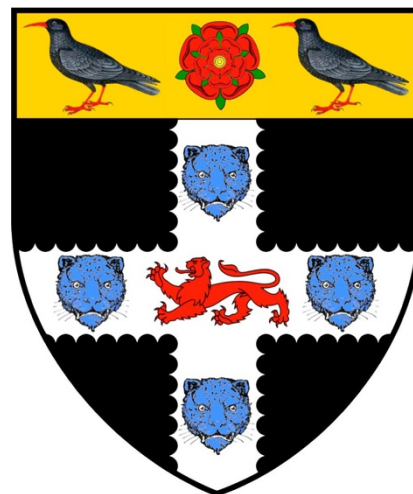


Synthesis and Reactivity Studies of Low Valent Germanium Compounds



Xueer Zhou, Christ Church

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A thesis submitted for the degree of Doctor of
Philosophy

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This thesis is dedicated to my mother, who raised me up alone from the day I was born and never stops working hard to give me the best opportunities to achieve great things in life.

This thesis describes the synthesis, characterisation and reactivity studies of NHC-amido and phosphine-amido stabilised low valent heavier group 14 compounds.

In Chapter 1, a general introduction of the development of interesting main group compounds in the recent decades is provided. The classes of compound include carbenes, metallylenes, low valent germanium cations and the heavier group 14 alkyne analogues. The reactivity patterns of these types of compound are also discussed. The aims of this DPhil project are described.

In Chapter 2, the experimental techniques and analytical methods employed in this project are summarised. Details of starting materials syntheses following modified literature procedures are also given.

In Chapter 3, the synthesis and structural properties of a series of low valent monohalo germanium, tin and lead compounds stabilised by a chelating $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand system are described and compared. These compounds serve as precursors towards more reactive derivatives in the following chapters. The synthesis of a Ge(I) dimer upon reduction and its preliminary reactivity towards dihydrogen are also explored.

In Chapter 4, the synthesis of two novel germyliumylidene cations featuring a $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand system and their activation of O-H and N-H bonds via metal ligand cooperation, as well as the oxidative addition of C-Cl bond in dichloromethane, are detailed.

In Chapter 5, the synthesis of low valent germanium(II) compounds stabilised by a $N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ ligand is investigated. From a common chlorogermylene precursor, a novel germyliumylidene and other Cl-substituted Ge(II) derivatives can be achieved. Attempts to synthesise a Ge(II) hydride in situ are described and the isolated Ge(II) naphthoxide is shown to act as an effective pre-catalyst in hydroboration reactions.

Abbreviations

Ar = general aryl group (unless otherwise stated)	HOMO = Highest Occupied Molecular Orbital
Ad = 1-admantyl	HSQC = Heteronuclear Single Quantum Coherence
atm = atmospheric pressure	ⁱ Bu = isobutyl
br = broad	ⁱ Pr = isopropyl
COSY = homonuclear correlation spectroscopy	J = coupling constant
Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl	L = ligand
cyclam = 1,4,8,11-tetraazacyclotetradecane	LUMO = Lowest Unoccupied Molecular Orbital
d = doublet	m = multiplet
DCM = dichloromethane	Me = Methyl
DFT = Density Functional Theory	Mes = 2,4,6-Trimethylphenyl (mesityl)
DIBAL = Diisobutylaluminium hydride	mol = moles
Dipp = 2,6-Diisopropylphenyl	ⁿ Bu = <i>normal</i> -butyl
equiv. = equivalent	NMR = Nuclear Magnetic Resonance
Et = Ethyl	<i>o</i> = ortho
FT-IR = Fourier Transform Infrared	<i>p</i> = para
G = Gibbs free energy	Ph = Phenyl
<i>H/h</i> = enthalpy/hours	PMDTA = <i>N,N,N',N'',N'''</i> -pentamethyldiethylenetriamine
HBpin = pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborole)	ppm = parts per million
HBCat = catecholborane (1,3,2-benzodioxaborolane)	q = quartet
HMBC = Heteronuclear Multiple Quantum Coherence	R/R ₁ /R ₂ = general substituents (unless otherwise stated)

S/s = entropy/singlet

^sBu = sec-butyl

sep = septet

t = triplet

tacn = 1,4,7-triazacyclononane

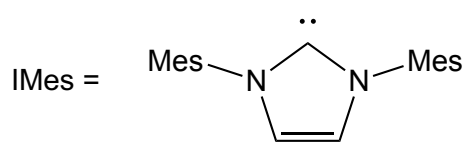
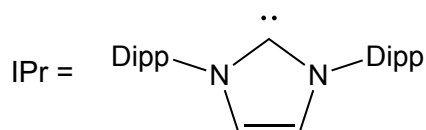
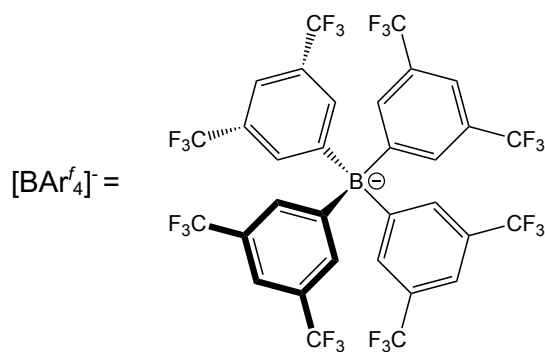
^tBu = *tert*-butyl

THF = Tetrahydrofuran

Trip = 2,4,6-Triisopropylphenyl

WCA = weakly coordinating anion

X = generic halide



Compound numbering: In Chapter 1, all known compounds are numbered as **1.x** in sequence. In the introduction sections of Chapter 3-5 known compounds are numbered using Roman numerals starting from **I** in each chapter. All novel compounds are numbered using single integers starting from **1**.

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Appendix

Chapter I

Introduction

1.1 “Transition metal-like” behaviour of main group compounds

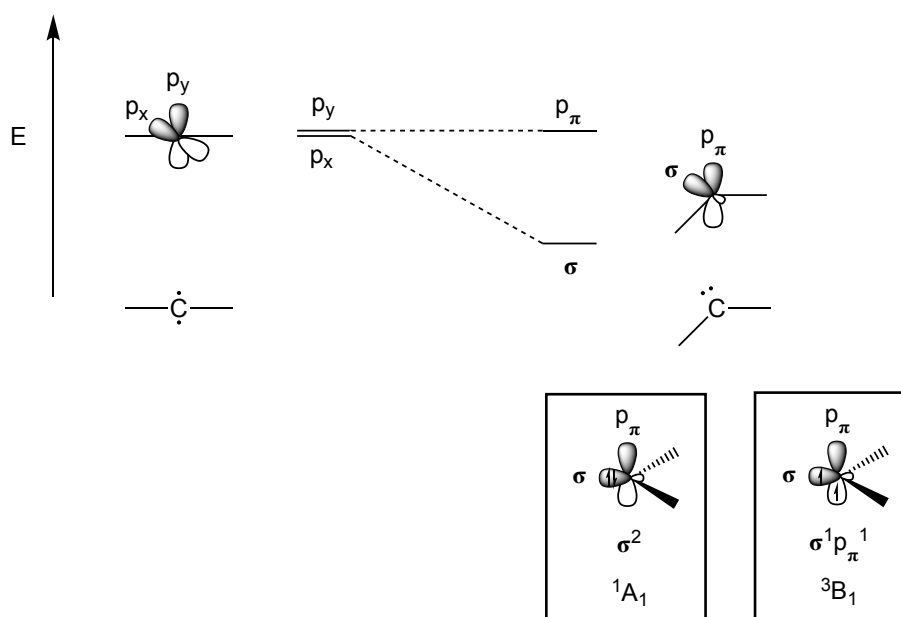
Transition metal complexes play a key role in homogenous catalysis of important industrial processes, for example the hydrogenation of alkenes by Wilkinson’s catalyst and the carbonylation of methanol to generate acetic acid via the Monsanto process.¹ These catalytic cycles proceed via a series of elementary reaction steps at the metal centre (typically including oxidative addition, migratory insertion and reductive elimination), which involve small molecules such as dihydrogen, carbon monoxide and olefins. Key to this reactivity is the fact that transition metal complexes possess energetically accessible, partially occupied valence orbitals which are capable of interacting with small molecules.² Their drawbacks have also started to become apparent, and their toxic effects on living organisms and harmful impact on the environment cannot be ignored.³ Difficulties in extraction may also lead to elevated prices and socio-economic risks.⁴ Moreover, some industrially attractive reactions involving the oxidative addition of the N-H bond in ammonia (and amines) by transition metal complexes remain extremely challenging, as almost all form simple coordination adducts instead.^{5–7}

In recent decades, major advances have been made in the synthesis of isolable low-valent main group compounds, and investigation of their previously elusive reactivity in small molecule activation and catalysis.^{8–10} In 2005, a germanium analogue of an alkyne was shown to oxidatively add hydrogen under ambient conditions, the first main group compound to do so.¹¹ As with transition metal systems, the proposed mechanism involves interactions between the closely separated frontier orbitals of the digermynes and those of hydrogen. Subsequently, a wide range of group 13–15 compounds including singlet carbenes and metallocenes, tetrelonium cations, heavier alkyne analogues, monovalent group 13 complexes and frustrated Lewis pairs¹² have demonstrated “transition metal-like” behaviour in the activation of saturated

and unsaturated substrates, including ammonia. Despite this, reversible bond activation and reductive elimination are rare and the applications of single-site systems in catalysis remain a largely unrealised research focus with huge potential.

1.2 N-heterocyclic carbenes (NHCs)

Carbenes feature a neutral, divalent carbon with two nonbonding electrons and six valence electrons in total. Bending at the carbene centre breaks the degeneracy of the p_x and p_y orbitals and enforces s/p mixing (and p_x , p_y orbitals become the so-called σ and p_π orbitals respectively). The ground-state spin multiplicity of a carbene can be a singlet (1A_1) or a triplet (3B_1), depending on the relative energies of the two frontier orbitals. Reactivity-wise, singlet carbenes are potentially ambiphilic in nature with both a filled σ orbital and a vacant p_π orbital, whereas triplet carbenes possess diradical character (**Scheme 1.2.1**).¹³



Scheme 1.2.1: Frontier orbitals of linear and bent carbenes and the ground state singlet and triplet electronic configurations.

The ground-state multiplicity of carbenes can be influenced by two factors - electronic effects and steric effects. The use of sterically bulky substituents is an effective way of kinetically stabilising triplet carbenes by widening the angle at carbon. Electronically, electronegative (σ -

electron withdrawing) substituents inductively stabilise the σ orbital by increasing its s character, leading to a bigger HOMO-LUMO energy gap, and thereby favouring the singlet ground state. In addition, π -electron donating substituents destabilise the vacant p_π orbital and widen the HOMO-LUMO gap (mesomeric effect). N-heterocyclic carbenes (NHCs) are cyclic aminocarbenes that possess singlet ground states. The (one or two) adjacent π -donating and σ -withdrawing amino groups stabilise the carbon centre via push, push mesomeric-pull, pull inductive effects. Moreover, sterically bulky substituents prevent dimerisation of the carbene. As such, NHCs have been extensively explored in recent years.¹⁴

Early efforts to synthesise NHC-metal complexes were made by Wanzlick et al. and Öfele in 1968, leading to the first examples of NHC-Hg and NHC-Cr complexes.^{15,16} In 1988, Bertrand et al. reported a carbene intermediate from the photolysis of a (trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane.¹⁷ The first singlet carbene (**1.1**) that was thermally stable and characterised in the solid state was reported by Arduengo in 1991, in a communication entitled *A Stable Crystalline Carbene*.¹⁸ The target N-heterocyclic carbene was synthesised by C2-deprotonation from the corresponding imidazolium salt by NaH. The relatively high stability of the compound was attributed to a combination of thermodynamic/electronic (i.e. the mesomeric and inductive effects of the two amido nitrogens adjacent to the carbene centre) and kinetic/steric factors (i.e. bulky adamantyl substituents).

However in a subsequent publication it was shown that steric factors play a reduced role in the stability and isolation of imidazol-2-ylidenes.¹⁹ The unsaturation of the imidazolium C=C backbone was also shown to provide only a small enhancement of stabilisation compared to a saturated backbone through potential 6π aromaticity in heterocycle.²⁰ The first acyclic diaminocarbene (**1.2**) was isolated and shown to possess significant C-N double bond character; this system is slightly less stable and more air-sensitive than cyclic NHCs.²¹ Carbene N-C-N ring expansion can also be achieved, as manifested by the isolation of NHCs

(1.3) featuring six-, seven- and eight-membered rings, and their applications in *s*- and *d*-block metal complexes.^{22–24} In addition, a metal-free “abnormal” N-heterocyclic carbene (aNHC) (1.4) was first isolated in 2009, which is considered to be more basic than normal NHCs.²⁵ More recently, the synthesis and isolation of a monosubstituted carbene (1.5), employing a carefully designed substituent at the single N_{amino} group was reported, and shown to be stable in the solid-state at room temperature for more than a month.²⁶ DFT calculations combined with experimental evidence imply that it is one of the most electrophilic carbenes isolated to date.

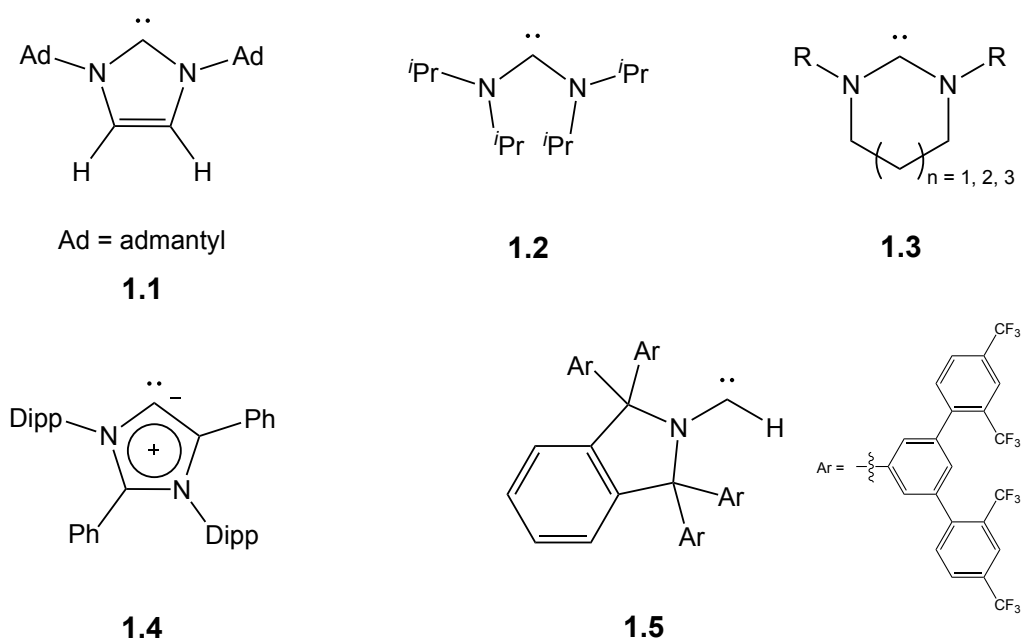


Figure 1.2.1: Representative examples of NHCs.

NHCs have been shown to possess stronger σ -donating properties as ligands within transition metal complexes than tertiary phosphine ligands, and have been widely applied in homogeneous catalysis.²⁷ Major breakthroughs include NHC-Ru(II) complexes for olefin metathesis and NHC-Pd(0) complexes for C-C and C-N cross-coupling reactions.^{28,29} The role of NHCs as organocatalysts has also been intensively explored.³⁰

In a similar fashion to phosphine ligands, the electronic and steric properties of NHCs can be probed and analysed quantitatively.^{31–33} The overall donating ability of a ligand at a transition metal can be quantified by the Tolman Electronic Parameter (TEP),³⁴ which exploits the effects

on the infra red stretching frequency of metal-bound carbonyl coligands of variation in the electron-donating capabilities of the ligand in question. $\nu(\text{CO})$ reflects combined σ -donating and π -accepting properties of the carbene. As illustrated by NHC-containing nickel(0) and iridium(I) carbonyl complexes, the σ -donating ability of NHCs is typically higher than phosphine ligands.^{35–38} The π -accepting ability of NHCs can be independently evaluated through the ^{31}P NMR chemical shift of the derived carbene-phenylphosphinidene complex, or the ^{77}Se NMR resonance of the corresponding Se adduct.^{39–42} In both cases the resonance shifts downfield as the π -accepting ability of the carbene increases. One commonly-used method of determining the overall *steric* impact of an NHC is by determining its “percentage buried volume” ($\%V_{\text{bur}}$) from either X-ray crystallography data or quantum chemical calculations.^{32,36,43,44} This parameter represents the percentage of volume of a sphere with radius r around the metal centre which is occupied by atoms of the NHC ligand.

Another key development in the area of NHCs is in the stabilisation of low-valent main group element compounds.^{45,46} The first NHC-Ge(II) adduct (**1.6**) was structurally characterised by Arduengo et al. in 1993.⁴⁷ Since then, NHCs have been extensively utilised in stabilising low-valent main group compounds due to their strongly σ -donating properties. Notably, the first dichlorosilylene was isolated at room temperature, stabilised as an NHC adduct.^{48,49} Moreover, NHCs have been shown to stabilise an otherwise transient diorganogermylene $\text{Ge}(\text{Mes})_2$.⁵⁰ Rivard et al. conducted a series of studies on heavier methylene (**1.7**) and ethylene analogues based on stabilisation by a donor-acceptor adduct model.^{51–54} NHCs are able to stabilise a series of main group diatomic allotropes with a formal oxidation state of zero,^{55–57} including examples for boron,⁵⁸ silicon,⁵⁹ germanium,⁶⁰ tin,⁶¹ phosphorus⁶² and arsenic.⁶³ Cyclic (**1.8**) and acyclic germa-dicarbenes featuring a monomeric germanium(0) centre have also been reported.^{64–66}

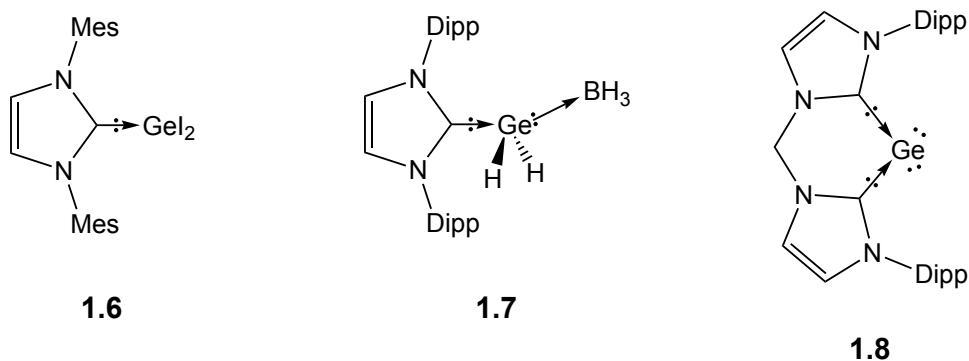
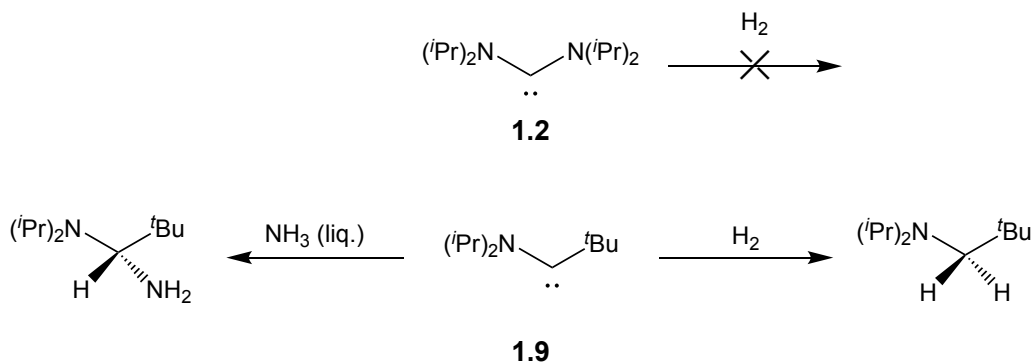


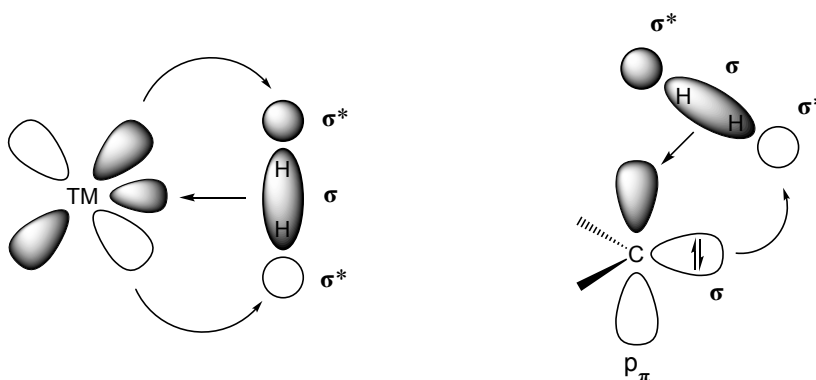
Figure 1.2.2: NHC-stabilised low valent germanium compounds and tethered-NHC ligands.

Bertrand et al. introduced the first acyclic (alkyl)(amino)carbene (**1.9**) in 2004 and revealed that such systems possess a higher energy HOMO and a smaller HOMO-LUMO gap than both Arduengo's di(amino)carbene (**1.1**) and the (hypothetical) acyclic carbene $C(NH_2)_2$.^{67,68} Consequently, (alkyl)(amino)carbenes are considered to be both more nucleophilic and electrophilic than NHCs. Consistently, and in contrast to di(amino)carbenes (which do not react at C2 position with CO or H_2),^{69,70} acyclic and cyclic (alkyl)(amino)carbenes react with CO to form the corresponding ketenes.^{71,72} In 2007, Bertrand et al. demonstrated in another groundbreaking report that two singlet (alkyl)(amino)carbenes (cyclic and acyclic) are able to mimic transitional metal behaviour by effecting the oxidative addition of H_2 at the carbene centre under mild conditions.⁷³ They are also capable of oxidatively activating NH_3 at $-78^\circ C$ (**Scheme 1.2.2**). This contrasts with the behaviour of electrophilic transition metal centres, which (with very few exceptions) form Lewis Acid-Base (Werner-like) adducts with amines. The isolation of an amido hydride complex of iridium was reported by Hartwig et al. only in 2005.⁶ Analogous activation reactions are not achievable using di(amino)carbenes (e.g. **1.2**); compared to (alkyl)(amino)carbenes, the p_π orbital (LUMO) in di(amino)carbenes is destabilised and raised in energy. The σ orbital (HOMO) is lowered in energy slightly and the HOMO-LUMO gap is therefore significantly larger, which disfavours the activation of E-H bonds.



Scheme 1.2.2: Oxidative addition of H₂ and NH₃ by an acyclic (alkyl)(amino)carbene; comparative lack of reaction with a di(amino)carbene.

In terms of reaction pathways, DFT calculations and experimental evidence both support the idea that the activation of H₂ by (alkyl)(amino)carbenes is a nucleophilic activation process, which involves a primary interaction of the lone pair of carbene with the σ^* anti-bonding orbital of H₂, followed by a hydride transfer to the positively polarised carbon centre. This is in the opposite sense to H₂ activation by a transition metal centre, in which the primary interaction is between the vacant *d* orbital of the metal and the σ bonding orbital of H₂. Depending on the strength of back-donation from the filled *d* orbital of the metal to the σ^* anti-bonding orbital of H₂, the H-H bond can then be cleaved.^{74,75}



Scheme 1.2.3: Models of orbital interactions of H₂ with a transition metal centre (left) and with a carbene centre (right).

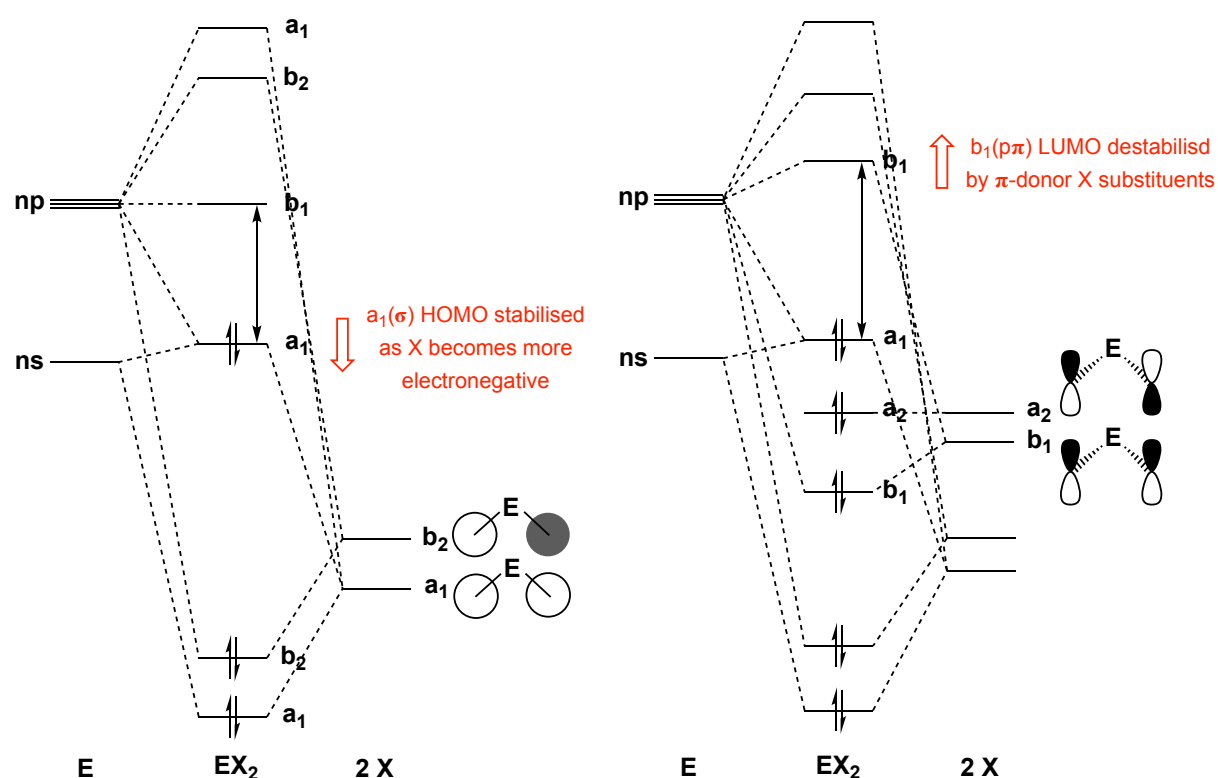
1.3 Metallylenes*

Metallylenes are the heavier group 14 analogues of carbenes with the general formula of R_2E , namely silylenes (R_2Si), germylenes (R_2Ge), stannylenes (R_2Sn) and plumbylenes (R_2Pb). These compounds feature the group 14 element with a formal oxidation state of +2 and six electrons in the valence shell. Compared to the simplest carbene CH_2 , which has a triplet ground state, the heavier analogues (e.g. SiH_2) possess singlet ground states, and are more bent (i.e. have H-E-H angles closer to 90°). This can be rationalised by the increase in atomic radii of E, poorer orbital overlap and weaker E-H bonds. There is less s/p mixing on going down group 14, and the σ orbital goes from approximately " sp^2 " for C to almost pure s for Pb - leading to a bigger HOMO-LUMO gap.⁷⁶ Therefore, in contrast to carbenes, metallylenes almost always possess a singlet ground state. Such systems have low tendency to undergo s/p mixing and possess a lone pair with high s character (σ) and a vacant p orbital (p_π), consistent with their ambiphilic character.⁷⁷ Since metallylenes with simple R groups are highly reactive and polymerise easily, kinetic and/or electronic strategies are needed to stabilise monomeric species.⁷⁸ Sterically bulky ligands are usually required to prevent oligomerisation. Intramolecular or intermolecular ligands involving π -donating heteroatoms (e.g. N, O, P) are often used to stabilise the highly reactive vacant p_π orbital (LUMO) via mesomeric effects.^{13,77}

Consistent with the contrasting capabilities in small molecule activation of di(amino)carbenes and (alkyl)(amino)carbenes (section 1.2), the reactivity of metallylenes is often directly related to the singlet-triplet energy gap, which in turn can be related to the HOMO-LUMO gap between the frontier orbitals (σ and p_π).⁷⁹ A smaller HOMO-LUMO energy gap generally leads to higher reactivity. The electronic properties of the R substituents and the R-E-R bond angle at the metal centre are closely related to the energy of HOMO and LUMO orbitals (**Scheme 1.3.1**).⁸⁰ Bent's Rule states that an orbital has more s character when bonding to a more electropositive

* The main focus of this section is on germylenes, reflecting the corresponding focus of the experimental work described in Chapters 3-5.

group,⁸¹ which indicates that when the substituent R is more σ -donating, the lone pair σ orbital (HOMO) acquires more p character and become destabilised, hence narrowing the HOMO-LUMO gap (and vice versa). This theory is analogous to the inductive effect described above in the case of carbenes. Since a wider R-E-R angle can be caused by a more electropositive R substituent, it is also strongly associated with the destabilisation of the HOMO and a smaller HOMO-LUMO gap. On the other hand, a more π -donating ligand will destabilise the p_π orbital (LUMO) and widen the HOMO-LUMO gap, akin to the mesomeric effect for carbenes.¹³ Overall, the balance between stabilising the metallylene ground state and enhancing reactivity is a primary consideration when designing the ligand set around the metal centre.



Scheme 1.3.1: Molecular orbital diagrams demonstrating the effect on the HOMO/LUMO energies by σ -withdrawing (left) and π -donating ligands (right) respectively.

