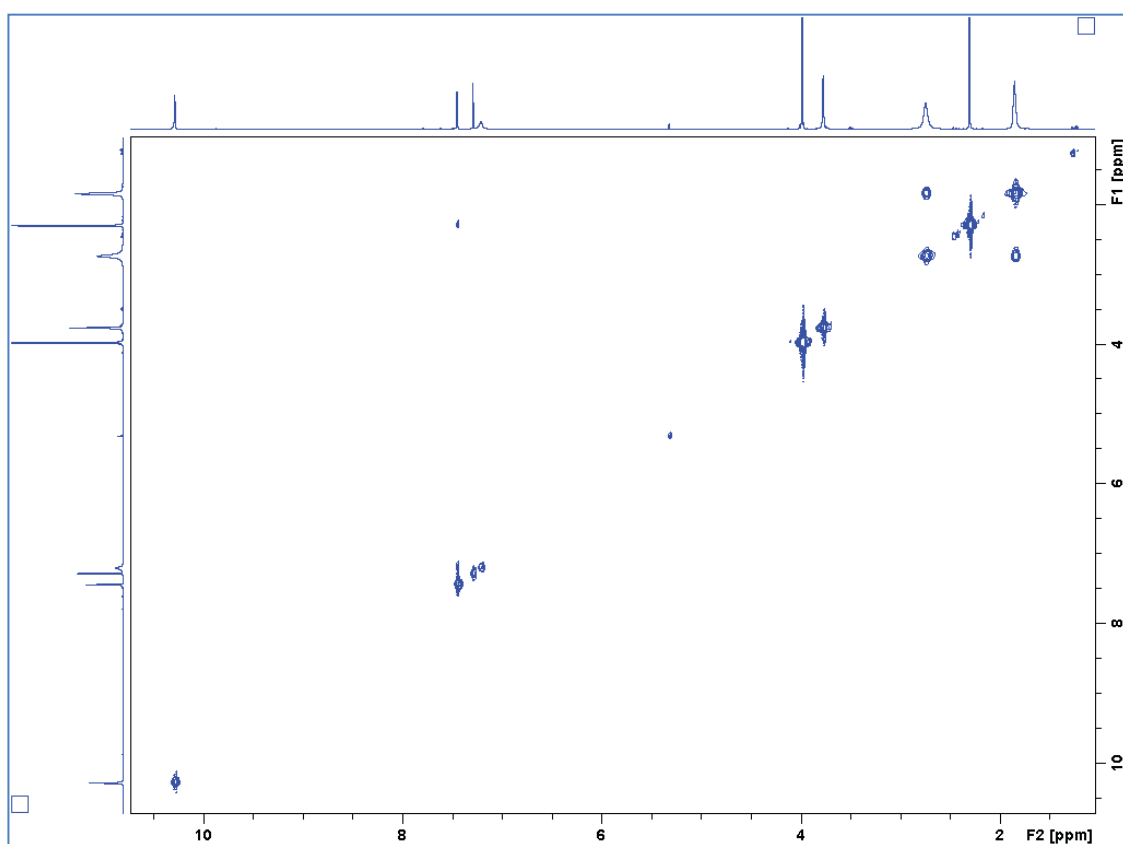
To a solution of Et_3N (0.88 g, 8.73 mmol) in dry CH_2Cl_2 (60 ml) were added simultaneously over 30 minutes solutions of **1** (2.00 g, 8.73 mmol) and 1,4-dioxo-8-azaspiro[4,5]decane (1.25 g, 8.73 mmol), each dissolved in dry CH_2Cl_2 (40 ml). The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 150 ml) and the organic phase dried over anhydrous Na_2SO_4 . Removal of the solvent afforded a yellow solid, which was dried *in vacuo* for 24 h. Yield (2.31 g, 91%). Mp 146-150 °C. IR (KBr pellet): 1678 (s, C=O), 1471 (m, Ar-C=C), 1094 (s, C-O), 1151 (s, C-O) cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.88; H, 7.16; N, 4.73. ^1H NMR (CDCl_3 , 500 MHz): δ 1.84 (br, 4H, NCH_2CH_2), 2.30 (s, 3H, ArCH_3), 2.74 (br, 4H, NCH_2CH_2), 3.77 (s, 2H, ArCH_2N), 3.98 (s, 4H, CHOCH_2), 7.26 (br, 1H, Ar-H), 7.44 (d, $J = 1.32$ Hz, 1H, Ar-H), 10.28 (s, 1H, CHO). ^{13}C NMR (CDCl_3 , 500 MHz): δ 192.1, 159.2, 136.8, 129.0, 128.4, 123.5, 122.2, 106.4, 64.3, 58.6, 50.9, 34.4, 20.2 ppm. ES^+ -MS (m/z) 292 $[\text{M}+\text{H}]^+$.



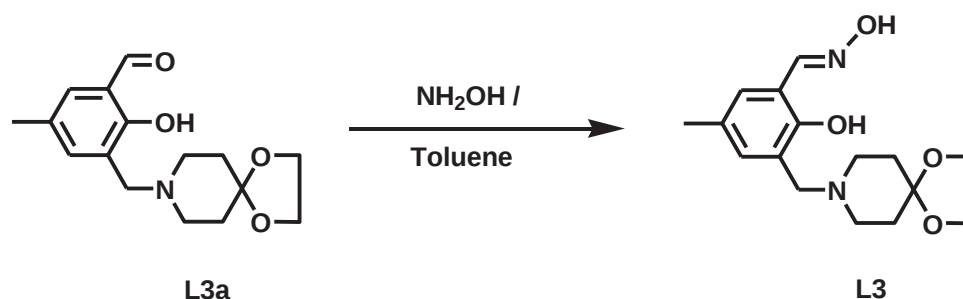




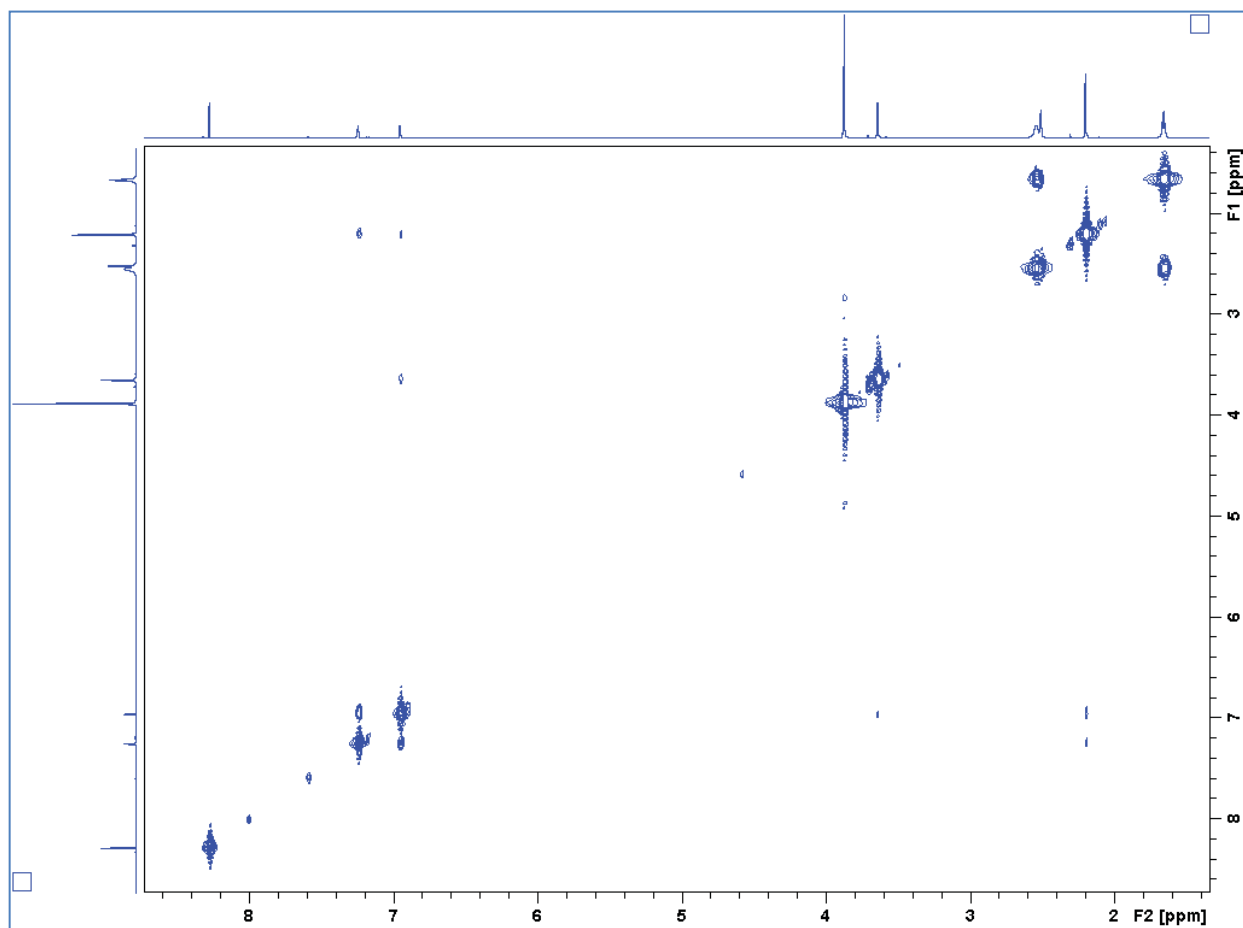
HMQC experiment of **L3a**



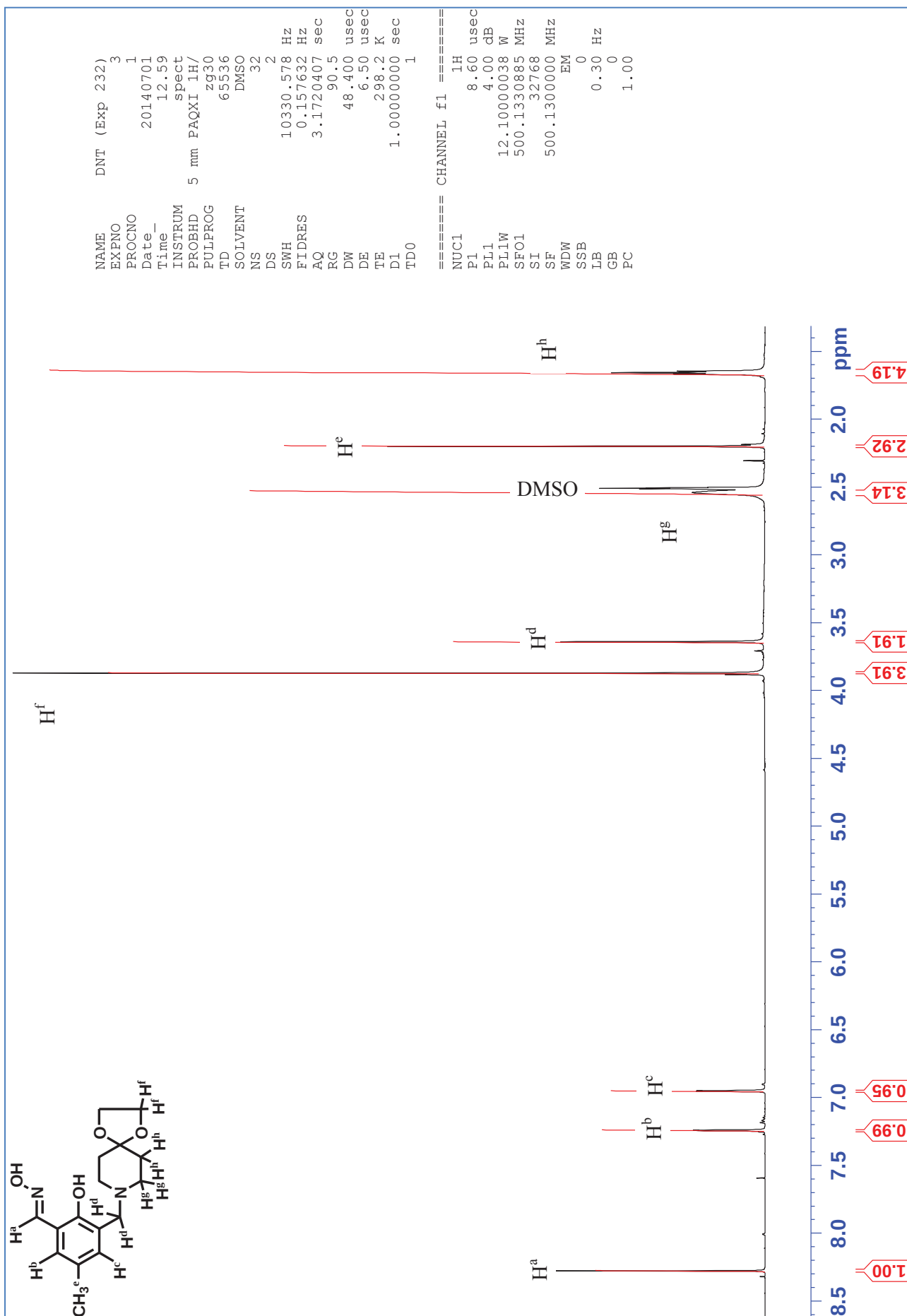
COSY experiment of **L3a**

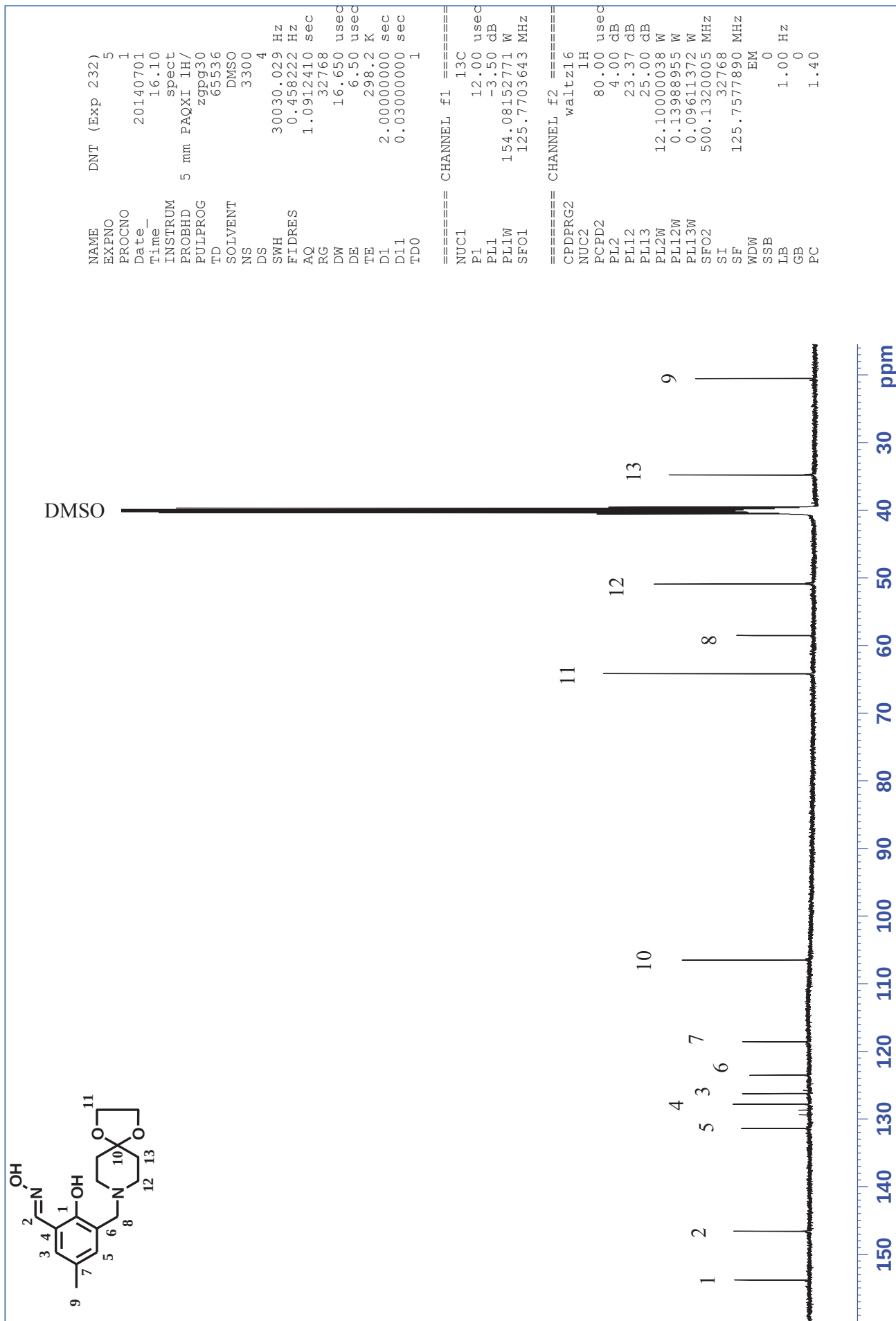
2-hydroxy-5-methyl-3-(4-(1,4-dioxo-8-azaspiro[4,5]dec-8-ylmethyl))-benzaldehydeoxime

A solution of potassium hydroxide (0.768 g, 13.70 mmol) in dry ethanol (50 ml) was added to a solution of hydroxylamine hydrochloride (0.952 g, 13.70 mmol) in dry ethanol (50 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L3a** (2.000 g, 6.84 mmol) in dry toluene (100 ml) over 30 min. The pale yellow solution was stirred for a further 24 h at RT. A white powder precipitated and was filtered, washed with EtOH (100 ml), and dried *in vacuo* for 24 h. Yield (1.7 g, 83%). Mp 189-193 °C. IR (KBr pellet): 1610 (s, C=N), 2942 (m, C-H), 1469 (s, C-H), 1091 (s, C-O) cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.82; H, 7.29; N, 8.96. ^1H NMR (DMSO, 500 MHz): δ 1.64 (t, $J = 5.55$ Hz, 4H, NCH_2CH_2), 2.20 (s, 3H, ArCH_3), 2.54 (br, 4H, NCH_2CH_2), 3.64 (s, 2H, ArCH_2N), 3.87 (s, 4H, CHOCH_2), 6.95 (d, $J = 1.80$ Hz, 1H, Ar-H), 7.24 (d, $J = 1.76$ Hz, 1H, Ar-H), 8.27 (s, 1H, CHN). ^{13}C NMR (DMSO, 500 MHz): δ 153.8, 146.5, 131.3, 127.7, 126.2, 123.5, 118.5, 106.4, 64.1, 58.4, 50.8, 34.8, 20.5 ppm. ES^+ -MS (m/z) 330 $[\text{M}+\text{Na}]^+$.

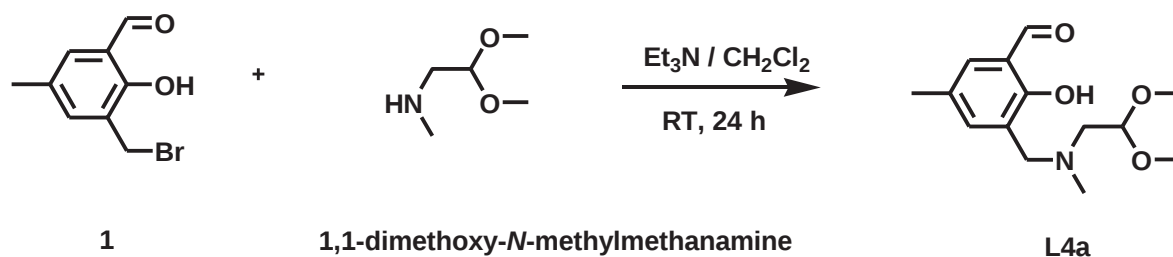


COSY experiment of **L3**

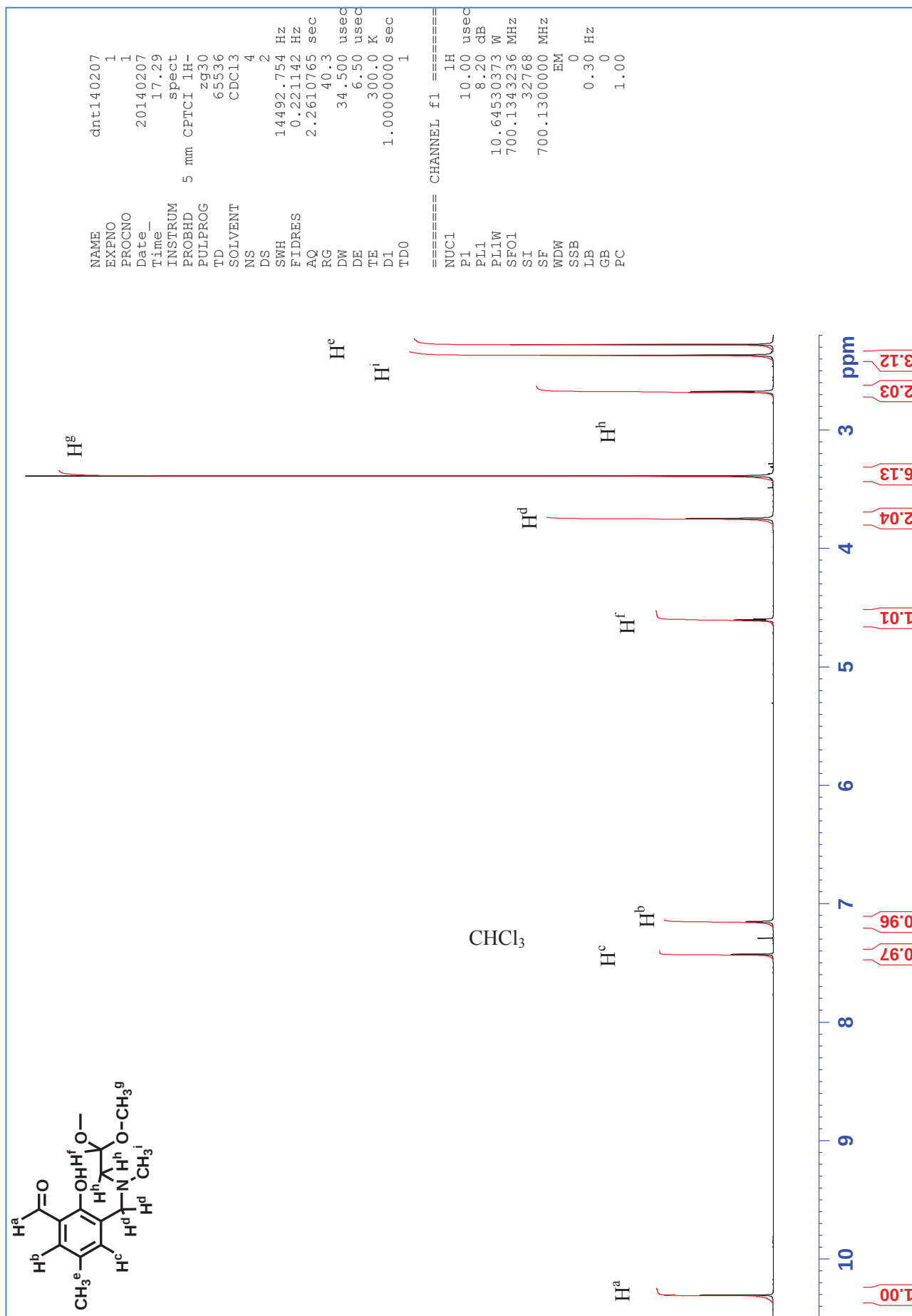


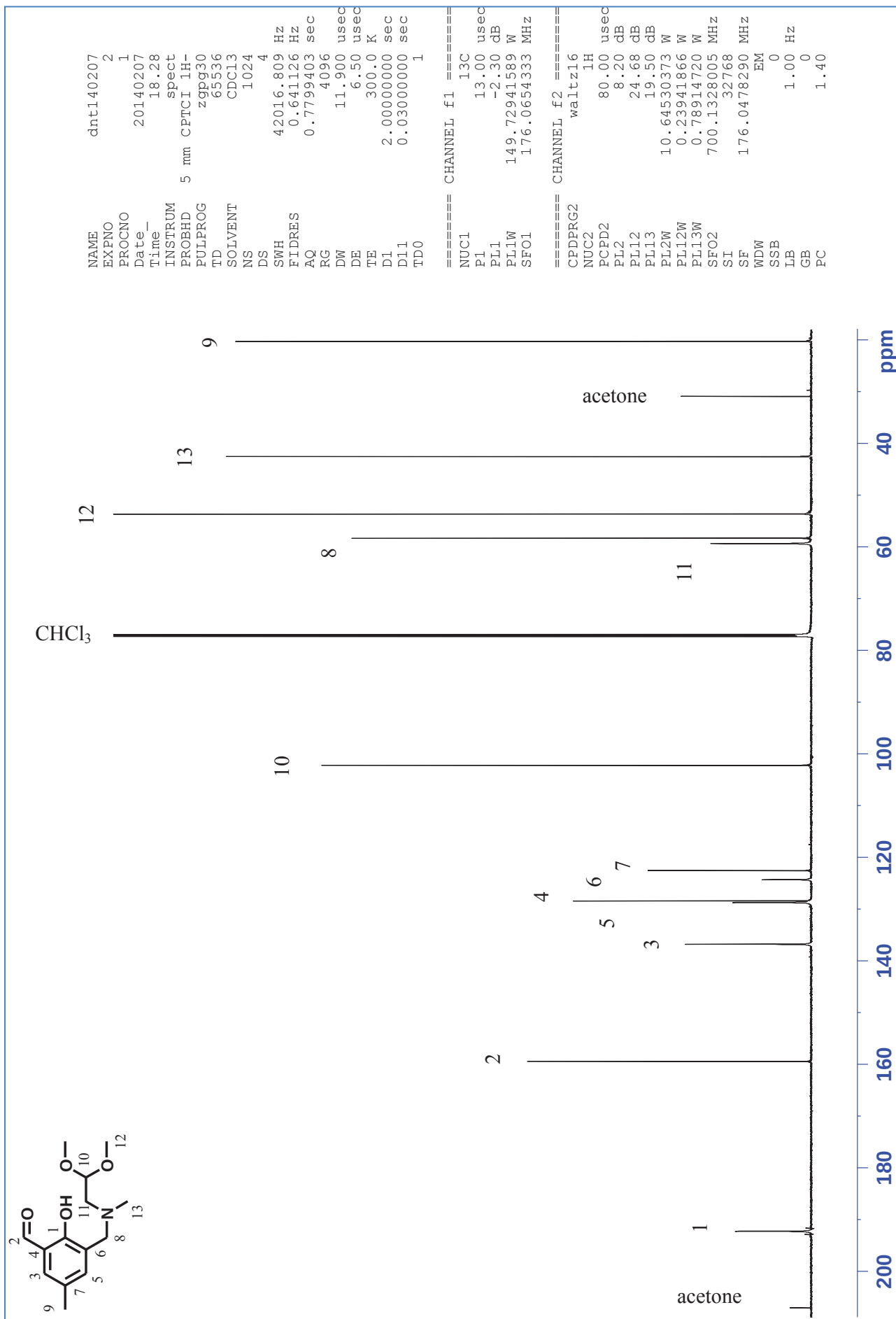


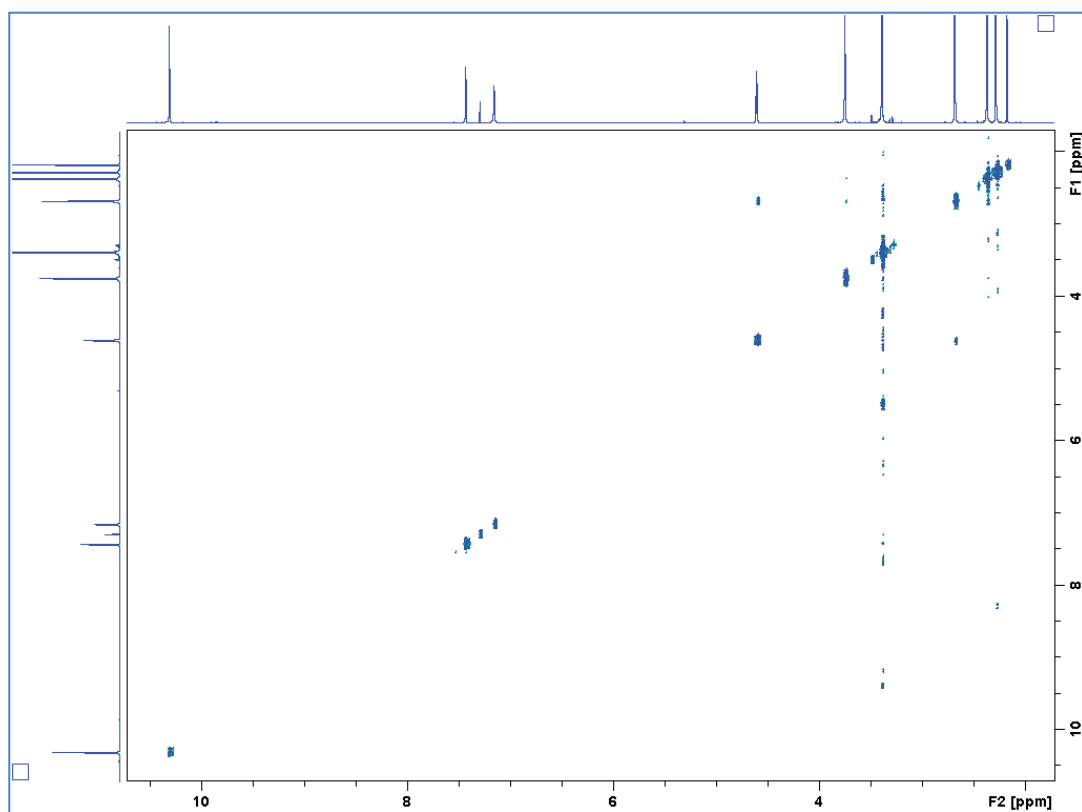
2-hydroxy-5-methyl-3-(4-(1,1-dimethoxy-N-methylmethanamino))-benzaldehyde



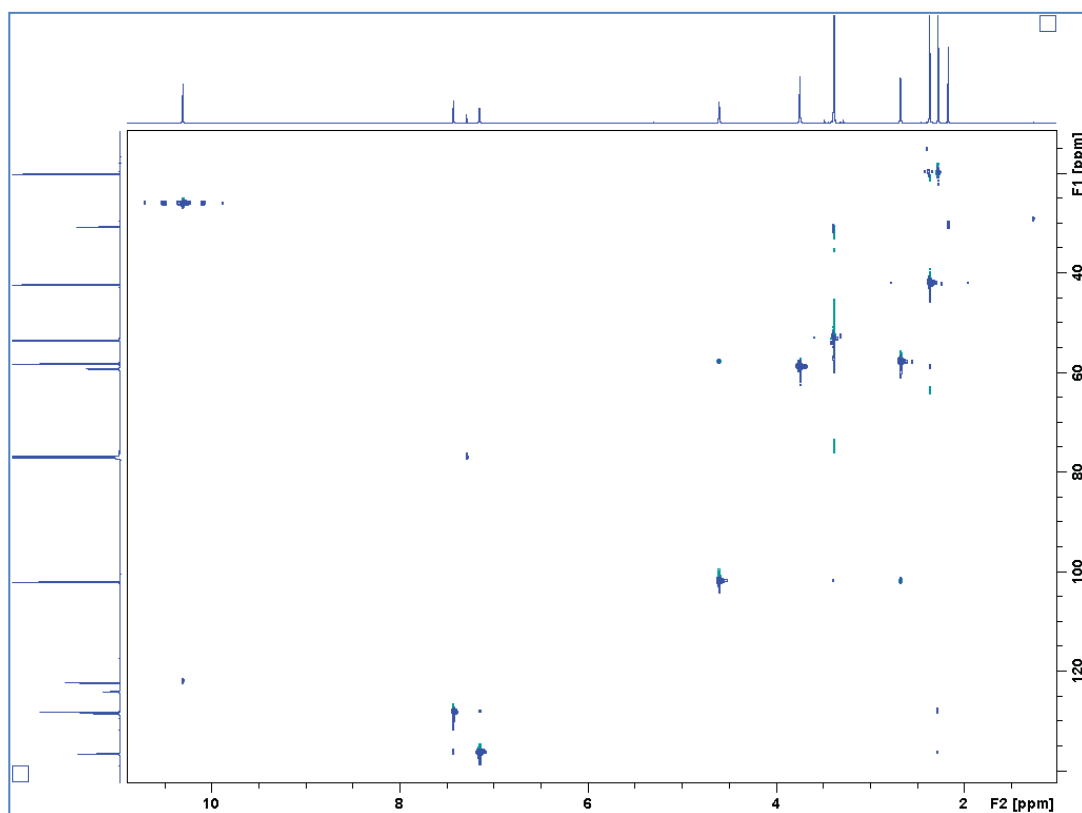
To a solution of Et₃N (0.84 g, 8.39 mmol) in dry CH₂Cl₂ (60 ml) were added simultaneously over 30 minutes solutions of **1** (1.92 g, 8.39 mmol) and 1,1-dimethoxy-N-methylmethanamine (1.00 g, 8.39 mmol) each dissolved in dry CH₂Cl₂ (40 ml). The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 150 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a yellow oil, which was dried *in vacuo*. Yield (1.95 g, 87%). IR (KBr pellet): 1677 (s, C=O), 1467 (m, Ar-C=C), 1088 (s, C-O), 1148 (s, C-O) cm⁻¹. Anal. Calcd for C₁₄H₂₁NO₄: C, 62.90; H, 7.92; N, 5.24. Found: C, 62.91; H, 8.10; N, 5.23. ¹H NMR (CDCl₃, 700 MHz): δ 2.27 (s, 3H, ArCH₃), 2.36 (s, 3H, NCH₃), 2.67 (s, 2H, ArCH₂N(CH₃)CH₂-), 3.38 (s, 6H, -OCH₃), 3.74 (s, 2H, ArCH₂N), 4.59 (t, *J* = 5.35 Hz, 1H, -CH₂CH(OCH₃)₂), 7.15 (br, 1H, Ar-H), 7.42 (d, *J* = 1.81 Hz, 1H, Ar-H), 10.30 (s, 1H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 192.1, 159.2, 136.6, 128.5, 128.2, 124.1, 122.3, 102.1, 59.3, 58.3, 53.6, 42.5, 20.2 ppm. ES⁺-MS (*m/z*) 268 [M+H]⁺.





