



Synthetic, Structural and Decomposition Studies of Aluminium Precursors to Functional Materials

This thesis is submitted in partial fulfilment of the requirements for
the Degree of Doctor of Philosophy (Chemistry)

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I, Samuel P. Douglas, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

This thesis describes the synthesis of a range of aluminium precursors, the majority of which are novel, in order to assess their suitability towards low temperature decomposition to aluminium functional materials, namely aluminium metal and/or oxide *via* thermogravimetric analysis (TGA).

Chapter 1 sets the scene for the thesis, beginning with a preface for this work, project aims and a thesis synopsis. It then proceeds with a brief introduction covering topics such as general precursor chemistry, why aluminium was chosen as the metal centre to investigate and a review of several deposition techniques in which precursors can be used to deposit metal and/or metal oxide films

Chapter 2 details all the experimental and characterisation procedures conducted in this research project, for the research discussed in Chapters 3–6.

Chapters 3 and 4 describe the synthesis of several novel tris(β -ketoiminate) aluminium and novel bis(β -ketoiminate) aluminium monochloride compounds, respectively. Each family of compounds is fully characterised including by SCXRD, multi-nuclear NMR spectroscopy, mass spectrometry and elemental analysis. Each set of precursors is assessed by analysing their decomposition behaviour *via* TGA and some through pyrolysis experiments.

Chapter 5 involves the synthesis of two types of aluminium hydride compound; mono(β -diketiminato) aluminium dihydrides a family of complexes better known for catalytic small molecule activation and amine-stabilised alanes, a more well-known family of precursors to Al functional materials. Again, the suitability of both families of compounds towards low temperature decomposition is assessed using TGA.

Chapter 6 involves the solution-based deposition of two of the best performing precursors thermally analysed in this work, followed by their low temperature thermal sintering. The films were analysed using a multitude of techniques to gauge the effectiveness of the most promising formulations.

Chapter 7 concludes the work detailed within this thesis and provides some insight into how this research can be expanded in the future.

Impact Statement

The metal of interest in this project is aluminium, as it is both highly conductive and has a low work function in the zerovalent state. Equally, its oxides, namely alumina, has a host of potential applications, including as a replacement for silica as a high- κ gate dielectric materials. Using aluminium, which has the highest molar crustal abundance of any metal, better future-proofs technologies of today and tomorrow. The research into aluminium containing precursors towards functional materials has been conducted since the late 1960's, however only over the last decade or so has research concentrated on the solution-based deposition of such materials. Current research has focussed mainly on known precursors that are extremely reactive such that they are not suitable for industrial scale-up.

This thesis aims to have a more synthetic outlook to metal functional material deposition, by concentrating on precursor design and analysis. The main objective of this work is to produce compounds that decompose to aluminium metal and/or oxide (depending on the conditions used) at low temperature ($<200\text{ }^{\circ}\text{C}$) such that aluminium functional materials can be deposited onto low-cost, flexible substrates. This research begins by studying the use of β -ketoiminates as ligands, a historically popular class of compound and then compares precursors synthesised with similar compounds in the literature, as well as, the leading standards. Finally, the best performing precursors have been used to deposit functional material at low temperature onto a range of low-cost flexible substrates, as a consequence this strategy has much potential in the realisation of flexible and paper-based printing of highly conductive Al for use in electronic devices.

The results presented within this thesis introduce a series of new compounds and helps to elucidate structural and thermal trends as ligand and/or precursor structure is sequentially varied, as well as, providing the first solution-based deposition of aluminium metal without the need for an additional reducing catalyst.

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List of Publications

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5. C. E. Knapp, E. A. Metcalf, S. Mrig, C. Sanchez-Perez, S. P. Douglas, P. Choquet and N. D. Boscher, *ChemistryOpen*, 2018, **7**, 850–857.

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List of Abbreviations

AA	<i>Adjacent averaging</i>
AACVD	<i>Aerosol-assisted CVD</i>
acac	<i>Acetylacetonate / β-diketonate</i>
acnac	<i>β-ketoiminate</i>
ALD	<i>Atomic layer deposition</i>
amd	<i>Amindinate</i>
Anal.	<i>Analysed</i>
Ar	<i>Aryl</i>
Ar^{mes}	<i>2,4,6-Trimethylphenyl / mesityl</i>
at. %	<i>Atomic %</i>
Avg.	<i>Average</i>
AZO	<i>Aluminium zinc oxide</i>
bi	<i>Bidentate</i>
br	<i>Broad signal (in NMR spectroscopy)</i>
Calc.	<i>Calculated</i>
CBE	<i>Chemical beam epitaxy</i>
COSY	<i>Correlated Spectroscopy (in NMR spectroscopy)</i>
Cp	<i>Cyclopentadienyl</i>
Cp*	<i>1,2,3,4,5-Pentamethylcyclopentadiene</i>
CVD	<i>Chemical vapour deposition</i>
d	<i>Doublet signal (in NMR spectroscopy)</i>
d.p.	<i>Decimal places</i>
DCM	<i>Dichloromethane</i>
dipp	<i>2,4,-Diisopropylphenyl</i>
DMEA	<i>N,N'-dimethylethylamine</i>
DMEAA	<i>Dimethylethylamine alane</i>
DSC	<i>Differential scanning calorimetry</i>
DTG	<i>Differentiated thermogravimetry</i>
EA	<i>Elemental analysis</i>
EDS	<i>Energy-dispersive X-ray spectroscopy</i>
eq.	<i>Equivalents</i>

ESI	<i>Electrospray ionisation</i>
Et	<i>Ethyl</i>
Fw	<i>Formula weight</i>
GIXRD	<i>Grazing incidence X-ray diffraction</i>
guan	<i>Guanidinate</i>
hept	<i>Heptet signal (in NMR spectroscopy)</i>
HMBC	<i>Heteronuclear multiple bond correlation (in NMR spectroscopy)</i>
HSQC	<i>Heteronuclear single quantum coherence (in NMR spectroscopy)</i>
DiPEA	<i>Diisopropyl ether alane</i>
ⁱPr	<i>Isopropyl</i>
IR	<i>Infrared</i>
ITO	<i>Indium tin oxide</i>
LiHMDS	<i>Lithium bis(trimethylsilyl)amide</i>
m	<i>Multiplet signal (in NMR spectroscopy)</i>
Me	<i>Methyl</i>
mmp	<i>1-Methoxy-2-methyl-2-propoxide</i>
mo	<i>Monodentate</i>
MOCVD	<i>Metal-organic CVD</i>
MOD	<i>Metal-organic decomposition</i>
mp	<i>Melting point</i>
MS	<i>Mass spectrometry</i>
nanac	<i>β-diketiminate</i>
DBEA	<i>Dibutyl ether alane</i>
NMP	<i>N-methylpyrrolidine</i>
NMR	<i>Nuclear magnetic resonance</i>
NP	<i>Nanoparticle</i>
ⁿPr	<i>n-Propyl</i>
OLED	<i>Organic light emitting diode</i>
PEN	<i>Polyethylene naphtholate</i>
PET	<i>Polyethylene terephthalate</i>
Pet.	<i>Petroleum</i>
Ph	<i>Phenyl</i>
PI	<i>Polyimide</i>

ppm	<i>Parts per million</i>
PVD	<i>Physical vapour deposition</i>
q	<i>Quartet signal (in NMR spectroscopy)</i>
QUIN	<i>Quinuclidine</i>
R2R	<i>Roll-to-roll</i>
RFID	<i>Radio frequency identification</i>
RT	<i>Room temperature</i>
s	<i>Singlet signal (in NMR spectroscopy)</i>
SC	<i>Solar cell</i>
SCXRD	<i>Single crystal X-ray diffraction</i>
SEM	<i>Scanning electron microscopy</i>
t	<i>Triplet signal (in NMR spectroscopy)</i>
TAAA	<i>Triallylamine alane</i>
TCO	<i>Transparent conducting oxide</i>
TEA	<i>triethylaluminium</i>
TEAA	<i>Triethylamine</i>
TFT	<i>Thin film transistor</i>
TGA	<i>Thermogravimetric analysis</i>
THF	<i>tetrahydrofuran</i>
TIBA	<i>Triisobutylaluminium</i>
TMA	<i>Trimethylaluminium</i>
TMAA	<i>Trimethylamine</i>
TMEDA	<i>Tetramethylethylenediamine</i>
TMEDAA	<i>N,N,N',N'-tetramethyl-1,3-propane-diamine</i>
TTIP	<i>Titanium isopropoxide</i>
UV	<i>Ultraviolet</i>
VSEPR	<i>Valence shell electron pair repulsion</i>
VT	<i>Variable temperature</i>
XPS	<i>X-ray photoelectron spectroscopy</i>
XRD	<i>X-ray diffraction</i>
3c-2e	<i>3-Centre-2-electron</i>

List of Symbols

$\downarrow$	<i>Precipitation of product</i>
J	<i>NMR coupling constant</i>
m/z	<i>Mass to charge ratio (in mass spectrometry)</i>
pK_a	<i>Acid dissociation constant</i>
R	<i>R-factor (in crystallography)</i>
R_s	<i>Sheet resistance</i>
T_d	<i>Decomposition temperature</i>
Z	<i>Number of formula units in the unit cell (in crystallography)</i>
δ	<i>NMR chemical shift</i>
$\Delta_f H^\theta$	<i>Standard enthalpies of formation</i>
η^n	<i>Ligand denticity, where n denotes the number of binding sites</i>
θ	<i>X-ray incident beam angle</i>
κ	<i>Dielectric constant</i>
λ	<i>Wavelength</i>
ρ	<i>Resistivity</i>
ρ_{calc}	<i>Calculated unit cell density (in crystallography)</i>
τ	<i>Structure parameter</i>
Φ	<i>Work function</i>

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Chapter 1

Introduction

This Chapter sets the scene for the thesis, beginning with a preface for this work, project aims and a thesis synopsis. The Chapter then proceeds with a brief introduction covering topics such as general precursor chemistry, why aluminium was chosen as the metal centre to investigate and a review of several deposition techniques in which precursors can be used to deposit metal and/or metal oxide films.

1.1 Preface

The market for printed, organic and flexible electronics is predicted to be worth \$74 billion in 2030.¹ Perhaps unintuitively, there is both a need for compounds that can be deposited to produce functional materials for electronics, that can either be highly conductive or insulating. Highly conductive materials, namely in the form of conductive metal interconnects, can be used as the circuitry in a host of printable devices such as solar cells (SCs), radio frequency identification (RFID) antennas and organic light emitting diodes (OLEDs). Non-conductive materials are useful as insulating layers in electronic devices, most noticeably in thin film transistors (TFTs). There is a push from market leaders for the fabrication of electronics on large scales, incorporating processes that are material-, energy- and time- efficient. One potential approach to achieve these goals is through the use of metal-organic decomposition (MOD).

The metal of interest in this project is aluminium, Al as it is both highly conductive ($\rho = 2.65 \mu\Omega \text{ cm}$, 20 °C, the fourth most conductive element after silver, copper and gold),² and has a low work function in the zerovalent state. Conversely, its oxide, namely alumina, Al_2O_3 has a host of potential applications, including as a replacement for silica, SiO_2 as a high- κ gate dielectric material.³ Using aluminium, which has the highest molar crustal abundancy of any metal, better future-proofs technologies of today and tomorrow.²

1.2 Project aims

The aims of this thesis are detailed below:

- To synthesise a range of aluminium compounds, novel or otherwise, in order to assess their stability with regards to their long-term storage, handleability and decomposition temperature.
- To fully characterise a range of novel aluminium compounds, drawing trends between chemical structure and stability.
- To formulate the most suitable precursors into MOD inks, followed by their solution-based deposition at low temperature in order to form highly conductive aluminium metal and/or oxide films.

- To fully characterise aluminium thin films, drawing conclusions between MOD ink formulation and film quality.

1.3 Thesis overview

Chapter 1 of this work introduces the context of the project presenting research aims and an introduction to MOD precursors, the usefulness of depositing aluminium-containing thin films along with various deposition types that can be used to achieve this is given. Chapter 2 contains details of laboratory procedures and characterisation techniques for all experimental results that are subsequently discussed in latter Chapters (3–6). Chapter 3 details the novel synthesis, full characterisation and thermal analysis of a series of novel tris(β -ketoiminate) aluminium compounds, whilst Chapter 4 continues to develop synthetic routes for a family of bis(β -ketoiminate) aluminium monochloride compounds. Chapter 5 details the synthesis, characterisation and thermal analysis of a series of aluminium hydride containing compounds (mono(β -diketiminato) aluminium dihydride compounds and amine-stabilised alanes) and Chapter 6 finishes off this work by utilising the best thermally performing compounds from Chapters 3–5 as MOD inks, to deposit conductive aluminium metal films, which themselves are fully analysed by a multitude of film characterisation techniques. Chapter 7 concludes the work within this thesis, detailing areas in which this work can be further investigated.

1.4 Introduction

1.4.1 What is a precursor?

Within the field of materials deposition, specifically in the field of deposition of inorganic materials techniques such as chemical vapour deposition (CVD), precursors are defined as “*molecular compounds containing one or more atoms or groups of atoms that are constituents of the particular target material, which are selectively deposited upon decomposition of the precursor during materials synthesis and processing.*”⁴ Thus in this context, precursors are not “building blocks” like monomers in polymer chemistry or subunits in supramolecular chemistry. Typically, the molecular structure of precursors are completely dismantled, rather than integrated to an extent in the final material.

Precursor chemistry is rooted deep within the traditions of classical inorganic solid-state chemistry, where precursors act as “molecular containers” for the delivery of the smallest possible unit for chemical construct: the atom. It proceeds that the major issue in precursor

chemistry is ascertaining a detailed understanding and control of the decomposition of a precursor under the conditions defined by the requirements and limitations of the particular fabrication process of the target material or device.⁴

Organometallic compounds by definition contain a formal metal-carbon bond whereas metal-organic compounds contain both metal and carbon atoms, but no formal metal-carbon bond, however these terms are often, perhaps incorrectly, interchanged in materials chemistry. Both types are of particular interest since their composition and structure can be easily changed by varying the ligands attached to the metal centres. Simple inorganic molecular precursors, such as the molecular elements, binary hydrides or halides do not offer such degrees of freedom, but are advantageous due to their chemical simplicity. The increase in precursor complexity likely complicates rather than remedies the overall chemical intricacy of materials synthesis. The target of precursor engineering is finding an optimum compromise between the conditions of materials synthesis and processing, with the possibilities and limitations of precursor chemistry.⁴

1.4.2 Requirements of a precursor

Since the advent of organometallic CVD in the late 1960's by Manasevit *et al.*,⁵ numerous alternative methods have been used to deposit organometallic and metal-organic complexes and although specific requirements must be met, the general requirements of a precursor have remained the same. First and foremost, the precursor/s must contain all of the constituent elements/s required in the desired material. This can be achieved in a number of ways, most commonly through the use of 'single source' or 'dual source' precursor set-ups. Single source precursors are particularly desired as they often contain preformed bonds required in the target material, which removes an energy barrier for deposition and can also facilitate the deposition of metastable materials, that perhaps cannot be derived by other methods. In addition to this, they often simplify the accompanying gas phase reactions, thus reducing the process parameters to be controlled and optimised.⁴

Precursors should always be designed to limit contaminants in the resulting functional material, since purity is essential to reliable functional application – this is often why carbon and halogen contents in precursors are kept to a minimum. Environmental impact and cost are other important factors, in particular when industrial scale fabrications are considered. Finally, it is advantageous for precursors to have low toxicity and high stability, for storage

and handling purposes. Toxicity limits the choice of donor atoms chosen in metal-organic precursor chemistry. Carbon atoms form covalent bonds with a selection of heteroatoms, most commonly O, N, P, S, As and halogens, with the halogens being excluded as metal donor atoms as they are monovalent and therefore cannot bridge between a central metal ion and a hydrocarbon radical. Due to the formation of toxic and noxious fumes upon thermal decomposition of As and P compounds, they are less regularly used heteroatoms. Therefore in most cases, only metal-organic compounds with O, S and/or N heteroatoms are considered as viable MOD precursors.⁶

Historically there has also been a requirement for compounds to be volatile, such that the vapour phase can be readily accessible, for use in techniques such as CVD and atomic layer deposition (ALD). Precursor stability and volatility have an inverse relationship, which traditionally resulted in industrial processes making a stability compromise, often employing pyrophoric reagents.⁷ Due to increased prevalence of solution-based techniques such as aerosol-assisted (AA)CVD, coating and printing techniques, precursor volatility is no longer an essential requirement, so precursors have evolved to become more handleable. Particularly through the popularity of low-cost flexible (and sometimes transparent) substrates such as paper and plastics, precursor decomposition temperature has become an escalating hot-topic, with sub 200 °C temperatures required in order to not damage substrate integrity.

1.4.3 Metal-organic decomposition (MOD) precursors

When designing a suitable metal-organic precursor for a metal ink, considerations must be made, as highlighted in Section 1.4.2. Whilst precursors for transparent conducting oxides (TCOs), photoelectrical materials and photovoltaics have been intensively researched over the last few decades, these often involve the tailoring of ligands to form oxides or nitrides.⁸ Arguably the most difficult task when designing precursors are those that under particular conditions (most likely decomposition under an inert atmosphere and solventless or using benign solvents) decompose to zerovalent state, as most metals prefer to exist in higher oxidation states. Among common MOD precursors, only the metal carbonyls begin the process in the formal zerovalent state, so some form of metal reduction is often required during decomposition. While metal carbonyls seem as if they would make ideal candidates for metal deposition, this is only true for nickel tetracarbonyl, Ni(CO)_4 as in most cases, the metal surface is reactive enough to split carbon monoxide, CO, producing films that are contaminated with carbon and oxygen.^{9,10}

With regards to CVD, which is the most commonplace area for using such precursors, only 67 (of around 95) of the naturally occurring metallic elements have had useful deposition processes to the zerovalent state identified.¹⁰ Accessible elements include those bordering the metalloid line along the p-block elements to the vanadium triad in the d-block. None of the elements to the left of this group (group I and II metals), including the f-block elements have been deposited in the zerovalent state by a useful CVD process. These elements represent the most electropositive examples in the periodic table, and are typically found in their highest possible oxidation state when bonded, with metal centres in such compounds difficult to reduce.¹⁰

There are three generic reactions that can be used for precursor reduction and deposition (see example Eqn.'s 1.1–1.3):

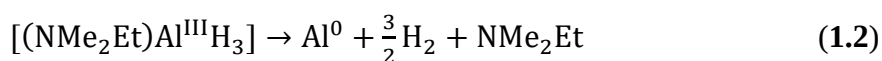
1. Addition of an external reducing agent such as hydrogen

It is well known that addition of a reducing agent can aid precursor transformation into a desired material, for example Eqn. 1.1 illustrates the use of hydrogen gas, H₂ to reduce tungsten hexafluoride, WF₆ to tungsten metal.¹¹ Hydrogen is used in many CVD processes even when its role as a stoichiometric reductant may seem superfluous – in such depositions, it serves as both a carrier gas and to aid metal film purity, as it helps to remove carbon, oxygen and/or other impurities which may derive from ligands in the precursor. Other popular reducing agents include alcohols and silanes.



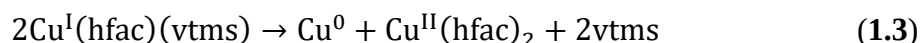
2. Reductive elimination of ligands

The use of amine-stabilised alanes to deposit metallic aluminium (also see Chapter 5) is an exemplar of when reductive elimination is used to reduce the metal centre (Eqn. 1.2).¹² The hydride ligands (formally H⁻) provide electrons when they dissociate as molecular hydrogen from the aluminium surface. As later described, reductive elimination of hydrogen serves as the electron source in every useful aluminium CVD process, even in examples where no hydrides are present in the precursor (*e.g.*, Al[CH₂CH(CH₃)₂]₃).¹³



3. Disproportionation

Disproportionation involves one metal serving as both the electron donor and acceptor. Monovalent copper is one of the more common examples that exhibit this phenomenon ($\text{Cu(I)} \rightarrow \text{Cu(0)} + \text{Cu(II)}$) and it features in one of the most important copper CVD processes (Eqn. 1.3, where hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, vtms = vinyltrimethylsilane).¹⁴

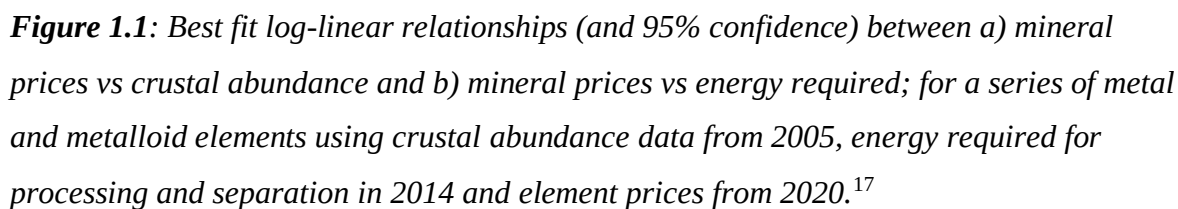


To decompose compounds to metal oxide or nitrides, the most common functional materials with metals in non-zerovalent states, the non-metallic elements can either derive from the precursor (*i.e.* alkoxides, β -diketonates, alkylamides, amines) and/or through reaction with the carrier gas upon decomposition (commonly, O_2 , H_2O vapour or NH_3). Often reactive carrier gasses are used even when it may seem unnecessarily to ensure films are formed stoichiometrically, as well as, helping to remove impurities.^{15,16}

1.4.3.1 MOD precursor metal choice

When selecting the metal centre of a MOD precursor several considerations must be made. First, and foremost, the metal centre must be suitable for the desired use, be that in the zerovalent state when deposited for metal circuitry in a host of devices or in the oxidised state, for example as the metal oxide, which can be used in numerous applications such as gas sensing, in TCO devices or for corrosion/wear resistance. Ideally a single precursor could fabricate films containing either the zerovalent or oxidised metal depending on the deposition parameters, however oftentimes precursors tend to be specialised.

Another major decision when selecting the metal centre of a MOD precursor is often its availability and cost, which are inherently linked. Figure 1.1 gives the crustal abundances, extraction and processing energy cost for a series of metallic and metalloid elements. One great example of when a metal's scarcity and cost has hampered its wide-spread continued use and research is indium. Indium, a constituent element in indium tin oxide (ITO) a highly employed TCO used in touchscreen electronic displays, has been prone to extreme price fluctuations due to limits in supply and increased demand, such that there has been a great push to replace this material entirely, with groups undertaking more research on more sustainable compounds such as aluminium zinc oxide (AZO), despite its poorer base performance. By



In addition to the generic requirements of a precursor (Section 1.4.2), ligands can be selected that facilitate one of the three precursor reduction and deposition reactions (Section 1.4.3). MOD precursors can require auxiliary ligands that aid complex solubility, handleability and/or promote/aid decomposition. It must be noted that frequently, particular ligands can play or play parts in several of these roles – for example, the amine ligand in amine-stabilised alanes acts twofold in that it can partake in the reductive elimination reaction and it allows the AlH_3 moiety to be dissolved in a range of organic solvents. Additionally, changing the amine can vary storage conditions and decomposition temperatures.¹⁸

Aluminium is a readily available metallic element, being the third most abundant element in the Earth's crust behind oxygen and silicon, which are non-metals. Aluminium's high natural abundance in tandem with its relatively simple two-step extraction process from bauxite first to alumina, Al_2O_3 (Bayer process)¹⁹ followed by smelting to the metal (Hall-Hérout process),²⁰ means aluminium has a comparatively low price compared to most other

metals (Figure 1.1). In addition to aluminium's practicality, zerovalent and oxidised aluminium-based materials have a host of useful functional applications.

In the metallic state, aluminium's high electrical conductivity ($\rho = 2.65 \mu\Omega \text{ cm}$, 20°C)² makes it an excellent choice as a metal interconnect in numerous electrical devices, whilst its low work function ($\Phi = 4.08 \text{ eV}$)² makes it an appealing inorganic electrode material. Aluminium's aforementioned low-cost compares well to the three other most electrically conductive metallic elements, being approximately 30,000 times as inexpensive as gold, 400 times that of silver and 4 times that of copper.²¹

One major issue with using aluminium metal as a conductive material is that it is susceptible to electromigration under high current densities.²² Electromigration is the transport of metal atoms along grain boundaries propelled by the force exerted by flowing electrons under high current densities, which results in voids and extrusions at opposite ends of metal lines.⁷ Electromigration can be reduced by two approaches: the first is by increasing grain size which reduces the surface area of grain boundaries and the second is by filling grain boundaries with an alloying element to reduce the rate of grain boundary diffusion. For this reason, aluminium interconnects are commonly alloyed with copper and silicon, well above their solid solubility in aluminium at room temperature, causing the alloyed elements to precipitate out at the grain boundaries, thereby decreasing grain boundary diffusion.⁷ Alloying aluminium with palladium is another appealing method of reducing the effects electromigration, with Al-Pd less susceptible to corrosion than Al-Cu.²³ Other beneficial uses of aluminium include metal coatings on packaging to prevent gas diffusion and applications that take advantage of aluminium's high reflectivity, being the second most reflective metal only behind silver.⁷

1.4.4.1 Precursors to aluminium metal

Al(III) compounds are used exclusively in the deposition of aluminium metal using MOD inks, as Al(I) compounds are extremely unstable, requiring harsh conditions and bulky ligands to adequately protect the metal centre respectively.²⁴ Traditionally, deposition of aluminium metal films using molecular precursors was achieved *via* CVD, a technique that forms thin films using the chemical reaction of compounds in the vapour phase. Up until the 1990's, aluminium alkyls such as triisobutylaluminium (TIBA) and trimethylaluminium (TMA) were mainly used as aluminium metal CVD precursors due to their commercial availability. Breaking the Al–C bonds is the rate determining step in the decomposition of these species

and the efficacy of low temperature clean decomposition to metallic films is greatly improved by having β -hydrides present in the alkyl ligands (as for TIBA, but not for TMA). For the majority of aluminium alkyls, higher temperatures ($>200\text{ }^{\circ}\text{C}$) are required for cleaner deposition.^{7,10,13}

An alternative approach is to use aluminium trihydride, AlH_3 (or alane) based compounds, with alane itself showing clean decomposition at temperatures as low as $60\text{ }^{\circ}\text{C}$, due to it only containing three weak Al–H intramolecular bonds.²⁵ Trimethylamine alane (TMAA), dimethylethylamine alane (DMEAA) and triethylamine alane (TEAA) have been the focus of a number of more recent metal-organic (MO)CVD publications, where tertiaryamine adducts of alane have been used to deposit Al films at low temperatures (below $100\text{ }^{\circ}\text{C}$) in relatively short times.^{12,26,27} These precursors are synthesised from one-step reactions involving lithium aluminium hydride, LiAlH_4 and the hydrochloride salt of the amine or through ligand replacements reactions of diethyl ether-stabilised alane solution produced from reacting LiAlH_4 with aluminium trichloride, AlCl_3 . Their extremely low decomposition temperatures does lead to storage issues, with refrigeration the only option for longer term use. The versatility of these compounds is considerable, as there are many Lewis base compounds to choose from including tertiaryamines and ethers. Rockenberger *et al.*²⁸ in their 2010 patent listed a broad array of stabilised aluminium compounds, capable of decomposing at temperatures around $100\text{ }^{\circ}\text{C}$ in the form of aluminium inks (precursors dissolved in solution.) Since 2010, research into the solution-based deposition use of these precursors has become more common, including the first literature use of an ether-stabilised alane, dibutyl ether alane (DBEA) to deposit aluminium metal films when used alongside a reducing agent.²⁹ A selection of precursors that have been used to deposit thin films of aluminium metal is given in Figure 1.2.

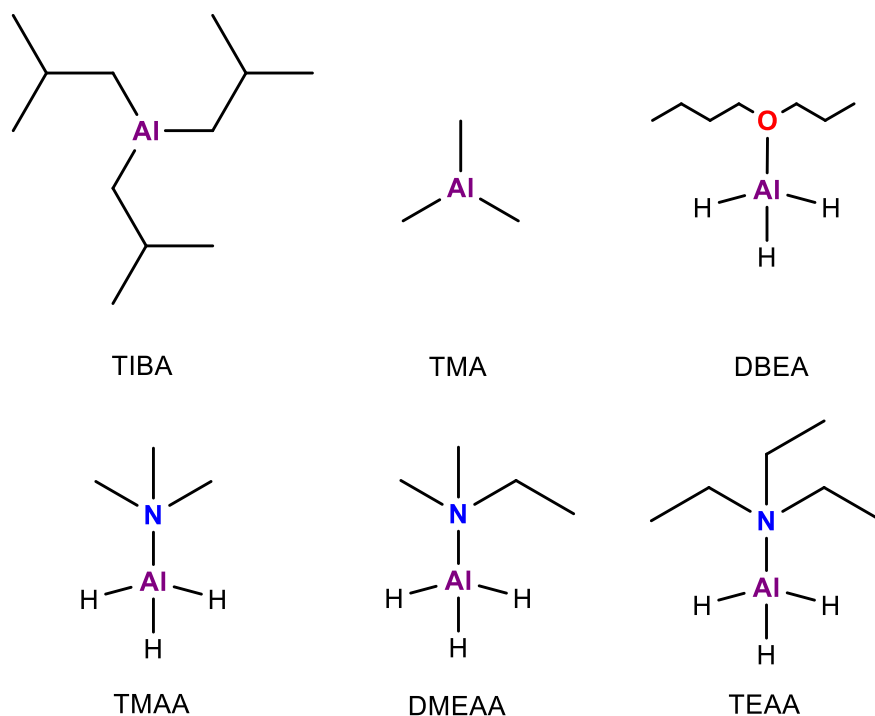


Figure 1.2: A selection of aluminium compounds used as precursors to deposit aluminium metal thin films within the literature.

1.4.5 Aluminium oxide

Thin films of aluminium oxide (alumina) have found a diverse range of applications over the last few decades. Alumina is a relatively hard, unreactive electrically insulating material that can be transparent in some modifications (optical band gap 8.7 eV).¹⁵ These properties make Al₂O₃ useful for several applications in a wide field of engineering, such as use as insulating layers in electronic devices,³⁰ as anti-reflective coatings on glass surfaces,³¹ or in the fields of mechanical engineering where it is utilised in either protective layers or hard coatings.³² The properties of Al₂O₃ films are strongly influenced by the crystal structure deposited, with several different phases of alumina existing. The most stable form of aluminium oxide and therefore the most common is α -Al₂O₃ (corundum), which is the hardest phase which displays excellent thermal stability, making it ideal for the mechanical engineering sector. Other prevalent phases of alumina films include the metastable phase γ -Al₂O₃ (Al₂OMgO₄-type), along with amorphous films Al₂O₃, which tend to be softer (Mohs scale) than the crystalline films.³³

1.4.5.1 Precursors to aluminium oxide

As with aluminium metal thin film fabrication, Al(III) compounds are exclusively used in the deposition of oxide films, with the deposition field of CVD once again playing a crucial role in the development of precursors. Early studies into the MOCVD of Al₂O₃ involved the hydrolysis or oxidation of aluminium trihalides, such as AlCl₃, however, the high deposition temperatures required (typically 700–950 °C) were unsuitable for microelectronic applications.^{34,35} Lower deposition temperatures (<400 °C–650 °C) were obtained through the use of alkyl aluminium compounds such as TMA and triethylaluminium (TEA) in the presence of either O₂^{36,37} or N₂O.³⁸ Gustin *et al.*³⁹ compared both oxidising agents and concluded that using O₂ produced superior films. The high reactivity of alkyl aluminium compounds towards O₂ can lead to problems, with premature reactions causing particulate films which have poor substrate adhesion, whilst incomplete ligand oxidation can lead to carbon contamination.

The use of aluminium isopropoxide, [Al(OⁱPr)₃], with O₂^{40,41} or N₂O⁴² avoids the problem of pre-reaction and allows the MOCVD of Al₂O₃ at low temperature (200–750 °C). However, [Al(OⁱPr)₃] is a trimeric solid (mp = 118 °C) which has a tendency to oligomerise upon prolonged storage, which consequently changes its vapour pressure and therefore has a significant effect on the deposition rate of the Al₂O₃ film. A solution to this issue is to synthesise [Al(OⁱPr)₃] *in-situ* in the gas-phase by mixing vapours of TMA and isopropanol upstream from the reactor cell, which allowed the growth of high purity Al₂O₃ (C <0.5 at.%) by conventional MOCVD over the temperature range 400–600 °C.⁴³ [Al(acac)₃] (where acac = acetylacetonate) has also been investigated, with films grown in the absence of O₂,⁴⁴ or in the presence of air,⁴⁵ showing significant carbon contamination, although those grown using [Al(acac)₃] with O₂ or H₂O were of higher quality.^{46,47} Lewis base-stabilised alanes, such as amine-stabilised alanes have also more recently been used to deposit Al₂O₃ films at low temperature (200–300 °C) in the presence of an oxygen source, however the use of these precursors is not as common place as one might expect.⁴⁸

ALD is another popular method of Al₂O₃ deposition, with many precursors overlapping both fields. Earlier studies include the use of AlCl₃, [Al(OEt)₃], [Al(OⁿPr)₃] and TMA in combination with H₂O, O₂, ROH, H₂O₂ or O₃.^{3,49–51} More contemporary depositions generally concentrated on using TMA, due to its high reactivity with H₂O along with its relatively high thermal stability, making it an almost ideal ALD precursor.⁵² However, TMA is less well

adapted to liquid injection ALD and so the much less reactive $[\text{Al}(\text{mmp})_3]$ (where mmp = 1-methoxy-2-methyl-2-propoxide) has been used alongside H_2O .⁵³ Self-limiting growth was observed at low temperatures (250 °C), however trace carbon (2.4 at.%) was observed in the Al_2O_3 films. A selection of precursors that have been used to deposit thin films of aluminium oxide is given in Figure 1.3, it is interesting to note that there are examples of aluminium precursors that do not contain oxygen, that can be used to deposit the oxide.

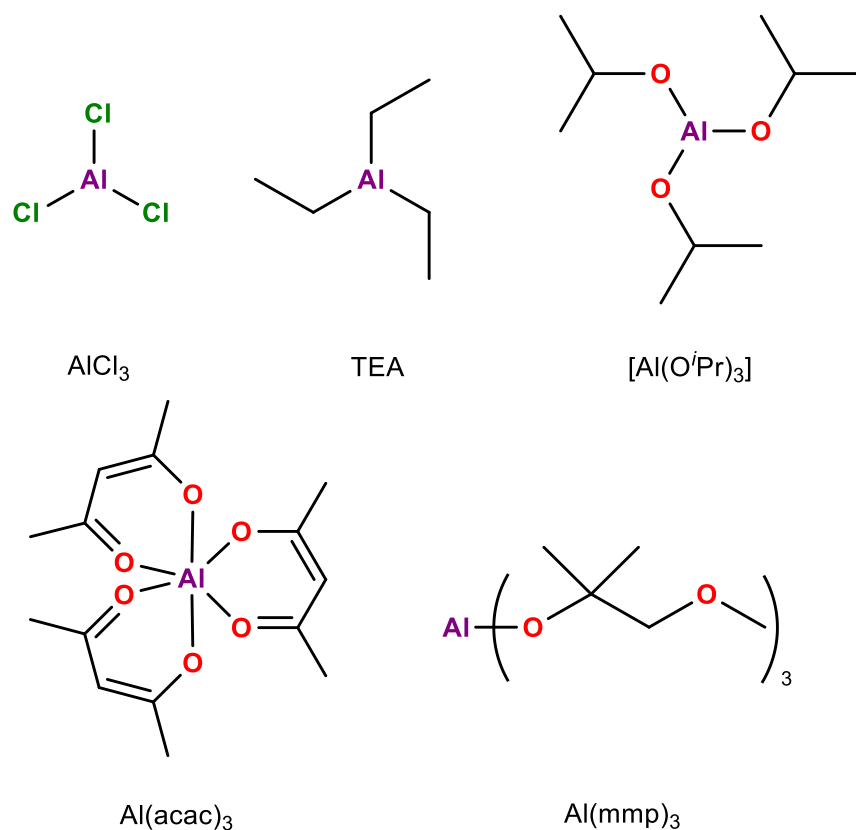


Figure 1.3: A selection of aluminium compounds used as precursors to deposit aluminium oxide thin films within the literature.

1.4.6 Vapour-based deposition techniques

There are many methods of depositing organometallic and metal-organic precursors in the vapour state, with many types already aforementioned. The type of thin film deposition method is usually dependent on three main factors; the nature of the precursor, properties of the material/device required and the scale of fabrication. In addition to the method of thin film deposition,⁵⁴ the type of substrate,⁵⁵ annealing temperatures and duration⁵⁶ are major factors in defining film morphology, quality and hence characteristic properties of the deposited functional material.

1.4.6.1 Metal-organic chemical vapour deposition (MOCVD)

CVD involves thin solid film deposition onto a substrate, *via* decomposition of a vapour-phase precursor or the chemical reaction of vapour phase precursors, which can occur both in the gas phase and on the substrate. It can be differentiated from physical vapour deposition (PVD) processes, which include evaporation, ion-plating and reactive sputtering, which require the adsorption of atomic or molecular species onto a substrate.^{57,58} CVD reactions can be promoted or initiated by heat (considerably the most common), ionising radiation and/or plasma. Precursors can be pulsed sequentially using an inert gas (ALD – see Section 1.4.6.2) or can react with gaseous co-precursors under high vacuum producing single-crystal/epitaxial films on epitaxial substrates (chemical beam epitaxy, CBE). Because of its versatility, there are many variations of CVD.⁵⁸

MOCVD

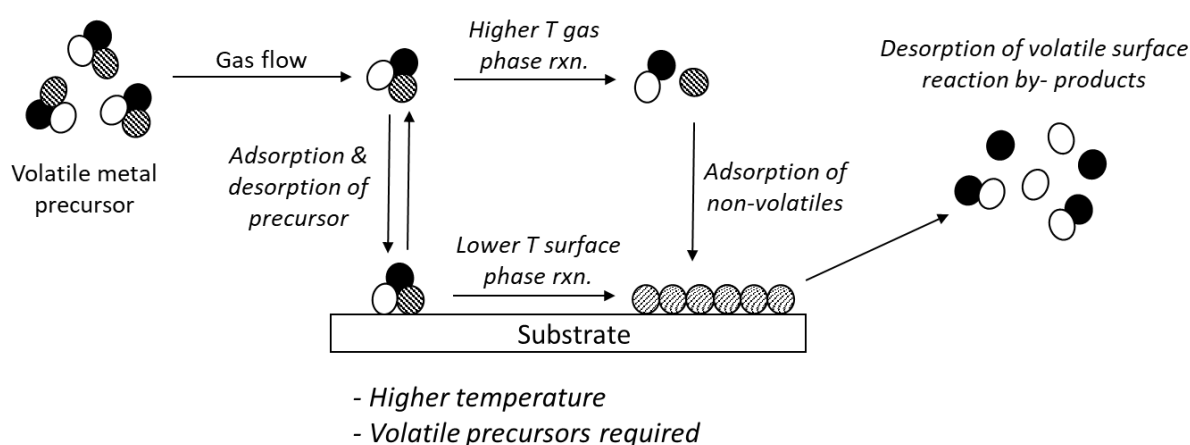


Figure 1.4: Schematic of MOCVD processes.

One such variation is MOCVD, which utilises metal-organic (or organometallic) precursors. As aforementioned, the strict definition of a metal-organic compound is one that contains metal and carbon atoms but doesn't have a direct metal-carbon bond (*e.g.* metal-alkoxides, metal- β -diketonates, metal alkylamides, alanes), however MOCVD oftentimes covers organometallic compounds which do (*e.g.* metal alkyls, metal carbonyls). As seen in the above Sections, the field of MOCVD and its related techniques have been at the forefront of metal-organic precursor research for decades.

MOCVD shows great promise in the formation of metal-based thin films, as it provides many advantages over more traditional deposition methods such as sputtering. Firstly, growth rates and composition are no longer highly temperature sensitive, due to the mass transport control temperature window that many MOCVD processes operate in. Secondly, MOCVD depositions can be undertaken at lower deposition temperatures, with well-defined and controllable stoichiometric quantities of precursors. Furthermore, there are capabilities to deposit thin films using MOCVD with selective area or patterns and films with superior uniformity and purity can be produced. Finally, the experimental ease of MOCVD deposition from starting materials and the potential to up-scale to larger production processes are increased.⁵⁸

1.4.6.2 Atomic layer deposition (ALD)

ALD is a modified variant of CVD, developed more than three decades ago. Chemical reactants are introduced into a vacuum chamber, but unlike vacuum variants of CVD, reactants are supplied sequentially, where the steps are separated by an additional gas purge. The reactants undergo a chemical reaction with the substrate surface in precise monolayers.⁵⁹ If ALD is used to deposit a metal oxide or nitride film (*e.g.* Al_2O_3 , TaN) the first reactant contains the metal and the second the non-metal (*i.e.* oxygen or nitrogen), which forms a monolayer of compound with the metal. Each reaction is self-limiting, meaning that wholly conformal depositions are possible under ideal conditions. Deposition temperatures for ALD are usually low (200–400 °C) compared to CVD (500–1500 °C), however deposition rates are very low, at around $0.1 \text{ nm cycle}^{-1}$.⁵⁸ Due to this low deposition rate ALD can be used for ultra-thin films only. Over the past decade, the significance of such ultra-thin films has grown rapidly such that ALD has become a prominent deposition technique.

1.4.7 Inkjet printing and other solution-based deposition techniques

The deposition of functional materials *via* soluble precursors can be achieved using both coating and printing techniques. Coating techniques include slot-die, dip-⁶⁰ and spin-coating⁶¹ which generally tend to use larger amounts of ink as the processes are usually more wasteful. Printing techniques include screen and gravure printing, as well as, solution stamping,²⁹ but also include highly advanced direct-write technologies in the form of inkjet printing, which many in the field of microelectronics view as the ideal deposition technique. Traditionally,

using solution-based techniques has led to the formation of thicker films, however with the development of microdosage and microprinting tools, thinner films can now be produced.⁵⁷

Since its foundation in the early nineteenth century, inkjet printing technology has become one of the most widely used printing techniques in the publishing and graphics industries, however it is only more recently that this technology has been used in the deposition of functional materials.⁶² Inkjet printing (also known as drop-on-demand printing) allows a more efficient usage of expensive materials and greater flexibility in pattern design.⁶³ Printing of conductive materials using MOD precursors was first published by Vest *et al.*⁶⁴, who has since contributed enormously to this field. Traditionally the use of MOD compounds in printing processes has focussed on metallic patterning for use in the circuitry of electronic devices such as SCs, RFID tags,⁶⁵ OLEDs,⁶⁶ sensors⁶⁷ and supercapacitors⁶⁸ *etc.* (Figure 1.5), however more recently other functional materials such as TCOs have been deposited.⁶⁹

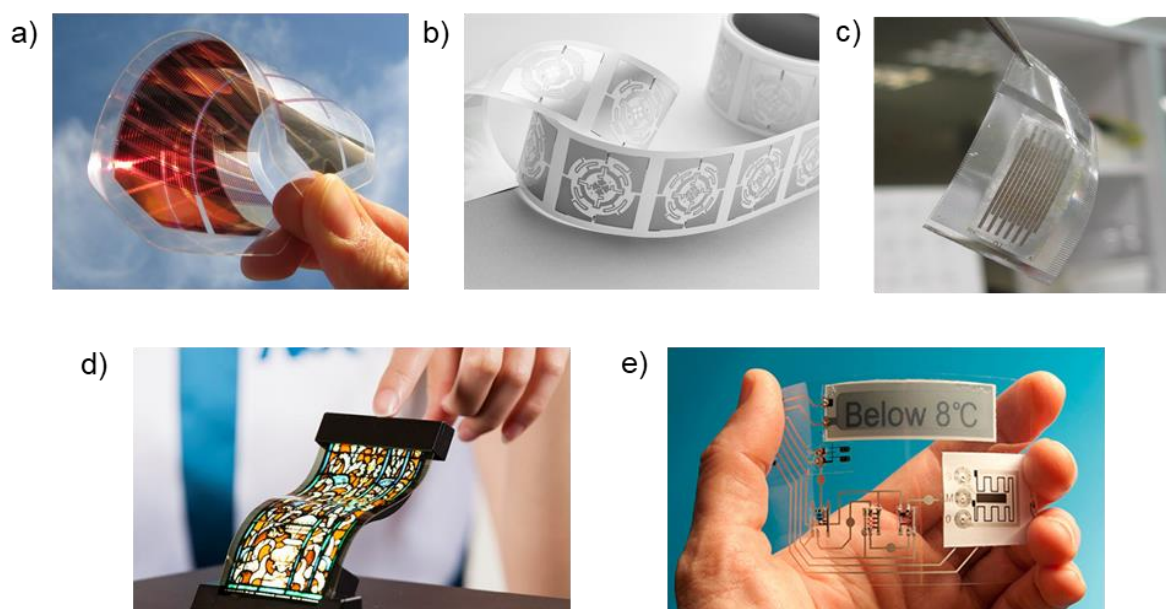


Figure 1.5: Various examples of printed electronics a) SC; b) RFID; c) supercapacitor; d) OLED display; e) temperature sensor.

1.4.7.1 Requirements of metal-based inks

Inks are comprised of a liquid-vehicle (water or an organic solvent) which governs the basic properties of the ink and a dispersed or dissolved constituent, which provides the desired functionality *i.e.* the active precursor. For a metal-based ink to be effective it must satisfy several criteria. Firstly, the printed films must be of sufficient quality to satisfy the functional

application. For example, printed metal films produced must display good conductivity, comparable to the bulk metal ($\leq \times 2-3$). This is why some of the least resistive metals; silver, copper and aluminium are most highly researched.⁷⁰ The resistivities of the deposits are also affected by their morphology.⁵⁵ Although large grains are more conductive than a microstructures consisting of small grains, large grains are frequently accompanied by high porosity which significantly hampers conductivity (Figure 1.6).⁶⁷ Using co-complexing agents to reduce particle size⁶¹ and printing multiple layers to reduce porosity⁷¹ are methods of improving film conductivity.

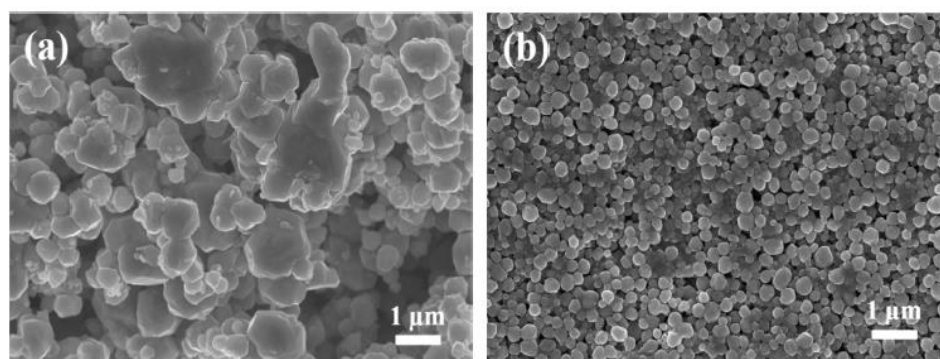


Figure 1.6: Microstructures of a (a) deposit with large particle size and high porosity (poor conductivity) and (b) deposit with small particle size and low porosity (good conductivity).⁶¹

Care must be taken to avoid a phenomenon known as the “coffee ring effect”, which often occurs at drying droplets upon printing, due to material transport within the droplet from its centre to rim, causing inhomogeneous thicknesses.⁷² Inks must exhibit good mechanical properties (adhesion, durability and flexibility of films). Inks should also display good printability, resolution and chemical stability, as well as, requiring minimum printer maintenance, which depend on the viscosity, surface tension and wettability of the ink. Finally, it is favourable for the inks to be cured at lower temperatures ($<200\text{ }^{\circ}\text{C}$)⁷⁰ for short periods of time, so films can be printed on cheap, flexible substrates with fast production speeds.⁷⁰ Such substrates include polymers like polyethylene terephthalate (PET),⁷² polyethylene naphtholate (PEN)⁷¹ and polyimide (PI)⁶⁵ substrates, as well as, paper.⁶⁰ To simultaneously achieve all of the above is problematic and hence there are many challenges in the fabrication of printed metal films.

Historically, MOD inks have been rarely used in the fabrication of electronics. There are numerous limitations that currently exist, particularly the requirement for high sintering

temperatures⁷³ and low times,⁷⁴ in addition to, an artificial atmosphere upon ink deposition.⁶⁵ Many publications highlight low quality deposits with poor electrical⁶⁵ and mechanical properties,⁷⁴ along with long-term storage issues.⁷⁵ Currently the most common method of depositing metallic films through solution-based deposition processes is through using metal nanoparticles (NPs).^{21,70}

1.4.7.2 Alternative types of metal-based ink

The main competitor to MOD inks are NP inks, with the latter currently more widely used, especially when regarding metal deposition, as there is no redox process required in the conversion to metal and oftentimes they can be loaded with higher metal content as ligands are not required.²¹ However, there are issues associated with the use of NP-based inks, not least contamination from capping agents. They must be stable to aggregation and precipitation, in order to produce a highly reproducible performance; hence the addition of an organic stabilising agent (also referred to as a capping agent) is often needed. This stabilising agent can cause issues upon ink drying, as it and other non-metallic components prevent formation of continuous interconnections between individual particles in the printed pattern. This creates insulating regions between particles, resulting in low electrical conductivity when producing metal films. To obtain good conductivity, an additional post-printing step is commonly required, but this limits particular substrate use.⁷¹ Another main challenge for NP-based inks is the rapid oxidation of more reactive metals at ambient conditions, such as copper and aluminium.

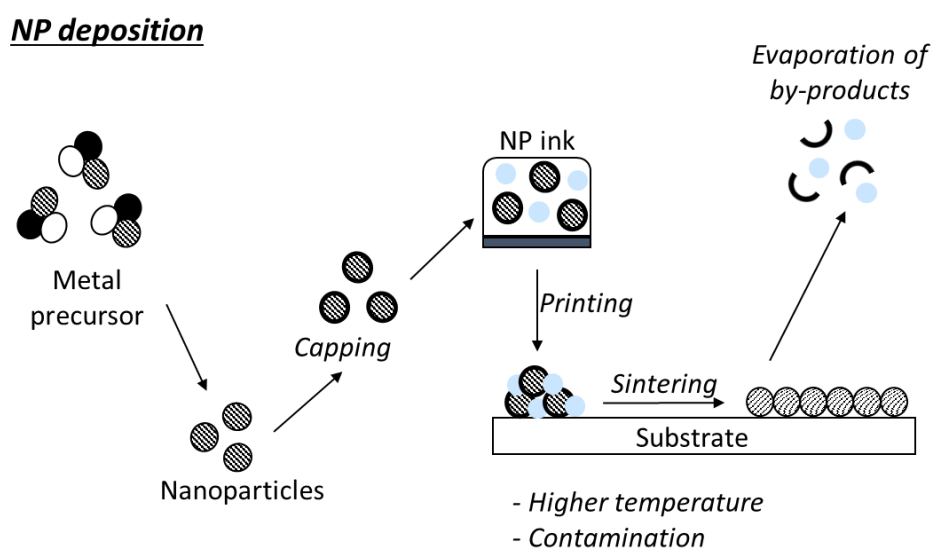


Figure 1.7: Schematic of NP ink formulation and deposition.

Presently, most NP inks are silver-based, due to silver's high conductivity and its resistance to oxidation. Many examples of silver-based NP inks are commercially available but they are expensive.⁶⁹ In addition, the suspension of silver particles in NP inks can often clog the nozzle upon printing, especially upon higher metal loading.⁷⁶ It is also a common occurrence that silver NPs are synthesised in an organic solvent that is primarily composed of hazardous material, which ideally would be avoided.⁷⁷ Copper and aluminium NP inks have been synthesised, with the former commercially available, but they often require sophisticated reaction conditions, such as deposition under a reducing atmosphere.^{21,70,78} Still, the future of NP inks is promising and they are MOD ink's main contender in the metallic ink printing industry.

1.4.8 Sintering methods

Sintering is the process of welding particles together at temperatures below their melting point. Sintering is particularly prevalent in the deposition of metal films, where it allows conductive particles to form continuous interconnections, lowering porosity and results in lower resistivity films. Sintering is less common when depositing other types of functional materials, but it can be useful in removing organic residues and densify films.⁷⁹ The sintering processes described in this Section can be applied to all the abovementioned deposition techniques towards metal-containing functional materials.

Undoubtedly the most common type of sintering for MOD compounds towards functional materials is thermal sintering (Figure 1.8).⁷¹ Other sintering methods include electromagnetic radiation (microwave,⁸⁰ infrared (IR),⁶³ ultraviolet (UV)⁸¹), plasma⁸² and laser sintering⁸³ which have been used solely or in parallel with thermal sintering in order to lower sintering times and/or temperatures.⁷² A more expansive range of alternative methods to thermal sintering have been successfully used in NP inks, which have a greater requirement of sintering, in order to form the connections between neighbouring particles necessary to achieving highly conductive films.⁸⁴

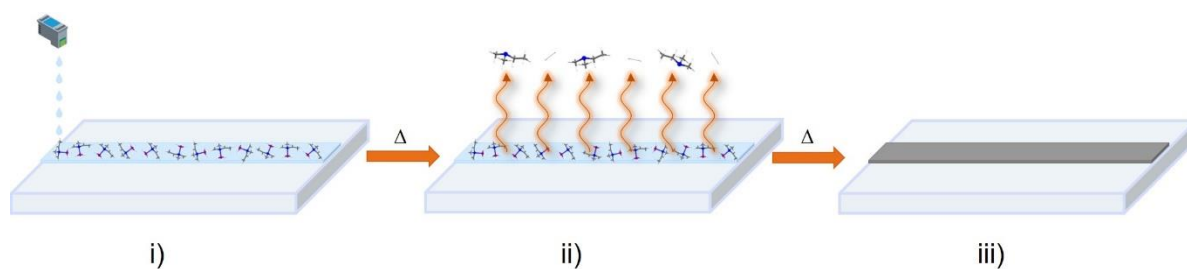


Figure 1.8: A typical sintering process for a MOD ink which has been inkjet printed onto a substrate. i) The ink is deposited on the substrate. ii) The ink is thermally sintered resulting in the MOD ink decomposition and evaporation of volatile by-products. iii) Sintering leaves behind pure metal particles that bind together to form a conductive film.⁷¹

1.5 Summary

This Section has identified the key objectives this research looks to achieve, presented an overview of the work featured within and introduced important concepts that link to the research conducted from the literature.

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Chapter 2

Experimental Procedures

This Chapter details the experimental and characterisation procedures conducted in this research project, for the work discussed in Chapters 3–6.

2.1 General considerations

2.1.1 Synthetic procedures

All reagents were procured from Sigma Aldrich/Merck unless stated otherwise. Reactions involving the formation of lithium salts of ligands and aluminium metal-organic complexes were performed using standard Schlenk and glove box techniques, both using N₂ as the inert gas. All glassware used in air-sensitive reactions was heated to *ca.* 150 °C prior to use. Precursors that were solids were dried *in vacuo* prior to use and those that were liquids were either distilled or degassed prior to use. Owing to their lower thermal stability, amine-stabilised alane complexes were stored in a 4 °C refrigerator inside a glove box, whilst all other aluminium metal-organic complexes were stored in the glove box without refrigeration. All non-deuterated solvents were dried over activated alumina *via* the Grubbs method using anhydrous engineering equipment, ensuring that the concentration of water in the solvents was below 5–10 ppm and were stored over the appropriately sized molecular sieves (3 or 4 Å).¹ Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed and stored over 4 Å molecular sieves. Amines were used as supplied for ligand synthesis, however those that were used to react directly with alane were either distilled *in vacuo* or degassed depending on purity, but were not left under molecular sieves, due to some observed instability. All anhydrous reagents that are liquid at room temperature were stored in vessels sealed with a Teflon valve (Young's tap flasks). AlCl₃ anhydrous powder, sublimed for synthesis, ≥98.0% was procured from Merck Millipore and LiAlH₄ powder, reagent grade, 95% was procured from Sigma Aldrich and was purified by dissolution in and recrystallisation from diethyl ether using a literature procedure.² Lithium bis(trimethylsilyl)amide (LiHMDS) was purchased from Sigma Aldrich and purified *via* sublimation (<0.01 mbar, >90 °C). Triethyloxonium tetrafluoroborate, [Et₃O][BF₄] was purchased from Sigma Aldrich and used as received – it was also stored and used under an inert environment.

2.1.2 Characterisation

2.1.2.1 Precursor characterisation

Nuclear magnetic resonance (NMR): ¹H and ¹³C{¹H} NMR spectrums were collected on either Bruker 300, 500, 600 or 700 MHz NMR instruments at 298 K. ¹H NMR were calibrated using the CDCl₃ or C₆D₆ peak at 7.26 or 7.16 ppm respectively. ¹³C{¹H} NMR were calibrated using the CDCl₃ or C₆D₆ peak at 77.16 or 128.06 ppm respectively. ¹H and ¹³C{¹H} NMR assignments were confirmed by ¹H–¹H (COSY) and ¹H–¹³C{¹H} (HSQC and HMBC)

experiments where necessary. NMR spectra for all synthesised compounds can be found in the Appendices. **Single crystal X-ray diffraction (SCXRD):** suitable crystals were immersed in mineral oil before being selected and mounted on a nylon loop on a SuperNova Atlas (Dual) diffractometer using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). All crystals were kept at 150.00(10) K during data collection for compounds **6** (153(4) K) and **9** (151(2) K). Compounds were solved using Olex2.³ The structure of compounds **1, 2, 6–9, 21** was solved with the olex2.solve⁴ structure solution program using charge flipping and refined with the ShelXL⁵ refinement package using least squares minimisation. The structure of compounds **3–5, 10** the structure was solved with the ShelXT⁶ structure solution program using intrinsic phasing and refined with the ShelXL⁵ refinement package using either least squares minimisation (**3, 5, 8, 10**) or Gauss-Newton minimisation (**4**). **Elemental analysis (EA):** was used to determine the percentage of C, H and N in each sample using either a Carlo Erba CE1108 Elemental Analyser (London Metropolitan University) or Carlo Erba EA1110 Elemental Analyser (Elemental Lab). **Mass spectrometry (MS):** compounds were dissolved in dry toluene, were ionised using electrospray ionisation and detected in positive (ESI+) or negative mode (ESI-) on a Waters LCT Premier XE. **Thermogravimetric analysis (TGA):** measurements were made using two different instruments depending on the volatility of the sample. More volatile samples were measured using a Netzsch STA 449C Jupiter instrument, whilst lesser volatile samples were measured using a PerkinElmer STA6000 TGA. Both instruments had a sensitivity of 0.1 mg and used He and N₂ as shield gasses respectively. For each, samples (5–10 mg) were placed in 85 μL aluminium pans that were sealed in a glove box and were pierced just before measurement to allow for mass loss. The samples were heated from 30 °C (room temperature) up to a maximum of 500 °C, at a heating rate of 5–10 °C min⁻¹ and under flow of shield gas (N₂) with a flow rate of 60 mL min⁻¹. The majority of TGA measurements were conducted in triplicate to ensure reliability of data.

2.1.2.2 Depositions characterisation

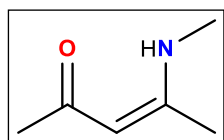
Thin films were analysed as deposited, on their respective substrates. **Lowest resistance measurements:** were recorded using a Kewtech KT116 multimeter. Resistivities were calculated with these values for the thicknesses of films produced, full details of calculating the values are given in Section 2.5.1 of this Chapter. **Grazing incidence X-ray diffraction (GIXRD):** patterns were measured using Bruker-Axs diffractometer with parallel beam optics, fitted with a PSD LynxEye silicon strip detector. X-rays were generated using a copper source with Cu K α_1 ($\lambda = 1.54056 \text{ \AA}$) and Cu K α_2 ($\lambda = 1.54439 \text{ \AA}$) radiation with an intensity

ratio of 2:1. The incident beam angle, θ was kept at 2° , with the angular range of scans collected between $20^\circ < 2\theta < 66^\circ$. Data was collected using a step size of 0.05° counted at 2 s per step. **X-ray photoelectron spectroscopy (XPS):** analysis of the films was carried out using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al K_α source in order to identify constituent elements, their speciation and at.%. The peaks were modelled using CasaXPS⁷ software with binding energies adjusted to adventitious carbon 1s standard peak (284.8 eV) in order to compensate for charging of the surface. Survey scans were collected in the range of 0–1350 eV (binding energy) at a pass energy of 40 eV and were used to estimate atomic%. C 1s, Cu 2p, N 1s and O 1s were also scanned. For each scan, two levels were collected each for 20 s; at the surface and after a 400 s etch. Etching was achieved using an Ar ion etch beam at 1 keV with a current of $1.55 \mu\text{A}$. **Scanning electron microscopy (SEM):** images were collected using a JEOL JSM-6301F Field Emission SEM at an accelerating voltage of 5 kV. **Energy-dispersive X-ray spectroscopy (EDS):** was also measured with an acceleration voltage of 20 kV. Samples were cut into small squares, as well as, coated with a fine layer of gold and stuck with copper tape to an aluminium mount to avoid charging.

2.2 Synthesis of six-membered ring chelates

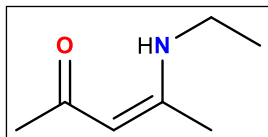
2.2.1 Synthesis of β -ketoimine compounds

2.2.1.1 Synthesis of *N*-methyl-4-amino-3-penten-2-one, (MeCN{H}(Me)CHC=OMe) (**Me-acnach**)



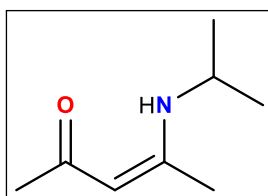
Methylamine (20.4 mL, 40 wt.% in H_2O , 209 mmol) was added slowly to acetylacetone (20 mL, 196 mmol) in 100 mL toluene at 0°C . The yellow biphasic solution stirred at room temperature overnight, before the organic phase was separated and the aqueous phase washed $2 \times 50 \text{ mL}$ with toluene. The organic fractions were combined, dried (MgSO_4), filtered, and concentrated *in vacuo* until a white solid precipitated. The product was recrystallised from toluene at -20°C to yield colourless crystals, which were washed with ice-cold hexane and dried *in vacuo* to yield pure product. Yield: 14.64 g (66%). ^1H NMR (700 MHz, CDCl_3) δ 10.71 (s, 1H, NH), 4.97 (s, 1H, CH), 2.93 (d, 3H, CH_3) 2.00 (d, 3H, CH_3CO), 1.92 (s, 3H, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz) δ 194.77 (CH_3CO), 164.16 (CH_3CN), 95.16 (CH), 29.49 (CH_3), 28.76 (CH_3CO), 18.71 (CH_3CN). NMR data is consistent with spectra reported in the literature.⁸

2.2.1.2 Synthesis of *N*-ethyl-4-amino-3-penten-2-one, (MeCN{H}(Et)CHC=OMe) (**Et-acnach**)



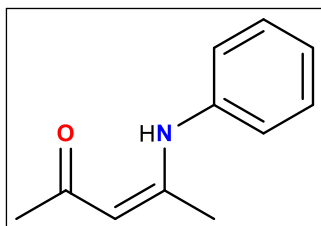
Ethylamine (16.6 mL, 70 wt.% in H₂O, 209 mmol) was added slowly to acetylacetone (20 mL, 196 mmol) in 100 mL toluene at 0 °C. The yellow biphasic solution stirred at room temperature overnight, before the organic phase was separated and the aqueous phase washed 2 × 50 mL with toluene. The organic fractions were combined, dried (MgSO₄), filtered, and solvent was removed *in vacuo* producing a yellow oil. Yield: 18.40 g (74%), ¹H NMR (500 MHz, C₆D₆) δ 11.07 (s, 1H, NH), 4.88 (s, 1H, CH), 2.53 (m, 2H, CH₂), 2.04 (s, 3H, CH₃CO), 1.37 (s, 2H, CH₃CN), 0.68 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 194.20 (CH₃CO), 161.72 (CH₃CN), 95.15 (CH), 37.28 (CH₂), 28.98 (CH₃CO), 18.19 (CH₃CN), 15.30 (CH₃). NMR data is consistent with spectra reported in the literature.⁹

2.2.1.3 Synthesis of *N*-isopropyl-4-amino-3-penten-2-one, (MeCN{H}(Pr)CHC=OMe) (**Pr-acnach**)



Isopropylamine (12.00 g, 203 mmol) was added slowly to acetylacetone (20.33 g, 203 mmol) in 100 mL toluene at 0 °C. Yellow solution refluxed at 115 °C overnight, forming a clear yellow solution. The solution was dried (Na₂SO₄), filtered and the solvent was removed *in vacuo* producing an orange oil. Yield: 24.43 g (85%). ¹H NMR (700 MHz, C₆D₆) δ 11.20 (s, 1H, NH), 4.86 (s, 1H, CH), 3.08 (m, 1H, CH(CH₃)₂), 2.04 (s, 3H, CH₃CO), 1.44 (s, 3H, CH₃CN), 0.78 (d, *J* = 6.5 Hz, 6H, CH₃). ¹³C{¹H} NMR (176 MHz, C₆D₆) δ 194.68 (CH₃CO), 161.15 (CH₃CN), 95.76 (CH(CH₃)₂), 44.88 (CH), 29.54 (CH₃CO), 24.27 (CH₃CN), 18.76 (CH₃). NMR data is consistent with spectra reported in the literature.¹⁰

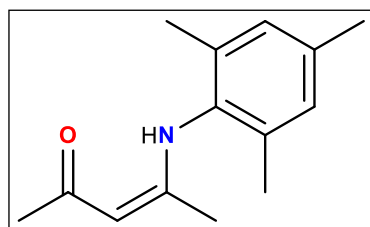
2.2.1.4 Synthesis of *N*-phenyl-4-amino-3-penten-2-one, (MeCN{H}(Ph)CHC=OMe) (**Ph-acnach**)



Aniline (12.4 mL, 136 mmol) was added to acetylacetone (70 mL, 682 mmol) and was refluxed at 150 °C overnight. Excess acetylacetone was removed *in vacuo* to produce a viscous brown solution. This brown solution was distilled at 125 °C under vacuum (*ca.* 0.04 mbar). The distillate collected solidified at room temperature yielding a yellow solid, which was recrystallised from hexane at −20 °C, separated by filtration and washed with ice-cold hexane, to produce off-white crystals. Yield: 19.76 g (83%). ¹H NMR (500 MHz, CDCl₃) δ 12.47 (s, 1H, NH), 7.33 (m, 2H, Ar-H-*meta*),

7.19 (m, 1H, Ar-H-para), 7.09 (m, 2H, Ar-H-ortho), 5.19 (s, 1H, CH), 2.10 (s, 3H, CH₃CO), 1.99 (s, 4H, CH₂CN). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 196.29 (CH₃CO), 160.38 (CH₃CN), 138.87, 129.21, 125.69, 124.89 (Ar-C), 97.73 (CH), 29.30 (CH₃CO), 19.97 (CH₃CN). NMR data is consistent with spectra reported in the literature.⁹

2.2.1.5 Synthesis of *N*-(2,4,6-trimethylphenyl)-4-amino-3-penten-2-one, (MeCN{H}(Ar^{mes})CHC=OMe, where Ar^{mes} = 2,4,6-trimethylphenyl) (**Ar^{mes}-acnacH**)

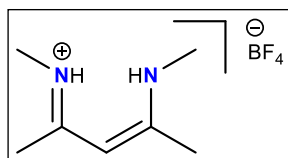


2,4,6-trimethylaniline (19 mL, 136 mmol) was added to acetylacetone (70 mL, 682 mmol) and was refluxed at 150 °C overnight. Excess acetylacetone was removed *in vacuo* to produce a viscous brown solution. This brown solution was distilled at 135 °C under vacuum (*ca.* 0.04 mbar). The distillate

collected solidified at room temperature yielding a yellow solid, which was recrystallised from hexane at -20 °C, separated by filtration and washed with ice-cold hexane, to produce white crystals. Yield: 21.37 g (72%). ¹H NMR (500 MHz, CDCl₃) δ 11.84 (s, 1H, NH), 6.90 (s, 2H, Ar-H), 5.19 (s, 1H, CH), 2.28 (s, 3H, CH₃CO), 2.15 (s, 9H, Ar-CH₃), 2.12 (s, 3H, CH₃CN). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 195.71 (CH₃CO), 163.84 (CH₃CN), 137.30, 135.78, 133.90, 129.06 (Ar-C), 95.65 (CH), 29.01 (CH₃CO), 21.07 (CH₃), 19.09 (CH₃CN), 18.28 (CH₃). NMR data is consistent with spectra reported in the literature.⁹

2.2.2 Synthesis of tetrafluoroborate salt intermediates

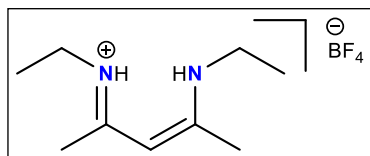
2.2.2.1 Synthesis of *N*-*N'*-dimethyl-4-amino-3-penten-2-immonium tetrafluoroborate, ([MeCN{H}(Me)CHC=N{H}(Me)Me][BF₄]) (**[Me₂-nacnacH₂][BF₄]**)



[Et₃O][BF₄] (18.84 g, 97.6 mmol) in 25 mL of dry DCM was added to **Me-acnacH** (10.00 g, 88.4 mmol) in 30 mL dry DCM, which was stirred for 30 min. After, methylamine (13.5 mL, 33% wt. in EtOH, 110 mmol), was added and the reaction was stirred for a further

30 min, forming a cloudy pale-yellow solution. The solution was heated to dissolve the white precipitate and stored at -20 °C. Overnight, white crystals formed which were washed with ice-cold DCM. Yield (15.13 g, 80%).

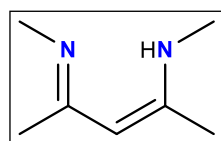
2.2.2.2 Synthesis of *N*-*N'*-diethyl-4-amino-3-penten-2-immonium tetrafluoroborate, ([MeCN{H}(Et)CHC=N{H}(Et)Me][BF₄]) (**[Et₂-nacnacH₂][BF₄]**)



[Et₃O][BF₄] (8.37 g, 44.1 mmol) in 15 mL of dry DCM was added to **Et-acnacH** (5.05 g, 39.7 mmol) in 30 mL dry DCM, which was stirred for 30 min. After, ethylamine (23.5 mL, 2M in MeOH, 47.2 mmol), was added and the reaction was stirred for a further 30 min, forming a cloudy pale-yellow solution. The solution was heated to dissolve the white precipitate and stored at -20 °C. Overnight, white crystals formed which were washed with ice-cold DCM. Yield (5.44 g, 57%).

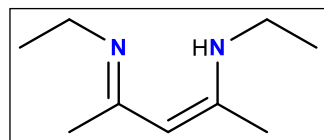
2.2.3 Synthesis of β -diketimine compounds

2.2.3.1 Synthesis of *N*-*N'*-dimethyl-4-amino-3-penten-2-imine, (MeCN{H}(Me)CHC=N(Me)Me) (**Me₂-nacnacH**)



NaOMe (12 mL, 25 wt.% in MeOH, 52.4 mmol) was added to **[Me₂nacnacH₂][BF₄]** (10.00 g, 47 mmol) in anhydrous MeOH and the resultant cloudy suspension was stirred for 1 h. The volatiles were then removed *in vacuo*, 50 mL of toluene was added, and the clear supernatant was isolated *via* filtration. The white solids were washed with 2 × 20 mL toluene, the fractions were combined and the solvent was removed *in vacuo* to produce an off-white solid. Yield: 4.43 g (84%). ¹H NMR (300 MHz, C₆D₆) δ 11.51 (1H, s, NH), 4.64 (s, 1H, CH), 2.79 (s, 6H, CH₃), 1.66 (s, 6H, CH₃CN). ¹³C{¹H} NMR (75 MHz, C₆D₆) δ 161.44 (CH₃CN), 94.85 (CH), 33.28 (CH₃), 19.01 (CH₃CN). NMR data is consistent with spectra reported in the literature.⁸

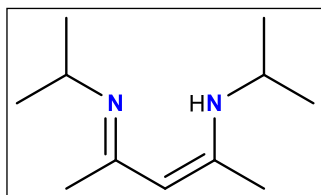
2.2.3.2 Synthesis of *N*-*N'*-diethyl-4-amino-3-penten-2-imine, (MeCN{H}(Et)CHC=N(Et)Me) (**Et₂-nacnacH**)



NaOMe (5.2 mL, 25 wt.% in MeOH, 22.7 mmol) was added to **[Et₂nacnacH₂][BF₄]** (5.02 g, 20.7 mmol) in anhydrous MeOH and the resultant cloudy suspension was stirred for 1 h. The volatiles were then removed *in vacuo*, 50 mL of toluene was added, and the clear supernatant was isolated *via* filtration. The white solids were washed with 2 × 20 mL toluene, the fractions were combined and the solvent was removed *in vacuo* to produce brown-yellow oil. Yield: 1.08 g (34%). ¹H NMR (500 MHz, CDCl₃) δ 11.09 (s, 1H, NH), 4.48 (s, 1H, CH), 3.27 (q, *J* = 7.2 Hz, 3H, CH₂), 1.88 (s, 6H, CH₃CN), 1.24 (t, *J* = 7.2 Hz, 6H, CH₃). ¹³C{¹H} NMR

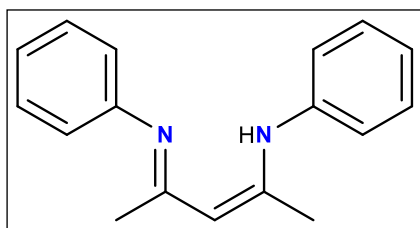
(126 MHz, CDCl₃) δ 160.80 (CH₃CN), 93.64 (CH), 41.07 (CH₂), 19.36 (CH₃CN), 16.45 (CH₃). NMR data is consistent with spectra reported in the literature.⁸

2.2.3.3 Synthesis of *N-N'*-diisopropyl-4-amino-3-penten-2-imine, (MeCN{H}(iPr)CHC=N(iPr)Me) (**Pr₂-nacnach**)



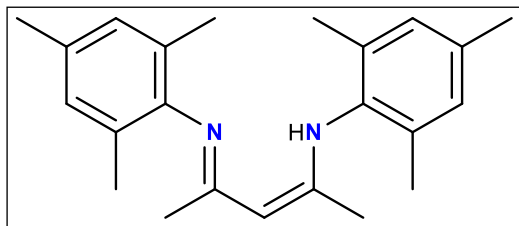
Dimethyl sulphate (7 mL, 74.0 mmol) was added to **Pr-acnach** (10.00 g, 70.8 mmol) which was stirred overnight to produce a viscous pale yellow oil. Isopropylamine (7.2 mL, 84.5 mmol) was slowly added at 0 °C to produce a viscous orange oil after 1 h. NaOMe (17 mL, 25 wt.% in MeOH, 74.3 mmol) was added and the reaction was stirred for 1 h, producing a cloudy yellow solution, which was filtered to produce a yellow solid. The product was extracted with hexane (3 × 20 mL), which was removed *in vacuo* to produce a dark brown oil. Yield oil: 8.08 g (63%), yield desired product: 7.03 g (54%) – NMR analysis showed product was in a *ca.* 87:13 ratio of product to starting material (unable to separate). ¹H NMR (300 MHz, CDCl₃) δ 11.40 (s, 1H, NH), 4.37 (s, 1H, CH), 3.64 (hept, *J* = 6.2 Hz, 2H, CH(CH₃)₃), 1.88 (s, 6H, CH₃CN), 1.16 (d, *J* = 6.4 Hz, 12H, CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 158.70 (CH₃CN), 93.61 (CH), 46.85 (CH(CH₃)₂), 24.81 (CH₃CN), 18.89 (CH₃). NMR data is consistent with spectra reported in the literature.¹¹

2.2.3.4 Synthesis of *N-N'*-diphenyl-4-amino-3-penten-2-imine, (MeCN{H}(Ph)CHC=N(Ph)Me) (**Ph₂-nacnach**)



HCl (37%, 9 mL, 107 mmol) was added to a solution of acetylacetone (10 mL, 97.4 mmol) and aniline (19.5 mL, 214 mmol) at 0 °C. The solution stirred at room temperature overnight forming a yellow solid. The yellow solid was dissolved in DCM (4 mL) and water (50 mL) before being neutralised with triethylamine (15 mL, 107 mmol). The product was extracted with pet. ether 40-60 (2 × 150 mL), which was removed *in vacuo* to produce a yellow oil. The resulting yellow oil was recrystallised from EtOH at low temperature as small yellow plates. Yield: 10.99 g (45%). ¹H NMR (CDCl₃, 300 MHz) δ 12.73 (1H, s, NH), 7.30 (4H, m, Ar-H), 7.07 (2H, m, Ar-H), 6.98 (4H, d, *J* = 7.8 Hz, Ar-H), 4.90 (1H, s, CH), 2.02 (6H, s, CH₃CN). ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 159.61 (CH₃CN), 145.86, 128.91, 123.33, 122.75 (Ar-C), 97.47 (CH), 20.97 (CH₃CN). NMR data is consistent with spectra reported in the literature.¹²

2.2.3.5 Synthesis of *N*-*N'*-di(2,4,6-trimethylphenyl)-4-amino-3-penten-2-imine, (MeCN{H}(Ar^{mes})CHC=N(Ar^{mes})Me), where Ar^{mes} = 2,4,6-trimethylphenyl) (**Ar^{mes}₂-nacnacH**)



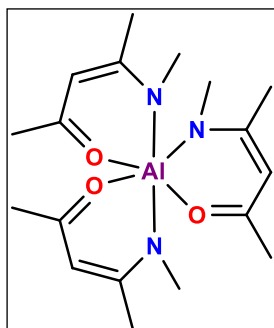
HCl (37%, 3.5 mL, 54.8 mmol) was added to a solution of acetylacetone (5 mL, 48.7 mmol) and 2,4,6-trimethylaniline (15 mL, 107 mmol) in EtOH (100 mL) at 0 °C which was refluxed for 3 days resulting in a darkening of the solution. The

resulting brown solution was cooled before the EtOH was removed *in vacuo* the remaining residue was neutralised with a saturated solution Na₂CO₃, before being extracted with DCM (3 × 100 mL). The organic layers were collected, dried and filtered, before the DCM was removed *in vacuo* producing a dark brown solid. The product was purified by crystallisation from MeOH at low temperature, producing a golden yellow solid after washing. Yield: 8.81 g (52%). ¹H NMR (CDCl₃, 300 MHz) δ 12.14 (1H, s, NH), 6.85 (4H, s, Ar-H), 4.85 (1H, s, CH), 2.25 (6H, s, *para*-CH₃), 2.11 (12H, s, *ortho*-CH₃), 1.68 (6H, s, CH₃CN). ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 161.09 (CH₃CN), 141.28, 133.63, 131.94, 128.54 (Ar-C), 93.40 (CH), 20.95 (CH₃), 20.41 (CH₃CN), 18.40 (CH₃). NMR data is consistent with spectra reported in the literature.¹²

2.3 Synthesis of aluminium compounds

2.3.1 Synthesis of tris(β-ketoiminate) aluminium compounds

2.3.1.1 Synthesis of [Al(MeCN(Me)CHC=OMe)₃] (**[Al(Me-acnac)₃]**, **1**)

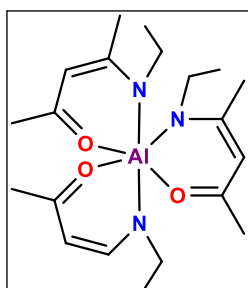


Me-acnacH (1.91 g, 16.88 mmol) in 20 mL diethyl ether was added to a solution of TMAA (TMAA synthesised in Section 2.3.4.1) (0.49 g, 5.50 mmol) in 20 °C at −78 °C. The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. Any insolubles were removed by filtration. The filtrate was concentrated and stored at −20 °C. Overnight, white crystals of **1** suitable for single crystal X-ray measurement

precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 1.08 g (54%). ¹H NMR (C₆D₆, 500 MHz) δ 5.03 (1H, s, CH), 4.97 (1H, s, CH), 4.87 (1H, s, CH), 2.92 (3H, s, CH₃), 2.79 (6H, s, CH₃), 1.99 (3H, s, CH₃CO), 1.93 (3H, s, CH₃CO), 1.90 (3H, s, CH₃CO), 1.59 (3H, s, CH₃CN), 1.56 (3H, s, CH₃CN), 1.55 (3H, s, CH₃CN). ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 178.77, 178.46, 176.10 (CH₃CO), 171.21,

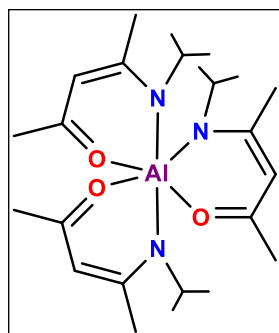
171.07, 170.02 (CH_3CN), 99.41, 98.93, 98.15 (CH), 36.92, 36.77, 36.49 (CH_3), 26.49, 26.18, 25.63 (CH_3CO), 21.89, 21.47, 20.93 (CH_3CN). **MS:** m/z [ESI+] 363 $[\text{M}]^+$, 362 $[\text{M} - \text{H}]^+$, 447.31 $[\text{M}]^+$, 283.22 $[\text{2L} + \text{H}]^+$, 142.10 $[\text{L} + \text{H}]^+$. **EA: Anal. Calcd. For $\text{C}_{18}\text{H}_{30}\text{O}_3\text{N}_3\text{Al}$:** C, 59.49, H, 8.32, N, 11.56. **Found:** C, 59.43, H, 8.47, N, 11.46.

2.3.1.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Et-acnac})_3]$, **2**)



Et-acnacH (2.15 g, 16.9 mmol) in 20 mL diethyl ether was added to a solution of TMAA (0.50 g, 5.61 mmol) in 20 °C at -78 °C. The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. Any insolubles were removed by filtration. The filtrate was concentrated and stored at -20 °C. Overnight, white crystals of **2** suitable for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 1.45 g (64%). ^1H NMR (500 MHz, C_6D_6) δ 5.00 (s, 1H, CH), 4.96 (s, 1H, CH), 4.88 (s, 1H, CH), 3.30 (m, 6H, CH_2), 1.97 (s, 3H, CH_3CO), 1.91 (s, 3H, CH_3CO), 1.87 (s, 3H, CH_3CO), 1.74 (s, 3H, CH_3CN), 1.69 (s, 3H, CH_3CN), 1.66 (s, 3H, CH_3CN), 1.27 (t, $J = 7.1$ Hz, 3H, CH_3), 1.21 (d, $J = 7.1$ Hz, 3H, CH_3), 1.06 (t, $J = 7.2$ Hz, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 177.84, 177.80, 175.01 (CH_3CO), 170.63, 169.59, 169.47 (CH_3CN), 128.25, 128.06, 127.87 (CH_2), 99.86, 99.23, 98.55 (CH), 26.44, 25.83, 25.47 (CH_3CO), 20.93, 20.86, 20.27 (CH_3CN), 16.01, 15.38, 15.01 (CH_3). **MS:** m/z [ESI+] 405 $[\text{M}]^+$, 404 $[\text{M} - \text{H}]^+$. **EA: Anal. Calcd. For $\text{C}_{21}\text{H}_{36}\text{O}_3\text{N}_3\text{Al}$:** C, 62.20, H, 8.85, N, 10.36. **Found:** C, 62.13, H, 8.89, N, 10.21.

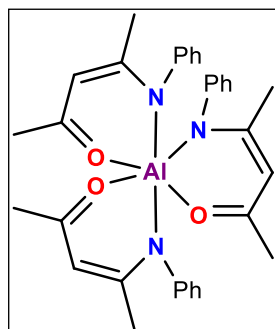
2.3.1.3 Synthesis of $[\text{Al}(\text{MeCN}(\textit{i}\text{Pr})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\textit{i}\text{Pr-acnac})_3]$, **3**)



***i*Pr-acnacH** (2.38 g, 17.0 mmol) in 20 mL diethyl ether was added to a solution of TMAA (0.50 g, 5.61 mmol) in 20 °C at -78 °C. The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. Any insolubles were removed by filtration. The filtrate was concentrated and stored at -20 °C. Overnight, white crystals of **3** suitable for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 1.53 g (61%). ^1H NMR (25 °C, 500 MHz, C_6D_6) δ 4.95 (br s, 3H, CH), 4.15 (br s, 3H, $\text{CH}(\text{CH}_3)_2$), 1.87 (s, 9H, CH_3CO), 1.83 (s, 9H, CH_3CN), 1.33 (s, 18H, CH_3). ^1H NMR (75 °C, 500 MHz, C_6D_6) δ 4.95 (s, 3H, CH), 4.15 (hept, $J = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.87 (s, 9H, CH_3CO), 1.82 (s, 9H, CH_3CN), 1.32 (d,

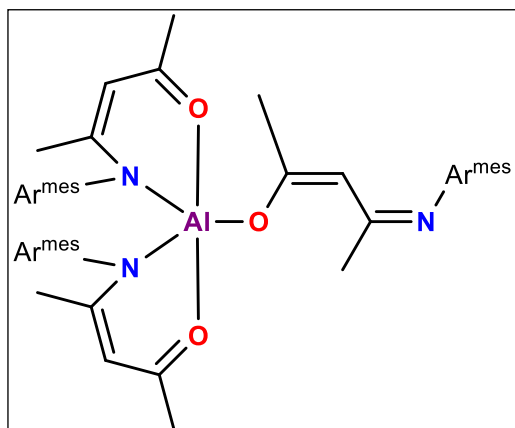
$J = 6.8$ Hz, 18H, $\underline{\text{CH}_3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (25°C, 126 MHz, C_6D_6) δ 169.88 ($\text{CH}_3\underline{\text{CN}}$), 101.01 ($\underline{\text{CH}}$), 49.47 ($\underline{\text{CH}}(\text{CH}_3)_2$), 25.57 ($\underline{\text{CH}_3\text{CO}}$), 23.74 ($\underline{\text{CH}_3\text{CN}}$), 22.28 ($\underline{\text{CH}_3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 °C, 126 MHz, C_6D_6) δ 169.47 ($\text{CH}_3\underline{\text{CN}}$), 101.94 ($\underline{\text{CH}}$), 50.05 ($\underline{\text{CH}_3}$), 25.34 ($\underline{\text{CH}_3\text{CO}}$), 22.74 ($\underline{\text{CH}_3\text{CN}}$). **MS:** m/z [ESI+] 447 $[\text{M}]^+$, 446 $[\text{M} - \text{H}]^+$. **EA:** **Anal. Calcd. For $\text{C}_{24}\text{H}_{42}\text{O}_3\text{N}_3\text{Al}$:** C, 64.40, H, 9.46, N, 9.39. **Found:** C, 64.35, H, 9.60, N, 9.27.

2.3.1.4 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{OMe})_3]$ (**[Al(Ph-acnac)₃]**, **4**)



Ph-acnacH (2.95 g, 16.9 mmol) in 20 mL diethyl ether was added to a solution of TMAA (0.50 g, 5.61 mmol) in 20 °C at -78 °C. The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution. Diethyl ether solvent removed *in vacuo* and the resultant pale cloudy solid was dissolved in 20 mL toluene. Any insolubles were removed by filtration. The filtrate was concentrated and stored at -20 °C. Overnight, white crystals of **4** suitable for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 2.01 g (65%). ^1H NMR (C_6D_6 , 500 MHz) δ 7.50 – 6.86 (15H, m, Ar- $\underline{\text{H}}$), 5.12 (1H, s, $\underline{\text{CH}}$), 4.87 (1H, s, $\underline{\text{CH}}$), 4.57 (1H, s, $\underline{\text{CH}}$), 2.04 (3H, s, $\underline{\text{CH}_3\text{CO}}$), 1.53 (3H, s, $\underline{\text{CH}_3\text{CO}}$), 1.50 (3H, s, $\underline{\text{CH}_3\text{CO}}$), 1.47 (3H, s, $\underline{\text{CH}_3\text{CN}}$), 1.44 (3H, s, $\underline{\text{CH}_3\text{CN}}$), 1.34 (3H, s, $\underline{\text{CH}_3\text{CN}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 180.65, 179.82, 177.92 ($\text{CH}_3\underline{\text{CO}}$), 171.49, 170.07, 169.83 ($\text{CH}_3\underline{\text{CN}}$), 151.84, 151.02, 150.86, 128.58, 128.25, 128.17, 128.06, 127.87, 127.76, 127.57, 127.36, 126.93, 126.51, 125.13, 124.80, 124.13, 124.04, 123.91 (Ar- $\underline{\text{C}}$), 99.10, 98.45, 98.29 ($\underline{\text{CH}}$), 26.34, 25.28, 25.21 ($\underline{\text{CH}_3\text{CO}}$), 24.06, 23.64, 23.56 ($\underline{\text{CH}_3\text{CN}}$). **MS:** m/z [ESI+] 549 $[\text{M}]^+$, 548 $[\text{M} - \text{H}]^+$. **EA:** **Anal. Calcd. For $\text{C}_{33}\text{H}_{36}\text{O}_3\text{N}_3\text{Al}$:** C, 72.11, H, 6.60, N, 7.65. **Found:** C, 71.76, H, 6.62, N, 7.57. NMR data is consistent with spectra reported in the literature.¹³

2.3.1.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_3]$, where Ar^{mes} = 2,4,6-trimethylphenyl ($[\text{Al}(\text{Ph-acnac})_3]$, **5**)

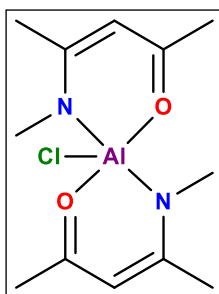


Ar^{mes}-acnacH (3.66 g, 16.9 mmol) in 20 mL diethyl ether was added to a solution of TMAA (0.50 g, 5.61 mmol) in 20 °C at -78 °C. The reaction mixture was stirred at room temperature overnight to form a cloudy white solution. Any insolubles were removed by filtration. The filtrate was concentrated and stored at -20 °C. Overnight, white crystals of **5** formed. The crystals were

separated from the supernatant solution and dried under reduced pressure. Yield: 1.80 g (47%). ^1H NMR (C_6D_6 , 500 MHz) δ 6.83, 6.81, 6.74 (6H, s, Ar-H), 5.10 (1H, s, CH mo), 4.91 (2H, s, CH bi), 2.79 (3H, s, CH₃CO mo), 2.45, 2.41, 2.31, 2.21, 2.20, 1.94 (27H, s, CH₃), 1.51 (3H, s, CH₃CN mo), 1.30 (6H, s, CH₃CO bi), 1.21 (6H, s, CH₃CN bi). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 180.34 (CH₃CO bi), 176.06 (CH₃CN bi), 164.90, 163.45, 149.39–126.82 (Ar-C), 99.76 (CH bi), 99.25 (CH mo), 27.55 (CH₃CO mo), 25.59 (CH₃CN mo), 23.99 (CH₃CN bi), 23.67 (CH₃CO bi), 21.09–18.33 (CH₃). **MS: m/z [ESI+]** 675 $[\text{M}]^+$, 674 $[\text{M} - \text{H}]^+$. **EA: Anal. Calcd. For $\text{C}_{42}\text{H}_{54}\text{O}_3\text{N}_3\text{Al}$:** C, 74.64, H, 8.05, N, 6.22. **Found:** C, 73.23, H, 8.06, N, 6.06.

2.3.2 Synthesis of bis(β -ketoiminate) aluminium monochloride compounds

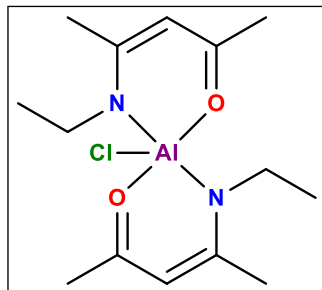
2.3.2.1 Synthesis of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Me-acnac})_2\text{Cl}]$, **6**)



LiHMDS (1.02 g, 6.10 mmol) in 20 mL toluene was added to a solution of **Me-acnacH** (0.68 g, 6.01 mmol) in 20 mL toluene at -78 °C. The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. The volatiles were removed *in vacuo* to produce a pale-yellow solid, which was re-dissolved in 20 mL toluene and added to a slurry of AlCl_3 (0.40 g, 3.00 mmol) in 20 mL toluene at -78 °C. The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution, which was filtered, with the clear pale-yellow filtrate concentrated and stored at -20 °C. Overnight, white crystals suitable of **6** for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 0.82 g (95%). ^1H NMR (500 MHz, C_6D_6) δ 4.81 (s, 2H, CH), 3.11 (s, 6H, CH₃), 1.79 (s, 6H, CH₃CO), 1.30 (s, 6H, CH₃CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ

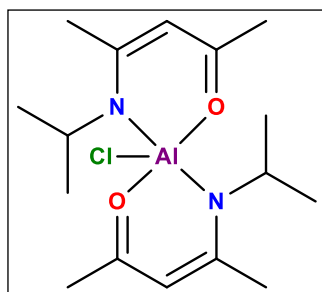
173.92 (CH_3CO), 171.80 (CH_3CN), 100.57 (CH), 37.31 (CH_3), 24.82 (CH_3CO), 20.91 (CH_3CN). **MS: m/z [ESI+]** 251 $[\text{M} - \text{Cl}]^+$. **EA: Anal. Calcd. For $\text{C}_{12}\text{H}_{20}\text{O}_2\text{N}_2\text{AlCl}$:** C, 50.27, H, 7.03, N, 9.77. **Found:** C, 50.11, H, 7.07, N, 9.50.

2.3.2.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Et-acnac})_2\text{Cl}]$, **7**)



LiHMDS (1.00 g, 5.98 mmol) in 20 mL toluene was added to a solution of **Et-acnacH** (0.77 g, 6.05 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. The volatiles were removed *in vacuo* to produce a pale-yellow solid, which was re-dissolved in 20 mL toluene and added to a slurry of AlCl_3 (0.40 g, 3.00 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution, which was filtered to produce a clear solution of the same colour. The solvent was removed *in vacuo* to yielding a pale-yellow solid, which was recrystallised from hexane and toluene overnight at -20°C . White crystals suitable of **7** for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 0.79 g (84%). ^1H NMR (C_6D_6 , 500 MHz) δ 4.81 (2H, s, CH), 3.88 (2H, s, CH_2), 3.41 (2H, s, CH_2), 1.78 (6H, s, CH_3CO), 1.47 (6H, s, CH_3CN), 1.20 (6H, t, $J = 7.1$ Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ 173.33 (CH_3CO), 171.37 (CH_3CN), 100.99 (CH), 44.30 (CH_2), 24.60 (CH_3CO), 20.34 (CH_3CN), 15.30 (CH_3). **MS: m/z [ESI+]** 315 $[\text{M}]^+$, 279 $[\text{M} - \text{Cl}]^+$. **Anal. Calcd. For $\text{C}_{14}\text{H}_{24}\text{O}_2\text{N}_2\text{AlCl}$:** C, 53.42, H, 7.68, N, 8.90. **Found:** C, 52.95, H, 7.72, N, 8.72.

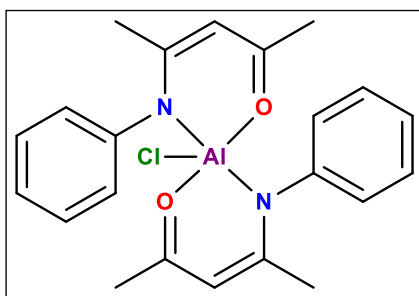
2.3.2.3 Synthesis of $[\text{Al}(\text{MeCN}(i\text{Pr})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(i\text{Pr-acnac})_2\text{Cl}]$, **8**)



LiHMDS (0.58 g, 3.47 mmol) in 20 mL toluene was added to a solution of ***i*Pr-acnacH** (0.54 g, 3.85 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution. The volatiles were removed *in vacuo* to produce a pale-yellow solid, which was re-dissolved in 20 mL toluene and added to a slurry of AlCl_3 (0.23 g, 1.72 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution, which was filtered, with the clear pale-yellow filtrate concentrated and stored at -20°C . Overnight, white crystals suitable for single crystal X-ray measurement precipitated. The crystals were separated from the

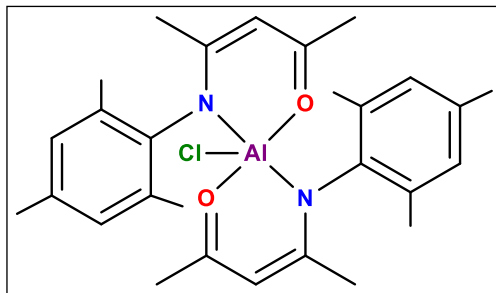
supernatant solution and dried under reduced pressure. Yield: 0.51 g (86%). ^1H NMR (600 MHz, C_6D_6) δ 4.75 (s, 2H, CH), 4.57 (br s, 2H, $\text{CH}(\text{CH}_3)_2$), 1.76 (s, 6H, CH_3CO), 1.65 (s, 6H, CH_3CN), 1.41 (br s, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 171.90 (CH_3CO), 170.58 (CH_3CN), 101.77 (CH), 51.26 ($\text{CH}(\text{CH}_3)_2$), 24.52 (CH_3CO), 23.66 (CH_3CN), 22.47, 21.85 (CH_3). **MS:** m/z [ESI+] 283 $[\text{M} - \text{Al} - \text{Cl} + 3\text{H}]^+$. **E.A:** **Anal. Calcd. For $\text{C}_{16}\text{H}_{28}\text{O}_2\text{N}_2\text{AlCl}$:** C, 56.05, H, 8.23, N, 8.17. **Found:** C, 55.85, H, 8.33, N, 8.12.

2.3.2.4 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{OMe})_2\text{Cl}]$ (**[Al(Ph-acnac) $_2$ Cl]**, **6**)



LiHMDS (1.00 g, 5.98 mmol) in 20 mL toluene was added to a solution of **Ph-acnacH** (1.11 g, 6.37 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution. The volatiles were removed *in vacuo* to produce a pale-yellow solid, which was re-dissolved in 20 mL toluene to reform a cloudy, pale-yellow solution which was added to a slurry of AlCl_3 (0.40 g, 3.00 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution, which was filtered, with the clear pale-yellow filtrate concentrated and stored at -20°C . Overnight, white crystals of **9** suitable for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 0.64 g (52%). ^1H NMR (C_6D_6 , 500 MHz) δ 7.67, 7.16 – 6.99 (10H, m, Ar- H), 4.88 (3H, s, CH), 1.47 (6H, s, CH_3CO), 1.36 (6H, s, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ 176.87 (CH_3CO), 173.03 (CH_3CN), 149.01, 126.62, 125.23 (Ar- C), 100.74 (CH), 24.02 (CH_3CO), 23.41 (CH_3CN). **MS:** m/z [ESI+] 411 $[\text{M}]^+$, 375 $[\text{M} - \text{Cl}]^+$. **EA:** **Anal. Calcd. For $\text{C}_{22}\text{H}_{24}\text{O}_2\text{N}_2\text{AlCl}$:** C, 64.31, H, 5.89, N, 6.82. **Found:** C, 62.83, H, 5.80, N, 6.54.

2.3.2.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_2\text{Cl}]$, where Ar^{mes} = 2,4,6-trimethylphenyl ($[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$, **10**)

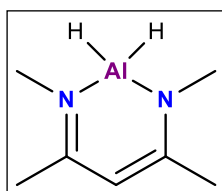


LiHMDS (1.00 g, 5.98 mmol) in 20 mL toluene was added to a solution of $\text{Ar}^{\text{mes}}\text{-acnacH}$ (1.37 g, 6.33 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a transparent, pale-yellow solution. The volatiles were removed *in vacuo* to

produce a pale-yellow solid, which was re-dissolved in 20 mL toluene and added to a slurry of AlCl_3 (0.40 g, 3.00 mmol) in 20 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy, pale-yellow solution, which was filtered, with the clear pale-yellow filtrate concentrated and stored at -20°C . Overnight, white crystals of **10** suitable for single crystal X-ray measurement precipitated. The crystals were separated from the supernatant solution and dried under reduced pressure. Yield: 0.78 g (53%). ^1H NMR (C_6D_6 , 500 MHz) δ 6.84 (1H, s, Ar-H), 6.75 (1H, s, Ar-H), 4.97 (2H, s, CH), 2.52 (3H, s, CH_3), 2.19 (3H, s, CH_3), 2.00 (3H, s, CH_3), 1.35 (6H, s, CH_3CO), 1.29 (6H, s, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ 181.53 (CH_3CO), 176.50 (CH_3CN), 146.01, 134.13, 133.55, 131.23, 129.81, 128.53, 128.35 (Ar-C), 99.91 (CH), 24.24 (CH_3CO), 23.80 (CH_3CN), 20.86, 19.45, 18.96 (CH_3). **MS:** m/z [ESI-] 466 $[\text{M} - \text{Al} - \text{H}]^-$. **Anal. Calcd. For $\text{C}_{28}\text{H}_{36}\text{O}_2\text{N}_2\text{AlCl}$:** C, 67.94, H, 7.33, N, 5.66. **Found:** C, 66.47, H, 7.27, N, 5.50.

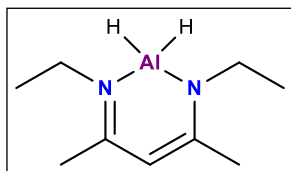
2.3.3 Synthesis of mono(β -diketiminate) aluminium dihydride compounds

2.3.3.1 Synthesis of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{N}(\text{Me})\text{Me})\text{H}_2]$ ($[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$, **11**)

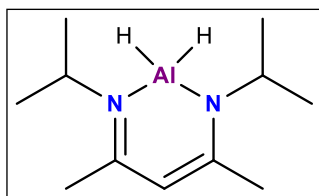


$\text{Me}_2\text{-nacnacH}$ (0.33 g, 2.61 mmol) in 15 mL toluene added to TMAA (0.26 g, 2.92 mmol) in 15 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy off-white solution. The volatiles were removed *in vacuo* to produce an off-white

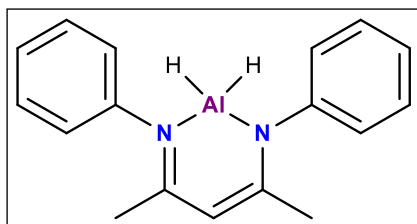
solid, which was washed with 25 mL hexane and filtered to form a pale yellow solution and a fine white precipitate. Yield 0.33 g (82%). ^1H NMR (300 MHz, C_6D_6) δ 4.84 (br s, 2H, AlH_2), 4.44 (s, 1H, CH), 2.52 (s, 6H, CH_3), 1.35 (s, 6H, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 169.82 (CH_3CN), 96.99 (CH), 34.05 (CH_3), 20.79 (CH_3CN). NMR data is consistent with spectra reported in the literature.¹⁴

2.3.3.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{N}(\text{Et})\text{Me})\text{H}_2]$ ($[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$, **12**)

Et₂-nacnacH (0.81 g, 5.25 mmol) in 15 mL toluene added to TMAA (0.50 g, 5.61 mmol) in 15 mL toluene at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature overnight to form a transparent yellow solution. The volatiles were removed *in vacuo* to produce a sticky pale-orange residue, which was washed with 25 mL hexane and filtered at $-78\text{ }^{\circ}\text{C}$ to form a yellow solution and a yellow oil when warmed to room temperature. Yield: 0.50 g (52%). ^1H NMR (500 MHz, C_6D_6) δ 4.75 (br s, 2H, AlH_2), 4.40 (s, 1H, CH), 3.05 (q, $J = 7.2\text{ Hz}$, 4H, CH_2), 1.51 (s, 6H, CH_3CN), 1.06 (t, $J = 7.2\text{ Hz}$, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 168.26 (CH_3CN), 97.04 (CH), 42.50 (CH_2), 20.33 (CH_3CN), 15.25 (CH_3). **MS: m/z [ESI-]** 153 [$\text{M} - \text{Al}$] $^+$. **EA: Anal. Calcd. For $\text{C}_9\text{H}_{19}\text{N}_2\text{Al}$:** C, 59.32, H, 10.51, N, 15.37. **Found:** C, 58.39, H, 9.90, N, 14.93.

2.3.3.3 Synthesis of $[\text{Al}(\text{MeCN}(i\text{Pr})\text{CHC}=\text{N}(i\text{Pr})\text{Me})\text{H}_2]$ ($[\text{Al}(i\text{Pr}_2\text{-nacnac})\text{H}_2]$, **13**)

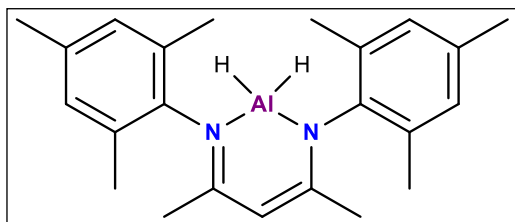
***i*Pr₂-nacnacH** (0.90 g, 4.94 mmol) in 15 mL toluene added to TMAA (0.44 g, 4.94 mmol) in 15 mL toluene at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature overnight to form a transparent yellow solution. The volatiles were removed *in vacuo* to produce a sticky pale-orange residue, which was washed with 25 mL hexane and filtered at $-78\text{ }^{\circ}\text{C}$ to form a yellow solution and a fine off-white precipitate. Yield: 0.12 g (12%). ^1H NMR (300 MHz, C_6D_6) δ 4.41 (s, 1H, CH), 3.46 (hept, $J = 6.5\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 1.53 (s, 6H, CH_3CN), 1.33 (d, $J = 6.5\text{ Hz}$, 12H, CH_3), AlH_2 not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 166.61 (CH_3CN), 97.36 (CH), 50.24 ($\text{CH}(\text{CH}_3)_2$), 22.77 (CH_3CN), 21.54 (CH_3). NMR data is consistent with spectra reported in the literature.¹⁴

2.3.3.4 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{N}(\text{Ph})\text{Me})\text{H}_2]$ ($[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$, **14**)

Ph-nacnacH (1.27 g, 5.07 mmol) in 25 mL toluene added to TMAA (0.52 g, 5.83 mmol) in 25 mL toluene at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature overnight to form a cloudy yellow solution, which was filtered to produce a transparent yellow solution. The volatiles were removed *in vacuo* to produce a sticky pale-yellow residue, which was washed with 25 mL hexane and filtered to form a yellow solution and a fine off-white precipitate, which was re-dissolved in toluene and stored at $-20\text{ }^{\circ}\text{C}$. Overnight, pale-yellow

crystals suitable for single crystal X-ray measurement precipitated. Yield: 0.88 g (63%). ^1H NMR (500 MHz, C_6D_6) δ 7.10 – 7.01 (m, 8H, Ar-H), 6.91 (m, 2H, Ar-H), 4.89 (br s, 2H, AlH₂), 4.73 (s, 1H, CH), 1.54 (s, 6H, CH₃CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 168.97 (CH₃CN), 145.39, 129.81, 126.29, 125.97 (Ar-C), 98.01 (CH), 22.63 (CH₃CN). NMR data is consistent with spectra reported in the literature.¹⁵

2.3.3.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{N}(\text{Ar}^{\text{mes}})\text{Me})_2]$, where Ar^{mes} = 2,4,6-trimethylphenyl ($[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$, **15**)

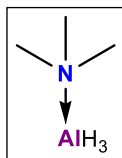


Ar^{mes}₂-nacnacH (1.70 g, 5.08 mmol) in 15 mL toluene added to TMAA (0.50 g, 5.61 mmol) in 15 mL toluene at -78°C . The reaction mixture was stirred at room temperature overnight to form a cloudy yellow solution. The volatiles were

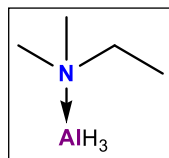
removed *in vacuo* to produce a cream solid, which was washed with 25 mL hexane and filtered to form a yellow solution and a fine off-white precipitate. Yield 1.52 g (83%). ^1H NMR (600 MHz, C_6D_6) δ 6.77 – 6.72 (m, 4H, Ar-H), 4.80 (s, 1H, CH), 2.33 (s, 12H, *ortho*-CH₃), 2.10 (s, 6H, *para*-CH₃), 1.49 (s, 6H, CH₃CN), AlH₂ not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 169.73 (CH₃CN), 139.79, 135.86, 133.56, 129.98, 128.35 (Ar-C), 95.86 (CH), 22.09 (*para*-CH₃), 20.92 (CH₃CN), 18.52 (*ortho*-CH₃). NMR data is consistent with spectra reported in the literature.¹⁶

2.3.4 Synthesis of tertiary amine-stabilised alanes

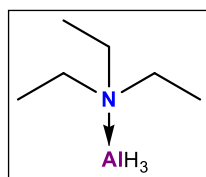
2.3.4.1 Synthesis of trimethylamine alane (TMAA), $[\text{AlH}_3\cdot\text{NMe}_3]_2$ (**16**)



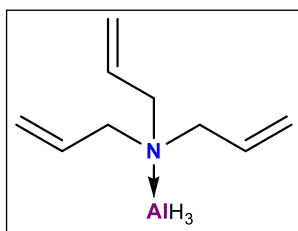
LiAlH_4 (1.21 g, 31.9 mmol) in 20 mL diethyl ether was added to dried $[\text{HNMe}_3][\text{Cl}]$ (2.50 g, 26.2 mmol) in 20 mL diethyl ether at -78°C . After 10 min, a white suspension had formed, which was allowed to warm to room temperature and stirred overnight. The white suspension was filtered to produce a colourless transparent solution. The volatiles were removed *in vacuo* to produce a white solid, which was purified by sublimation. Several batches of crystalline white solid were collected. Yield: 1.79 g, (77%). ^1H NMR (500 MHz, C_6D_6) δ 4.12 (br s, 6H, AlH₆), 1.84 (s, 18H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 47.68 (CH₃). NMR data is consistent with spectra reported in the literature.¹⁷

2.3.4.2 Synthesis of dimethylethylamine alane (DMEAA), $[\text{AlH}_3 \cdot \text{NMe}_2\text{Et}]$ (17)

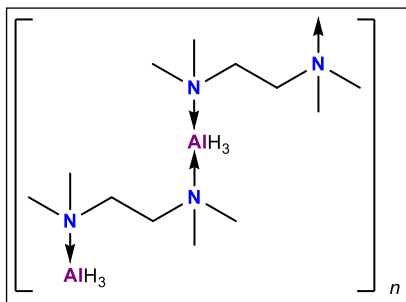
A slurry of AlCl_3 (1.06 g, 7.95 mmol) in 20 mL hexane was added to a slurry of LiAlH_4 (1.00 g, 26.4 mmol) in 20 mL hexane at -78°C , which was stirred for 30 min. Following this, DMEA (DMEA = *N,N'*-dimethylethylamine) (3.8 mL, 35.1 mmol) was added at -78°C . The reaction was stirred under cooling for 30 min, before being left to stir overnight whilst warming to room temperature. The resultant cloudy white mixture was filtered to produce a transparent colourless solution, which was concentrated by half before being cooled to -78°C to form a white solid in a transparent colourless solution. The solid was separated from the solution by cannula filtration under cooling. The solid was re-dissolved with another 20 mL hexane and warmed to room temperature, before being separated at -78°C as before. Finally, the white solid was dried *in vacuo* under cooling ($<-10^\circ\text{C}$) to remove any excess solvent, to produce a colourless transparent liquid. Yield: 2.16 g (66%). ^1H NMR (500 MHz, C_6D_6) δ 3.84 (br, 3H, AlH_3), 2.38 (q, $J = 7.3$ Hz, 2H, CH_2), 2.00 (s, 6H, CH_3), 0.83 (t, $J = 7.3$ Hz, 3H, CH_3CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 53.60 (CH_2), 44.06 (CH_3), 9.11 (CH_3CH_2). NMR data is consistent with spectra reported in the literature.¹⁷

2.3.4.3 Synthesis of triethylamine alane (TEAA), $[\text{AlH}_3 \cdot \text{NEt}_3]$ (18)

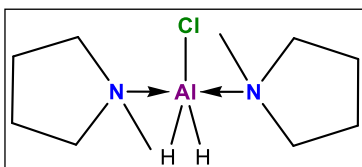
A slurry of AlCl_3 (1.07 g, 8.02 mmol) in 20 mL hexane was added to a slurry of LiAlH_4 (1.00 g, 26.4 mmol) in 20 mL hexane at -78°C , which was stirred for 30 min. Following this, triethylamine (4.9 mL, 35.2 mmol) was added at -78°C . The reaction was stirred under cooling for 30 min, before being left to stir overnight whilst warming to room temperature. The resultant cloudy white mixture was filtered to produce a transparent colourless solution, which was concentrated by half before being cooled to -78°C to form a white solid in a transparent colourless solution. The solid was separated from the solution by cannula filtration under cooling. The solid was re-dissolved with another 20 mL hexane and warmed to room temperature, before being separated at -78°C as before. Finally, the white solid was dried *in vacuo* under cooling ($<-10^\circ\text{C}$) to remove any excess solvent, to produce a colourless transparent liquid. Yield: 3.63 g (86%). ^1H NMR (500 MHz, C_6D_6) δ 4.09 (br, 3H, AlH_3), 2.35 (q, $J = 7.3$ Hz, 6H, CH_2), 0.85 (t, $J = 7.3$ Hz, 9H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 48.21 (CH_2), 9.05 (CH_3). NMR data is consistent with spectra reported in the literature.¹⁸

2.3.4.4 Synthesis of triallylamine alane (**TAAA**), $[\text{AlH}_3 \cdot (\text{N}\{\text{H}_2\text{C}=\text{CHCH}_2\}_3)]$ (**19**)

A solution of AlCl_3 (0.59 g, 4.42 mmol) in 25 mL diethyl ether was added to a solution of LiAlH_4 (0.50 g, 13.2 mmol) in 25 mL diethyl ether at -78°C , which was stirred for 1 h. Following this, TAA triallylamine (3.8 mL, 22.0 mmol) was added at -78°C . The reaction was stirred under cooling for 30 min, before being left to stir overnight whilst warming to room temperature. The resultant white mixture was filtered, to produce a transparent colourless solution, with the filtrate being washed with 2 x 25 mL diethyl ether. The solvent was removed *in vacuo* to produce a white solid. Yield: 2.15 g (73%). ^1H NMR (500 MHz, C_6D_6) δ 6.00 (ddt, $J = 17.3, 10.2, 7.2$ Hz, 3H, CH), 4.96 (ddm, $J = 45.0, 13.5$ Hz, 6H, $=\text{CH}_2$), 4.19 (br s, 3H, AlH_3), 3.08 (d, $J = 7.2$ Hz, 6H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 130.27 (CH), 122.48 ($=\text{CH}_2$), 58.30 (CH_2). NMR data is consistent with spectra reported in the literature.¹⁹

2.3.4.5 Synthesis of tetramethylethylenediamine alane (**TMEDAA**), $[\text{AlH}_3 \cdot (\{\text{CH}_3\}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\}_n)]$ (**20**)

TMEDA (TMEDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine) (0.4 mL, 2.67 mmol) added to **TMAA** (0.21 g, 2.36 mmol) in 10 mL of diethyl ether at -78°C . The reaction mixture was stirred at room temperature overnight to form a clear colourless solution with a small amount of insoluble white precipitate. The solution was filtered and the volatiles were removed *in vacuo* to produce a fine white solid. Yield 0.09 g (26%). ^1H NMR (300 MHz, C_6D_6) δ 3.96 (br s, 3H, AlH_3), 2.44 (s, 4H, CH_2), 2.05 (s, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 55.81 (CH_2), 45.54 (CH_3). NMR data is consistent with spectra reported in the literature.¹⁸

2.3.4.6 Synthesis of bis(*N*-methylpyrrolidine) monochloroalane, $[\text{AlH}_2\text{Cl} \cdot 2(\{\text{CH}_3\}_2\text{N}\{\text{CH}_2\}_4)]$ (**AIH₂Cl·2(NMP)**, **21**)

A solution of LiAlH_4 (0.50 g, 13.2 mmol) in 25 mL diethyl ether was added to a solution of AlCl_3 (1.76 g, 13.2 mmol) in 35 mL diethyl ether at -78°C , which was stirred for 1 h. Following this, excess NMP (NMP = *N*-methylpyrrolidine) (6.9 mL, 66.4 mmol) was added at -78°C . The reaction was stirred under cooling for 30 min,

before being left to stir overnight whilst warming to room temperature. The resultant cloudy white mixture was filtered and 50 mL hexane was added to further precipitate any LiCl, before the mixture was filtered again to produce a transparent colourless solution. The volatiles were removed *in vacuo* to produce a white solid. White crystals suitable of **21** for single crystal X-ray measurement were grown from hexane. Yield: 3.87 g (62%). ^1H NMR (300 MHz, C_6D_6) δ 2.70 (m, 8H, CH_2N), 2.27 (s, 6H, CH_3), 1.42 (m, 8H, CH_2), AlH_2 not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 55.71 (CH_2N), 44.21 (CH_3), 23.92 (CH_2). **EA: Anal. Calcd. For $\text{C}_{12}\text{H}_{20}\text{O}_2\text{N}_2\text{AlCl}$:** C, 51.17, H, 10.30, N, 11.93. **Found:** C, 51.09, H, 10.35, N, 11.80.

2.4 Decomposition analysis of aluminium compounds

The decomposition of precursors **1–21** was analysed using two techniques; thermogravimetric analysis (TGA) and pyrolysis experiments.

2.4.1 Thermogravimetric analysis (TGA)

TGA is a technique that allows the continuous measurement of mass of a sample while subjecting the sample to a controlled thermal program, commonly through constant heating. For the complexes included in this study, decomposition occurs through the loss of organic ligand, resulting in a decrease in mass. By plotting the percentage mass as a function of increasing temperature, decomposition characteristics exhibited by the complex can be elucidated, such as decomposition temperature ranges, the number of decomposition stages (including initial decomposition temperatures), sublimation/volatilisation, total mass loss, and residual mass.

Thermal analysis of precursors allows an initial assessment of the complexes as potential precursors for aluminium metal deposition *via* any number of deposition techniques such as those mentioned in Chapter 1. Ideal precursors would exhibit a TGA profile displaying a low temperature decomposition (50–200 °C, not too low as to severely compromise handleability under ambient conditions, not too high as to limit the substrate scope), with rapid decomposition at elevated temperatures within the range set. Furthermore, the residual mass left behind after decomposition can be an indicator as to the purity of the aluminium metal deposits (closer to expected mass of pure Al, the less film impurity), with greater impurities leading to lower conductivity. Likely impurities include soot and aluminium oxides (if O is present in precursor or from non-perfect inert atmosphere), however high boiling point polymeric adducts may also form from unwanted side-reactions.

All analyses were carried out in sealed aluminium crucibles that were pierced just before measurement to allow for mass loss, under an inert atmosphere (He or N₂), in part due to the tendency of nanoparticulate aluminium metal to form its oxides (especially at elevated temperatures). This meant that there was an upper limit of 660 °C (melting point of the aluminium crucible), however it was decided to only test the thermal properties of the precursors up to a maximum of 500 °C (ramp rate 5–10 °C min⁻¹), since decomposition at such a high temperature would render these precursors unfit for low temperature (<200 °C) depositions, regardless. A high flow rate of inert gas 60 mL min⁻¹ was used to best prevent oxidative degradation from air. The majority of TGA measurements were conducted in triplicate to ensure reliability of data (full data sets given in the Appendices).

Differential scanning calorimetry (DSC) is a technique often employed in combination with TGA and can provide excellent added insights in the behaviour of a material as it heated in the form of exothermic and/or endothermic peaks. In relation to the compounds used in these studies, exothermic peaks would most likely be as a result of compound decomposition (oxidative), whilst endothermic peaks would most likely be a result of either sublimation, melting and/or vaporisation. Unfortunately, for both the TGA set-ups used accurate DSC data could not be collected due to a number of different reasons, with the most important factor likely being the modified set-ups used, to accommodate for the air-sensitive compounds.

Each compound was analysed using TGA multiple times until three agreeable thermal profiles were measured. This is because TGA is a technique that depends on many variables (sample batch purity, sample batch grain size, distributions of sample in the crucible, amount of residual O₂/air in the inert atmosphere, even the size of the hole made in the crucible and how well it has been crimped *etc.*) and although attempts were made to have as little variation between analysing the same sample as possible, inconsistencies can arise. In cases with high instrumental noise, adjacent averaging (AA) smoothing was performed. This smoothing is noted in the captions of smoothed thermograms.

Mean decomposition temperatures, T_d and mass losses with associated errors were calculated using three agreeable TGA data sets. Decomposition temperatures were calculated using differentiated thermogravimetry (DTG) curves (first derivative of the TGA curve, given in Appendices). The point at which the last stage of decomposition started was selected as the decomposition temperature. The start of the last decomposition stage was chosen as firstly, the start temperature of decomposition is the point at which the minimum energy for a

particular decomposition stage has been met and the slope/speed of decomposition is dependent on the heating rate chosen (therefore the midpoint of a decomposition step is a less accurate point of measurement) and secondly, the last decomposition step was chosen, as the compound must be heated to this particular temperature to allow it to fully decompose. Mass losses were not calculated directly from the TGA profiles and were in fact calculated by manually measuring the starting and end masses of the crucibles during a TGA experiment – this technique was chosen as it was deemed this would give more accurate results with the modified experimental set-up used.

The thermograms displayed throughout this thesis are there to give the reader an idea of the shape of the decomposition profile for each precursor, with one thermogram chosen for each sample to illustrate a representative curve (full sets of TGA data are given as Appendix 103–137).

2.4.2 Pyrolysis experiments

Residues after TGA could not be analysed by techniques such as EA, XRD and XPS to further probe their composition as the TGA machines used here exposed samples to atmospheric conditions after measurement, which would oxidise any Al(0) residue formed during the thermal degradation. To confirm whether each precursor decomposed to aluminium metal under inert conditions, inert furnace heating experiments (pyrolysis) were undertaken. Two precursors were chosen for initial experiments; [Al(Et-acnac)₃] (2) and [Al(Ph-acnac)₃] (4).

2.4.2.1 Pyrolysis of [Al(Et-acnac)₃] (2)

Free-flowing off-white powdery [Al(Et-acnac)₃] (0.15 g, 0.370 mmol) was loaded into a ceramic crucible and placed in the centre of a quartz tube fitted with take-off adaptors in a glove box. Once sealed this was removed from the glove box and attached to a nitrogen line fitted with a flow meter and placed into a tube furnace. The tube furnace was heated to 350 °C for 45 min, with a flow rate of 0.5 L min⁻¹, following this time it was allowed to cool to room temperature and was taken back into the glove box for analysis. A two-point probe confirmed the resulting brown powder was not conductive, XRD analysis showed only amorphous material present. This experiment was repeated at 400 and 500 °C, and also at 350 °C under dynamic vacuum on the Schlenk line, yielding the same amorphous brown powder.

2.4.2.2 Pyrolysis of [Al(Ph-acnac)₃] (4)

Free-flowing off-white powdery [Al(Ph-acnac)₃] (0.15 g, 0.273 mmol) was loaded into a ceramic crucible and placed in the centre of a quartz tube fitted with take-off adaptors in a glove box. Once sealed this was removed from the glove box and attached to a nitrogen line fitted with a flow meter and placed into a tube furnace. The tube furnace was heated to 350 °C for 45 min, with a flow rate of 0.5 L min⁻¹, following this time it was allowed to cool to room temperature and was taken back into the glove box for analysis. A two-point probe confirmed the resulting brown powder was not conductive, XRD analysis showed only amorphous material present. This experiment was repeated at 400 and 500 °C, and also at 350 °C under dynamic vacuum on the Schlenk line, yielding the same amorphous brown powder.

2.5 Deposition of aluminium compounds

Al metal thin films were deposited onto numerous substrates: glass, polyimide (PI), polyethylene terephthalate (PET) and paper (Fujifilm instax) substrates with thicknesses of 1.00, 1.06, 1.05 and 0.85 mm respectively *via* a drop-casting process. 25 µL of neat liquid compound (DMEAA or TEAA) was pipetted onto a preheated substrate (±1 °C error in the temperature measurement of the hot surface) under an N₂ atmosphere inside a glove box for fixed time periods. Films were sintered using a hotplate, employing a Kewtech KT116 multimeter as an external temperature control. Films were stored in the glove box prior to analysis.

2.5.1 Metal film conductivity measurements

Resistance values were measured for all depositions using a two-point probe (Kewtech KT116 multimeter). Resistance measurements were converted to resistivity values as a direct comparison to the electrical properties of the bulk metal itself, as well as, films fabricated in the literature. Upper and lower mean thicknesses (measured using side-on SEM images in Section 6.2.5) were used to calculate upper and lower estimates of resistivity for all depositions using:

$$\rho = \frac{R \cdot A}{L} \quad (2.1)$$

where ρ = resistivity (Ω m), R = resistance of two-point probe measurement (Ω), A = cross-sectional area of sample (m²), L = distance between two probes (m).

The cross sectional area of the sample was estimated using:

$$A = B \cdot C \quad (2.2)$$

where B = thickness of deposited film (m), C = diameter of two-point probe points in contact with deposited film.

The constants used were:

$$L = 0.25 \text{ cm}$$

$$B_{lower} = 15.44 \text{ } \mu\text{m} \text{ and } B_{upper} = 16.46 \text{ } \mu\text{m}$$

(for Al coating on PET and on PI respectively, taken from SEMs shown in Section 6.2.5) .

$$C = 0.50 \text{ mm}$$

Mean resistivities (in all cases) was calculated by average the three lower and upper estimates for each sample. The $\pm$ error in the resistivity measurement, was calculated used the standard error in the mean, $\sigma_{\bar{x}}$:

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \quad (2.3)$$

where σ = standard deviation of the population, n = size (number of observations) of the sample

Best resistivities of *ca.* twenty times bulk Al metal were calculated, which was the lowest resistivities able to be calculated with the two-point probe set-up for the thicknesses of film that were produced.

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Chapter 3

Tris(β -ketoiminate) Aluminium Compounds for use as Aluminium Precursors

This Chapter describes the synthesis of several novel tris(β -ketoiminate) aluminium compounds, with full characterisation including SCXRD, multi-nuclear NMR spectroscopy, mass spectrometry and elemental analysis. Finally, the suitability of these precursors is assessed by analysing their decomposition behaviour via TGA and pyrolysis experiments.

3.2 Introduction

This introduction includes many of the topics needed to comprehend results discussed in Chapters 3–5, giving a brief overview of aluminium complex chemistry, as well as, introducing six-membered ring chelates and the types of complexes they can form with aluminium. The introduction concludes by concentrating on the types of complexes that feature within this Chapter in particular, namely homoleptic aluminium complexes that feature three chelating ligands.

3.2.1 General aluminium complex chemistry

The vast majority of inorganic aluminium compounds, including all minerals and commercially significant compounds, feature aluminium in the +3 oxidation state, due to it containing three valence electrons. The coordination number of such ionic compounds varies, but generally ionically bonded Al^{3+} is either four- or six-coordinate. Almost all compounds Al(III) are colourless.¹ Al(III) is also undoubtedly the most prevalent oxidation state for organometallic and metal-organic aluminium complexes. Neutral Al(III) complexes tend to form either tetra-, penta-, or hexa-coordinate structures which have a preference for tetrahedral, trigonal bipyramidal and octahedral geometries, respectively. The first organoaluminium compound: $(\text{C}_2\text{H}_5)_3\text{AlI}_3$ was discovered in 1859.²

Lower valent aluminium centres can exist, under more extreme conditions or ligand systems and are extremely reactive/air-sensitive being highly sensitive towards oxidation or disproportionation. Al(II) organometallic/metal-organic compounds are considerably the least common and only occur in complexes that feature an Al-Al bond. Al(I) compounds, albeit uncommon, are more prevalent than those for Al(II) .³ As with Al(II) , a large majority of Al(I) complexes can only be formed when trapped and studied in inert gas matrices. In 1991, the first Al(I) compound to be isolated and structurally characterised was $[\text{AlCp}^*]_4$ [$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$], which forms an Al_4 tetrahedral core, with each vertex capped by a Cp^* ligand.³ Since then, other tetrameric Al(I) complexes have been synthesised using sterically bulky ligands. In 2000, the first monomeric Al(I) complex was achieved through the reduction of a bulky β -diketiminate Al(III) diiodide complex using potassium metal. This methodology has since become a commonplace for producing such complexes, which are stable analogues to carbenes.⁴

3.2.2 Conjugated six-membered ring chelates

Conjugated six-membered ring chelates are prominent class of ligands in the field of metal-organic chemistry, with several comprehensive reviews published.⁵⁻⁷ In their most basic form, they consist of a core conjugated five-membered chain containing three unsaturated carbon atoms and two terminal heteroatoms. At any one point of time during conjugation, they contain one L type ($=O$, $=S$, $-NR_2$, $-PR_2$ etc.) and one X type ($-O^-$, $-S^-$, $-NR^-$, $-PR^-$ etc.) donor, making them monoanionic bidentate ligands. Any number of group four and five heteroatom combinations can exist, but this overview will only focus on the most prevalent conjugated six-membered ring chelates *i.e.* those that contain either oxygen or nitrogen atoms or both.

Conjugated six-membered ring chelates that contain two oxygen heteroatom donors are called β -diketonates or “acacs”, those that contain one oxygen and one nitrogen donor are known as β -ketoiminates or “acnacs” and those that contain two nitrogen donors are known as β -diketimimates or “nacnacs” (Figure 3.1). Each motif can also exist as the protonated uncomplexed organic compound (β -diketone, β -ketoimine and β -diketimine respectively.) There has been a particular interest in these ligand systems for use in precursors over the last few decades, especially in the field of microelectronics, where techniques such as MOCVD and ALD have been used to deposit thin films of metal-based functional materials.

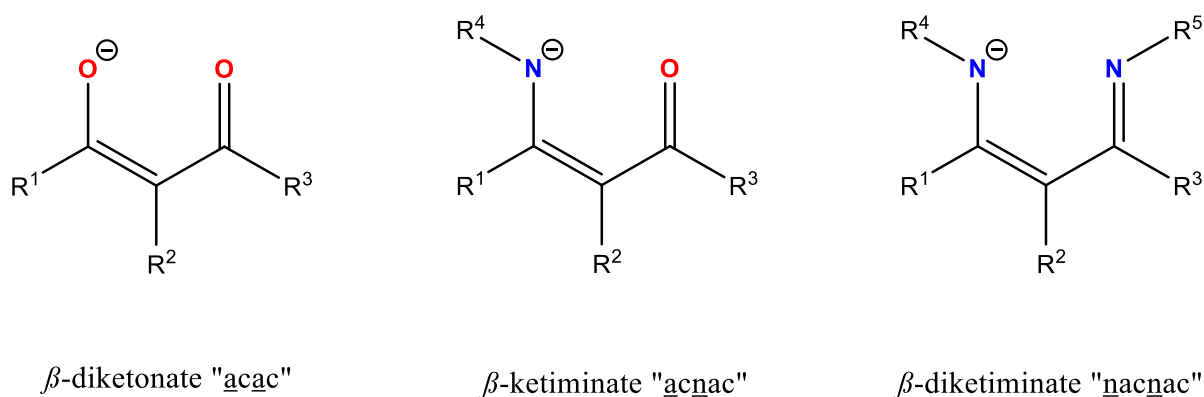


Figure 3.1: Several conjugated six-membered ring chelates.