In the 1970s, Lappert et al. introduced the synthesis of organogermanium/tin/lead derivatives (**1.10**) stabilised by bis(trimethylsilyl)amino ligands, which can act as versatile precursors to other divalent species such as dialkyl metallylenes (**1.11**).^{82–85} The same group also reported the first examples of two-coordinate germylenes and stannylenes that are monomeric in the

solid state (**1.12**).⁸⁶ Interestingly, Jutzi et al. structurally characterised a monomeric dialkyl germylene (**1.13**) with just one more trimethylsilyl group on the alkyl substituents than Lappert's dialkyl germylene (**1.11**), which is a dimer in the solid state.^{87,88}

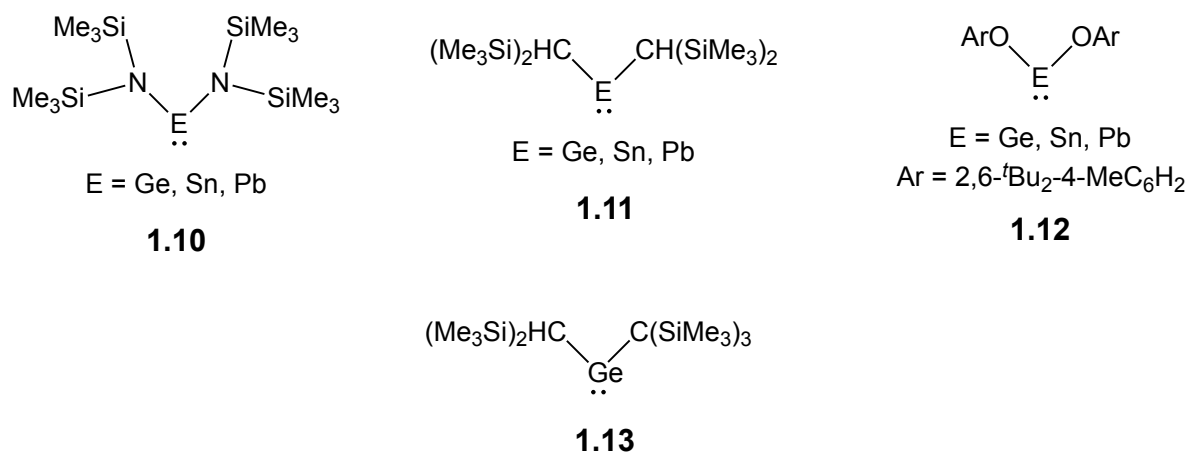


Figure 1.3.1: First examples of isolable two-coordinate divalent metallylenes.

More recently, great advances were made in the last two decades in the development of novel synthetic methods which have allowed exploration of the reactivity of heavier carbene analogues. By fine-tuning the electronic and steric properties of the ancillary ligands around the metal centre, low-valent heavier group 14 compounds can be isolated and their ambiphilic nature illustrated by means of small molecule activation chemistry, which in some cases closely resembles that of transition metal complexes. As an example, Power's terphenyl-stabilised germylene was shown to be capable of oxidatively splitting H₂ at room temperature (vide infra).⁸⁹

1.3.1 β -Diketiminato stabilised metallylenes

Anionic, chelating β -diketiminato ("Nacnac") ligand systems and their derivatives have been extensively applied to the synthesis of germylenes and stannylenes. They are ideal for stabilising low-valent metal centres due to the presence of two π donating N-donors within a chelating framework (which would destabilise the p_π orbital), and the steric bulk provided by the tuneable substituents on the ligand backbone.⁹⁰ In 2001, Roesky et al. reported the first

applications of $[N(Ar)CMe]_2CH^-$ ($Ar = 2,6\text{-}i\text{-Pr}_2C_6H_3$) (" $[Nacnac^{Dipp}]^-$ ") in the chemistry of the heavier group 14 elements germanium and tin. This led to the synthesis and structural characterisation of the three-coordinate, monomeric chloro-germylene **1.14** and stannylene **1.15**.⁹¹ These compounds were synthesised via salt metathesis using the lithiated ligand and the corresponding metal dihalides. Subsequently, the chloride group could be substituted by $t\text{Bu}$, OSO_2CF_3 , N_3 , F , Me groups as well as by more σ -donating groups such as $O^t\text{Bu}$, 2-thienyl, $N(H)Dipp$, PPh_2 to generate a series of $Ge(II)$ and $Sn(II)$ derivatives.^{91–94}

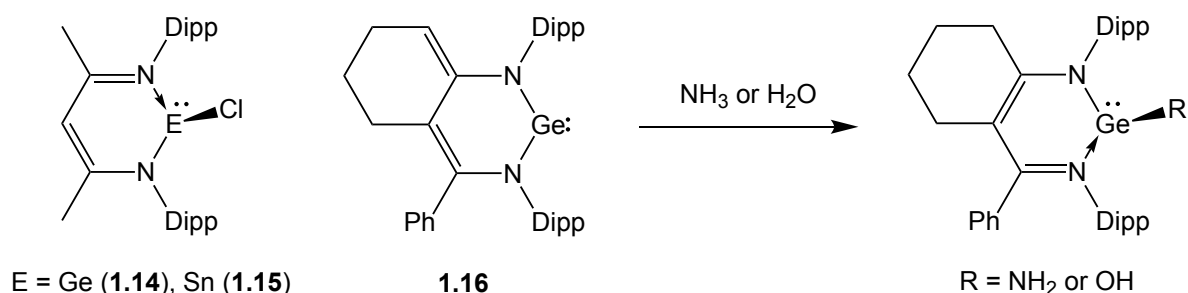
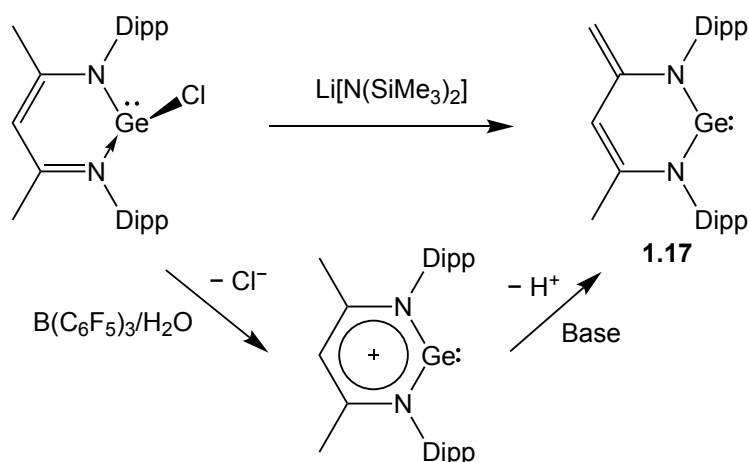


Figure 1.3.2: Heterocyclic germynes **1.14**, **1.15**, **1.16** and E-H bond activation products of **1.16**.

The hydrolysis of the $(Nacnac^{Dipp})GeCl$ (**1.14**) yielded the first example of a $Ge(II)$ hydroxide, $(Nacnac^{Dipp})Ge(OH)$.⁹⁵ The product was synthesised by reacting **1.14** with a slight excess of water and one equivalent of free NHC to bind the in situ generated HCl . The solid-state structure of the hydrolysis product reveals an intermolecular interaction between the O-H hydrogen and the Ge centre of the two halves of the overall dimer. A related example of a germylene with a terminal hydroxy group was reported by Driess et al. from the reaction of a heterocyclic germylene (**1.16**) with water and ammonia.⁹⁶ In both cases the E-H bond was cleaved across the ligand backbone $C=C$ bond and the $Ge(II)$ centre in a cooperative manner. In contrast to $(Nacnac^{Dipp})Ge(OH)$, the structure of the hydrolysis product was shown to be monomeric with no $OH\cdots Ge$ interaction, presumably owing to the increased steric hinderance around the metal centre. Alternatively, $(Nacnac^{Dipp})Ge(OH)$ can be generated via O-H activation across the ligand and metal centre of N-heterocyclic germylene **1.17** which

incorporates a deprotonated Nacnac^{Dipp} ligand.⁹⁷ This compound was first introduced by Driess et al. in 2006 and can be accessed via two different synthetic routes.⁹⁸

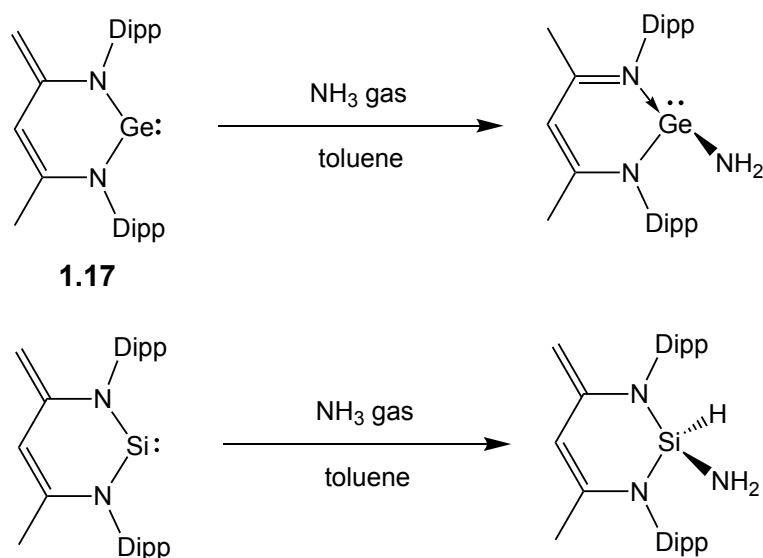


Scheme 1.3.2: Two synthetic routes to diamidogermylene **1.17**.

The reactivity of β -diketiminato stabilised metallyenes towards ammonia has also been investigated, and the mode of N-H bond activation was shown to be dependent on the nature of the group 14 element. Roesky et al. showed that germylene **1.17** undergoes cooperative 1,4-addition of the N-H bond in the presence of excess dry ammonia gas.⁹⁹ The structure of the activation product is monomeric with no significant intermolecular hydrogen bonding. Under the same reaction conditions however, the silylene analogue oxidatively adds the N-H bond at the Si(II) centre in 1,1-fashion.¹⁰⁰ The contrasting reactivity reflects the fact that silicon is less stable in a +2 oxidation state than germanium.

The contrast in reactivity was studied and rationalised theoretically using DFT calculations from the perspective of both kinetics and thermodynamics.¹⁰¹ For both silylene and germylene systems the initial interaction is between the NH_3 lone pair and the vacant p orbital (LUMO), to form an NH_3 adduct intermediate. A second molecule of ammonia is believed to be involved in the process, and facilitates proton shuttling by making the spatial deposition of the orbitals of the interacting species to properly overlap, which significantly lowers the activation barrier for the 1,1-addition product formation. For the silylene, the 1,1-addition product is more

thermodynamically favoured than the 1,4-addition product, whereas the opposite applies to germylene since the lone pair of Ge(II) has more s character and is more inert. As such the 1,4-addition product is more kinetically and thermodynamically favoured. Moreover, neither of the metallylenes showed reactivity towards dihydrogen, in line with the wide singlet-triplet energy separations for both systems, and hence the correspondingly high activation barriers. This result implies that the reaction pathways towards the apolar H-H bond and the protic N-H bonds are different for metallylenes.



Scheme 1.3.3: Contrast reactivity towards ammonia by a germylene **1.17** and a silylene.

Main group metal hydrides are important intermediates which are often employed as precursors or reducing agents in inorganic and organic transformations. They are relatively underdeveloped, primarily due to their extremely air-/moisture-sensitive nature and low thermal stability.¹⁰² After multiple attempts with various hydride sources, the first terminal germanium(II) (**1.18**) and tin(II) (**1.19**) hydrides stabilised by the Nacnac^{Dipp} ligand were isolated by Roesky et al. in 2006, via the reaction of chloro-germylene/stannylene precursors with Me₃N·AlH₃ or K[BEt₃H].^{103,104} X-ray crystallography reveals the monomeric nature of the Ge(II) hydride in the solid state, whereas the Sn(II) system forms a hydride-bridged dimer with a weak intermolecular interaction between the tin lone pair and the hydrogen atom from the two “half dimers”. Subsequently, the Ge(II) hydride was shown to undergo hydrogermylation

with unsaturated molecules such as CO₂, N₂O, aldehydes and ketones.^{104,105} Notably, the CO₂ activation product (i.e. a germanium ester of formic acid) could further react with a hydrogen source (LiH₂NBH₃ or H₃N·BH₃) to regenerate the starting hydride.¹⁰⁶ The Ge(II) hydride could also undergo oxidative addition-insertion to form a Ge(IV) dithiocarboxylate acid analogue with elemental sulfur.¹⁰⁴

Interestingly, the first monomeric germanium(I) radical (**1.20**) was reported in 2011,^{107,108} incorporating a bulkier β-diketiminato ligand ([Nacnac^{*t*Bu}][−] = [N(Dipp)C^{*t*}Bu₂CH][−]). The compound was synthesised by reacting the (Nacnac^{*t*Bu})GeCl precursor with a stoichiometric amount of Na(C₁₀H₈) or {(Nacnac^{Mes})Mg}₂^{109–111} ([Nacnac^{Mes}][−] = [N(Mes)CMe₂CH][−]) and characterised by X-ray crystallography and EPR spectroscopy. Bulky Dipp groups on the backbone provide sufficient steric shielding to prevent dimerisation upon reduction. Reaction of the Ge(I) radical with ¹¹⁹Bu₃SnH or of the germylene precursor with K[BEt₃H] leads to protonation at the imine carbon, instead of the formation of (Nacnac^{*t*Bu})GeH (cf. (Nacnac^{Dipp})GeH). The contrast in reactivity was rationalised on the basis of less electron delocalisation in the ring resulting from a bulkier ligand which causes the nucleophilic attack on the imine carbon by the in situ generated Ge(II)H functional group.

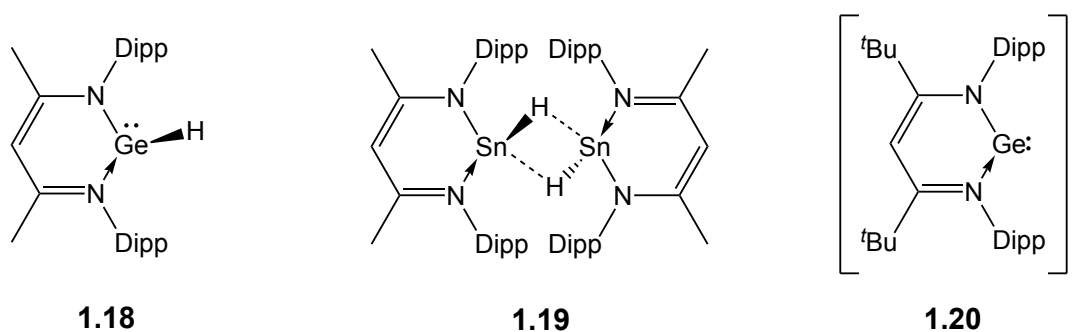
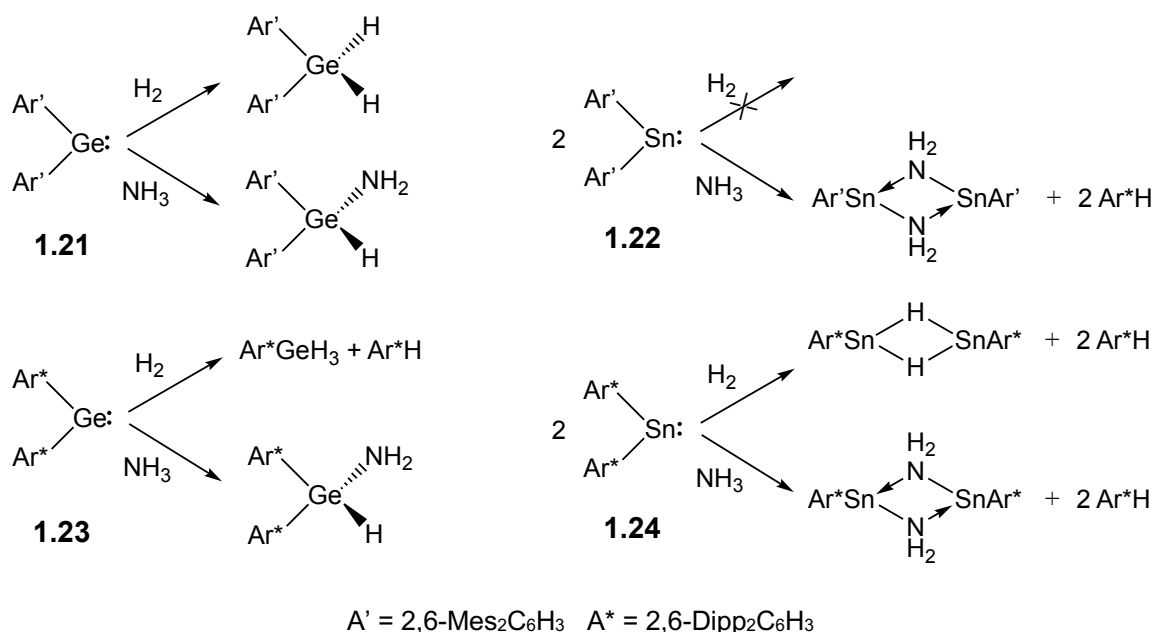


Figure 1.3.3: First examples of Ge(II) and Sn(II) hydrides **1.18** and **1.19**, and Ge(I) radical **1.20**.

1.3.2 Terphenyl stabilised metallylenes

Power et al. first introduced the monomeric, two-coordinate metallylenes (2,6-Ar₂C₆H₃)₂M (M = Ge, Sn, Pb; Ar = Mes, Dipp) incorporating the σ-bonded, non-chelating terphenyl

ligands.^{112,113} In contrast to an N-donor chelating ligand (e.g. β -diketiminato donors), these metallylenes are stabilised by more σ -donating substituents and possess a much wider inter-ligand angle. Hence they generally have a smaller singlet-triplet energy gap and enhanced reactivity towards E-H bond activation.



Scheme 1.3.4: H_2 and NH_3 activation by terphenyl stabilised germynes and stannynes.

The activation reactions of dihydrogen and ammonia by $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{M}$ ($\text{M} = \text{Ge}$ (**1.21**), Sn (**1.22**)) and $(2,6\text{-Dipp}_2\text{C}_6\text{H}_3)_2\text{M}$ ($\text{M} = \text{Ge}$ (**1.23**), Sn (**1.24**)) were investigated both experimentally and computationally with the results summarised in **Scheme 1.3.4**.^{89,114} DFT calculations reveal that for both germynes and stannynes the first step in the activation reaction involves interaction between the σ bond of H_2 and the vacant p orbital of the metal centre. In the case of diaryl germynes, a more sterically-demanding ligand (i.e. **1.23** rather than **1.21**) leads to the more thermodynamically favoured arene elimination product instead of the direct oxidative addition product. For stannynes the arene elimination/dimerisation products are both kinetically and thermodynamically favoured. The observation of no reaction between **1.22** and H_2 is presumably due to the relatively large singlet-triplet gap compared to **1.24**. For NH_3 activation, the initial step involves complexation through the lone pair of nitrogen in NH_3 and vacant $4p/5p$ orbitals of Ge/Sn . A second molecule of NH_3 is essential in the

reaction pathway in order to lower the activation barriers by solvating the coordinated NH_3 through intermolecular $\text{N}\cdots\text{H}$ interactions. In a similar manner to the N-heterocyclic germylene (**1.17**) and silylene, the initial step involves formation of the metallylene- NH_3 adduct intermediates. Both germylenes favour oxidative addition kinetically whereas the arene elimination/dimerisation products are thermodynamically more stable for the stannylenes. As such, it has been demonstrated that the type of H_2/NH_3 activation product formed relates to the combination of metal lone pair stability, singlet-triplet separation of the metallylene and the steric properties of the ligand.

In contrast to H_2 and NH_3 activation, treatment of germylene **1.21** with various Brønsted acids such as HCN , HN_3 and $\text{H}[\text{BF}_4]$ affords exclusively the oxidative addition products. Similarly, reaction of stannylene **1.22** with $\text{H}[\text{BF}_4]$ leads only to oxidation with no arene elimination.¹¹⁵ The mechanisms of these reactions are proposed to involve protonation at the metal centre followed by nucleophilic attack from the conjugate base. Regarding hydroxyl O-H bonds, **1.21** undergoes oxidative addition with water and methanol to form the respective Ge(IV) products, whereas **1.22** again reacts via arene elimination and dimerisation.¹¹⁶ The mechanism of oxidative insertion into the O-H bond by **1.21** resembles the pathway of NH_3 activation, which involves proton shuttling aided by a second molecule of H_2O . The kinetic products of **1.22** are the oxo-bridged stannylene dimer, which was proposed to be generated via a one-step σ bond metathesis from the Sn-OH_2 adduct intermediate.

Bulky terphenyl ligand systems have also been employed in forming chloro-germylene/stannylene precursors which can react further with a reducing agent to generate the corresponding multiply bonded species (*vide infra*).¹¹⁷ Use of the less bulky 2,6-Mes₂C₆H₃ ligand leads to dimerisation of the chloro-germylene (**1.25**) and stannylene (**1.26**).¹¹² Monomeric chlorometallylenes (**1.27**) could however be accessed by employing the bulkier 2,6-Trip₂C₆H₃ ligand.¹¹⁸ The first example of a Sn(II) hydride (of any sort) was achieved by

reacting monomeric (2,6-Trip₂C₆H₃)SnCl with DIBAL, resulting in a hydrido-bridged dimer which structurally resembles dimeric {(2,6-Mes₂C₆H₃)SnCl}₂.¹¹⁹

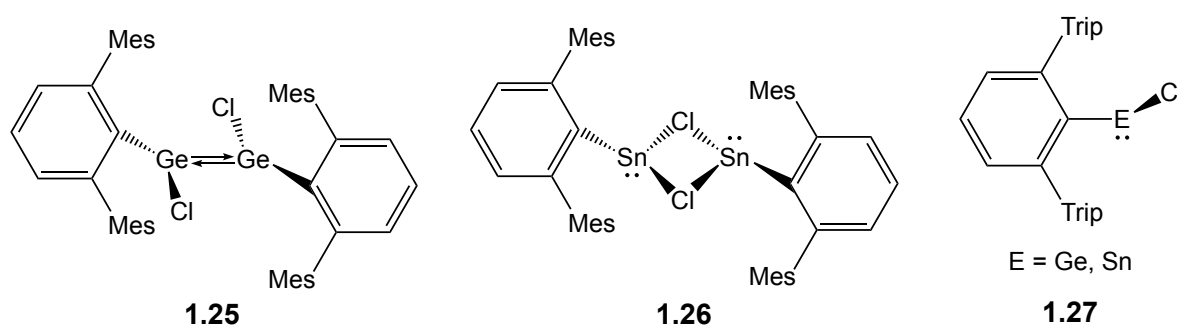


Figure 1.3.4: Terphenyl-stabilised chloro-germylenes and stannylenes.

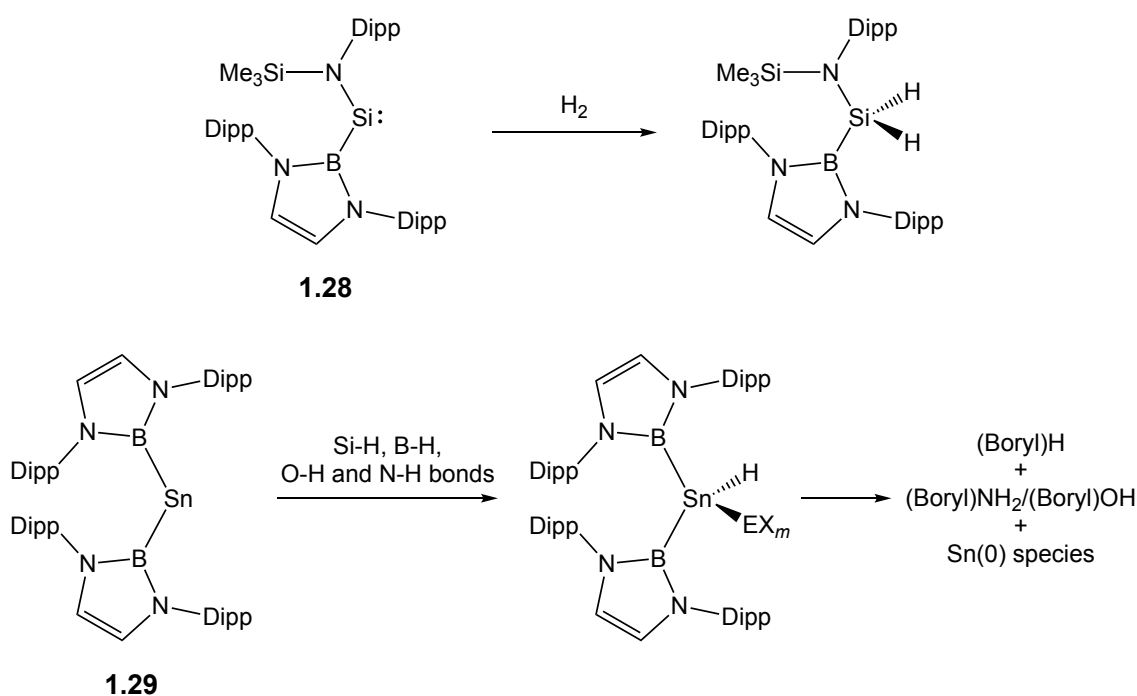
1.3.3 Boryl-substituted metallylenes

By utilising sterically hindered, strongly σ -donating boryl substituents, metallylenes with a narrow HOMO-LUMO gap can be synthesised and their enhanced reactivity towards small molecules demonstrated. Aldridge et al. successfully isolated the first example of a two-coordinate, acyclic silylene (**1.28**), stabilised by a bulky boryl substituent B{N(Dipp)CH}₂ and an amido group.¹²⁰ As expected based on the electropositive nature of the boryl group, this compound possesses a small HOMO-LUMO gap, which increases its reactivity towards E-H bond activation. Experimentally **1.28** was shown to oxidatively activate dihydrogen at 0°C, a reaction which was unprecedented for silylenes. DFT calculations reveal that the activation reaction is both thermodynamically and kinetically favourable despite the presence of a π -donating amido group.

A subsequent study systematically investigated the synthesis and reactivity towards small molecules of a series of sterically encumbered two-coordinate germylenes, employing a Mes/Dipp terphenyl group and an amido/phosphide/alkyl/silyl/boryl substituent.⁸⁰ Fine-tuning of the electronic properties of the substituents at the germanium centre enabled the manipulation of the HOMO-LUMO energy separation, leading to different reactivity towards

apolar H₂ and other hydridic/protic E-H bonds. It was reported that the silyl-substituted germylene formed oxidative addition products with H₂ and NH₃, while germylenes bearing less σ -donating/ π -accepting ligands showed no hint of reaction. The (boryl)amidogermylene $\{(\text{NDippCH})_2\text{B}\}\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}$ had a relatively small HOMO-LUMO gap (180 kJ mol⁻¹) and oxidatively activated both B-H and Si-H bonds and activated H₂ to give an unsymmetrical digermane.

Both oxidative addition and reductive elimination reactions have been shown to be achievable with a bis(boryl)stannylene **1.29**.¹²¹ Having two strongly σ -donating boryl ligands significantly reduces the HOMO-LUMO gap by destabilising the HOMO, which facilitates facile (yet irreversible) oxidative addition of H₂, B-H and Si-H bonds at the tin centre. However, in the cases of protic O-H and N-H bonds, **1.29** undergoes oxidative addition followed by reductive elimination to give O- or N- borylated products with tin reduced from Sn(IV) back to Sn(II) and then Sn(0). The favourable nature of the elimination reactions can be attributed to the weaker Sn-E bond strength compared the lighter congeners in group 14, the more favourable Sn(II)/Sn(IV) redox potential, and the formation of strong B-N or B-O bonds. Again, the reaction pathway for N-H activation was considered to be initial coordination of NH₃ (intermediate isolated), followed by an N-to-Sn proton shuttle facilitated by a second molecule of NH₃.



Scheme 1.3.5: E-H bond activation by boryl-substituted silylene **1.28** and stannylene **1.29**.

1.3.4 Extremely bulky amido ligand stabilised metallylenes

Jones et al. introduced a range of two-coordinate monohalo metallylenes (**1.30**) stabilised by extremely bulky monodentate amido ligands.¹²² While the chloro-germylenes and stannylenes are monomeric in the solid state, the plumbylenes are dimeric, forming chloride-bridged structures owing to the larger covalent radius of lead. These compounds have served as precursors to more reactive germanium(II) and tin(II) derivatives, such as heavier group 14 alkyne analogues and low-valent metal hydrides.¹²³ It was proposed that having a vacant *p* orbital at the metal centre would significantly enhance the reactivity of the corresponding hydrido-germylene and stannylene species in hydrometallation reactions compared to (for example) the corresponding (Nacnac)EH systems.

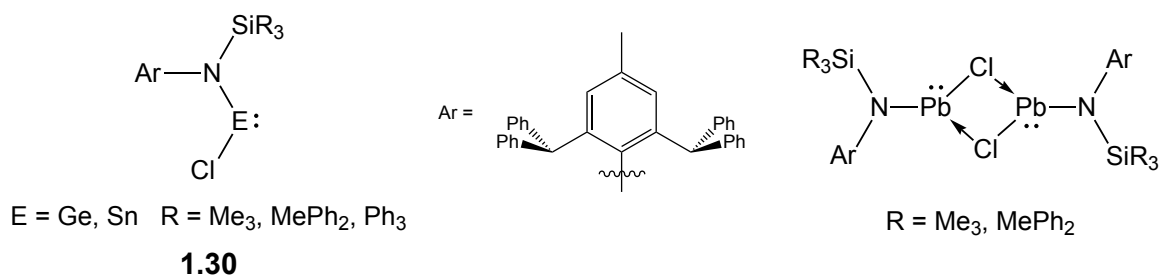
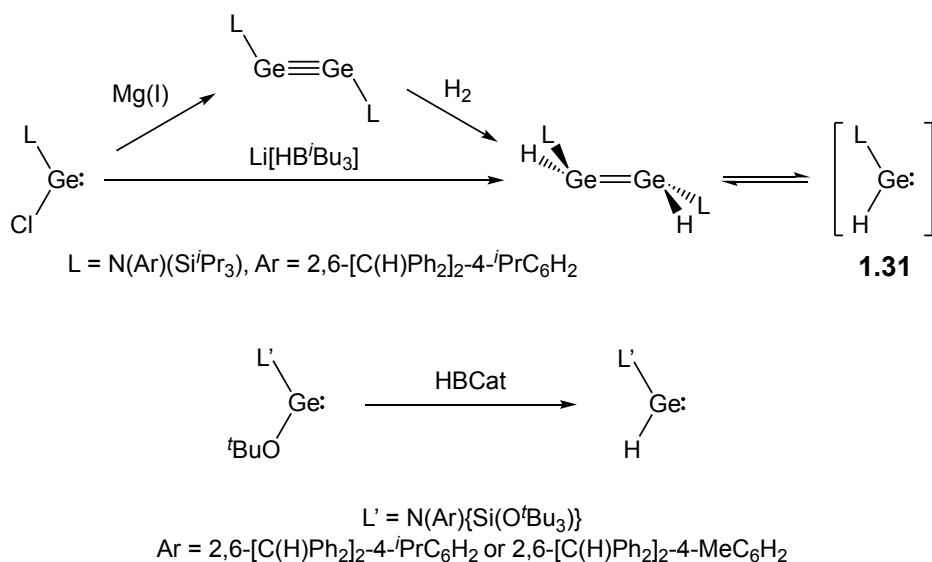


Figure 1.3.5: Two-coordinate metallylenes stabilised by bulky amido ligands.