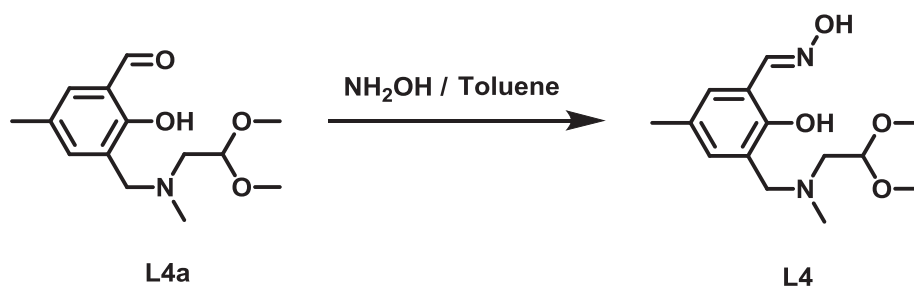


ROESY experiment of **L4a**

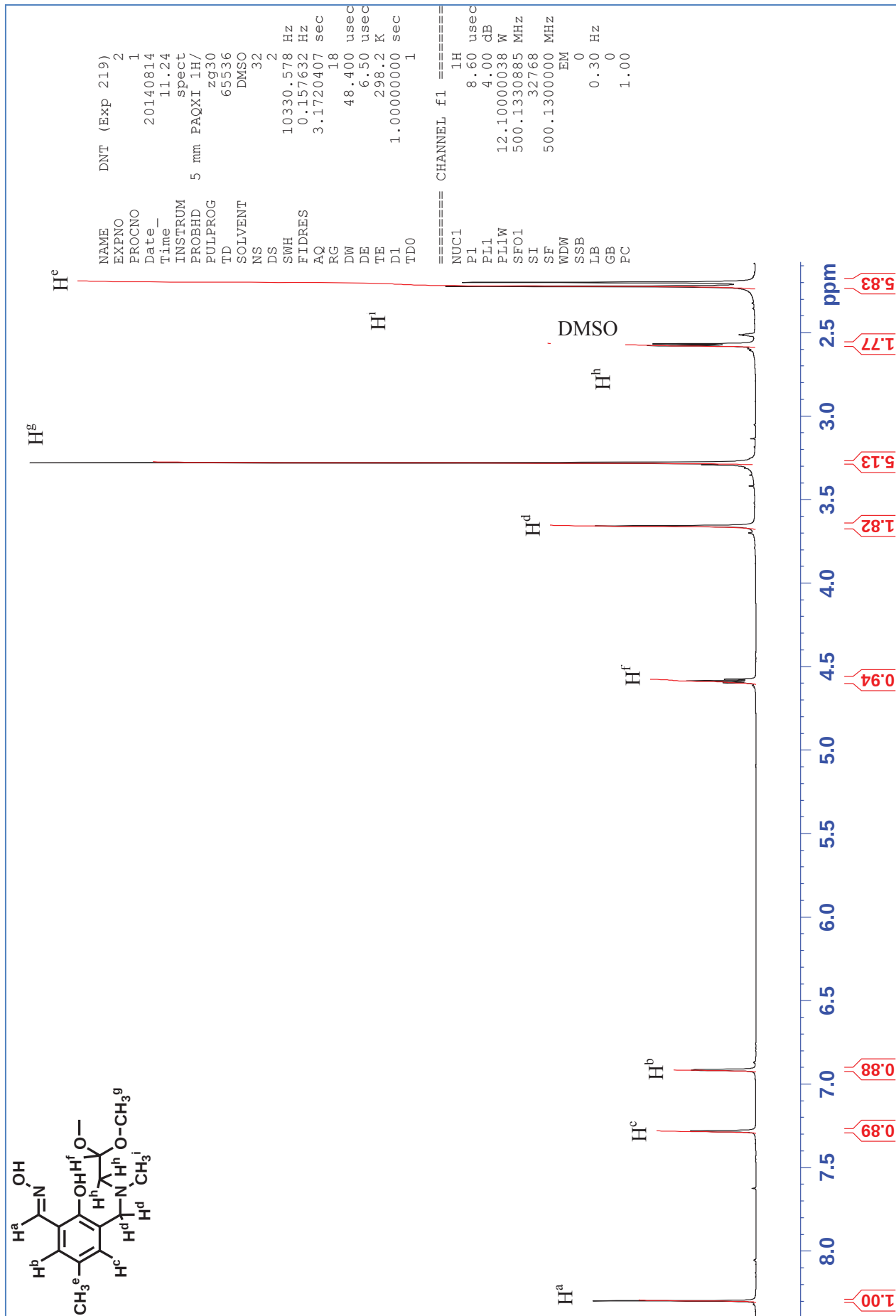


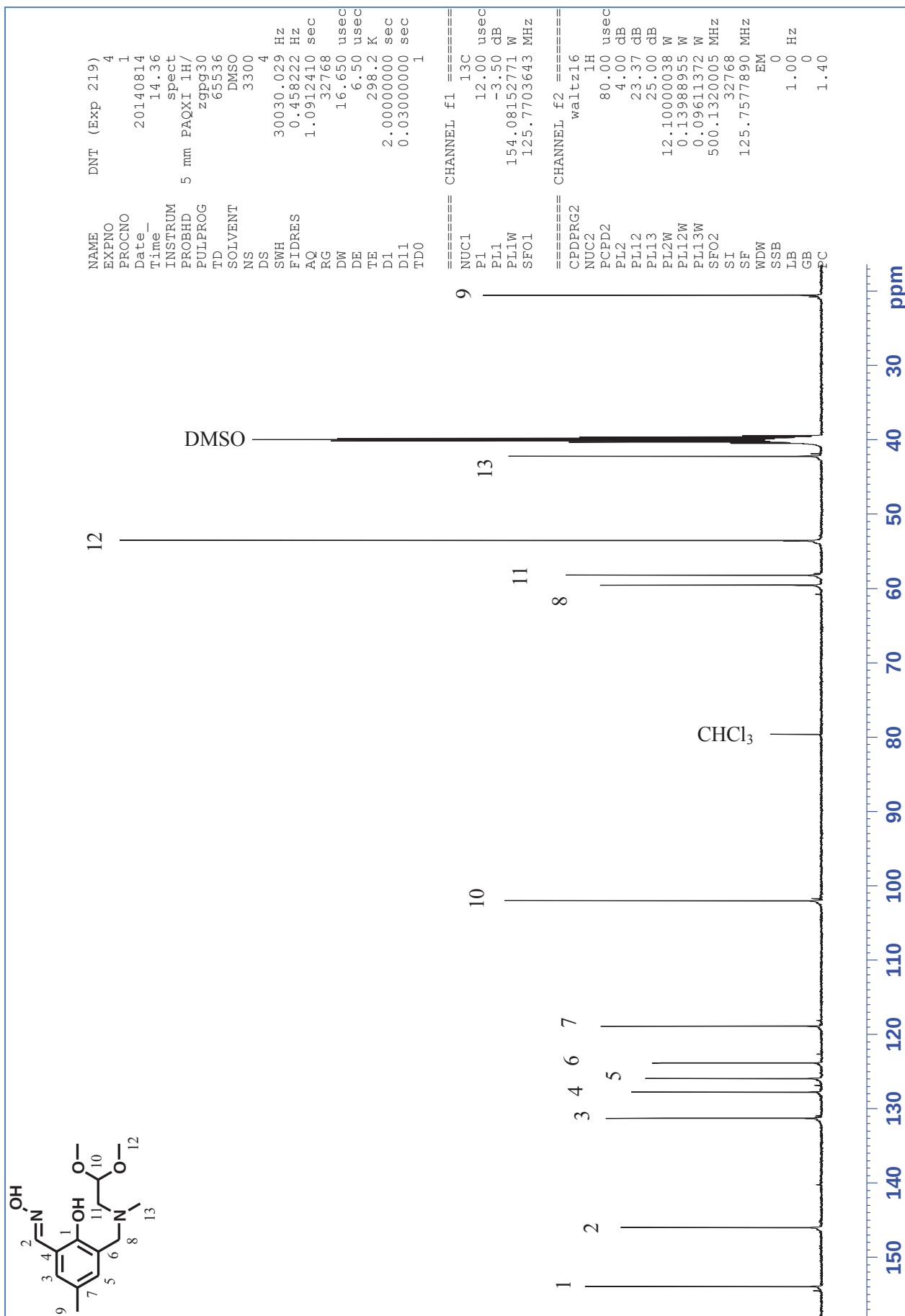
HSQC experiment of **L4a**

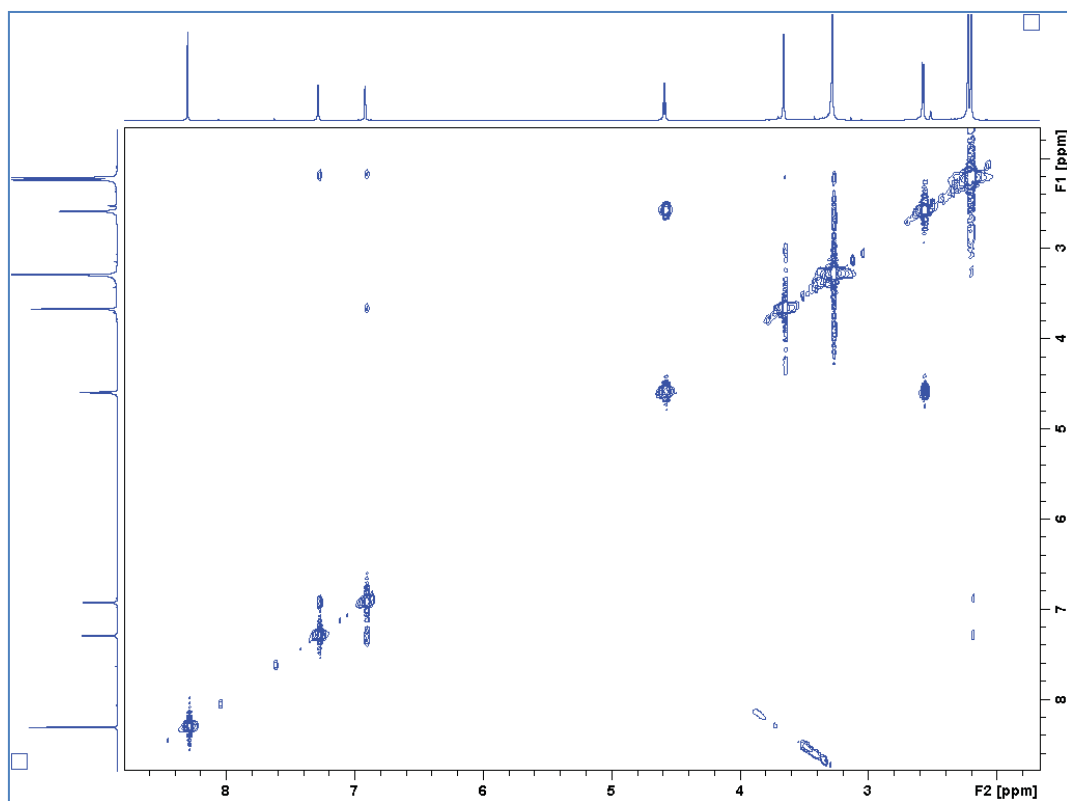
2-hydroxy-5-methyl-3-(4-(1,1-dimethoxy-N-methylmethanamino))-benzaldehydeoxime



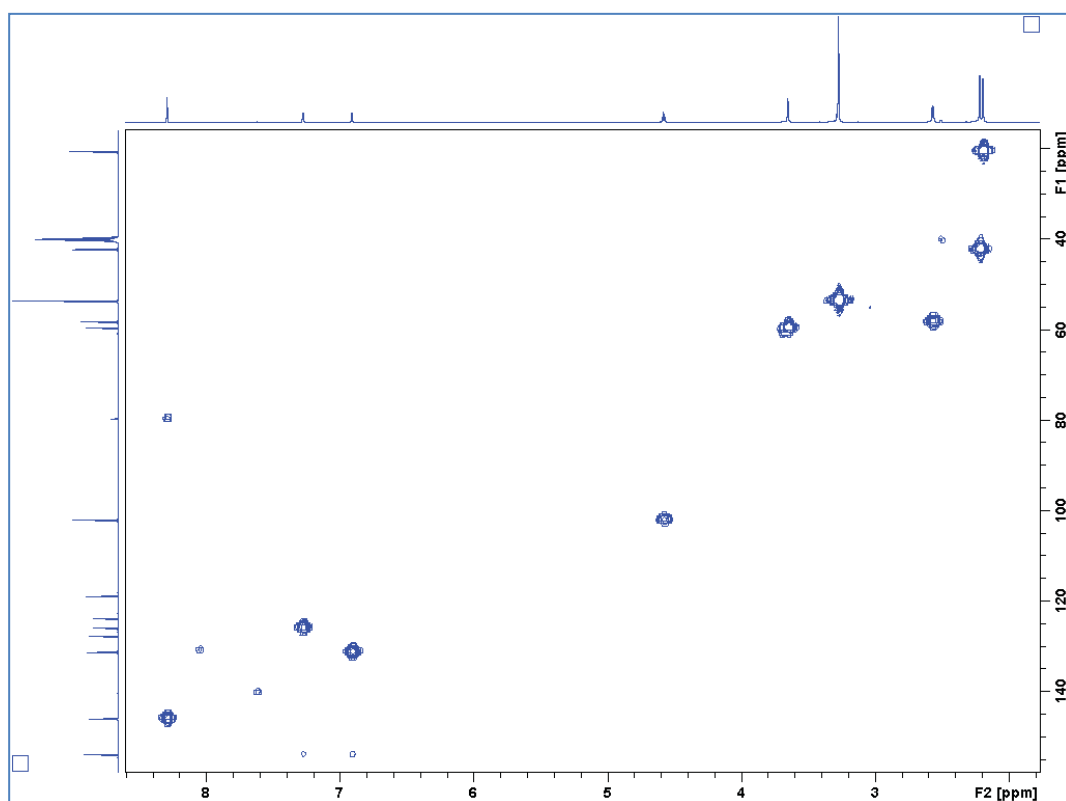
A solution of potassium hydroxide (0.210 g, 3.74 mmol) in dry ethanol (60 ml) was added to a solution of hydroxylamine hydrochloride (0.260 g, 3.74 mmol) in dry ethanol (60 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L4a** (1.000 g, 3.74 mmol) in dry toluene (100 ml) over 30 min. The pale yellow solution was stirred for a further 24 h at RT. The solvent was removed under reduced pressure and the yellow oil afforded was dissolved in CHCl_3 . The solution was washed with water (3 x 220 ml) and the organic phase dried over anhydrous Na_2SO_4 . Removal of the solvent afforded a yellow oil, which was dried *in vacuo*. Yield (0.765 g, 74%). IR (KBr pellet): 1611 (s, C=N), 2943 (m, C-H), 1468 (s, C-H), 1088 (s, C-O) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_4 \cdot 0.2\text{CHCl}_3$: C, 55.70; H, 7.31; N, 9.15. Found: C, 55.81; H, 7.44; N, 9.14. ^1H NMR (DMSO, 500 MHz): δ 2.19 (s, 3H, ArCH_3), 2.21 (s, 3H, NCH_3), 2.56 (d, $J = 5.57$ Hz, 2H, $\text{ArCH}_2\text{N}(\text{CH}_3)\text{CH}_2$ -), 3.27 (s, 6H, $-\text{OCH}_3$), 3.65 (s, 2H, ArCH_2N), 4.57 (t, $J = 5.36$ Hz, 1H, $-\text{CH}_2\text{CH}(\text{OCH}_3)_2$), 6.91 (d, $J = 1.64$ Hz, 1H, Ar-H), 7.27 (d, $J = 1.45$ Hz, 1H, Ar-H), 8.29 (s, 1H, CHN). ^{13}C NMR (DMSO, 500 MHz): δ 153.8, 145.9, 131.2, 127.6, 125.8, 123.7, 118.8, 102.0, 59.5, 58.2, 53.5, 42.1, 20.5 ppm. ES^+ -MS (m/z) 283 $[\text{M}+\text{H}]^+$.



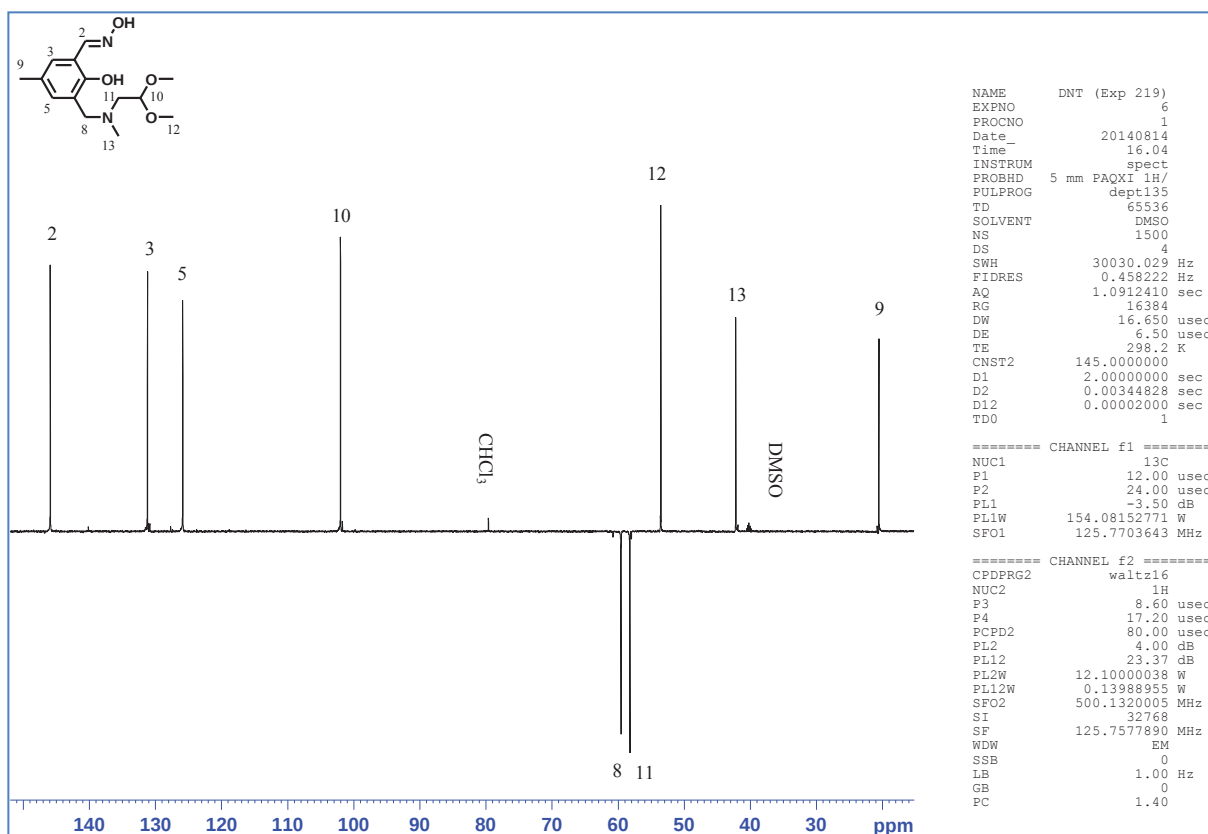




COSY experiment of **L4**



HMQC experiment of **L4**

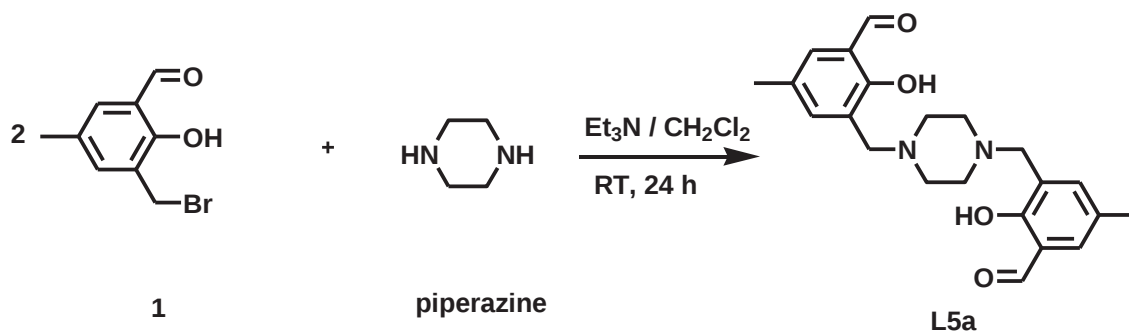


DEPT 135 experiment of **L4**

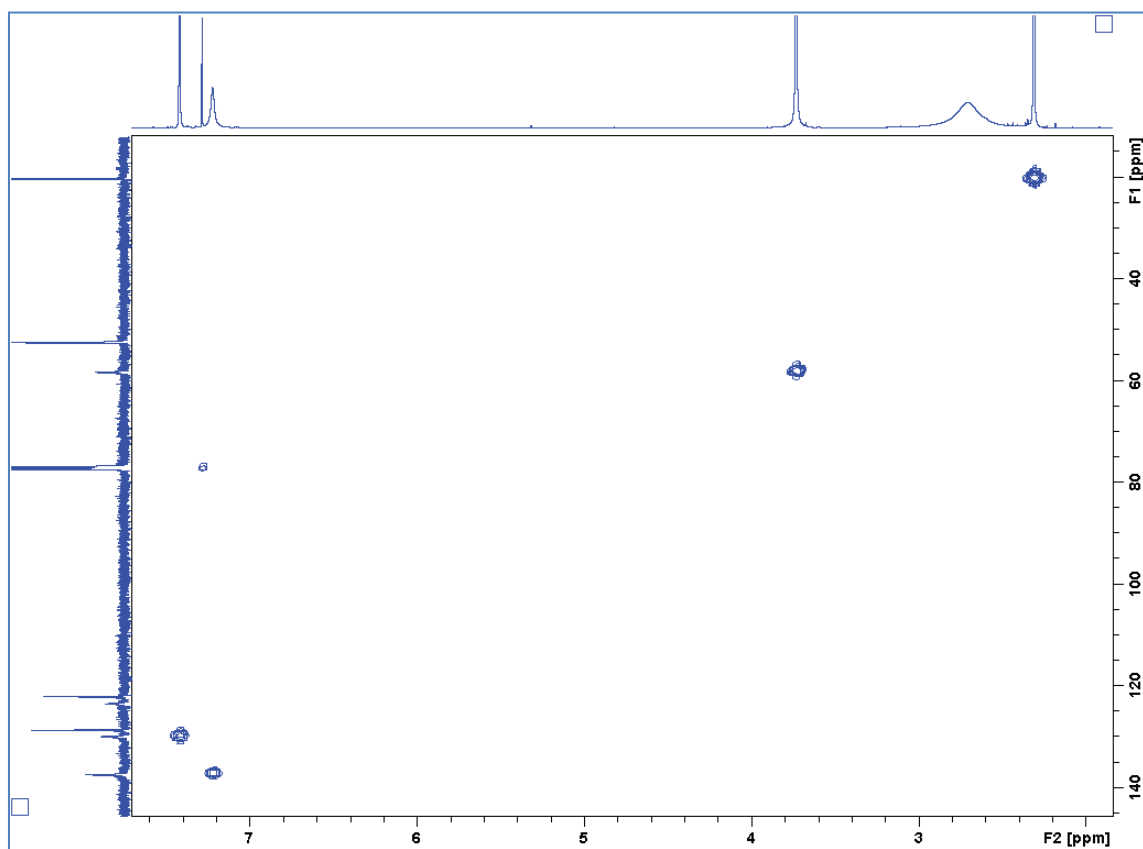
A.2.2 Synthesis of double-headed oxime ligands

L5a

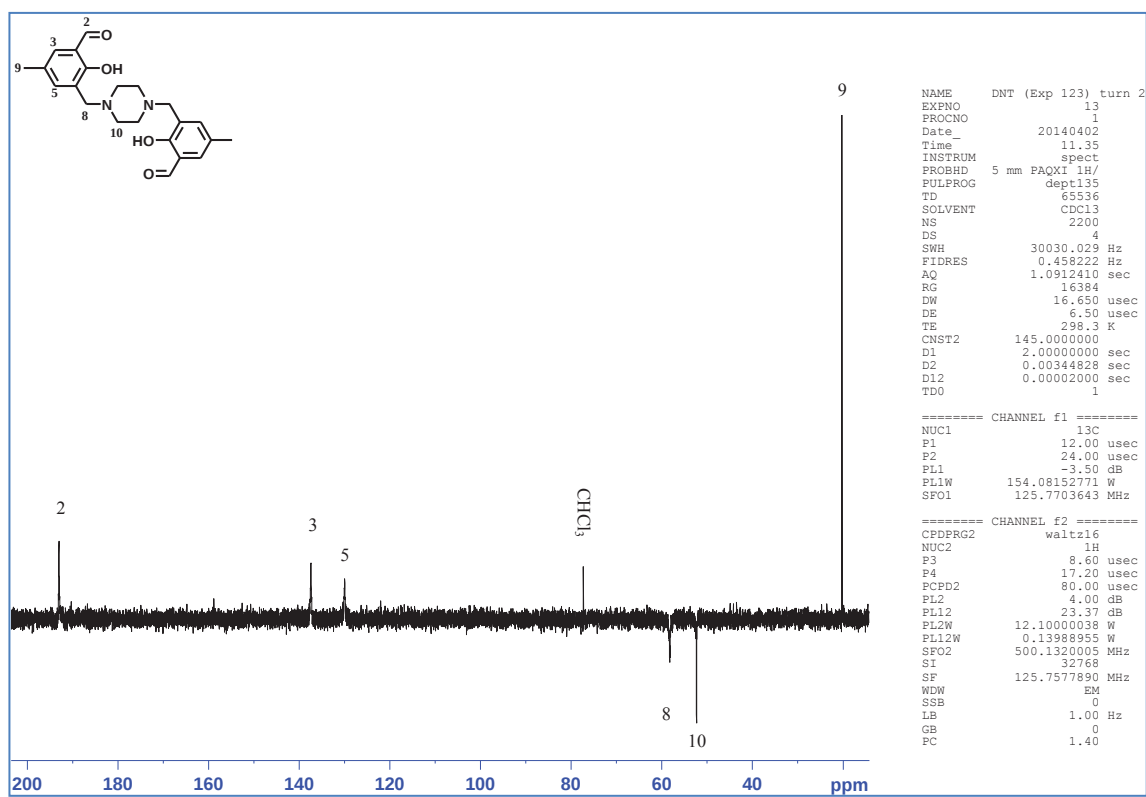
3,3'-[1,4-piperazinediylbis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde]



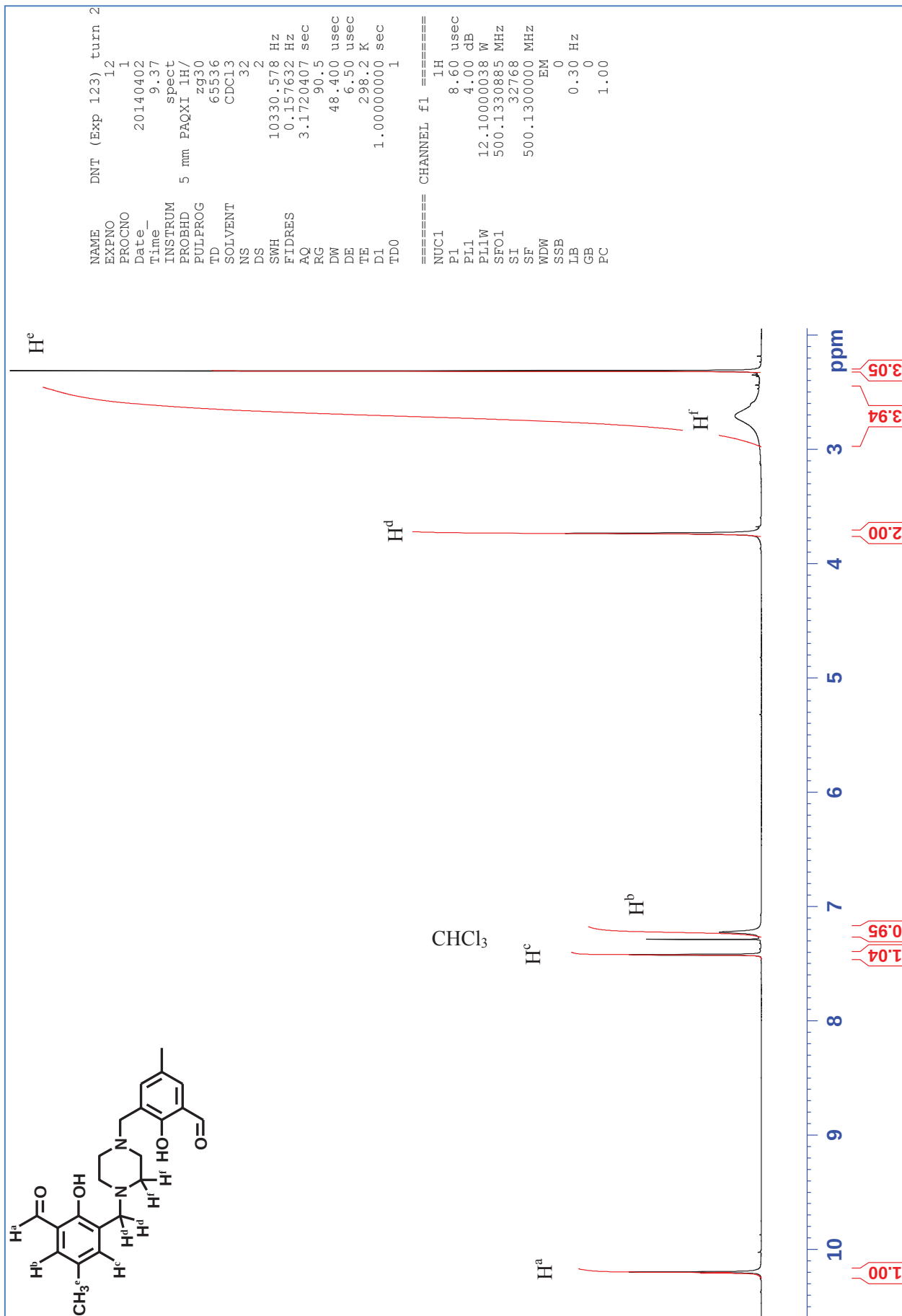
To a solution of Et₃N (1.11 g, 11.0 mmol) in dry CH₂Cl₂ (20 ml) were added over 30 minutes solutions of **1** (1.27 g, 5.54 mmol) and piperazine (0.24 g, 2.77 mmol) each dissolved in dry CH₂Cl₂ (15 ml). The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 70 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a brown solid, which was purified by adding EtOH to a concentrated solution of the compound in CHCl₃ to afford a pale brown powder which was dried *in vacuo*. Yield (0.90 g, 85%). Mp 221–222 °C. IR (KBr pellet): 1679 (s, C=O) cm⁻¹. Anal. Calcd for C₂₂H₂₆N₂O₄·0.3C₂H₅OH: C, 68.44; H, 7.09; N, 7.04. Found: C, 68.14; H, 6.74; N, 7.26. ¹H NMR (CDCl₃, 500 MHz): δ 2.29 (s, 6H, CH₃), 2.66 (br, 8H, CH₂), 3.70 (s, 4H, Ar-CH₂N), 7.17 (d, *J* = 1.75 Hz, 2H, Ar-H), 7.41 (d, *J* = 1.61 Hz, 2H, Ar-H), 10.21 (s, 2H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 192.6, 158.8, 137.0, 129.5, 128.4, 123.5, 122.0, 58.5, 52.4, 20.2 ppm. ES⁺-MS (*m/z*) 383 [M+H]⁺.

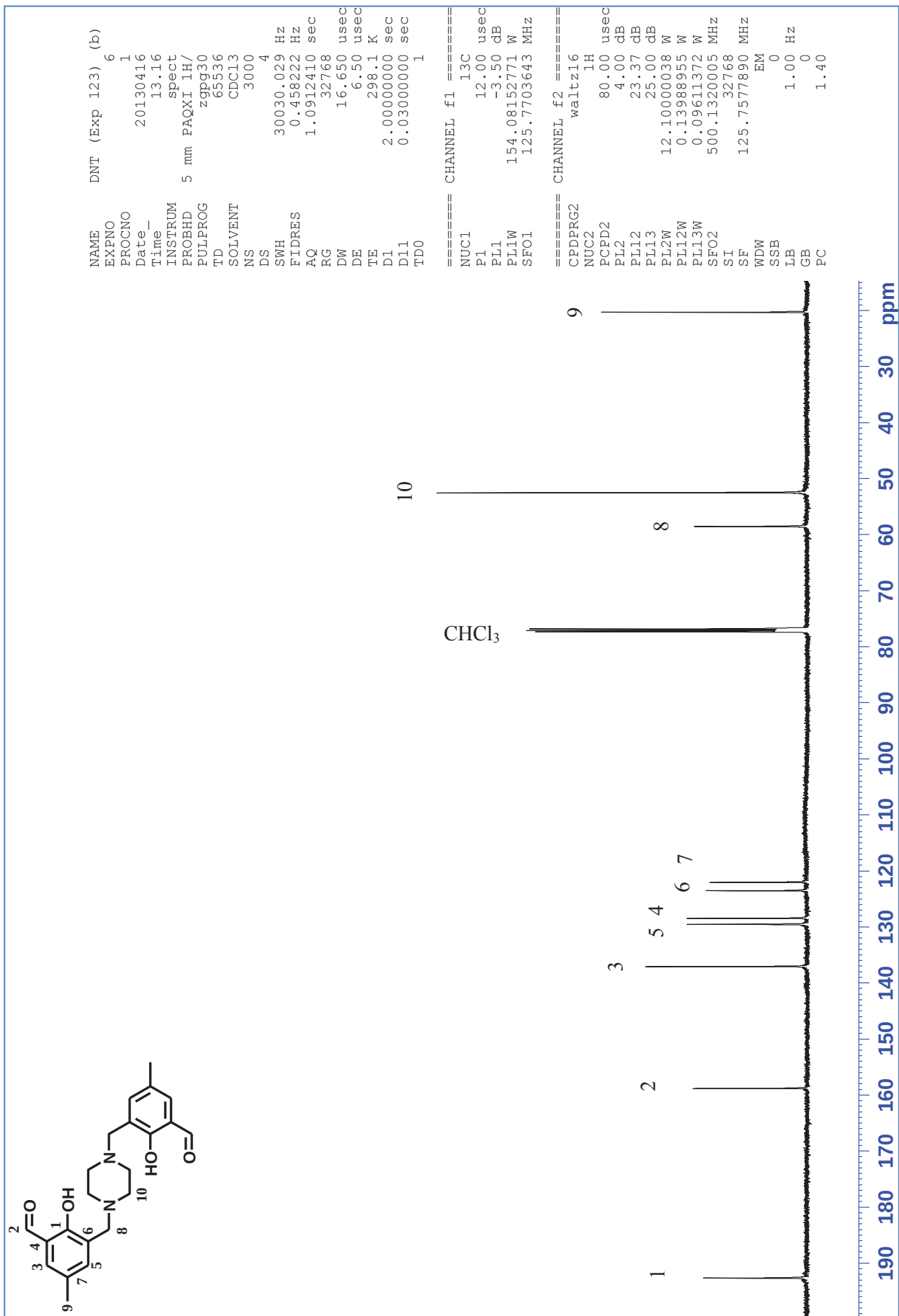


HMQC experiment of **L5a**

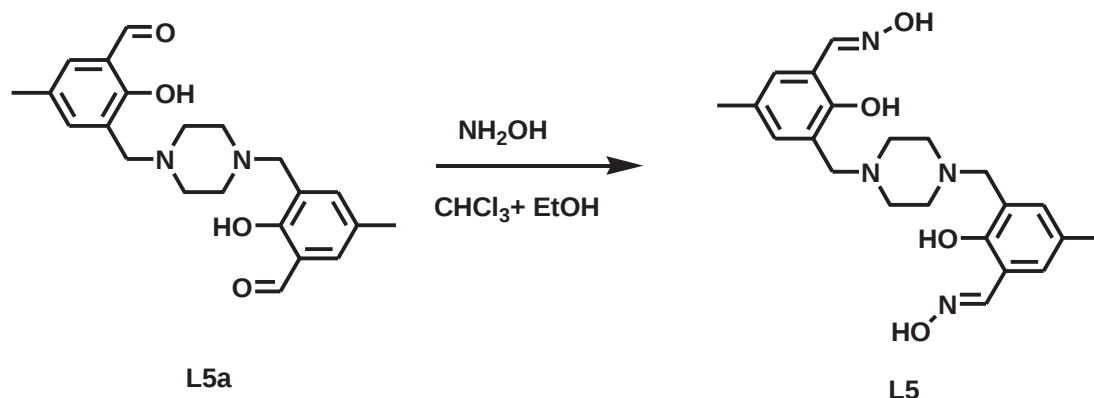


DEPT 135 experiment of **L5a**

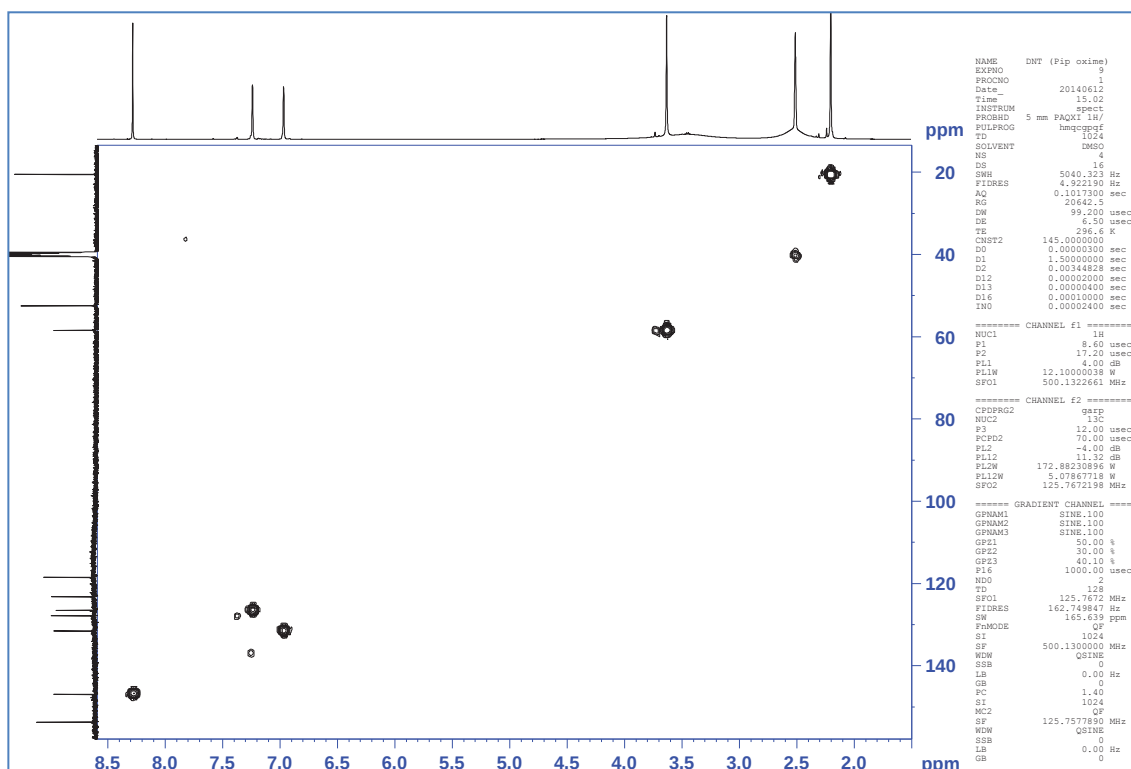




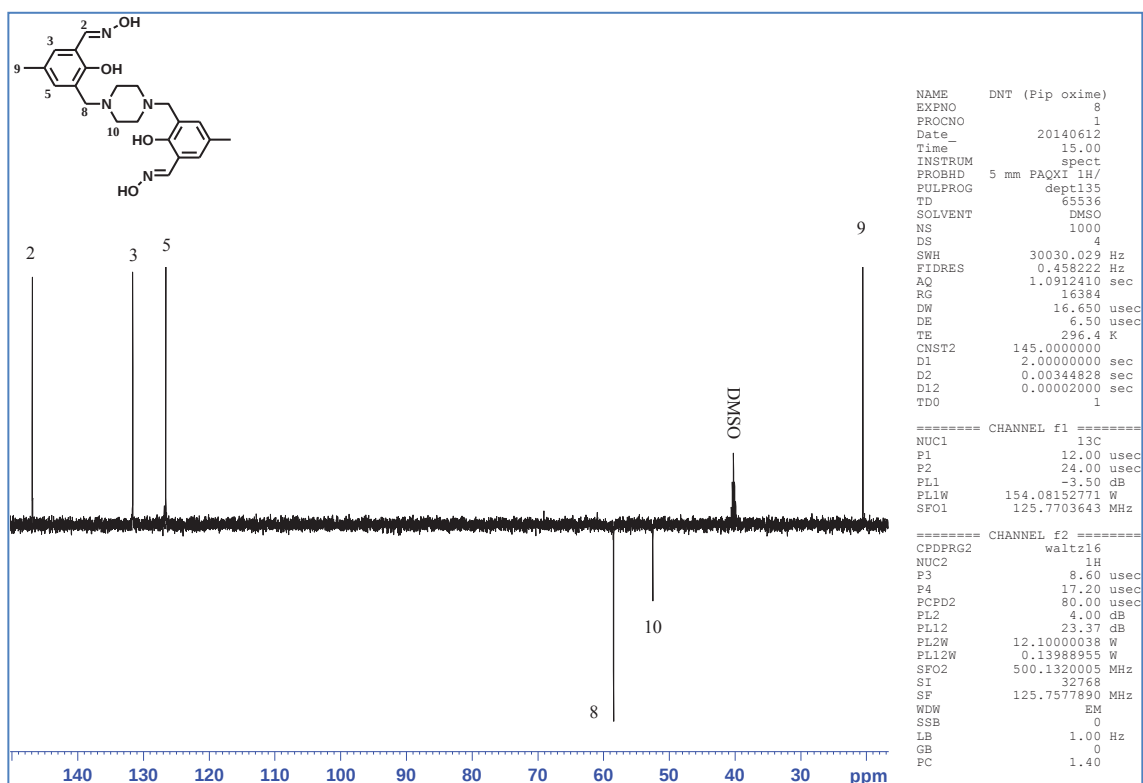
3,3'-[1,4-piperazinediylbis(methylene)]bis[2-hydroxy-5-methylbenzaldehydeoxime]



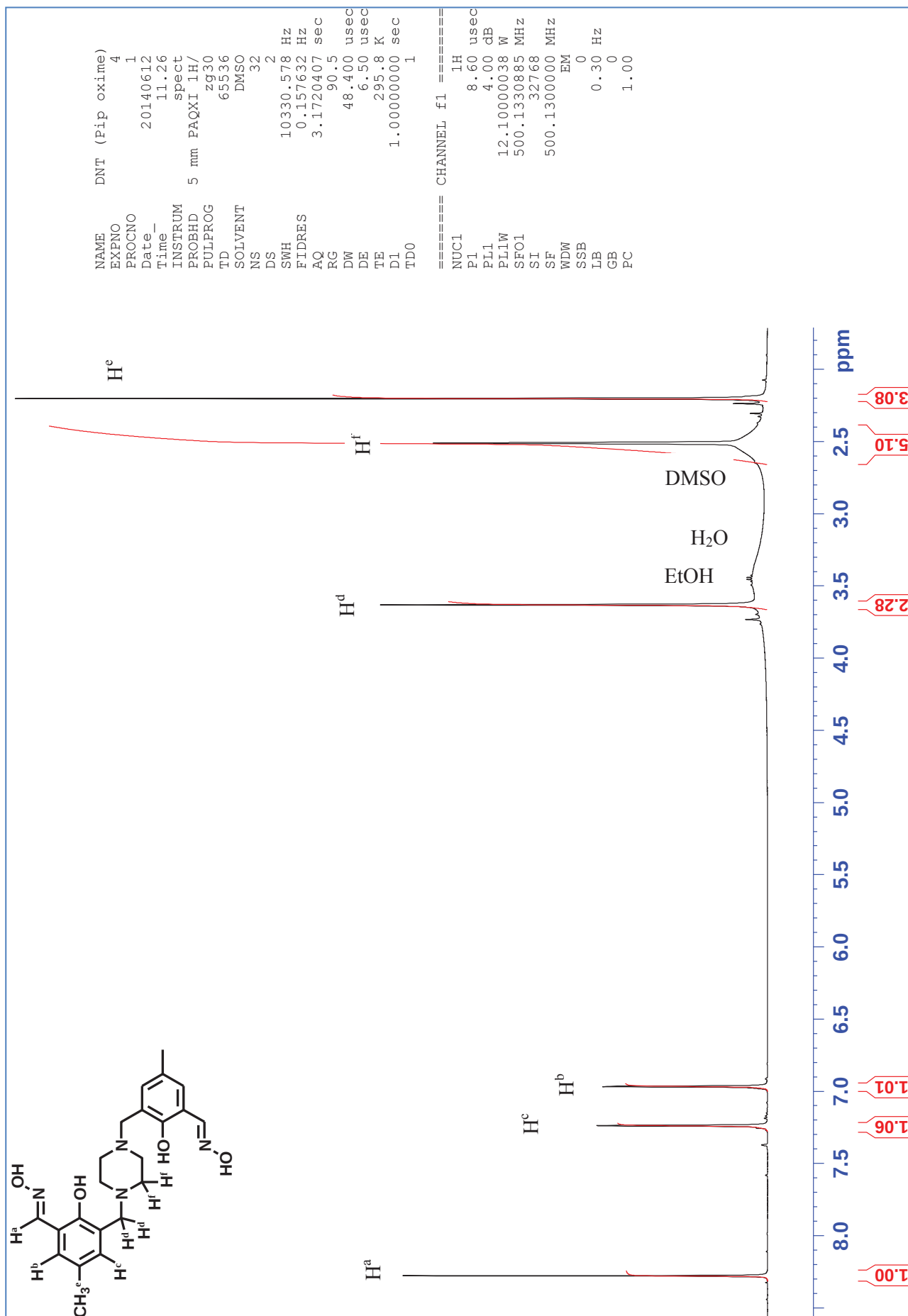
A solution of hydroxylamine hydrochloride (0.400 g, 5.76 mmol) in dry ethanol (60 ml) was added to a solution of potassium hydroxide (0.324 g, 5.76 mmol) in dry ethanol (60 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L5a** (0.727 g, 1.9 mmol) in a chloroform : dry ethanol ratio of 5 : 95 ml over 30 min. The pale yellow solution was stirred for a further 24 h at RT, during which time a pale yellow precipitate was formed. The precipitate was filtered and the remaining solvent was removed under reduced pressure. The combined pale yellow residues were then washed with chloroform (3 x 30 ml) and dried *in vacuo*. Yield (0.321 g, 41%). Mp 245-246 °C. IR (KBr pellet): 1625 (s, C=N), 1470 (s, -CH₂), (C-O), 1136 (s, N-O), 822 (s, Ar-H) cm⁻¹. Anal. Calcd for C₂₂H₂₈N₄O₄·0.2C₂H₅OH: C, 63.80; H, 6.98; N, 13.29. Found: C, 63.59; H, 6.84; N, 13.58. ¹H NMR (DMSO, 500 MHz): δ 2.19 (s, 6H, CH₃), 3.59 (s, 8H, CH₂), 3.62 (s, 4H, Ar-CH₂N), 6.96 (d, *J* = 1.92 Hz, 2H, Ar-H), 7.23 (d, *J* = 1.74 Hz, 2H, Ar-H), 8.27 (s, 2H, CHN). ¹³C NMR (DMSO, 500 MHz): δ 153.6, 146.9, 131.6, 127.8, 126.5, 123.2, 118.5, 58.4, 52.4, 20.5 ppm. ES⁺-MS (*m/z*) 413 [M+H]⁺.