3.2.2.1 β -diketones and aluminium β -diketonate complexes

Various polydentate ligands have been used to increase metal complex stability through the anchoring of coordination sites and the chelate effect. One such type of polydentate ligand that has arguably drawn the most attention are β -diketonate ligands, with their ligation investigated with virtually every metal and metalloid centre in the periodic table.⁸

β -diketones, which usually exist in their dicarbonyl form, undergo keto-enol tautomerism, allowing them to chelate in a bidentate mode to a metal centre once deprotonated. Group 13 β -diketonates are a well-known family of compounds, existing as tris ligated systems when no other types of ligands are present. Aluminium acetylacetonate, [Al(acac)₃] is undoubtedly the most synonymous Group 13 compound containing β -diketonate ligands, which has had a rich history in deposited aluminium oxides films through MOCVD as highlighted in Chapter 1.⁹

Whilst the majority of β -diketonate aluminium complexes are tris ligated, with variants changing the groups on the backbone of the ligand (namely R¹ and R³, or R² at any one given time – see Figure 3.1),^{10,11} rarer examples of mono and bis(β -diketonate) aluminium complexes do exist when other X type co-ligands are present.^{12,13}

3.2.2.2 β -ketoimines and aluminium β -ketoiminate complexes

Despite the great historic interest in β -diketonate ligands, the lack of opportunity to functionalise these ligands closer to the metal binding site (due to the oxygen atoms being fully coordinated) means that there are fewer opportunities to customise the ligand in order to change the properties of the resultant metal complex. One ligand system that is closely related to β -diketonates are the β -ketoiminates. These ligand systems also contain a conjugated core, however one carbonyl/enol group has been replaced by an enamine group. They are most commonly synthesised by the condensation reaction of a β -diketone with a primary amine in the presence of a catalytic acid. Functionalisation at the enamine group can drastically change the resultant properties of the ligand (and hence metal complex), however for the ligand to bind conventionally to a metal centre, the ligand must retain one hydrogen atom on the enamine group as to undergo a σ -bond metathesis reaction. Many variations of β -ketoimine compounds have been prepared, including examples where the R group is alkyl,¹⁴ aryl¹⁵ or even silyl.¹⁶ There are also examples of β -ketoimine compounds where the choice of R group leads to ligand systems with a greater denticity than two.^{17,18}

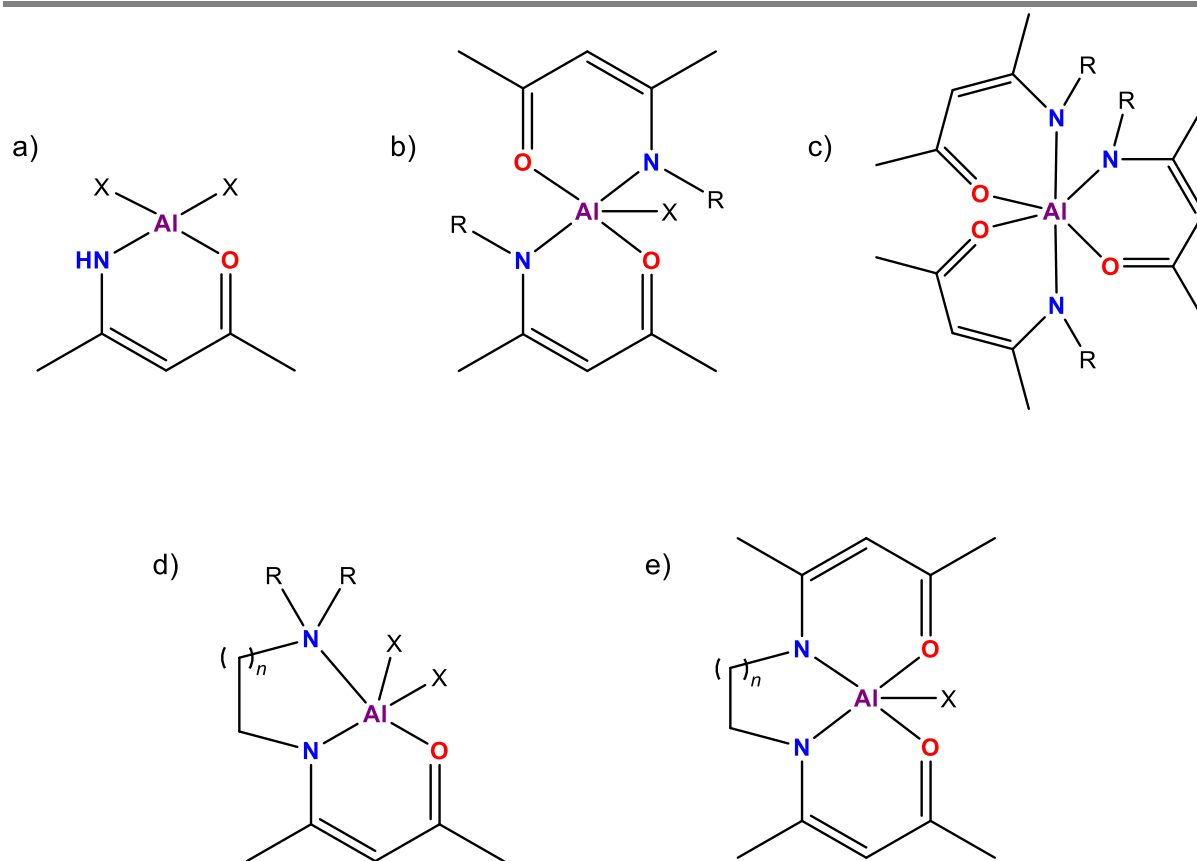


Figure 3.2: Commonly encountered structural motifs for Al compounds containing β -ketoiminate ligand/s, where X represents other X-type co-ligands. a) Mono(β -ketoiminate) Al complex, b) bis(β -ketoiminate) Al complex, c) tris(β -ketoiminate) Al complex, d) mono three coordinate β -ketoiminate with pendant tertiary amine arm Al complex ($n = 1, 2$), e) mono four-coordinate β -ketoiminate with two units bridged together by alkyl chain Al complex ($n = 1, 2$).

Once again, all Al complexes featuring these ligands feature Al(III). Interestingly, mono (Figure 3.2a) and bis (Figure 3.2b) ligated systems using these ligands are much more common for β -ketoiminates than for the β -diketonates, with the prevalence heteroleptic structures being much greater. Despite there being several mono and bis ligated system featuring alkyl,¹⁹ alkoxide¹⁰ and halide¹⁹ co-ligands, only one example of an aluminium compound featuring β -ketoiminate and hydride ligands exists, which was synthesised by Kuo *et al.*²⁰ who used the very bulky 2,6-diisopropylphenyl (dipp) group as the *N*-substituent. Hydrides are particularly sought after co-ligands as they are hypothesised to aid clean metal centre reduction. Impressive work by Kuo *et al.*²⁰ also led to a range of similar complexes using other uncommon co-ligands in this field such as carboxyl, isocyanate and dithiocarboxyl. Bis(β -ketoiminate) complexes are the topic of Chapter 4, so a more detailed discussion of such complexes will feature therein.

Tris(β -ketoiminate) Al complexes do exist (Figure 3.2c), although surprisingly they are not as commonplace as for the β -diketonates. Interestingly there are only two tris(β -ketoiminate) Al complexes featured within the literature with the first contribution in 2014 by Altaf *et al.*²¹ and the second in 2017 by Jana *et al.*,¹⁵ with both complexes containing aryl *N*-substituents (see Figure 3.6 later). As tris(β -ketoiminate) complexes are the feature of this Chapter, they will be discussed in more detailed subsequently, in Section 3.1.4.

The option to attach additional donating groups to increase the density of β -ketoimine compounds has also been applied to their subsequent aluminium complexes with tertiary amine pendant arms (Figure 3.2d) and linking to another β -ketoiminate subunit *via* an alkyl bridge (Figure 3.2e) being popular choices, with the latter providing a system where the constraint of the ligand results in a square pyramidal geometry around the Al centre, compared to the more common trigonal bipyramidal for bis complexes of this type.²²

3.2.2.3 β -diketimines and aluminium β -diketiminato complexes

The β -diketiminato ligands as shown in Figure 3.1 on the right, represent another class of polydentate ligand that closely links to β -diketonate and β -ketoiminates. Again, β -diketiminato ligands feature the conjugated core as seen previously and offer the great potential for customisability being able to be functionalised along the backbone and at both nitrogen atoms, through one imine and one enamine group that are in constant flux. Although not as commonplace as one might expect, each nitrogen atom can be functionalised differently to produce extremely diverse ligand systems. β -diketiminato aluminium complexes are featured in Chapter 5, so will be discussed in more depth later in Section 5.1.5.

3.2.2.4 Conjugated six-membered ring chelates as precursors

As mentioned earlier, six-membered ring chelating metal compounds have a rich history in precursor chemistry, particularly in the deposition of metal oxide films.^{23–25} Examples of the use of such ligands to produce the metallic element upon deposition do exist, but are rare.²⁶ Much of the research in acac deposition chemistry has concentrated on increasing the volatility of such ligands through adding fluorinated groups, less so into lowering decomposition temperatures. With regards to aluminium, [Al(acac)₃] and its derivatives have been investigated extensively in the deposition Al₂O₃ thin films since the 1960's, as was highlighted in Chapter 1.²⁷ Aluminium's high affinity to oxygen means it is highly unlikely that such precursors will

ever be able to convert to the metallic element, even under the harshest of conditions, unlike what is seen in copper metal deposition chemistry.²⁶

β -ketoimine compounds have also been used in Al-based deposition chemistry, albeit infrequently, where they are more prominently used for the group 2 metals, where they have allowed the preparation of volatile monomeric compounds.²³ Pugh *et al.*²⁸ synthesised a series of Group 13 β -ketoiminate complexes (using tetradentate β -ketoimine variants), however interestingly they only opted to deposit the gallium variants *via* MOCVD as they were the only complexes that included the hydride co-ligand the group sought after. Knapp *et al.*²⁹ working in the same group also synthesised a range of Group 13 β -ketoiminate complexes, using similar ligand systems and were able to deposit Al₂O₃ using a complex with an isopropoxide co-ligand.

To the author's knowledge no β -diketimate complexes have been used in the deposition of either aluminium or aluminium oxide, despite their historic use in the deposition of other metals. As with β -ketoiminates, the enhanced steric bulk of β -diketimate ligands greater allows for monomeric species of larger metal centres, leading to more volatile precursors.³⁰

3.2.3 Isomerism and chirality in octahedral complexes

The tris(β -ketoiminate) Al compounds which are the main focus of this Chapter are mostly six-coordinate and therefore possess octahedral geometry about the metal centre. For this reason, it is important to introduce some key particularities found in octahedral coordination compounds.

When two or more types of ligand (L^1 , L^2 , ...) are coordinated to an octahedral metal centre (M), the complex can exist as different isomers, with the naming system for these isomers depending upon the number and arrangement of the different ligands.

3.2.3.1 Cis and trans isomerism

For systems where there are two types of ligand, four of one type and two of the other *i.e.* $ML^1_4L^2_2$, two isomers exist. These isomers of $ML^1_4L^2_2$ are *cis*, if the L^2 ligands are mutually adjacent, and *trans*, if the L^2 groups are situated 180° to each other. This type of isomerism is analogous to what is seen in square planar complexes.

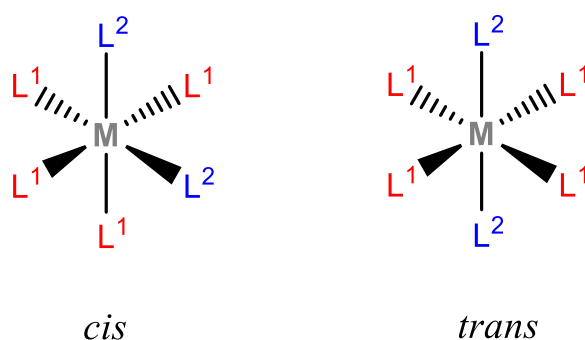


Figure 3.3: Isomerism shown in octahedral complexes with the general formula: $ML^1_4L^2_2$.

3.2.3.2 Facial and meridional isomerism

For systems where there are two types of ligand, three of one type and three of the other *i.e.* $ML^1_3L^2_3$, two isomers are also possible. The first is a facial (*fac*) isomer in which each set of three identical ligands occupies one face of the octahedron surrounding the metal centre, where any two of these three ligands are mutually *cis*. The second is a meridional (*mer*) isomer in which each set of three identical ligands lies along a plane passing through the metal centre.

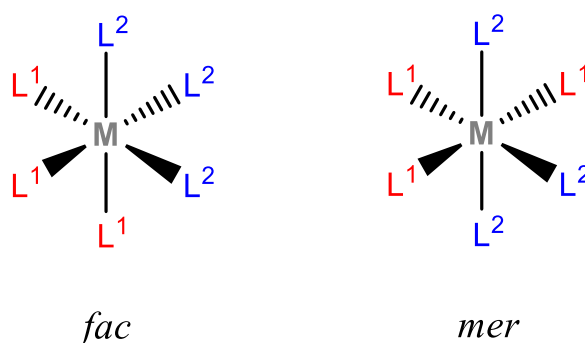


Figure 3.4: Isomerism shown in octahedral complexes with the general formula: $ML^1_3L^2_3$.

3.2.3.3 Isomerism and chirality in more complex compounds

More complex coordination compounds, with several different types of ligands or with bidentate ligands (*e.g.* $\text{Al}(\text{R-acnac})_3$) can also be chiral, meaning that pairs of isomers are non-superimposable mirror images (or enantiomers) of one other. Octahedral complexes can either have a lambda, Λ (left-handed) or delta, Δ (right-handed) chirality. Often such tris bidentate complexes tend to crystallise out in racemic mixtures, with all molecules in one unit cell being all of one isomer and another unit cell containing all molecules of the opposite isomer, as seen in Jana *et al* (Section 3.1.4).¹⁵

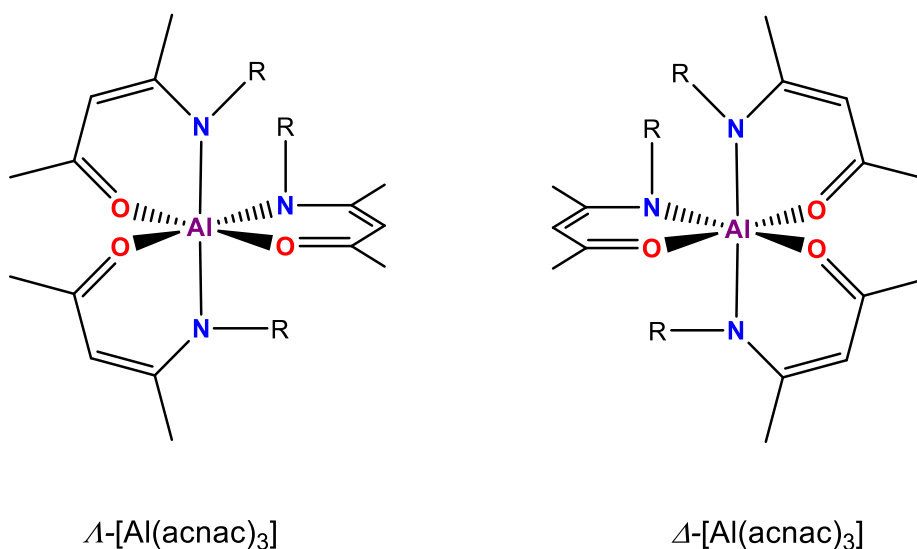


Figure 3.5: Chirality shown in octahedral complexes with three identical bidentate ligands.

It must be noted in octahedral complexes where more than two types of ligand are present (*i.e.* $\text{L}^1\text{--L}^6$) the number of isomers and enantiomeric pairs increases up to a maximum of 30 and 15 respectively, for a system with six different ligands about a metal centre.

3.2.4 Tris(β -ketoiminate) aluminium complexes

As mentioned, there are only two tris(β -ketoiminate) aluminium complexes reported in the literature. The first complex of this type was synthesised by Altaf *et al.*,²¹ who produced a tris(β -ketoiminate) complex using a β -ketoiminate ligands with a 4-tertbutylphenyl *N*-substituent. The complex was synthesised in a glove box by reaction three equivalents of ligand with $[\text{AlH}_3\cdot\text{NMe}_3]$, TMAA in toluene at low temperature. The yellow oily product was recrystallised from toluene and hexane to produce colourless crystals in moderate yield (44%). Three β -ketoiminate ligands arranged themselves around the Al(III) centre in an octahedral arrangement and the crystal structure has a *Pbca* space group. Interestingly, the ^1H and $^{13}\text{C}\{^1\text{H}\}$

NMR spectra of the tris complex displayed three sets of peaks for each ligand, likely owing to the *mer*-configuration (see Figure 3.6a and also Section 3.1.3.2) about the Al centre, however individual peaks were not assigned to specific ligands. Altaf synthesised the tris complex as a proof of concept, as it was noticed that many reactions with β -diketimines bearing the *para*-substituted *N*-phenyl group often led to the formation of tris ligated aluminium complexes as the major products, even in scenarios where lower than three equivalents of ligand were used. Mono and bis ligated complexes with methyl co-ligands were used to activate ring-opening polymerisation reactions, whilst the tris ligated complex was not chosen, likely owing to the lack of access to the reactive Al centre.

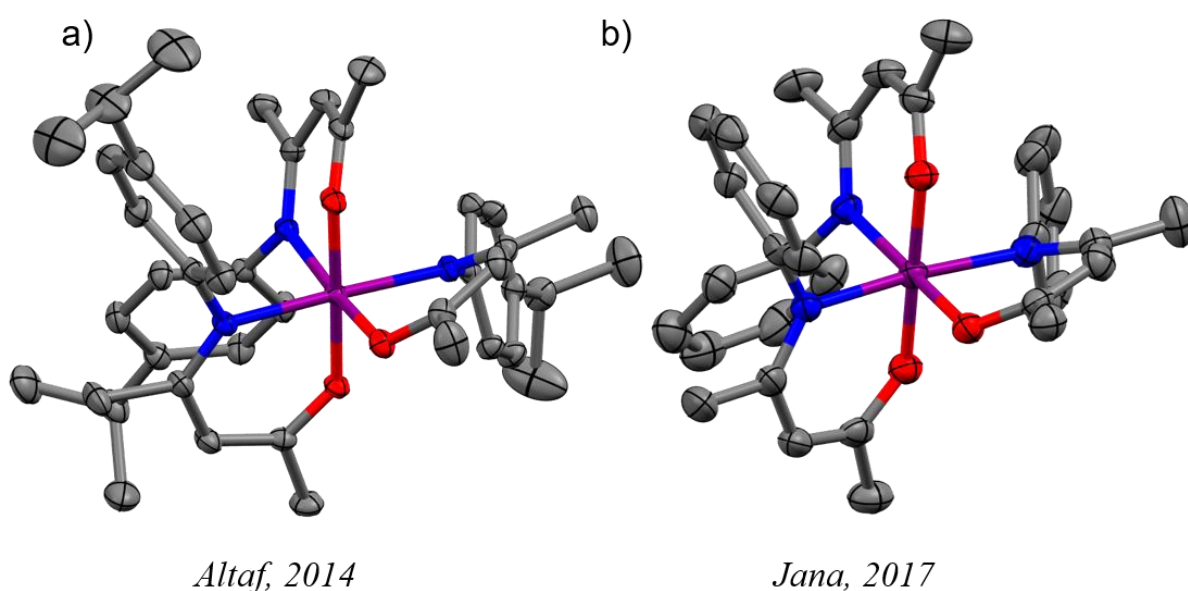


Figure 3.6: *Tris(β -ketoiminate) aluminium complexes of the type $[AlL_3]$ (where L = bidentate β -ketoiminate) in the literature (hydrogen atoms omitted for clarity). a) Altaf's²¹ and b) Jana's¹⁵ complexes, respectively.*

The second tris(β -ketoiminate) Al complex reported was synthesised by Jana *et al.*¹⁵ who were investigating Group 13 complexes containing β -ketoiminate and β -diketiminate ligands. Jana initially synthesised the tris complex (Figure 3.6b) with phenyl *N*-substituents by reacting two equivalents of ligand with $[AlH_3 \cdot NMe_2Et]$, DMEAA in hexane, in a non-stoichiometric reaction. Their hypothesis was that equimolar equivalents of a tris(β -ketoiminate) aluminium complex and a mono(β -ketoiminate) aluminium dihydride complex were synthesised, however the compound could not be isolated in as single crystals. The failure to make a 1:2 product with one hydride co-ligand, along with their being only one structure of this ilk in the literature (Kuo *et al.*)²⁰ proves that these complexes are difficult to make. To synthesise the tris complex

quantitatively, Jana reacted DMEAA with three equivalents of β -ketoimine. As with Altaf's complex, the Al centre was six-coordinate in an octahedral *mer*-arrangement, in a *Pbca* crystal space group. Jana commented on this isomerism, stating that the *mer*-adduct was likely formed over the *fac*-adduct (see Section 3.1.3.2) in order to facilitate a reduction of steric stress around the aluminium atom, which was to expected when using the bulky β -diketiminato ligand with phenyl *N*-substituents. Interestingly, once again each ligand had its own set of environments in both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and Jana was able to attribute each peak to each individual ligand environment.

3.2.4.1 Analogues to tris(β -ketoiminate) aluminium complexes

Due to the lack of tris(β -ketoiminate) aluminium complexes in the literature, it can be useful to look at other analogues that closely relate, namely Al complexes that contain three ligands containing conjugated centres that bind in a bidentate mode. Undoubtedly the most similar analogue in the literature is the tris(β -diketiminato) aluminium complex synthesised by Kuhn *et al.*³¹ using methyl groups on the *N*-substituents, the only complex of its type (Figure 3.7a). Three equivalents of ligand was reaction with TMAA and produced a distorted octahedral complex that was fully analysed including by SCXRD. It is likely other complexes of this motif have not been synthesised owing to the greater steric hindrance of the ligand system owing to there being two R groups on the ligand. Tris complexes involving β -diketiminato ligands with larger R groups (*i.e.* aryl groups), do exist for systems that involve larger metal centres such as Riedhammer's³² uranium complexes. Another bidentate ligand systems that feature a conjugated centre that has been placed around Al in three equivalent are pyrazolates, shown eloquently by Deacon's³³ complex which has a trigonal prismatic geometry (Figure 3.7b). These complexes contain the two donor atoms adjacent to one another, so have a smaller bite angle and thus there is a greater potential to use bulkier ligand backbones.

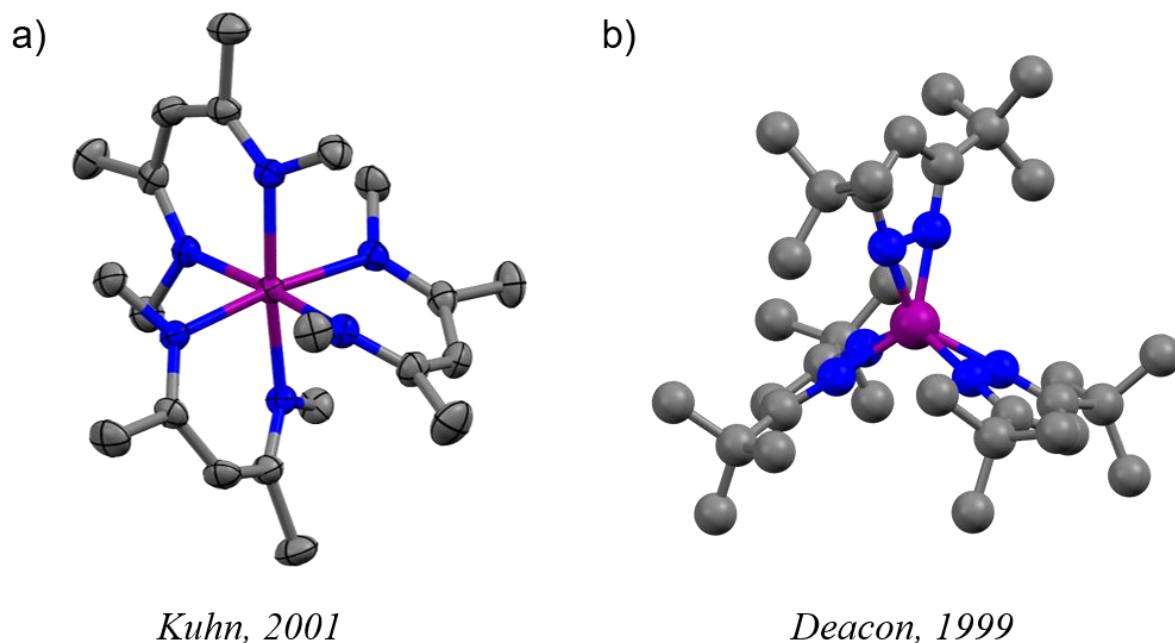
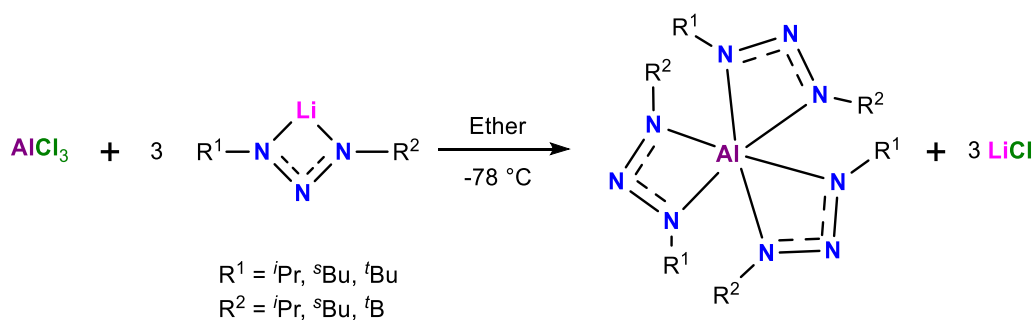


Figure 3.7: Tris ligated aluminium complexes of the type $[Al(L)_3]$ (where L = bidentate N-donating ligands) in the literature (hydrogen atoms omitted for clarity). a) Kuhn's³¹ and b) Deacon's³³ complexes, respectively.

Amindinate (amd) and guanidinate (guan) ligands are popular ligand systems in precursor chemistry and tris adducts of aluminium ($[Al(amd)_3]$, $[Al(guan)_3]$) have been synthesised producing octahedral complexes, however these particular types of compounds have not been used as precursors in MOCVD or ALD process due to insufficient volatility.^{34,35} Triazenide ligands can be also used to produce six-coordinate Al complexes, with Leman producing several contributions in this field producing octahedral complexes with aryl R groups.^{36,37} Early this year, Samii *et al.*³⁸ reported six-coordinate octahedral complexes using triazenides complexes with unsymmetrical alkyl R groups (*i.e.* R^1 and R^2 – see Scheme 3.1) to improve volatility, compared to the homoleptic aryl variants synthesised by Leman for example, for use as aluminium nitride, AlN ALD precursor.



Scheme 3.1: Reaction utilised by Samii et al.³⁸ for the Synthesis of $[\text{Al}(\text{guan})_3]$ type compounds with unsymmetrical R groups.

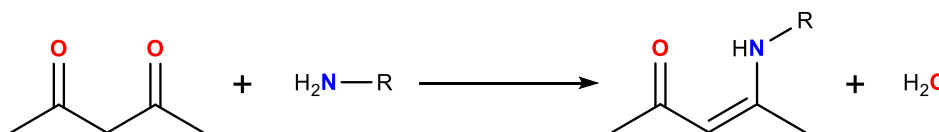
3.3 Results and discussion

Ligand substitution reactions have been employed to yield a library of tris(β -ketoiminate) aluminium compounds. The effect of steric bulk of the coordinating ligand on the geometry at the metal centre is explored, with particular focus on X-ray crystal structural and thermal decomposition analysis.

3.3.1 Synthesis of β -ketoimine compounds

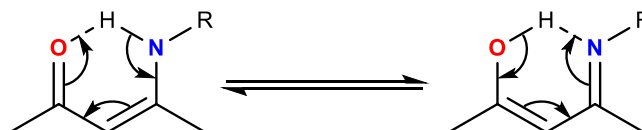
β -ketoimine compounds can be synthesised *via* the facile condensation reaction of β -diketones with primary amines, as shown in Scheme 3.2. Many techniques have been used to synthesise such compounds including the use of solid acid catalysts, catalytic iodine and microwave-assisted processes.^{8,39,40} However, the processes followed to synthesise β -ketoimine compounds featured herein use the simplistic reaction of acetylacetone with a primary amine, either at room temperature or heated to reflux, as this was the simplest and most cost-effective method offering good yields.⁴¹ Solid products were purified *via* recrystallisation, whilst liquid products were purified *via* distillation, when required. Yields were generally high (>66%) and could potentially be increased by driving the reaction *via* water elimination, either using a Dean-Stark apparatus and/or using drying agent during the synthesis. The β -ketoimines; N -methyl-4-amino-3-penten-2-one (**Me-acnach**), 4 N -ethyl-4-amino-3-penten-2-one (**Et-acnach**), N -isopropyl-4-amino-3-penten-2-one (**iPr-acnach**), N -phenyl-4-amino-3-penten-2-one (**Ph-acnach**) and N -(2,4,6-trimethylphenyl)-4-amino-3-penten-2-one (**Ar^{mes}-acnach**) were synthesised due to their differences in steric bulk and electron donating properties of the N -substituent. The alkyl-substituted ligands required very little purification if any (solids were recrystallised), whilst the aryl-substituted ligands first required distillation before recrystallisation. A more detailed description of each synthesis follows in Sections

3.2.1.1–3.2.1.5. As detailed in Section 3.1.2.2, functionalisation of the β -ketoimine imino group can vastly change the resultant properties of the synthesised complexes.



Scheme 3.2: Reaction scheme for the synthesis of β -ketoimines by the condensation reaction between β -diketones (i.e. acetylacetone) and primary amines.

Formation of the β -ketoimine compounds is easily identified by the characteristic chemical downfield shift of the broad NH proton resonance in the primary amine to that of the β -chelating compound at *ca.* δ 11–12 ppm. This chemical shift occurs due to deshielding effect of imino group intramolecularly hydrogen bonded with the adjacent carbonyl group. β -ketoimines undergo rapid proton exchange between the nitrogen and oxygen atoms and thus exists in two tautomeric forms that rapidly interconvert as illustrated in Scheme 3.3. The presence of just one broad heteroatomic proton signal for the two tautomers suggests that exchange must be very fast, with respect to the NMR timescale.



Scheme 3.3: Tautomeric forms (conjugation) of β -ketoimines.

3.3.1.1 Synthesis of *N*-methyl-4-amino-3-penten-2-one, (MeCN{H}(Me)CHC=OMe) (**Me-acnacH**)

The reaction of methylamine (in water) with acetylacetone at ambient temperature afforded **Me-acnacH** as a white solid after work-up, which was recrystallised from toluene at -20 °C. The resulting colourless crystals were synthesised in excellent purity and good yield (66%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁴²

3.3.1.2 Synthesis of *N*-ethyl-4-amino-3-penten-2-one, (MeCN{H}(Et)CHC=OMe) (**Et-acnacH**)

The reaction of ethylamine (in water) with acetylacetone at ambient temperature afforded **Et-acnacH** as a yellow oil which was synthesised in excellent purity and good yield (74%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the literature.⁴³

3.3.1.3 Synthesis of *N*-isopropyl-4-amino-3-penten-2-one, (MeCN{H})(*i*Pr)CHC=OMe) (***i*Pr-acnacH**)

The reaction of isopropylamine with acetylacetone, which was refluxed at 115 °C in toluene, afforded ***i*Pr-acnacH** as a clear yellow solution, which was dried *in vacuo*. The resulting orange oil was synthesised in excellent purity and yield (85%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.²⁹

3.3.1.4 Synthesis of *N*-phenyl-4-amino-3-penten-2-one, (MeCN{H})(Ph)CHC=OMe) (**Ph-acnacH**)

The reaction of aniline with excess acetylacetone, which was refluxed at 150 °C in the absence of solvent, afforded **Ph-acnacH** as a viscous brown solution, which was distilled at 125 °C at reduced pressure. The resulting yellow solid that formed upon cooling was recrystallised from hexane at –20 °C and the product was washed with ice-cold hexane. Off-white crystals were formed in excellent purity and yield (83%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the literature.⁴³

3.3.1.5 Synthesis of *N*-(2,4,6-trimethylphenyl)-4-amino-3-penten-2-one, (MeCN{H})(Ar^{mes})CHC=OMe, where Ar^{mes} = 2,4,6-trimethylphenyl) (**Ar^{mes}-acnacH**)

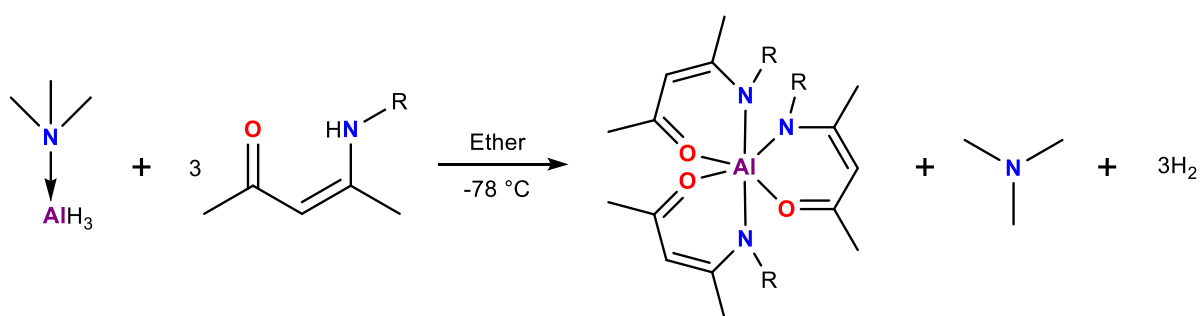
The reaction of 2,4,6-trimethylaniline with excess acetylacetone which was refluxed at 150 °C, in the absence of solvent, afforded **Ar^{mes}-acnacH** as a viscous brown solution, which was distilled at 135 °C at reduced pressure. The resulting yellow solid that formed upon cooling was recrystallised from hexane at –20 °C and the product was washed with ice-cold hexane. White crystals were formed in excellent purity and good yield (72%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁴³

3.3.2 **Synthesis of tris(β -ketoiminate) aluminium compounds**

With a view of forming aluminium complexes with low decomposition temperatures, the β -ketoimine compounds were complexed to aluminium *via* the reaction with [Me₃N·AlH₃], TMAA. TMAA itself is a precursor that can be used to deposit aluminium metallic films at low temperature, however it is extremely air and temperature sensitive and thus is less suitable for industrial procedures (see Chapter 5). Through numerous reactions using different molar ratios of β -ketoimine, it was found that to sufficiently stabilise the aluminium centre, three equivalents were required, liberating three equivalents of dihydrogen gas as an entropic driving force, as shown in Scheme 3.4. Smaller ratios of ligand gave lower yields of the tris adducts, whilst using large amounts resulted in wasted reagent – the formation of a mono or bis species

could not be isolated and characterised. In addition to dihydrogen, the formation of the low boiling trimethylamine (3 °C) as the only other by-product makes the workup of this complex relatively easy. The complexes with alkyl R groups (**1–3**) were soluble in diethyl ether and hence were recrystallised from the reaction solvent (once any insolubles were removed) at –20 °C, whilst complexes with aryl groups (**4,5**) were not soluble in diethyl ether due to a larger hydrophobic character of the R groups and hence were recrystallised from the less polar solvent toluene at –20 °C. Yields were moderate, ranging from 47–66%, with differences mainly due to ligand purity and how efficient the recrystallisation purification process was performed, with syntheses often requiring multiple crystal batches to maximise yield. A more detailed description of each synthesis, as well as, the crystal structure descriptions and comparisons for each novel compound follows in Sections 3.2.2.1–3.2.2.6.

As introduced in Section 3.1.4, there are only two other tris(β -ketoiminate) aluminium compounds in the literature, Jana's¹⁵ phenyl and Altaf's²¹ bulkier (4-tertbutylphenyl) complexes, with no alkyl adducts known. Other conventional tris coordinated aluminium complexes featuring bidentate ligands are limited to range of tris(β -diketonate) aluminium analogues, one tris(β -diketiminate) aluminium complex (Kuhn's methyl complex – see Section 3.1.4.1),³¹ as well as, others that employ less comparable ligand systems.



Scheme 3.4: General reaction scheme of the tris(β -ketoiminate) aluminium complexes.

3.3.2.1 Synthesis of [Al(MeCN(Me)CHC=OMe)₃] ([Al(Me-acnac)₃], **1**)

Compound **1**, [Al(Me-acnac)₃], was prepared by the σ -bond metathesis reaction of **TMAA** with 3 eq. of **Me-acnacH** in diethyl ether at low temperature. White crystals were formed from a concentrated diethyl ether solution at –20 °C and the recrystallised compound had excellent purity, as demonstrated by ¹H and ¹³C{¹H} NMR spectra. The yield was moderate (54%) due to inefficiency of the recrystallisation process and potentially could be improved by moderating the solvent system and collecting more batches. The crystal structure of compound **1** was

determined via SCXRD and is displayed in Figure 3.8. The details of the determined crystallographic data are given in Table 3.7 with selected bond lengths and angles given in Table 3.1 and 3.8.

Table 3.1: Selected bond lengths and angles for compound **1**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Me-acnac) ₃] (1)			
Lengths / Å		Angles / °	
Al – O	1.871	O – Al – N (bite)	88.86
Al – N	2.033	O – Al – N (trans)	174.93(4)
C – O	1.251	O – Al – O (trans)	175.27(4)
C – N (backbone)	1.307	N – Al – N (trans)	176.45(4)
C – N (N-substituent)	1.467		

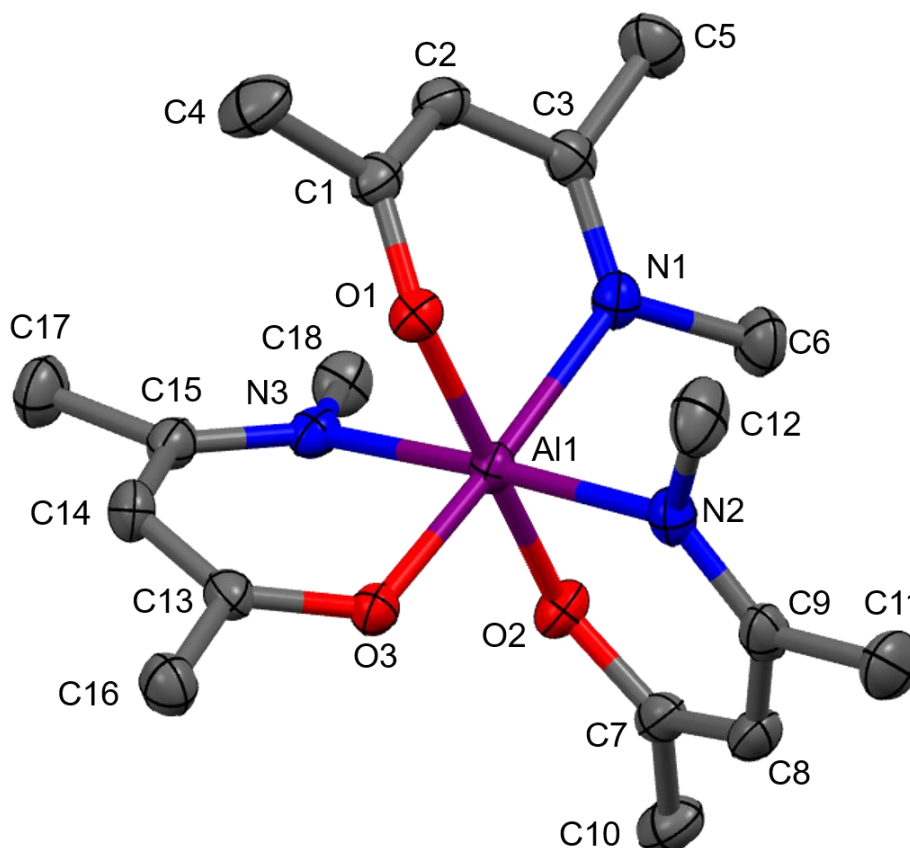


Figure 3.8: Molecular structure of compound **1**. Thermal ellipsoids are drawn at 50% probability with hydrogen atoms omitted for clarity.

Compound **1** crystallised in the triclinic space group $P\bar{1}$. The complex is a 1:3 monomer, with three chelating bidentate β -ketoiminate ligands that each bind *via* one O and one N atom. The ONC_3 backbone of each of the three β -ketoiminate ligands coordinate to the Al centre have a delocalised π -electronic system, similar to compounds of this motif.^{15,21} The three ligands form a rare example of an octahedral arrangement around the six-coordinate Al metal centre in a *mer* configuration, as seen in the only other tris(β - ketoiminate) aluminium complexes reported by Jana¹⁵ and Altaf²¹ – this has previously been understood as a method of reducing steric clash between the bulky imino groups, however it may also be due to better packing within the crystal. The distortion found in octahedral arrangement of the ligands is to the point that each bidentate ligand cannot be generated by symmetry and thus although each ligand environment is chemically identical, they are crystallographically different leading to a host of different bond lengths and angles – this is likely due to the *mer*-configuration of the ligands around the Al centre leading to varying steric clashes, as well as, different *cis/trans* heteroatom relationships.

The angles in complex **1** agree well with those found in Jana's structure (Al–O: 1.839(1)–1.865(1) Å, Al–N: 2.040(2)–2.062(2) Å), as well as, Altaf's complex (Al–O: 1.8321(9)–1.8764 (10) Å, Al–N: 2.0403(11)–2.0671(11) Å).^{15,21} Due to the steric constraints of the bidentate ligands, the octahedral geometry is slightly distorted, which can be seen in the O(1)–Al(1)–N(1) angle of 86.73(4)°, deviating from 90 ° linearity. Thus, there is also distortion of the angles between O(1) and N(1) to other heteroatoms in the structure, such as the O(1)–Al(1)–O(2) and N(1)–Al(1)–O(3) angles of 175.27(4) and 174.93(4)° respectively. Similar distortions are seen in the complexes of Jana and Altaf.^{15,21} The Al–N–C–C–C–O– six-membered chelate rings are slightly puckered, as reflected by the internal sum of bond angles (ring of ligand 1 = 704.6°, where 720° is expected for a hexagon).

As expected, the Al–O bond lengths from 1.8589(9) to 1.8769(9) Å are shorter compared to the Al–N bond lengths of 2.0306(10) to 2.0352(11) Å, which is caused by the smaller radius of the oxygen atoms and larger ionic contribution to the Al–O bond. The chelate rings are delocalised as evidenced by the pattern of bond lengths, (O(1)–C(1): 1.2934(15) Å, C(1)–C(2): 1.3699(18) Å, C(2)–C(3): 1.4244(18) Å, C(3)–N(1): 1.3084(17) Å) – compared with the free β -ketoimine compound, there is lengthening of the O(1)–C(1) and C(2)–C(3) bonds and a shortening of the N(1)–C(3) bond, as the bonds gain less and more double bond character respectively.⁴⁴

Bond lengths of the three ligands vary only slightly between one another and in most cases are within three estimated standard deviations of one another, hence they are classed as crystallographically identical. The only notable bond length differences between ligands include O–C and N–C backbone bond lengths which are crystallographically identical for two ligands but crystallographically different for ligand 3 (*i.e.* O(3) and N(3) containing ligand), with this most likely occurring due the first and second ligand have more steric clash between their respective *N*-substituents. Bond angles within the ligand are less similar when comparing the three chelates, most often not falling within three estimated standard deviations of another. One example of this is the bond angle of the methine environment which varies from 123.36(11)–125.42(12)° across the three ligands. These observations are seen for all complexes featured within this Section so ligand specific bond lengths and angles will not be further discussed.

In addition to SCXRD characterisation, compound **1** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. The ^1H NMR spectrum of compound **1** does not show any resonances for the NH proton of the free β -ketoiminate ligand and peaks are shifted from the uncomplexed compound as expected. Interestingly, **1** shows complicated NMR spectra, with most methyl groups showing different resonances, as well as, there being three different methine environments in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, attributable to the aforementioned *mer*-geometry. Due to different *cis* and *trans* heteroatomic relationships across the aluminium centre, as well as, varying amounts of steric clash, no proton/carbon environment across the three ligands is the same and hence they are shifted from one another. This phenomenon is most elegantly exhibited by the presence of three CH peaks in the ^1H NMR spectrum at δ 5.03, 4.97 and 4.87 ppm in a 1:1:1 ratio. Methine protons are followed by two singlet peaks (lost doublet character due to loss of enamino proton) at δ 2.92 and 2.79 ppm corresponding to the *N*-substituent CH_3 groups in a 1:2 ratio. It is important to note that only two peaks are observed in this region, from the two environments intrinsic to the *mer* conformation (two methyl imino groups *trans* to one another, and one Me–N *trans* to O). While it could be argued that two separate environments may have coalesced due to a very small change in chemical shift between peaks, this is unlikely as the peak with the larger integration actually as a smaller peak width (2.76 Hz compared to 3.12 Hz) of the methine environments. Finally, there are six methyl groups corresponding to three CH_3CO and three CH_3CN groups at δ 1.99, 1.93, 1.90 ppm and δ 1.59, 1.56, 1.55 ppm respectively, with each integrating to 3H. Chemically identical but crystallographically different $^{13}\text{C}\{^1\text{H}\}$ NMR environments also split

into three for each of the three ligands, with the $^{13}\text{C}\{^1\text{H}\}$ environments consistent with the formation of **1**.

3.3.2.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_3]$ (**[Al(Et-acnac)₃]**, **2**)

Compound **2**, **[Al(Et-acnac)₃]**, was synthesised by the same procedure as the methyl analogue, with white crystals precipitated from a concentrated diethyl ether solution at $-20\text{ }^\circ\text{C}$ in excellent purity and in good yield (64%). The crystal structure of compound **2** was determined *via* SCXRD and is displayed in Figure 3.9. The details of the determined crystallographic data are given in Table 3.7 with selected bond lengths and angles given in Table 3.2 and 3.8. Compound **2** crystallised in the higher symmetry monoclinic space group $P2_1/n$. Three bidentate ligands bind to the metal centre in the same manner as with compound **1** ($\text{R} = \text{Me}$), although compound **2** ($\text{R} = \text{Et}$) crystallises out as the mirror image/enantiomer (see Section 3.1.3.3).

Table 3.2: Selected bond lengths and angles for compound **2**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Et-acnac)₃] (2)			
Lengths / Å		Angles / °	
Al – O	1.861	O – Al – N _(bite)	89.18
Al – N	2.047	O – Al – N _(trans)	173.84(4)
C – O	1.293	O – Al – O _(trans)	176.30(4)
C – N _(backbone)	1.308	N – Al – N _(trans)	174.19(4)
C – N _(N-substituent)	1.475		

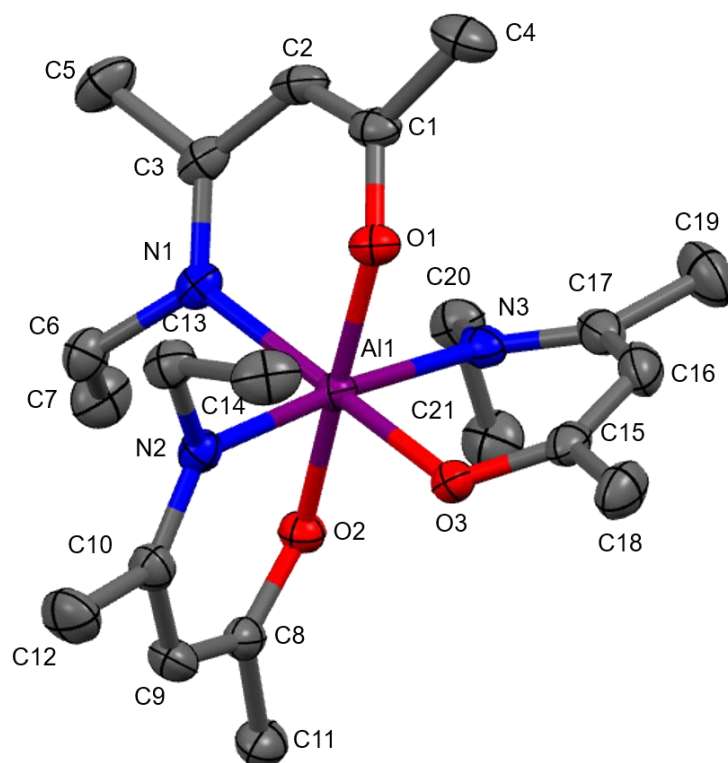


Figure 3.9: Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability with hydrogen atoms omitted for clarity.

Again, the complex is in a distorted octahedral geometry in *mer*-configuration, with most distortions in the ethyl analogue being similar to those of the methyl. One angle that shows more distortion in the ethyl complex, is the N(1)–Al(1)–N(3) angle which is 95.82(4)°, as opposed to 91.56(4)°. This can be understood as the alkyl constituents on N(1) and N(3) are the closest together, spanning out into the same plane, hence they distort further away from the 90 ° optimum geometry in the case of the larger ethyl groups, as there is a greater likelihood of steric clash.

The Al–O bond lengths are slightly shorter than the methyl analogue, ranging from 1.8512(9)–1.8693(9) Å, whilst the Al–N bond distances are slightly larger, ranging from 2.0442(10)–2.0498(10) Å. These findings can be rationalised as the N atoms binding further away from the Al centre due to the added steric bulk of the ethyl group, resulting in the O atoms binding closer to supply the Al centre with sufficient electron density, in combination with the delocalised nature found in these β -ketoiminate ligands. The O(1)–C(1) bond distance for the ethyl analogue is very similar to that the methyl complex (O(1)–C(1); **1**: 1.2934(15) Å, **2**: 1.2966(15)), which is also true for the N(1)–C(3) bond distances (N(1)–C(3); **1**: 1.3084(17), **2**: 1.3122(16)). There is a noticeable difference in the N(1)–C(6) bond distance, with it being

larger in the ethyl complex (**2**), compared to that of the methyl analogue (**1**), with bond distances of 1.4764(16) and 1.4681(16) Å respectively. This longer bond length in the ethyl complex can be attributed to the increased steric strain of the complex, as the dangling ethyl groups from each ligand have to contort further away from the ligand backbone to avoid clashing with the other ligands. As seen for the methyl complex variant, there are similar trends in differences in bond lengths and angles between each of the three chelating ligands.

In addition to SCXRD characterisation, compound **2** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. Again, the ^1H NMR spectrum of compound **2** does not show any resonances for the NH proton of the free β -ketoimine compound, peaks are shifted and there is a loss of multiplicity due to the removal of the enamino proton upon complexation. As with the methyl analogue, **2** shows complicated NMR spectra. All methyl, methylene and methine groups have different resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, due to the *mer*-geometry of the complex. Once more, the highest downfield environments are the methine groups on the ligand backbone occurring between δ 5.00–4.88 ppm, followed by the methylene groups of the ethyl *N*-substituent at δ 3.40–3.19 ppm, whilst the methyl groups on the ethyl group are shifted upfield to δ 1.27–1.06 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR environments were also consistent with the formation of **2**.

3.3.2.3 Synthesis of $[\text{Al}(\text{MeCN}(\textit{i}\text{Pr})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\textit{i}\text{Pr-acnac})_3]$, **3**)

Compound **3**, $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$, was synthesised by the same procedure as the other alkyl analogues, with white crystals precipitated from a concentrated diethyl ether solution at $-20\text{ }^\circ\text{C}$ in excellent purity and in good yield (61%). The crystal structure of compound **3** was determined *via* SCXRD and is displayed in Figure 3.10. The details of the determined crystallographic data are given in Table 3.7 with selected bond lengths and angles given in Tables 3.3 and 3.8. Compound **3** crystallised in the triclinic space group $P\bar{1}$. Three bidentate ligands bind to the metal centre in the same manner as with the other tris(β -ketoiminate) aluminium compounds.

Table 3.3: Selected bond lengths and angles for compound **3**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(<i>i</i>-Pr-acnac)₃] (3)			
Lengths / Å		Angles / °	
Al – O	1.862	O – Al – N (bite)	88.54
Al – N	2.059	O – Al – N (trans)	174.38(5)
C – O	1.295	O – Al – O (trans)	177.26(4)
C – N (backbone)	1.309	N – Al – N (trans)	174.75(4)
C – N (N-substituent)	1.491		

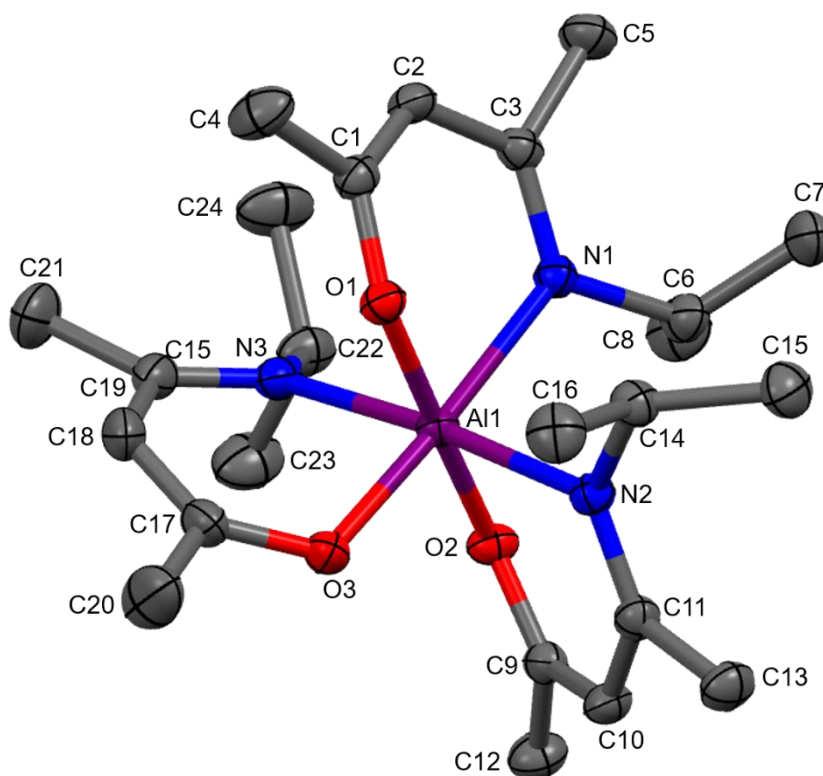


Figure 3.10: Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability with hydrogen atoms omitted for clarity.

As seen in the other complexes of this motif, complex **3** adopts a distorted octahedral geometry as the *mer*-stereoisomer. Overall, the isopropyl complex is more distorted than the ethyl analogue due to the added steric bulk of the N-substituent, which is exhibited by a larger distortion in the ligand pincer bonding angle, O(1)–Al(1)–N(1), of 87.34(4)°, compared to 88.00(4)°. Distortions such as the O(1)–Al(1)–N(1), O(1)–Al(1)–O(2) and N(1)–Al(1)–O(3) bond angles of 88.10(4), 177.26(4) and 173.38(5)° are generally greater than those found in the complexes of Jana and Altaf, which indicates that the isopropyl group, having great steric bulk

closer the complex centre, creates a larger distortion, which agrees well with Tolman cone angle values for the different R groups.^{15,21,45,46}

As expected, we see the same trend in increasing the steric bulk of the *N*-substituent as before, with an increase in Al–N bond lengths, ranging from 2.0530(12)–2.0638(11) Å (change in Al–O bond distances negligible, Al–O: 1.8445(9)–1.8743(9) Å). As expected, the N(1)–C(3) and N(1)–C(6) bond lengths are longer in the isopropyl complex, which logical due to the increased bulk of the alkyl group. Comparing aluminium heteroatom bonds to the literature, the bonds agree well with those found in Jana’s tris(phenyl β -ketoiminate) aluminium structure (Al–O: 1.839(1)–1.865(1) Å, Al–N: 2.040(2)–2.062(2)), as well as, Altaf’s complex (Al–O: 1.8321(9)–1.8764 (10) Å, Al–N: 2.0403(11)–2.0671(11)).^{15,21} It is interesting to note that although one could assume that the isopropyl groups in **3** would cause less steric clash between ligands than the aryl groups, it seems this is not the case as **3** has slightly longer bond Al–O and Al–N lengths to reduce this clash between ligands. This can be rationalised as the planar phenyl group that is only bulky in two dimensions can arrange itself to minimise steric clash more easily and the 4-tertbutylphenyl group in Altaf’s complex is only three-dimensionally bulky when it is far enough away from the centre of the complex, as to not cause large steric clash.⁴⁶ As seen for the methyl and ethyl complexes, there are similar trends in differences in bond lengths and angles between each of the three chelating ligand.

In addition to SCXRD characterisation, compound **3** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, MS and EA. Once again, the ^1H NMR spectrum of compound **3** does not show any resonances for the NH proton of the free β -ketoimine compound, as well as, peaks being shifted and a loss of multiplicity due to the removal of the enamino proton upon complexation. As for the other alkyl analogues, **3** shows an intriguing NMR spectra. All methyl, methylene and methine groups have different resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, due to the *mer*-geometry of the complex.

^1H NMR peaks at δ 4.95 (CH), 4.15 ($\text{CH}(\text{CH}_3)_2$), 1.87 ($\text{CH}_3\text{CO CH}_3$), 1.82 (CH_3CN) and 1.32 (CH_3) ppm, and δ 1.27, 1.21, 1.06 (CH_3) ppm in the expected ratios and a sufficient shift from the uncomplexed compound confirm the presence of **3**. Interestingly, unlike the other complexes of this type in this Chapter, despite being analysed in the same deuterated solvent (C_6D_6), peaks do not split between each ligand, appearing as broad peaks. In order to probe this behaviour, in addition to room temperature (RT) NMR, both low (7 °C) and high (75 °C) temperature ^1H NMR experiments were conducted. Whilst the low temperature NMR spectrum

did not provide any extra useful information, the high temperature NMR spectrum (Appendix 34) elucidated the splitting of the protons on the ^iPr imino groups – in all cases the ligands did not split into three peaks as with the other tris analogues (Appendix 31–34). Interestingly the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3** displayed very weak peaks despite highly concentrated samples (>100 mM) and longer scans. The most resolved $^{13}\text{C}\{^1\text{H}\}$ NMR was measured at high temperature (75°C) using a highly concentrated sample, however despite this some expected peaks were still undetectable. $^{13}\text{C}\{^1\text{H}\}$ NMR environments at δ 169.88 ($\text{CH}_3\text{C}\equiv\text{N}$), 101.01 ($\text{C}\equiv\text{N}$), 49.47 ($\text{CH}(\text{CH}_3)_2$), 25.57 (CH_3CO), 23.74 (CH_3CN), 22.28 (CH_3) ppm were consistent with the formation of **3**, however during numerous experiments under differing conditions the signal for the CH_3CO environment could not be identified, which is likely owing to the speed of dynamics with this R group.

3.3.2.4 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Ph-acnac})_3]$, **4**)

Compound **4**, $[\text{Al}(\text{Ph-acnac})_3]$, was synthesised by the same procedure as the other analogues, although white crystals were precipitated from a concentrated toluene solution at -20°C in excellent purity and in good yield (65%). The crystal structure of compound **4** was determined *via* SCXRD and is displayed in Figure 3.11 – it must be noted that compound **4** has previously been synthesised and characterised *via* SCXRD by Jana, with bond lengths and angles occurring within three standard deviations with one another.¹⁵ The details of the determined crystallographic data are given in Table 3.7 with selected bond lengths and angles given in Tables 3.4 and 3.8. Compound **4** crystallised in the high symmetry orthorhombic space group *Pbca*. Three bidentate ligands bind to the metal centre producing distorted octahedral geometry with *mer*-stereoisomerism as previously seen for compounds **1–3**.

Table 3.4: Selected bond lengths and angles for compound **4**. Average values can be identified by the fact no estimated standard deviations values are given.

$[\text{Al}(\text{Ph-acnac})_3]$ (4)			
Lengths / Å		Angles / °	
Al – O	1.855	O – Al – N (bite)	89.20
Al – N	2.051	O – Al – N (trans)	175.14(4)
C – O	1.287	O – Al – O (trans)	176.70(4)
C – N (backbone)	1.314	N – Al – N (trans)	173.87(4)
C – N (N-substituent)	1.439		

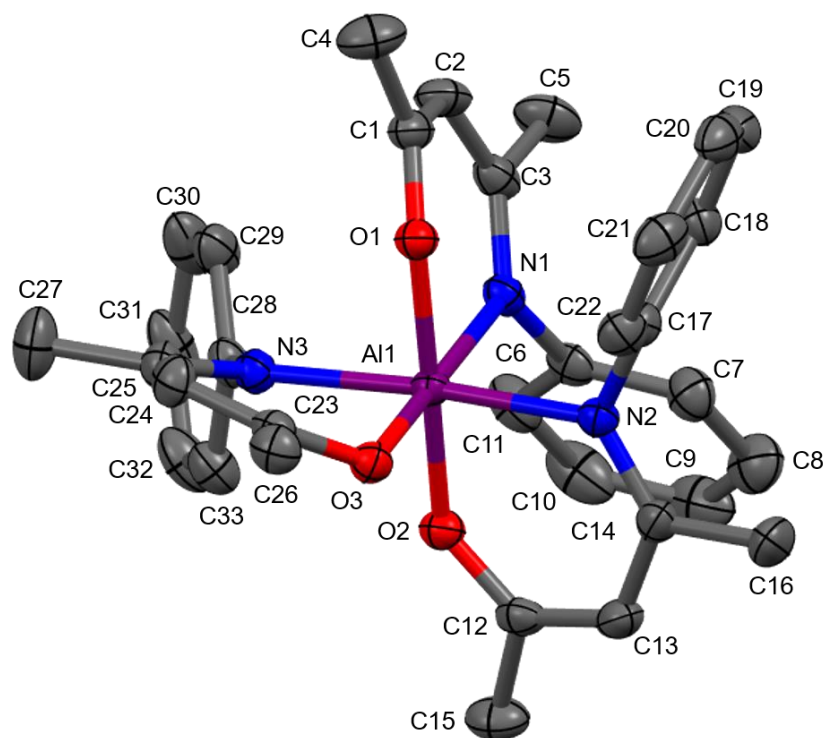


Figure 3.11: Molecular structure of compound **4**. Thermal ellipsoids are drawn at 50% probability with hydrogen atoms omitted for clarity.

In addition to SCXRD characterisation, compound **4** formation was also confirmed *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA and agrees with the literature.¹⁵ Once again, the ^1H NMR spectrum of compound **4** does not show resonances accounted with the NH proton of the free β -ketoimine compound, as well as, peaks being shifted and a loss of multiplicity due to the removal of the enamino proton upon complexation. Additionally, each chemically identical ^1H environment of the three ligands are crystallographically different leading to different resonances for each methyl, methylene and methine group as seen for compounds **1** and **2**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is in agreement with the ^1H NMR spectrum.

3.3.2.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_3]$ (**5**), where Ar^{mes} = 2,4,6-trimethylphenyl ($[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$, **5**)

Compound **5**, $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$, was synthesised by the same procedure as the phenyl analogue, with white crystals precipitated from a concentrated toluene solution at $-20\text{ }^\circ\text{C}$ in excellent purity and in moderate yield (47%). Despite numerous attempts, crystals grown of compound **5** were not of sufficient quality that they could only be refined by a model with a high R-factor (14.35%), this appears to be a feature of the crystal growth, since multiple attempts yielded the same high mosaicity in the collected frames. Nevertheless, the crystal

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structure of compound 5 is displayed in Figure 3.12, with the details of the determined crystallographic data given in Table 3.7 with selected bond lengths and angles given in Tables 3.5 and 3.8.

Table 3.5: Selected bond lengths and angles for compound 5. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Ar ^{mes} -acnac) ₃] (5)			
Lengths / Å		Angles / °	
Al – O	1.802	O – Al – N (bite)	89.80
Al – N	1.976	O – Al – O (trans)	175.9(2)
C – O	1.303	O – Al – O (obtuse)	94.7(2)
C – N (backbone)	1.327	N – Al – N	126.4(2)
C – N (N-substituent)	1.438		

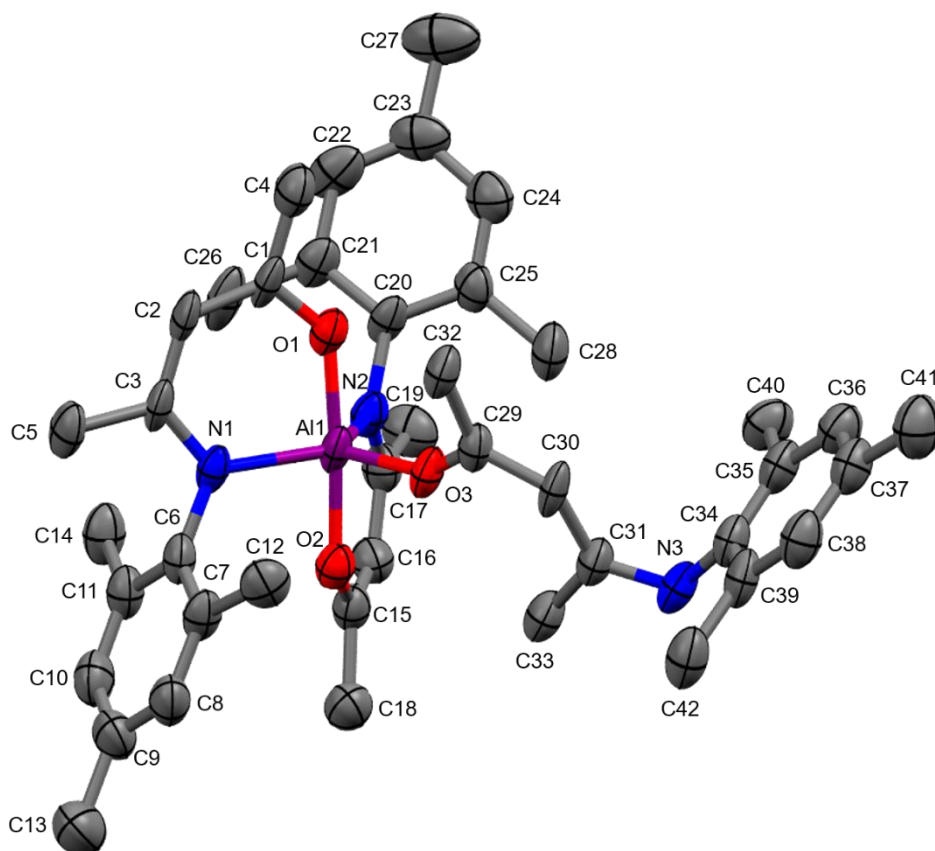


Figure 3.12: Molecular structure of compound 5. Thermal ellipsoids are drawn at 50% probability with hydrogen atoms omitted for clarity.

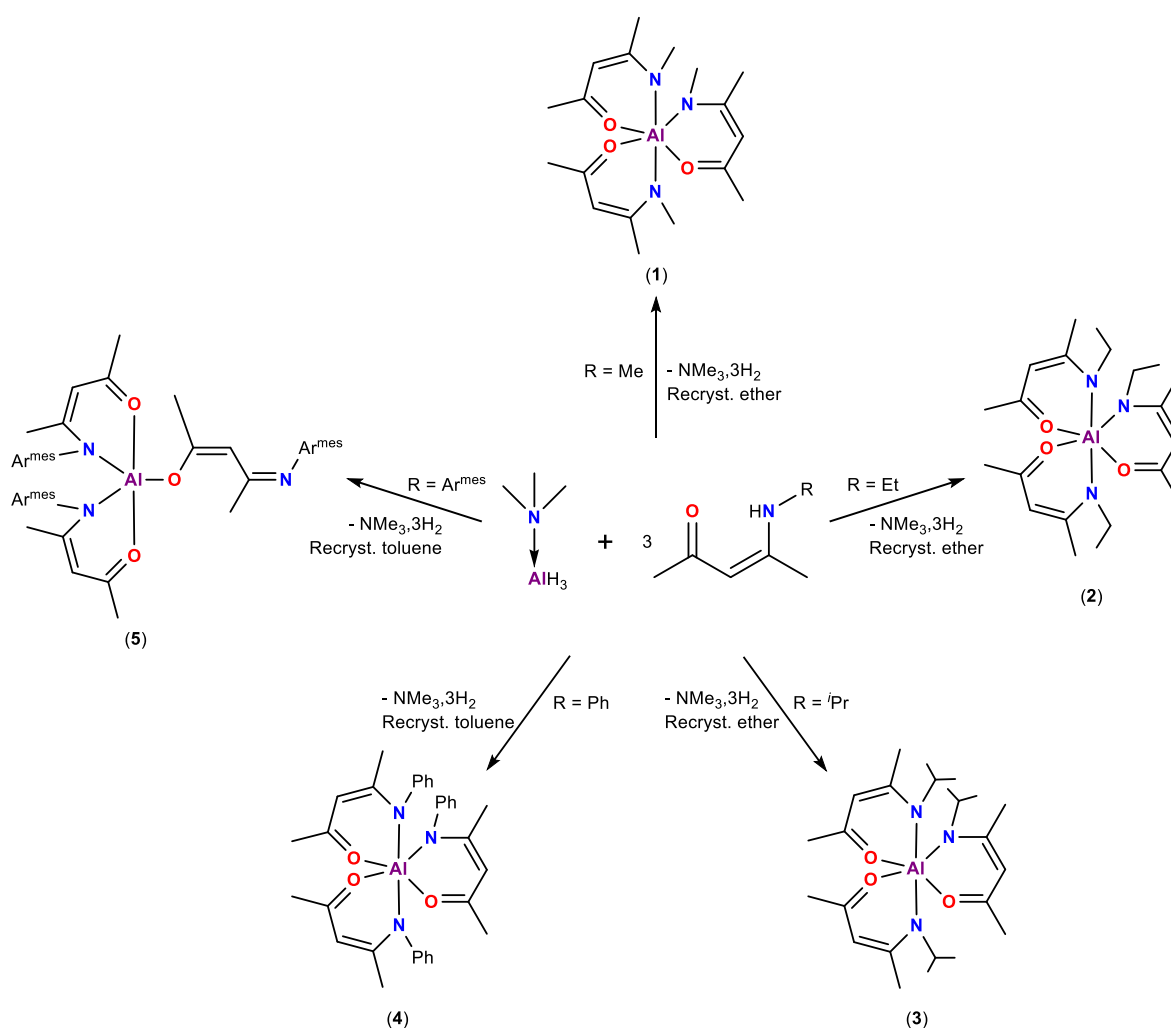
Due to this poor agreement between the crystallographic model and the experimental X-ray diffraction data, crystal symmetry, bonds lengths and angles *etc.* will not be discussed at great length and will only be used help observations in the TGA data (*via* trends). Interestingly however, this *pseudo*-crystallographic model does give us some key information of the structure of **5**, which would have been very difficult to elucidate without it. Due to the large steric bulk of the mesityl (2,4,6-trimethylphenyl) R group, the size of the compounds used to synthesise complex **5** are so bulky they have exceeded the size limit for fitting three β -ketoiminate ligands around the metal centre in a six-coordinate octahedral mode. Instead, only a five-coordinate trigonal bipyramidal geometry can be formed, with axial O-binding of two chelated ligands and one ligand only binding in a monodentate mode. Intuitively, the monodentate β -ketoiminate binds to the Al centre through the oxygen atom, with the biggest contributing factor likely being due to sterics, as the bulky mesityl group is situated further away from the crowded complex centre. Al also has a higher affinity to bind to O, so this bonding motif is also supported by electronics.

In addition to SCXRD characterisation, compound **5** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. Again, the ^1H NMR spectrum of compound **5** does not show any resonances for the NH proton of the free β -ketoimine compound, as well as, peaks being shifted and a loss of multiplicity due to the removal of the enamino proton upon complexation. As for the other analogues, **5** all methyl, methylene and methine groups have different resonances leading to exceedingly crowded ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which does agree well with the unique crystal structure. Environments on both the mono and bis ligated systems have been assigned where sufficiently confident judgements can be made.

3.3.2.6 Comparison of crystal structures

Scheme 3.5 summarises the reaction and recrystallisation conditions for compounds **1–5**. Table 3.6 shows a comparison of the average Al–O and Al–N bond lengths as well as, the average O–Al–N ligand pincer angles found in each of the four novel complexes (in addition to Jana's¹⁵ structure) featured within this Section. For the tris bidentate complexes (R = Me, Et, *i*Pr and Ph) there is a general trend between increasing Al–N bond length with increasing steric bulk of the R group (*i*Pr being the bulkiest as aforementioned).^{45,46} The effects of hyperconjugation do not play a key role in determining the Al–N bond distances between differing N-substituents as shorter bond distances for longer/more branched alkyl chains are not observed. The lengthening of the Al–N bond is generally accompanied by a trend of the

shortening of the Al–O bond, however the i Pr analogue conflicts with this observation slightly and is likely due to greater steric clash with adjacent imino groups on other ligands if the O atoms are pulled in more closely. The five-coordinate trigonal bipyramidal complex formed when $R = Ar^{mes}$ has both the shortest average Al–N and Al–O bonds and this can be attributed to having to fit less donor atom around the relatively small Al centre. Trends in the average O–Al–N ligand pincer angles are less clear, however the less crowded Ar^{mes} complexes is able get closest to the optimum 90° angle expected for bidentate ligands binding in both the axial and equatorial positions in both geometries, with this most likely being a consequence of fitting fewer donor atoms around the Al centre. Further evidence that the i Pr complex is the most sterically encumbered complex out of all the octahedral adducts is shown by the smallest ligand pincer angle out of the four complexes.



Scheme 3.5: *Synthesis and recrystallisation conditions of various tris(β -ketoiminate) aluminium complexes with the formula: $[AlL_3]$ (where L = bidentate β -ketoiminate).*

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Table 3.6: Comparison of average Al–O and Al–N bond lengths, as well as, O–Al–N pincer angles for complexes **1**–**5**.

R Group	Me (1)	Et (2)	ⁱ Pr (3)	Ph (4)	Ar ^{mes} (5)
Avg. Bond Length					
Al—O	1.871	1.861	1.862	1.855	1.802
Al—N	2.033	2.047	2.059	2.051	1.976
Avg. Bond Angle					
	88.86	89.18	88.54	89.20	89.80

Table 3.7: Crystallographic data for structurally characterised compounds 1–5.

Compound	[Al(Me-acnac) ₃] (1)	[Al(Et-acnac) ₃] (2)	[Al(ⁱ Pr-acnac) ₃] (3)	[Al(Ph-acnac) ₃] (4)	[Al(Ar ^{mes} -acnac) ₃] (5)
Empirical formula	C ₁₈ H ₃₀ AlN ₃ O ₃	C ₂₁ H ₃₆ AlN ₃ O ₃	C ₂₄ H ₄₂ AlN ₃ O ₃	C ₃₃ H ₃₆ AlN ₃ O ₃	C ₄₃ H ₅₅ AlN ₃ O ₂
Fw / g mol ⁻¹	363.43	405.51	447.58	549.65	672.88
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	8.4187(3)	10.0045(2)	9.8466(3)	13.2786(1)	19.971(3)
<i>b</i> / Å	9.4139(3)	16.6360(2)	11.4889(3)	13.5525(1)	13.5282(7)
<i>c</i> / Å	13.8037(4)	13.8351(2)	11.7060(4)	33.3317(2)	15.1341(12)
α / °	100.453(2)	90	84.747(2)	90	90
β / °	102.868(2)	98.5520(10)	82.406(2)	90	109.101(11)
γ / °	104.650(3)	90	77.341(2)	90	90
<i>V</i> / Å ³	998.51(6)	2277.04(6)	1278.05(7)	5998.31(7)	3863.7(7)
<i>Z</i>	2	4	2	8	4
ρ_{calc} / g cm ⁻³	1.209	1.183	1.163	1.2172	1.157
μ / mm ⁻¹	1.059	0.977	0.913	0.886	0.75
Reflections collected	15602	35979	19433	97192	21034
Independent reflections	3880	4558	5044	6023	7329
<i>R</i> _{int}	0.0286	0.0396	0.0259	0.0485	0.0638
<i>R</i> ₁ and <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0334, 0.0898	0.0358, 0.0957	0.0353, 0.0891	0.0380, 0.1012	0.1435, 0.3583
<i>R</i> ₁ and <i>wR</i> ₂ [all data]	0.0365, 0.0928	0.0396, 0.1003	0.0417, 0.0938	0.0402, 0.1041	0.1667, 0.3772

Table 3.8: Selected bond lengths (Å) and angles (°) for compounds 1–5.

Compound	[Al(Me-acnac) ₃] (1)	[Al(Et-acnac) ₃] (2)	[Al(ⁱ Pr-acnac) ₃] (3)	[Al(Ph-acnac) ₃] (4)	[Al(Ar ^{mes} -acnac) ₃] (5)
Lengths / Å					
Al(1) – O(1)	1.8769(9)	1.8613(9)	1.8684(9)	1.8589(9)	1.823(5)
Al(1) – O(2)	1.8589(9)	1.8512(9)	1.8445(9)	1.8384(8)	1.824(5)
Al(1) – O(3)	1.8675 (9)	1.8693(9)	1.8743(9)	1.8657(8)	1.759(4)
Al(1) – N(1)	2.0352(11)	2.0498(10)	2.0638(11)	2.0591(10)	1.982(5)
Al(1) – N(2)	2.0331(11)	2.0442(10)	2.0597(11)	2.0406(10)	1.969(5)
Al(1) – N(3)	2.0306(10)	2.0469(11)	2.0530(12)	2.0493(10)	-
O(1) – C(1)	1.2934(15)	1.2966(15)	1.2888(15)	1.2792(15)	1.294(7)
N(1) – C(3)	1.3084(17)	1.3122(16)	1.3135(16)	1.3130(16)	1.339(8)
N(1) – C(6)	1.4681(16)	1.4764(16)	1.4919(16)	1.4444(15)	1.431(8)
Angles / °					
O(1) – Al(1) – O(2)	175.27(4)	176.30(4)	177.26(4)	176.70(4)	175.9(2)
O(1) – Al(1) – O(3)	88.33(4)	88.00(4)	87.06(4)	87.94(4)	94.7(2)
O(1) – Al(1) – N(1)	86.73(4)	88.10(4)	87.34(4)	88.25(4)	90.2(2)
O(1) – Al(1) – N(2)	93.56(4)	92.92(4)	91.73(4)	91.52(4)	89.7(2)
O(1) – Al(1) – N(3)	89.80(4)	89.01(4)	91.19(4)	90.20(4)	-
N(1) – Al(1) – O(3)	174.93(4)	173.84(4)	173.38(5)	175.14(4)	119.3(2)
N(1) – Al(1) – N(2)	89.79(4)	89.72(4)	92.24(4)	91.87(4)	126.4(2)
N(1) – Al(1) – N(3)	91.56(4)	95.82(4)	92.25(4)	94.06(4)	-
N(2) – Al(1) – N(3)	176.45(4)	174.19(4)	174.75(4)	94.06(4)	-

3.3.3 Thermal decomposition analysis of tris(β -ketoiminate) aluminium precursors

The thermal decomposition properties of the tris(β -ketoiminate) aluminium compounds **1–5** were analysed by thermal gravimetric analysis (TGA). The thermograms of the β -ketoimine compounds used to synthesise complexes featured within this Chapter are given in the Appendices (Appendix 103). As expected, β -ketoimine compounds decompose fully (*i.e.* 100% mass loss). Full TGA and DTG analysis of complexes **1–5** is featured in the Appendices (Appendix 105–114).

3.3.3.1 Thermal decomposition of [Al(Me-acnac)₃] (**1**)

The thermogram of [Al(Me-acnac)₃] (**1**) (Figure 3.13) shows decomposition at low temperature with significant mass loss beginning at 152 °C. A mass loss of 89% was recorded, with a mass loss of 93% expected if pure Al metal is formed and 72% if pure Al₂O₃ is formed. The decomposition properties for this complex are extremely promising, showing that it is likely this precursor decomposes to the metal rather than the oxide under inert conditions, with very little carbon contamination. The recorded mass loss of this precursor maybe overestimated as there is a small decrease in mass leading up to the decomposition onset (small shoulder at 140 °C, seen in all repeats.) This slow mass loss could also be due to **1** being volatile, even at modest temperatures.

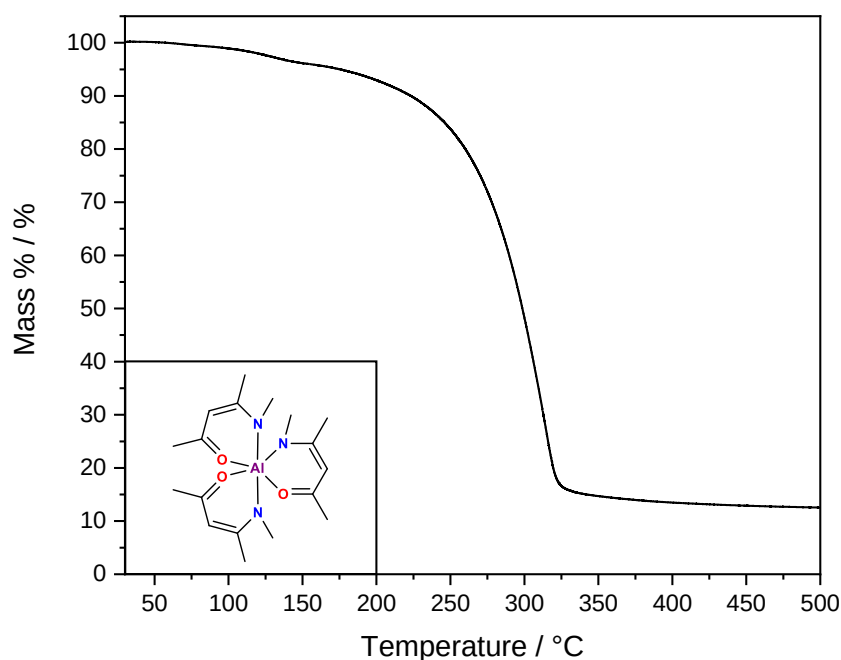


Figure 3.13: Thermogram of compound [Al(Me-acnac)₃] (**1**).

3.3.3.2 Thermal decomposition of $[\text{Al}(\text{Et-acnac})_3]$ (**2**)

The thermogram of $[\text{Al}(\text{Et-acnac})_3]$ (**2**) (Figure 3.14) shows decomposition at low temperature with significant mass loss beginning at 141 °C. A mass loss of 80% was recorded, with a mass loss of also 93% expected if pure Al metal is formed and 75% if pure Al_2O_3 is formed. Here we see mass loss beginning at an even lower temperature than in **1**, however the total mass loss is not as promising as when $\text{R} = \text{Me}$. The mass loss expected if pure Al_2O_3 is formed is 75%, so again the decomposition profile of this precursor indicates that it decomposes to Al metal along with residual carbonaceous decontaminants under inert conditions.

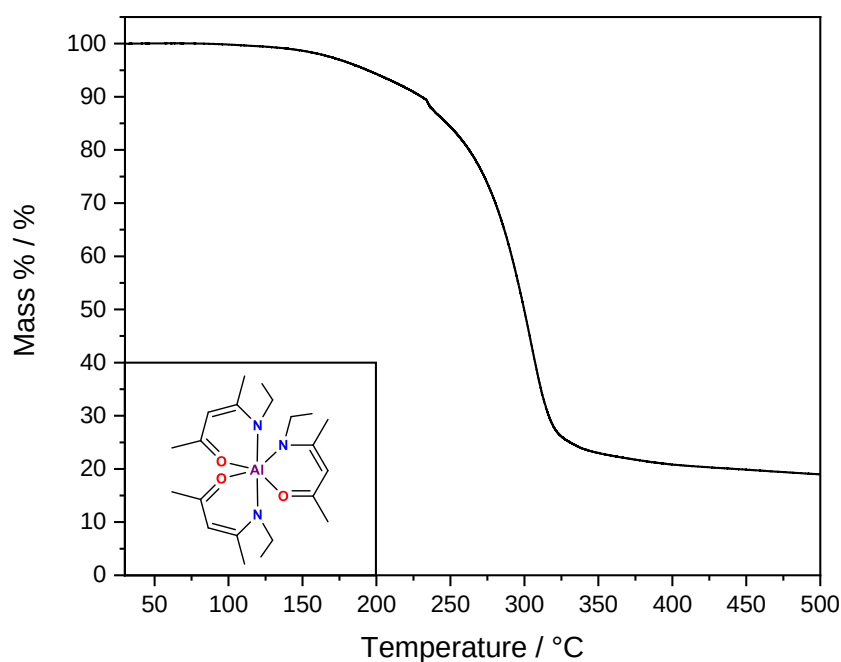


Figure 3.14: Thermogram of compound $[\text{Al}(\text{Et-acnac})_3]$ (**2**).

3.3.3.3 Thermal decomposition of $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$ (3)

The thermogram of $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$ (3) (Figure 3.15) shows decomposition at low temperature with significant mass loss beginning at the lowest temperature of all tris complexes at 114 °C. A mass loss of 69% was recorded, with a mass loss of also 94% expected if pure Al metal is formed and 77% if pure Al_2O_3 is formed. This precursor's decomposition temperature is extremely promising however the mass loss is less than satisfactory, producing either aluminium metal or aluminium oxide films with a considerable amount of carbon contamination. The compound likely decomposes at lower temperatures than the other analogues tested in this Chapter due to the steric bulk of the isopropyl *N*-substituent, which is sterically impeding in three dimensions close to the metal centre, so less activation energy for decomposition is required, as decomposition significantly reduces the steric strain imposed upon the bonds.

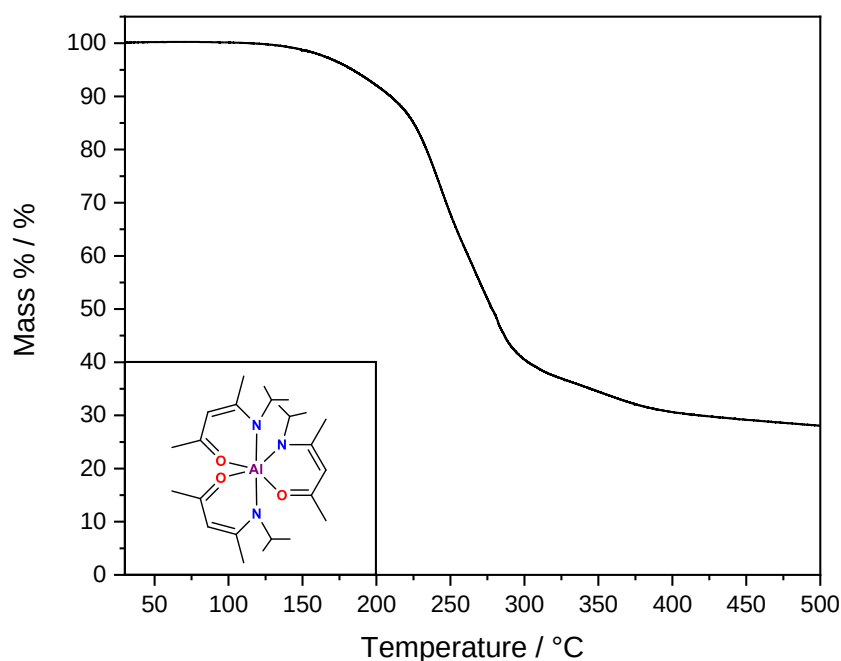


Figure 3.15: Thermogram of compound $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$ (3).

3.3.3.4 Thermal decomposition of $[\text{Al}(\text{Ph-acnac})_3]$ (4)

The thermogram of $[\text{Al}(\text{Ph-acnac})_3]$ (4) (Figure 3.16) shows decomposition at low temperature with significant mass loss beginning at 280 °C. A mass loss of 78% was recorded, with a mass loss of also 95% expected if pure Al metal is formed and 81% if pure Al_2O_3 is formed. Interestingly thermograms show a shoulder at *ca.* 180 °C, which may due to decomposition in the presence of residual oxygen, as also seen in when $\text{R} = \text{Me}$. The relatively compact aryl group (only sterically bulky in two directions) means there is little steric strain in this complex, so we do not observe the low decomposition temperature as with complex 3 ($\text{R} = \text{'Pr}$). The very high decomposition temperature is likely due to the presence of strong aromatic C–C bonds which required large amounts of energy to break in order to volatilise by-products that contribute towards mass loss.

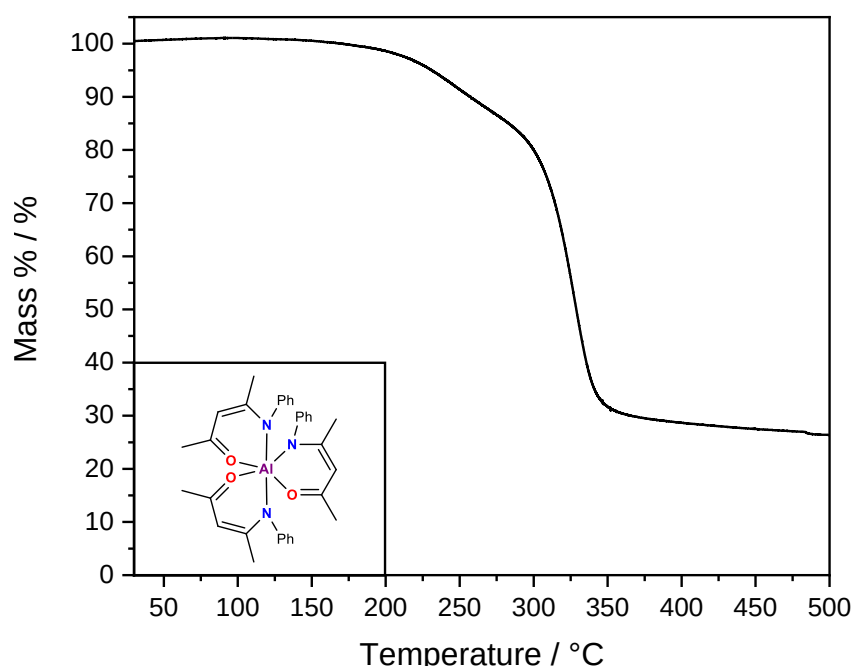


Figure 3.16: Thermogram of compound $[\text{Al}(\text{Ph-acnac})_3]$ (4).

3.3.3.5 Thermal decomposition of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5)

The thermogram of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5) (Figure 3.17) shows decomposition at low temperature with significant mass loss beginning at 256 °C. A mass loss of 79% was recorded, with a mass loss of also 96% expected if pure Al metal is formed and 85% if pure Al_2O_3 is formed. Interestingly, this complex has the second highest decomposition onset temperature of all those featured and this again may be due to aromatic nature of the R group, despite it's greater steric hindrance. There is likely less steric strain in this complex compared to when $\text{R} = i\text{Pr}$ due to complex **5** adopting a less sterically hindered five-coordinate structure as previously described in Section 3.2.2.5. The mass loss is almost identical to complex **4** ($\text{R} = \text{Ph}$) and this is likely due to the presence of the aromatic ring in the R group and similar ligand masses.

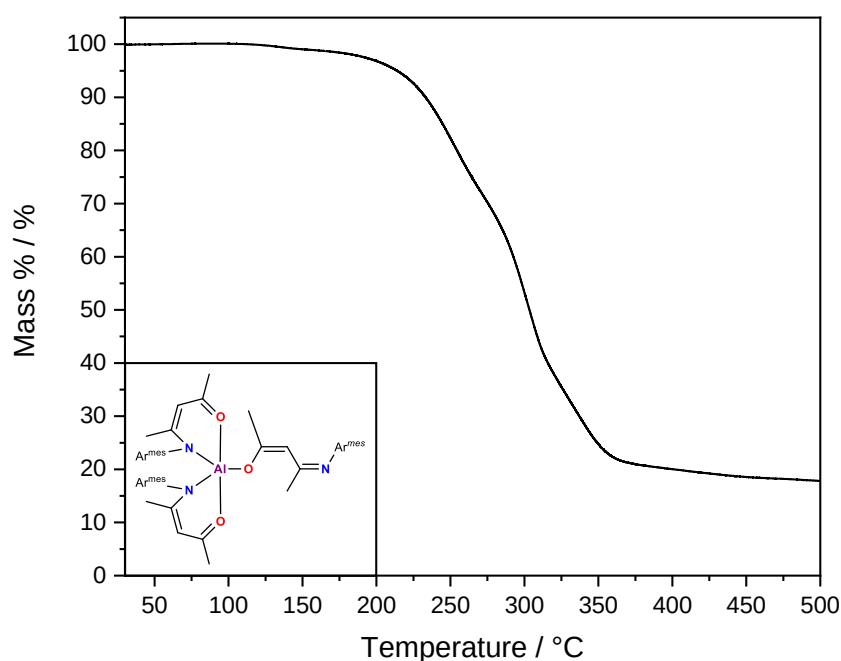


Figure 3.17: Thermogram of compound $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).

3.3.3.6 Thermal decomposition summary

This work exemplifies the usefulness in the iterative approach of changing one group on a molecule of interest at a time. In this case the *N*-substituent on the ligand of the tris(β -ketoiminate) aluminium complexes is changed in order to probe thermal trends, which would be very difficult to hypothesise without experimental results (Table 3.9).

Table 3.9: *Expected % residue, % of non-volatile residue and onset/end of volatilisation/decomposition for complexes 1–5.*

Precursor	Expected Mass Loss % for Al, Al ₂ O ₃	% Av. Non-volatile Residue	Av. Onset Temp.	Av. End Temp.
[Al(Me-acnac) ₃] (1)	93%, 72%	89%	152 °C	322 °C
[Al(Et-acnac) ₃] (2)	93%, 75%	80%	141 °C	328 °C
[Al(^{<i>i</i>} Pr-acnac) ₃] (3)	94%, 77%	69%	114 °C	415 °C
[Al(Ph-acnac) ₃] (4)	95%, 81%	78%	280 °C	346 °C
[Al(Ar ^{mes} -acnac) ₃] (5)	96%, 85%	79%	256 °C	366 °C

Figures 3.18 and 3.19 graph the onset temperature and mass loss data with associated errors for each of the five complexes thermally analysed respectively. Evidently, there is no real trend that could be predicted without the aid of these experimental results and there are many contributing factors that cause variations in decomposition characteristics such as onset temperature and complex mass loss. Only the three alkyl complexes fall within the temperature bracket desired (50–200 °C), with only the methyl and ethyl variants exhibiting exemplar mass loss properties.

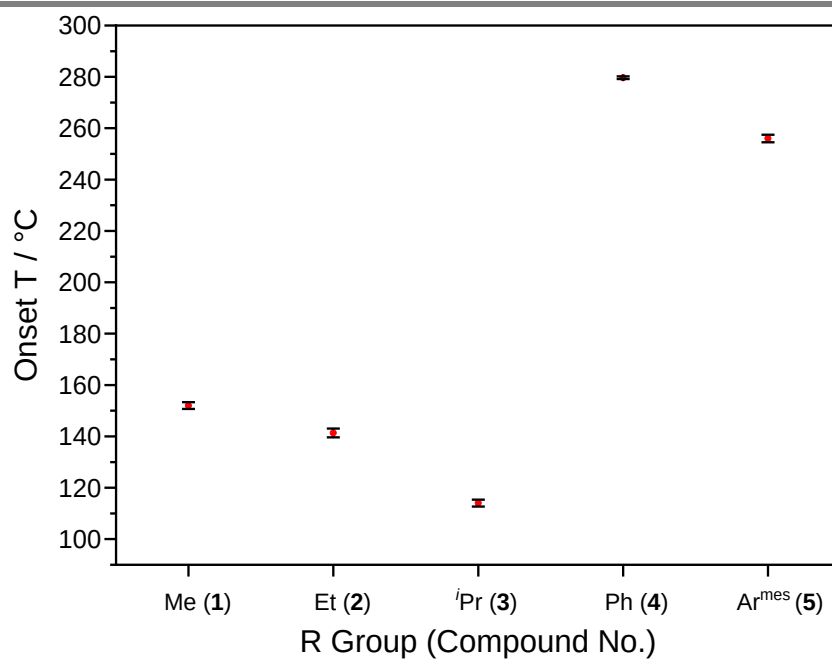


Figure 3.18: Comparison of precursor (1–5) onset decomposition temperatures with associated errors.

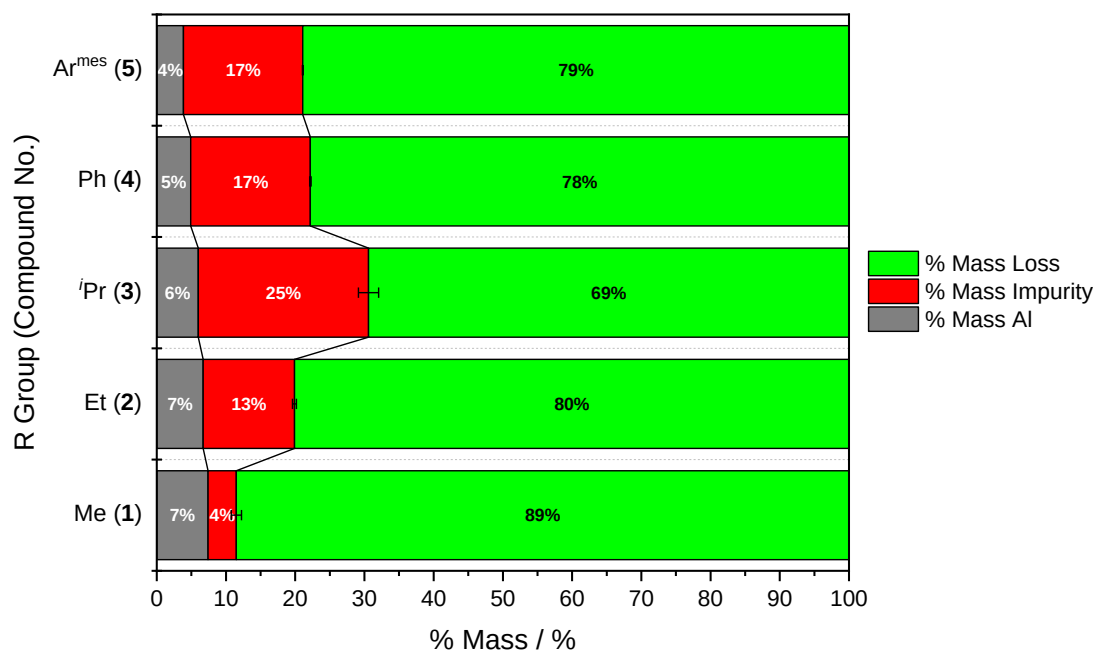


Figure 3.19: Comparison of precursor (1–5) mass loss %'s with associated errors.

3.3.4 Pyrolysis of tris(β -ketoiminate) aluminium compounds

Preliminary pyrolysis studies indicate that these compounds do not convert to aluminium metal when heated. $[\text{Al}(\text{Et-acnac})_3]$ (**2**) and $[\text{Al}(\text{Ph-acnac})_3]$ (**4**) were investigated, initially 0.5 g of each compound was loaded into a crucible in a tube furnace under a flow of N_2 and heated to 350, 400 and 500 °C in subsequent experiments. Brown powdery deposits were not conductive and XRD analysis revealed amorphous material. Since Al_2O_3 is not crystalline when formed at temperatures below 900 °C, this was not detected in the XRD pattern. Repeat experiments under vacuum yielded identical results. The investigation of these compounds as precursors to aluminium oxide represents a target for future work.

3.4 Summary

One family of compounds containing three β -ketoiminate ligands surrounding an Al centre have been synthesised, including the first examples where the *N*-substituent is an alkyl group. Like the only two other complexes of this motif in the literature, each novel complex with an alkyl *N*-substituent forms an octahedral arrangement around the Al centre as the *mer* stereoisomer, likely owing to the reduction in steric strain this causes. Interestingly, although high quality crystal structure of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$, **5** could not be obtained, the structure indicates that one of the three ligands only binds in a monodentate fashion, due to the steric congestion at the Al centre – this is the only complex of this niche motif and signifies the steric limit at which three β -ketoiminate ligands with bulky *N*-substituents can no longer all bind in a bidentate mode around the metal centre.

To assess this family's suitability as MOD precursors, each compound was thermally analysed *via* TGA. Compounds generally showed good decomposition properties, with the best precursor $[\text{Al}(\text{Me-acnac})_3]$, **1** displaying excellent mass loss properties and a low onset decomposition temperature (<200 °C), lesser than that of $[\text{Al}(\text{acac})_3]$, a well-known comparable precursor in the synthesis of Al_2O_3 thin films.

Pyrolysis experiments were less successful and perhaps these precursors need more complex set-ups in order to decompose cleanly, with deposition *via* CVD techniques an interesting avenue for the future. These compounds could have potential in a range of deposition techniques including MOCVD and ALD and since they are highly soluble in a range of organic solvents, it is hypothesised that they may be particularly applicable in solution-based techniques such as AACVD and inkjet printing.

3.5 References

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Chapter 4

Bis(β -ketoiminate) Aluminium Monochloride Compounds for use as Aluminium Precursors

This Chapter involves the synthesis of several novel bis(β -ketoiminate) aluminium monochloride compounds, with full characterisation including that by SCXRD. Finally, the suitability of these precursors is assessed by analysing their decomposition behaviour via TGA.

4.1 Introduction

General aluminium complex chemistry, as well as, the popularity and use of six-membered ring chelating ligands including β -ketoiminate ligands has been introduced in Chapter 3. This Chapter will focus on heteroleptic aluminium complexes that include halide co-ligands and β -ketoiminate ligand systems, which were introduced in Chapter 3.

4.1.1 Aluminium trichloride

Anhydrous aluminium trichloride serves as the starting material for the precursors synthesised within this Chapter. Pure aluminium chloride is white, however most commercial product has a yellow tinge due to iron chloride impurities. It reacts vigorously with water, evolving hydrogen chloride and dissolves readily in polar organic solvents. As a Lewis acid it forms adducts with numerous electron donors such as ethers, amines and alcohols. It is an important material commercially, which is mainly produced and consumed in the manufacture of aluminium metal, however it is also a popular Friedel-Crafts catalyst in the chemical and petrochemical industries.¹ AlCl_3 adopts different structures depending on its temperature and state. Solid aluminium chloride is sheet-like layered cubic close packed layers, in which the Al centres adopt octahedral geometry, sharing Cl atoms between adjacent metal centres.² As mentioned in Chapter 1, AlCl_3 can be used to deposit aluminium oxide films, however high temperatures are required and most often HCl is produced as a by-product, which can affect film quality, as well as, cause issues relating to the handling of exhaust gases and corrosion. Using metal-organic precursors can help lower deposition temperatures, in addition to, increase deposition rates.³

4.1.2 Salt metathesis reactions

Salt metathesis reactions are used to synthesise the compounds featured within this Chapter. A salt metathesis reaction, sometimes referred to as a double displacement reaction, is a chemical reaction which involves the exchange of bonds between two reaction species creating products with similar or identical (or closely similar) bonding affiliations to those in the reactants.⁴ The bonds between the reacting species can be either ionic or covalent, with the driving force of the reaction most often being the high enthalpy of formation of the resultant binary salt (*i.e.* LiCl , $\Delta_f H^\circ = -408.6 \text{ kJ mol}^{-1}$).⁵ Classically, these reactions result in the precipitation of one product. Eqn. 4.1 depicts a generic salt metathesis reaction.



4.1.3 Five-membered complexes

The complexes that dominate the bulk of this Chapter are five-coordinate at the metal centre. When a complex is five-coordinate at the metal centre, it can adopt one of two confirmations; trigonal bipyramidal or square pyramidal (Figure 4.1).

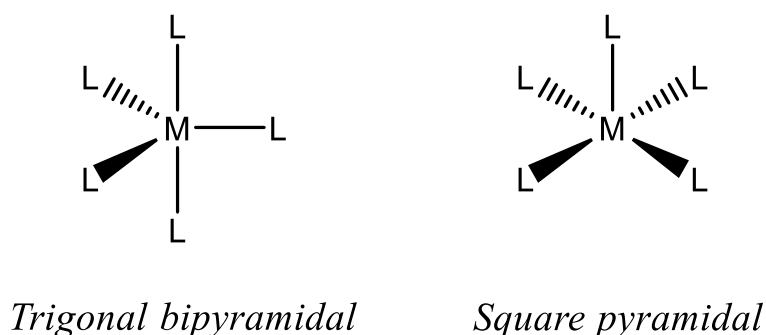


Figure 4.1: Coordination geometries for five-coordinate complexes.

In trigonal bipyramidal complexes, the five atoms bonded to the central atom at the corners of a triangular bipyramid. Not all corner atoms are equivalent, with two different types of position defined, namely: axial and equatorial. The two axial atoms sit above and below the plane of the molecule: the points of the two imaginary pyramids that molecules is formed of. Axial atoms are at 180° angle to each other when there is no molecule distortion. The three equatorial atoms lie along the plane of the molecule and at the corners of the base of the two imaginary pyramids. Equatorial atoms are at 120° angle to each other when there is no molecule distortion. Valence shell electron pair repulsion (VSEPR) theory states that an axial position is more crowded because it has three neighbouring equatorial atoms (on the same central atom) at a 90° bond angle, whilst an equatorial atom only has two neighbouring atoms at a 90° bond angle. For molecules with five identical ligands, the axial bond lengths tend to be longer as the ligand atom due to the distribution of molecular orbitals around a trigonal bipyramidal centre, as evidenced in both PF_5 and PCl_5 .⁶

In square pyramidal geometry, five atoms are bonded to the central atom at the corners of a square-based pyramid. Again not all corner atoms are equivalent, with four making up the base and one making up the point of the pyramid. This geometry is common for particular main group compounds *i.e.* XF_5 (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) that have a stereochemically active lone pair, as detailed by VSEPR theory.⁷

4.1.4 The structural parameter (τ)

The structural parameter (τ) is used to elucidate the geometry and measure the degree of distortion around a metal centre, which can be useful in determining precursor thermal stability. Compounds which are more heavily distorted from idealised geometry have a greater misalignment between bonding orbitals and can cause elongated bonds, which require less energy to break, thus lowering the temperature required for decomposition.⁸ Values range from 0 to 1, which indicates what geometry the coordination centre is in. A value of 0.5 indicates that the compound is the most distorted it can possibly be, being a hybrid of both idealised geometries. The first such parameter was developed for five-coordinate compounds (τ_5) in 1984 and a calculation for four-coordinate complexes (τ'_4) has since been developed.^{9,10}

For four-coordinate structures (featured mainly in Chapter 5), τ'_4 is defined as:

$$\tau'_4 = \frac{\beta - \alpha}{250.5^\circ} + \frac{180^\circ - \beta}{70.5^\circ} \quad (4.2)$$

Where β and α are the two largest angles at the coordination centre and $\beta > \alpha$. $\tau'_4 = 0$ indicates an idealised square planar geometry and $\tau'_4 = 1$ indicates an idealised tetrahedral geometry. Intermediate values reveal the level of distortion from either idealised geometry.⁹

For five-coordinate structures (featured in this Chapter), τ_5 is defined as:

$$\tau_5 = \frac{\beta - \alpha}{60^\circ} \quad (4.3)$$

Where β and α are the two largest angles at the coordination centre and $\beta > \alpha$. $\tau_5 = 0$ indicates an idealised square pyramidal geometry and $\tau_5 = 1$ indicates an idealised trigonal bipyramidal geometry. Again, intermediate values reveal distortion from idealised geometries.¹⁰

4.1.5 Conjugated six-membered ring chelates with halide co-ligands

Perhaps surprisingly, there is only a small selection of aluminium compounds that contain both conjugated six-membered ring chelates and halide co-ligands. No aluminium compounds containing both β -diketonate and halide ligands have been previously reported, with dileptic aluminium compounds featuring β -diketonate ligands extremely rare.^{11,12}

Aluminium complexes involving β -ketoiminate ligands and halide co-ligands do exist, however they are sparse. Interestingly, the only crystallographically characterised complexes

that feature one β -ketoiminate ligand are those that coordinate in a tridentate mode. Tridentate ligands feature a pendant tertiary amine arm ($-\text{CH}_2\text{CH}_2\text{NR}_2$, R = Me, Et) that can sufficiently stabilise the AlCl_2 moiety in a trigonal bipyramidal geometry, with contributions to the literature from Beavers *et al.*¹³ and Steiniger and co-workers¹⁴ respectively (Figure 4.2).

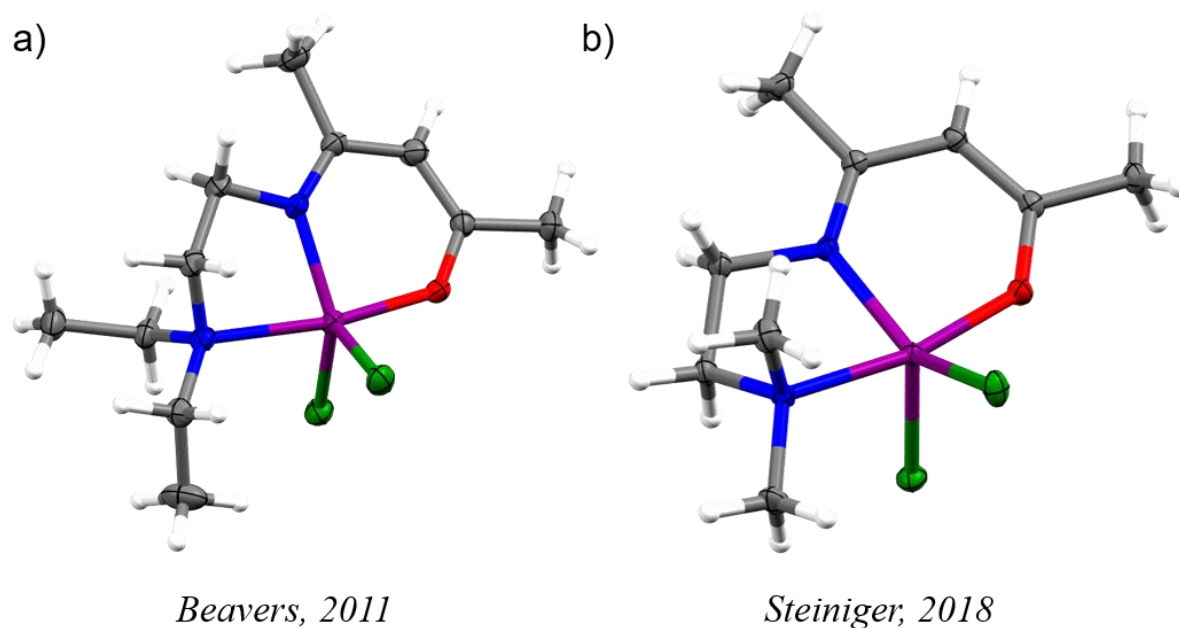
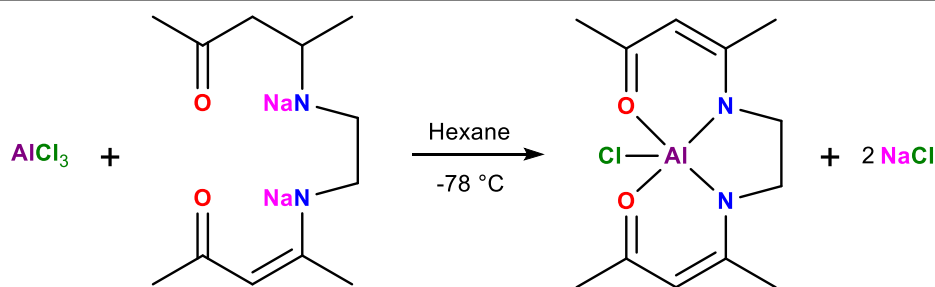


Figure 4.2: Mono(β -ketoiminate) aluminium dichloride complexes of the type $[\text{Al}(\text{L})\text{Cl}_2]$ (where L = tridentate β -ketoiminate ligand) in the literature. a) Beavers's¹³ and b) Steiniger's¹⁴ complexes, respectively.

Beavers *et al.*¹³ synthesised their complex using a salt metathesis reaction, whilst Steiniger opted to use a ligand substitution reaction by reacting the $[\text{LAlClMe}]$ (L = $(\text{MeCN}(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{CHC}=\text{OMe})_2$) variant with GaCl_3 resulting in the formation of $[\text{LAlCl}_2]$. Both Beaver's and Steiniger's complexes adopt a trigonal bipyramidal geometry with chloride ligands and the N atom from the ligand backbone in the equatorial positions. Trileptic tridentate β -ketoiminate variants also exist, with one chloride and one methyl co-ligand each, as seen above in the synthesis by Steiniger *et al.*¹⁴, as well as, by Lugo and co-workers.¹⁵

Pugh *et al.*¹⁶ report the synthesis of a tetradentate β -ketoiminate aluminium complex with one co-chloride ligand, however crystals grown were unsuitable for SCXRD analysis, with crystal structures of this complex type still eluding the literature. The tetradentate ligand featured two β -ketoiminate subunits linked by an alkyl bridge and the complex was synthesised by an elementary salt metathesis reaction (Scheme 4.1.)



Scheme 4.1: Synthesis of Pugh's tetradentate β -ketoiminate aluminium monochloride complex.¹⁶

Aluminium complexes featuring two β -ketoiminate ligands and a halide co-ligand of the type: $[\text{AlL}_2\text{Cl}]$ (L = bidentate β -ketoiminate ligand) also exist, however once again examples within the literature are infrequent. Yu *et al.*¹⁷ have made several contributions to aluminium complex chemistry using β -ketoiminate ligands, including two bis(β -ketoiminate) aluminium complexes which contain either a chloride or fluoride co-ligand. The chloride analogue was synthesised by reacting two equivalents of ligated ligand with AlCl_3 , with LiCl formation the thermodynamic driving force for the reaction (Figure 4.3a). Yu's fluoride analogue was synthesised by reacting the chloride complex with silver tetrafluoroborate, AgBF_4 in a ligand substitution reaction. The β -ketoiminate ligand used featured a bulky dipp (dipp = diisopropylaniline) *N*-substituent, with the complex forming a trigonal bipyramidal geometry with the oxygen and chlorine atoms in the equatorial positions. Interestingly, efforts were also made to synthesise the mono(β -ketoiminate) ligated product and although an impure product could be formed, crystals suitable for analysis *via* SCXRD could not be grown.

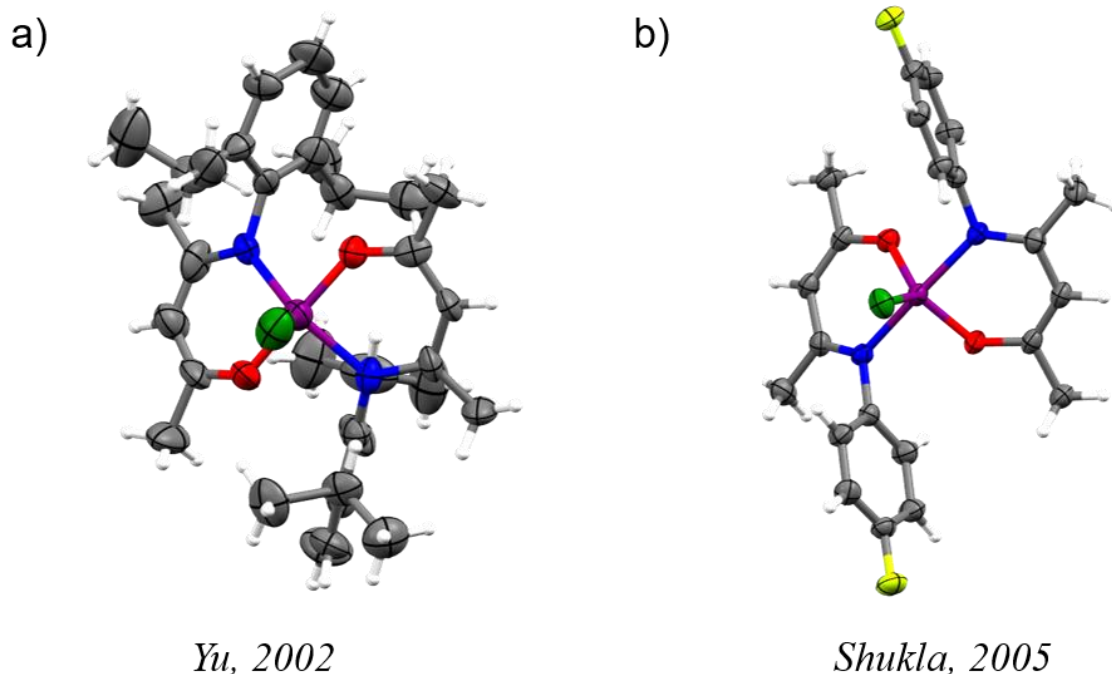


Figure 4.3: Bis(β -ketoiminate) aluminium monochloride complexes of the type $[\text{Al}(\text{L})_2\text{Cl}]$ (where L = bidentate β -ketoiminate ligand) in the literature. a) Yu's¹⁷ and b) Shukla's¹⁸ complexes, respectively.

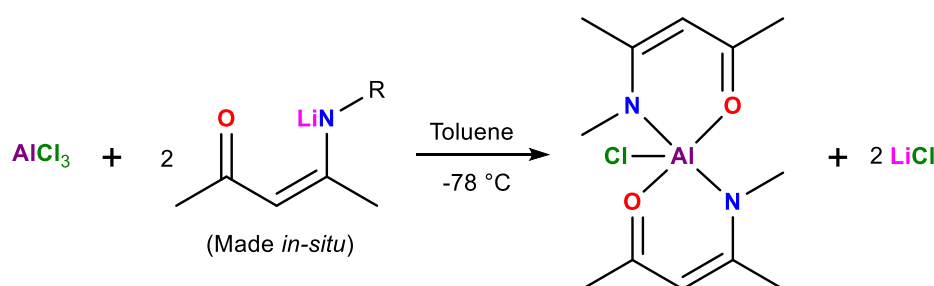
Shukla *et al.*¹⁸ also synthesised a bis(β -ketoiminate) aluminium complex using fluoroaryl *N*-substituents with a chlorine co-ligand (Figure 4.3b). Once again the halide atom occupies the equatorial positions of the trigonal bipyramidal complex, however interestingly, the oxygen atoms of the β -ketoiminate ligand now occupy the equatorial positions, with this shift likely being due to the lower steric bulk of the fluoroaryl *N*-substituent, such that they can occupy the more crowded axial positions as detailed in Section 4.1.3. The compound was synthesised *via* two routes, the first using a standard salt metathesis reaction and the second by reacting two equivalents of ligand with dimethylaluminium chloride, $[\text{AlMe}_2\text{Cl}]$, liberating methane as the entropic driving force. Other relatable compounds in the literature include Doherty's range of ethoxy bridged complexes.¹⁹

4.2 Results and discussion

Salt metathesis reactions have been employed to yield a library of bis(β -ketoiminate) aluminium monochloride compounds of the type $[\text{Al}(\text{L})_2\text{Cl}]$, where $\text{L} = \beta$ -ketoiminate. The effect of steric bulk of the coordinating ligand on the geometry at the metal centre is explored, with particular focus on X-ray crystal structural and thermal decomposition analysis.

4.2.1 Synthesis of bis(β -ketoiminate) aluminium monochloride compounds

With a view to forming aluminium complexes with low decomposition temperatures, β -ketoimine compounds were complexed to an aluminium chloride moiety *via* the reaction of lithiated β -ketoiminate (made and used *in-situ*, synthesis of which is discussed in Section 4.2.1.1–4.2.1.5) with AlCl_3 . Through numerous reactions using different molar ratios of lithium salt of the ligand, it was found that to sufficiently stabilise the aluminium centre, two equivalents were required, liberating two equivalents of LiCl as an enthalpic driving force, as shown in Scheme 4.2.



Scheme 4.2: General reaction scheme for the formation of the bis(β -ketoiminate) aluminium monochloride complexes.

LiCl being the only by-product of this reaction can be easily removed *via* filtration and the aluminium chloride complexes were generally recrystallised from toluene at -20°C . Using smaller ratios of ligand salt to AlCl_3 still resulted in the formation bis ligated adducts, but in lower yields (no mono ligated adducts could be isolated). Additionally, using greater than two equivalents would likely result in the tris complexes featured in Chapter 3. Yields were moderate, ranging from 52–95%, with differences attributed to ligand purity, effectiveness of *in-situ* ligand salt formation and how efficient the recrystallisation purification process was carried out, with syntheses often requiring multiple crystal batches to maximise yield.

There are only two similar bis(β -ketoiminate) aluminium monochloride compounds in the literature as introduced in Section 4.1.5; Yu's¹⁷ bulky dipp and Shukla's¹⁸ fluoroaryl complexes

(see Figure 4.3), with no adducts with alkyl *N*-substituents published. To the author's knowledge, no mono(bidentate β -ketoiminate) aluminium chloride complexes have ever been characterised by SCXRD, however tridentate β -ketoiminate analogues with a $-\text{CH}_2\text{CH}_2\text{NR}_2$ pendent arm have been able to sufficiently stabilise the AlCl_2 moiety as shown by Beavers¹³ and Steiniger (see Figure 4.2).¹⁴

4.2.1.1 Synthesis of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Me-acnac})_2\text{Cl}]$, **6**)

Compound **6** was prepared by the salt metathesis reaction of AlCl_3 with 2 *eq.* of lithium salt of **Me-acnacH** (made *in-situ*) in toluene at low temperatures. White crystals were formed from a filtered and concentrated toluene solution at $-20\text{ }^\circ\text{C}$ and the recrystallised compound had excellent purity, as demonstrated by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The yield was excellent (95%) due to a high efficiency of the intermediate salt formation, as well as, the recrystallisation process. The crystal structure of compound **6** was determined *via* SCXRD and is displayed in Figure 4.4. The details of the determined crystallographic data are given in Table 4.7 with selected bond lengths and angles given in Tables 4.1 and 4.8.

Table 4.1: Selected bond lengths and angles for compound **6**. Average values can be identified by the fact no estimated standard deviations values are given.

$[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6)			
Lengths / Å		Angles / °	
Al – O	1.786	O – Al – N (bite)	91.12
Al – N	1.993	O – Al – O	124.24(5)
Al – Cl	2.220	N – Al – N	176.53(5)
C – O	1.315	O – Al – Cl	117.87
C – N (backbone)	1.302	N – Al – Cl	91.42
C – N (<i>N</i> -substituent)	1.471		

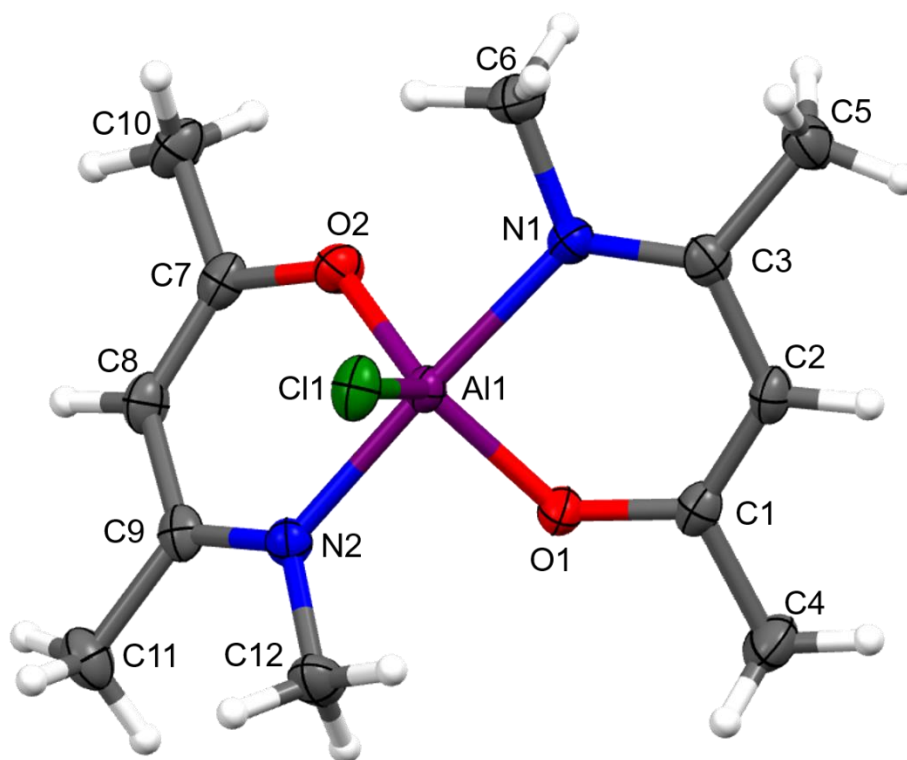


Figure 4.4: Molecular structure of compound **6**. Thermal ellipsoids are drawn at 50% probability.

Compound **6** crystallised in the orthorhombic space group *Pbca*. The complex is a 1:2 monomer, forming a mildly distorted trigonal bipyramidal arrangement around the Al centre ($\tau_5 = 0.87$), which is common for penta-coordinate Al complexes. The chelating β -ketoiminate ligands bind in a bidentate fashion, as seen in the tris(β -ketoiminate) aluminium complexes introduced in Chapter 3. The Cl and O atoms occupy the equatorial positions, whilst the N atoms occupy the axial positions, as shown by the N(1)–Al(1)–N(2) angle deviating slightly from linearity ($176.53(5)^\circ$). This motif is likely preferred for ligands with less bulky R groups as it allows the O atoms to bind in the equatorial positions, with equatorial bonds often being shorter, allowing a stronger binding interaction between Al and O, which have a very high affinity to bond to one another due to the respective electronegativities of the elements. There are only two compounds of this motif in the literature – interestingly Yu’s¹⁷ bulky dipp analogue positions the O atoms axially, whilst Shukla’s¹⁸ less bulky fluoroaryl analogue follows the same bonding mode as compound **6**, with the N atoms positioned axially.

The trigonal bipyramidal geometry is distorted with the two five-membered rings (comprised of the two bidentate ligands complexed to the Al centre) angling away from the large Cl atom, with the N(1)–Al(1)–Cl(1) and N(2)–Al(1)–Cl(1) angles being $91.20(4)^\circ$ and $91.64(3)^\circ$

respectively. There is also distortion between the axial and equatorial positions caused due to the steric constraints of the bidentate ligand, displayed by the pincer angles O(1)–Al(1)–N(1) and O(2)–Al(1)–N(2) of 90.90(4) and 91.33(4)° respectively. Finally, there are distortions between equatorial atoms, with O(1)–Al(1)–Cl(1) and O(2)–Al(1)–Cl(1) angles being 118.65(3) and 117.09(4)° respectively, deviating from the expected 120 ° angle expected for linearity, which are caused by the presence of the large electronegative Cl atom in the equatorial plane. These distortions are considerably more evident in similar structures in the literature owing to the much bulkier *N*-substituents.^{17,18} Comparing to the O–Al–N pincer angles of 90.90(4) and 91.22(4)° of complex **6** to the tris complexes in Chapter 3 (where the O(1)–Al(1)–N(1) angles range from 86.73(4)–88.10(4)°), the more acute angles found in the tris complexes are likely the result of having to crowd six ligating atoms around the Al centre, compared to five. The N–C–C–O chelate rings are also slightly less puckered than seen in the tris complexes featured in Chapter 3, as reflected by the sum of bond angles (ring of ligand 1 = 718.13°, where 720 ° is expected for a hexagon), which also agrees well with having to fit fewer chelates around the Al centre.

As expected, the Al–O bond lengths from 1.7849(9) and 1.7874(9) Å are shorter compared to the Al–N bond lengths of 1.9950(11) and 1.9915(11) Å which is caused by the smaller size and larger ionic contribution of the oxygen atoms, as seen for compound seen in Chapter 3. Longer Al–O bond lengths result in shorter Al–N bond distances on the same chelate, which is understood by the delocalised nature of the bidentate ligand. The Al–Cl bond is 2.2197(5) Å, which compares well with the few examples of these compounds in the literature (Al–Cl, Yu: 2.170(6) Å, Shukla: 2.1925(18) Å).^{17,18} Bond lengths and angles of the two β -ketoiminate ligands vary only slightly between one another and in most cases are within three estimated standard deviations of one another, hence they are classed as crystallographically identical. These observations are seen for all complexes featured within this Section so ligand specific bond lengths and angles will not be further discussed.

In addition to SCXRD characterisation, compound **6** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. The ^1H NMR spectrum of compound **6** does not show any resonances for the NH proton of the free β -ketoimine compound, the doublet *N*-methyl peak has lost its multiplicity and all peaks are shifted from the uncomplexed compound. This shift is especially seen for the *N*-substituent CH_3 group which has drastically shifted downfield by δ 1.11 ppm, due to N electron donation to the Al centre and the resulting

hyperconjugation. The environment observed furthest downfield is at δ 4.81 ppm which can be assigned to the single methine proton, whilst the peak at δ 3.11 ppm integrates to 3H for the enamino methyl protons. The terminal methyl groups on the backbone of the ligand can be observed at δ 1.79 and 1.30 ppm, which are also in agreement with the formation of the desired product. $^{13}\text{C}\{^1\text{H}\}$ NMR environments agree well with the ^1H NMR spectrum.

4.2.1.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_2\text{Cl}]$ (**[Al(Et-acnac) $_2$ Cl]**, **7**)

Compound **7** was synthesised by the same procedure as the methyl analogue, however white crystals precipitated from a concentrated mixed hexane and toluene solution at $-20\text{ }^\circ\text{C}$ in excellent purity and yield (84%). Compound **7** had particular issues crashing out from just toluene at low temperature, so action was taken to dissolve the compound in the less polar hexane, which could not be achieved until a small amount of toluene was added. Upon placing the concentrated solution in the freezer ($-20\text{ }^\circ\text{C}$) overnight, a large batch of pure compound precipitated out. The crystal structure of compound **7** was determined *via* SCXRD and is displayed in Figure 4.5. The detail of the determined crystallographic data are given in Table 4.7 with selected bond lengths and angles given in Tables 4.2 and 4.8.