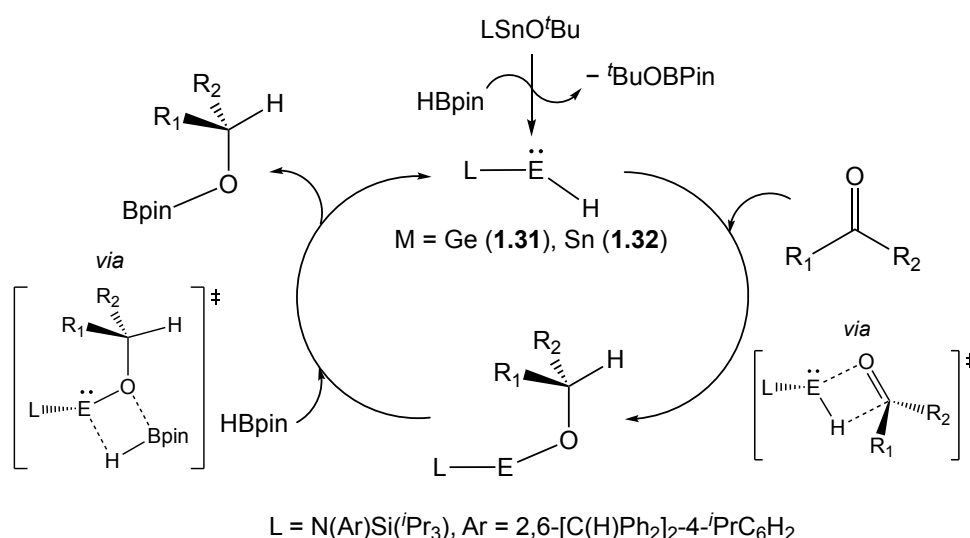
The two-coordinate hydrido-germylenes could be synthesised via three different routes - (i) reaction of the monohalide Ge(II) precursor with a hydride source, such as $\text{Li}[\text{HB}^i\text{Bu}_3]$ (ii) reaction of a Ge(II) alkyoxide derivative with a neutral hydroborane, such as HBpin or HBCat (iii) hydrogenation of the digermynes species generated from reduction of the monohalo Ge(II) precursor.^{124,125} With the systems featuring less bulky substituents on the amido silyl substituent (^iPr), the Ge(II) hydride forms a dimer in the solid state which was shown to exist in an equilibrium with the monomeric species in solution (vide infra). Alternatively, the use of more sterically hindered O^iBu groups resulted in the isolation of the first two-coordinate hydrido-germylenes at room temperature.



Scheme 1.3.6: Different routes to access two-coordinate hydrido-germylenes.

The reactivities of the two-coordinate amido Ge(II) and Sn(II) hydride complexes were explored, particularly in catalytic transformations.¹²⁶ **1.31** and **1.32** (the tin analogue of **1.31**)

were shown to act as the first low-valent *p*-block metal hydride catalysts in the hydroboration of aldehydes and ketones. The Ge(II) hydride employed is dimeric in the solid state, but is assumed to dissociate fully in solution. The Sn(II) hydride decomposes slowly in solution, and therefore a more air-/moisture-stable Sn(II) *tert*-butoxide was employed as a pre-catalyst. Compared to transition metal catalysts and other main group compounds capable of catalysing this type of reaction, these group 14 metal hydrides demonstrate among the highest catalytic efficiency, with **1.32** having a turnover frequency as high as 13300 h⁻¹. In terms of the reaction mechanism, kinetic studies revealed that there is first-order dependence in the HBpin and catalyst and zero-order in the carbonyl substrate, implying that the rate determining step is metathesis of the alkoxide intermediate with HBpin.



Scheme 1.3.7: Proposed catalytic cycle for hydroboration of carbonyl compounds by **1.31** and **1.32**.

The highly efficient catalytic performance has been attributed to the empty *p* orbital on the Ge(II) and Sn(II) centres which enhances their reactivity towards bulky, unactivated ketones. In contrast, the intramolecular base stabilised system (Nacnac)EH only reacts with activated ketones stoichiometrically under forcing conditions. Moreover, the two-coordinate nature of Jones' systems allows the intermediate easier access to HBpin in the rate-determining step. The Sn(II) hydride catalyses the reactions more efficiently than the germanium analogue due

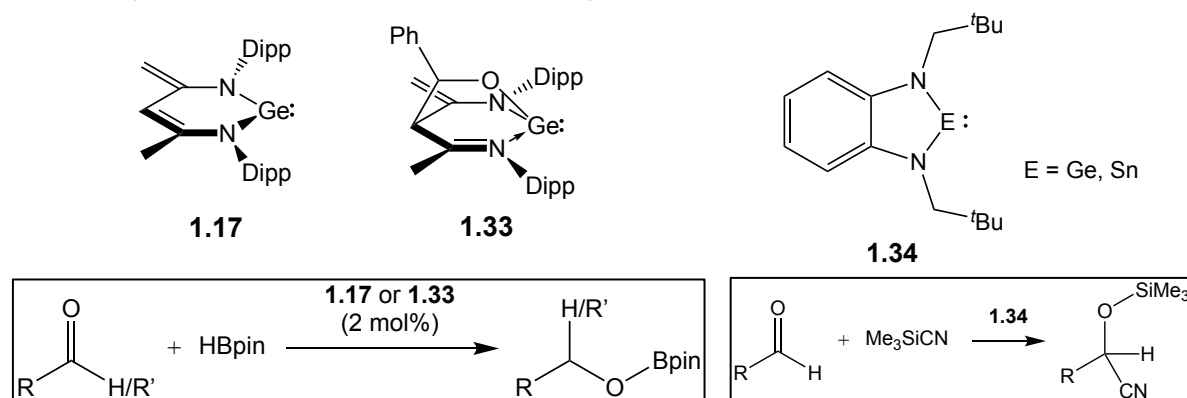
to the more Lewis acidic nature of the metal centre and the more polarised nature of the Sn-O bond of the intermediate which facilitates its reactivity towards HBpin.

In addition to these hydroboration reactions, **1.31** and **1.32** were also shown to act as effective catalysts for the reduction of CO₂ to methanol-like products (i.e. H₃COBCat/H₃COBpin) in the presence of HBCat or HBpin. The tin(II) hydride was shown to be the most efficient and selective main group catalyst reported for this type of reaction.¹²⁷

1.3.5 Other metallylenes with applications in catalysis

Following the report of the first examples of catalytic hydroboration by extremely bulky amido Ge(II) and Sn(II) hydrides by Jones et al., two previously synthesised germylenes were studied further for their applications in this transformation. The neutral N-heterocyclic germylene **1.17** activates a wide range of functionalised aldehydes and ketones via metal-ligand cooperativity to give the 1,4-addition product **1.33**, which acts as the active catalytic species in the cycle leading to the generation of the corresponding hydroboration products.¹²⁸

Another example involves previously reported benzannulated N-heterocyclic germylene/stannylenes **1.34**, and their catalytic reactivity in the cyanosilylation and hydroboration of aldehydes.¹²⁹ The mechanism for both transformations is proposed to involve initial coordination of the trimethylsilyl cyanide/pinacol borane to the Ge(II) or Sn(II) centre followed by σ -bond metathesis with the aldehyde.



Scheme 1.3.8: Catalytic applications of germylene **1.17**, **1.33** and **1.34**.

1.4 Low-valent germanium cations

Cationic compounds of the heavier group 14 elements have been popular synthetic targets over the last few decades, due to their unique chemical properties and high reactivity.^{130,131} Their lighter congeners (carbocations) represent cationic compounds with carbon as the tetrel element, and can be categorised into two classes: three coordinate carbenium ions (CR_3^+) and pentacoordinated carbonium ions (CR_5^+).¹³² While the structures and reactivity of carbocations have been extensively explored in organic chemistry, heavier group 14 (Si-Pb) cations are relatively underdeveloped. These compounds can be classified into two categories: tetrylium ions (R_3E^+), featuring a tetravalent centre with six valence electrons analogous to carbocations; and tetrylium-ylidenes ($\text{RE}^+:$), featuring a divalent centre with a lone pair of electrons. The work described in this thesis focuses mainly on low valent germanium cations, in particular germylium-ylidenes ($\text{RGe}^+:$). These compounds are cationic and highly electrophilic. The germanium centre is electron-deficient with only four valence electrons and two empty valence *p* orbitals, whilst the lone pair on Ge makes it nucleophilic to some extent. Therefore germylium-ylidenes are ambiphilic in nature, which underpins the sophisticated strategies required for their synthesis and isolation, as well as their interesting reactivity in small molecule activation and (potentially) in catalysis.

The formation and stabilisation of the reactive cationic species in the condensed phases requires the presence of a counterion (and a suitable solvent) which is weakly or nearly non-coordinating, which would ideally lead to a so-called “pseudo-gas-phase condition”. Germylium-ylidenes of this type can be synthesised by replacing a coordinating halide substituent at the metal centre with a more weakly interacting anion via salt metathesis. Although an authentic non-coordinating anion is yet to be reported, several categories of weakly coordinating anion (WCA) have been developed and widely utilised in Ge cation synthesis. The most versatile WCAs are normally bulky and non-nucleophilic/basic moieties

which allow the diffuse distribution of the negative charge over the entire entity. They also need to be able to accommodate strongly electrophilic or oxidising group 14 cations.^{133,134}

One of the main classes of WCAs are fluorinated boron-centred anions based on tetrafluoroborate anion $[\text{BF}_4]^-$. Formally substituting the four fluorine groups on the boron centre with larger, fluorinated phenyl groups such as $[\text{C}_6\text{F}_5]^-$ or $[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]^-$ generates the less nucleophilic anions **1.35** and **1.36**.¹³³ Additionally, the tetramethylammonium salt of **1.36** was proved to have a higher solubility in organic solvents than the corresponding $[\text{BPh}_4]^-$ salt due to the presence of the electron-withdrawing *meta*-substituents. **1.36** is also more robust towards decomposition under acidic conditions than either $[\text{BPh}_4]^-$ or borates bearing phenyl groups with less electron-withdrawing substituents such as $\text{C}(\text{CF}_3)_2\text{OCH}_3$.¹³⁵ The preparation of sodium salt of **1.36** from $\text{Na}[\text{BF}_4]$ is straightforward and can be achieved on a multi-gram scale.¹³⁶

Another commonly used class of WCA are alkoxy/aryloxymetallates with an oxophilic central atom such as aluminium(III) or boron(III).^{133,137} The most striking examples are the $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ salts **1.37** reported by Krossing et al. in 2001 (often referred to as the “Krossing anion” due to the extensive application by that group).¹³⁸ The perfluorinated alkoxyaluminate is considered to be one of the weakest coordinating anions presently available. The anion is highly resistant to hydrolysis, an attribute accredited to the bulky and electron-withdrawing $\text{C}(\text{CF}_3)_3$ ligands, which effectively shield the oxygen atoms from the attack by protic reagents. Practically, the synthesis of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ is very convenient and cheap with a high yield (up to 200 g) and purity of product available within two or three days. Hence it was selected to be the main source of WCA for the synthesis of novel Ge cations described in this thesis.

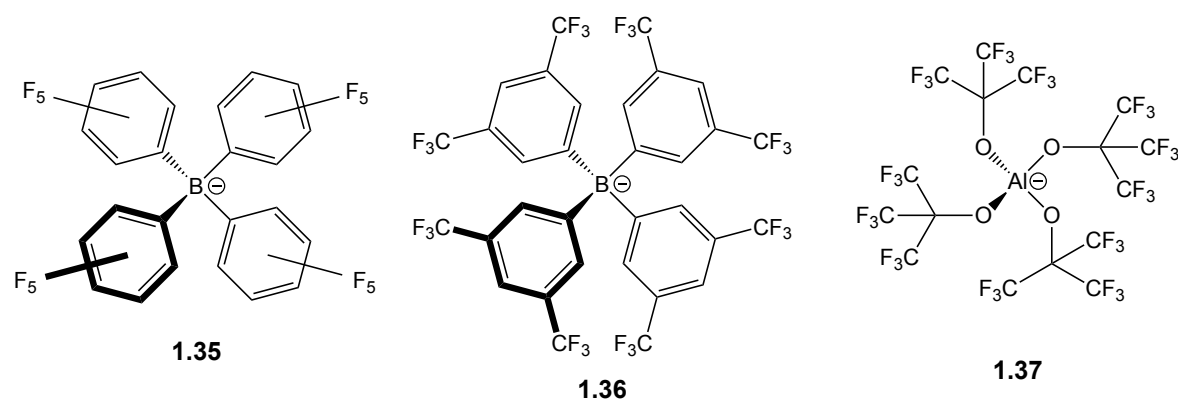


Figure 1.4.1: Examples of borate-based WCAs and the “Crossing anion”.

Compared with the neutral germylenes, cationic compounds possess ideal kinetic properties for E-H bond activation. Previous work has shown that the positive charge can lower the energies of the frontier orbitals and reduce the HOMO-LUMO gap, leading to a higher reactivity.¹³⁹ It has also been proposed that the net positive charge at the germanium centre could provide an electrostatic disincentive to prevent Ge=E (e.g. E = C, N, O) bonds oligomerising/polymerising to form thermodynamically favourable Ge-E single (σ) bonds.¹⁴⁰ Due to its highly electrophilic nature, an authentic one-coordinate germylium-ylidene still remains elusive. However, various kinetic and/or electronic stabilisation strategies have been employed to design ligands that support the synthesis and isolation of higher coordinate divalent germanium cations. Generally speaking, these ligands feature one (or a combination of) anionic or neutral arene rings, macrocycles, N donors, phosphino, strongly σ -donating N-heterocyclic carbene/silylene or boryl ligands.

1.4.1 Germylium-ylidenes stabilised by ligands without N donors

The first examples of germylium-ylidenes date back to 1980, when the bulky pentamethylcyclopentadienyl (Cp^*) ligand was employed to stabilise the $[Cp^*Ge]^+$ cation (**1.38**) both kinetically and electronically through coordination as a pentahapto coordinated, 5-electron donor.^{141,142} Neutral aromatic hydrocarbons such as [2,2,2]-paracyclophane were also shown to be able to facilitate the isolation of Ge(II) cations via strong η^6 coordination from

the three benzene rings.¹⁴³ Remarkably, a monodentate carbodiphosphorane ligand has been shown to act simultaneously as a σ and π donor to stabilise a two-coordinate cationic GeCl fragment (**1.39**).¹⁴⁴ The central carbon of this ligand (supported by two triphenylphosphine groups) donates two orthogonal electron pairs to the electron-deficient germanium centre. Alternatively, bis(phosphino)borate ligand systems have been shown to successfully stabilise chlorogermylum-ylidenes, forming the zwitterionic complex (**1.40**) incorporating a six-membered ring.¹⁴⁵ In contrast to covalently bonded ligands, the two phosphino groups engage solely in dative interactions with the cationic Ge(II) centre. When a 2:1 ratio of ligand to germanium precursor was applied, the chloride could be replaced by a pendant phosphine group which exhibited Lewis base character.

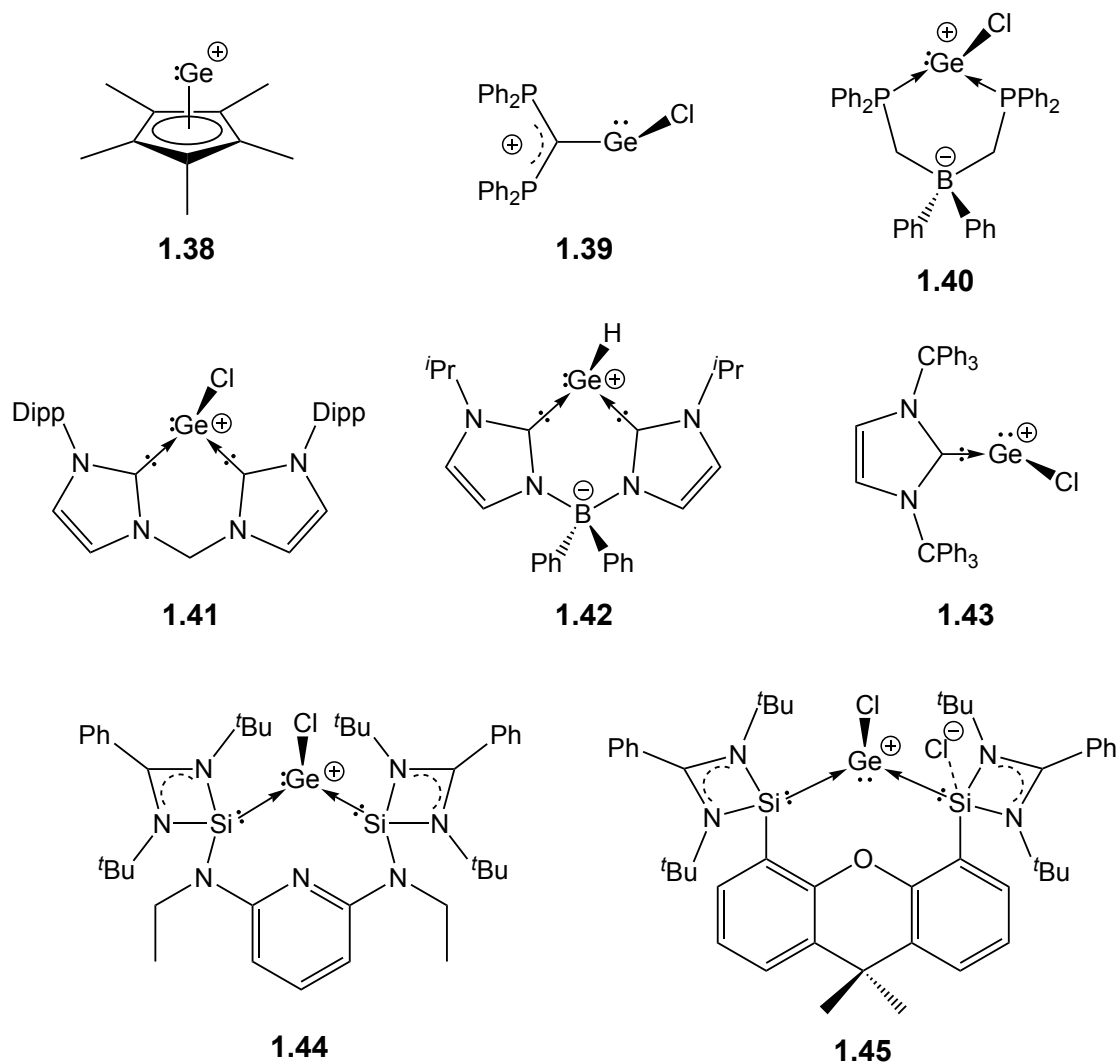


Figure 1.4.2: Germylum-ylidenes stabilised by ligands without N donors (**1.38-1.45**).

In addition to bis(phosphino) ligands, σ -donating bis(carbene) donors represent another type of versatile ancillary ligand with the possibility to support low-valent germanium complexes. In the quest for an isolable “germylone”, Driess et al. reacted a chelating dicarbene with $\text{GeCl}_2 \cdot \text{dioxane}$, leading to the first example of bis(NHC) stabilised cationic chlorogermylene (**1.41**), which was then dehalogenated to furnish the targeted $\text{Ge}(0)$ complex.⁶⁴ When allowed to react with sodium azide, the chlorogermylum-ylidene can be transformed into the first isolable azidogermylum-ylidene azide.¹⁴⁶ Following these results, the same group investigated zwitterionic bis(NHC) borate systems, and reported the first germylum-ylidene hydride (**1.42**).¹⁴⁷ The product was accessed via Cl/H exchange in the presence of a hydride source. Intriguingly, the potassiated ligand underwent facile rearrangement from a bis(NHC) borate to the isomeric (imidazolyl)(NHC) when using toluene instead of THF. The resulting NHC-imido stabilised chlorogermylum-ylidene was also used to access a cationic $\text{Ge}(\text{II})$ hydride.¹⁴⁸ In another example, a bis(NHC) borate ligand, $(p\text{-tolyl})_2\text{B}[1\text{-(1-adamantyl)-3-yl-2-ylidene}]_2$, was developed to afford a light-sensitive phosphaketanyl-substituted $\text{Ge}(\text{II})$ cation.¹⁴⁹ In a recent report a (bis)IMe-stabilised germylum-ylidene, $[\text{Mes}^-\text{TerGe}(\text{IMe})_2]^+$ ($\text{Mes}^-\text{Ter} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$), was synthesised and reacted with N_2O to generate a germa-acylium ion.¹⁵⁰ Finally, an NHC with trityl N-substituents (which possesses the highest percent volume buried ($\%V_{\text{bur}}$) yet reported) was used to stabilise a chlorogermylum-ylidene (**1.43**) in the presence of a borate WCA.¹⁵¹

A more strongly σ -donating silicon analogue of the bis(carbene) ligand, namely a bis(N-heterocyclic silylenyl)pyridine pincer ligand, has been shown to stabilise a chlorogermylum-ylidene (**1.44**), but not the germylone targeted by reduction, due to electronic oversaturation at the $\text{Ge}(0)$ centre, owing to the electron-rich pyridine pincer system.¹⁵² By changing the ligand backbone to a xanthene scaffold, a novel bis(NHSi) stabilised germylone was able to be isolated by reduction of the corresponding chlorogermylum-ylidene chloride (**1.45**). The

resulting zero-valent germanium complex displays intriguing reactivity towards Lewis acids, as well as frustrated Lewis pair type behaviour in the heterolytic activation of dihydrogen.¹⁵³

1.4.2 Germylium-ylidenes stabilised by ligands with one or more N donors

A significant number of germylium-ylidene cations have been reported which contain one or more neutral imine and/or anionic amido donors to stabilise the electrophilic low-valent Ge centres both sterically and electronically. One of the strategies is to deploy an LX type, bidentate N-heterocyclic system incorporating bulky amido and imino groups. The N donors stabilise the electron-deficient germanium centre acting as σ and π donors through the identical, partially dative Ge-N bonds. Such examples were first reported in 1997, when an aminotroponimate (ATI) ligand featuring a conjugated backbone with ten delocalised π electrons was utilised to stabilise a two-coordinate Ge(II) cation (**1.46**).¹⁵⁴ Synthetically this was accomplished via halide abstraction from the chlorogermylene precursor in the presence of a WCA source. Cationic Ge(II) derivatives of similar ligand systems were later investigated for their roles as pre-catalysts in hydroboration reactions.¹⁵⁵ In similar fashion, the sterically encumbered (Nacnac^{Dipp}) ligand was also shown to stabilise a cationic [(Nacnac^{Dipp})Ge]⁺ fragment (**1.47**),¹⁵⁶ and a chiral bis(oxazoline) ligand was found to support the Lewis base complexes of a germylium-ylidene with the S-configuration of the chiral carbons on the ligand backbone being retained throughout the synthesis.¹⁵⁷ Notably, protonation of a germanium analogue of a NHC furnished a non-conjugated germylium-ylidene cation (**1.48**) stabilised by an anionic amido and intramolecular dative interaction with a neutral imino group.¹⁵⁸

Alternatively, cationic [GeX]⁺ fragments (together with the [GeX₃]⁻ anions) can be synthesised and isolated via auto-ionisation reactions of a GeCl₂·dioxane or GeBr₂ precursor, mediated by a neutral di/tridentate Lewis base containing multiple N donors. As a L₂ type ligand, 2,2'-bipyridine was shown to generate [GeBr(bipy)]⁺[GeBr₃]⁻ (**1.49**) from GeBr₂,¹⁵⁹ while forming a neutral adduct with chlorogermylene analogue, which could react further with one or two

equivalents of trimethylsilyl triflate to furnish a Ge(II) monocation and a dication respectively.¹⁶⁰

In a similar fashion, a neutral bidentate ligand featuring chelating pyridino/imino donors was shown to induce facile dissociation of GeCl_2 to give the corresponding ion pair $[\text{LGeCl}]^+[\text{GeCl}_3]^-$. On the other hand this ligand was shown to form neutral adducts with the more Lewis acidic GeCl_4 .¹⁶¹ Auto-ionisation of GeX_2 could also be achieved with tridentate Lewis bases such as PMDTA or the substituted Schiff base (2,6-diacetylpyridinebis(2,6-diisopropylanil)) to give cationic $[\text{GeX}]^+$ and anionic $[\text{GeX}_3]^-$ species (latter: **1.50**).^{159,162} In addition, an ethylene-bridged bis(N-heterocyclic imine) ligand $[\{\text{C}(\text{H})\text{NMes}\}_2\text{C}=\text{N}(\text{CH}_2)]_2$ was shown to initiate auto-ionisation of $\text{GeCl}_2 \cdot \text{dioxane}$ to generate $[(\text{bis-NHI})\text{GeCl}]^+[\text{GeCl}_3]^-$.¹⁶³ In contrast, ligand exchange instead of auto-ionisation occurred when combining a bis(P=N) ylide ligand with $\text{GeCl}_2 \cdot \text{dioxane}$, furnishing a “naked” chlorogermylum-ylidene (**1.51**) and a remote chloride counter ion.¹⁶⁴ Another example of similar chemistry involves a bis(imidazolyl) stabilised chlorogermylum-ylidene (**1.52**) featuring two Ge-Cl units.¹⁶⁵

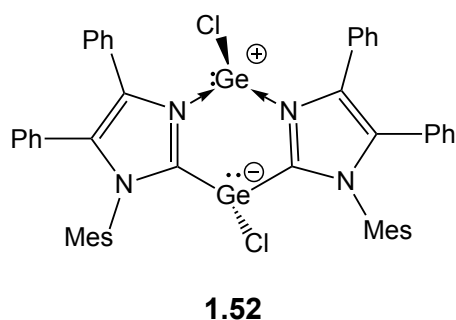
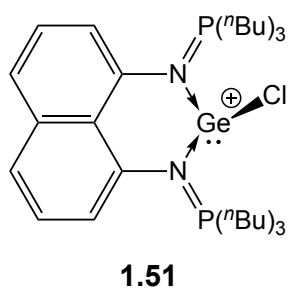
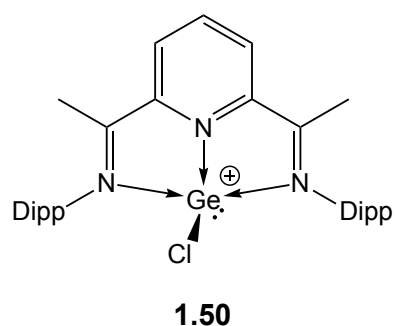
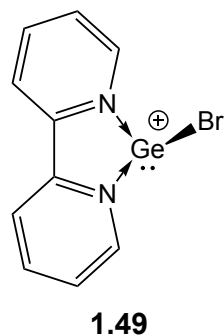
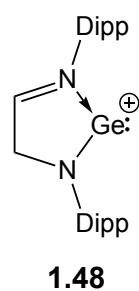
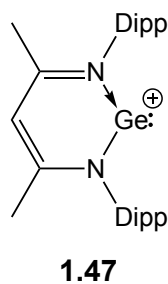
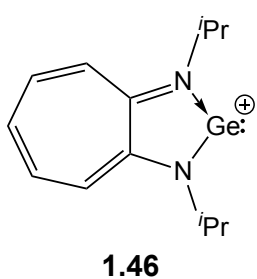


Figure 1.4.3: Germylium-ylidenes stabilised by N donor ligands (**1.46-1.52**).

A bulky Dipp-substituted imidazolin-2-iminato ligand was studied as a suitable ancillary ligand for stabilising the electrophilic Ge(II) cations due to its inherently strong donating capacity (up to six electrons, $2\sigma+4\pi$). An amido(imino)germylene $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}\{\text{NC}(\text{N}(\text{Dipp})\text{CH})_2\}$ was first synthesised as a precursor. Upon treatment with $\text{B}(\text{C}_6\text{F}_5)_3$, methyl abstraction occurred to give the monocationic species (**1.53**) featuring a four-membered metallacycle.¹⁶⁶ Strikingly, treating the germylene precursor with BF_3 yielded a germylene stabilised fluorogermlyium-ylidene (**1.54**), which reacted further with a triflate salt to give an unprecedented dication with bi(germylium-ylidene) character.¹⁶⁷

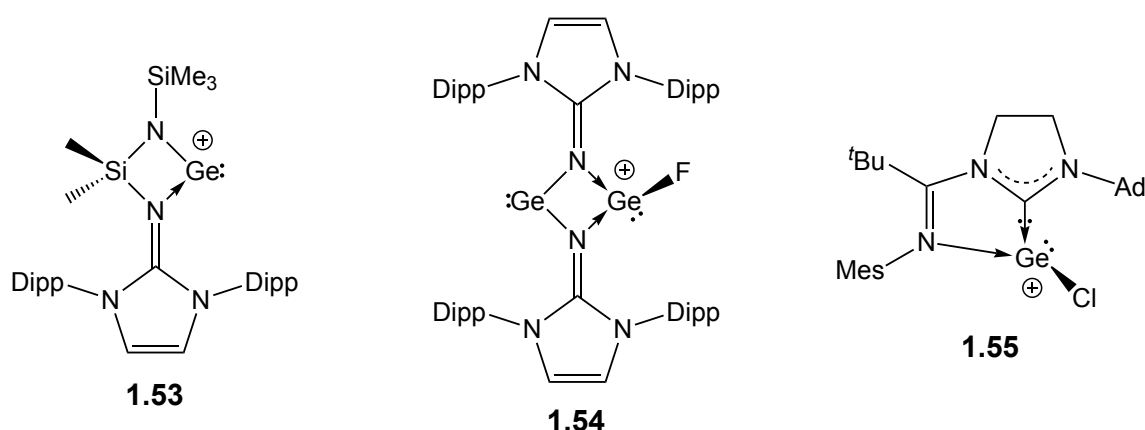


Figure 1.4.4: Imidazalin-2-iminato or imino-NHC stabilised germylium-ylidenes.