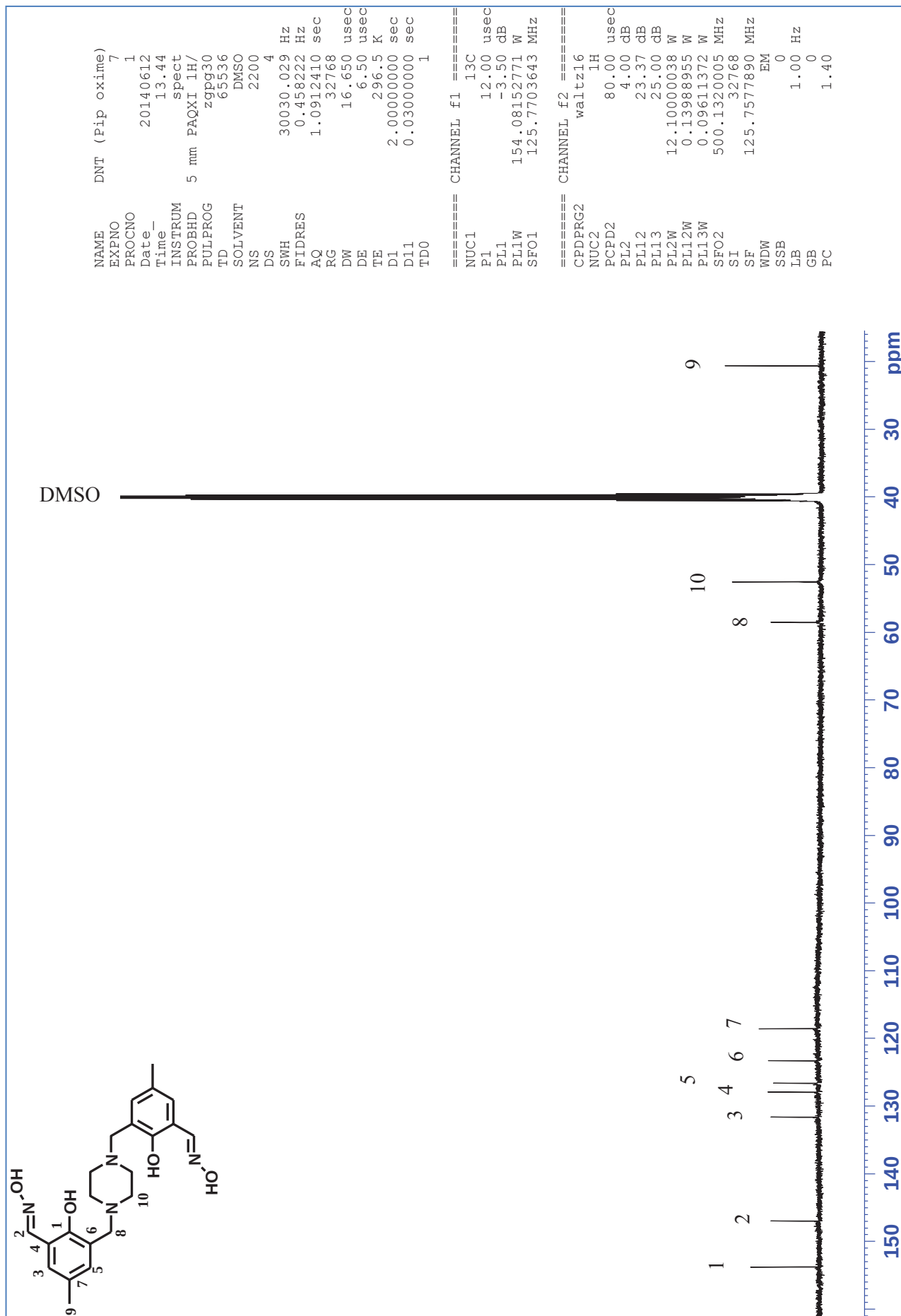


HMQC experiment of L5



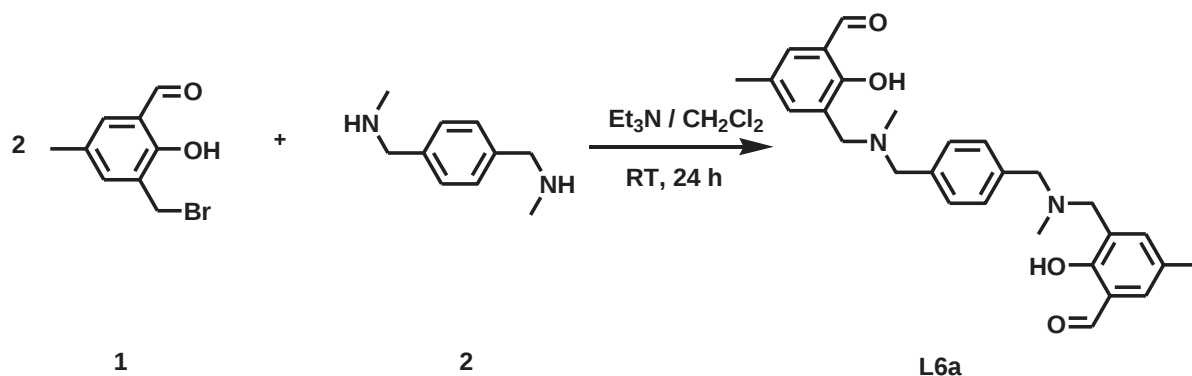
DEPT 135 experiment of L5



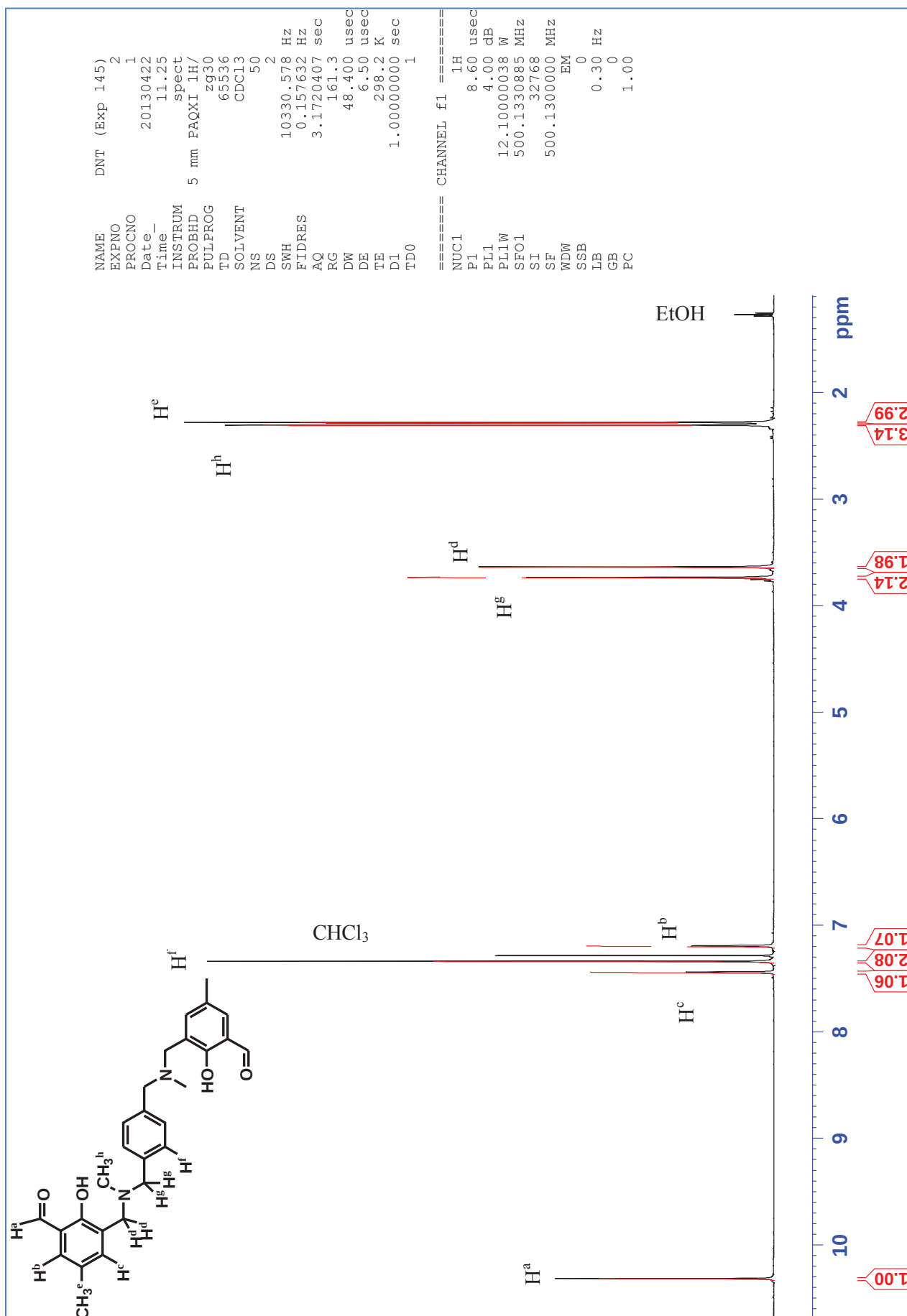


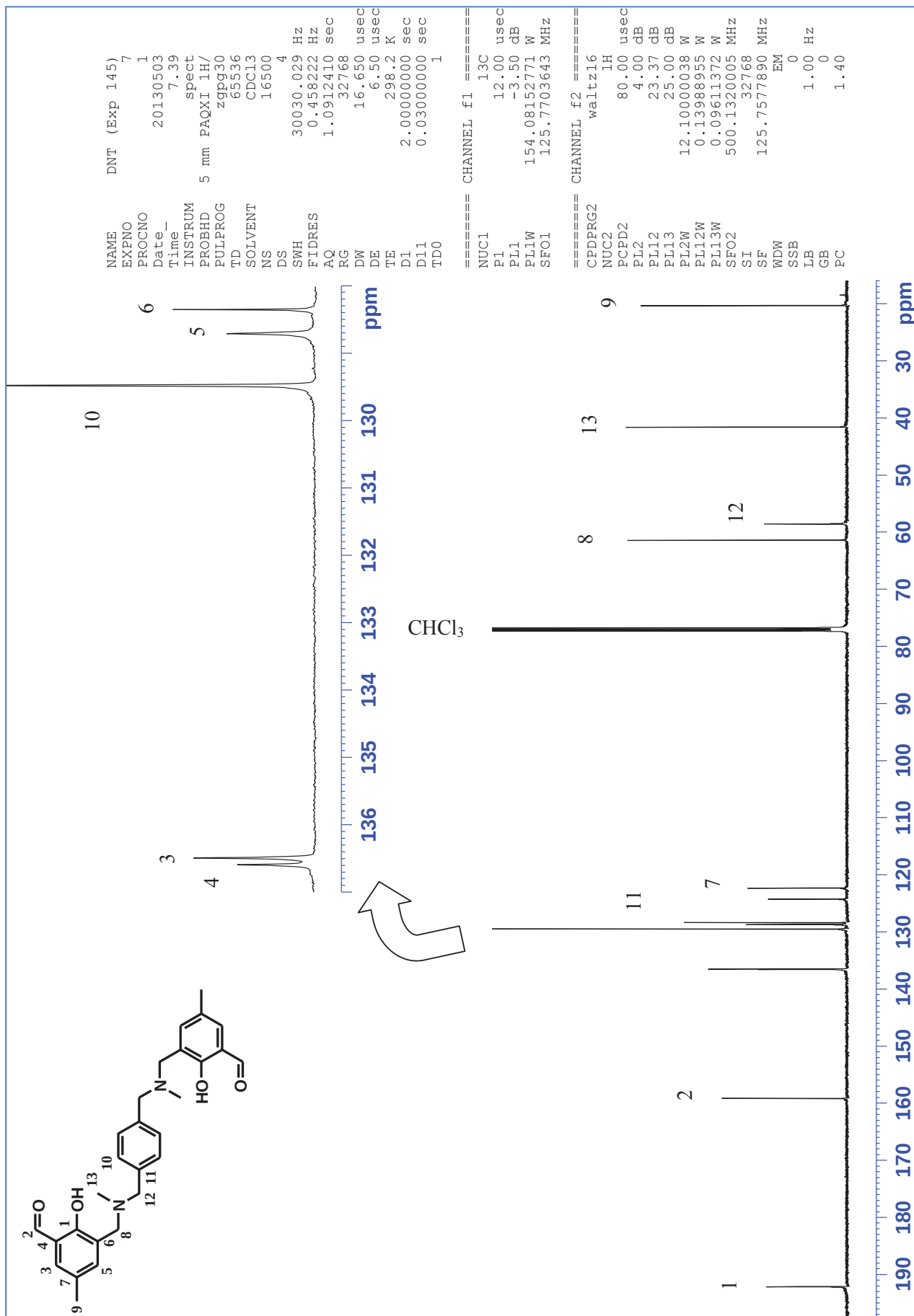
L6a

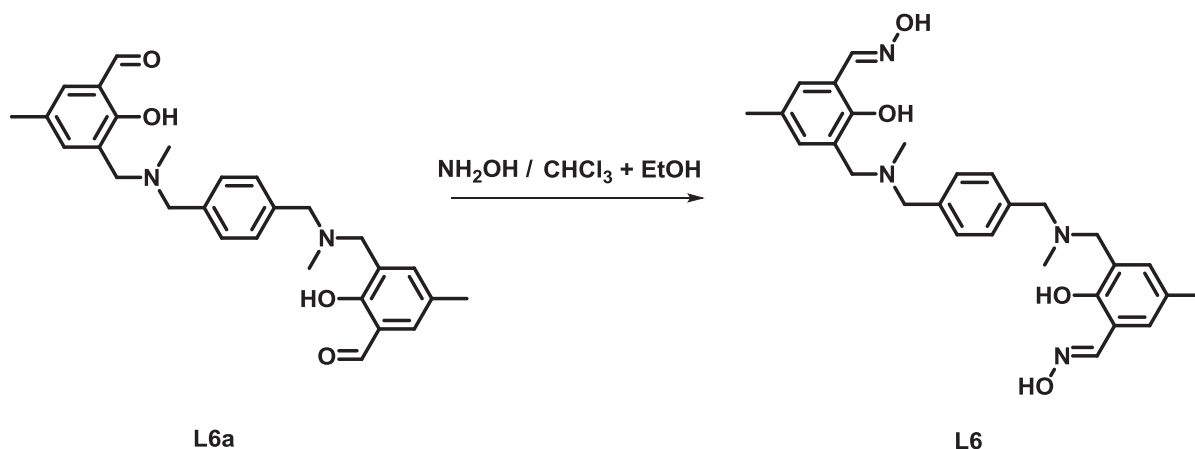
3,3'-[1,4-phenylenebis[methylene(methylimino)methylene]]bis[2-hydroxy5-methyl-benzaldehyde]



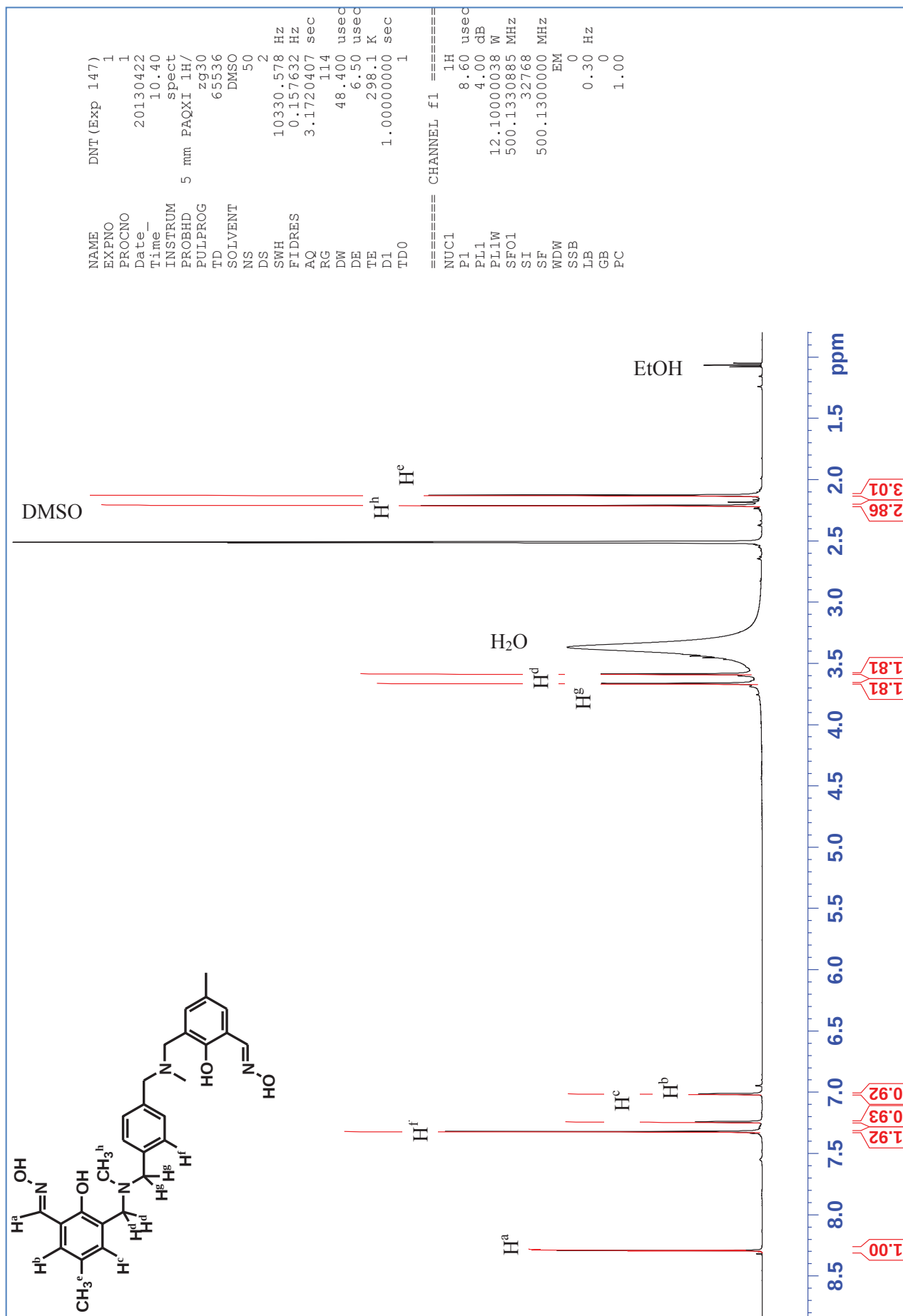
To a solution of Et₃N (1.11 g, 11.00 mmol) in dry CH₂Cl₂ (20 ml) were added over 30 minutes solutions of **1** (1.27 g, 5.54 mmol) and **2** (0.46 g, 2.77 mmol) each dissolved in dry CH₂Cl₂ (15 ml). The yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 70 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a pale yellow solid, which was recrystallised by adding EtOH to a concentrated solution of the compound in CHCl₃ to afford yellow crystals which were dried *in vacuo*. Yield (1.16 g, 90%). Mp 152–155 °C. IR (KBr pellet): 1678 (s, C=O), 3449 (br, O-H), 828 (s, Ar-H) cm⁻¹. Anal. Calcd for C₂₈H₃₂N₂O₄: C, 73.02; H, 7.00; N, 6.08. Found: C, 72.60; H, 6.87; N, 6.03. ¹H NMR (CDCl₃, 500 MHz): δ 2.28 (s, 6H, CH₃), 2.30 (s, 8H, CH₂), 3.63 (s, 4H, Ar-CH₂N), 3.73 (s, 4H, Ar-CH₂N), 7.19 (d, *J* = 1.79 Hz, 2H, Ar-H), 7.34 (s, 4H, Ar-H), 7.44 (d, *J* = 1.57 Hz, 2H, Ar-H), 10.31 (s, 2H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 192.1 (CHO), 159.1, 136.6, 136.5, 129.4, 128.7, 128.3, 124.2, 122.3 (ArC), 61.4 (CH₂), 58.5, 58.5 (CH₂), 41.5 (CH₃), 20.3 (CH₃) ppm. ES⁺-MS (*m/z*) 461 [M+H]⁺.

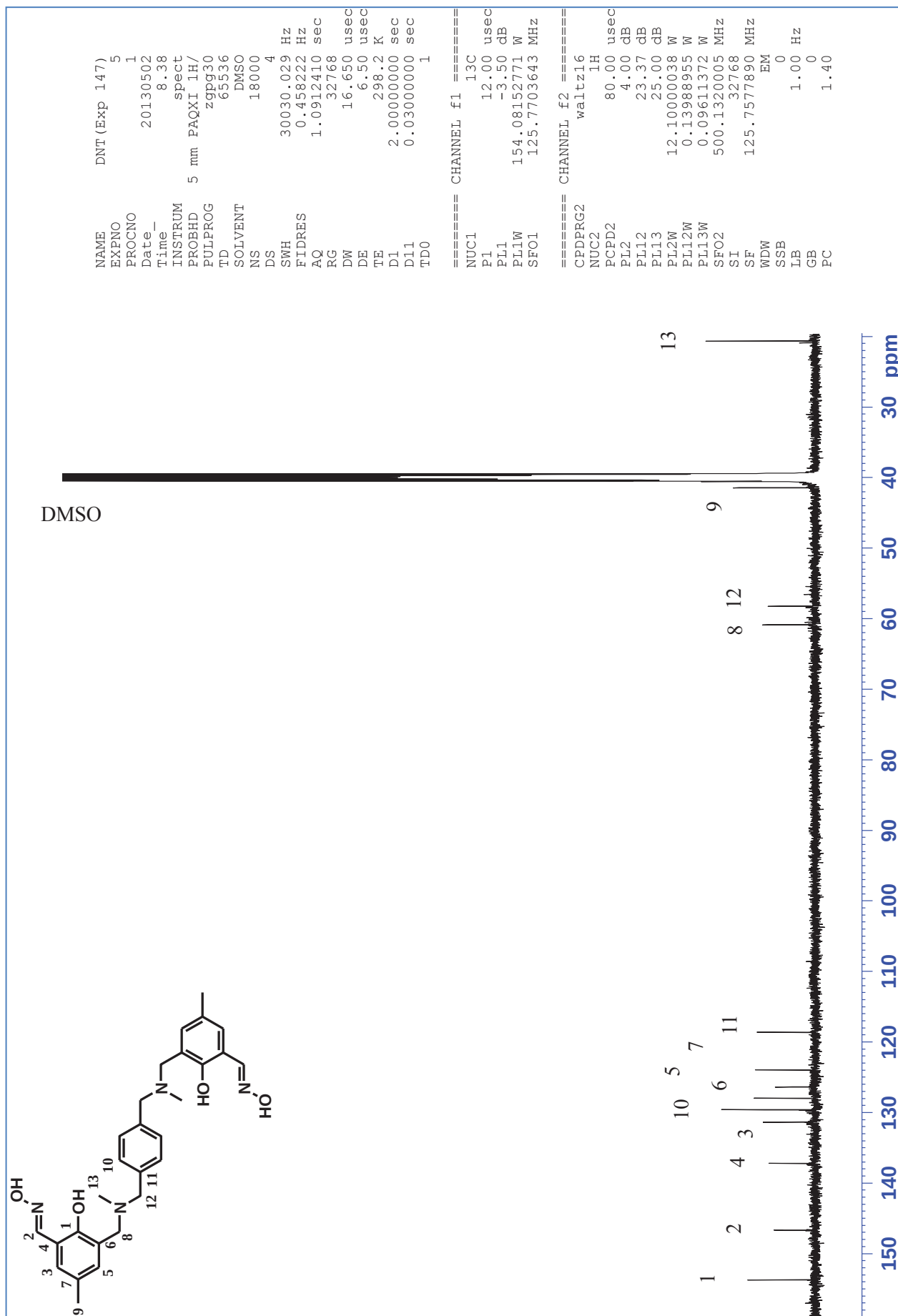


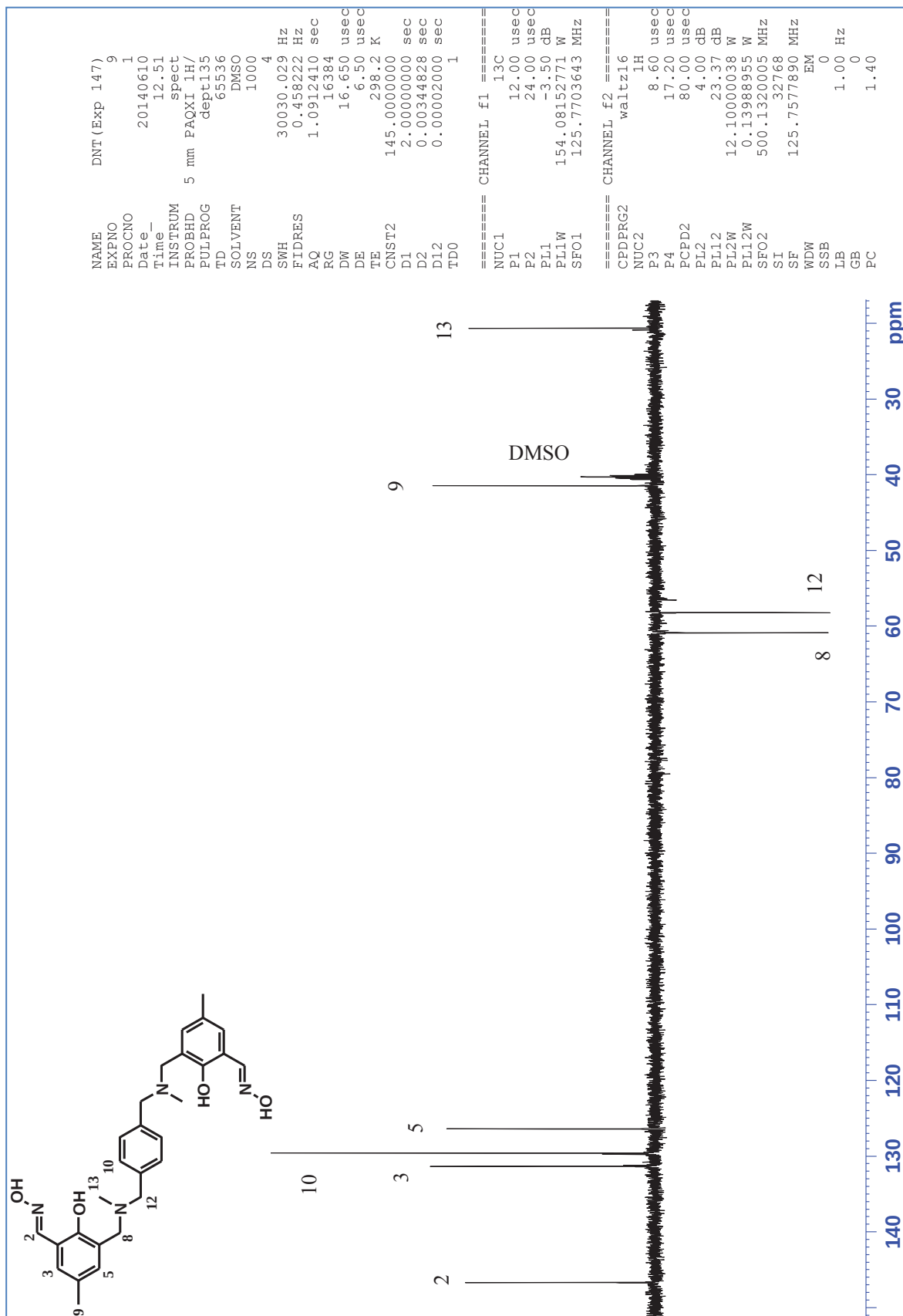


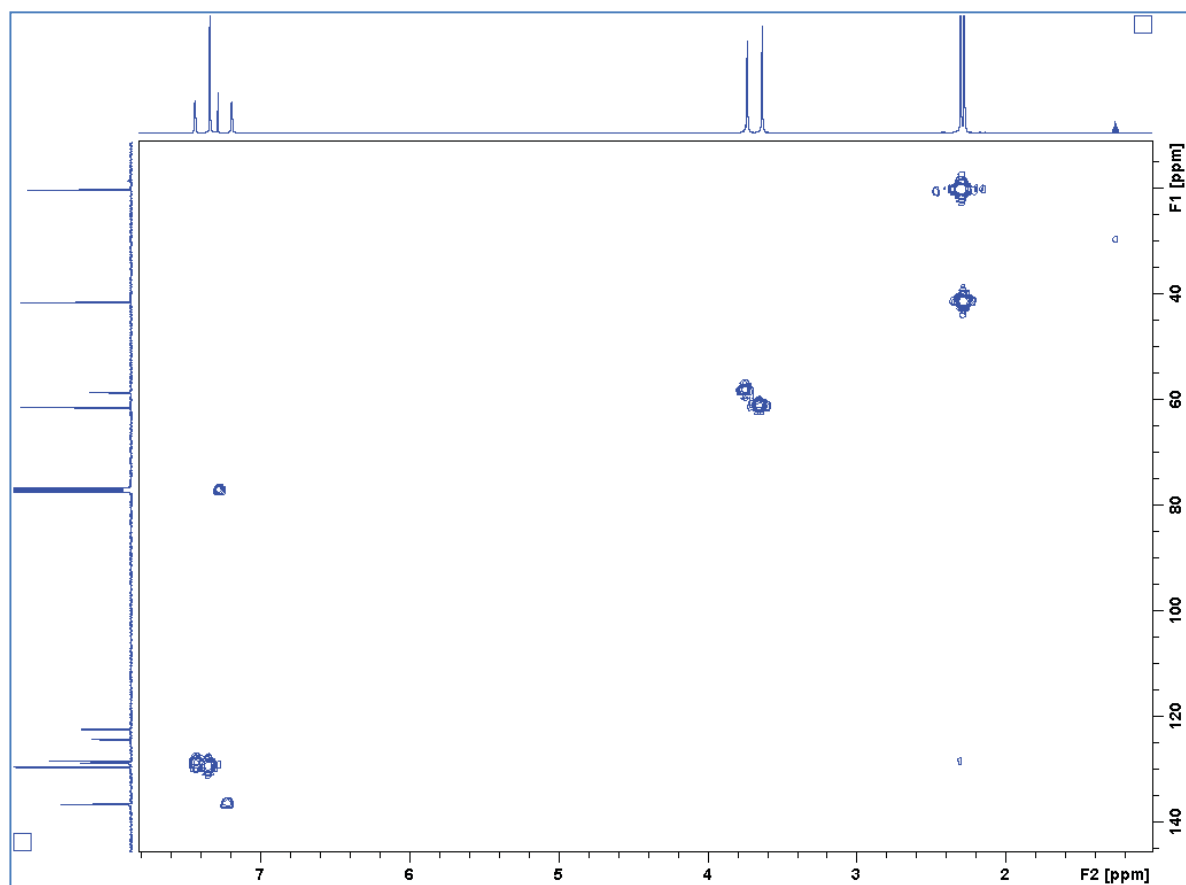
3,3'-[1,4-phenylenebis[methylene(methylimino)methylene]]bis[2-hydroxy-5-methyl]-1,1'-dioxime

A solution of hydroxylamine hydrochloride (0.377 g, 5.43 mmol) in dry ethanol (60 ml) was added to a solution of potassium hydroxide (0.377 g, 5.43 mmol) in dry ethanol (60 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L6a** (1.000 g, 2.171 mmol) in a chloroform : dry ethanol ratio of 5 : 95 ml over 30 minutes. The pale yellow solution was stirred for further 48 h at RT, after which time a pale yellow precipitate was obtained. The combined residues were filtered, washed with chloroform (3 x 30 ml) followed by ethanol (3 x 30 ml). The final product was dried *in vacuo*. Yield (0.978 g, 92%). Mp 203-204 °C. IR (KBr pellet): 1610 (m, C=N), 2955 (m, C-H), 1469 (vs, -CH₂), 1285 (s, C-O), 1020 (m, N-O) cm⁻¹. Anal. Calcd for C₂₈H₃₄N₄O₄·0.5C₂H₅OH: C, 67.81; H, 7.26; N, 10.91. Found: C, 67.01; H, 6.96; N, 10.89. ¹H NMR (DMSO, 500 MHz): δ 2.12 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 3.58 (s, 4H, Ar-CH₂N), 3.66 (s, 4H, Ar-CH₂N), 7.01 (d, *J* = 1.64 Hz, 2H, Ar-H), 7.24 (d, *J* = 1.80 Hz, 2H, Ar-H), 8.28 (s, 2H, CHN). ¹³C NMR (DMSO, 500 MHz): δ 153.6 (CN), 146.9, 137.1, 131.3, 129.5, 127.9, 126.3, 123.9, 118.5 (ArC), 60.7 (CH₂), 58.1 (CH₂), 41.3 (CH₃), 20.5 (CH₃) ppm. ES⁺-MS (*m/z*) 491 [M+H]⁺.