Table 4.2: Selected bond lengths and angles for compound **7**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Et-acnac)$_2$Cl] (7)			
Lengths / Å		Angles / °	
Al – O	1.783	O – Al – N (bite)	91.37
Al – N	2.003	O – Al – O	122.09(5)
Al – Cl	2.215	N – Al – N	178.81(5)
C – O	1.317	O – Al – Cl	118.96
C – N (backbone)	1.304	N – Al – Cl	90.43
C – N (N- substituent)	1.477		

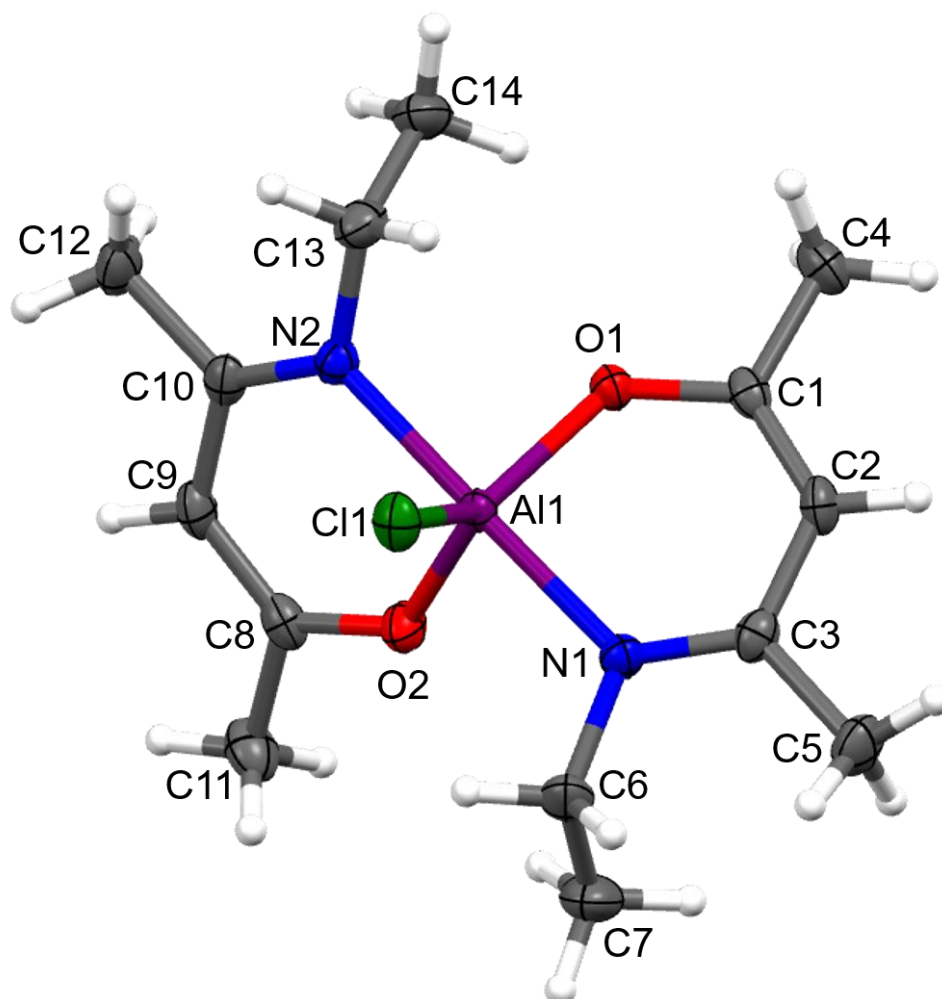


Figure 4.5: Molecular structure of compound **7**. Thermal ellipsoids are drawn at 50% probability.

Compound **7** crystallised in the lower symmetry triclinic space group $P\bar{1}$. Two bidentate ligands bind to the metal centre in the same mode as with compound **6** ($R = \text{Me}$). There are two independent molecules in the unit cell for complex **7**; however, only one is described due to their similarity – this is also observed for Yu’s dipp analogue.¹⁷ As with complex **6**, there is trigonal bipyramidal arrangement around the metal centre with the N atoms bonded axially, as seen when less bulky *N*-substituents are present. Interestingly, there are overall smaller distortions in the ethyl analogue compared to the methyl ($\tau_5 = 0.95$), displayed by the N(1)–Al(1)–N(2), O(1)–Al(1)–Cl(1) and O(2)–Al(1)–Cl(1) angles of 178.81(5), 120.61(4), and 117.30(4)° respectively. Al–O bonds are marginally shorter (Al(1)–O(1): 1.7839(10) Å, Al(1)–O(2): 1.7817(10) Å), whilst Al–N bonds are marginally longer (Al(1)–N(1): 2.0009(11) Å, Al(1)–N(2): 2.0050(11) Å) which is most likely due to the added size of the ethyl group and delocalised nature of the ligands, which was also a trend for the tris structures in Chapter 3.

The Al(1)–Cl(1) bond of the ethyl complex (2.2150(5) Å) is slightly shorter than in the methyl complex, which may be as a result of greater N atom electron donating effects caused by greater hyperconjugation from the longer carbon chain supplying more electron density to the Al centre, which can in turn donate more electron density to the Cl atom producing a shorter bond.

In addition to SCXRD characterisation, compound **7** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. Again, as expected the ^1H NMR spectrum of compound **7** does not show any resonances for the NH proton of the free β -ketoimine compound, there is a loss of multiplicity at the *N*-adjacent methylene group and peaks are shifted. Interestingly, the complexation of this compound to the aluminium centre results in geminal coupling at the methylene, CH_2 groups, shown by the separation of the environment into two broad peaks at δ 3.80 and 3.41 ppm in a 2:2 ratio. Coordination results in the proton environments becoming inequivalent and their broad nature suggests a degree of fluxionality, which could be further investigated by variable temperature (VT) NMR studies. There have been instances where the extent of fluxionality of chelating ligands to a centre in a precursor was directly related to its thermal decomposition profile, with more fluxionality resulting in lower decomposition temperatures.²⁰ The methine proton of complex is once again the most downfield peak and is also found at δ 4.81 ppm. After the diastereotopic methine proton environments come the terminal protons for the keto (δ 1.78 ppm) and enamino (δ 1.47 ppm) groups on the backbone, which both integrate to 6H each for the two ligands in the complex. The lowest ppm protons are the methyl protons (δ 1.20 ppm) which have been upfield shifted from the region in complex **6** (R = Me), due to being one further methylene group away from the electron-withdrawing nitrogen atom. $^{13}\text{C}\{^1\text{H}\}$ NMR environments are in agreement with the ^1H NMR spectrum.

4.2.1.3 Synthesis of [Al(MeCN(*i*Pr)CHC=OMe)₂Cl] ([Al(*i*Pr-acnac)₂Cl], **8**)

Compound **8** was also synthesised using a salt metathesis reaction as with **6** and **7**, again, with the lithium salt synthesised *in-situ*. Compound **8** was recrystallised from a concentrated toluene solution at $-20\text{ }^{\circ}\text{C}$ as seen before in excellent purity and yield (86%). The crystal structure of compound **8** was determined via SCXRD and is displayed in Figure 4.6. The detail of the determined crystallographic data are given in Table 4.7 with selected bond lengths and angles given in Tables 4.3 and 4.8.

Table 4.3: Selected bond lengths and angles for compound **8**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(<i>i</i> Pr-acnac) ₂ Cl] (8)			
Lengths / Å		Angles / °	
Al – O	1.7714(11)	O – Al – N (bite)	92.06(5)
Al – N	2.0255(13)	O – Al – O	121.25(8)
Al – Cl	2.2131(8)	N – Al – N	178.30(8)
C – O	1.3123(19)	O – Al – Cl	119.38(4)
C – N (backbone)	1.305(2)	N – Al – Cl	90.85(4)
C – N (<i>N</i> -substituent)	1.497(2)		

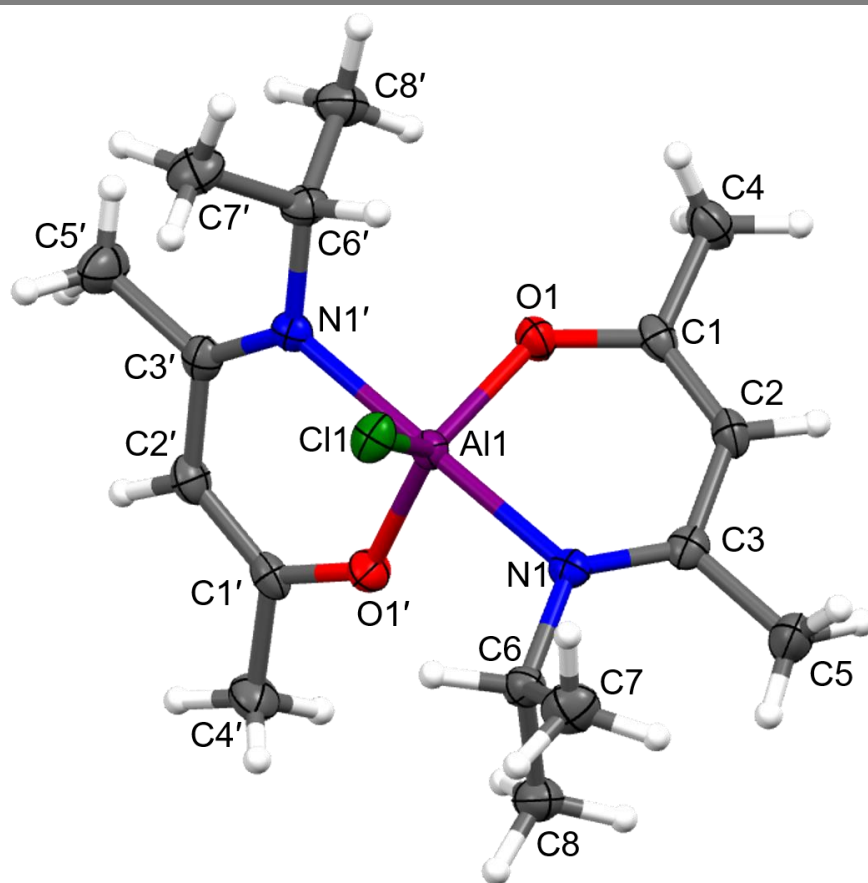


Figure 4.6: Molecular structure of compound **8**. Thermal ellipsoids are drawn at 50% probability.

Compound **8** crystallised in the monoclinic space group $C2/c$. Two bidentate ligands bind to the metal centre in the same mode as with compounds **6** and **7**, however in this complex, the second ligand is generated by symmetry *via* a twofold rotation axis that lies along the Al(1)–Cl(1) bond, as seen in Shukla’s fluoroaryl complex.¹⁸ Again the trigonal bipyramidal arrangement around the metal centre is distorted, with the N atoms bonded axially, indicating that the isopropyl groups are still not bulky enough to shift to an O axial structure. As expected, the isopropyl analogue has marginally more bond angles compared to the ethyl complex, with N(1)–Al(1)–N(1)’ and O(1)–Al(1)–Cl(1) of 178.30(8) and 119.38(4)° respectively, however overall the complex displays near identical distortion from ideal trigonal bipyramidal geometry ($\tau_5 = 0.95$). Interestingly, like the ethyl complex, compound **8** is not as distorted as the methyl analogue. The O(1)–Al(1)–N(1) angle of this complex departs the most from linearity compared the other synthesised structures of this motif, due the three-dimensional steric bulk of the isopropyl group, wanting to be further away from the adjacent backbone CH₃ group below it. Al–O (Al(1)–O(1): 1.7714(11) Å) and Al–N (Al(1)–N(1): 2.0255(13) Å) bonds follow the observed trends in increasing steric bulk of the *N*-substituent

and there is a very marginal change in Al–Cl bond distance from the methyl and ethyl complexes (Al(1)–Cl(1): 2.2131(8) Å).

In addition to SCXRD characterisation, compound **8** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. As expected, the ^1H NMR spectrum of compound **8** does not show any resonances for the NH proton of the free β -ketoimine compound evidencing completion of the reaction. There is a loss of multiplicity at the *N*-adjacent methylene group and peaks are shifted. Interestingly, multiplicity is not resolved at the terminal methyl groups on the isopropyl R group, which is not observed for the terminal methyl group on complex **8** (R = Et). As expected, the methine proton on the ligand backbone is the furthest downfield peak at δ 4.75 ppm, closely followed by the methine proton adjacent to the N atom. The remaining peaks correspond to the terminal protons for the keto (δ 1.76 ppm) and enamino (δ 1.65 ppm) groups on the backbone, as well as, the methyl groups of the isopropyl group (δ 1.41 ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR environments are agreement with proton NMR, showing non-equivalent terminal methyl groups on the isopropyl group.

4.2.1.4 Synthesis of [Al(MeCN(Ph)CHC=OMe)₂Cl] ([Al(Ph-acnac)₂Cl], **9**)

Compound **9** was synthesised by the same using the LiHMDS procedure as for the other compounds featured within this Chapter, with white crystals precipitated from a concentrated toluene solution at $-20\text{ }^\circ\text{C}$ in excellent purity and moderate yield (52%). The crystal structure of compound **9** was determined *via* SCXRD and is displayed in Figure 4.7. The detail of the determined crystallographic data are given in Table 4.7 with selected bond lengths and angles given in Tables 4.4 and 4.8.

Table 4.4: Selected bond lengths and angles for compound **9**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Ph-acnac) ₂ Cl] (9)			
Lengths / Å		Angles / °	
Al – O	1.7718(9)	O – Al – N (bite)	90.16(4)
Al – N	2.0377(11)	O – Al – O	121.66(7)
Al – Cl	2.1895(7)	N – Al – N	173.00(6)
C – O	1.3088(16)	O – Al – Cl	119.17(3)
C – N (backbone)	1.3113(17)	N – Al – Cl	93.50(3)
C – N (<i>N</i> -substituent)	1.4487(16)		

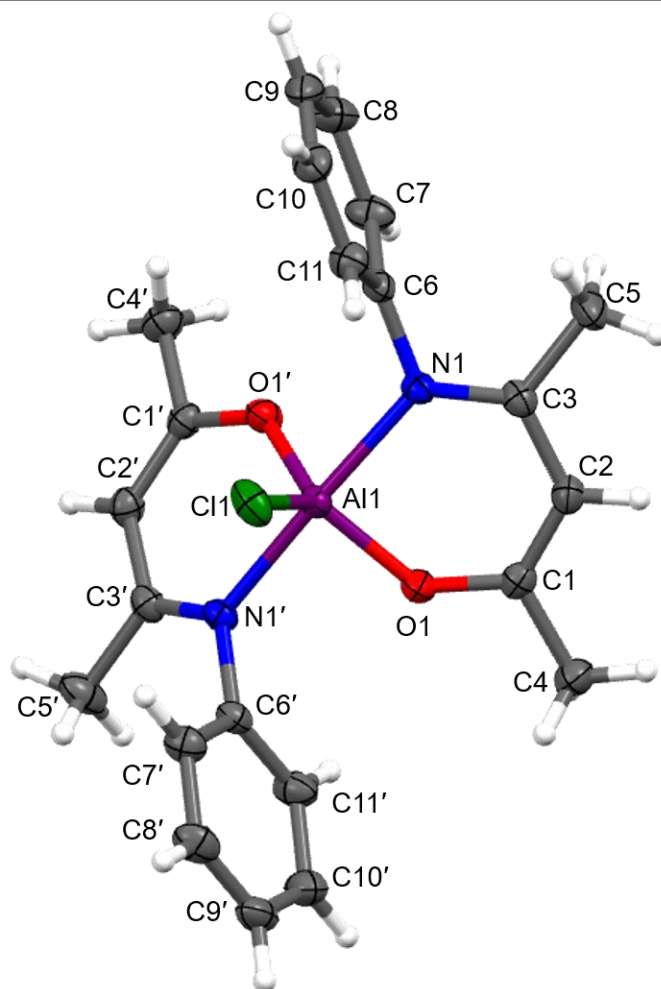


Figure 4.7: Molecular structure of compound **9**. Thermal ellipsoids are drawn at 50% probability.

Compound **9** crystallised in the monoclinic space group $C2/c$. Two bidentate ligands bind to the metal centre in the same mode as with the other compounds in this Chapter and like compound **8** ($R = iPr$), the second ligand is generated by symmetry via a twofold rotation axis that lies along the $Al(1)–Cl(1)$ bond. The trigonal bipyramidal arrangement around the metal centre is the most distorted from the idealised geometry of all the complexes featured within this Section ($\tau_5 = 0.86$), with the N atoms bonded axially, indicating that the phenyl groups are again not bulky enough to the shift to an O axial structure, which can be comprehended as Shukla's marginally bulkier fluoroaryl complex still adopts this conformation.¹⁸ Interestingly, unlike in the tris complexes featured in Chapter 3, the bis Ph-acnac, **9** analogue has greater distortions from linearity than the bis iPr -acnac, **8** complex. This is most significantly depicted by the axial $N(1)–Al(1)–N(1')$ angle of $173.00(6)^\circ$ in **9** (compared to $178.30(8)^\circ$ in **8**). Thus, the ligands bend further away from the Cl atom and may be a result of the orientation of the

phenyl groups, orienting themselves in such a way to lower clash between each ligand in the bis complex. Intriguingly, the O(1)–Al(1)–N(1) pincer angle of $90.16(4)^\circ$ is the lowest of all the crystal structures in this Section, which is most likely due to the low axial N–Al–N angle. There is an extremely small difference in the Al–O bond distance compared to the isopropyl analogue ($1.7718(9)$ Å in **9**, compared to $1.7714(11)$ Å in **8**) however there is a noticeable difference in the Al–N bond distance (**9**: $2.0377(11)$ Å, **8**: $2.0377(11)$ Å) with the longest axial Al–N bond length featured in this Chapter, due to the bulky phenyl group. The longest axial Al–N bond length, results in the shortest Al–Cl length of $2.1895(7)$ Å.

In addition to SCXRD characterisation, compound **9** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. Again, the ^1H NMR spectrum of compound **9** does not show any resonances for the NH proton of the free β -ketoimine compound, in addition to, there being peaks shifted. Singlet peaks at δ 4.88 ppm (CH), 1.47 (CH_3CO), and 1.36 ppm (CH_3CN) in a 2:6:6 ratio agree with the formation of the **9**. The aromatic region in the ^1H NMR spectrum is difficult to fully characterise, due to their being broad overlapping peaks, as well as, the solvent C_6D_6 peak at δ 7.16 ppm occurring in the same region, however the overall integration of this region does sum to ten protons. $^{13}\text{C}\{^1\text{H}\}$ NMR environments agree with peaks in the ^1H NMR spectrum.

4.2.1.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$, **10**), where Ar^{mes} = 2,4,6-trimethylphenyl

Compound **10** was synthesised using the aforementioned salt metathesis reaction, with white crystals precipitated from a concentrated toluene solution at -20°C in excellent purity (as confirmed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR) and moderate yield (53%). The crystal structure of compound **10** was determined *via* SCXRD and is displayed in Figure 4.8a, along with a view of the structure along the O–Al–O axis in Figure 4.8b. The detail of the determined crystallographic data are given in Table 4.7 with selected bond lengths and angles given in Tables 4.5 and 4.8.

Table 4.5: Selected bond lengths and angles for compound **10**. Average values can be identified by the fact no estimated standard deviations values are given.

[Al(Ar ^{mes} -acnac) ₂ Cl] (10)			
Lengths / Å		Angles / °	
Al – O	1.8286(12)	O – Al – N (bite)	90.30
Al – N	1.9718(13)	O – Al – O	179.77(8)
Al – Cl	2.2176(8)	N – Al – N	119.82(8)
C – O	1.288(2)	O – Al – Cl	89.88(4)
C – N (backbone)	1.331(2)	N – Al – Cl	120.09(4)
C – N (N- substituent)	1.449(2)		

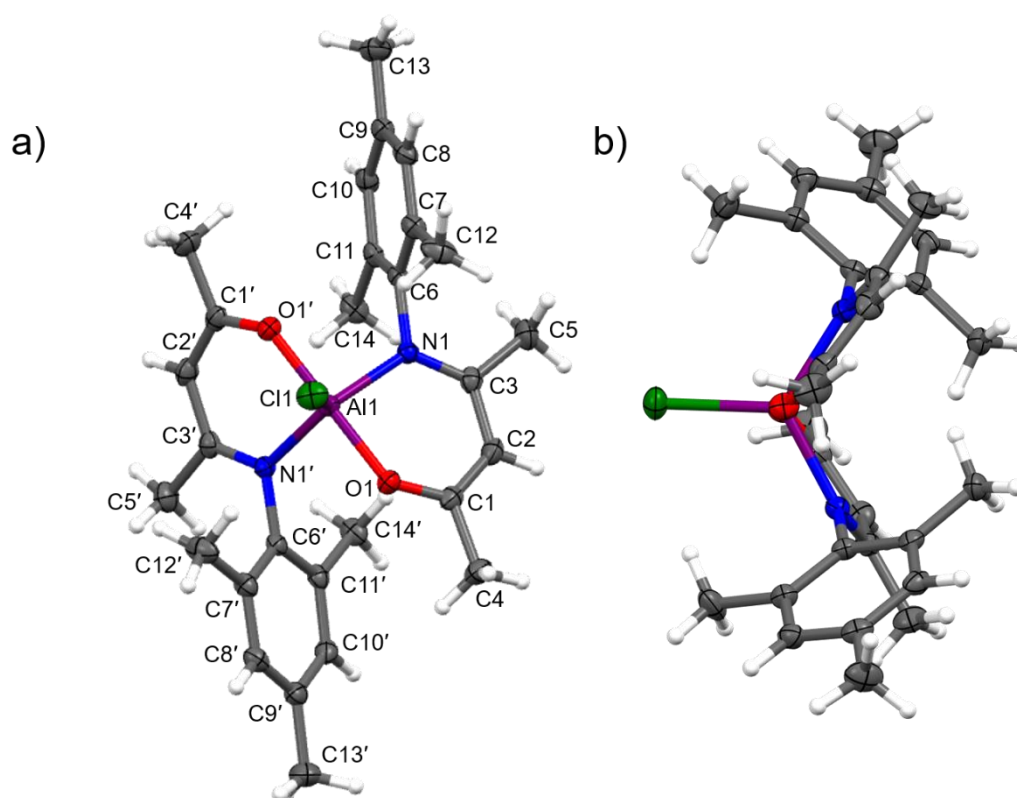


Figure 4.8: a) Molecular structures of compound **10**. Thermal ellipsoids are drawn at 50% probability. b) Compound **10** along O–Al–O axis.

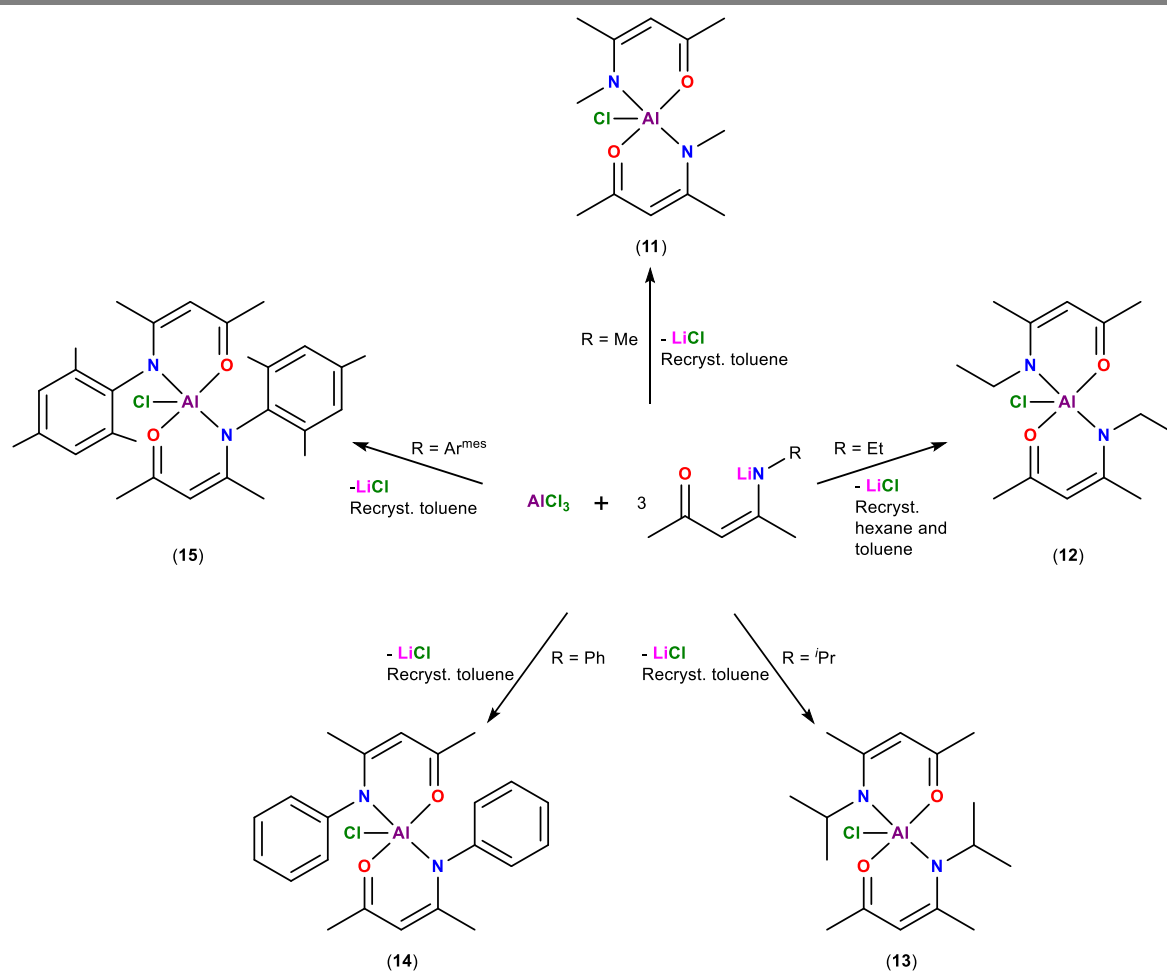
Compound **10** crystallised in the tetragonal space group $P4_32_12$. Two bidentate ligands bind to the metal centre as with compounds **6–9** and the second ligand is generated by symmetry via a twofold rotation axis that lies along the Al(1)–Cl(1) bond, such as for compounds **8** (R = *i*Pr) and **9** (R = Ph). However, one striking difference between compound **10** and the others featured in this Chapter is that the O atoms, rather than the N atoms, occupy the axial

positions in the trigonal bipyramidal geometry, exemplified by an O(1)–Al(1)–O(1)' angle of nearly 180 °, deviating slightly from linearity at 179.77(8)°. This bonding motif was previously seen in Yu's bulky dipp analogue, suggesting that the steric bulk of the Ar^{mes} group is great enough to cause this shift.¹⁷ This shift may be caused by being able to more efficiently pack molecules in the unit cell when the very bulky imino groups are in the equatorial positions or may be a method in achieving the most idealised trigonal bipyramidal geometry, as shown by an essentially perfect structure parameter for a trigonal bipyramidal complex ($\tau_5 = 1.00$, when rounded to 2 d.p.). Comparing the axial angle to Yu's complex (O(1)–Al(1)–O(2): 168.8(5)°) we can see that Yu's bulkier dipp complex has a greater effect on the ligands pulling away from the Cl atom. Just like the axial angle, the equatorial angles (N(1)–Al(1)–N(1)': 119.82(8)°, N(1)–Al(1)–Cl(1): 120.09(4)°) deviate only minimally from linearity, unlike that of Yu's complex (N(1)–Al(1)–N(1)': 134.6(4)°, N(1)–Al(1)–Cl(1): 117.2(3)°, N(2)–Al(1)–Cl(1): 108.2(4)). Comprehensibly, the Al–O bond length has increased (1.8286(12) Å) and Al–N bond length has decreased (1.9718(13) Å) compared to the other complexes featured within this Chapter, due to the tendency of axial bonds being longer and equatorial bonds being shorter than their opposite counterparts, as stated by orbital overlap theory. The Al–Cl bond length of 2.2176(8) Å is comparable to all structures featured, apart from the phenyl analogue which is shorter, as discussed in the following Section (4.2.1.6).

In addition to SCXRD characterisation, compound **10** was also identified *via* ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR (with aid of 2D spectra), MS and EA. The ^1H NMR spectrum of compound **10** does not show any resonances for the NH proton of the free β -ketoimine compound, with all peaks shifted from the uncomplexed β -ketoimine compound. Interestingly, complexation of the β -ketoimine compound to the aluminium centre results in a splitting of the Ar–H (δ 6.84, 6.75 ppm) and *ortho* Ar–CH₃ (δ 2.52, 2.00 ppm) signals, suggesting groups are no longer equivalent as a result of not being able to rotate about the N–C bond due to steric clash. VT NMR may be able to elucidate whether this rotation is unfeasible or just slow with respect to the NMR timescale. Other notable signals include the methine protons at δ 4.97 ppm, the *para* Ar–CH₃ groups at δ 2.19 ppm and the terminal methyl groups of the keto and enamino groups at δ 1.35 and 1.29 ppm respectively. $^{13}\text{C}\{^1\text{H}\}$ NMR environments are in agreement with the formation of **10**.

4.2.1.6 Comparison of crystal structures

Scheme 4.3 summarises the reaction and recrystallisation conditions for compounds **1–5**. Table 4.6 shows a comparison of the average Al–O, Al–N and Al–Cl bond lengths, as well as, the average O–Al–N ligand pincer angles found in each of the five novel complexes featured within this Section. There is a clear trend in the lengthening of the axial nitrogen atoms as the size of the *N*-substituent increases from methyl through to phenyl, which is most likely explained due to sterics, as when larger R groups are present on the N atom, the ligand must pull further away from the complex centre to avoid steric clash. The effects of hyperconjugation do not play a key role in determining the Al–N bond distances between differing *N*-substituents, as shorter bond distances for longer/more branched alkyl chains are not observed. The lengthening of the Al–N bond is accompanied by the trend of shortening of the Al–O bond from methyl through to phenyl, due to the synergistic binding nature of the chelating ligands. We see a drastic reduction in the Al–N bond length and increase in the Al–O bond length compared to other complexes for when $R = Ar^{mes}$, and this is due to the N and O atoms switching from their axial and equatorial positions respectively, a phenomenon observed previously for other bulky complexes of this motif as highlighted in Section 4.1.5. The Al–Cl bond distances do not vary much between complexes, apart from for that when $R = Ph$, with this most likely being due to a combination of complex geometry and mesomeric electron withdrawing effects of the phenyl ring on the N lone pair, which results in a longer Al–N bond and thus the Cl atom can bind closer to the metal centre – this observation is not seen for the other complex with aryl substituents (**10**) due to the shift in axial and equatorial positions for the O and N atoms. The O–Al–N pincer angles vary across the series and most interestingly, the aryl adducts display pincer angles closest to the expected angle of 90°. The largest pincer angle of 92.06° is a result of the bulky ⁱPr *N*-substituents being in the axial position.



Scheme 4.3: Synthesis and recrystallisation conditions of various bis(β -ketoiminate) aluminium chloride complexes with the formula: $[\text{AlL}_2\text{Cl}]$ (where $L =$ bidentate β -ketoiminate).

Table 4.6: Comparison of average Al–O and Al–N bond lengths, as well as, O–Al–N pincer angles for complexes **6**–**10**.

R Group	Me (6)	Et (7)	ⁱ Pr (8)	Ph (9)	Ar ^{mes} (10)
Avg. Bond Length					
Al—O	1.786	1.783	1.771	1.772	1.829
Al—N	1.993	2.003	2.023	2.038	1.972
Al—Cl	2.220	2.215	2.213	2.190	2.218
Avg. Bond Angle					
	91.12	91.37	92.06	90.16	90.30

Table 4.7: Crystallographic data for structurally characterised compounds 6–10.

Compound	[Al(Me-acnac) ₂ Cl] (6)	[Al(Et-acnac) ₂ Cl] (7)	[Al(ⁱ Pr-acnac) ₂ Cl] (8)	[Al(Ph-acnac) ₂ Cl] (9)	[Al(Ar ^{mes} -acnac) ₂ Cl] (10)
Empirical formula	C ₁₂ H ₂₀ AlClN ₂ O ₂	C ₁₄ H ₂₄ AlClN ₂ O ₂	C ₁₆ H ₂₈ AlClN ₂ O ₂	C ₂₂ H ₂₄ AlClN ₂ O ₂	C ₂₈ H ₃₆ AlClN ₂ O ₂
Fw / g mol ⁻¹	286.73	314.78	342.83	410.86	495.02
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Tetragonal
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 4 ₃ 2 ₁ 2
<i>a</i> / Å	9.92920(10)	8.97922(17)	11.3290(3)	12.1425(2)	15.91110(10)
<i>b</i> / Å	12.27050(10)	13.8461(3)	11.3991(3)	12.2037(2)	15.91110(10)
<i>c</i> / Å	24.4057(2)	15.05909(3)	14.1862(3)	13.9522(3)	10.56760(10)
α / °	90	68.945(2)	90	90	90
β / °	90	85.2964(17)	94.627(2)	93.853(2)	90
γ / °	90	72.7480(18)	90	90	90
<i>V</i> / Å ³	2973.50(5)	1668.01(7)	1826.04(7)	2062.81(7)	2675.33(4)
<i>Z</i>	8	4	4	4	4
ρ_{calc} / g cm ⁻³	1.281	1.253	1.247	1.323	1.229
μ / mm ⁻¹	2.827	2.563	2.381	2.212	1.787
Reflections collected	47242	24221	12215	15305	44166
Independent reflections	2956	6554	1269	2036	2657
<i>R</i> _{int}	0.0451	0.0305	0.0215	0.0322	0.0355
<i>R</i> ₁ and <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0295, 0.0838	0.0337, 0.0916	0.0252, 0.0714	0.0309, 0.0853	0.0262, 0.0727
<i>R</i> ₁ and <i>wR</i> ₂ [all data]	0.0313, 0.0862	0.0349, 0.0928	0.0268, 0.0729	0.0325, 0.0870	0.0264, 0.0731

Table 4.8: Selected bond lengths (Å) and angles (°) for compounds 6–10.

Compound	[Al(Me-acnac) ₂ Cl] (6)	[Al(Et-acnac) ₂ Cl] (7)	[Al(ⁱ Pr-acnac) ₂ Cl] (8)	[Al(Ph-acnac) ₂ Cl] (9)	[Al(Ar ^{mes} -acnac) ₂ Cl] (10)
Lengths / Å					
Al(1) – O(1)	1.7849(9)	1.7839(10)	1.7714(11)	1.7718(9)	1.8286(12)
Al(1) – O(2)	1.7874(9)	1.7817(10)	-	-	-
Al(1) – N(1)	1.9950(11)	2.0009(11)	2.0255(13)	2.0377(11)	1.9718(13)
Al(1) – N(2)	1.9915(11)	2.0050(11)	-	-	-
Al(1) – Cl(1)	2.2197(5)	2.2150(5)	2.2131(8)	2.1895(7)	2.2176(8)
O(1) – C(1)	1.3158(15)	1.3169(16)	1.3123(19)	1.3088(16)	1.288(2)
N(1) – C(3)	1.3045(17)	1.3032(18)	1.305(2)	1.3113(17)	1.331(2)
N(1) – C(6)	1.4723(17)	1.4778(17)	1.497(2)	1.4487(16)	1.449(2)
Angles / °					
O(1) – Al(1) – O(1)'	-	-	121.25(8)	121.66(7)	179.77(8)
O(1) – Al(1) – O(2)	124.24(5)	122.09(5)	-	-	-
O(1) – Al(1) – N(1)	90.90(4)	91.04(5)	92.06(5)	90.16(4)	90.30(5)
O(1) – Al(1) – N(1)'	-	-	87.11(5)	86.43(4)	89.82(6)
O(1) – Al(1) – N(2)	85.99(4)	87.81(5)	-	-	-
O(1) – Al(1) – Cl(1)	118.65(3)	120.61(4)	119.38(4)	119.17(3)	89.88(4)
O(2) – Al(1) – N(2)	91.33(4)	91.69(5)	-	-	-
O(2) – Al(1) – Cl(1)	117.09(4)	117.30(4)	-	-	-
N(1) – Al(1) – O(2)	89.16(4)	88.65(5)	-	-	-
N(1) – Al(1) – N(1)'	-	-	178.30(8)	173.00(6)	119.82(8)
N(1) – Al(1) – N(2)	176.53(5)	178.81(5)	-	-	-
N(1) – Al(1) – Cl(1)	91.20(4)	90.74(4)	90.85(4)	93.50(3)	120.09(4)
N(2) – Al(1) – Cl(1)	91.64(3)	90.12(4)	-	-	-

4.2.2 Thermal decomposition analysis of bis(β -ketoiminate) aluminium monochloride compounds

The thermal decomposition properties of the bis(β -ketoiminate) aluminium compounds **6–10** were analysed by TGA using the methodology as stated in Chapter 2. The thermal analysis of the ligands used in this Chapter are featured in the Appendices (Appendix 103). Full TGA and DTG analysis of complexes **6–10** is featured in the Appendices (Appendix 115–124).

4.2.2.1 Thermal decomposition of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (**6**)

The thermogram of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (**6**) (Figure 4.9) shows decomposition at low temperature with significant mass loss beginning at 166 °C. A mass loss of 74% was recorded, with a mass loss of 91% expected if pure Al metal is formed and 64% if pure Al_2O_3 is formed. The decomposition of compound **6** is promising as it lies within the temperature range desired for low temperature deposition techniques (50–200 °C) and its high mass loss likely indicates aluminium metal is formed (in preference to aluminium oxide) along with carbon-based impurities. It could be postulated that the recorded mass loss of this precursor maybe slightly overestimated as there is a small decrease in mass leading up to the decomposition onset (small shoulder at 115 °C, seen in all repeats.) This slow mass low could also be due to **1** being volatile, even at modest temperatures, which could relate to the $\text{R} = \text{Me}$ β -ketoimine compound itself having the highest volatility of all the β -ketoimine compounds used, a phenomenon which was also seen for the methyl variant of the tris complexes in Chapter 3.

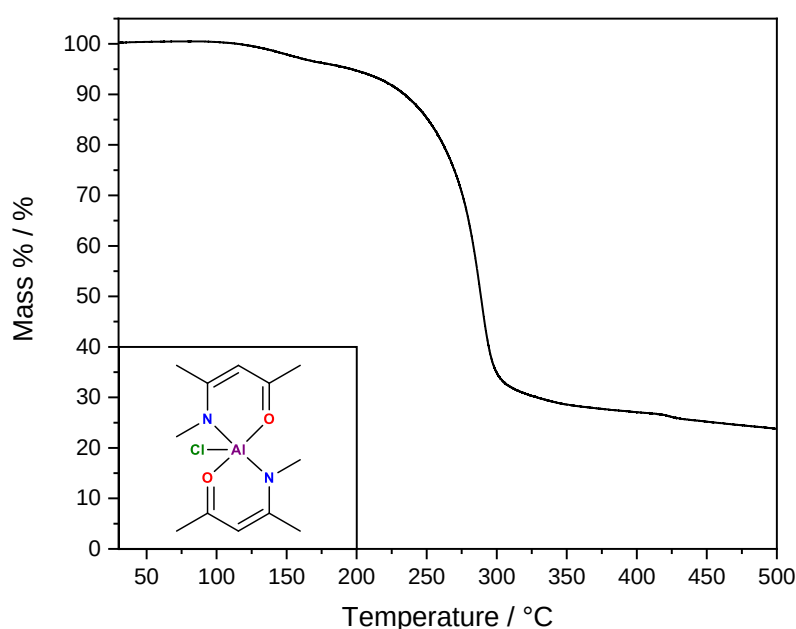


Figure 4.9: Thermogram of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (**6**).

4.2.2.2 Thermal decomposition of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7)

The thermogram of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7) (Figure 4.10) shows decomposition at very low temperature with significant mass loss beginning at 116 °C. A mass loss of 71% was recorded, with a mass loss of also 91% expected if pure Al metal is formed and 68% if pure Al_2O_3 is formed. Complex 7's thermal properties are very promising, exhibiting the lowest decomposition temperature out of all complexes of this type (and lowest of all novel complexes synthesised in this thesis). The mass losses calculated are slightly less than those for when $\text{R} = \text{Me}$, however the decrease in onset for decomposition of around 50 °C greatly outweighs this. Once again, the mass loss indicates that compound decomposes to aluminium metal with carbon impurities rather than aluminium oxides.

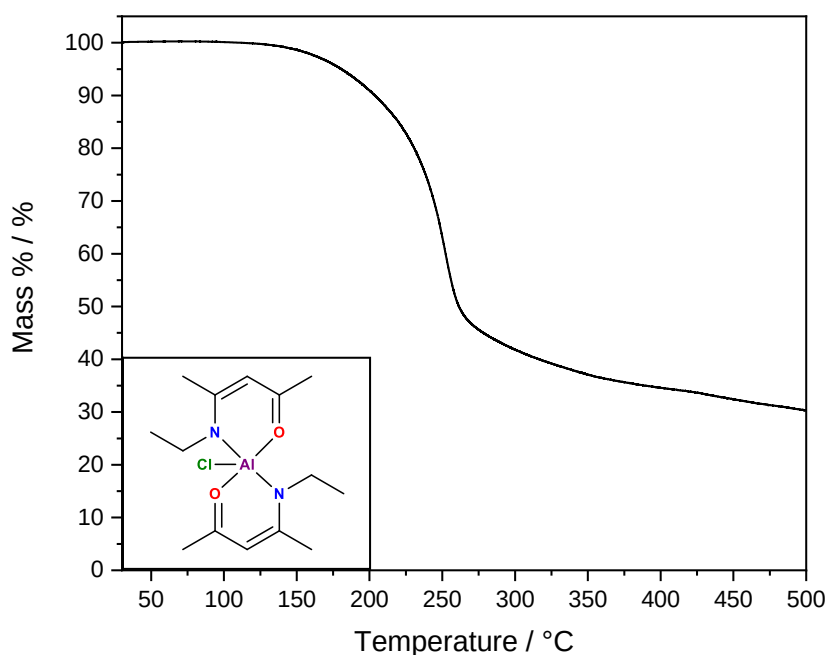


Figure 4.10: Thermogram of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).

4.2.2.3 Thermal decomposition of $[\text{Al}(\text{}^i\text{Pr-acnac})_2\text{Cl}]$ (**8**)

The thermogram of $[\text{Al}(\text{}^i\text{Pr-acnac})_2\text{Cl}]$ (**8**) (Figure 4.11) shows decomposition at low temperature with significant mass loss beginning at 186 °C. A mass loss of 69% was recorded, with a mass loss of also 92% expected if pure Al metal is formed and 70% if pure Al_2O_3 is formed. Although the decomposition temperature for complex **8** is promising, lying with the 50–200 °C window desired, its low mass loss is less promising. Interestingly, in Chapter 3 we saw that when $\text{R} = \text{}^i\text{Pr}$ for the tris complexes, the highest impurity remained and for the bis complexes featured within this Chapter, when $\text{R} = \text{}^i\text{Pr}$, the second largest impurity remains, however this is not a property of ligand decomposition itself, as evidenced by the good thermal properties of the ligand itself featured in the Appendices.

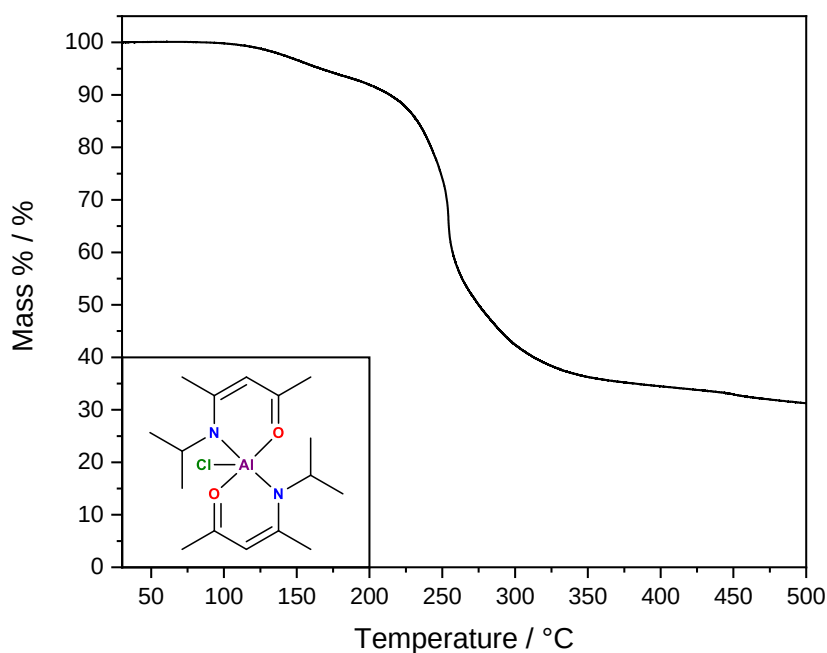


Figure 4.11: Thermogram of $[\text{Al}(\text{}^i\text{Pr-acnac})_2\text{Cl}]$ (**8**).

4.2.2.4 Thermal decomposition of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9)

The thermogram of **$[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9)** (Figure 4.12) shows decomposition at low temperature with significant mass loss beginning at 199 °C. A mass loss of 63% was recorded, with a mass loss of also 93% expected if pure Al metal is formed and 75% if pure Al_2O_3 is formed. Although this compound has a decomposition onset just within the desired temperature window, it exhibits the lowest mass loss of all complexes featured within this Chapter, likely owing to the higher temperatures required to break and volatilise the aromatic C–C bonds.

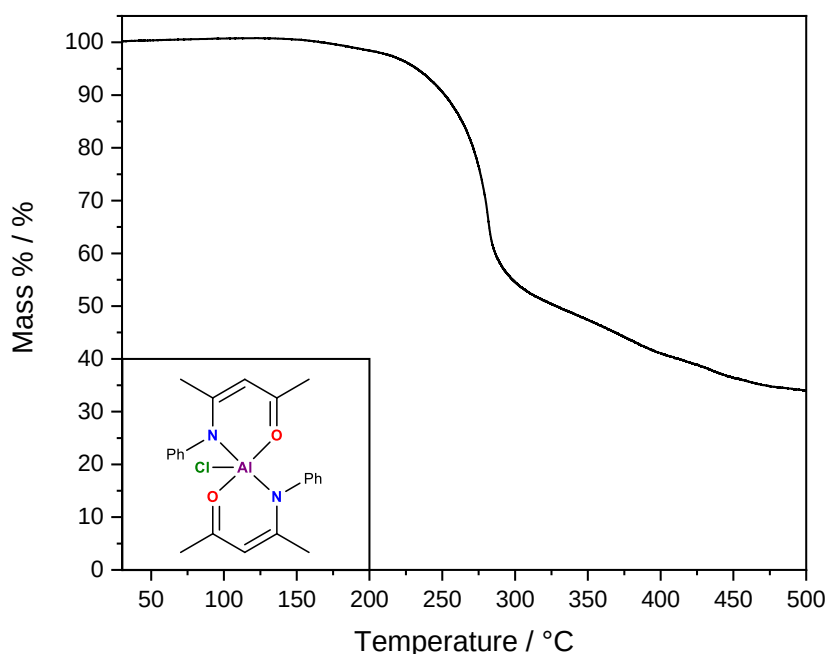


Figure 4.12: Thermogram of **$[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9)**.

4.2.2.5 Thermal decomposition of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (**10**)

The thermogram of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (**10**) (Figure 4.13) shows decomposition at low temperature with significant mass loss beginning at 278 °C. A mass loss of 76% was recorded, with a mass loss of also 95% expected if pure Al metal is formed and 79% if pure Al_2O_3 is formed. Complex **10** displays the highest decomposition temperature of all those featured within this Chapter and this is likely due to a secondary decomposition step (see DTG – Appendix 124) which is most likely due to a decomposition process related to the aromatic ring within the ligand.

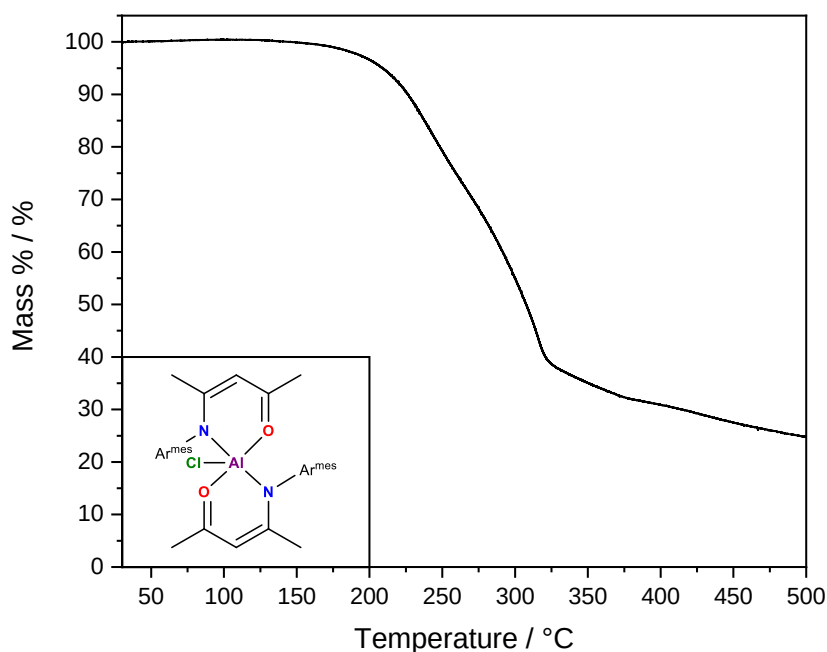


Figure 4.13: Thermogram of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (**10**).

4.2.2.6 Thermal decomposition summary

This work, like that featured in Chapter 3, demonstrates the worth of changing one group on a molecule of interest at a time in order to probe thermal trends. Like with Chapter 3, the group that is changed between each complex is the *N*-substituent on the ligand, with alterations once again having substantial effects on the thermal properties of each bis(β -ketoiminate) aluminium monochloride complex, which are difficult to predict (Table 4.9).

Table 4.9: *Expected % residue, % of non-volatile residue and onset/end of volatilisation/decomposition for complexes 6–10.*

Precursor	Expected Mass Loss % for Al, Al ₂ O ₃	% Av. Non-volatile Residue	Av. Onset Temp.	Av. End Temp.
[Al(Me-acnac) ₂ Cl] (6)	91%, 64%	74%	166 °C	305 °C
[Al(Et-acnac) ₂ Cl] (7)	91%, 68%	71%	116 °C	266 °C
[Al(^{<i>i</i>} Pr-acnac) ₂ Cl] (8)	92%, 70%	69%	186 °C	266 °C
[Al(Ph-acnac) ₂ Cl] (9)	93%, 75%	63%	199 °C	289 °C
[Al(Ar ^{mes} -acnac) ₂ Cl] (10)	95%, 79%	76%	256 °C	500+ °C

Figures 4.15 and 4.16 graph the onset temperature and mass loss data with associated errors for each of the five complexes thermally analysed respectively. As we can see from the bonds lengths and angles around the Al centre (previously given in Table 4.6), there are no strong correlations between complex structure and thermal properties such as onset temperature and mass loss. There also doesn't seem to be a strong correlation between precursor τ_5 values and decomposition temperatures, with values tending to 0.5 expected to give lower temperatures (Appendix 127). Promisingly, despite the presence of the chlorine co-ligand which can hamper metal film conductivity if incorporated (unlikely due to the high volatility of Cl), most complexes exhibit the beginnings of significant mass loss within the temperature window desired (50–200 °C), with complex **7** (R = Et) being of particular interest. Perhaps intuitively, complexes featured within this Chapter have very similar decomposition properties to those featured in Chapter 3, with both families of complexes possessing the same choice of β -ketoiminate ligands. Pyrolysis experiments were not conducted on any bis(β -ketoiminate) aluminium monochloride compounds, due in part to the lack of successful results when analysing the tris compounds in Chapter 3.

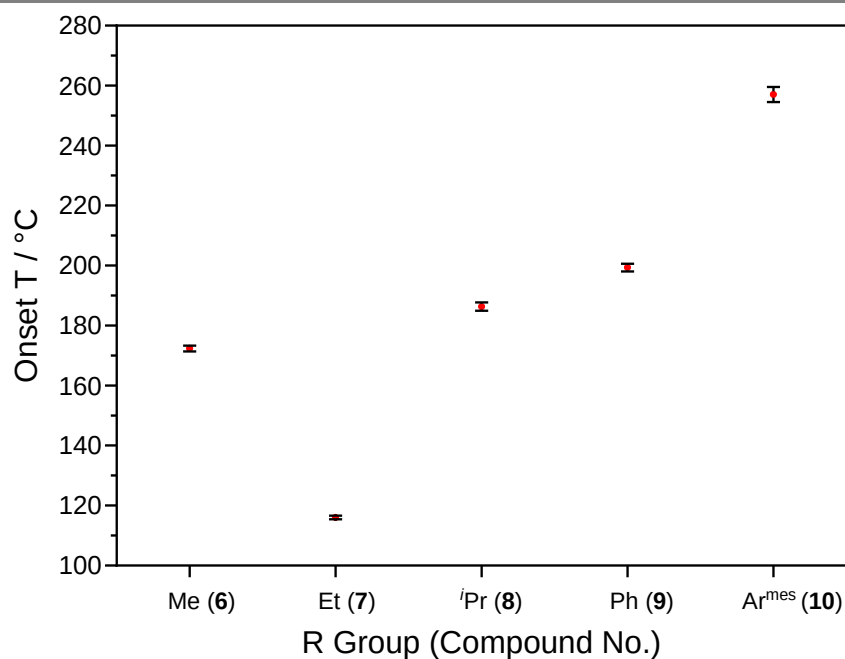


Figure 4.14: Comparison of precursor (6–10) onset decomposition temperatures with associated errors.

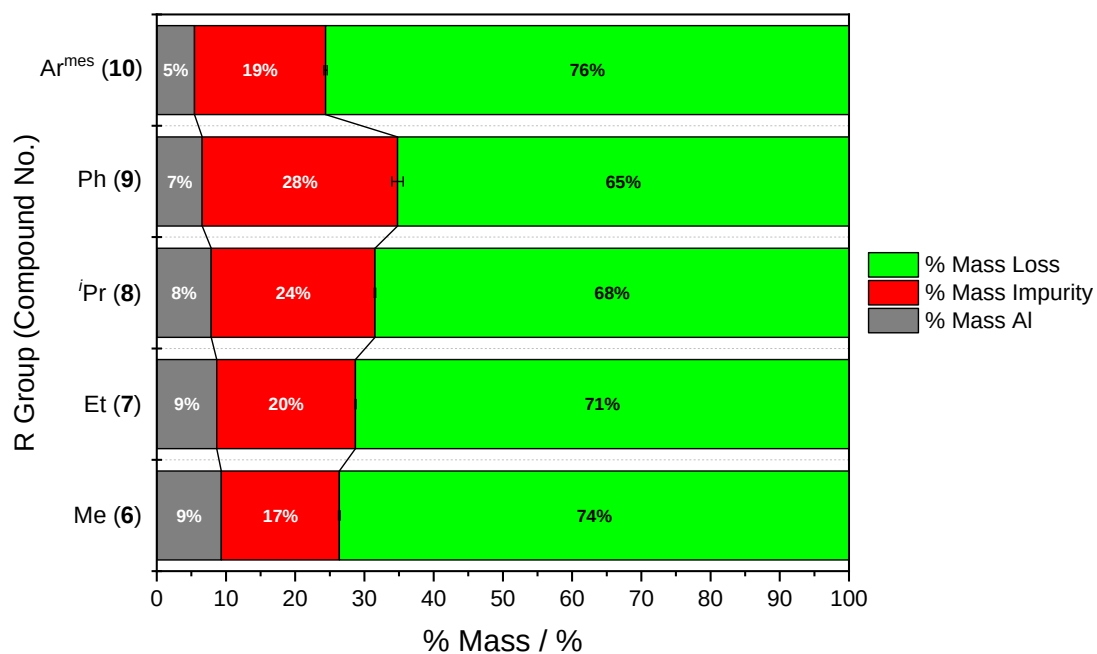


Figure 4.15: Comparison of precursor (6–10) mass loss %'s with associated errors.

4.3 Summary

A family of compounds containing two β -ketoiminate and one chlorine co-ligand bonded to an Al centre have been synthesised, which includes the first examples where the *N*-substituent is an alkyl group. As seen with the only other two complexes of this type in the literature, each complex adopts a trigonal bipyramidal geometry around the Al centre, with the Cl atom in the equatorial position for each of the five complexes. When less bulky *N*-substituents are used, the N atoms occupy the equatorial positions and when bulkier R groups are used (complex **10**) the O atoms of the ligand occupy the equatorial positions, which are both bonding motifs that compare well to the literature.

In order to probe this set of complexes suitability as MOD precursors, each compound was thermally analysed *via* TGA. Compounds generally showed reasonable decomposition properties, with the best precursor **[Al(Et-acnac)₂Cl]**, **7** displaying good mass loss properties and a low onset decomposition temperature (<200 °C), again lower than that of [Al(acac)₃], a well-known standard precursor in the synthesis of Al₂O₃ thin films. Decomposition properties are comparable to the tris complexes synthesised in Chapter 3.

The next step in for the future of this work would be an investigation into the decomposition products, which would be a step closer to application of these compounds as precursors to functional materials. Like the compounds investigated in the previous Chapter, these compounds maybe be better suited to deposition *via* CVD techniques (MOCVD or ALD) due to their decomposition properties. Furthermore, their solubility in a range of solvents could potentially render them useful solution-based precursors in deposition techniques such as AACVD and inkjet printing. Another future avenue of research for this family of complexes could involve using the chloride co-ligand as a reaction handle, in order to change functionalisation at the metal centre.

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Chapter 5

Aluminium Hydride Compounds for use as Aluminium Precursors

This Chapter involves the synthesis of two types of aluminium hydride compound; mono(β -diketiminato) aluminium dihydrides a family of complexes better known for catalytic small molecule activation and amine-stabilised alanes, a more well-known family of precursors to Al functional materials. The suitability of both families of compounds towards low temperature decomposition is assessed using TGA.

5.1 Introduction

Whilst Chapters 3 and 4 focussed on the complexation of β -ketoiminate ligands to aluminium, this Chapter focuses on two new ligand systems; β -diketiminates and amines, both of which form aluminium complexes with hydride co-ligands, a rather rare type of bond. Both ligand systems lack oxygen atoms in their structure and should therefore prevent the chance of aluminium oxide formation under an inert atmosphere. Hydride co-ligands are hypothesised to aid complex reduction to the metal through the production of a reducing atmosphere upon decomposition.

5.1.1 Group 13 binary hydrides

Hydride complexes of the Group 13 elements arguably best exemplify their individualism. In the diversity and abundance of its hydride chemistry, boron gives little indication of the lack of comparative features that dominate much of the hydride chemistry for the heavier Group 13 elements.¹ Over 100 borane compounds are known, typically as discrete molecules that possess remarkable bonding properties that have challenged and reshaped our understanding of chemical bonding.² By contrast, aluminium forms only one binary hydride stable under normal conditions as various polymorphs of a polymeric solid: alane, $[\text{AlH}_3]_n$. Attempts to prepare the gallium analogue were problematic and it took around half a century from the first reported sighting to establish the true credentials of gallane, $[\text{GaH}_3]_n$, which now emerges as showing obvious affinities to diborane in the vapour state (*i.e.* $n = 2$) while being relatively short-lived under normal conditions.³

The first dependable synthesis of indane, $[\text{InH}_3]_n$ was only reported within the last two decades despite there being spectroscopic evidence for InH , InH_2 , and InH_3 molecules for some time.⁴ Thallium binary hydride chemistry is extremely sparse with TlH_x ($x = 1-3$) compounds accessible only in the gas phase or when cryogenic matrices are used.^{2,4,5} The lack of prominence of the latter two Group 13 binary trihydrides (InH_3 and TlH_3) is most likely owing to the “inert pair effect” with the unimolecular decomposition of MH_3 (to give $\text{MH} + \text{H}_2$) having been shown to become energetically more favourable on descending the group – the abstraction of dihydrogen from InH_3 and TlH_3 being calculated to be exothermic.²

The hydrides of the Group 13 metals carry bonds which are polarised: $\text{M}^{\delta+}-\text{H}^{\delta-}$. The *pseudo*-anionic hydrogen ligand is thus vulnerable to electrophilic attack, and the metal centre to

nucleophilic attack, which is partly due to its partial positive charge and partly by virtue of the vacant orbital which it bears.¹

Group 13 binary hydride compounds contain 3-centre 2-electron bonds (3c-2e) *i.e.* electron-deficient chemical bonds where three atoms share two electrons. The combination of three atomic orbitals form three molecular orbitals: one bonding, one non-bonding, and one anti-bonding. The two electrons go into the bonding orbital, resulting in a net bonding effect which results in chemical bond forming between all three atoms. 3-2e bonds can be classified into three types according to whether the bridging atom contributes zero (μ -Z), one (μ -X) or two (μ -L) electrons (Figure 5.1).⁶

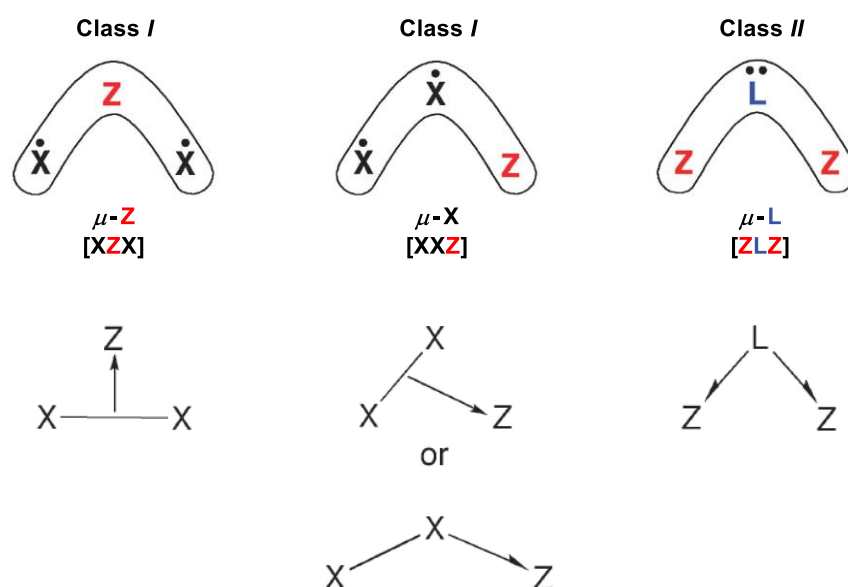


Figure 5.1: Classification of 3-centre 2-electron (3c-2e) interactions according to the nature of the specified bridging atom.⁶ Adapted from reference 6.

Group 13 binary hydride compounds contain the very common Class I μ -X 3c-2e bonds, *i.e.* those that feature a μ -X bridge. Compounds with bridging μ -X atoms can either be depicted by drawing an arrow from the centre of the X–X bond to the outer Z atom or represented by using the X–X, Z ‘half-arrow’ notation in which the ‘half-arrow’ is drawn from the central X atom to the outer Z atom (Figure 5.1). The former motif is most commonly employed if the angle at the central atom is distinctly nonlinear and the outer Z atom is considered to be within a bonding distance to both X atoms (*i.e.* a ‘closed’ system), whilst the latter representation is employed if the [XXZ] interaction is almost linear (*i.e.* an ‘open’ system).⁶ The half arrow

notation is the better representation for the 3c-2e bonding found in crystalline Group 13 binary hydrides.

5.1.2 Alane and Lewis base-stabilised alanes

As introduced in Chapter 1, Lewis base-stabilised alanes offer the viability of aluminium metal deposition at low temperatures. Alane, AlH_3 was first synthesised as an impure solid by Stecher and Wiberg in 1942.⁷ The procedure utilised electrical glow discharges in mixtures of $[\text{AlMe}_3]$ and H_2 followed by addition of NMe_3 to the resultant mixtures. This resulted in several base-stabilised adducts with the formula $[\text{Me}_x\text{AlH}_{3-x}\cdot\text{NMe}_3]$ ($x = 0-3$), however only trimethylamine alane (TMAA), $[\text{AlH}_3\cdot\text{NMe}_3]$ was obtained as a crystalline solid. This crystalline solid was thermolysed to produce impure alane.

In 1946, Finholt, Bond and Schlesinger were first to synthesise lithium aluminium hydride, LiAlH_4 from the reaction of four equivalents of lithium hydride, LiH with aluminium trichloride, AlCl_3 in ether.⁸ They also found by reacting three equivalents of their newly discovered LiAlH_4 with another equivalent of AlCl_3 in ether produced an ethereal solution of alane which was not stable and quickly deposited a white solid in the form of ether-stabilised alane, $[\text{AlH}_3\cdot\{\text{O}(\text{Et})_2\}]$, which today is still a popular starting reaction for many alane-based compounds. The ether could not be fully removed without decomposition of the compound. The same product was also produced from the reaction of three equivalents of LiH with AlCl_3 in ether, but the authors found the former reaction was preferred as it proceeded faster and more smoothly.

Brower *et al.*⁹ were the first to synthesise non-solvated alane. They stated that the rapid precipitation observed by Finholt *et al.*⁸ was due to crystallisation from a supersaturated solution, rather than by polymerisation. Like with Finholt's work, Brower and co-workers observed that that pure alane etherate decomposes to the elements if heated under vacuum, but if excess LiAlH_4 was present, desolvation of the ether could occur without decomposition. They also found that using lithium borohydride, LiBH_4 in combination with LiAlH_4 further lowered the temperature at which desolvation could occur. Further heating steps of the dry etherate phase, mixed with LiAlH_4 and LiBH_4 , led to pure alane.

Under normal conditions there is only one stable form of alane – the α -form, however at least seven structural polymorphs are known, which are all non-volatile, insoluble polymeric solids, $[\text{AlH}_3]_n$ thus making alane unfit for purpose in the deposition of aluminium metal

films.^{9–12} Alane polymerises through Al–H–Al bridging units, so that each aluminium centre can possess a full octet of electrons for added stability.

In addition to several polymorphs, alane forms complexes with a number of Lewis base donor ligands (L) including; carbenes,¹³ phosphines,¹⁴ amines,¹⁵ ethers,⁹ as well as, other heteroatom donating and mixed donor ligands.¹⁶ Such donors often prevent the formation of polymeric chains of alane moieties through homolytic, symmetrical cleavage of Al–H–Al bridging units. This can be understood as each Lewis base donating two electrons to each aluminium centre, giving each centre a full octet of electrons and thus negating polymerisation.¹⁰

Lewis base-stabilised alane compounds are generally solids or liquids under standard conditions and can oftentimes be miscible/dissolved in a range of aprotic organic solvents due to the lipophilic nature of the Lewis base ligands. Protic solvents are not compatible with alane precursors as they react vigorously with one another, frequently producing hydrogen gas as a by-product.¹⁷ Lewis base-stabilised alanes maintain low decomposition temperatures, which relate to the strength of the weak donor-acceptor bond, (as well as, the sterics involved), which is a function of the donating capability of the Lewis base ligand (indicated by the pK_a of its conjugate acid) – see Section 5.1.3.4 for a more in depth discussion of this.¹⁸ Many stabilised alanes are temperature sensitive so they must be refrigerated, otherwise they will decompose over time at room temperature.^{19,20}

Due to the interesting properties of alane and its donor stabilised compounds, they have been subject of interest in many different scientific fields in recent history, not just for the deposition of aluminium metal, pioneered by the metal CVD field.²¹ For example, the remarkable hydrogen content of the alane moiety (10.1% by mass) has attracted extensive research to use alane compounds as an alternative energy sources *via* its hydrogen storing capabilities.²² Other major interests of aluminium hydride compounds is their use as potential rocket fuels,²³ explosives^{24,25} and as catalytic reducing agents for a number of different functional groups.²⁶

5.1.3 Structural preferences of Lewis base-stabilised alanes

$[AlH_3 \cdot nL]$ adducts tend to conform to one of six basic structural types including monomers, dimers, as well as, polymers with alane-to-ligand ratios of 1:1 and 1:2 considerable the most common (Figure 5.2). The aluminium centres in these complexes are either tetra- or penta-

coordinate, with higher coordinate AlH_3 centres being very uncommon, requiring dimerisation²⁷ or tetraborate ligands.^{2,28,29}

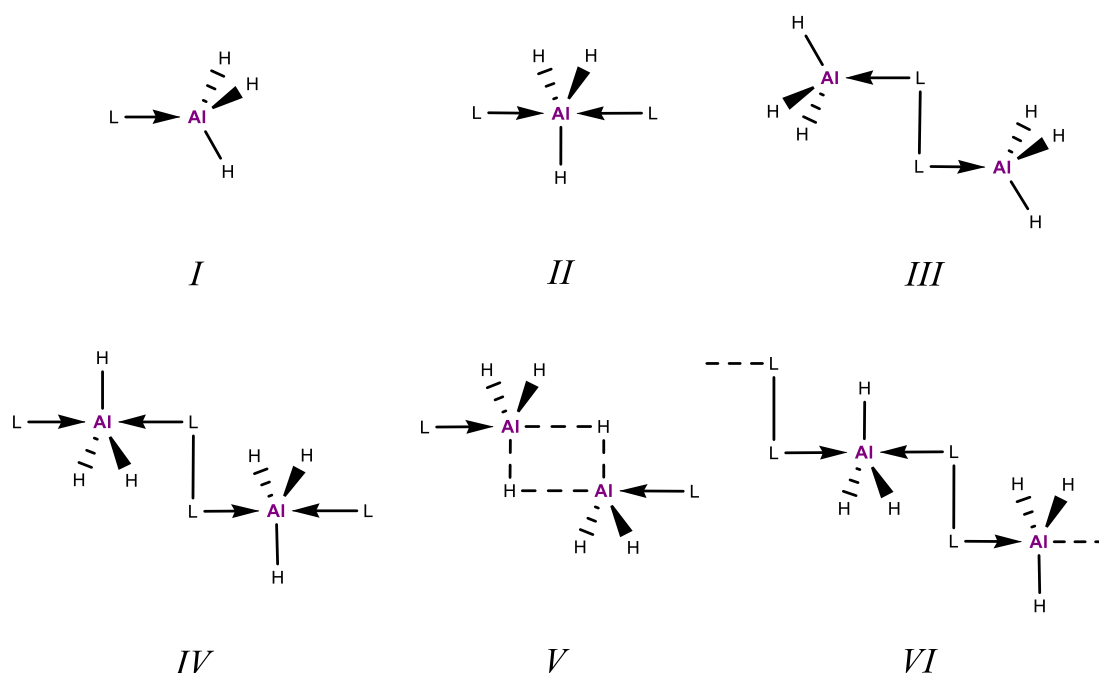


Figure 5.2: Typical structural paradigms for neutral adducts of Lewis base-stabilised alanes.

For all Group 13 Lewis base-stabilised hydrides, such as Lewis base-stabilised alanes, coordination numbers of four and five are certainly the most common (Figure 5.2). The specific geometry adopted is not only a function of the metal centre (Al, Ga, In, Th), but also the steric and electronic properties of the Lewis base ligands, as will be discussed in more depth later (Section 5.1.3.4). Complexes featuring a four-coordinate structure (Figure 5.2: type *I* and *III*) form tetrahedral arrangements and have shorter metal-ligand bonds than those found in related five-coordinate systems (Figure 5.2: type *II*, *IV* or *VI*) which form trigonal bipyramidal geometries – this is due to both the increased steric crowding at the metal centre and its reduced Lewis acidity.³⁰ Evidence for this statement is provided by the Al–N bond lengths of $[\text{AlH}_3 \cdot \text{NMe}_3]$ (type *I*, in the vapour phase), $[\text{AlH}_3 \cdot (\text{NMe}_3)_2]$ (type *II*) and $[\text{AlH}_3 \cdot \text{Me}_2\text{N}(\text{CH}_2)_3\text{NMe}_2]_n$ (type *VI*) which are 2.063(7), 2.18(1) and 2.209(4) Å respectively.²

Structural type *V*, a 2:1 adduct of a *N*- or *O*-donor Lewis base with an Al_2H_6 moiety, features a weakly bound bridging hydride in the fifth coordination position and is a hybrid of four- and five-coordinate alane complexes. Although, the metal centre is best described as trigonal

bipyramidal (given that the sum of the three AlH_2 angles is approx. 360°), it is important to note that the $\text{Al-H}\cdots\text{Al}$ bridging interaction is weak and that the Al-L bond lengths are closer to those measured for typical tetra-coordinate (type *I*) adducts, than for ‘true’ penta-coordinate systems of type *II*. The Al-N distance in $[\text{AlH}_3\cdot\text{NMe}_3]_2$ (type *V*, 2.09(2) Å) is more reminiscent of gaseous $[\text{AlH}_3\cdot\text{NMe}_3]$ (type *I*; 2.063(7) Å) than of $[\text{AlH}_3\cdot(\text{NMe}_3)_2]$ (type *II*; 2.18(1) Å).^{31–33} An interesting property of type *V* dimers *via* $\text{Al-H}\cdots\text{Al}$ interactions is the possibility for coordination of an $[\text{AlH}_3\cdot\text{L}]$ fragment with a transition metal centre *via* $\text{Al-H}\cdots\text{M}$ interaction, with some complexes of this type included in a review by Butler and Crimmin.³⁴

5.1.3.1 $[\text{AlH}_3\cdot\text{L}]$ Adducts

Stabilised alane compounds with a 1:1 ratio of alane moiety to ligand form either monomeric (type *I*) or dimeric adducts (type *V*) and generally adopts a *pseudo*-tetrahedral configuration. Examples of such 1:1 monomeric complexes include those where the ligand is a tertiary amine of phosphine, such as where *L* is quinuclidine (QUIN),³⁵ tri-*n*-butylamine,³⁶ tricyclohexylphosphine¹⁴ and tri-*t*-butylphosphine.³⁷ Closely related to the monomeric 1:1 analogues are the 1:1 dimeric complexes, in which bridging hydride moieties span two *Al* centres (type *V*).¹⁸ The Al-H bonds are unsymmetrical, with characteristic bond distances of 2.08 and 1.60 Å for the bridging and terminal hydrides respectively.²⁸ Examples of such complexes include where *L* is trimethylamine,³⁸ *N,N'*-dimethylethylamine (DMEA),²⁸ benzyldimethylamine,³² 1-methyl-tetrahydropyridine,³² 4-dimethylaminopyridine, triallylamine,³⁹ tetrahydrofuran (THF)⁴⁰ and 3-(dimethylamino)propyl chloride, $\text{NMe}_2(\text{CH}_2)_3\text{Cl}$.⁴¹

5.1.3.2 $[\text{AlH}_3\cdot 2\text{L}]$ Adducts

Stabilised alane compounds with a ratio of alane moiety to ligand of 1:2 (type *II*, *IV*) form five-coordinate aluminium centres in a trigonal bipyramidal arrangement, with three equatorial hydrides and two axial ligands. This type of alane adduct is the least common with only a few compounds known including where *L* is QUIN,⁴² THF⁴⁰ and trimethylamine.³¹

5.1.3.3 Polymeric alane adducts $[\text{AlH}_3\cdot\text{L}]_n$

Polymeric stabilised alane adducts are much more common and they also consist of a trigonal bipyramidal arrangement around the aluminium centre (type *VI*), with three equatorial hydrides and two axial bidentate ligands than branch two alane moieties. Examples

of polymeric alane complexes include where L is *N,N,N',N'*-tetramethyl-ethylenediamine (TMEDA),⁴³ *N,N,N',N'*-tetramethyl-1,3-propane-diamine⁴⁴ and 1,2-bis(di-isopropylphosphino)-ethane.¹⁴ If the bidentate ligand does not cause polymerisation, possibly due to sterics, type *III* structures are formed.

5.1.3.4 Lewis base size and basicity effects

Although there were many reports detailing the synthesis and characterisation of $[\text{AlH}_3 \cdot \text{L}]_n$ adducts, for a long time there was no systematic investigation of what factors favour which structure being formed. A pioneering two-part investigation by Humphries *et al.*^{18,28} involving density functional theory analysis and SCXRD, which was accompanied by a large range of other different characterisation techniques, linked how the size and basicity of L (where L is a Lewis base) determined the value of *n* and when *n* = 1, whether $[\text{AlH}_3 \cdot \text{L}]$ is likely to be monomeric or dimeric in the solid state.

They found that as the $\text{p}K_a$ of the Lewis base increases, so does the likelihood of a monomer being formed (rather than a dimer), for a 1:1 adduct, as its ability to satisfy the Lewis acidic aluminium centre electronically is enhanced. As the $\text{p}K_a$ of the Lewis base decreases, the formation of bridging Al–H bonds between two AlH_3 moieties helps to stabilise the structure in the solid state. Empirically, they stated that Lewis base ligands whose $\text{p}K_a$ is 9.76 or lower (L = trimethylamine) prefer to dimerise, while monomeric complexes are preferred at a $\text{p}K_a$ of 9.99 (L = DMEA) or higher. They also elucidated that bulky Lewis bases with large ligand cone angles tend to favour the formation of 1:1 monomers, whilst 1:1 dimeric or 1:2 structures form when the ligand cone angle is less than 125°.

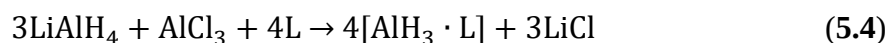
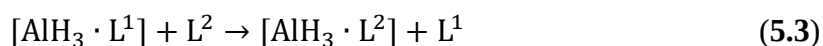
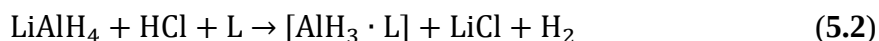
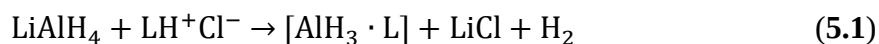
However, by the end of their investigations it was still unclear as to whether the basicity or the steric bulk of the ligand is the key factor in determining structural preferences of the complex. The catalogue of information reported using several analysis techniques enabled the group to state with confidence that the previously disputed structure of TEAA is a 1:1 monomer and the previously unknown structure of DMEAA is also a 1:1 monomeric adduct.¹⁸

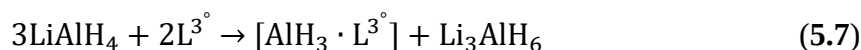
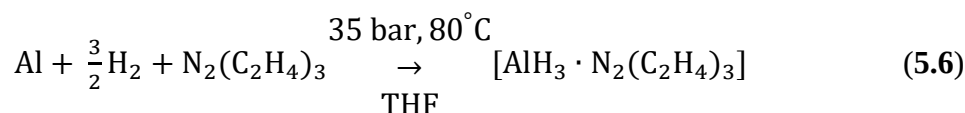
5.1.4 Amine-stabilised alanes

Whilst there are several different atoms that can be bound to aluminium hydride species such as O, P and C, the most prevalent category of ligand donates through an N atom. N donor ligands are essential to coordination chemistry and can be divided into two main classes; I) the aliphatic amines (primary, secondary or tertiary) and II) the aromatic amines typified by

pyridine, pyrrole and their derivatives. Ammonia itself, as well as, primary and secondary amines do not feature strongly in Al metal chemistry because of the propensity of the hydrides, AlH_3 and halides, AlX_3 , to eliminate H_2 or HX respectively, producing nitrides, amines or imides as by-products. As a result, tertiary amines such as trimethylamine predominate as convenient Lewis base adducts. Recently, the use of QUIN, as a less sterically hindered tertiary amine has been used to complex to alane.⁴⁵

As previously stated, Wiberg *et al.*⁷ were first to isolate an amine-stabilised alane compound in the form of TMAA which was a precursor to make free alane. However, the process was arduous and led to an impure product. Currently, there are several preferred methods of synthesis for adducts of alane. There is the reaction of amine hydrochloride³² or a 1:1 mixture of Lewis base and HCl , with LiAlH_4 (Eqn. 5.1 and 5.2).⁴⁶ Next, there are ligand displacements reactions whereby readily available Lewis base alane complexes such as $[\text{AlH}_3 \cdot \text{Et}_2\text{O}]$ (Finholt method),⁸ $[\text{AlH}_3 \cdot \text{NMe}_3]$ (Ruff and Hawthorne method),⁴⁶ or $[\text{AlH}_3 \cdot \text{THF}]$ (Brown and Yoon method)⁴⁷ are treated with a stronger donating Lewis base, resulting in a ligand exchange (Eqn. 5.3). Another popular synthetic route is addition of the amine to a slurry of AlCl_3 and LiAlH_4 in a hydrocarbon solvent such as pentane or hexane, as was first carried out by Frigo *et al.* (Eqn. 5.4).¹⁵ The majority of the abovementioned preferred methods generally lead to 1:1 adducts, however quantitative addition of the ligand can produce the 1:2 adduct; depending on the nature of the ligand. Less common methods of producing amine-stabilised alanes include; the reduction of an aluminium halide with a hydride source, direct hydrogenation of Al powder under high pressure H_2 ⁴⁸ and the addition of a tertiary amine directly to LiAlH_4 (Eqn. 5.5, 5.6 and 5.7 respectively).^{49,50}





Like with other Lewis base-stabilised alanes, the amine adducts are air-sensitive and either solids (many with moderately low melting points) or liquids at room temperature. They are generally volatile and sublime readily at ambient temperatures, but are metastable in the gas phase.^{51,52} Upon thermolysis (>100 °C) under inert conditions, the ligand dissociates leaving behind polymeric alane, which immediately decomposes *via* an autocatalytic process, forming aluminium metal and releasing hydrogen.^{14,18,28,53} Thermolysis with some oxygen present in the atmosphere (or potentially in the ligand in mixed donor systems, if a strong reducing catalyst isn't present – as seen for ether-stabilised alanes decomposition) will inevitably lead to aluminium oxide, Al_2O_3 being formed.¹⁹ The production of high purity aluminium metal at low temperatures is the reason why there has been much interest in such compounds as precursors to aluminium metal films *via* CVD, with DMEAA being a popular precursor.^{54–56} The advantages of using amine-stabilised alanes over conventional aluminium alkyl precursors include facile Al–H and Al–N cleavage compared to Al–C cleavage (no β -hydrides required), and the lower levels of carbon contamination of the deposited metal.⁵⁷

5.1.5 Amine-stabilised halidoalanes

In addition to the many amine-stabilised alanes in the literature, there are a few examples of amine-stabilised halidoalane compounds of the formula; $[\text{AlH}_2\text{X} \cdot 2\text{L}]$ and $[\text{AlHX}_2 \cdot 2\text{L}]$ where X = Cl, Br, I and L is an aliphatic tertiary amine. Contributions by Veith include the synthesis of the bis(*N*-methylpiperidine) aluminium chloro^{58,59}, bromo⁶⁰ and iodo⁶⁰ alane adducts, as well as, mixed halido adducts.⁶⁰ Veith's monochloro and dichloro alane complexes are shown in Figure 5.3 and it is interesting to note how the *N*-methylpiperidine ligands bind differently between one another. The synthetic method used by Veith reacted equimolar quantities of LiAlH_4 and an aluminium trihalide, before complexing the halidoalane centre with two

equivalents of amine. QUIN adducts have also been made by Alexander *et al.*⁶¹ and Jones *et al.*⁶² These classes of compounds are seen as less viable precursors to high quality aluminium metal films as halogen incorporation into films lowers film conductivity, plus gases produced can be highly toxic and detrimental to the environment.

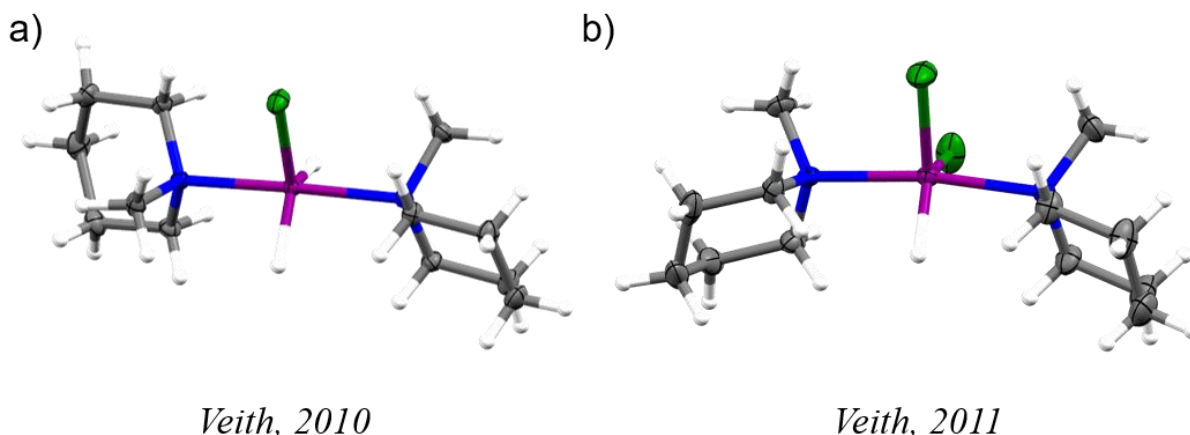


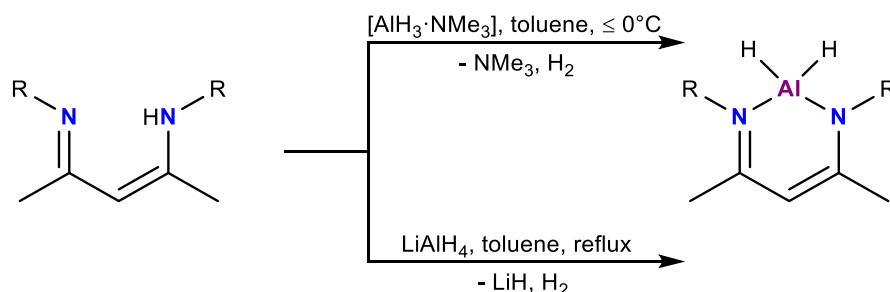
Figure 5.3: Amine-stabilised chloroalane compounds synthesised by Veith *et al.* of the formula: i) $[AlH_2Cl \cdot 2L]^{53}$ and ii) $[AlHCl_2 \cdot 2L]^{59}$

5.1.6 Mono(β -diketiminate) aluminium dihydrides

As mentioned in Chapters 3 and 4, β -diketonate ligands (Figure 3.1) are prevalent in aluminium chemistry, with $[Al(acac)_3]$ and its derivatives being popular precursors to aluminium oxide thin films.⁶³ β -ketoiminate ligands are less prominently featured, however several examples do exist within the literature, in addition to, several examples of such compounds being synthesised in Chapters 3 and 4.^{64–68} These compounds most often feature, alkyl, halide and/or alkoxide co-ligands, with only one complex in the literature featuring both hydride and β -ketoiminate ligands, which was synthesised by Kuo *et al.*⁶⁹ As hypothesised in Chapter 3 and 4, the lack of β -ketoiminate aluminium hydride complexes is likely owing to the lack of steric protection these ligands can offer, due to the impossibility of adding a protecting substituent onto the O atom (as you can for a N atom.)

The β -diketiminate ligands are also well-known in aluminium chemistry.^{70,71} They are particularly prevalent in Al(I) chemistry, where bulky substituents are placed on the N atoms of the ligand to effectively stabilise the highly reactive Al(I) centre complexes with the formula: $[Al(L)]$.⁷² Since the discovery of this family of complexes in 2000 by Cui *et al.*⁷³ there has been great interest in reactivity at the aluminium(I) centre, where such compounds have been

used to activate small molecules and catalyse organic transformations, forming trivalent complexes/intermediates with the formula: $[Al(L)X_2]$.^{74–78} Interestingly these compounds can be reacted with dihydrogen gas to form mono(β -diketiminate) aluminium dihydrides, $[AlH_2 \cdot L]$, however the two more conventional preparation methods are by reacting β -diketimine compounds with either equimolar equivalents of TMAA or a slight excess of $LiAlH_4$ (Scheme 5.1).^{71,76}



Scheme 5.1: Synthesis of mono(β -diketimate) aluminium dihydrides, $[Al(L)H_2]$.

Unlike those that feature β -ketoiminate ligands, aluminium complexes featuring mono(β -diketimate) aluminium dihydrides are prominent in the literature, with one potential explanation being the presence of two *N*-substituents in the ligand structure that can protect the reactive AlH_2 moiety.^{78–86} mono(β -diketimate) aluminium dihydrides have also been investigated as catalysts in deprotonation, insertion, and activation type reactions, however their decomposition properties with regards to forming low temperature aluminium metal films are unknown within the literature.⁸⁷

In addition to the more conventional bidentate β -diketimate ligand systems (Figure 5.4a), tri- and tetra- β -diketimate systems with pendant arms containing additional donor atoms have been used to complex to aluminium. Using a tridentate ligand system containing one dimethylethylamine pedant arm (Figure 5.4b), Nako *et al.*⁵⁰ were able to make the only example of a five-coordinate Al centre with one β -diketimate type ligand and two hydride ligands. Using a tetradentate ligand system, containing two β -diketimate units (Figure 5.4c), Goedken *et al.*⁸⁸ were able to synthesised a five-coordinate Al centre with one ethyl co-ligand – a hydride complex of this type has yet to be synthesised. Sequential alternations of ligand systems, including potentially adding more Lewis base donors, can lead to iterations that change the properties of the final molecule.

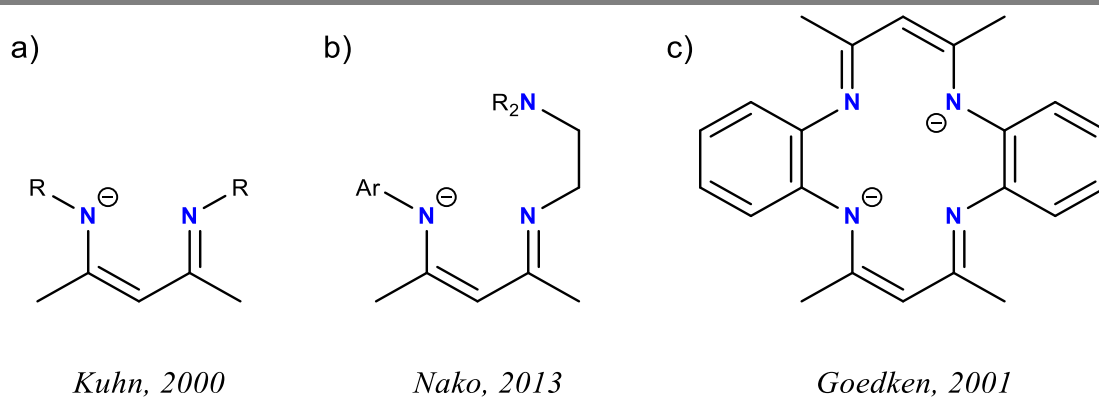


Figure 5.4: Exemplar β -diketiminato ligands of varying denticity, that have been used to complex to metal centres within the literature: a) bidentate, b) tridentate, c) tetradentate.

Whilst most β -diketiminato aluminium chemistry is concerned with the use of bulky ligands, Kuhn *et al.*⁸⁴ have produced several contributions to non-bulky mono(β -diketiminato) aluminium dihydride chemistry, which may be a better fit for materials chemistry due to a lower potential for carbon contamination. In 2000, Kuhn and co-workers⁸³ synthesised several mono(β -diketiminato) aluminium dihydride complexes with the formula: $[\text{Al}(\text{C}_5\text{H}_7\text{N}_2\text{R}_2)\text{H}_2]$ ($\text{R} = \text{Me}, ^i\text{Pr}, \text{Ph}$) by reacting TMAA with equimolar amounts of the analogous β -diketiminato ligands at low temperature (as seen in Scheme 5.1). The methyl (Figure 5.5a) and isopropyl (Figure 5.5b) analogues were characterised by SCXRD and exhibited near planar ring geometries.

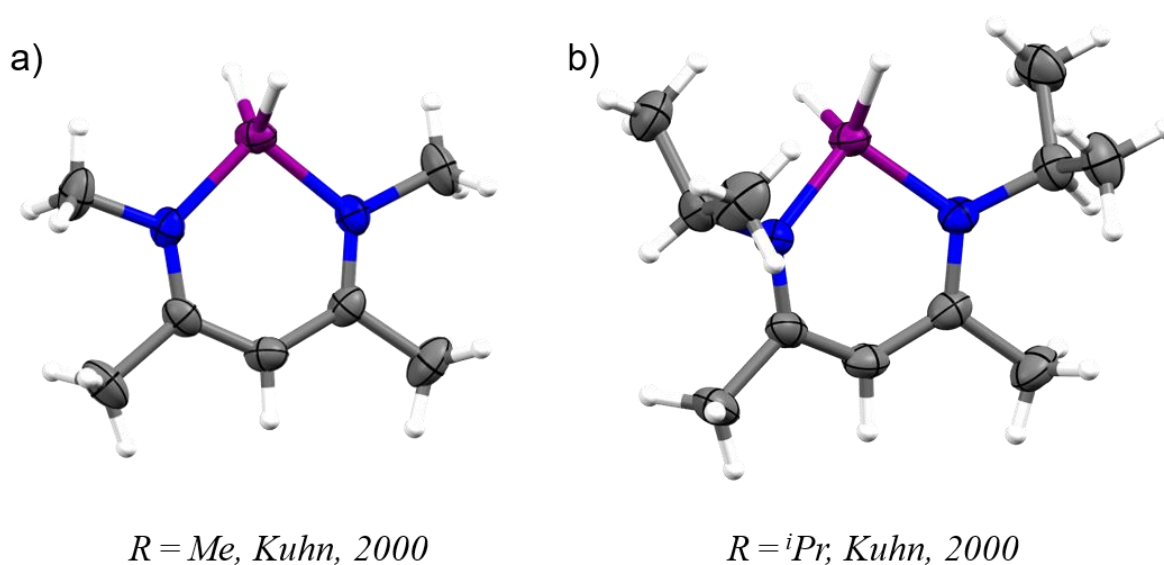


Figure 5.5: Mono(β -diketiminato) aluminium dihydride complexes of the type $[\text{Al}(\text{C}_5\text{H}_7\text{N}_2\text{R}_2)\text{H}_2]$ synthesised by Kuhn *et al.*⁸³ a) $\text{R} = \text{Me}$ and b) $\text{R} = ^i\text{Pr}$ complexes.

Kuhn and co-workers also revealed that if excess hydride reagent was added during synthesis, using the isopropyl β -diketiminate ligand and TMAA as reagents, a perhydrogenated ring system could be formed with the structure: $[\text{Al}_2\text{H}_4 \cdot (\text{C}_{11}\text{H}_{24}\text{N}_2)]_2$. Two units of $[\text{Al}_2\text{H}_4 \cdot (\text{C}_{11}\text{H}_{24}\text{N}_2)]$ are connected *via* hydrogen bridges and form a central planar Al_2H_2 core (Figure 5.6a).⁸³ In a subsequent communication,⁸⁹ they found that reaction of the dihydride complexes with trimethylamine salts, $\text{Me}_3\text{N} \cdot \text{HX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) yielded dihalide complexes, which had been previously synthesised by the reaction of β -diketiminate ligand with AlX_3 .⁸³ It is also interesting to note that in 2001, Kuhn and co-workers⁹⁰ were able to synthesise the first tris(β -diketiminate) metal complex; $[\text{Al}(\text{C}_7\text{H}_{13}\text{N}_2)_3]$ by reacting TMAA with three equivalents of β -diketimine, which was previously mentioned in Chapter 3 (see Section 3.1.4.1, Figure 3.7a). Jana *et al.*⁶⁵ have also made several β -diketiminate aluminium complexes, including the mono(phenyl β -diketiminate) aluminium dihydride and a very interesting tetra-coordinate β -diketiminate aluminium complex, with the other co-ligand a protonated form of a β -diketiminate at the imine group (Figure 5.6b). They were formed by reacting DMEAA with one and two equivalents of the β -diketimine respectively.

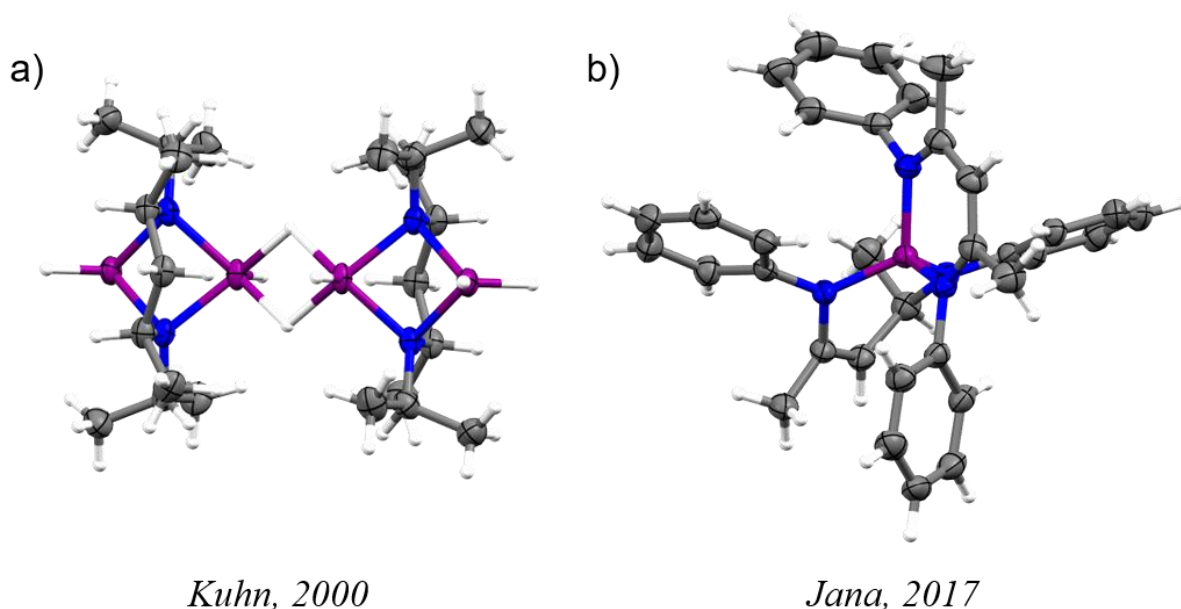


Figure 5.6: β -diketiminate aluminium complexes. a) Kuhn's⁸³ bridging and b) Jana's⁶⁵ four-coordinate β -diketiminate aluminium complexes, respectively.

5.2 Results and discussion

5.2.1 Synthesis of β -diketiminate ligands

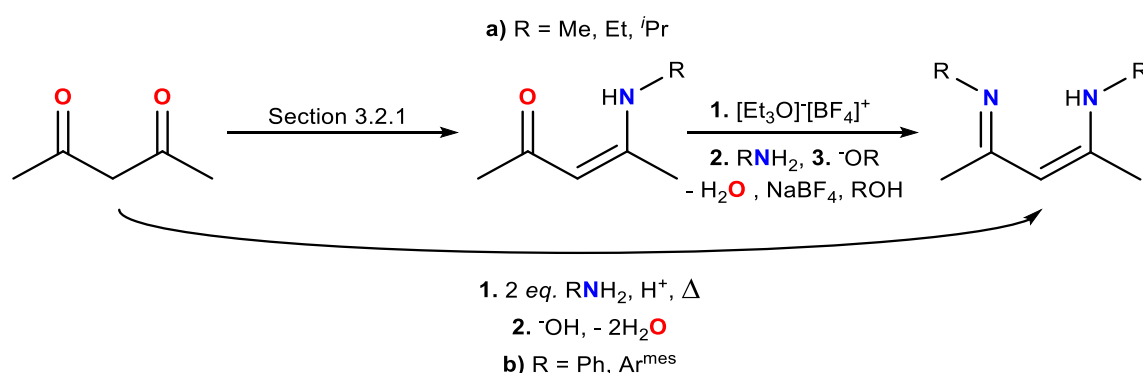
As introduced in Section 3.1.2.3, β -diketimines are a relatively unexplored ligand system in metal-organic complex chemistry, despite offering excellent versatility through variation of the imine and enamine groups. *N*-substituents include hydrogen, alkyl, aryl or silyl groups, with the stress of such groups potentially having a directly impact on how the metal centre bonds. *N*-substituents also offer the potential to increase the denticity of ligands, when added bonding groups are present. Finally β -diketimines can be customised through the more passive backbone, having less of an impact on the environment around the metal centre, but still potentially changing the properties of the resultant complex, such as its solubility. Despite the strong metal-ligand bonds this type of compound forms through the *N,N'*-chelating binding mode, it is believed with the correct customisation there is a potential to tune the decomposition temperature of metal β -diketiminate complexes to within the temperature range required, whilst maintaining suitable compound handleability.

β -diketimine compounds can be synthesised *via* the formation and isolation of β -ketoimine compounds (Section 2.2.1), followed by a subsequent condensation reaction with one equivalent of primary amine or *via* a one-pot condensation reaction of a β -diketone (acetylacetone) with two equivalents of primary amine, with both methods shown in Scheme 5.2. These reactions often require acid or alkyl templating, which renders the second carbonyl group more prone to nucleophilic attack, as the second condensation reaction is less facile. There are many other variations of β -diketimine synthesis including by first converting a β -diketone to a ketoketal before a subsequent reaction with primary amine or by substituting the β -diketone with 1,1,3,3-tetraethoxypropane, which results in a range of products.⁷⁰ Herein, a range of templated methods were found to give the purest product in good yields.

It was noted that when R = alkyl a two-step method was preferred – the β -ketoimine was first synthesised (see Section 2.2.1), then the remaining carbonyl group was activated by *O*-alkylation using triethyloxonium tetrafluoroborate (Meerwein's salt), [Et₃O][BF₄] (see Section 2.2.2) followed by the subsequent reaction with a second equivalent of primary amine, with resulting salt reacted with a base (NaOMe) to form the desired product. Anhydrous solvents were used during the latter steps as triethyloxonium tetrafluoroborate is highly water-sensitive. Although not attempted in this work, the two-step β -diketimine synthesis enables the manufacture of unsymmetrical β -diketimine compounds with varying R groups, which

may exhibit contrasting properties to their symmetrical counterparts, especially when complexed to a metal centre.

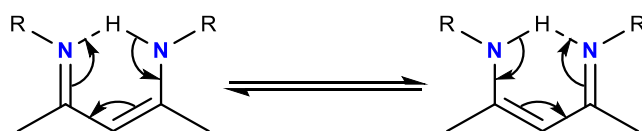
When R = aryl, a more facile acid-templated one-pot reaction of β -diketone with two equivalents of primary amine was favoured as pure product was formed without the need of the water-sensitive triethyloxonium tetrafluoroborate. For both synthetic routes, solid products were purified *via* recrystallisation, whilst liquid products were purified *via* distillation, when required. The β -diketimines; *N*-*N*'-dimethyl-4-amino-3-penten-2-imine (**Me₂-nacnacH**), *N*-*N*'-diethyl-4-amino-3-penten-2-imine (**Et₂-nacnacH**), *N*-*N*'-diisopropyl-4-amino-3-penten-2-imine (**ⁱPr₂-nacnacH**), *N*-*N*'-diphenyl-4-amino-3-penten-2-imine (**Ph₂-nacnacH**) and *N*-*N*'-di(2,4,6-trimethylphenyl)-4-amino-3-penten-2-imine (**Ar^{mes}₂-nacnacH**) were synthesised due to their differences in steric bulk and electron donating properties of the *N*-substituent.



Scheme 5.2: Reaction schemes for the synthesis of β -diketimines by a) the templated reaction of β -ketoimines with primary amines or b) the double condensation reaction between β -diketones and primary amines.

Formation of the β -diketimine compound is identified by several means, depending on the starting reagents used. If synthesising from the β -ketoimine compound (which also exhibit downfield NH peaks), there are several indicators of reaction success. Firstly, there is a reduction in the number of environments, as the resultant β -diketimine compounds are now symmetrical; secondly, there is a doubling of the integration of the *N*-substituent groups (when the second R group added is identical to the first, as is the case here); thirdly for alkyl R groups, there is a loss of multiplicity at the proton environment neighbouring the NH proton environment due to the proton becoming fluxional and finally, there is a shifting of the peaks (upfield and downfield depending for differing proton environments), the most notable being

when looking the NH region (as it is separate from the other peaks), which all exhibit downfield shifts to *ca.* δ 11–12 ppm, due to increased imine character (compared to enamine), due to removal of the carbonyl group, since enol formation is less favourable compared with enamine formation in β -ketoimines (Scheme 5.3).



Scheme 5.3: Tautomeric forms (conjugation) of β -diketimines.

If synthesising straight from the β -diketone with two equivalents of primary amine, there is a drastic downfield shift of the amine NH peak to the product NH peak, which was also seen for the β -ketoimine compounds seen in Section 3.2.1. This drastic downfield chemical shift occurs due to deshielding effect of the imino group intramolecularly hydrogen bonding with the adjacent enamino group. β -diketimines undergo rapid proton exchange between the imino and enamino groups (Scheme 5.3) meaning these compounds are conjugated enabling them to bind to metal centre in a delocalised bidentate fashion, as seen previously for β -ketoimines. Swapping an O atom for a N atom allows for stronger donation of the lone pair of electrons due to reduced donor atom electronegativity and more customisability of the ligand system, due to the presence of a second R group. Many different β -diketimine compounds have been synthesised previously with the same,⁹¹ different⁹² and even bridging⁹³ or pendent⁹⁴ R groups. As detailed in previous Chapters, functionalisation of the N group can vastly change the decomposition properties of synthesised complexes, with aryl substituted β -ketoiminate aluminium complexes having high decomposition onset temperature and lower mass losses.

Of the alkyl-substituted ligands, only the dimethylated species (**Me₂-nacnacH**) gave a high yield (84%), while the related diethyl compound (**Et₂-nacnacH**) gave only 34%. While these species both used [Et₃O][BF₄] to activate the remaining carbonyl group, the diisopropyl variant (**ⁱPr₂-nacnacH**) used dimethyl sulphate, due to following a differing literature procedure, yielding a dark brown oil in moderate yield (54%). Despite attempting numerous synthetic methods to yield pure **ⁱPr₂-nacnacH**, only a best ratio of product : starting reagent of 87:13 could be achieved. Different purification techniques were also used including distillation and column chromatography, with little success.

Of the aryl-substituted ligands, both the diphenyl (**Ph₂-nacnacH**) and dimesityl (**Ar^{mes}₂-nacnacH**) compounds gave moderate yields (45 and 52% respectively) both by means of a one-pot synthesis method using HCl as the acid catalyst. Differences in literature procedures meant that the former was reacted dry (*i.e.* solventless) whilst the latter used ethanol, with compound work-up and recrystallisation also varying depending on what yielded the best results.

A more detailed description of each synthesis follows in Sections 5.2.1.1–5.2.1.5.

5.2.1.1 Synthesis of *N-N'*-dimethyl-4-amino-3-penten-2-imine, (MeCN{H}(Me)CHC=N(Me)Me) (**Me₂-nacnacH**)

The tetrafluoroborate salt of the methyl substituted ligand ([Me₂nacnacH₂][BF₄]) synthesis was synthesised using a standard literature procedure, isolated and characterised by NMR as show in Section 2.2.2.1.⁹⁵ The reaction of sodium methoxide (in methanol) with [Me₂nacnacH₂][BF₄] in toluene at ambient temperature afforded **Me₂-nacnacH** as a white solid after work-up, which was synthesised in excellent purity and yield (84%). ¹H and ¹³C{¹H} NMR spectra were consistent with the formation of the desired product.⁹⁵

5.2.1.2 *N-N'*-diethyl-4-amino-3-penten-2-imine, (MeCN{H}(Et)CHC=N(Et)Me) (**Et₂-nacnacH**)

[Et₂nacnacH₂][BF₄] synthesis was synthesised using a standard literature procedure, isolated as show in Section 2.2.2.2.⁹⁵ The reaction of sodium methoxide (in methanol) with [Et₂nacnacH₂][BF₄] in toluene at ambient temperature afforded **Et₂-nacnacH** as a white solid after work-up, which was synthesised in excellent purity and moderate yield (34%). ¹H and ¹³C{¹H} NMR spectra were consistent with the literature.⁹⁶

5.2.1.3 Synthesis of *N-N'*-diethyl-4-amino-3-penten-2-imine, (MeCN{H}(^{*i*}Pr)CHC=N(^{*i*}Pr)Me) (**^{*i*}Pr₂-nacnacH**)

The reaction of dimethyl sulphate with **^{*i*}Pr-acnacH**, followed by the addition of isopropylamine at low temperature yielded an orange oil. This residue was reacted with sodium methoxide (in methanol) and yielded a dark brown oil after work-up in moderate purity and yield (54%). NMR analysis showed product was in a *ca.* 87:13 ratio of product (**^{*i*}Pr₂-nacnacH**) to the starting reagent (**^{*i*}Pr-acnacH**). The starting material impurity could not be separated despite numerous different methods (distillation, column chromatography *etc.*)

and repeat attempts. Despite the impurity, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁸³

5.2.1.4 Synthesis of *N-N'*-diphenyl-4-amino-3-penten-2-imine, (MeCN{H}(Ph)CHC=N(Ph)Me) (**Ph₂-nacnacH**)

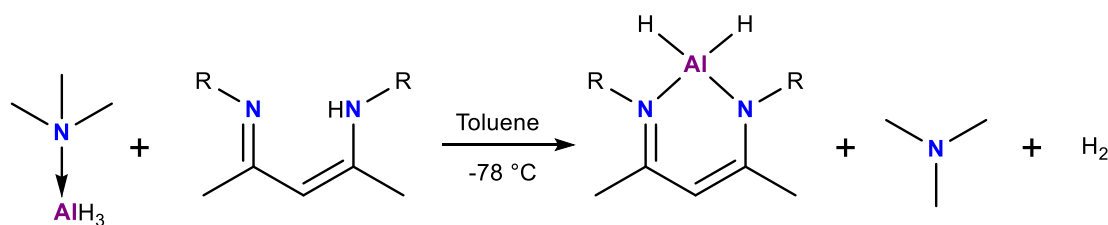
The reaction of aniline with acidified acetylacetone at low temperature for 1 day afforded **Ph₂-nacnacH** as a yellow oil after work-up, which was purified by recrystallisation from ethanol producing yellow plates in moderate yield (45%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the literature.⁹⁷

5.2.1.5 Synthesis of *N-N'*-di(2,4,6-trimethylphenyl)-4-amino-3-penten-2-imine, (MeCN{H}(Ar^{mes})CHC=N(Ar^{mes})Me), where Ar^{mes} = 2,4,6-trimethylphenyl) (**Ar^{mes}₂-nacnacH**)

The reaction of aniline with an acidified solution of acetylacetone in ethanol refluxed for 3 days afforded **Ar^{mes}₂-nacnacH** as a dark brown solid after work-up, which was purified by recrystallisation from methanol producing a golden yellow solid in moderate yield (52%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁹⁷

5.2.2 Synthesis of mono(β -diketiminato) aluminium dihydride compounds

With a view of forming aluminium complexes with hydride co-ligands, with low decomposition temperatures, the β -diketimine compounds were complexed to an aluminium dihydride moiety via the reaction with TMAA as shown in Scheme 5.4. By-products include dihydrogen and the low boiling point trimethylamine, which are easily removed *in vacuo*.



Scheme 5.4: Reaction scheme of the mono(β -diketiminato) aluminium dihydride complexes.

These complexes are well known in the literature, having historically been used in catalytic small molecule activation.⁹⁸ However, the materials chemistry of these compounds has not been probed to date, with information crucial for their application in Al deposition, such as decomposition temperatures, absent from the literature. Numerous attempts to isolate bis(β -diketiminato) aluminium monohydrides, a currently undiscovered family of complexes, were

unsuccessful. Interestingly, unlike the bis(β -ketoiminate) aluminium monochloride compounds featured in Chapter 4, no example of bis(β -diketiminato) aluminium monochlorides feature in the literature. In both cases, for the ligands that contain larger R groups, this is comprehensible as there would be too much steric clash between the ligands. On the contrary, ligands with a smaller R groups such as the methyl derivative, may suffer the same fate as the bis(β -ketoiminate) hydride compounds that could not be successfully isolated in Chapters 3 and 4, in that they may suffer from not being able to sufficiently sterically protect the reactive AlH moiety. The steric clash of having two R groups on each ligand is less problematic when the R group is smaller, which is elegantly shown by the synthesis of the only tris(β -diketiminato) aluminium compound known: $[\text{Al}(\text{C}_7\text{H}_{13}\text{N}_2)_3]$ by Kuhn *et al.*, as detailed in Section 5.1.6.⁹⁰

Several mono(β -diketiminato) aluminium dihydride compounds were formed with varying yields (12–83%) – as these are previously reported, the focus of these syntheses was to produce high purity product for thermal analysis, not improve on yields found within the literature, with yields mainly dependent on ligand purity and how effective the compounds were recrystallised. A more detailed description of each synthesis follows in Sections 5.2.2.1–5.2.2.5.

5.2.2.1 Synthesis of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{N}(\text{Me})\text{Me})\text{H}_2]$ (**[Al(Me₂-nacnac)H₂], 11**)

Compound **11** was prepared by the σ -bond metathesis reaction of TMAA with 1 *eq.* of **Me₂-nacnacH** in toluene at low temperature. Any insolubles were removed by filtration to form a transparent pale yellow solution. The volatiles were removed *in vacuo* to produce an off-white precipitate, in excellent purity and yield (82%). Compound **11** has previously been synthesised and characterised *via* SCXRD by Kuhn *et al.*⁸⁴ ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁸⁴

5.2.2.2 Synthesis of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{N}(\text{Et})\text{Me})\text{H}_2]$ (**[Al(Et₂-nacnac)H₂], 12**)

Moving from R = Me to Et, reaction of **Et₂-nacnacH** *via* σ -bond metathesis reaction with TMAA with in toluene at low temperature afforded compound **12**. Any insolubles were removed filtration to form a transparent pale orange solution. The volatiles were removed *in vacuo* to produce a sticky pale-orange residue which was washed with hexane to form a pale yellow oil in excellent purity and 52% yield. Compound **12** has not previously been synthesised and characterised *via* SCXRD, however single crystals of sufficient quality could

not be grown despite numerous attempts. ^1H NMR peaks at δ 4.75 (AlH_2), 4.40 (CH), 3.05 (CH_2), 1.51 (CH_3), 1.06 ppm (CH_3CN) in a 2:1:4:6:6 ratio and sufficient shift from the uncomplexed compound confirm the presence of **12**. Formation of **12**, is also supported by the very clean shifted $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, as well as, 2D NMR techniques.

5.2.2.3 Synthesis of $[\text{Al}(\text{MeCN}(\textit{i}\text{Pr})\text{CHC}=\text{N}(\textit{i}\text{Pr})\text{Me})\text{H}_2]$ ($[\text{Al}(\textit{i}\text{Pr}_2\text{-nacnac})\text{H}_2]$, **13**)

Compound **13** was prepared by the σ -bond metathesis reaction of TMAA with 1 *eq.* of ***i*Pr₂-nacnacH** in toluene at low temperature. Any insolubles were removed by filtration to form a transparent pale orange solution. The volatiles were removed *in vacuo* to produce a sticky pale-orange residue which was washed with hexane to form an off-white precipitate in excellent purity and low yield (12%). Compound **13** has previously been synthesised and characterised *via* SCXRD by Kuhn *et al.*⁸⁴ ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁸⁴

5.2.2.4 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{N}(\text{Ph})\text{Me})\text{H}_2]$ ($[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$, **14**)

Coordination of $\text{Ph}_2\text{-nacnac}$ to AlH_2 (**14**) was achieved by σ -bond metathesis reaction of TMAA with 1 *eq.* of **Ph₂-nacnacH** in toluene at low temperature. Any insolubles were removed by filtration to form a transparent pale yellow solution. The volatiles were removed *in vacuo* to produce a sticky pale-yellow residue which was washed with hexane to form an off-white precipitate which was recrystallised from toluene in excellent purity and moderate yield (63%). Compound **14** has previously been synthesised and characterised *via* SCXRD by Jana *et al.* and crystals synthesised in this work were cell-matched to their structure as a proof of concept.⁷⁷ ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the literature.⁸²

5.2.2.5 Synthesis of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{N}(\text{Ar}^{\text{mes}})\text{Me})\text{H}_2]$, where Ar^{mes} = 2,4,6-trimethylphenyl ($[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$, **15**)

Synthesis of **15** was carried out as per the procedure laid out for **11–14**, by the σ -bond metathesis reaction of TMAA with 1 *eq.* of **Ar^{mes}₂-nacnacH** in toluene at low temperature. Any insolubles were removed by filtration to form a transparent pale yellow solution. The volatiles were removed *in vacuo* to produce a pale-yellow solid which was washed with hexane to form an off-white precipitate which was recrystallised from toluene in excellent purity and good yield (83%). Compound **15** has previously been synthesised and characterised by Gonzalez-Gallardo *et al.*⁸⁶ ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the formation of the desired product.⁸⁶

5.2.2.6 Comparison of crystal structures from the literature

Table 5.1 gives average Al–H and Al–N bond lengths, as well as, N–Al–N pincer angles for complexes 11–15 from the literature, which may help to elucidate trends observed in the thermal properties as the *N*-substituents are changed sequentially. One observation of note is the large variation in Al–H bond length across the series, likely owing to the differing steric and hyperconjugation power of the different R groups.

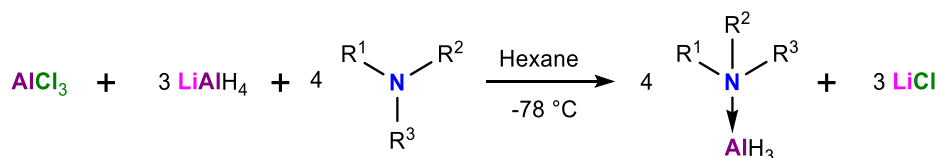
Table 5.1: Comparison of average Al–H and Al–N bond lengths, as well as, N–Al–N pincer angles for complexes 11, 13–15.^{65,84,86}

R Group	Me (11)	ⁱ Pr (13)	Ph (14)	Ar ^{mes} (15)
Bond Length				
Al—H	1.508	1.536	1.552	1.516
Al—N	1.880	1.899	1.893	1.890
Bond Angle				
	97.44	97.88	96.40	96.37

5.2.3 Synthesis of tertiary amine-stabilised alanes

To compare precursors featured in Chapters 3–5, several (tertiary) amine-stabilised alanes were also synthesised. Stabilised alanes have been perceived as the best molecular precursors to aluminium metal coatings for some time, with seminal work done by Glatfelter *et al.*^{54,99,100} in the field of aluminium CVD and more recently by Lee and co-workers^{101–103} in the area of aluminium MOD ink chemistry. This is mainly due to their low decomposition temperatures, however this does come at a cost of stability, which may limit industrial scale-up. Although there has been lots of research in synthesising these types of compounds, there has been a lack of a systematic approach in cataloguing their materials chemistry properties. Many decomposition temperatures of potentially viable stabilised alanes are missing or are reported

as large ranges in the literature, as shown in the article by Humphries *et al.*¹⁸ This Chapter includes a study of these complexes as a comparison to lesser known Al precursors, elucidating information useful to the materials chemist. The general method of synthesising amine-stabilised alanes is shown in Scheme 5.5 and is referred to as the “slurry method” due to the low solubility of the reactants in hexane.



Scheme 5.5: General reaction scheme of amine-stabilised alane complexes.

One equivalent of aluminium(III) trichloride, AlCl_3 was reacted with just over three equivalents of lithium aluminium hydride, LiAlH_4 (to ensure no partially halogenated aluminium species were formed) in hexane at low temperature, before a slight excess of tertiary amine was added with cooling, which was allowed to stir overnight to enable full complexation. The lithium chloride, LiCl by-product was removed by filtration and the product was recrystallised from hexane. Variations from this methodology occur due to a number of reasons, such as the tertiary amine being gaseous at room temperature or there being precedent for different starting reagents/solvents in the literature.

Several amine-stabilised alanes were synthesised from the literature, most with good yields (>60%). The purity of all products was high, as confirmed *via* NMR. High volatility solids (namely TMAA) and liquid precursors were particularly difficult to purify as the vigorous solvent removal by vacuum process (which was needed to have high purity compounds to test *via* thermal analysis) often led to the loss of product. A more detailed description of each synthesis follows in Sections 5.2.3.1–5.2.3.6.

5.2.3.1 Synthesis of trimethylamine alane (TMAA), $[\text{AlH}_3 \cdot \text{NMe}_3]_2$ (**16**)

Compound **16** was synthesised using a different method to Scheme 5.5, as trimethylamine is a gas at room temperature. Instead, lithium aluminium hydride was added to the solid ammonium salt: $[\text{HNMe}_3][\text{Cl}]$ (dried *in vacuo*) in diethyl ether at low temperature. After filtering, removal of solvent and purification *via* sublimation white crystalline product was formed in excellent purity and good yield (77%). Formation of **16** was confirmed by the presence of ^1H NMR peaks at δ 4.12 and 1.84 ppm in a 6:18 ratio, corresponding to the

hydrogen environments $\text{Al}\underline{\text{H}}_3$ and $\text{C}\underline{\text{H}}_3$ respectively. The single $^{13}\text{C}\{^1\text{H}\}$ NMR environment at δ 47.68 ($\text{C}\underline{\text{H}}_3$) ppm was also consistent with the formation of the desired product.¹⁸

5.2.3.2 Synthesis of dimethylethylamine alane (**DMEAA**), $[\text{AlH}_3 \cdot \text{NMe}_2\text{Et}]$ (**17**)

Compound **17** was synthesised overnight using the slurry method, as shown in Scheme 5.5, using dimethylethylamine as the Lewis base. The LiCl by-product was removed by filtration to produce a clear transparent solution, which was concentrated by *approx.* half before being cooled to -78°C to allow for the product to crystallise out as a white solid, which was cold filtered. The white solid was re-dissolved in fresh hexane and the cold filtration process was repeated to ensure high purity. The double filtered white solid isolated at low temperature was dried *in vacuo* cautiously (*i.e.* maintaining cooling temperatures of $<-10^\circ\text{C}$) to ensure no volatile product was lost. Finally, the white solid was allowed to warm to room temperature, melting to form a transparent colourless liquid in excellent purity and good yield (66%). Formation of **17** was confirmed by the presence of ^1H NMR peaks at δ 3.84, 2.38, 2.00 and 0.83 ppm in a 3:2:6:3 ratio, corresponding to the hydrogen environments $\text{Al}\underline{\text{H}}_3$, $\text{C}\underline{\text{H}}_2$, $\text{C}\underline{\text{H}}_3$ and $\text{C}\underline{\text{H}}_3\text{CH}_2$ respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR environments at δ 53.60 ($\text{C}\underline{\text{H}}_2$), 44.06 ($\text{C}\underline{\text{H}}_3$), 9.11 ($\text{C}\underline{\text{H}}_3\text{CH}_2$) ppm were in agreement with the literature.¹⁸

5.2.3.3 Synthesis of triethylamine alane (**TEAA**), $[\text{AlH}_3 \cdot \text{NEt}_3]$ (**18**)

Compound **18** was synthesised and purified as for compound **17**, however triethylamine was the Lewis base used. A transparent colourless liquid was formed in excellent purity and yield (86%). Formation of **18** was confirmed by the presence of ^1H NMR peaks at δ 4.09, 2.35 and 0.85 ppm in a 3:6:9 ratio, corresponding to the hydrogen environments $\text{Al}\underline{\text{H}}_3$, $\text{C}\underline{\text{H}}_2$ and $\text{C}\underline{\text{H}}_3$ respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR environments at δ 48.21 ($\text{C}\underline{\text{H}}_2$), 9.05 ($\text{C}\underline{\text{H}}_3$) ppm were also consistent with the formation of the desired product.²⁸

5.2.3.4 Synthesis of triallylamine alane (**TAAA**), $[\text{AlH}_3 \cdot (\text{N}\{\text{H}_2\text{C}=\text{CHCH}_2\}_3)]$ (**19**)

As with compounds **17** and **18**, compound **19** was synthesised using the same slurry method, with triallylamine as the Lewis base used. A transparent colourless liquid was formed in excellent purity and good yield (73%). Formation of **19** was confirmed by the presence of ^1H NMR peaks at δ 6.00, 4.96, 4.19 and 3.08 ppm in a 6:12:6:12 ratio, corresponding to the hydrogen environments $\text{C}\underline{\text{H}}$, $=\text{C}\underline{\text{H}}_2$, $\text{Al}\underline{\text{H}}_3$, $\text{C}\underline{\text{H}}_2$ and $\text{C}\underline{\text{H}}_3$ respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR environments at δ 130.27 ($\text{C}\underline{\text{H}}$), 122.48 ($=\text{C}\underline{\text{H}}_2$), 58.30 ($\text{C}\underline{\text{H}}_2$) ppm were also consistent with the literature.³⁹

5.2.3.5 Synthesis of tetramethylethylenediamine alane (**TMEDAA**), $[\text{AlH}_3 \cdot (\{\text{CH}_3\}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\})_n]$ (**20**)

Compound **20** was synthesised *via* the ligand exchange reaction of TMEDA with **TMAA** overnight at low temperature. Any insolubles were removed filtration to form a transparent colourless solution. The solvent was removed *in vacuo* to produce a fine white solid (poor solubility in all common aprotic solvents) in excellent purity and low yield (26%). Formation of **20** was confirmed by the presence of ^1H NMR peaks at δ 3.96, 2.44 and 2.05 ppm in a 3:4:12 ratio, corresponding to the hydrogen environments $\text{Al}\underline{\text{H}}_3$, $\text{C}\underline{\text{H}}_2$ and $\text{C}\underline{\text{H}}_3$ respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR environments at δ 55.81 ($\underline{\text{C}}\text{H}_2$), 45.54 ($\underline{\text{C}}\text{H}_3$) ppm were also consistent with the formation of the desired compound.²⁸

5.2.3.6 Synthesis of bis(*N*-methylpyrrolidine) monochloroalane, $[\text{AlH}_2\text{Cl} \cdot 2(\{\text{CH}_3\}_2\text{N}\{\text{CH}_2\}_4)]$ (**[AlH₂Cl·2(NMP)]**, **21**)

Compound **21** was synthesised by the 1:1 reaction of AlCl_3 , with LiAlH_4 , in diethyl ether at low temperature, before adding five equivalents of *N*-methylpyrrolidine at low temperature. The diethyl ether was replaced with hexane, the solution was filtered and the volatiles were removed *in vacuo* to produce a white powder. This white powder was recrystallised from hexane at low temperature to produce colourless crystals in excellent purity and good yield (62%).

The crystal structure of compound **21** was determined *via* SCXRD and is displayed in Figure 5.7. The detail of the determined crystallographic data is given in Table 5.2 with selected bond lengths and angles given in Table 5.3.

Table 5.2: Selected bond lengths and angles for compound **21**.

[AlH₂Cl·2(NMP)] (21)			
Lengths / Å		Angles / °	
Al(1)–Cl(1)	2.2167(5)	N(1)–Al(1)–Cl(1)	92.07(3)
Al(1)–N(1)	2.1198(11)	N(2)–Al(1)–Cl(1)	91.63(3)
Al(1)–N(2)	2.1273(11)	N(1)–Al(1)–N(2)	175.53(4)

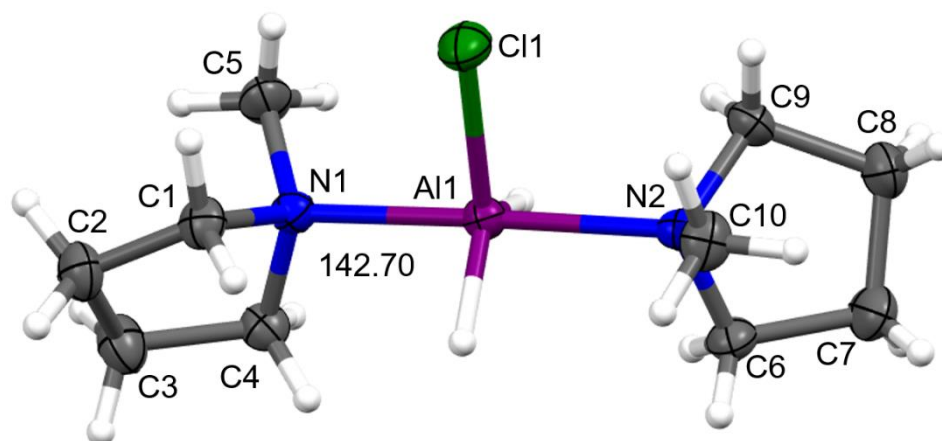


Figure 5.7: Molecular structure of compound **21**. Thermal ellipsoids are drawn at 50% probability.

Compound **21** crystallised in the monoclinic space group $P2_1/n$. The complex is a 1:2 monomer, forming a trigonal bipyramidal arrangement around the Al centre with X ligands equatorial ($X = H^-$, Cl^-) and L ligands (two NMP ligands) axial. This geometry is to be expected, as it is seen for many compounds of this type.^{58,60,62} The trigonal bipyramidal arrangement is slightly distorted, with $Cl(1)-Al(1)-N(1)$ and $Cl(1)-Al(1)-N(2)$ angles being $92.08(3)^\circ$ and $91.64(3)^\circ$ respectively, which is understood as the greater size and electronegativity of the Cl atom compared to the H atoms repels the bulky NMP ligands. This distortion is also reflected by the $N(1)-Al(1)-N(2)$ angle of $175.52(4)^\circ$, which deviates 4.48° from linearity. This distortion also occurs in the structurally similar compound $[(N\text{-methylpiperidine})_2AlH_2Cl]$, which has a $N-Al-N$ angle that deviates from linearity by 2.7° .⁵⁸ The distortion may be greater in the five-membered-ring adduct due to the shorter Al–N bonds of 2.1202(11) and 2.1271(11) Å respectively, whilst the average Al–N bond is 2.1618(4) Å in the six-membered ring adduct.

In addition to SCXRD characterisation, compound **21** was also identified *via* ^1H , $^{13}C\{^1H\}$ NMR (with aid of 2D spectra) and EA (was too reactive for MS set-up). The ^1H NMR spectrum of compound shows a shift of the amine signals, as well as, increased broadness, in addition to, a broad peak around δ 4 ppm for the hydride signals which are both characteristic features for these types of complexes. Peaks at δ 4.17 (AlH_2Cl), 2.38 (CH_2N), 2.01 (CH_3) and 1.34 ppm (CH_2) ratio agree with the formation of the desired product. $^{13}C\{^1H\}$ NMR environments at δ 56.78 (CH_2N), 44.80 (CH_3), 23.98 (CH_2) ppm were also consistent with the formation of **21**.

Table 5.3: Crystallographic data for structurally characterised compound **21**.

Compound	[AlH ₂ Cl·2(NMP)] (21)
Empirical formula	C ₁₀ H ₂₄ AlClN ₂
Fw / g mol ⁻¹	234.74
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	10.7772(3)
<i>b</i> / Å	6.96649(13)
<i>c</i> / Å	18.3655(4)
<i>α</i> / °	90
<i>β</i> / °	104.454(2)
<i>γ</i> / °	90
<i>V</i> / Å ³	1335.23(5)
<i>Z</i>	4
<i>ρ</i> _{calc} / g cm ⁻³	1.168
<i>μ</i> / mm ⁻¹	2.912
Reflections collected	20084
Independent reflections	2681
<i>R</i> _{int}	0.033
<i>R</i> ₁ and <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0298, 0.0781
<i>R</i> ₁ and <i>wR</i> ₂ [all data]	0.0318, 0.0798

5.2.4 Thermal decomposition of precursors

The thermal decomposition properties of the bis(β -ketoiminate) aluminium compounds **11–15** and amine-stabilised alane compounds **16–21** were analysed by TGA using the same methodology as stated in Section 2.4.1. TGA analysis of each β -diketimine compound (Appendix 104), as well as, full TGA and DTG analysis of complexes **11–21** is featured in the Appendices (Appendix 126–135).