Ligands incorporating both an imine donor and a strongly donating NHC have been investigated for the stabilisation of both germanium(II) cations and zero-valent germylone species. Accordingly, the chlorogermylium-ylidene (**1.55**) can be synthesised via an auto-ionisation reaction between the imino-NHC ligand and GeCl₂·dioxane. The corresponding germylone LGe (L = imino-NHC ligand) following reduction was shown to exist in two resonance forms with either one or two lone pair(s) at the germanium(0) centre which are available for binding electrophiles and group 6 metal complexes.^{168,169} In a recent report the germylene {C₄H₄C=CHN(Mes)}Ge stabilised by a non-innocent, bidentate α -iminopyridine ligand was also shown to exhibit reactivity as a α -iminopyridine-coordinated germylone which reacts with GeCl₂·dioxane to form a [LGeCl]⁺[GeCl₃]⁻ ion pair and Ge(0) species.¹⁷⁰ Finally, a diimino N-heterocyclic carbene (dimNHC) stabilised germylone [{(Mes)N=C(Ph)}₂NHC]Ge was shown to react with excess GeCl₂·dioxane or one equivalent of GeCl₄ to generate [(dimNHC)GeCl]⁺[GeCl₃]⁻.¹⁷¹

Despite the lack of authentic one-coordinate germylium-ylidene $[\text{RGe:}]^+$, a small number of Ge(II) monocations that are supported by a single covalently bonded amide group have been reported (with additional weak intramolecular interactions with pendant arene group(s)). One of these reported by Jones et al. (**1.56**) deploys an extremely bulky amide substituent.¹⁷² Apart from the amido linkage, the cationic Ge(II) centre established an η^2 -arene interaction with one of the flanking phenyl rings in the solid-state. A more recent example features a Ge(II) cation (**1.57**) stabilised by a sterically-hindered, modified carbazole moiety.¹⁷³ The two 3,5-*tert*-butyl phenyl substituents of the carbazole framework enhance the solubility and steric bulk of the ligand scaffold, as well as promoting Menshutkin-type interactions* with the cationic Ge(II) centre as electron-rich arenes.

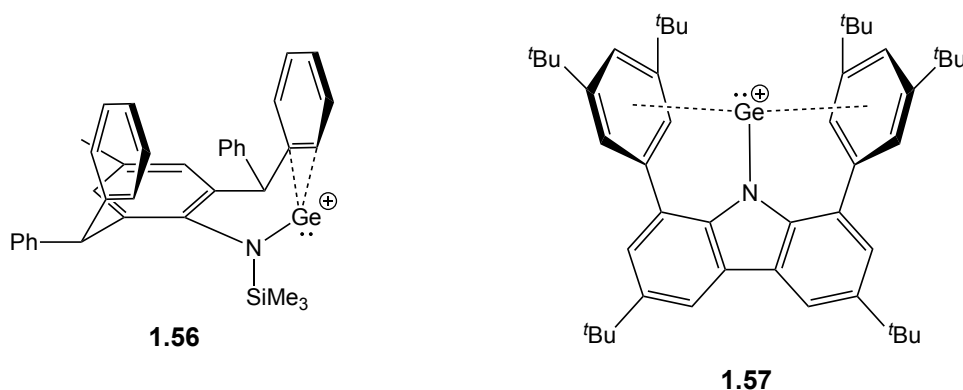


Figure 1.4.5: Pseudo one-coordinate germylium-ylidenes.

1.4.3 Germanium dications

Dicationic germanium(II) complexes can be isolated by using one of a series of neutral mono- or polydentate ligands, including σ -donating NHC or isocyanide ligands and electron-rich macrocycles such as crown ethers and azamacrocycles. An early study from Baines et al. demonstrated that a germanium-centred dication (**1.58**) could be generated by the coordination of three bulky N-heterocyclic carbenes.¹⁷⁴ Later, (four) isoelectronic cyanide ligands were proven to be sufficient in stabilising a dication through σ -donation to central germanium centre.¹⁷⁵ The majority of Ge(II) dications have been stabilised by incorporating

* A weak π -interaction between main group elements and arenes.²³⁰

macrocycles following the discovery of a cryptand[2.2.2]-encapsulated Ge dication (**1.59**),¹⁷⁶ where the dicationic fragment was protected in a bicyclic, three-dimension cavity and engaged in weak donor-acceptor interactions with N and O lone pairs. Other crown ethers of various sizes such as [12]crown-4, [15]crown-5 and [18]crown-6, as well as azamacrocycles such as M₄-cyclam and M₃-tacn, were tested their abilities and different coordination modes in stabilising the Ge(II) dications.^{177,178} Preliminary reactivities studies on the [15]crown-5 stabilised dication revealed simple coordination of H₂O and NH₃ to the germanium centre.¹⁷⁹

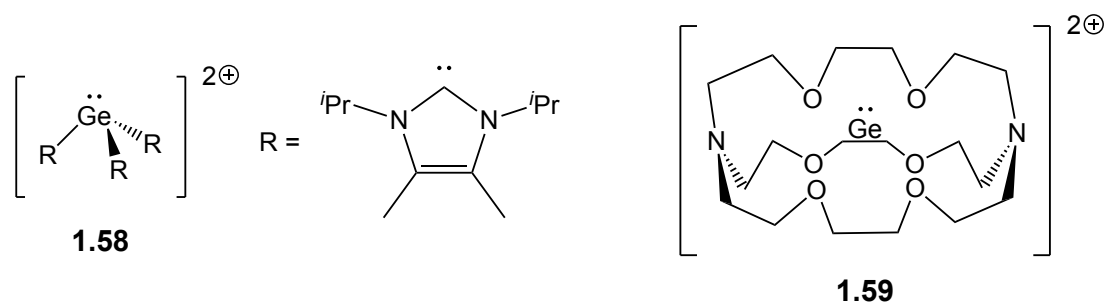
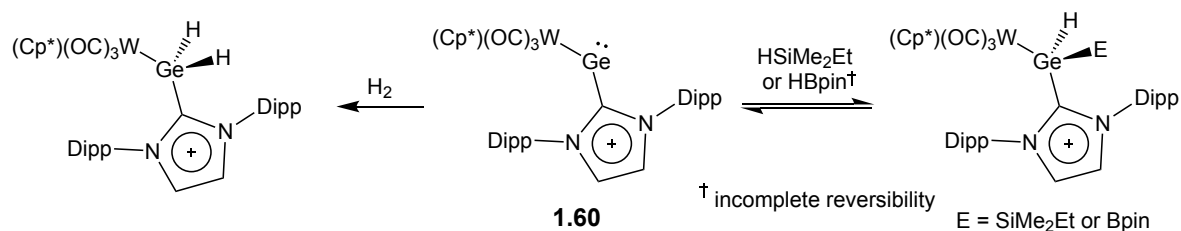


Figure 1.4.6: Examples of Ge(II) dications.

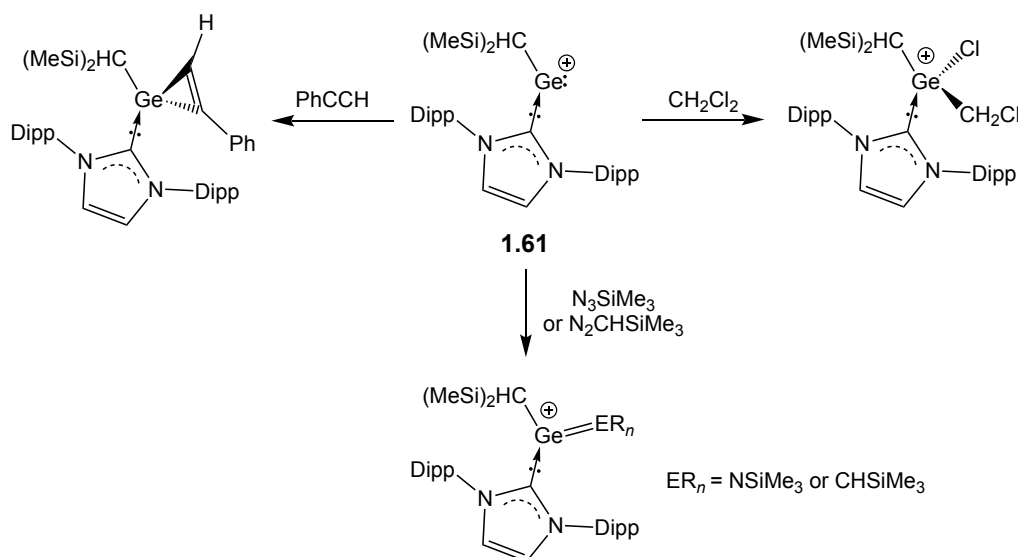
1.4.4 Small molecule activation and catalytic applications

Despite the numerous examples of isolable germylium-ylidenes described above, their reactivity (e.g. towards small molecule activation) has been little explored, largely due to the fact that interactions with additional π -donating ligands and/or a small chelating angle around the germanium centre lead to a wide HOMO-LUMO gap. A breakthrough in this respect was made by Tobita et al., who reported a two-coordinate Ge(II) cation (**1.60**) incorporating an anionic electron-rich tungsten fragment and a σ -donating NHC which was shown to be capable of oxidatively adding dihydrogen at elevated temperatures.^{139,180} Strikingly, the same complex was able to reversibly activate B-H and Si-H bonds. The novel reactivity illustrated by this cation (but not the neutral chlorogermylene precursor) was rationalised by the lowering of both the HOMO and LUMO orbitals (and a smaller HOMO-LUMO gap) owing to the net positive charge. This is thought to allow frontier orbital interactions which facilitate a more-or-less concerted mechanism for H₂ activation.



Scheme 1.4.1: E-H bond activation by Tobita's Ge(II) cation.

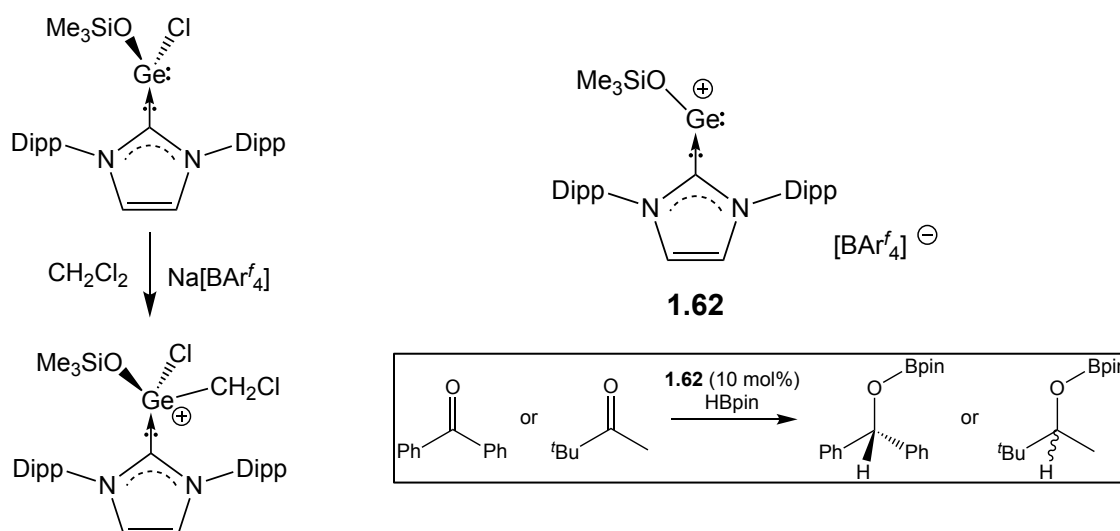
Several novel NHC-stabilised germylium-ylidenes have been isolated and studied in the Aldridge group which avoid the incorporation of transition metal substituents at the germanium centre. An acyclic germylium-ylidene (**1.61**) stabilised by a combination of alkyl and NHC ligands acquired a relatively small HOMO-LUMO gap, and thus high reactivity, due to the lack of π -donation and the wide chelate angle.¹⁴⁰ **1.61** undergoes oxidative insertion into the C-Cl bond of dichloromethane and [2+1] cycloaddition with C $\equiv$ C bond in phenylacetylene. Moreover, it was also shown that complexes featuring Ge=E (E = C or N) double bonds could be synthesised from this cation without the need to utilise bulky substituents or a higher coordination number to prevent oligomerisation.



Scheme 1.4.2: Reactivities of alkyl-NHC stabilised germylium-ylidenes.

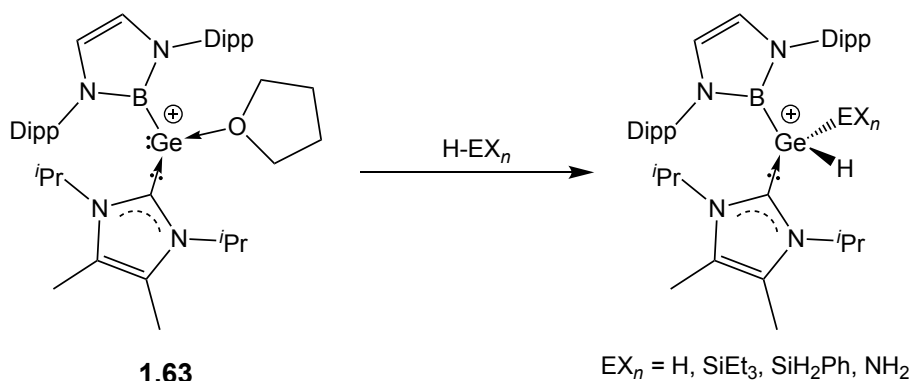
In contrast, when the same NHC and a π -donating trimethylsiloxy ligand were applied to stabilise a cationic Ge(II) centre, the HOMO-LUMO gap was found to be widened, and thus

not suitable for E-H bond activation.¹⁸¹ The chlorogermylene precursor however, was shown to oxidatively activate the C-Cl bond of CH₂Cl₂ in the presence of a WCA in dichloromethane (**Scheme 1.4.3**, left). In addition, the germylium-ylidene **1.62** acts as a pre-catalyst in hydroboration reactions of hindered ketones and pinacolborane.



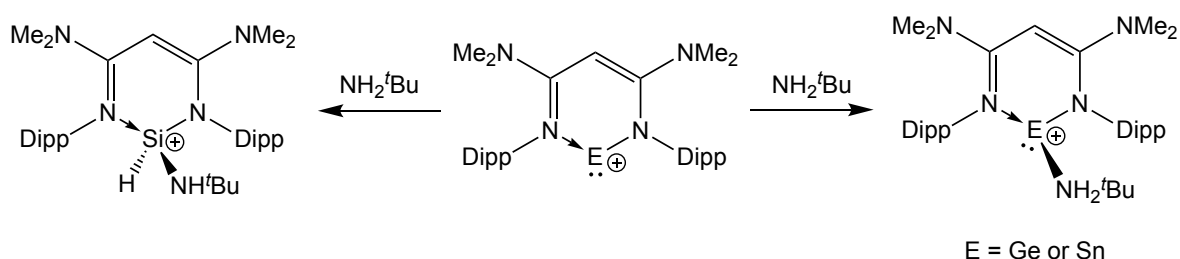
Scheme 1.4.3: Reactivities of siloxy-NHC stabilised germylene and germylium-ylidene.

Formally replacing the siloxy group with a very strongly σ -donating boryl results in a Ge(II) cation (**1.63**) with a narrow HOMO-LUMO gap.¹⁸² **1.63** adopts a dicationic, dimeric form in the solid-state and dissociates to a monomer upon coordination of a labile THF or pyridine molecule. Unsurprisingly, it undergoes facile oxidative addition reaction with dihydrogen, silanes and ammonia to generate the according Ge(IV) derivatives.



Scheme 1.4.4: Reactivities of boryl-NHC stabilised germylium-ylidenes.

A recent study in our group investigated the contrasting reactivities of N-nacnac ($[\{N(\text{Dipp})C(\text{NMe}_2)\}_2\text{CH}]^-$) supported cationic silylene, germylene and stannylene towards the activation/coordination of the N-H bond in ammonia and the primary amine $^t\text{BuNH}_2$.¹⁸³ N-nacnac ligands feature an amido/imino substituent combination with no strongly σ -donating group, hence the HOMO-LUMO gap is expected to be relatively large and concerted E-H bond activation expected to be disfavoured. Interestingly, while the germylum-ylidene and stannylum-ylidene form simple Werner-type adducts with the amine, the silylum-ylidene inserts into the N-H bond and furnishes a primary amido/hydrido Si(IV) derivative. It was proposed that the net positive charge on the Si(II) centre could increase the Lewis acidity and promote coordination of the N lone pair to the vacant p_π orbital of Si(II), followed by proton shuttling, despite a large HOMO-LUMO gap. The distinct difference in reactivity shown by the germylum-ylidene and stannylum-ylidene systems was rationalised by a lowering of $E^{\text{II}}/E^{\text{IV}}$ redox potential going down group 14. Hence only the initial Ge-N and Sn-N adducts were obtained with the heavier derivatives.

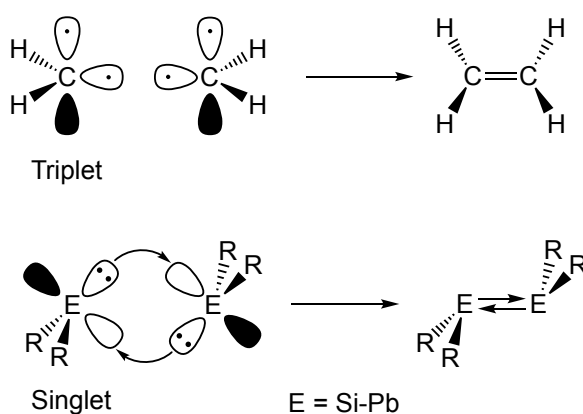


Scheme 1.4.5: Contrasting behaviour towards a N-H bond by Si(II) vs. Ge(II)/Sn(II) cations.

1.5 Heavier group 14 alkyne analogues

As the “Double Bond Rule” used to state, elements with a principal quantum number of three or higher are considered to be unable to form multiple bonds.¹⁸⁴ However this view was challenged in the 1970s, when Lappert’s landmark dialkyl germylene and stannylene (**1.11**) were reported to have dimeric structures in the solid state (which dissociate into the monomeric species in solution).^{84,85,88}

In contrast with their planar, lighter congener (i.e. alkenes), both digermenes and distannenes possess *trans*-bent geometries, featuring pyramidalised metal centres and a non-zero out-of-plane fold angle θ . These “non-classical” double bonds between heavier group 14 elements can be rationalised in terms of valence bond theory or molecular orbital (MO) theory. From the standpoint of the valence bond approach, the ground-state of methylene is a triplet and the heavier analogues are singlets owing to the increasing $\Delta E_{S \rightarrow T}$ gaps and weakening of E-E π bonds upon descending group 14. As a result, two metallylenes prefer to form two $n_{\sigma} \rightarrow p_{\pi}$ semipolar bent “paw-paw” bonds upon dimerisation instead of σ and π bonds.^{77,185}



Scheme 1.5.1: *Trans*-bent geometry of heavier alkene analogues.

In 1980-90, the Carter-Goddard-Malrieu-Trinquier (CGMT) model was developed which relates the *trans*-folded distortion of the ditetrelenes to the singlet-triplet energy gap ($\Delta E_{S \rightarrow T}$) and the combined energies of the σ and π bonds ($E_{\sigma+\pi}$) of the corresponding tetrelene. In this model the bond dissociation energy is represented by the expression $D = 2(\Delta E_{S \rightarrow T}) - (E_{\sigma+\pi})$. It was proposed that if $(\Delta E_{S \rightarrow T}) > \frac{1}{2} (E_{\sigma+\pi})$, the tetrelene would retain monomeric and not form multiple bonds. Furthermore, if $(\Delta E_{S \rightarrow T}) < \frac{1}{4} (E_{\sigma+\pi})$, the ditetrelene would have a planar geometry (as with ethylene), while if $(\Delta E_{S \rightarrow T}) \geq \frac{1}{4} (E_{\sigma+\pi})$, the ditetrelene would have a *trans*-bent geometry as summarised in **Table 1.5.1**.^{186–188}

	$\Delta E_{S \rightarrow T}$	$\frac{1}{4} E_{\sigma+\pi}$	$\frac{1}{2} E_{\sigma+\pi}$	Expected structure
H ₂ C=CH ₂	-9	43	86	Planar
H ₂ Si=SiH ₂	18-21	18-19	35-38	<i>Trans</i> -bent (borderline)
H ₂ Ge=GeH ₂	22	15-17	30-35	<i>Trans</i> -bent
H ₂ Sn=SnH ₂	23	15-17	30-35	<i>Trans</i> -bent
H ₂ Pb=PbH ₂	41	12-15	25-30	Doubly H-bridged

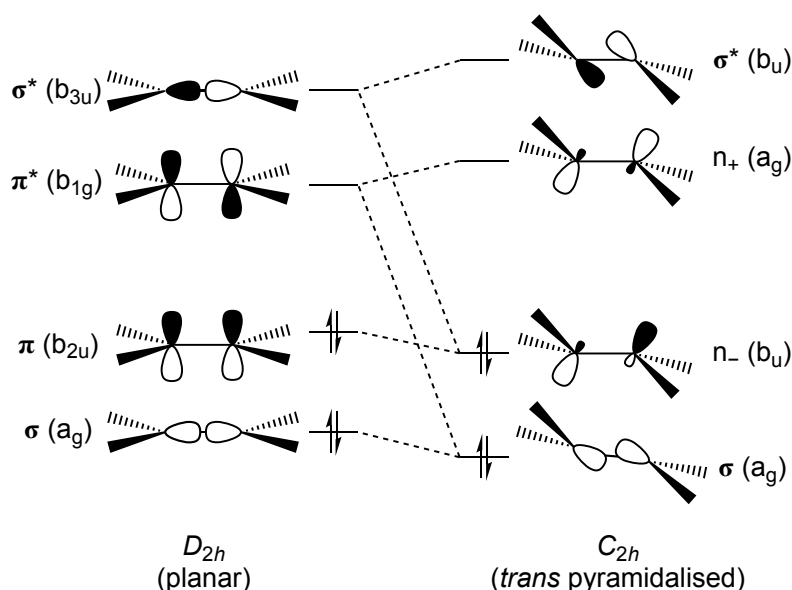
Table 1.5.1: Singlet-triplet gaps, σ and π bond energies and geometries for ethylene and heavier analogues (energies in kilocalories per mole).

Subsequent DFT studies have suggested that the total interaction energy between the Ge/Sn monomer fragments in the dimer is a combination of Pauli repulsion energy, electrostatic interaction, donor-acceptor orbital interaction and attractive dispersion forces. In the case of bulky substituents (e.g. trimethylsilylalkyl ligands), the dispersion interaction plays a vital role and greatly increases the binding energies of the Ge and Sn dimers. For (hypothetical) smaller complexes (e.g. GeH₂ and SnH₂), the influence of orbital interactions is much more significant than dispersion forces.^{189,190}

From a molecular orbital (MO) theory perspective, the *trans*-bent geometry of the heavier alkene analogues can be rationalised on the basis of the second order Jahn-Teller effect. Upon changing from the planar (D_{2h}) geometry to *trans*-bent (C_{2h}), the change of symmetry enables orbital mixing. The symmetry-allowed mixing of the new MOs (π and σ^*) result in a more “lone pair” character in the π bonding MO (n), hence the distorted “folded” structures of the dimetallaylenes.

Upon descending group 14, the degree of interaction becomes more pronounced as bond strengths become weaker, causing the π and σ^* orbitals to be closer in energy thereby

enabling enhanced mixing. As such, the degree of *trans*-bending becomes greater on going from disilylene to diplumbylene (fold angle θ increases).^{191–193}



Scheme 1.5.2: Molecular orbital diagram explanation of *trans*-bent dimetallenes.

Another type of multiple bonding between heavier group 14 elements arises for the (nominally triply-bonded) dimetallynes (i.e. alkyne analogues). Bulky terphenyl ligands were first proven to be effective in kinetically stabilising such dimetallene systems.¹⁹⁴ Power et al. reported the isolation of germanium, tin and lead analogues of alkynes (and further reduction products) employing the Dipp and/or Trip terphenyl substituents.^{117,195–198} Rather than having the linear geometry of alkynes, dimetallynes features a *trans*-bent distortion, which becomes more pronounced on going from Si to Pb.¹⁹⁹ The structure of the plumbylene $\{(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{Pb}\}_2$ features a Pb-Pb-C angle close to 90° and a long Pb-Pb bond, which implies almost no mixing of the 6s/6p orbitals.¹⁹⁶ The germanium and tin analogues have a degree of *trans*-bent distortion between the carbon and lead congeners. The groundbreaking first silicon analogue of alkyne was isolated by Sekiguchi in 2004, featuring a Si-Si “triple” bond with a bond order of ca. 2.6 and stabilised by two bulky silyl substituents and in a *trans*-bent geometry.²⁰⁰

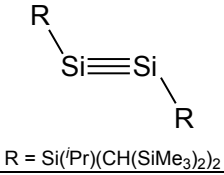
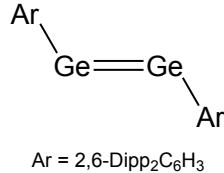
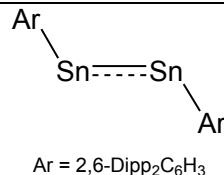
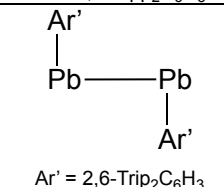
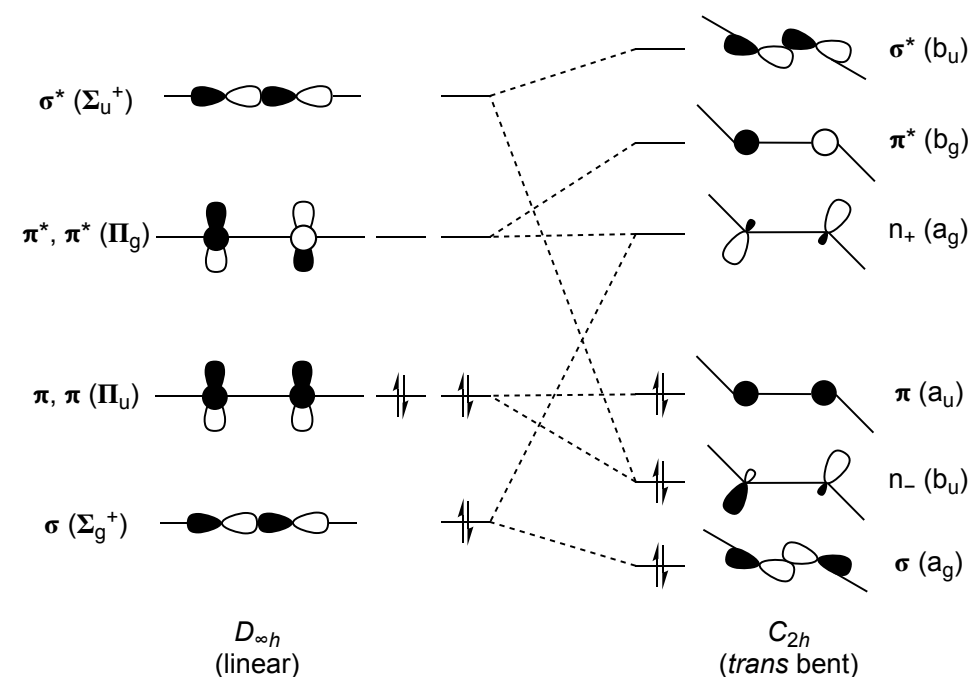
Compounds	E≡E (Å)	E≡E-C bending angle (°)
 $R = \text{Si}(i\text{Pr})(\text{CH}(\text{SiMe}_3)_2)_2$	2.0622(9)	137.44(4)
 $\text{Ar} = 2,6\text{-Dipp}_2\text{C}_6\text{H}_3$	2.285(6)	128.67(8)
 $\text{Ar} = 2,6\text{-Dipp}_2\text{C}_6\text{H}_3$	2.6675(4)	125.1(2)
 $\text{Ar}' = 2,6\text{-Trip}_2\text{C}_6\text{H}_3$	3.1811	94.26(4)

Table 1.5.2: Structural parameters comparison between dimetallynes.⁸

Similar bonding concepts can be applied to explain the *trans*-bent structures of the heavier analogues of alkynes. Upon descending group 14 the heavier elements have lower degree of *s/p* hybridisation due to poorer orbital overlap and weaker bonds formed than the lightest carbon congener (“inert pair effect”). In other words, as the doublet-quartet splitting of the ER fragments widens on going from carbon to lead, the E-E bond lengthens and the two π bonds gradually becomes two non-bonded lone pairs at the group 14 centres, leading to an increasingly *trans*-bent geometry.^{191,193} However in contrast to the dimetallenes, the donor/acceptor bonding model does not apply in the case of diplumbylene since the interaction between the lone pair and vacant p_π orbital cannot exist.²⁰¹

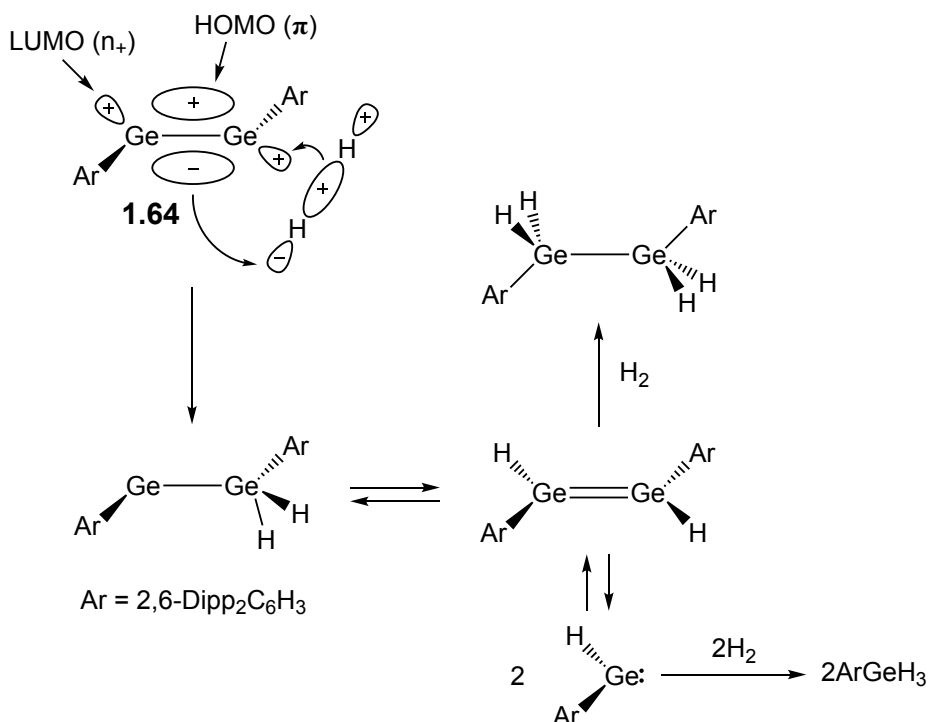
Instead, the non-linear structure of dimetallynes is perhaps best rationalised based on a molecular orbital analysis. A second order Jahn-Teller effect allows mixing of the π and σ^* MOs as the geometry change from linear ($D_{\infty h}$) to *trans*-bent (C_{2h}), resulting in three new occupied

MOs ($\pi(a_u)$, $n_-(b_u)$ and $\sigma(a_g)$). On going from silicon to tin, the occupied $n_-(b_u)$ orbital gradually possesses less π bond character and is progressively better viewed as a non-bonding orbital. As a result, there is increasing non-bonding electron density on the tetrel atoms and the bond order is reduced from 3 to ca. 2. The original E-E σ bond is also weakened due to poorer orbital overlap on mixing. Notably, the $\pi(a_u)$ (HOMO) and $n_+(a_g)$ (LUMO) can potentially act as an electron pair donor and acceptor, which underlies the unique reactivities of this type of compounds.^{193,202}



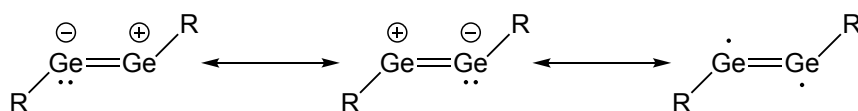
Scheme 1.5.3: Molecular orbital diagram explanation of *trans*-bent dimetallynes.