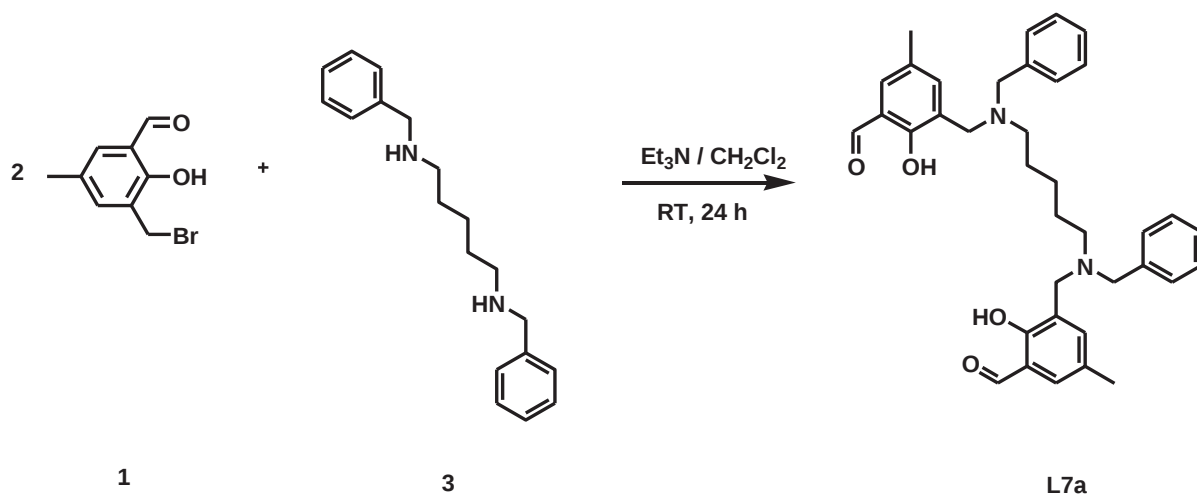




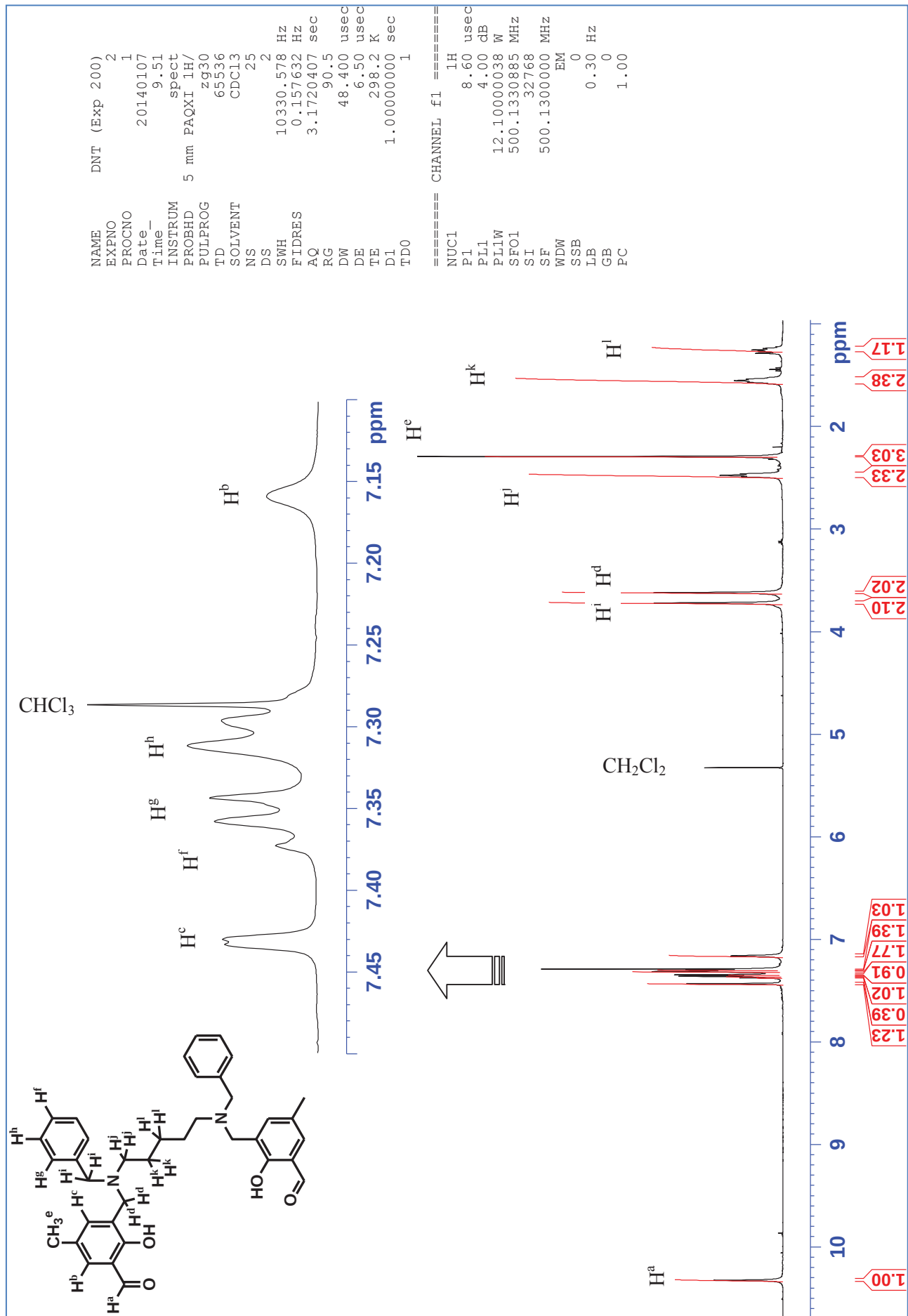


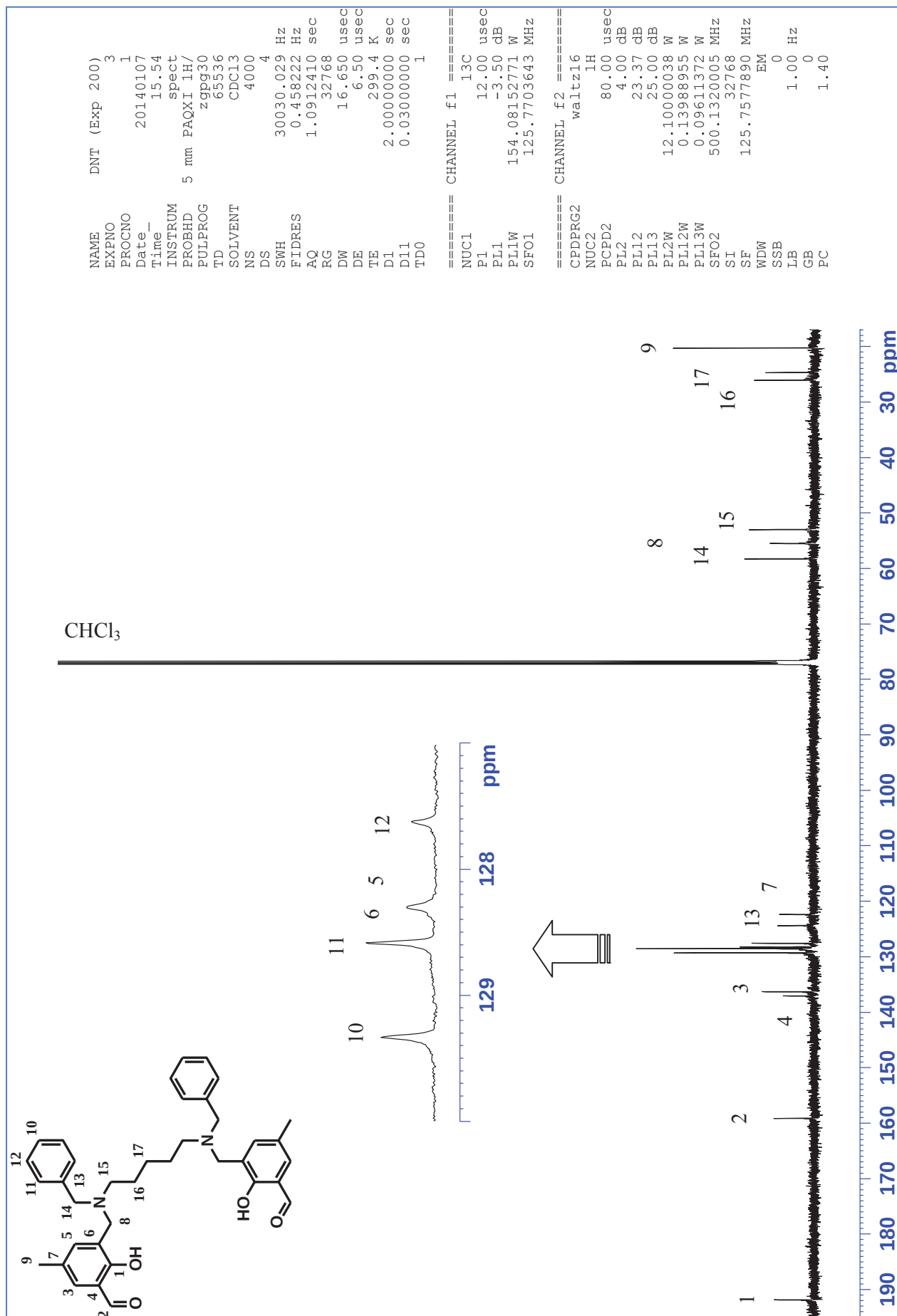
L7a

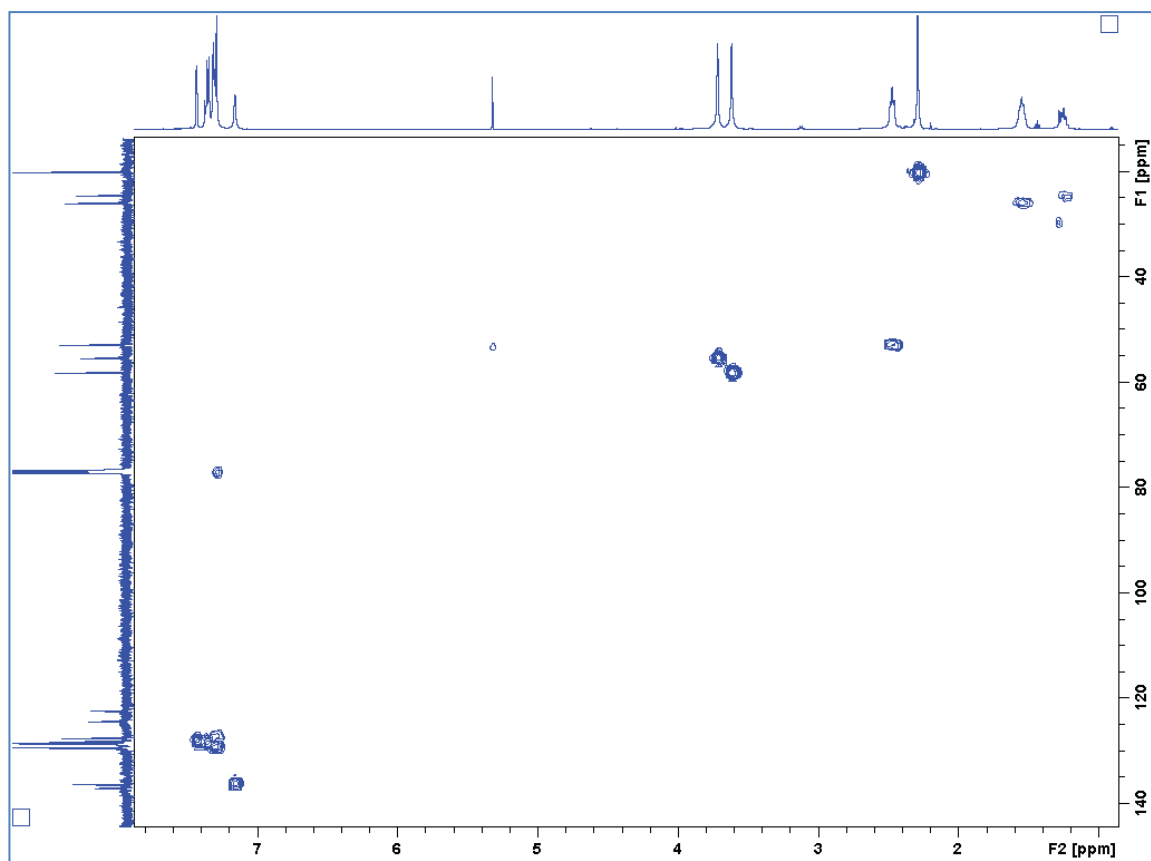
3,3'-[N,N'-dibenzyl-1,5-pentanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde]



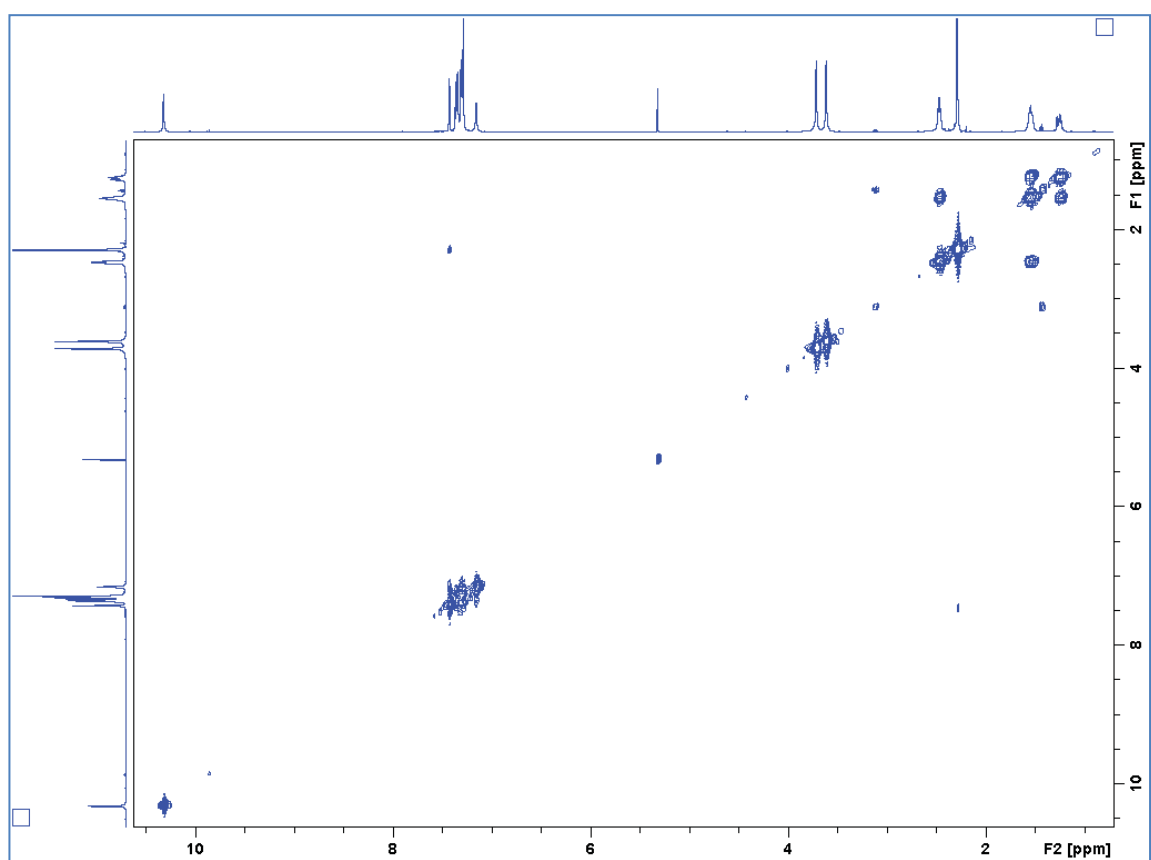
To a solution of Et₃N (1.11 g, 8.05 mmol) in dry CH₂Cl₂ (30 ml) were added over 30 minutes solutions of **1** (1.00 g, 8.05 mmol) and **3** (EtOAc : Et₃N / 9 : 1, *R_f* = 0.5), (0.81 g, 2.77 mmol) each dissolved in dry CH₂Cl₂ (20 ml). The yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 100 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a bright yellow semi-solid, which was dried *in vacuo* for 24h. Yield (2.04 g, 86%). IR (KBr pellet): 1681 (s, C=O), 2851 (s, C-H), 3028 (m, Ar-C-H), 1471 (m, Ar-C=C) cm⁻¹. Anal. Calcd for C₃₇H₄₂N₂O₄·H₂O: C, 74.47; H, 7.43; N, 4.69. Found: C, 74.61; H, 7.37; N, 4.73. ¹H NMR (CDCl₃, 500 MHz): δ 1.22 (q, *J* = 7.53 Hz, 2H, CH₂), 1.53 (q, *J* = 6.85 Hz, 4H, CH₂), 2.28 (s, 6H, CH₃), 2.45 (s, *J* = 6.88 Hz, 4H, NCH₂), 3.61 (s, 4H, NCH₂Ar), 3.71 (s, 4H, Ar-CH₂NCH₂), 7.15 (s, 2H, Ar-H), 7.29 (d, *J* = 7.69 Hz, 4H, Ar-H), 7.34 (d, *J* = 7.28 Hz, 4H, Ar-H), 7.37 (s, 2H, Ar-H), 7.43 (d, *J* = 1.62 Hz, 2H, Ar-H), 10.32 (s, 2H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 191.8 (CHO), 159.2, 137.1, 136.3, 129.3, 128.5, 128.3, 128.2, 127.6, 124.4, 122.4 (ArC), 58.2 (CH₂), 55.5 (CH₂), 55.0 (CH₂), 26.0 (CH₂) 24.7 (CH₂), 20.3 (CH₃) ppm. ES⁺-MS (*m/z*) 580 [M+H]⁺.





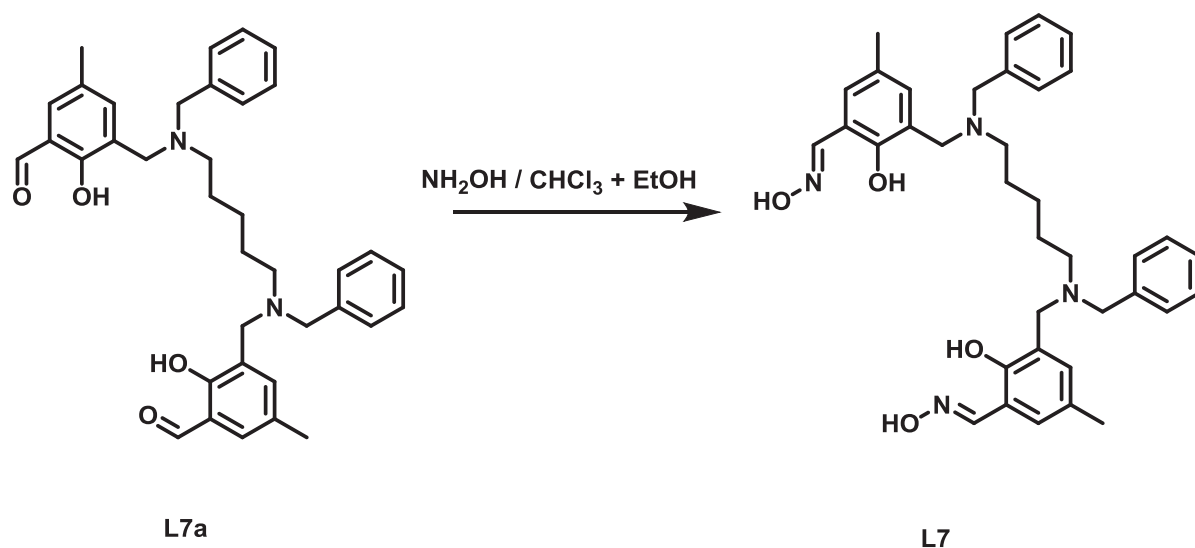


HMQC experiment of **L7a**

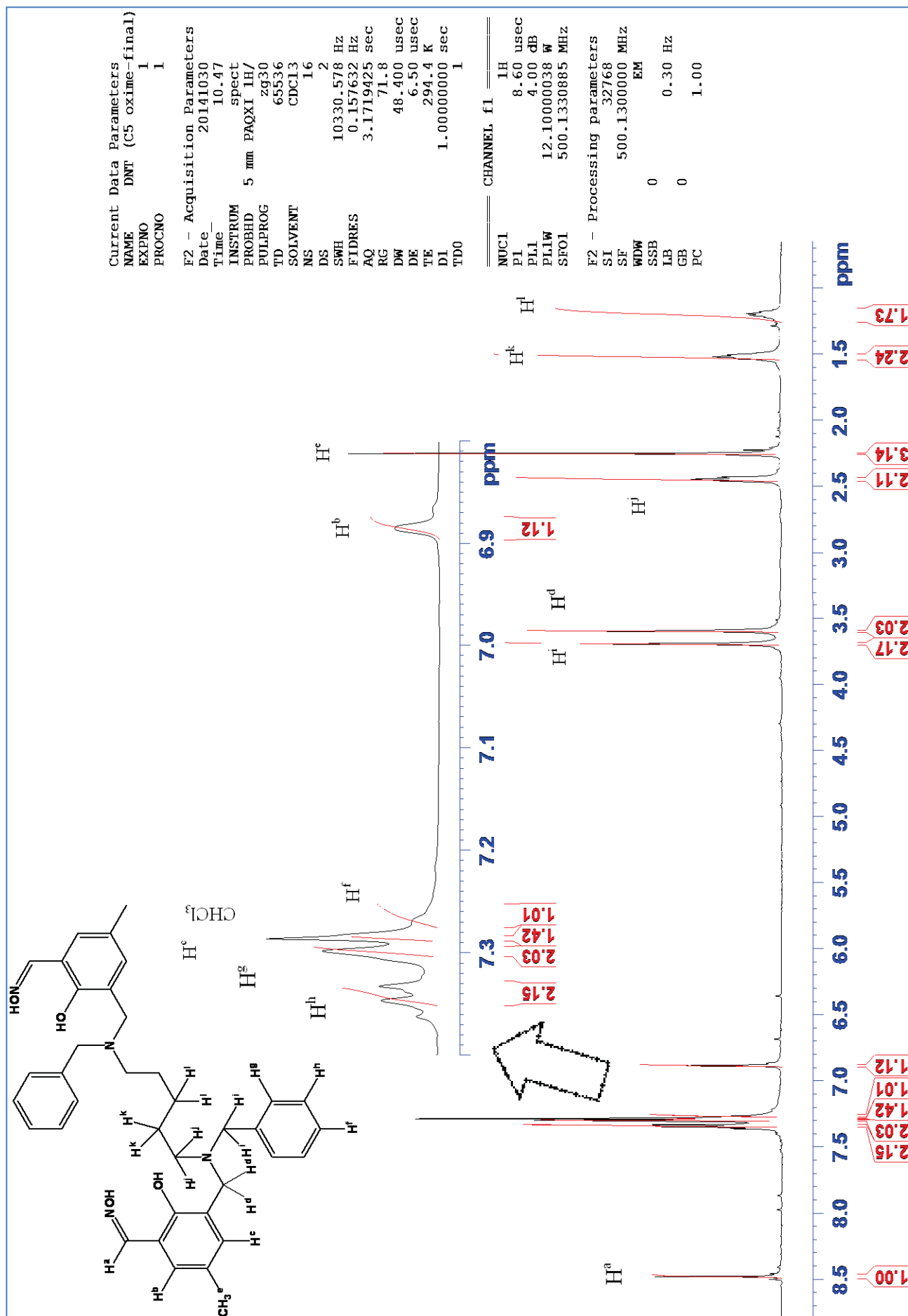


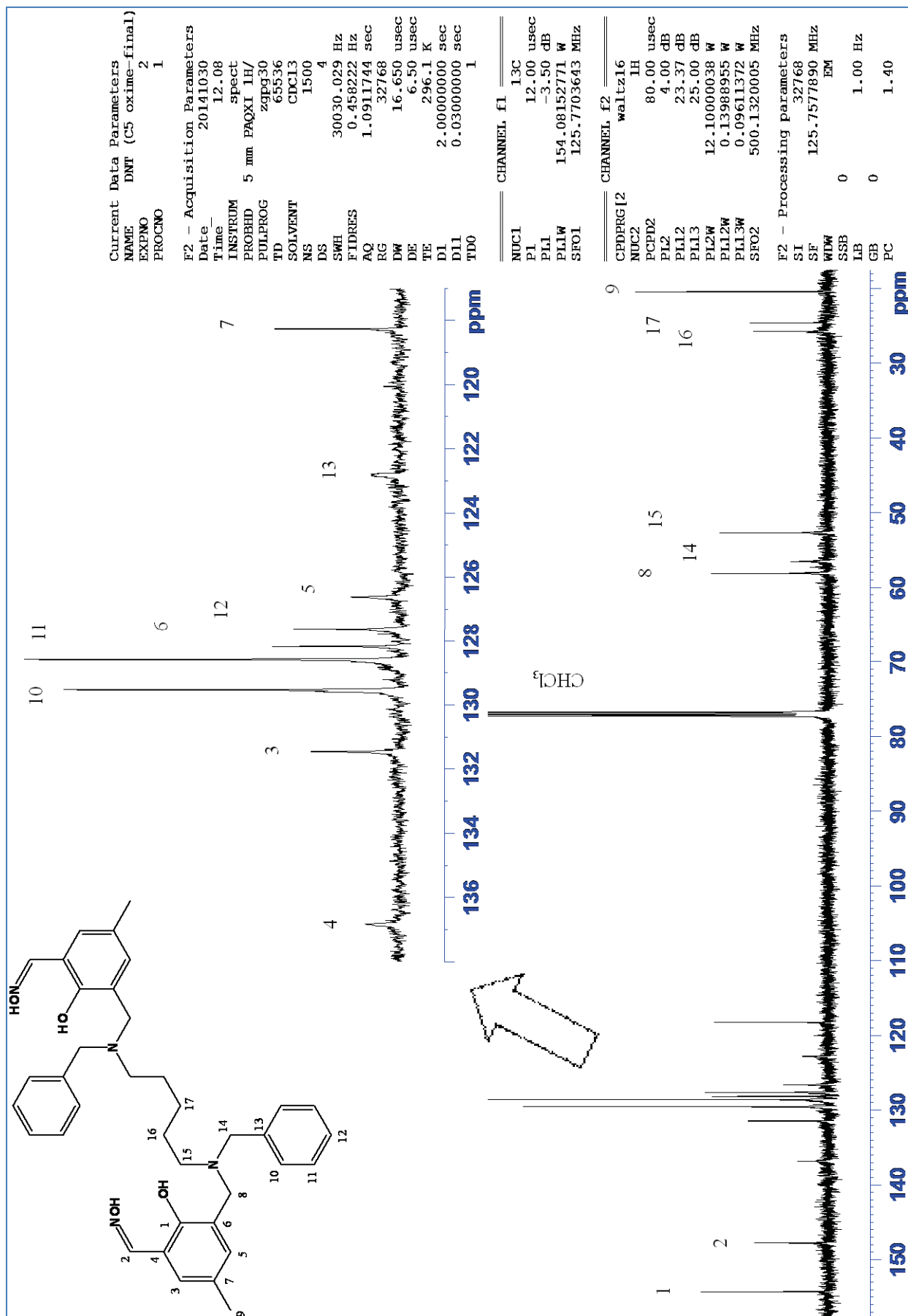
COSY experiment of **L7a**

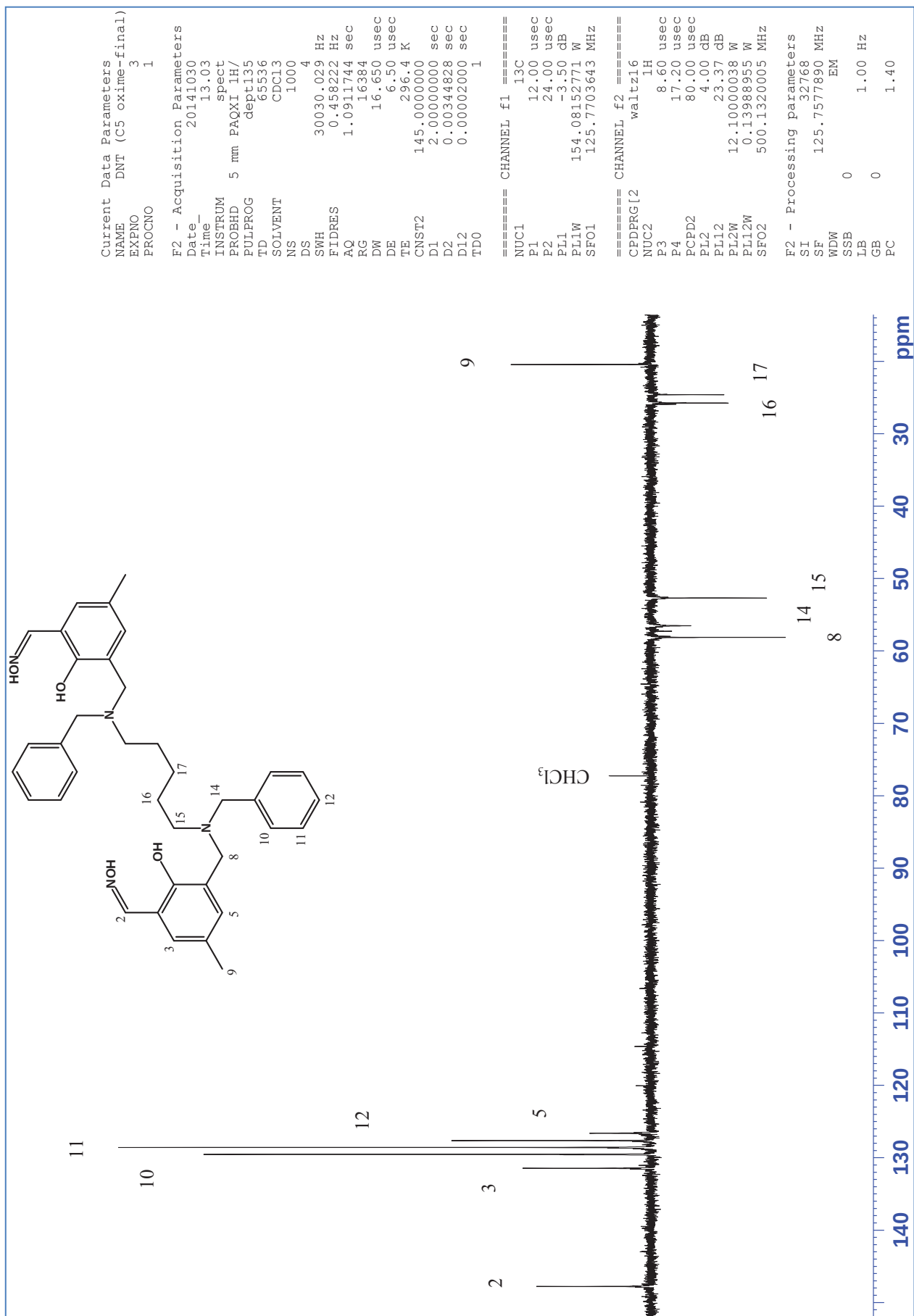
3,3'-[*N,N'*-dibenzyl-1,5-pentanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehydeoxime]

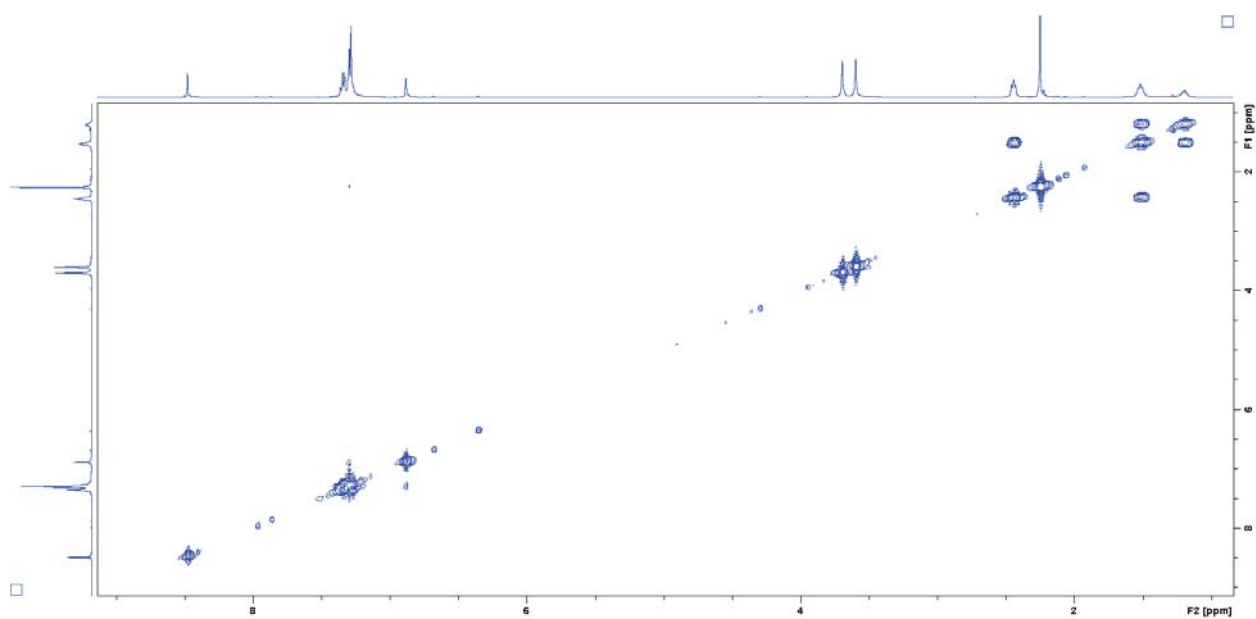


A solution of hydroxylamine hydrochloride (0.342 g, 4.92 mmol) in dry ethanol (20 ml) was added to a solution of potassium hydroxide (0.276 g, 4.92 mmol) in dry ethanol (60 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L7a** (1.000 g, 1.64 mmol) in dry toluene (30 ml) over 30 minutes. The pale yellow solution was stirred for further 48 h at RT, after which time a white precipitate was obtained. The combined residues were filtered, washed with chloroform (3 x 30 ml) followed by ethanol (3 x 30 ml). The final yellow waxy product was dried *in vacuo*. Yield (0.892 g, 85%). IR (KBr pellet): 1612 (m, C=N), 1280 (s, C-O), 1022 (m, N-O) cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{44}\text{N}_4\text{O}_4$: C, 73.00; H, 7.29; N, 9.20. Found: C, 72.87; H, 6.98; N, 8.92. ^1H NMR (CDCl_3 , 500 MHz): δ 1.18 (q, $J = 7.22$ Hz, 2H, CH_2), 1.51 (q, $J = 6.83$, 4H, CH_2), 2.25 (s, 6H, CH_3), 2.44 (s, $J = 6.99$ Hz, 4H, NCH_2), 3.59 (s, 4H, NCH_2Ar), 3.69 (s, 4H, $\text{Ar-CH}_2\text{NCH}_2$), 6.86 (br, 2H, Ar-H), 7.26 (br, 4H, Ar-H), 7.28 (br, 4H, Ar-H), 7.29 (br, 4H, Ar-H), 7.33 (t, $J = 7.82$ Hz, 4H, Ar-H), 8.48 (s, 2H, CHN). ^{13}C NMR (CDCl_3 , 500 MHz): δ 154.2 (ArC-O), 147.7 (CHN), 136.8, 131.4, 129.5, 128.5, 128.1, 127.6, 126.6, 122.7, 118.2, 122.4 (ArC), 58.1 (CH_2), 56.5 (CH_2), 52.6 (CH_2), 25.7 (CH_2), 24.6 (CH_2), 20.4 (CH_3) ppm. ES^+ -MS (m/z) 609 $[\text{M}+\text{H}]^+$.