5.2.4.1 Thermal decomposition of mono(β -diketiminate) aluminium dihydrides

5.2.4.1.1 Thermal decomposition of $[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$ (**11**)

The TGA thermogram of $[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$ (**11**) (Figure 5.8) shows decomposition at low temperature with significant mass loss beginning at 265 °C. A mass loss of 46% was recorded after heating to 500 °C, with a mass loss of 83% expected if pure Al metal is formed and 34% if pure Al_2O_3 is formed. Although the thermogram appears as if this it levelling out at around 500 °C, it is likely the compound has not fully decomposed at this temperature making it unfit for purpose as a precursor for a MOD ink, especially as aluminium itself melts at 660 °C. If the compound has fully decomposed at 500 °C, the carbon contamination is on a scale that would be of significant detriment to any films produced.

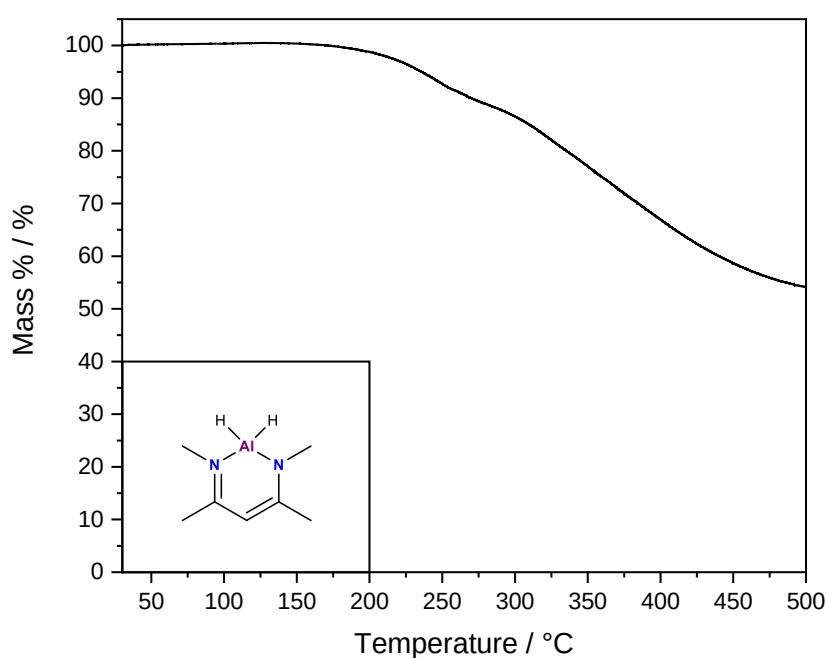


Figure 5.8: Thermogram of $[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$ (**11**).

5.2.4.1.2 Thermal decomposition of $[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$ (**12**)

The TGA thermogram of $[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$ (**12**) (Figure 5.9) shows decomposition at low temperature with significant mass loss beginning at 256 °C. A mass loss of 59% was recorded after heating to 500 °C, with a mass loss of 85% expected if pure Al metal is formed and 44% if pure Al_2O_3 is formed. Unlike that for complex **11** ($\text{R} = \text{Me}$), **12** may fully decompose by the maximum heating temperature, however the high decomposition onset temperature and slow decomposition would indicate a lack of suitability for use as a MOD precursor.

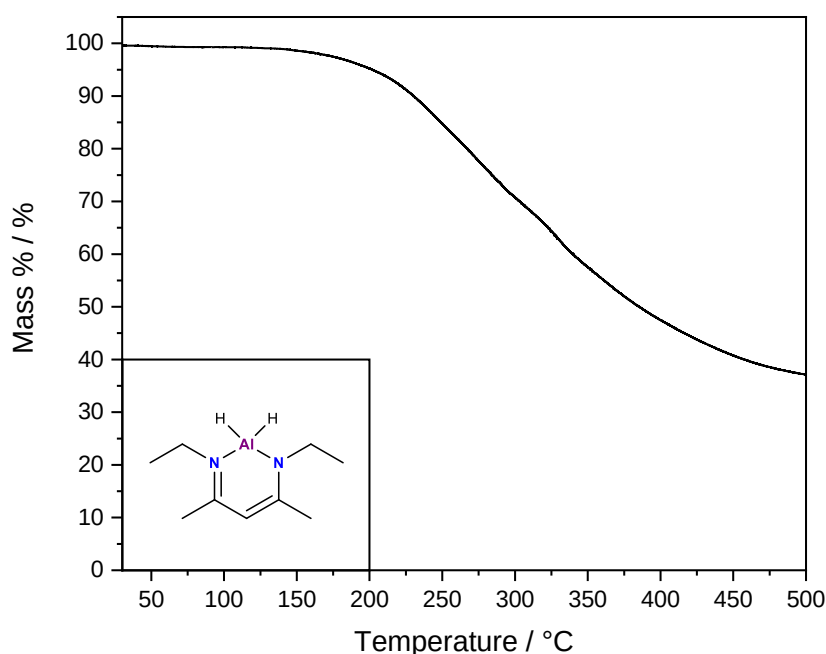


Figure 5.9: Thermogram of $[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$ (**12**).

5.2.4.1.3 Thermal decomposition of $[\text{Al}(\text{iPr}_2\text{-nacnac})\text{H}]$ (**13**)

On comparison with complex **12** ($\text{R} = \text{Et}$) the TGA thermogram of $[\text{Al}(\text{iPr}_2\text{-nacnac})\text{H}]$ (**13**) (Figure 5.10) shows full decomposition by the maximum heating temperature. Decomposition of **13** begins at low temperature with significant mass loss beginning at 293 °C, as with **12** decomposition is slow, and therefore out of range for use as a precursor. A mass loss of 69% was recorded after heating to 500 °C, with a mass loss of 87% expected if pure Al metal is formed and 52% if pure Al_2O_3 is formed.

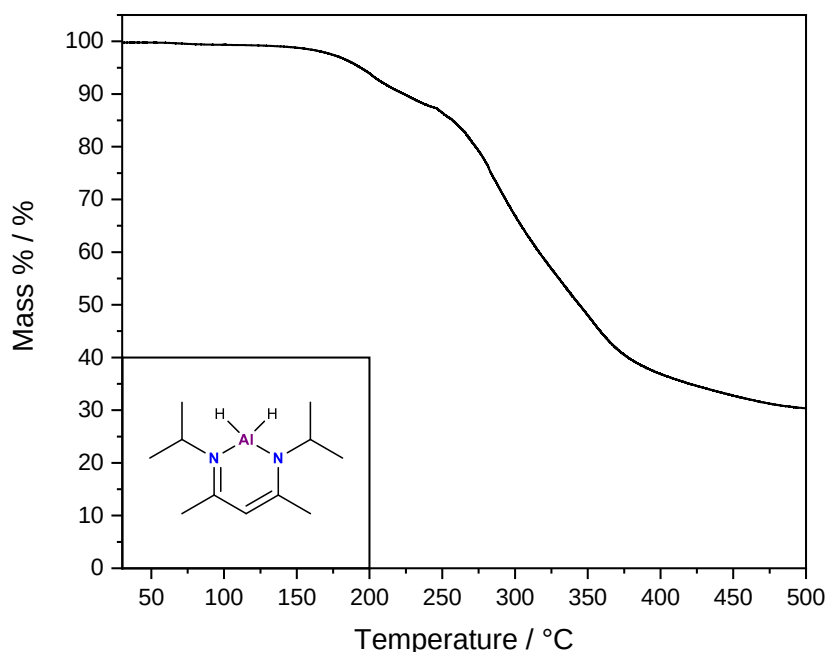


Figure 5.10: Thermogram of $[\text{Al}(\text{iPr}_2\text{-nacnac})\text{H}_2]$ (**13**).

5.2.4.1.4 Thermal decomposition of $[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$ (**14**)

The larger aryl R group, Ph, in **14** can be seen to delay the onset of decomposition in this compound, as evidenced in the TGA thermogram of $[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$ (**14**) (Figure 5.11). A mass loss of 38% was recorded after heating to 500 °C, with a mass loss of 90% expected if pure Al metal is formed and 63% if pure Al_2O_3 is formed. Compound **14** displays the least favourable decomposition properties for the purpose required, with mass loss beginning at 383 °C and the highest decomposition temperature and lowest mass loss, likely owing to the presence of the unsubstituted phenyl group, which has shown to be a detriment to low temperature decomposition for the other families of complexes pyrolysed in Sections 3.3 and 4.3.

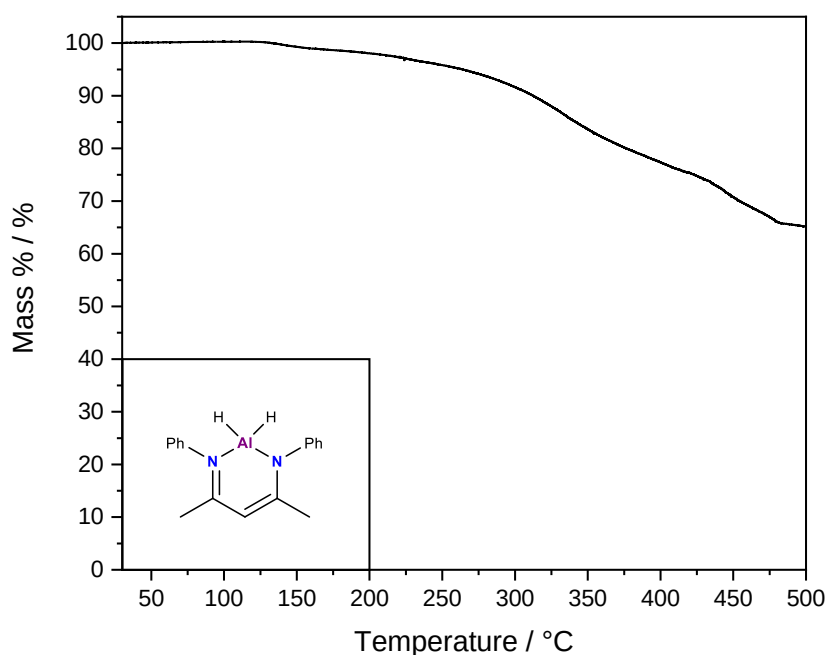


Figure 5.11: Thermogram of $[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$ (**14**).

5.2.4.1.5 Thermal decomposition of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$ (**15**)

The TGA thermogram of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$ (**15**) (Figure 5.12), the compound with the largest R group, shows decomposition at low temperature with significant mass loss beginning at 282 °C. A mass loss of 65% was recorded after heating to 500 °C, with a mass loss of 93% expected if pure Al metal is formed and 72% if pure Al_2O_3 is formed. Interesting **15** shows better decomposition characteristics than when **14** ($\text{R} = \text{Ph}$) and this has previous seen for the complexes analysed in Section 3.3 and 4.3 and this is likely due to the ease at which the ligand breaks down when methyl groups are present on the aryl ring.

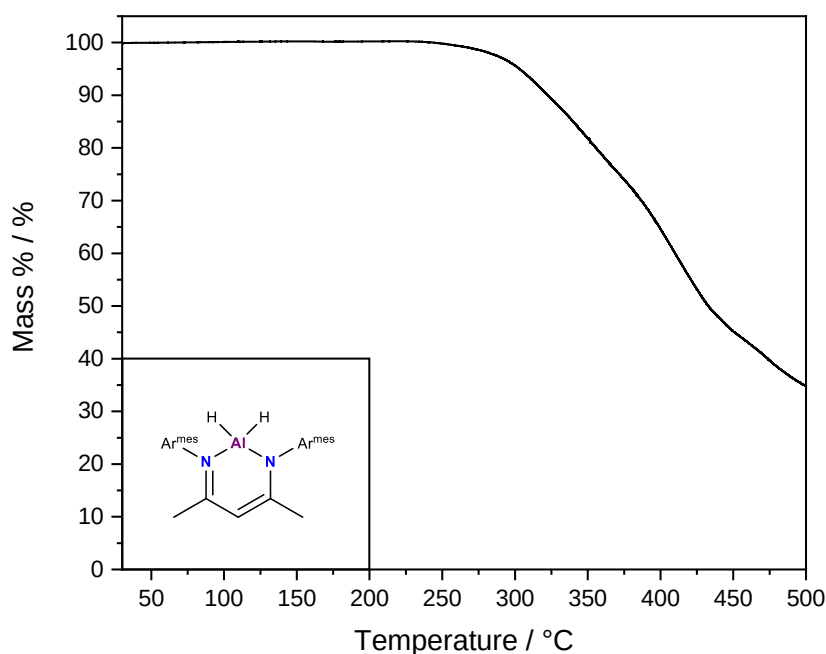


Figure 5.12: Thermogram of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$ (**15**).

5.2.4.1.6 Thermal decomposition summary

Thermal analysis of the mono(β -diketiminate) aluminium dihydrides complexes **11–15** show that they decompose at elevated temperatures (>250 °C) and are thus not suitable for purpose in the pursuit of depositing aluminium metal at low temperature. They also generally decompose at higher temperatures than those featured in Chapters 3 and 4, despite them containing the sought-after hydride co-ligand and containing no O atoms, which when present increase the potential of Al_2O_3 formation. Like for complexes **1–10** we see similar trends in decomposition temperatures as the *N*-substituent is changed, which are hard to predict without experimental data (Table 5.4).

Table 5.4: Expected % residue, % of non-volatile residue and onset/end of volatilisation/decomposition for complexes **11–15**.

Precursor	Expected Mass Loss % for Al, Al_2O_3	% Av. Non-volatile Residue	Av. Onset Temp.	Av. End Temp.
[Al(Me-nacnac) $_2\text{H}_2$] (11)	83%, 34%	46%	265 °C	500+ °C
[Al(Et-nacnac) $_2\text{H}_2$] (12)	85%, 44%	59%	256 °C	500+ °C
[Al(<i>i</i> -Pr-nacnac) $_2\text{H}_2$] (13)	87%, 52%	69%	293 °C	500+ °C
[Al(Ph-nacnac) $_2\text{H}_2$] (14)	90%, 63%	38%	383 °C	500+ °C
[Al(<i>Ar</i> ^{mes} -nacnac) $_2\text{H}_2$] (15)	93%, 72%	65%	282 °C	500+ °C

Figures 5.13 and 5.14 graph the onset temperature and mass loss data with associated errors for each of the five complexes thermally analysed respectively. Evidently, there is no real trend that could be predicted without the aid of these experimental results and there are many contributing factors that cause variations in decomposition characteristics such as onset temperature and complex mass loss. All complexes do not lie within the temperature bracket desired (50–200 °C) and exhibit poorer mass loss properties compared to the compounds featured in Chapter 3 and 4. As the β -diketimine compounds have similar decomposition properties as the β -ketoimines (Appendix 103 and 104), it is likely that the β -diketiminate ligands bind more strongly to Al centres than the β -ketoimines.

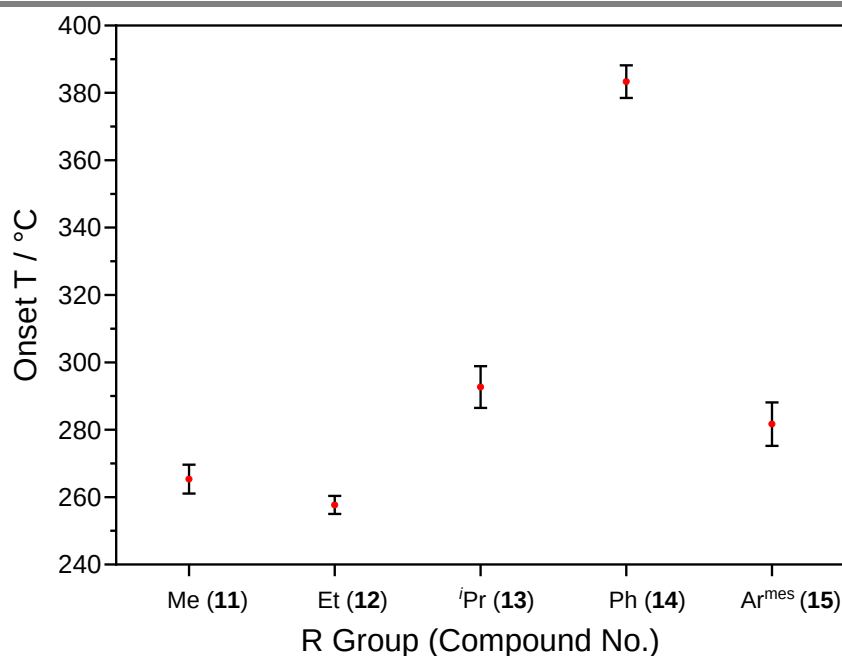


Figure 5.13: Comparison of precursor (11–15) onset decomposition temperatures with associated errors.

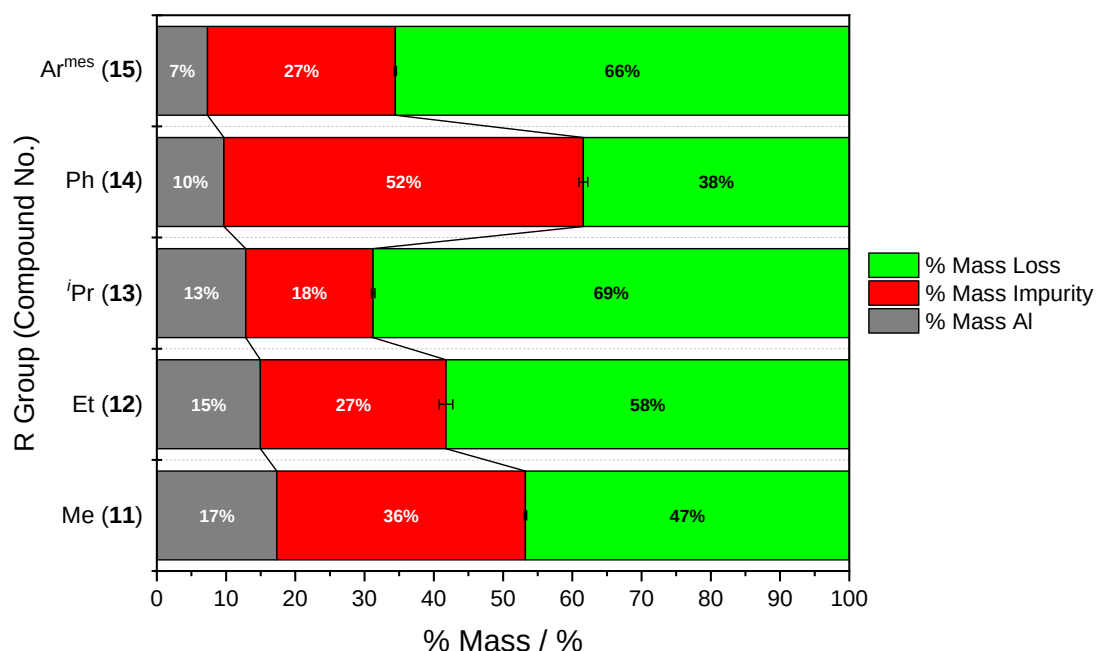


Figure 5.14: Comparison of precursor (11–15) mass loss %'s with associated errors.

Due to each compound only containing one β -diketiminato ligand and two small hydride co-ligands, each complex can achieve near optimal tetrahedral geometry at the metal centre ($\tau'_4 = 0.94, 0.94, 0.96, 0.95$ for complexes **11**, **13–15** respectively – calculated using crystal structure data from original sources). As complex distortion about the metal centre can lead to significant variations in metal-ligand bond distances, which can in turn affect

decomposition properties, the drastic difference in decomposition properties observed in this series (which do not have large distortion differences between complexes) are likely due to other factors (decomposition temperature vs structure factor plot given in Appendix 136). One factor that may give clues into the decomposition behaviour across the series in the correlation between shorter Al–H bond lengths and lower complex decomposition, which one may find anti-intuitive. More complexes across the series need to be analysed thermally to further elucidate these findings (decomposition temperature vs Al–H bond length plot given in Appendix 137).

5.2.4.2 Thermal decomposition of tertiary amine-stabilised alanes

Thermal analysis of the amine-stabilised alane compounds **16–21** show that they generally display decomposition temperatures in the window that enables deposition of aluminium onto low-cost flexible substrates (50–200 °C). Here we see a how compound decomposition temperature is dependent on the pK_a of the Lewis basic ligand as highlighted by Humphries *et al.*²⁸ Usually, upon thermal decomposition of a Lewis base-stabilised AlH_3 complex, the ligand dissociates to leave binary AlH_3 , which then immediately decomposes *via* an autocatalytic process to Al metal and H_2 . This mode of decomposition is preferential as it means no carbon residues should be incorporated into the metal films, as the ligand has already been removed. Although these compounds have been previously thermally analysed, a systematic approach of analysing each compound under the same repeatable conditions has not been undertaken previous to this work, to select the best precursor for solution-based aluminium deposition.

5.2.4.2.1 Thermal decomposition of **TMAA (16)**

The Thermogram of **TMAA (16)** (Figure 5.15) shows a clean single-step decomposition at very low temperature with significant mass loss beginning at 69 °C. A mass loss of 86% was recorded after heating to 300 °C, with a mass loss of 70% expected if pure Al metal is formed and a mass gain of 14% if pure Al_2O_3 is formed. **TMAA** sublimes at modest temperatures (vapour pressure: 1.1 Torr, 19°C)¹⁷ and the fact we see a greater mass loss than expected if pure aluminium metal is formed is evidence that sample was lost from the crucible before decomposition occurs. Although high volatility can ease compound purification as seen in Section 5.2.3.1, it can also leads to complications when designing an ideal MOD ink, as it not only can higher volatility make the ink more difficult to handle, it can lead to precursor loss from a hot surface (*i.e.* sintering conditions) before it decomposes to the desired material. Nevertheless, the high mass loss recorded for this precursor is extremely promising as it means very little non-metallic content is left behind, which would hamper film conductivity. The mass increase at *ca.* 130 °C is could be due to decomposed material settling in the pan after being blown upwards by the escaping gas from degradation, however the shallower mass gain is likely owing to the aluminium metal slowly oxidising due to the atmosphere not being perfectly inert.

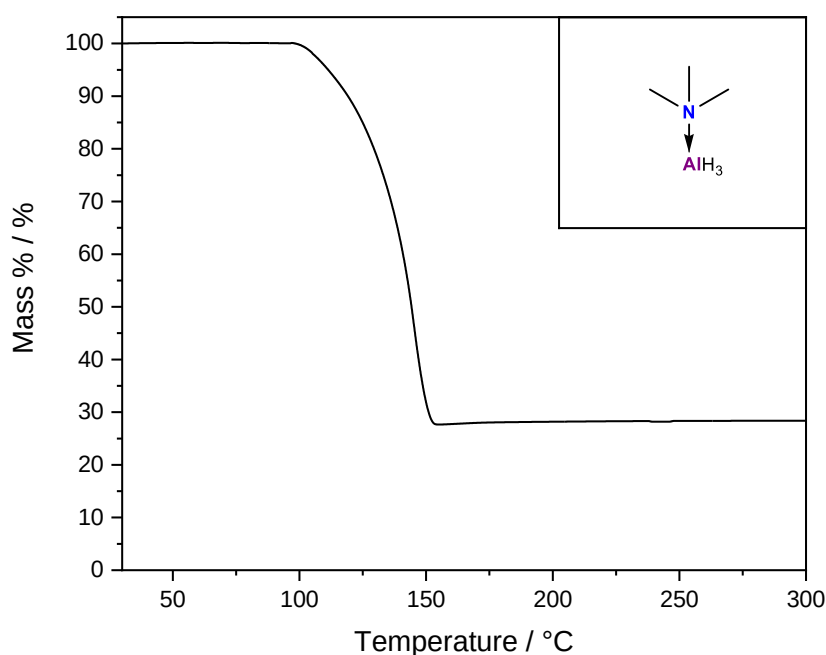


Figure 5.15: Thermogram of **TMAA (16)**. (AA smooth, points of window = 100).

5.2.4.2.2 Thermal decomposition of **DMEAA (17)**

The Thermogram of **DMEAA (17)** (Figure 5.16) shows a clean single-step decomposition at very low temperature with significant mass loss beginning at 72 °C. A mass loss of 71% was recorded after heating to 300 °C, with mass losses of 74% expected if pure Al metal is formed and 1% if pure Al_2O_3 is formed. **DMEAA** is also volatile at modest temperatures (vapour pressure: 1.5 Torr, 25°C),¹⁷ so it is likely mass was lost from the system before decomposition occurs which will affect the mass loss value, although this effect is less apparent than for deposition involving **TMAA (16)**. As with **16**, the high mass loss is promising as it means very little non-metallic residues left behind. There is very little to choose between **TMAA** and **DMEAA** in terms of decomposition properties. This is understandable as there is only a small difference in the strength of amine lone pair donation to the alane moiety ($\text{p}K_a$ of conjugate acids; trimethylamine = 9.76, DMEA = 9.99),¹⁰⁴ meaning that the donor-acceptor bond strengths are similar, which results in there being only a small difference in the activation energy (heat supplied correlating to temperature in the case of TGA) required to break the amine-alane bond before full decomposition can occur. Additionally, the steric bulk of each amine ligand is comparable, so any reductions in steric strain upon decomplexation are likely to be minimal.

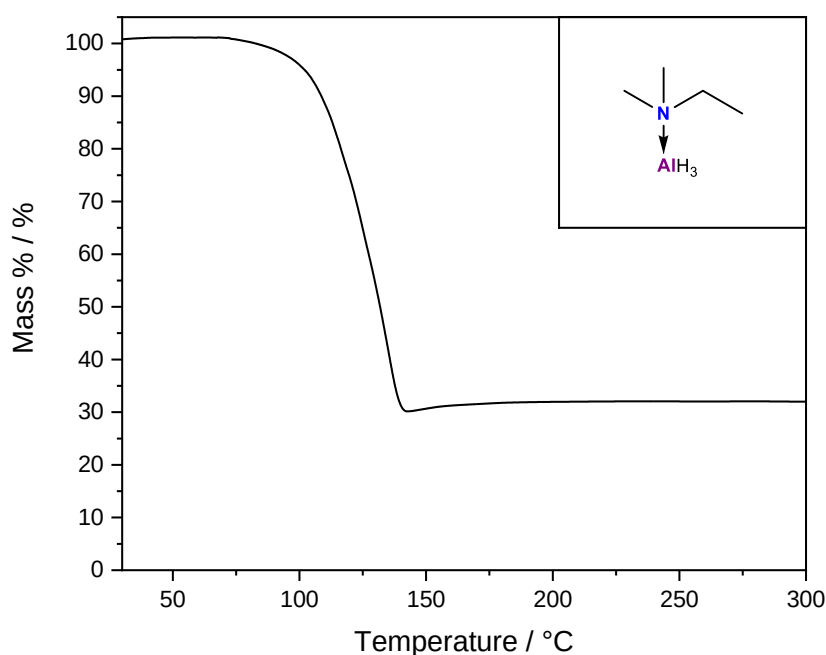


Figure 5.16: Thermogram of **DMEAA (17)**. (AA smooth, points of window = 50).

5.2.4.2.3 Thermal decomposition of **TEAA (18)**

The Thermogram of **TEAA (18)** (Figure 5.17) shows a clean single-step decomposition at very low temperature with significant mass loss beginning at 59 °C. A mass loss of 66% was recorded after heating to 300 °C, with mass losses of 79% expected if pure Al metal is formed and 22% if pure Al_2O_3 is formed. Again, **TEAA** is volatile at modest temperatures (vapour pressure: 0.5 Torr, 25 °C)¹⁷, albeit less so, so again it is likely mass was lost from the system before decomposition occurs which will affect the mass loss value. As with the other amine-stabilised alanes, the high mass loss is promising, however, in this case we do start to see a significant difference between measured mass loss and expected mass loss, meaning it is probable there is a significant amount of carbon residues remaining, likely owing to the increased carbon content in the precursor. The extended decomposition range is most likely due to the increase basicity of the TEA ligand ($\text{p}K_a$ of the conjugate acid = 10.66),¹⁰⁴ meaning greater amounts of energy are required to break the dative bond, this may also explain by decomposition occurs over a longer temperature range/period of time.

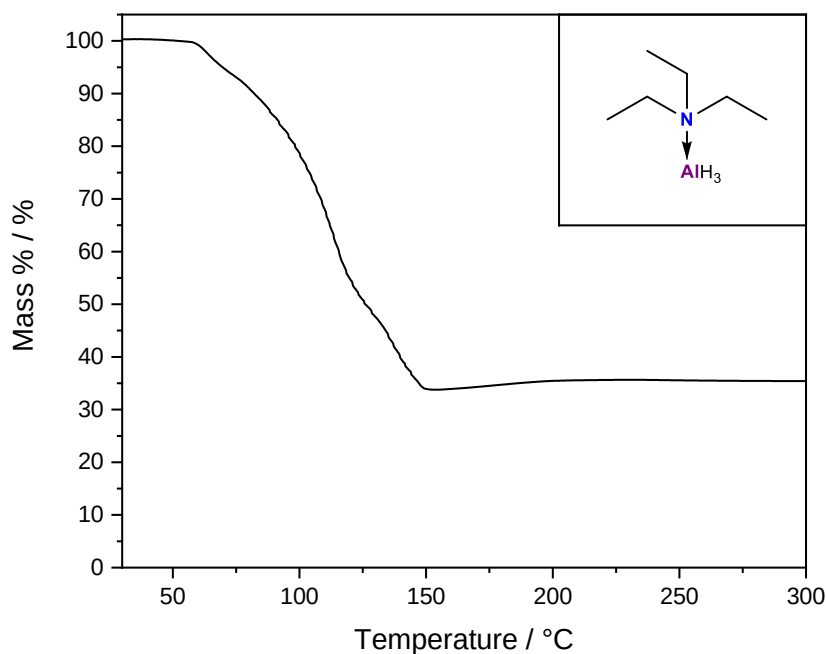


Figure 5.17: Thermogram of **TEAA (18)**

5.2.4.2.4 Thermal decomposition of **TAAA (19)**

The Thermogram of **TAAA (19)** (Figure 5.18) shows a two-step decomposition at low temperature with the final decomposition stage occurring at 117 °C. Here we see a two-step mass loss process, likely due to the complex more structure of the high boiling point amine (bp = 150 °C),¹⁰⁵ which may form a higher decomposition temperature by-product (polymeric) on the way to full decomposition. A total mass loss of 68% was measured after heating to 300 °C, with a mass loss of 84% expected if pure Al is formed and 39% if pure Al₂O₃ is formed. Here the alane adduct is less volatile due to the higher boiling point Lewis base, so mass loss measurements are likely to be more accurate. Like with **TEAA**, a larger ligand carbon content in the ligand results in more organic residues being left behind after decomposition, however in this case, using a higher boiling point amine ensures even more residual amine remains in the crucible when amine decomposition occurs. Interestingly, the basicity of TAA is the lowest of all the amines used (p*K*_a of conjugate acid = 8.31),¹⁰⁴ which means the alane-amine bond should be the weakest of all the others synthesised for 1:1 adducts, however this is not reflected in the decomposition data of the complex likely owing to the decomposition characteristics of the amine itself.

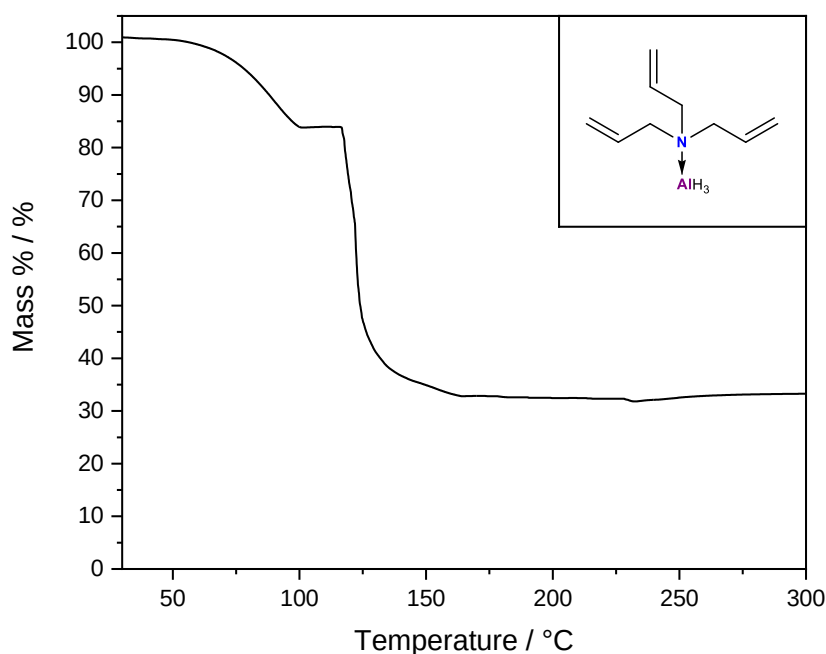


Figure 5.18: Thermogram of **TAAA (19)**.

5.2.4.2.5 Thermal decomposition of **TMEDAA (20)**

The Thermogram of **TMEDAA (20)** (Figure 5.19) shows a two-step decomposition with the final decomposition stage occurring at 216 °C. Here we see a two-step mass loss process, likely due to the complex more structure of the high boiling point amine (bp = 121 °C),¹⁰⁵ which may form a higher decomposition temperature by-product (polymeric) on the way to full decomposition. A total mass loss of 63% was measured after heating to 300 °C, with a mass loss of 82% expected if pure Al is formed and 30% if pure Al₂O₃ is formed. As with **TAAA**, the decomposition properties of the high boiling point amine hampers the compound losing its non-metallic mass at low temperatures and here with the polymeric nature may add extra stability that such higher temperatures are required to first sequester the polymeric adduct before it can undergo full decomposition.

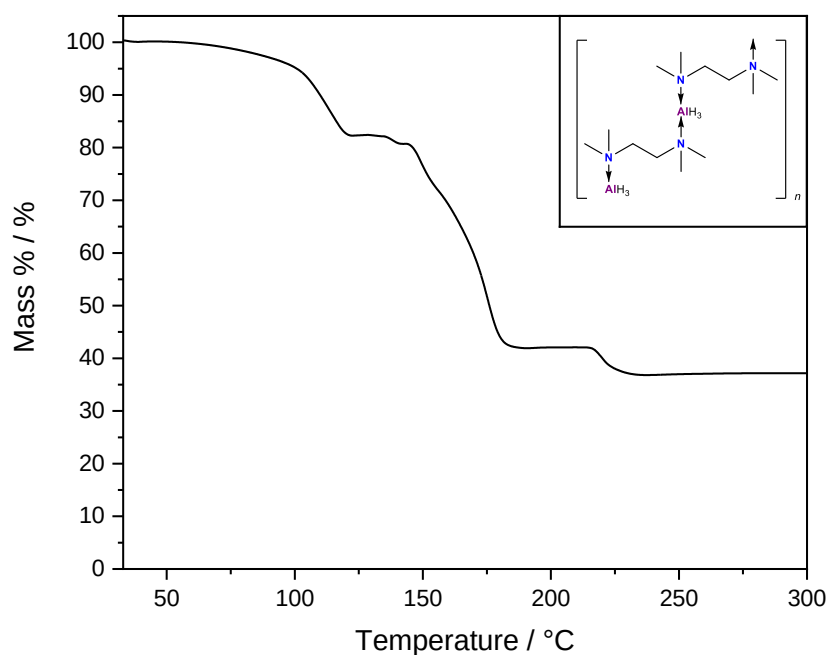


Figure 5.19: Thermogram of **TMEDAA (20)**. (AA smooth, points of window = 50).

5.2.4.2.6 Thermal decomposition of $[\text{AlH}_2\text{Cl}\cdot 2(\text{NMP})]$ (**21**)

The Thermogram of **21** (Figure 5.20) shows a clean single-step decomposition at low temperature with significant mass loss beginning at 126 °C. A mass loss of 68% was recorded after heating to 300 °C, with mass losses of 89% expected if pure Al metal is formed and 57% if pure Al_2O_3 is formed. The % mass loss for the chloride co-ligand is 15%, so if this was incorporated into the residual mass, a mass loss of only 73% would be expected, which is in a much greater agreement with the experimental mass loss measured. The integration of Cl into the residual mass may explain the small residual mass loss from 161°C up to 300 °C as anhydrous AlCl_3 (*i.e.* potentially some impurity) sublimates at 180 °C.¹⁰⁵

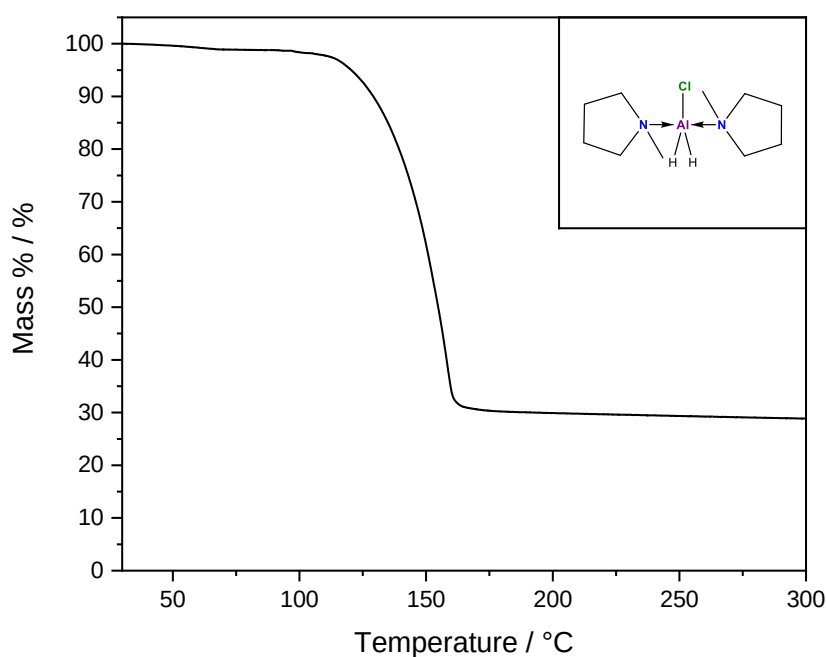


Figure 5.20: Thermogram of $[\text{AlH}_2\text{Cl}\cdot 2(\text{NMP})]$ (**21**).

5.2.4.2.7 Thermal decomposition summary

Thermal analysis of the amine-stabilised alane compounds **16–21** show that they generally decompose at low temperatures (<200 °C) as expected and the majority are well-suited for purpose in the pursuit of depositing aluminium metal at low temperature (Table 5.5).

Table 5.5: Expected % residue, % of non-volatile residue and onset/end of volatilisation/decomposition for complexes **16–21**.

Precursor	Expected Mass Loss % for Al, Al ₂ O ₃	% Non-volatile Residue	Onset Temp.	End Temp.
TMAA (16)	70%, gain 14%	86%	69 °C	153 °C
DMEAA (17)	74%, 1%	71%	72 °C	141 °C
TEAA (18)	79%, 22%	66%	59 °C	151 °C
TAAA (19)	84%, 39%	68%	117 °C	163 °C
TMEDAA (20)	82%, 30%	63%	216 °C	231 °C
[AlH ₂ Cl·2(NMP)] (21)	89%, 57%	68%	126 °C	169 °C

As previously mentioned, work by Humphries *et al.*¹⁸ ligand basicity affects compound thermal stability and we generally see this within the results collected (Figure 5.21, lower pK_a, weaker amine-alane bond, lower decomposition temperature) however there are many other factors at play such as ligand cone angle and what type of adduct (1:1, 1:2, polymeric) the complexes form, as well as, the decomposition properties of the amines themselves. Also more accurate decomposition temperatures for the more volatile compounds would be of great value and are more likely to be accurately identified using DSC, as highlighted in Section 2.4.1.

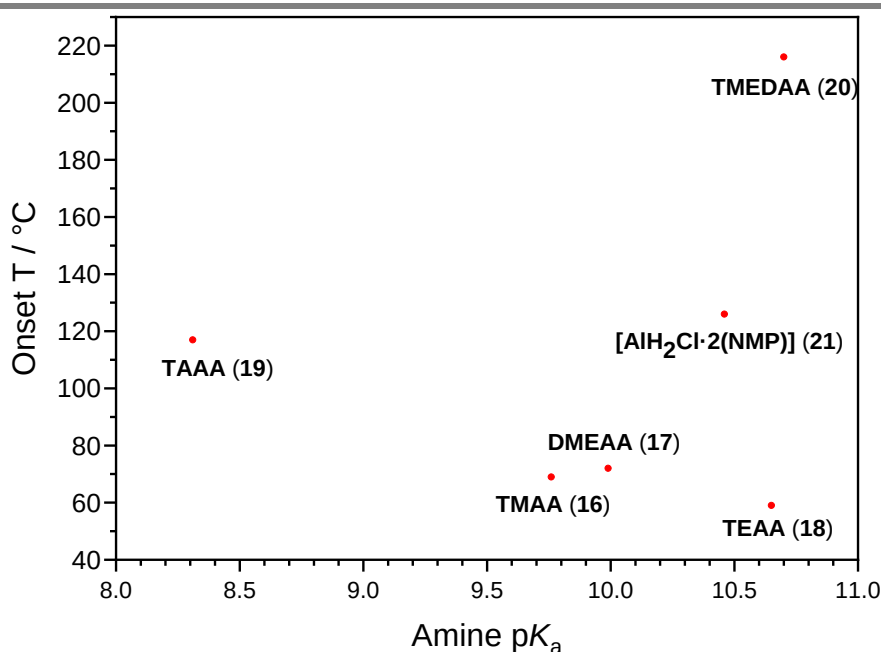


Figure 5.21: Comparison of precursor (16–21) onset decomposition temperatures and amine pK_a. pK_a values taken from literature sources.¹⁰⁴

Alanes generally decompose with low levels of impurity present (<23%) however the results for the more volatile precursors are obscured due to volatilisation/sublimation before decomposition takes place (Figure 5.22) – there is currently no TGA experimental set-up that can remedy this issue.

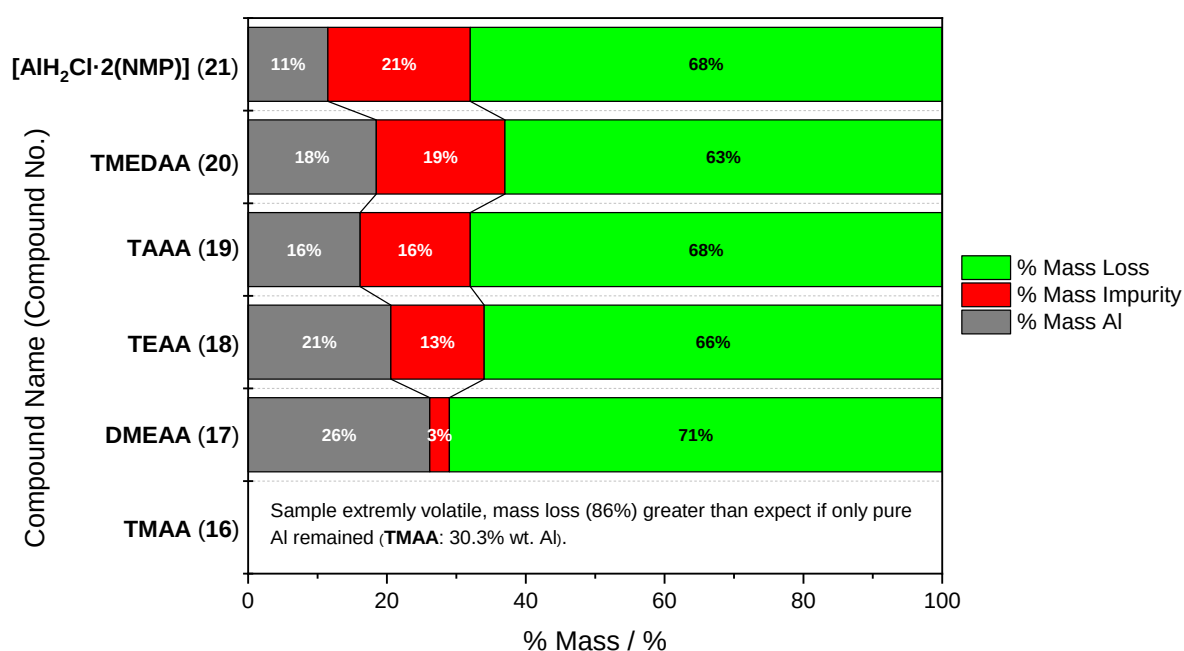


Figure 5.22: Comparison of precursor (16–21) mass loss %'s with associated errors.

5.3 Summary

Two families of compounds, both containing Al–N and Al–H bonds (in addition to an absence of Al–O bonds) have been synthesised: mono(β -diketiminate) aluminium dihydrides and amine-stabilised alanes, which have been analysed thermally (many for the first time) to gauge their suitability as MOD precursors to aluminium metal coatings *via* low temperature solution-based processing. β -diketiminate complexes were found to decompose at too high temperatures ($>250\text{ }^{\circ}\text{C}$) to be fit for purpose and decomposition left large amounts of impurities. Initial results suggest that for this family of precursors, compound decomposition temperature may correlate to the Al–H bond distances found in these structures, however more investigation into this is required. Amine-stabilised alane compounds, being more well-known in precursor chemistry, exhibited excellent decomposition properties, generally decomposing at low temperatures ($<200\text{ }^{\circ}\text{C}$), with small amounts of impurities present. Here we see how the complexed amine plays a key role in precursor decomposition characteristics, particular its basicity and denticity (which dictates donor-acceptor bond strength and which type of adduct is formed), boiling point and steric bulk. Of all the amine-stabilised alanes analysed, two liquid precursors with the best thermal properties: **DMEAA** and **TEAA** were chosen to fabricate coatings of aluminium metal in the subsequent Chapter.

5.4 References

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Chapter 6

Deposition of MOD Precursors to form Aluminium Metal Films

This Chapter involves the solution-based deposition of two of the best performing MOD precursors thermally analysed in this work, followed by their low temperature thermal sintering. The films were analysed using a multitude of techniques to gauge the effectiveness of the most promising formulations.

6.1 Introduction

As introduced in earlier Chapters, although there is much interest in producing high quality aluminium oxide films, ideally aluminium precursors would decompose to the metal under inert conditions. This would yield versatile aluminium precursors that can decompose to different materials under varying conditions. Conductive metal coatings are highly sought after and so precursors that can produce either metal (when deposited in the absence of air) or metal oxide (when decomposed in air/in the presence of a solvent that is an oxide source) are of great interest. This Chapter focusses on the deposition of two amine-stabilised alanes; **DMEAA** and **TEAA**, to form aluminium metal films without the need of a reducing agent.

6.1.1 Deposition of aluminium metal films

There is a great desire to deposit tracks of aluminium metal in the electronics industry due to it possessing several favourable characteristics such as its high electrical conductivity ($\rho = 2.65 \times 10^{-8} \Omega \text{ m}$, 20 °C),¹ low work function ($\Phi = 4.08 \text{ eV}$)² and high Earth abundancy as introduced in Chapter 1.³ As with other conductive metals, there is a particular driving force to deposit aluminium metal films at low temperature to enable deposition onto low-cost flexible substrates such as paper, plastics and textiles to enable a multitude of different applications.^{4,5} Traditional methods of metal deposition include dip- and powder- coating methods, electrochemical and electroless depositions from liquid solutions, as well as, by PVD and CVD.⁶ This Chapter aims to deposit metal films using aluminium containing species suspended in a liquid vehicle, more commonly known as aluminium metal inks.

Historically, research into the formulation and deposition of aluminium metal inks has been lacking, most likely owing to aluminium's high reactivity making it particularly prone to oxidation to non-conductive oxides, inhibiting film performance. Due to aluminium's affinity to react with oxygen and water in air, aluminium precursors and their formulations must be designed, stored and the latter deposited under inert conditions, using methods and equipment which are often laborious and expensive. Like with other conductive metal inks, aluminium metal tracks can be deposited using either metal-organic decomposition (MOD) precursor or nanoparticle (NP) formulations.^{4,5} Whilst both fields are in their infancy in relation to aluminium, the former has been more extensively researched and is also the subject of research in this Chapter. A summation of the introduction is given in Section 6.1.4, alongside Table 6.1 which summarises (and compares) the majority of the literature covered henceforth.

6.1.2 Depositing aluminium metal films using MOD precursors

As highlighted in Chapter 1, in 2010 Rockenberger *et al.*⁷ listed a broad array of stabilised aluminium compounds, most of which are base-stabilised alane compounds, capable of decomposing at temperatures around 100 °C, however the document gives no description of the specific precursors, formulations and processes used to achieve the best aluminium metal films. Curtis and co-workers⁸ had previously published a patent in 2009, with some details of the deposition of amine-stabilised alane on a silicon substrate, which was heated to a temperature of above 140 °C, under an inert atmosphere. The lack of academic literature at this time into the solution-based deposition of these compounds, showed that the researchers within this field were excited about the viability of industrial application.

Unquestionably the research by Lee *et al.* over the last decade has significantly contributed to the Al MOD ink field, being the first group to publish their work within academic literature. They first debuted their novel warm solution-stamping process in 2011 (Figure 6.1), using an ether-stabilised alane, $[\text{AlH}_3 \cdot \{\text{O}(\text{i-Bu})_2\}]$ (DBEA) with all procedures performed in an Ar-filled glove box, to prevent formation of aluminium hydroxide, $\text{Al}(\text{OH})_3$, aluminium oxide, Al_2O_3 and aluminium nitride, AlN , which would reduce the conductivity of the Al films produced.⁹

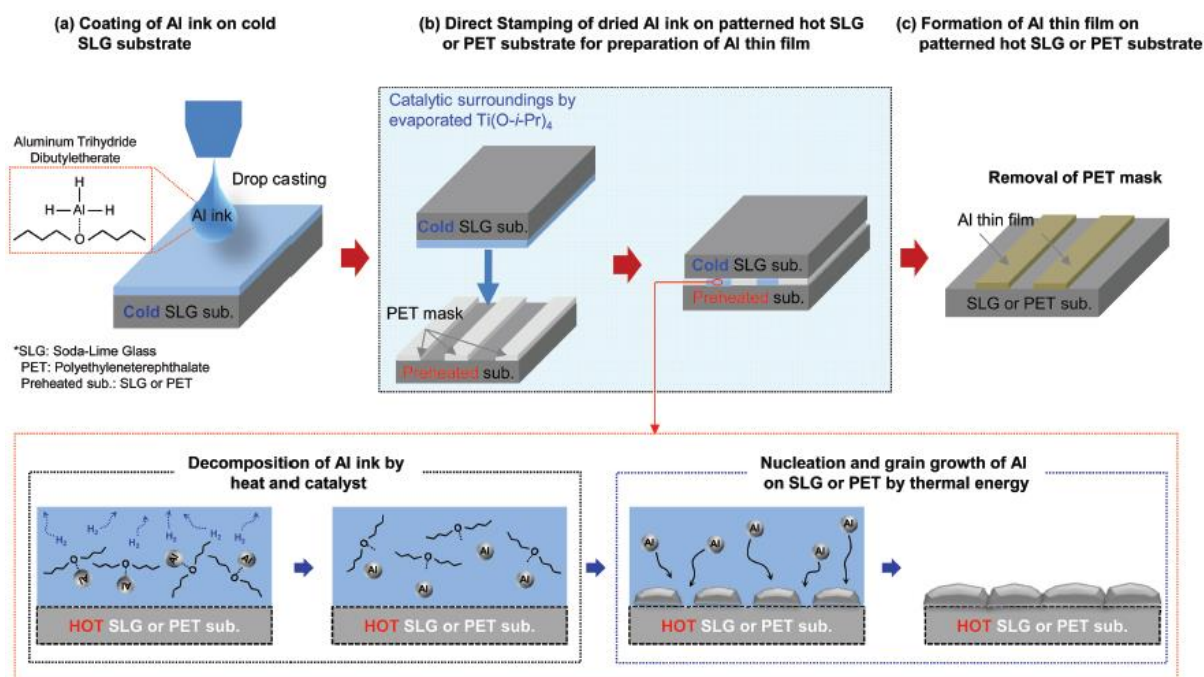
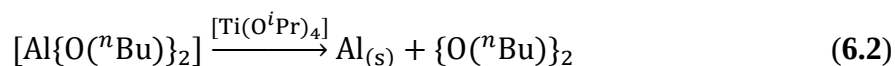
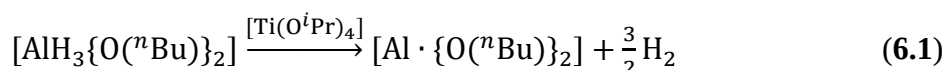


Figure 6.1: Lee's novel solution-stamping process to deposit highly conductive Al films using DBEA.⁹

The solution-stamping process yielded films with excellent electrical and promising mechanical properties on both rigid and flexible substrates, with a minimum electrical resistivity of $8 \mu\Omega \text{ cm}$ achieved using a sintering temperature of 150°C . A minimum sintering temperature of 90°C was investigated, however a film with more modest resistivity of *ca.* $1.5 \mu\Omega \text{ cm}$ was produced. The etherate precursor thermally decomposed in a two-step process as first detailed by Brower *et al.*,¹⁰ with the novel additional aid of evaporated titanium isopropoxide (TTIP), $[\text{Ti}(\text{O}^i\text{Pr})_4]$ to assist reduction/prevent oxidation of the Al centre (Eqn. 6.1 and 6.2). In the absence of the TTIP “catalyst” exposure process, the decomposition of the Al precursor ink occurred at a higher temperature of 165°C . The authors state that when the Al MOD ink is exposed to a high temperature atmosphere of the catalyst, the etherate decomposes spontaneously due to the low Gibbs free energy of the reaction.^{9,11}



After optimisation of the solution-stamping procedure, films showed uniform thicknesses. Uniform film thicknesses are imperative, as a metal film’s thickness is proportional to its electrical conductivity, as highlighted in Section 2.5.1. The effect of film morphology at varying sintering temperatures was also analysed, which showed that when the ink was sintered at higher temperatures, surface grain sized decreased resulting in smoother films (Figure 6.2).

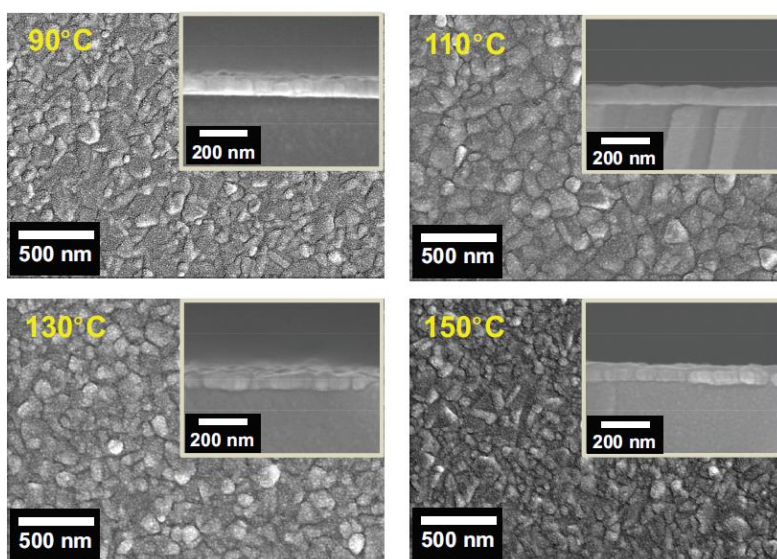


Figure 6.2: SEM images showing DBEA depositions with differing morphologies under varied sintering temperatures.⁹

A year later, Lee and co-workers¹² used the same solution-stamping process analyse aluminium metal deposition on various types of paper. Films were *approx.* 50 μm in thickness and their morphology varied slightly depending on the paper type, with all films exhibiting excellent electrical and mechanical properties (Figure 6.3a and b). The best films were deposited onto inkjet printing paper, with a minimum resistivity of *ca.* 60 $\mu\Omega\text{ cm}$ recorded.

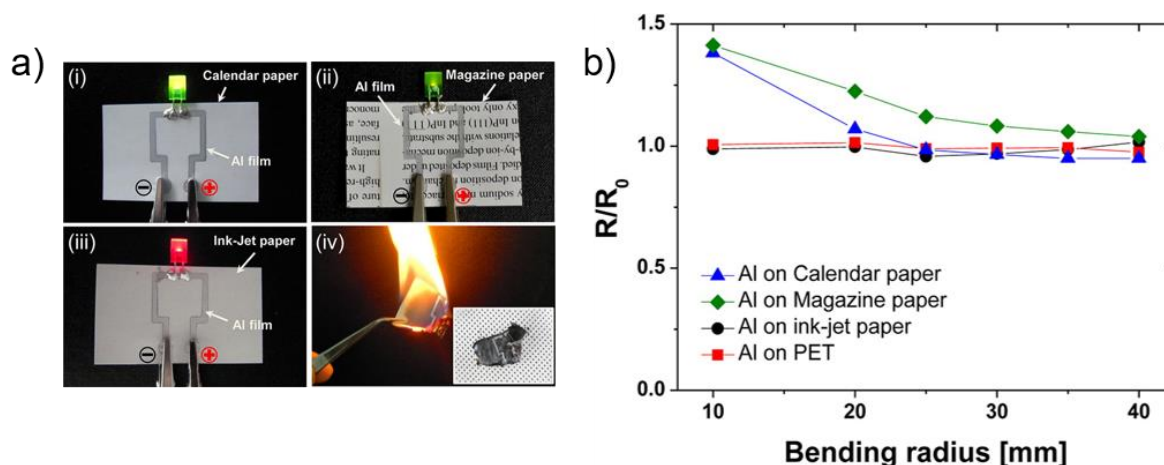


Figure 6.3: a) Electronic circuits formed from DBEA depositions on various paper substrates, along with combustion of a circuit to show little waste is produced. b) Electrical resistance change of said Al features on various paper and PET substrates under various bending radii.¹²

Fei *et al.*¹³ used a variation of Lee's solution-stamping process, depositing diisopropyl ether-stabilised alane (DiPEA), $[\text{AlH}_3 \cdot \{\text{O}(i\text{Pr})_2\}]$ in the presence of a titanium tetrachloride, TiCl_4 reduction catalyst. The best metallic feature was sintered at 80 $^\circ\text{C}$ for 30 s to form a 50 nm thick cathode with a sheet resistance, R_s of 2.09 $\Omega\text{ sq}^{-1}$ and a work function of 3.67 eV. They state that by swapping from dibutyl ether to diisopropyl ether, lower sintering temperatures were possible allowing them to deposit onto a larger range of substrates. They state that the more well-known diethyl ether alane analogue (introduced in Chapter 1) was not used as it is extremely flammable, even at temperatures as low as -5 $^\circ\text{C}$.

In 2013, Lee *et al.*¹⁴ employed a different deposition technique opting for a novel solution-dipping process, once using their DBEA precursor (Figure 6.4). The process involved dipping a pre-heated (100 $^\circ\text{C}$) and pre-treated (TTIP coated) substrate into the precursor solution at room temperature. The technique allowed preparation of films with a large surface area and could also be used to deposit conductive patterns when used with a mask as with the solution-stamping process. As dipping time increased, the standard deviation in both film thickness and

electrical resistance increased. Films showed good sheet resistance values on glass and PET substrates (lowest $R_s = 2.6 \, \Omega \, \text{sq}^{-1}$ reported on PET) with only a small decrease after adhesion (Scotch tape) and bending (10,000 cycles) testing. In 2015, Choi *et al.*,¹⁵ working in the Lee group, were able to deposit Al metal on catalytically treated (TTIP) tissue paper with a high electrical conductivity ($R_s = \sim 0.700 \, \Omega \, \text{sq}^{-1}$), which was used in high performance lithium-sulphur batteries.

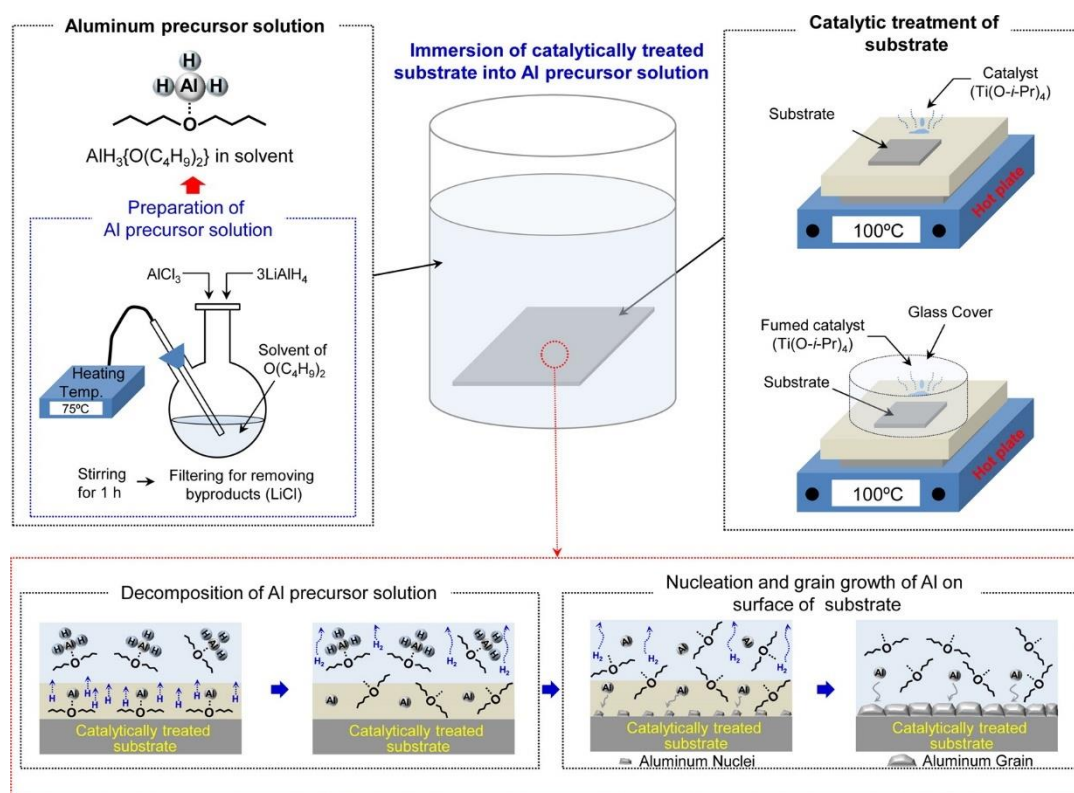


Figure 6.4: Lee's novel solution-dipping process to deposit highly conductive Al films using DBEA.¹⁴

DBEA has limited stability over time and as such Lee *et al.*¹⁶ reported the inventive solution of producing an ink which could be formulated by dissolving a solid alane precursor in solvent (Figure 6.5a). $[\text{AlH}_3 \cdot \text{NMe}_3]$, TMAA was chosen as not only was it a solid under standard conditions, amines are stronger bases than ethers so tend to form more stable adducts. All featured inks were deposited on glass and PET using the aforementioned solution-stamping process (substrate at $130 \, ^\circ\text{C}$) under an inert atmosphere. Little decomposition of the precursor occurred when refrigerated (*ca.* $5 \, ^\circ\text{C}$), with only small differences in the quality of film produced between inks using the as-prepared and 180 day stored alane precursor. The solubility and efficacy of dissolving the powder-type alane in several solvents (diethyl ether, dibutyl ether and toluene, Figure 6.5b) was also assessed, with no clear winner (all $\rho < 8 \, \mu\Omega \, \text{cm}$, Figure 6.5c).

Interestingly, there has been no follow up work in the Lee group investigating amine-stabilised alanes. Shen¹⁷ had previously suggested the use of amine-stabilised alanes as MOD precursors to aluminium metal, opting to use the liquid $[\text{AlH}_3 \cdot \text{NEt}_3]$, TEAA under standard conditions. Their deposition process was expensive (Pt catalyst required) and produced films of high surface roughness.

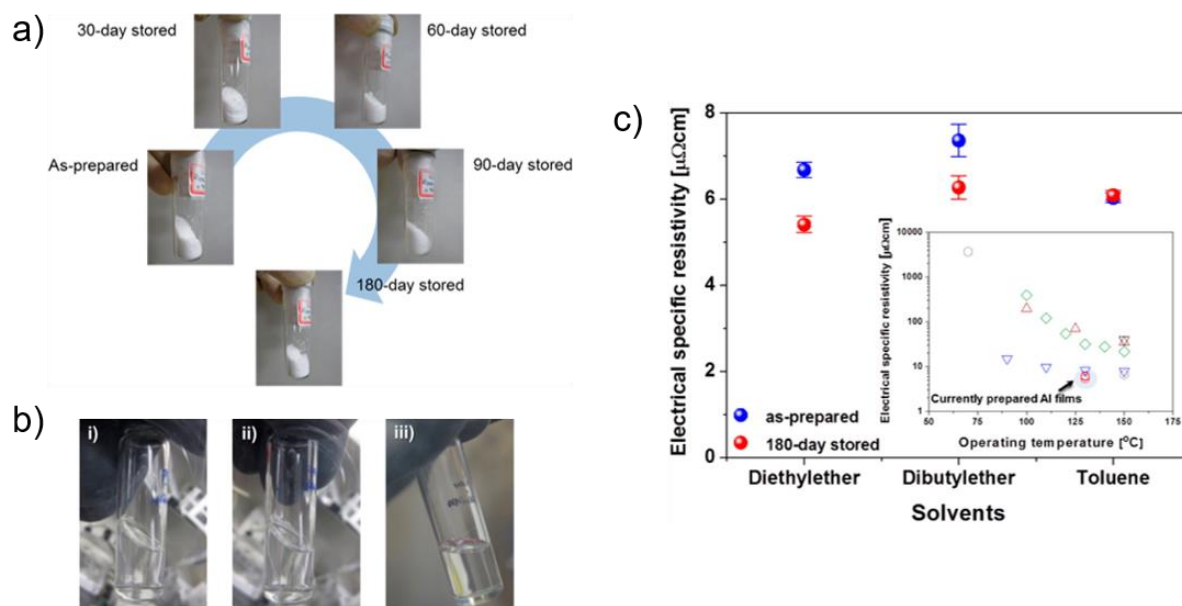


Figure 6.5: a) As-prepared and 30–180-day stored TMAA powders at $\sim 5^{\circ}\text{C}$. b) Al MOD inks prepared by fully solving the 180-day stored TMAA powders in i) diethyl ether, ii) dibutyl ether and iii) toluene. c) Electrical specific resistivity of as-prepared and 180-day stored TMAA depositions using different ink solvents, sintered at 130°C (inset: comparison of Al films prepared in Lee's research with previously reported samples).¹⁶

In 2018, Jung *et al.*¹¹, working in Lee's research group, took major steps in industrialising their Al deposition process, one again using their DBEA precursor, by applying it to a roll-to-roll (R2R) printing process to deposit metallic thin films on PI (Figure 6.6a).¹¹ R2R printing is the industrial counterpart of inkjet printing, which enabling large scale manufacture. Although this technique is not as technologically advanced as inkjet printing, being able to produce less intricate designs, it is much better suited to high throughput device fabrication and has traditionally only been used for more standard inks.¹⁸ Lee's group took dried PI substrates (overnight at 80°C) and exposed them to a diluted catalyst (100:1 volumetric ratio of dibutyl ether to TTIP, before coating them with their DBEA MOD ink using a slit-die-coating method. High quality Al lines were produced with a width of 130 mm at a speed of 5 cm s^{-1} (Figure 6.6b). Deposits exhibited high durability and adhesion, with a lowest resistivity of

$1.70 \times 10^5 \Omega \text{ m}$ for a 60.9 nm thick film. The Al metal films were resistant to oxidation, with only a minor change in their resistivity when they were heated to 100 °C in air for 10 days, or when they were exposed to H₂O or ethanol. To demonstrate the applicability of the R2R-process, the Al metal films produced was used to fabricate a flexible touch panel.¹¹

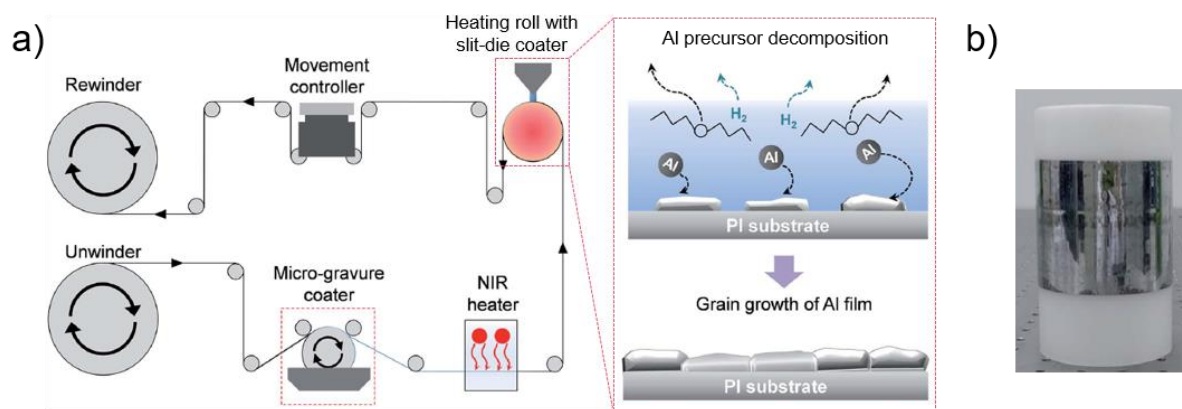


Figure 6.6: a) Schematic of the fabricated R2R machine and decomposition mechanism. b) Prepared Al film on the PI substrate, straight edge created using mask.¹¹

6.1.3 Depositing aluminium metal films using NP precursors

As introduced in Chapter 1, the main competitor to MOD inks in depositing metal films are NP formulations. At present, most commercially available metal NP inks are Ag or Cu based, due to their high conductivity of the metallic and lower tendency to oxidise in the zerovalent state. The problem of NP oxidation (which is also experienced in Cu NP chemistry) is amplified when using Al as the source metal, as it suffers drastically from the highly thermodynamically stable surface oxide layer forming. When used in the bulk, the native oxide layer of Al (~3–5 nm) is negligible, however in NPs, the surface-to-volume ratio of oxide to metal limits electrical performance. Thus, it is essential to use capping agents to prevent surface oxidation, which has also been seen in Cu NP chemistry, where materials such as carbon,¹⁹ organic surfactants,²⁰ metal salts²¹ and secondary metals²² have been used. A bonus of using organic surfactants as capping agents is that they aid in preventing aggregation and precipitation, as introduced in Chapter 1. A similar capping approach curbing Al reactivity has been applied to Al NP-based fuels and rocket propellants.^{23,24}

Lee *et al.*²⁵ are one of the only groups to research Al NPs for use in conductive inks. Al NPs were synthesised using an adapted version of the Haber and Buhro²⁶ method using DMEAA as the Al source and TTIP as the decomposition catalyst. Oleic acid was used to cap the NPs, with particle size dependent on the capping agent injection time. All synthetic procedures were

conducted in an Ar-filled glove box to prevent oxidation. Surface capping was confirmed via XPS which also showed the absence of an oxide layer. The prepared NPs were stored in a low humidity desiccator for 2 days prior to XPS analysis, meaning that the oxidation stability study of NPs in this work was limited to 2 days in air.

Conductive films were depositing using a 30 wt.% solution in toluene *via* spin-coating, with films sintered in a reducing atmosphere (10% H₂ with 90% Ar) at temperatures of 200–600 °C. The transformation of the particles into continuous film was observed using SEM (Figure 6.7a–c). As expected, the surface morphologies of the films differed depending on the sintering temperature. When the NPs were sintered at 200 °C, small particle sizes that did not physically contact each other were observed, leading to poor resistivity. The coalescence of NPs started from 400 °C, which was intuitive as at this temperature, oleic acid could be efficiently removed (bp = 360 °C). When the Al NPs were sintered at over 400 °C, little aggregation between particles was observed and the average particle size gradually increased as sintering temperature increased. The best films were deposited at 600 °C with a lowest $\rho = 4.12 \times 10^{-7} \Omega \text{ m}$, approximately ten times greater than bulk Al, as this temperature allowed for the greater coalescence of particles. Whilst these processing temperatures are high, the work function of the exemplar film was calculated to be 4.22 eV, indicating that Al NPs are more efficient than noble metals such as Ag and Cu for use in electrodes.

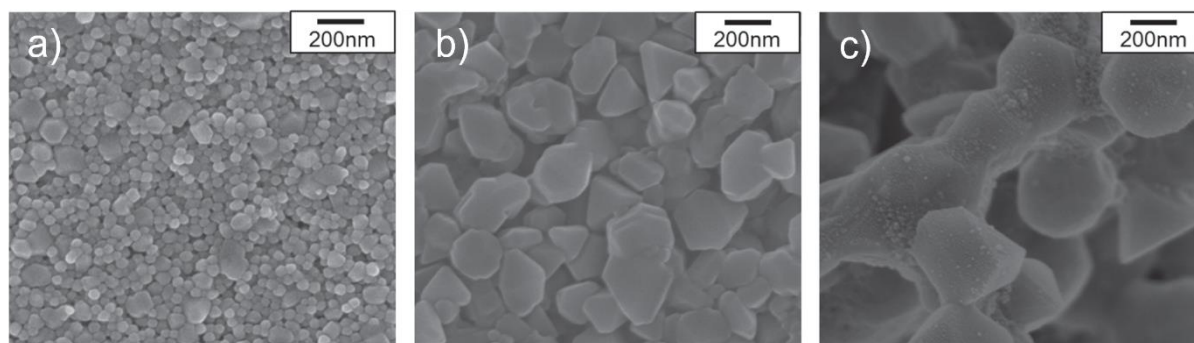


Figure 6.7: Surface morphology of Lee's Al NP films after sintering at a) 200 °C, b) 400 °C, c) 600 °C.²⁵

6.1.4 Solution-based Al deposition summary

A range of solution-based deposition processes has been used to deposit aluminium metal films, all of which have used Lewis base-stabilised alanes as the Al source. To date, all depositions have been conducted under either inert conditions, with the majority also opting to deposit in the presence of a decomposition catalyst. Currently, only thermal sintering has been explored to improve film quality, with other sintering techniques such as using UV radiation or plasma, offering unrealised potential to further lower deposition temperatures. NP Al ink chemistry is in its infancy, with there being plenty of scope to apply practices seen in Cu NP chemistry. Table 6.1 provides a detailed summary of the literature introduced in this Section, allowing the reader to compare and contrast the Al precursors and substrates used, as well as, deposition and sintering conditions, alongside best resistivities reported.

Table 6.1: Important discoveries using non-commercial Al MOD and NP inks to deposit Al metal films. Inks appear in the order they are mentioned. For ease of comparison, all conductivity values have been converted to volume resistivity in units of $\Omega \text{ m}$ (note: $\Omega \text{ m} = (\text{S m}^{-1})^{-1}$). Sheet resistance values have not been converted as information is not always given as to the volume of the films. Detailed descriptions of substrate pre-treatments are not listed here. *Value has been extrapolated from graph in the respective paper.

Ink composition	Substrate/s	Deposition Technique	Sintering Conditions	Resistivity/Resistance	Reference
DBEA	Glass, PET	Solution-stamping	Chemical and thermal: TTIP substrate, 150 °C, <1 min, under Ar	$\rho \approx 8.00 \times 10^{-8} \Omega \text{ m}^*$	Lee ⁹
DBEA	Paper	Solution-stamping	Chemical and thermal: TTIP treated substrate, 110 °C, 1 min, under Ar	$R_s \leq 2 \Omega \text{ sq}^{-1}$	Lee ¹²
DiPEA	PET	Solution-stamping	Chemical and thermal: TiCl_4 treated substrate, 80 °C, 30 s, under inert conditions	$R_s = 2.09 \Omega \text{ sq}^{-1}$	Fei ¹³
DBEA	PET	Solution-dipping	Chemical: TTIP substrate, solution-dipped at RT for 20 min, dried at RT, under Ar	$R_s \approx 2.60 \Omega \text{ sq}^{-1}$	Lee ¹⁴
DBEA	Tissue paper	Solution-dipping	Chemical: TTIP substrate solution-dipped for 2 h, dried at RT, under Ar	$R_s \approx 0.700 \Omega \text{ sq}^{-1*}$	Choi ¹⁵
TMAA	Glass	Solution-stamping	Chemical and thermal: TTIP treated substrate, 130 °C, 1 min, under Ar	$\rho = 5.80\text{--}7.00 \times 10^{-8} \Omega \text{ m}$	Lee ¹⁶
TEAA	Substrate patterned with Pt nanocrystals	Solution-dipping	Thermal: 105–120 °C, 30 min–2 h, under N_2	$\rho = 2.80\text{--}3.50 \times 10^{-8} \Omega \text{ m}$	Shen ¹⁷
DBEA	PI	Slit-die-coating (R2R printing)	Chemical and thermal: TTIP treated substrate 150 °C, web speed of 3 m min^{-1} , under Ar	$\rho = 1.70 \times 10^{-7} \Omega \text{ m}$	Jung ¹¹
Oleic acid capped Al NPs	Glass	Spin-coating	Thermal: 600 °C, under Ar/H_2 environment	$\rho = 4.12 \times 10^{-7} \Omega \text{ m}$	Lee ²⁵

6.2 Results and discussion

6.2.1 MOD precursor choice

As emphasised throughout this project, one major aim of this work is to deposit conductive aluminium metal films using aluminium MOD inks containing aluminium metal-organic precursors. To assess precursor viability, each family of aluminium precursor were thermally analysed using TGA (in order of appearance: Chapter 3: tris(β -ketoiminate) aluminium complexes; Chapter 4: bis(β -ketoiminate) aluminium monochlorides; Chapter 5: mono(β -diketiminato) aluminium dihydrides and amine-stabilised alanes). Although the families of complexes containing either β -ketoiminate or β -diketiminato ligands showed much greater handleability, this unfortunately came at the cost of poor decomposition characteristics such as high temperature requirements and unclean decomposition under inert gas flow. Solution-depositing these types of complex would likely not show any marked improvement of what has already been undertaken within the literature, as these complexes look better suited to vapour deposition techniques. Alane-based precursors are currently the only family of aluminium compound used to deposit aluminium metal films using solution-based techniques and this is further emphasised by thermal analysis within this project – many of them exhibit considerably lower decomposition temperatures than those using the chelating ligands, with fewer impurities remaining.

Of the many amine-stabilised alanes synthesised, **DMEAA** and **TEAA** were chosen as they both exhibit excellent thermal decomposition characteristics and are liquids at room temperature, so no solvent is required to liquid-deposit them. As mentioned in Chapter 1, one criticism of MOD inks is that their metal weight loading in solution is comparatively low when compared to their NP equivalents – by using liquid precursors, no additional solvent is required thus resulting in higher Al weight loadings (**DMEAA** = 26.2%, **TEAA** = 20.6% Al by mole fraction respectively).

6.2.2 Depositions of MOD precursors

Highly conductive aluminium films on a range of substrates (glass, polyimide (PI), polyethylene terephthalate (PET) and paper – assigned red, black, blue and green colours respectively in the below Figures) were deposited *via* drop-casting at low temperatures (100–120 °C) using **DMEAA** and **TEAA** under an atmosphere of nitrogen. Drop-casting was chosen as the deposition technique of choice as not only it is a good preface to more complex printing techniques, it only requires small amounts of material and a relatively simplistic set-up.

Different low-cost flexible substrates were chosen to analyse the compatibility of the ink (without added solvent) to different surface functional groups. A simple heating setup was used (Figure 6.8) with both compounds deposited on all substrates at 100 °C and 120 °C. Sintering temperatures at higher temperatures (*i.e.* 140 °C) were not thoroughly investigated as significantly warping of the paper substrate was observed, whilst efforts to deposit at 80 °C were unsuccessful, producing non-conductive films despite long sintering times (>20 min, more than the 5 min timing threshold set). Depositions were not aided by the use of a reducing agent (like many of the depositions listed in Table 6.1) as no method to separate the metal films and the oxidised by-products could be devised and thus the by-products could lower film conductivity.

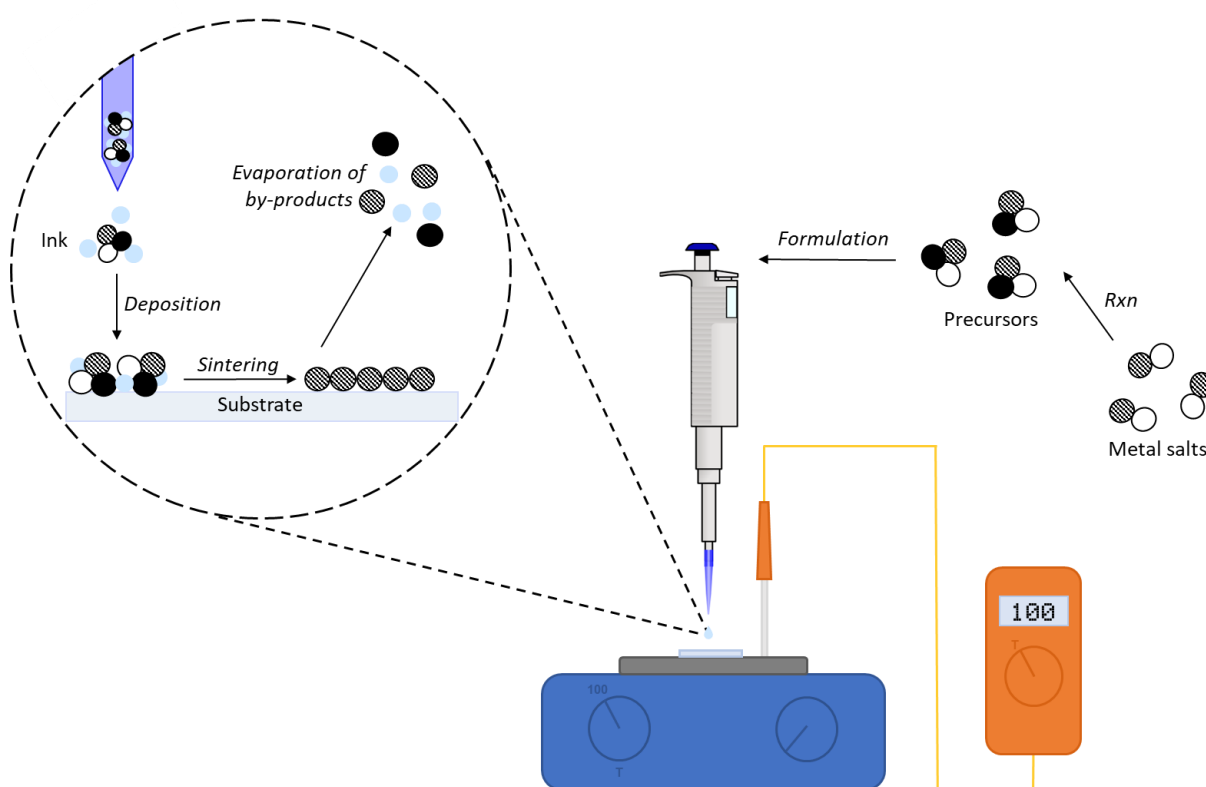


Figure 6.8: Schematic of MOD ink formulation and deposition process.

All depositions were undertaken in a glove box, with the expected decomposition products at elevated temperature (*i.e.* sintering conditions) being aluminium metal, hydrogen gas, and free amine. Finally, all depositions were repeated in triplicate to increase their repeatability. Conductive aluminium coatings ($\rho = 4.10 \times 10^{-5} - 5.32 \times 10^{-7} \Omega \text{ m}$) were formed, with a best deposition only twenty times that of bulk metal ($\rho = 2.65 \times 10^{-8} \Omega \text{ m}$, 20 °C)¹ – a full set of depositions is given in Table 6.2. Depositions at 100 and 120 °C produced metallic films with

those on paper the best adhered whilst samples on PI, PET and glass were easily scraped off the surface using a steel stylus.

6.2.3 Resistivity measurements of deposited films

Resistance values were measured for all depositions using a two-point probe and calculated as detailed in Section 2.5.1. A full set of results for both **DMEAA** and **TEAA** are given in the Appendices (Appendix 138 and 139 respectively), whilst a condensed set of results giving the mean resistivity for each type of deposition are given in Table 6.2. Resistivities are also represented pictorially in Figure 6.9.

Table 6.2: Resistivity values for depositions using **DMEAA** and **TEAA** onto various substrates at 120 and 100 °C.

Precursor	Substrate	Temperature / °C	Time / min:s	Resistivity / Ω m	
DMEAA	Glass	100	1:30	8.29×10^{-6}	$\pm 6.28 \times 10^{-7}$
	Glass	120	1:00	1.60×10^{-6}	$\pm 4.21 \times 10^{-7}$
	PI	100	1:30	6.38×10^{-6}	$\pm 1.46 \times 10^{-6}$
	PI	120	1:00	9.57×10^{-7}	$\pm 2.33 \times 10^{-7}$
	PET	100	2:30	1.91×10^{-6}	$\pm 2.35 \times 10^{-7}$
	PET	120	1:30	2.34×10^{-6}	$\pm 4.86 \times 10^{-7}$
	Paper	100	2:00	2.98×10^{-6}	$\pm 1.38 \times 10^{-6}$
	Paper	120	1:30	2.66×10^{-6}	$\pm 7.77 \times 10^{-7}$
TEAA	Glass	100	1:30	5.32×10^{-7}	$\pm 1.35 \times 10^{-7}$
	Glass	120	0:30	4.25×10^{-6}	$\pm 6.76 \times 10^{-8}$
	PI	100	2:00	4.10×10^{-5}	$\pm 1.31 \times 10^{-6}$
	PI	120	1:30	7.44×10^{-7}	$\pm 6.81 \times 10^{-8}$
	PET	100	2:30	3.01×10^{-5}	$\pm 4.54 \times 10^{-6}$
	PET	120	2:00	3.67×10^{-6}	$\pm 4.66 \times 10^{-7}$
	Paper	100	2:00	4.00×10^{-5}	$\pm 2.15 \times 10^{-5}$
	Paper	120	2:00	5.32×10^{-6}	$\pm 3.06 \times 10^{-6}$

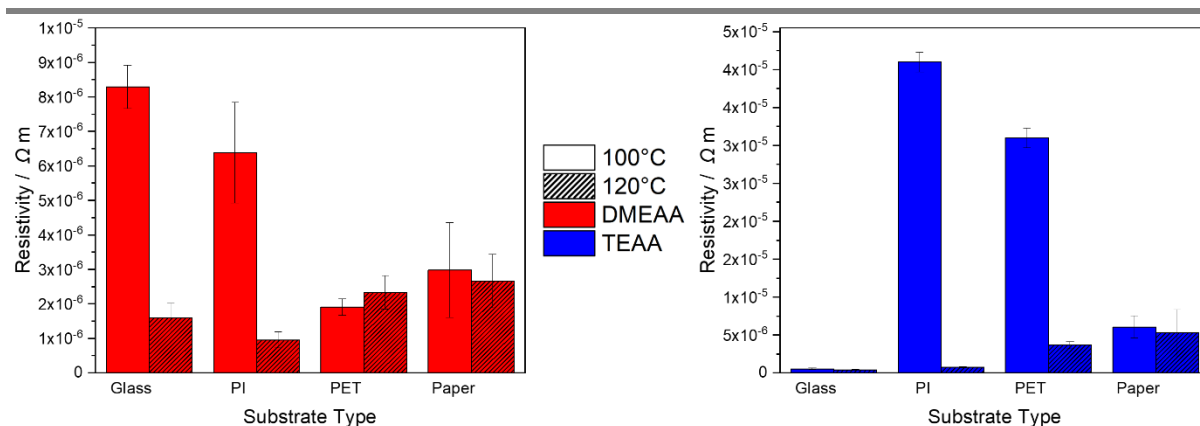


Figure 6.9: Resistivities for depositions using **DMEAA** (red) or **TEAA** (blue) at either 100 °C (plain) or 120 °C (hashed) on different substrates.

6.2.4 X-ray diffraction analysis of deposited films

X-ray diffraction patterns were collected for all films in the range of $20^\circ < 2\theta < 66^\circ$. One exemplar XRD pattern for each substrate for both precursors and temperatures are displayed in Figure 6.10a–d, with background substrate XRD patterns and full (unnormalised) XRD data given in the Appendices (Appendix 140–142). All diffraction patterns (bar **TEAA** on paper at 100 °C, *vide infra*) contain three Bragg peaks at 38.5, 44.8 and 65.2°, corresponding to the presence of aluminium metal (cubic space group: $Fm\bar{3}m$) (Figure 6.10a–d). Bragg peaks deriving from the substrate are also observed in some diffraction patterns, with substrate XRD data also given in the Appendices. X-ray patterns between substrates vary in intensity due to several affects including the thicknesses of the film (relating due to substrate wettability), adherence of the film and the normalisation process in relation to the additional peaks due to breakthrough of the X-ray beam to the substrate. The only set of three depositions to not display diffraction patterns corresponding to aluminium metal was the deposition of **TEAA** on paper at the lower temperature of 100 °C – this is comprehensible as **TEAA** decomposes over a longer heat range than **DMEAA** as shown by thermal analysis in Section 5.3.2 and paper had the highest specific heat capacity of all the substrates used.

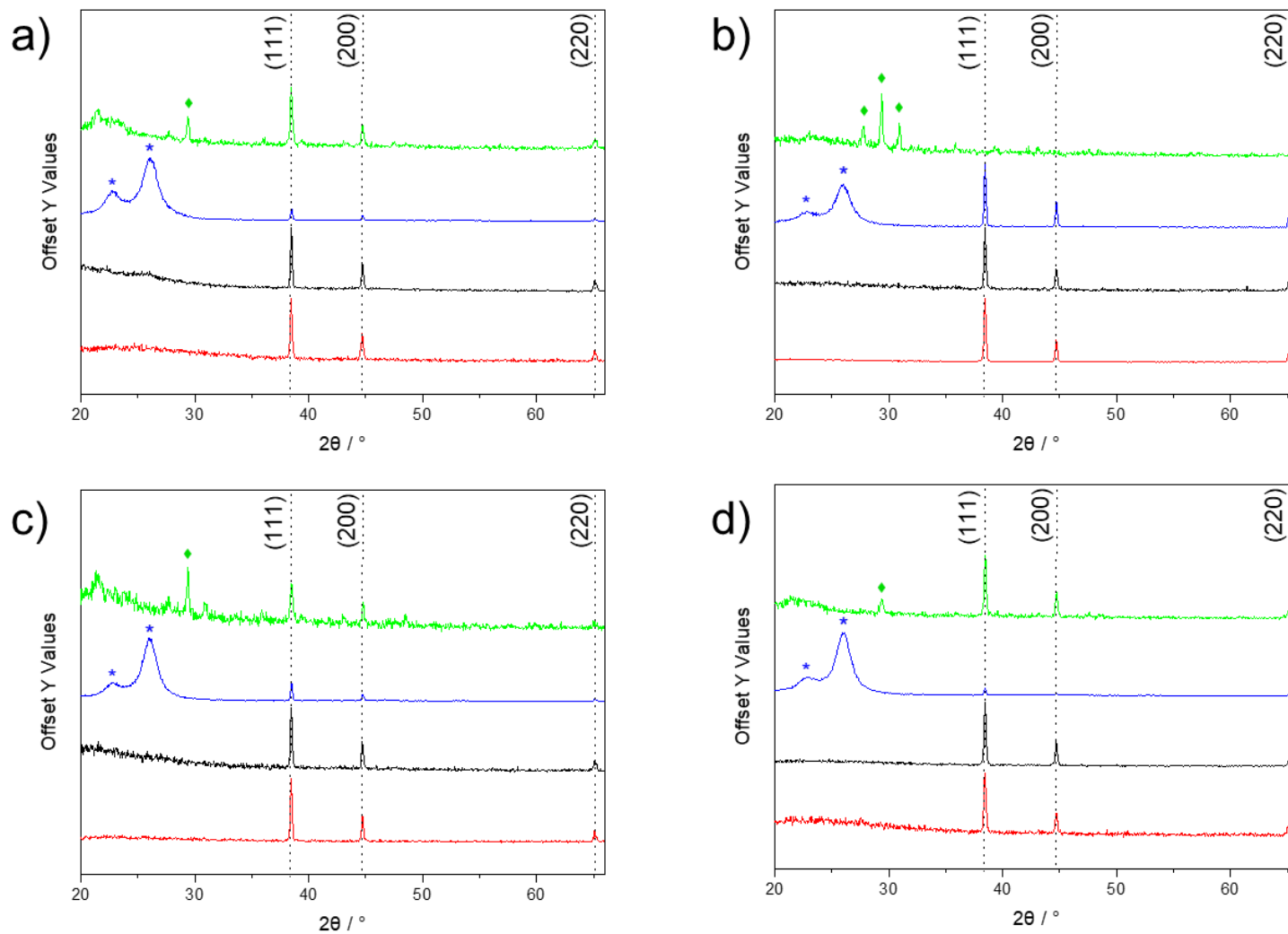


Figure 6.10: Representative XRD patterns of films deposited using a) **DMEAA** and b) **TEAA** at 120 °C, and c) **DMEAA** and d) **TEAA** at 100 °C on substrates: glass (red), PI (black), PET (blue) and paper (green). * and ♦ indicates PET and paper substrate peaks respectively.

6.2.5 Scanning electron microscopy analysis of deposited films

Scanning electron microscopy (SEM) images were taken from a representative selection of samples in order to study their surface morphology (Figure 6.11a–d). The morphology of the Al particles on glass, PI and PET are alike, showing coalesced spherical grains due to sintering (Figure 6.11a–c). Average grain sizes of $1.43 \pm 0.09 \mu\text{m}$, $1.08 \pm 0.05 \mu\text{m}$ and $1.03 \pm 0.06 \mu\text{m}$ were measured on glass, PI and PET substrates respectively. Average grain sizes were calculated by measuring across the longest midpoint of each individual particle in each respective SEM images, with full data presented as histograms shown in Figure 6.12. Although the large grain sizes produced can lead to highly porous films (lower conductivity), increasing grain size can lessen the detrimental effects of electromigration, a characteristic aluminium films are usually plagued with, as introduced in Section 1.4.4.

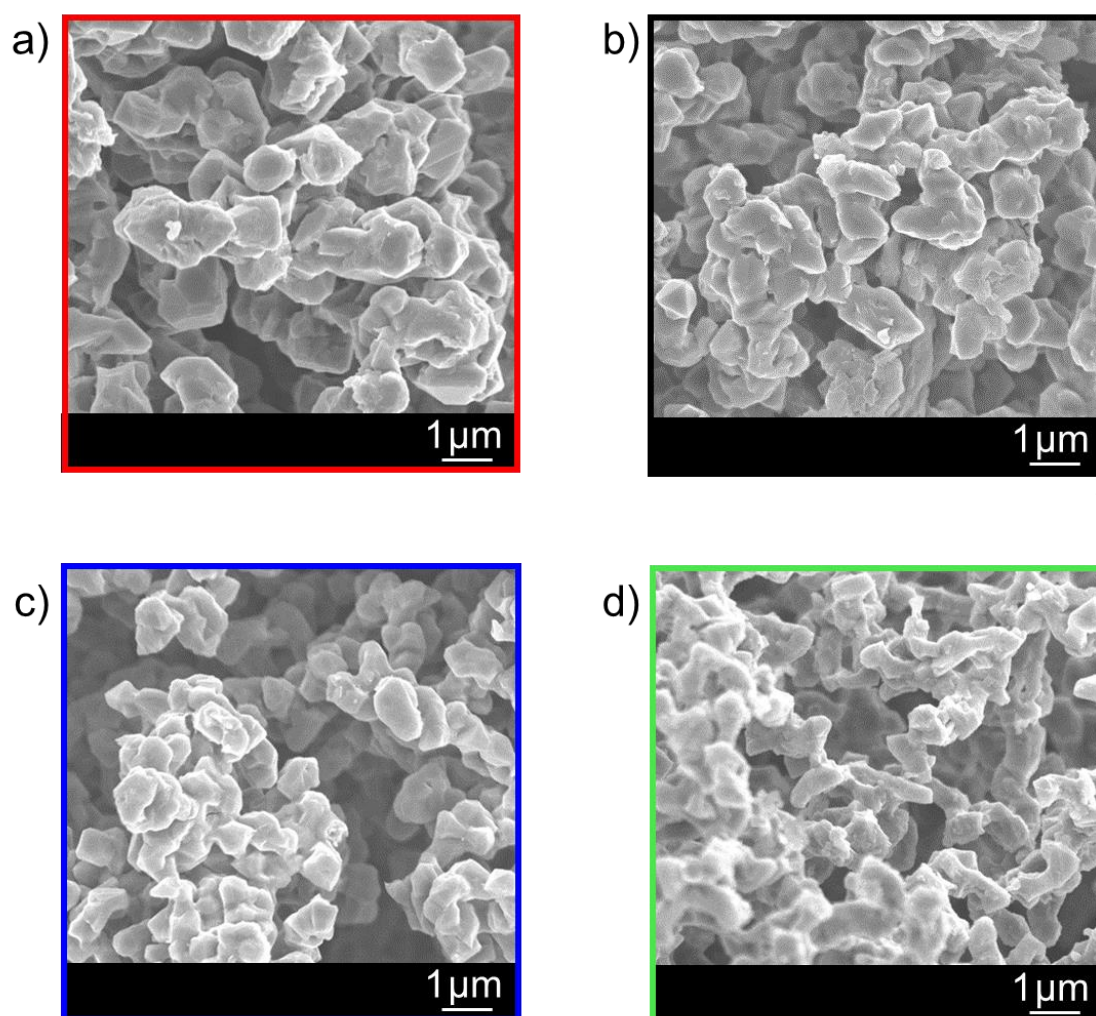


Figure 6.11: Representative top-down SEM images taken of aluminium films on a) glass, b) PI, c) PET and d) paper, respectively.

The morphology of the aluminium films on paper differs to the other substrates, displaying a vermicular structure which is likely owing to the porous nature of the substrate (Figure 6.11d).²⁷ In all samples, the frequency of coalesced grains is high, with few isolated spherical particles providing proof that particles are sintered together and is supported by the excellent conductivity of the deposits (Table 6.2).

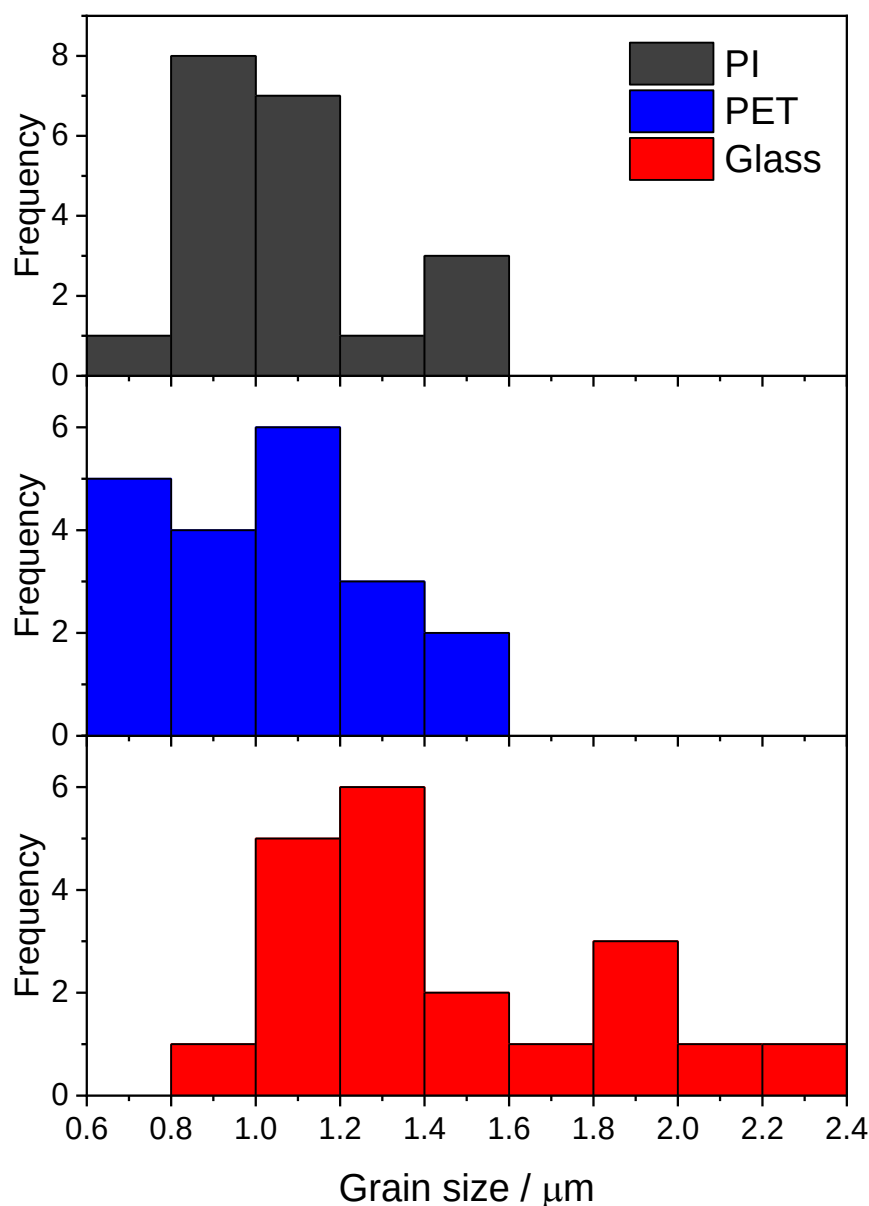


Figure 6.12: Grain size analysis for top-down SEMs for deposition on glass (red), PET (blue) and PI (grey).

Cross-sectional SEM images were obtained for films on PI and PET (Figure 6.13a and b). Adequate quality cross-sectional images for glass and paper substrates could not be obtained due to problems involving sample preparation (scoring glass and cutting paper destroyed film

edge). Film thicknesses were estimated for PI and PET by taking an average of three points along the film, with marginally thicker coatings on PET (PET = 16.5 μm , PI = 15.4 μm).

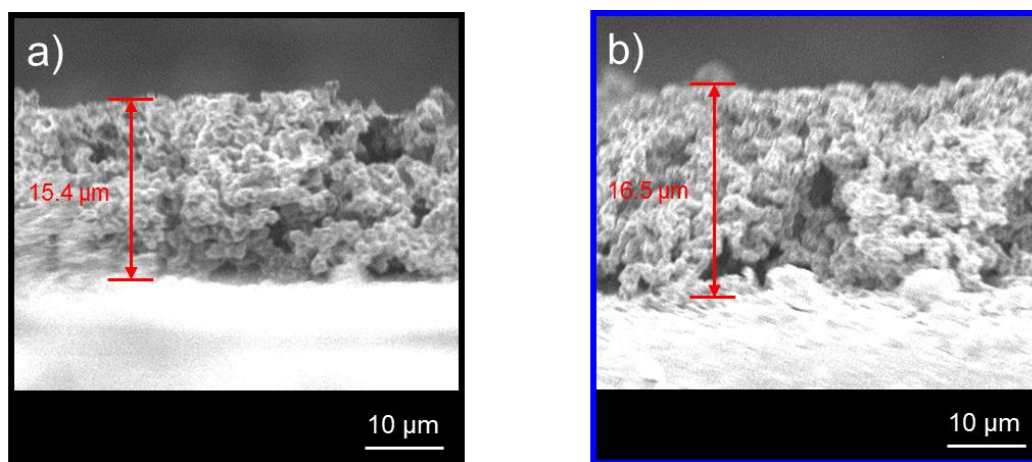


Figure 6.13: Representative cross-sectional SEM images taken of aluminium films on a) PI and b) PET, respectively.

6.2.6 Energy-dispersive X-ray spectroscopy of deposited films

Energy-dispersive X-ray spectroscopy (EDS) analysis of the Al films confirmed the presence of Al, with very small amounts of O present (<5.4% in all cases, see Table 6.3, Figure 6.14). Intriguingly, when **TEAA** was used to deposit Al on paper and glass (at 120 and 100 °C, respectively) EDS showed Al content of 93.2% and 96.6% respectively, whilst when **DMEAA** was used to deposit Al on PI and PET (at 120 °C), coatings with 85.1% and 78.5% Al which can be attributed to varying levels of carbon detection. Carbon contamination varied greatly between substrates, with PI and PET substrates containing the highest amount (11.4% and 16.1% respectively). This is likely owing to the electron beam breaking through the porous films to the carbon-based substrates, as the carbon contamination for the less porous film on paper is very small (3.4%) and null for glass (0.0%), which isn't a carbon-based substrate. This theory is substantiated by the EDS layered spectra (Figure 6.14a–d).

Table 6.3: Tabulated EDS data showing %Al, C, O and N amounts for four depositions using a combination of precursors, substrates and sintering temperatures.

SEM/EDS	Precursor	Substrate	T / °C	EDS			
				%Al	%C	%O	%N
a)	DMEAA	PI	120	85.1	11.4	3.6	0.0
b)	DMEAA	PET	120	78.5	16.1	5.4	0.0
c)	TEAA	Paper	120	93.2	3.4	3.4	0.0
d)	TEAA	Glass	100	96.6	0.0	3.4	0.0

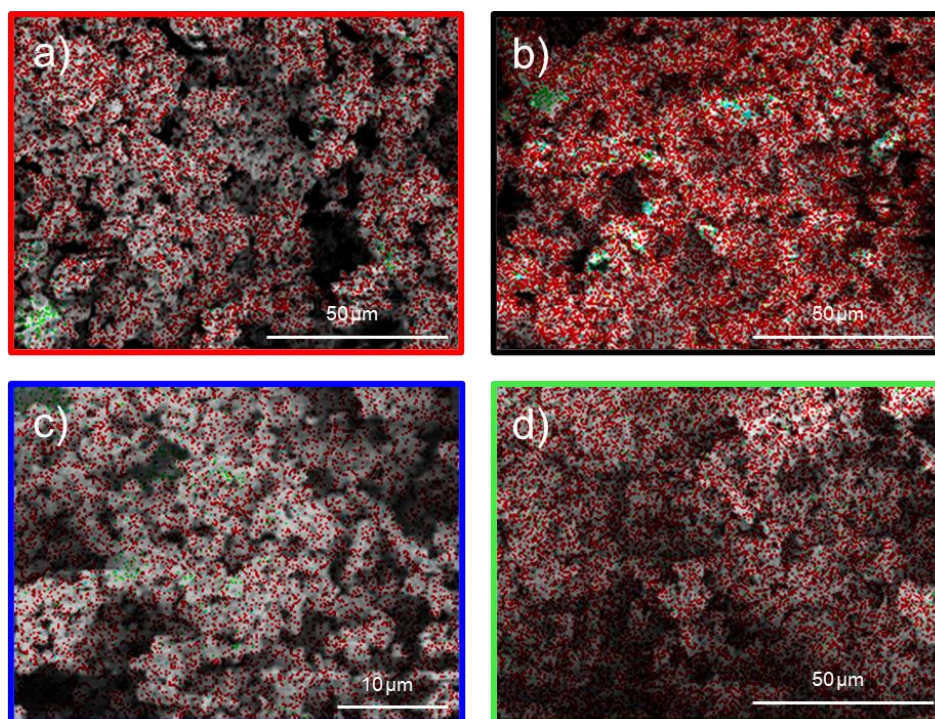


Figure 6.14: Representative EDS layered spectra of top-down SEM images of films on a) glass, b) PI, c) PET and d) paper. Image b) was collected for a longer scan period, evidenced by the higher frequency of red points (red spot = Al, green spot = C from substrate breakthrough).

6.2.7 X-ray photoelectron spectroscopy of deposited films

X-ray photoelectron spectroscopy (XPS) measurements were conducted to probe the Al 2p (exemplar spectra shown in Figure 6.15), C1s, N1s and O1s regions at the surface and after a 300 s Ar ion etch of each type of deposition, with elemental %'s for each analysed deposition given in Table 6.4. Each deposition shows variations in the amount of carbon and oxygen contamination however promisingly, undetectable amounts of nitrogen content in all films are recorded, which agrees with the notion that the volatile amine adducts found in the MOD complexes are completely removed, before their full decomposition occurs.

Specifically looking at the Al 2p scans, which provide us with the most valuable information, two environments are present at each level for every film pertaining to one environment each for aluminium oxide and aluminium metal, which agrees with XPS data for naturally oxidised aluminium metal foil.²⁸ Aluminium oxide was observed in all surface scans at *ca.* 74.5 eV, which agrees with the literature and is expected since XPS is a surface-sensitive technique, with many metals (including Al) forming passive oxide layers.³² Aluminium metal is also present at the surface in a lower proportion at *ca.* 71.7 eV, which is also in agreement with the literature, detailing that the entirety of the metal surface has not been oxidised. Intuitively, after 300 s etches the ratios of oxide to metal decrease, as surface oxide is removed. Interestingly, aluminium oxide is still present after 300 s etches in all samples, which is most likely due to the porous morphology of the films, allowing oxygen to penetrate forming a 3D network of surface alumina – this is most likely a consequence of the gaseous by-products formed upon sintering of MOD inks. A small shift in the binding energy of aluminium metal is observed (to *ca.* 71.8 eV) but is within error limits. An exemplar survey scan is shown in Figure 6.15c, as well as, a full list of elemental percentages calculated from the survey scans of all samples given in the Table 6.4.

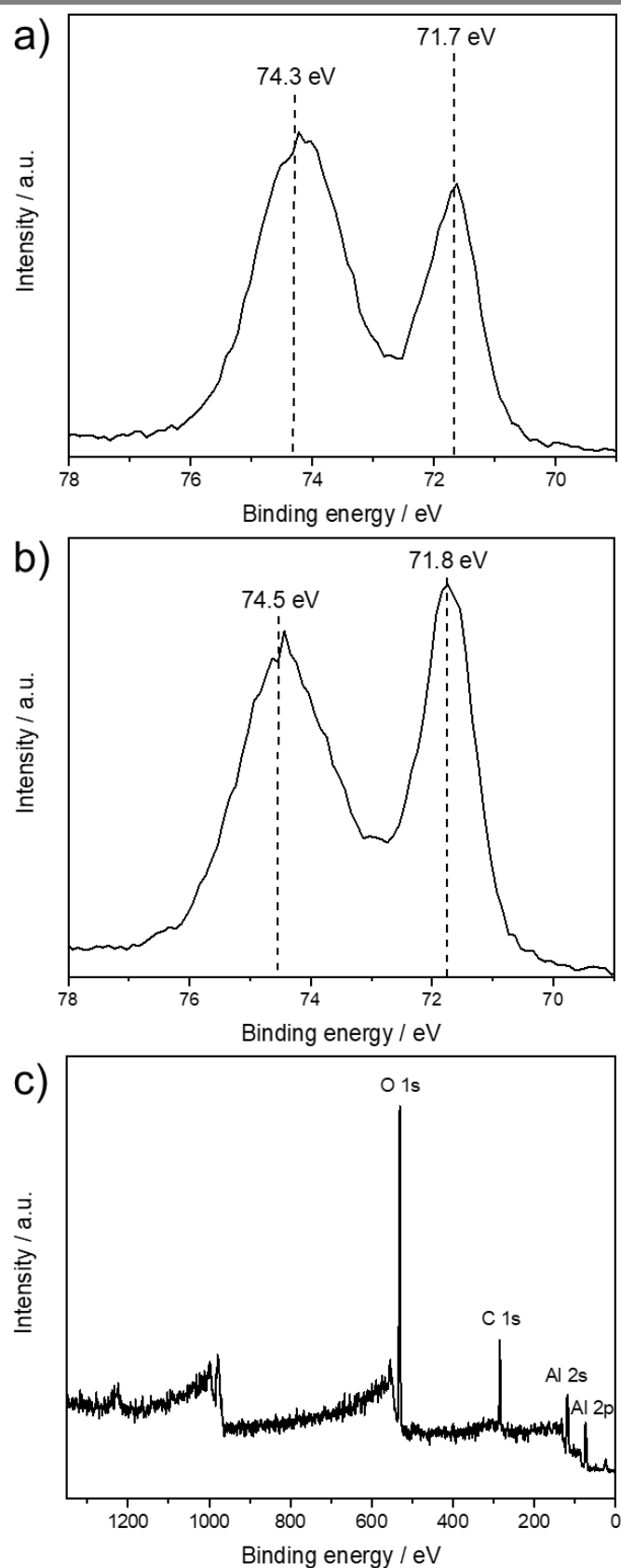


Figure 6.15: Exemplar Al 2p XPS spectra from a film deposited at 100 °C from DMEAA on paper a) surface scan b) after 300 s etch. c) Exemplar XPS survey spectrum showing the Al 2s and 2p transitions for aluminium metal on paper.

Table 6.4: Tabulated XPS data showing %Al, C, O and N amounts for a series of depositions using a combination of precursors, substrates and sintering temperatures.

Precursor	Temperature	Substrate	Etch / s	%Al	%C	%O	%N
DMEAA	120	PI	0	24.0	48.3	27.7	0.0
			300	38.7	29.4	31.8	0.0
		PET	0	20.9	46.0	33.2	0.0
			300	32.7	31.6	35.7	0.0
		Paper	0	26.1	32.6	41.3	0.0
			300	42.4	13.2	44.5	0.0
	100	PI	0	11.5	64.0	24.5	0.0
			300	31.6	34.3	34.2	0.0
		Paper	0	34.5	22.7	42.9	0.0
			300	44.3	21.4	34.3	0.0
TEAA	120	PI	0	32.7	23.6	43.7	0.0
			300	43.7	10.7	45.6	0.0
		PET	0	23.4	37.9	38.6	0.0
			300	37.8	5.3	56.9	0.0
		Paper	0	32.3	27.7	40.0	0.0
			300	46.8	11.3	41.9	0.0
	100	Glass	0	23.1	32.7	44.2	0.0
			300	46.6	13.4	40.0	0.0
		PI	0	22.8	24.0	53.3	0.0
			300	32.0	0.0	68.1	0.0
		PET	0	25.9	31.0	43.0	0.0
			300	39.8	12.6	47.6	0.0
		Paper	0	0.0	34.1	65.9	0.0
			300	50.0	0.0	50.0	0.0

6.2.8 Device fabrication using deposited films

Whilst all deposits of Al reported were highly conductive, depositions from **DMEAA** proved to be of superior quality, which adherent films being deposited on paper substrates at shorter times than the comparative depositions carried out at both 100 and 120 °C from **TEAA** (Table 6.2, Figure 6.9). As such an example of an aluminium film deposited using **DMEAA** on paper at 100 °C was cut to shape and used to light an LED in a circuit highlighting the potential application (Figure 6.16).

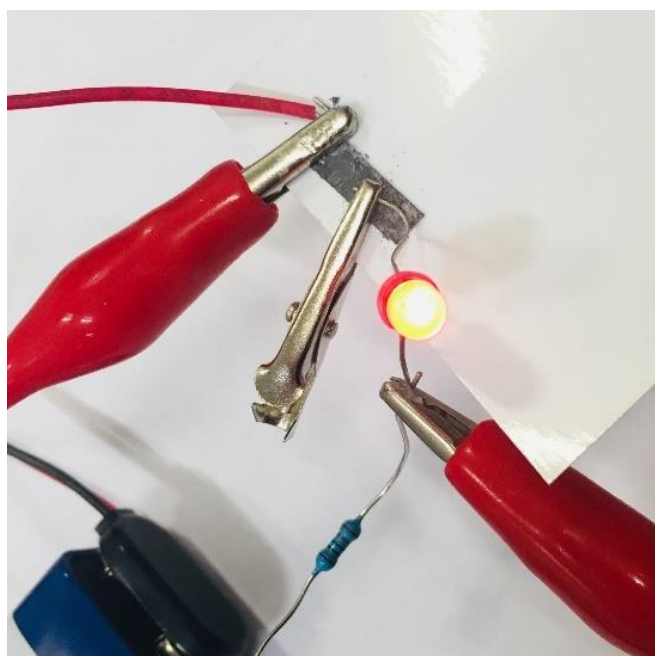


Figure 6.16: Example of an aluminium film deposited from DMEAA on paper at 100 °C cut to shape and used to light an LED in a circuit.

6.2.9 Deposition summary

Both precursors produced extremely low resistivity coatings at both temperatures (100, 120 °C) with **DMEAA** producing the most consistent results, with resistivities in the range of $8.29 \times 10^{-6} - 9.57 \times 10^{-7} \Omega \text{ m}$, just one order of magnitude higher than bulk Al. Whilst all films displayed exceptional conductivity, the best films were deposited at 120 °C on glass and PI. Greater variation in resistivity was observed for the depositions using **TEAA** as presented in Table 6.25. and in Figure 6.9 measured resistivities range from $4.00 \times 10^{-5} - 4.25 \times 10^{-7} \Omega \text{ m}$ with the best films deposited onto glass at 100 and 120 °C and on PI at 120 °C. The coatings with the highest resistivities were found on PI, PET and paper at the lower decomposition temperature, 100 °C – this information is consistent with the TGA

data (Chapter 5, Figures 5.16, 5.17), which shows complete decomposition of **DMEAA** at a lower temperature than for **TEAA** attributed to the difference in ligand pK_a , as previously explained in Section 5.1.3.4. Sintering times vary between substrates as expected due to a combination of their different thicknesses and thermal conductivities.

Both hydride precursors have proven to be highly appropriate for deposition of conductive aluminium due to the presence of reactive Al–H bonds. The hydride ligand acts threefold: firstly the weak bond presents a low thermodynamic barrier to cross, secondly each hydrogen in the AlH_3 moiety provides an electron to reduce the (formally) Al(III) centre to Al(0) and finally, since it is a gaseous by-product highly conductive features are afforded since contamination (typically carbon) is avoided in this entropically driven process.

6.3 Summary

Two liquid precursors which displayed the best thermal properties of all the compounds analysed in Chapter 3–5: **DMEAA** and **TEAA** were chosen to fabricate coatings of aluminium metal using a solution-based deposition technique onto a range of substrates. **DMEAA** deposited the best films, with a particular highlight being the deposition of both precursors onto paper which deposited highly conductive films that adhered excellently. Metallic films adhered less well to other the substrates, which is a commonly observed in metallic coatings using precursors. Surfaces may require pre-treatment before deposition to produced better adhered films, with this being just one avenue to improve deposited film in the future.

Other future work in this field should focus on how amine-stabilised alane precursors can be formulated to make superior inks (better viscosities, produce films with better adhesion, more dilute and hence faster sintering), as the work done in this Chapter only utilised the precursors neat. Care must be taken when selecting solvent systems as these compounds are highly reactive towards protic solvents. Research into new amine-stabilised alanes may also yield exciting results, whether that be producing compounds that decompose at even lower temperatures, although this may mean they are less easy to handle and store, or produce more amiable precursors that achieve a good balance between decomposition temperature and handleability.

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Chapter 7

Conclusions and Future Work

This Chapter concludes the work detailed within this thesis and provides some insight into how this research can be expanded in the future.

7.1 Conclusions

The overarching concept for the research detailed in this thesis has been to produce a series of aluminium precursors that can produce aluminium functional films, namely aluminium metal or oxide, upon decomposition at low temperature (<200 °C). Throughout this research there was a particular emphasis on changing the substitution around the donor nitrogen atom in each of the four families of complexes investigated, in order to probe how decomposition properties were affected.

Chapters 3 and 4 focussed on the development of two families of complexes involving the use of β -ketoimine compounds as ligands. β -ketoiminates are surprisingly under-investigated in the stabilisation of aluminium centres, especially considering the prevalence of aluminium β -diketonates within the literature, which have widely been used as single-source precursors in the deposition of oxide films. In addition to their simplistic synthesis and purification, the appeal of using β -ketoiminates as a class of ligand arises from the potential to functionalise at the imino position, which can directly affect the coordination of the ligand to the metal centre, with the affects of using a range of both alkyl and aryl substituents of varying steric bulk investigated within this work.

The reactivity of the β -ketoimines was initially investigated in ligand substitution reactions in Chapter 3 *via* the reaction with TMAA, a popular aluminium precursor in its own right. The intention of this research was to substitute the monodentate amine ligand with that of the bidentate β -ketoiminate in order to produce more stable complexes *via* the chelation effect, which still maintaining low decomposition temperatures. This was a driving force for research as popular amine-stabilised alane precursors such as TMAA, which have very low decomposition temperatures, tend to be extremely reactive towards air and moisture making them unsuitable for industrial use. Despite attempting various equivalents of β -ketoimine to alane, the only experiments that yielded pure product in good yield was when a 3:1 ligand : alane ratio was used. Five complexes, four of which were novel, were synthesised including the first three examples of those that feature aliphatic *N*-substituents. The majority of complexes synthesised were six-coordinate around the Al centre, with three ligands binding in a *mer* octahedral arrangement, with slight distortions observed in all cases. Interestingly, the complex that featured the mesityl group at the imino position was only five-coordinate at the metal centre. This is the first example of where the steric bulk of the *N*-substituent drastically changes the ligand coordination around the metal centre in these tris(β -

ketoiminate) aluminium complexes. Compounds generally showed good decomposition properties, with the best precursor **[Al(Me-acnac)₃]**, **1** displaying excellent mass loss properties and a low onset decomposition temperature (<200 °C), less than that of [Al(acac)₃], a well-known standard precursor in the synthesis of Al₂O₃ thin films.

In order to synthesise complexes with lower equivalents of β -ketoimine compounds, salt metathesis reactions were employed using the reaction of AlCl₃ with intermediate lithium salts formed by deprotonation of the β -ketoimines with LiHMDS. Both 1:1 and 1:2 equivalents of AlCl₃ : lithium salt were attempted in order to form compounds different to that observed in Chapter 3. After numerous reactions it was observed that only 1:2 reactions gave pure product in good yield. Five novel complexes were synthesised including the first three examples of those that feature aliphatic *N*-substituents. Each synthesised complex was five-coordinate around the Al centre in a trigonal bipyramidal geometry, again with slight distortions observed in all cases. In each complex, two β -ketoiminate ligands bind in a bidentate mode, in addition to one chloride co-ligand, which always binds in the equatorial position. Interestingly, of the four complexes with the least bulky substituents, the β -ketoiminate ligands bind to the Al centre with the N atoms in the equatorial positions however when bulkier imino groups are used (R = mesityl) the O atoms of the ligand occupy the equatorial positions, which are both bonding motifs that compare well to the literature. Decomposition properties are comparable to the complexes synthesised in Chapter 3, with the presence of the chloride co-ligand having no detrimental effect to decomposition. The best precursor **[Al(Et-acnac)₂Cl]**, **7** displayed good mass loss properties and a low onset decomposition temperature (<200 °C).

Chapter 5 introduced two other types of ligand systems; β -diketiminates which relate closely to the systems utilised in Chapter 3 and 4 and tertiary amines, a standard L type donor system, which feature in amine-stabilised alanes, a family of compounds that have been previously used in the deposition of aluminium. Two families of precursors, both containing Al–N and Al–H bonds (in addition to an absence of Al–O bonds) have been synthesised: mono(β -diketiminato) aluminium dihydrides and amine-stabilised alanes, which have been analysed thermally (many of which for the first time) to gauge their suitability as MOD precursors to aluminium metal coatings *via* low temperature solution-based processing. Despite the presence of hydride co-ligands which are hypothesised to aid decomposition, β -diketiminato compounds were found to decompose at too high temperatures (>250 °C) to be fit for purpose

and decomposition left large amounts of impurities. Initial results suggest that for this family of precursors, compound decomposition temperature may correlate to the Al–H bond distances found in these structures, however more investigation into this is required. Amine-stabilised alane compounds, being more well-known in precursor chemistry, exhibited excellent decomposition properties, generally decomposing at low temperatures (<200 °C), with small amounts of impurities present. Here we see how the complexed amine plays a key role in precursor decomposition characteristics, particular its basicity and denticity (which dictates donor-acceptor bond strength and which type of adduct is formed), boiling point and steric bulk.

In Chapter 6, two liquid amine-stabilised alane precursors with the best thermal properties: **DMEAA** and **TEAA** were chosen to fabricate coatings of aluminium metal using a solution-based deposition technique onto a range of substrates. **DMEAA** deposited the best films, with a particular highlight being the deposition of both precursors onto paper which deposited highly conductive films that adhered excellently.

7.2 Future work

Despite the successes of this research, there is still plenty of scope to expand the work conducted within this thesis. Results have shown β -ketoiminates to be a potentially useful class of compound for the deposition of aluminium functional films, namely aluminium oxide due to the presence of O in the ligand system. Members of both the tris(β -ketoiminate) aluminium and bis(β -ketoiminate) aluminium monochloride compounds show good decomposition properties, with similar trends observed in both complexes, showing that properties are highly dependent on the ligand system used. Interestingly the decomposition properties of the ligand do not seem to directly correlate to the decomposition properties of the constituent precursor. These trends need to be probed further so that persuasive conclusions can be drawn. One such method of achieving this would be to analyse said compounds using differential scanning calorimetry (DSC)/TGA in tandem as decomposition temperature values would be easier to decipher from precursor volatility. Using gas chromatography/mass spec analysis of any by-products during thermal decomposition could potentially help decipher degradation mechanisms. It would also be extremely beneficial to apply the complexes in Chapters 3 and 4 to MOCVD processes, as their decomposition properties are in the window that are well-suited to this deposition technique.

The mono(β -diketiminate) aluminium dihydride compounds featured in Chapter 5 have too high decomposition temperatures to be of interest in further projects, however the tris(β -diketiminate) compound synthesised by Kuhn *et al.*¹ and subsequent variants (if they can be synthesised) should be investigated as the lack of oxygen in the ligand structure makes them potentially viable aluminium metal and oxide precursors depending on the deposition conditions used. Lewis base-stabilised alanes, namely amine-stabilised alanes, offer the most viable route to successful deposition results in the near future and instead of focussing on precursor development, more focus should be applied to the formulation of these precursors into inks (better viscosities, produce films with better adhesion, potentially using decomposition catalysts, more dilute and hence faster sintering), which can be deposited using additive direct-writing techniques, namely inkjet printing. Research into new amine-stabilised alanes may also yield exciting results, whether that be producing compounds that decompose at even lower temperatures, although this may mean they are less easy to handle and store or produce more amiable precursors that achieve a good balance between decomposition temperature and handleability.

7.3 References

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Appendices

Appendices for the work conducted in this thesis are featured herein. The NMR spectra of each compound synthesised in this work will first be presented, next full crystallographic data will be given and finally supplementary thermal and materials analysis will be provided for the work discussed in Chapter 3–6. A separate contents page is provided for ease of access.