In 2005, Power reported H_2 activation by a terphenyl-stabilised digermynes (**1.64**), the first example of such reactivity showcased by a main group compound under ambient conditions.¹¹ The hydrogenation products were shown to be a mixture of digermene, digermane and primary germane, with the relative ratios depending on the number of equivalents of H_2 added. The three products were characterised and identified by 1H NMR and X-ray crystallography. The initial step of this unprecedented transition-metal like reactivity was suggested to involve interactions between the σ orbital of H_2 and the LUMO(n_+) of **1.64**, and between the HOMO(π) of **1.64** and the σ^* orbital of H_2 .¹⁹²



Scheme 1.5.4: H₂ activation by terphenyl-stabilised digermynes **1.64**.

It was also proposed that the high reactivity of **1.64** might also result from a resonance form with singlet diradical (diradicaloid) character (**Scheme 1.5.5**).^{203,204} This idea was validated by DFT calculations²⁰⁵ and experimentally demonstrated by reacting **1.64** with a series of electron-rich unsaturated molecules, such as PhCCPh and PhCN to form the cycloaddition and the 2-electron reductive coupling products, respectively.²⁰⁶ However in contrast, the digermynes reported by Tokito et al. (stabilised by bulky 2,6-bis[bis-(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) ligand) displayed no diradical character with no radical reactivity being observed towards H₂O, Et₂SiH or 2,3-dimethyl-1,3-butadiene.²⁰⁷



Scheme 1.5.5: Resonance forms of **1.64** illustrating singlet diradical character.

Furthermore, **1.64** reacts with excess ^tBuNC to form the 1:1 Lewis base adduct with only a small increase of the Ge-Ge distance and retention of multiple bond character. Replacing

^tBuNC with MesNC leads to coordination of a second Lewis base to the Ge centres and greater lengthening of the Ge-Ge bond - which effectively becomes a single bond (**Figure 1.5.1**, left).²⁰⁸ This result is consistent with the molecular orbital picture of **1.64**. With one Lewis base, the additional electron pair fills the LUMO, which is a non-bonding orbital ($a_g(n_+)$), and the GeGe bonding interaction is only affected slightly. When there is additional coordination, the second pair of electrons populate the anti-bonding orbital ($b_g(\pi^*)$), thereby reducing the bond order between the two Ge centres, resulting in a single bond. Sterically speaking, the mesityl isonitrile is likely to form the double coordination product because it is flatter and can be orientated in parallel to avoid steric repulsion comparing to the bulky tert-butyl substituents.

Alternatively, by incorporating a chelating $N_{dido}^{\wedge}N_{amine}$ ligand (which is similar to a Nacnac ligand), dimers with Ge-Ge single bonds can be achieved. Jones et al. reported the synthesis of Ge(I) dimers (**1.65**) stabilised by amidinate and guanidinate ligands, which involve a π -donating N_{amido} group and an imine σ -donor ligand.²⁰⁹ Each Ge centre is three-coordinate with a lone pair possessing a high degree of s character. The solid-state structures of the Ge dimers reveal that they feature long Ge-Ge bonds that are comparable to the average Ge-Ge single bond length, as well as acute *trans*-bent angles closed to 90°. Therefore little GeGe multiple bonding is postulated based on the structural evidence.

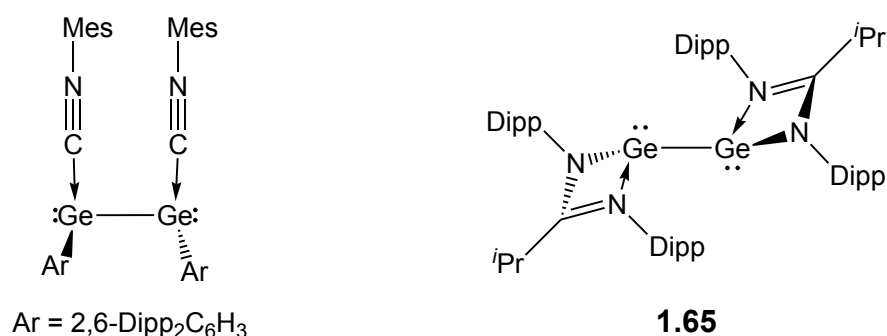
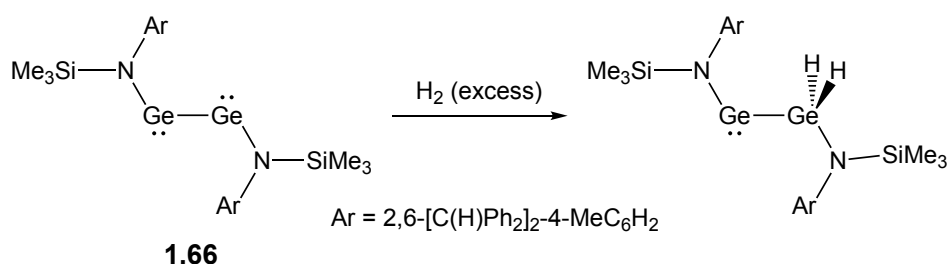


Figure 1.5.1: Lewis base(s) coordinated **1.64** and **1.65** with Ge-Ge single bond.

The first example of a two-coordinate digermynes with a Ge-Ge single bond was reported in 2011, and its reactivity towards H_2 investigated.²¹⁰ Reducing a chlorogermylene

$\{(\text{Ar})(\text{SiMe}_3)\text{N}\}\text{GeCl}$; ($\text{Ar} = 2,6\text{-}[\text{C}(\text{H})\text{Ph}_2]_2\text{-4-MeC}_6\text{H}_2$) employing a super bulky amido substituent with half equivalent of $\{(\text{Nacnac}^{\text{Mes}})\text{Mg}\}_2$ led to the synthesis of the digermynes **1.66** featuring a GeGe single bond. X-ray crystallography showed the solid-state structure to have a *trans*-bent geometry, featuring the longest Ge-Ge bond and the narrowest *trans*-bent angle among all the reported digermynes. Each Ge centre is two-coordinate, which underpins its higher reactivity towards small molecule activation than **1.65**. The bulky amido substituents were postulated to provide kinetic stabilisation and also enhanced π -donation from the lone pair of N_{amido} to the empty $4p$ orbital on the Ge(I) centre, thereby preventing the formation of GeGe multiple bonds.

In terms of reactivity, DFT calculations revealed that digermine **1.66** has a small HOMO-LUMO energy gap. It was shown experimentally to activate dihydrogen under ambient conditions, forming an oxidative addition product with mixed-valence Ge(I) and Ge(III) centres. Additionally, reacting the chlorogermylene precursor with a hydride source ($\text{Li}[\text{HB}^s\text{Bu}_3]$ or $\text{K}[\text{HBEt}_3]$) offered the same product (and other by-products). Unlike Power's terphenyl substituted digermine, **1.66** did not undergo further hydrogenation with further H_2 . Based on the singly bonded nature and the activation of H_2 solely at one Ge centre, the mechanism of this reaction was proposed to be analogous to germylene **1.21**, and involves interactions of the σ orbital of H_2 and the vacant $4p$ orbital of Ge, along with the back-donation from the lone pair of Ge to σ^* orbital of H_2 .²¹⁰

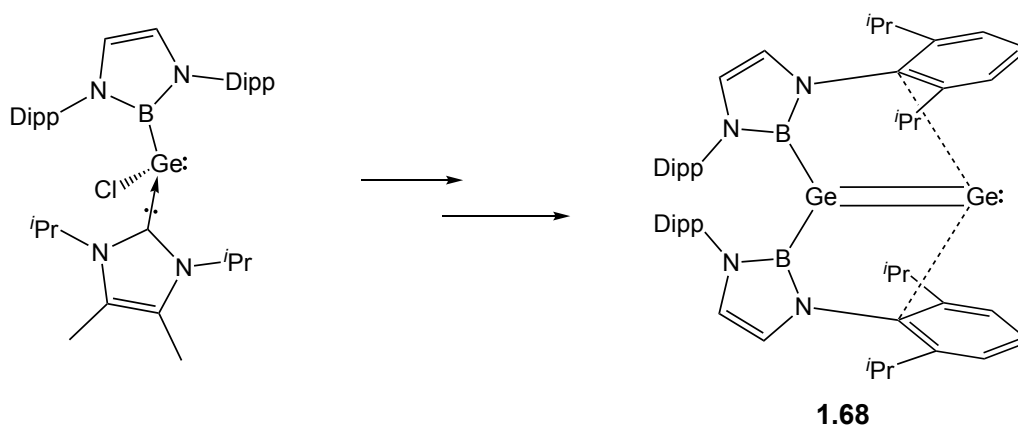


Scheme 1.5.6: Bulky amido-stabilised digermine **1.66** and its H₂ activation product.

A related digermine (**1.67**) incorporating an even bulkier amido ligand was subsequently introduced.¹²⁴ Modifying the ligand by replacing the methyl groups with isopropyl on both of the substituents of the N_{amido} donor resulted in significant structural differences in the digermine formed. In the case of the bulkier ligand scaffold, a shorter Ge-Ge bond and a less acute *trans*-bent angle suggested multiple bonding between GeGe, as confirmed by the solid-state structure. This was explained on the basis of a sterically inaccessible π interaction between the N lone pair and the Ge 4p orbital; the enhanced steric bulk prevents the respective orbitals from being coplanar. As with **1.66**, **1.67** also has a small HOMO-LUMO gap, hence its reactivity towards dihydrogen was investigated. Unlike **1.66**, however, the activation product is a symmetrical hydrido-digermene and no further hydrogenation was observed. Experimental evidence suggests that the hydrido-digermene exists in equilibrium with the dissociated hydrido-germylene monomer in solution. Moreover, the hydrido-digermene could be synthesised by combining the chlorogermylene precursor with Li[HB^tBu₃].

Interestingly, a germanium analogue of vinylidene (**1.68**) was reported by Aldridge et al., which represents the first heavier group 14 compound with the formula R₂EE.²¹¹ **1.68** was synthesised by first reducing a chlorogermylene stabilised by an NHC and a strongly σ -donating boryl ligand with either potassium metal or KC₈. This step generated an anionic, formally Ge(0)-Ge(0) dimer with two potassium counter cations. Partial reoxidation led to the formation of (boryl)₂Ge(II)Ge(0) (**1.68**) in which both boryl groups are on one Ge centre, i.e. a 1,1-substitution pattern. Previous DFT calculations suggested that H₂GeGe is more

energetically favoured than HGeGeH. As the substituents on Ge become bulkier, the 1,2-pattern is more favoured. The boryl substituents are thought to be labile across the Ge₂ core unit. This is reflected by adding an NHC to **1.68**, which results in the formation of a 1,2-substituted Ge dimer with one coordinated NHC. In addition, **1.68** undergoes H₂ activation forming a symmetrical 1,2-diboryl-digermane with boryl migration.



Scheme 1.5.7: A germanium analogue of vinylidene **1.68** and its ultimate chlorogermylene precursor.

N-heterocyclic carbenes (NHCs) have proved to be capable of stabilising a range of zero-valent group 13/14 main group compounds, including examples bearing germanium. The reduction of (IPr)GeCl₂ with one equivalent of {(Nacnac^{Mes})Mg}₂ reducing agent results in a NHC-stabilised Ge(0) dimer (**1.69**).⁶⁰ The product featured a *trans*-bent conformation with a GeGe bond length close to a double bond. The same NHC ligand has also been shown to stabilised zero-valent Si(0)=Si(0) and Sn(0)=Sn(0) species (**Figure 1.5.2**).^{59,61}

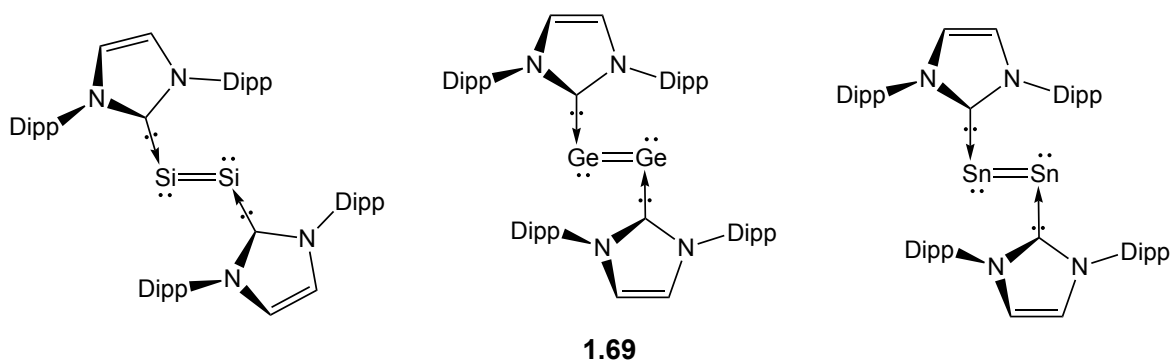


Figure 1.5.2: NHC-stabilised Ge(0) dimer **1.69** and the Si(0) and Sn(0) analogues.

1.6 Ligand scaffolds exploited in this thesis

The scarcity of reactive low valent germanium complexes manifesting E-H bond activation behaviour, especially in a reversible manner, prompted us to develop new divalent germylenes and germanium cations incorporating ligand systems where both steric protection and electronic stabilisation are provided. Based on the precedented success we considered utilising a strong σ -donating (e.g. NHC or phosphine) and a π -donating amido group could potentially lead to interesting reactivity, such as (reversible) E-H bond activation. Accordingly, two chelating ligand scaffolds were exploited.

In 2003 Arnold et al. reported the synthesis of an anionic amido-tethered NHC ligand (**Figure 1.6.1**, left) and its application in lanthanide and early transition metal chemistry.²¹² Later, the same group proposed the synthesis and applications of the alcohol-functionalised protio-ligands.²¹³ Subsequently, a series of tethered-NHC ligated *s*-, *d*- and *f*-block element complexes has been synthesised and their patterns of reactivity studied.^{214–221} Notable examples included the first magnesium-NHC complex to initiate lactide polymerisation and amino-NHC Ni/Al mediated *para* C-H bond activation of pyridine and quinoline derivatives.^{222,223} Additionally, amido-NHC ligands were shown to mediate C-C coupling of benzene and pyridine via a proposed radical mechanism.²²⁴

Bidentate amido phosphine chelate ligands (**Figure 1.6.1**, right) feature an amino and a hemilabile phosphine group. This type of ligand has been widely explored in transition metal coordination and reactivity chemistry due to its “softer” donating properties at phosphorus centre.^{225–227} For example, such ligands have been found to stabilise rare earth bis-alkyl complexes and the reactivity in initiating ring-opening polymerisation has been investigated.²²⁸ However there have been no investigations involving coordinating these ligands to main group elements.

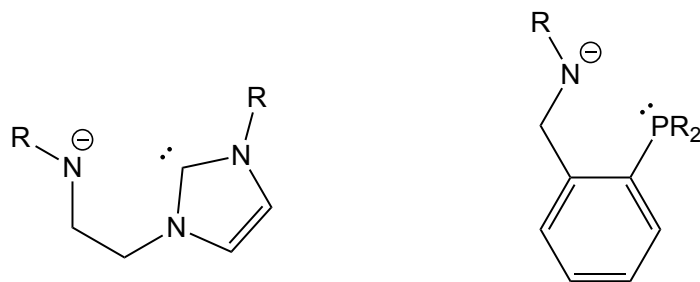


Figure 1.6.1: Generic amido functionalised NHC ligands and one type of aminophosphine chelate ligand.

We therefore targeted the synthesis of halo-metallylenes (i.e. LGe-hal) featuring these ligand types, which could then be converted into more reactive Ge(II) derivatives such as tetra-germylenium salts or Ge(II) hydrides, and the metal-metal complexes. Once isolated, their reactivity with dihydrogen, protic or hydrido E-H (in particular N-H) sources could be investigated using DFT calculations and experimental methods. Finally, their applications as (pre)catalysts in catalytic hydroboration reactions can be investigated.

During the first few months of work into this project, a relevant paper on anionic amido-tethered NHC stabilised Ge(II) and Sn(II) monohalo precursors, cations and their preliminary reactivity studies was published.²²⁹ As no unambiguous structural evidence for the cations or definitive results of the reaction with e.g. H₂ were given, the aims of this project were to fully characterise novel cations employing this ligand system and conduct a conclusive reactivity study towards E-H bonds.

1.7 References

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Chapter II

Experimental Methods

2.1 Manipulation of air- and moisture-sensitive compounds

The majority of compounds reported in this thesis are highly air- and moisture-sensitive. Therefore it was necessary to employ inert atmosphere techniques to manipulate them.

2.1.1 Inert atmosphere techniques

Schlenk lines and inert-atmosphere gloveboxes both offer an adequate air- and moisture-free environment to allow the handling and storage of sensitive compounds under nitrogen or argon. Solution-phase reactions involving such compounds were generally carried out using a Schlenk line in order to minimise exposure to air or moisture. The line was equipped with a double Pyrex manifold, with one glass tube connected to an inert gas supply (argon or nitrogen) and the other one to a high vacuum pump. The excess gas pressure was vented through a mercury bubbler. The ground glass joints and four taps on the line were connected using high vacuum grease to give an air-tight seal. The vacuum pressure inside the line was constantly monitored by a digital pressure gauge and normally maintained at 10^{-2} mbar. A trap cooled by liquid nitrogen was set up between the line and the vacuum pump to prevent any volatile contaminants from entering the pump.¹⁻³

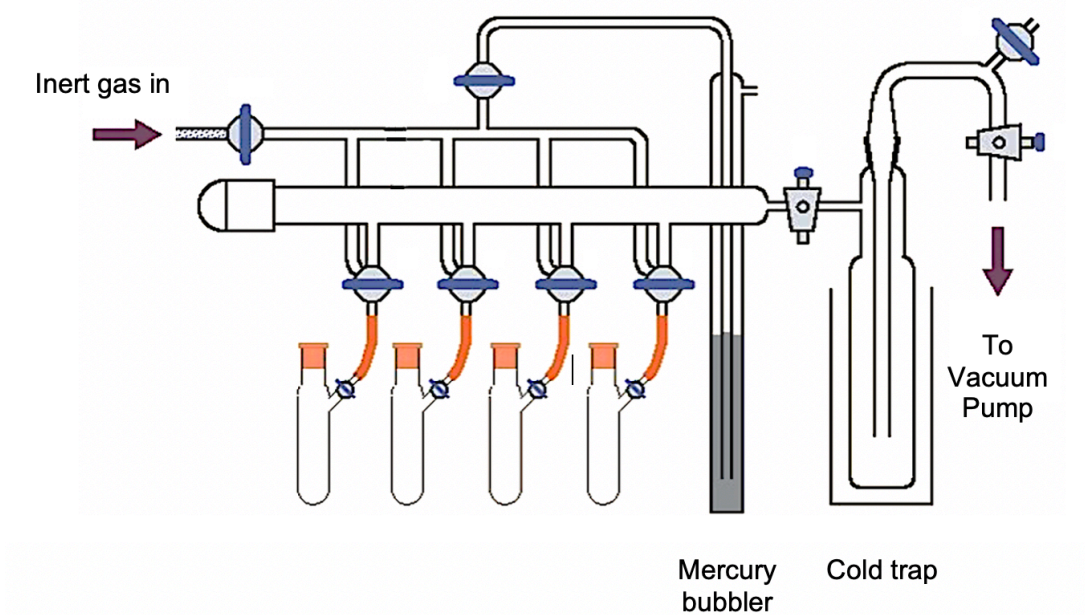


Figure 2.1.1: A typical Schlenk line.

The reaction vessels were connected to the line through rubber tubing, and the two-way taps allowed access to both the inert atmosphere and the vacuum. To evacuate the glass vessels, three “pump and purge” cycles were applied involving evacuation and back-filling with argon (or nitrogen). The first iteration normally involved using a Bunsen burner to heat the glass surface under vacuum to get rid of trace moisture adsorbed on the inner surfaces. Liquid transfers between reaction vessels under inert atmosphere were conducted using cannulae or disposable syringes evacuated three times with argon. Micro-syringes were used when manipulating smaller quantities of liquid (less than 1 mL). Filtrations were carried out using cannulae fitted with glass-fibre filter paper. Dry solvents used were either collected from a MBRAUN solvent purification system or distilled over an appropriate drying agent, degassed by purging with argon (or freeze-pump-thaw cycling), and stored over molecular sieves or potassium/sodium mirrors.^{2,3}

A glovebox filled with a nitrogen atmosphere was employed for weighing and storing sensitive compounds and preparing NMR samples. The atmosphere inside was recirculated and

purified using external columns of molecular sieves, activated copper(I) catalyst and charcoal to remove moisture, oxygen and fine particles respectively. The dry box was equipped with two neoprene gloves built into the side to allow access to the sealed system. Items were brought into the dry box after “pump and purge” with vacuum and nitrogen three times in an ante-chamber.^{2,3}

2.2 Spectroscopic and analytical techniques

The work in this thesis utilised a range of characterisation techniques, the details of which are given below.

2.2.1 NMR spectroscopy

NMR spectra were measured by the author on a Bruker Avance III HD nanobay 400 MHz, Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz NMR spectrometer; or by Ms. Tina Jackson on a Bruker Avance 500 MHz NMR spectrometer equipped with a ^{13}C detect cryoprobe. Variable temperature NMR experiments and data simulation were assisted by Dr. Nick Rees. All air or moisture sensitive samples were prepared using a Schenk line or in a glovebox and stored under argon or nitrogen in NMR tubes fitted with J Young’s valves. ^1H and ^{13}C spectra were referenced to the residual protio solvent signal and the deuterated solvent signal, respectively. Chemical shifts are reported relative to $(\text{CH}_3)_4\text{Si}$ at 0 ppm. ^7Li , ^{11}B , ^{19}F , ^{27}Al , ^{31}P and ^{207}Pb NMR spectra are referenced against the standard reference compounds LiCl , $\text{BF}_3\cdot\text{OEt}_2$, CFCl_3 , $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, H_3PO_4 and Me_4Pb respectively. 2D experiments (COSY, HSQC, HMBC) were carried out in order to assist the assignment of the signals.

2.2.2 Infrared spectroscopy

Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. The sample was prepared in the glovebox as a Nujol mull before sealed between airtight NaCl crystal windows.

2.2.3 Elemental analysis

Elemental analyses were carried out at London Metropolitan University. All samples were prepared in sealed glass tubes or vials in the glovebox. Attempts were made to obtain microanalytical data for most of the isolated compounds, with the exception of the adventitious water activation products (compound **12** and **13**) and the germanium-gold complex (compound **24**), where samples were challenging to obtain in pure crystalline form. In some cases, the highly air and/or moisture sensitive nature of the compounds, or the presence of a trace of oily residue prevented reliable microanalysis. For example, in the case of compound **26**, the crystalline material was consistently contaminated by 6% of protio-ligand, as shown by the ^1H NMR spectrum.

2.2.4 X-ray crystallography

Single-crystal X-ray diffraction data for all compounds were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector (unless otherwise stated). Data collection and structure determination were carried out by Dr. Jamie Hicks, Dr. Maria Ángeles Fuentes, Dr. Eugene L. Kolychev, Andreas Heilmann or Caitilín McManus of the Aldridge group. Single crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.⁴ Data were collected at 150K (unless otherwise stated) using mirror monochromated Cu K_α ($\lambda = 1.5418 \text{ \AA}$) or Mo K_α ($\lambda = 0.7107 \text{ \AA}$) radiation. Data for $\{(\text{L}^{\text{tBu}})\text{Ge}\}_2$ was collected at 173(2)K using synchrotron radiation ($\lambda = 0.6889 \text{ \AA}$) at the Diamond Light Source. Diffraction data were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro). Equivalent reflections were merged, and diffraction patterns processed with the CrysAlisPro suite. The structures were then solved ab initio from

the integrated intensities using SHELXT⁵ and refined on F² using SHELXL⁵ with the graphical interface Olex2⁶ or X-Seed.⁷

2.2.5 DFT calculations

All computational work was performed at the density functional theory (DFT) by Dr. Petra Vasko of the Aldridge group, using Gaussian16 (Revision C.01) program package. Geometry optimisations of the compounds were achieved using the PBE1PBE exchange correlation functional^{8–10} and the Def-TZVP basis set.^{11–13} The minimum nature of the stationary points found on the potential energy surface was confirmed by full frequency calculations (no imaginary frequencies). All calculated energies were reported in gas phase and at zero Kelvin.

2.3 Preparation and purification of starting materials

Information about commercially available materials used in this thesis including supplier, purity and purification methods can be found in the Appendix. The following known compounds were prepared according to the literature procedure: (2,4,6-trimethylphenyl)-imidazole (crude product purified via sublimation instead of column chromatography),¹⁴ 1-*tert*-butylimidazole,^{15,16} Li[Al{OC(CF₃)₃}₄],¹⁷ 2-(*o*-bromophenyl)-1,3-dioxolane,¹⁸ 2-(*o*-diphenylphosphinophenyl)-1,3-dioxolane,¹⁸ 2-(diphenylphosphino)-benzaldehyde,¹⁸ *o*-(PPh₂)-C₆H₄C(H)=NC₆H₃-2,6-*i*-Pr₂¹⁹ and *o*-(PPh₂)-C₆H₄(CH₂)N(H)C₆H₃-2,6-*i*-Pr₂.¹⁹ Details of known compounds which were prepared using modified literature procedures are given below.

Preparation of **Br(CH₂)₂N(H)^tBu·HBr**

Three different synthetic routes were explored for the preparation of **Br(CH₂)₂N(H)^tBu·HBr**.

¹H NMR data (in D₂O) in each case were consistent with literature values.²⁰

Route 1:

2-Chloroethanol (13.4 mL, 0.20 mol) and *tert*-butylamine (46.0 mL, 2.0 mol) were dissolved in distilled H₂O (10.8 mL) and the reaction mixture refluxed at 50°C overnight. 48% HBr (50.1

mL, 0.44 mol) was then added and the reaction mixture refluxed at 120°C overnight. Excess HBr and H₂O were removed in vacuo and the crude product was washed with ethanol to give a white crystalline solid.²⁰ Yield: 8.15 g, 16%.

Route 2:

Commercially available 2-*tert*-butylaminoethanol (5.86 g, 50.0 mmol) and 48% HBr (18.2 mL, 160 mmol, 3.2 equiv.) were mixed in a round-bottomed flask and the reaction mixture refluxed at 120°C overnight. Three additional portions of HBr (3 × 18.2 mL) were added over the course of four days of reflux, before the excess HBr and H₂O were removed in vacuo. The crude product was washed with ethanol to give a white crystalline solid. Yield: 6.59 g, 50%.

Route 3:

Commercially available 2-*tert*-butylaminoethanol (5.00 g, 42.7 mmol, 1 equiv.) was dissolved in CHCl₃ and SOBr₂ (6.62 mL, 85.3 mmol, 2 equiv.) added dropwise at room temperature. The reaction mixture was refluxed for 2 h and turned into a red solution with a yellow precipitate. After cooling to room temperature, Et₂O was added to give an orange solution. The product was then precipitated by adding EtOH, and isolated as a white crystalline solid after washing with cold EtOH.²¹ Yield: 9.00 g, 80%.