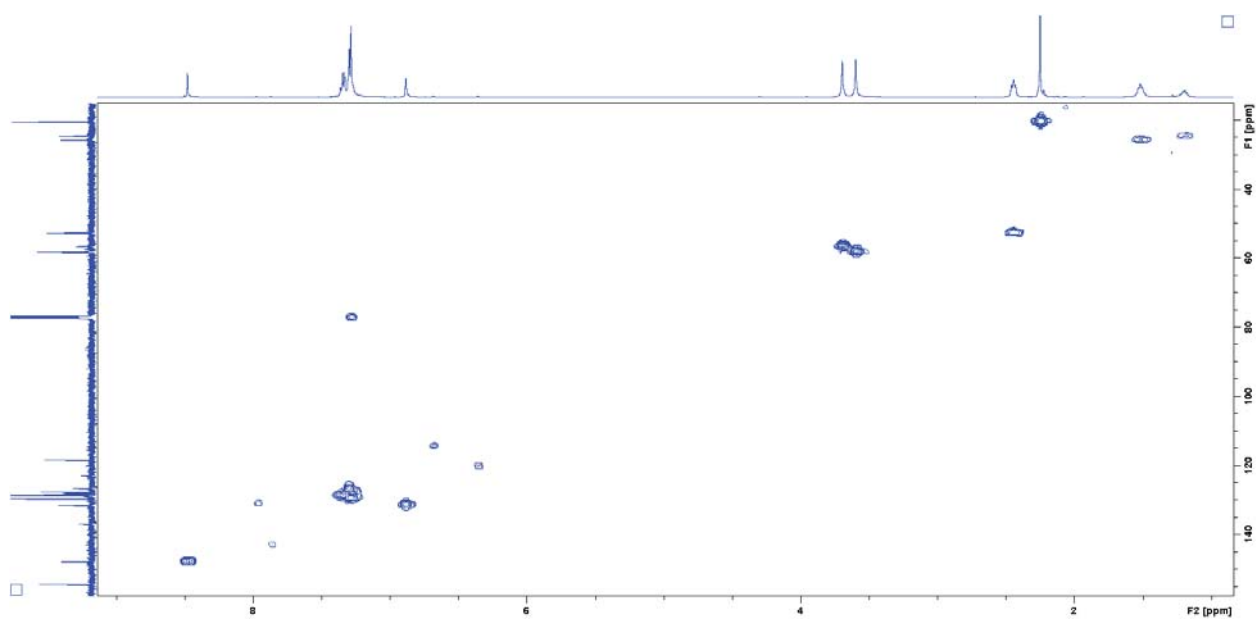








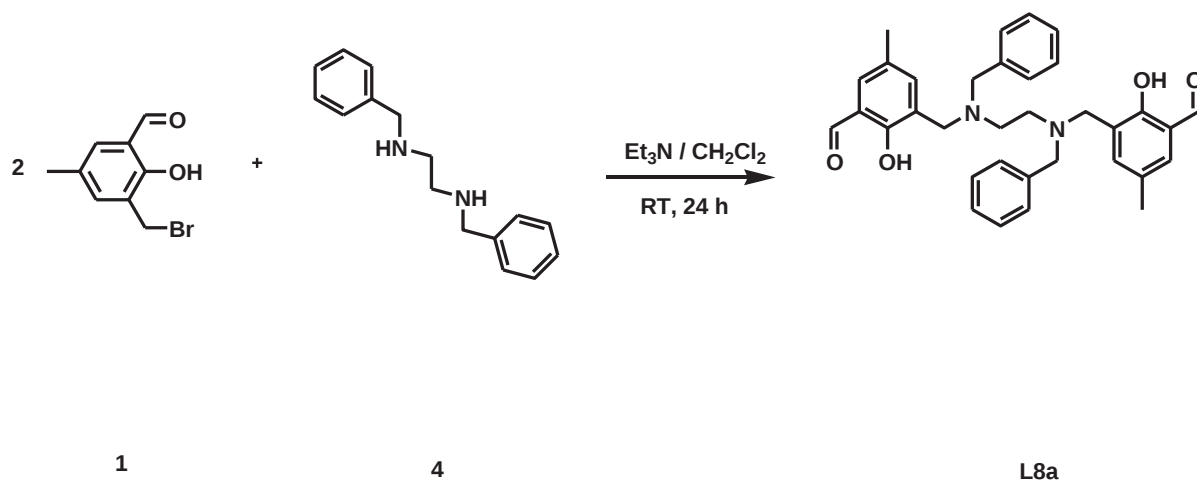
COSY experiment of **L7**



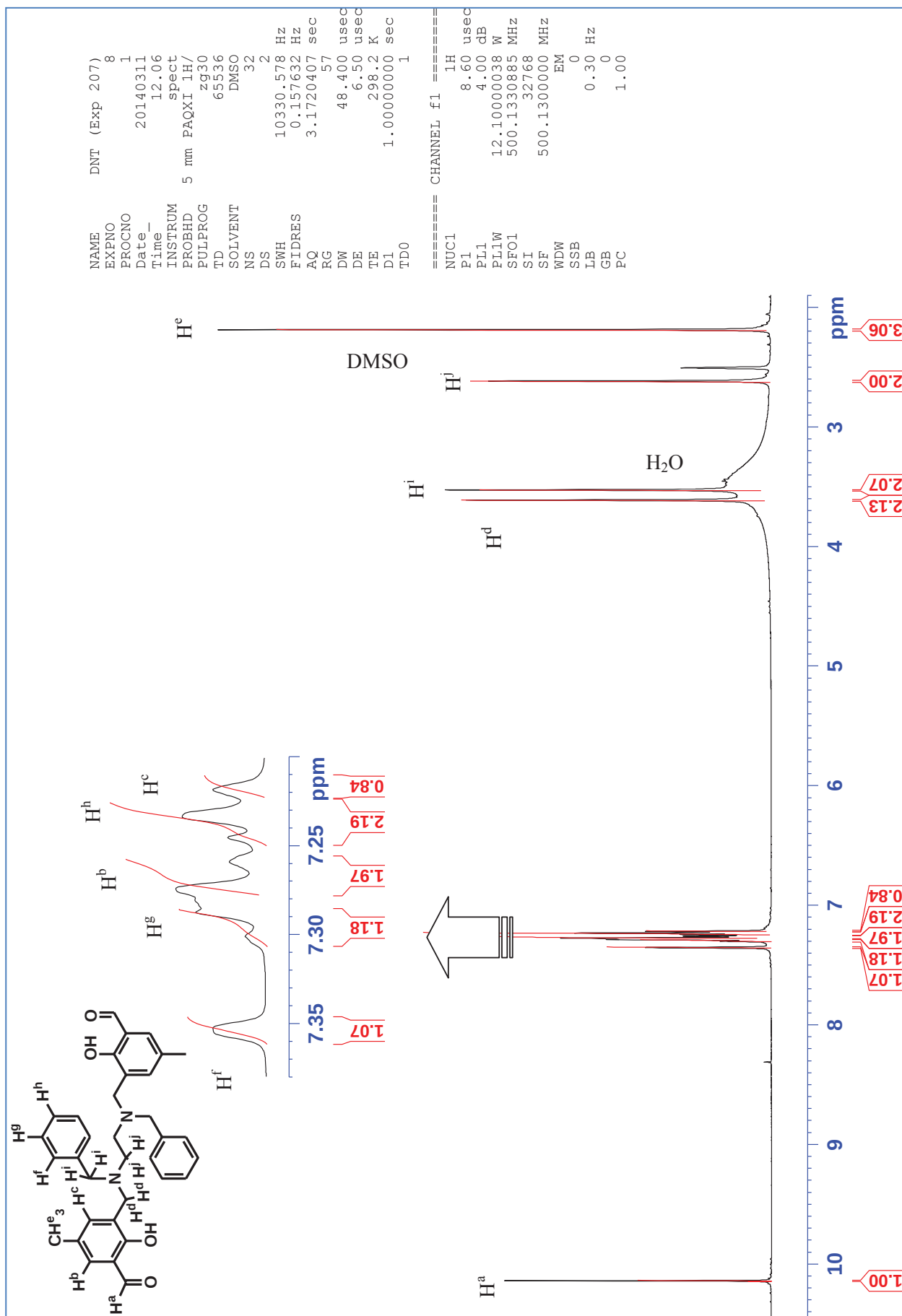
HMQC experiment of **L7**

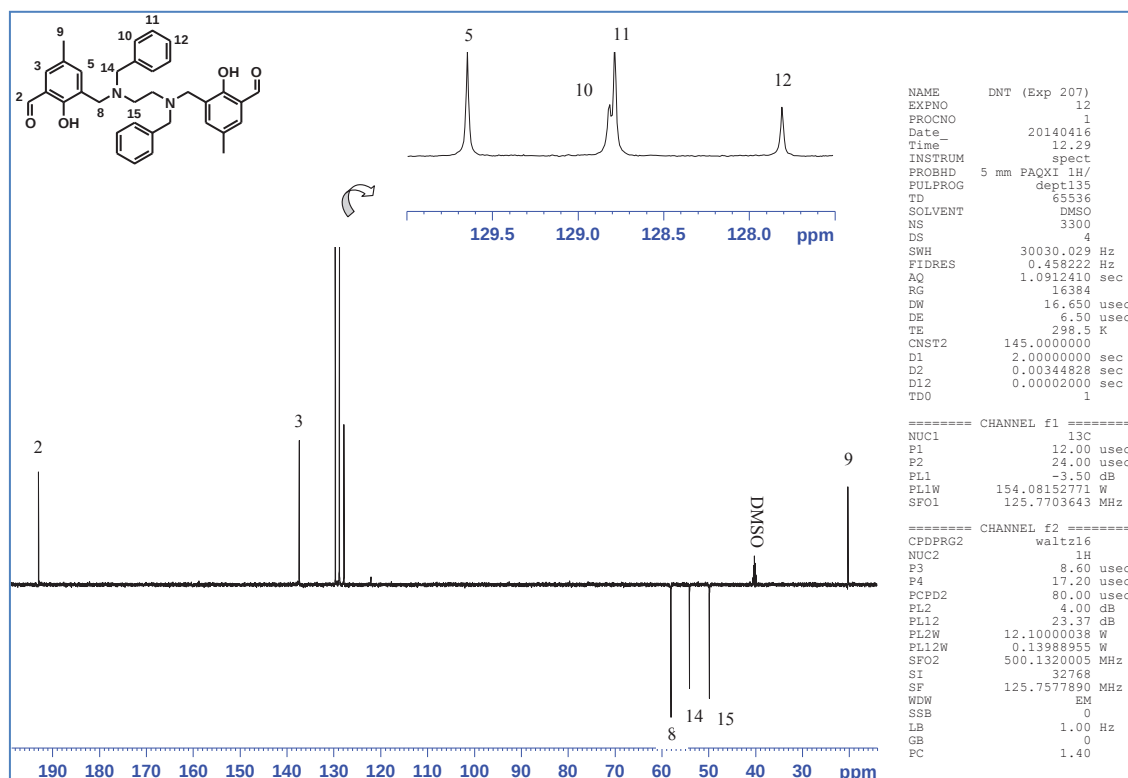
L8a

3,3'-[N,N'-dibenzyl-1,2-ethanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde]

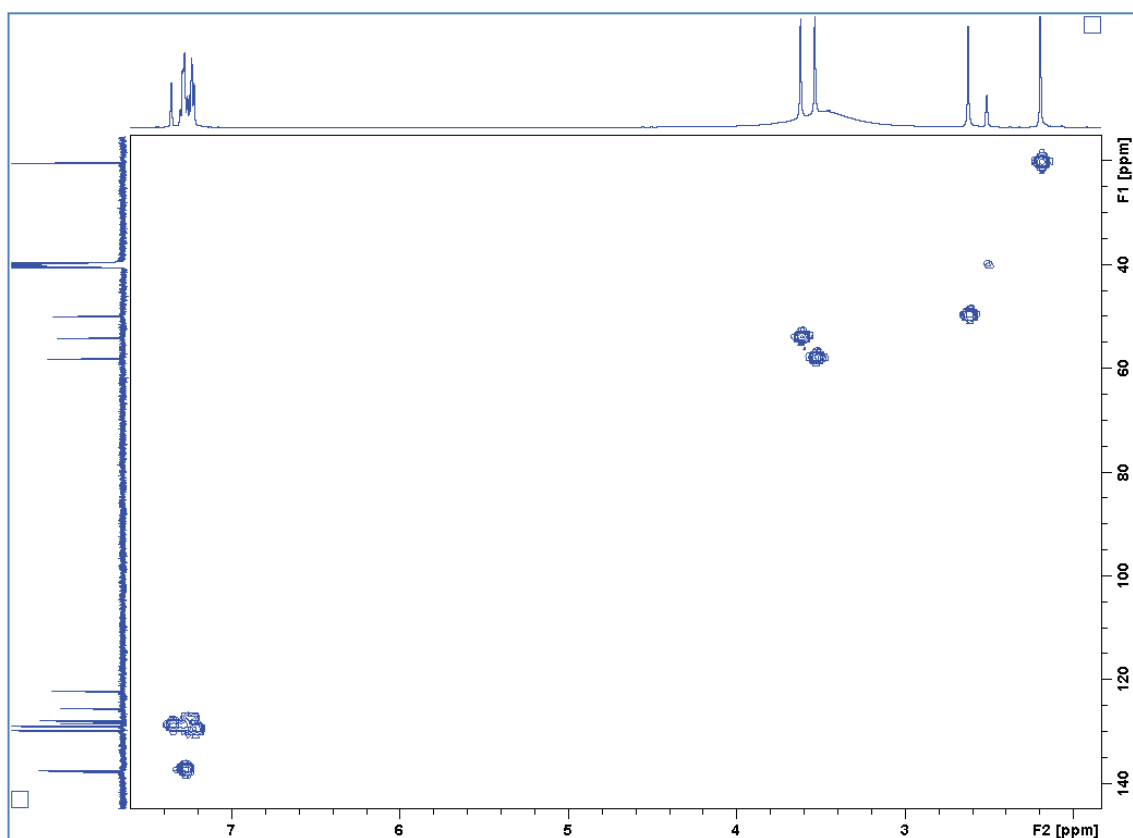


To a solution of Et₃N (1.85 g, 18.30 mmol) in dry CH₂Cl₂ (60 ml) were added over 30 minutes solutions of **1** (4.19 g, 18.30 mmol) and **4** (EtOAc : Et₃N / 9 : 1, *R_f* = 0.5), (2.20 g, 9.15 mmol) each dissolved in dry CH₂Cl₂ (40 ml). The yellow solution was stirred for 24 h at RT. The solution was washed with water (3 x 150 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a bright yellow semi-solid, which was dried *in vacuo*. Yield (4.51 g, 85%). Mp 158-164 °C. IR (KBr pellet): 1673 (s, C=O), 1470 (m, Ar-C=C) cm⁻¹. Anal. Calcd for C₃₄H₃₆N₂O₄·0.75H₂O: C, 74.84; H, 6.83; N, 5.13. Found: C, 75.03; H, 6.69; N, 5.17. ¹H NMR (DMSO, 500 MHz): δ 2.19 (s, 6H, CH₃), 2.61 (s, 4H, NCH₂CH₂), 3.53 (s, 4H, Ar-CH₂N), 3.61 (s, 4H, Ar-CH₂N), 7.22 (br, 4H, Ar-H), 7.23 (s, 4H, Ar-H), 7.27 (br, 2H, Ar-H), 7.28 (m, H, Ar-H), 7.35 (br, 2H, Ar-H), 10.14 (s, 2H, CHO). ¹³C NMR (DMSO, 500 MHz): δ 192.9 (CHO), 158.6, 137.6, 137.3, 129.6, 128.8, 128.7, 128.3, 127.8, 125.4, 122.0, (ArC), 58.0 (CH₂), 54.0 (CH₂), 49.8 (CH₂), 20.3 (CH₃) ppm. ES⁺-MS (*m/z*) 538 [M+H]⁺.



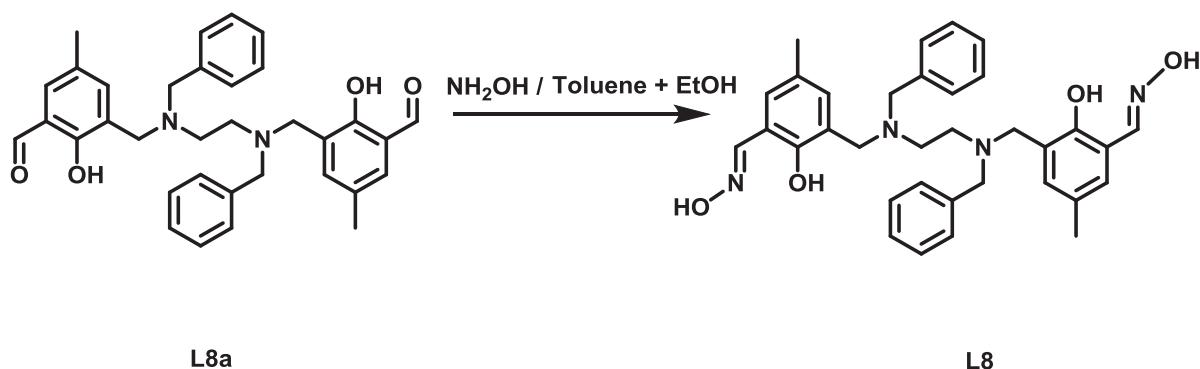


DEPT 135 experiment of **L8a**

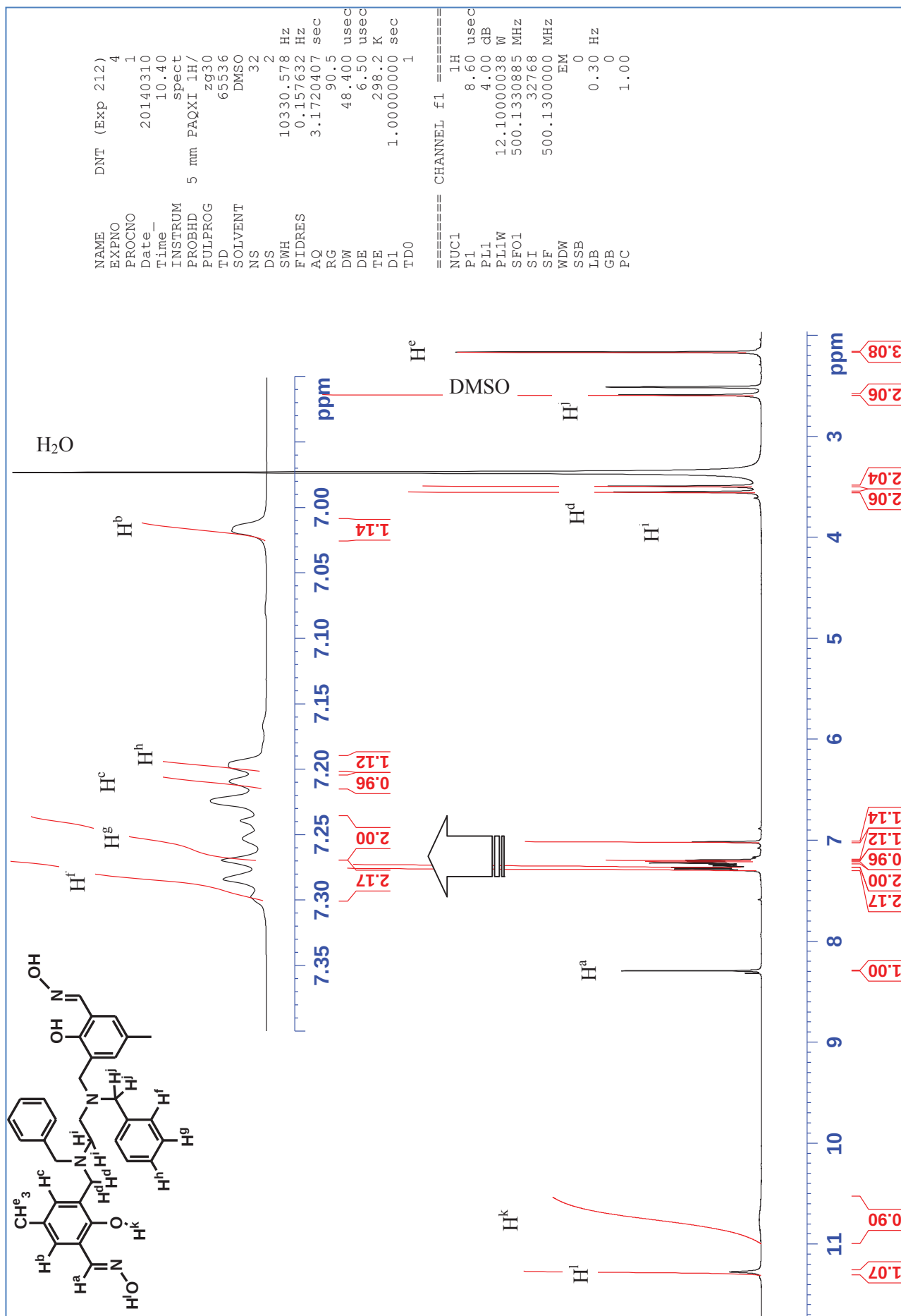


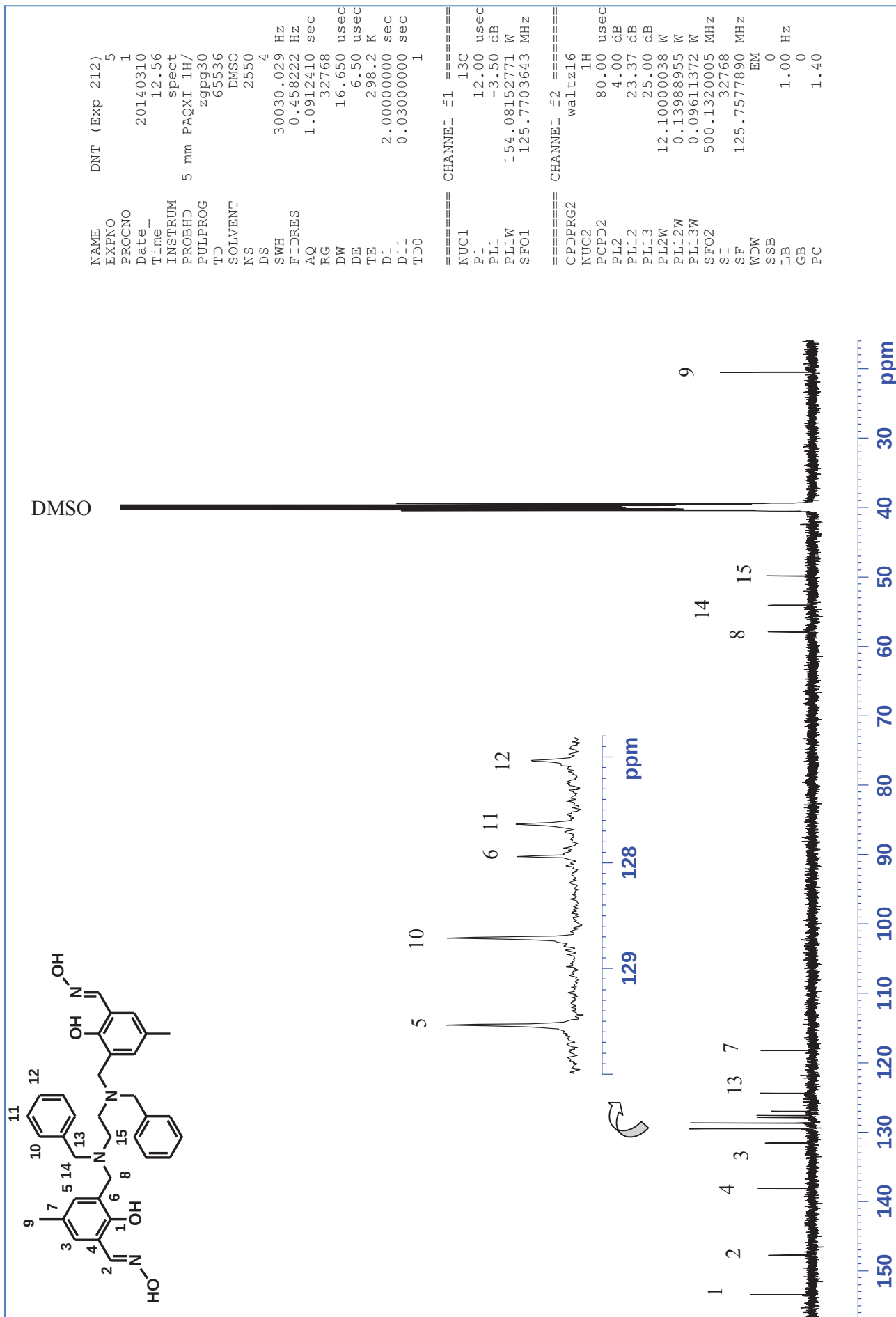
HMQC experiment of **L8a**

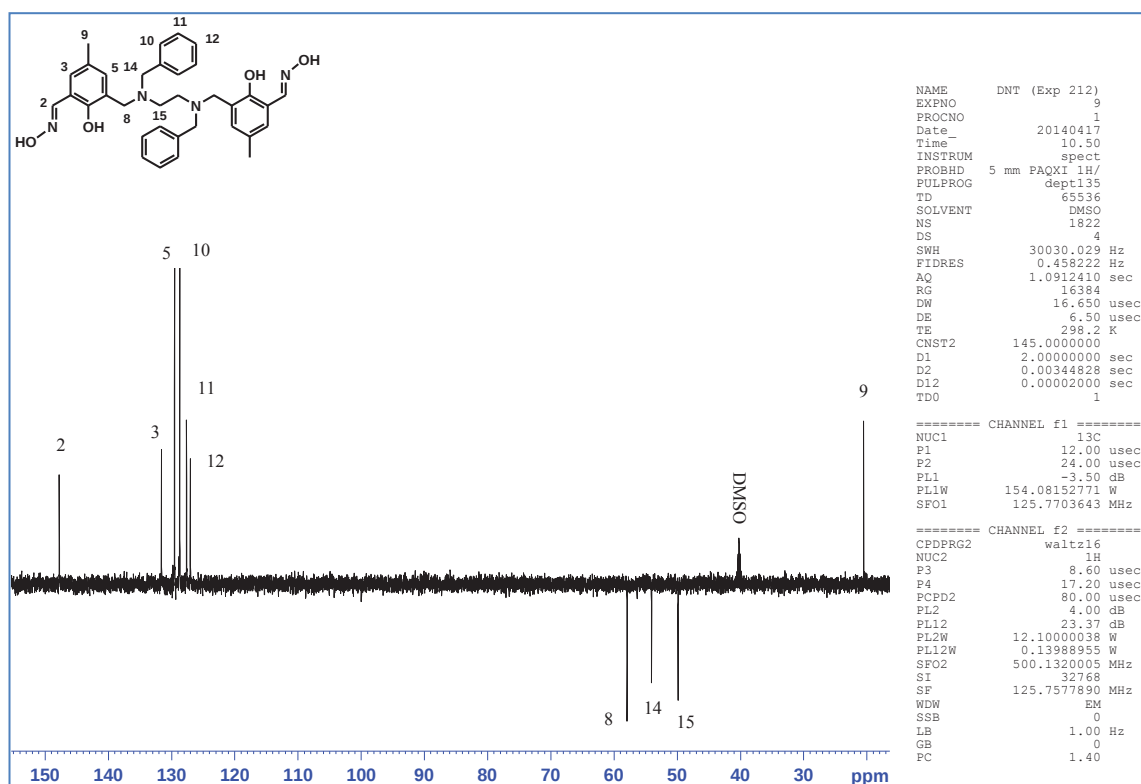
3,3'-[*N,N'*-dibenzyl-1,2-ethanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehydeoxime]



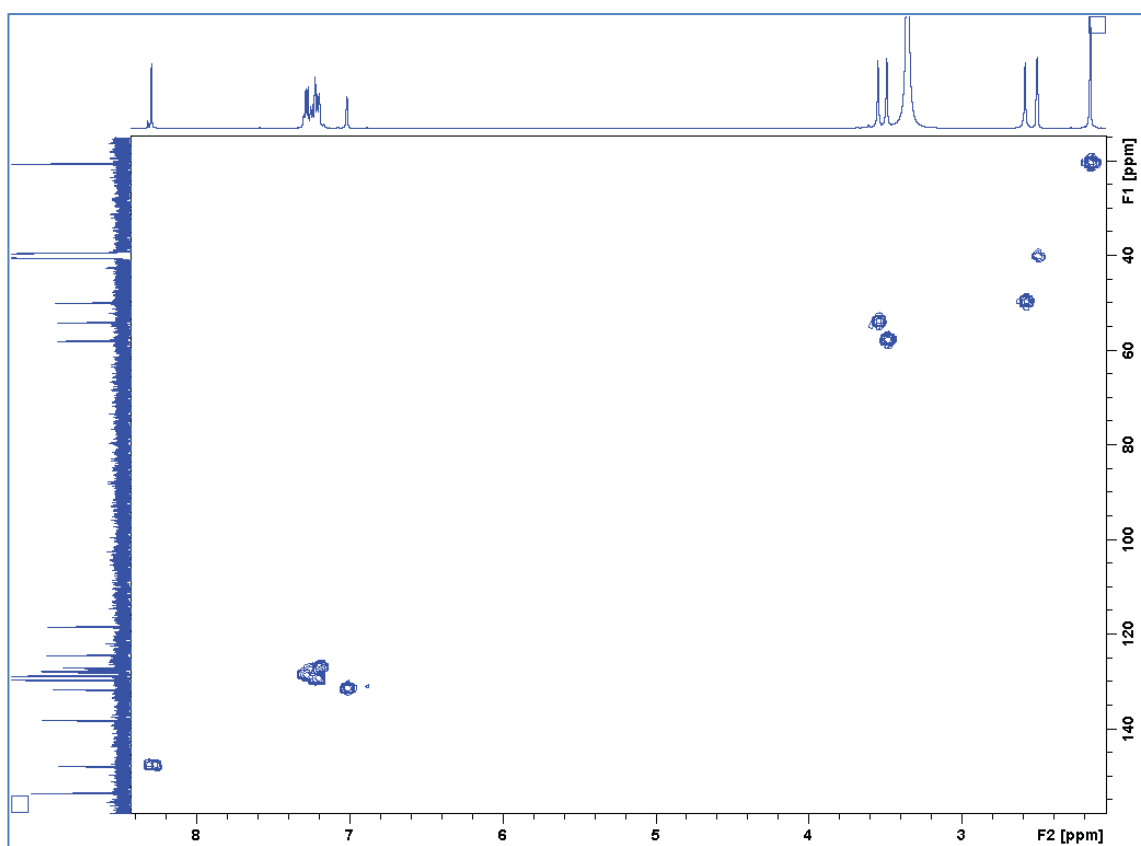
A solution of hydroxylamine hydrochloride (0.587 g, 8.45 mmol) in dry ethanol (20 ml) was added to a solution of potassium hydroxide (0.474 g, 8.45 mmol) in dry ethanol (60 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L8a** (0.908 g, 1.69 mmol) in dry toluene (30 ml) over 30 minutes. The pale yellow solution was stirred for further 48 h at RT, after which time a white precipitate was obtained. The combined residues were filtered, washed with chloroform (3 x 30 ml) followed by ethanol (3 x 30 ml). The final product was dried *in vacuo*. Yield (0.863 g, 90%). Mp 195-196.4 °C. IR (KBr pellet): 1610 (m, C=N), 2952 (m, C-H), 1475 (s, -CH₂), 1285 (s, C-O), 1070 (m, N-O), 742 (Ar-H) cm⁻¹. Anal. Calcd for C₃₄H₃₈N₄O₄·1.6 H₂O: C, 68.57; H, 6.97; N, 9.41. Found: C, 68.45; H, 6.96; N, 9.39. ¹H NMR (DMSO, 500 MHz): δ 2.16 (s, 6H, CH₃), 2.58 (s, 4H, Ar-CH₂N), 3.49 (s, 4H, Ar-CH₂N), 3.54 (s, 4H, Ar-CH₂NCH₂CH₂), 7.01 (br, 2H, Ar-H), 7.19 (br, 2H, Ar-H), 7.21 (br, 2H, Ar-H), 7.24 (m, 4H, Ar-H), 7.28 (m, 4H, Ar-H), 8.29 (s, 2H, CHN). ¹³C NMR (DMSO, 500 MHz): δ 153.4 (ArC), 147.7 (CN), 138.1, 131.5, 129.5, 128.7, 127.9, 127.6, 127.0, 124.2, 118.2 (ArC), 57.9 (CH₂), 54.0 (CH₂), 49.8 (CH₂), 20.5 (CH₃) ppm. ES⁺-MS (*m/z*) 568 [M+H]⁺.







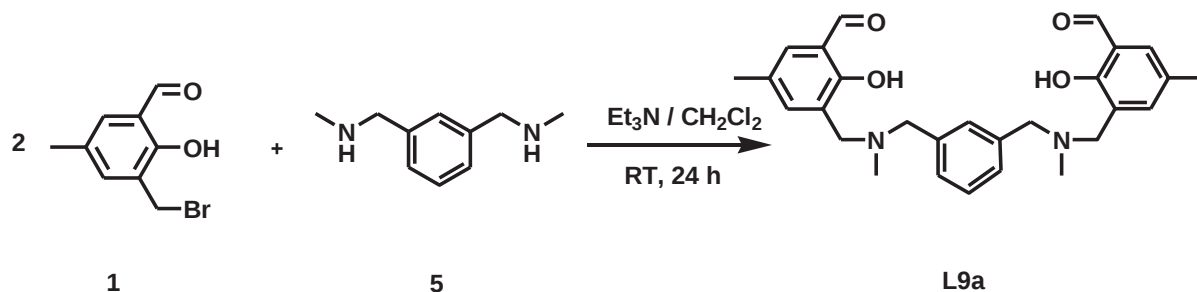
DEPT 135 experiment of **L8**



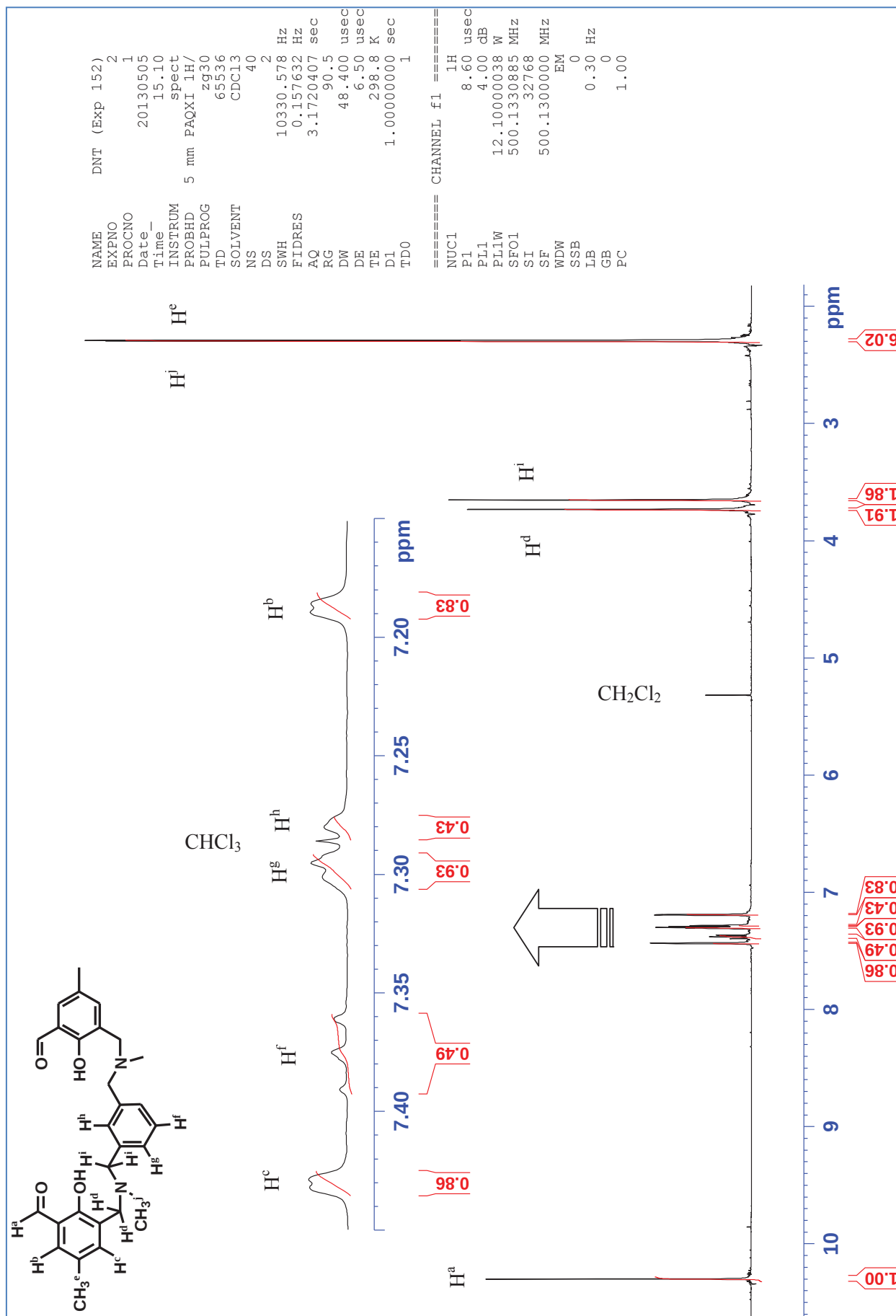
HMQC experiment of **L8**

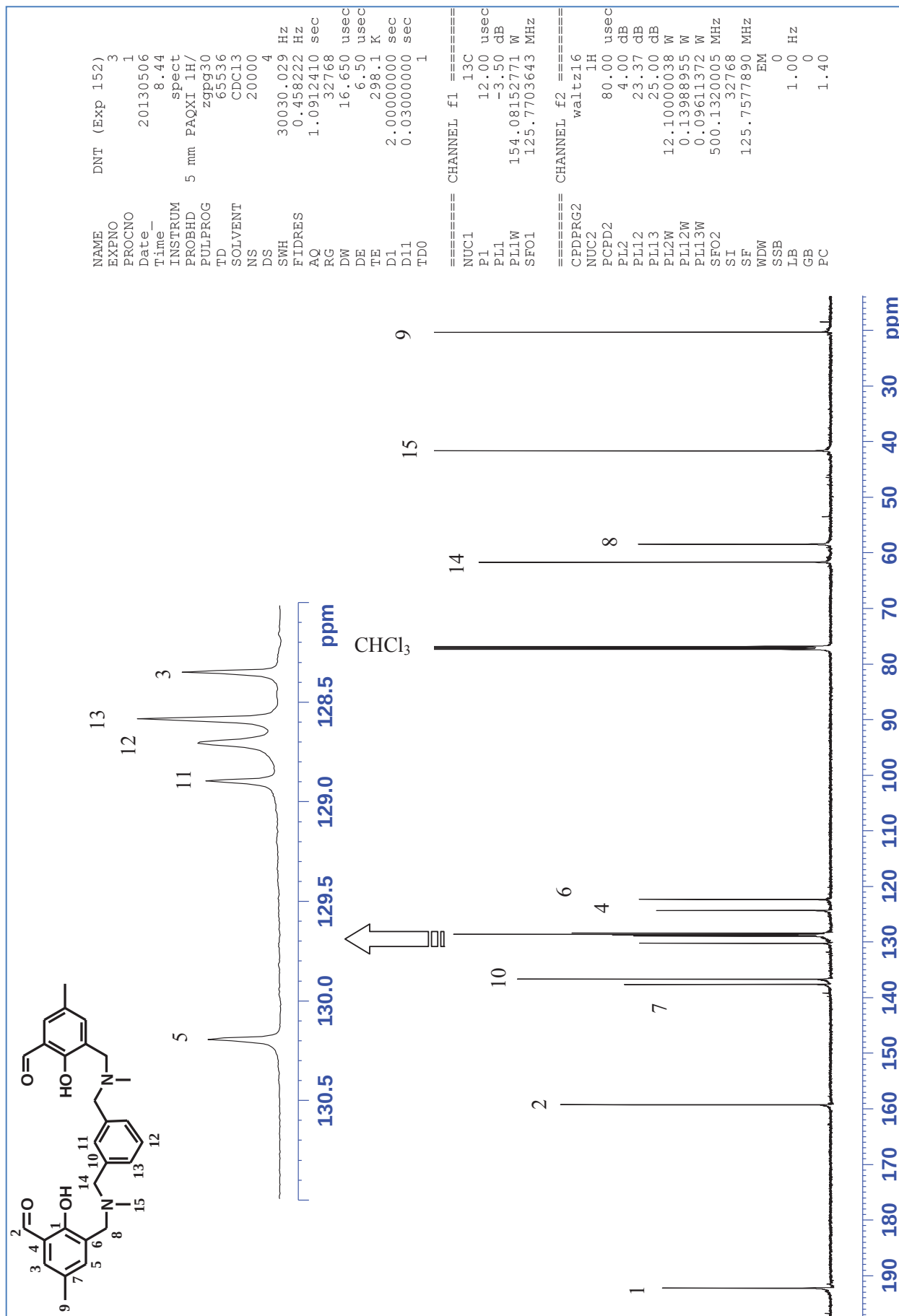
L9a

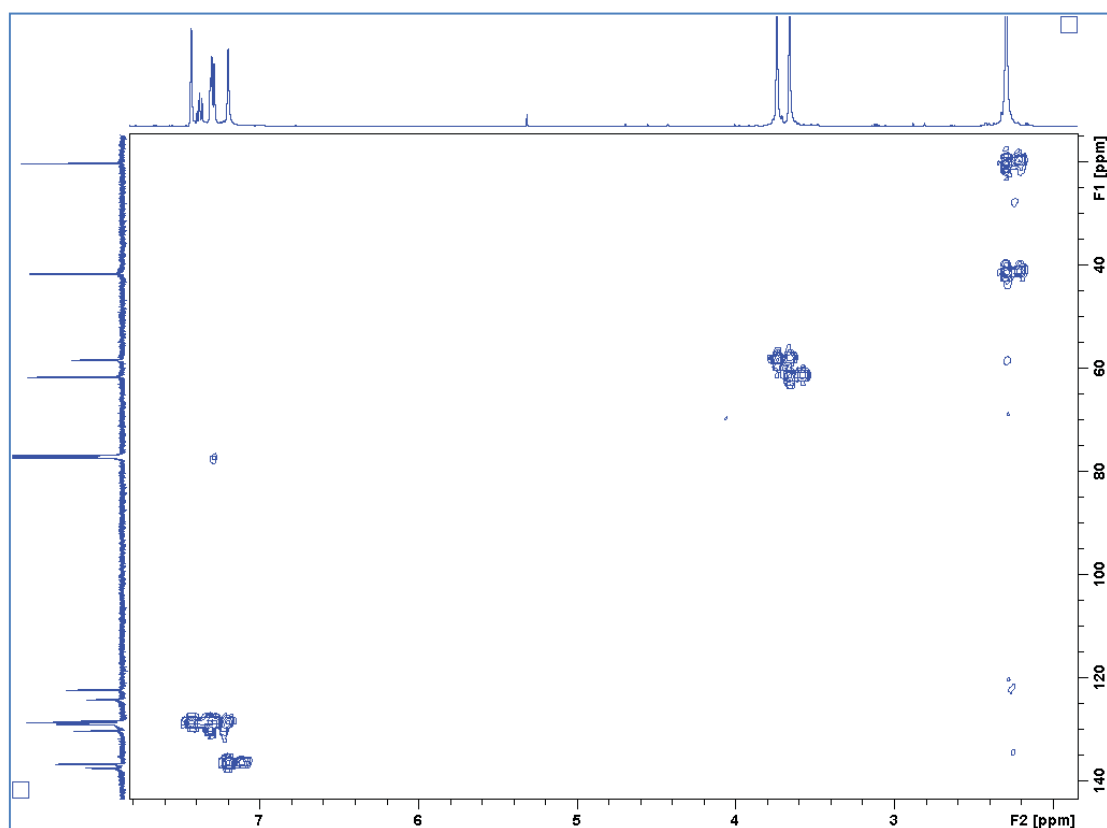
3,3'-[1,3-phenylenebis[methylene(methylimino)methylene]]bis[2-hydroxy-5-methylbenzaldehyde]