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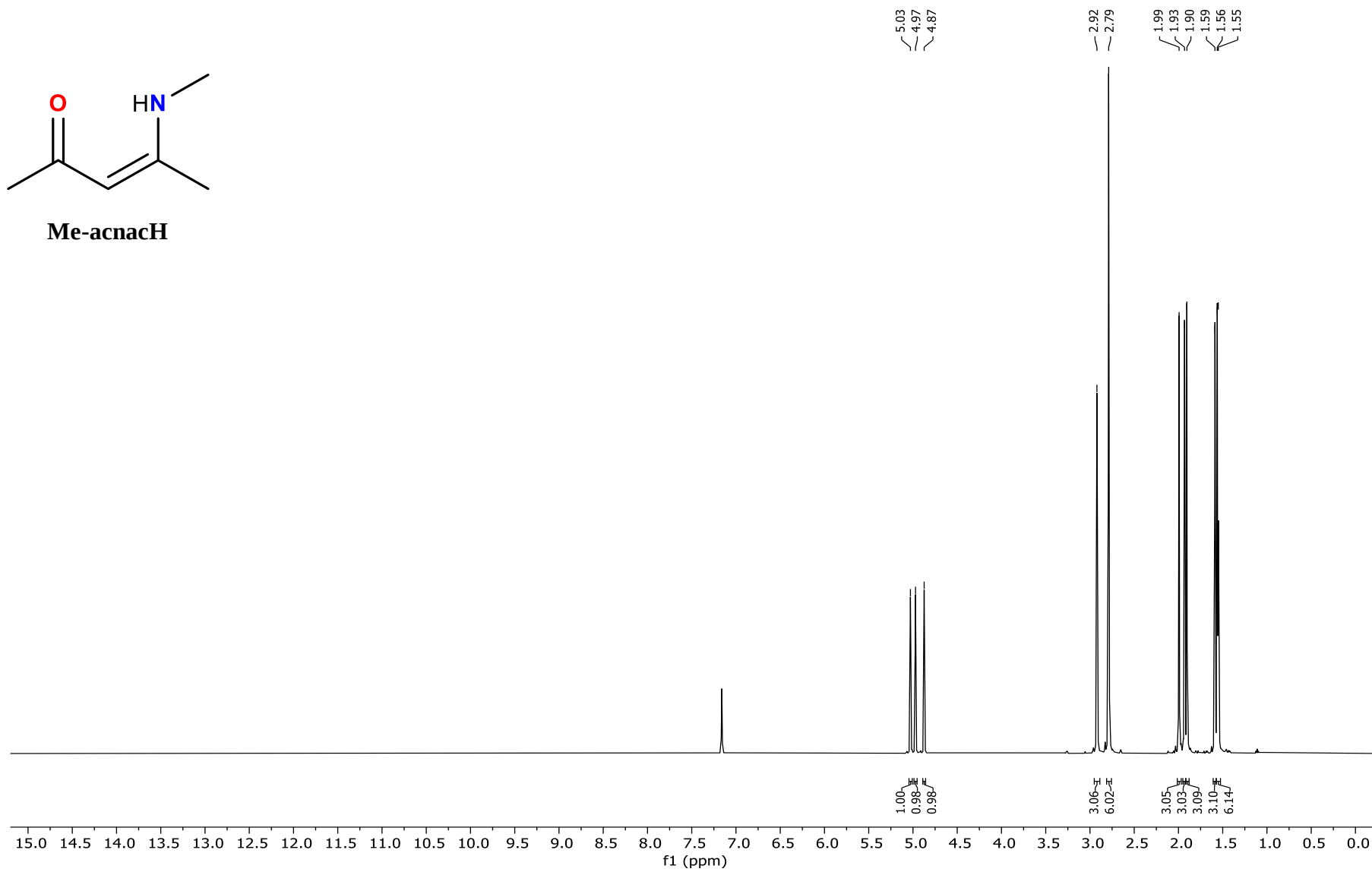
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<i>TGA (Appendix 103–137).....</i>	<i>CLIII</i>
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NMR (Appendix 1–91)

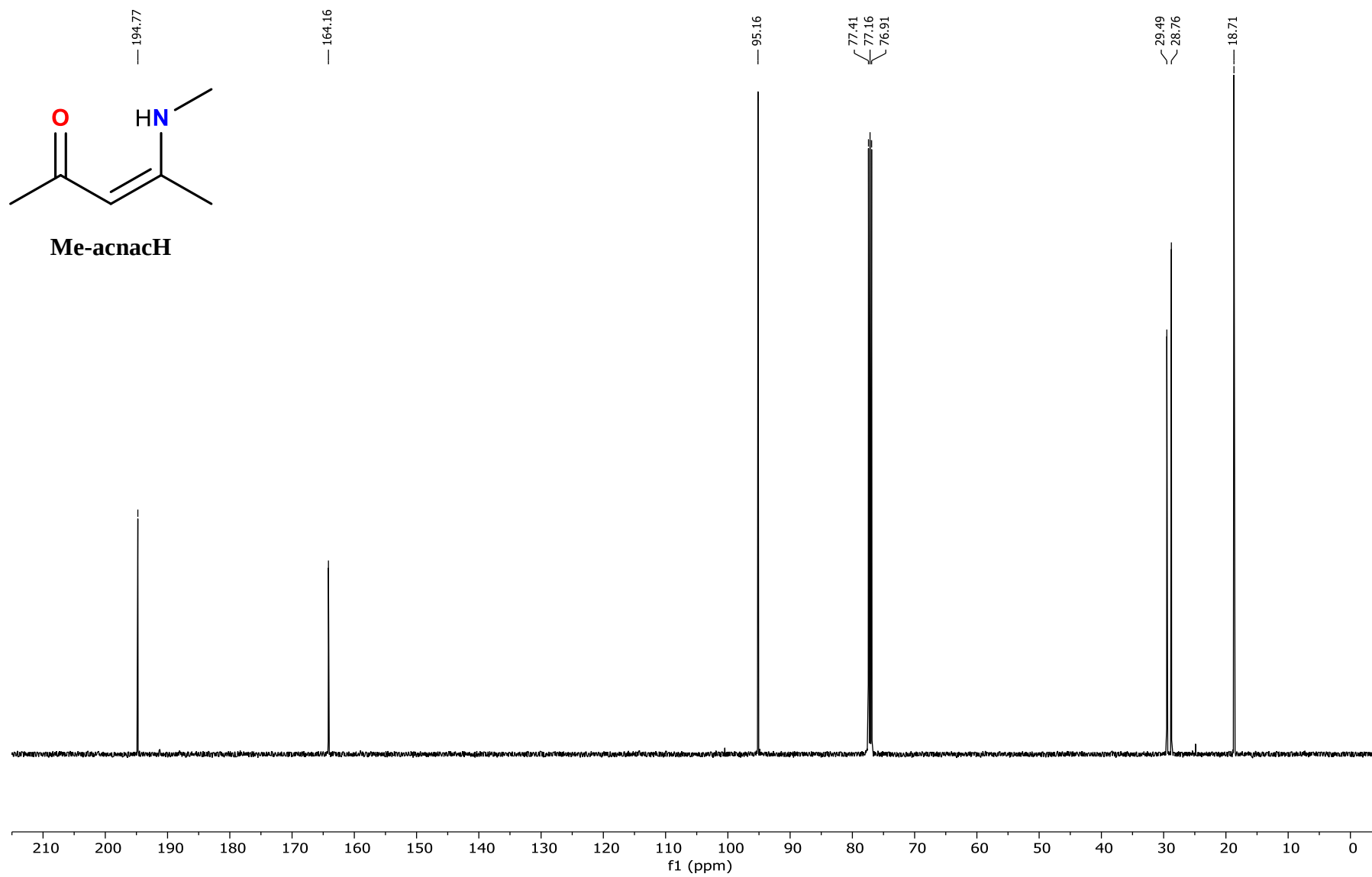
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Appendix 16: ^{13}C NMR of ⁱPr₂-nacnacH	XXI
Appendix 17: ^1H NMR of Ph₂-nacnacH	XXII
Appendix 18: ^{13}C NMR of Ph₂-nacnacH	XXIII
Appendix 19: ^1H NMR of Ar^{mes}₂-nacnacH	XXIV
Appendix 20: ^{13}C NMR of Ar^{mes}₂-nacnacH	XXV
Appendix 21: ^1H NMR of [Al(Me-acnac)₃] (1)	XXVI
Appendix 22: ^{13}C NMR of [Al(Me-acnac)₃] (1)	XXVII
Appendix 23: COSY NMR of [Al(Me-acnac)₃] (1)	XXVIII
Appendix 24: HSQC NMR of [Al(Me-acnac)₃] (1)	XXIX
Appendix 25: HMBC NMR of [Al(Me-acnac)₃] (1)	XXX
Appendix 26: ^1H NMR of [Al(Et-acnac)₃] (2)	XXXI
Appendix 27: ^{13}C NMR of [Al(Et-acnac)₃] (2)	XXXII
Appendix 28: COSY NMR of [Al(Et-acnac)₃] (2)	XXXIII
Appendix 29: HSQC NMR of [Al(Et-acnac)₃] (2)	XXXIV
Appendix 30: HMBC NMR of [Al(Et-acnac)₃] (2)	XXXV
Appendix 31: ^1H NMR of [Al(ⁱPr-acnac)₃] (3) at 25 °C	XXXVI
Appendix 32: ^1H NMR of [Al(ⁱPr-acnac)₃] (3) at 75 °C	XXXVII

Appendix 33: ^{13}C NMR of $[\text{Al}(\text{iPr-acnac})_3]$ (3) at 25 °C.	XXXVIII
Appendix 34: ^{13}C NMR of $[\text{Al}(\text{iPr-acnac})_3]$ (3) at 75 °C.	XXXIX
Appendix 35: ^1H NMR of $[\text{Al}(\text{Ph-acnac})_3]$ (4).....	XL
Appendix 36: ^{13}C NMR of $[\text{Al}(\text{Ph-acnac})_3]$ (4).....	XLI
Appendix 37: COSY NMR of $[\text{Al}(\text{Ph-acnac})_3]$ (4).	XLII
Appendix 38: HSQC NMR of $[\text{Al}(\text{Ph-acnac})_3]$ (4).....	XLIII
Appendix 39: HMBC NMR of $[\text{Al}(\text{Ph-acnac})_3]$ (4).....	XLIV
Appendix 40: ^1H NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	XLV
Appendix 41: ^{13}C NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	XLVI
Appendix 42: COSY NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	XLVII
Appendix 43: HSQC NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	XLVIII
Appendix 44: HMBC NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	XLIX
Appendix 45: ^1H NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	L
Appendix 46: ^{13}C NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	LI
Appendix 47: COSY NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	LII
Appendix 48: HSQC NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	LIII
Appendix 49: HMBC NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	LIV
Appendix 50: ^1H NMR of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	LV
Appendix 51: ^{13}C NMR of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	LVI
Appendix 52: COSY NMR of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	LVII
Appendix 53: HSQC NMR of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	LVIII
Appendix 54: HMBC NMR of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	LIX
Appendix 55: ^1H NMR of $[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$ (8).	LX
Appendix 56: ^{13}C NMR of $[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$ (8).	LXI
Appendix 57: COSY NMR of $[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$ (8).	LXII
Appendix 58: HSQC NMR of $[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$ (8).	LXIII
Appendix 59: HSQC NMR of $[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$ (8).	LXIV
Appendix 60: ^1H NMR of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	LXV
Appendix 61: ^{13}C NMR of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	LXVI
Appendix 62: COSY NMR of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	LXVII
Appendix 63: HSQC NMR of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	LXVIII
Appendix 64: HSQC NMR of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	LXIX
Appendix 65: ^1H NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	LXX

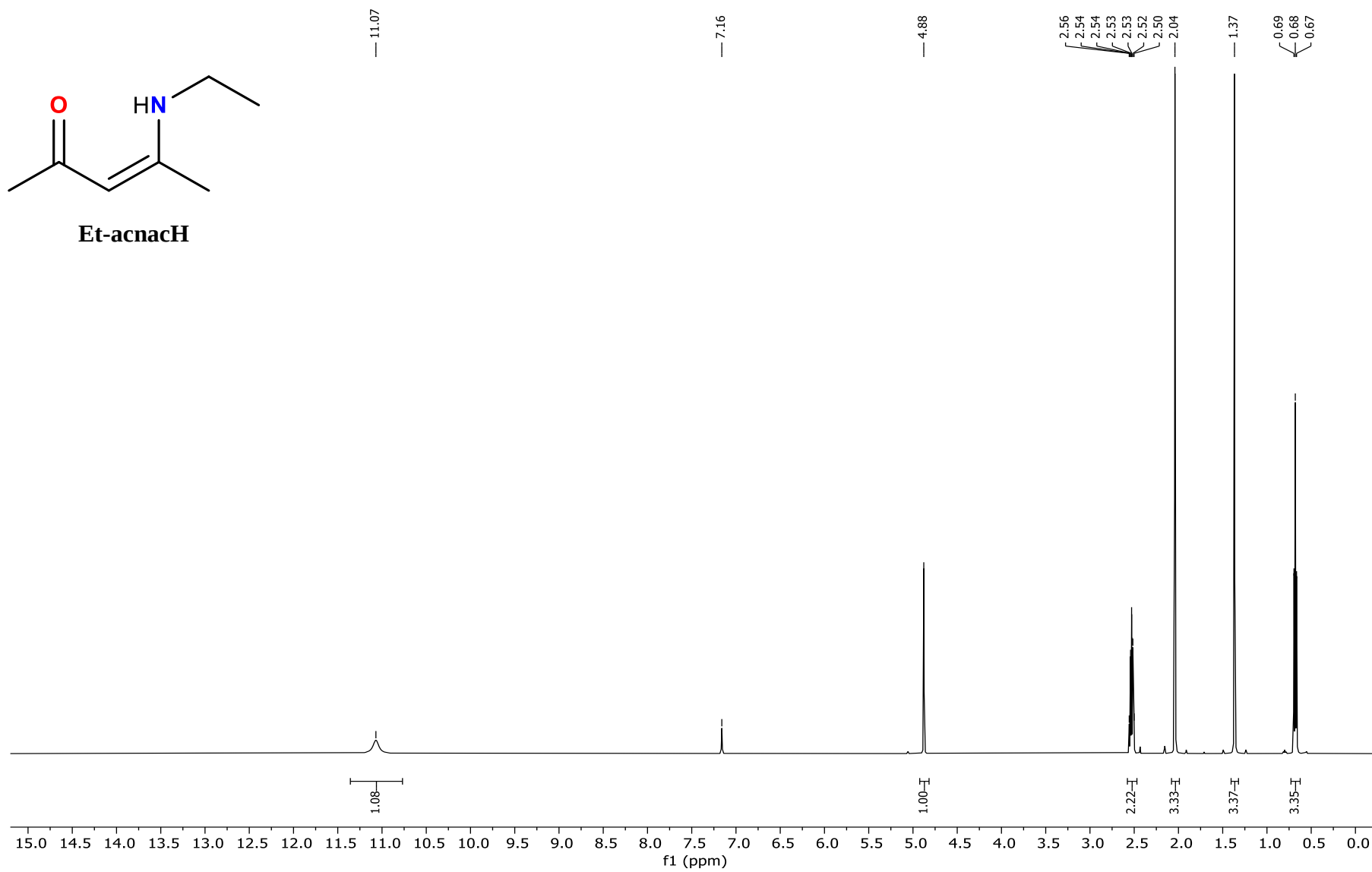
Appendix 66: ^{13}C NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	LXXI
Appendix 67: COSY NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	LXXII
Appendix 68: HSQC NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	LXXIII
Appendix 69: HMBC NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	LXXIV
Appendix 70: ^1H NMR of $[\text{Al}(\text{Me}_2\text{-nacnac})_2\text{H}_2]$ (11).	LXXV
Appendix 71: ^{13}C NMR of $[\text{Al}(\text{Me}_2\text{-nacnac})_2\text{H}_2]$ (11).	LXXVI
Appendix 72: ^1H NMR of $[\text{Al}(\text{Et}_2\text{-nacnac})_2\text{H}_2]$ (12).	LXXVII
Appendix 73: ^{13}C NMR of $[\text{Al}(\text{Et}_2\text{-nacnac})_2\text{H}_2]$ (12).	LXXVIII
Appendix 74: ^1H NMR of $[\text{Al}(\text{iPr}_2\text{-nacnac})_2\text{H}_2]$ (13).	LXXIX
Appendix 75: ^{13}C NMR of $[\text{Al}(\text{iPr}_2\text{-nacnac})_2\text{H}_2]$ (13).	LXXX
Appendix 76: ^1H NMR of $[\text{Al}(\text{Ph}_2\text{-nacnac})_2\text{H}_2]$ (14).	LXXXI
Appendix 77: ^{13}C NMR of $[\text{Al}(\text{Ph}_2\text{-nacnac})_2\text{H}_2]$ (14).	LXXXII
Appendix 78: ^1H NMR of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})_2\text{H}_2]$ (15).	LXXXIII
Appendix 79: ^{13}C NMR of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})_2\text{H}_2]$ (15).	LXXXIV
Appendix 80: ^1H NMR of TMAA (16).	LXXXV
Appendix 81: ^{13}C NMR of TMAA (16).	LXXXVI
Appendix 82: ^1H NMR of DMEAA (17).	LXXXVII
Appendix 83: ^{13}C NMR of DMEAA (17).	LXXXVIII
Appendix 84: ^1H NMR of TEAA (18).	LXXXIX
Appendix 85: ^{13}C NMR of TEAA (18).	XC
Appendix 86: ^1H NMR of TAAA (19).	XCI
Appendix 87: ^{13}C NMR of TAAA (19).	XCII
Appendix 88: ^1H NMR of TMEDAA (20).	XCIII
Appendix 89: ^{13}C NMR of TMEDAA (20).	XCIV
Appendix 90: ^1H NMR of $[\text{AlH}_2\text{Cl}\cdot 2(\text{NMP})]$ (21).	XCV
Appendix 91: ^{13}C NMR of $[\text{AlH}_2\text{Cl}\cdot 2(\text{NMP})]$ (21).	XCVI



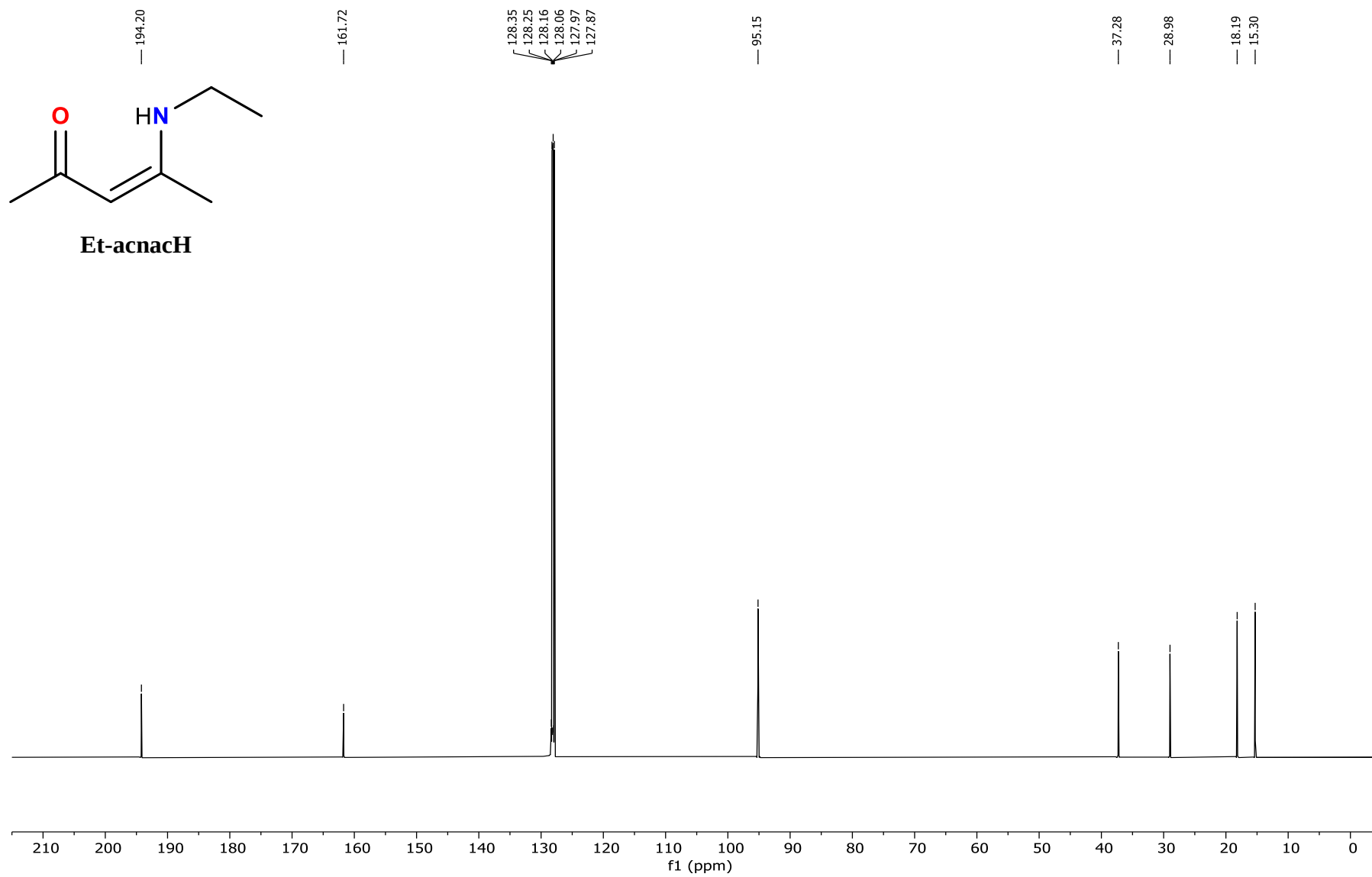
Appendix 1: ^1H NMR of Me-acnacH.



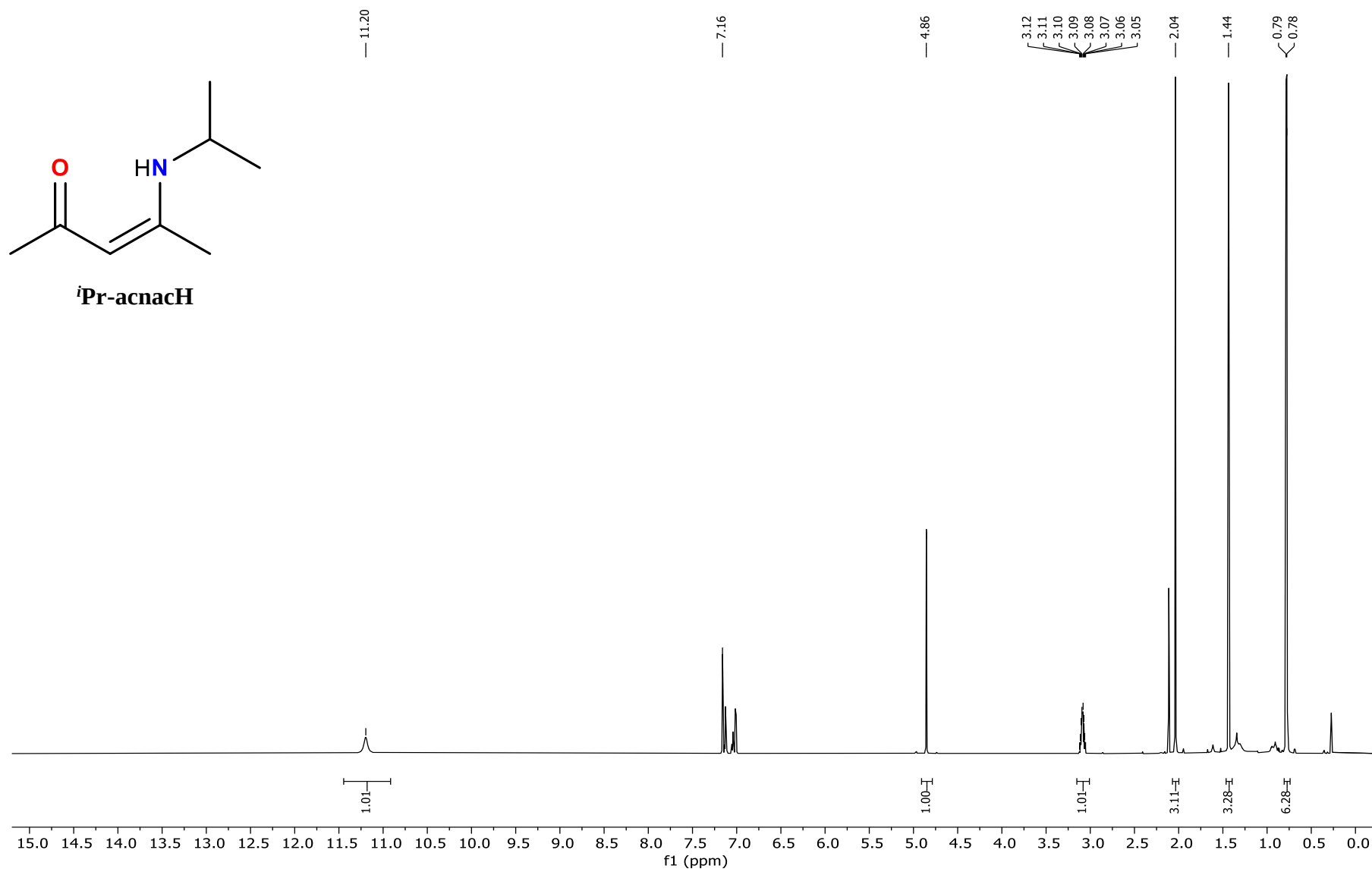
Appendix 2: ^{13}C NMR of Me-acnacH.



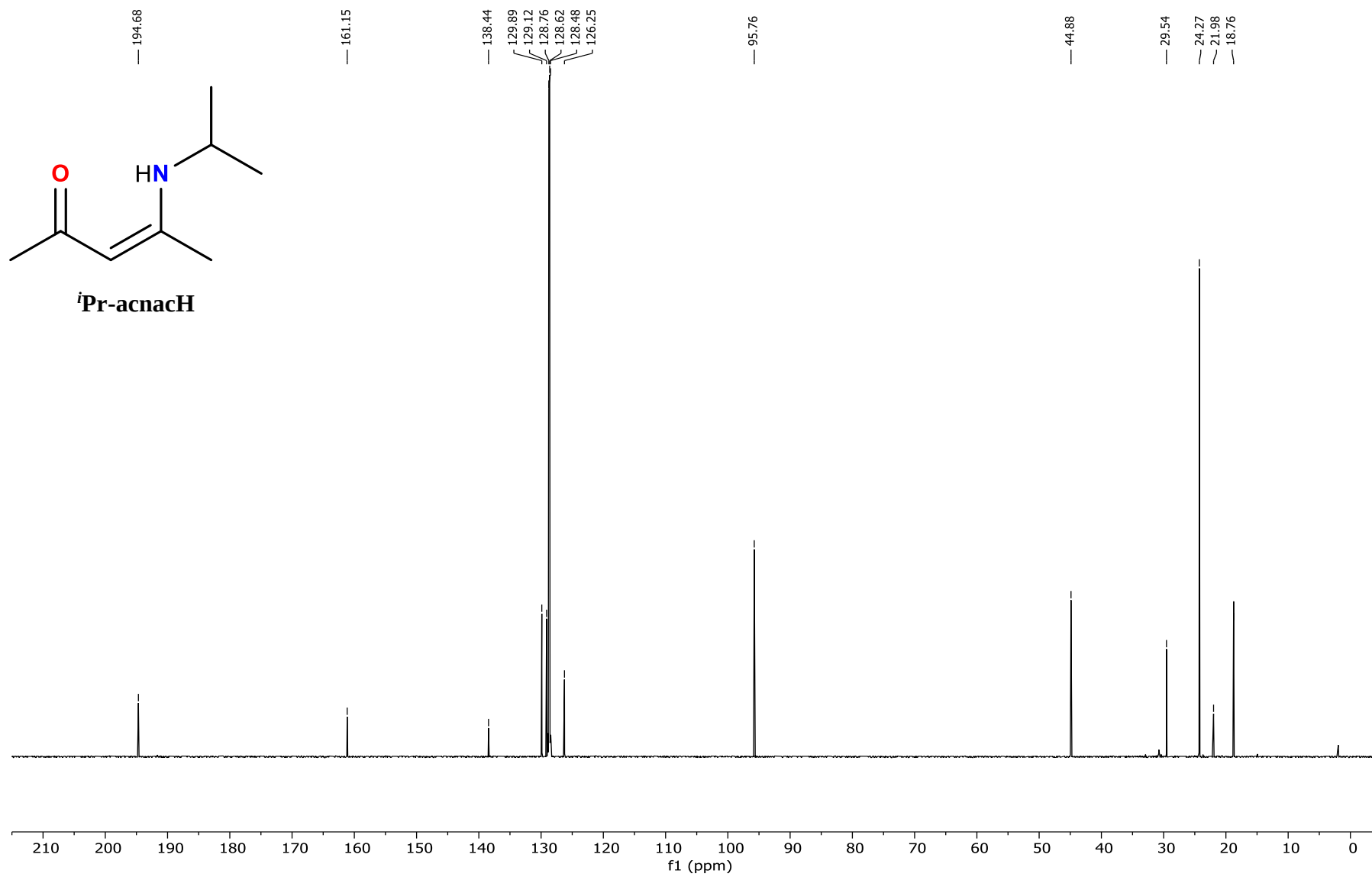
Appendix 3: ^1H NMR of Et-acnacH.



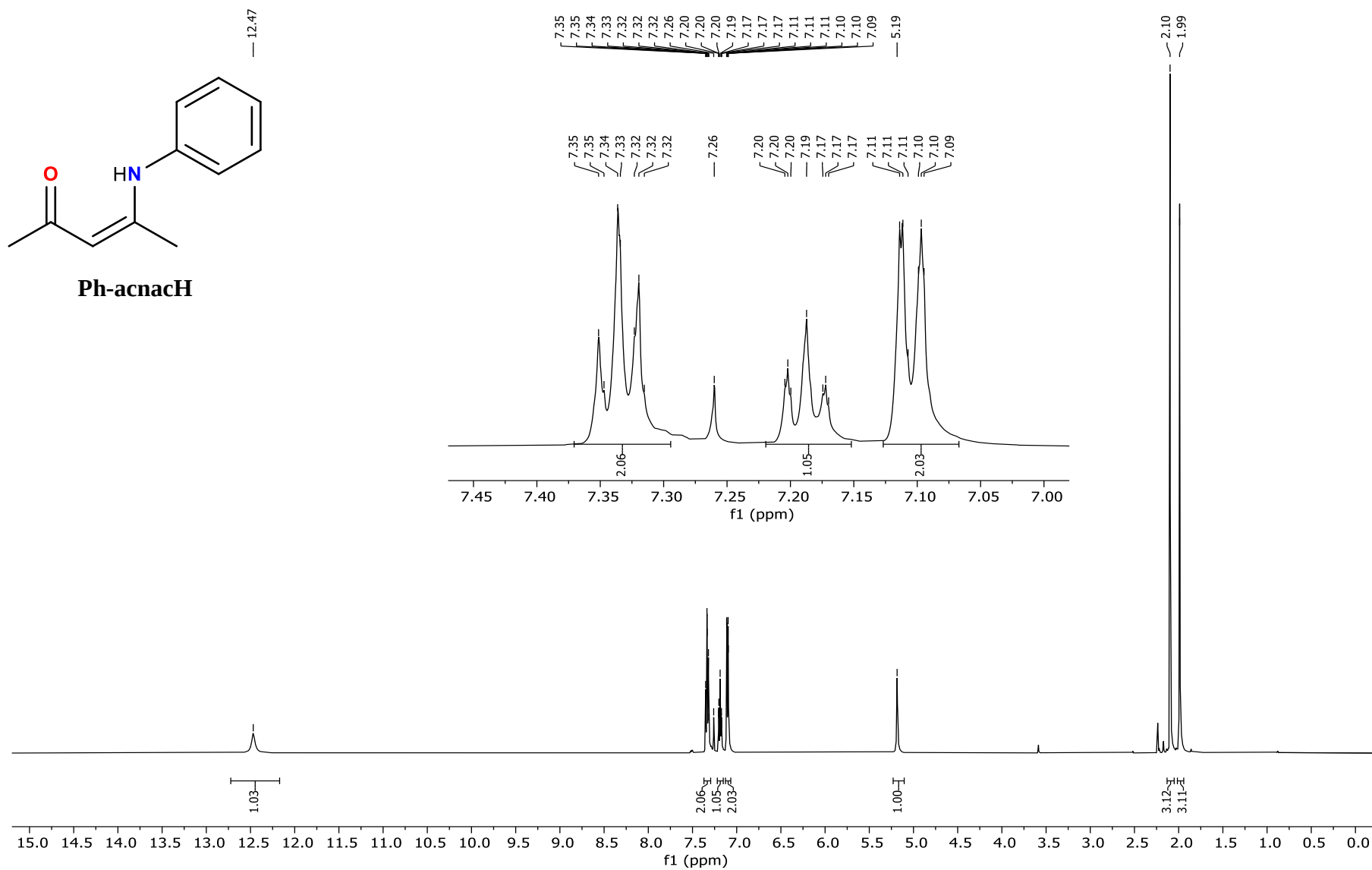
Appendix 4: ^{13}C NMR of *Et-acnacH*.

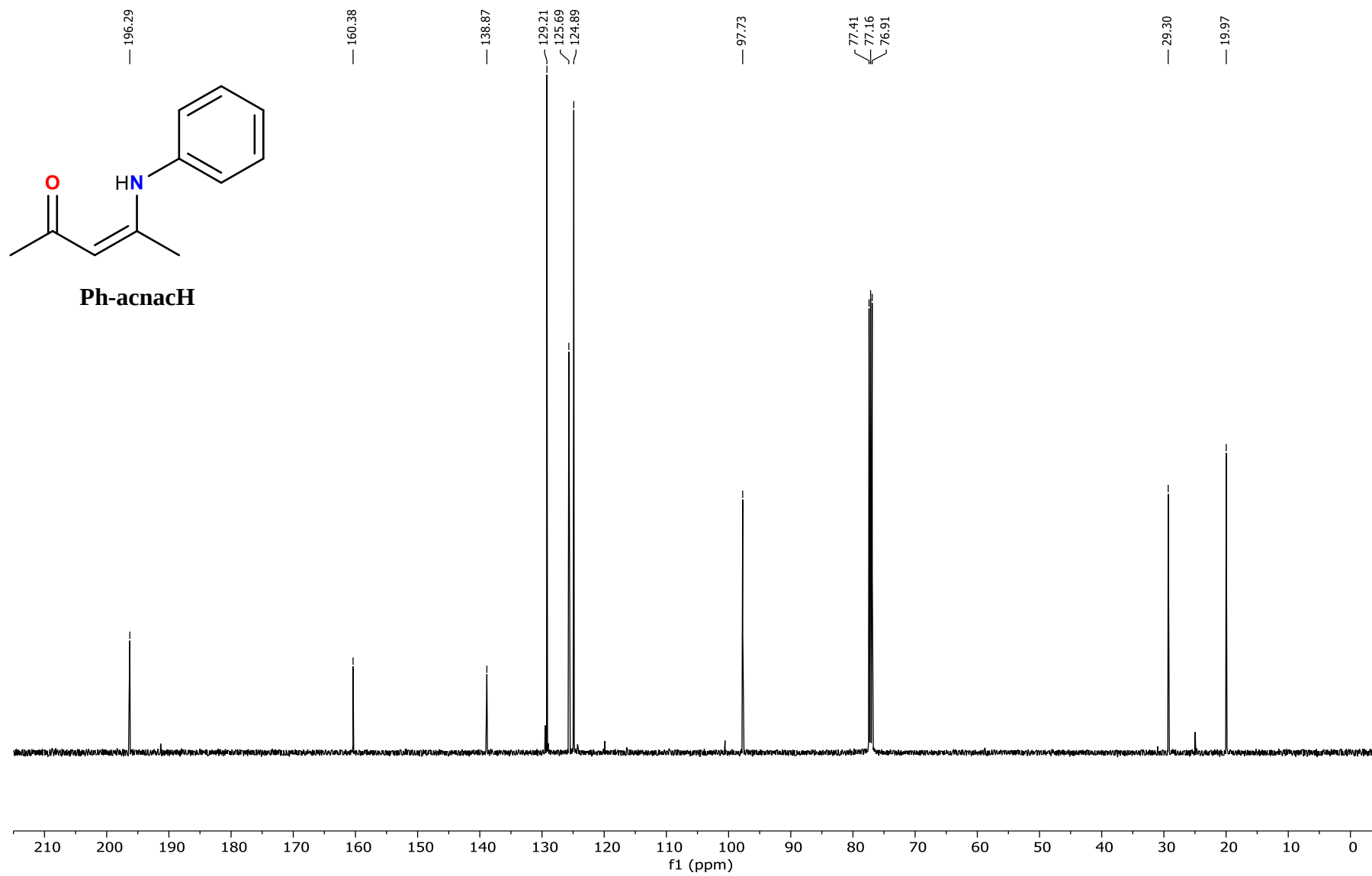


Appendix 5: ^1H NMR of *i*Pr-acnacH.

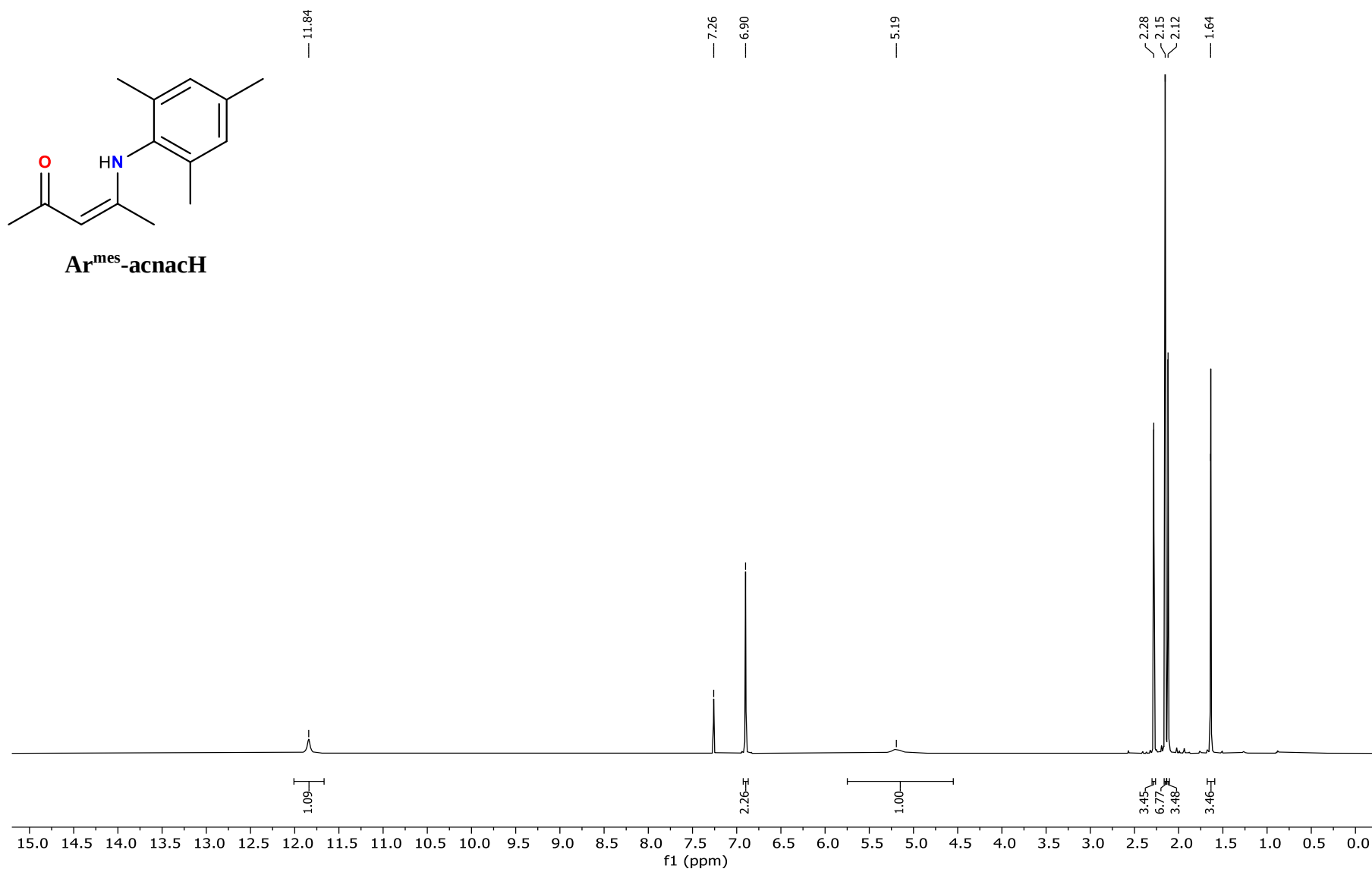


Appendix 6: ^{13}C NMR of *i*Pr-acnacH.

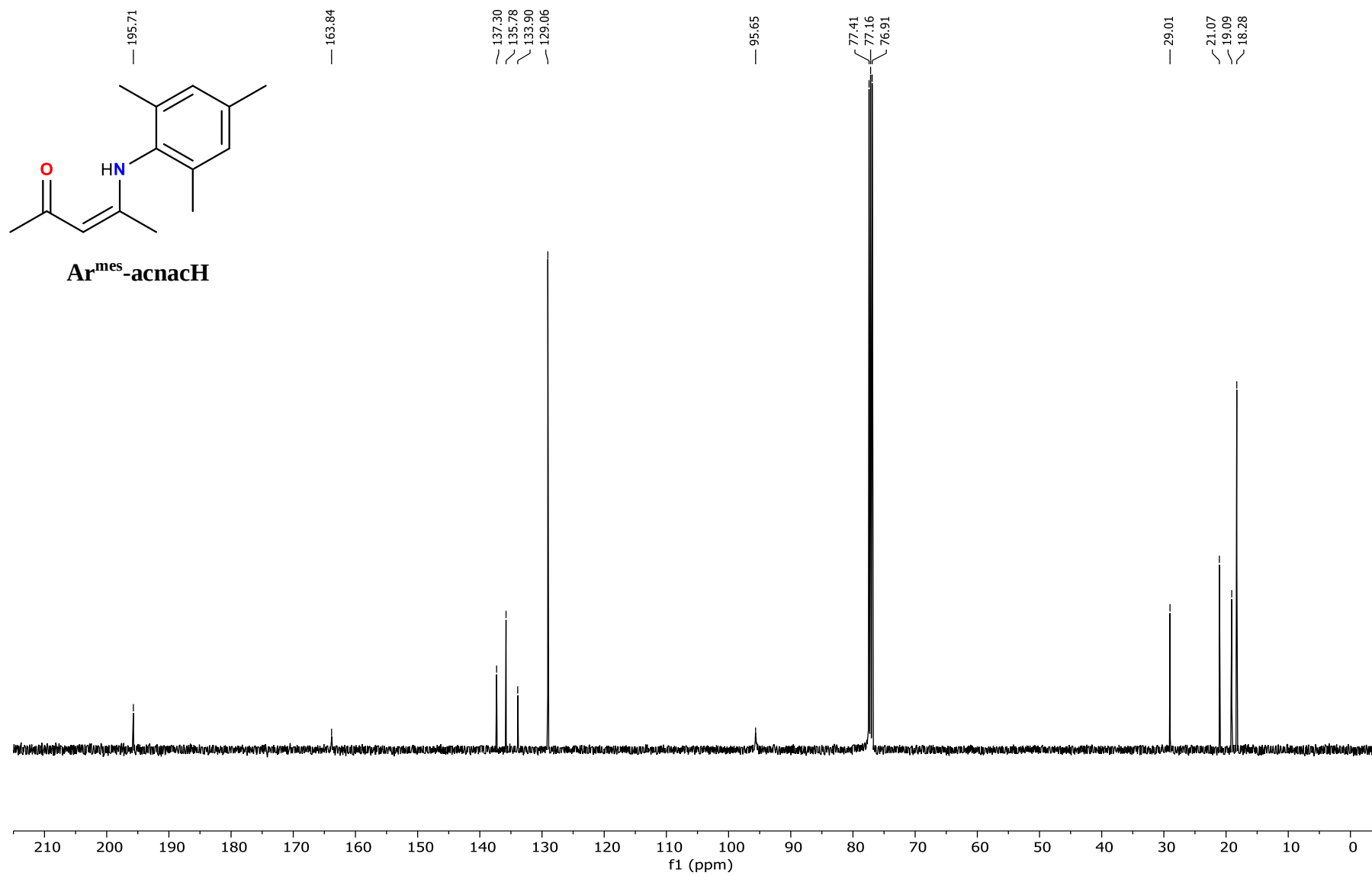
Appendix 7: ^1H NMR of Ph-acnacH.



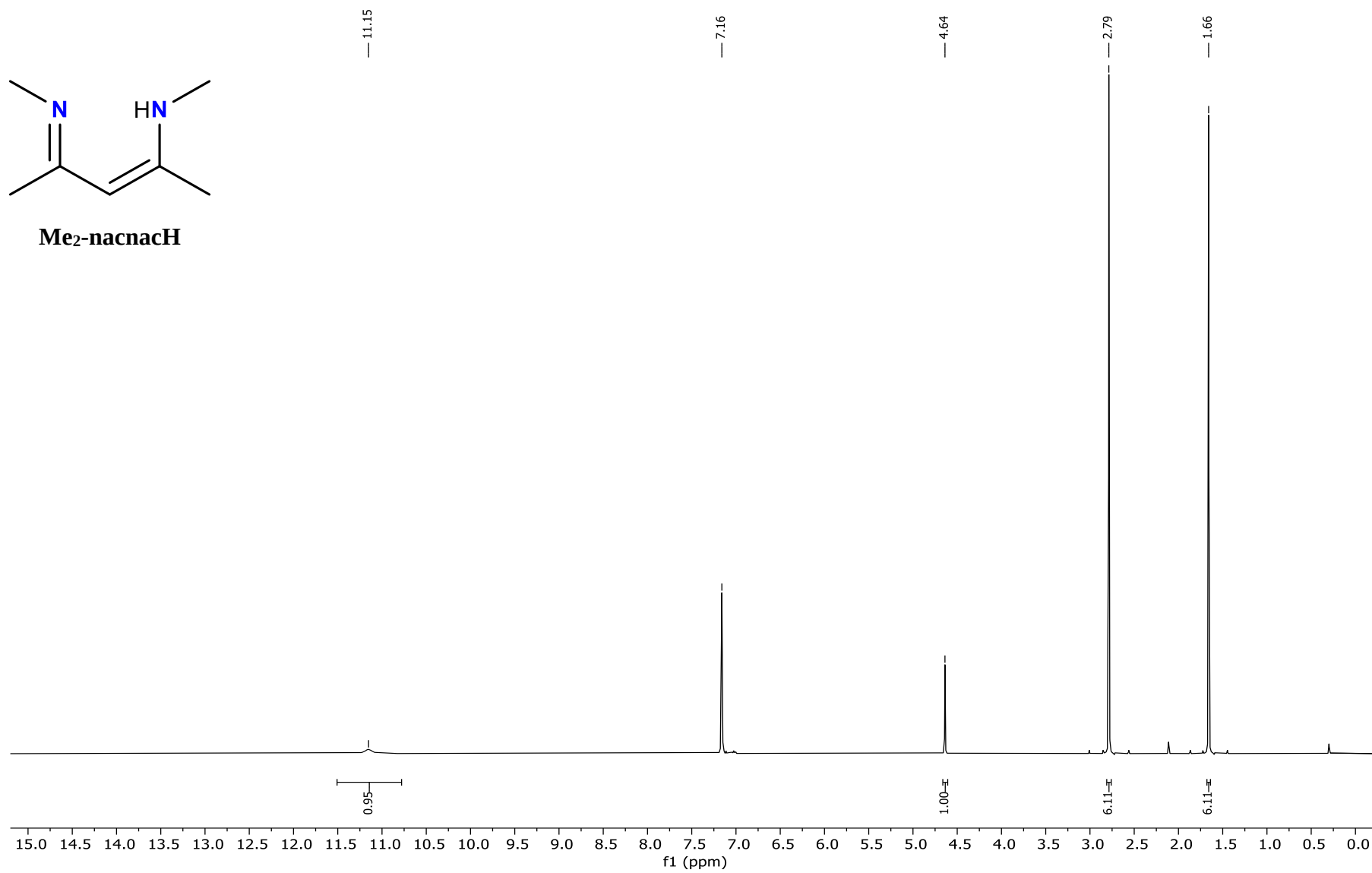
Appendix 8: ^{13}C NMR of *Ph-acnacH*.



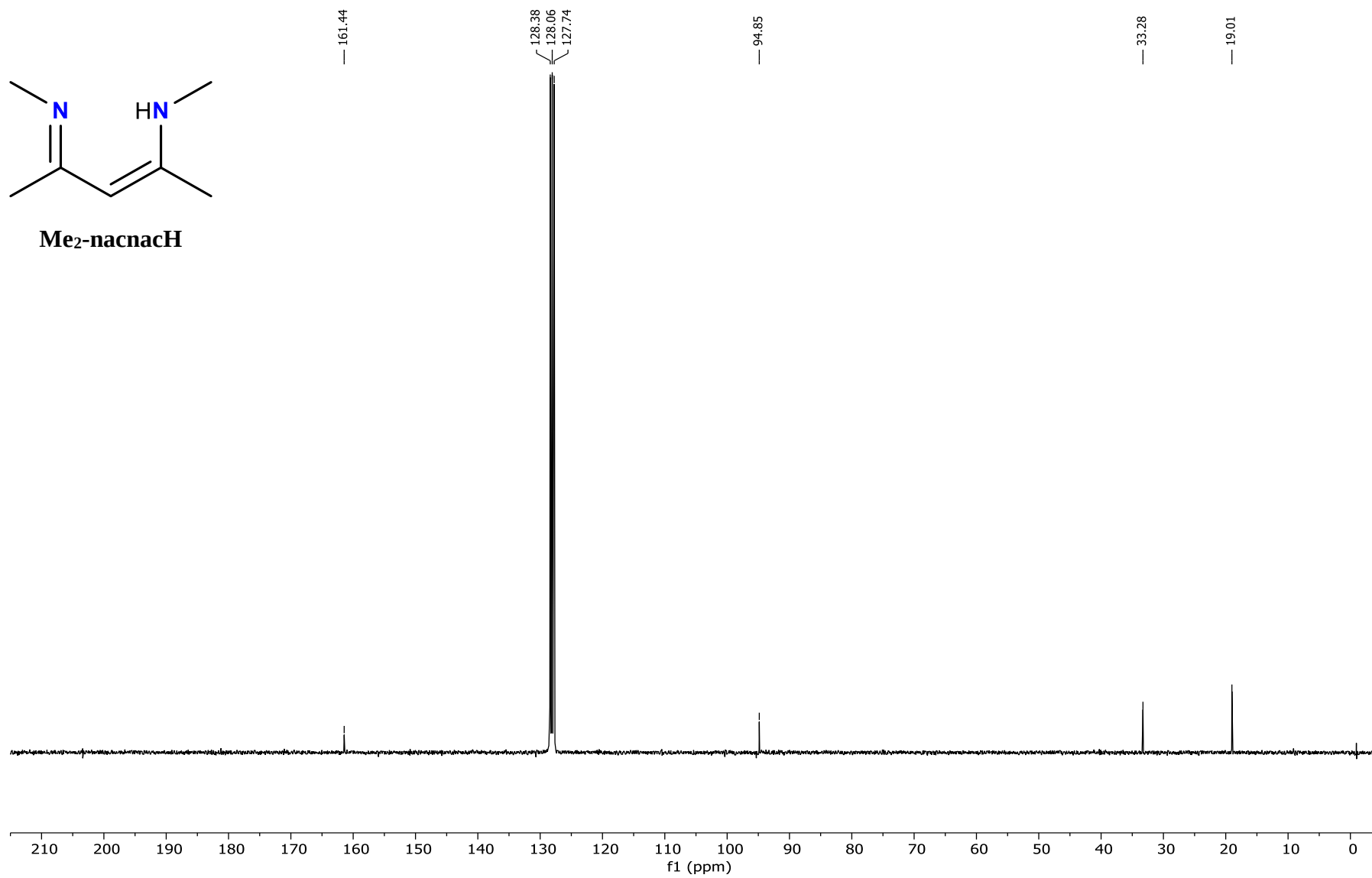
Appendix 9: ¹H NMR of Ar^{mes}-acnacH.



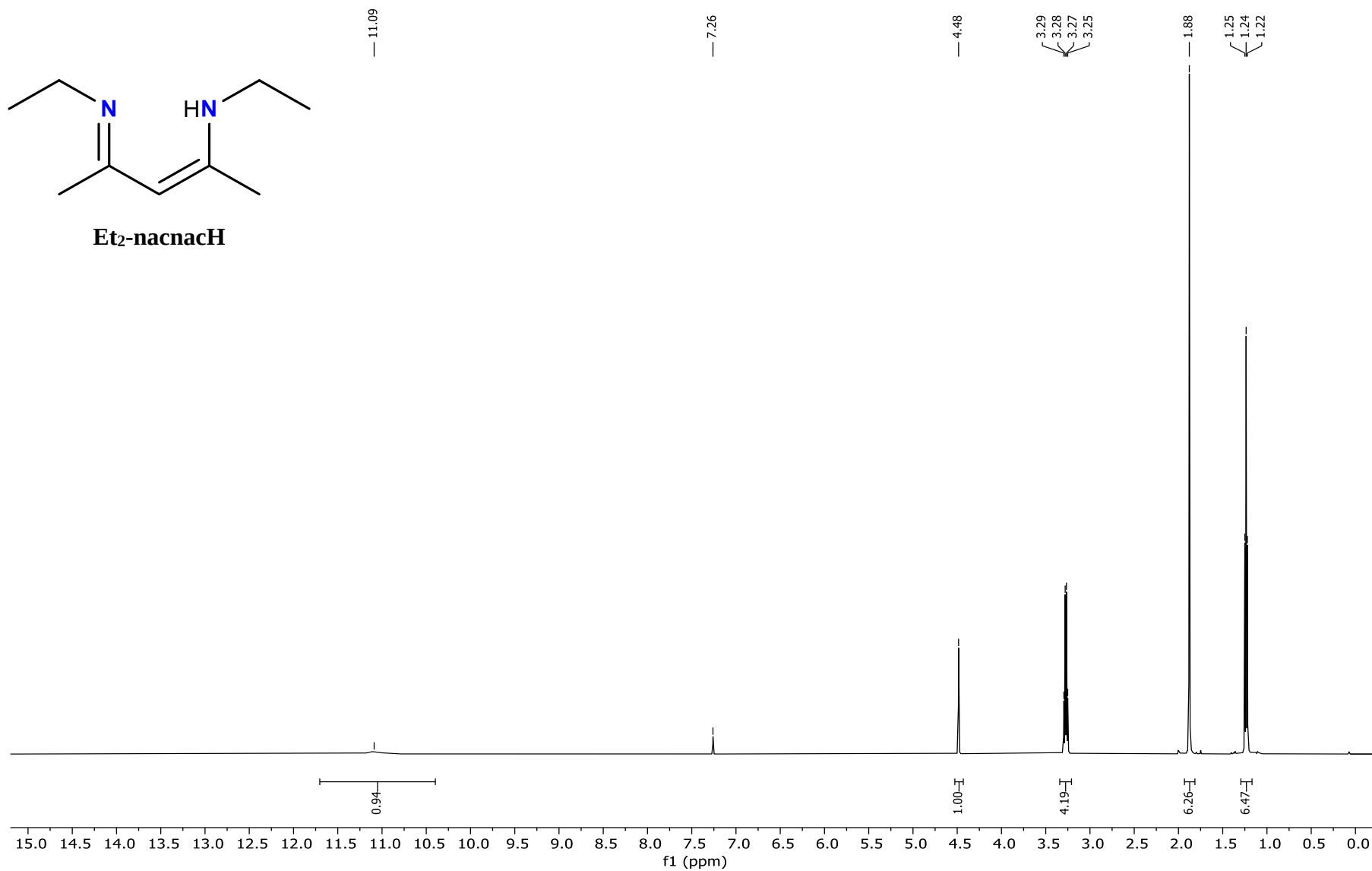
Appendix 10: ^{13}C NMR of Ar^{mes} -acnacH.



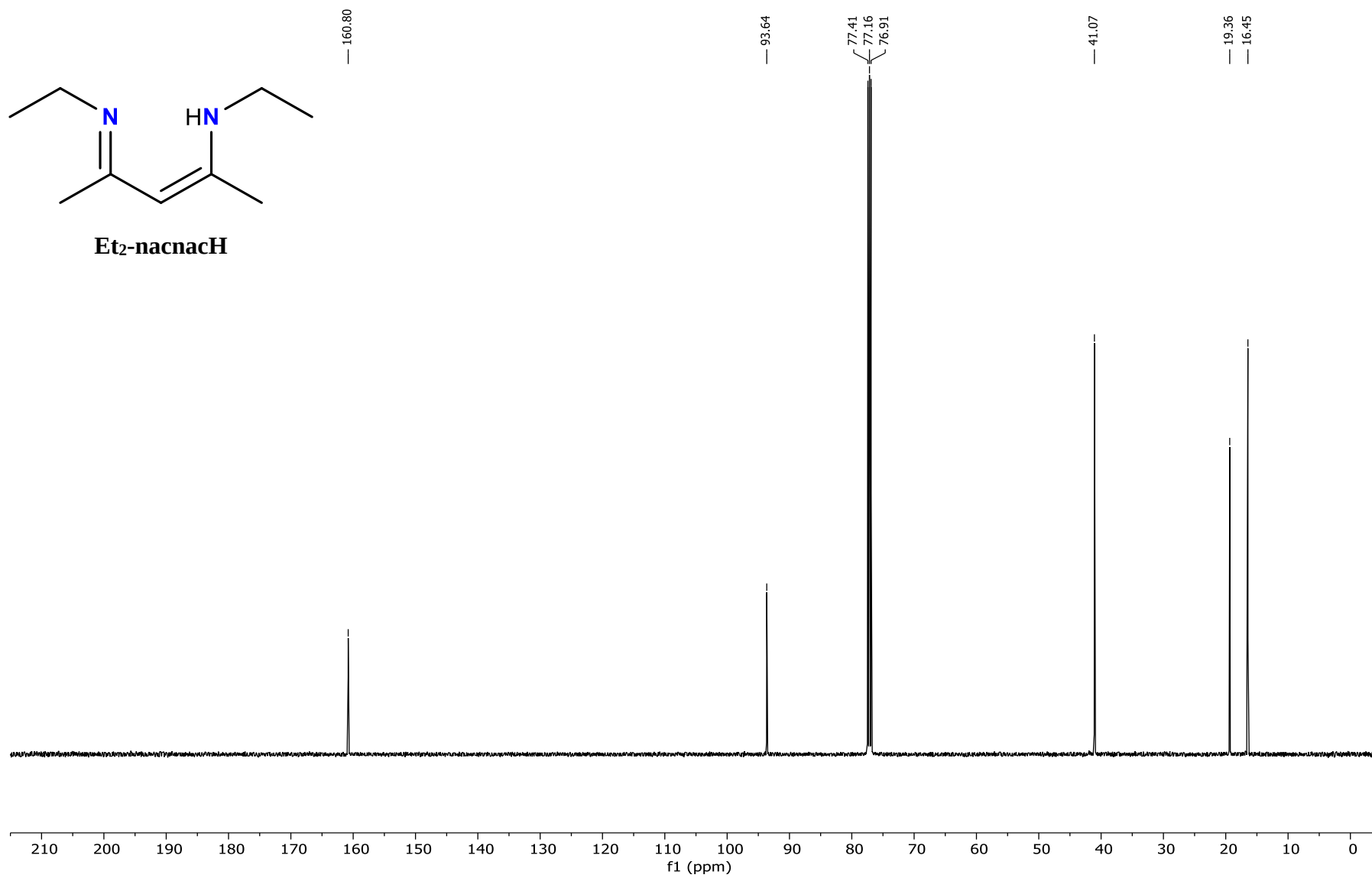
Appendix 11: ¹H NMR of Me₂-nacnacH.



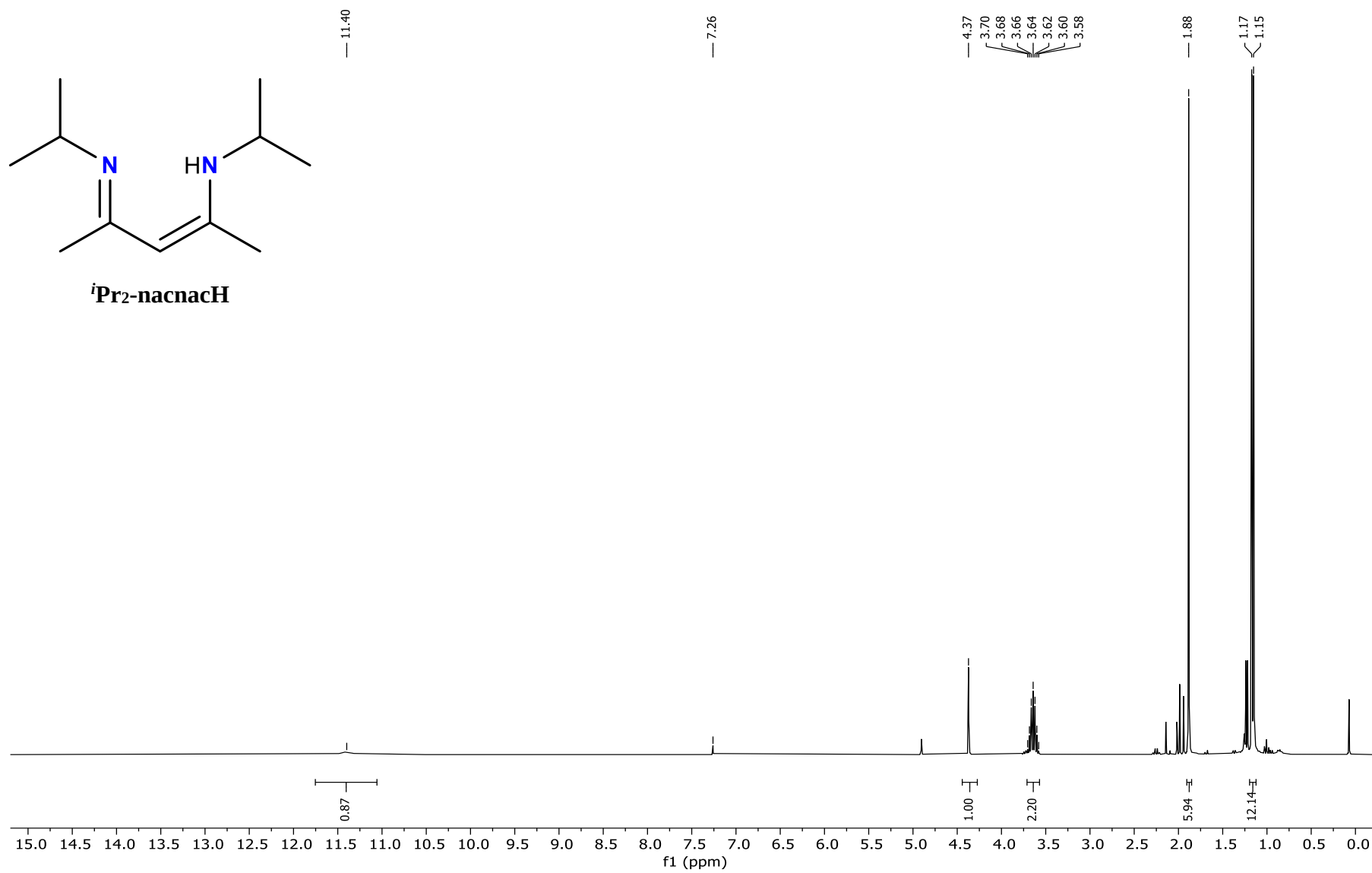
Appendix 12: ^{13}C NMR of Me₂-nacnacH.



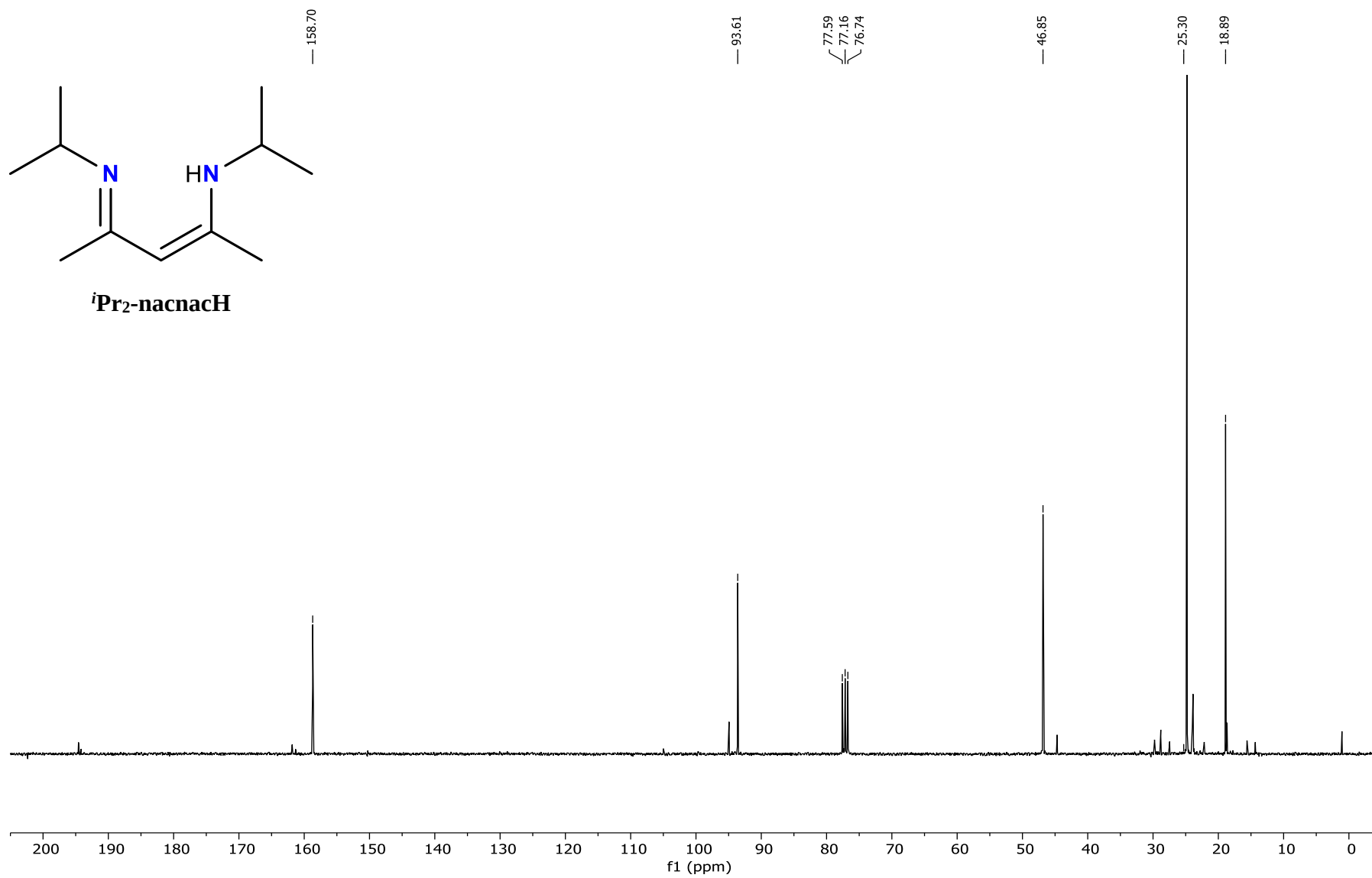
Appendix 13: ¹H NMR of Et₂-nacnacH.



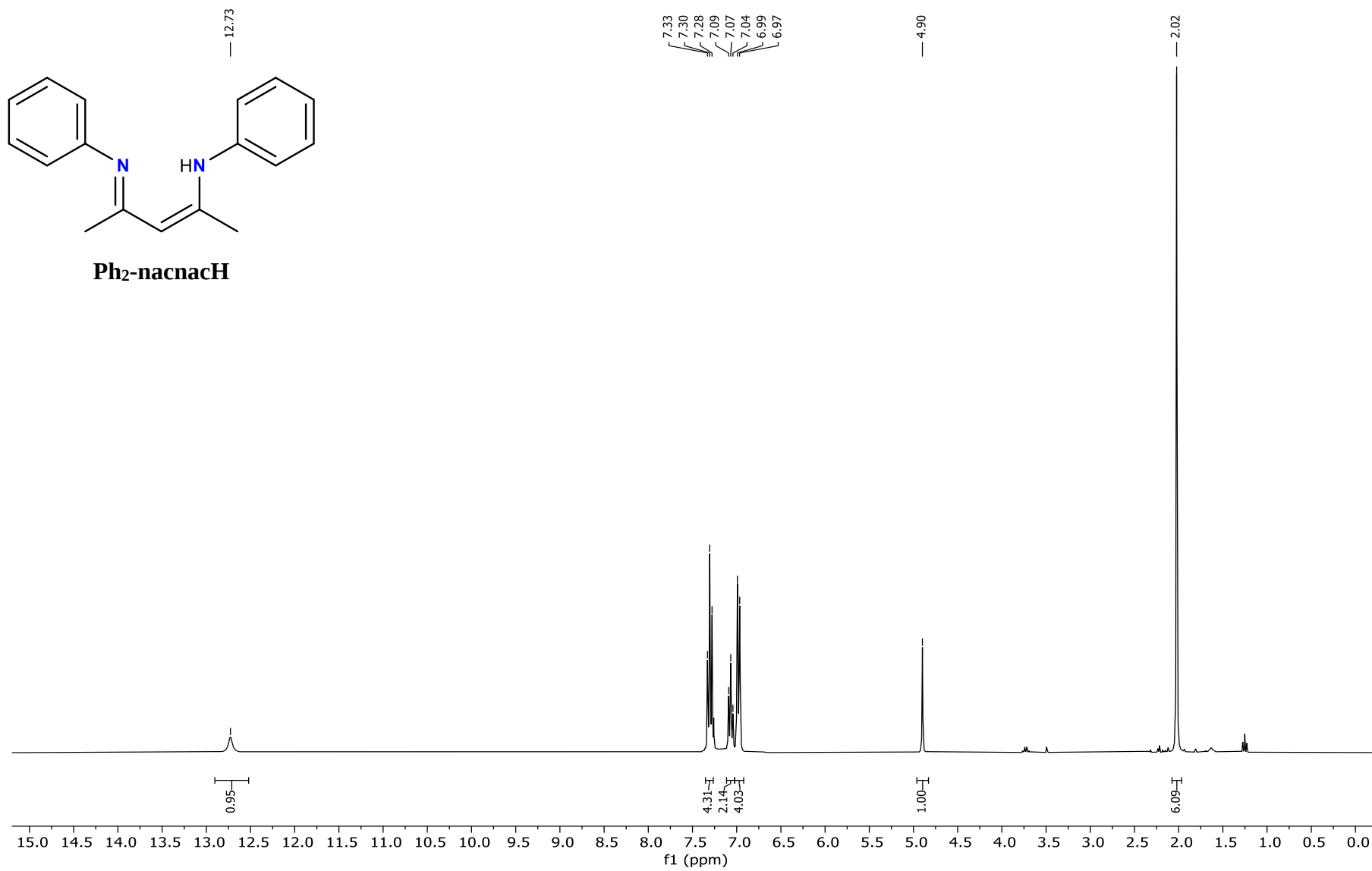
Appendix 14: ¹³C NMR of Et₂-nacnacH.

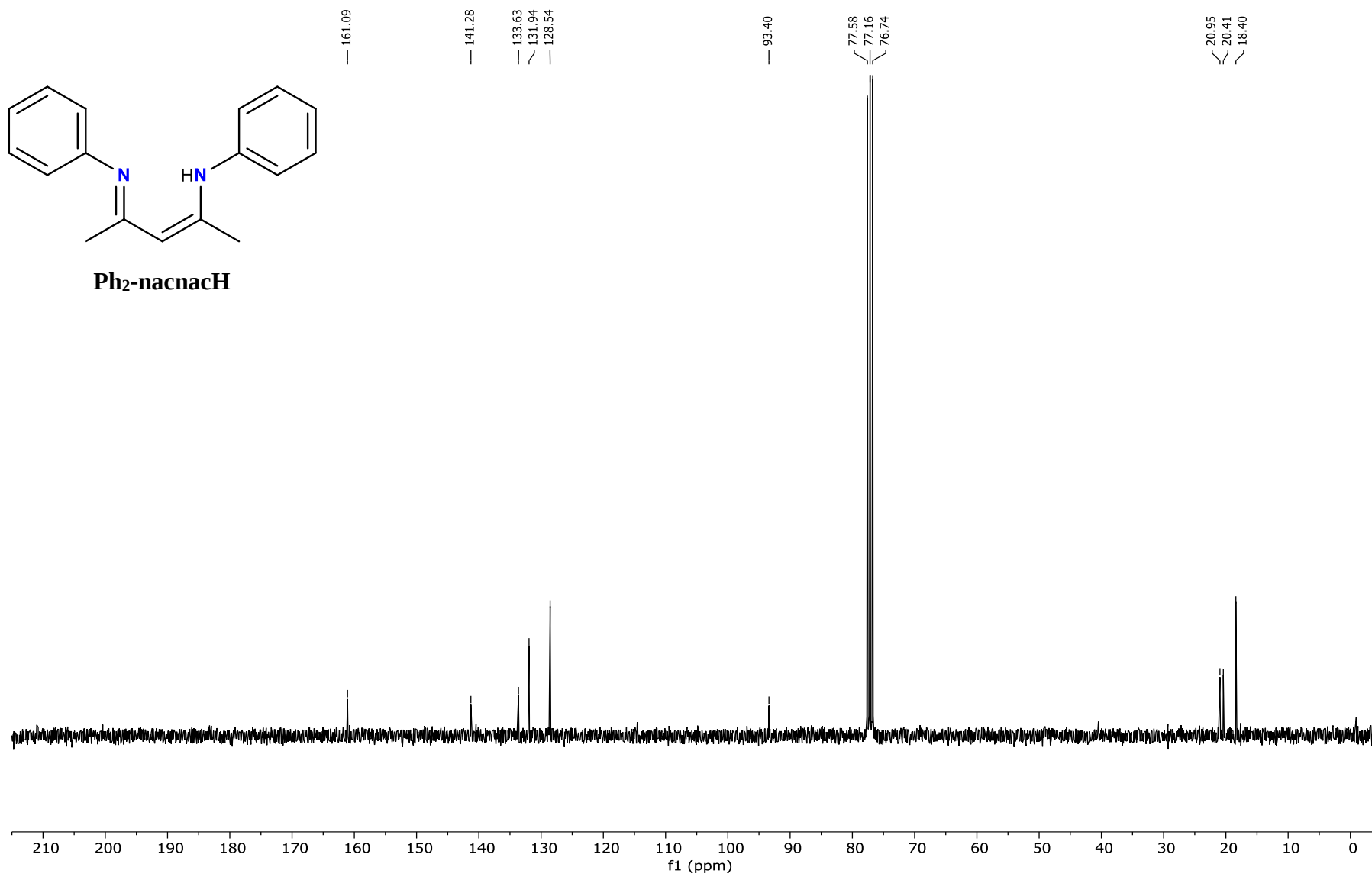


Appendix 15: ¹H NMR of *i*Pr₂-nacnacH.

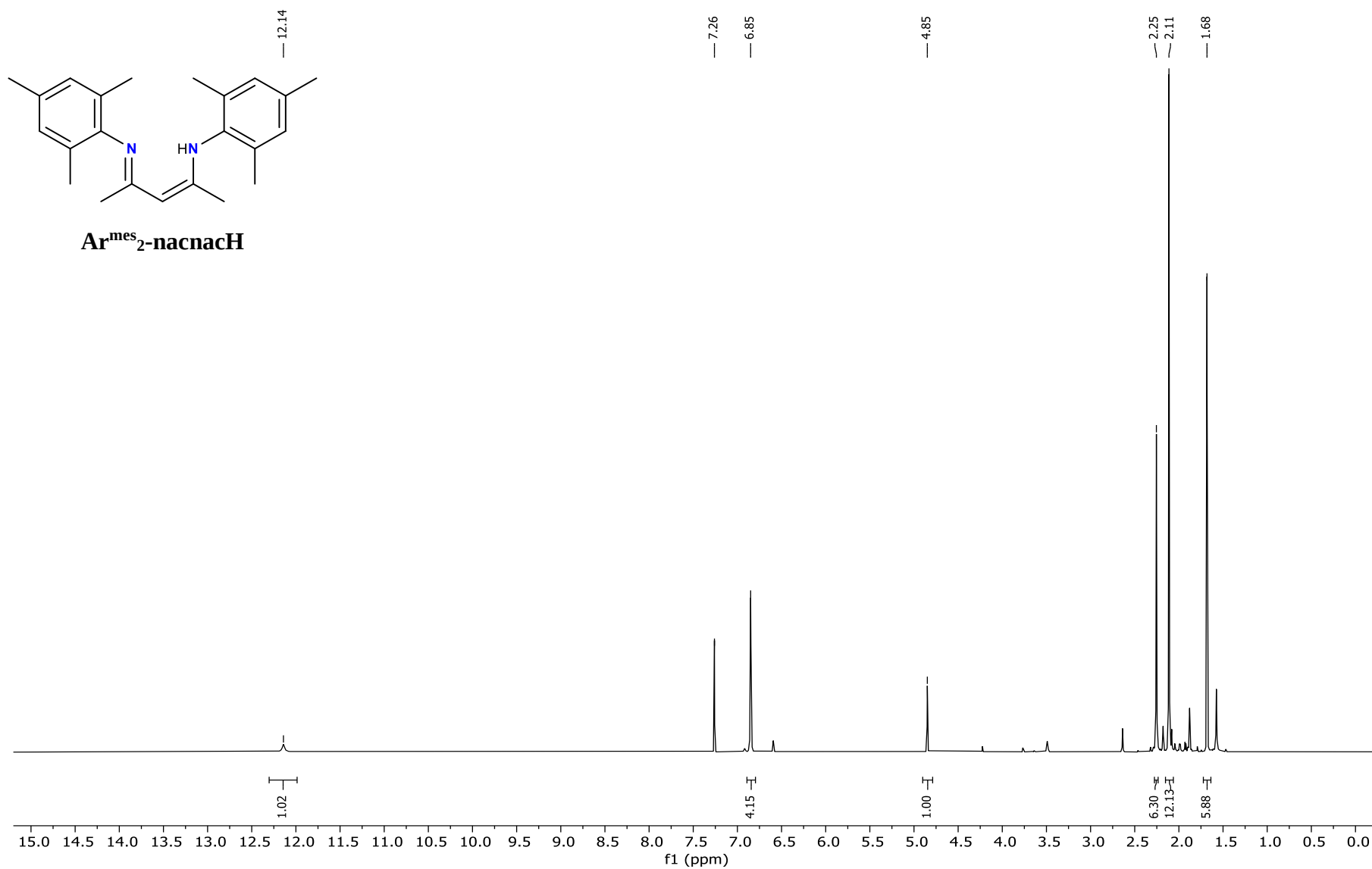


Appendix 16: ^{13}C NMR of *i*Pr₂-nacnacH.

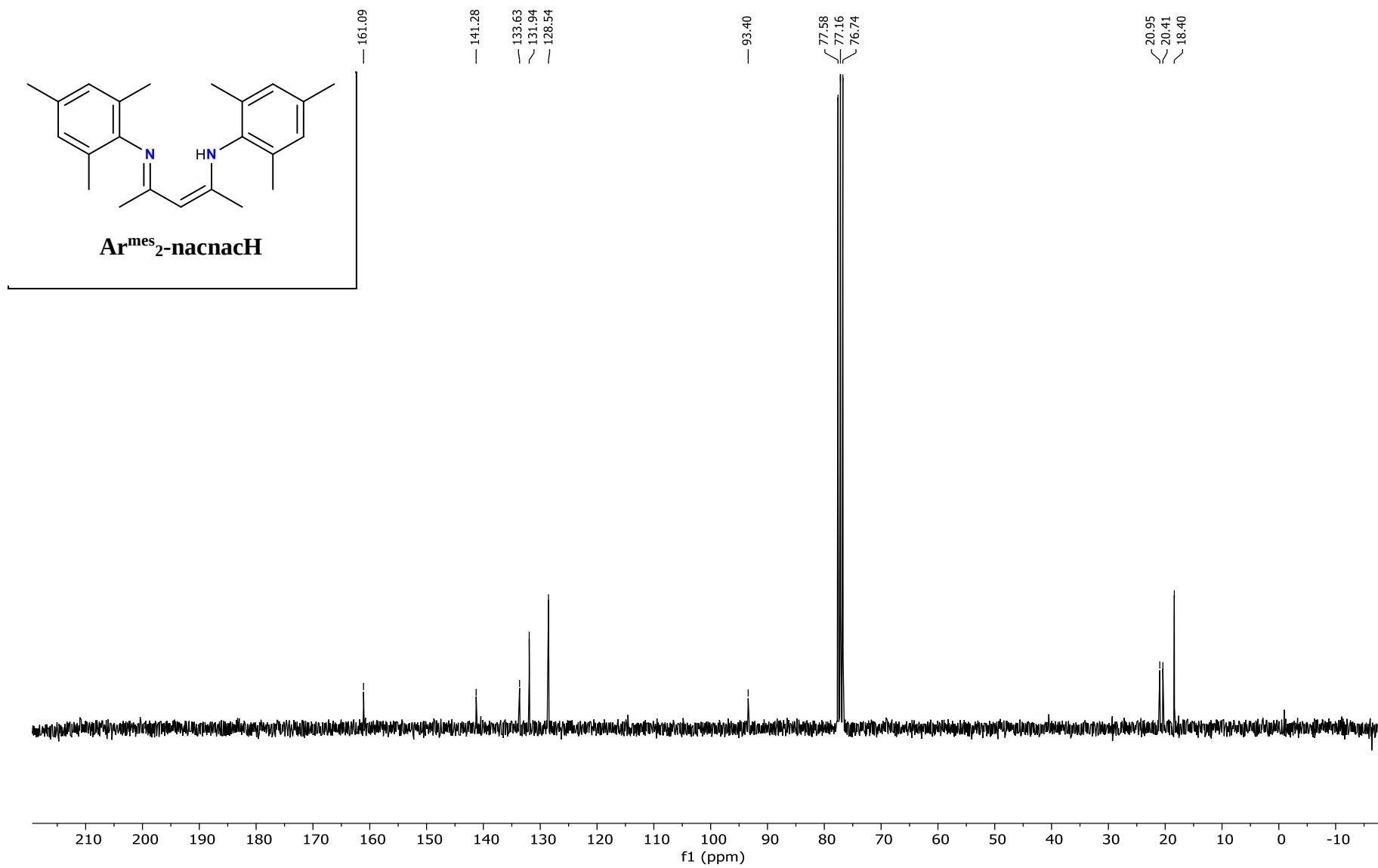
Appendix 17: ¹H NMR of Ph₂-nacnacH.

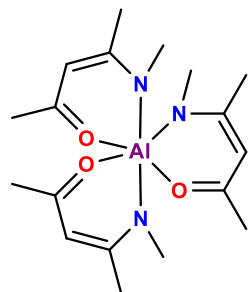


Appendix 18: ¹³C NMR of Ph₂-nacnacH.

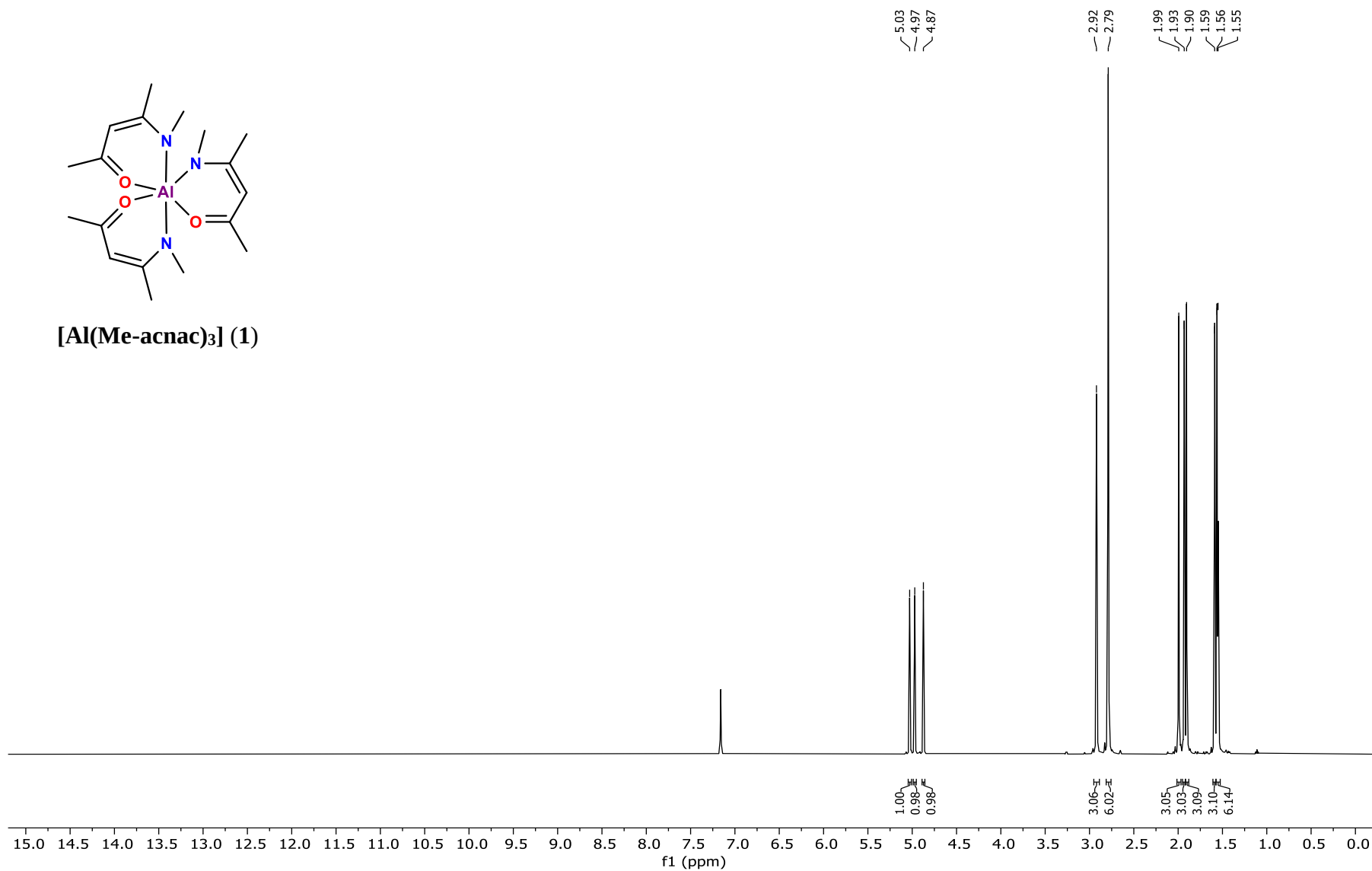


Appendix 19: ^1H NMR of $\text{Ar}^{\text{mes}}_2\text{-nacnacH}$.

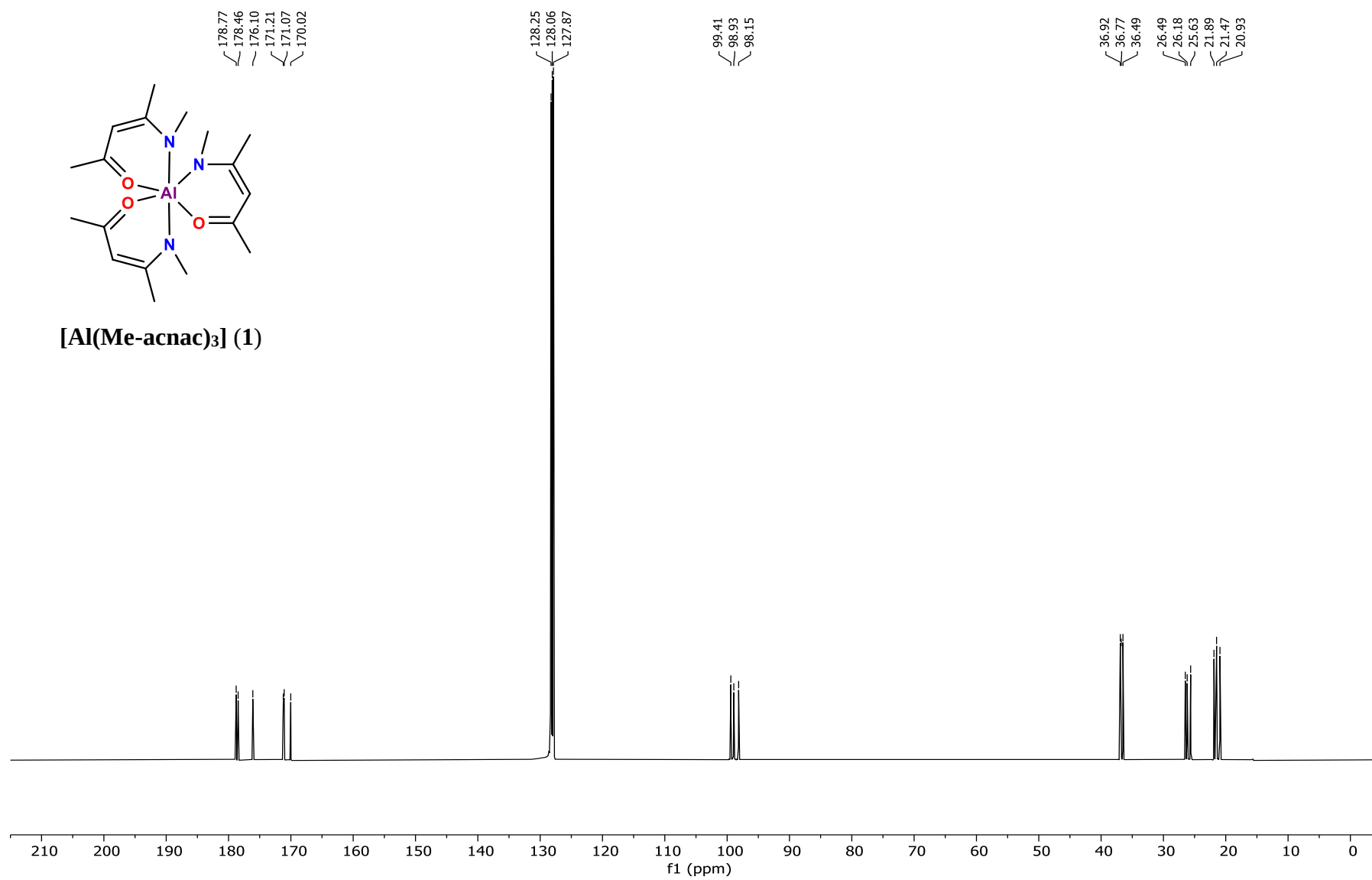
Appendix 20: ^{13}C NMR of $\text{Ar}^{\text{mes}}_2\text{-nacnacH}$.



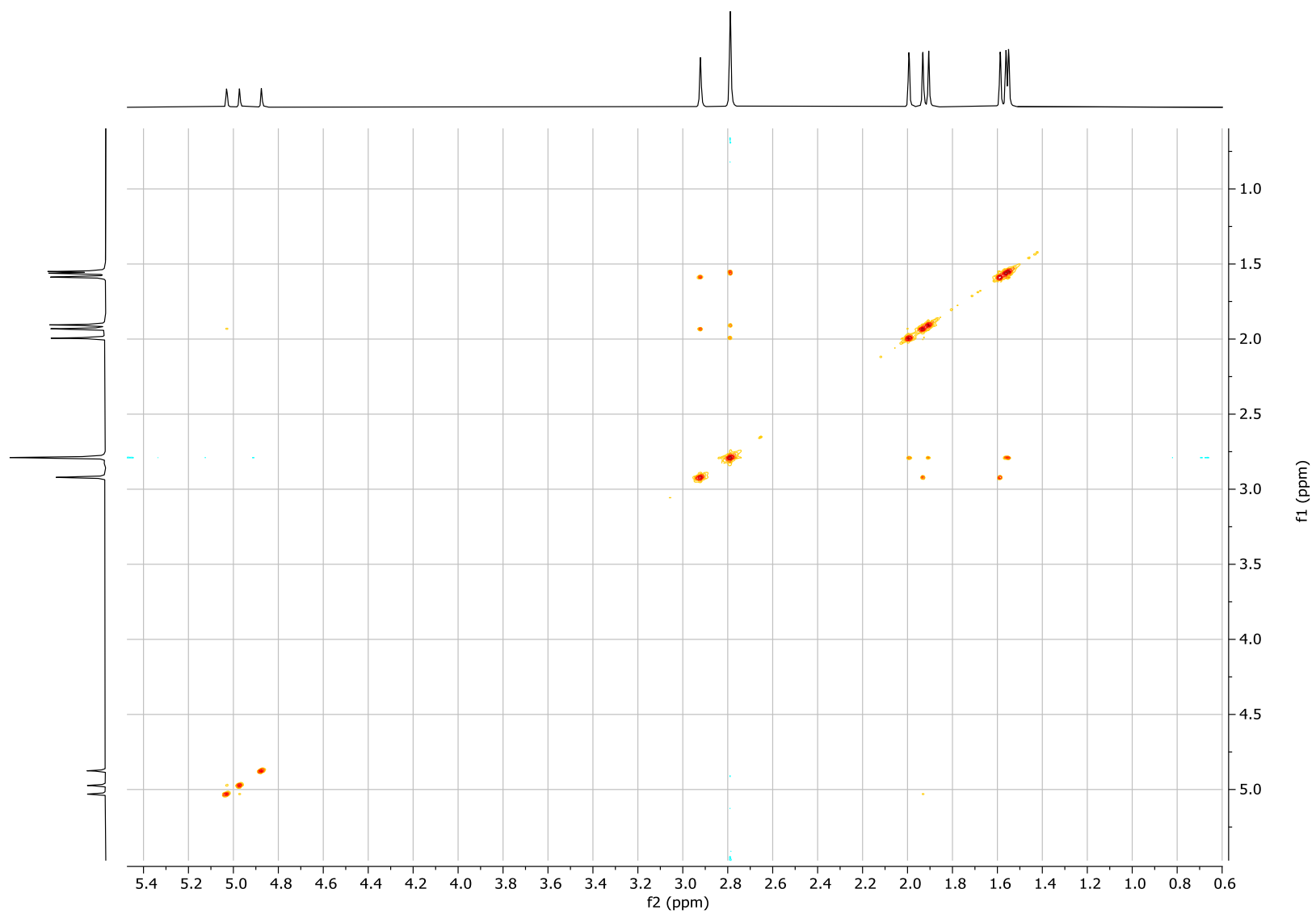
[Al(Me-acnac)₃] (1)



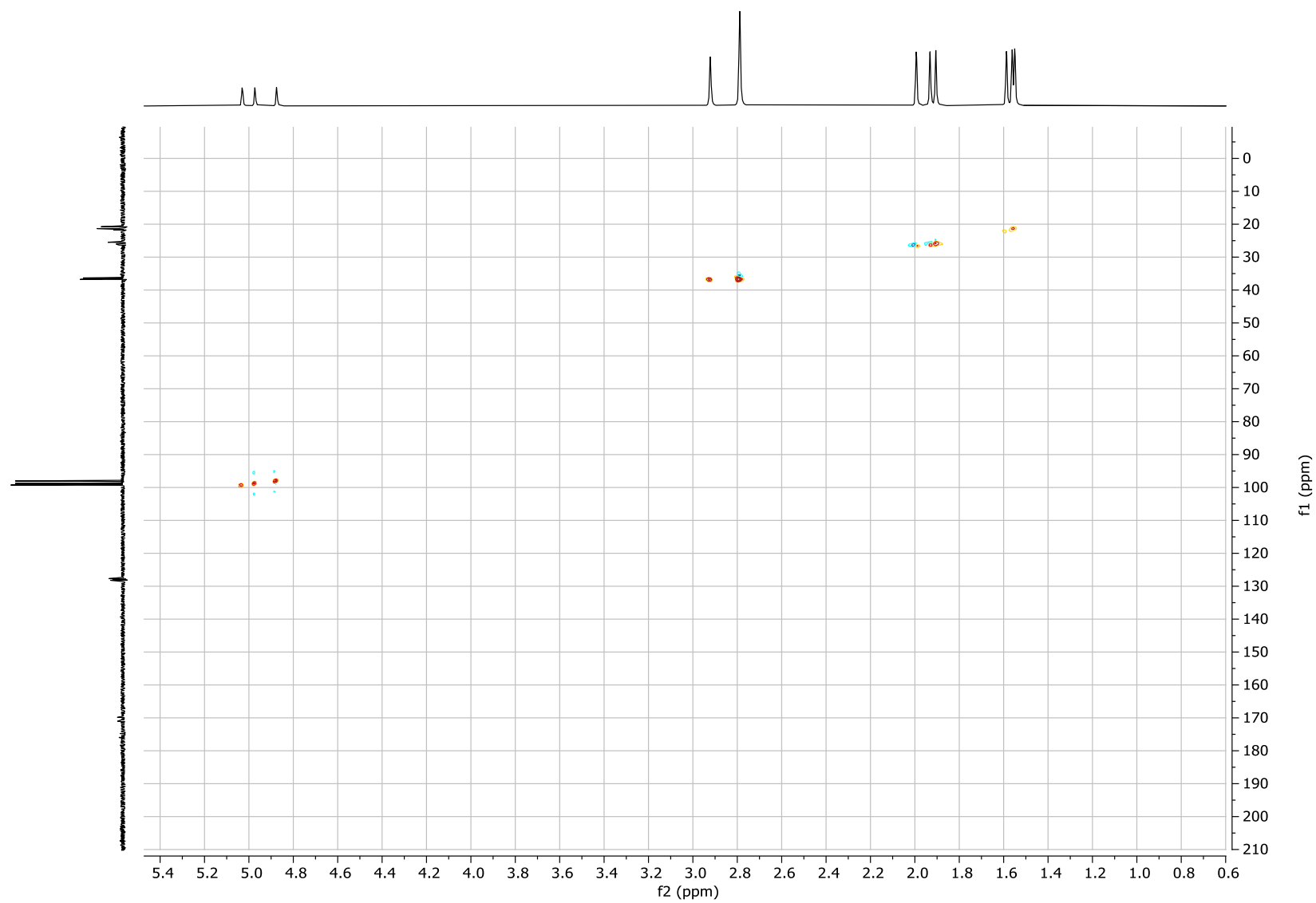
Appendix 21: ¹H NMR of [Al(Me-acnac)₃] (1).



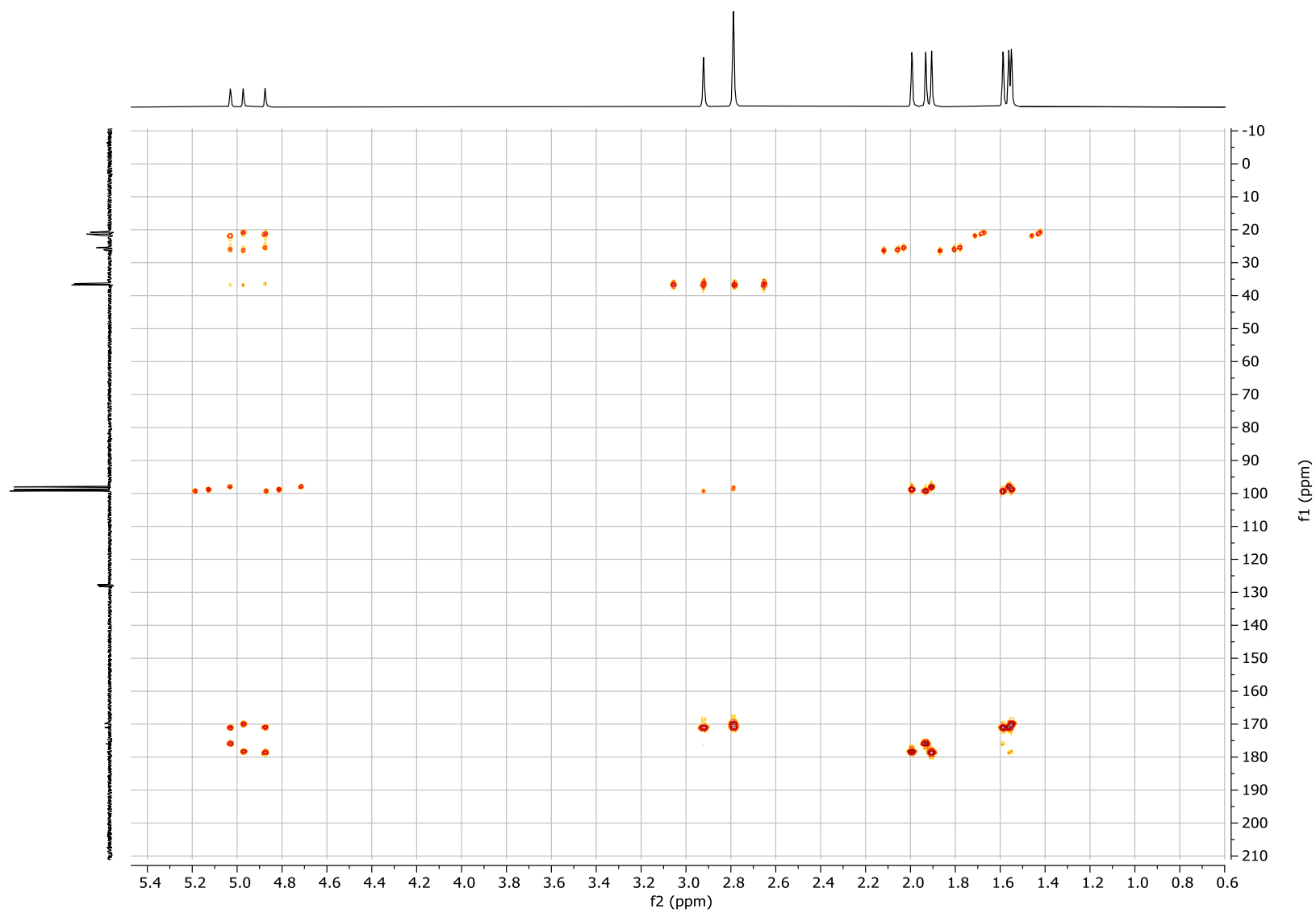
Appendix 22: ¹³C NMR of [Al(Me-acnac)₃] (1).



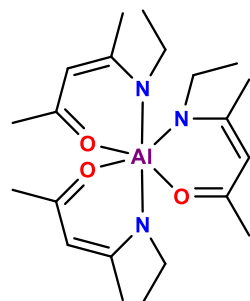
Appendix 23: COSY NMR of $[Al(Me-acnac)_3]$ (1).



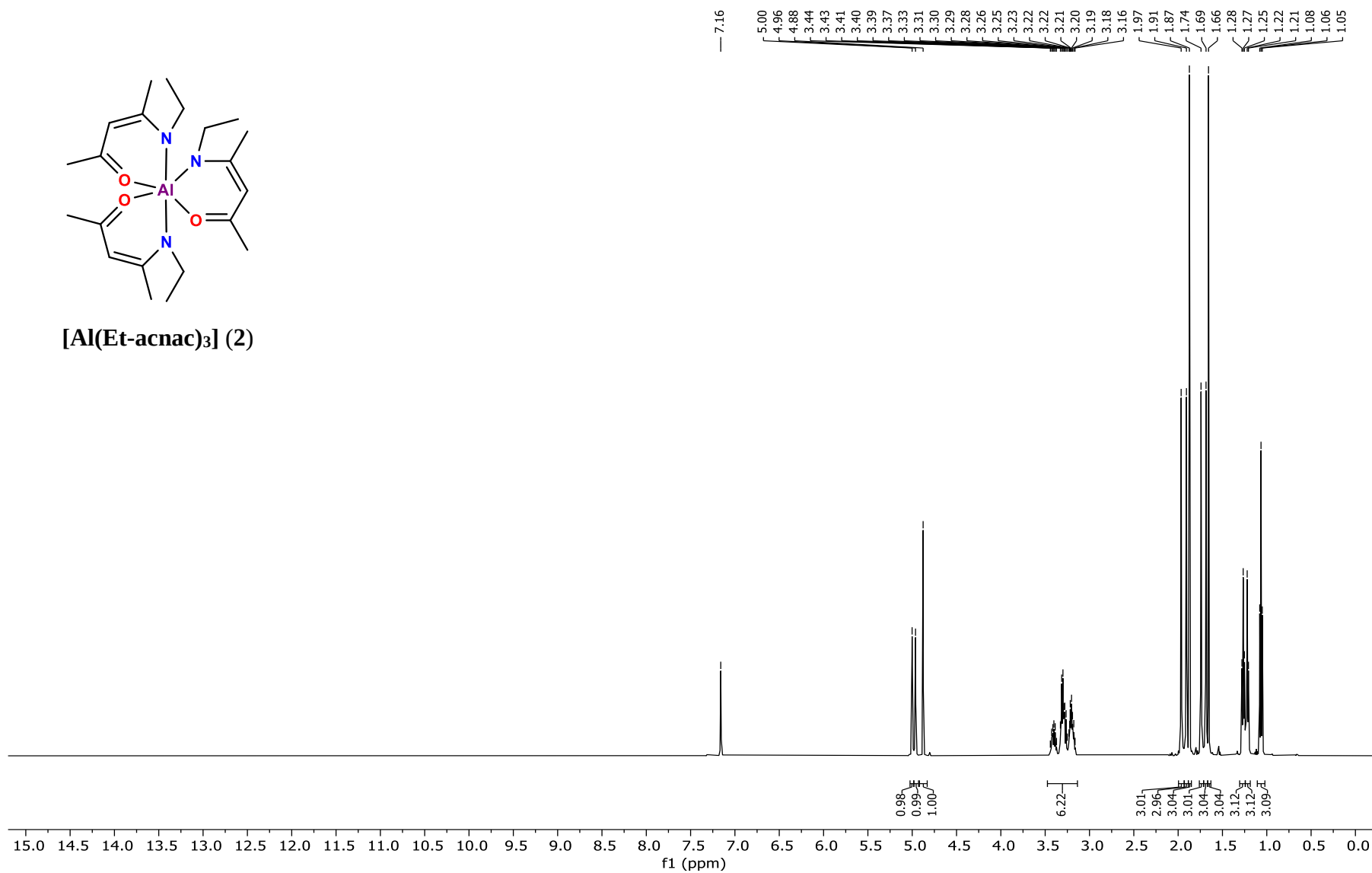
Appendix 24: HSQC NMR of [Al(Me-acnac)₃] (1).



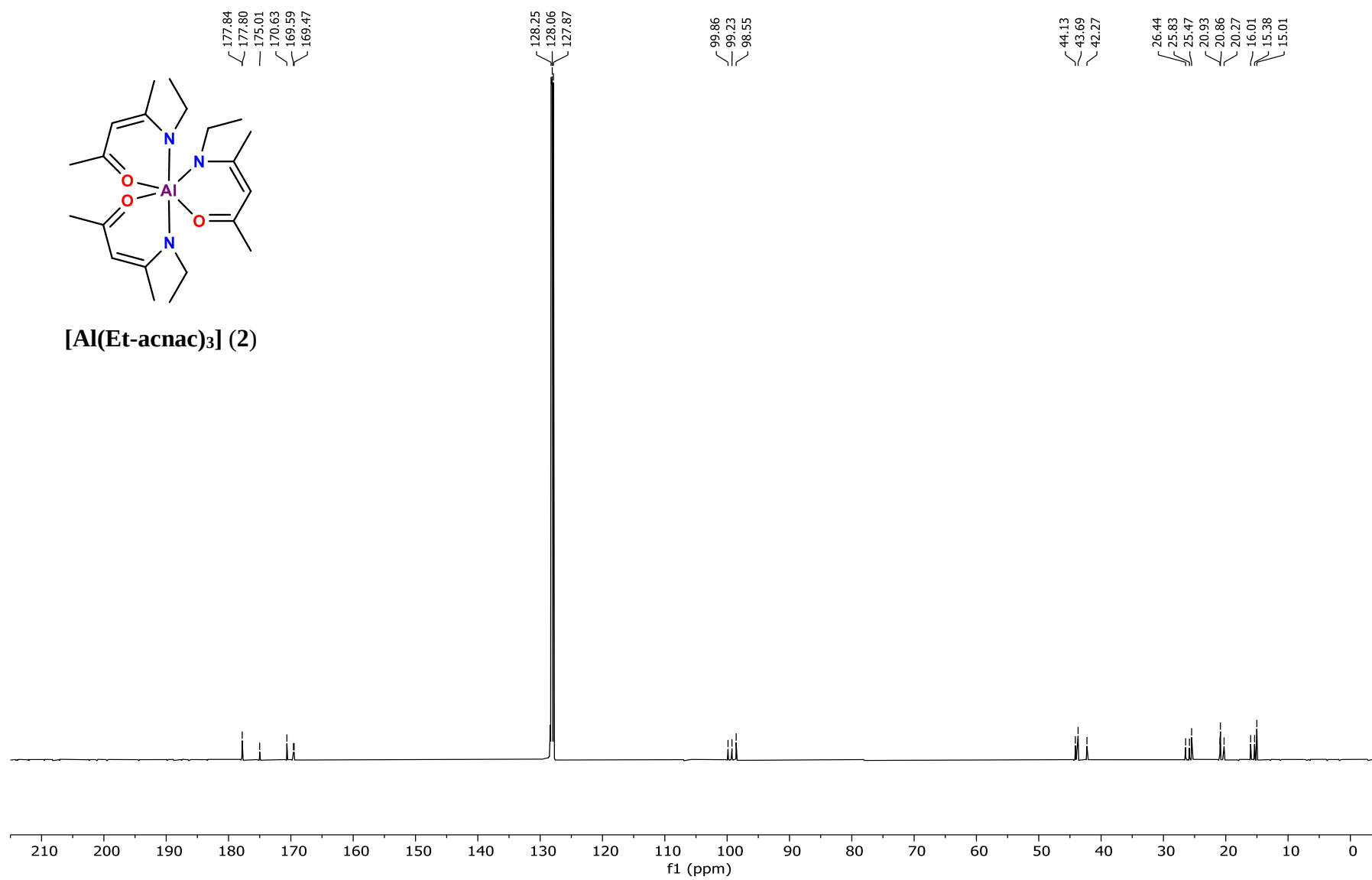
Appendix 25: HMBC NMR of $[Al(Me-acnac)_3]$ (1).



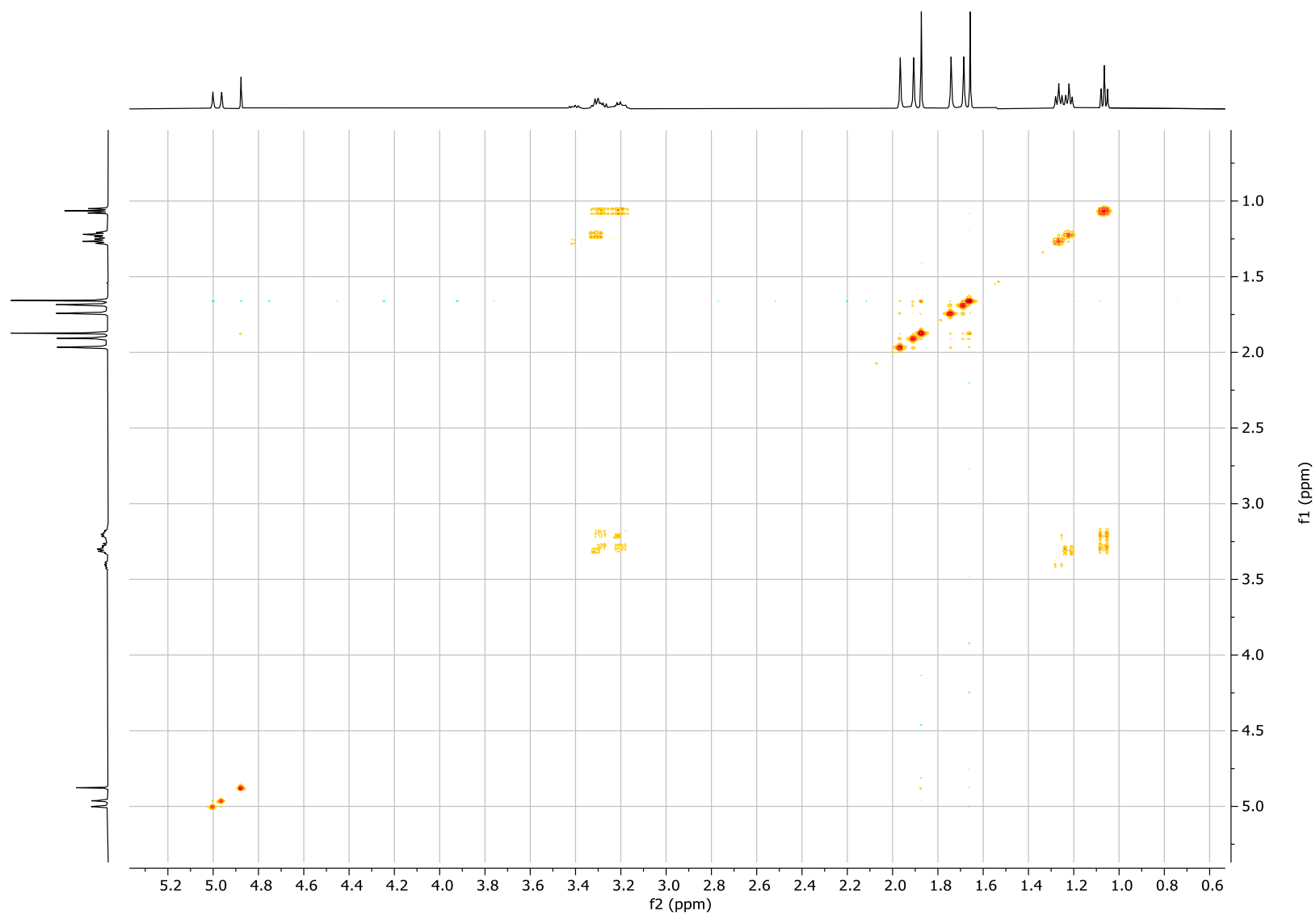
[Al(Et-acnac)₃] (2)



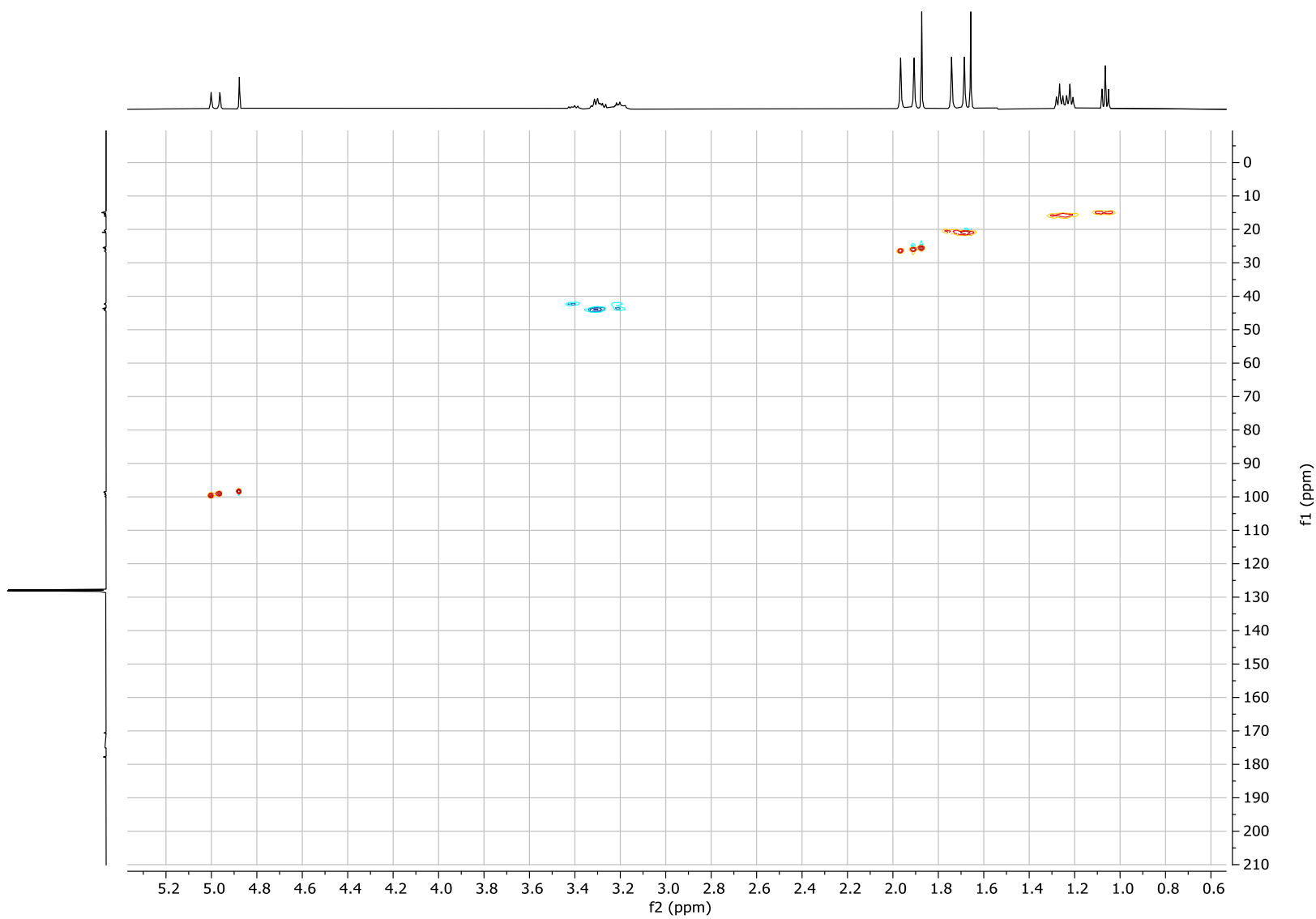
Appendix 26: ¹H NMR of [Al(Et-acnac)₃] (2).



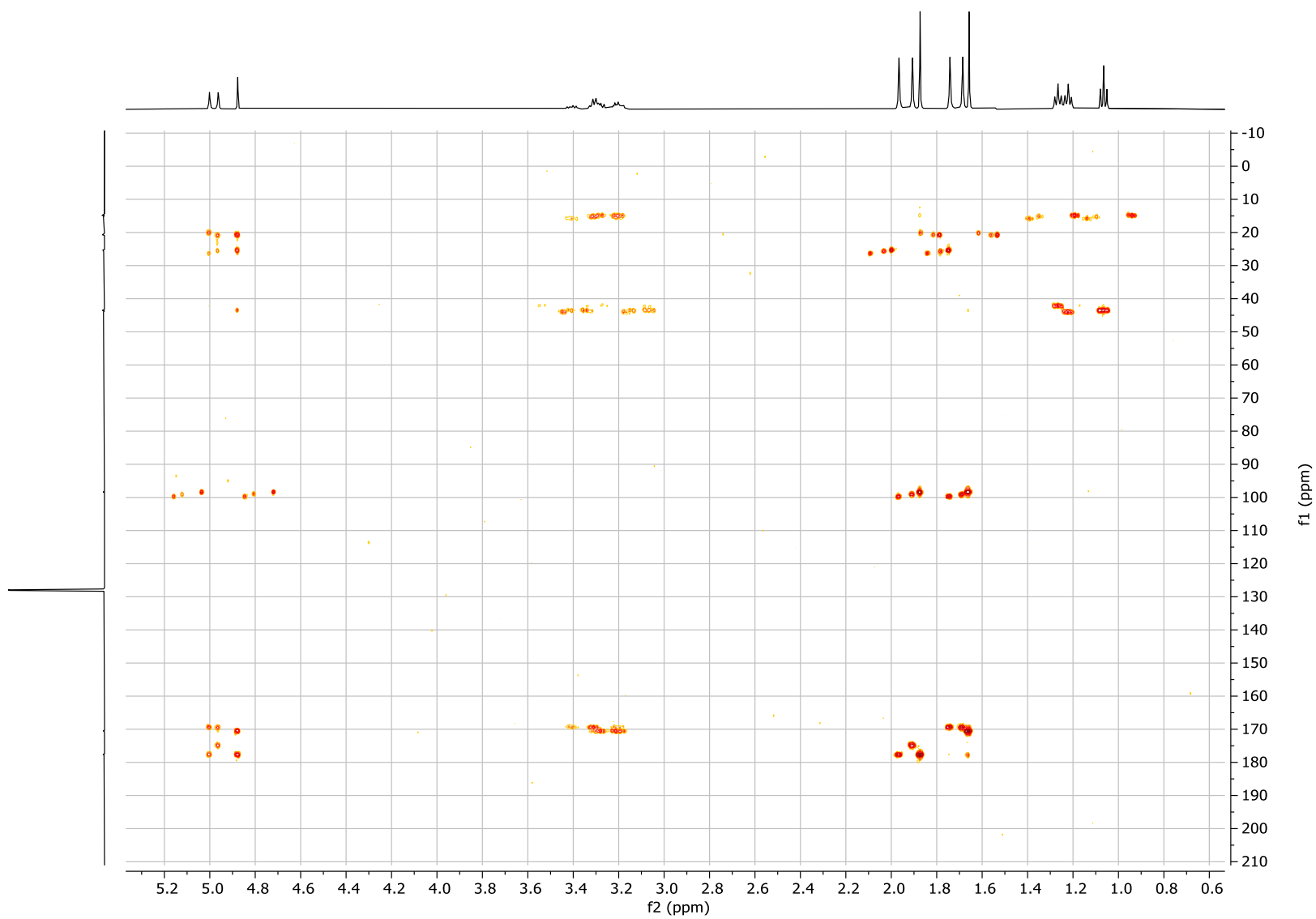
Appendix 27: ¹³C NMR of [Al(Et-acnac)₃] (2).



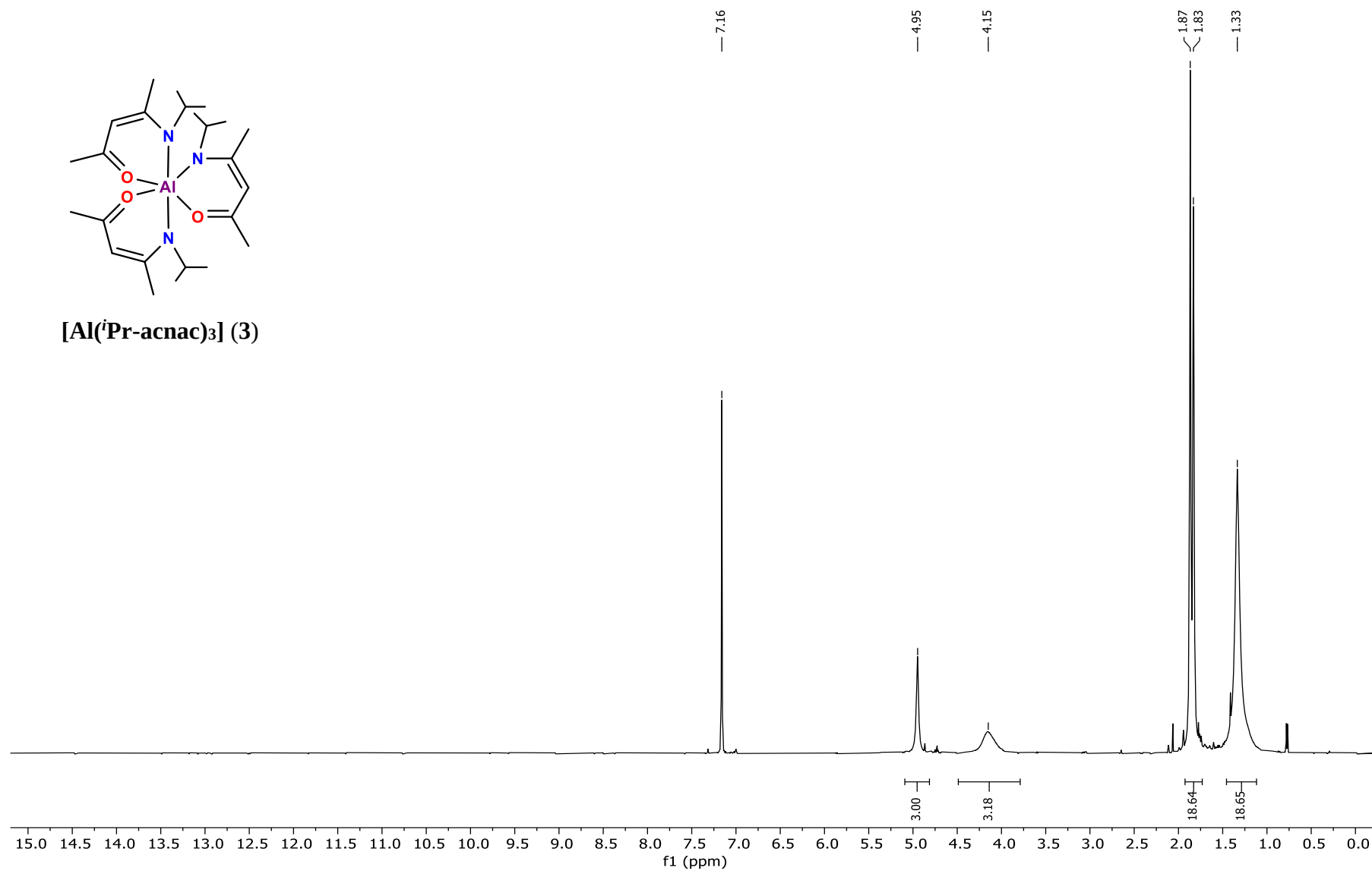
Appendix 28: COSY NMR of $[Al(Et-acnac)_3]$ (2).



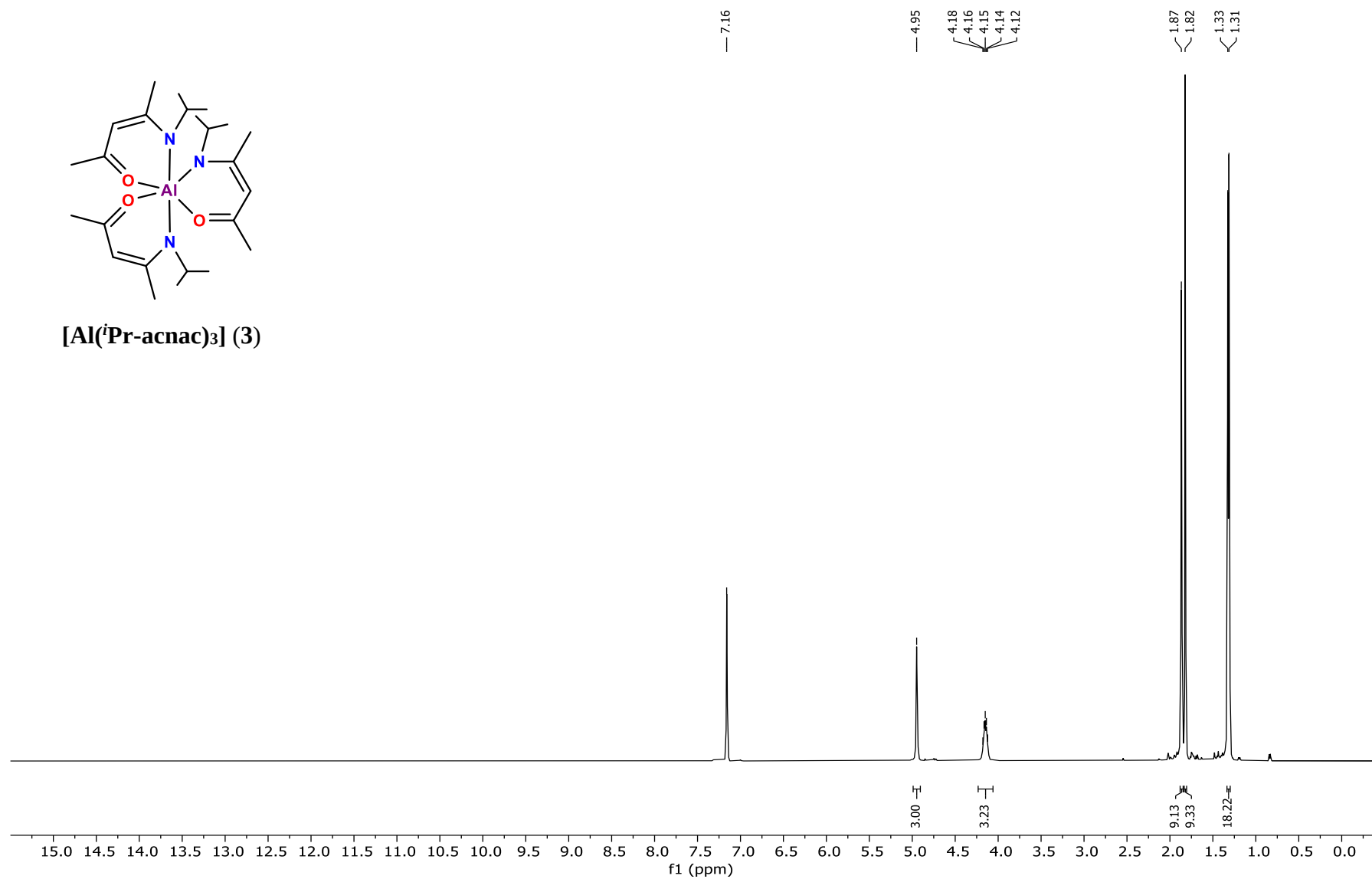
Appendix 29: HSQC NMR of [Al(Et-acnac)₃] (2).



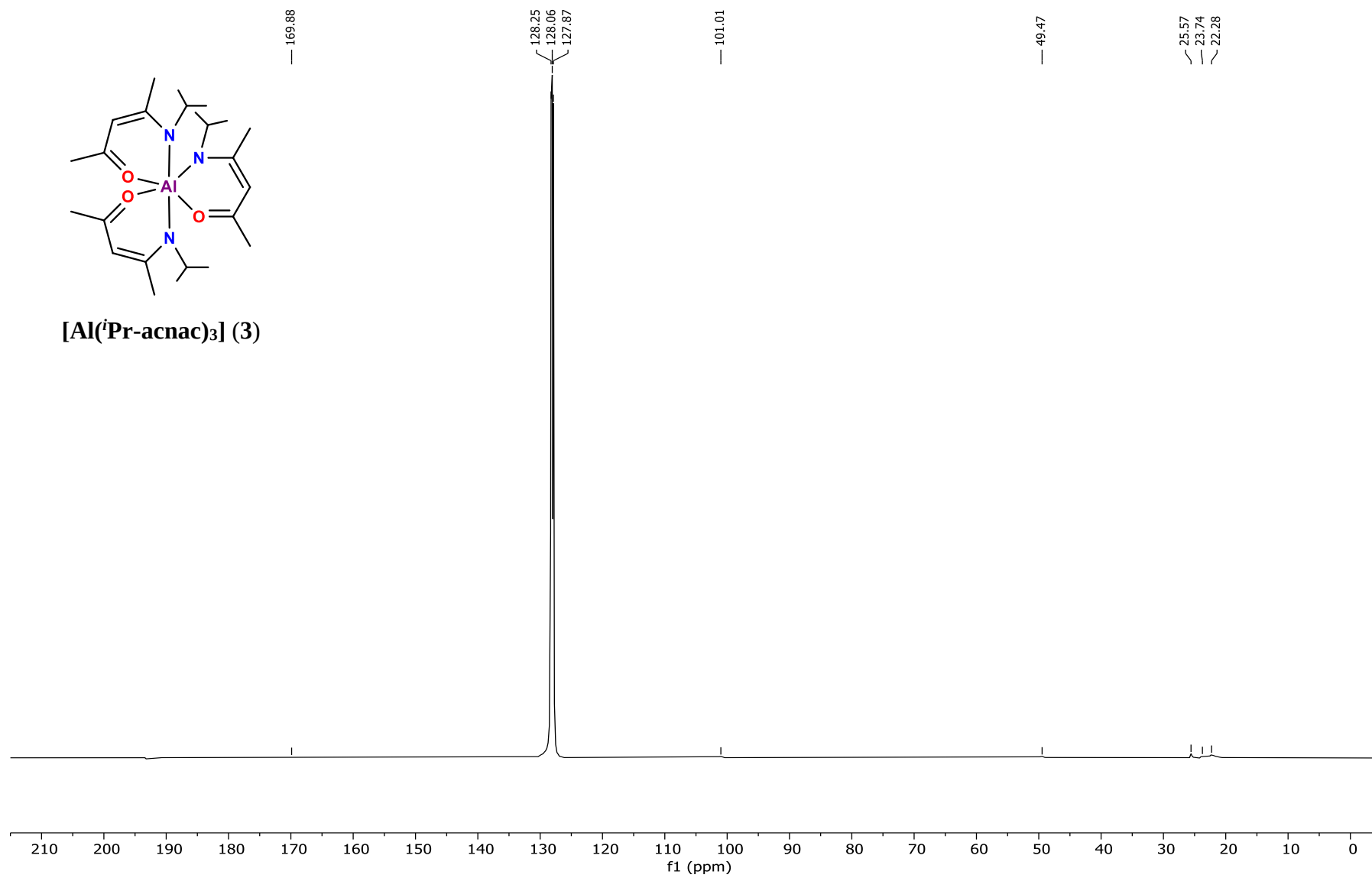
Appendix 30: HMBC NMR of $[Al(Et-acnac)_3]$ (2).