General procedure for the preparation of [(L^R)H₃]Br₂ (R = ^tBu/Mes)

Br(CH₂)₂N(H)^tBu·HBr (2.50 g, 9.58 mmol) and 1-*tert*-butylimidazole (1.19 g, 9.58 mmol) or (2,4,6-trimethylphenyl)-imidazole (1.78 g, 9.58 mmol) were mixed in acetonitrile and refluxed at 86°C for 48 h, after which time an orange/yellow solution and a white solid precipitate were formed. The reaction mixture was filtered and the product isolated as a white powder.²² Yield: 2.47 g, 67% (^tBu) and 3.30 g, 77% (Mes). ¹H NMR data (in CDCl₃) for both compounds deviated slightly from literature values^{23,24} as follows:

[(L^{^tBu})H₃]Br₂ δ_H 1.57 (10H, s, ^tBu C(CH₃)₃, overlapped with NH), 1.75 (9H, s, ^tBu C(CH₃)₃), 3.52 (2H, br m, ethylene CH₂), 5.17 (2H, br m, ethylene CH₂), 7.38 (1H, br m, imidazolylidene backbone CH), 7.66 (1H, br m, imidazolylidene backbone CH), 10.13 (1H, br m, NCHN).

$[(L^{Mes})H_3]Br_2$ δ_H 1.57 (10H, s, tBu C(CH₃)₃, overlapped with NH), 2.19 (6H, s, Mes *ortho* CH₃), 2.34 (3H, s, Mes *para* CH₃), 3.70 (2H, t, $^3J_{H-H}$ = 5.8 Hz, ethylene CH₂), 5.34 (2H, t, $^3J_{H-H}$ = 5.8 Hz, ethylene CH₂), 7.00 (2H, s, Mes *meta* CH), 7.20 (1H, br m, imidazolylidene backbone CH), 8.12 (1H, br m, imidazolylidene backbone CH), 10.06 (1H, br m, NCHN).

General procedure for the preparation of $[(L^R)H_2]Br$ (R = tBu /Mes)

$[(L^R)H_3]Br_2$ (2.60 g, 6.73 mmol) was dissolved in distilled H₂O (30 mL), and K₂CO₃ (4 to 5 fold excess) was added at room temperature. The reaction mixture was stirred for 3 h before the volatiles were removed in vacuo to leave a white solid residue. The product was extracted into CHCl₃ (3 × 15 mL) and the filtrate concentrated and dried in vacuo to generate the product as a white powder. Yield: 1.59 g, 77% (tBu) and 2.24 g, 91% (Mes). ¹H NMR data (in CDCl₃) for both compounds deviated slightly from literature values^{23–25} as follows:

$[(L^{tBu})H_2]Br$ δ_H 0.97 (9H, s, tBu C(CH₃)₃), 1.26 (1H, s, NH), 1.70 (9H, s, tBu C(CH₃)₃), 2.96 (2H, br m, ethylene CH₂), 4.52 (2H, br m, ethylene CH₂), 7.35 (1H, br m, imidazolylidene backbone CH), 7.60 (1H, br m, imidazolylidene backbone CH), 10.47 (1H, br m, NCHN).

$[(L^{Mes})H_2]Br$ δ_H 0.98 (9H, s, tBu C(CH₃)₃), 1.51 (1H, s, NH), 2.05 (6H, s, Mes *ortho* CH₃), 2.32 (3H, s, Mes *para* CH₃), 3.00 (2H, br m, ethylene CH₂), 4.79 (2H, br m, ethylene CH₂), 6.98 (2H, s, Mes *meta* CH), 7.09 (1H, br m, imidazolylidene backbone CH), 7.92 (1H, br m, imidazolylidene backbone CH), 9.95 (1H, br m, NCHN).

Synthesis of $Ge\{N(SiMe_3)_2\}_2$

GeCl₂·dioxane (1.77 g, 7.64 mmol, 1 equiv.) and Li[N(SiMe₃)₂] (2.56 g, 15.3 mmol, 2 equiv.) were mixed in a Schlenk tube and dissolved in Et₂O (25 mL) at room temperature to give a red/orange solution. The reaction mixture was stirred at room temperature overnight, before volatiles were removed in vacuo to generate a yellow orange solid. Pentane (30 mL) was added to extract the product, and the orange filtrate was concentrated in vacuo to give a yellow

orange crystalline solid.²⁶ Yield: 2.60 g, 87%. ¹H NMR (400 MHz, benzene-d₆, 298K): δ_H 0.32 (18H, s, Si(CH₃)₃).

Synthesis of **Sn{N(SiMe₃)₂}₂**

SnBr₂ (0.97 g, 3.48 mmol, 1 equiv.) and Li[N(SiMe₃)₂] (1.20 g, 6.97 mmol, 2 equiv.) were mixed in a Schlenk tube and dissolved in Et₂O (15 mL) at room temperature to give a red/orange solution. The reaction mixture was stirred at room temperature overnight, before volatiles were removed in vacuo to generate an orange solid. Pentane (20 mL) was added to extract the product and the orange filtrate was concentrated in vacuo to give an orange crystalline solid.²⁶ Yield: 1.53 g, 72%. ¹H NMR (400 MHz, benzene-d₆, 298K): δ_H 0.29 (18H, s, (Si(CH₃)₃)₂).

Synthesis of **Pb{N(SiMe₃)₂}₂**

PbCl₂ (2.50 g, 8.99 mmol, 1 equiv.) and Li[N(SiMe₃)₂] (3.00 g, 18.0 mmol, 2 equiv.) were mixed in a Schlenk tube and dissolved in Et₂O (15 mL) at -78°C to give white suspension, which turned bright yellow when warmed to room temperature. After stirring overnight, volatiles were removed in vacuo to generate an orange oily solid. Pentane (20 mL) was added to extract the product and the orange filtrate was concentrated in vacuo to give a bright yellow crystalline solid.²⁶ Yield: 4.10 g, 86%. ¹H NMR (400 MHz, benzene-d₆, 298K): δ_H 0.25 (18H, s, (Si(CH₃)₃)₂).

Preparation of **Li[O(C₁₀H₇-1)]**

To a solution of 1-naphthol (1 g, 6.94 mmol) in Et₂O was added 1.2 equiv. *n*-BuLi (1.6 M in hexane, 5.20 ml, 8.33 mmol) at -78°C. The reaction mixture was slowly warmed to room temperature and left to stir overnight, over which time a yellow solution was formed. Volatiles were removed in vacuo, and the crude product was generated as an off white powder. After washing with hexane (2 × 10 mL), the product was isolated as a white powder and used without further purification. Yield: 0.60 g, 58%.

2.4 References

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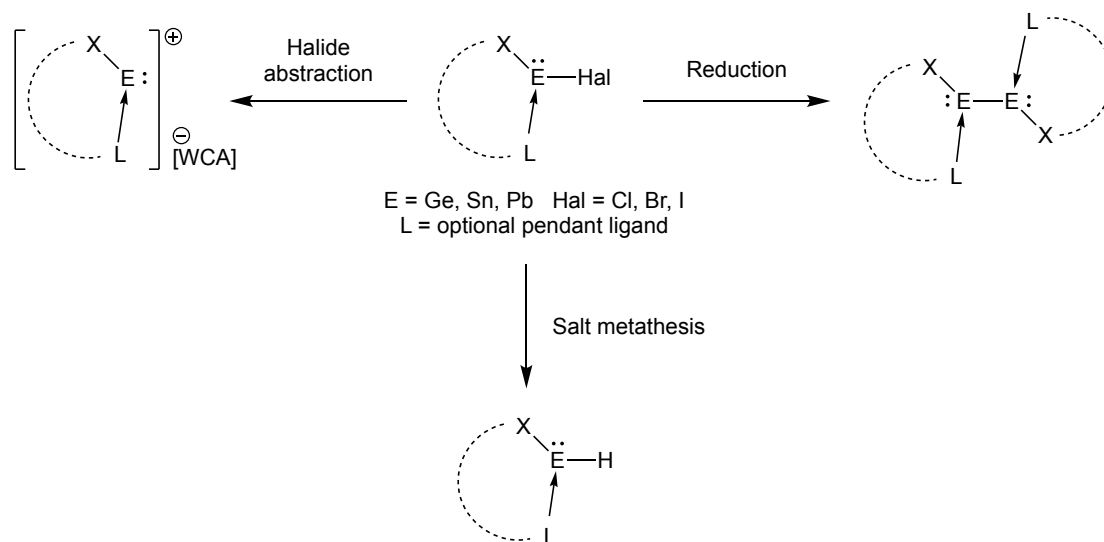
Chapter III

Synthesis and Reduction of Group 14 Halo-Metallylenes

Incorporating a N_{amido}⁺C_{NHC} Chelating Ligand System

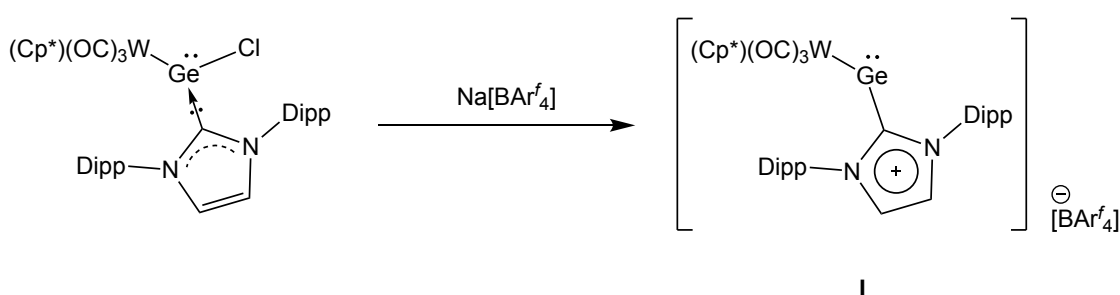
3.1 Introduction

In recent decades, heavier group 14 element(II) complexes have attracted a significant amount of research interest due to their “transition metal-like” reactivity in small molecule activation and potential applications in catalysis.^{1–4} In addition to tetrelenes (of general formula R₂E),^{5–8} three general categories of such complex are in focus, namely cationic divalent group 14 complexes (tetrylium-ylidenes),⁹ heavier group 14 element(I) alkyne analogues (ditetrelynes)^{10–12} and heavier group 14 element(II) hydride complexes.^{13,14} Two or three-coordinate halo-metallylenes, incorporating a monoanionic group (e.g. halide, alkyl, boryl or amido) and a halide group as ligands, serve as common precursors to each of these synthetic targets (**Scheme 3.1.1**).



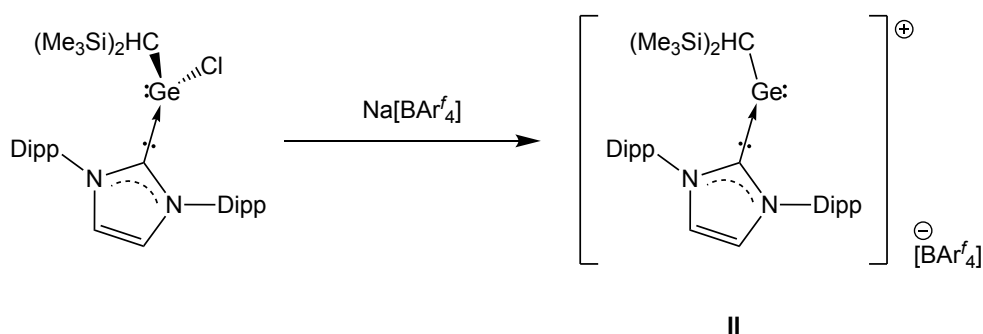
Scheme 3.1.1: Halide-substituted metallylenes can act as versatile precursors for heavier group 14 element(II) complexes of interest in bond activations/catalysis.

The synthesis of cationic germylium-ylidene complexes is usually accomplished via halide abstraction from the related halide-substituted germylenes.^{15–22} Within this area, in 2014, Tobita et al. reported the first example of a cationic metallogermylene (**I**), employing a $(\text{Cp}^*)\text{W}(\text{CO})_3$ fragment.²³ This complex has a narrower HOMO-LUMO energy gap (ca. 179 kJ mol⁻¹) than related neutral germylenes, and brings about both facile cleavage of H₂ and the reversible activation of B-H and Si-H bonds. This cationic species can be synthesised by chloride abstraction from the corresponding NHC-stabilised chlorometallogermylene using Na[BAr^f₄].²⁴ (**Scheme 3.1.2**)



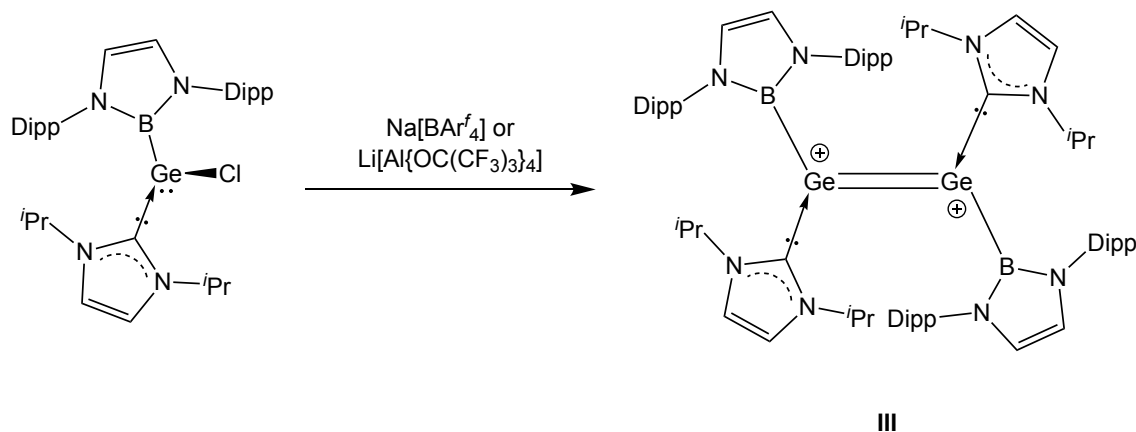
Scheme 3.1.2: Synthesis of the first cationic metallogermylene.

Subsequently, our group reported the isolation of the first example of an acyclic two-coordinate germylium-ylidene cation (**II**) with no π -stabilisation.²⁵ This cation features a relatively small HOMO-LUMO energy gap and undergoes facile oxidative addition of dichloromethane and [2+1] cycloaddition with phenylacetylene. It also allows access to the first examples of cationic systems featuring Ge=E multiple bonds (E = C, N). This cation can also be accessed through chloride abstraction from the corresponding chlorogermylene system by Na[BAr^f₄] (**Scheme 3.1.3**).



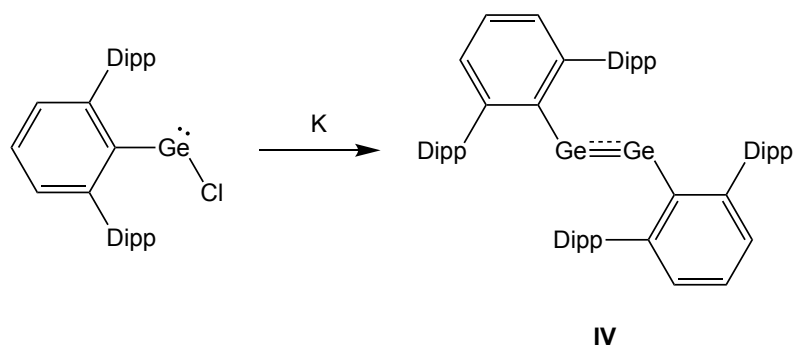
Scheme 3.1.3: Synthesis of the first two-coordinate germanium cation with no π stabilisation.

Another example of an NHC-supported germanium cation (**III**) reported by our group was synthesised via chloride abstraction using either $\text{Na}[\text{Barf}_4]$ or $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$.²⁶ This boryl-stabilised germanium cation undergoes facile oxidative addition with H_2 , NH_3 and silanes due to the narrowing of the HOMO-LUMO gap by the strongly σ -donating ancillary ligand.



Scheme 3.1.4: Synthesis of an NHC-stabilised germanium cation incorporating a boryl ligand (anions omitted for clarity).

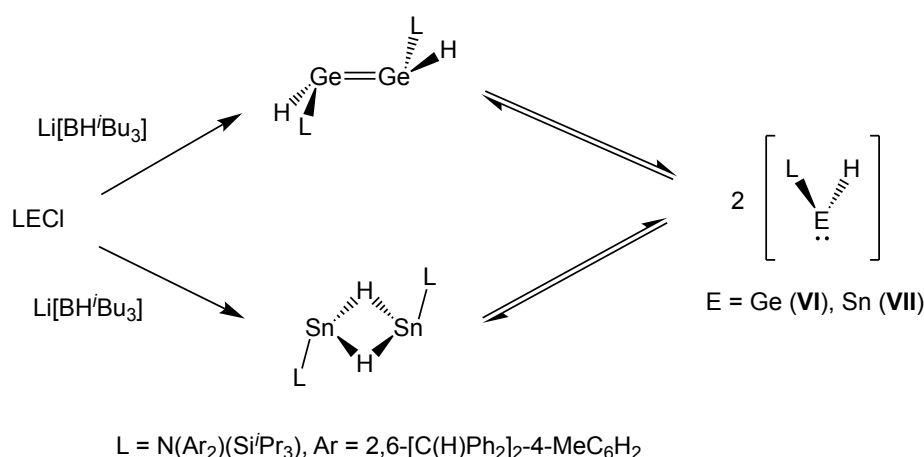
Heavier group 14 element(I) alkyne analogues are usually synthesised by the reduction of the corresponding halo-metallaylenes using a reducing agent such as alkali metals (e.g. Li, Na, K or KC_8) or $\{(\text{Nacnac}^{\text{Mes}})\text{Mg}\}_2$.^{27–36} In 2002, Power et al. reported the isolation of the first example of a stable digermene (**IV**) via the reduction of a terphenyl ligated chlorogermylene; this compound was later shown to be the first main group metal complex to be capable of activating H_2 under ambient conditions (**Scheme 3.1.5**).^{37,38}



Scheme 3.1.5: Synthesis of the first stable digermynes.

In 2011, Jones and co-workers reported a related digermynes LGeGeL ($\text{L} = \text{N}(\text{SiMe}_3)(\text{Ar})$; $\text{Ar} = 2,6\text{-}[\text{C}(\text{H})\text{Ph}_2]_2\text{-4-MeC}_6\text{H}_2$ (**V**) containing a Ge-Ge single bond, again synthesised by the reduction of the chlorogermylene precursor. This complex is stabilised by very bulky amido ligands, and the digermynes is able to activate H_2 even at -10°C .²⁸

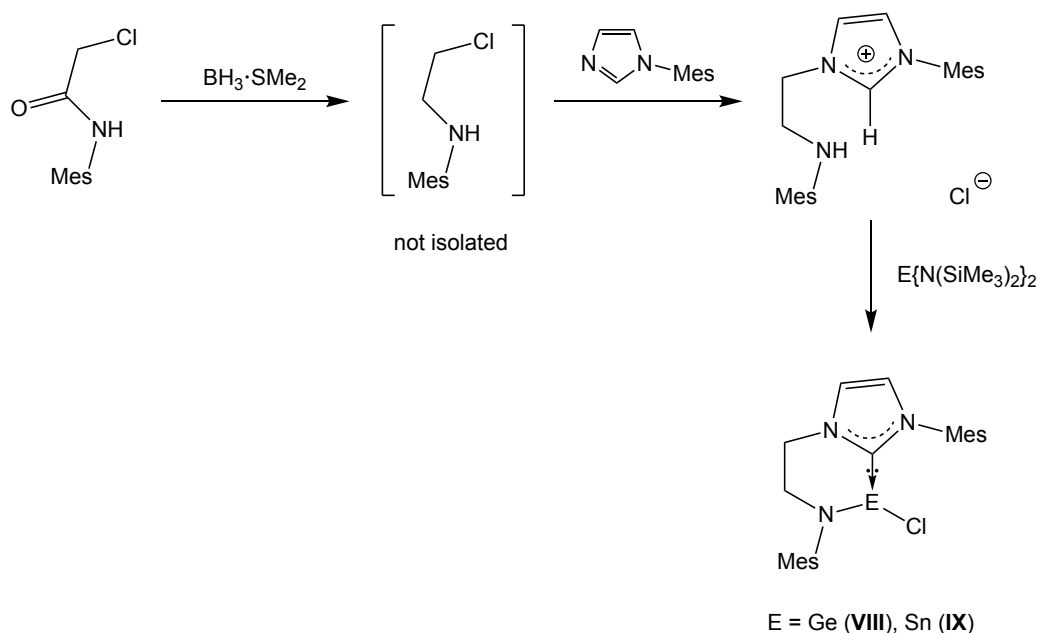
Heavier group 14 element(II) hydride complexes are usually synthesised via salt metathesis reactions between halido-metallenes and a hydride source such as $\text{M}[\text{BH}_4]$ ($\text{M} = \text{Na}, \text{Li}$), $\text{Li}[\text{AlH}_4]$, $\text{Me}_3\text{N}\cdot\text{AlH}_3$ or $\text{Li}[\text{R}_3\text{BH}]$ ($\text{R} = ^i\text{Bu}, \text{Et}$ etc.).^{21,27,38–53} In 2014, Jones et al. reported the first examples of monomeric, two-coordinate germanium (**VI**) and tin (**VII**) hydrides, together with their ability to act as efficient catalysts for hydroboration reactions.^{55–57} The hydrides **VI** and **VII** were synthesised by reacting the chlorogermylene or -stannylene with $\text{Li}[\text{HB}^i\text{Bu}_3]$ (**Scheme 3.1.6**). Alternatively, they can be accessed through reduction of the metallene followed by reaction with H_2 .



Scheme 3.1.6: Synthesis of amido-stabilised hydrido germylene and stannylenes.

3.2 Project aims

The aim of this project at the outset was to develop one (or more) synthetic routes for the isolation and characterisation of a range of heavier group 14 halo-metallylene precursors incorporating a $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ chelating ligand system.^{58,59} These systems (for germanium, tin and lead) would then undergo various functionalisation reactions to form low valent group 14 complexes with interesting reactivity (via halide abstraction, metathesis or reduction). A publication from Hahn and Glorius et al. reported the synthesis and subsequent reactivity of a germylene (**VIII**) and a stannylene (**IX**) employing similar ligand systems, although no further chemistry was definitively established.⁶⁰ The synthetic methods used for the protio-ligand and halo-metallylenes described in their paper are summarised in **Scheme 3.2.1**.



Scheme 3.2.1: Synthesis of halo-metallylenes in a related publication by Hahn and Glorius.

In this chapter we report synthetic routes to two novel sets of halo-metallylene systems featuring two different amido R groups (**Figure 3.2.1**). By varying the ligand framework, we wished to examine the difference in the structure and reactivity of the coordinated complexes due to the changes in steric and electronic properties. In our synthesis, each known intermediate can be isolated and characterised by ^1H NMR spectroscopy. In addition to germylenes and stannylenes, two novel plumbylenes are also isolated and fully characterised. Furthermore, the reduction chemistry of the two germylenes has been attempted, and the preliminary results of this chemistry are discussed.

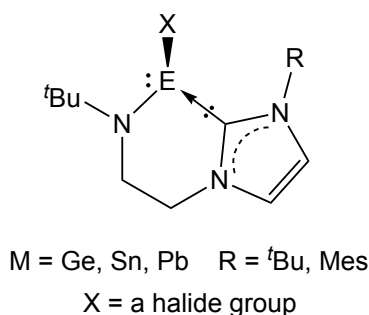
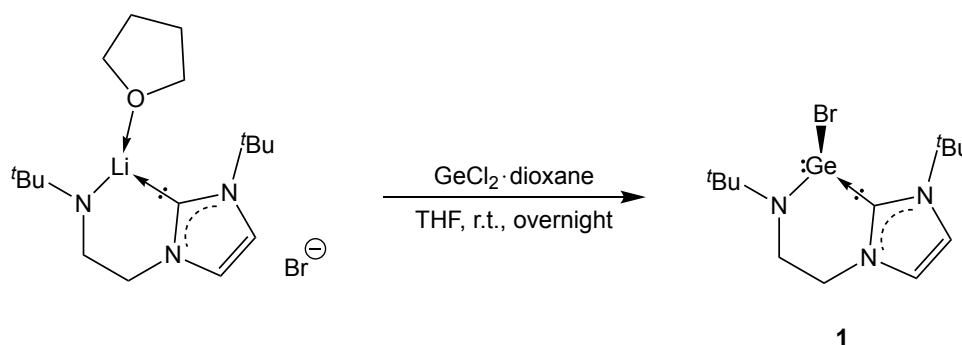


Figure 3.2.1: Generic structure of the target complexes.

3.3 Results and discussion

3.3.1 Synthesis and characterisation of (L^{tBu})GeBr, **1**

Two different synthetic routes towards bromo-substituted germylene complex **1** were investigated and compared. Initially, salt metathesis was carried out by combining the previously reported lithiated ligand⁶¹ and the commercially available germanium dichloride dioxane complex in THF at room temperature and stirring overnight (**Scheme 3.3.1**).



Scheme 3.3.1: Initial synthetic route to (L^{tBu})GeBr, **1**.

Both reactants are soluble in THF and the reaction mixture forms a pale yellow solution. After removing all THF in vacuo, extracting the product into toluene and concentrating to reduce the volume of solvent, bromogermylene **1** was isolated as a pale yellow powder. Despite the reported insolubility of the lithiated ligand in benzene- d_6 , its ^1H NMR spectrum can be measured and used as a reference for the formation of a new product during the course of reaction. The enhanced solubility in benzene- d_6 might be due to the coordination of one molecule of THF revealed in the resulting ^1H NMR spectrum.

The ^1H NMR spectrum of **1** shows a different pattern of signals to the lithiated precursor, (corresponding to one ligand environment) consistent with the formation of a single new product. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution of **1** in toluene stored at -30°C for several days. Compound **1** crystallises in the monoclinic $P2_1/c$ space group and the asymmetric unit consists of a monomeric bromogermylene molecule (**Figure 3.3.1**). Interestingly, due to the relatively higher solubility

of LiBr than LiCl in THF, anion exchange occurred during the formation of **1**, leading to a bromide ligand being incorporated at the germanium centre, instead of the expected chloride. The geometric parameters obtained from the solid-state structure are in line with those reported for related compounds, typically featuring a Ge(2)-Br(1) bond almost perpendicular to the N(3)-Ge(2)-C(11) chelate moiety (mean bond angle 96.5°).^{60,62–68} This suggests a low degree of hybridisation between the *s* and *p* orbitals of the germanium centre.⁶⁹ For detailed discussion of key structural parameters see section 3.3.7.

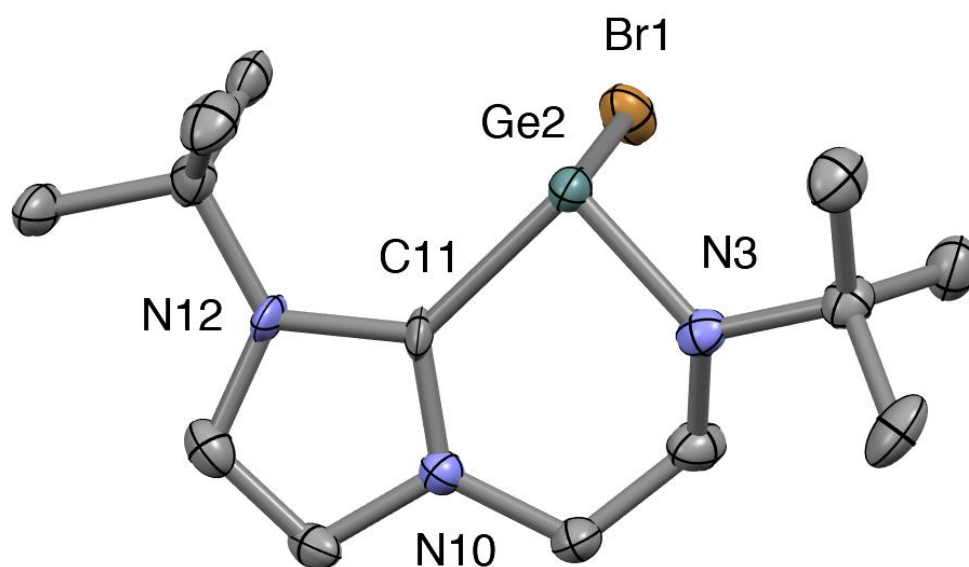
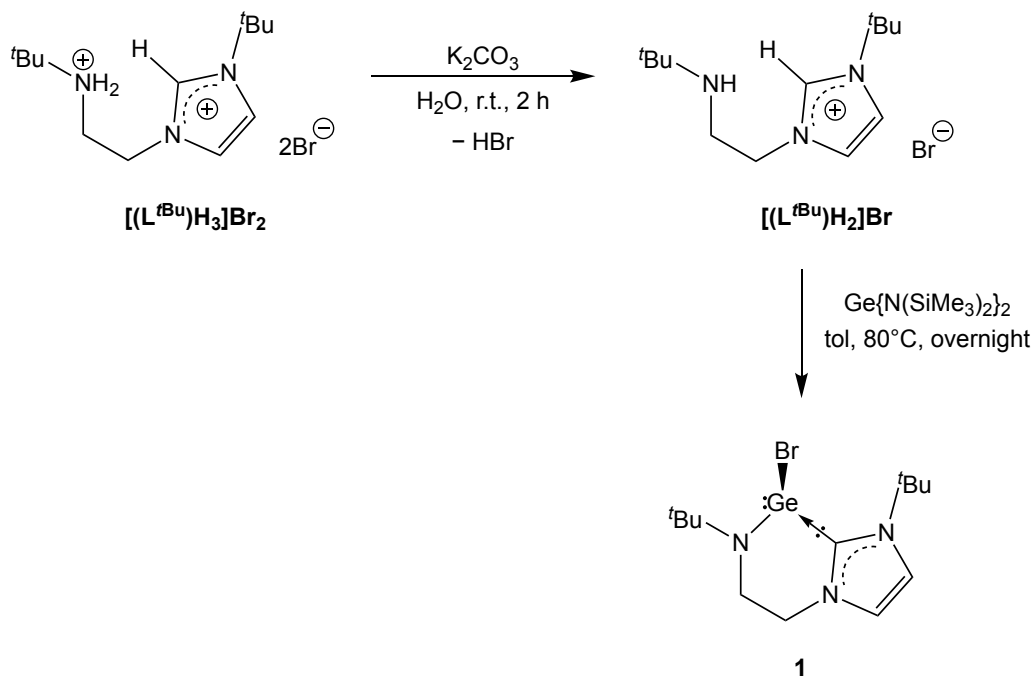


Figure 3.3.1: Molecular structure of (L^{tBu})GeBr, **1**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ge(2)-Br(1) 2.611(2), Ge(2)-N(3) 1.856(11), Ge(2)-C(11) 2.062(13), C(11)-Ge(2)-Br(1) 94.4(4), N(3)-Ge(2)-Br(1) 98.6(4), N(3)-Ge(2)-C(11) 90.1(5).