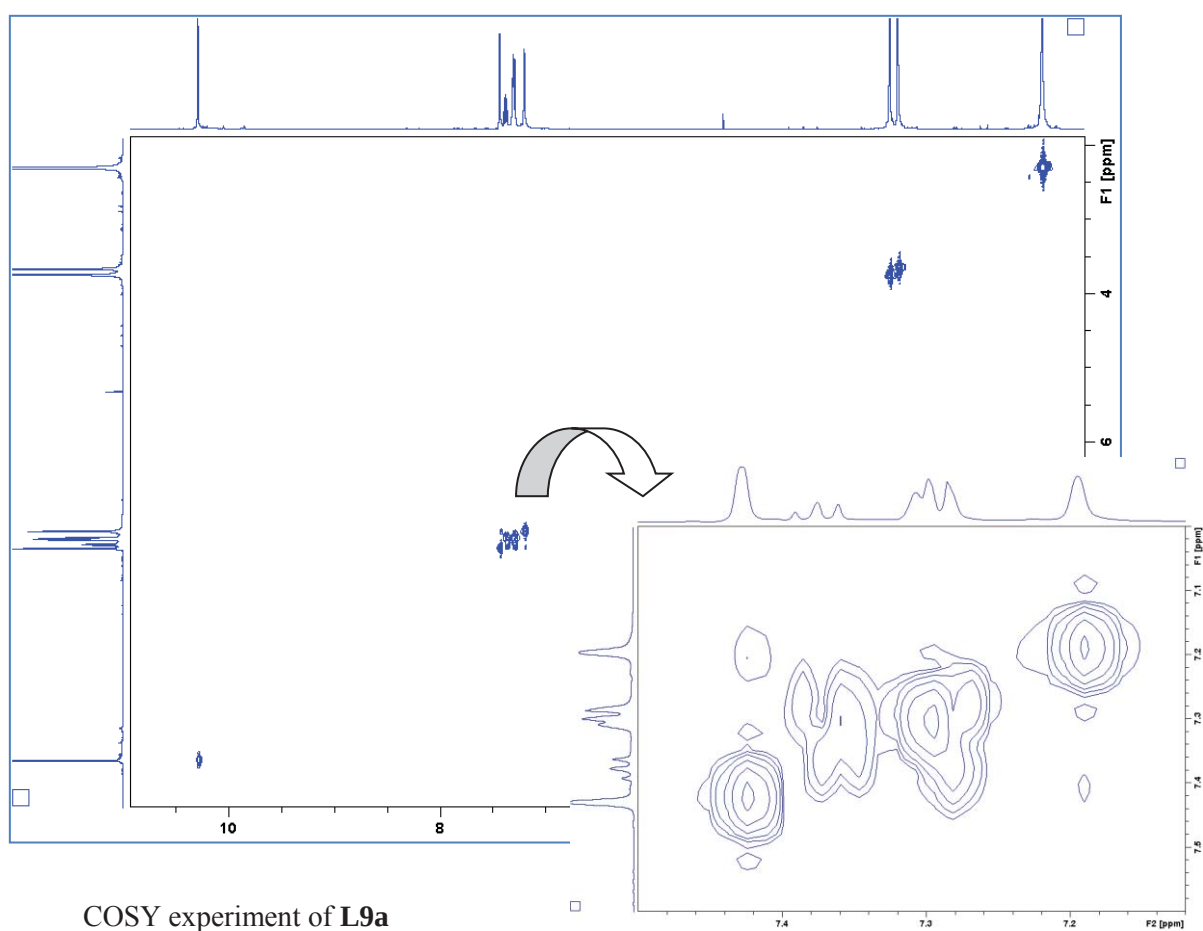
To a solution of Et₃N (1.11 g, 11.00 mmol) in dry CH₂Cl₂ (20 ml) were added over 30 minutes solutions of **1** (1.27 g, 5.54 mmol) and **5** (0.46 g, 2.77 mmol) each dissolved in dry CH₂Cl₂ (15 ml). The yellow solution was stirred for a further 24 h at RT. The solution was washed with water (3 x 70 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded a bright yellow waxy solid, which was dried *in vacuo*. Yield (1.19 g, 92%). IR (KBr pellet): 1679 (s, C=O), 3511 (br, Ar-O-H), 2845 (m, C-H), 1473 (s, Ar-C=C), 1608 (s, Ar-C=C) cm⁻¹. Anal. Calcd for C₂₈H₃₂N₂O₄·0.1CH₂Cl₂: C, 71.95; H, 6.92; N, 5.97. Found: C, 72.10; H, 7.01; N, 6.01. ¹H NMR (CDCl₃, 500 MHz): δ 2.28 (s, 6H, CH₃), 2.29 (s, 6H, CH₃), 3.73 (s, 4H, Ar-CH₂N), 3.74 (s, 4H, Ar-CH₂N), 7.18 (d, *J* = 1.75 Hz, 2H, Ar-H), 7.28 (s, 1H, Ar-H), 7.29 (d, *J* = 2.84 Hz, 2H, Ar-H), 10.29 (s, 2H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 192.1 (CHO), 159.1, 137.5, 136.5, 130.1, 128.8, 128.7, 128.5, 128.3, 124.2, 122.2 (ArC), 61.6 (CH₂), 58.4 (CH₂), 41.6 (CH₃), 20.2 (CH₃) ppm. ES⁺-MS (*m/z*) 461 (M+H)⁺.



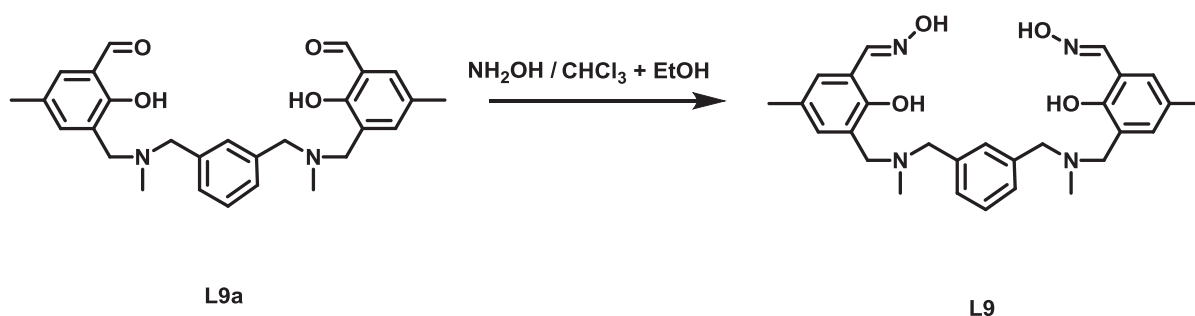




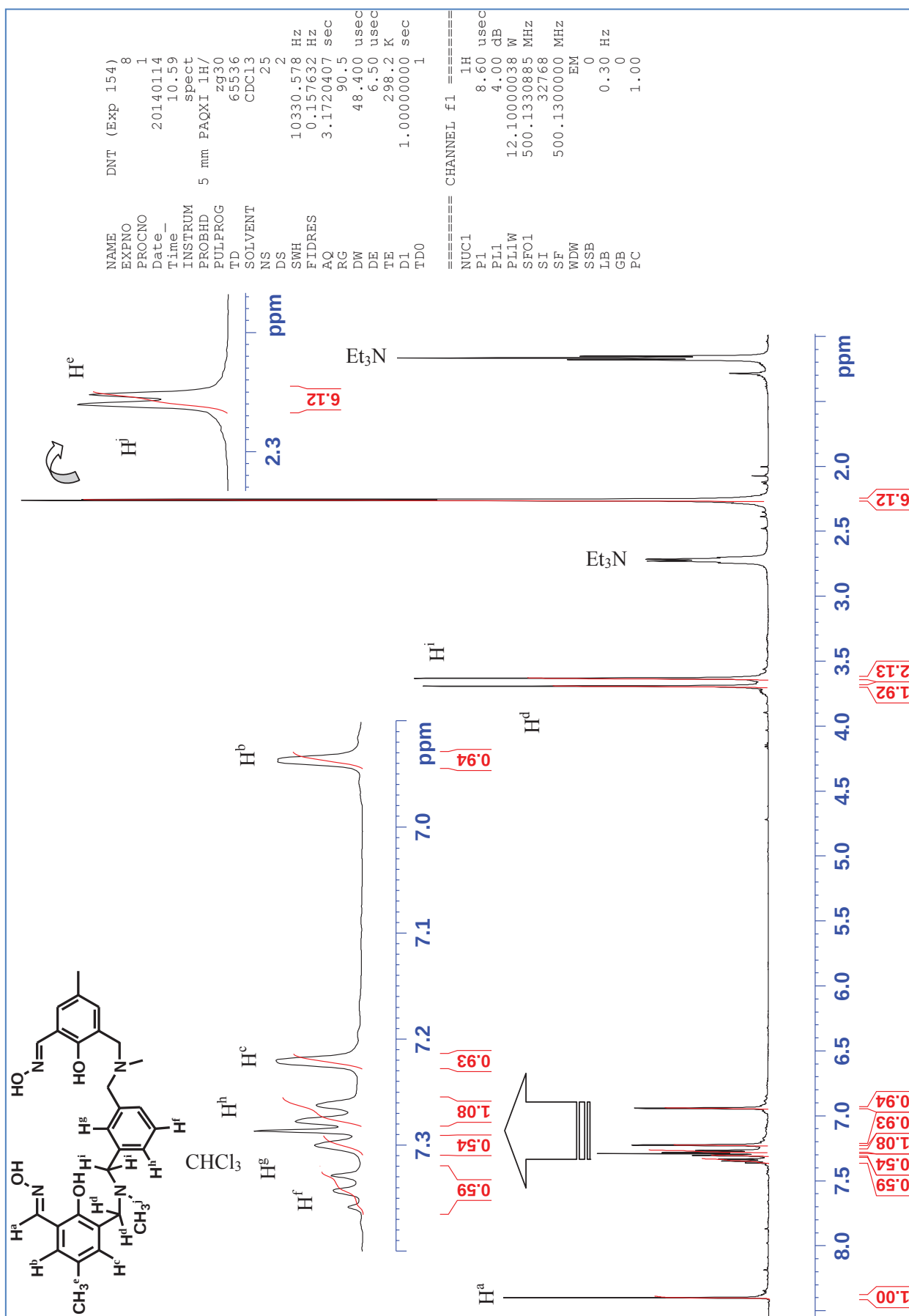
HMQC experiment of **L9a**

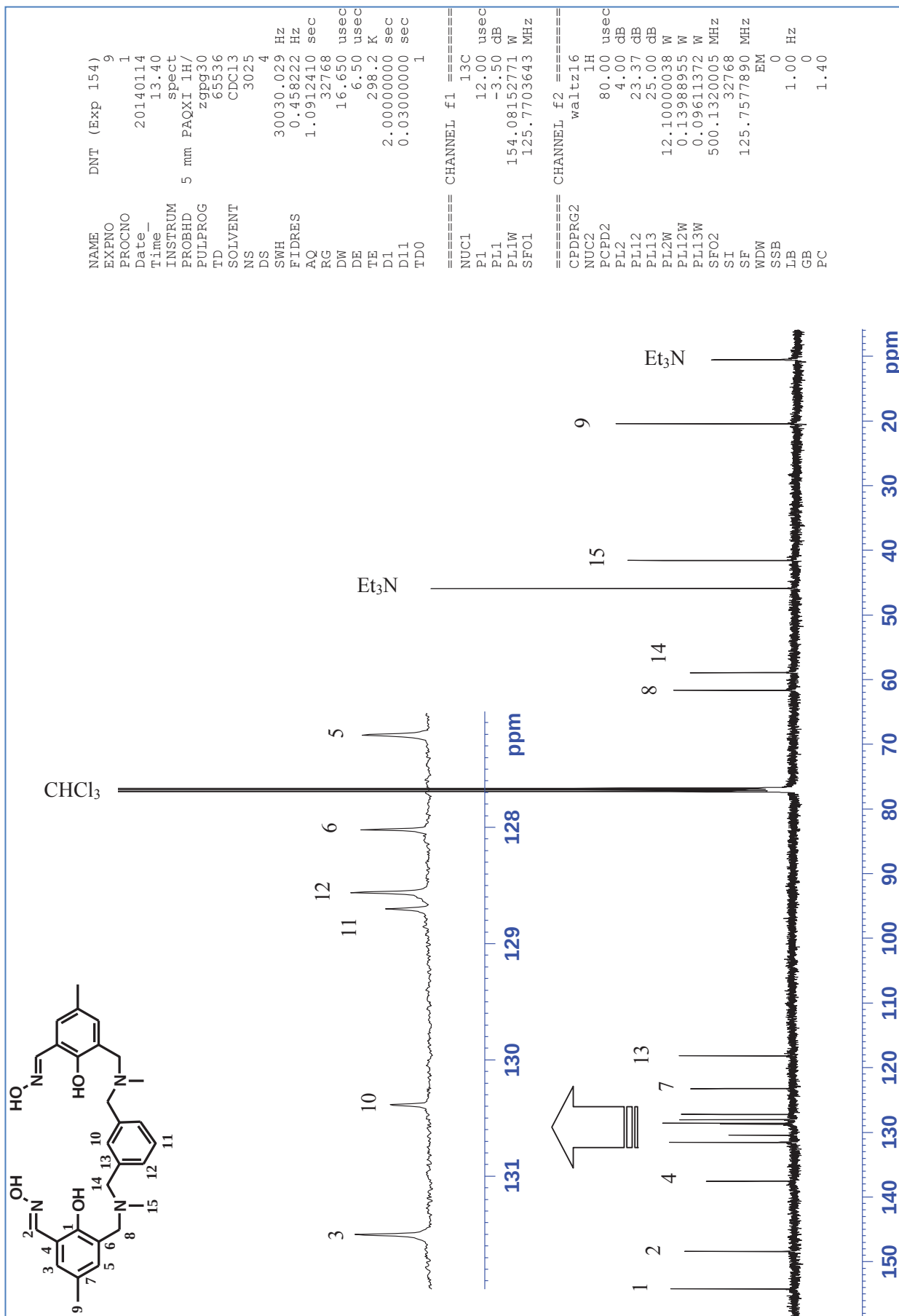


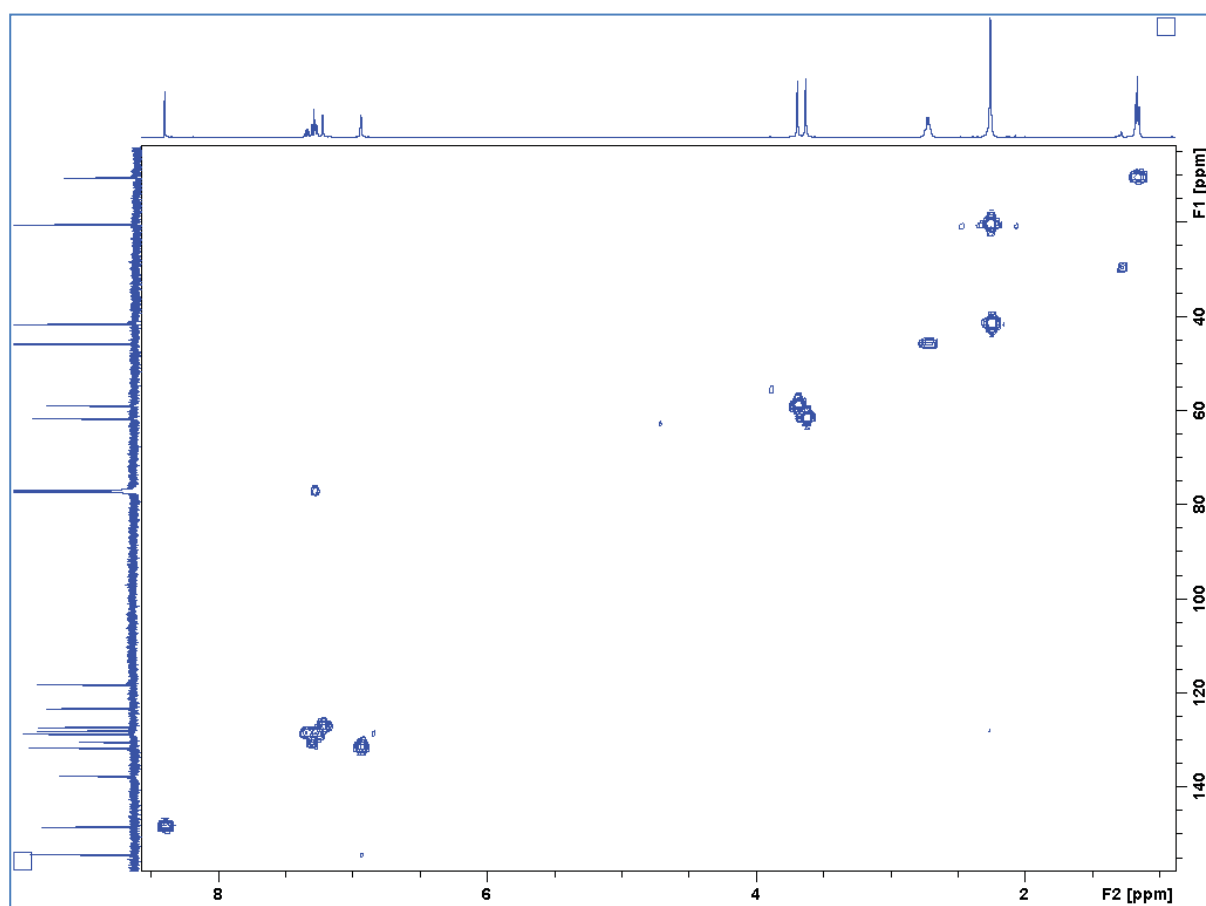
COSY experiment of **L9a**

3,3'-[1,3-phenylenebis[methylene(methylimino)methylene]]bis[2-hydroxy-5-methyl]-1,1'-dioxime

A solution of hydroxylamine hydrochloride (1.21 g, 17.37 mmol) in dry ethanol (240 ml) was added to a solution of potassium hydroxide (0.97 g, 17.37 mmol) in dry ethanol (240 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L9a** (4.00 g, 8.68 mmol) in a chloroform : dry ethanol ratio of 20 : 380 ml over 30 minutes. The pale yellow solution was stirred for further 48 h at RT. The solvent was removed under reduced pressure, the pale yellow residue afforded was then dissolved in chloroform (300 ml), was washed with water (3 x 250 ml), and the organic phase was dried over anhydrous Na₂SO₄ followed by the removal of the solvent under reduced pressure, after which the pale yellow sticky solid was obtained. The product was then column purified with Et₃N : EtOAc / 1 : 9 (*R_f* = 0.74) and dried *in vacuo*. Yield (3.842 g, 90%). IR (KBr pellet): 2975 (m, C-H), 1618 (m, C=N), 1467(s, -CH₂), 1288 (s, C-O), 1018 (m, N-O), 734 (s, Ar-H) cm⁻¹. Anal. Calcd for C₂₈H₃₄N₄O₄·0.5C₆H₁₅N: C, 68.80; H, 7.73; N, 11.65 Found, C, 68.93; H, 7.58; N, 11.54. ¹H NMR (CDCl₃, 500 MHz): δ 2.25 (s, 6H, Ar-CH₃), 2.26 (s, 6H, NCH₃), 3.63 (s, 4H, Ar-CH₂N), 3.69 (s, 4H, Ar-CH₂N), 6.93 (d, *J* = 1.10 Hz, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 7.26 (d, *J* = 7.67 Hz 4H, Ar-H), 7.30 (s, 1H, Ar-H), 7.32 (t, *J* = 7.12 Hz, 1H, Ar-H), 8.39 (s, 2H, CHN). ¹³C NMR (CDCl₃, 500 MHz): δ 154.1 (C=O), 148.3 (CHN), 137.5, 131.5, 130.3, 128.7, 128.5, 128.0, 127.2, 123.2, 118.1 (ArC), 61.6 (CH₂), 58.9 (CH₂), 41.5 (CH₃), 20.4 (CH₃) ppm. ES⁺-MS (*m/z*) 492 [M+H]⁺.



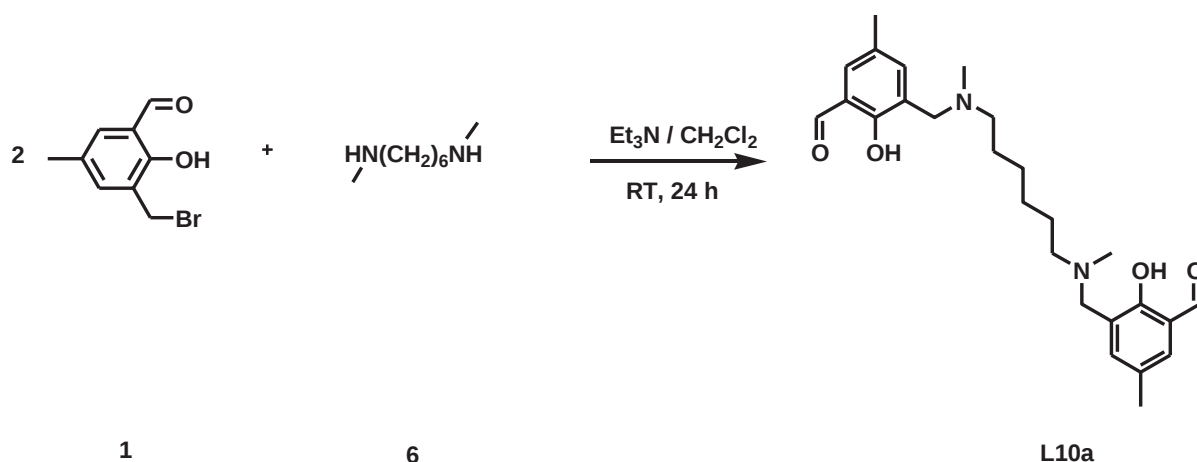




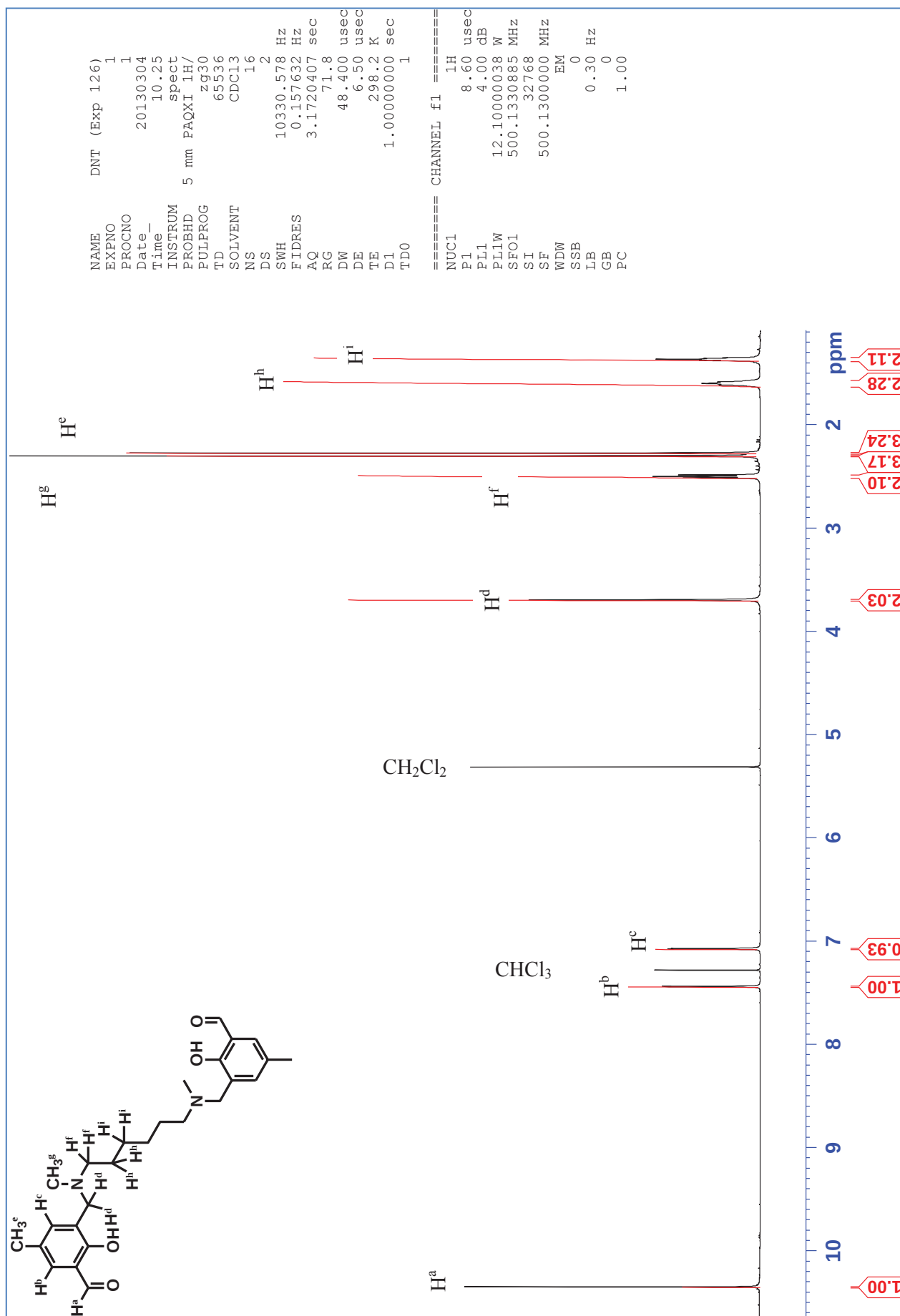
HMQC experiment of **L9**

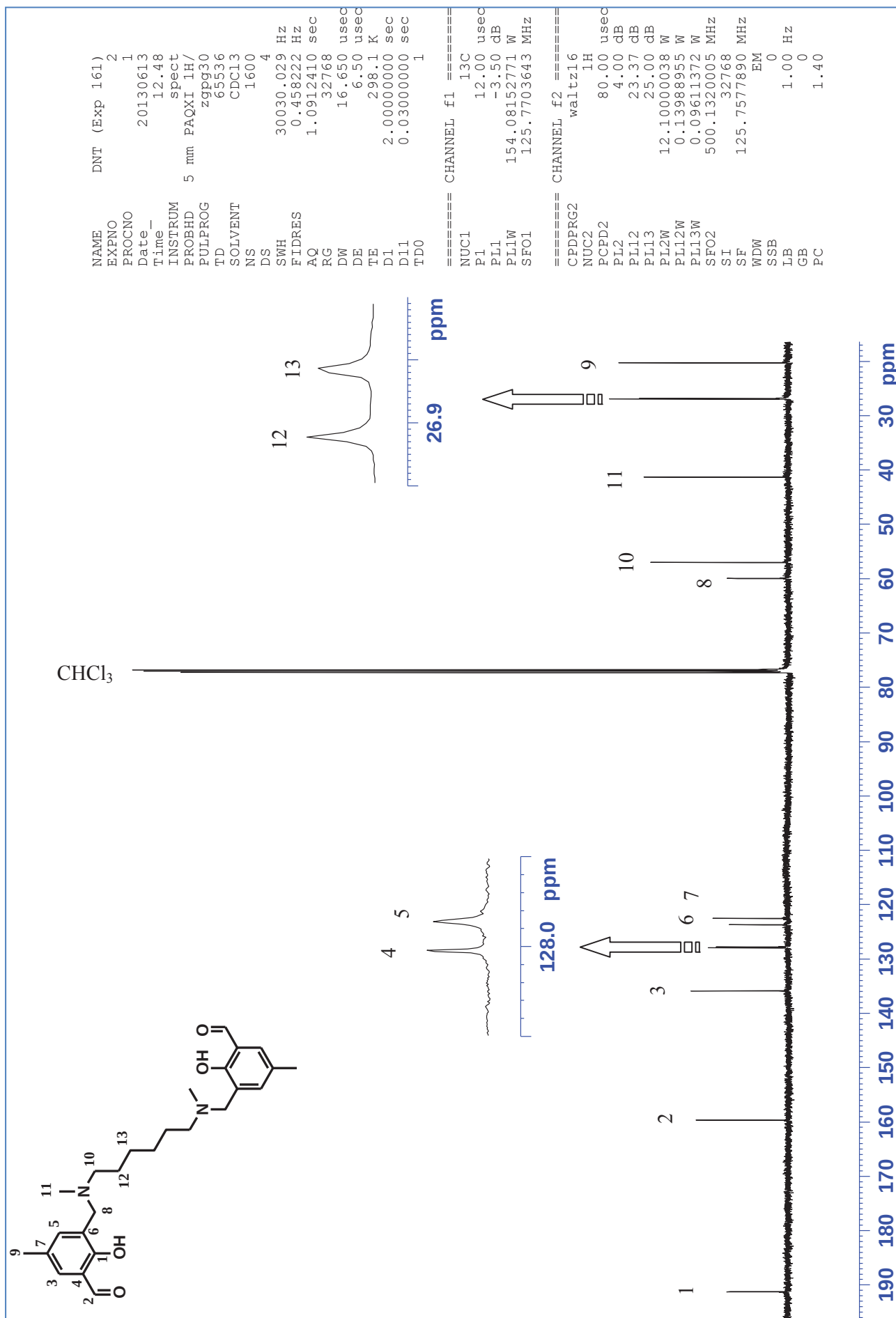
L10a

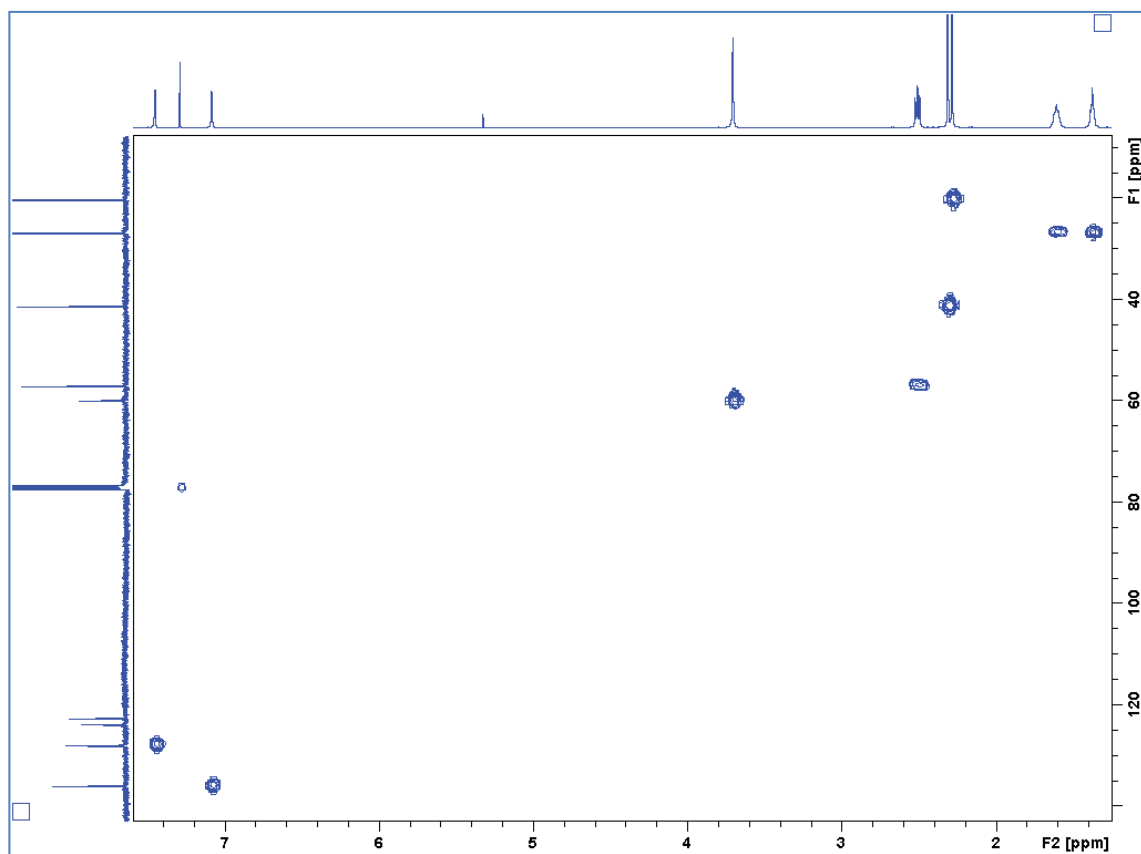
3,3'-[1,6-hexanediylbis[(methylimino)methylene]]bis[2-hydroxy-5-methylbenzaldehyde]



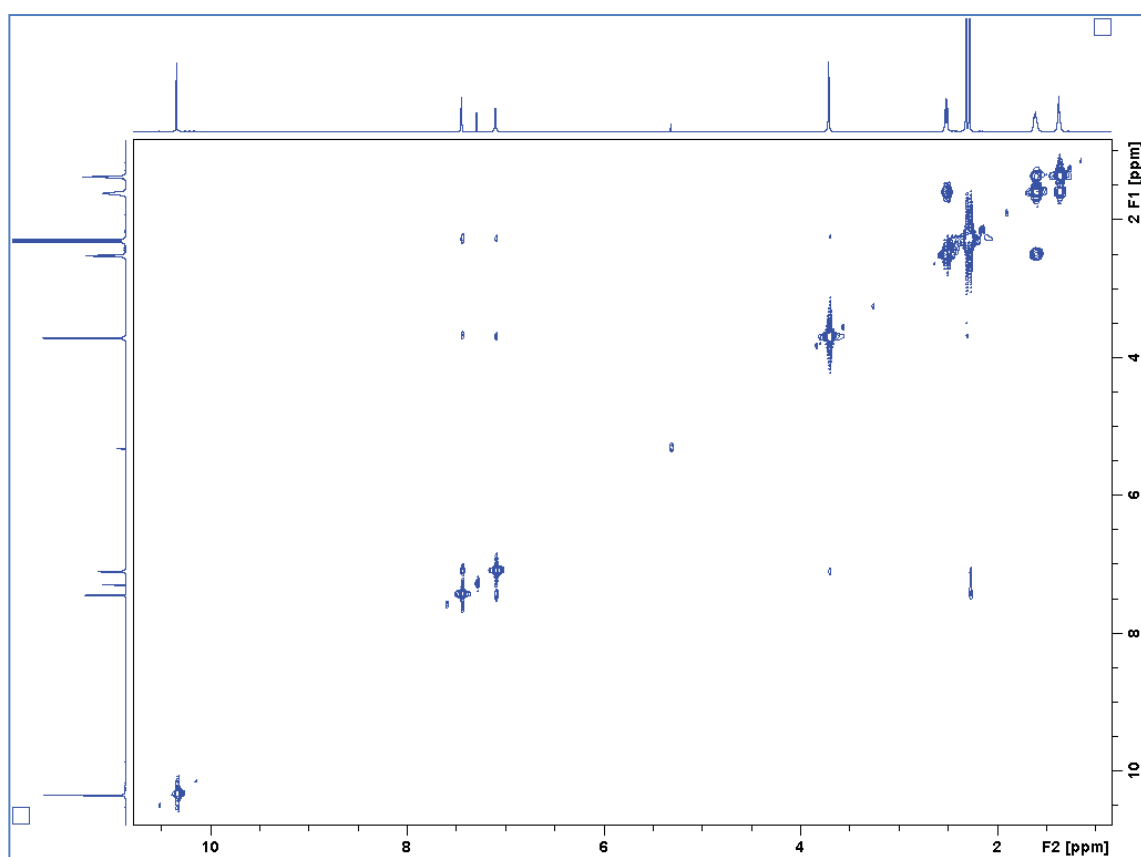
To a solution of Et₃N (0.88 g, 8.73 mmol) in dry CH₂Cl₂ (40 ml) were added over 30 minutes solutions of **1** (2.00 g, 8.73 mmol) and **6** (0.63 g, 4.36 mmol) each dissolved in dry CH₂Cl₂ (30 ml). The resulting yellow solution was stirred for 24 h at RT, after which time the solution was washed with water (3 x 150 ml) and the organic phase dried over anhydrous Na₂SO₄. Removal of the solvent afforded an oil which became a yellow solid *in vacuo*. Yield (2.02 g, 92%). Mp 111-112 °C. IR (KBr pellet): 1682 (s, C=O), 3456 (br, Ar-O-H), 2862 (m, C-H), 1602 (s, Ar-C=C) cm⁻¹. Anal. Calcd for C₂₆H₃₆N₂O₄: C, 70.88; H, 8.24; N, 6.36. Found, C, 70.54; H, 8.61; N, 6.31. ¹H NMR (CDCl₃, 500 MHz): δ 1.35 (q, *J* = 3.64 Hz, 4H, CH₂), 1.58 (q, *J* = 7.10 Hz, 4H, CH₂), 2.27 (s, 6H, Ar-CH₃), 2.30 (s, 6H, CH₃N), 2.48 (t, *J* = 7.42 Hz, 4H, NCH₂), 3.69 (s, 4H, Ar-CH₂N), 7.07 (d, *J* = 1.65 Hz, 2H, Ar-H), 7.44 (d, *J* = 1.65 Hz, 2H, Ar-H), 10.35 (s, 2H, CHO). ¹³C NMR (CDCl₃, 500 MHz): δ 191.2 (CHO), 159.7, 135.9, 128.0, 127.8, 123.7, 122.6 (Ar-C), 59.9 (ArCH₂N), 57.0 (CH₂CH₂CH₂N), 41.3 (CH₃N), 26.9, 26.8 (CH₂CH₂CH₂N), 20.2 (CH₃Ar) ppm. ES⁺-MS (*m/z*) 441(M+H)⁺.