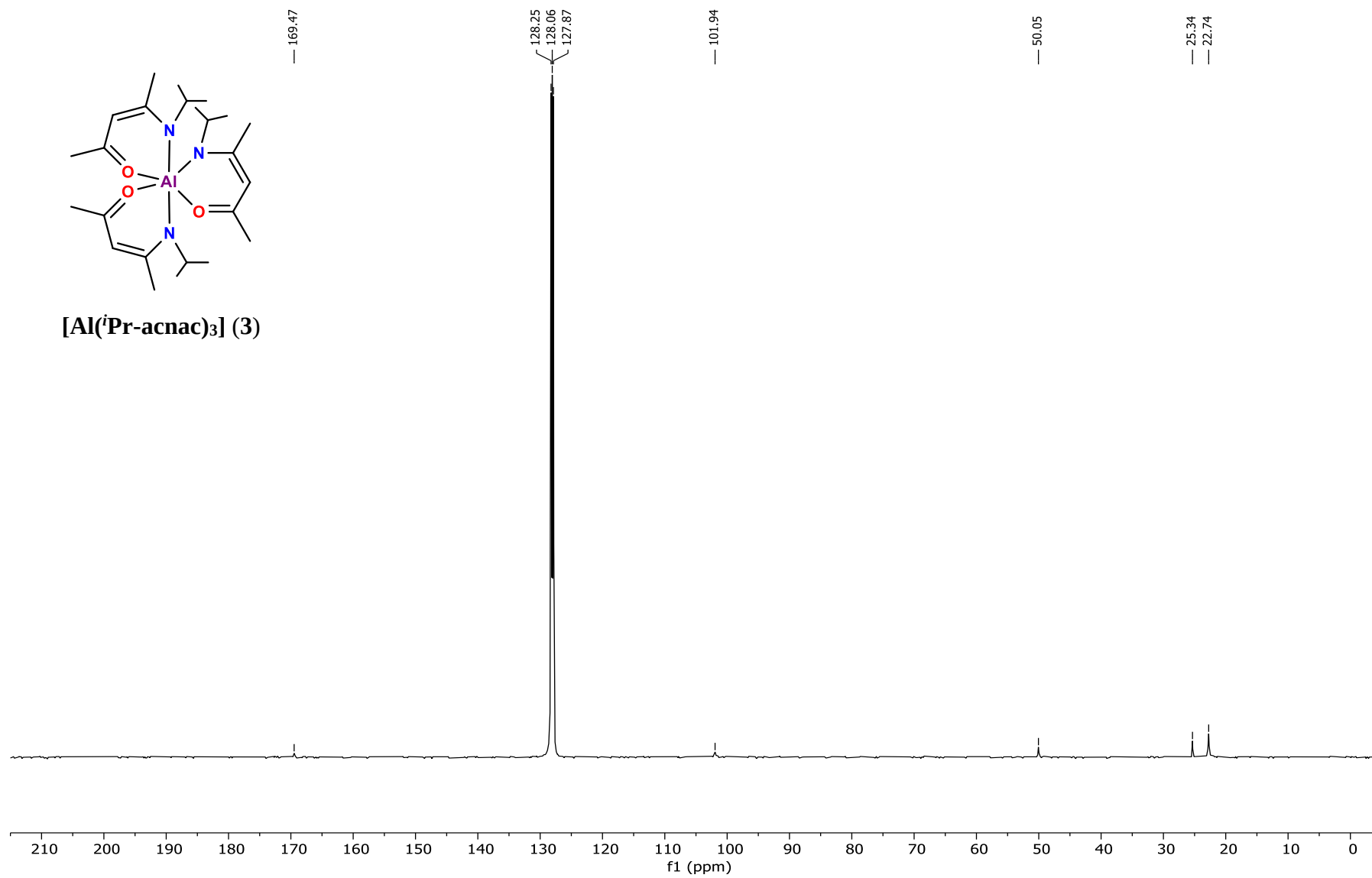
Appendix 31: ^1H NMR of $[Al(iPr-acnac)_3]$ (3) at 25 °C.



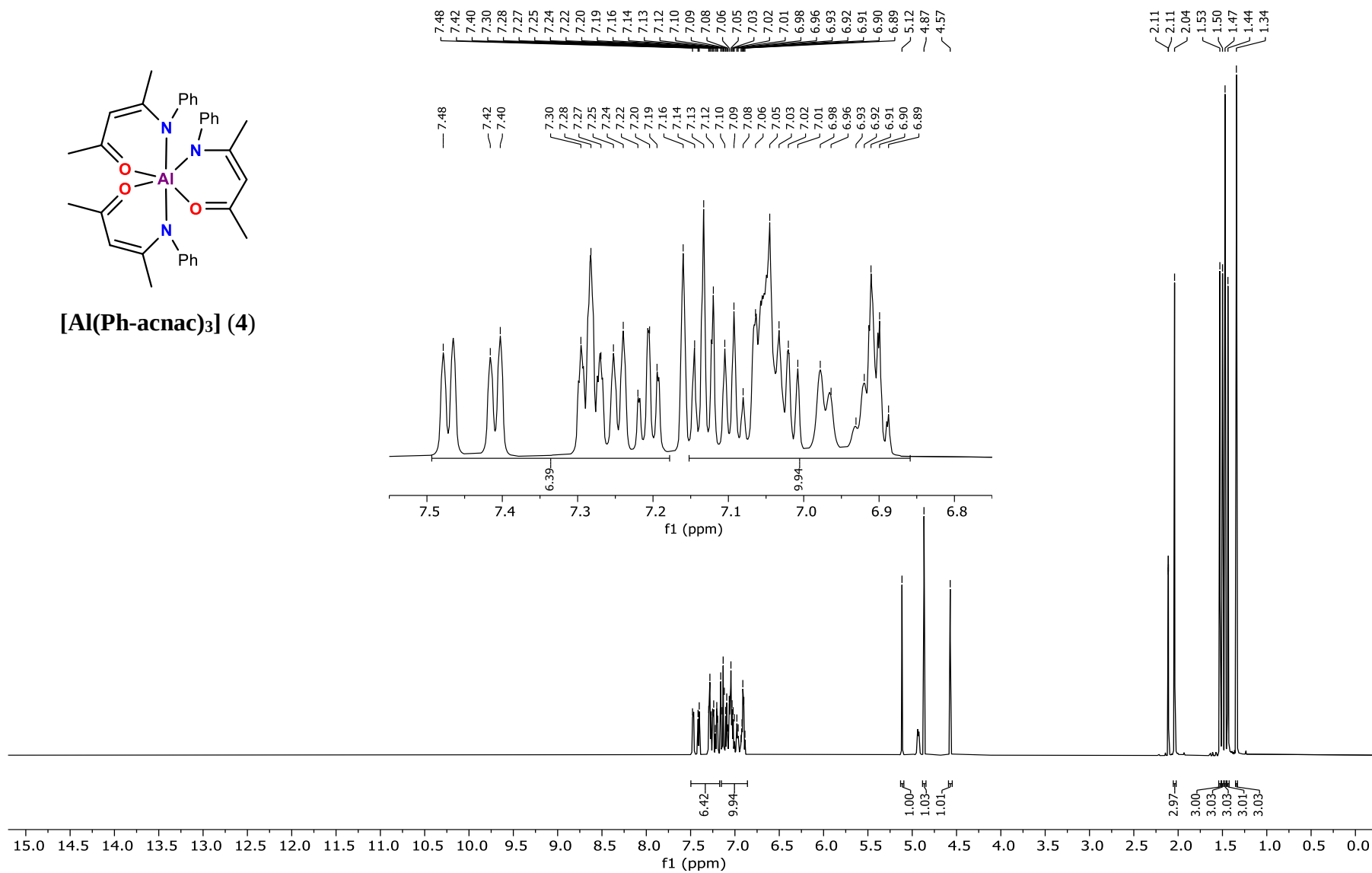
Appendix 32: ^1H NMR of $[Al(iPr-acnac)_3]$ (3) at 75 °C.

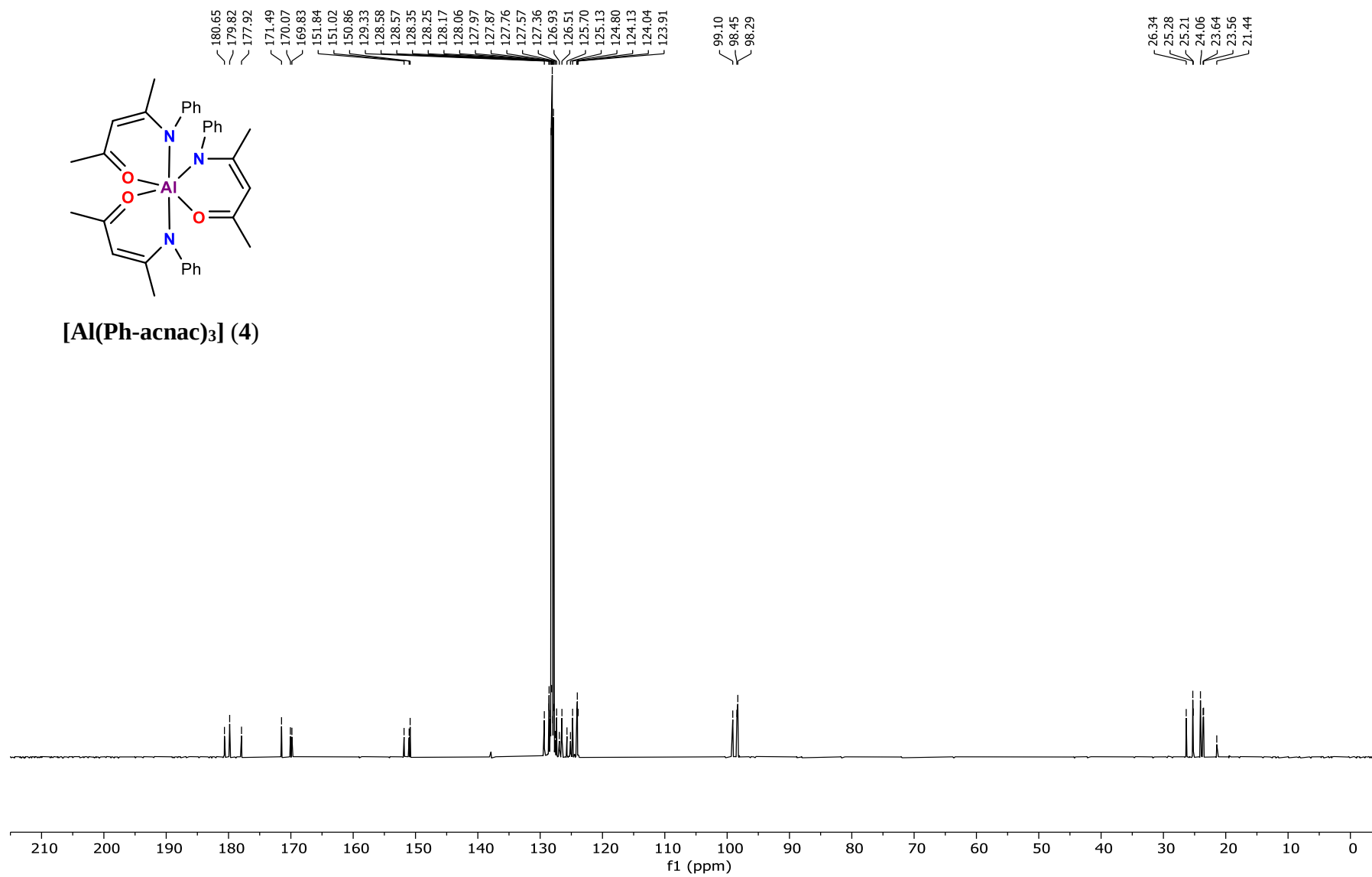


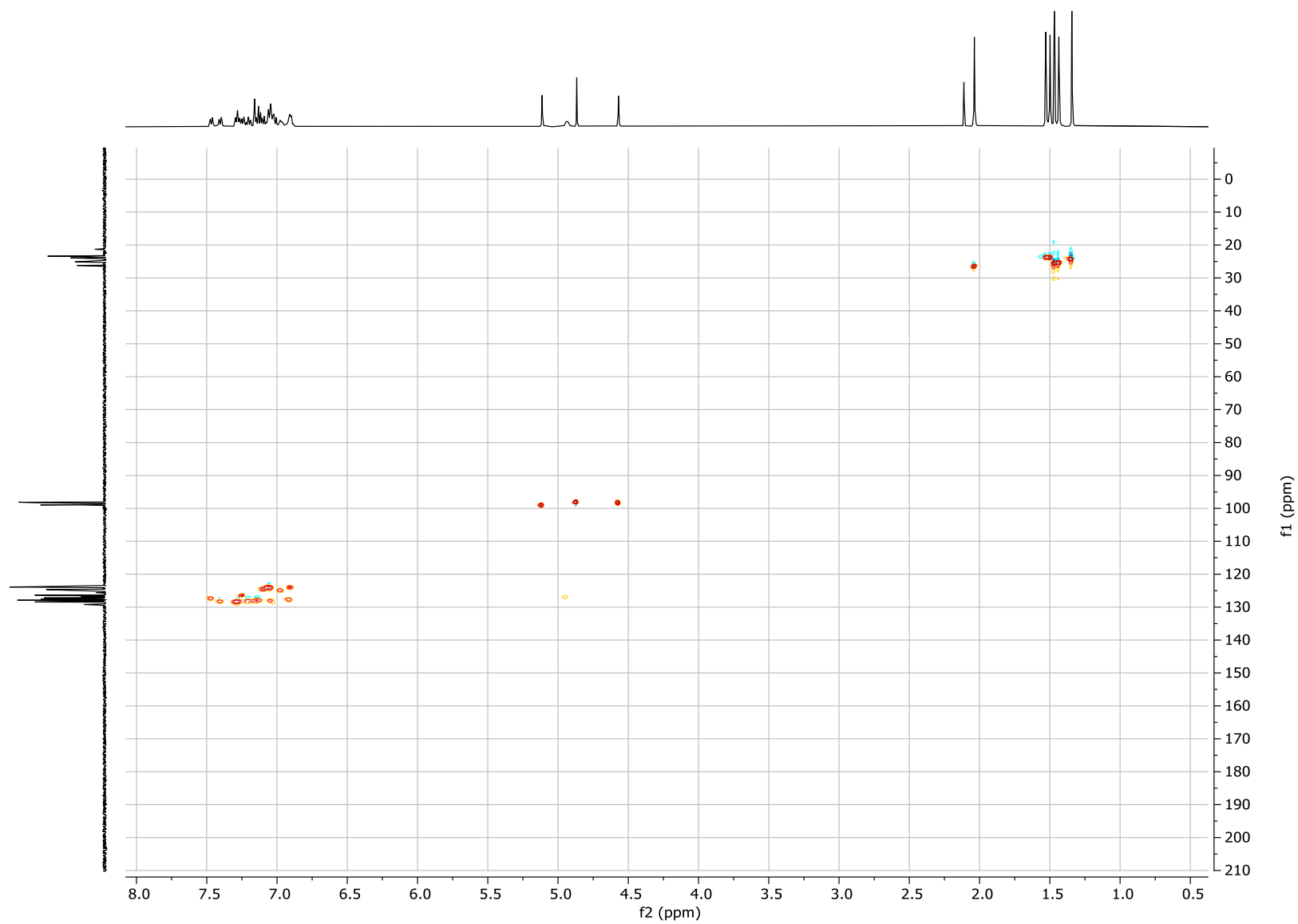
Appendix 33: ^{13}C NMR of $[Al(iPr-acnac)_3]$ (3) at 25 °C.



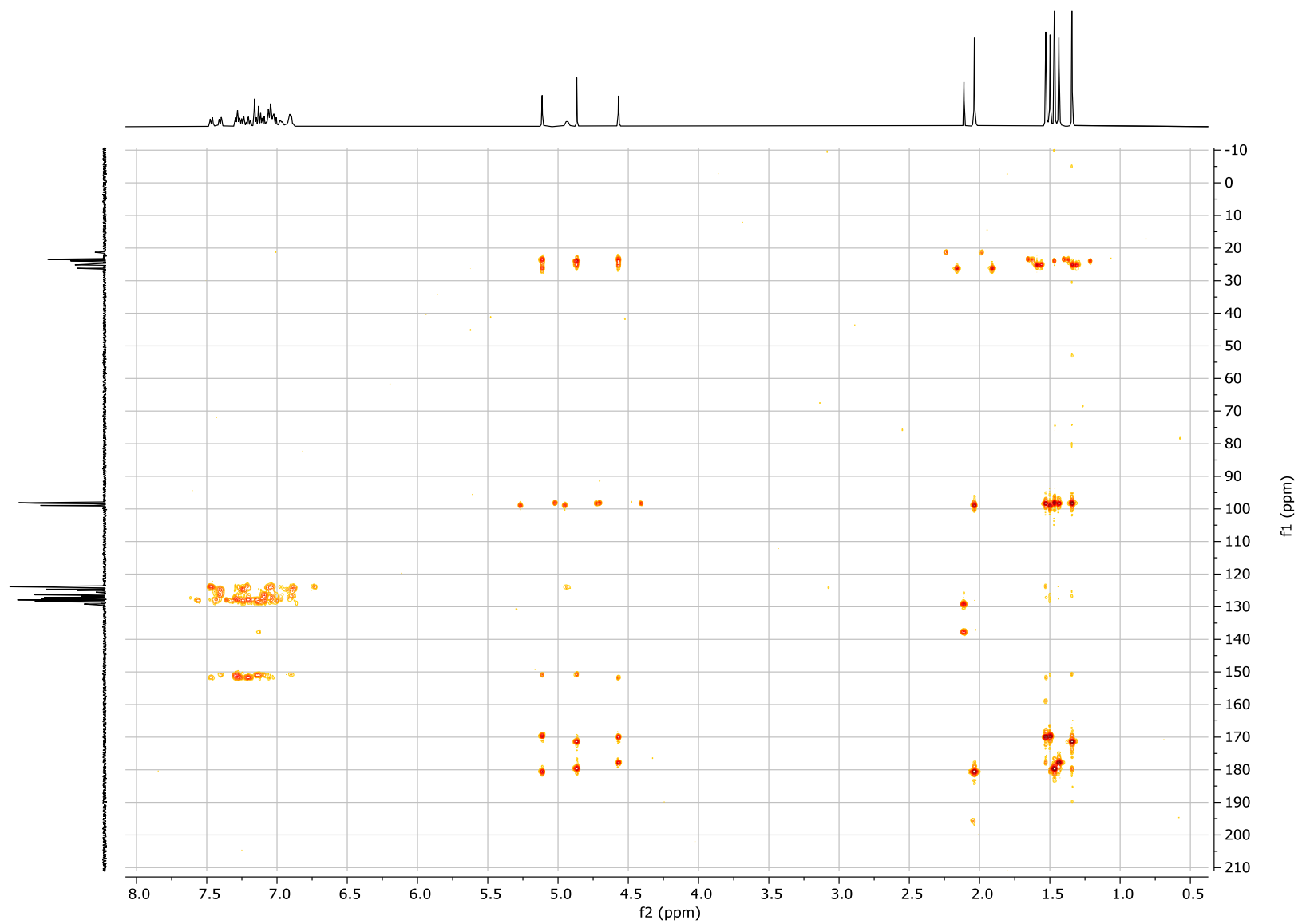
Appendix 34: ^{13}C NMR of $[\text{Al}(\text{iPr-acnac})_3]$ (3) at 75 °C.

Appendix 35: ¹H NMR of [Al(Ph-acnac)₃] (4).

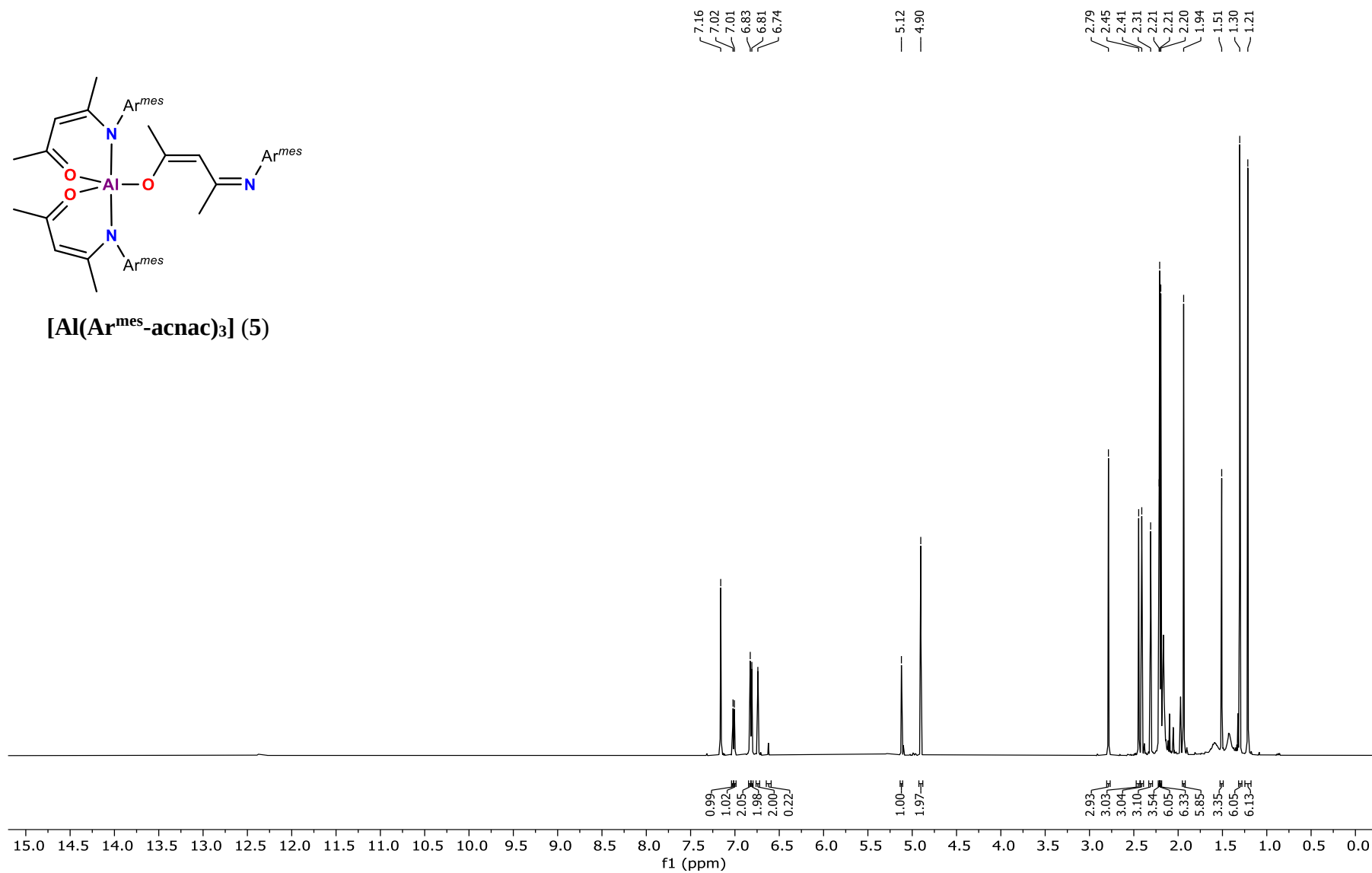
Appendix 36: ¹³C NMR of [Al(Ph-acnac)₃] (4).

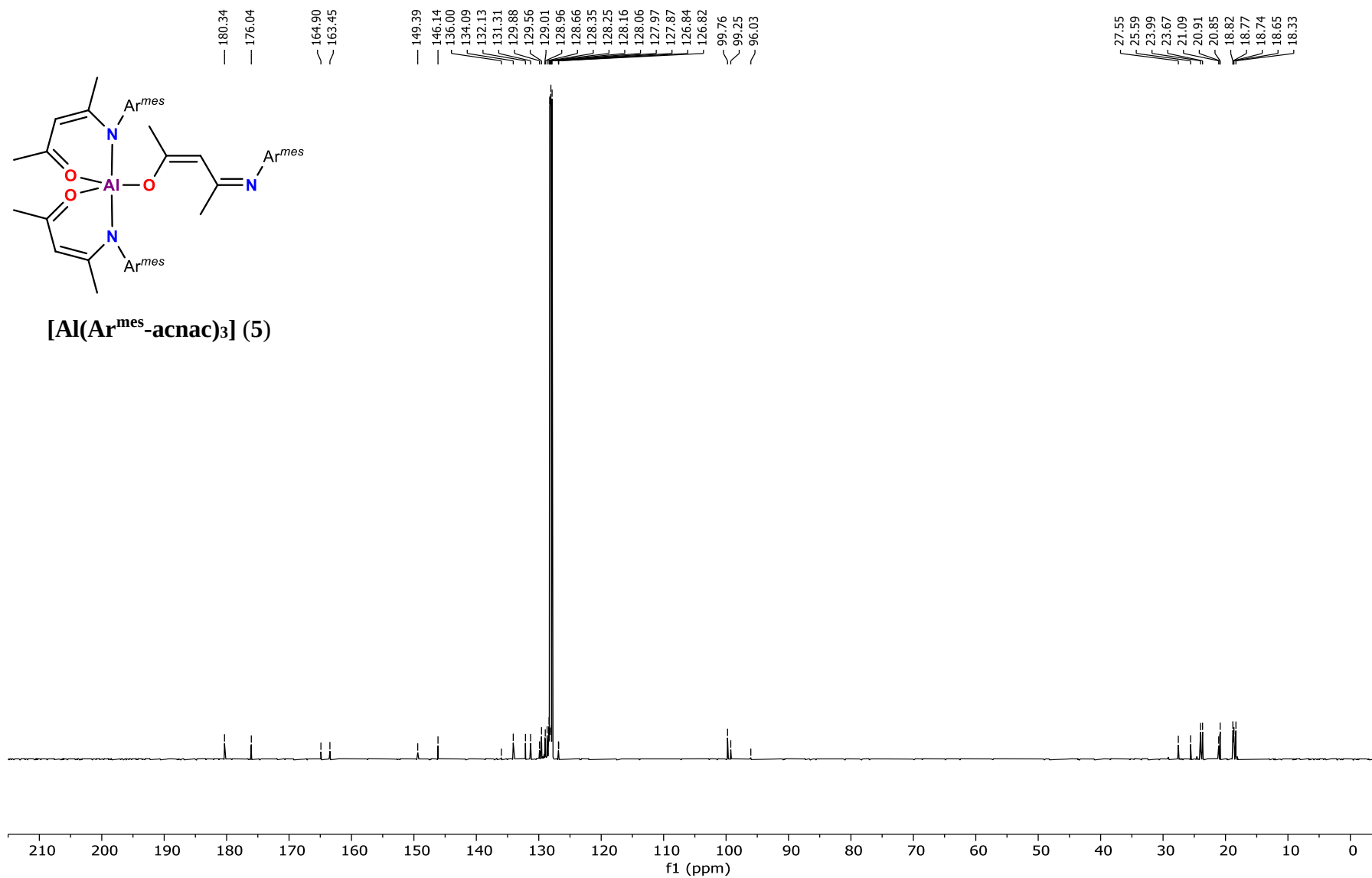


Appendix 38: HSQC NMR of $[Al(Ph-acnac)_3]$ (4).

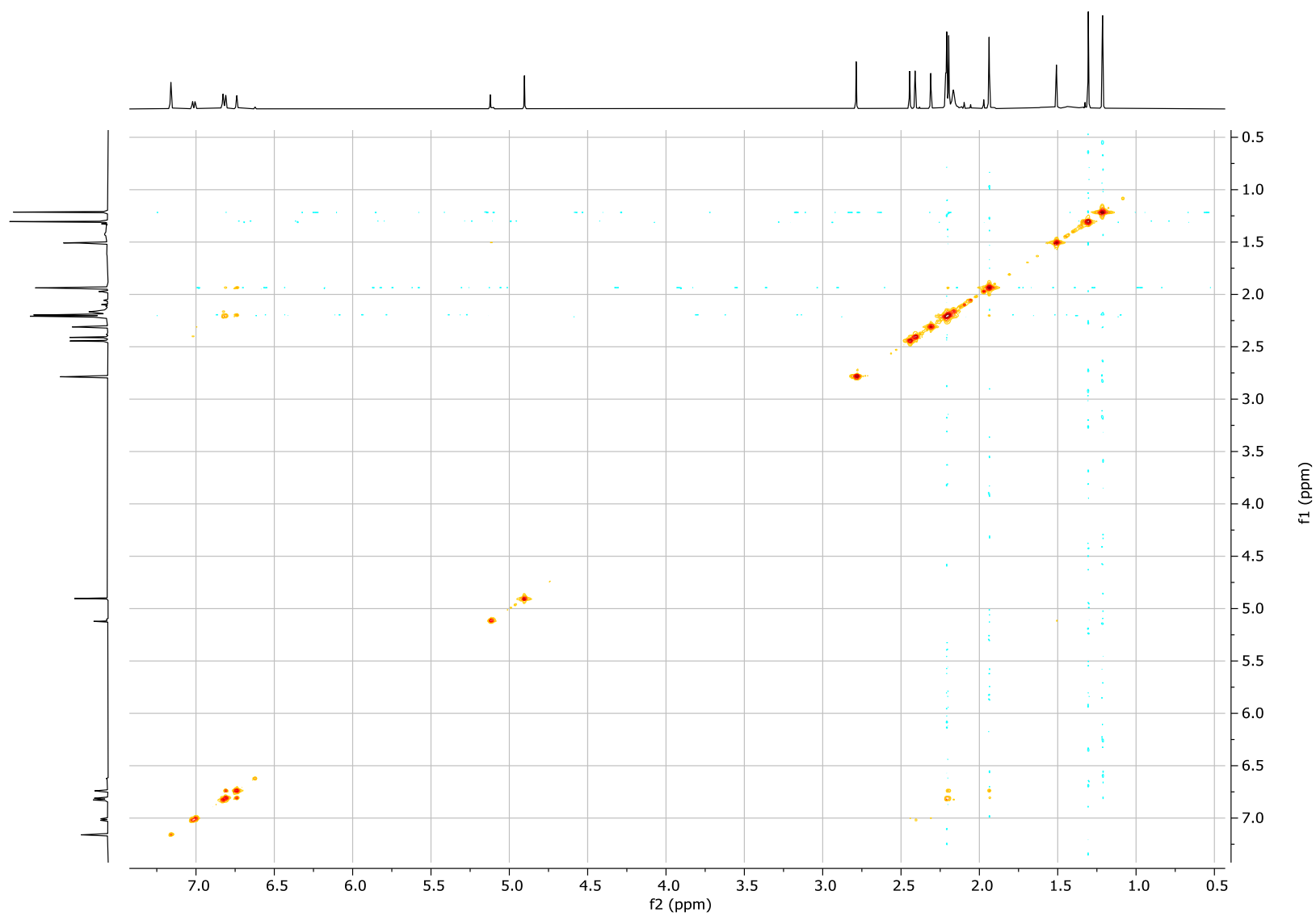


Appendix 39: HMBC NMR of $[Al(Ph-acnac)_3]$ (4).

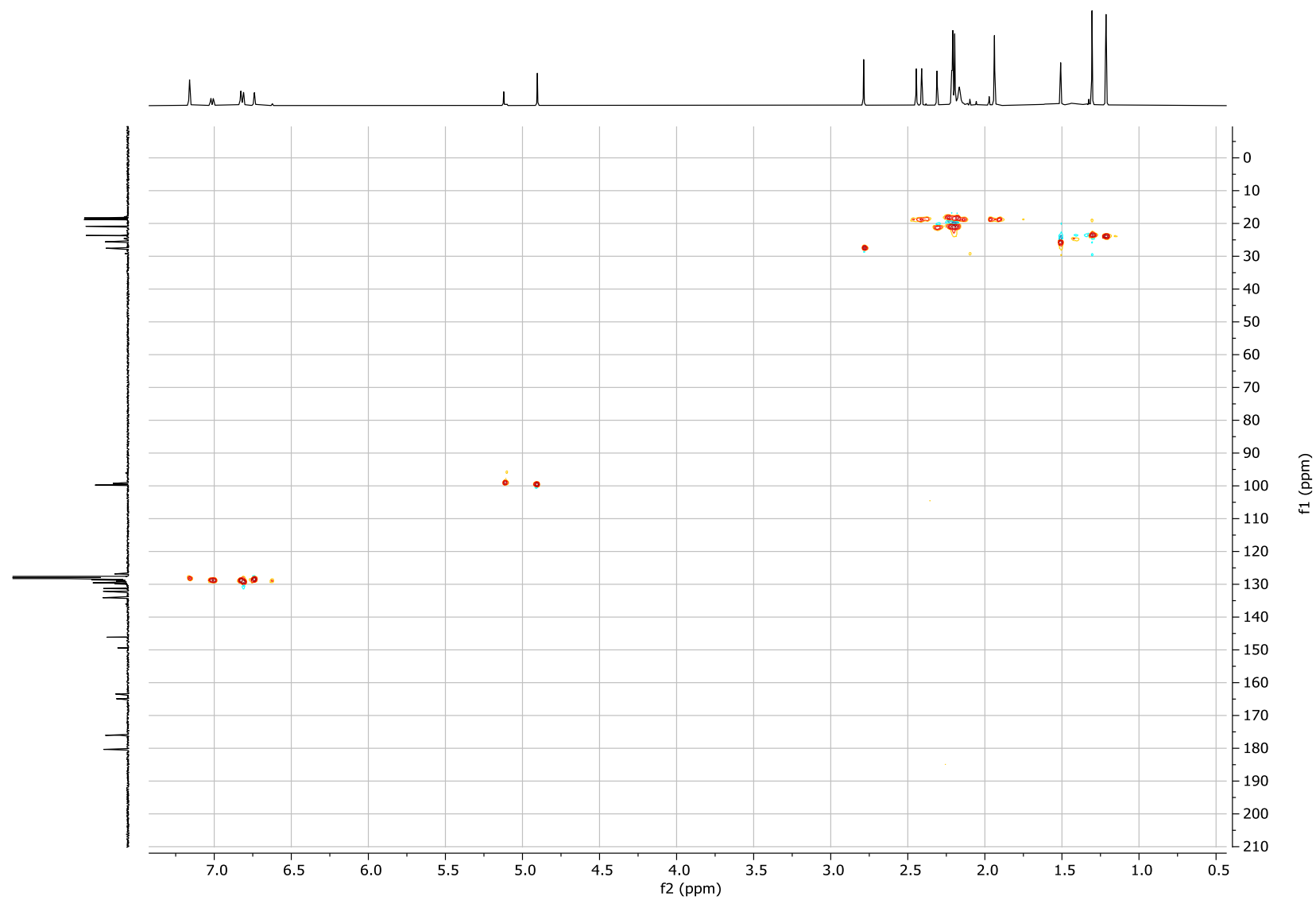
Appendix 40: ^1H NMR of $[Al(Ar^{mes}\text{-}acnac)_3]$ (5).



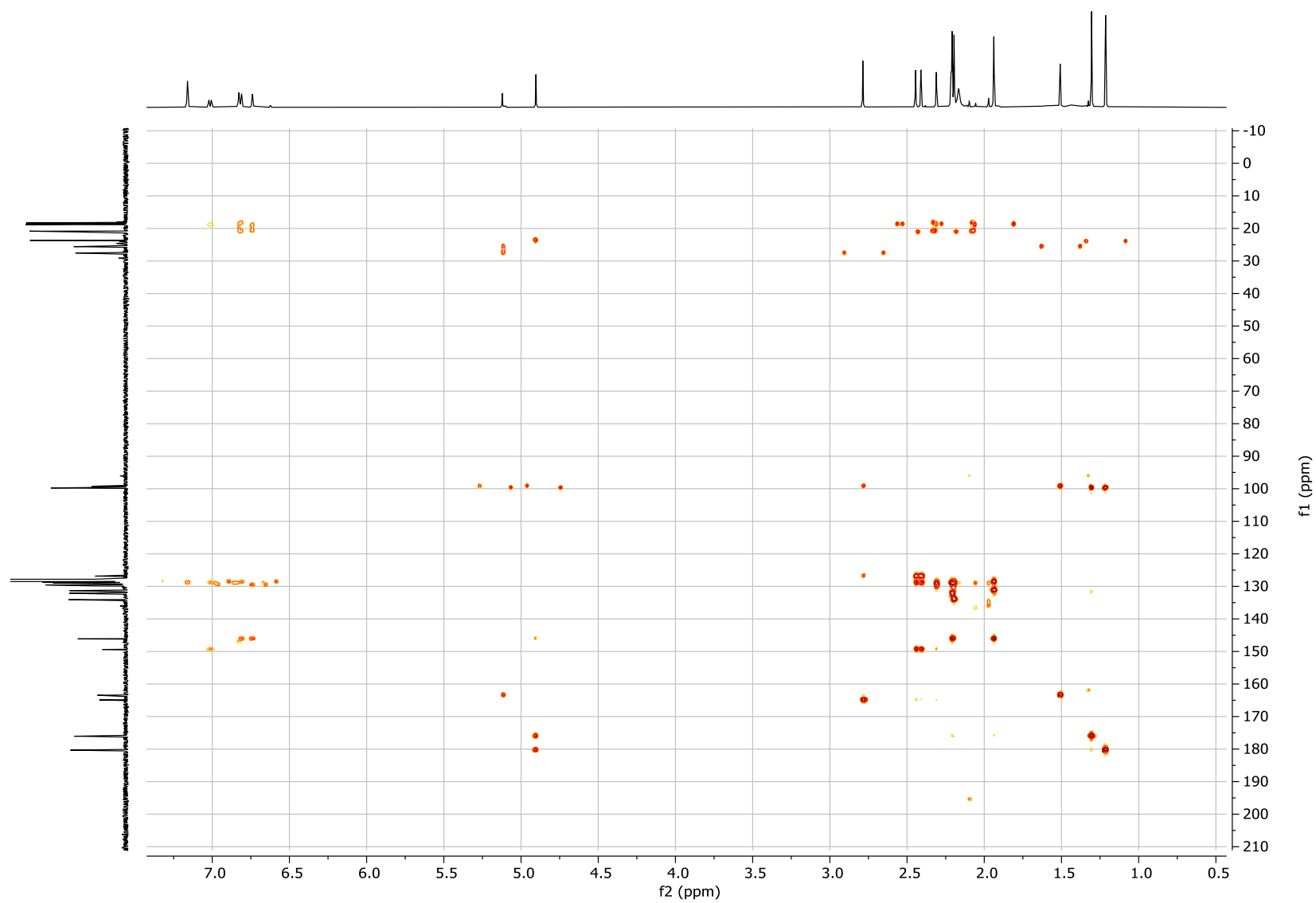
Appendix 41: ^{13}C NMR of $[Al(Ar^{mes}\text{-}acnac)_3]$ (5).



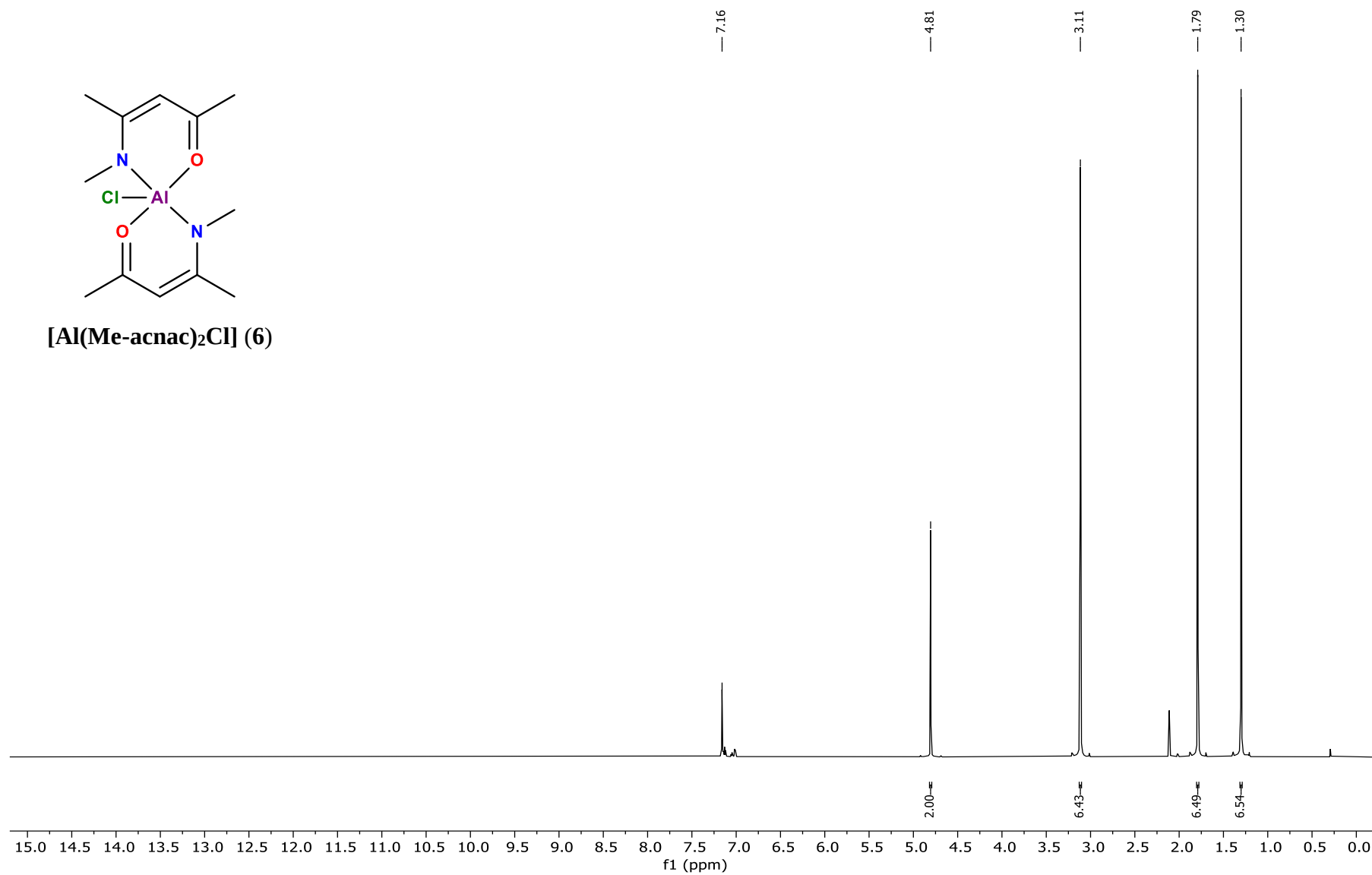
Appendix 42: COSY NMR of $[Al(Ar^{mes}\text{-}acnac)_3]$ (5).



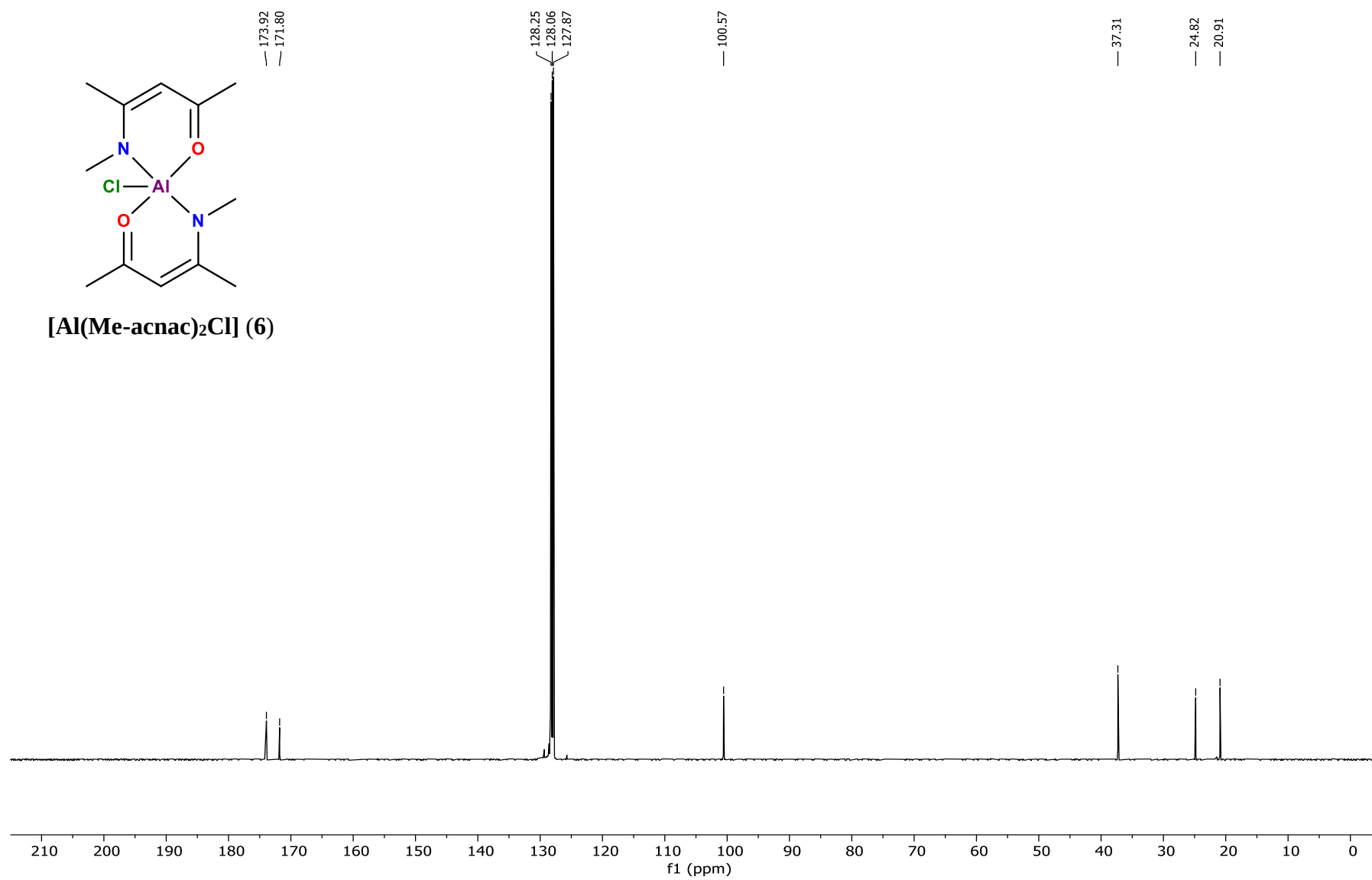
Appendix 43: HSQC NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).



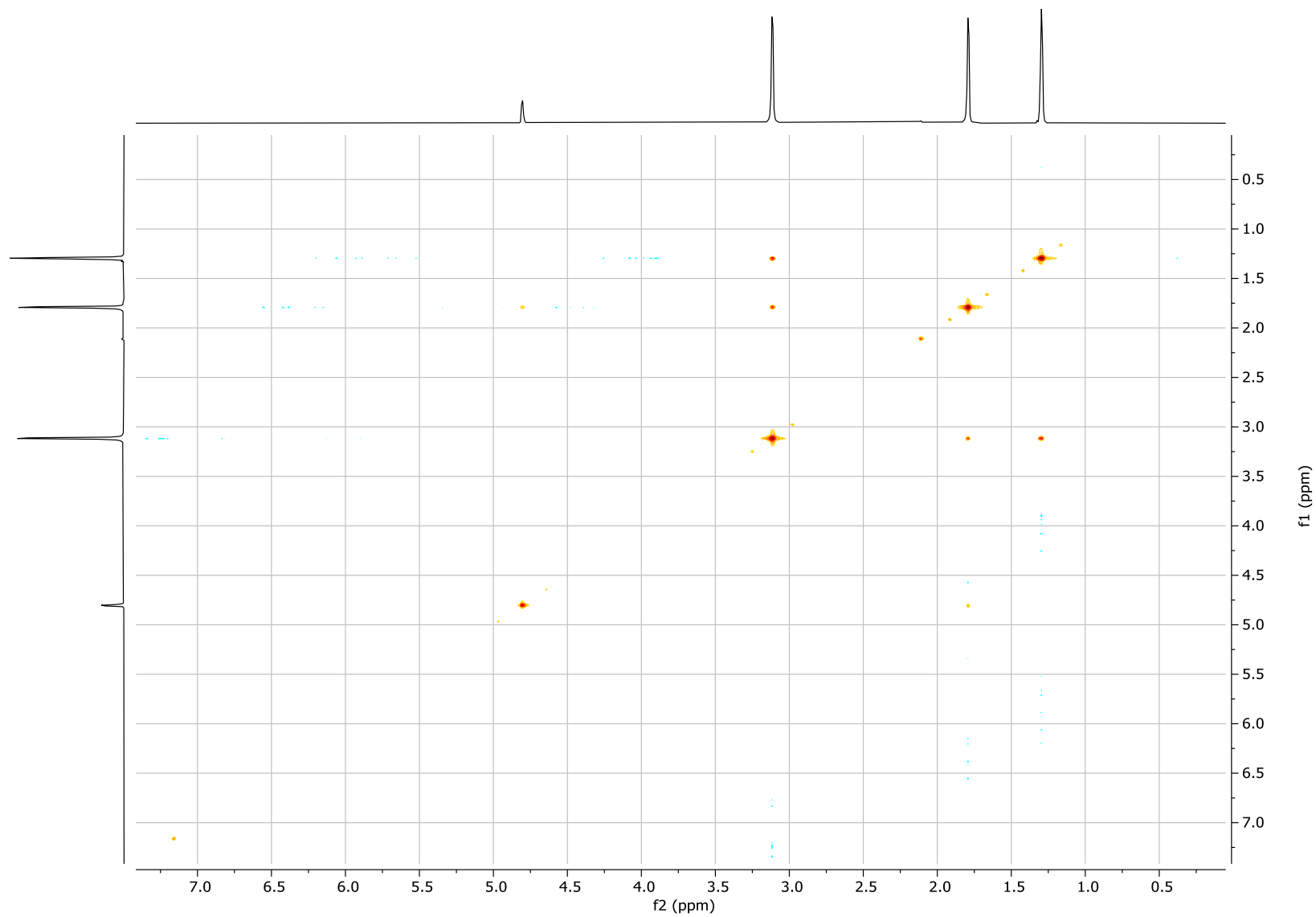
Appendix 44: HMBC NMR of $[Al(Ar^{mes}\text{-}acnac)_3]$ (5).



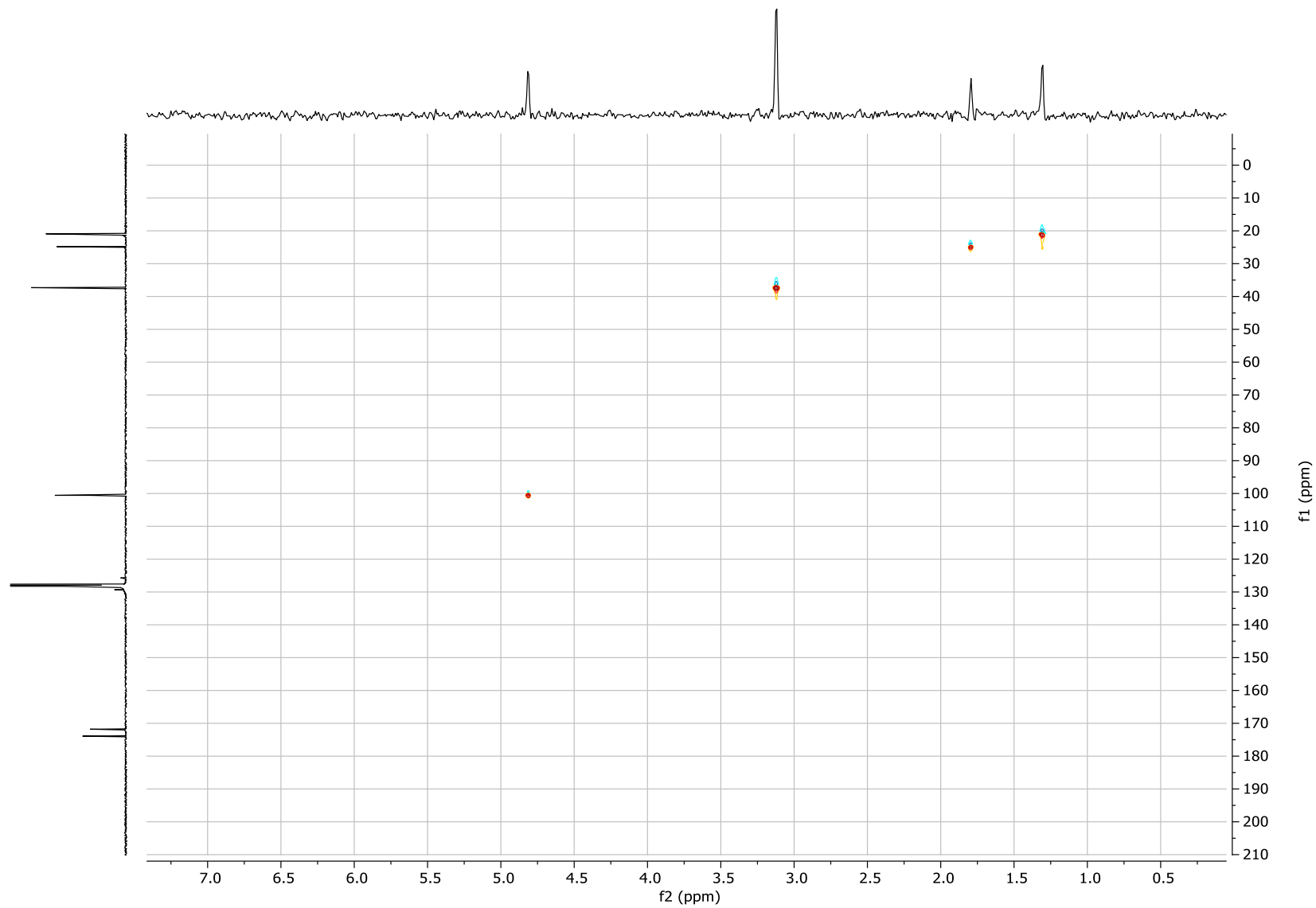
Appendix 45: ^1H NMR of $[Al(Me-acnac)_2Cl]$ (6).



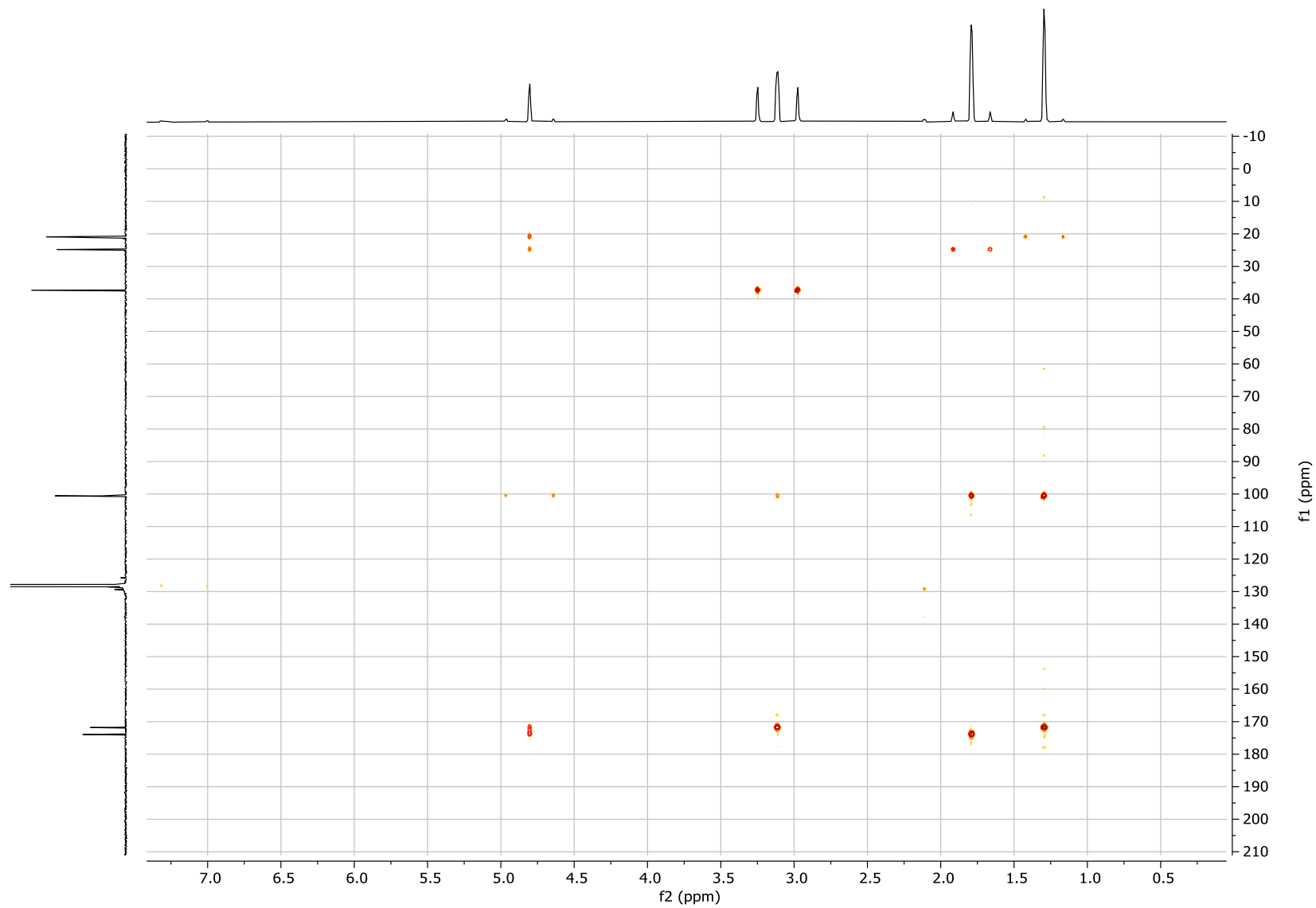
Appendix 46: ¹³C NMR of [Al(Me-acnac)₂Cl] (6).



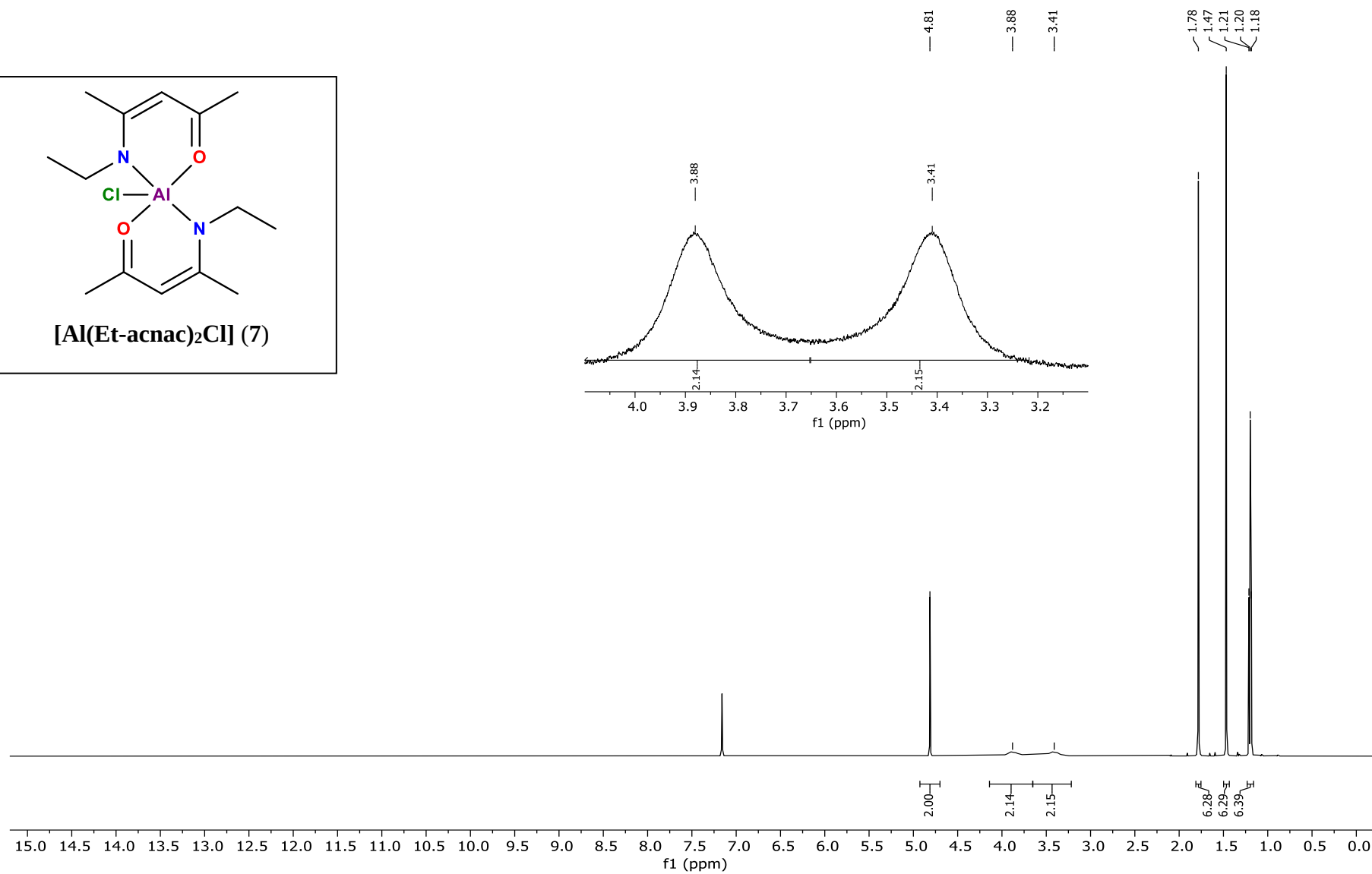
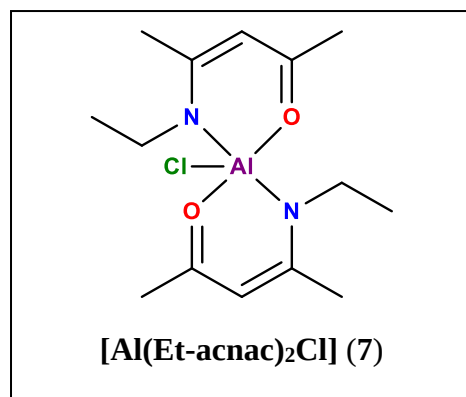
Appendix 47: COSY NMR of $[Al(Me-acnac)_2Cl]$ (6).



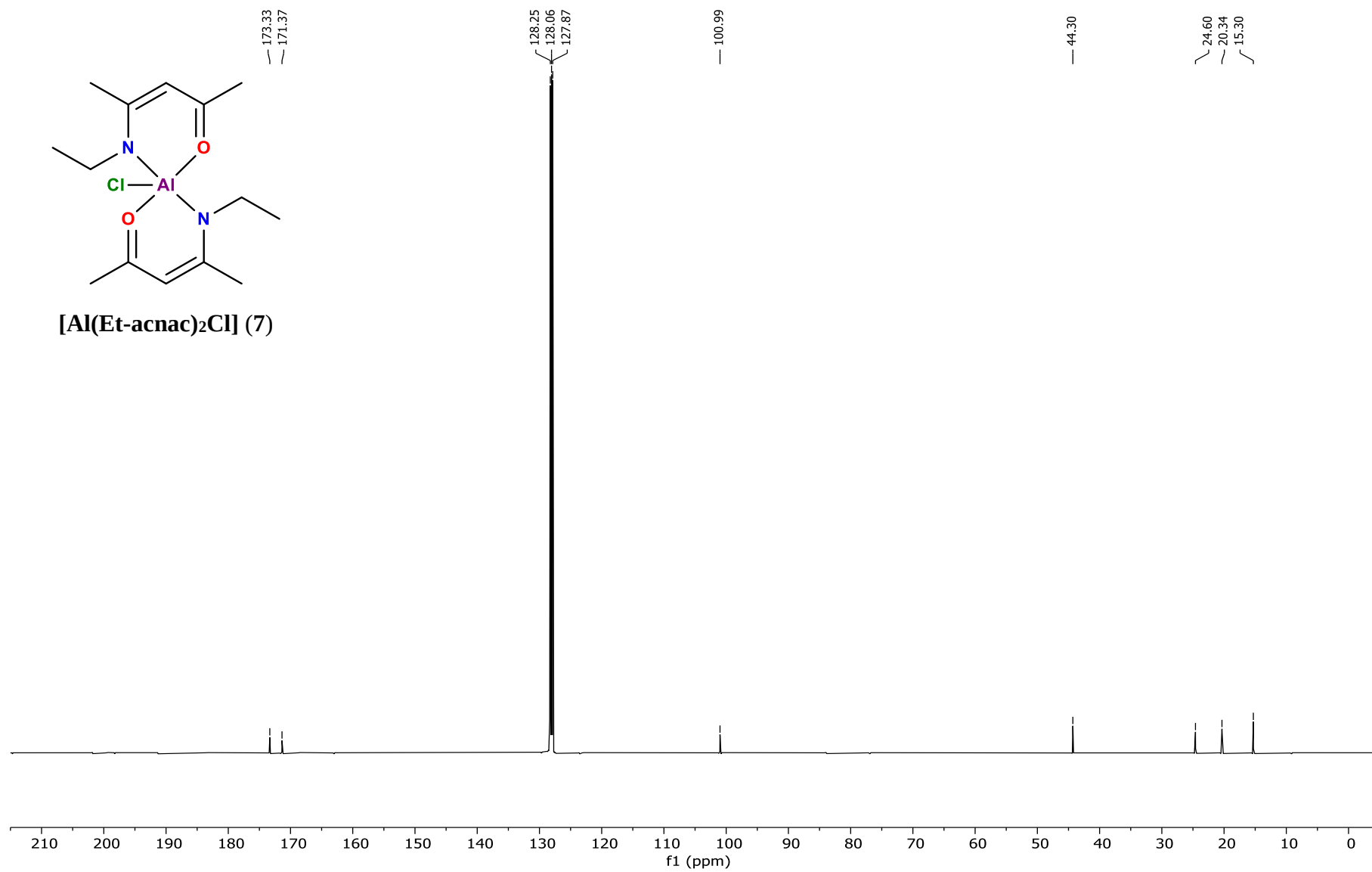
Appendix 48: HSQC NMR of $[Al(Me-acnac)_2Cl]$ (6).



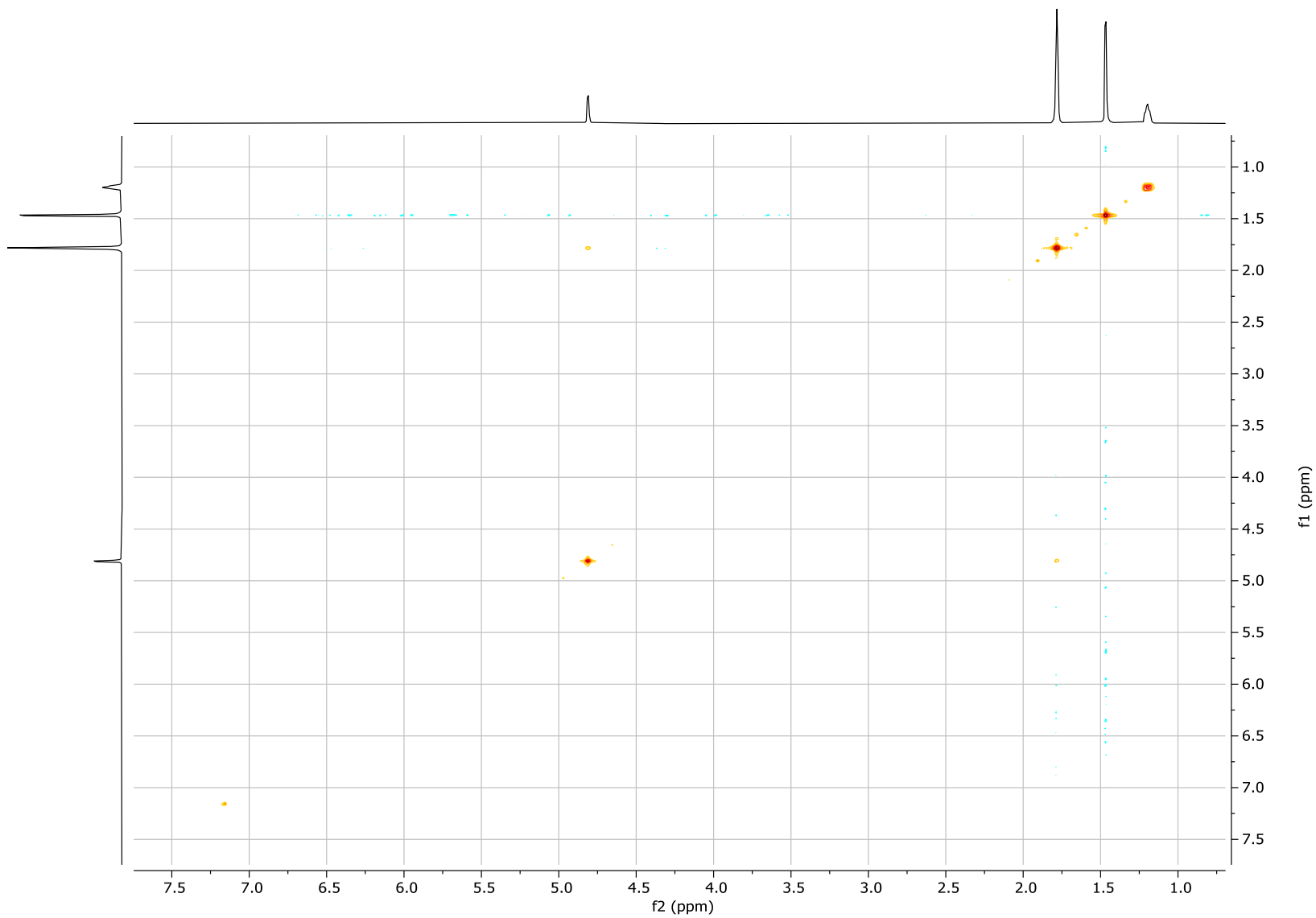
Appendix 49: HMBC NMR of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).



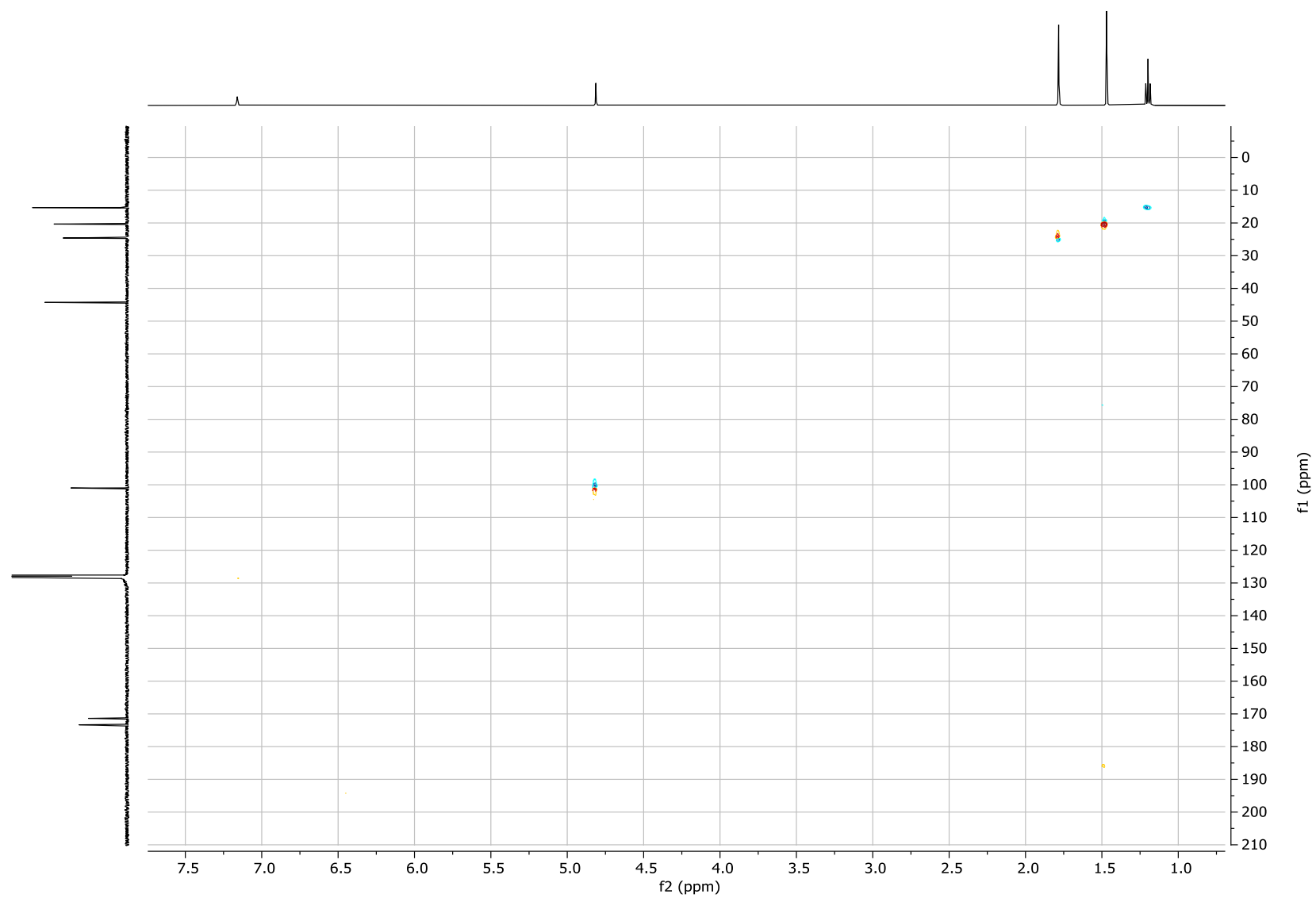
Appendix 50: ¹H NMR of [Al(Et-acnac)₂Cl] (7).



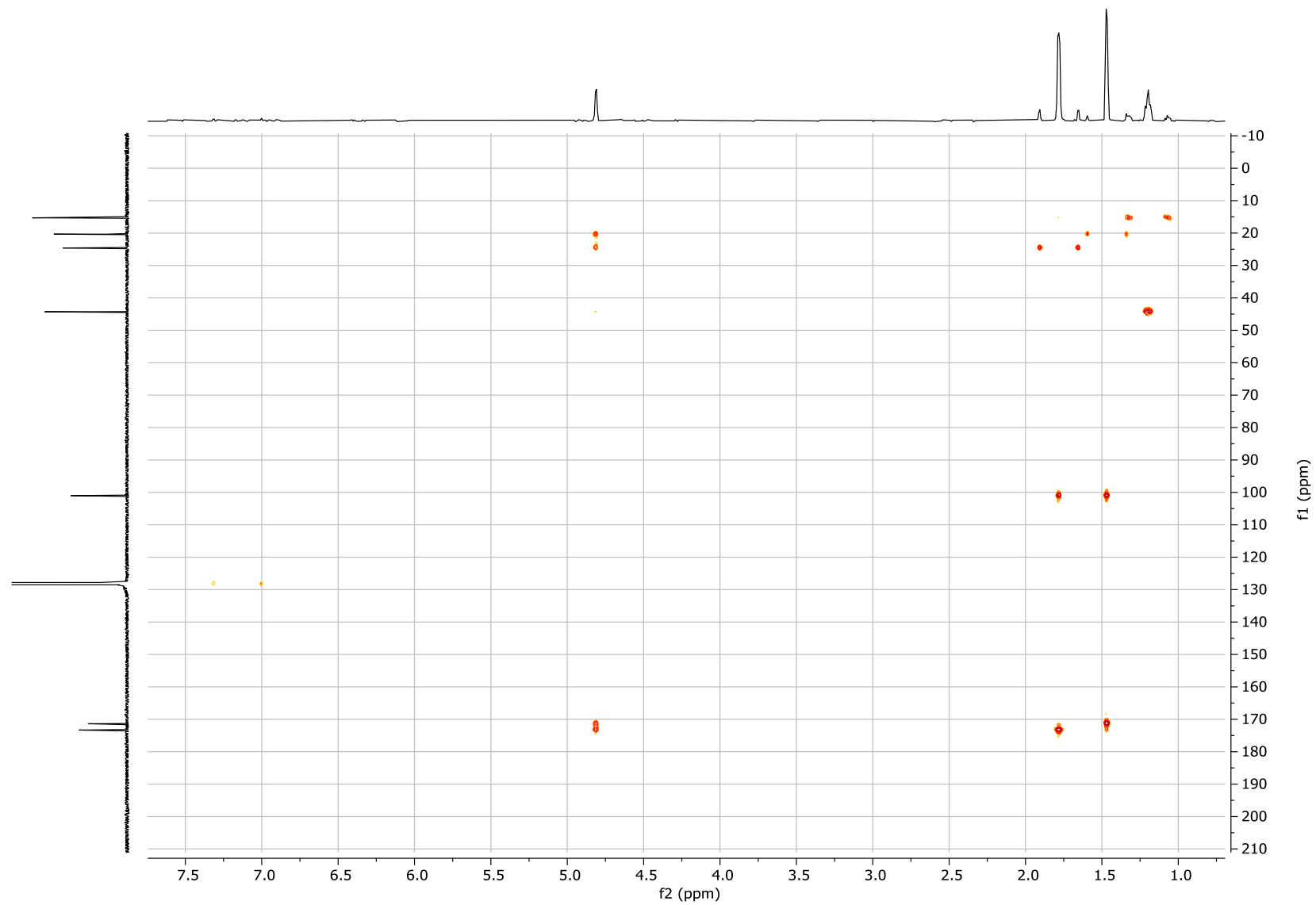
Appendix 51: ^{13}C NMR of $[Al(Et-acnac)_2Cl]$ (7).



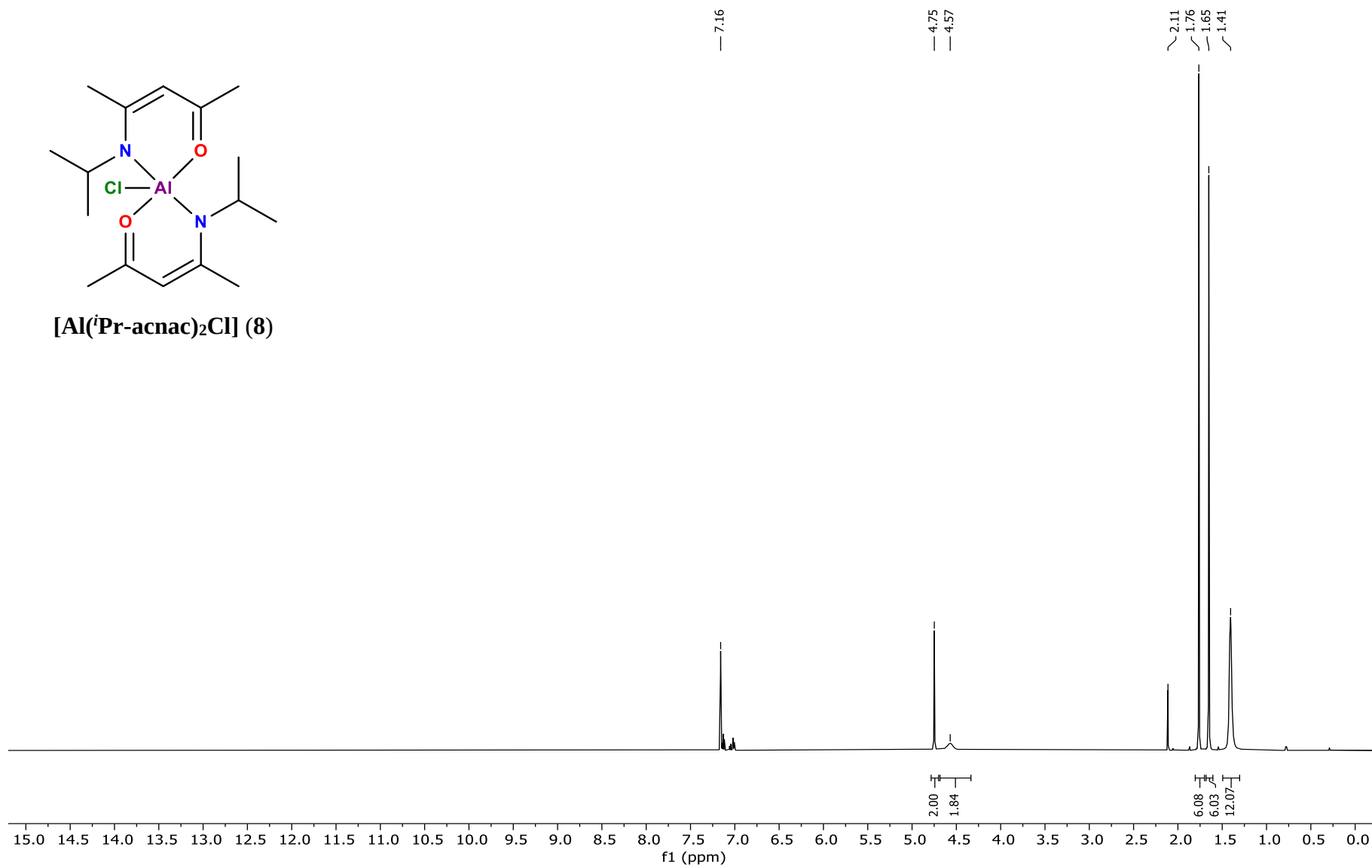
Appendix 52: COSY NMR of $[Al(Et-acnac)_2Cl]$ (7).



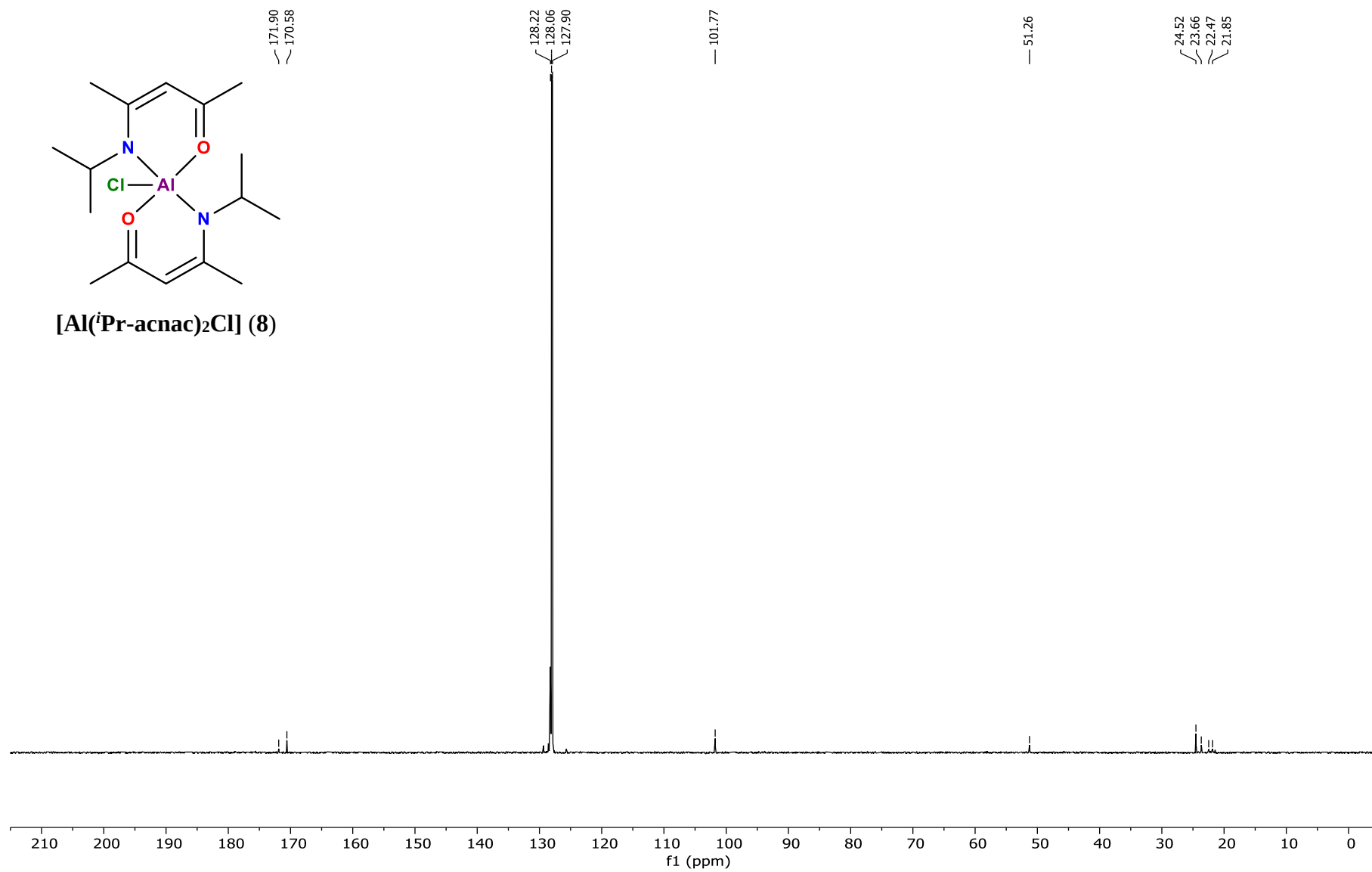
Appendix 53: HSQC NMR of $[Al(Et-acnac)_2Cl]$ (7).



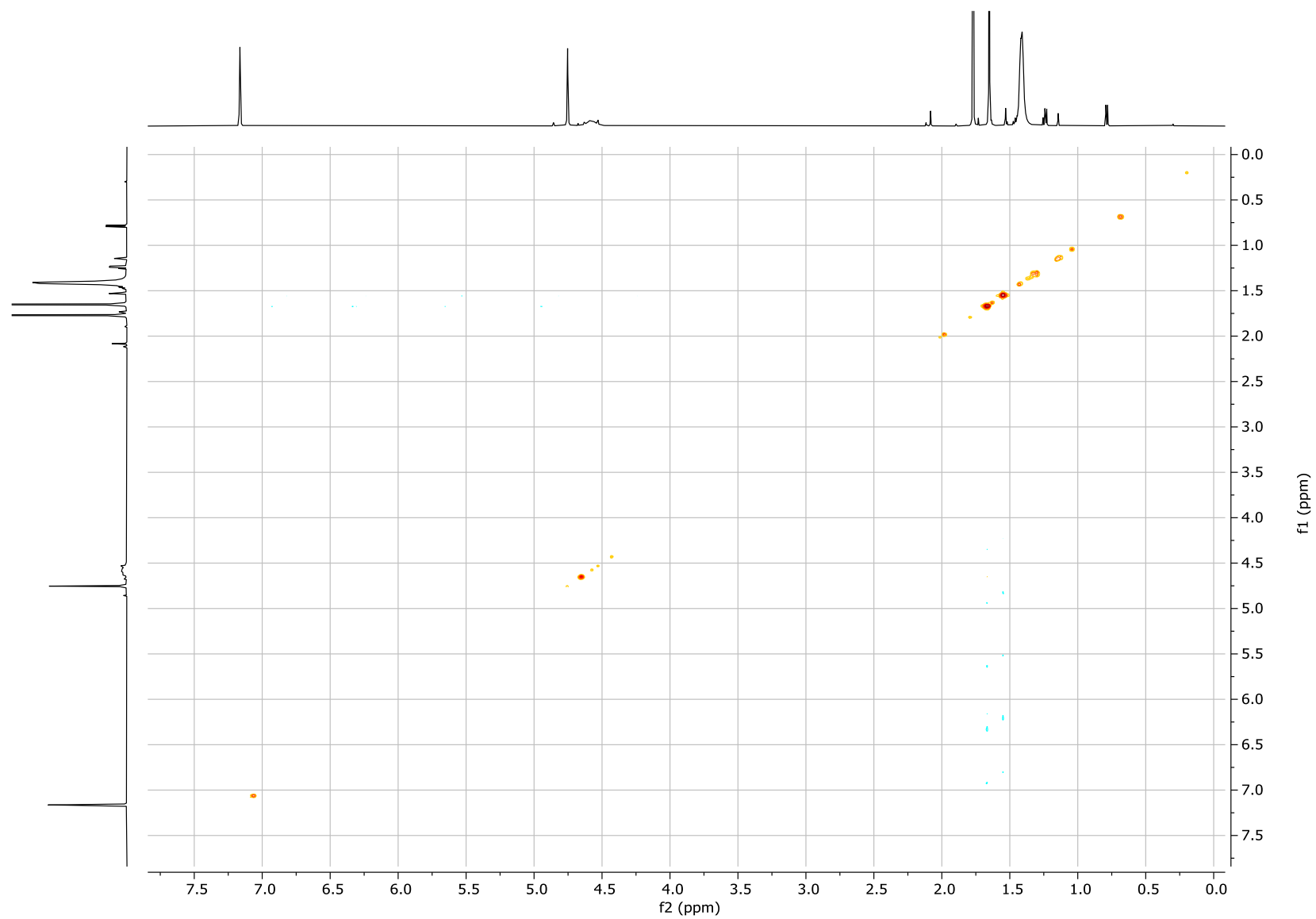
Appendix 54: HMBC NMR of $[Al(Et-acnac)_2Cl]$ (7).



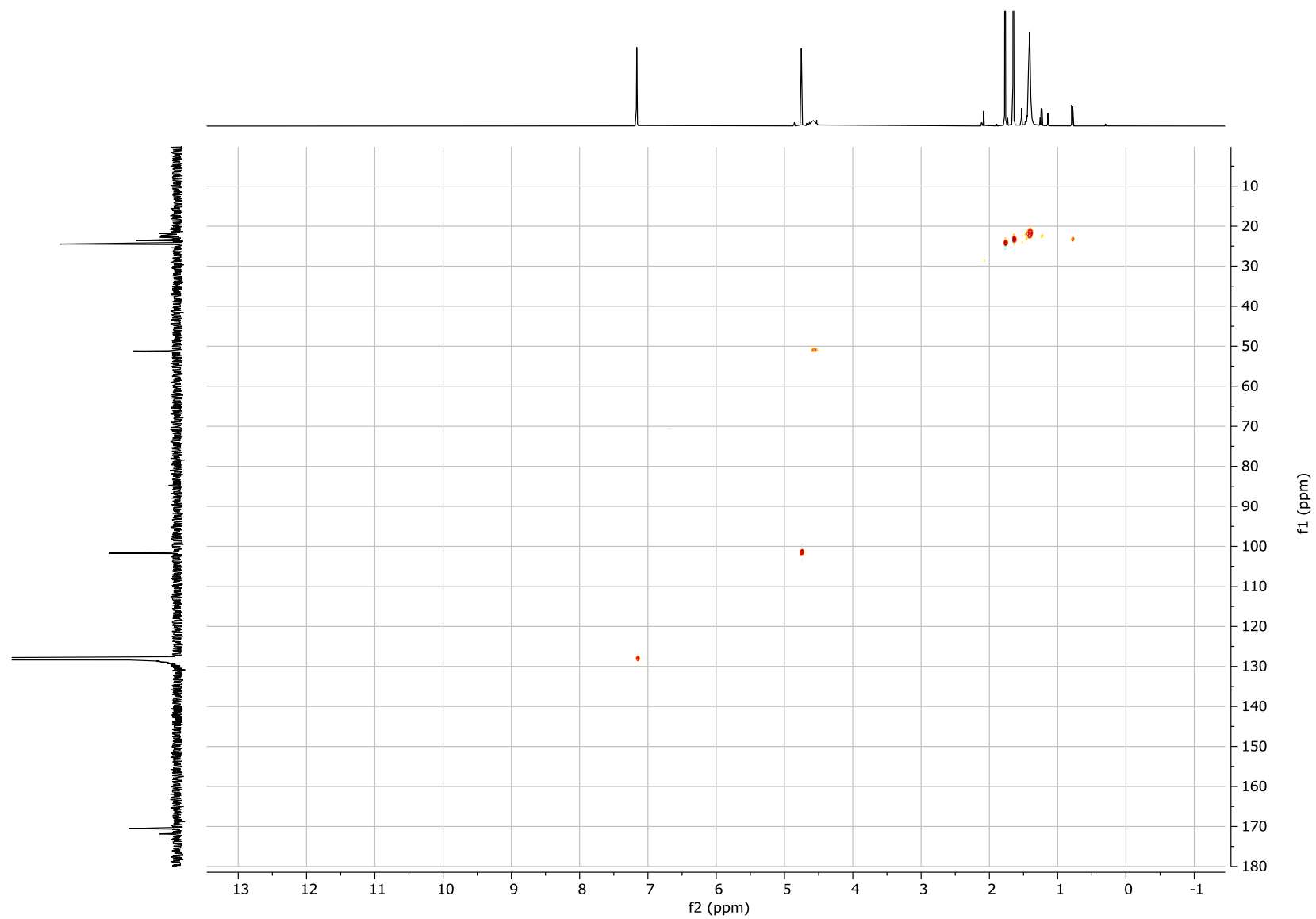
Appendix 55: ^1H NMR of $[\text{Al}(\textit{i}\text{Pr-acnac})_2\text{Cl}]$ (8).



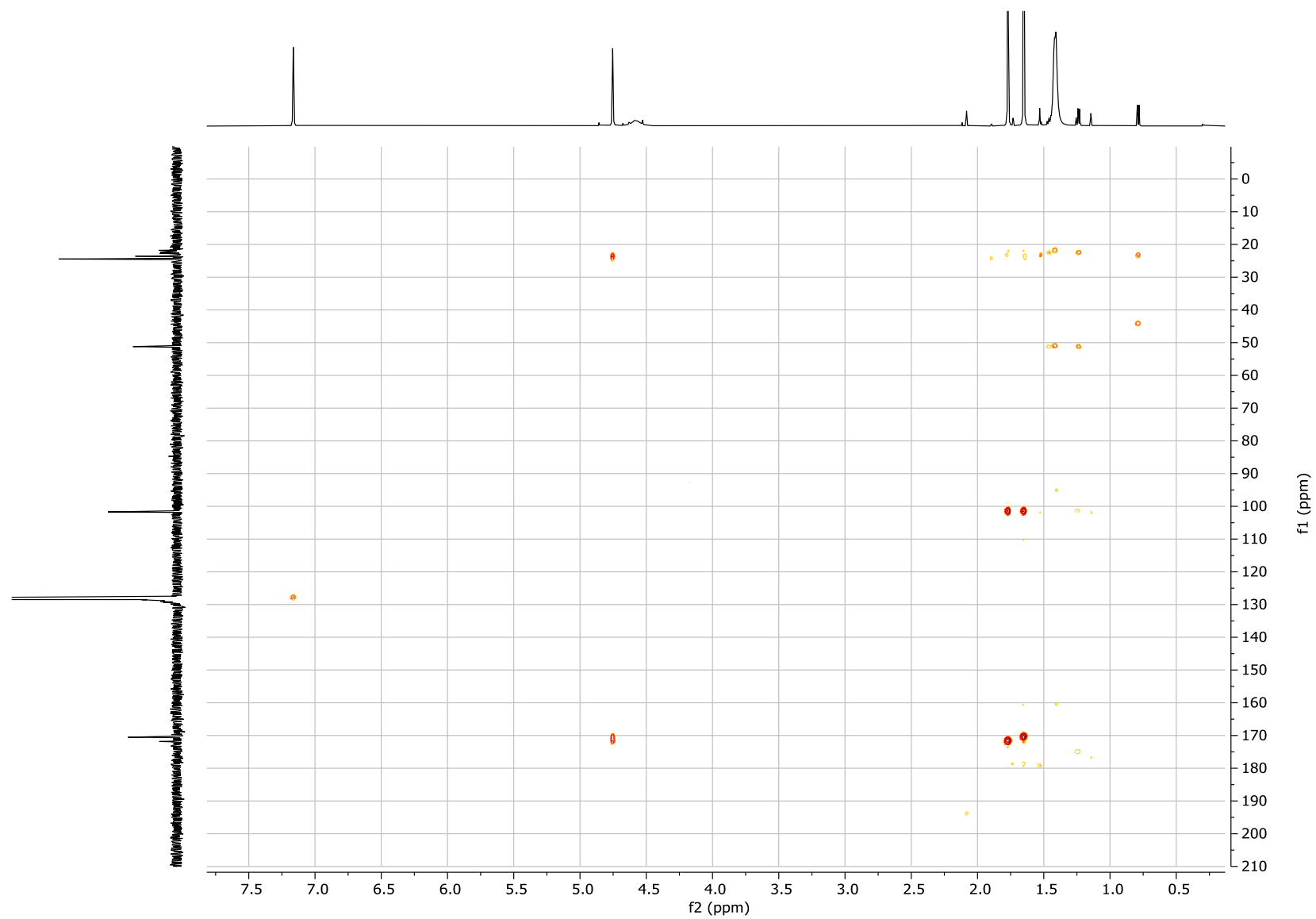
Appendix 56: ^{13}C NMR of $[Al(iPr-acnac)_2Cl]$ (8).



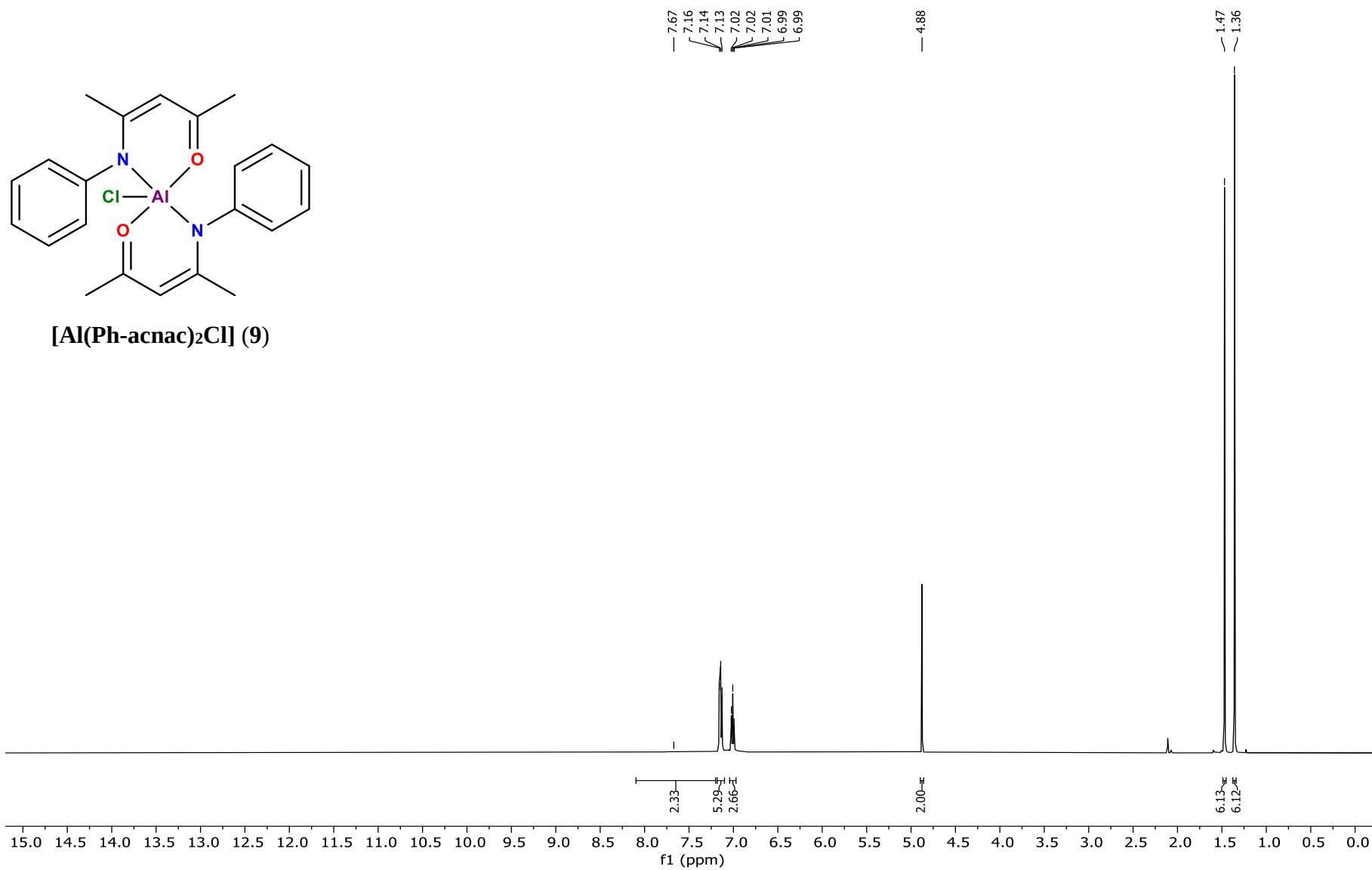
Appendix 57: COSY NMR of $[Al(iPr-acnac)_2Cl]$ (8).



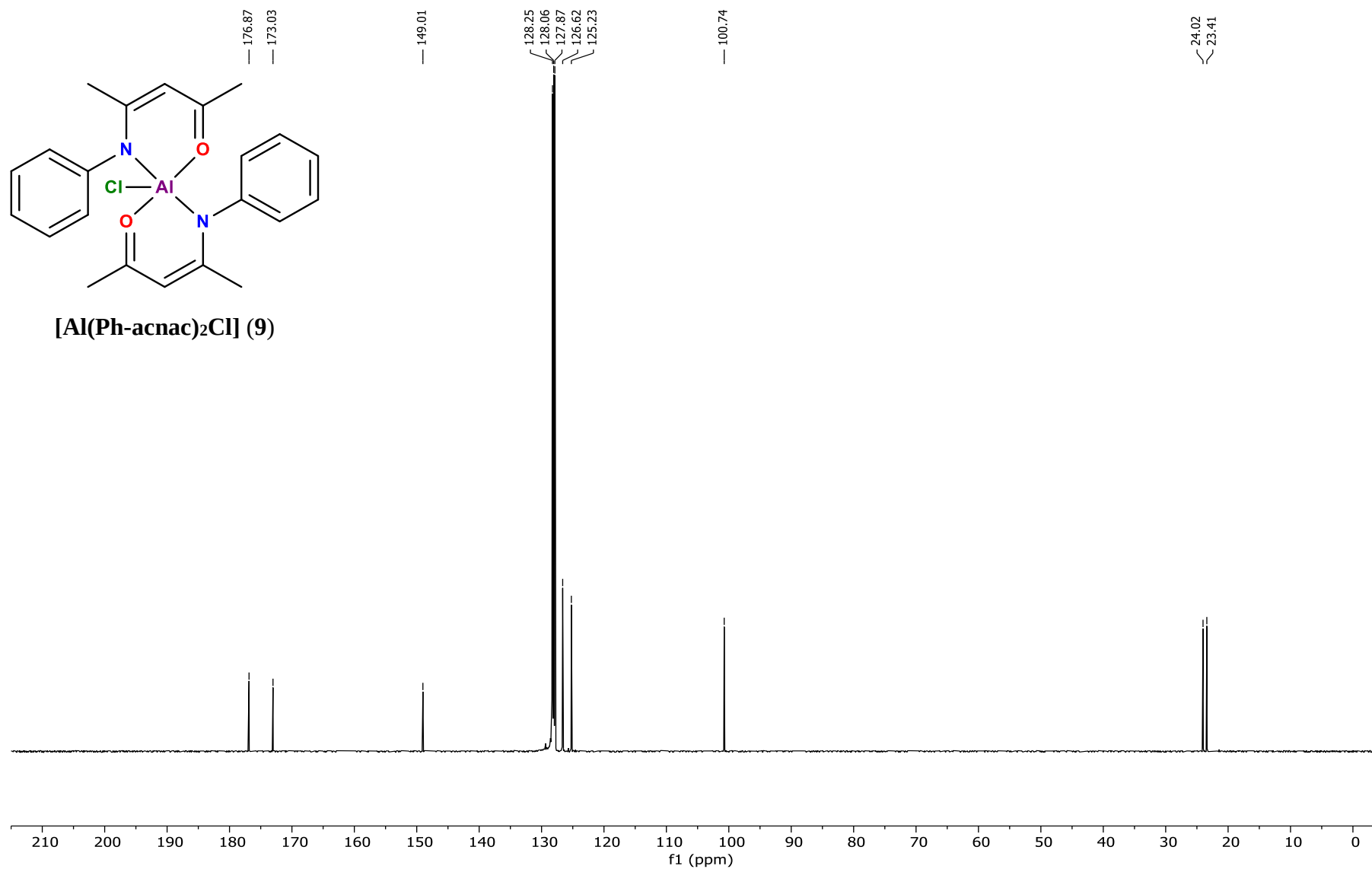
Appendix 58: HSQC NMR of $[Al(iPr-acnac)_2Cl]$ (8).



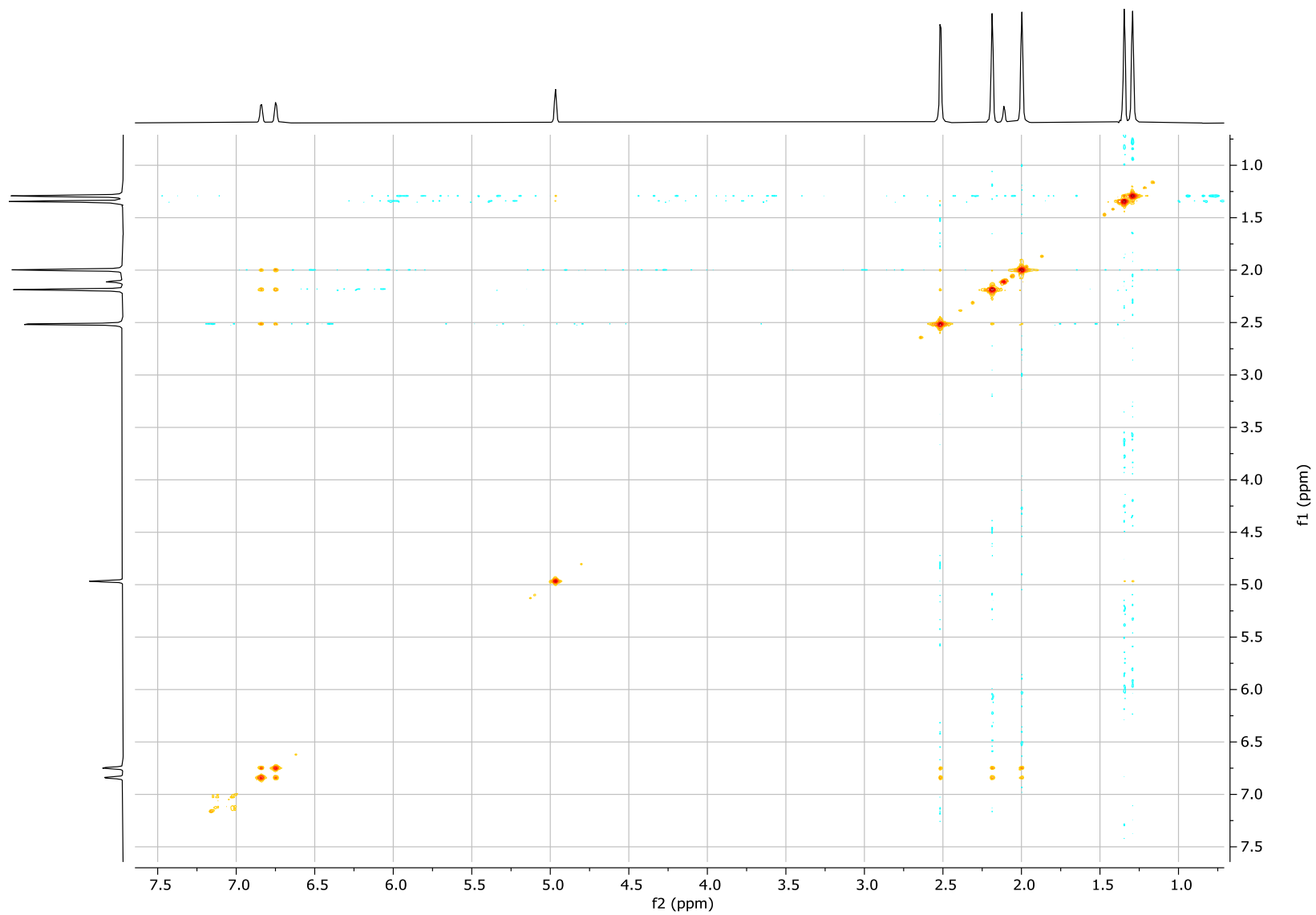
Appendix 59: HSQC NMR of $[Al(iPr-acnac)_2Cl]$ (8).



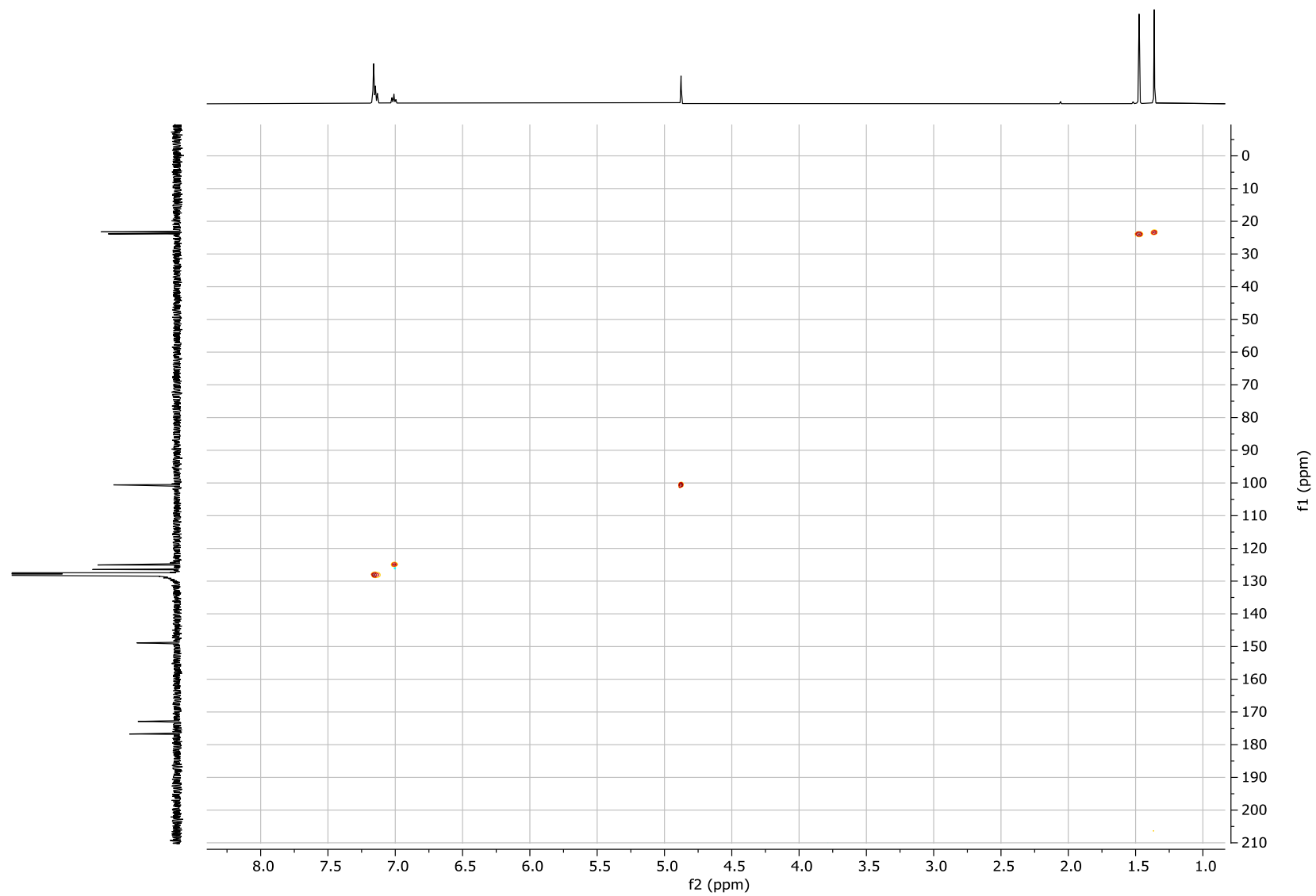
Appendix 60: ^1H NMR of $[Al(Ph-acnac)_2Cl]$ (9).



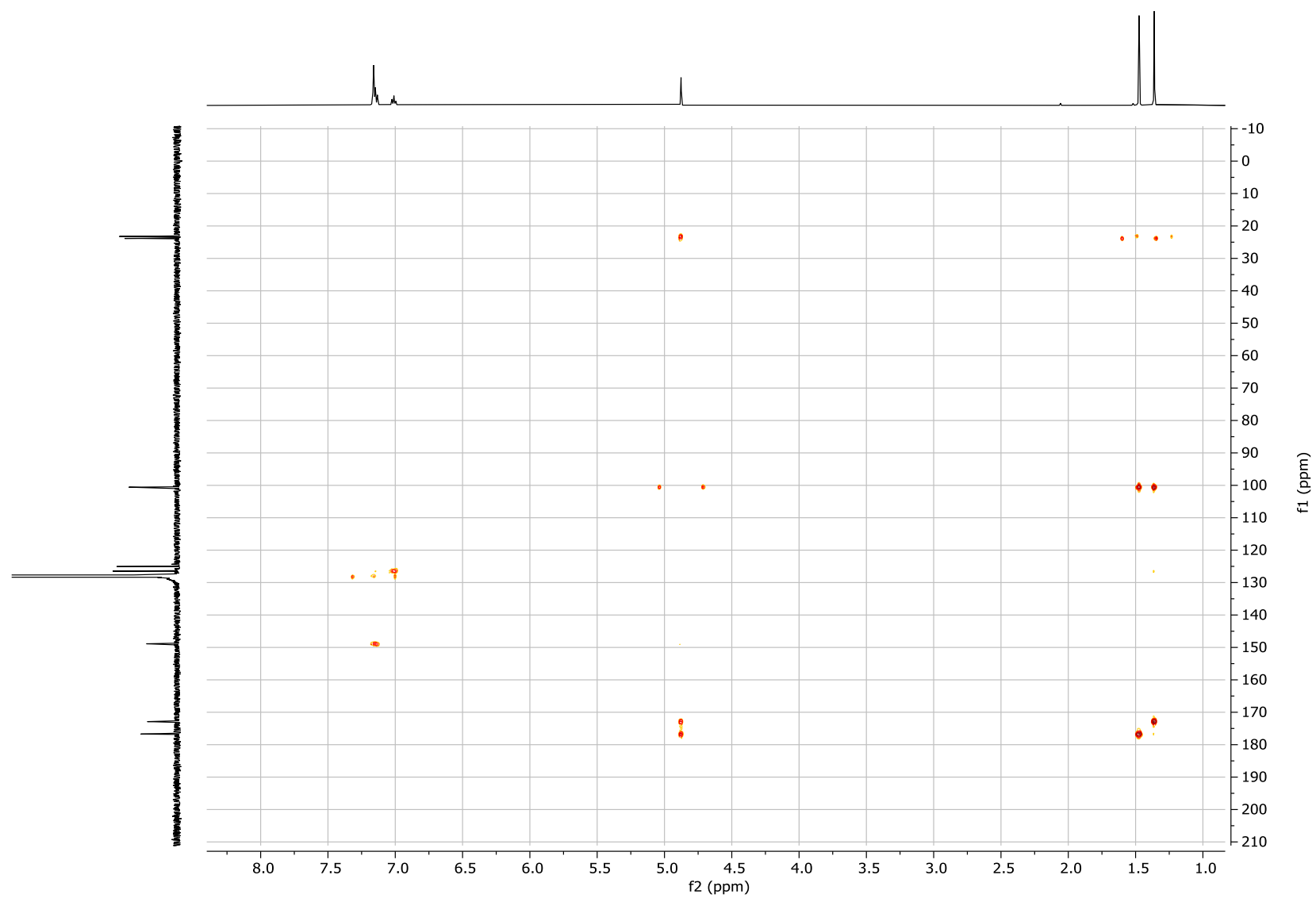
Appendix 61: ^{13}C NMR of $[Al(Ph-acnac)_2Cl]$ (9).



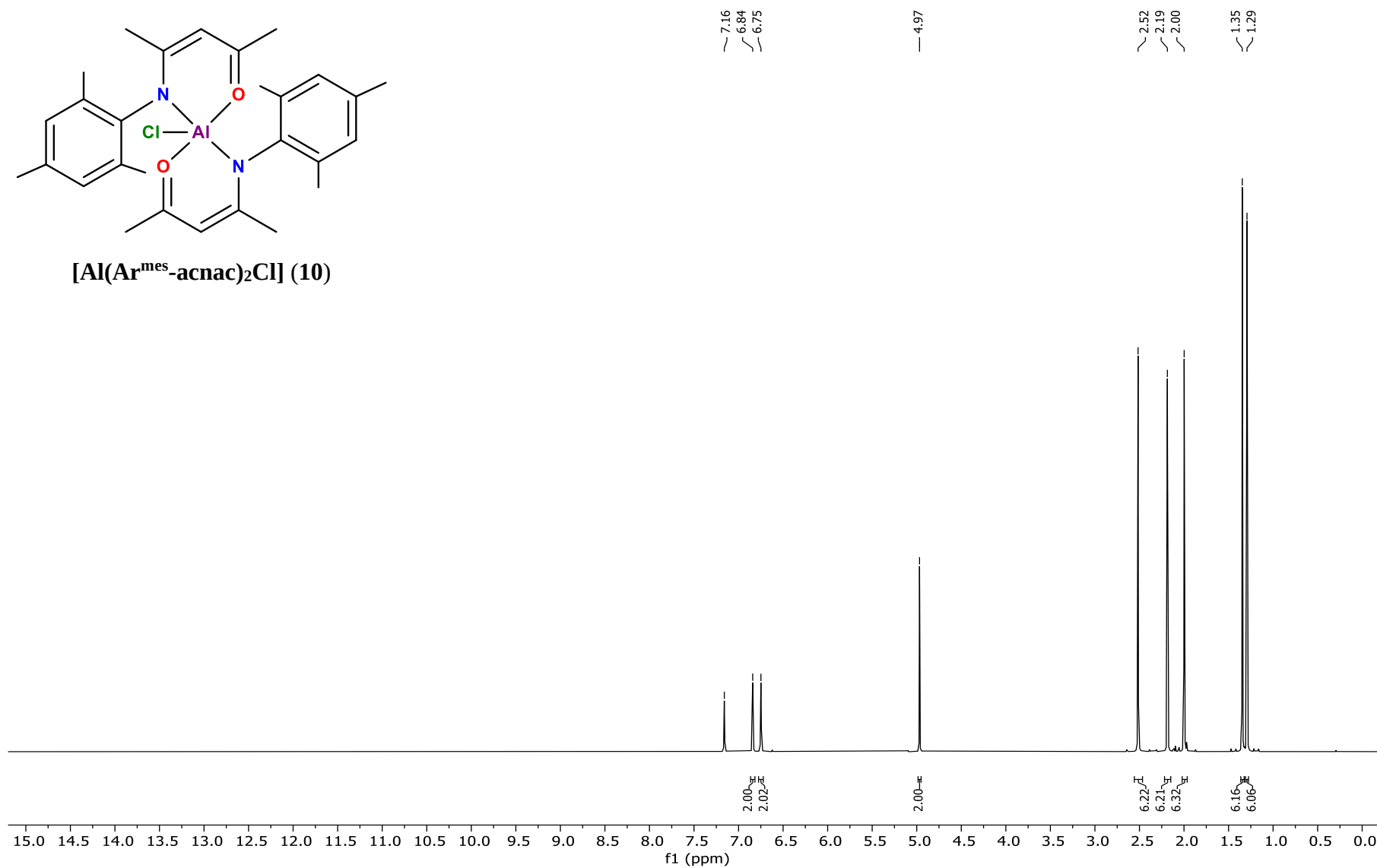
Appendix 62: COSY NMR of $[Al(Ph-acnac)_2Cl]$ (9).



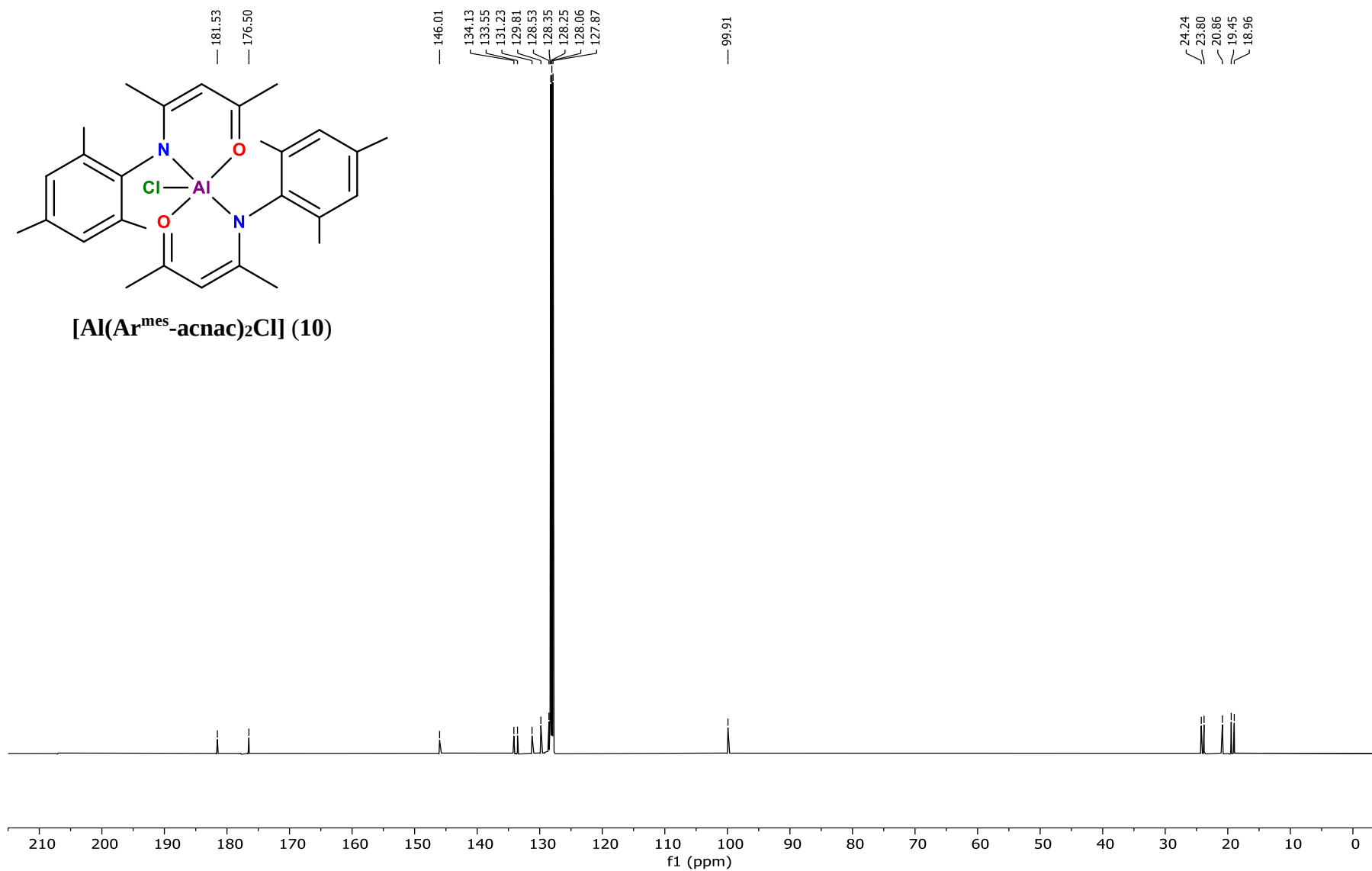
Appendix 63: HSQC NMR of $[Al(Ph-acnac)_2Cl]$ (9).



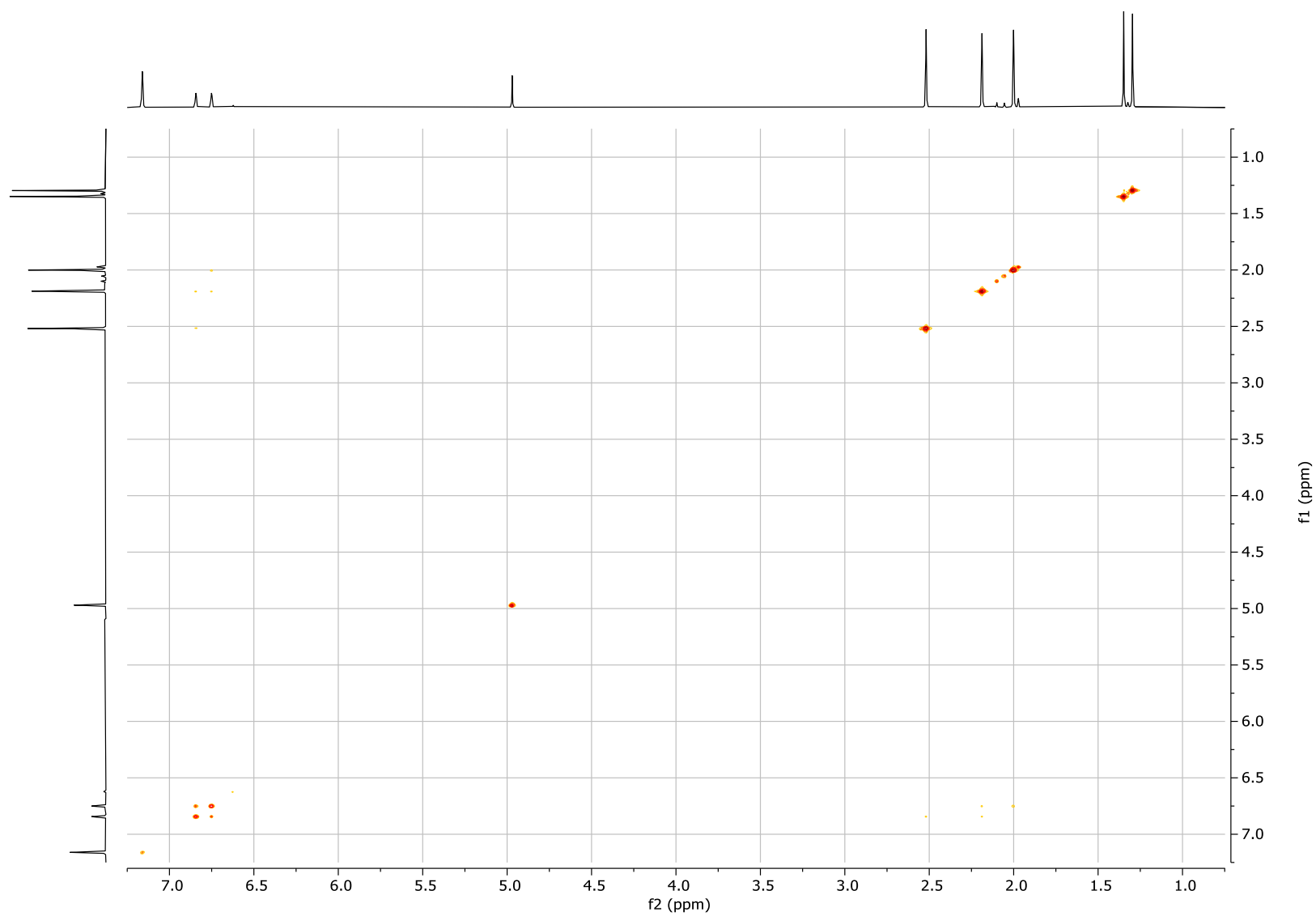
Appendix 64: HSQC NMR of $[Al(Ph-acnac)_2Cl]$ (9).



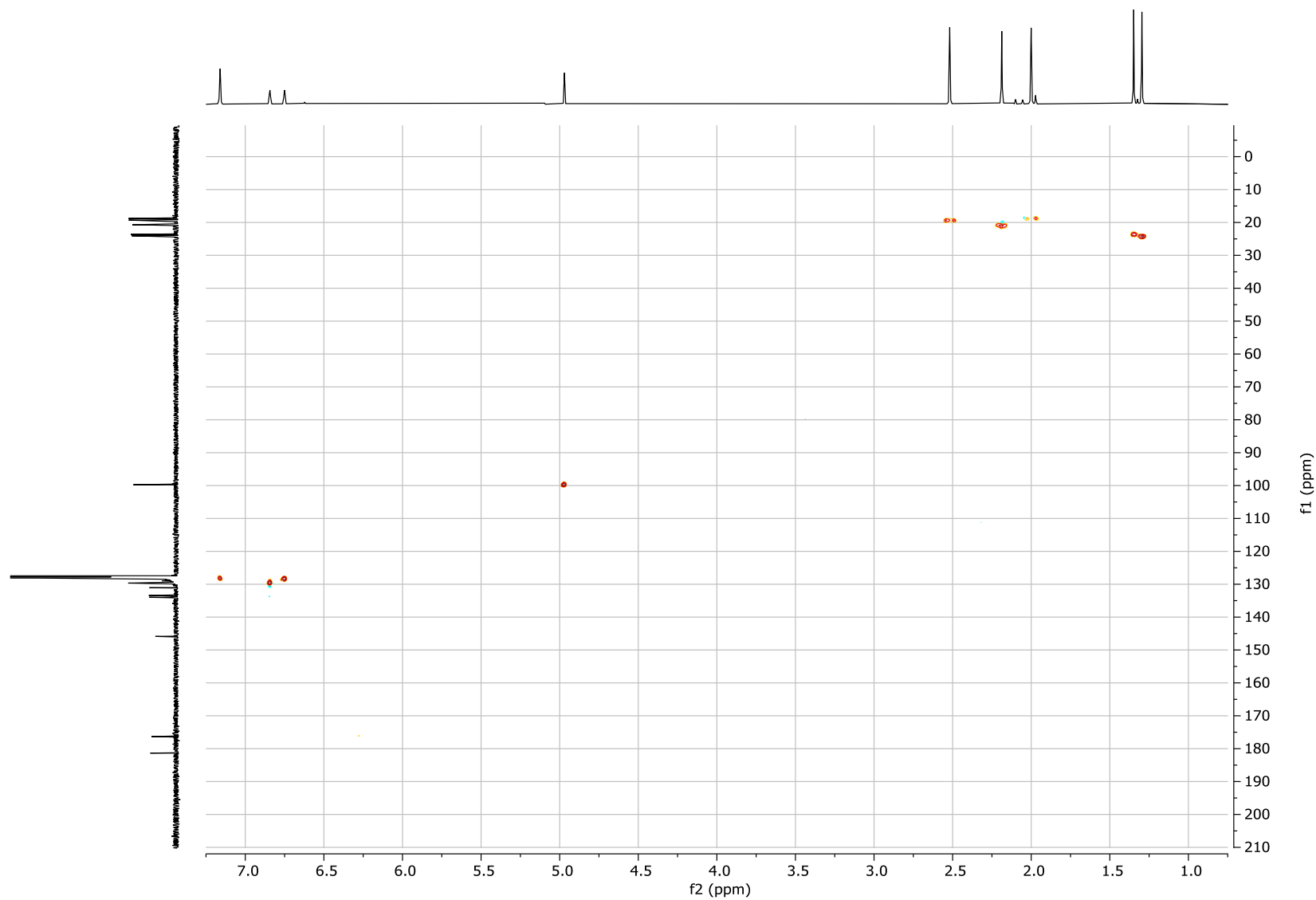
Appendix 65: ^1H NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).