This synthetic method, however, is not ideal for the isolation of bulk quantities of **1** and its use in further reaction chemistry. The yield of the isolated product is very low (ca. 10%), and the purity of **1** as an isolated powder is also not ideal, with a small amount of free ligand always present in the ^1H NMR spectrum. Therefore, an alternative synthetic route was designed and explored, in hope of offering higher yield and purity.

With this in mind, the monocationic protio-ligand [L^{tBu}] H_2]Br could be synthesised from the corresponding dication [L^{tBu}] H_3]Br₂ using a procedure modified slightly from the published

literature (**Scheme 3.3.2**).^{70,71} Deprotonation was performed using an excess of a weak base (potassium carbonate) and subsequent reaction with germanium bis(trimethylsilyl)amide⁷² in toluene at 80°C overnight successfully generated the same bromogermylene product **1** in significantly higher yield (ca. 90%) and purity.



Scheme 3.3.2: Alternative synthetic route of $(L^{tBu})GeBr$, **1**.

Due to the low solubility of the protio-ligands in hydrocarbon solvents such as benzene or toluene, they were mainly characterised by 1H NMR spectroscopy in $CDCl_3$. After heating the reaction mixture at 80°C overnight under argon, a cloudy yellow/orange suspension turned into a clear pale-yellow solution, indicating that the reaction has occurred to give a new product which has a relatively higher solubility in toluene than the protio-ligand. The 1H NMR spectrum of the isolated product is consistent with the formation of **1**, with almost no contamination by the free ligand. In the aliphatic region, two sharp singlets integrating to 9H each (at $\delta_H = 1.39$ and 1.50 ppm) correspond to the tBu groups attached to the amido and imidazolylidene nitrogens, respectively. In the aromatic region, two broad doublets integrating to 1H each at $\delta_H = 5.94$ and 6.21 ppm correspond to the two imidazolylidene backbone protons. At room temperature, the $^{13}C\{^1H\}$ NMR spectrum shows the carbenic carbon resonance at $\delta_C = 168.6$

ppm, which is in the typical range for compounds of this type (e.g. chlorogermylene **VIII** δ_C = 171.4 ppm).^{22,45,60} The molecular structure of **1** in the solid state shows that the ethylene linkage between the amido and carbene components of the ligand does not lie co-planar with the N_{amido}-Ge-C_{NHC} scaffold. As such, it should give rise to four distinct chemical environments for the sidearm protons in the ¹H NMR spectrum. However, only a single broad resonance integrating to 4H at δ_H = 3.54 ppm is observed at room temperature. Hypothesising that this might be due to a fluxional process occurring under ambient conditions, VT-NMR measurements were attempted at low temperature. Unfortunately, these measurements were not particularly informative, due to the low solubility of **1** in toluene-d₈ below 253K.

In terms of synthetic protocols, the second method described is also advantageous because in contrast to the lithiated ligand, both [(L^{tBu})H₃]Br₂ and [(L^{tBu})H₂]Br are air and moisture stable, which means that they are easier and safer to handle than lithiated intermediates. This route was subsequently employed in all syntheses of **1**, and also extended to the preparation of other group 14 halo-metallylenes.

3.3.2 Synthesis and characterisation of (L^{tBu})SnBr, **2**

Encouraged by the success of the synthesis of **1**, the same ligand was utilised for the formation of the tin analogue, (L^{tBu})SnBr **2**. In similar fashion to **1**, initial attempts at synthesising **2** using the lithiation method were less than ideal, with the same problems of low yield and purity of the isolated product. Nonetheless, evidence for the formation of **2** was obtained from aliquots taken from the reaction mixture. The ¹H NMR spectrum clearly indicates the formation of a new species featuring a single ligand environment, and which is not the free ligand. Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a hexane solution.* The solid-state structure of this new species was studied by X-ray crystallography

* This part was performed in collaboration with Dr Andrey Protchenko from the Aldridge group.

and shown to be monomeric **2** (**Figure 3.3.2**). Further investigation showed that **2** could also be crystallised by layering a concentrated solution of toluene with hexane stored at -30°C .

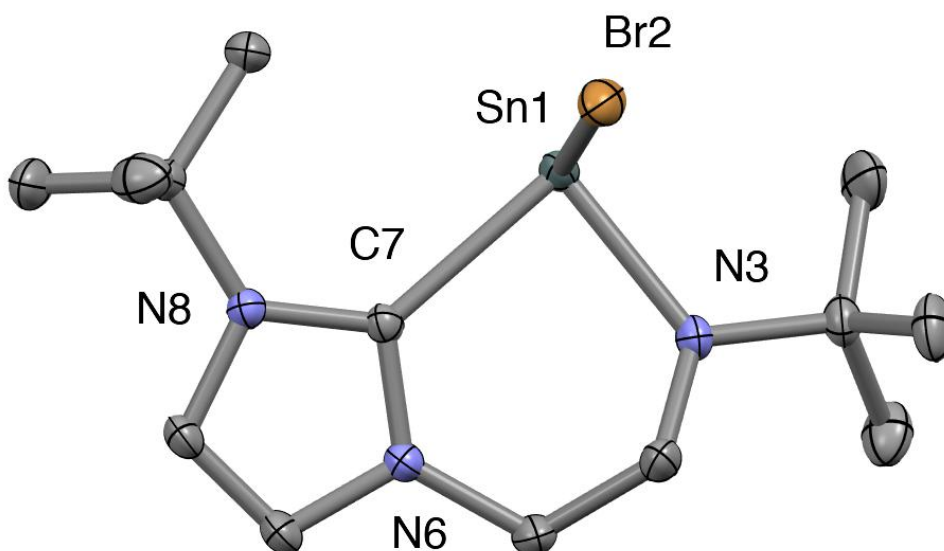
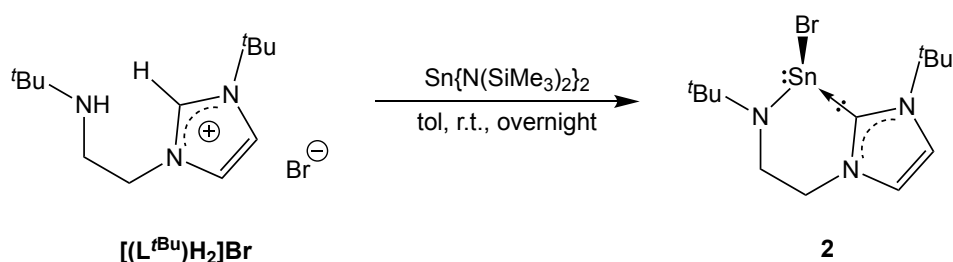


Figure 3.3.2: Molecular structure of $(\text{L}^{\text{tBu}})\text{SnBr}$, **2**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Sn(1)–Br(2) 2.7559(5), Sn(1)–N(3) 2.074(3), Sn(1)–C(7) 2.319(4), C(7)–Sn(1)–Br(2) 91.20(9), N(3)–Sn(1)–Br(2) 96.96(10), N(3)–Sn(1)–C(7) 88.26(13). Detailed discussion see section 3.3.7.

As expected, the solid-state structure of **2** features a bromide group oriented almost perpendicular to the N(3)–Sn(1)–C(7) plane (mean bond angle 94.08°). Key bond lengths are also consistent with typical halide substituted stannylenes.^{60,62,63,73–79}

The alternative synthetic route outlined in **Scheme 3.3.3** was then adopted for **2**, given its improved performance in the synthesis of **1**. Treatment of $[(\text{L}^{\text{tBu}})\text{H}_2]\text{Br}$ with tin bis(trimethylsilyl)amide⁷² afforded **2** in a higher isolated yield (ca. 53%). Notably, the reaction conditions for the formation of **2** are milder than for the corresponding germylene **1**: the reaction occurs at room temperature with no heating required. This can be attributed to the larger covalent radius of Sn(II) (1.39(4) Å, cf. 1.20(4) Å for Ge(II)) and the fact that Sn–N bonds are consequently weaker than their germanium counterparts.⁶²



Scheme 3.3.3: Synthesis of $(L^{tBu})SnBr$, **2**, from the corresponding bis(amide).

The 1H NMR spectrum of **2** measured at 298K in toluene- d_8 features two broad multiplets which integrate to 2H each (at $\delta_H = 3.60$ and 3.86 ppm) for the ethylene backbone. In the $^{13}C\{^1H\}$ NMR spectrum, the carbenic carbon resonance is measured at $\delta_C = 173.7$ ppm. This is in line with other related stannylenes of this type (e.g. chlorostannylene **IX**, $\delta_C = 178.6$ ppm).^{45,60}

Both ^{117}Sn and ^{119}Sn isotopes are NMR active having spins of $\frac{1}{2}$. In the current study, ^{119}Sn NMR data were measured; previous research has shown that the ^{119}Sn chemical shift can be used as an indication of the coordination number around the tin centre in solution. Higher coordination numbers generally lead to a more shielded ^{119}Sn NMR signal. However ^{119}Sn NMR spectroscopy can be highly sensitive to small structural changes.^{80,81} In the case of **2**, a single resonance was observed at $\delta_{Sn} = -51.7$ ppm, which reflects a three-coordinate Sn(II) centre. The ^{119}Sn NMR chemical shift of **2** is comparable to several reported NHC-stabilised stannylenes, for example $\delta_{Sn} = -61.5$ ppm for saturated 1,3-dimesitylimidazolin-ylidene backbone and -63.9 ppm for $IMes \cdot SnCl_2$, as well as $\delta_{Sn} = -68.7$ ppm for $IPr \cdot SnCl_2$.^{45,82} It is also similar to a three-coordinate chlorostannylenes incorporating an aminotroponimate ligand system, $[(^iPr)_2ATI]SnCl$ ($\delta_{Sn} = -68$ ppm) (**Figure 3.3.3**).^{66,83} Notably, the ^{119}Sn chemical shift of the chlorostannylene (**IX**) reported in Hahn's paper is at $\delta_{Sn} = -149$ ppm, which indicates a more electron-rich tin centre compared to compound **2**.⁶⁰

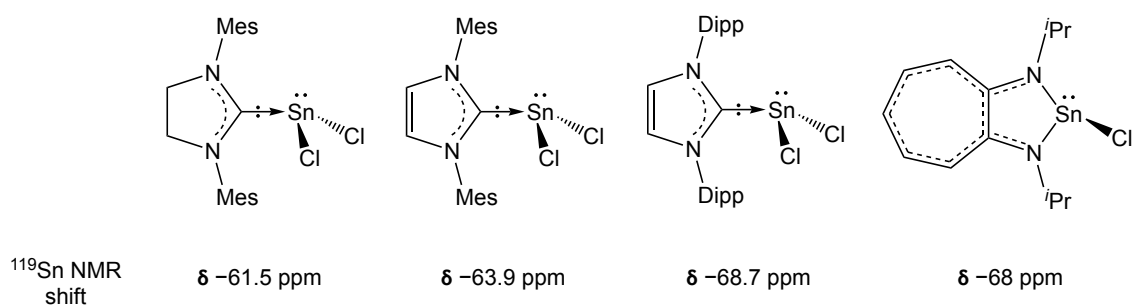
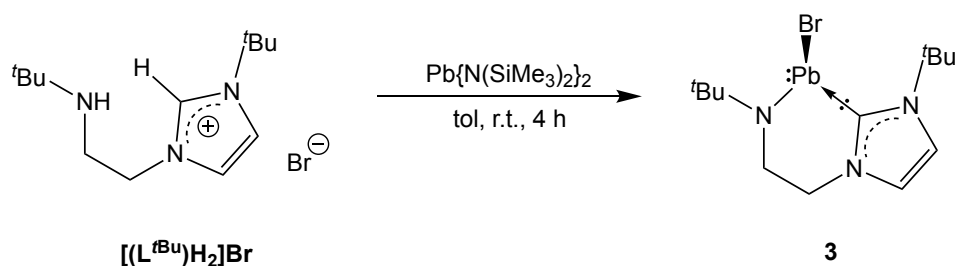


Figure 3.3.3: Previously reported three-coordinate stannylenes and their ¹¹⁹Sn NMR chemical shifts.

3.3.3 Synthesis and characterisation of (L^{tBu})PbBr, **3**

By reacting the [(L^{tBu})H₂]Br with lead bis(trimethylsilyl)amide,⁷² a three-coordinate bromoplumbylene **3** can be synthesised and isolated as green powder in reasonable yields (ca. 48%) (**Scheme 3.3.4**).



Scheme 3.3.4: Synthesis of (L^{tBu})PbBr, **3**, from the corresponding bis(amidate).

As expected, given the even weaker Pb-N covalent interaction, the reaction conditions employed for **3** were even milder than those for **2**. Compound **3** is prone to decomposition upon heating, with signs of a dark precipitate, that is thought to be lead metal. In comparison with the relatively more stable germanium/tin compounds **1** and **2**, this can be rationalised by the larger covalent atomic radius of Pb(II) (1.46(5) Å), leading to weaker interaction with the ligand.

In a similar fashion to compounds **1** and **2**, ¹H NMR spectrum of **3** exhibits two sharp singlets in the aliphatic region (^tBu groups) and two doublets in the aromatic region (imidazolyliidene

CH). In the case of **3**, the ethylene backbone protons appear to be better resolved into two doublets of triplets with couplings of $^2J_{\text{HH}} = 1.4$ Hz and $^3J_{\text{HH}} = 3.7$ Hz. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the carbenic carbon at $\delta_{\text{C}} = 204.0$ ppm. It is comparable to other reported NHC-stabilised plumbylene, for example $\text{IPr}\cdot\text{PbBr}_2$ ($\delta_{\text{C}} = 218.9$ ppm).⁸⁴

^{207}Pb NMR was also used to characterise **3** and probe the coordination environment around the Pb(II) centre. Due to the variability of ^{207}Pb NMR chemical shifts for Pb(II) compounds, a wide range ($\delta_{\text{Pb}} = -3000$ to 6000 ppm) was examined. A broad singlet resonance at $\delta_{\text{Pb}} = 2093$ ppm was found. Compared with related compounds, the chemical shift of this resonance appears to be consistent with a coordination number of three around the lead centre in solution (**Figure 3.3.4**).^{76,85–87}

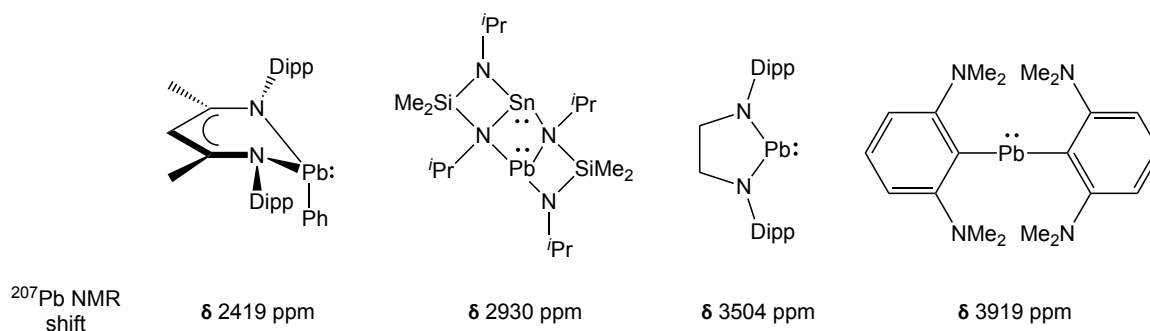


Figure 3.3.4: Previously reported two or three-coordinate plumbylenes and their ^{207}Pb NMR chemical shifts.

Single crystals of **3** suitable for X-ray crystallography were obtained by storing a concentrated toluene solution at -30°C . Consistent with the hypotheses made for the structure in solution on the basis of the NMR data, the molecular structure of **3** in the solid is shown to be monomeric, with the typical features of a halo-metallylene (**Figure 3.3.5**).

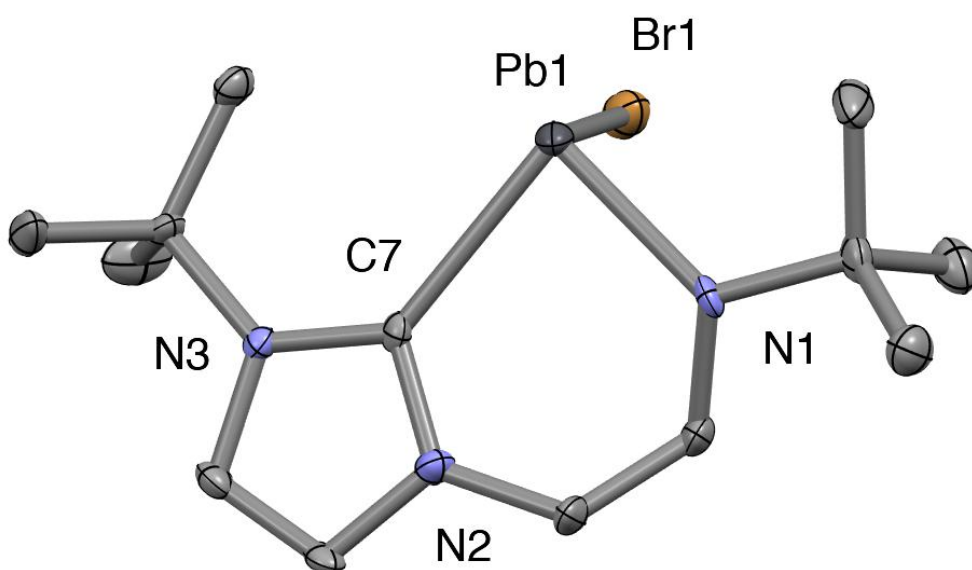
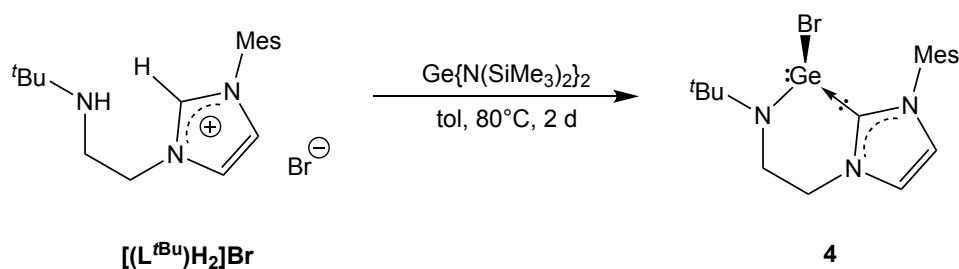


Figure 3.3.5: Molecular structure of $(L^{\text{tBu}})\text{PbBr}$, **3**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Pb(1)–Br(1) 2.8489(14), Pb(1)–N(1) 2.170(9), Pb(1)–C(7) 2.412(11), C(7)–Pb(1)–Br(1) 86.5(3), N(1)–Pb(1)–Br(1) 98.0(3), N(1)–Pb(1)–C(7) 86.5(3). Detailed discussion see section 3.3.7.

3.3.4 Synthesis and characterisation of $(L^{\text{Mes}})\text{GeBr}$, **4**

Encouraged by the synthesis, isolation and characterisation of halo-metallaylenes **1-3**, we sought to develop a second set of related systems employing a similar ligand system, by using the same synthetic strategy. By changing the R group on the imidazolyliidene fragment from ^tBu to Mes, the resulting structural and chemical properties might vary due to the changes in electronic and steric properties. In addition, the availability of two (related) ligand systems was thought to offer increased prospects for obtaining compounds as single crystals suitable for X-ray crystallography. The protio-ligand $[(L^{\text{Mes}})\text{H}_2]\text{Br}$, featuring an imidazolyliidene-appended mesityl group was synthesised following a modified reported procedure.⁸⁸

In a similar manner to the synthetic route used for **1**, mixing $[(L^{\text{Mes}})\text{H}_2]\text{Br}$ and germanium bis(trimethylsilyl)amide generates bromogermylene complex **4** (**Scheme 3.3.5**) in high yield (ca. 99%) and purity. The reaction requires heating in toluene at 80°C for two days for a complete conversion. Compound **4** is isolated as a pale yellow powder.



Scheme 3.3.5: Synthesis of $(L^{Mes})GeBr$, **4**, from the corresponding bis(amide).

The 1H NMR spectrum of **4** shows a singlet (9H, $\delta_H = 1.42$ ppm) for the tBu protons and a singlet (3H, $\delta_H = 2.00$ ppm) for the *para* methyl group of the mesityl substituent. A broad singlet (6H, $\delta_H = 2.06$ ppm) is assigned to the *ortho*-methyl groups, rather than a sharp singlet. This can be explained by the slow rotation of the mesityl group on the NMR timescale. The two sets of diastereotopic protons on the ethylene backbone again appear as a broad singlet (4H, $\delta_H = 3.43$ ppm) as described in the case of compound **1**. As in the case of compound **1**, VT NMR was not informative due to the low solubility below 253K. As expected, in the aromatic region, two doublets and a singlet are assigned to the imidazolyliene C-H and mesityl C-H groups, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows the carbenic carbon at $\delta_C = 169.5$ ppm (cf. $\delta_C = 168.6$ ppm for **1**).

Single crystals suitable for X-ray crystallography were obtained by layering a concentrated solution of **4** in THF with hexane at room temperature. Compound **4** crystallises in an orthorhombic space group ($Pbca$) and the asymmetric unit is comprised on a single (monomeric) bromogermylene molecule (**Figure 3.3.6**). The solid-state structure of **4** displays typical structural features of a monohalide germylene.

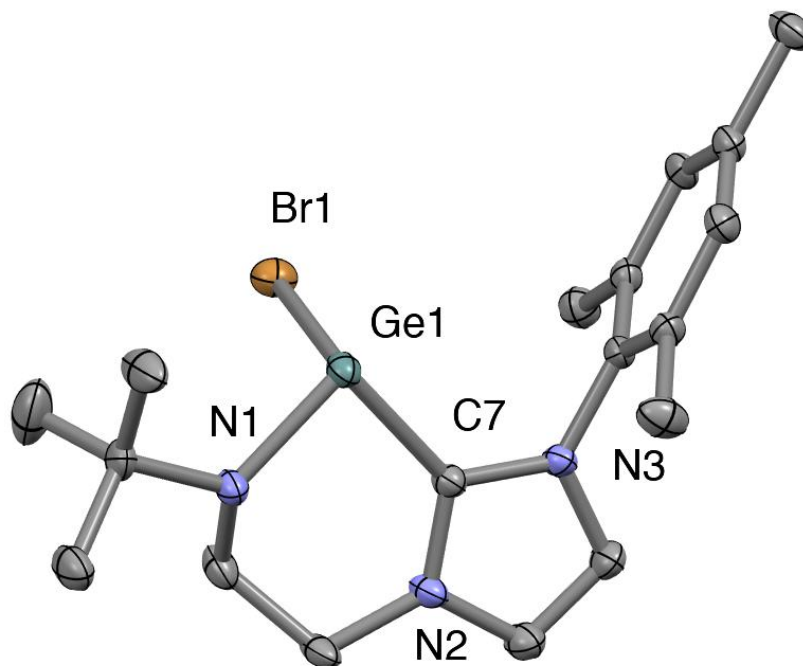
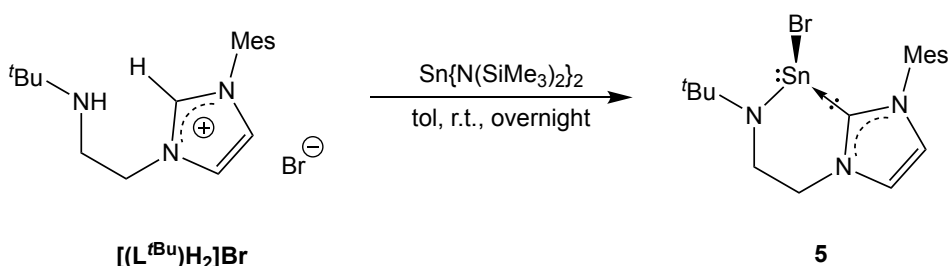


Figure 3.3.6: Molecular structure of (L^{Mes})GeBr, **4**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-Br(1) 2.6118(6), Ge(1)-N(1) 1.891(3), Ge(1)-C(7) 2.059(3), C(7)-Ge(1)-Br(1) 94.42(10), N(1)-Ge(1)-Br(1) 98.93(10), N(1)-Ge(1)-C(7) 89.96(13). Detailed discussion see section 3.3.7.

3.3.5 Synthesis and characterisation of (L^{Mes})SnBr, **5**

Following the same method, bromostannylene **5** can be synthesised in relatively high yield (ca. 65%) and good purity (**Scheme 3.3.6**) and characterised by multinuclear NMR, X-ray crystallography and elemental microanalysis.



Scheme 3.3.6: Synthesis of (L^{Mes})SnBr, **5**, from the corresponding bis(amide).

The ^1H NMR resonances can be assigned in a similar manner to germylene **4**, with a singlet (9H, δ_{H} = 1.37 ppm) for the $t\text{Bu}$ protons, a singlet (3H, δ_{H} = 1.98 ppm) for the *para*-methyl

group of the mesityl substituent and a broad singlet (6H, $\delta_{\text{H}} = 2.00$ ppm) for the *ortho*-methyl groups, rather than a sharp singlet. The four ethylene backbone protons were again shown as a broad multiplet at $\delta_{\text{H}} = 3.45$ ppm at 298K. In order to resolve the individual signals for these protons, ^1H NMR spectra were measured at 193, 198, 208, 218, 223, 233, 243, 253, 263 and 298K. As the sample was cooled down, more distinct and well-resolved signals can be observed for the four inequivalent ethylene protons, as well as the two *ortho* CH_3 and *para* CH on the mesityl group. At/below approximately 208K the system is in the slow exchange regime on the NMR timescale. Lowering the temperature further leads to broadening of the signals due to the lowered solubility.

The rate of exchange (k) can be calculated by ^1H NMR simulation. As shown by the stacked spectra (**Figure 3.3.7**), the simulated spectra are in good agreement with the experimental data. Kinetic data (i.e. the energy barrier) for the exchange process can then be calculated using the rate constants obtained from the simulations.

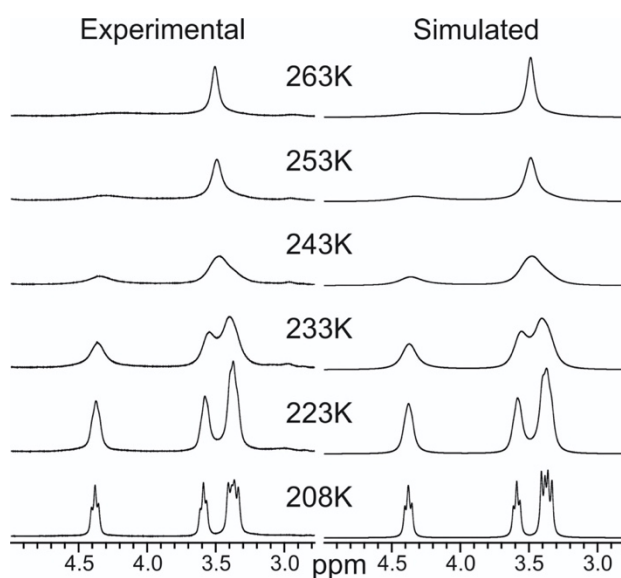


Figure 3.3.7: Experimental and simulated ^1H NMR spectra ($\delta_{\text{H}} = 3.0\text{-}4.5$ ppm) of stannylene **5**.

A straight line graph was generated by plotting $\ln(k/T)$ against $1/T$ at $T = 223, 233, 243, 253\text{K}$ (**Figure 3.3.8**). $\Delta H^\ddagger$ and $\Delta S^\ddagger$, and hence $\Delta G^\ddagger$ can be worked out from the gradient and intercept

of this Eyring type plot. The energy barrier $\Delta G^\ddagger$ at the coalescence temperature T_c (253K) is 49(1) kJ mol⁻¹. $\Delta H^\ddagger = 27.5(0.8)$ kJ mol⁻¹ and $\Delta S^\ddagger = -84(3)$ J mol⁻¹ K⁻¹.