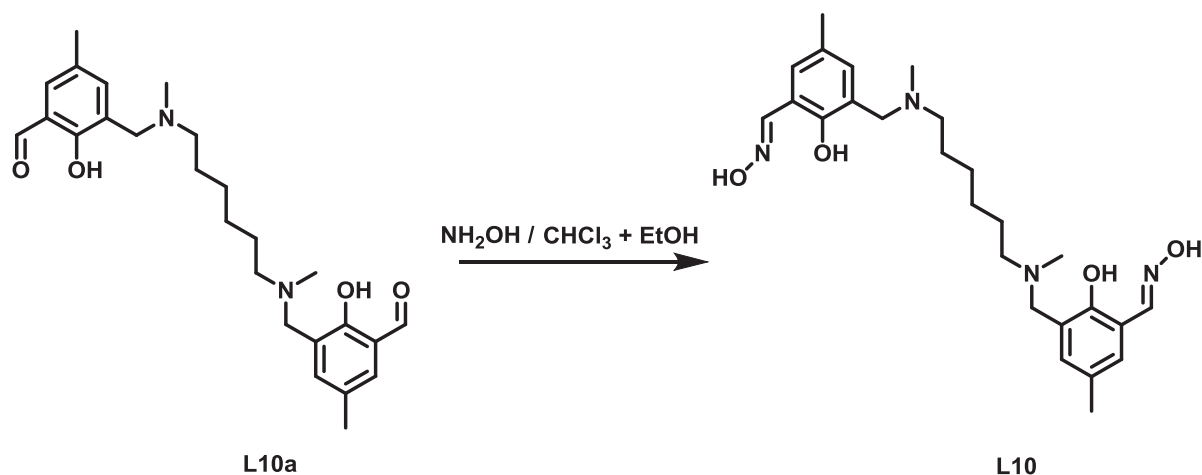


HMQC experiment of **L10a**

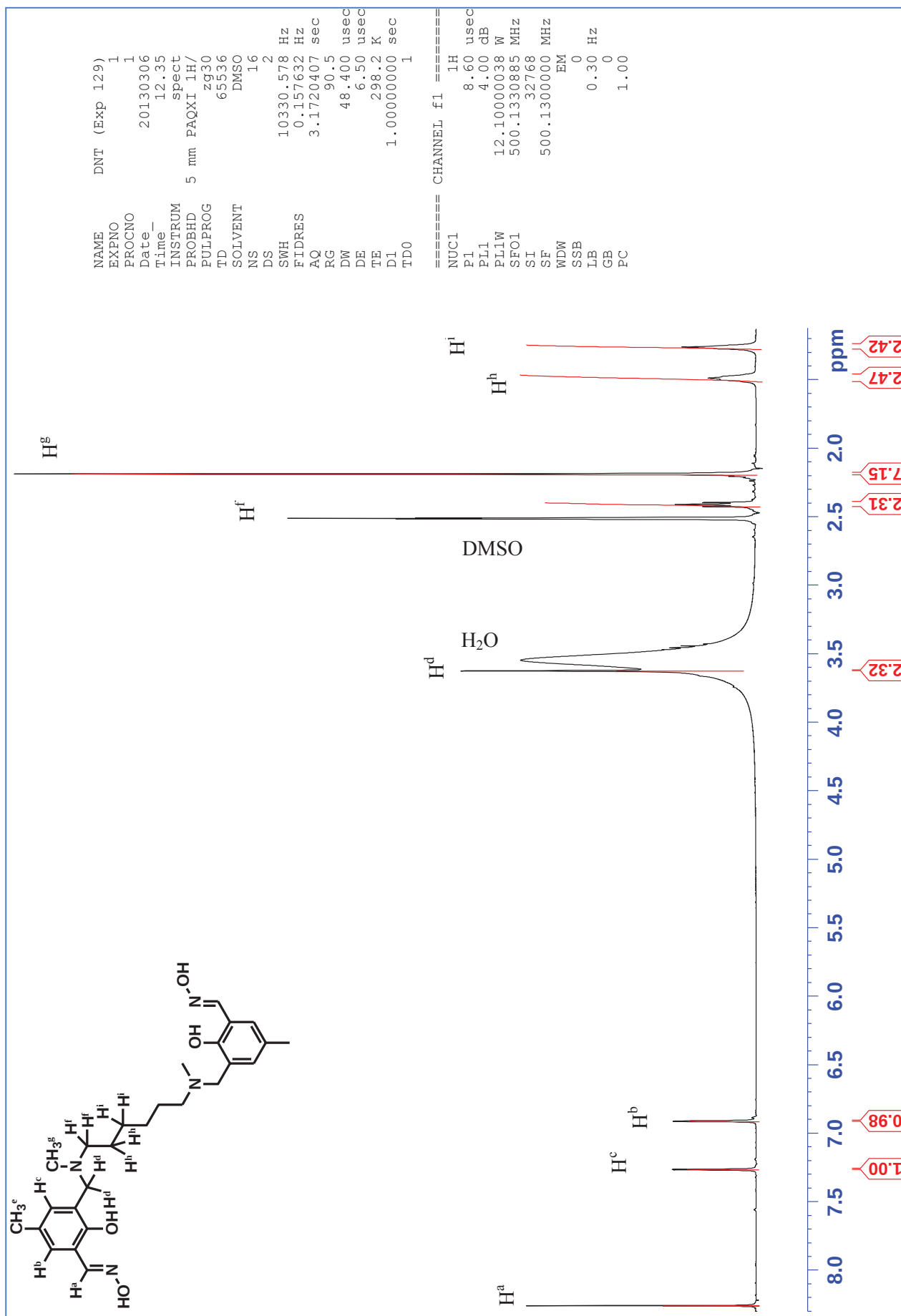


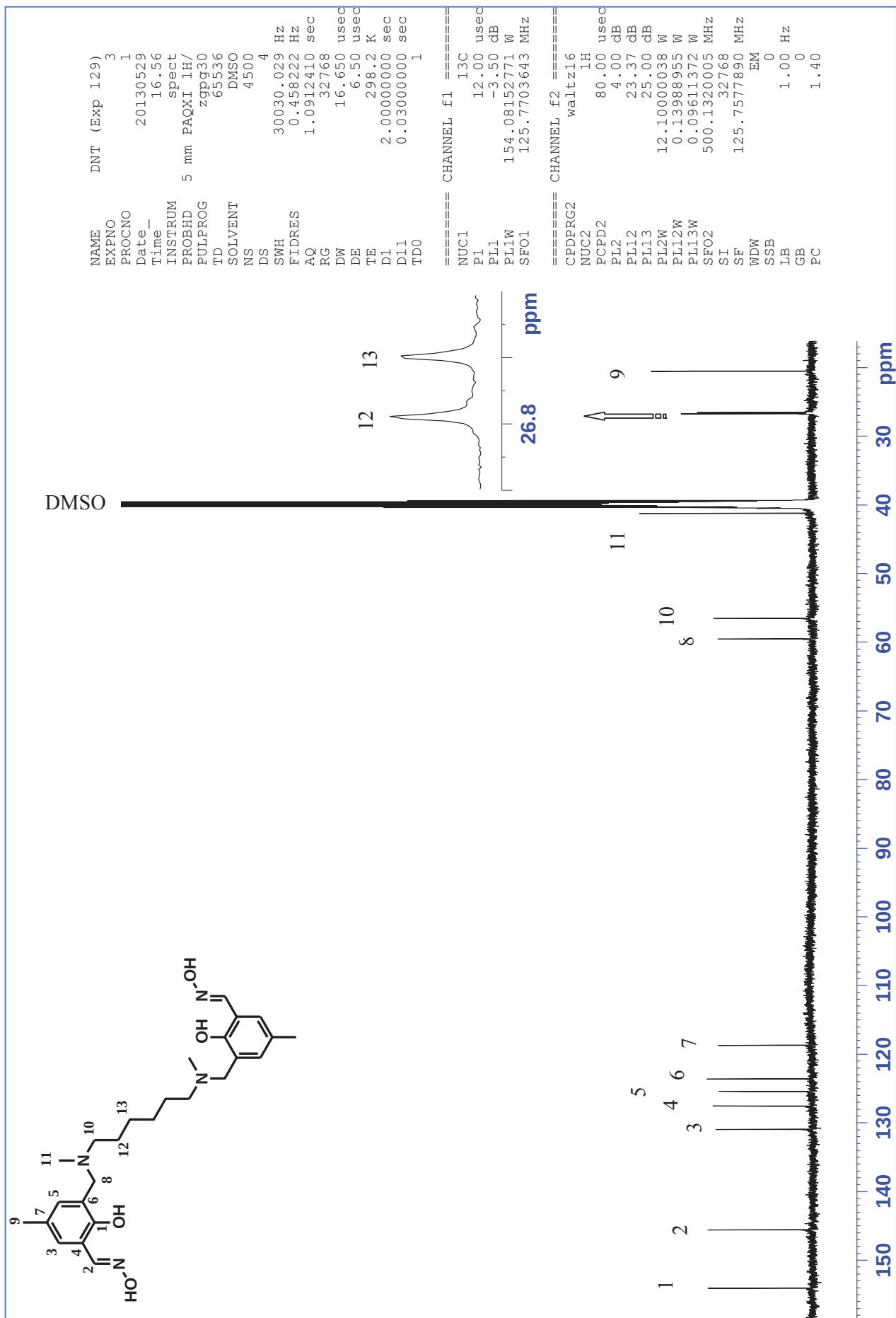
COSY experiment of **L10a**

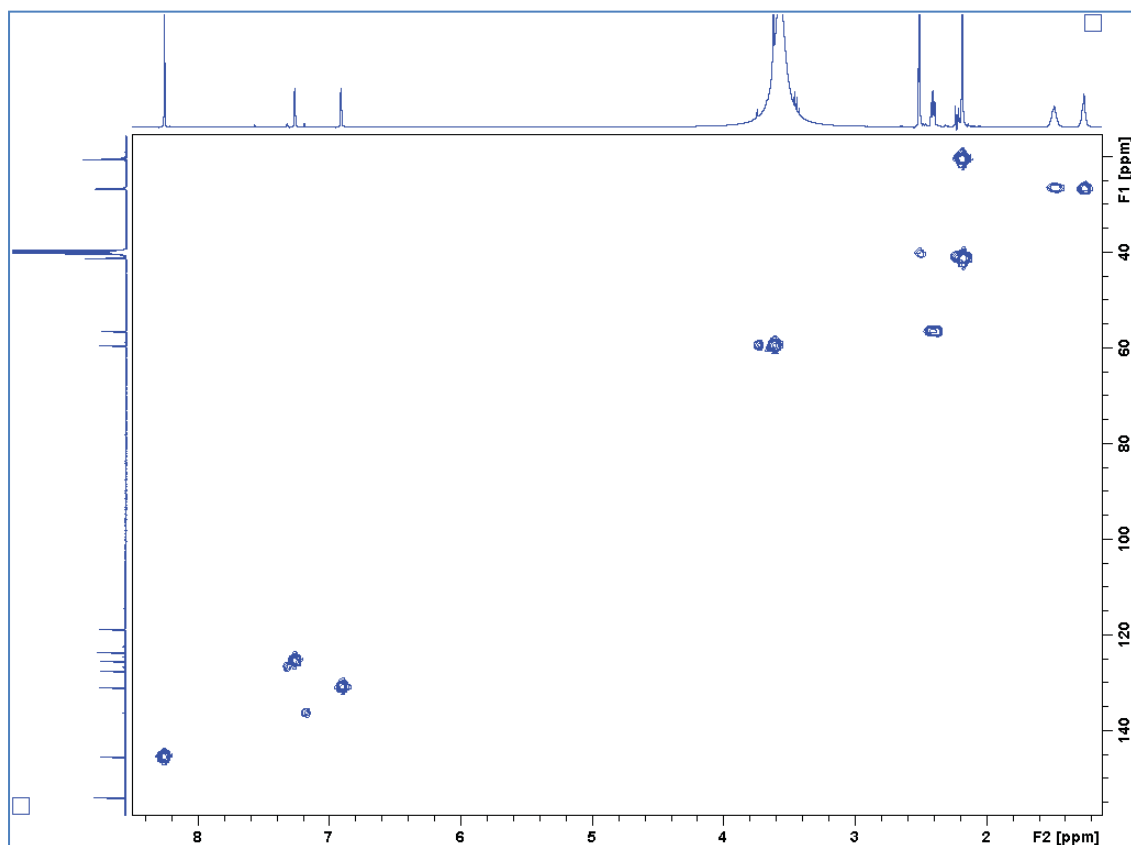
3,3'-[1,6-hexanediylbis[(methylimino)methylene]]bis[2-hydroxy-5-methyl]-1,1'-dioxime



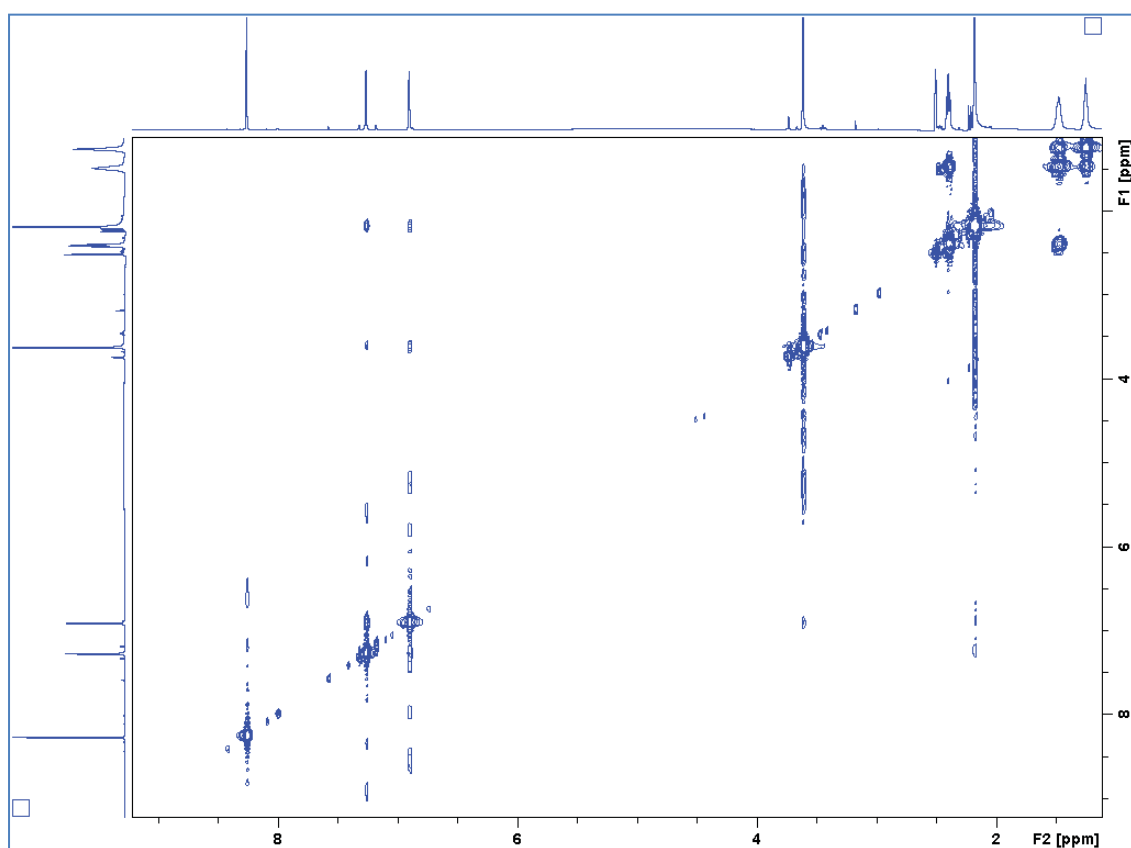
A solution of hydroxylamine hydrochloride (0.636 g, 9.16 mmol) in dry ethanol (100 ml) was added to a solution of potassium hydroxide (0.514 g, 9.16 mmol) in dry ethanol (100 ml). The resulting white precipitate was removed. The filtrate was added to a solution of **L10a** (2.020 g, 4.58 mmol) in a chloroform : dry ethanol ratio of 7.5 : 142.5 ml over 30 minutes. The white solution was stirred for a further 48 h at RT, after which time a pale yellow compound precipitated. The precipitate was filtered and washed with ethanol (3 x 30 ml). The final product was dried *in vacuo*. Yield (1.660 g, 77%). Mp 194-195 °C. IR (KBr pellet): 1624 (s, C=N), 1473 (s, -CH₂), 1269 (s, C-O), 1019 (m, N-O), 849 (s, -Ar-H) cm⁻¹. Anal. Calcd for C₂₆H₃₈N₄O₄: C, 66.36; H, 8.14; N, 11.91. Found: C, 66.50; H, 8.33; N, 12.00. ¹H NMR (DMSO, 500 MHz): δ 1.25 (q, 4H, CH₂), 1.48 (q, 4H, CH₂), 2.18 (s, 6H, Ar-CH₃), 2.18 (s, 6H, CH₃N), 2.39 (t, *J* = 7.38 Hz, 4H, NCH₂), 3.62 (s, 4H, Ar-CH₂N), 6.90 (d, *J* = 1.69 Hz, 2H, Ar-H), 7.25 (d, *J* = 1.57 Hz, 2H, Ar-H), 8.25 (s, 2H, CHN). ¹³C NMR (DMSO, 500 MHz): δ 154.1 (CHNOH), 145.5, 131.0, 127.6, 125.4, 123.6, 118.7 (Ar-C), 59.5 (ArCH₂N), 41.2 (CH₃N), 28.6 (CH₂CH₂CH₂N), 26.7, 26.6 (CH₂CH₂CH₂N), 20.5 (CH₃Ar) ppm. ES⁺-MS (*m/z*) 509 [M+K]⁺.







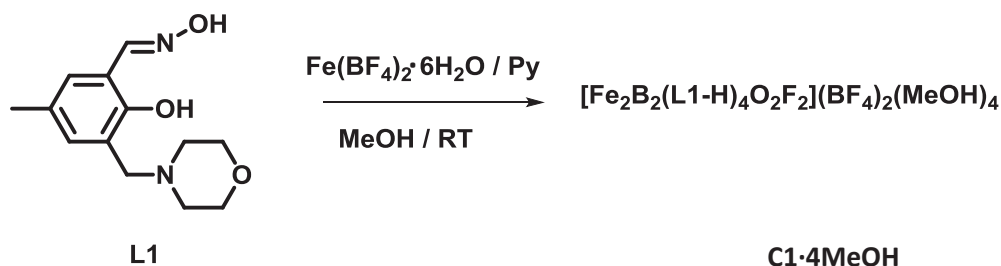
HMQC experiment of **L10**



COSY experiment of **L10**

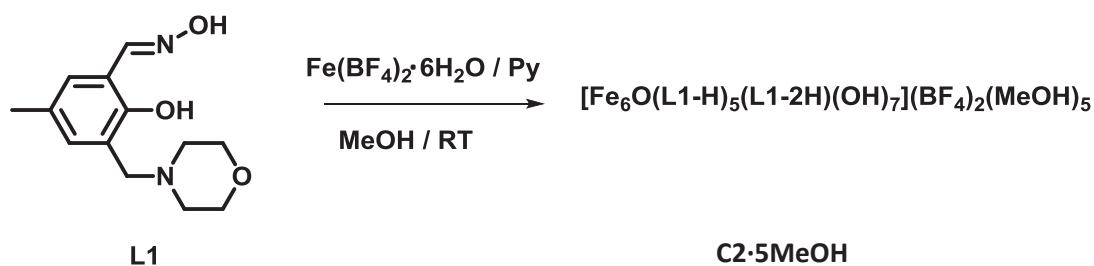
A.2.3 Synthesis of metal clusters

$[Fe_2B_2O_2(L1-H)_4(F)_2](BF_4)_2$ (C1)



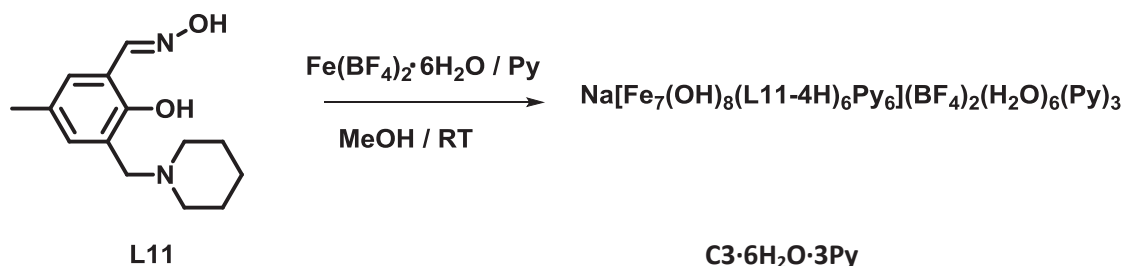
To the ligand **L1** (0.125 g, 0.50 mmol) dissolved in MeOH (12.5 ml), was added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.169 g, 0.50 mmol) dissolved in MeOH (12.5 ml). After full dissolution, pyridine (2 ml) was added to the maroon coloured solution. The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Yield (0.091 g, 49 %). Anal. Calcd for $\text{C}_{52}\text{H}_{68}\text{B}_4\text{F}_{10}\text{Fe}_2\text{N}_8\text{O}_{14} \cdot 8\text{H}_2\text{O}$: C, 41.14; H, 5.58; N, 7.38. Found: C, 40.93; H, 5.31; N, 7.63.

$[Fe_6O(L1-H)_5(L1-2H)(OH)_7](BF_4)_2$ (C2)



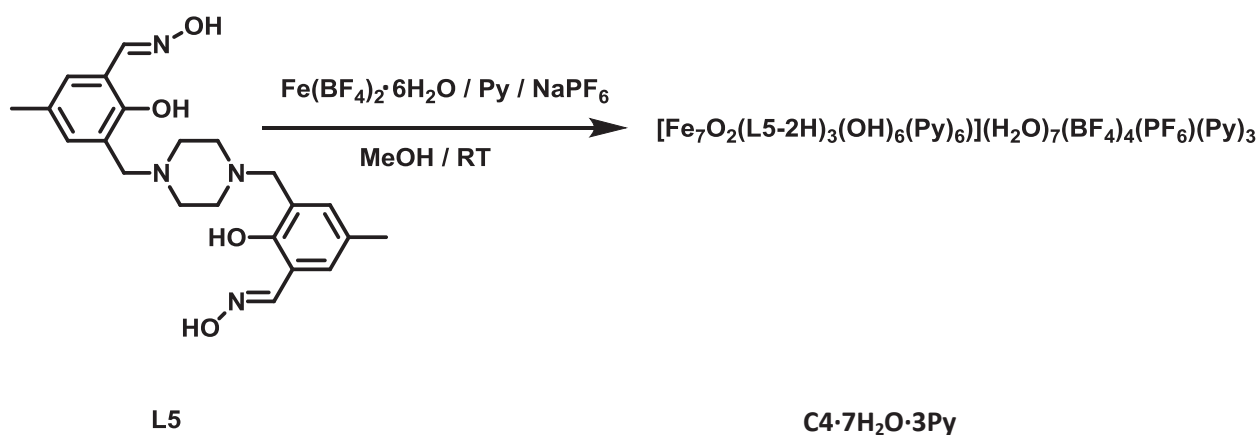
To the ligand **L1** (0.125 g, 0.50 mmol) dissolved in MeOH (12.5 ml), was added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.169 g, 0.50 mmol) dissolved in MeOH (12.5 ml). After full dissolution, pyridine (2 ml) was added to the maroon coloured solution. The solution was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Yield (0.202 g, 59 %). Anal. Calcd for $\text{C}_{78}\text{H}_{102}\text{B}_2\text{F}_8\text{Fe}_6\text{N}_{12}\text{O}_{26}$: C, 43.93; H, 4.82; N, 7.88. Found: C, 43.94; H, 4.92; N, 7.98. IR (KBr pellet): 1617(s), 1465(vs), 1084(m), 520(s), 454(m) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 222. ES^+ -MS (m/z) 988.16 $[\text{NaFe}_3\text{O}_2(\text{L1-H})_3(\text{OH})]^{2+}$.

Na[Fe₇(OH)₈(L11-2H)₆(Py)₆](BF₄)₂ (C3)



To the ligand **L11** (0.145 g, 0.50 mmol) dissolved in MeOH (12.5 ml), was added Fe(BF₄)₂·6H₂O (0.169 g, 0.50 mmol) in MeOH (12.5 ml). After full dissolution, NaPF₆ (0.167 g, 1.00 mmol) and pyridine (2 ml) were added to the maroon coloured solution. The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Yield (0.180 g, 67 %). Anal. Calcd for C₁₁₇H₁₆₅B₂F₈Fe₇N₁₅O₂₀Na: C, 52.37; H, 5.97; N, 7.83. Found: C, 52.63; H, 6.35; N, 7.58. IR (KBr pellet): 1605(m), 1458(vs), 1084(m), 732(s), 534(s), 437(m) cm⁻¹. UV-Vis (λ_{max} nm) in MeOH: 266, 221.

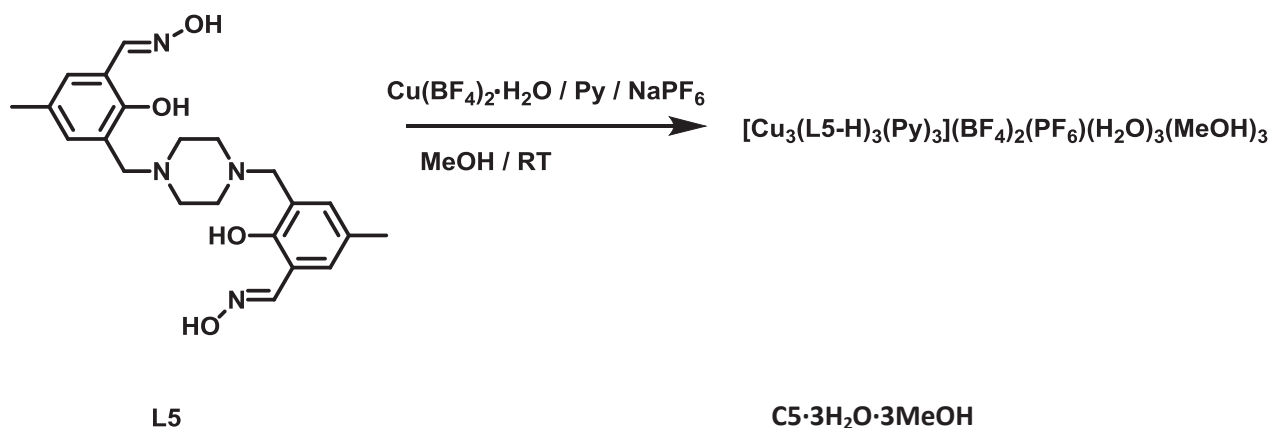
[Fe₇O₂(L5-2H)₃(OH)₆(Py)₆](BF₄)₄PF₆ (C4)



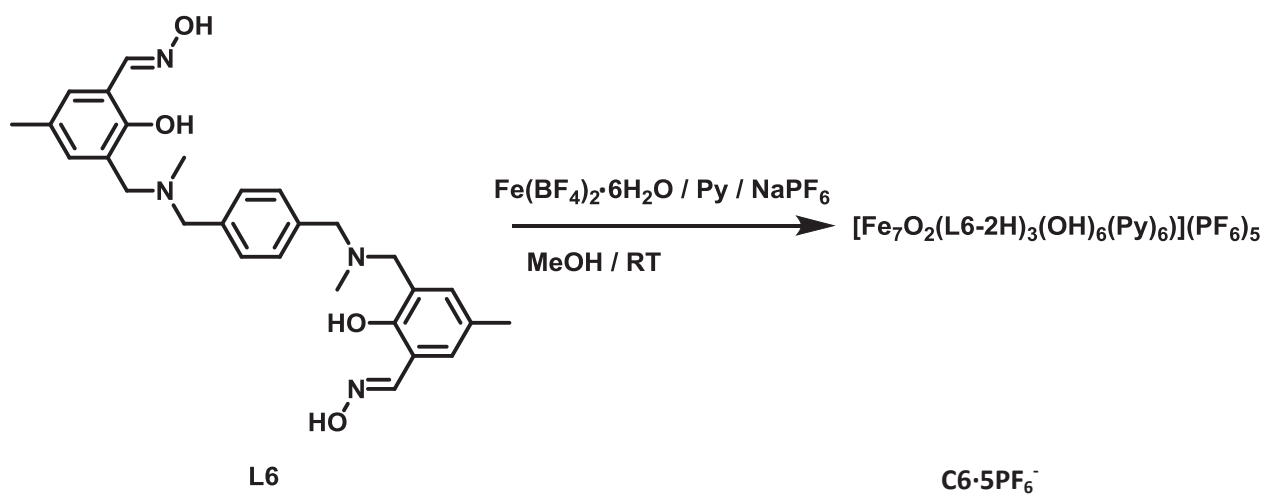
To the ligand **L5** (0.206 g, 0.50 mmol) suspended in MeOH (12.5 ml), was added Fe(BF₄)₂·6H₂O (0.348 g, 1.00 mmol) dissolved in MeOH (12.5 ml). After full dissolution, NaPF₆ (0.167 g, 1.00 mmol) and pyridine (2 ml) were added to the maroon coloured solution. The solution was stirred for 3 h, filtered, and the filtrate was left to

evaporate slowly. X-ray quality crystals were produced after 2 weeks. Yield (0.200 g, 47 %). Anal. Calcd for $C_{96}H_{108}B_4F_{22}Fe_7N_{18}O_{20}P \cdot 7H_2O$: C, 40.55; H, 4.33; N, 8.87. Found: C, 40.24; H, 4.44; N, 8.84. IR (KBr pellet): 1613(m), 1463(vs), 1307(s), 1084(m), 757(s), 483(s) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 228.

$[Cu_3(L5-H)_3(Py)_3](BF_4)_2(PF_6)(C5)$

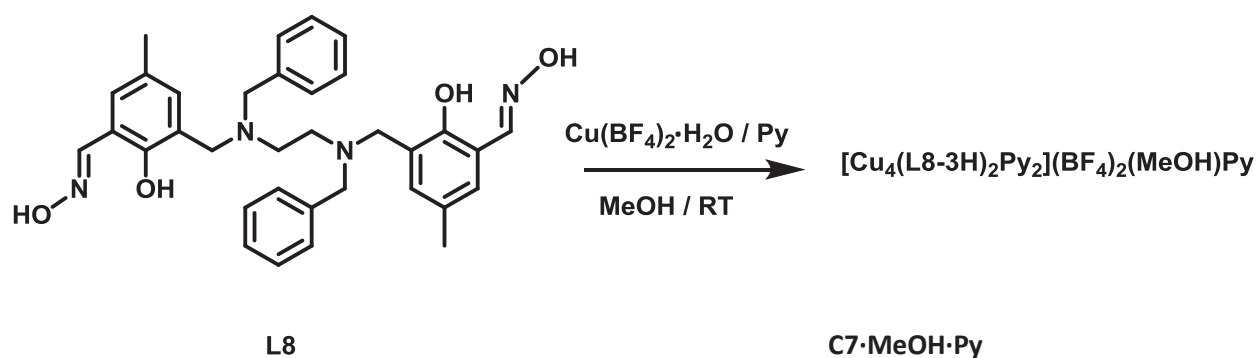


To the ligand **L5** (0.206 g, 0.50 mmol) suspended in MeOH (12.5 ml), was added $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (0.255 g, 1.00 mmol) dissolved in MeOH (12.5 ml). After full dissolution, pyridine (2 ml) was added to the green coloured solution followed by NaPF_6 (0.042, 0.25 mmol). The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. The compound was then purified by diffusing DEE into the complex dissolved in DMF. Yield (0.320 g, 91 %). Anal. Calcd for $C_{81}H_{96}B_2Cu_3F_{14}N_{15}O_{12}P \cdot \text{DMF}$: C, 49.12; H, 5.05; N, 10.91. Found: C, 49.05; H, 5.32; N, 10.58. ES^+ -MS (m/z) 474.1210 $[\text{Cu}_3(\text{L5-H})]^+$, 535.0393 $[\text{Cu}_2(\text{L5-3H})]^+$, 949.2635 $[\text{Cu}_2(\text{L5-H})(\text{L5-2H})]^+$, 1010.1864 $[\text{Cu}_3(\text{L5-H})(\text{L5-3H})]^+$. IR (KBr pellet): 1683(s), 1470(s), 1327(s), 1023(m), 1006(m), 824(s), 620(s) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 323, 225.



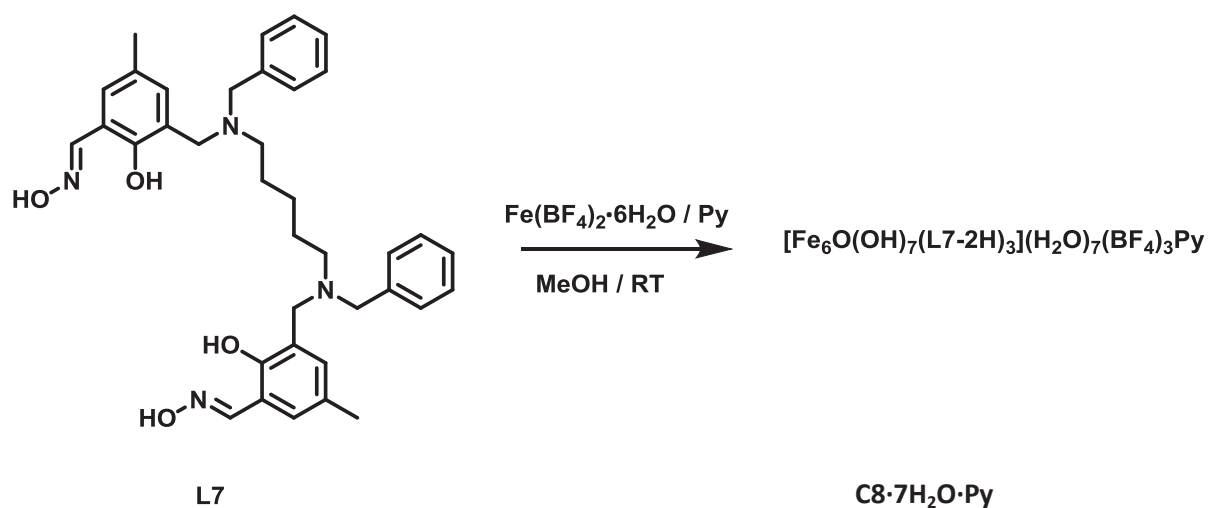
To the ligand **L6** (0.245 g, 0.50 mmol) suspended in MeOH (12.5 ml), was added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.337 g, 1.00 mmol) dissolved in MeOH (12.5 ml). After full dissolution, NaPF_6 (0.167 g, 1.00 mmol) and pyridine (2 ml) was added to the maroon coloured solution. The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Anal. Calcd for $\text{C}_{114}\text{H}_{126}\text{Fe}_7\text{N}_{18}\text{O}_{20} \cdot 5\text{PF}_6^-$: C, 43.00; H, 3.99; N, 7.92. Found: C, 42.84; H, 4.24; N, 7.92. IR (KBr pellet): 1617(m), 1465(s), 1299(s), 1084(m), 1006(m), 756(s), 522(m), 440(w) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 226, 220.

[Cu₄(L8-3H)₂Py₂](BF₄)₂ (C7)



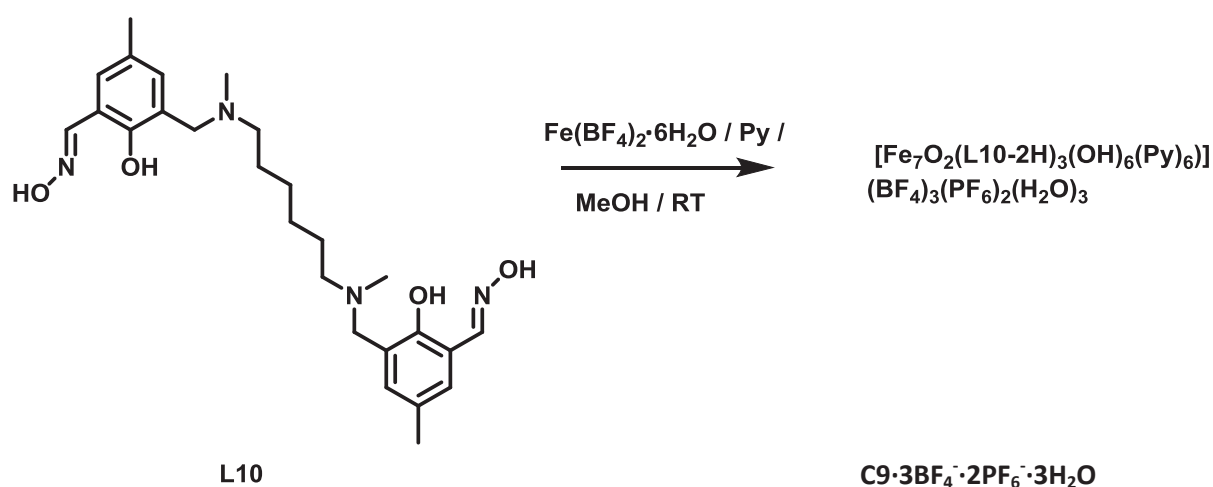
To the ligand **L8** (0.056 g, 0.10 mmol) dissolved in MeOH (12.5 ml), was added Cu(BF₄)₂·H₂O (0.051 g, 0.20 mmol) dissolved in MeOH (12.5 ml). To the green coloured solution, was added pyridine (1 ml). The mixture was stirred for 3 h, filtered, and then the filtrate was left to evaporate slowly. X-ray quality green, rhombic shaped crystals were produced after 2 weeks. Yield (0.041 g, 24 %). Anal. Calcd for C₇₈H₈₀B₂Cu₄F₈N₁₀O₈·8.5H₂O: C, 50.19; H, 5.24; N, 7.50. Found: C, 50.08; H, 4.89; N, 7.60. IR (KBr pellet): 1611(w), 1463(vs), 1280(s), 1084(m), 1070(m), 734(m), 634(m) cm⁻¹. UV-Vis (λ_{max} nm) in MeOH: 323, 226.