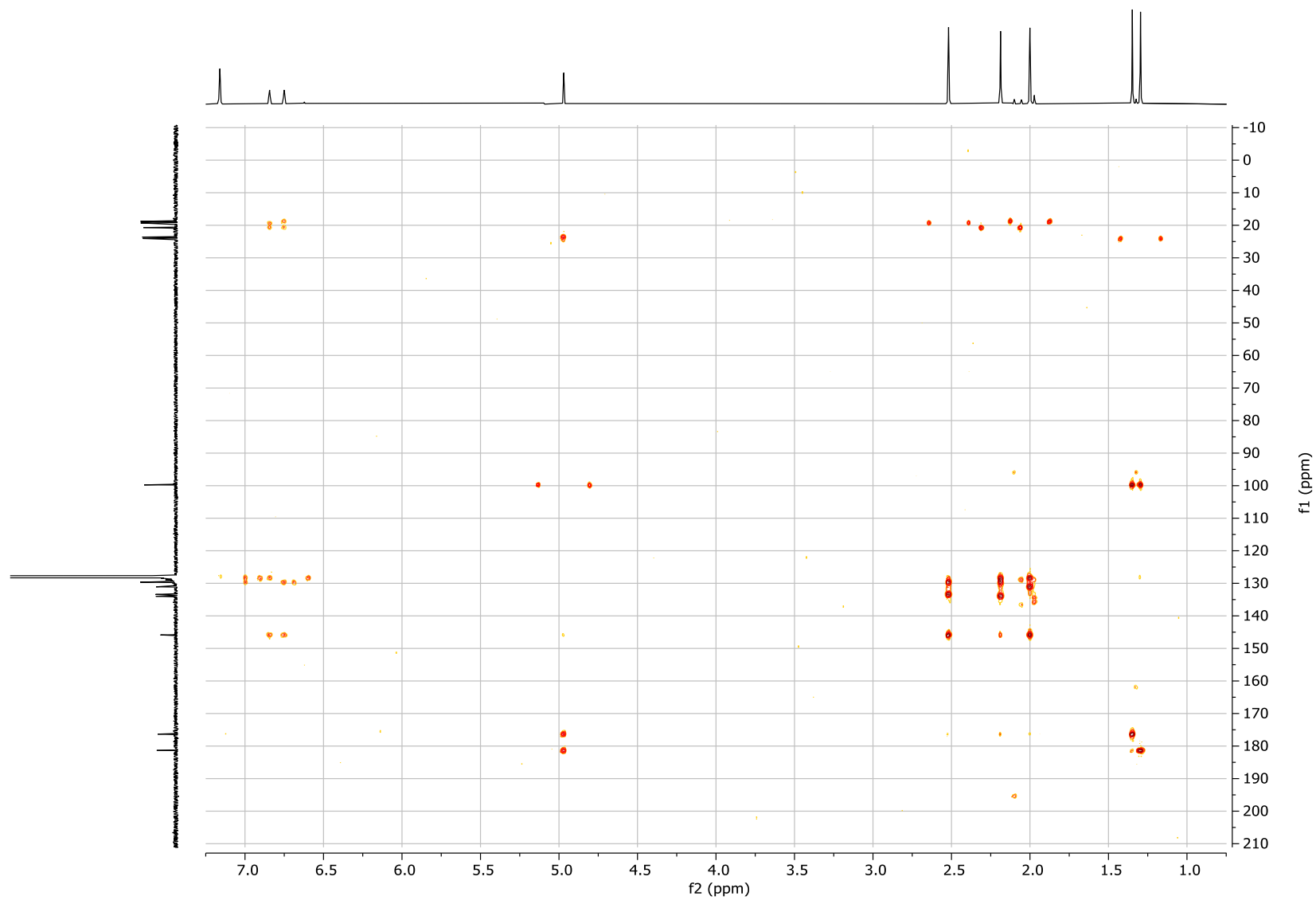
Appendix 66: ^{13}C NMR of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).



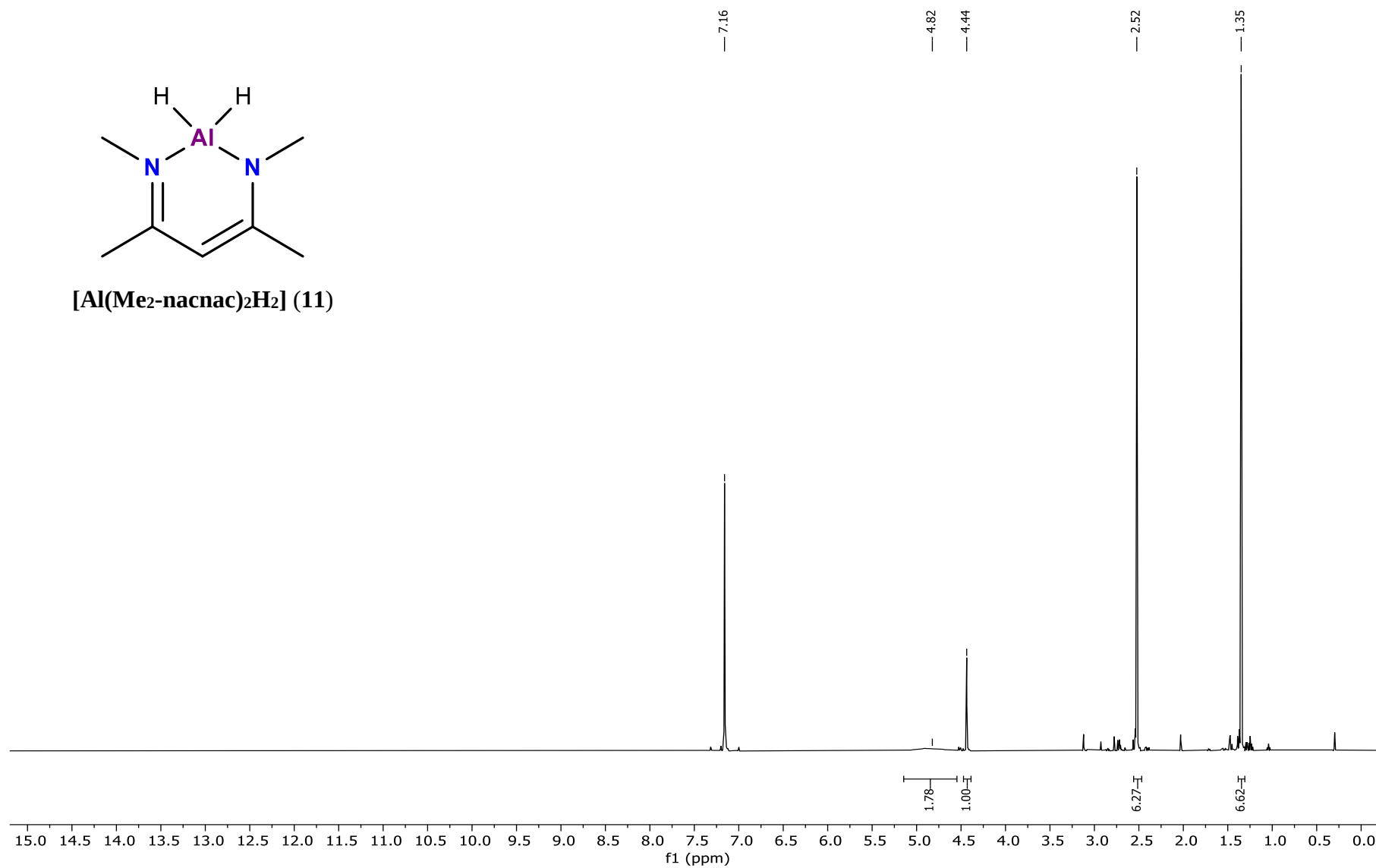
Appendix 67: COSY NMR of $[Al(Ar^{mes}\text{-}acnac)_2Cl]$ (10).



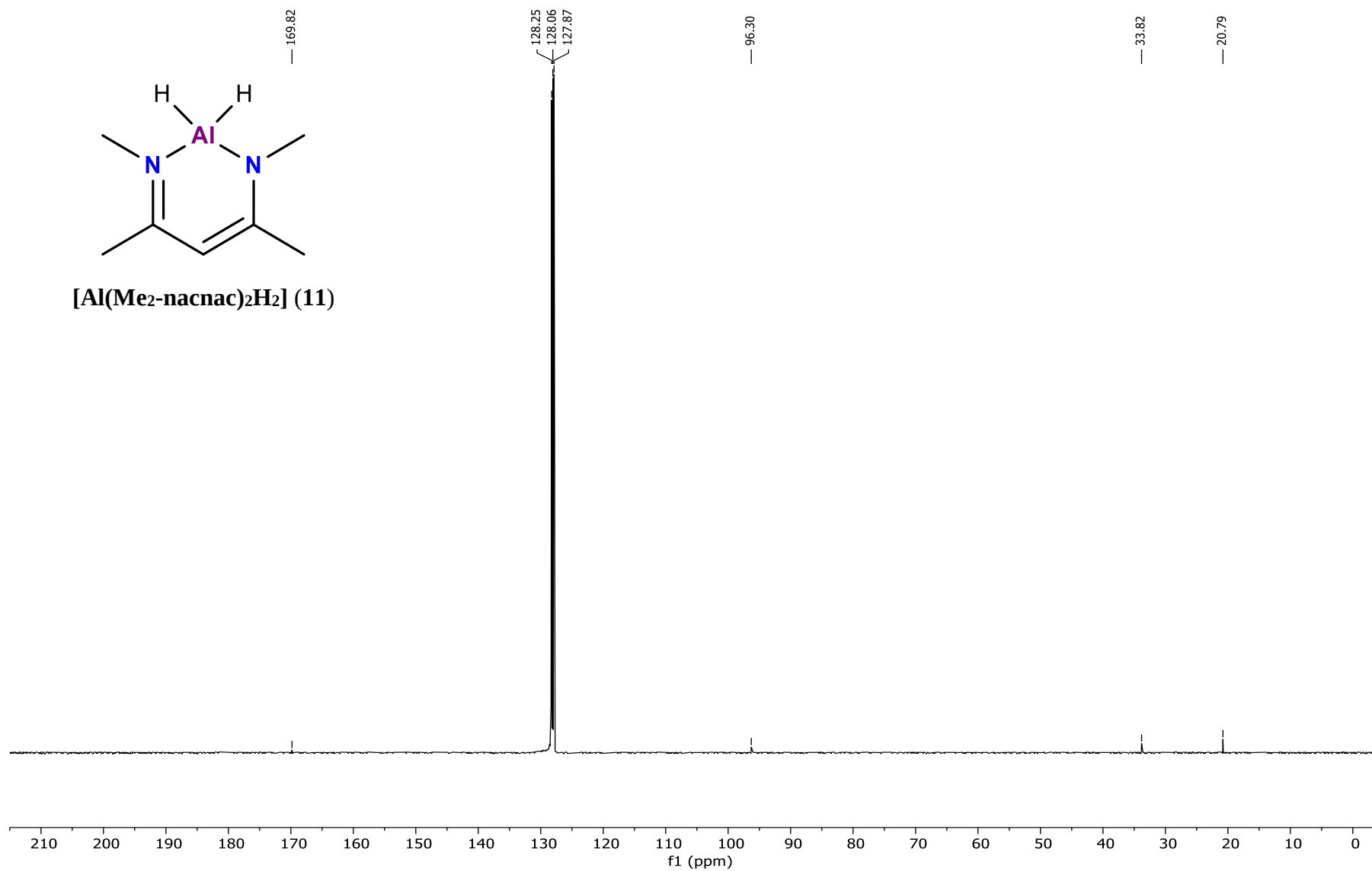
Appendix 68: HSQC NMR of $[Al(Ar^{mes}\text{-}acnac)_2Cl]$ (10).



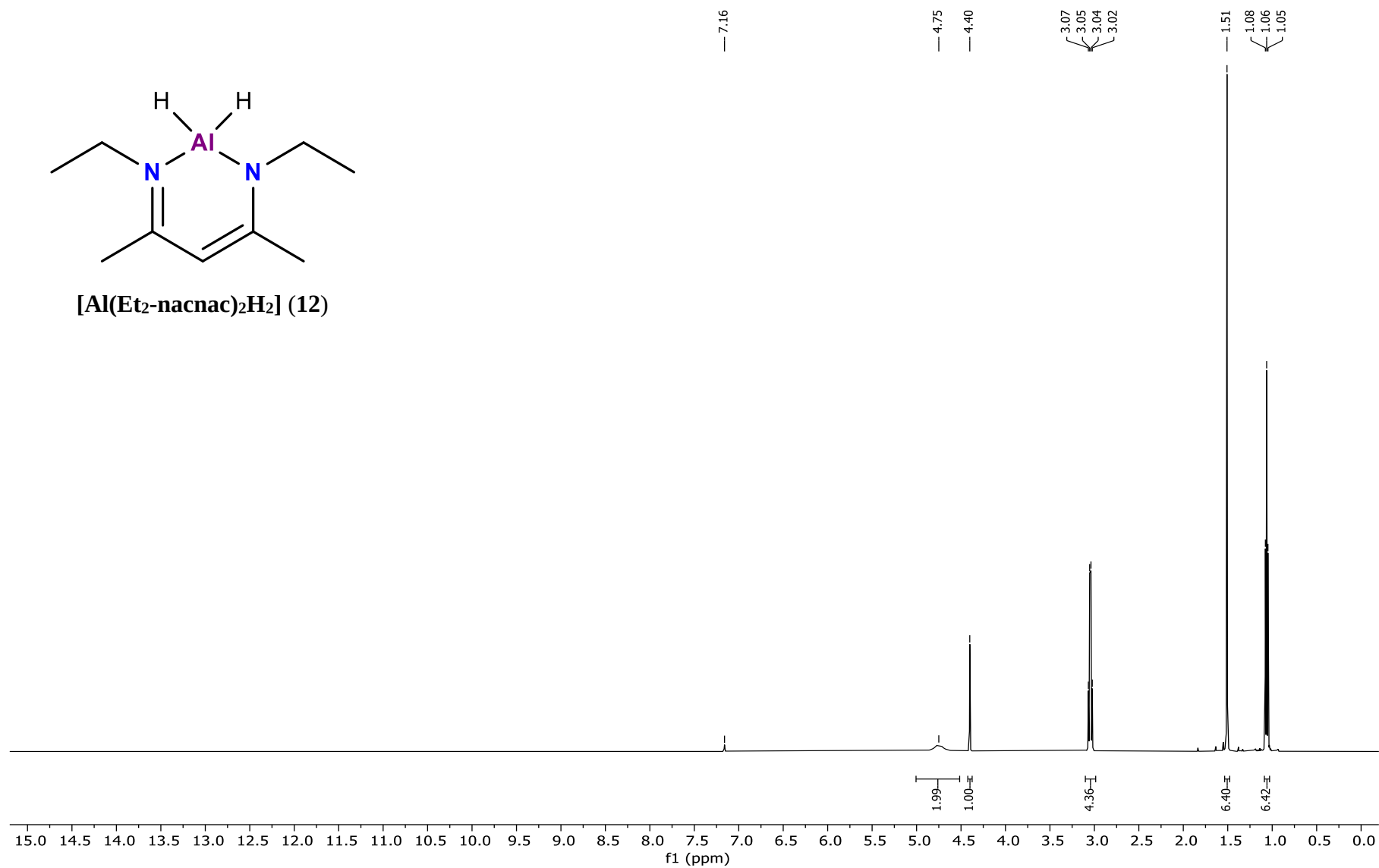
Appendix 69: HMBC NMR of $[Al(Ar^{mes}\text{-}acnac)_2Cl]$ (10).



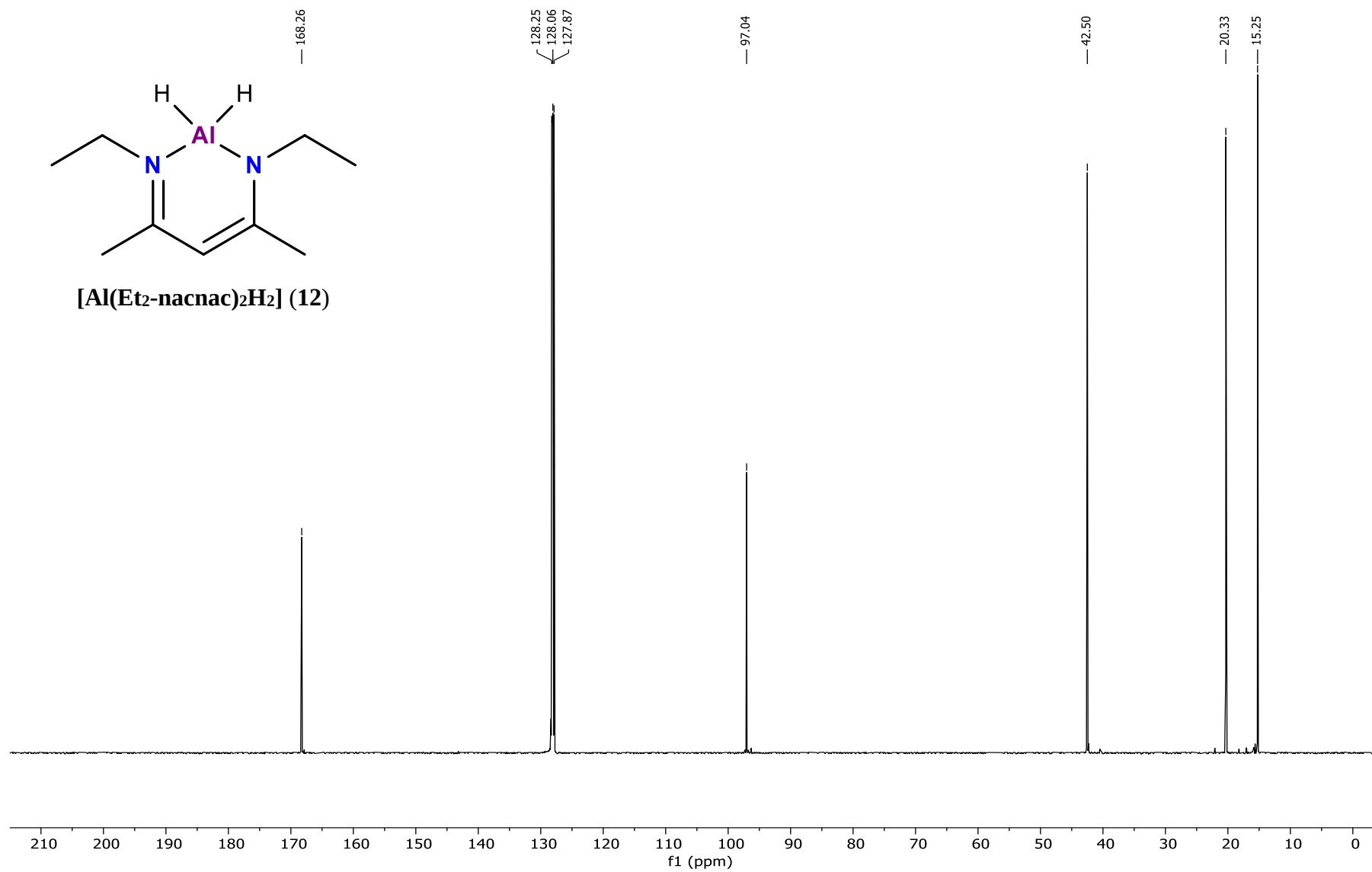
Appendix 70: ^1H NMR of $[\text{Al}(\text{Me}_2\text{-nacnac})_2\text{H}_2]$ (11).



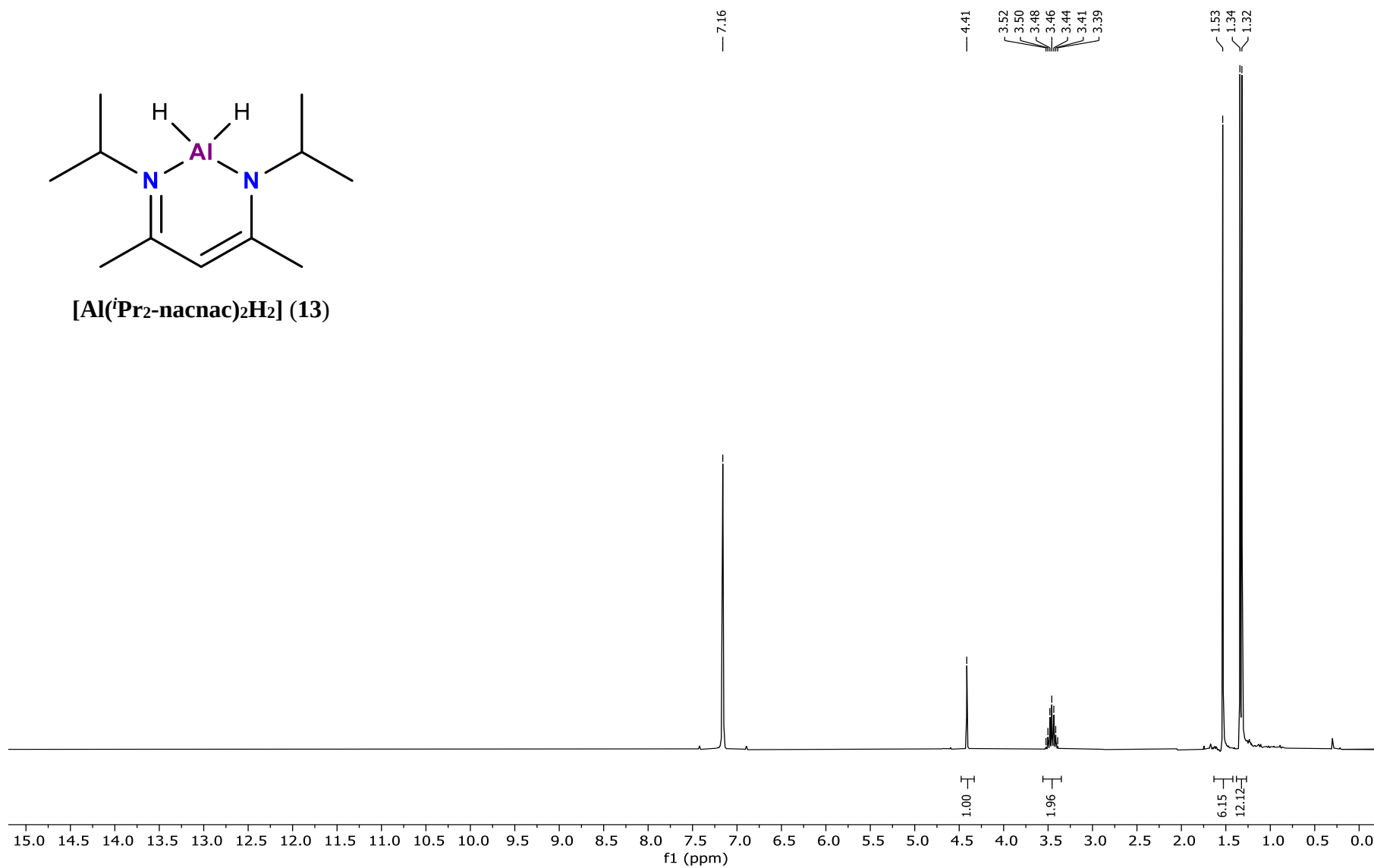
Appendix 71: ^{13}C NMR of $[\text{Al}(\text{Me}_2\text{-nacnac})_2\text{H}_2]$ (11).



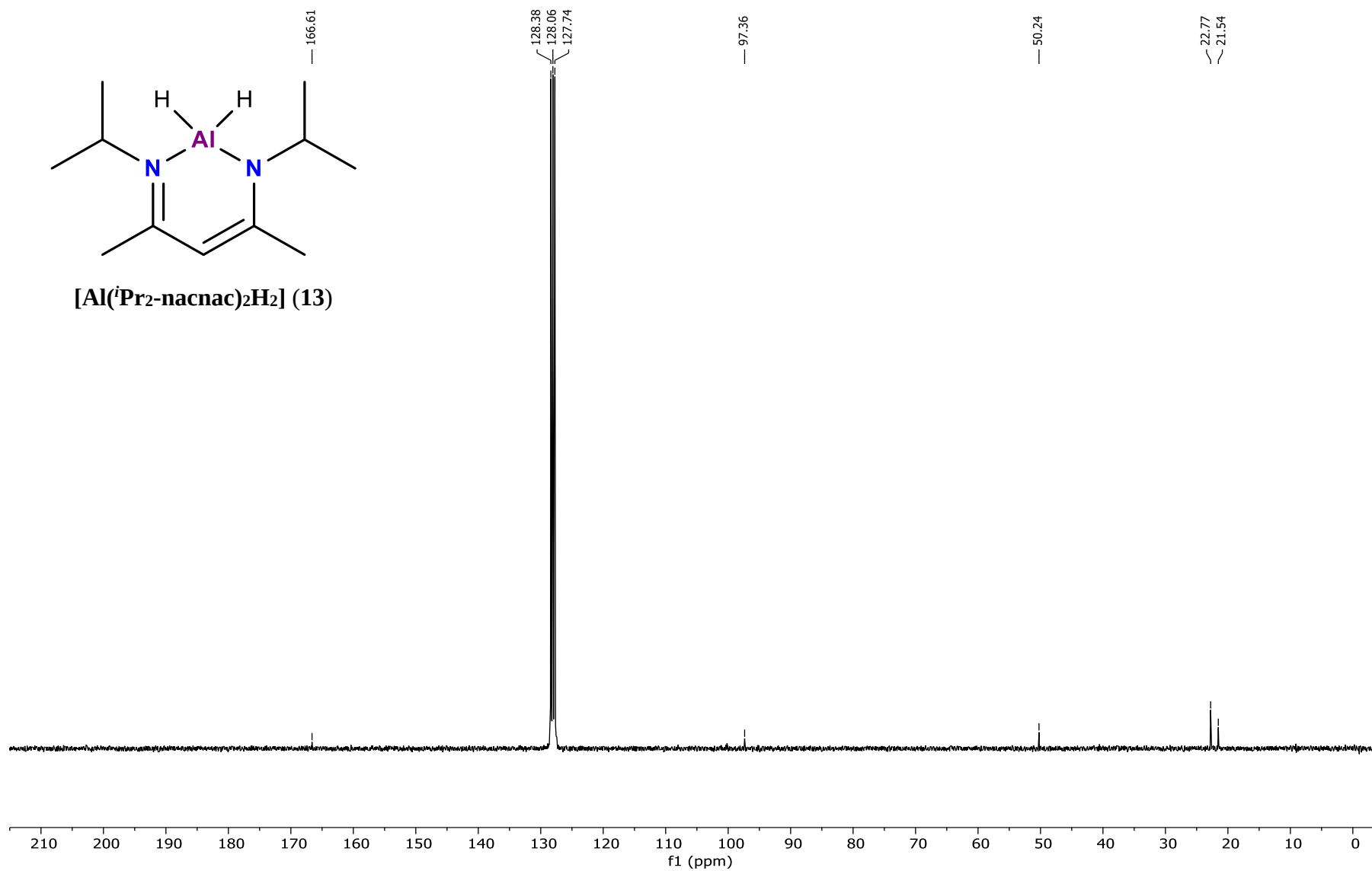
Appendix 72: ^1H NMR of $[Al(Et_2\text{-nacnac})_2H_2]$ (12).



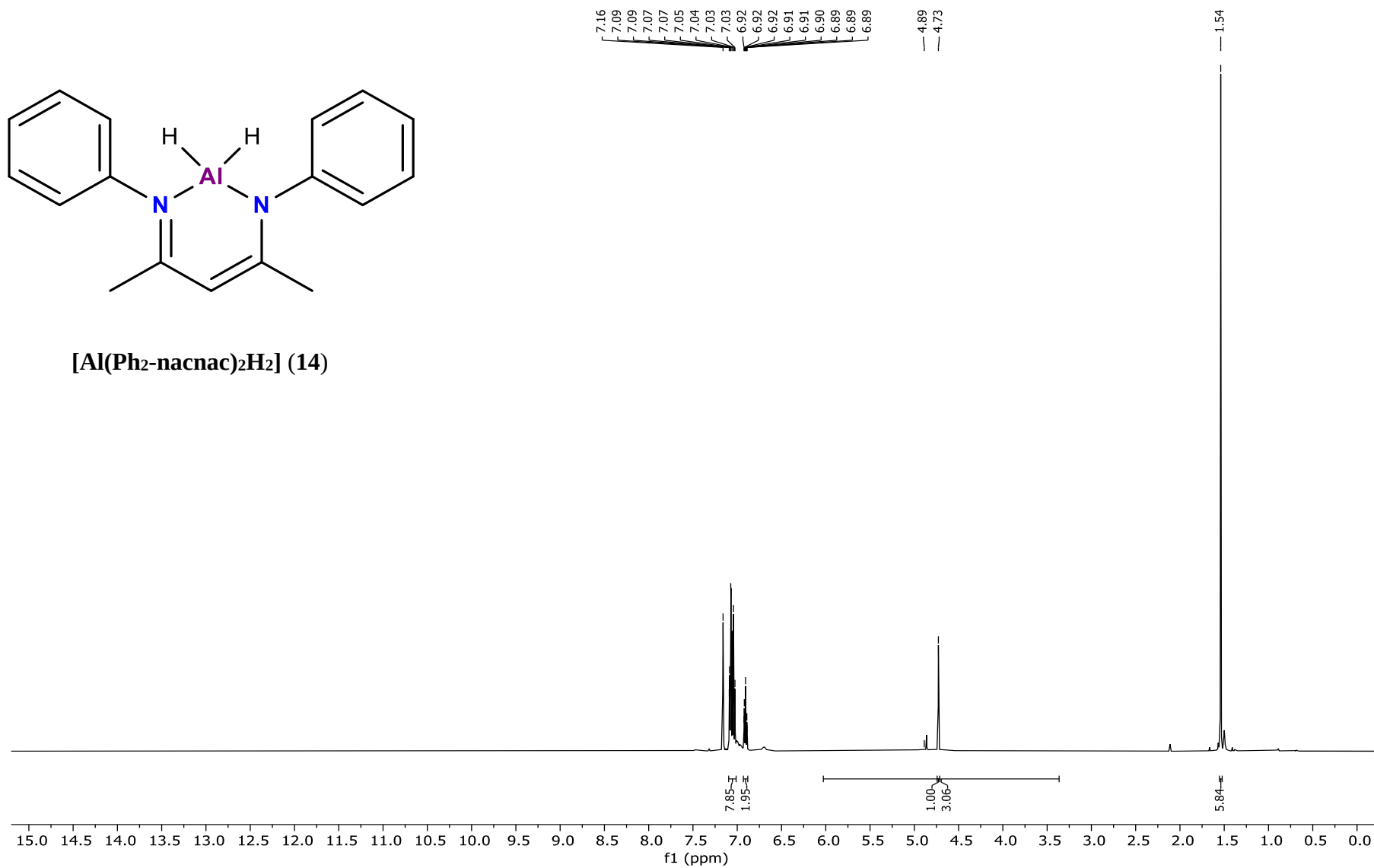
Appendix 73: ^{13}C NMR of $[\text{Al}(\text{Et}_2\text{-nacnac})_2\text{H}_2]$ (12).



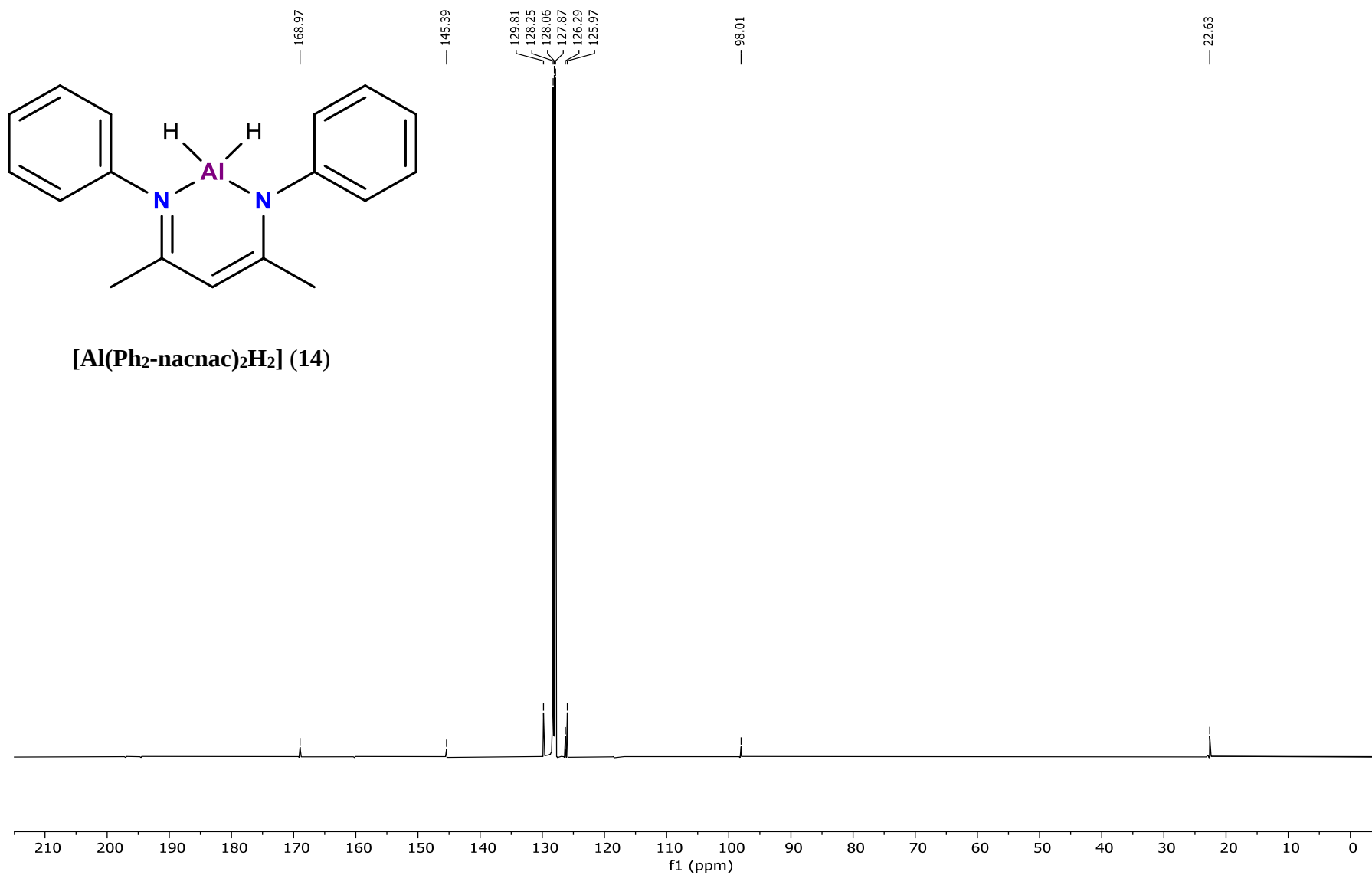
Appendix 74: ^1H NMR of $[\text{Al}(\text{iPr}_2\text{-nacnac})_2\text{H}_2]$ (13).



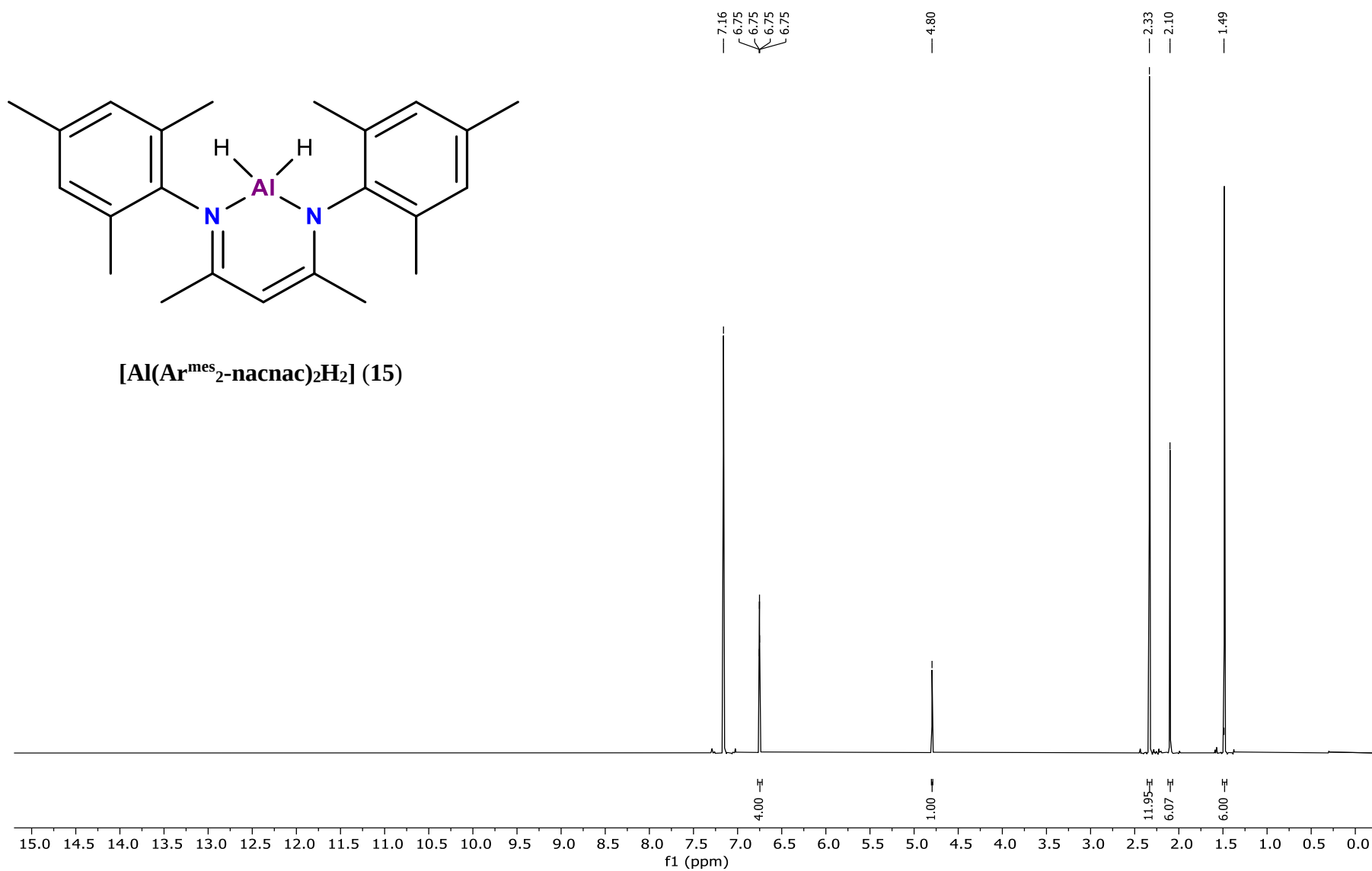
Appendix 75: ^{13}C NMR of $[Al(iPr_2-nacnac)_2H_2]$ (13).



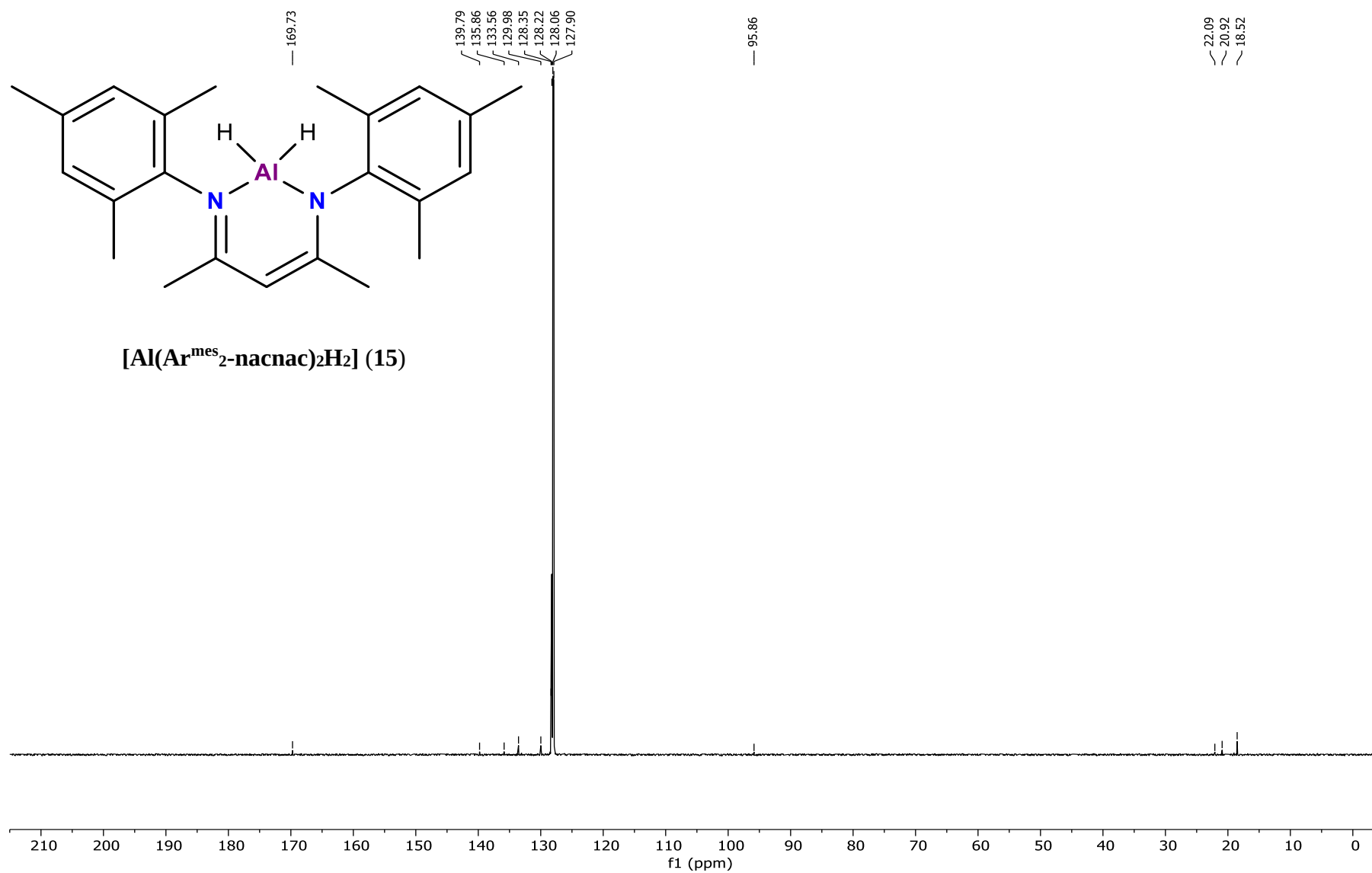
Appendix 76: ¹H NMR of [Al(Ph₂-nacnac)₂H₂] (14).



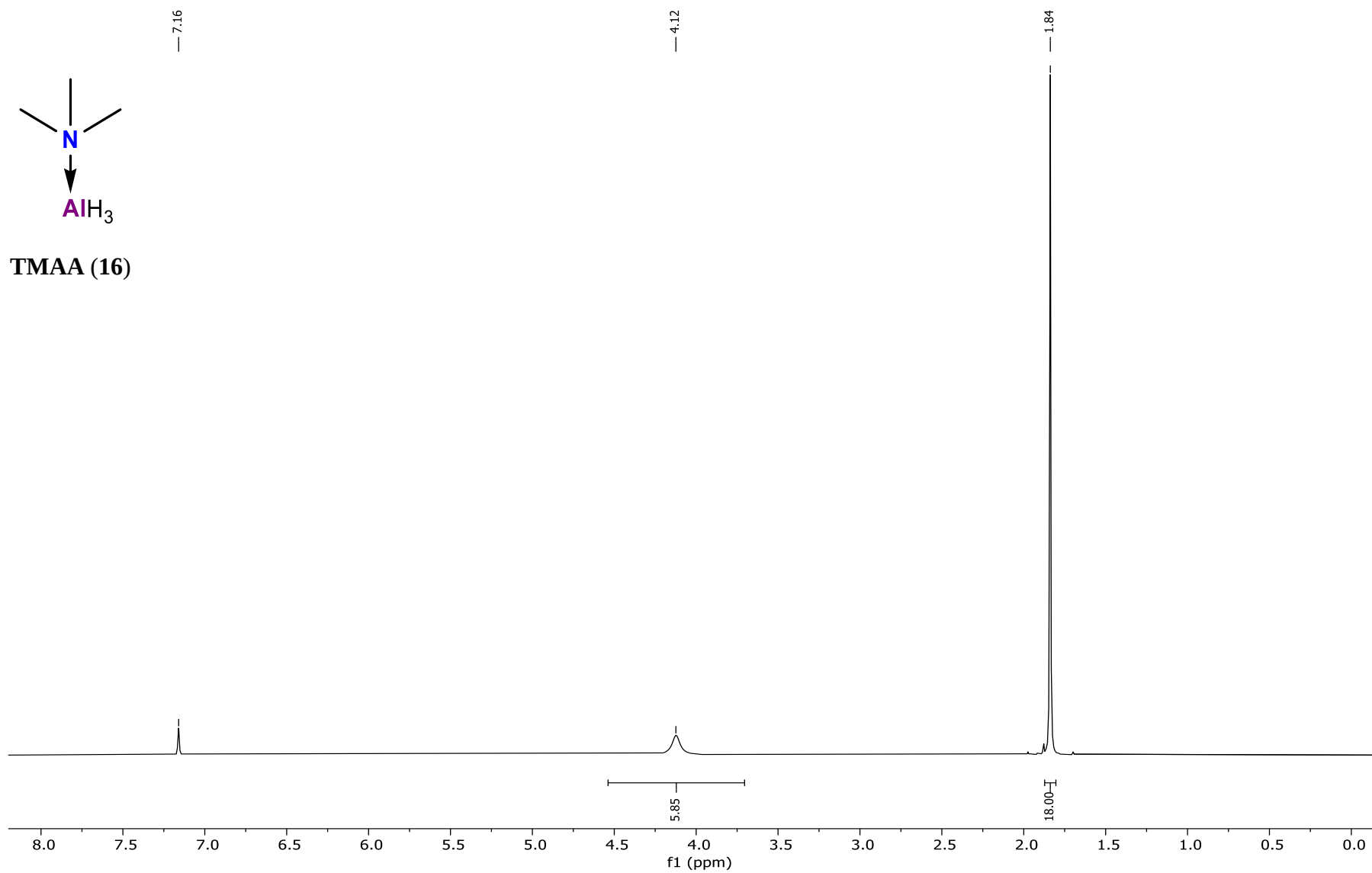
Appendix 77: ^{13}C NMR of $[Al(Ph_2-nacnac)_2H_2]$ (14).



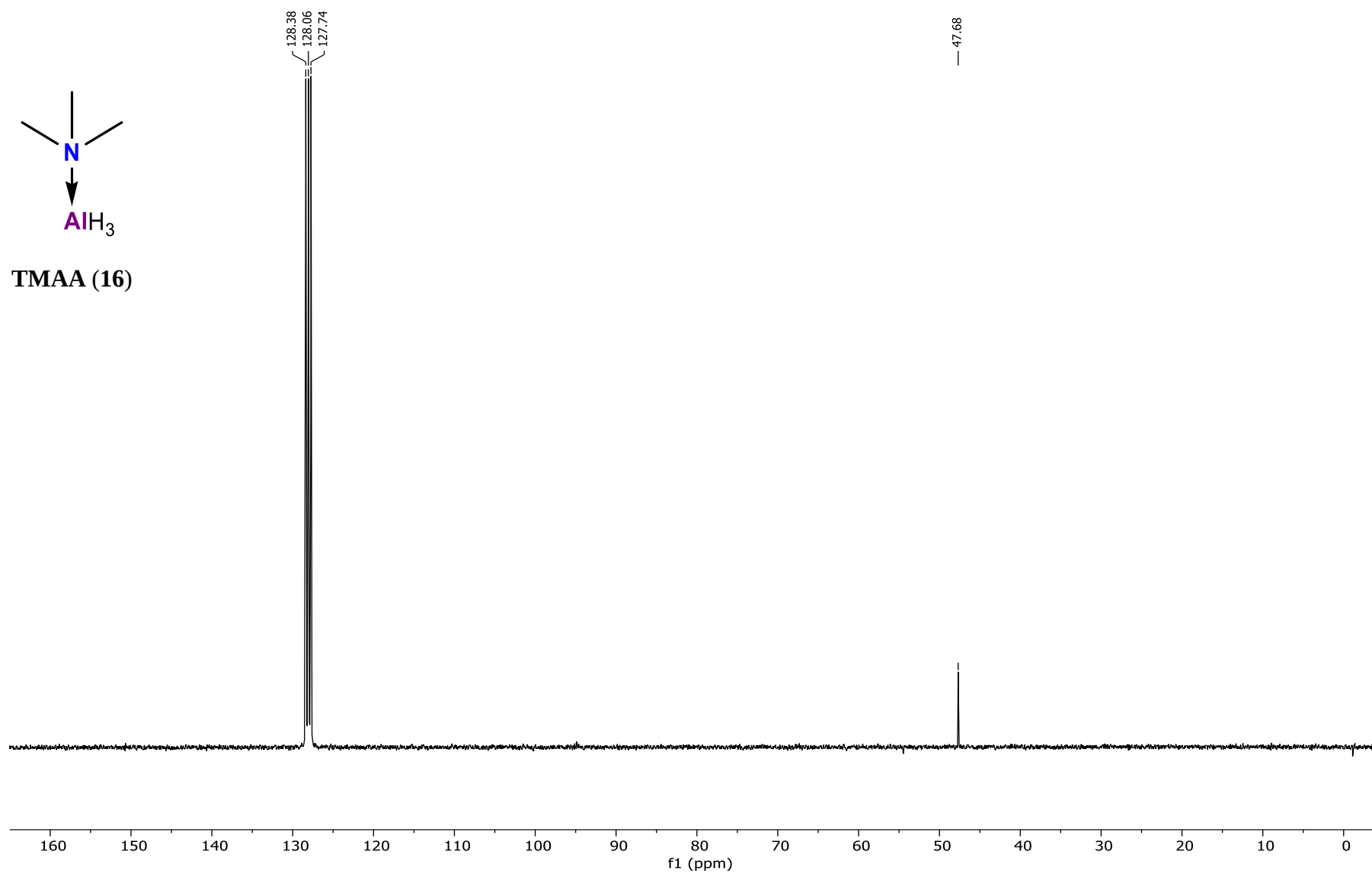
Appendix 78: ^1H NMR of $[Al(Ar^{mes}_2-nacnac)_2H_2]$ (15).



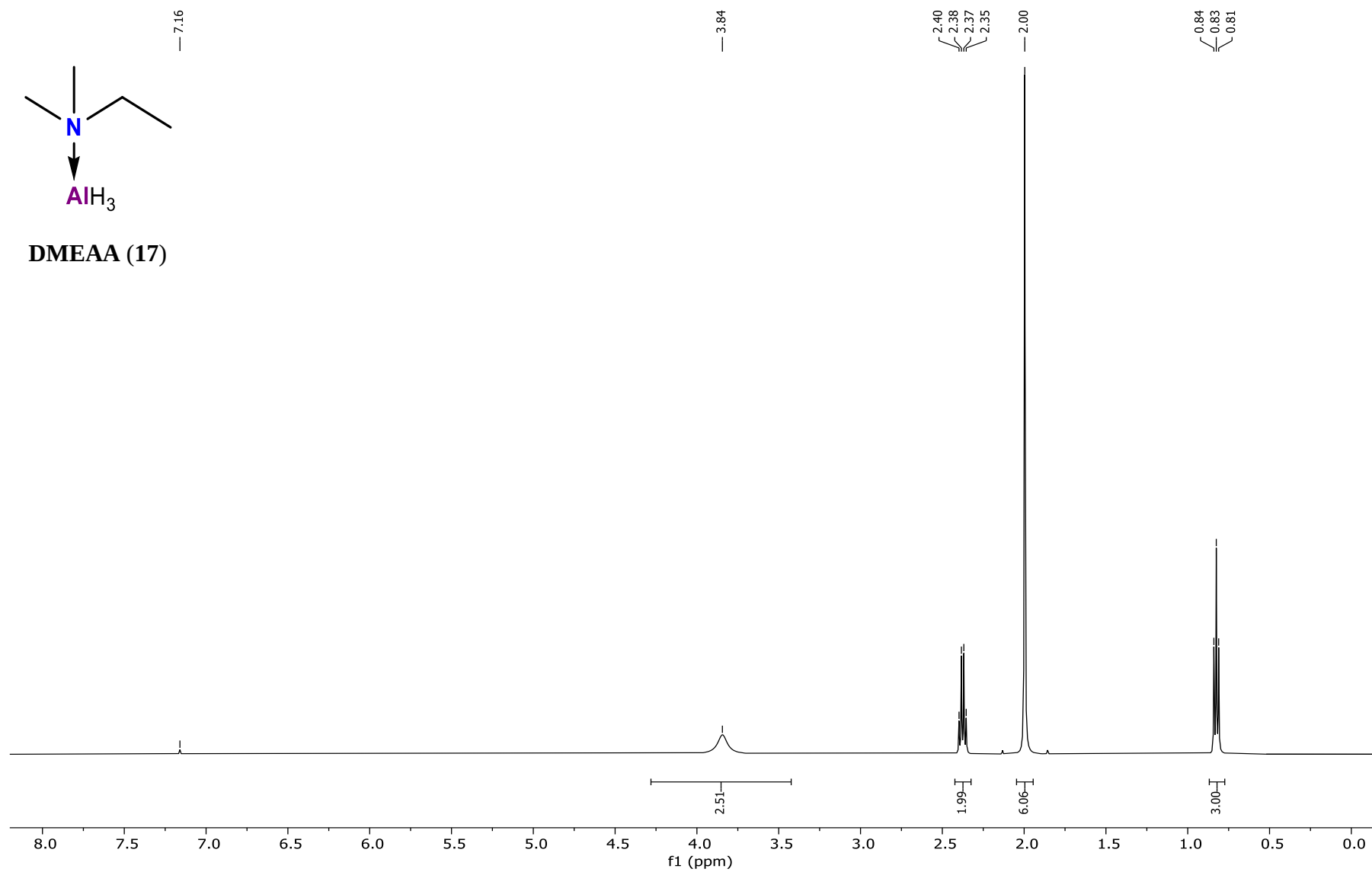
Appendix 79: ^{13}C NMR of $[Al(Ar^{mes}_2-nacnac)_2H_2]$ (15).



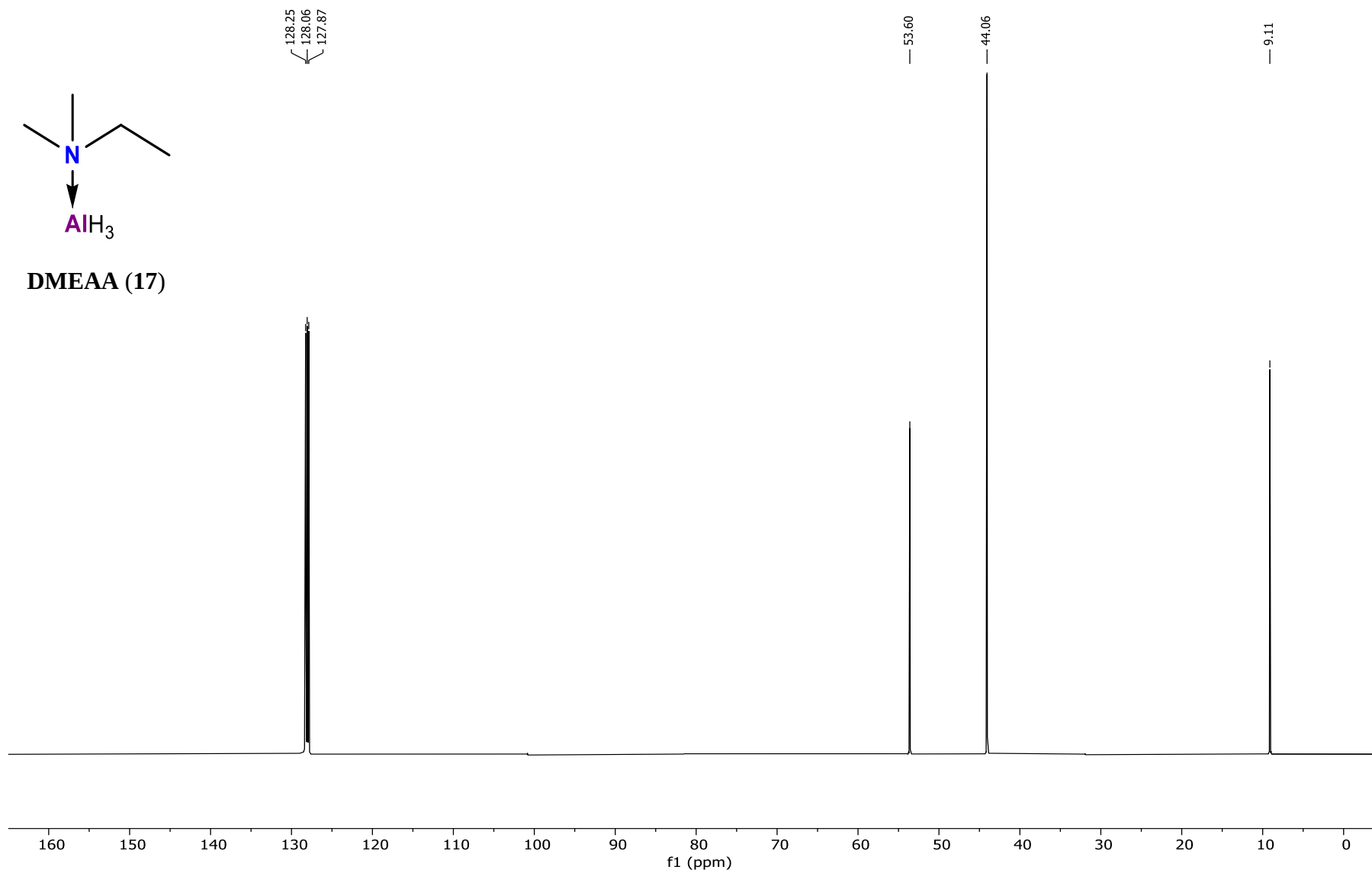
Appendix 80: ¹H NMR of TMAA (16).



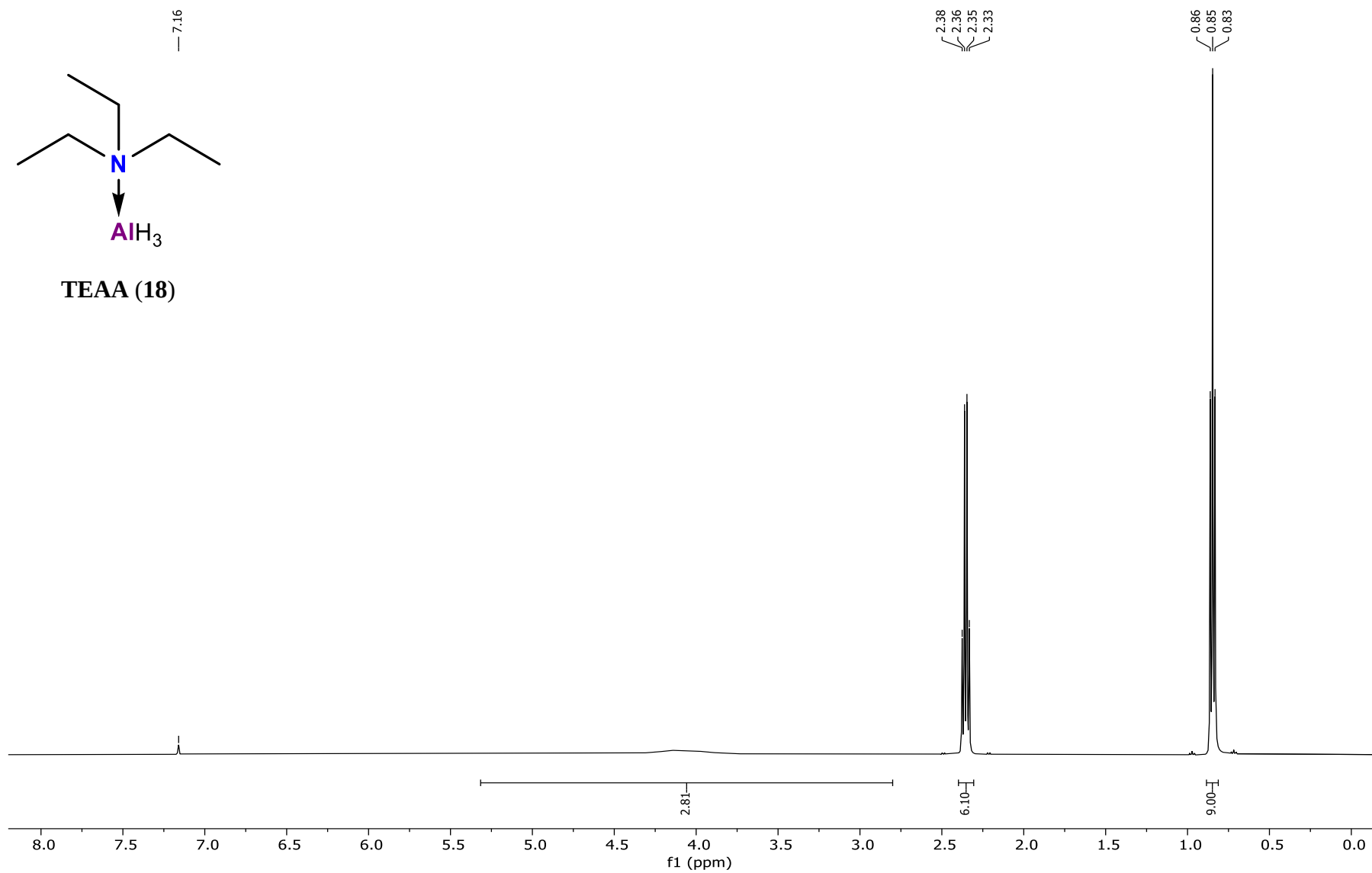
Appendix 81: ^{13}C NMR of TMAA (16).



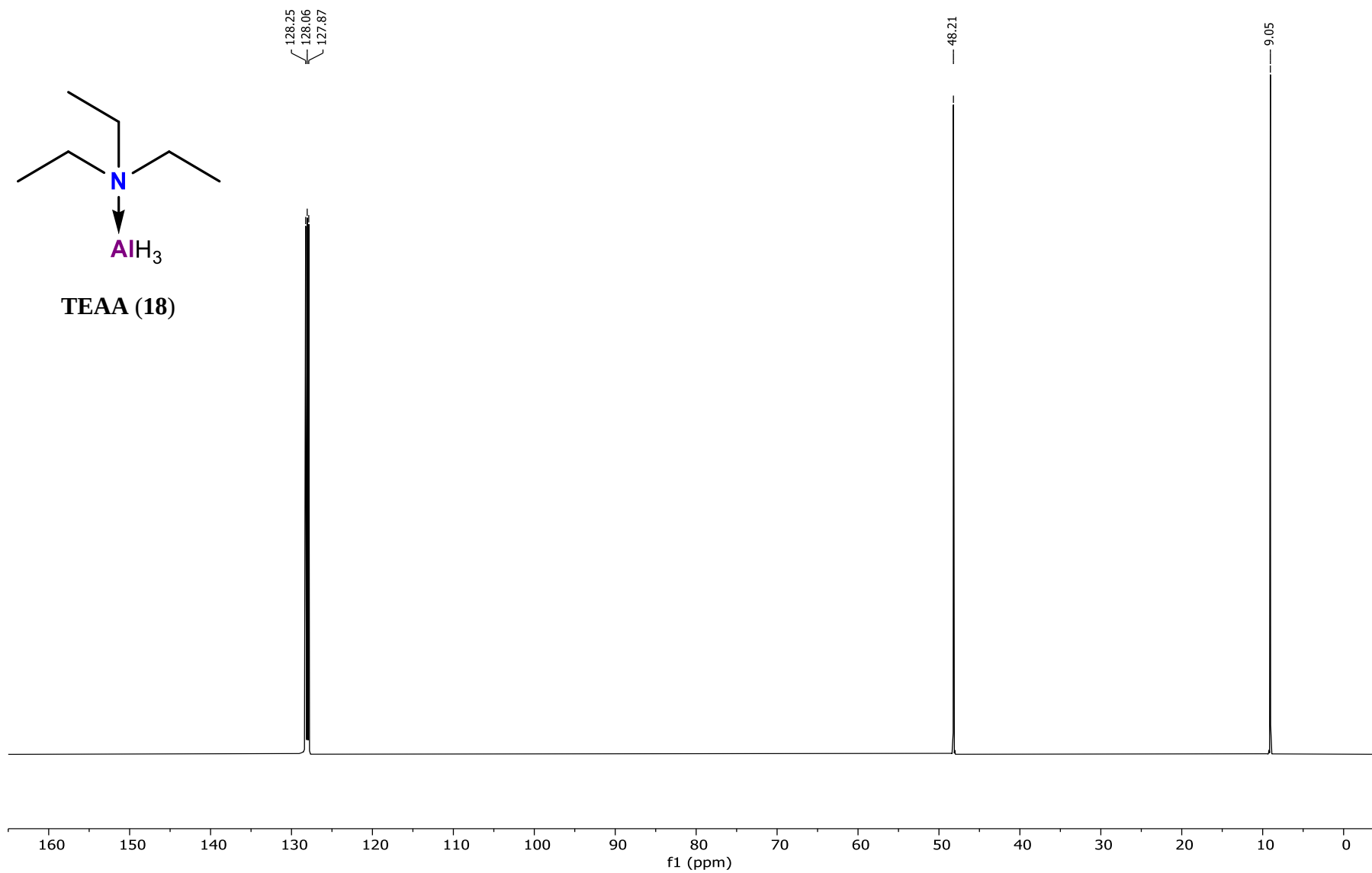
Appendix 82: ^1H NMR of DMEAA (17).



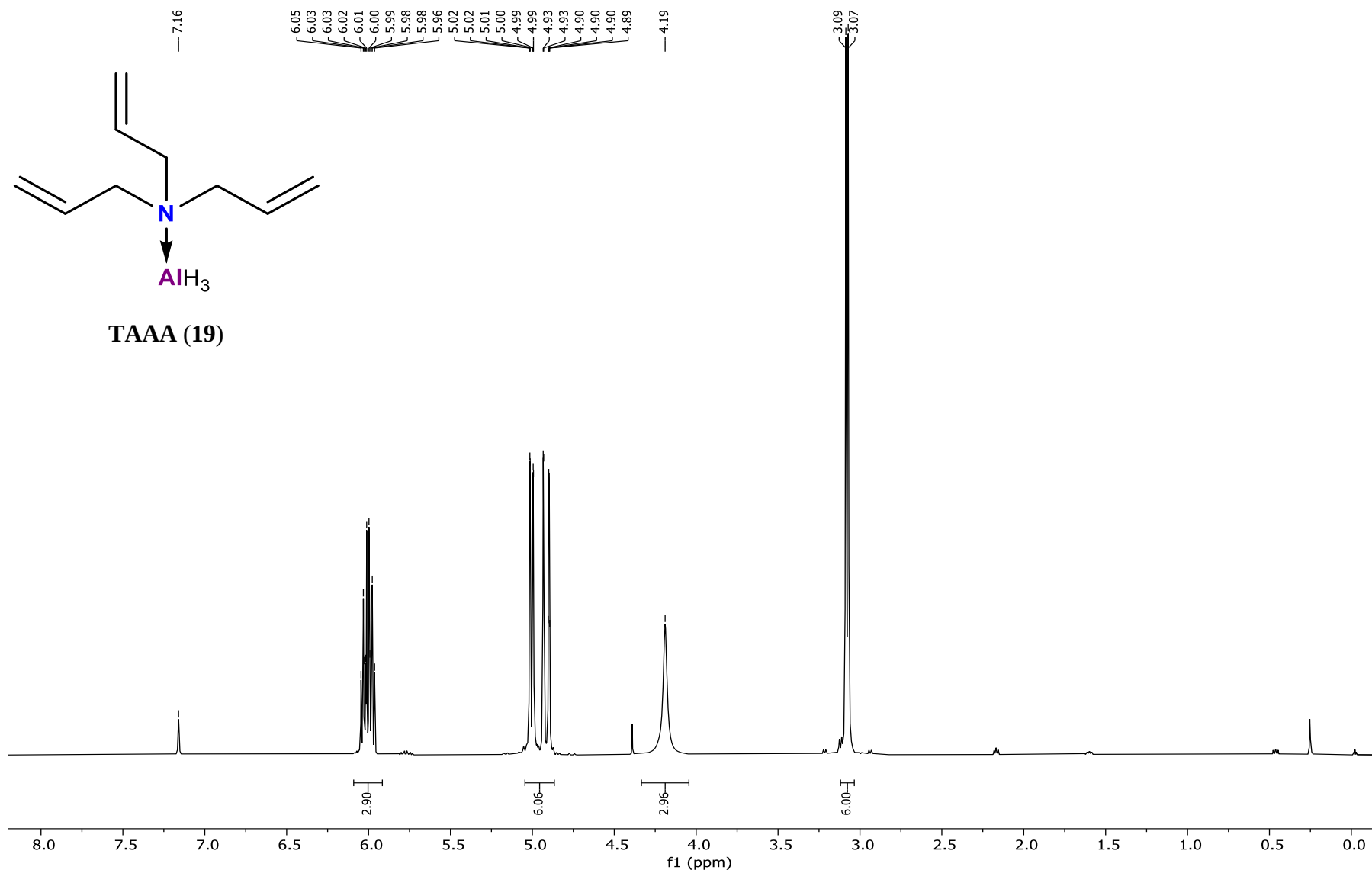
Appendix 83: ^{13}C NMR of DMEAA (17)



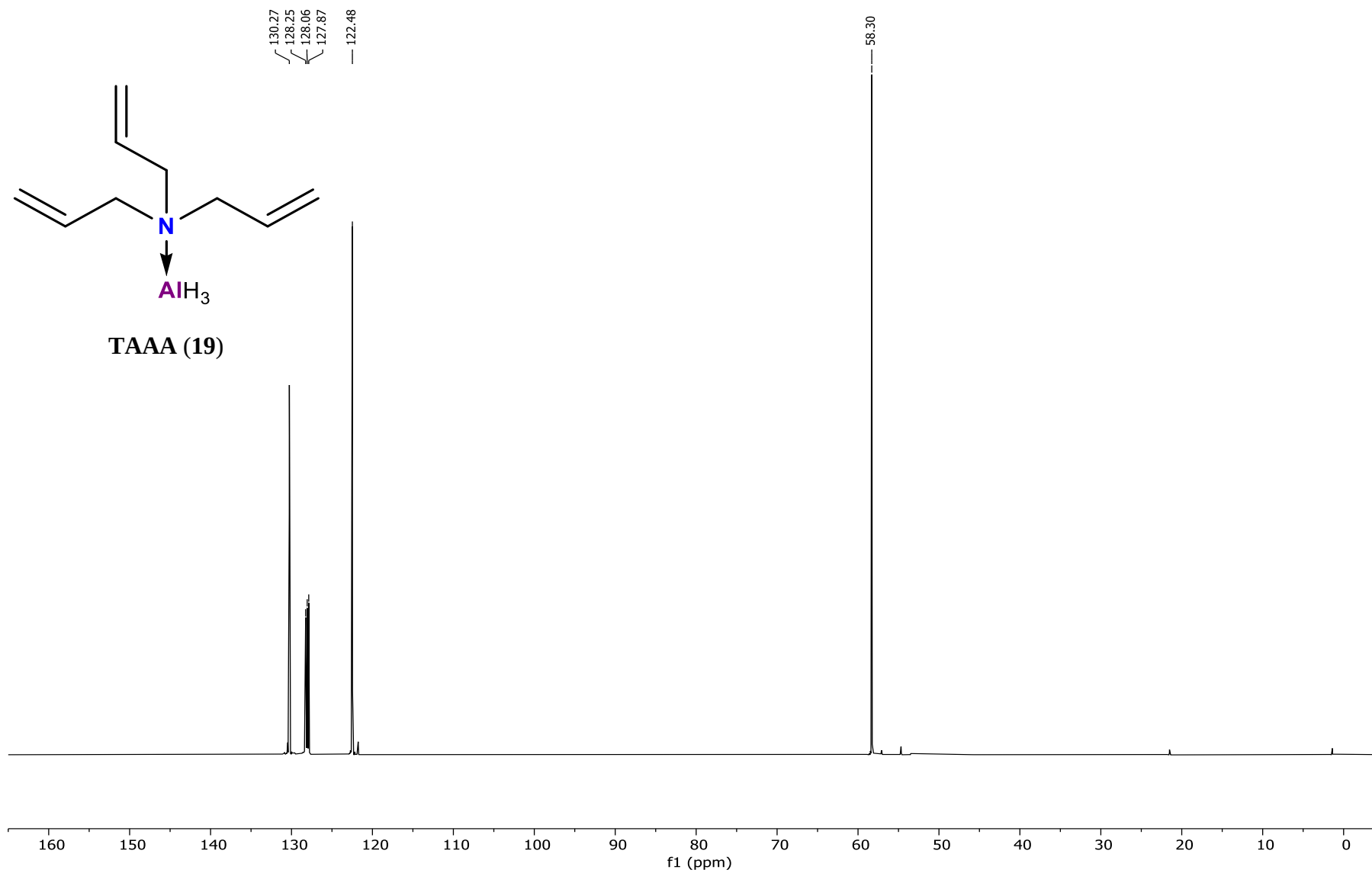
Appendix 84: ¹H NMR of TEAA (18).



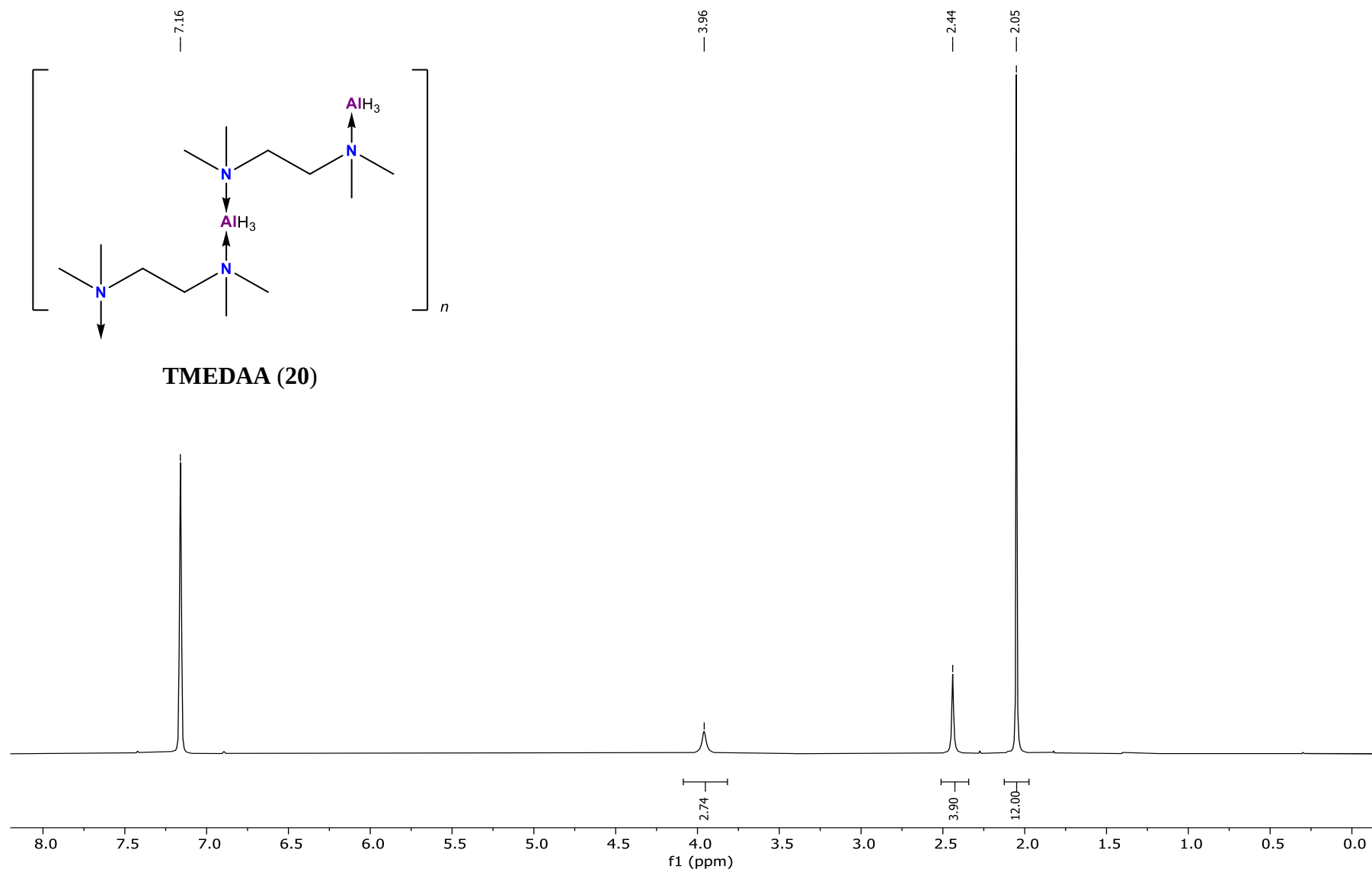
Appendix 85: ^{13}C NMR of TEAA (18).



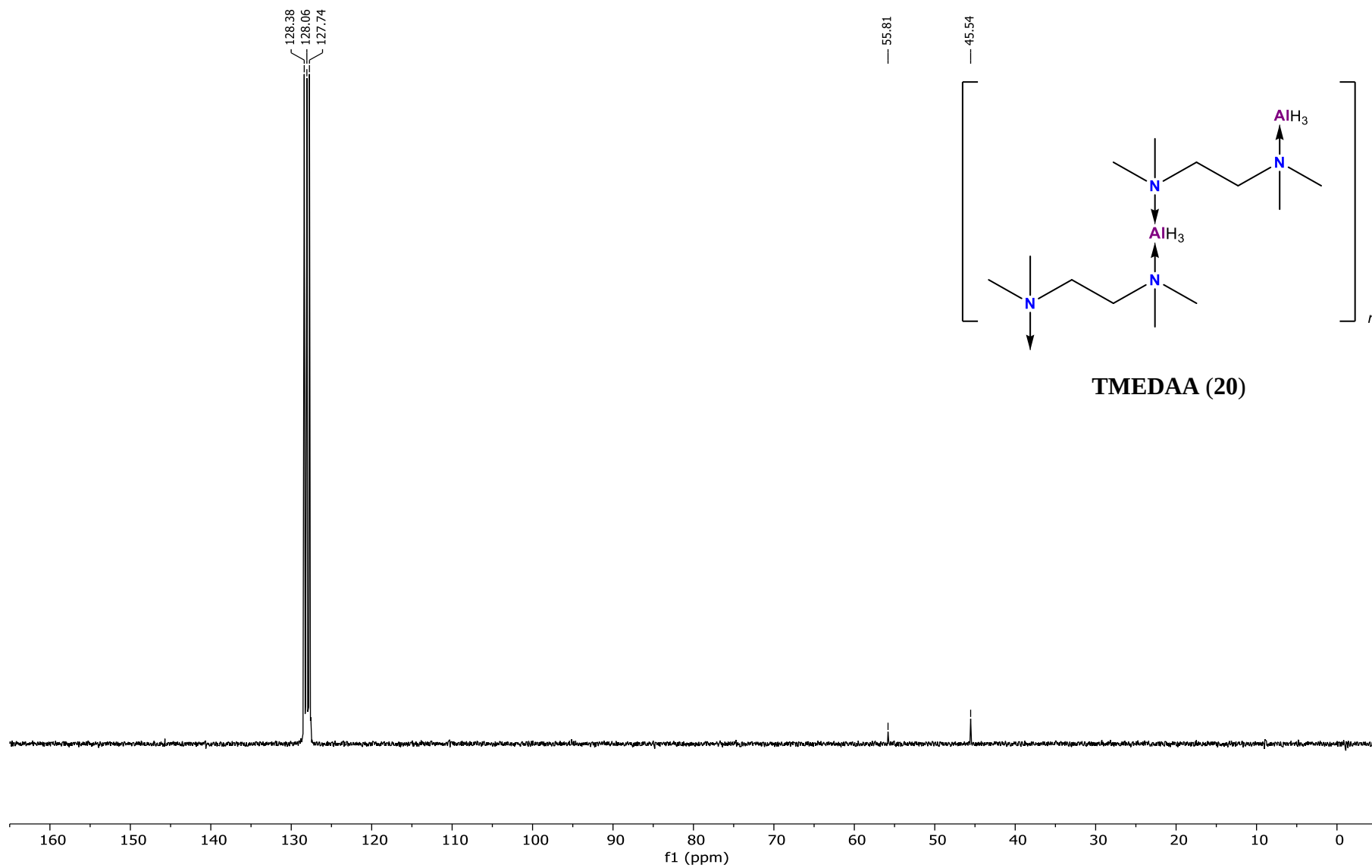
Appendix 86: ^1H NMR of TAAA (19).



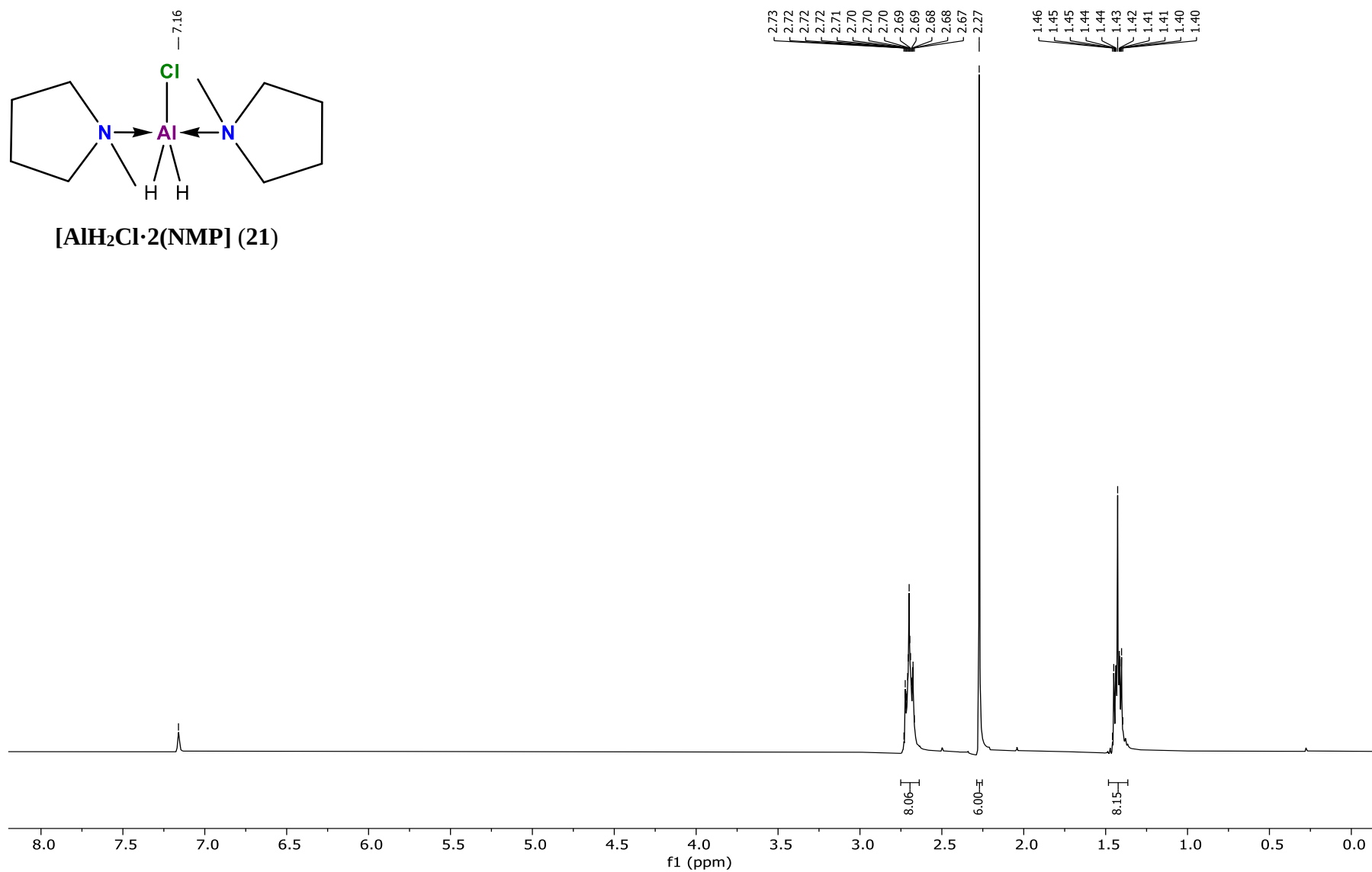
Appendix 87: ^{13}C NMR of TAAA (19).



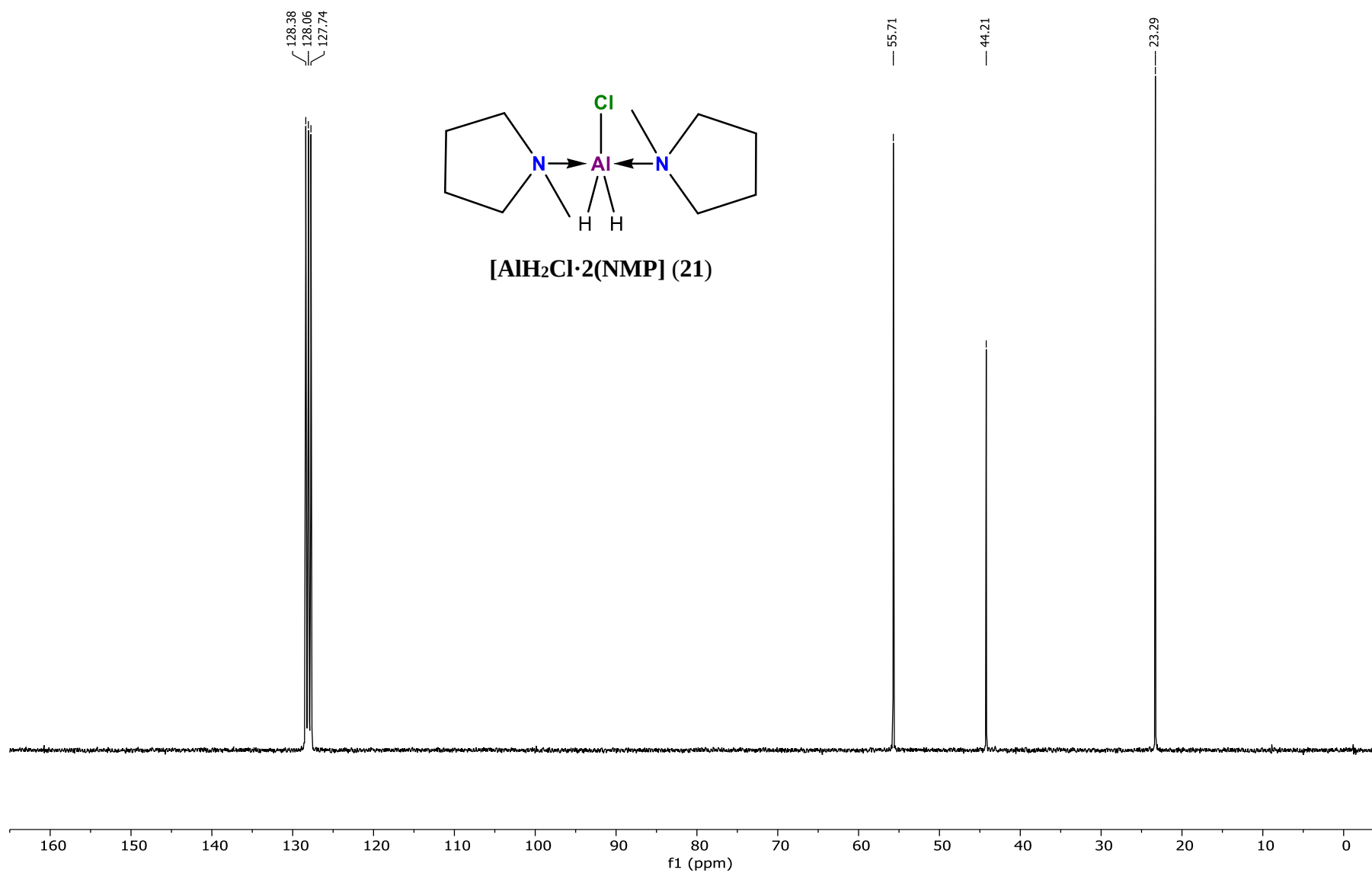
Appendix 88: ¹H NMR of TMEDAA (20).



Appendix 89: ^{13}C NMR of TMEDAA (20).



Appendix 90: ^1H NMR of $[AlH_2Cl \cdot 2(NMP)]$ (21).



Appendix 91: ^{13}C NMR of $[AlH_2Cl \cdot 2(NMP)]$ (21).

Crystallography (Appendix 92–102)

Appendix 92: Crystal data of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Me-acnac})_3]$, 1).	XCVIII
Appendix 93: Crystal data of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Et-acnac})_3]$, 2).	CIII
Appendix 94: Crystal data of $[\text{Al}(\text{MeCN}(\text{iPr})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{iPr-acnac})_3]$, 3).	CVI
Appendix 95: Crystal data of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Ph-acnac})_3]$, 4).	CXII
Appendix 96: Crystal data of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_3]$ ($[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$, 5). ...	CXIX
Appendix 97: Crystal data of $[\text{Al}(\text{MeCN}(\text{Me})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Me-acnac})_2\text{Cl}]$, 6)	CXXVII
Appendix 98: Crystal data of $[\text{Al}(\text{MeCN}(\text{Et})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Et-acnac})_2\text{Cl}]$, 7)...	CXXXI
Appendix 99: Crystal data of $[\text{Al}(\text{MeCN}(\text{iPr})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{iPr-acnac})_2\text{Cl}]$, 8)	CXXXVIII
Appendix 100: Crystal data of $[\text{Al}(\text{MeCN}(\text{Ph})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$, 9). CXLII	
Appendix 101: Crystal data of $[\text{Al}(\text{MeCN}(\text{Ar}^{\text{mes}})\text{CHC}=\text{OMe})_2\text{Cl}]$ ($[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$, 10)	CXLVI
Appendix 102: Crystal data bis(<i>N</i> -methylpyrrolidine) monochloridoalumane, $[\text{AlH}_2\text{Cl} \cdot 2(\{\text{CH}_3\}_2\text{N}\{\text{CH}_2\}_4)]$ ($[\text{AlH}_2\text{Cl} \cdot 2(\text{NMP})]$, 21)	CL

Appendix 92: Crystal data of $[Al(MeCN(Me)CHC=OMe)_3]$ ($[Al(Me-acnac)_3]$, **1**).

Crystal data and structure refinement for compound **21**.

Empirical formula	C ₁₈ H ₃₀ AlN ₃ O ₃
Formula weight	363.43
Temperature/K	150.03(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.4187(3)
b/Å	9.4139(3)
c/Å	13.8037(4)
$\alpha/^\circ$	100.453(2)
$\beta/^\circ$	102.868(3)
$\gamma/^\circ$	104.650(3)
Volume/Å ³	998.51(6)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.209
μ/mm^{-1}	1.059
F(000)	392.0
Crystal size/mm ³	0.26 × 0.2 × 0.19
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	10.036 to 145.598
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -17 ≤ l ≤ 16
Reflections collected	15602
Independent reflections	3880 [R_{int} = 0.0286, R_{sigma} = 0.0202]
Data/restraints/parameters	3880/0/235
Goodness-of-fit on F ²	1.061
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0334, wR_2 = 0.0898
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0928

Largest diff. peak/hole / e Å⁻³ 0.27/-0.20

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for compound **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Al1	5442.9(4)	2364.4(4)	2720.0(2)	19.34(11)
O1	3429.9(10)	2922.7(9)	2559.9(6)	22.21(19)
O2	7486.6(11)	1910.9(10)	2806.7(6)	25.0(2)
O3	4084.6(11)	336.9(9)	2316.8(6)	23.16(19)
N3	5321.2(13)	2318.8(12)	1228.4(8)	21.9(2)
N1	6735.3(13)	4623.7(12)	3173.5(8)	23.2(2)
N2	5663.6(13)	2329.9(12)	4211.9(8)	24.1(2)
C1	3159.5(16)	4018.8(15)	2169.7(9)	24.6(3)
C7	8341.5(16)	1390.8(13)	3481.6(10)	24.9(3)
C13	2825.1(16)	-249.2(14)	1480.7(9)	23.5(3)
C14	2677.1(17)	298.6(15)	623.9(9)	26.9(3)
C3	6153.3(16)	5650.3(14)	2822.9(9)	24.2(3)
C8	8004.0(18)	1283.9(15)	4394.7(10)	29.2(3)
C9	6741.2(17)	1799.5(14)	4763.4(9)	27.4(3)
C15	3987.6(17)	1473.1(14)	476.3(9)	25.1(3)
C2	4423.4(17)	5304.7(15)	2230.4(10)	26.5(3)
C18	6718.6(17)	3328.1(16)	974.8(10)	28.5(3)
C5	7280.7(19)	7259.5(15)	3029.2(11)	33.6(3)
C10	9803.6(17)	937.2(16)	3213.5(12)	33.1(3)
C16	1517.2(18)	-1669.2(15)	1482.8(11)	30.9(3)
C6	8474.9(17)	5129.2(16)	3873.5(11)	33.1(3)
C12	4483(2)	2876.1(19)	4707.1(11)	38.1(3)
C17	3776.8(19)	1638.5(18)	-607.5(10)	35.2(3)

C11	6745(2)	1729.7(18)	5847.5(11)	40.3(4)
C4	1315.6(18)	3813.6(18)	1659.3(13)	39.4(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Al1	18.81(19)	21.65(19)	16.50(18)	5.46(14)	2.99(14)	5.64(14)
O1	21.6(4)	24.0(4)	22.4(4)	7.7(3)	6.4(3)	7.7(3)
O2	21.7(4)	31.3(5)	23.5(4)	10.8(4)	4.1(3)	9.8(4)
O3	24.9(4)	22.7(4)	19.5(4)	5.8(3)	2.5(3)	6.3(3)
N3	22.0(5)	25.5(5)	20.6(5)	7.6(4)	6.8(4)	9.4(4)
N1	21.6(5)	25.1(5)	19.4(5)	5.3(4)	3.2(4)	3.8(4)
N2	25.2(5)	25.2(5)	18.3(5)	4.5(4)	4.4(4)	3.9(4)
C1	26.3(6)	28.9(6)	21.5(6)	6.7(5)	6.9(5)	13.0(5)
C7	21.5(6)	18.9(6)	29.2(6)	7.2(5)	0.1(5)	3.0(5)
C13	24.1(6)	21.8(6)	22.4(6)	1.4(5)	4.3(5)	8.1(5)
C14	25.4(6)	28.4(7)	20.4(6)	2.5(5)	-0.6(5)	6.1(5)
C3	30.1(7)	23.0(6)	19.7(6)	5.5(5)	9.7(5)	6.2(5)
C8	33.3(7)	26.3(6)	25.6(6)	10.4(5)	-0.4(5)	9.7(5)
C9	35.0(7)	21.3(6)	20.2(6)	6.0(5)	2.7(5)	2.5(5)
C15	29.3(7)	28.3(6)	19.4(6)	6.0(5)	4.9(5)	13.7(5)
C2	31.9(7)	25.7(6)	25.7(6)	10.3(5)	8.3(5)	12.6(5)
C18	28.2(7)	35.4(7)	25.7(6)	10.7(5)	12.2(5)	10.2(5)
C5	40.8(8)	25.5(7)	32.0(7)	9.0(5)	11.0(6)	3.7(6)
C10	24.4(7)	33.3(7)	43.0(8)	15.6(6)	4.5(6)	11.1(6)
C16	30.3(7)	27.3(7)	29.6(7)	4.5(5)	5.0(5)	4.1(5)
C6	26.0(7)	30.7(7)	31.5(7)	5.9(6)	-2.8(5)	0.2(5)
C12	38.7(8)	56.5(9)	22.2(7)	8.7(6)	11.6(6)	18.2(7)
C17	40.5(8)	42.9(8)	20.5(6)	9.9(6)	4.5(6)	11.9(6)
C11	57.6(10)	41.6(8)	23.0(7)	12.9(6)	7.6(6)	17.2(7)

C4	28.3(7)	43.5(8)	49.6(9)	20.0(7)	5.1(6)	15.7(6)

Bond Lengths for compound **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O1	1.8769(9)	N2	C12	1.4671(18)
Al1	O2	1.8589(9)	C1	C2	1.3699(18)
Al1	O3	1.8675(9)	C1	C4	1.5017(18)
Al1	N3	2.0306(10)	C7	C8	1.3676(19)
Al1	N1	2.0352(11)	C7	C10	1.4986(19)
Al1	N2	2.0331(11)	C13	C14	1.3668(18)
O1	C1	1.2934(15)	C13	C16	1.5026(18)
O2	C7	1.2926(15)	C14	C15	1.4305(18)
O3	C13	1.2995(15)	C3	C2	1.4244(18)
N3	C15	1.3042(16)	C3	C5	1.5075(17)
N3	C18	1.4656(16)	C8	C9	1.427(2)
N1	C3	1.3084(17)	C9	C11	1.5092(18)
N1	C6	1.4681(16)	C15	C17	1.5080(17)
N2	C9	1.3082(17)			

Bond Angles for compound **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	N3	89.80(4)	C9	N2	Al1	125.04(9)
O1	Al1	N1	86.73(4)	C9	N2	C12	116.62(11)
O1	Al1	N2	93.56(4)	C12	N2	Al1	118.29(8)
O2	Al1	O1	175.27(4)	O1	C1	C2	123.90(12)
O2	Al1	O3	94.46(4)	O1	C1	C4	114.93(11)
O2	Al1	N3	86.41(4)	C2	C1	C4	121.14(12)
O2	Al1	N1	90.54(4)	O2	C7	C8	123.98(12)

O2	Al1	N2	90.30(4)	O2	C7	C10	115.16(11)
O3	Al1	O1	88.33(4)	C8	C7	C10	120.84(12)
O3	Al1	N3	89.56(4)	O3	C13	C14	124.73(12)
O3	Al1	N1	174.93(4)	O3	C13	C16	115.07(11)
O3	Al1	N2	89.38(4)	C14	C13	C16	120.14(11)
N3	Al1	N1	91.56(4)	C13	C14	C15	124.45(11)
N3	Al1	N2	176.45(4)	N1	C3	C2	121.69(11)
N2	Al1	N1	89.79(4)	N1	C3	C5	121.60(12)
C1	O1	Al1	125.16(8)	C2	C3	C5	116.71(11)
C7	O2	Al1	130.37(8)	C7	C8	C9	125.42(12)
C13	O3	Al1	123.96(8)	N2	C9	C8	122.69(11)
C15	N3	Al1	122.17(8)	N2	C9	C11	121.51(13)
C15	N3	C18	117.89(10)	C8	C9	C11	115.78(12)
C18	N3	Al1	119.83(8)	N3	C15	C14	121.99(11)
C3	N1	Al1	123.76(8)	N3	C15	C17	121.76(12)
C3	N1	C6	117.55(11)	C14	C15	C17	116.21(11)
C6	N1	Al1	118.52(9)	C1	C2	C3	123.36(11)

Appendix 93: Crystal data of $[Al(MeCN(Et)CHC=OMe)_3]$ ($[Al(Et-acnac)_3]$, 2).

Crystal data and structure refinement for compound 2.

Empirical formula	$C_{21}H_{36}AlN_3O_3$
Formula weight	405.51
Temperature/K	150.02(10)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	10.0045(2)
$b/\text{\AA}$	16.6360(2)
$c/\text{\AA}$	13.8351(2)
$\alpha/^\circ$	90
$\beta/^\circ$	98.5520(10)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2277.04(6)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.183
μ/mm^{-1}	0.977
$F(000)$	880.0
Crystal size/ mm^3	$0.18 \times 0.14 \times 0.09$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	8.368 to 146.844
Index ranges	$-12 \leq h \leq 12, -20 \leq k \leq 20, -17 \leq l \leq 17$
Reflections collected	35979
Independent reflections	4558 [$R_{\text{int}} = 0.0396, R_{\text{sigma}} = 0.0175$]
Data/restraints/parameters	4558/0/262
Goodness-of-fit on F^2	1.024
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0358, wR_2 = 0.0957$
Final R indexes [all data]	$R_1 = 0.0396, wR_2 = 0.1003$

Largest diff. peak/hole / e Å⁻³ 0.31/-0.21

Bond Lengths for compound 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O1	1.8613(9)	C8	C9	1.3656(19)
Al1	O2	1.8512(9)	C8	C11	1.5030(17)
Al1	O3	1.8693(9)	C1	C2	1.3662(19)
Al1	N2	2.0442(10)	C1	C4	1.5011(18)
Al1	N1	2.0498(10)	C2	C3	1.4222(19)
Al1	N3	2.0469(11)	C3	C5	1.5170(17)
O1	C1	1.2966(15)	C10	C9	1.4348(18)
O2	C8	1.2930(15)	C10	C12	1.5143(18)
O3	C15	1.2893(15)	C15	C16	1.373(2)
N2	C10	1.3044(16)	C15	C18	1.5035(18)
N2	C13	1.4750(15)	C13	C14	1.5178(19)
N1	C3	1.3122(16)	C6	C7	1.5230(18)
N1	C6	1.4764(16)	C20	C21	1.5209(19)
N3	C20	1.4729(16)	C16	C17	1.429(2)
N3	C17	1.3072(17)	C17	C19	1.5182(19)

Bond Angles for compound 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	O3	88.00(4)	C17	N3	C20	118.10(11)
O1	Al1	N2	92.92(4)	O2	C8	C9	124.48(11)
O1	Al1	N1	88.10(4)	O2	C8	C11	114.44(11)
O1	Al1	N3	89.01(4)	C9	C8	C11	121.08(12)
O2	Al1	O1	176.30(4)	O1	C1	C2	124.36(12)
O2	Al1	O3	93.52(4)	O1	C1	C4	114.84(12)
O2	Al1	N2	90.56(4)	C2	C1	C4	120.78(12)
O2	Al1	N1	90.66(4)	C1	C2	C3	123.59(11)
O2	Al1	N3	87.64(4)	N1	C3	C2	122.31(11)
O3	Al1	N2	85.72(4)	N1	C3	C5	122.96(12)
O3	Al1	N1	173.84(4)	C2	C3	C5	114.71(11)
O3	Al1	N3	88.87(4)	N2	C10	C9	122.62(11)
N2	Al1	N1	89.72(4)	N2	C10	C12	122.60(12)
N2	Al1	N3	174.19(4)	C9	C10	C12	114.78(11)
N3	Al1	N1	95.82(4)	O3	C15	C16	124.03(12)
C1	O1	Al1	125.95(8)	O3	C15	C18	114.52(12)
C8	O2	Al1	129.76(8)	C16	C15	C18	121.44(12)
C15	O3	Al1	124.55(8)	N2	C13	C14	112.18(10)
C10	N2	Al1	124.25(8)	C8	C9	C10	125.39(12)
C10	N2	C13	117.99(10)	N1	C6	C7	114.04(11)
C13	N2	Al1	116.97(8)	N3	C20	C21	111.96(11)
C3	N1	Al1	123.55(9)	C15	C16	C17	124.32(12)
C3	N1	C6	118.51(10)	N3	C17	C16	122.72(12)
C6	N1	Al1	117.89(8)	N3	C17	C19	122.22(13)
C20	N3	Al1	120.26(8)	C16	C17	C19	115.06(12)
C17	N3	Al1	121.58(9)				

Appendix 94: Crystal data of $[Al(MeCN(iPr)CHC=OMe)_3]$ ($[Al(iPr-acnac)_3]$, **3**).Crystal data and structure refinement for compound **3**.

Empirical formula	C ₂₄ H ₄₂ AlN ₃ O ₃
Formula weight	447.58
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.8466(3)
b/Å	11.4889(3)
c/Å	11.7060(4)
$\alpha/^\circ$	84.747(2)
$\beta/^\circ$	82.406(2)
$\gamma/^\circ$	77.341(2)
Volume/Å ³	1278.05(7)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.163
μ/mm^{-1}	0.913
F(000)	488.0
Crystal size/mm ³	0.25 × 0.2 × 0.2
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	7.636 to 146.79
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -13 ≤ l ≤ 14
Reflections collected	19433
Independent reflections	5044 [R_{int} = 0.0259, R_{sigma} = 0.0208]
Data/restraints/parameters	5044/0/292
Goodness-of-fit on F ²	1.071
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0353, wR_2 = 0.0891
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.0938

Largest diff. peak/hole / e Å⁻³ 0.29/-0.21

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Al1	7110.2(4)	7699.9(3)	2784.4(3)	18.62(10)
O1	9057.0(9)	7510.7(8)	2516.6(8)	21.61(19)
O2	5195.0(9)	7826.5(8)	3005.4(8)	22.7(2)
O3	7028.6(10)	9342.9(8)	2808.0(8)	25.8(2)
N2	7149.0(11)	7593.6(9)	4546.2(9)	20.3(2)
N1	7411.1(11)	5868.1(9)	2746.0(9)	20.0(2)
N3	6947.2(11)	7954.5(10)	1044.9(9)	24.2(2)
C9	4338.9(13)	8356.3(11)	3834.8(11)	21.4(3)
C10	4721.5(13)	8568.9(11)	4858.4(11)	23.7(3)
C11	6084.1(14)	8135.9(11)	5230.3(11)	21.9(3)
C1	9890.3(13)	6784.7(12)	1831.3(11)	22.4(3)
C2	9602.1(13)	5741.9(11)	1547.1(11)	23.5(3)
C3	8457.1(13)	5247.0(11)	2092.2(11)	21.9(3)
C6	6388.2(14)	5271.2(12)	3503.2(12)	26.0(3)
C13	6117.9(15)	8344.2(13)	6484.3(12)	29.1(3)
C19	7556.7(15)	8728.6(13)	404.6(12)	30.2(3)
C14	8521.3(13)	7050.6(12)	4979.0(12)	24.4(3)
C17	7740.6(15)	9904.9(12)	2019.0(13)	30.8(3)
C12	2830.7(14)	8702.5(13)	3609.2(13)	30.0(3)
C18	8092.0(16)	9598.3(12)	901.0(13)	32.7(3)
C22	6073.1(15)	7258.7(13)	561.2(12)	29.7(3)
C7	7059.9(17)	4196.2(13)	4261.7(13)	34.4(3)
C5	8605.3(16)	3945.0(12)	1865.0(13)	31.2(3)
C16	9373.8(15)	7997.2(14)	5069.7(14)	32.9(3)

C15	8475.9(16)	6191.2(13)	6055.9(13)	32.2(3)
C4	11251.6(15)	7135.0(15)	1370.6(14)	35.9(3)
C8	5237.0(16)	4993.3(15)	2877.9(15)	38.4(4)
C21	7737(2)	8806.3(16)	-906.8(13)	45.3(4)
C23	4740.5(17)	8062.8(17)	161.9(15)	43.3(4)
C24	6831.1(19)	6373.7(16)	-335.0(15)	44.0(4)
C20	8153(2)	10974.6(15)	2406.5(17)	51.4(5)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Al1	19.83(19)	17.42(18)	17.8(2)	-2.76(13)	-0.20(14)	-2.60(13)
O1	21.7(4)	22.0(4)	21.0(5)	-4.1(3)	0.2(4)	-4.8(3)
O2	21.1(4)	25.0(4)	21.4(5)	-6.3(4)	-1.6(4)	-2.1(3)
O3	30.4(5)	18.5(4)	26.3(5)	-2.9(4)	4.7(4)	-4.5(4)
N2	20.3(5)	20.3(5)	20.4(5)	-2.4(4)	-1.9(4)	-4.3(4)
N1	20.1(5)	19.7(5)	20.5(5)	-2.0(4)	-0.6(4)	-5.1(4)
N3	24.4(5)	24.8(5)	20.5(6)	-3.2(4)	-1.8(4)	1.4(4)
C9	20.5(6)	18.8(6)	23.8(7)	-1.8(5)	0.5(5)	-3.5(5)
C10	22.0(6)	24.9(6)	22.2(7)	-5.2(5)	2.6(5)	-2.3(5)
C11	25.7(6)	20.9(6)	19.7(6)	-3.2(5)	-0.7(5)	-6.3(5)
C1	21.0(6)	26.3(6)	18.8(6)	-1.0(5)	-1.7(5)	-3.0(5)
C2	22.7(6)	24.5(6)	20.8(7)	-5.6(5)	2.1(5)	-0.9(5)
C3	24.5(6)	19.9(6)	20.9(6)	-3.0(5)	-4.7(5)	-1.8(5)
C6	25.4(7)	23.6(6)	29.3(7)	-3.2(5)	4.0(5)	-9.1(5)
C13	31.4(7)	33.9(7)	20.9(7)	-6.7(5)	-1.7(6)	-3.5(6)
C19	31.2(7)	30.1(7)	22.2(7)	2.3(5)	1.7(6)	4.5(6)
C14	22.6(6)	26.5(6)	23.7(7)	-1.8(5)	-4.1(5)	-3.4(5)
C17	32.8(7)	18.9(6)	36.8(8)	0.7(6)	5.2(6)	-3.3(5)

C12	21.4(6)	35.7(7)	31.6(8)	-6.1(6)	-1.8(6)	-2.2(5)
C18	36.5(8)	25.9(7)	30.1(8)	6.4(6)	5.8(6)	-3.5(6)
C22	29.3(7)	35.9(7)	22.9(7)	-7.3(6)	-6.1(6)	-0.4(6)
C7	40.1(8)	26.0(7)	34.6(8)	1.5(6)	6.2(6)	-9.1(6)
C5	35.6(8)	22.5(7)	34.6(8)	-9.1(6)	1.9(6)	-4.8(6)
C16	26.9(7)	37.9(8)	36.5(8)	-1.4(6)	-8.2(6)	-10.2(6)
C15	32.3(7)	34.4(7)	28.2(8)	2.5(6)	-6.6(6)	-3.3(6)
C4	27.8(7)	42.7(8)	39.1(9)	-13.6(7)	7.2(6)	-13.6(6)
C8	30.5(8)	40.8(8)	48.2(10)	-7.2(7)	-0.8(7)	-17.2(7)
C21	56.6(11)	50.4(10)	22.1(8)	4.4(7)	2.7(7)	-3.5(8)
C23	30.5(8)	56.9(10)	38.7(9)	-6.6(8)	-8.9(7)	3.5(7)
C24	44.7(9)	51.9(10)	33.4(9)	-19.9(7)	-9.3(7)	3.8(8)
C20	66.3(12)	30.3(8)	58.1(12)	-10.7(8)	19.9(9)	-23.7(8)

Bond Lengths for compound **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O1	1.8684(9)	C10	C11	1.4350(18)
Al1	O2	1.8445(9)	C11	C13	1.5146(18)
Al1	O3	1.8743(9)	C1	C2	1.3688(18)
Al1	N2	2.0597(11)	C1	C4	1.5017(18)
Al1	N1	2.0638(11)	C2	C3	1.4234(18)
Al1	N3	2.0530(12)	C3	C5	1.5155(17)
O1	C1	1.2888(15)	C6	C7	1.532(2)
O2	C9	1.3003(15)	C6	C8	1.531(2)
O3	C17	1.2960(16)	C19	C18	1.425(2)
N2	C11	1.3084(16)	C19	C21	1.519(2)
N2	C14	1.4918(16)	C14	C16	1.5309(19)
N1	C3	1.3135(16)	C14	C15	1.5305(19)

N1	C6	1.4919(16)	C17	C18	1.367(2)
N3	C19	1.3061(18)	C17	C20	1.500(2)
N3	C22	1.4878(18)	C22	C23	1.532(2)
C9	C10	1.3603(19)	C22	C24	1.5320(19)
C9	C12	1.5030(18)			

Bond Angles for compound 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	O3	87.06(4)	C10	C9	C12	120.45(12)
O1	Al1	N2	91.73(4)	C9	C10	C11	125.22(12)
O1	Al1	N1	87.34(4)	N2	C11	C10	122.20(12)
O1	Al1	N3	91.19(4)	N2	C11	C13	125.14(12)
O2	Al1	O1	177.26(4)	C10	C11	C13	112.63(11)
O2	Al1	O3	95.21(4)	O1	C1	C2	123.64(12)
O2	Al1	N2	89.89(4)	O1	C1	C4	115.57(11)
O2	Al1	N1	90.40(4)	C2	C1	C4	120.78(12)
O2	Al1	N3	87.36(4)	C1	C2	C3	124.13(11)
O3	Al1	N2	87.39(4)	N1	C3	C2	122.22(11)
O3	Al1	N1	174.38(5)	N1	C3	C5	124.66(12)
O3	Al1	N3	88.40(4)	C2	C3	C5	113.09(11)
N2	Al1	N1	92.24(4)	N1	C6	C7	114.40(11)
N3	Al1	N2	174.75(4)	N1	C6	C8	114.23(12)
N3	Al1	N1	92.25(4)	C8	C6	C7	112.17(12)
C1	O1	Al1	126.10(8)	N3	C19	C18	121.62(13)
C9	O2	Al1	125.93(8)	N3	C19	C21	124.11(14)
C17	O3	Al1	121.52(8)	C18	C19	C21	114.26(13)
C11	N2	Al1	121.19(9)	N2	C14	C16	111.48(11)
C11	N2	C14	121.37(11)	N2	C14	C15	116.31(11)

C14	N2	Al1	116.66(8)	C15	C14	C16	112.98(12)
C3	N1	Al1	121.94(8)	O3	C17	C18	124.67(13)
C3	N1	C6	121.06(10)	O3	C17	C20	114.98(13)
C6	N1	Al1	117.00(8)	C18	C17	C20	120.33(13)
C19	N3	Al1	120.62(10)	C17	C18	C19	124.31(13)
C19	N3	C22	121.91(12)	N3	C22	C23	111.87(12)
C22	N3	Al1	117.44(9)	N3	C22	C24	116.54(12)
O2	C9	C10	124.54(12)	C23	C22	C24	112.40(13)
O2	C9	C12	114.99(11)				

Appendix 95: Crystal data of $[Al(MeCN(Ph)CHC=OMe)_3]$ ($[Al(Ph-acnac)_3]$, **4**).

Crystal data and structure refinement for compound **4**.

Empirical formula	$C_{33}H_{36}AlN_3O_3$
Formula weight	549.65
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.27860(10)
b/Å	13.55250(10)
c/Å	33.3317(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	5998.31(7)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.2172
μ/mm^{-1}	0.886
F(000)	2344.4
Crystal size/mm ³	$0.4 \times 0.2 \times 0.02$
Radiation	Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	8.52 to 147.06
Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 16, -41 \leq l \leq 41$
Reflections collected	97192
Independent reflections	6023 [$R_{\text{int}} = 0.0485, R_{\text{sigma}} = 0.0140$]
Data/restraints/parameters	6023/0/367
Goodness-of-fit on F^2	1.049
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0380, wR_2 = 0.1012$
Final R indexes [all data]	$R_1 = 0.0402, wR_2 = 0.1041$

Largest diff. peak/hole / e Å⁻³ 0.27/-0.27

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Al1	4992.1(2)	2687.1(2)	6153.82(9)	19.73(10)
O3	4709.5(6)	1541.7(6)	5864.4(2)	23.61(18)
O1	4288.9(6)	3388.7(6)	5765.0(2)	23.97(18)
O2	5735.3(6)	2055.3(6)	6541.8(2)	24.78(18)
N1	5183.0(7)	3991.8(7)	6461.1(3)	22.9(2)
N2	3695.3(7)	2379.3(7)	6457.5(3)	22.8(2)
N3	6293.6(7)	2841.8(7)	5829.5(3)	23.8(2)
C23	4866.4(9)	1439.3(9)	5484.2(3)	23.9(2)
C6	5462.0(9)	3938.2(9)	6879.4(4)	25.9(2)
C18	2498.8(10)	3731.2(10)	6359.5(4)	29.2(3)
C14	3622.6(9)	1740.3(9)	6752.2(4)	27.1(3)
C24	5642.3(9)	1884.5(10)	5281.5(4)	29.7(3)
C1	4306.2(9)	4304.6(9)	5672.5(4)	27.6(3)
C12	5460.9(10)	1517.3(9)	6842.3(3)	26.6(3)
C28	7142.2(9)	3377.6(9)	5986.8(4)	26.4(2)
C17	2785.8(8)	2762.2(9)	6285.3(3)	24.1(2)
C25	6389.4(9)	2482.9(9)	5464.5(4)	28.5(3)
C7	4724.5(11)	3779.9(10)	7165.5(4)	33.3(3)
C26	4145.7(10)	769.4(10)	5271.7(4)	30.4(3)
C13	4479.2(10)	1318.9(9)	6941.2(4)	30.7(3)
C29	7271.6(10)	4371.8(10)	5900.4(4)	34.1(3)
C20	1075.7(10)	3546.0(11)	5921.2(4)	35.4(3)
C19	1642.8(10)	4120.0(10)	6179.2(4)	34.0(3)
C22	2221.5(10)	2192.2(9)	6021.5(4)	30.3(3)

C2	4701.8(10)	5030.2(9)	5912.7(4)	32.7(3)
C21	1369.0(10)	2588.5(11)	5841.4(4)	35.1(3)
C3	5059.3(9)	4876.7(9)	6308.5(4)	28.0(3)
C11	6459.3(10)	4022.7(11)	6997.6(4)	36.1(3)
C33	7844.3(9)	2895.4(10)	6225.0(4)	32.4(3)
C30	8104.3(11)	4876.9(11)	6049.9(5)	43.4(4)
C15	6313.5(11)	1130.1(11)	7091.2(4)	38.0(3)
C32	8675.7(10)	3405.9(11)	6370.3(5)	41.4(3)
C5	5275.1(12)	5792.5(10)	6551.5(5)	40.9(3)
C4	3808.7(12)	4555.6(11)	5280.2(4)	43.2(3)
C8	4983.1(13)	3698.2(12)	7568.1(4)	43.1(4)
C31	8805.1(10)	4392.7(12)	6282.6(5)	45.8(4)
C9	5972.3(14)	3777.4(12)	7686.1(4)	47.7(4)
C16	2607.5(11)	1439.3(11)	6918.3(4)	40.3(3)
C10	6708.7(12)	3943.4(12)	7401.1(5)	47.1(4)
C27	7325.7(11)	2677.5(13)	5221.9(4)	44.6(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Al1	20.83(18)	17.24(19)	21.13(18)	0.22(12)	0.86(11)	0.15(12)
O3	27.0(4)	20.3(4)	23.5(4)	-1.2(3)	1.9(3)	-0.7(3)
O1	23.8(4)	21.8(4)	26.3(4)	1.0(3)	0.4(3)	2.7(3)
O2	28.4(4)	21.5(4)	24.4(4)	2.2(3)	-1.6(3)	0.6(3)
N1	22.5(4)	19.3(5)	26.8(5)	0.5(4)	0.7(4)	-1.9(4)
N2	24.7(5)	19.2(5)	24.4(5)	0.5(4)	2.9(4)	0.0(4)
N3	21.2(5)	23.6(5)	26.6(5)	-0.9(4)	1.5(4)	-0.5(4)
C23	27.0(6)	19.8(5)	25.0(5)	4.3(4)	-2.0(4)	-1.1(4)
C6	30.5(6)	19.0(6)	28.3(6)	2.4(5)	-2.2(5)	-6.8(4)

C18	28.7(6)	28.6(6)	30.1(6)	2.5(5)	4.8(5)	-1.3(5)
C14	34.9(6)	20.0(6)	26.4(6)	0.8(5)	8.2(5)	-0.4(4)
C24	33.7(6)	32.8(7)	22.5(5)	-1.5(5)	2.7(5)	-4.1(5)
C1	24.2(5)	25.4(6)	33.3(6)	2.0(5)	2.2(5)	7.2(5)
C12	38.6(7)	17.2(5)	23.8(5)	4.6(5)	-3.1(5)	-1.6(4)
C28	20.6(5)	26.1(6)	32.7(6)	-1.2(4)	4.7(4)	-4.8(5)
C17	21.8(5)	24.9(6)	25.6(5)	0.1(4)	6.4(4)	3.2(4)
C25	28.3(6)	29.7(6)	27.6(6)	-0.6(5)	5.5(5)	0.6(5)
C7	36.9(7)	33.6(7)	29.3(6)	1.0(5)	0.6(5)	-6.4(5)
C26	32.7(6)	28.6(6)	29.7(6)	-0.9(5)	-3.8(5)	-3.8(5)
C13	42.1(7)	23.4(6)	26.5(6)	4.0(5)	4.4(5)	6.3(5)
C29	26.8(6)	27.9(7)	47.6(7)	-1.8(5)	8.4(5)	-0.4(5)
C20	23.8(6)	44.6(8)	37.7(7)	1.4(5)	3.6(5)	13.6(6)
C19	32.6(6)	32.2(7)	37.2(7)	8.9(5)	8.2(5)	4.5(5)
C22	30.1(6)	25.4(6)	35.5(6)	-4.9(5)	2.1(5)	1.6(5)
C2	36.2(7)	19.9(6)	42.1(7)	1.2(5)	-2.4(5)	8.1(5)
C21	29.0(6)	39.3(7)	36.9(7)	-10.1(5)	-2.6(5)	7.4(6)
C3	23.9(6)	20.6(6)	39.6(7)	0.6(4)	1.9(5)	-2.1(5)
C11	31.6(7)	36.5(7)	40.3(7)	2.8(5)	-5.8(5)	-12.5(6)
C33	26.4(6)	29.9(7)	40.8(7)	2.0(5)	-1.1(5)	-6.9(5)
C30	32.0(7)	28.4(7)	69.7(10)	-7.8(6)	15.7(7)	-12.2(7)
C15	46.8(8)	32.8(7)	34.3(7)	4.4(6)	-12.3(6)	4.4(5)
C32	25.8(6)	44.6(8)	53.8(9)	5.1(6)	-5.2(6)	-18.7(7)
C5	46.6(8)	20.8(6)	55.3(9)	-0.3(6)	-8.2(7)	-4.2(6)
C4	49.5(8)	37.1(8)	43.0(8)	-0.6(6)	-12.5(6)	13.6(6)
C8	59.5(9)	42.1(8)	27.6(7)	0.7(7)	1.4(6)	-6.1(6)
C31	22.3(6)	44.3(9)	70.8(10)	-5.7(6)	6.5(6)	-28.9(8)
C9	71.5(11)	39.3(8)	32.2(7)	13.1(7)	-16.6(7)	-10.8(6)

C16	40.9(7)	36.1(8)	43.9(7)	2.7(6)	16.9(6)	12.3(6)
C10	46.1(8)	46.4(9)	48.8(8)	12.1(7)	-21.0(7)	-19.3(7)
C27	38.2(7)	57.8(10)	37.9(7)	-11.7(7)	14.5(6)	-9.5(7)

Bond Lengths for compound 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O3	1.8657(8)	C24	C25	1.4190(17)
Al1	O1	1.8589(9)	C1	C2	1.3726(19)
Al1	O2	1.8384(8)	C1	C4	1.5040(17)
Al1	N1	2.0591(10)	C12	C13	1.3713(19)
Al1	N2	2.0406(10)	C12	C15	1.4984(17)
Al1	N3	2.0493(10)	C28	C29	1.3885(18)
O3	C23	1.2917(14)	C28	C33	1.3881(18)
O1	C1	1.2792(15)	C17	C22	1.3897(18)
O2	C12	1.2913(15)	C25	C27	1.5063(17)
N1	C6	1.4444(15)	C7	C8	1.3895(19)
N1	C3	1.3130(16)	C29	C30	1.3925(19)
N2	C14	1.3130(15)	C20	C19	1.383(2)
N2	C17	1.4344(15)	C20	C21	1.381(2)
N3	C28	1.4393(15)	C22	C21	1.3894(19)
N3	C25	1.3164(16)	C2	C3	1.4172(19)
C23	C24	1.3720(17)	C3	C5	1.5096(18)
C23	C26	1.4972(16)	C11	C10	1.389(2)
C6	C7	1.3837(18)	C33	C32	1.3899(18)
C6	C11	1.3865(18)	C30	C31	1.378(2)
C18	C17	1.3896(17)	C32	C31	1.380(2)
C18	C19	1.3895(18)	C8	C9	1.375(2)
C14	C13	1.4200(18)	C9	C10	1.382(3)

C14 C16 1.5133(18)

Bond Angles for compound **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	O3	87.94(4)	C16	C14	C13	116.28(11)
O2	Al1	O3	94.83(4)	C25	C24	C23	124.38(11)
O2	Al1	O1	176.70(4)	C2	C1	O1	124.16(11)
N1	Al1	O3	175.14(4)	C4	C1	O1	114.90(11)
N1	Al1	O1	88.25(4)	C4	C1	C2	120.88(12)
N1	Al1	O2	89.08(4)	C13	C12	O2	124.43(11)
N2	Al1	O3	85.22(4)	C15	C12	O2	114.45(11)
N2	Al1	O1	91.52(4)	C15	C12	C13	121.10(11)
N2	Al1	O2	90.50(4)	C29	C28	N3	120.73(11)
N2	Al1	N1	91.87(4)	C33	C28	N3	119.78(11)
N3	Al1	O3	88.97(4)	C33	C28	C29	119.49(12)
N3	Al1	O1	90.20(4)	C18	C17	N2	120.10(11)
N3	Al1	O2	88.06(4)	C22	C17	N2	120.40(11)
N3	Al1	N1	94.06(4)	C22	C17	C18	119.35(11)
N3	Al1	N2	173.87(4)	C24	C25	N3	122.74(11)
C23	O3	Al1	124.35(8)	C27	C25	N3	120.73(11)
C1	O1	Al1	130.94(8)	C27	C25	C24	116.52(11)
C12	O2	Al1	131.08(8)	C8	C7	C6	120.20(13)
C6	N1	Al1	117.94(7)	C12	C13	C14	125.17(11)
C3	N1	Al1	125.18(8)	C30	C29	C28	120.08(13)
C3	N1	C6	116.87(10)	C21	C20	C19	119.66(12)
C14	N2	Al1	124.61(8)	C20	C19	C18	120.08(13)
C17	N2	Al1	115.98(7)	C21	C22	C17	119.85(12)
C17	N2	C14	118.43(10)	C3	C2	C1	124.47(12)

C28	N3	Al1	121.30(7)	C22	C21	C20	120.66(13)
C25	N3	Al1	122.09(8)	C2	C3	N1	122.45(11)
C25	N3	C28	116.58(10)	C5	C3	N1	121.28(12)
C24	C23	O3	123.85(11)	C5	C3	C2	116.26(11)
C26	C23	O3	115.23(10)	C10	C11	C6	119.77(14)
C26	C23	C24	120.91(11)	C32	C33	C28	119.89(13)
C7	C6	N1	119.45(11)	C31	C30	C29	120.23(14)
C11	C6	N1	121.01(11)	C31	C32	C33	120.51(14)
C11	C6	C7	119.53(12)	C9	C8	C7	120.40(15)
C19	C18	C17	120.38(12)	C32	C31	C30	119.79(13)
C13	C14	N2	122.56(11)	C10	C9	C8	119.47(13)
C16	C14	N2	121.13(11)	C9	C10	C11	120.63(14)

Appendix 96: Crystal data of $[Al(MeCN(Ar^{mes})CHC=OMe)_3]$ ($[Al(Ar^{mes}-acnac)_3]$, 5).

Crystal data and structure refinement for compound 5.