[Fe₆O(OH)₇(L7-2H)₃](BF₄)₃ (C8)

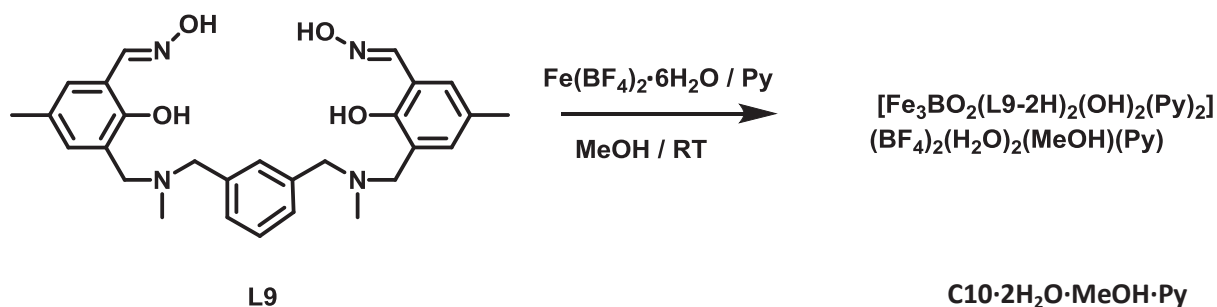


To the ligand **L7** (0.304 g, 0.50 mmol) dissolved in MeOH (12.5 ml), was added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.348 g, 1.00 mmol) dissolved in MeOH (12.5 ml). To the maroon coloured solution, was added pyridine (2 ml). The mixture was stirred for 3 h, filtered, and then the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Yield (0.190 g, 14 %). Anal. Calcd for $\text{C}_{111}\text{H}_{126}\text{B}_3\text{F}_{12}\text{Fe}_6\text{N}_{12}\text{O}_{20} \cdot 4\text{H}_2\text{O}$: C, 50.97; H, 5.16; N, 6.43. Found: C, 50.80; H, 5.02; N, 6.84. IR (KBr pellet): 1617(s), 1460(vs), 1293 (s), 1084(m), 759 (m), 522(m) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 220.

$[\text{Fe}_7\text{O}_2(\text{L10-2H})_3(\text{OH})_6(\text{Py})_6]$ (C9)



To the ligand **L10** (0.235 g, 0.50 mmol) in 12.5 ml of MeOH, $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.337 g, 1.00 mmol) in MeOH (12.5 ml) was added. After full dissolution, NaPF_6 (0.167 g, 1.00 mmol) and pyridine (2 ml) was added to the maroon coloured solution. The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Anal. Calcd for $\text{C}_{108}\text{H}_{138}\text{Fe}_7\text{N}_{18}\text{O}_{20} \cdot 3\text{BF}_4^- \cdot 2\text{PF}_6^- \cdot 3\text{H}_2\text{O}$: C, 43.19; H, 4.83; N, 8.39. Found: C, 43.06; H, 5.06; N, 8.32. IR (KBr pellet): 1603(w), 1459(m), 1301 (s), 1084(m), 521(m), 467(w) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 265, 221.



To the ligand **L9** (0.245 g, 0.50 mmol) dissolved in MeOH (12.5 ml), was added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.337 g, 1.00 mmol) dissolved in MeOH (12.5 ml). After full dissolution, pyridine (2 ml) was added to the maroon coloured solution. The mixture was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. Anal. Calcd for $\text{C}_{66}\text{H}_{76}\text{B}_3\text{F}_8\text{Fe}_3\text{N}_{10}\text{O}_{12} \cdot 4\text{H}_2\text{O}$: C, 48.77; H, 5.21; N, 8.62. Found: C, 48.78; H, 5.10; N, 8.90. IR (KBr pellet): 1617(s), 1465(vs), 1301 (C-O), 1039(s), 751(s), 522 (m), 423(m) cm^{-1} . UV-Vis (λ_{max} nm) in MeOH: 225.

References:

1. Aldered, R., Johnston, R., Levin, D., Neilan, J., *J. Chem. Soc. Perkin Trans.*, 1, **1994**, 1823.
2. Wang, Q., Wilson, C., Blake, A. J., Collinson, S. R., Tasker, P. A., Schröder, M., *Tetrahedron Lett.*, 47, **2006**, 8983.
3. Stevens, J. R., Plieger, P. G., *Dalton Trans.*, **2011**, 40, 12235.
4. Plieger, P. G., Tasker, P. A., Galbraith, S. G., *Dalton Trans.*, **2004**, 313.
5. Forgan, R. S., Davidson, J. E., Galbraith, S. G., Henderson, D. K., Parsons, S., Tasker, P., White, F. J., *Chem. Commun.*, **2008**, 4049.
6. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H., *J. Appl. Cryst.*, **2009**, 42, 339.
7. Kabsch, W., *Acta Cryst D*, **2010**, 66, 125.
8. Evans, P., *Acta Cryst D*, **2005**, 62, 72.
9. Winn, M. D., Ballard, C. C., Cowtan, K. D., Dodson, E. J., Emsley, P., Evans, P. R., Keegan, R. M., Krissinel, E. B., Leslie, A. G. W., McCoy, A., McNicholas, S. J., Murshudov, G. N., Pannu, N. S., Potterton, E. A., Powell, H. R., Read, R. J., Vagin, A., Wilson, K. S., *Acta Cryst D*, **2011**, 67, 235.

131B Fe₆ - morpholine

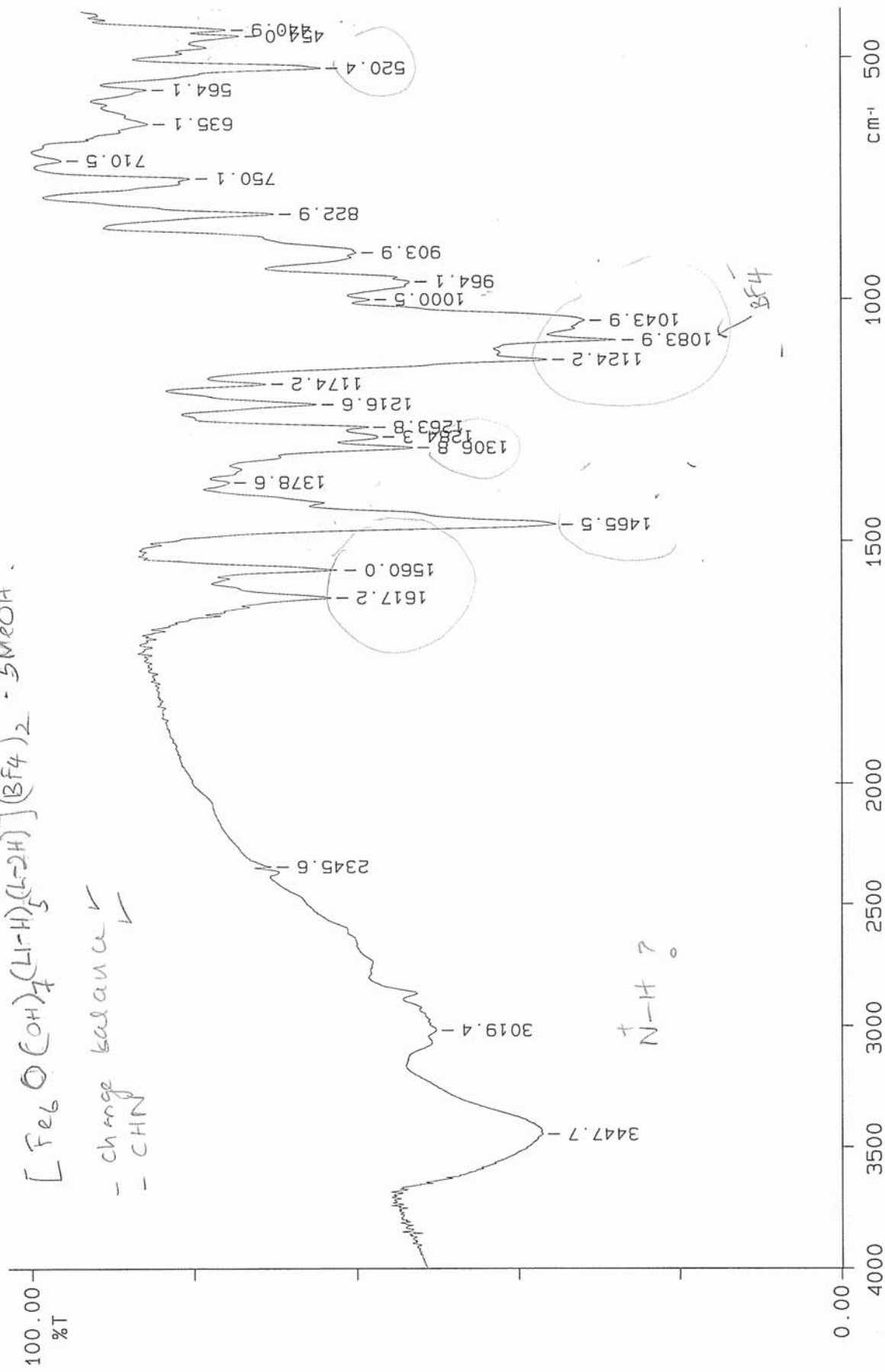
CZ

- no [Fe₃-H₃O]⁷⁺ (ν 480cm⁻¹)



- charge balance ✓
- CHN ✓

PERKIN ELMER



N-H ?

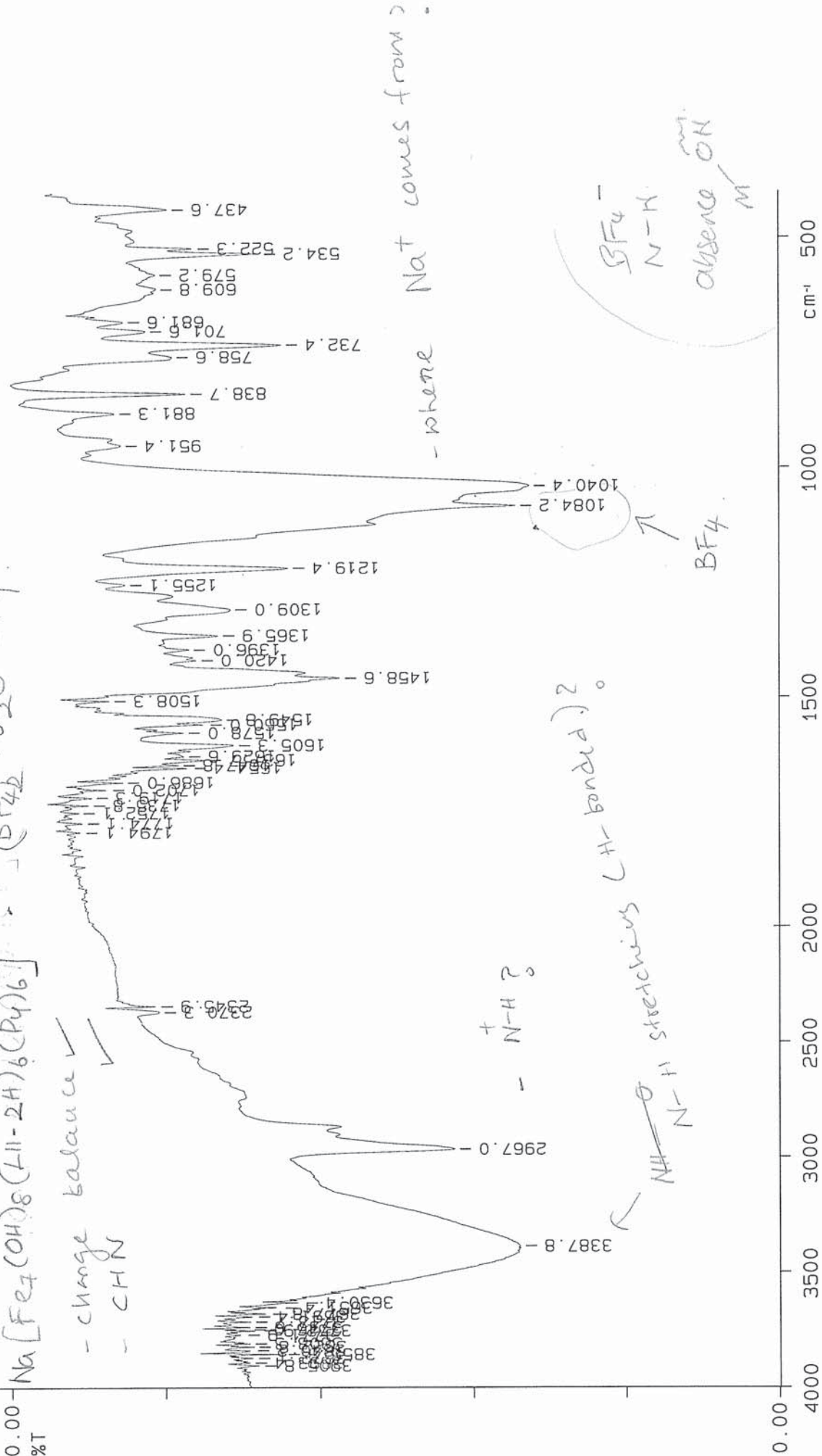
BF₄

PERKIN ELMER

20

$$[\text{Fe}_3-\text{P}_3\text{O}]^+$$
 $(\sim 480 \text{ nm})$
$$\text{Na}[\text{Fe}(\text{OH})_8(\text{LII}-2\text{H})_6(\text{Py})_6] \cdot (\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} \cdot 3\text{Py}$$

- charge ✓
- CHN ✓
balance ✓



$\text{NH} \equiv \text{O}$ stretching
 C-H bonded. 2

BF_4^-
 N-H
 absence of OH^-

$\text{CH}_3\text{N}^+\text{Na}^+$
 $\rightarrow \text{2-ray.}$
 Peak 5: Na^+

80/02/10 04:08 Operator:
X: 4 scans, 4.0cm-1, abex

204

Fe₇ - pip oxime.

NDS⁺ Fe₇ complex with
[Fe(BF₄)₂] · 6H₂O

Stilioni C. et al. 2009
in the complex (bidentate
bridging mode)
ν ~ 1600 (s) → C-N
ν ~ 1294 (w) → N-O

PERKIN ELMER

C4

100.00
%T

search

C-N stretch in pyridine
compare with
the ligand
peak.

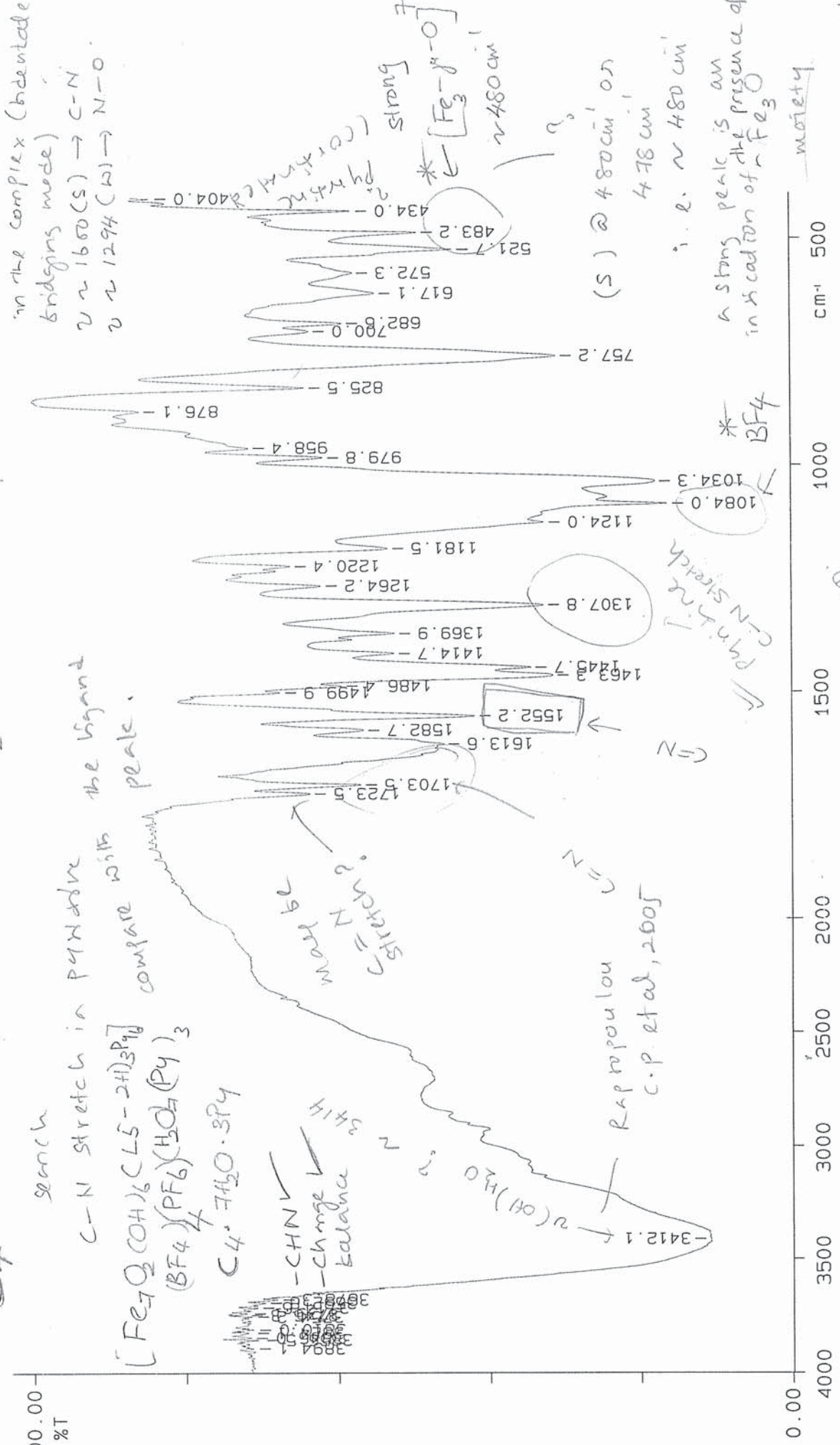
[Fe₇O₂(OH)₆(L₅-2H₂O)₂]
(BF₄)(PF₆)(H₂O)(Py)₃

C4 · 7H₂O · 3Py

-CHN ✓
-change
balance

stretch? C=N
stretch? C=N

Rapapoulou
C.P. et al, 2005



13/02/20 14:57 Operator:

X: 4 scans, 4.0cm-1, flat, abex

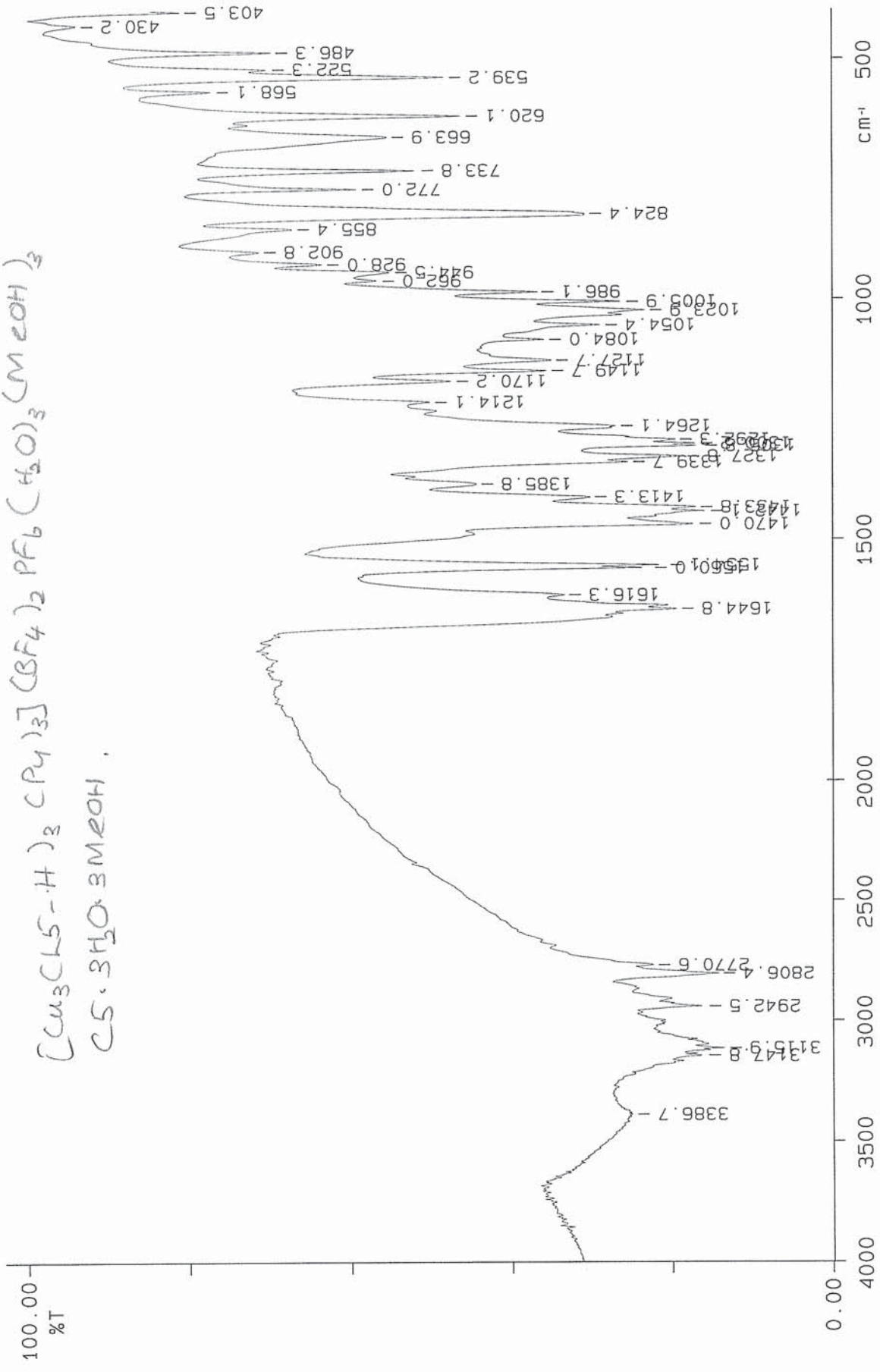
Rapapoulou C. P. et al, 2005

~~AD577~~

C5.

$[Cu_3(CLS-H)_3(CP_4)_3(BF_4)_2 PF_6(H_2O)_3(MEOH)_3]$
C5.3H₂O.3MeOH.

PERKIN ELMER



13/08/26 16:05 Operator:
X: 4 scans, 4.0cm-1, flat, abex

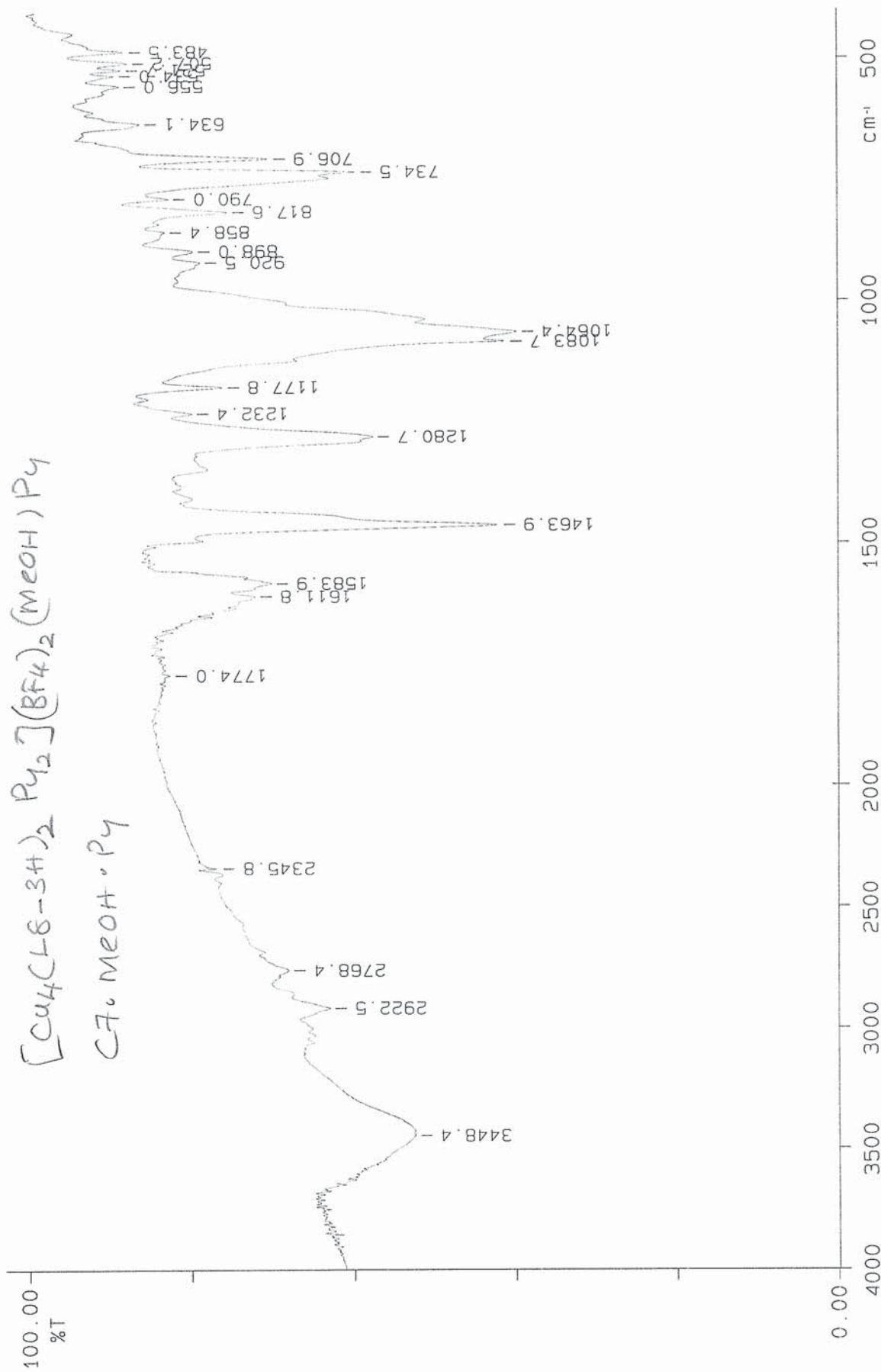
$$\text{No } [\text{Fe}_3 - \mu\text{O}]^+ + \text{ }^{-1} \text{ } (\sim 480 \text{ cm}^{-1})$$


NDS 735-5 (218-4) Cu₄-ethylene linked oxime.

$[Cu_4(L8-3H)_2P_4]_2(BF_4)_2(MeOH)_4$

C7, MeOH, Py

PERKIN ELMER



14/07/05 14:31 Operator:

X: 4 scans, 4.0cm-1, flat, abex

PERKIN ELMER

100.00
%T

0.00

4000

3500

3000

2500

2000

1500

1000

500

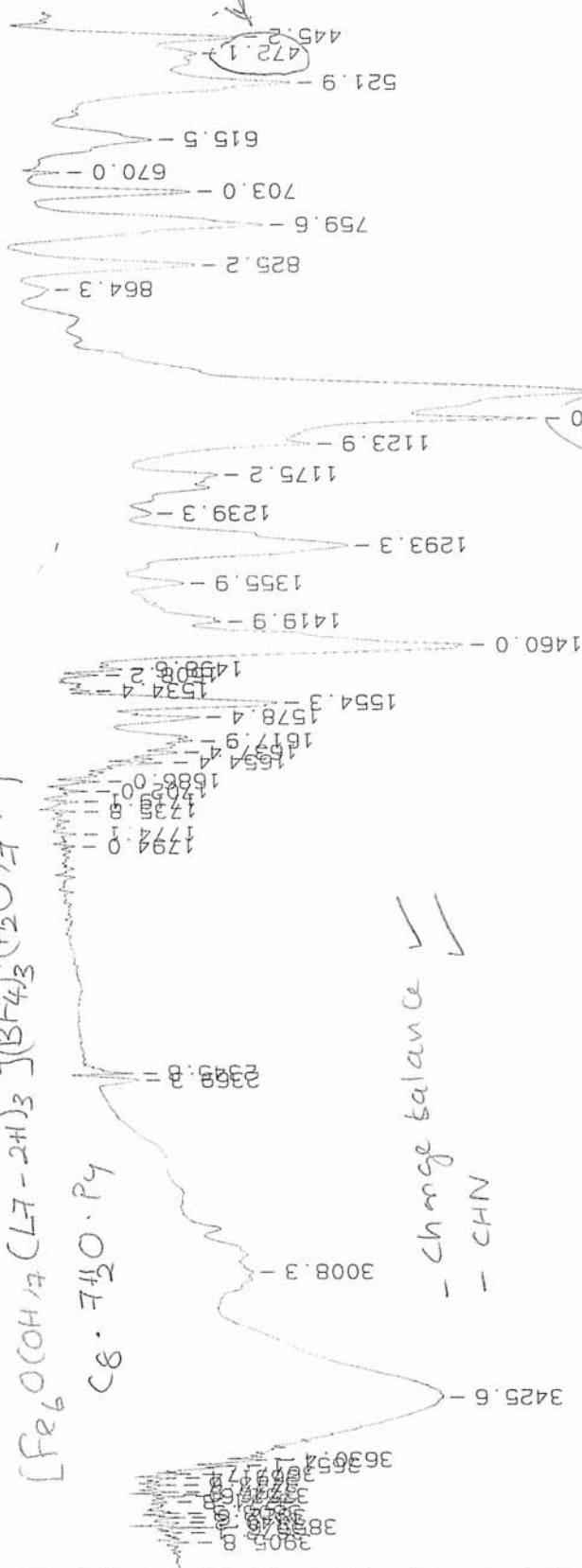
cm⁻¹

235-3, Fe₆-CS oxime.

C8

[Fe₆O(COH)₁₇(L7-2H)₃](BF₄)₃·(H₂O)₇·Py

C8·7H₂O·Py



- change balance ✓
- CHN ✓

N-H ?

BF₄

1500
1300
1100

1180
136
1316

1280
136
1416



480 cm⁻¹

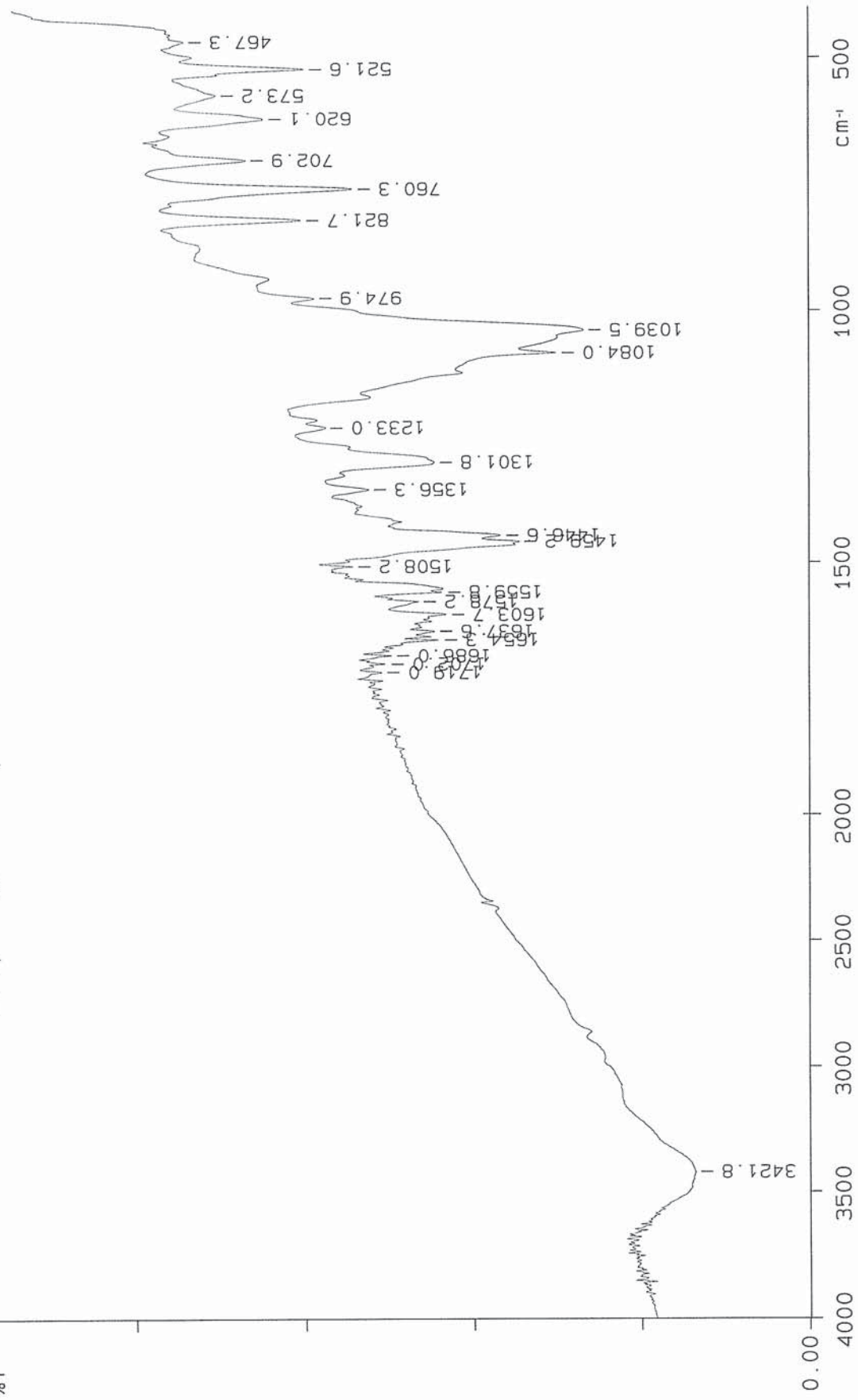
1x [Fe₃-μO]⁺¹

NDS 147

PERKIN ELMER

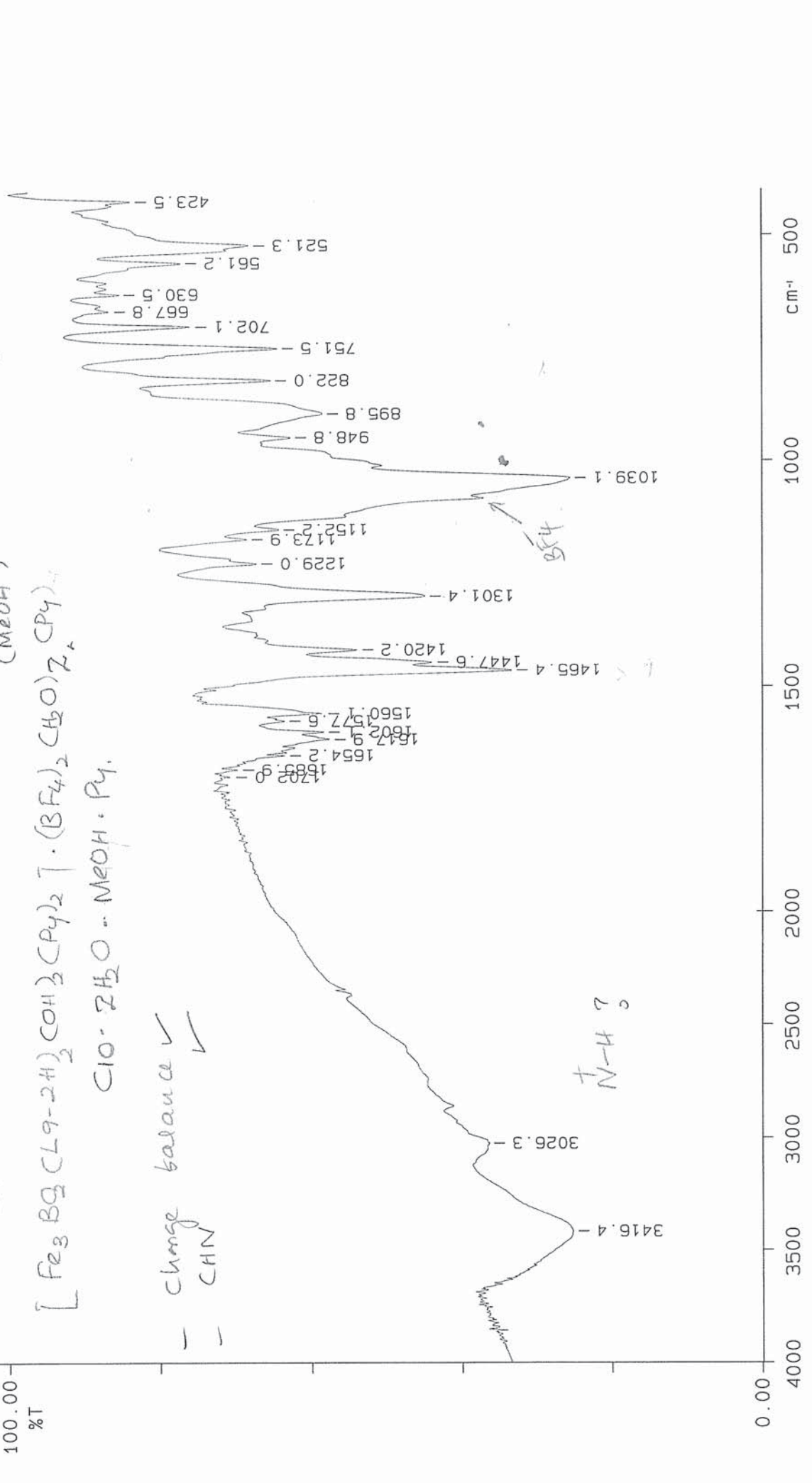
100.00
%T

Fe₇ - C₆ oxime
[Fe₇(OH)₈(L10-2H)₃(Py)₆](BF₄)₃(C₅O)₃(Py)₂
C₉.3BF₄·3H₂O·2Py



13/08/26 16:48 Operator:
X: 4 scans, 4.0cm-1, flat, abex

NDS 169
 Fe₃ - 1,3-xylyl linked oxime.
 C10
 (MeOH)
 [Fe₃BQ(L9-2H)₂(OH)₂(CPy)₂ · (BF₄)₂CH₃O)₂CPy)₂]
 C10 · 2H₂O · MeOH · Py.
 change balance ✓
 CHN ✓



13/08/26 16:38 Operator:
 X: 4 scans, 4.0cm-1, flat, abex