Empirical formula	C ₄₃ H ₅₅ AlN ₃ O ₂
Formula weight	672.88
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	19.971(3)
b/Å	13.5282(7)
c/Å	15.1341(12)
$\alpha/^\circ$	90
$\beta/^\circ$	109.101(11)
$\gamma/^\circ$	90
Volume/Å ³	3863.7(7)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.157
μ/mm^{-1}	0.750
F(000)	1452.0
Crystal size/mm ³	0.3 × 0.2 × 0.05
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	8.042 to 146.69
Index ranges	-24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -10 ≤ l ≤ 18
Reflections collected	21034
Independent reflections	7329 [R_{int} = 0.0638, R_{sigma} = 0.0591]
Data/restraints/parameters	7329/0/457
Goodness-of-fit on F ²	1.052
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.1435, wR_2 = 0.3583
Final R indexes [all data]	R_1 = 0.1667, wR_2 = 0.3772

Largest diff. peak/hole / e Å⁻³ 1.21/-0.76

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 5. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Al1	2827.3(10)	9339.1(11)	2628.8(12)	39.3(5)
O1	1959(2)	9926(3)	2182(3)	45.0(10)
O2	3724(2)	8840(3)	3075(3)	45.1(10)
N1	3126(3)	10021(3)	1660(3)	39.6(11)
O3	2494(2)	8127(3)	2421(3)	47.8(11)
N2	2931(3)	9842(3)	3888(4)	42.3(11)
N3	2405(3)	5153(4)	3190(4)	49.5(13)
C15	4212(4)	8819(5)	3886(5)	46.3(14)
C31	2502(4)	6046(4)	2910(4)	45.1(14)
C6	3805(3)	9782(5)	1590(4)	44.7(14)
C29	1960(3)	7548(4)	1964(4)	41.6(13)
C3	2735(4)	10681(4)	1047(4)	44.1(15)
C1	1667(4)	10546(4)	1517(4)	45.1(15)
C34	1736(4)	4684(4)	2802(5)	47.3(15)
C33	3222(4)	6455(5)	3336(5)	52.3(16)
C17	3494(4)	9753(5)	4649(4)	46.4(14)
C2	2041(4)	10928(4)	976(4)	48.0(16)
C25	1827(4)	9730(5)	4270(4)	49.0(15)
C20	2311(4)	10309(4)	4022(4)	43.5(14)
C30	1960(4)	6568(4)	2191(4)	44.5(15)
C39	1657(4)	3979(5)	2089(4)	52.4(17)
C8	4511(4)	8698(5)	1001(5)	56.6(17)
C16	4119(4)	9287(5)	4663(5)	52.0(16)
C11	4408(4)	10355(5)	2014(4)	48.5(15)

C5	3016(4)	11128(5)	317(5)	55.0(17)
C21	2193(4)	11318(5)	3837(4)	50.1(16)
C32	1350(4)	7988(5)	1210(5)	51.3(16)
C7	3865(4)	8927(4)	1077(4)	46.2(15)
C37	499(4)	3551(5)	2143(5)	57.1(18)
C18	4867(4)	8261(6)	3947(6)	59.2(18)
C22	1567(5)	11716(6)	3891(5)	64(2)
C4	911(4)	10746(5)	1336(5)	56.4(17)
C35	1204(4)	4830(5)	3179(5)	55.6(17)
C12	3238(4)	8254(5)	663(5)	55.4(17)
C9	5111(4)	9261(6)	1386(6)	60.1(18)
C10	5040(4)	10087(6)	1905(6)	60.1(18)
C38	1038(4)	3440(5)	1773(5)	57.7(18)
C19	3490(4)	10166(7)	5580(5)	64(2)
C24	1213(4)	10145(6)	4312(5)	59.5(18)
C23	1071(4)	11163(7)	4124(5)	64(2)
C36	582(4)	4268(5)	2848(5)	56.2(17)
C26	2716(5)	11921(5)	3552(5)	65(2)
C14	4356(4)	11240(5)	2601(5)	59.3(18)
C42	2230(5)	3841(6)	1656(6)	66(2)
C28	1968(4)	8629(5)	4475(5)	60.5(19)
C40	1276(4)	5602(5)	3941(5)	60.1(18)
C41	-156(5)	2933(6)	1819(7)	76(2)
C13	5800(5)	8983(8)	1265(8)	88(3)
C27	379(5)	11574(10)	4154(7)	93(3)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Al1	67.3(12)	22.4(8)	35.1(8)	3.0(6)	26.3(8)	-0.6(7)
O1	70(3)	32(2)	40(2)	3.5(17)	28(2)	4.0(18)
O2	61(3)	35(2)	45(2)	0.0(18)	25(2)	0.5(18)
N1	69(3)	22(2)	34(2)	-1.2(18)	25(2)	-1(2)
O3	75(3)	23.6(19)	49(2)	4.9(17)	25(2)	-2.4(18)
N2	63(3)	26(2)	43(3)	-2.6(19)	24(2)	0(2)
N3	75(4)	28(2)	43(3)	5(2)	16(3)	3(2)
C15	61(4)	34(3)	49(4)	2(3)	26(3)	-3(3)
C31	63(4)	32(3)	42(3)	7(2)	20(3)	-1(3)
C6	61(4)	36(3)	43(3)	7(2)	24(3)	-9(3)
C29	63(4)	32(3)	37(3)	2(2)	25(3)	-5(3)
C3	80(5)	19(2)	41(3)	6(2)	29(3)	-4(2)
C1	90(5)	18(2)	35(3)	6(2)	31(3)	6(2)
C34	65(4)	30(3)	45(3)	6(3)	16(3)	-6(3)
C33	74(5)	36(3)	47(3)	9(3)	20(3)	2(3)
C17	57(4)	45(3)	40(3)	-1(3)	21(3)	-6(3)
C2	85(5)	26(3)	42(3)	13(2)	33(3)	1(3)
C25	67(4)	48(4)	41(3)	5(3)	30(3)	0(3)
C20	79(4)	26(3)	34(3)	-2(2)	30(3)	6(3)
C30	86(5)	18(2)	32(3)	2(2)	23(3)	-6(2)
C39	84(5)	34(3)	39(3)	8(3)	20(3)	-10(3)
C8	73(5)	45(4)	63(4)	6(3)	38(4)	-1(3)
C16	50(4)	55(4)	53(4)	7(3)	21(3)	0(3)
C11	70(4)	40(3)	42(3)	-1(3)	27(3)	-11(3)
C5	94(5)	42(3)	42(3)	9(3)	39(3)	1(3)
C21	82(5)	36(3)	39(3)	-4(2)	28(3)	6(3)

C32	78(5)	31(3)	48(3)	9(3)	24(3)	-3(3)
C7	75(4)	29(3)	43(3)	-6(2)	31(3)	-4(3)
C37	74(5)	39(3)	55(4)	5(3)	16(3)	-8(3)
C18	65(5)	50(4)	68(5)	2(3)	29(4)	3(3)
C22	103(6)	53(4)	40(3)	-5(3)	29(4)	21(4)
C4	78(5)	48(4)	48(4)	11(3)	27(3)	1(3)
C35	74(5)	32(3)	58(4)	9(3)	18(3)	-2(3)
C12	67(5)	44(4)	60(4)	-16(3)	27(3)	-4(3)
C9	63(5)	59(4)	69(5)	4(4)	38(4)	-4(3)
C10	65(5)	50(4)	67(5)	8(3)	23(4)	-14(3)
C38	84(5)	38(3)	51(4)	-2(3)	21(4)	-9(3)
C19	68(5)	78(5)	47(4)	-9(4)	21(3)	2(4)
C24	67(5)	73(5)	47(4)	8(3)	29(3)	3(4)
C23	68(5)	81(6)	47(4)	-9(4)	24(3)	17(4)
C36	71(5)	40(3)	59(4)	2(3)	23(3)	2(3)
C26	132(7)	23(3)	52(4)	0(3)	47(4)	1(3)
C14	90(5)	42(4)	51(4)	-9(3)	31(4)	-17(3)
C42	106(6)	44(4)	55(4)	3(3)	37(4)	-7(4)
C28	89(5)	43(4)	58(4)	10(3)	36(4)	-9(3)
C40	77(5)	44(4)	60(4)	-7(3)	24(4)	4(3)
C41	96(6)	53(5)	81(6)	-6(4)	32(5)	-15(4)
C13	77(6)	75(6)	124(9)	7(6)	52(6)	0(5)
C27	94(7)	127(9)	60(5)	-10(5)	26(5)	42(6)

Bond Lengths for compound 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O1	1.823(5)	C34	C35	1.376(10)
Al1	O2	1.824(5)	C17	C16	1.394(10)

Al1	N1	1.982(5)	C17	C19	1.517(9)
Al1	O3	1.759(4)	C25	C20	1.389(9)
Al1	N2	1.969(5)	C25	C24	1.369(10)
O1	C1	1.294(7)	C25	C28	1.529(10)
O2	C15	1.294(8)	C20	C21	1.398(8)
N1	C6	1.431(8)	C39	C38	1.379(10)
N1	C3	1.339(8)	C39	C42	1.506(11)
O3	C29	1.322(7)	C8	C7	1.368(10)
N2	C17	1.326(8)	C8	C9	1.378(11)
N2	C20	1.462(8)	C11	C10	1.375(11)
N3	C31	1.315(8)	C11	C14	1.514(9)
N3	C34	1.422(9)	C21	C22	1.389(10)
C15	C16	1.399(10)	C21	C26	1.496(10)
C15	C18	1.485(10)	C7	C12	1.509(9)
C31	C33	1.477(9)	C37	C38	1.374(11)
C31	C30	1.444(9)	C37	C36	1.412(10)
C6	C11	1.400(9)	C37	C41	1.493(11)
C6	C7	1.419(9)	C22	C23	1.376(12)
C29	C30	1.369(8)	C35	C36	1.401(10)
C29	C32	1.493(9)	C35	C40	1.526(10)
C3	C2	1.395(9)	C9	C10	1.400(11)
C3	C5	1.518(8)	C9	C13	1.493(11)
C1	C2	1.378(8)	C24	C23	1.415(12)
C1	C4	1.468(10)	C23	C27	1.504(11)
C34	C39	1.410(9)			

Bond Angles for compound 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	O2	175.9(2)	N2	C17	C19	120.9(6)
O1	Al1	N1	90.2(2)	C16	C17	C19	115.5(6)
O1	Al1	N2	89.7(2)	C1	C2	C3	125.6(6)
O2	Al1	N1	87.1(2)	C20	C25	C28	120.3(6)
O2	Al1	N2	89.4(2)	C24	C25	C20	119.7(7)
O3	Al1	O1	94.7(2)	C24	C25	C28	120.0(6)
O3	Al1	O2	89.4(2)	C25	C20	N2	119.4(5)
O3	Al1	N1	119.3(2)	C25	C20	C21	121.2(6)
O3	Al1	N2	114.1(2)	C21	C20	N2	119.3(6)
N2	Al1	N1	126.4(2)	C29	C30	C31	126.9(6)
C1	O1	Al1	134.7(4)	C34	C39	C42	120.4(6)
C15	O2	Al1	134.7(4)	C38	C39	C34	119.1(7)
C6	N1	Al1	118.1(4)	C38	C39	C42	120.4(7)
C3	N1	Al1	125.1(4)	C7	C8	C9	123.5(7)
C3	N1	C6	116.8(5)	C17	C16	C15	123.8(6)
C29	O3	Al1	147.1(4)	C6	C11	C14	119.6(6)
C17	N2	Al1	126.9(4)	C10	C11	C6	119.0(6)
C17	N2	C20	115.7(5)	C10	C11	C14	121.4(6)
C20	N2	Al1	117.3(4)	C20	C21	C26	120.1(6)
C31	N3	C34	119.6(5)	C22	C21	C20	117.6(7)
O2	C15	C16	121.4(6)	C22	C21	C26	122.2(6)
O2	C15	C18	116.4(6)	C6	C7	C12	120.7(6)
C16	C15	C18	122.2(6)	C8	C7	C6	118.8(6)
N3	C31	C33	115.3(6)	C8	C7	C12	120.4(6)
N3	C31	C30	122.6(6)	C38	C37	C36	118.0(7)
C30	C31	C33	121.9(5)	C38	C37	C41	121.6(7)

C11	C6	N1	122.4(6)	C36	C37	C41	120.5(7)
C11	C6	C7	119.2(6)	C23	C22	C21	122.8(7)
C7	C6	N1	118.4(5)	C34	C35	C36	119.2(7)
O3	C29	C30	120.6(6)	C34	C35	C40	121.1(6)
O3	C29	C32	118.7(5)	C36	C35	C40	119.7(7)
C30	C29	C32	120.7(6)	C8	C9	C10	116.4(7)
N1	C3	C2	123.5(5)	C8	C9	C13	121.1(8)
N1	C3	C5	119.9(6)	C10	C9	C13	122.4(8)
C2	C3	C5	116.3(5)	C11	C10	C9	122.9(7)
O1	C1	C2	120.8(6)	C37	C38	C39	122.2(7)
O1	C1	C4	116.1(5)	C25	C24	C23	120.9(7)
C2	C1	C4	123.0(6)	C22	C23	C24	117.8(7)
C39	C34	N3	118.2(6)	C22	C23	C27	123.5(9)
C35	C34	N3	121.0(6)	C24	C23	C27	118.6(9)
C35	C34	C39	120.4(6)	C35	C36	C37	121.0(7)
N2	C17	C16	123.7(6)				

Appendix 97: Crystal data of $[Al(MeCN(Me)CHC=OMe)_2Cl]$ ($[Al(Me-acnac)_2Cl]$, **6**)

Crystal data and structure refinement for compound **6**.

Empirical formula	$C_{12}H_{20}AlClN_2O_2$
Formula weight	286.73
Temperature/K	153(4)
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.92920(10)
b/Å	12.27050(10)
c/Å	24.4057(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	2973.50(5)
Z	8
$\rho_{calc}/\text{g}/\text{cm}^3$	1.281
μ/mm^{-1}	2.827
F(000)	1216.0
Crystal size/mm ³	$0.38 \times 0.2 \times 0.09$
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	7.244 to 145.416
Index ranges	$-12 \leq h \leq 12, -15 \leq k \leq 14, -30 \leq l \leq 30$
Reflections collected	47242
Independent reflections	2956 [$R_{int} = 0.0451, R_{sigma} = 0.0131$]
Data/restraints/parameters	2956/0/169
Goodness-of-fit on F^2	1.068
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0295, wR_2 = 0.0838$
Final R indexes [all data]	$R_1 = 0.0313, wR_2 = 0.0862$

Largest diff. peak/hole / e Å⁻³ 0.26/-0.22

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl1	5681.3(3)	7068.0(3)	3926.0(2)	27.60(11)
Al1	4400.5(4)	5744.9(3)	3589.7(2)	18.53(12)
O1	2962.4(9)	5317.9(7)	3972.4(3)	23.5(2)
O2	4868.8(10)	5196.0(8)	2938.6(3)	25.3(2)
N2	3170.5(11)	6816.8(8)	3236.1(4)	21.4(2)
N1	5535.8(11)	4614.1(9)	3952.4(4)	22.7(2)
C1	2857.6(13)	4701.4(10)	4411.5(5)	23.0(3)
C7	4567.2(13)	5501.5(11)	2437.6(5)	23.2(3)
C9	2970.6(13)	6945.3(10)	2713.7(5)	22.5(3)
C2	3879.7(14)	4105.5(11)	4619.7(5)	24.4(3)
C3	5191.8(14)	4034.0(10)	4377.9(5)	23.0(3)
C8	3682.2(14)	6307.6(11)	2316.4(5)	25.5(3)
C12	2398.0(16)	7508.4(11)	3614.7(5)	30.7(3)
C11	1978.7(15)	7768.0(11)	2497.0(6)	30.8(3)
C10	5293.6(15)	4881.2(12)	1998.1(5)	31.0(3)
C5	6149.0(16)	3232.4(13)	4635.4(6)	34.7(3)
C4	1471.8(15)	4685.3(13)	4653.0(6)	35.1(3)
C6	6917.6(15)	4493.9(14)	3742.1(6)	37.8(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cl1	31.20(19)	28.96(19)	22.65(18)	0.61(11)	-2.14(11)	-10.00(12)
Al1	20.4(2)	19.9(2)	15.27(19)	0.55(13)	1.01(12)	-0.58(12)

O1	21.6(4)	25.6(5)	23.4(4)	5.0(3)	2.1(3)	-0.2(4)
O2	29.8(5)	27.5(5)	18.7(4)	-1.8(3)	1.3(3)	4.3(4)
N2	25.6(5)	19.2(5)	19.5(5)	-0.6(4)	0.7(4)	0.4(4)
N1	22.5(5)	25.1(6)	20.4(5)	1.3(4)	2.5(4)	3.1(4)
C1	25.8(6)	23.7(6)	19.4(6)	-1.6(5)	3.2(5)	-5.0(5)
C7	25.6(6)	25.9(6)	18.2(6)	-2.2(5)	2.5(5)	-8.1(5)
C9	23.2(6)	21.4(6)	22.8(6)	1.7(5)	-3.4(5)	-5.9(5)
C2	30.7(7)	26.3(6)	16.2(6)	2.5(5)	1.8(5)	-2.8(5)
C3	30.0(7)	21.4(6)	17.7(5)	-2.1(5)	-2.3(5)	1.9(5)
C8	31.5(7)	29.0(6)	15.8(5)	0.7(5)	-2.2(5)	-4.7(5)
C12	38.4(8)	27.5(7)	26.2(6)	-1.9(5)	2.2(6)	9.4(6)
C11	34.5(7)	28.7(7)	29.3(7)	3.8(5)	-8.4(6)	0.8(5)
C10	34.7(7)	35.9(7)	22.4(6)	-4.7(5)	7.2(5)	-3.3(6)
C5	42.5(8)	34.3(7)	27.2(7)	7.0(6)	1.5(6)	13.1(6)
C4	29.0(7)	42.6(8)	33.8(7)	5.9(6)	9.0(6)	-3.3(6)
C6	28.1(7)	51.1(9)	34.2(8)	10.0(7)	7.9(6)	12.5(7)

Bond Lengths for compound **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	Al1	2.2197(5)	N1	C6	1.4723(17)
Al1	O1	1.7849(9)	C1	C2	1.3502(19)
Al1	O2	1.7874(9)	C1	C4	1.4970(18)
Al1	N2	1.9915(11)	C7	C8	1.3557(19)
Al1	N1	1.9950(11)	C7	C10	1.5000(18)
O1	C1	1.3158(15)	C9	C8	1.4323(18)
O2	C7	1.3136(16)	C9	C11	1.5062(18)
N2	C9	1.2998(16)	C2	C3	1.4330(19)
N2	C12	1.4705(16)	C3	C5	1.5052(18)

N1 C3 1.3045(17)

Bond Angles for compound **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	Cl1	118.65(3)	C3	N1	C6	117.83(11)
O1	Al1	O2	124.24(5)	C6	N1	Al1	116.20(9)
O1	Al1	N2	85.99(4)	O1	C1	C2	123.95(12)
O1	Al1	N1	90.90(4)	O1	C1	C4	113.64(12)
O2	Al1	Cl1	117.09(4)	C2	C1	C4	122.37(12)
O2	Al1	N2	91.33(4)	O2	C7	C8	123.99(12)
O2	Al1	N1	89.16(4)	O2	C7	C10	114.28(12)
N2	Al1	Cl1	91.64(3)	C8	C7	C10	121.73(12)
N2	Al1	N1	176.53(5)	N2	C9	C8	121.49(12)
N1	Al1	Cl1	91.20(4)	N2	C9	C11	121.70(12)
C1	O1	Al1	131.16(8)	C8	C9	C11	116.81(11)
C7	O2	Al1	131.36(9)	C1	C2	C3	124.16(11)
C9	N2	Al1	126.78(9)	N1	C3	C2	122.17(12)
C9	N2	C12	117.82(11)	N1	C3	C5	121.57(12)
C12	N2	Al1	115.39(8)	C2	C3	C5	116.24(11)
C3	N1	Al1	125.79(9)	C7	C8	C9	124.80(11)

Appendix 98: Crystal data of $[Al(MeCN(Et)CHC=OMe)_2Cl]$ ($[Al(Et-acnac)_2Cl]$, 7)

Crystal data and structure refinement for compound 7.

Empirical formula	$C_{14}H_{24}AlClN_2O_2$
Formula weight	314.78
Temperature/K	150.0(6)
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	8.97922(17)
$b/\text{\AA}$	13.8461(3)
$c/\text{\AA}$	15.0590(3)
$\alpha/^\circ$	68.945(2)
$\beta/^\circ$	85.2964(17)
$\gamma/^\circ$	72.7480(18)
Volume/ $\text{\AA}^3$	1668.01(7)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.253
μ/mm^{-1}	2.563
$F(000)$	672.0
Crystal size/ mm^3	$0.34 \times 0.24 \times 0.2$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	7.142 to 146.872
Index ranges	$-10 \leq h \leq 11, -17 \leq k \leq 17, -18 \leq l \leq 18$
Reflections collected	24221
Independent reflections	6554 [$R_{\text{int}} = 0.0305, R_{\text{sigma}} = 0.0205$]
Data/restraints/parameters	6554/0/373
Goodness-of-fit on F^2	1.040
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0337, wR_2 = 0.0916$
Final R indexes [all data]	$R_1 = 0.0349, wR_2 = 0.0928$

Largest diff. peak/hole / e Å⁻³ 0.40/-0.29

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for compound **7**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl1	7078.5(4)	7585.6(3)	-688.6(2)	24.73(9)
Al1	5933.0(4)	7055.3(3)	689.4(3)	16.51(10)
O2	6234.4(12)	7556.9(8)	1575.8(7)	24.5(2)
O1	4748.6(11)	6170.2(7)	884.5(7)	21.1(2)
N2	4014.9(13)	8293.6(9)	174.0(8)	20.1(2)
N1	7819.2(13)	5799.3(9)	1215.6(8)	20.8(2)
C8	5600.7(17)	8501.6(11)	1669.8(10)	22.7(3)
C9	4391.4(17)	9274.5(11)	1120.8(10)	24.2(3)
C10	3578.3(15)	9157.8(11)	404.8(10)	21.7(3)
C13	3109.0(17)	8218.2(12)	-562.4(11)	28.5(3)
C14	1644.7(18)	7884.7(14)	-183.6(13)	36.2(4)
C11	6317(2)	8658.9(13)	2451.7(11)	34.1(3)
C12	2154.6(17)	10091.1(12)	-25.0(12)	31.3(3)
C1	5097.1(16)	5110.0(11)	1167.3(9)	20.7(3)
C2	6568.9(17)	4445.0(11)	1378.5(10)	24.0(3)
C3	7918.5(16)	4787.4(11)	1400.3(9)	22.3(3)
C6	9233.8(17)	6078.1(13)	1340.3(12)	30.9(3)
C7	9581(2)	5832.2(15)	2382.0(14)	42.4(4)
C4	3719.3(18)	4687.2(12)	1255.6(11)	29.6(3)
C5	9433.6(18)	3893.2(12)	1659.3(12)	33.1(3)
Cl2	1684.2(4)	7003.8(3)	5771.6(2)	26.62(9)
Al2	3264.8(5)	7836.7(3)	4787.2(3)	19.60(10)
O4	2418.7(13)	8959.0(8)	3755.7(7)	28.8(2)
O3	5302.4(12)	7345.4(8)	5057.8(8)	28.7(2)

N4	3077.1(15)	8792.8(10)	5544.6(9)	26.6(3)
N3	3459.6(14)	6896.6(9)	4008.2(8)	24.1(2)
C22	1668.3(17)	9964.9(11)	3647.0(11)	28.0(3)
C23	1551.6(19)	10385.0(12)	4342.7(12)	32.1(3)
C24	2279.7(18)	9813.7(12)	5271.0(12)	29.7(3)
C27	3811(2)	8254.5(14)	6508.3(11)	34.9(4)
C28	5321(2)	8512.2(17)	6581.0(14)	46.9(4)
C25	952(2)	10633.4(14)	2677.3(13)	43.1(4)
C26	2073(2)	10497.6(15)	5882.3(14)	42.4(4)
C15	6407.7(17)	6565.2(12)	4891.9(11)	28.9(3)
C16	6183.3(18)	6001.8(12)	4369.7(11)	29.8(3)
C17	4723.9(19)	6176.3(11)	3919.6(10)	27.1(3)
C20	1994.3(18)	7028.3(13)	3538.9(11)	29.0(3)
C21	1893(2)	7683.6(14)	2473.8(11)	36.8(4)
C18	7965(2)	6344.5(15)	5333.5(15)	45.2(4)
C19	4801(2)	5475.6(13)	3342.1(11)	36.5(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cl1	26.10(17)	22.33(17)	24.42(16)	-7.49(13)	8.76(12)	-8.09(13)
Al1	16.34(19)	13.96(18)	19.38(19)	-6.32(14)	1.68(14)	-4.32(14)
O2	28.1(5)	19.4(5)	26.4(5)	-10.5(4)	-3.1(4)	-3.2(4)
O1	20.0(5)	17.5(4)	25.5(5)	-6.3(4)	0.6(4)	-6.6(4)
N2	18.3(5)	17.9(5)	22.5(5)	-6.4(4)	1.6(4)	-4.0(4)
N1	17.1(5)	18.6(5)	25.4(6)	-6.7(4)	0.9(4)	-4.5(4)
C8	28.1(7)	21.7(6)	23.6(6)	-11.3(5)	7.8(5)	-12.5(6)
C9	26.2(7)	17.6(6)	31.8(7)	-12.7(5)	7.8(6)	-7.4(5)
C10	17.4(6)	16.8(6)	28.3(7)	-6.1(5)	6.4(5)	-5.0(5)

C13	27.2(7)	26.9(7)	28.4(7)	-9.5(6)	-7.0(6)	-1.8(6)
C14	23.5(7)	34.2(8)	52.2(10)	-18.0(7)	-9.7(7)	-3.9(6)
C11	49.1(10)	30.8(8)	30.1(8)	-15.5(6)	0.5(7)	-16.3(7)
C12	23.0(7)	19.5(7)	46.5(9)	-9.3(6)	1.3(6)	-2.1(6)
C1	27.9(7)	20.4(6)	17.9(6)	-9.0(5)	4.2(5)	-11.0(5)
C2	30.3(7)	15.4(6)	27.1(7)	-8.9(5)	3.9(6)	-6.8(5)
C3	23.8(7)	19.5(6)	21.0(6)	-7.9(5)	2.2(5)	-1.9(5)
C6	17.7(7)	28.1(7)	45.5(9)	-10.3(7)	-2.2(6)	-7.0(6)
C7	35.2(9)	40.0(9)	54.5(11)	-17.8(8)	-18.2(8)	-7.9(7)
C4	32.5(8)	28.6(7)	33.9(8)	-12.4(6)	4.1(6)	-17.0(6)
C5	28.2(8)	23.1(7)	41.7(9)	-11.0(6)	-0.1(6)	1.7(6)
Cl2	28.58(18)	25.19(17)	26.46(17)	-8.43(13)	7.07(13)	-10.77(13)
Al2	20.8(2)	16.97(19)	20.09(19)	-6.44(15)	1.00(15)	-4.27(15)
O4	35.6(6)	20.1(5)	26.1(5)	-5.9(4)	-0.8(4)	-3.7(4)
O3	23.2(5)	26.3(5)	35.5(6)	-11.5(4)	-2.0(4)	-4.1(4)
N4	29.2(6)	27.6(6)	27.3(6)	-12.1(5)	5.8(5)	-12.6(5)
N3	28.2(6)	23.0(6)	21.5(5)	-6.9(5)	3.0(5)	-9.7(5)
C22	22.8(7)	19.1(7)	35.2(8)	-2.3(6)	4.7(6)	-6.0(5)
C23	31.2(8)	18.5(7)	43.1(9)	-9.4(6)	7.8(6)	-5.5(6)
C24	29.5(8)	27.8(7)	39.5(8)	-18.1(6)	12.2(6)	-14.5(6)
C27	42.9(9)	40.7(9)	26.7(7)	-15.1(7)	2.5(6)	-16.3(7)
C28	47.2(11)	58.0(12)	44.9(10)	-23.4(9)	-5.2(8)	-20.1(9)
C25	45.9(10)	28.2(8)	37.1(9)	3.1(7)	0.3(7)	-2.4(7)
C26	50.9(11)	36.5(9)	51.6(10)	-27.0(8)	11.7(8)	-18.0(8)
C15	24.5(7)	23.1(7)	29.1(7)	-0.4(6)	2.6(6)	-3.9(6)
C16	29.7(8)	21.3(7)	29.1(7)	-5.4(6)	6.5(6)	0.3(6)
C17	38.0(8)	18.4(6)	20.9(6)	-4.3(5)	7.2(6)	-7.3(6)
C20	33.2(8)	30.8(8)	27.8(7)	-11.1(6)	1.3(6)	-15.5(6)

C21	45.8(10)	39.7(9)	27.6(8)	-8.3(7)	-3.4(7)	-19.3(8)
C18	26.5(8)	35.3(9)	63.5(12)	-8.3(8)	-8.1(8)	-2.7(7)
C19	54.1(10)	27.2(8)	25.9(7)	-11.0(6)	7.5(7)	-7.7(7)

Bond Lengths for compound 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	Al1	2.2150(5)	Cl2	Al2	2.2224(5)
Al1	O2	1.7817(10)	Al2	O4	1.7786(11)
Al1	O1	1.7839(10)	Al2	O3	1.7780(11)
Al1	N2	2.0050(11)	Al2	N4	2.0008(13)
Al1	N1	2.0009(11)	Al2	N3	2.0072(12)
O2	C8	1.3164(17)	O4	C22	1.3109(17)
O1	C1	1.3169(16)	O3	C15	1.3160(18)
N2	C10	1.3056(18)	N4	C24	1.308(2)
N2	C13	1.4778(17)	N4	C27	1.478(2)
N1	C3	1.3032(18)	N3	C17	1.3040(19)
N1	C6	1.4764(18)	N3	C20	1.4770(19)
C8	C9	1.353(2)	C22	C23	1.353(2)
C8	C11	1.4963(19)	C22	C25	1.494(2)
C9	C10	1.430(2)	C23	C24	1.434(2)
C10	C12	1.5093(19)	C24	C26	1.508(2)
C13	C14	1.522(2)	C27	C28	1.522(2)
C1	C2	1.354(2)	C15	C16	1.352(2)
C1	C4	1.4959(19)	C15	C18	1.498(2)
C2	C3	1.433(2)	C16	C17	1.441(2)
C3	C5	1.5089(19)	C17	C19	1.503(2)
C6	C7	1.519(2)	C20	C21	1.527(2)

Bond Angles for compound 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Al1	Cl1	117.30(4)	O4	Al2	Cl2	117.93(4)
O2	Al1	O1	122.09(5)	O4	Al2	N4	91.84(5)
O2	Al1	N2	91.69(5)	O4	Al2	N3	87.39(5)
O2	Al1	N1	88.65(5)	O3	Al2	Cl2	118.80(4)
O1	Al1	Cl1	120.61(4)	O3	Al2	O4	123.27(6)
O1	Al1	N2	87.81(5)	O3	Al2	N4	88.56(5)
O1	Al1	N1	91.04(5)	O3	Al2	N3	91.42(5)
N2	Al1	Cl1	90.12(4)	N4	Al2	Cl2	90.22(4)
N1	Al1	Cl1	90.74(4)	N4	Al2	N3	179.07(5)
N1	Al1	N2	178.81(5)	N3	Al2	Cl2	90.61(4)
C8	O2	Al1	130.87(9)	C22	O4	Al2	131.13(10)
C1	O1	Al1	131.88(9)	C15	O3	Al2	131.85(10)
C10	N2	Al1	125.04(10)	C24	N4	Al2	124.77(11)
C10	N2	C13	119.34(11)	C24	N4	C27	119.41(13)
C13	N2	Al1	115.53(9)	C27	N4	Al2	115.65(10)
C3	N1	Al1	125.93(10)	C17	N3	Al2	125.90(10)
C3	N1	C6	118.52(12)	C17	N3	C20	119.12(12)
C6	N1	Al1	115.43(9)	C20	N3	Al2	114.92(9)
O2	C8	C9	123.80(12)	O4	C22	C23	123.67(14)
O2	C8	C11	114.44(13)	O4	C22	C25	114.60(14)
C9	C8	C11	121.75(13)	C23	C22	C25	121.73(14)
C8	C9	C10	125.02(12)	C22	C23	C24	124.97(14)
N2	C10	C9	122.09(12)	N4	C24	C23	122.13(14)
N2	C10	C12	123.45(13)	N4	C24	C26	123.66(15)
C9	C10	C12	114.42(12)	C23	C24	C26	114.19(14)
N2	C13	C14	113.07(13)	N4	C27	C28	113.05(14)

O1	C1	C2	123.57(13)	O3	C15	C16	123.80(14)
O1	C1	C4	114.39(12)	O3	C15	C18	114.22(15)
C2	C1	C4	122.03(13)	C16	C15	C18	121.99(15)
C1	C2	C3	124.87(13)	C15	C16	C17	124.92(13)
N1	C3	C2	121.63(12)	N3	C17	C16	121.69(13)
N1	C3	C5	123.32(13)	N3	C17	C19	123.85(15)
C2	C3	C5	115.04(13)	C16	C17	C19	114.45(13)
N1	C6	C7	111.71(13)	N3	C20	C21	113.59(13)

Appendix 99: Crystal data of $[Al(MeCN(iPr)CHC=OMe)_2Cl]$ ($[Al(iPr-acnac)_2Cl]$, **8**)Crystal data and structure refinement for compound **8**.

Empirical formula	C ₁₆ H ₂₈ AlClN ₂ O ₂
Formula weight	342.83
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	11.3290(3)
b/Å	11.3991(3)
c/Å	14.1862(3)
$\alpha/^\circ$	90
$\beta/^\circ$	94.627(2)
$\gamma/^\circ$	90
Volume/Å ³	1826.04(7)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.247
μ/mm^{-1}	2.381
F(000)	736.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	11.028 to 115.754
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	12215
Independent reflections	1269 [R_{int} = 0.0215, R_{sigma} = 0.0096]
Data/restraints/parameters	1269/0/157
Goodness-of-fit on F ²	1.056
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0252, wR_2 = 0.0714
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0729

Largest diff. peak/hole / e Å⁻³ 0.34/-0.17

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
C2	1147.3(15)	-1229.1(15)	649.7(12)	24.6(4)
C5	3249.5(18)	-758(2)	1047.6(16)	36.2(5)
C3	1993.3(14)	-689.4(14)	1322.6(12)	21.9(4)
C6	2548.3(15)	360.0(15)	2802.9(12)	23.8(4)
C7	3167.4(18)	1425.9(18)	2418.4(15)	34.3(5)
C8	3381.6(17)	-504.4(19)	3328.3(14)	31.2(4)
C1	-26.7(15)	-1342.0(14)	739.3(11)	21.8(4)
C4	-834.3(18)	-1959.0(19)	19.3(13)	31.6(4)
N1	1675.7(11)	-211.8(11)	2099.0(9)	19.4(3)
Al1	0	-185.4(5)	2500	17.5(2)
Cl1	0	1756.0(4)	2500	24.4(2)
O1	-550.0(10)	-947.7(10)	1468.4(8)	24.9(3)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **8**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C2	31.3(10)	25.0(9)	18.2(9)	-3.4(7)	5.6(7)	1.9(7)
C5	26.2(11)	49.1(13)	34.1(12)	-10.3(10)	7.1(9)	1.3(9)
C3	23.4(9)	18.9(9)	23.5(9)	4.1(7)	3.8(7)	2.7(7)
C6	21.2(8)	24.3(9)	25.4(9)	-5.3(7)	-0.5(7)	0.0(7)
C7	30.5(10)	29.2(10)	42.9(12)	-3.3(9)	0.5(10)	-6.5(9)
C8	26.0(10)	35.7(11)	31.0(11)	-2.6(9)	-2.9(9)	3.1(9)
C1	31.5(10)	18.1(8)	15.8(8)	1.6(7)	2.2(7)	0.6(7)
C4	35.5(11)	36.0(11)	23.1(10)	-5.8(8)	0.2(8)	-5.6(9)

N1	20.9(7)	16.9(7)	20.3(7)	0.6(5)	0.3(6)	0.9(5)
Al1	18.8(4)	17.5(4)	16.4(4)	0	2.0(3)	0
Cl1	24.9(3)	17.3(3)	31.7(3)	0	6.7(2)	0
O1	24.6(6)	29.4(7)	20.8(6)	-5.7(5)	2.8(5)	-2.8(5)

Bond Lengths for compound **8**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C2	C3	1.435(2)	C1	C4	1.491(2)
C2	C1	1.352(2)	C1	O1	1.3123(19)
C5	C3	1.508(3)	N1	Al1	2.0255(13)
C3	N1	1.305(2)	Al1	N1 ¹	2.0255(13)
C6	C7	1.526(3)	Al1	Cl1	2.2131(8)
C6	C8	1.518(3)	Al1	O1 ¹	1.7714(11)
C6	N1	1.497(2)	Al1	O1	1.7714(11)

¹-X,+Y,1/2-ZBond Angles for compound **8**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C2	C3	125.96(15)	C6	N1	Al1	112.94(10)
C2	C3	C5	113.52(15)	N1	Al1	N1 ¹	178.30(8)
N1	C3	C2	121.69(15)	N1 ¹	Al1	Cl1	90.85(4)
N1	C3	C5	124.78(16)	N1	Al1	Cl1	90.85(4)
C8	C6	C7	114.01(15)	O1 ¹	Al1	N1	87.11(5)
N1	C6	C7	113.97(14)	O1	Al1	N1	92.06(5)
N1	C6	C8	113.33(14)	O1 ¹	Al1	N1 ¹	92.06(5)
C2	C1	C4	122.29(15)	O1	Al1	N1 ¹	87.11(5)
O1	C1	C2	123.48(15)	O1	Al1	Cl1	119.38(4)
O1	C1	C4	114.21(15)	O1 ¹	Al1	Cl1	119.38(4)

C3	N1	C6	122.18(13)	O1 ¹	Al1	O1	121.25(8)
C3	N1	Al1	124.87(11)	C1	O1	Al1	131.91(10)

¹-X,+Y,1/2-Z

Appendix 100: Crystal data of $[Al(MeCN(Ph)CHC=OMe)_2Cl]$ ($[Al(Ph-acnac)_2Cl]$, **9**)

Crystal data and structure refinement for compound **9**.

Empirical formula	C ₂₂ H ₂₄ AlClN ₂ O ₂
Formula weight	410.86
Temperature/K	151(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	12.1425(2)
b/Å	12.2037(2)
c/Å	13.9522(3)
$\alpha/^\circ$	90
$\beta/^\circ$	93.853(2)
$\gamma/^\circ$	90
Volume/Å ³	2062.81(7)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.323
μ/mm^{-1}	2.212
F(000)	864.0
Crystal size/mm ³	0.18 × 0.18 × 0.14
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	10.288 to 145.29
Index ranges	-15 ≤ h ≤ 14, -14 ≤ k ≤ 15, -17 ≤ l ≤ 15
Reflections collected	15305
Independent reflections	2036 [R_{int} = 0.0322, R_{sigma} = 0.0146]
Data/restraints/parameters	2036/0/130
Goodness-of-fit on F ²	1.064
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0309, wR_2 = 0.0853
Final R indexes [all data]	R_1 = 0.0325, wR_2 = 0.0870

Largest diff. peak/hole / e Å⁻³ 0.23/-0.24

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **9**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl1	5000	3557.3(3)	2500	30.19(15)
Al1	5000	5351.5(4)	2500	18.53(15)
O1	5625.1(7)	6059.1(8)	3503.4(7)	25.6(2)
N1	3506.5(9)	5453.5(8)	3078.4(8)	19.9(2)
C6	2541.6(10)	5087.5(11)	2498.7(10)	21.4(3)
C2	4219.2(11)	6233.2(11)	4571.5(10)	24.1(3)
C3	3339.1(11)	5838.7(11)	3933.8(10)	22.6(3)
C1	5279.8(11)	6336.5(10)	4338.3(9)	21.9(3)
C7	2241.4(11)	3992.8(11)	2507.6(10)	26.7(3)
C4	6156.0(11)	6816.4(12)	5014.7(10)	30.3(3)
C11	1910.1(11)	5821.8(12)	1939.2(11)	30.3(3)
C8	1306.9(12)	3636.7(12)	1968.9(11)	30.9(3)
C9	674.1(11)	4370.8(13)	1415.9(11)	30.9(3)
C10	973.1(12)	5460.8(13)	1402.3(12)	34.2(4)
C5	2198.5(12)	5918.6(15)	4292.3(12)	36.3(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **9**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cl1	31.2(3)	18.2(2)	42.8(3)	0	14.8(2)	0
Al1	17.6(3)	17.9(3)	20.2(3)	0	2.53(19)	0
O1	19.9(4)	33.2(5)	23.8(5)	-4.6(4)	3.3(4)	-2.6(4)
N1	18.5(5)	17.6(5)	23.8(6)	-1.1(4)	2.8(4)	-1.5(4)
C6	17.4(5)	23.2(6)	23.9(6)	-2.7(5)	4.6(5)	-1.8(5)

C2	27.5(7)	24.6(6)	20.5(6)	-2.6(5)	3.8(5)	-0.7(5)
C3	23.2(6)	19.5(6)	25.8(7)	0.0(5)	5.6(5)	-0.8(5)
C1	26.0(6)	18.7(6)	20.7(6)	0.7(5)	-0.8(5)	0.5(5)
C7	25.4(7)	22.2(7)	32.6(7)	-2.4(5)	1.3(5)	-1.3(5)
C4	28.9(7)	34.8(8)	26.6(7)	-3.4(6)	-2.3(6)	-3.0(6)
C11	23.0(7)	24.7(7)	43.1(9)	4.4(6)	0.1(6)	-2.4(5)
C8	28.5(7)	26.4(7)	38.0(8)	-9.2(6)	4.3(6)	-6.3(5)
C9	21.1(7)	43.5(8)	27.9(7)	-7.2(6)	1.7(5)	-6.4(6)
C10	22.8(7)	40.6(8)	38.6(9)	8.5(6)	-2.4(6)	-1.0(6)
C5	26.7(7)	46.1(9)	37.5(8)	-12.7(7)	12.0(6)	-5.3(6)

Bond Lengths for compound **9**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	Al1	2.1895(7)	C6	C11	1.386(2)
Al1	O1 ¹	1.7718(9)	C2	C3	1.4275(18)
Al1	O1	1.7718(9)	C2	C1	1.3552(19)
Al1	N1 ¹	2.0377(11)	C3	C5	1.5070(18)
Al1	N1	2.0377(11)	C1	C4	1.4936(18)
O1	C1	1.3088(16)	C7	C8	1.3880(19)
N1	C6	1.4487(16)	C11	C10	1.391(2)
N1	C3	1.3113(17)	C8	C9	1.382(2)
C6	C7	1.3851(19)	C9	C10	1.379(2)

¹1-X,+Y,1/2-ZBond Angles for compound **9**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1 ¹	Al1	Cl1	119.17(3)	C7	C6	C11	119.52(12)
O1	Al1	Cl1	119.17(3)	C11	C6	N1	120.75(12)

O1	Al1	O1 ¹	121.66(7)	C1	C2	C3	124.43(12)
O1	Al1	N1 ¹	86.43(4)	N1	C3	C2	122.20(12)
O1 ¹	Al1	N1 ¹	90.16(4)	N1	C3	C5	121.83(12)
O1	Al1	N1	90.16(4)	C2	C3	C5	115.95(12)
O1 ¹	Al1	N1	86.43(4)	O1	C1	C2	123.78(12)
N1	Al1	Cl1	93.50(3)	O1	C1	C4	113.99(11)
N1 ¹	Al1	Cl1	93.50(3)	C2	C1	C4	122.20(12)
N1	Al1	N1 ¹	173.00(6)	C6	C7	C8	120.22(13)
C1	O1	Al1	133.12(8)	C6	C11	C10	120.02(13)
C6	N1	Al1	117.90(8)	C9	C8	C7	120.21(13)
C3	N1	Al1	125.37(9)	C10	C9	C8	119.74(13)
C3	N1	C6	116.72(11)	C9	C10	C11	120.30(14)
C7	C6	N1	119.72(12)				

¹1-X,+Y,1/2-Z

Appendix 101: Crystal data of $[Al(MeCN(Ar^{mes})CHC=OMe)_2Cl]$ ($[Al(Ar^{mes}-acnac)_2Cl]$, **10**)

Crystal data and structure refinement for compound **10**.

Empirical formula	C ₂₈ H ₃₆ AlClN ₂ O ₂
Formula weight	495.02
Temperature/K	150.00(10)
Crystal system	tetragonal
Space group	P4 ₃ 2 ₁ 2
a/Å	15.91110(10)
b/Å	15.91110(10)
c/Å	10.56760(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	2675.33(4)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.229
μ/mm^{-1}	1.787
F(000)	1056.0
Crystal size/mm ³	0.2 × 0.2 × 0.15
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	7.858 to 145.296
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -12 ≤ l ≤ 12
Reflections collected	44166
Independent reflections	2657 [R_{int} = 0.0355, R_{sigma} = 0.0099]
Data/restraints/parameters	2657/0/160
Goodness-of-fit on F ²	1.075
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0262, wR_2 = 0.0727
Final R indexes [all data]	R_1 = 0.0264, wR_2 = 0.0731

Largest diff. peak/hole / e Å ⁻³	0.22/-0.18
Flack parameter	0.001(3)

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 10. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cl1	1926.7(2)	1926.7(2)	5000	27.99(16)
Al1	2912.2(3)	2912.2(3)	5000	16.61(16)
O1	3719.6(7)	2101.5(7)	4836.4(11)	22.7(3)
N1	3419.5(8)	3283.6(8)	6607.9(12)	18.2(3)
C3	4158.1(10)	3032.6(11)	7062.1(16)	21.6(3)
C6	2960.5(10)	3871.0(10)	7395.2(15)	18.4(3)
C11	3111.6(10)	4733.7(11)	7301.5(15)	20.1(3)
C7	2366.6(11)	3557.1(11)	8241.2(16)	22.0(3)
C2	4662.6(11)	2414.6(11)	6470.9(17)	24.9(4)
C10	2670.7(11)	5271.4(11)	8106.1(16)	22.7(4)
C9	2077.3(11)	4978.1(11)	8966.1(16)	24.2(3)
C1	4418.9(11)	1973.0(10)	5418.5(16)	22.3(4)
C8	1932.0(11)	4118.0(11)	9010.6(16)	23.6(3)
C14	3732.9(11)	5072.3(11)	6349.6(17)	25.2(4)
C5	4496.2(12)	3389.8(13)	8285.3(18)	30.9(4)
C12	2196.2(14)	2630.1(12)	8323.7(19)	33.2(4)
C4	4954.9(12)	1286.5(12)	4882.5(19)	32.7(4)
C13	1603.8(14)	5566.2(13)	9829(2)	35.1(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 10. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	24.69(19)	24.69(19)	34.6(3)	-2.92(17)	2.92(17)	-6.5(2)
Al1	16.6(2)	16.6(2)	16.7(3)	-0.40(17)	0.40(17)	0.8(2)
O1	23.6(6)	22.0(5)	22.4(6)	0.8(5)	0.6(5)	5.1(4)
N1	19.7(6)	17.6(6)	17.3(6)	0.6(5)	1.1(5)	0.7(5)
C3	21.5(8)	22.2(8)	21.2(8)	4.7(6)	-0.7(6)	-1.5(6)
C6	20.3(7)	20.2(7)	14.7(7)	-1.6(6)	-1.7(6)	1.0(6)
C11	21.8(7)	22.7(8)	16.0(7)	-1.1(6)	-4.2(6)	-1.8(6)
C7	24.2(8)	23.4(8)	18.5(7)	-1.2(6)	-0.5(6)	-2.1(6)
C2	18.4(8)	27.8(9)	28.7(9)	5.2(7)	-1.8(7)	3.5(6)
C10	29.5(9)	17.6(8)	20.9(8)	-1.3(6)	-5.6(7)	0.6(6)
C9	25.7(8)	27.4(8)	19.5(8)	-3.3(6)	-3.1(7)	5.1(7)
C1	20.6(7)	21.9(8)	24.5(8)	7.9(6)	5.5(6)	2.8(6)
C8	22.1(8)	29.8(9)	18.9(8)	-1.4(6)	1.5(6)	-1.7(7)
C14	30.0(9)	22.0(8)	23.7(8)	-0.2(6)	0.8(7)	-7.1(7)
C5	29.7(9)	36.8(10)	26.1(9)	-0.3(8)	-8.3(7)	3.1(8)
C12	45.1(11)	25.4(9)	29.1(9)	0.2(7)	14.5(9)	-8.3(8)
C4	31.2(9)	32.8(9)	34.2(10)	2.3(8)	4.6(8)	13.2(8)
C13	41.9(11)	34.0(10)	29.4(10)	-5.8(8)	6.1(8)	8.9(8)

Bond Lengths for compound 10.

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
Cl1	Al1	2.2176(8)	C6	C7	1.393(2)
Al1	O1	1.8286(12)	C11	C10	1.395(2)
Al1	O1 ¹	1.8287(12)	C11	C14	1.510(2)
Al1	N1 ¹	1.9718(13)	C7	C8	1.391(2)
Al1	N1	1.9718(13)	C7	C12	1.502(2)

O1	C1	1.288(2)	C2	C1	1.371(3)
N1	C3	1.331(2)	C10	C9	1.391(3)
N1	C6	1.449(2)	C9	C8	1.389(3)
C3	C2	1.415(2)	C9	C13	1.508(2)
C3	C5	1.511(2)	C1	C4	1.497(2)
C6	C11	1.397(2)			

¹+Y,+X,1-Z

Bond Angles for compound **10**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1 ¹	Al1	Cl1	89.89(4)	C7	C6	N1	118.62(14)
O1	Al1	Cl1	89.88(4)	C7	C6	C11	120.95(15)
O1	Al1	O1 ¹	179.77(8)	C6	C11	C14	120.70(15)
O1	Al1	N1	90.30(5)	C10	C11	C6	118.21(16)
O1	Al1	N1 ¹	89.82(6)	C10	C11	C14	121.09(15)
O1 ¹	Al1	N1	89.82(6)	C6	C7	C12	120.77(15)
O1 ¹	Al1	N1 ¹	90.30(5)	C8	C7	C6	118.82(16)
N1	Al1	Cl1	120.09(4)	C8	C7	C12	120.41(16)
N1 ¹	Al1	Cl1	120.09(4)	C1	C2	C3	123.62(16)
N1	Al1	N1 ¹	119.82(8)	C9	C10	C11	122.25(16)
C1	O1	Al1	132.36(11)	C10	C9	C13	121.72(17)
C3	N1	Al1	125.62(11)	C8	C9	C10	117.76(16)
C3	N1	C6	115.57(13)	C8	C9	C13	120.52(17)
C6	N1	Al1	118.80(10)	O1	C1	C2	123.39(16)
N1	C3	C2	123.39(15)	O1	C1	C4	115.30(16)
N1	C3	C5	120.67(15)	C2	C1	C4	121.30(16)
C2	C3	C5	115.92(15)	C9	C8	C7	121.98(16)
C11	C6	N1	120.42(14)				

¹+Y,+X,1-Z

Appendix 102: Crystal data bis(*N*-methylpyrrolidine) monochloridoalumane, $[AlH_2Cl \cdot 2(\{CH_3\}_2N\{CH_2\}_4)]$ ($[AlH_2Cl \cdot 2(NMP)]$, **21**)

Crystal data and structure refinement for compound **21**.

Empirical formula	$C_{10}H_{24}AlClN_2$
Formula weight	234.74
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	10.7772(3)
$b/\text{\AA}$	6.96649(13)
$c/\text{\AA}$	18.3655(4)
$\alpha/^\circ$	90
$\beta/^\circ$	104.454(2)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	1335.23(5)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.168
μ/mm^{-1}	2.912
$F(000)$	512.0
Crystal size/ mm^3	$0.1 \times 0.1 \times 0.05$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	8.688 to 147.618
Index ranges	$-13 \leq h \leq 12, -8 \leq k \leq 8, -22 \leq l \leq 22$
Reflections collected	20114
Independent reflections	2685 [$R_{\text{int}} = 0.0330, R_{\text{sigma}} = 0.0163$]
Data/restraints/parameters	2685/0/148
Goodness-of-fit on F^2	1.038
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0300, wR_2 = 0.0793$
Final R indexes [all data]	$R_1 = 0.0320, wR_2 = 0.0809$

Largest diff. peak/hole / e Å⁻³ 0.25/-0.30

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **21**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Al(2)	8414.2(4)	4825.6(5)	6131.1(2)	21.72(11)
N(1)	9327.4(10)	6486.6(15)	7086.7(6)	21.6(2)
N(3)	7639.1(10)	3182.0(16)	5151.8(6)	23.1(2)
C(11)	7947.0(15)	228(2)	4522.5(9)	37.7(3)
C(8)	8770.0(15)	6180(2)	7737.2(8)	32.1(3)
C(10)	8650.1(13)	1850(2)	5026.0(8)	27.2(3)
C(0AA)	10713.5(13)	5992(2)	7302.9(8)	28.4(3)
C(12)	6579.2(15)	260(2)	4629.3(9)	35.3(3)
C(7)	9349.6(14)	8575.3(19)	6911.9(8)	29.0(3)
C(13)	6603.9(13)	1825(2)	5217.7(8)	28.4(3)
C(5)	11404.3(15)	7722(2)	7737.8(10)	40.7(4)
C(14)	7194.9(17)	4423(2)	4481.9(8)	33.7(3)
C(6)	10507.4(15)	9423(2)	7476.0(9)	36.9(3)
Cl(1)	6540.8(3)	6205.5(5)	6079.4(2)	35.80(12)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound **21**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Al(2)	20.8(2)	22.21(19)	22.67(19)	1.95(14)	6.51(14)	-0.93(14)
N(1)	20.0(5)	21.8(5)	23.9(5)	2.1(4)	7.1(4)	1.0(4)
N(3)	22.7(5)	23.2(5)	23.2(5)	2.7(4)	5.6(4)	-0.8(4)
C(11)	37.9(8)	33.7(8)	44.0(8)	-10.2(6)	15.0(7)	-3.2(6)
C(8)	32.8(8)	40.5(8)	26.1(7)	-2.0(6)	13.1(6)	-5.2(6)
C(10)	24.9(7)	28.3(7)	30.5(7)	-0.3(5)	10.7(5)	-0.5(5)

C(0AA)	21.8(7)	30.6(7)	31.7(7)	-0.3(5)	4.6(5)	3.3(5)
C(12)	34.1(8)	32.0(7)	39.3(8)	-5.7(6)	8.0(6)	-8.9(6)
C(7)	31.5(7)	20.8(6)	33.3(7)	1.3(5)	5.7(6)	0.7(5)
C(13)	22.0(6)	31.5(7)	32.6(7)	-0.9(6)	8.6(5)	-4.9(5)
C(5)	27.8(8)	36.9(8)	51.5(9)	-3.0(7)	-0.9(7)	-5.0(6)
C(14)	43.4(9)	30.2(7)	24.3(7)	5.6(6)	2.2(6)	1.3(7)
C(6)	36.8(8)	29.0(7)	42.2(8)	-4.5(6)	4.8(7)	-5.8(6)
Cl(1)	25.31(19)	40.6(2)	39.2(2)	-5.59(14)	3.77(14)	6.91(13)

Bond Lengths for compound **21**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al(2)	N(1)	2.1273(11)	N(3)	C(14)	1.4820(17)
Al(2)	N(3)	2.1198(11)	C(11)	C(10)	1.535(2)
Al(2)	Cl(1)	2.2167(5)	C(11)	C(12)	1.535(2)
N(1)	C(8)	1.4805(16)	C(0AA)	C(5)	1.532(2)
N(1)	C(0AA)	1.4872(17)	C(12)	C(13)	1.530(2)
N(1)	C(7)	1.4916(16)	C(7)	C(6)	1.528(2)
N(3)	C(10)	1.4923(17)	C(5)	C(6)	1.529(2)
N(3)	C(13)	1.4903(17)			

Bond Angles for compound **21**.

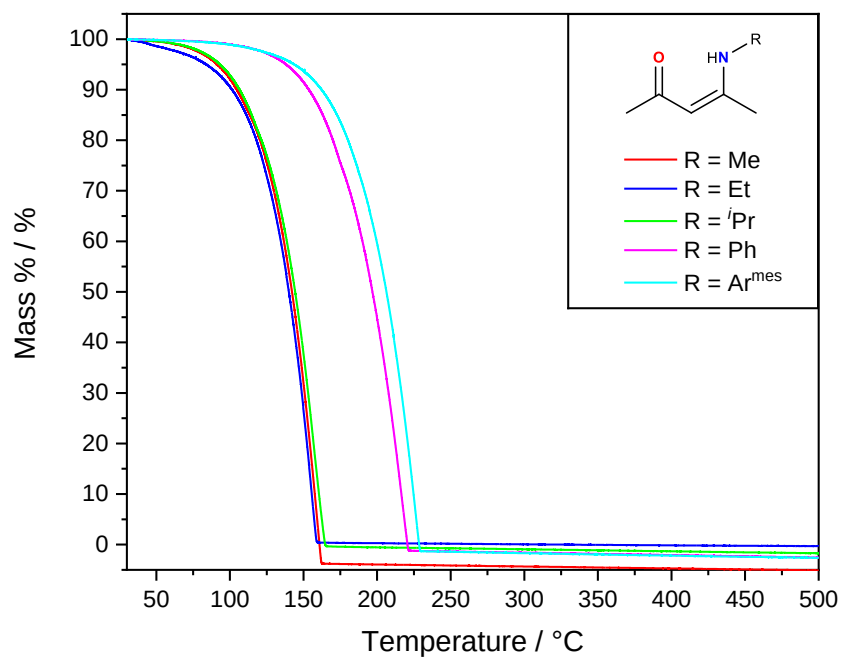
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(1)	Al(2)	Cl(1)	91.63(3)	C(14)	N(3)	Al(2)	111.49(9)
N(3)	Al(2)	N(1)	175.53(4)	C(14)	N(3)	C(10)	109.34(11)
N(3)	Al(2)	Cl(1)	92.07(3)	C(14)	N(3)	C(13)	110.14(11)
C(8)	N(1)	Al(2)	112.95(8)	C(12)	C(11)	C(10)	104.93(12)
C(8)	N(1)	C(0AA)	109.51(11)	N(3)	C(10)	C(11)	106.34(11)
C(8)	N(1)	C(7)	110.24(11)	N(1)	C(0AA)	C(5)	106.38(11)

C(0AA)	N(1)	Al(2)	108.74(8)	C(13)	C(12)	C(11)	104.63(12)
C(0AA)	N(1)	C(7)	102.39(10)	N(1)	C(7)	C(6)	106.59(11)
C(7)	N(1)	Al(2)	112.46(8)	N(3)	C(13)	C(12)	106.03(11)
C(10)	N(3)	Al(2)	108.60(8)	C(6)	C(5)	C(0AA)	105.01(12)
C(13)	N(3)	Al(2)	114.73(8)	C(7)	C(6)	C(5)	104.98(12)
C(13)	N(3)	C(10)	102.03(10)				

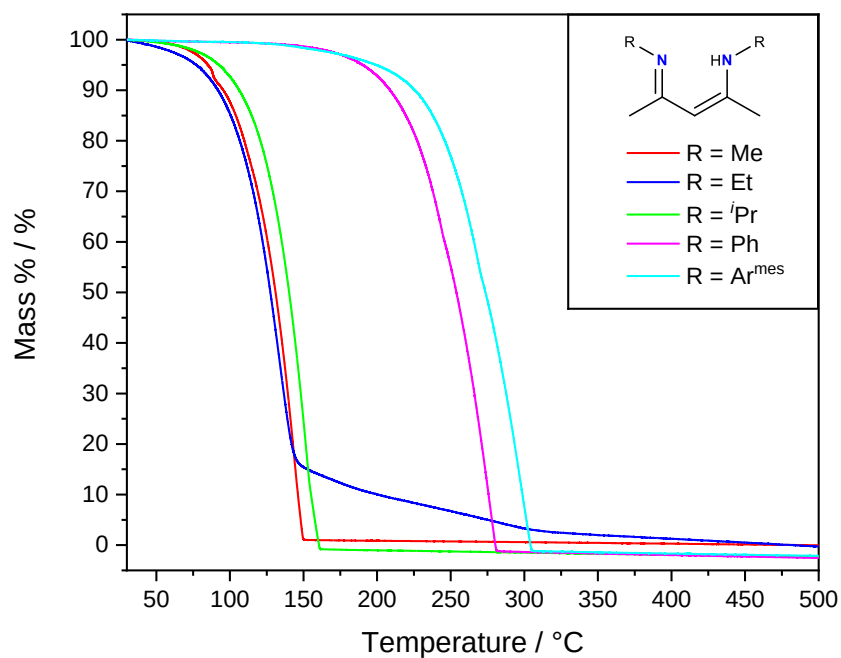
TGA (Appendix 103–137)

Appendix 103: Thermograms of β -ketoimine compounds.....	CLVI
Appendix 104: Thermograms of β -diketimine compounds.....	CLVI
Appendix 105: Thermograms of $[\text{Al}(\text{Me-acnac})_3]$ (1).	CLVII
Appendix 106: DTGs of $[\text{Al}(\text{Me-acnac})_3]$ (1).	CLVII
Appendix 107: Thermograms of $[\text{Al}(\text{Et-acnac})_3]$ (2).....	CLVIII
Appendix 108: DTGs of $[\text{Al}(\text{Et-acnac})_3]$ (2).....	CLVIII
Appendix 109: Thermograms of $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$ (2).....	CLIX
Appendix 110: DTGs of $[\text{Al}(\textit{i}\text{Pr-acnac})_3]$ (3).....	CLIX
Appendix 111: Thermograms of $[\text{Al}(\text{Ph-acnac})_3]$ (4).	CLX
Appendix 112: DTGs of $[\text{Al}(\text{Ph-acnac})_3]$ (4).....	CLX
Appendix 113: Thermograms of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).	CLXI
Appendix 114: DTGs of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_3]$ (5).....	CLXI
Appendix 115: Thermograms of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).....	CLXII
Appendix 116: DTGs of $[\text{Al}(\text{Me-acnac})_2\text{Cl}]$ (6).	CLXII
Appendix 117: Thermograms of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).	CLXIII
Appendix 118: DTGs of $[\text{Al}(\text{Et-acnac})_2\text{Cl}]$ (7).....	CLXIII
Appendix 119: Thermograms of $[\text{Al}(\textit{i}\text{Pr-acnac})_2\text{Cl}]$ (8).	CLXIV
Appendix 120: DTGs of $[\text{Al}(\textit{i}\text{Pr-acnac})_2\text{Cl}]$ (8).....	CLXIV
Appendix 121: Thermograms of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	CLXV
Appendix 122: Thermograms of $[\text{Al}(\text{Ph-acnac})_2\text{Cl}]$ (9).	CLXV
Appendix 123: Thermograms of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	CLXVI
Appendix 124: DTGs of $[\text{Al}(\text{Ar}^{\text{mes}}\text{-acnac})_2\text{Cl}]$ (10).	CLXVI
Appendix 125: Thermograms of $[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$ (11).....	CLXVII
Appendix 126: DTGs of $[\text{Al}(\text{Me}_2\text{-nacnac})\text{H}_2]$ (11).....	CLXVIII
Appendix 127: Comparison of onset temperature vs structural parameters for compounds 6–10.....	CLXVII
Appendix 128: Thermograms of $[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$ (12).	CLXVIII
Appendix 129: DTGs of $[\text{Al}(\text{Et}_2\text{-nacnac})\text{H}_2]$ (12).	CLXIX
Appendix 130: Thermograms of $[\text{Al}(\textit{i}\text{Pr}_2\text{-nacnac})\text{H}_2]$ (13).	CLXIX
Appendix 131: DTGs of $[\text{Al}(\textit{i}\text{Pr}_2\text{-nacnac})\text{H}_2]$ (13).	CLXX
Appendix 132: Thermograms of $[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$ (14).	CLXX
Appendix 133: DTGs of $[\text{Al}(\text{Ph}_2\text{-nacnac})\text{H}_2]$ (14).	CLXXI

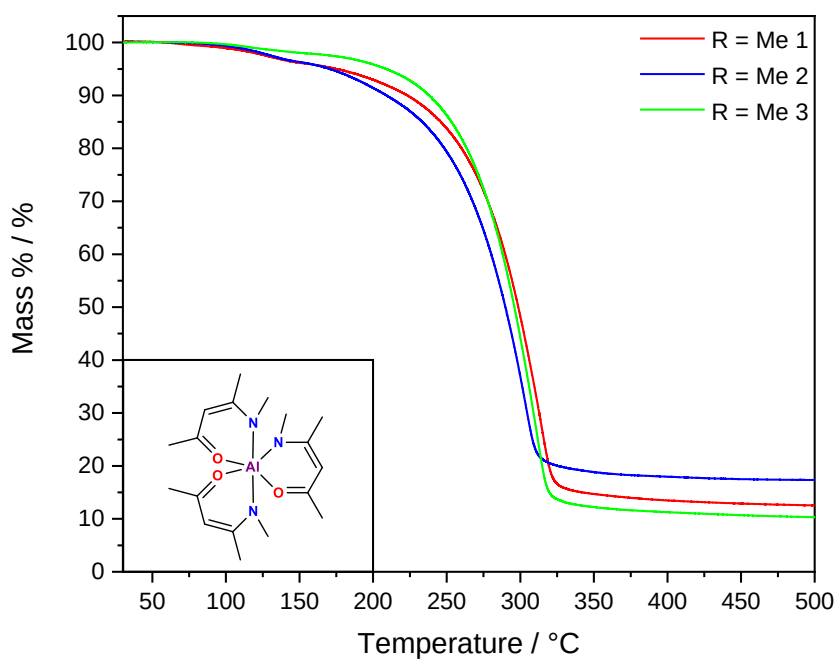
Appendix 134: Thermograms of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$ (15).	CLXXI
Appendix 135: DTGs of $[\text{Al}(\text{Ar}^{\text{mes}}_2\text{-nacnac})\text{H}_2]$ (15).	CLXXII
Appendix 136: Comparison of onset temperature vs structural parameters for compounds 11–15.	CLXXII
Appendix 137: Comparison of onset temperature vs Al–H bond length for compounds 11–15.	CLXXIII



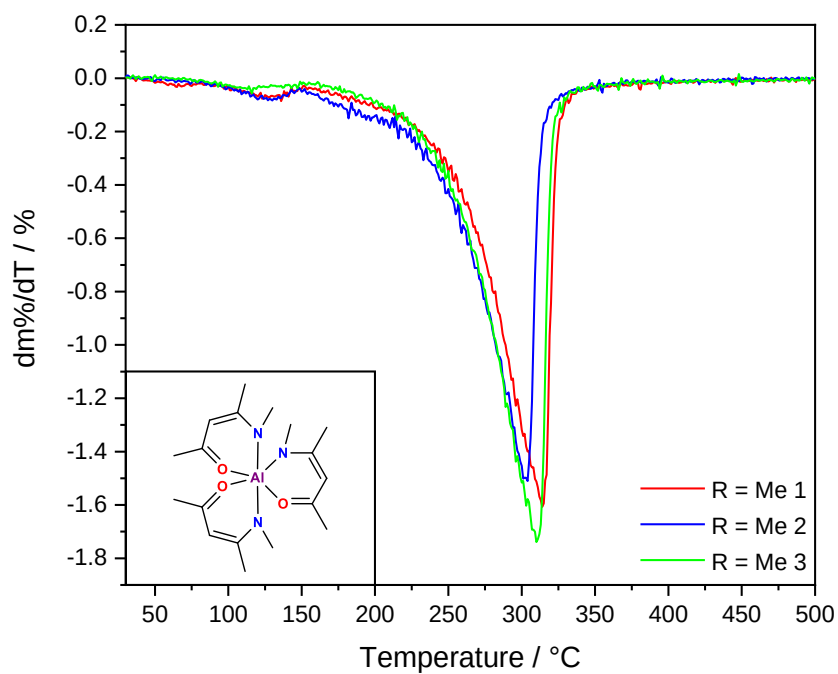
Appendix 103: Thermograms of β -ketoimine compounds.



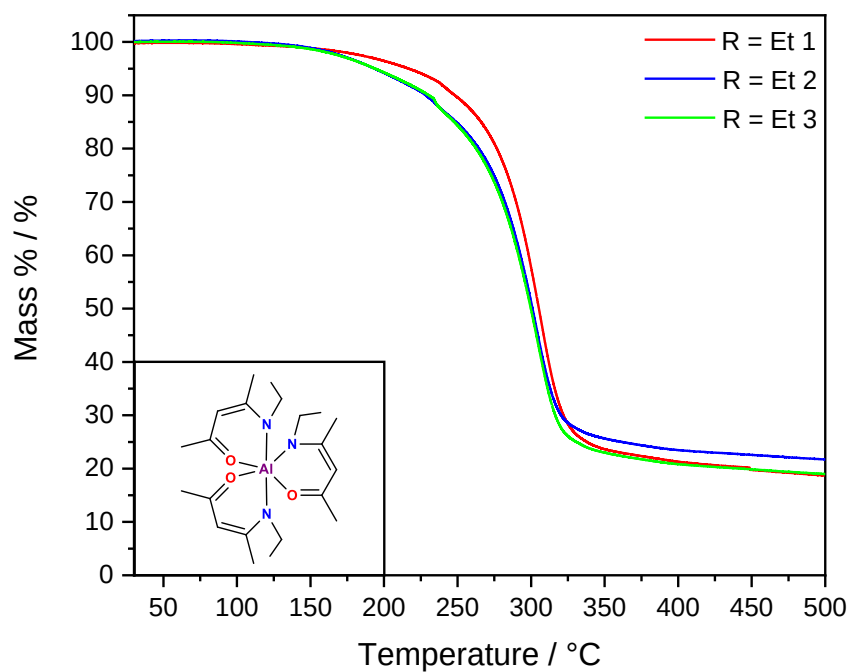
Appendix 104: Thermograms of β -diketimine compounds.



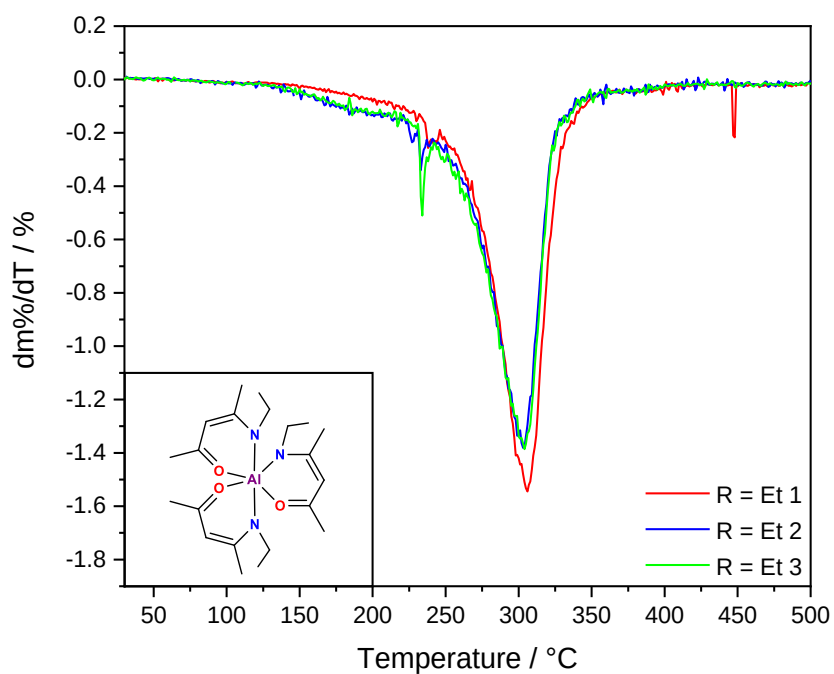
Appendix 105: Thermograms of $[Al(Me-acnac)_3]$ (1).



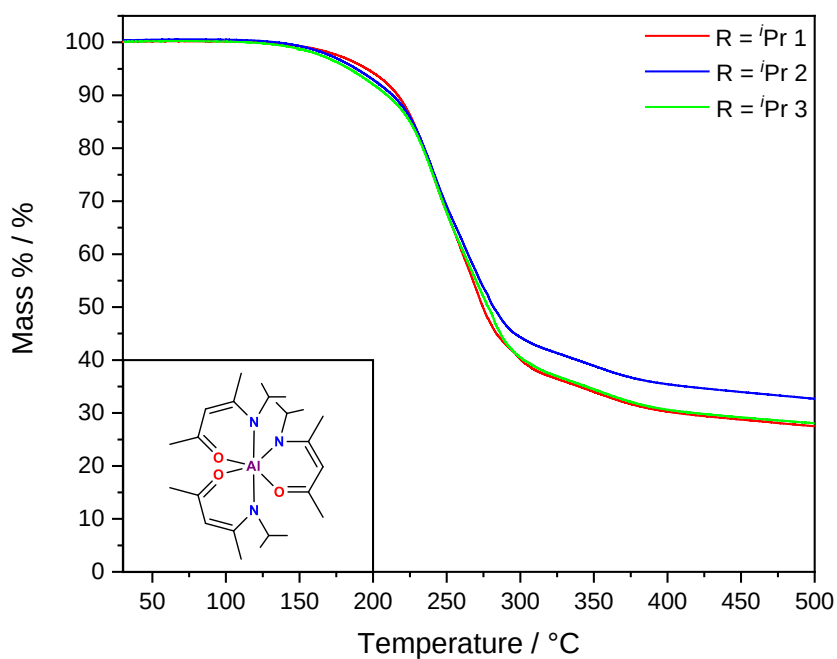
Appendix 106: DTGs of $[Al(Me-acnac)_3]$ (1).



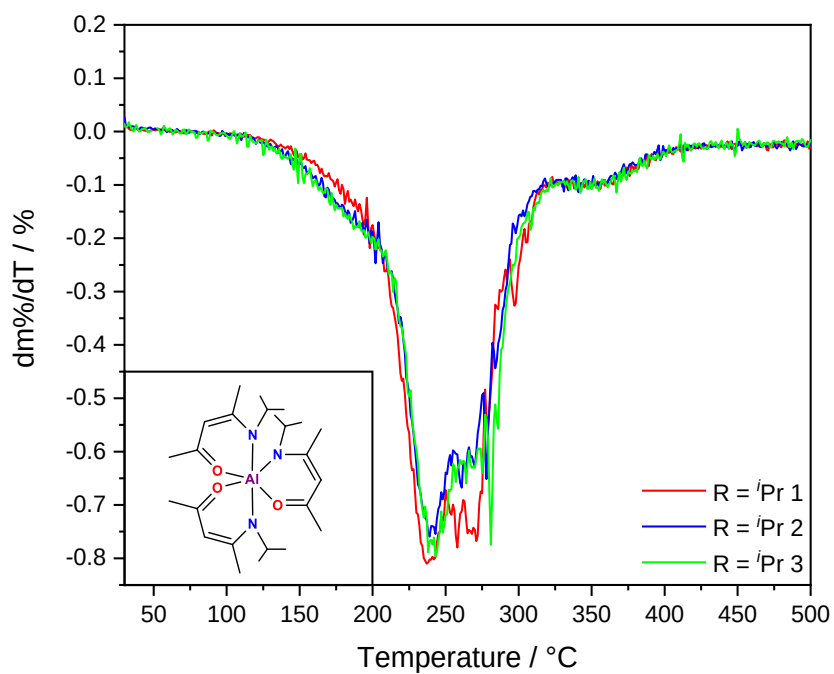
Appendix 107: Thermograms of $[Al(Et-acnac)_3]$ (2).



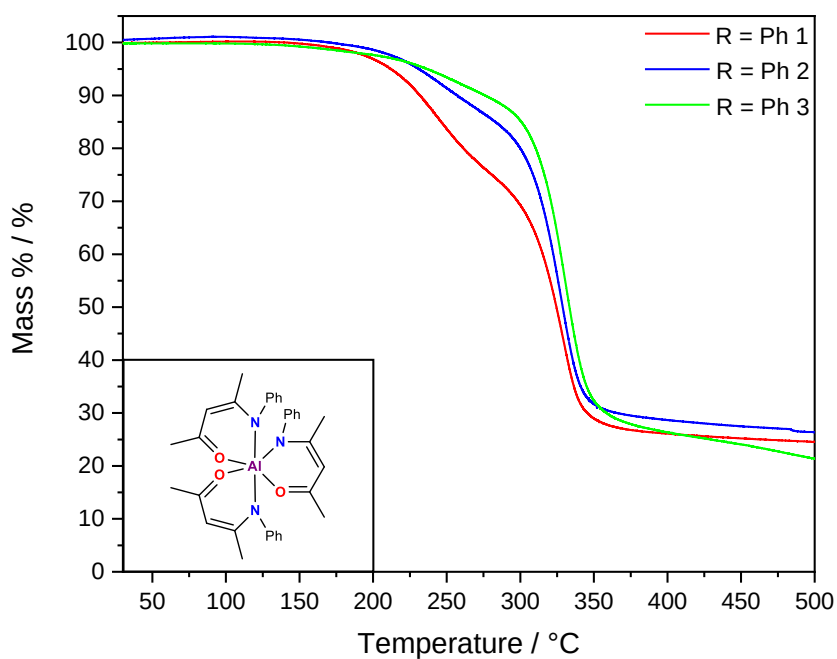
Appendix 108: DTGs of $[Al(Et-acnac)_3]$ (2).



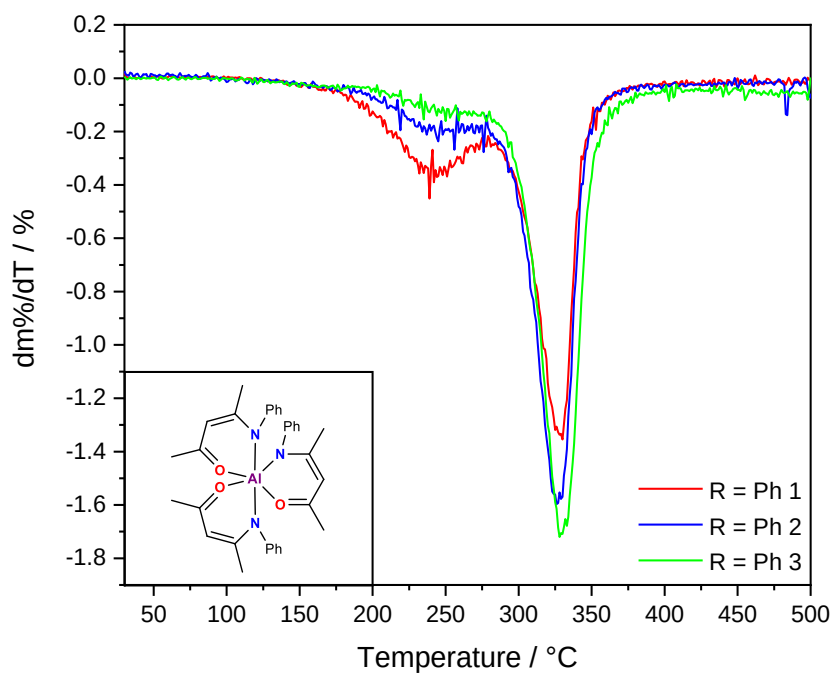
Appendix 109: Thermograms of $[Al(iPr-acnac)_3]$ (2).



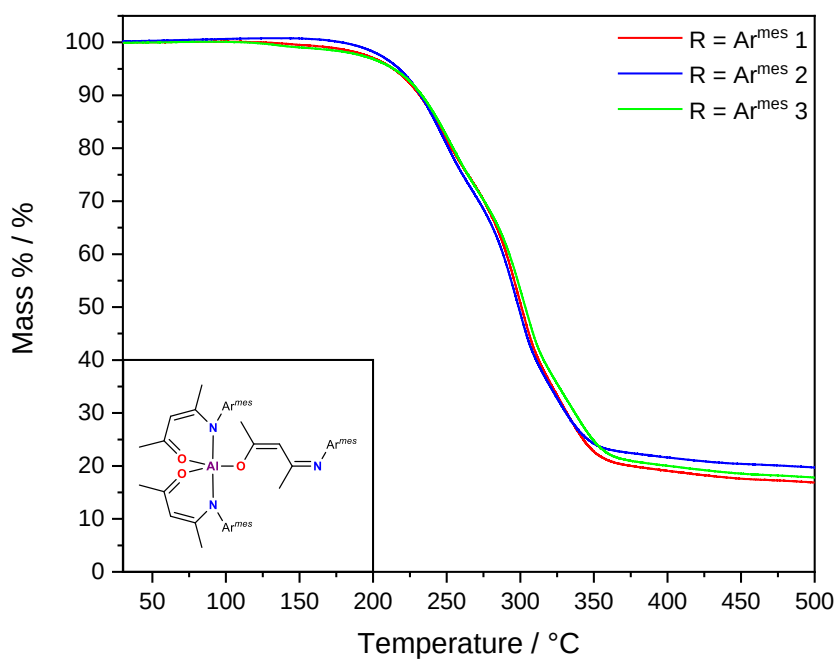
Appendix 110: DTGs of $[Al(iPr-acnac)_3]$ (3).



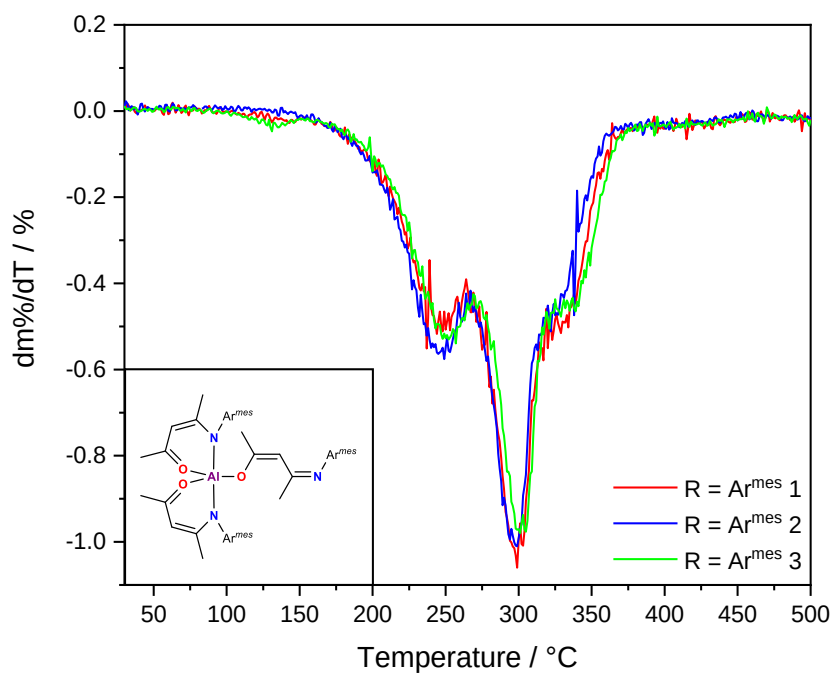
Appendix 111: Thermograms of $[Al(Ph-acnac)_3]$ (4).



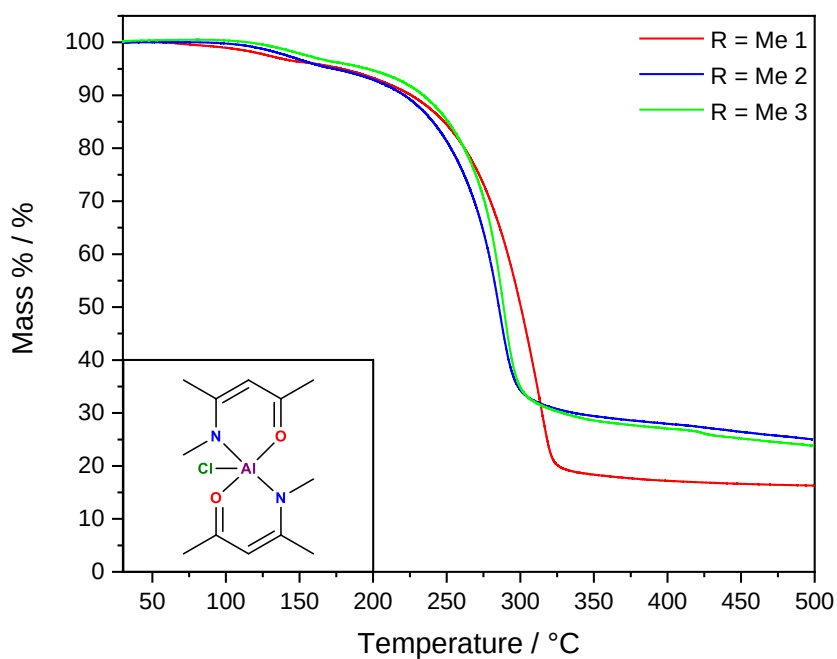
Appendix 112: DTGs of $[Al(Ph-acnac)_3]$ (4).



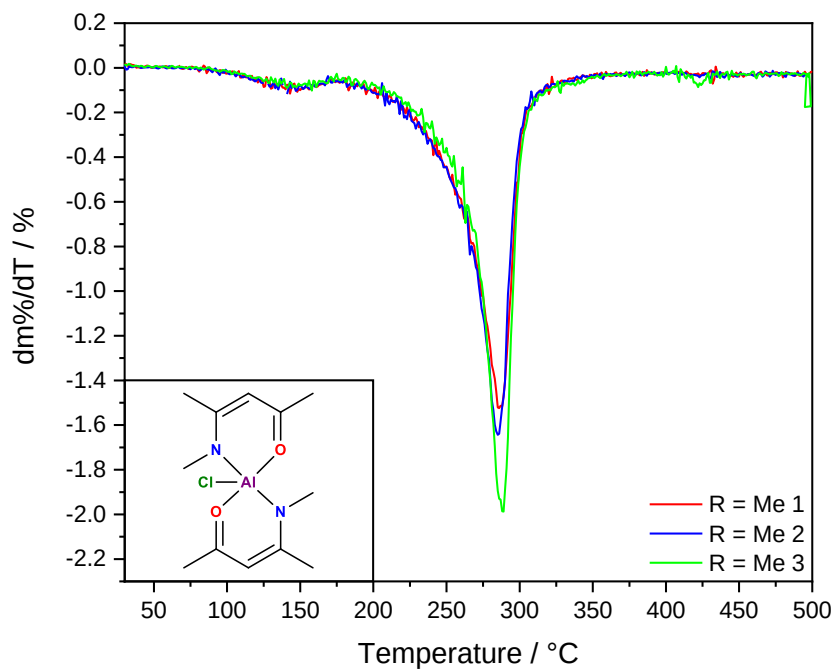
Appendix 113: Thermograms of $[Al(Ar^{mes}-acnac)_3]$ (5).



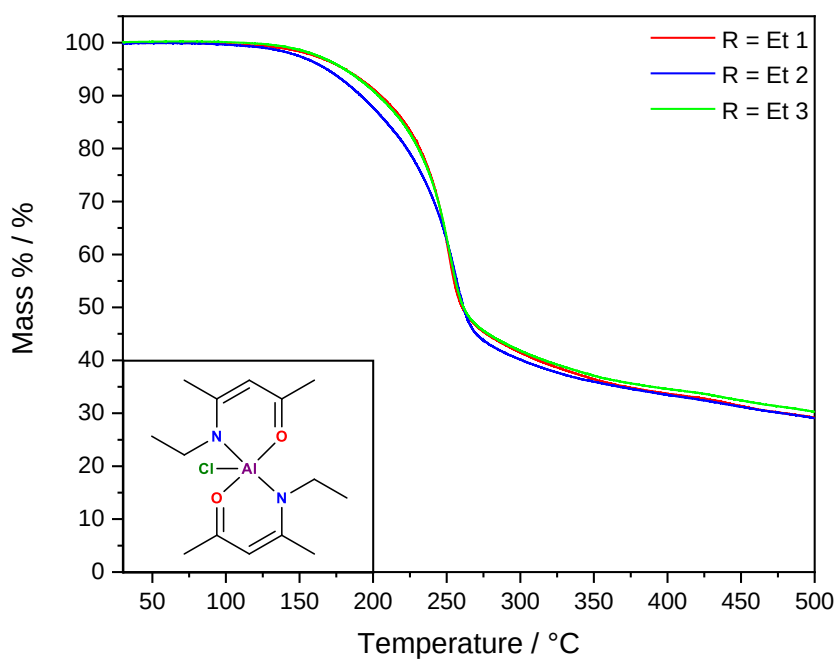
Appendix 114: DTGs of $[Al(Ar^{mes}-acnac)_3]$ (5).



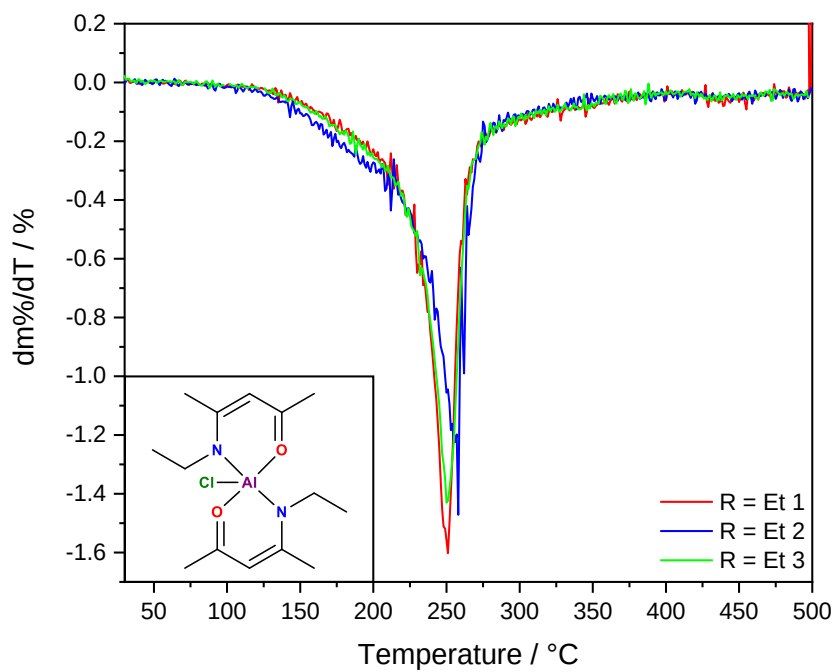
Appendix 115: Thermograms of $[Al(Me-acnac)_2Cl]$ (6).



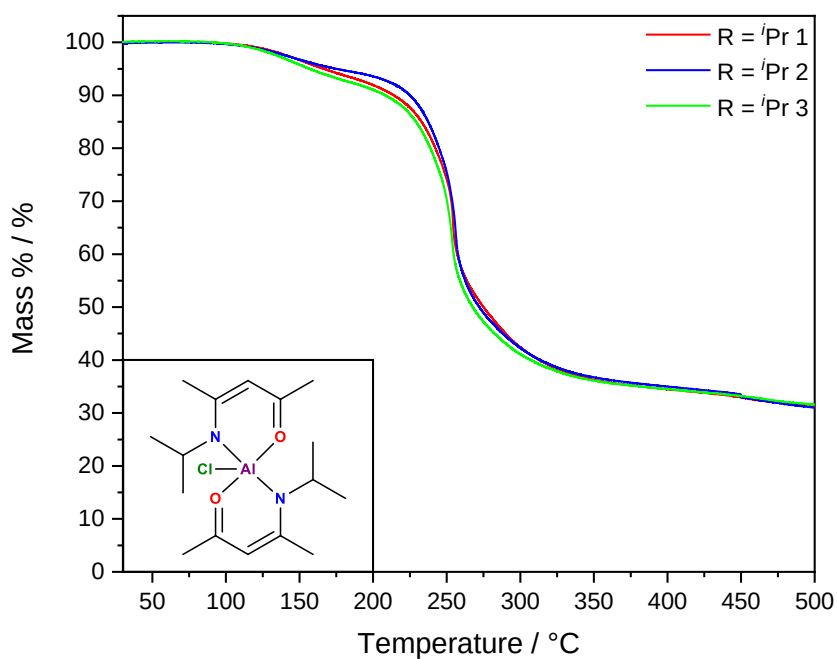
Appendix 116: DTGs of $[Al(Me-acnac)_2Cl]$ (6).



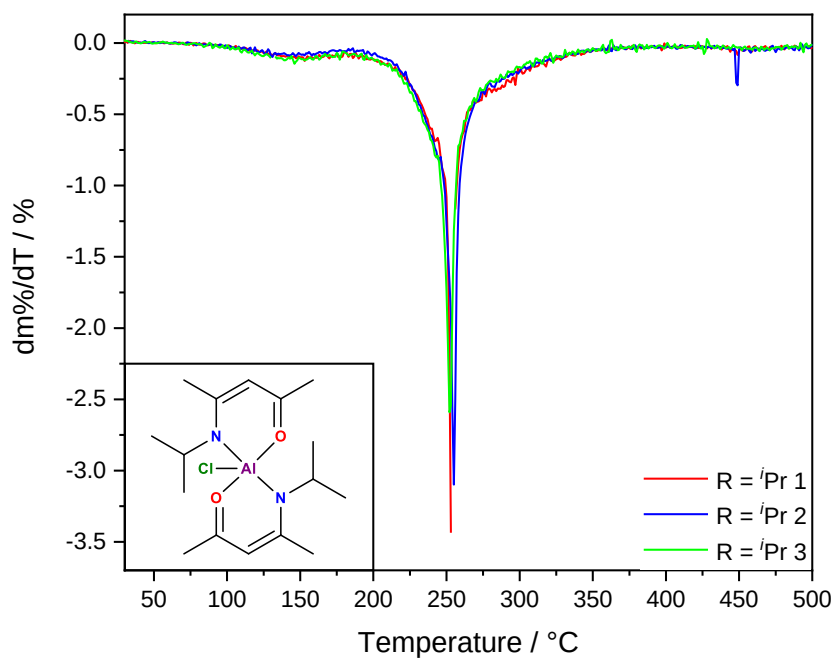
Appendix 117: Thermograms of $[Al(Et-acnac)_2Cl]$ (7).



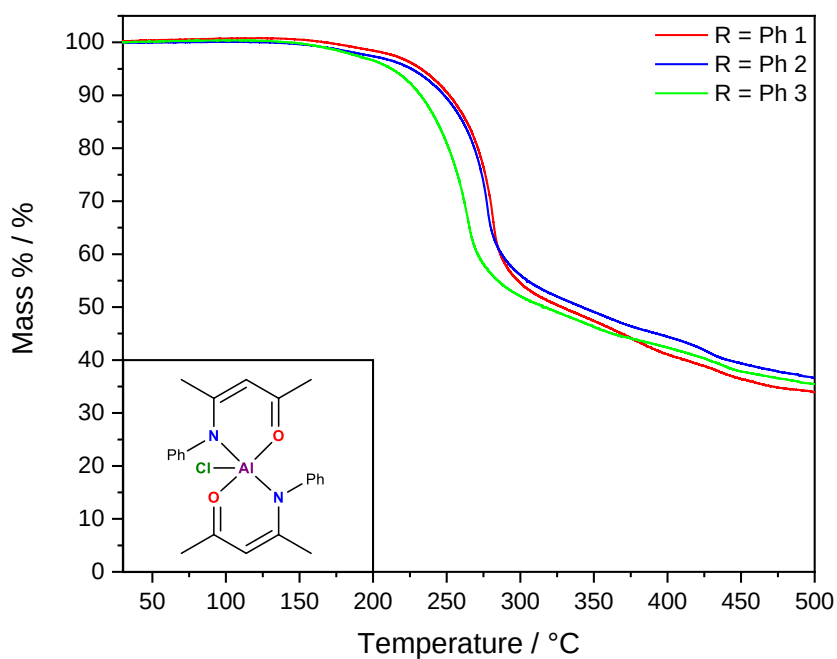
Appendix 118: DTGs of $[Al(Et-acnac)_2Cl]$ (7).



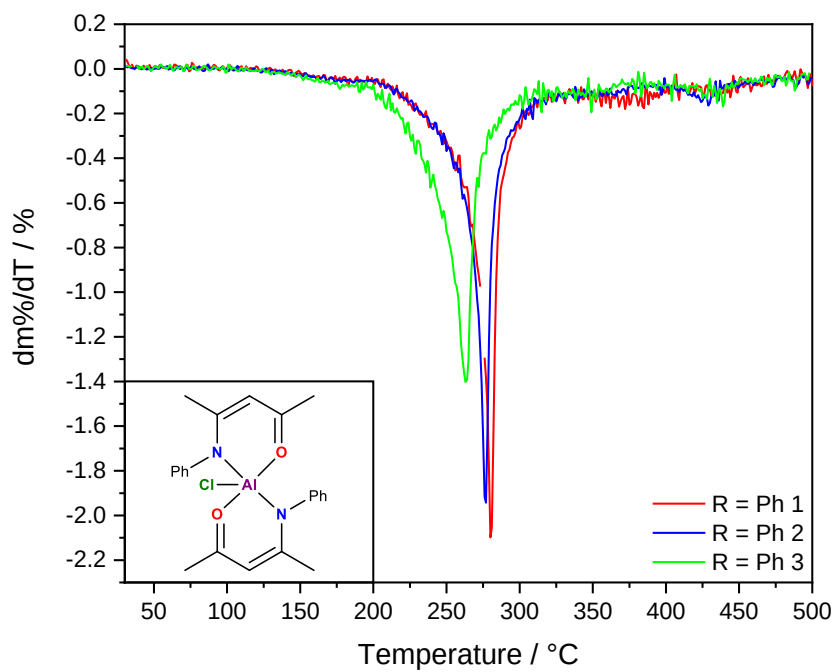
Appendix 119: Thermograms of $[Al(iPr-acnac)_2Cl]$ (8).



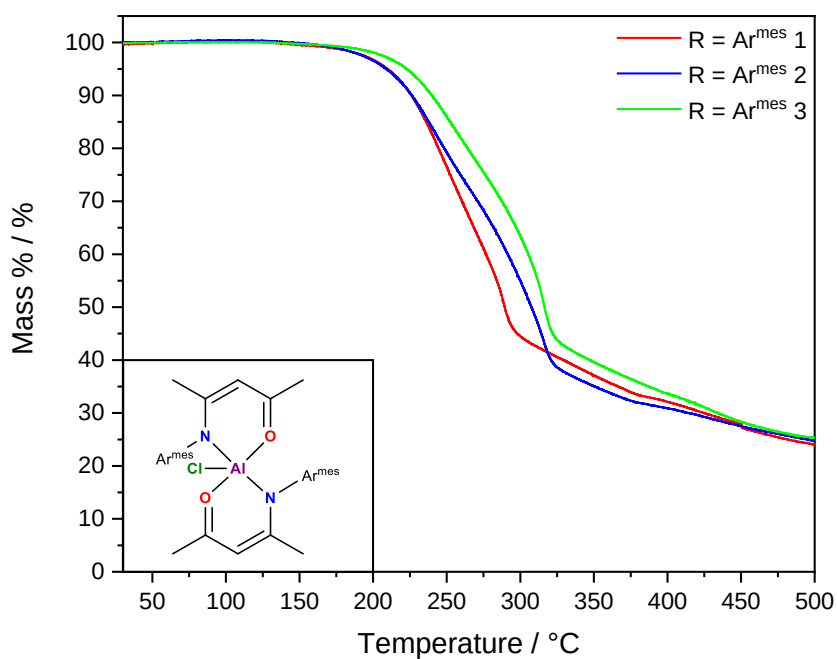
Appendix 120: DTGs of $[Al(iPr-acnac)_2Cl]$ (8).



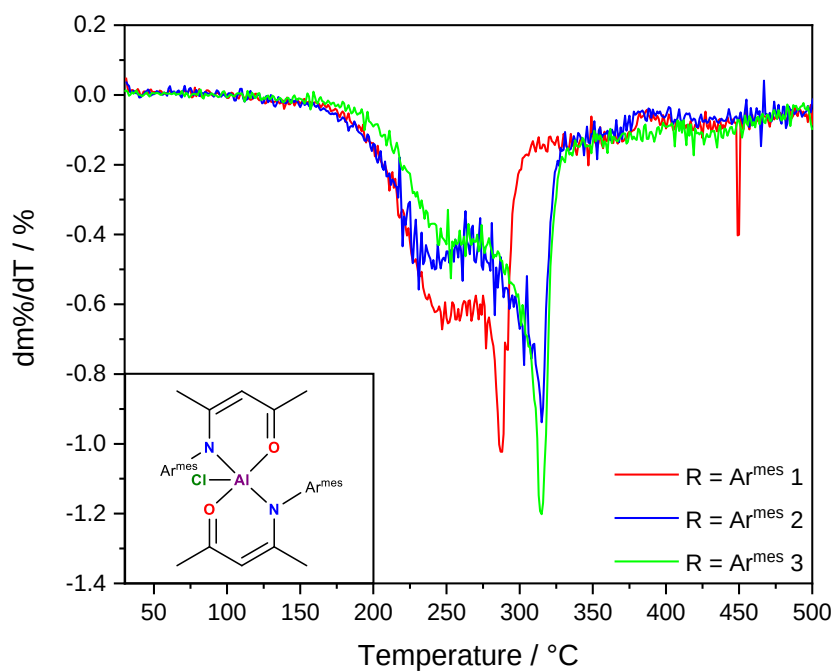
Appendix 121: Thermograms of $[Al(Ph-acnac)_2Cl]$ (9).



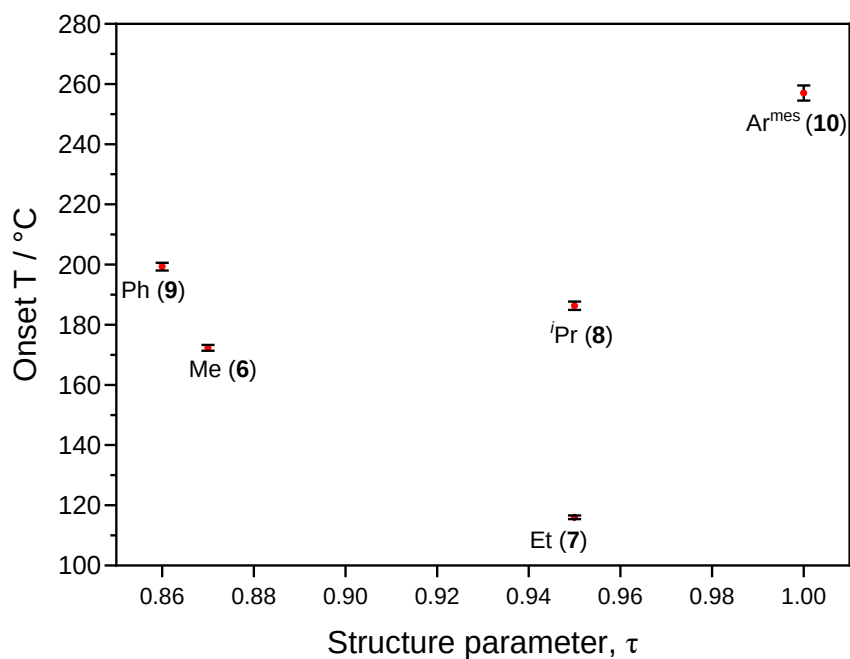
Appendix 122: Thermograms of $[Al(Ph-acnac)_2Cl]$ (9).



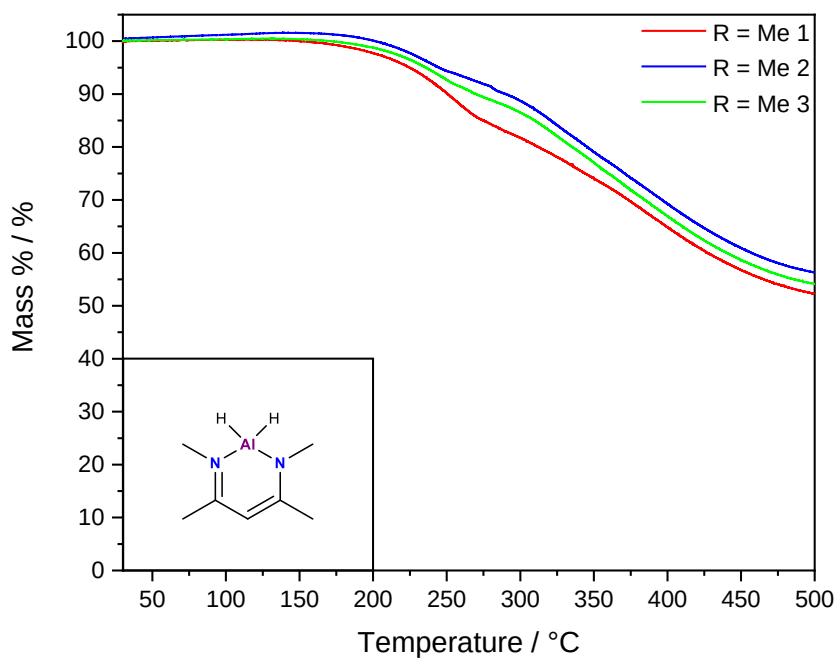
Appendix 123: Thermograms of $[Al(Ar^{mes}\text{-acnac})_2Cl]$ (10).



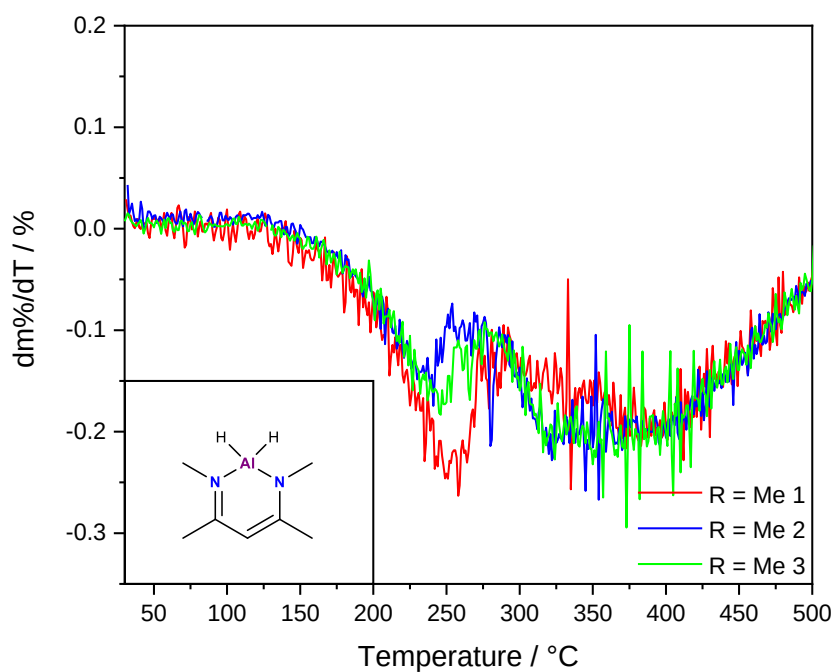
Appendix 124: DTGs of $[Al(Ar^{mes}\text{-acnac})_2Cl]$ (10).



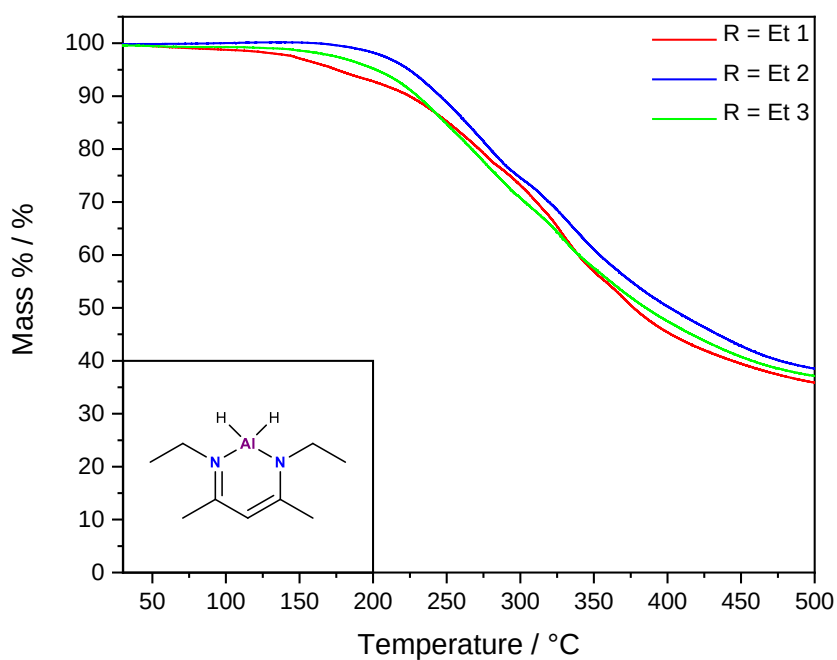
Appendix 125: Comparison of onset temperature vs structural parameters for compounds 6–10.



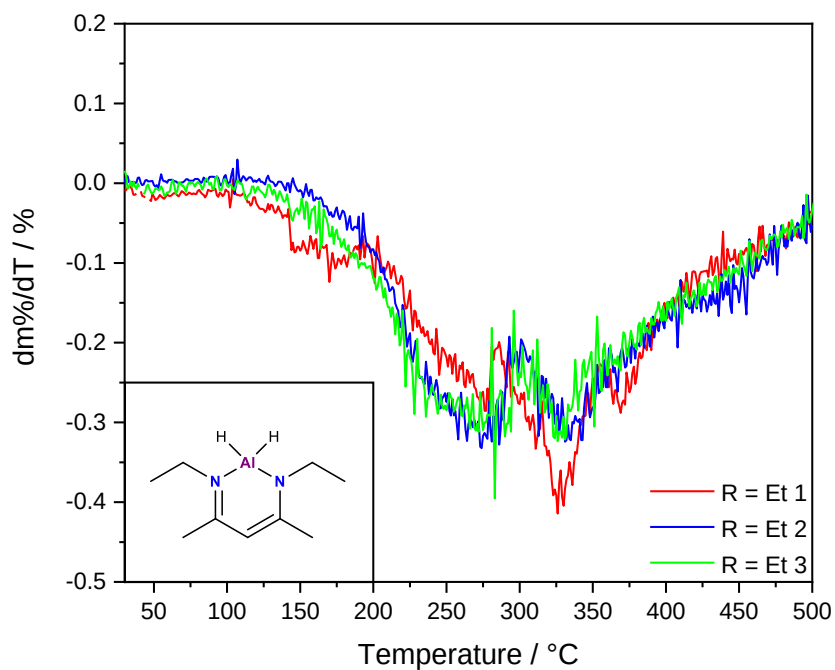
Appendix 126: Thermograms of $[Al(Me_2-nacnac)H_2]$ (11).



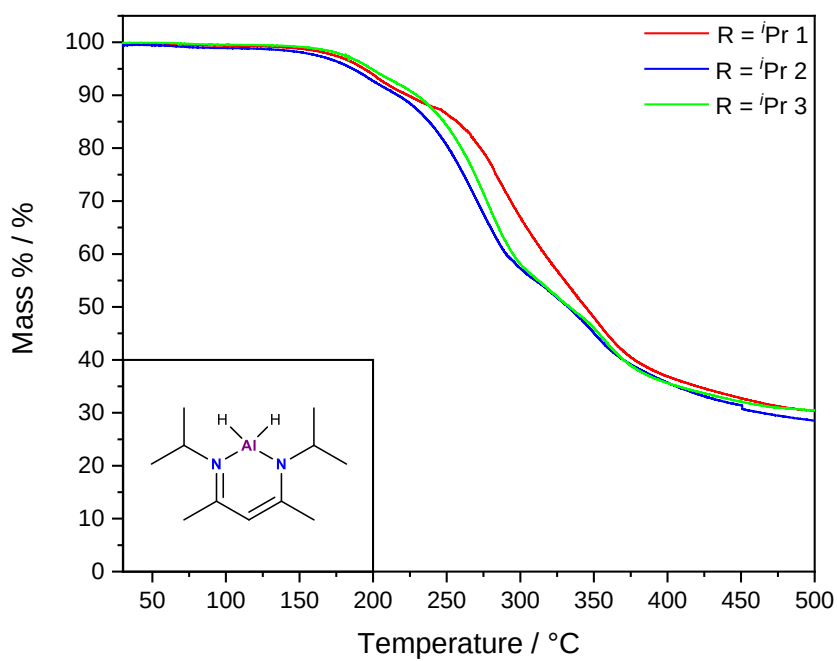
Appendix 127: DTGs of $[Al(Me_2-nacnac)H_2]$ (11).



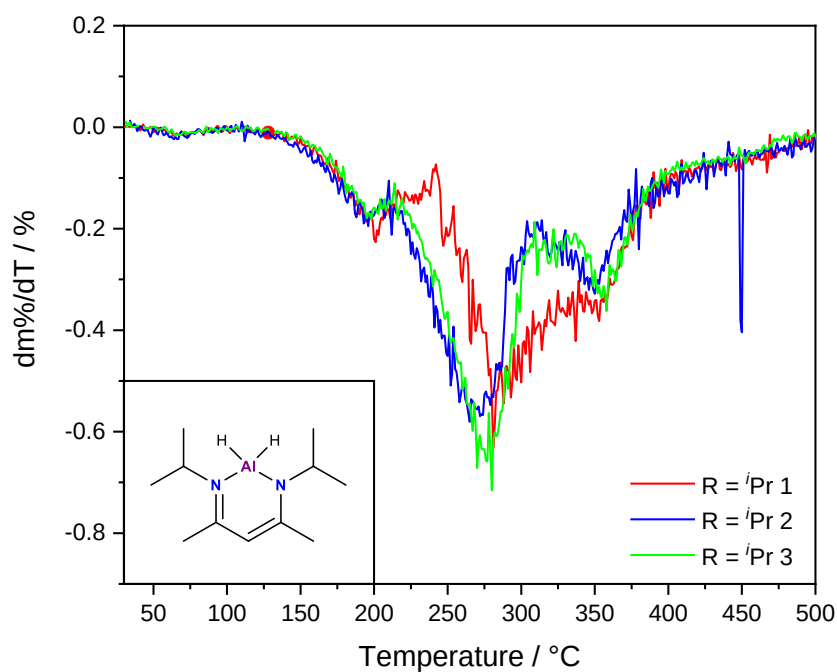
Appendix 128: Thermograms of $[Al(Et_2-nacnac)H_2]$ (12).



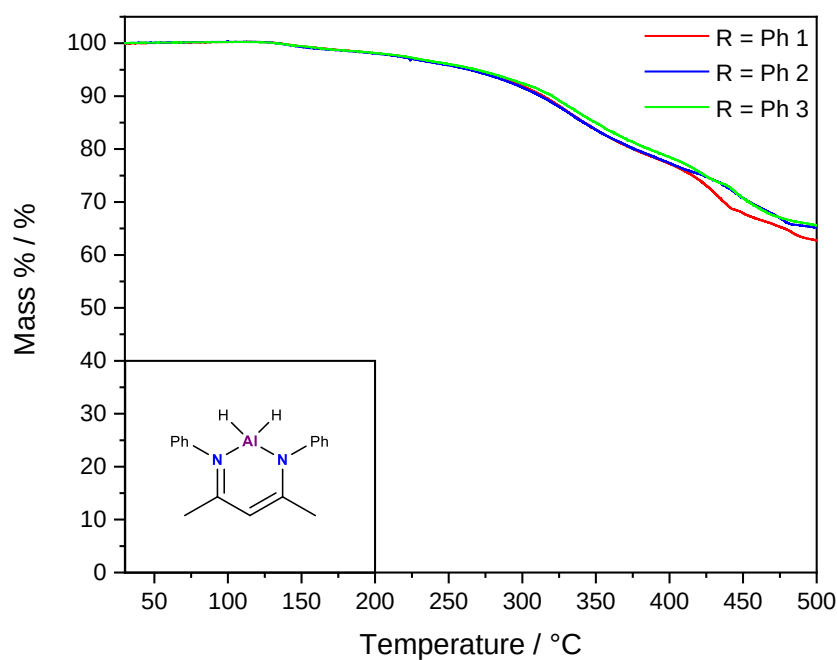
Appendix 129: DTGs of $[Al(Et_2\text{-nacnac})H_2]$ (12).



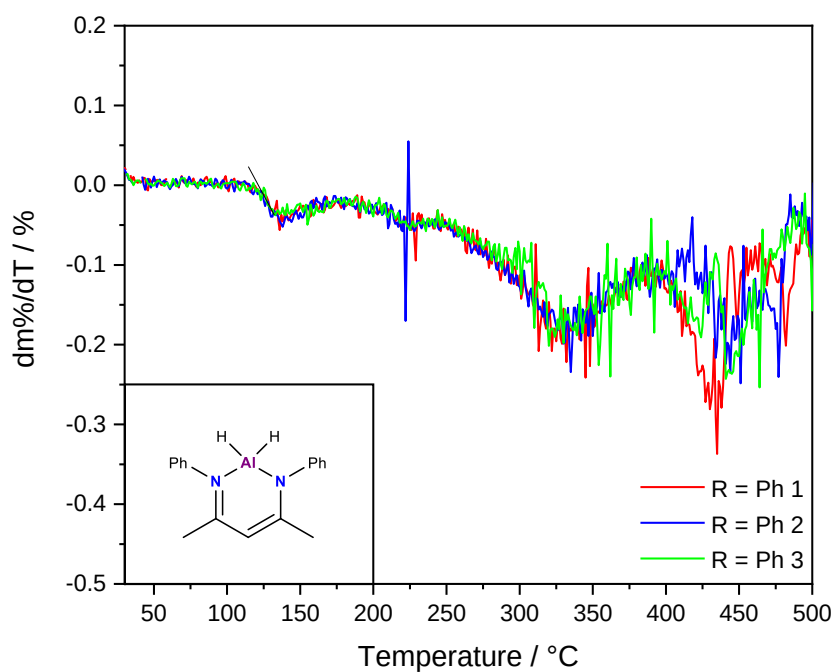
Appendix 130: Thermograms of $[Al(iPr_2\text{-nacnac})H_2]$ (13).



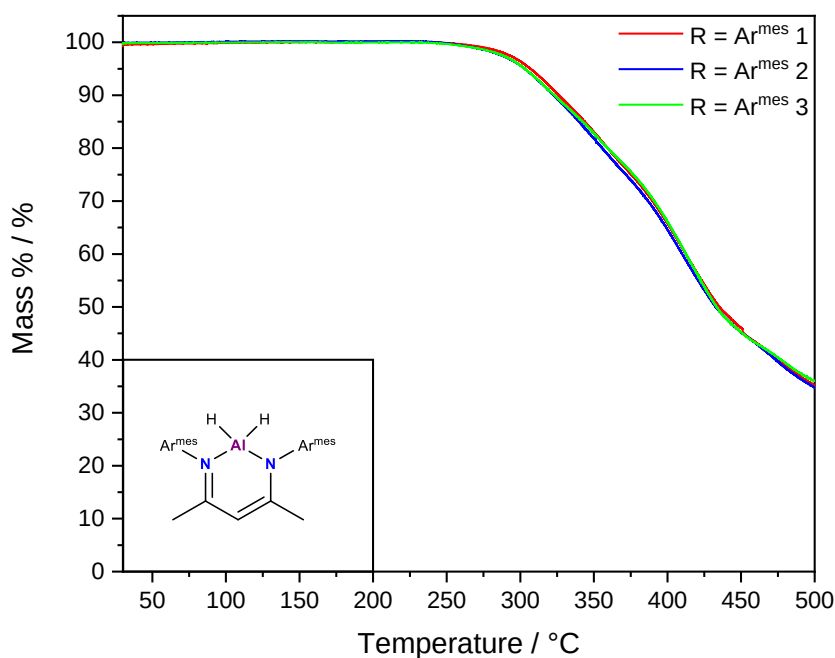
Appendix 131: DTGs of $[Al(iPr_2-nacnac)H_2]$ (13).



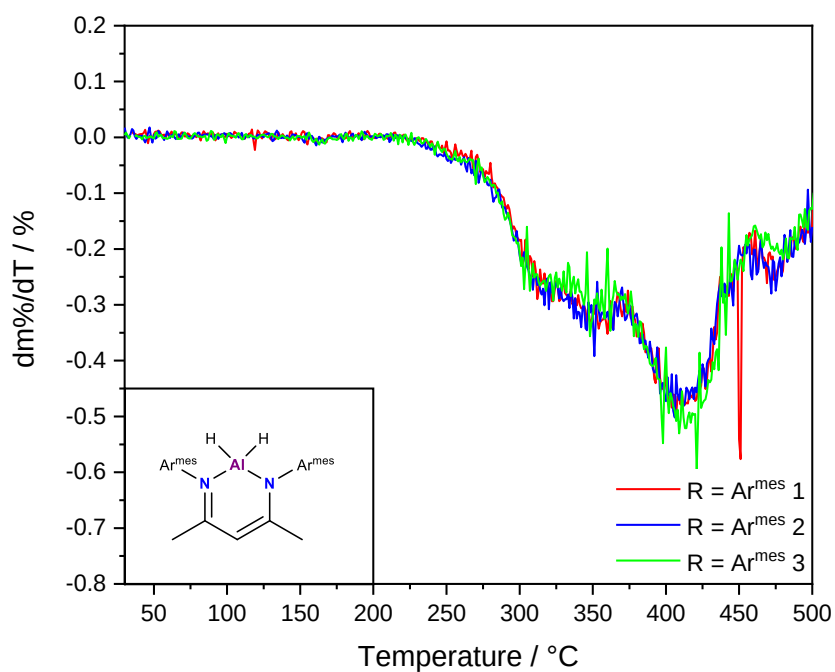
Appendix 132: Thermograms of $[Al(Ph_2-nacnac)H_2]$ (14).



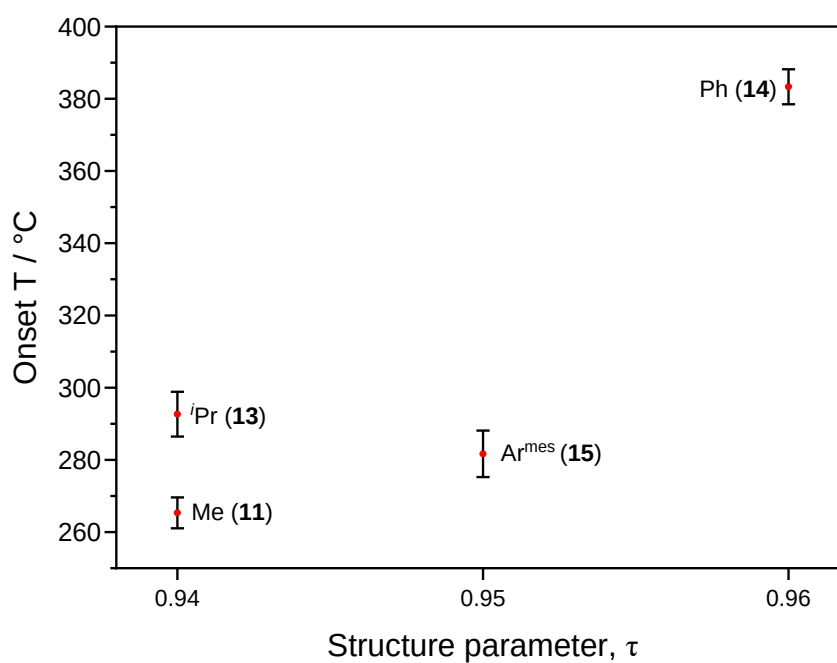
Appendix 133: DTGs of $[Al(Ph_2-nacnac)H_2]$ (14).



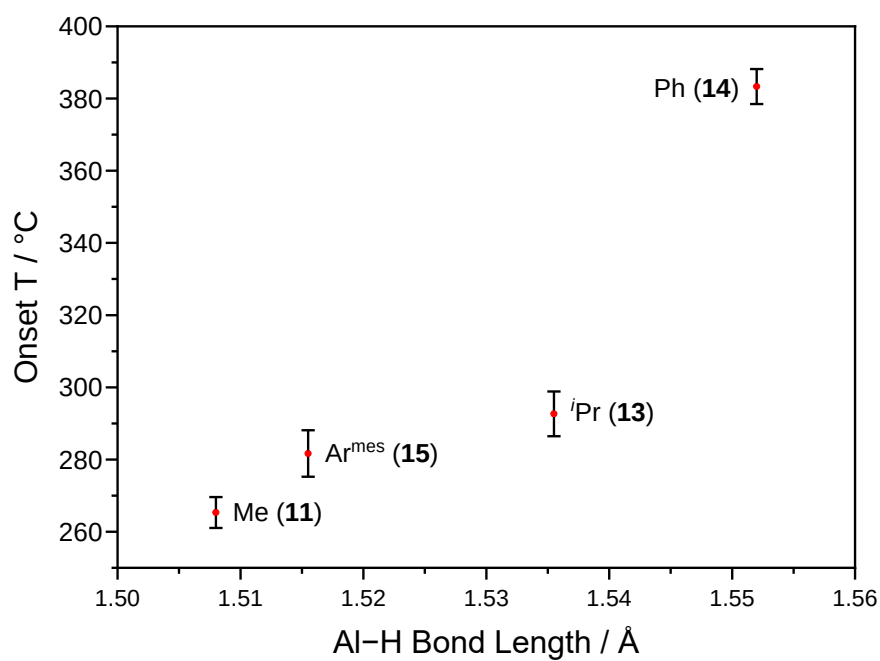
Appendix 134: Thermograms of $[Al(Ar^{mes}_2-nacnac)H_2]$ (15).



Appendix 135: DTGs of $[Al(Ar^{mes})_2-nacnac]H_2$ (15).



Appendix 136: Comparison of onset temperature vs structural parameters for compounds 11–15.



Appendix 137: Comparison of onset temperature vs Al-H bond length for compounds 11–15.

Film analysis (Appendix 138–143)

Appendix 138: Full resistivity data for depositions using **DMEAA** onto various substrates at 120 and 100 °C. CLXXV

Appendix 139: Full resistivity data for depositions using **TEAA** onto various substrates at 120 and 100 °C. CLXXVI

Appendix 140: Background XRD patterns of substrates..... CLXXVII

Appendix 141: Full (unnormalised) XRD data of samples deposited using DMEAA and TEAA on glass, PI, PET and paper for **DMEAA**. CLXXVII

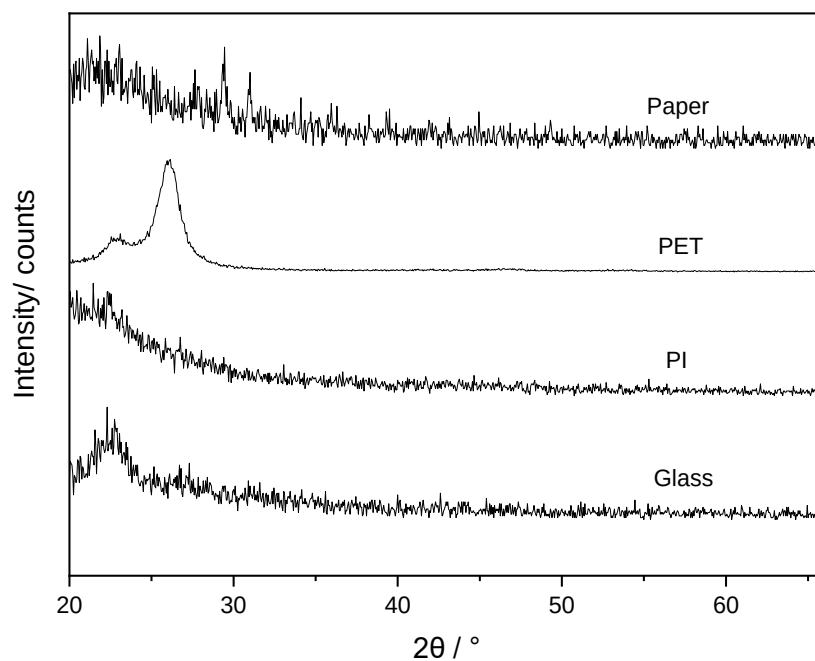
Appendix 142: Full (unnormalised) XRD data of samples deposited using DMEAA and TEAA on glass, PI, PET and paper for **TEAA**. CLXXVIII

Appendix 138: Full resistivity data for depositions using **DMEAA** onto various substrates at 120 and 100 °C.

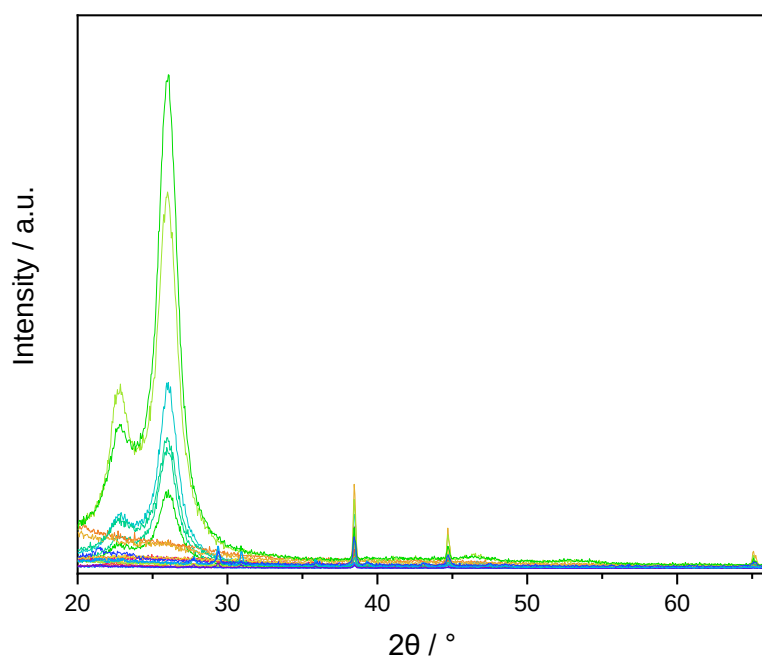
Precursor	Drop size / μ L	Substrate	Temperature / °C	Time / min:s	Resistivity / Ω m	
					Lower Value	Upper Value
DMEAA	25	Glass (G)	120	1:00	1.85E-06	1.98E-06
DMEAA	25	G	120	1:00	2.47E-06	2.63E-06
DMEAA	25	G	120	1:00	3.09E-07	3.29E-07
DMEAA	25	Polyimide (PI)	120	1:00	9.26E-07	9.88E-07
DMEAA	25	PI	120	1:00	3.09E-07	3.29E-07
DMEAA	25	PI	120	1:00	1.54E-06	1.65E-06
DMEAA	25	Polyethylene terephthalate (PET)	120	1:30	1.24E-06	1.32E-06
DMEAA	25	PET	120	1:30	1.85E-06	1.98E-06
DMEAA	25	PET	120	1:30	3.71E-06	3.95E-06
DMEAA	25	Paper (P)	120	1:30	1.54E-06	1.65E-06
DMEAA	25	P	120	1:30	1.24E-06	1.32E-06
DMEAA	25	P	120	1:30	4.94E-06	5.27E-06
DMEAA	25	G	100	1:30	6.79E-06	7.24E-06
DMEAA	25	G	100	1:30	7.41E-06	7.90E-06
DMEAA	25	G	100	1:30	9.88E-06	1.05E-05
DMEAA	25	PI	100	1:30	7.41E-06	7.90E-06
DMEAA	25	PI	100	1:30	1.85E-06	1.98E-06
DMEAA	25	PI	100	1:30	9.26E-06	9.88E-06
DMEAA	25	PET	100	2:30	2.47E-06	2.63E-06
DMEAA	25	PET	100	2:30	1.24E-06	1.32E-06
DMEAA	25	PET	100	2:30	1.85E-06	1.98E-06
DMEAA	25	P	100	2:00	9.26E-07	9.88E-07
DMEAA	25	P	100	2:00	7.10E-06	7.57E-06
DMEAA	25	P	100	2:00	6.18E-07	6.58E-07

Appendix 139: Full resistivity data for depositions using **TEAA** onto various substrates at 120 and 100 °C.

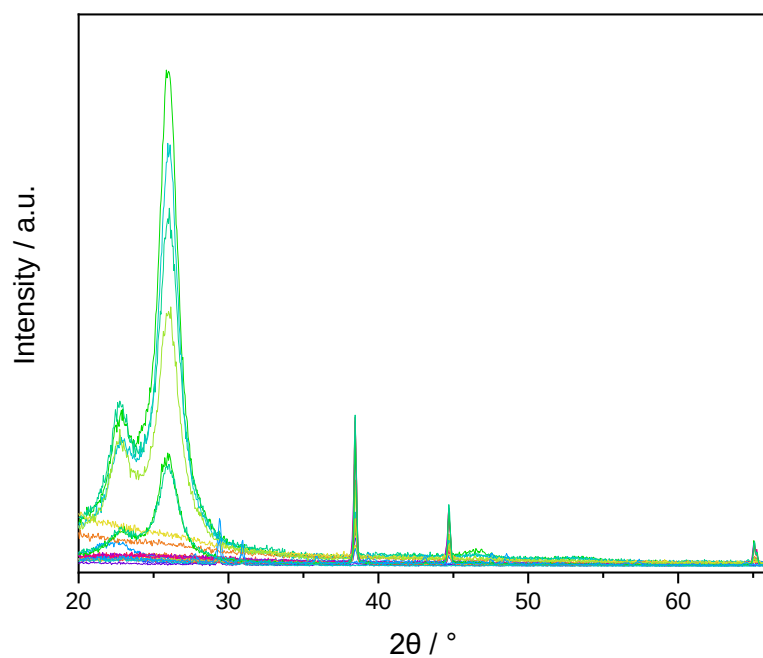
Precursor	Drop size / μ L	Substrate	Temperature / °C	Time / min:s	Resistivity / Ω m	
					Lower Value	Upper Value
TEAA	25	G	120	0:30	3.09E-07	3.29E-07
TEAA	25	G	120	0:30	3.09E-07	3.29E-07
TEAA	25	G	120	0:30	6.18E-07	6.58E-07
TEAA	25	PI	120	1:30	6.18E-07	6.58E-07
TEAA	25	PI	120	1:30	6.18E-07	6.58E-07
TEAA	25	PI	120	1:30	9.26E-07	9.88E-07
TEAA	25	PET	120	2:00	Not Conductive (NC)	NC
TEAA	25	PET	120	2:00	2.78E-06	2.96E-06
TEAA	25	PET	120	2:00	4.32E-06	4.61E-06
TEAA	25	P	120	2:00	1.45E-05	1.55E-05
TEAA	25	P	120	2:00	6.18E-07	6.58E-07
TEAA	25	P	120	2:00	3.09E-07	3.29E-07
TEAA	25	G	100	1:30	3.09E-07	3.29E-07
TEAA	25	G	100	1:30	9.26E-07	9.88E-07
TEAA	25	G	100	1:30	3.09E-07	3.29E-07
TEAA	25	PI	100	2:00	NC	NC
TEAA	25	PI	100	2:00	3.96E-05	4.23E-05
TEAA	25	PI	100	2:00	NC	NC
TEAA	25	PET	100	2:30	4.07E-05	4.34E-05
TEAA	25	PET	100	2:30	2.98E-05	3.18E-05
TEAA	25	PET	100	2:30	1.68E-05	1.79E-05
TEAA	25	P	100	2:00	7.10E-06	7.57E-06
TEAA	25	P	100	2:00	NC	NC
TEAA	25	P	100	2:00	4.63E-06	4.94E-06



Appendix 140: Background XRD patterns of substrates.



Appendix 141: Full (unnormalised) XRD data of samples deposited using DMEAA and TEAA on glass, PI, PET and paper for **DMEAA**.



Appendix 142: Full (unnormalised) XRD data of samples deposited using DMEAA and TEAA on glass, PI, PET and paper for **TEAA**.