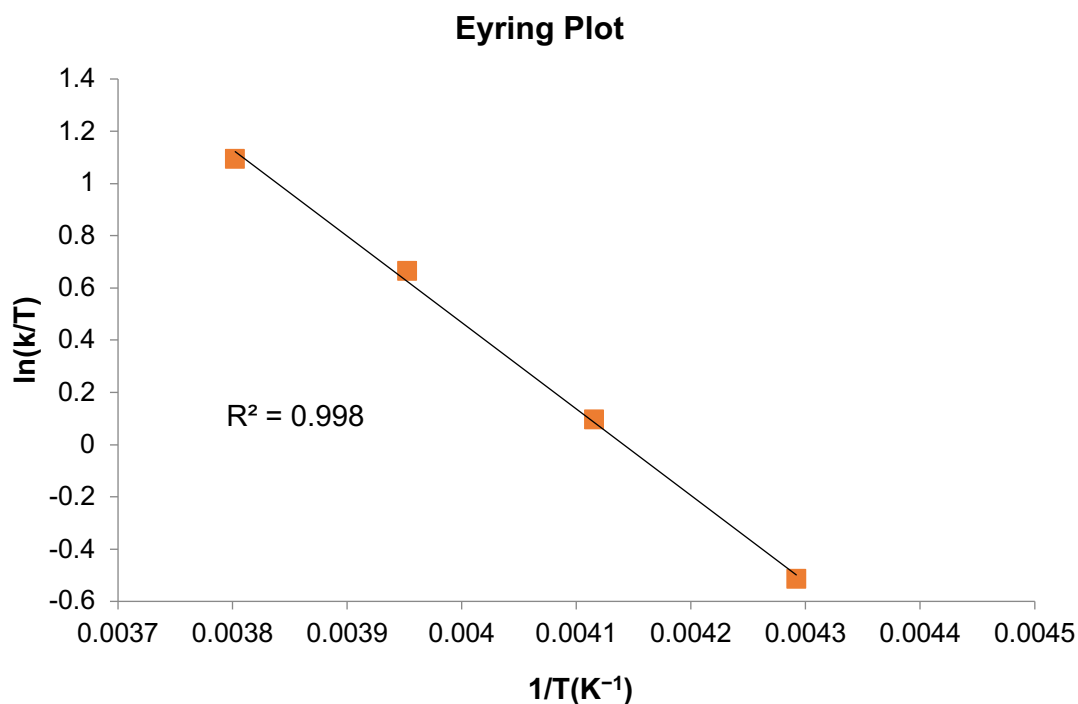
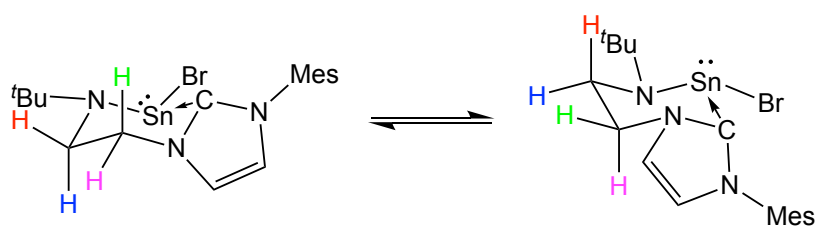


Figure 3.3.8: Eyring plot of the energy barrier to exchange of methylene resonances for stannylene **5**.

The mechanism of fluxional process is thought to involve a ring flip of the six-membered heterocycle in **5** (**Scheme 3.3.7**). As shown by the two chair conformations, the equatorial and axial ethylene protons are chemically inequivalent. When exchange process occurs rapidly on the NMR timescale, the two hydrogens within a given methylene (CH₂) unit become equivalent. As the temperature drops below the coalescence temperature T_c , the rate of exchange becomes slower and all four signals are distinguishable.



Scheme 3.3.7: Ring flip of **5**.

Finally, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** shows the carbenic carbon at $\delta_{\text{C}} = 174.7$ ppm (cf. $\delta_{\text{C}} = 173.7$ ppm for **2**), and the ^{119}Sn NMR spectrum shows a single resonance at $\delta_{\text{Sn}} = -67.8$ ppm (cf. $\delta_{\text{Sn}} = -51.7$ ppm for **2**), which is again consistent with a three-coordinate Sn(II) centre in solution.

Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of **5** in benzene (**Figure 3.3.9**). The molecular structure of **5** shows that it is monomeric and has the typical structural features of halo-stannylenes. It also confirms a three-coordinate tin centre in the solid state.

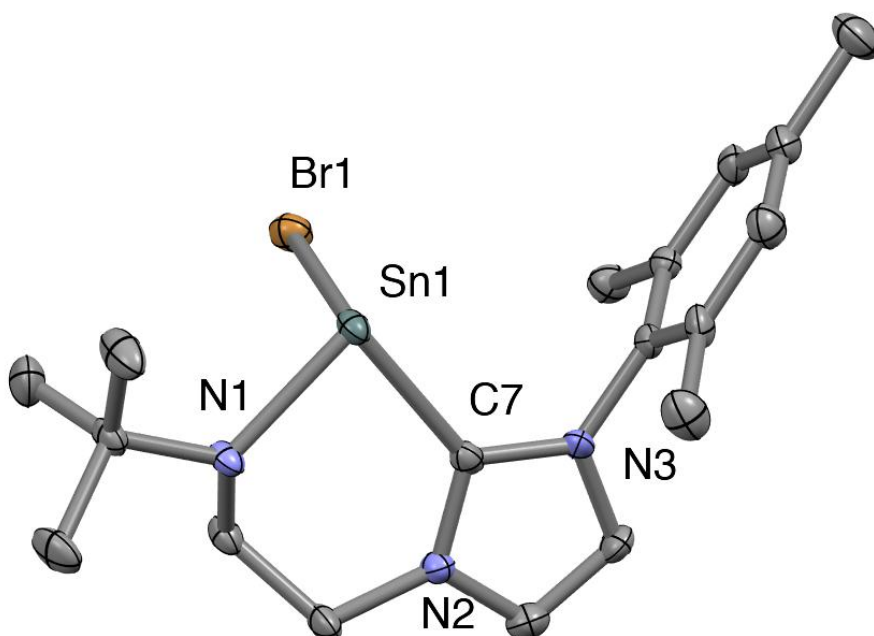
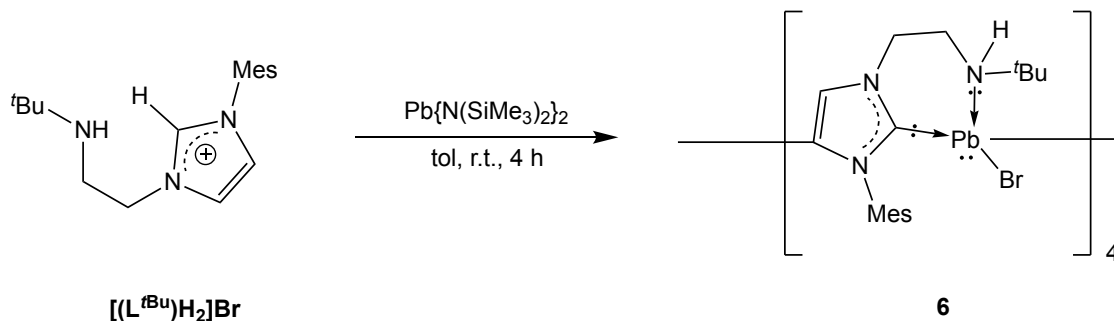


Figure 3.3.9: Molecular structure of $(\text{L}^{\text{Mes}})\text{SnBr}$, **5**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Sn(1)-Br(1) 2.7274(5), Sn(1)-N(1) 2.090(3), Sn(1)-C(7) 2.272(4), C(7)-Sn(1)-Br(1) 88.77(9), N(1)-Sn(1)-Br(1) 95.54(9), N(1)-Sn(1)-C(7) 85.30(13). Detailed discussion see section 3.3.7.

3.3.6 Synthesis and characterisation of $\{(\text{L}^{\text{Mes}'})\text{PbBr}\}_4$, **6**

Reaction of $[(\text{L}^{\text{Mes}})\text{H}_2]\text{Br}$ with one equivalent of lead bis(trimethylsilyl)amide under the same reaction conditions as used for the synthesis of plumbylene **3** leads to the formation of an unexpected isomeric species - namely the cyclotetramer **6** (**Scheme 3.3.8**). **6** is apparently

formed by the oligomerisation of four plumbylene monomers, via C-H activation at the imidazolylidene backbone. Compound **6** was isolated as a yellow-green powder in reasonable yield (ca. 45%).



Scheme 3.3.8: Unexpected formation of $\{(L^{Mes'})PbBr\}_4$, **6**, from the reaction of protio-ligand $[(L^{Mes})H_2]Br$ with lead bis(trimethylsilyl)amide.

The 1H NMR spectrum of an aliquot taken from the reaction mixture shows two sharp, well resolved 3H singlets ($\delta_H = 2.08$ and 2.14 ppm), which correspond to the two *ortho* CH_3 groups of the mesityl substituent, indicative of restricted rotation of the mesityl group about the N-C bond. Four relatively well-distinguished 1H multiplets between $\delta_H = 3$ -5 ppm can be assigned to the ethylene backbone protons, consistent with a conformationally fixed chelate ring. Furthermore, instead of the expected two doublets of 1H each (imidazolyliene C-H) and a signal for 2H (mesityl *meta* C-H), four 1H singlets are found in the aromatic region, with one significantly downfield shifted at $\delta_H = 7.66$ ppm. The $^{13}C\{^1H\}$ NMR shows the carbenic carbon resonance at $\delta_C = 201.8$ ppm (cf. $\delta_C = 204.0$ ppm for **3**). In addition, the ^{207}Pb NMR spectrum exhibits one broad singlet resonance at $\delta_{Pb} = 1358$ ppm, consistent with a coordination number at Pb(II) greater than three. Since the 1H (and ^{207}Pb) NMR spectroscopic data are intriguingly different from other halo-metallylenes reported in this chapter, X-ray crystallography was used to unambiguously determine the identity of the product in the solid state. Single crystals were obtained by storing a concentrated solution in toluene at $-30^\circ C$. The molecular structure of **6** so obtained reveals that the asymmetric unit is a cyclic tetramer, with each monomeric unit being an isomer of the expected monomeric plumbylene (**Figure 3.3.10**).

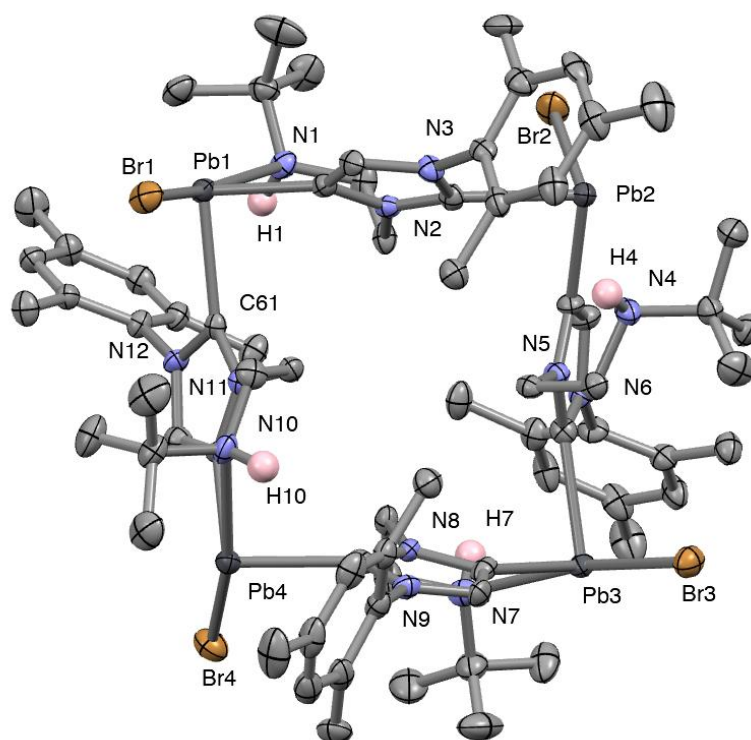
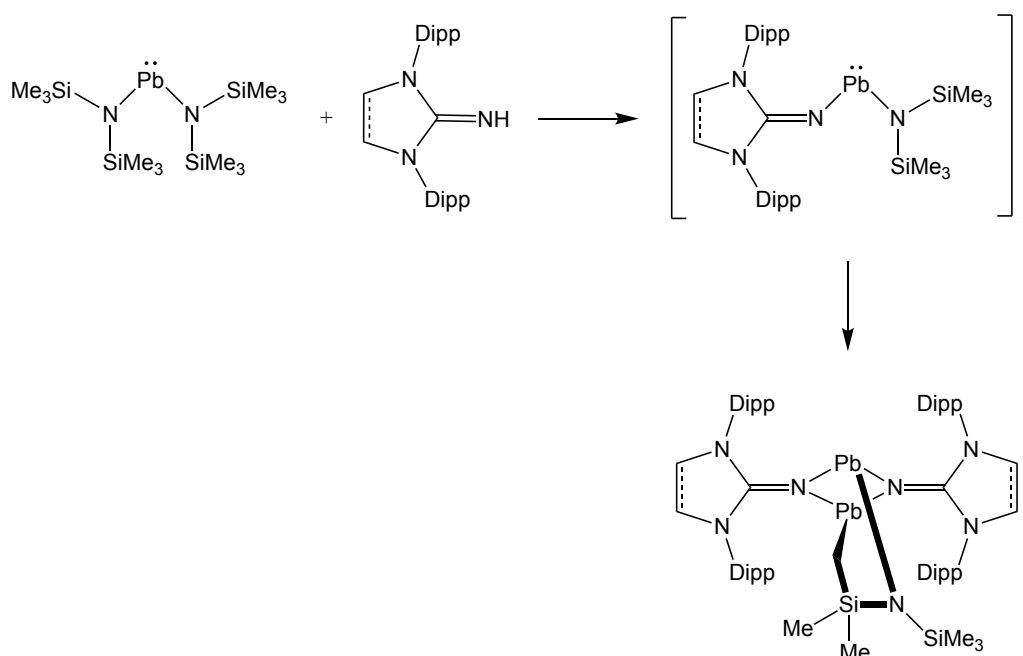


Figure 3.3.10: Molecular structure of $[L^{\text{Mes}^t}\text{PbBr}]_4$, **6**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)-N(1) 2.794(9), Pb(1)-Br(1) 2.9100(14), Pb(1)-C(8) 2.319(12), C(61)-Pb(1)-Br(1) 98.5(2), C(8)-Pb(1)-Br(1) 90.3(3), N(1)-Pb(1)-C(61) 90.9(3), C(8)-Pb(1)-C(61) 89.7(4).

From the X-ray structure, it can be seen that for each monomer fragment, one of imidazolylidene backbone C-H bonds has been activated across the Pb-N_{amido} bond, resulting in the formation of new Pb-C and N_{amido}-H bonds with coordination of the resulting neutral amine donor to the Pb(II) centre. This description is supported by the elongated Pb-N bond length (mean: 2.841 Å), compared to the amide donor in plumbylene **3** (2.170(9) Å). Since the reaction aliquot and the isolated crystals of **6** give the same set of resonances in the ¹H NMR spectra, it can be confirmed that the identity of the predominant product of the reaction mixture is in accordance with the solid-state structure. The two singlets in the ¹H NMR spectrum (δ_{H} = 6.71 and 7.66 ppm) can therefore be assigned to the single remaining imidazolylidene backbone C-H group and the N_{amido}-H unit, respectively.

The underlying reasons for the contrasting formation of **3** and **6** remain unknown. However, a precedent of sorts can be drawn from previous research on lead complexes in our group that

leads to similar C-H activation behaviour.⁸⁹ The reaction of a bulky guanidine protio-ligand with one equivalent of lead bis(trimethylsilyl)amide in benzene-d₆ initially forms the expected plumbylene complex. However this species then slowly undergoes intramolecular C-H activation on one of the methyl groups on the trimethylsilyl substituents across the Pb-N_{guan} bonds (**Scheme 3.3.9**) followed by reaction with a second equivalent of lead bis(trimethylsilyl)amide. Analogous processes in this case also do not occur for the germanium and tin analogues. Computational and experimental mechanistic studies have been undertaken on this system, with the C-H activation process being shown to be highly energetically favoured ($\Delta H = -240.2 \text{ kJ mol}^{-1}$).



Scheme 3.3.9: A previously reported example of intramolecular C-H activation by a plumbylene complex.

In addition, the backbone protons of the IMes carbene fragment have previously been shown to possess appreciable acidity. Robinson et al. reported the first anionic N-heterocyclic dicarbene via deprotonation IMes with ⁿBuLi.⁹⁰ Moreover, Pb{N(SiMe₃)₂}₂ is more ionic (and hence more basic) than the Sn/Ge analogues, leading to an increased possibility of deprotonation of carbene backbone.

3.3.7 Systematic comparison between the structures of compound **1-5** and related metallylenes **VIII** and **IX** by Hahn and Glorius et al.

Compound	Bond length (Å)	Bond angle (°)
(L ^{tBu})GeBr 1	Ge(2)-C(11) 2.062(13)	N(3)-Ge(2)-C(11) 90.1(5)
	Ge(2)-N(3) 1.856(11)	
	Ge(2)-Br(1) 2.611(2)	
(L ^{tBu})SnBr 2	Sn(1)-C(7) 2.319(4)	N(3)-Sn(1)-C(7) 88.26(13)
	Sn(1)-N(3) 2.074(3)	
	Sn(1)-Br(1) 2.7559(5)	
(L ^{tBu})PbBr 3	Pb(1)-C(7) 2.412(11)	N(1)-Pb(1)-C(7) 86.5(3)
	Pb(1)-N(1) 2.170(9)	
	Pb(1)-Br(1) 2.8489(14)	
(L ^{Mes})GeBr 4	Ge(1)-C(7) 2.059(3)	N(1)-Ge(1)-C(7) 89.96(13)
	Ge(1)-N(1) 1.891(3)	
	Ge(1)-Br(1) 2.6118(6)	
(L ^{Mes})SnBr 5	Sn(1)-C(7) 2.272(4)	N(1)-Sn(1)-C(7) 85.30(13)
	Sn(1)-N(1) 2.090(3)	
	Sn(1)-Br(1) 2.7274(5)	
Germylene VIII	Ge-C _{NHC} 2.062(2)	N _{amido} -Ge-C _{NHC} 88.27(9)
	Ge-N _{amido} 1.891(2)	
	Ge-Cl 2.03708(8)	
Stannylene IX	Sn-C _{NHC} 2.249(3)	N _{amido} -Sn-C _{NHC} 83.37(10)
	Sn-N _{amido} 2.088(2)	
	Sn-Cl 2.5069(10)	

Table 3.3.1: Key bond lengths and angles of compound **1-5** and metallylenes **VIII** and **IX**.

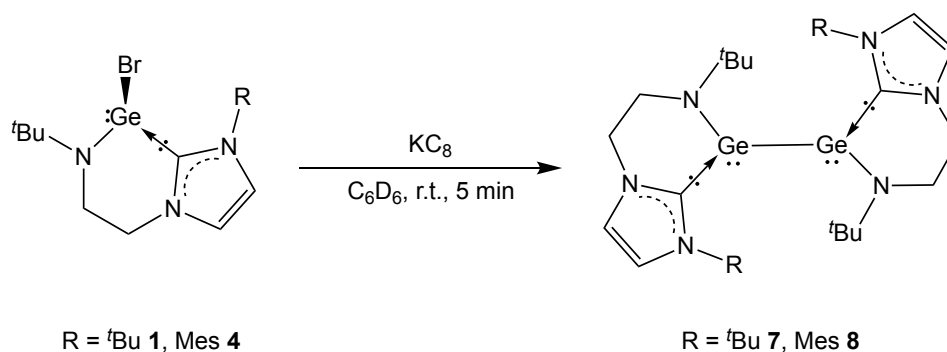
Selected structural parameters for compounds **1-5** are listed in **Table 3.3.1** for the purposes of structural comparison. Not surprisingly, on descending group 14, the E-C_{NHC}, E-N_{amido}, and E-Br distances increase from Ge to Pb. The observed changes are consistent with the increasing covalent atomic radii of the three elements (Ge 1.20(4) Å, Sn 1.39(4) Å, Pb 1.46(5) Å).^{91–93} The E-N_{amido} distances of the germylenes, stannylenes and plumbylene are comparable to the bulky amido stabilised, two coordinated halo-metallylenes.⁷³ As expected,

in each case, the $N_{\text{amido}}\text{-E-C}_{\text{NHC}}$ angle is close to 90° , consistent with a low degree of s/p orbital hybridisation. This angle becomes narrower from Ge to Pb, is in accordance with increases in the E-C_{NHC} and $\text{E-N}_{\text{amido}}$ bond lengths.

The E-C_{NHC} bond lengths of germylenes **1**, **4** and stannylenes **2**, **5** are very similar to the metallylenes **VIII**, **IX** reported in Hahn's paper.⁶⁰ In addition, the acute $N_{\text{amido}}\text{-E-C}_{\text{NHC}}$ chelate angle becomes slightly smaller as the ligand becomes less bulky from **1** to **4** to **VIII** and from **2** to **5** to **IX**.

3.3.8 Synthesis of two novel Ge(I) dimers **7** and **8** via reduction of **1** and **4**

With two bromogermylenes **1** and **4** in hand, we sought to investigate their reduction chemistry exploiting the widely-used reducing agent KC_8 . Treatment of **1** or **4** with one equivalent of KC_8 in benzene- d_6 affords the dimeric Ge(I) complexes **7** and **8**, respectively (**Scheme 3.3.10**). In both cases, an instant colour change from colourless to dark purple was observed after mixing the two reagents. The ^1H NMR spectra of the products reveal complete conversion to a single product in each case, with a set of shifted resonances for the chelating being observed compared to precursors **1** and **4**. For example for compound **7**, the two $t\text{Bu}$ singlets are at $\delta_{\text{H}} = 1.41$ and 1.58 ppm, four ethylene protons are in the range of $\delta_{\text{H}} = 3.15\text{--}6.27$ ppm, and the two imidazolylidene protons are at $\delta_{\text{H}} = 5.88$ and 6.27 ppm. Notably, four well-resolved resonances are measured for the ethylene backbone protons in each case, instead of a broad singlet, indicating a conformationally rigid, non-planar ring geometry.



Scheme 3.3.10: Reduction of bromogermylenes **1** and **4** with KC_8 .

The reduction products are extremely air and moisture sensitive and prone to decomposition at room temperature. Upon decomposition, the colour changes from dark purple to dark brown with a large amount of black precipitate being formed. The ^1H NMR spectra at this point show a mixture of unidentified products. Moreover, when performing the reduction using bromogermylene precursor **4**, the use of an excess of KC_8 leads to the formation of the over-reduction product $\text{K}[\text{L}^{\text{Mes}}]$ based on in situ ^1H NMR monitoring. The identity of the product was confirmed by the independent synthesis of $\text{K}[\text{L}^{\text{Mes}}]$ via the 2:1 reaction of potassium bis(trimethylsilyl)amide and the monocationic pro-ligand $[(\text{L}^{\text{Mes}})\text{H}_2]\text{Br}$.

Encouraged by the promising results shown by ^1H NMR spectroscopy, efforts were made to determine the solid-state structures of **7** and **8**, in order to study the chemical bonding between the germanium centres. Unfortunately, due to their unstable nature and high solubility in non-polar solvents such as hexane and pentane, crystallisation of these compounds proved to be challenging. Crystals of **7** were grown via slow evaporation of a concentrated solution in diethyl ether. While the diffraction data were too weak for discussion of structural metrics, a preliminary structure could nonetheless be obtained to confirm connectivity, and by implication, the success of the reduction process (**Figure 3.3.11**).*

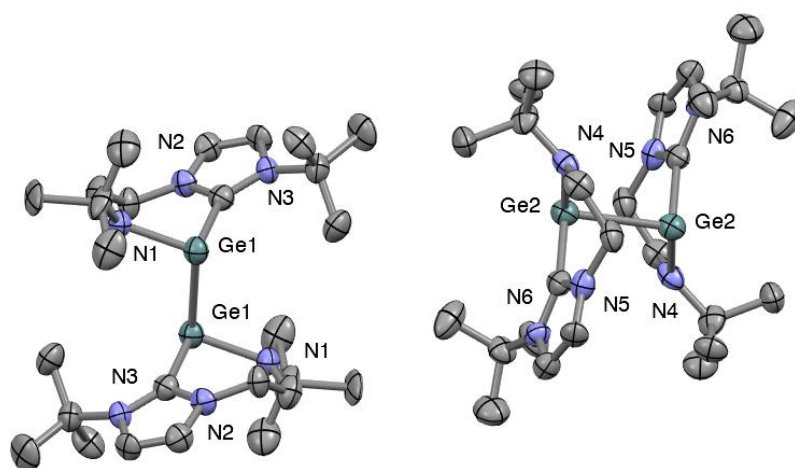


Figure 3.3.11: Molecular structure of $\{(\text{L}^{\text{tBu}})\text{Ge}\}_2$, **7**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity.

* This part was performed in collaboration with Dr Andrey Protchenko from the Aldridge group.

$\{(L^{tBu})Ge\}_2$, **7** crystallises in a triclinic space group (*P*-1) and has two independent molecules in the asymmetric unit. The structure features an inversion centre in the middle of the Ge(I)-Ge(I) bond, meaning that the asymmetric unit is two mono-germanium fragments. From the solid-state structure, it can be seen that **7** features a *trans*-bent geometry, which is a typical feature of heavier group 14 alkyne element analogues. Compound **7** is perhaps best described as a base-stabilised digermynes which possesses no Ge-Ge multiple bond character due to coordination of the NHCs via the (otherwise) vacant *p* orbitals at germanium.⁹⁴ Each of the germanium centres adopts a similar geometry to the bromogermylene precursors **1** and **4**. As such the coordination environment around each Ge centre is occupied by an amido group, an NHC, a Ge-Ge bond and a lone pair of electrons. Although a detailed discussion on the bond lengths and bond angles is not possible due to the poor quality of X-ray diffraction data, preliminary results reveals the mean Ge-Ge bond length to be 2.635 Å, which is consistent with a Ge-Ge single bond (ca. 2.61 Å).^{30–33,95}

In the case of the digermynes **IV**, which demonstrates “transition metal-like” behaviour by the activation of H₂ at ambient temperature, it has been shown that the initial step involves a synergistic interaction of the π bonding orbital (HOMO) of the digermynes and the σ^* antibonding orbital of H₂, as well as the n_+ orbital (LUMO) and the σ bonding orbital of H₂. This interaction is enabled by the relatively small HOMO-LUMO energy gap of the digermynes (ca. 2 eV).⁹⁶ We suspected that compound **7** might be able to activate H₂ in a similar manner only if the NHC coordination is labile enough to dissociate, leaving an empty 4*p* orbital and some degree of π -bonding between Ge-Ge, which enables it to interact with the frontier orbitals of H₂.¹ To prove this hypothesis, an in situ NMR-monitored reaction was performed to examine the reaction of **7** with H₂. Treatment with excess H₂ at 1 atm in benzene-*d*₆, however, reveals no reaction at room temperature, and heating at 80°C leads to decomposition. Based on this

result, we conclude that compound **7** features kinetically inert binding of the NHC groups, which do not dissociate easily under ambient conditions.

3.4 Conclusions

In summary, two different synthetic routes have been developed for the synthesis of halo-metallylenes employing a $N_{\text{amido}}C_{\text{NHC}}$ ligand scaffold. As a result, complexes **1-6** could be isolated in reasonable yields and fully characterised by multinuclear NMR spectroscopy, X-ray crystallography and elemental microanalysis. Bromogermynes **1** and **4** were isolated in particularly high yields (>90%). These compounds, along with the previously reported germylene **VIII** and stannylenes **IX**,⁶⁰ provide rare examples of intramolecular-NHC stabilised metallylenes. Reduction chemistry was attempted on compounds **1** and **4** and two novel base-stabilised Ge(I) dimers **7** and **8** were synthesised and characterised both in solution and the solid state (a preliminary molecular structure having been obtained for one such system by X-ray crystallography). Complexes **1-6** can be envisaged as building blocks in the synthesis of other interesting low valent group 14 derivatives (e.g. cationic species) - as outlined in Chapter 4.

3.5 Experimental details

(L^{*t*Bu})GeBr (1): To a mixture of $[(L^{\text{tBu}})_2\text{H}_2]\text{Br}$ (580 mg, 1.91 mmol) and $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2$ (750 mg, 1.91 mmol) was added toluene (15 mL) at -78°C . The reaction mixture was warmed to room temperature and then heated to 80°C for 12 h, over which time a colourless solution was formed. Volatiles were removed in vacuo, and the product isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene and stored at -30°C . Yield: 660 mg, 93%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 1.39 (9H, s, ^tBu C(CH $_3$) $_3$), 1.50 (9H, s, ^tBu C(CH $_3$) $_3$), 3.54 (4H, br m, ethylene CH $_2$), 5.94 (1H, br d, imidazolylidene backbone CH), 6.21 (1H, br d, imidazolylidene backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 ,

298K): δ_C 30.7 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 31.2 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 43.8 (ethylene C), 53.1 (ethylene C), 56.6 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 60.5 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 117.9 (imidazolylidene backbone C), 120.3 (imidazolylidene backbone C), 168.6 (carbenic $\underline{\text{NCN}}$). Elemental microanalysis: calc. for $\text{C}_{13}\text{H}_{24}\text{BrGeN}_3$: C 41.65% H 6.45% N 11.21%; meas. C 41.73% H 6.80% N 11.29%. Crystallographic data: $\text{C}_{13}\text{H}_{24}\text{BrGeN}_3$ ($M_r = 374.89$): monoclinic, $P2_1/c$, $a = 7.3992(2)$, $b = 10.0259(3)$, $c = 21.8229(8)$ Å, $\beta = 91.160(3)^\circ$, $V = 1618.57(9)$ Å³, $Z = 4$, $\rho_c = 1.538$ g cm⁻³, $T = 150$ K, $\mu(\text{Cu K}\alpha) = 3.105$ mm⁻¹, $\lambda = 1.54184$ Å. $R_1 = 0.1311$ for 3270 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.3312$ for all 3362 unique reflections. Max. and min. residual electron densities 3.29, -1.65 e Å⁻³.

($\text{L}^{t\text{Bu}}$)SnBr (2): To a mixture of [$\text{L}^{t\text{Bu}}\text{H}_2$]Br (200 mg, 0.657 mmol) and $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ (289 mg, 0.657 mmol) was added toluene (10 mL) at room temperature. The reaction mixture was stirred overnight, over which time a pale yellow solution was formed. Volatiles were removed in vacuo, and the product isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated toluene solution layered with hexane and stored at -30°C . Yield: 147 mg, 53%. Spectroscopic data: ^1H NMR (400 MHz, toluene- d_8 , 298K): δ_H 1.32 (9H, s, $^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 1.40 (9H, s, $^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 3.60 (2H, br m, ethylene CH_2), 3.86 (2H, br m, ethylene CH_2), 6.57 (1H, d, $^3J_{\text{HH}} = 1.9$ Hz, imidazolylidene backbone CH), 6.68 (1H, d, $^3J_{\text{HH}} = 1.9$ Hz, imidazolylidene backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_C 31.5 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 31.8 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 46.0 (ethylene C), 55.7 (ethylene C), 56.7 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 59.6 ($^t\text{Bu } \underline{\text{C}}(\text{CH}_3)_3$), 117.9 (imidazolylidene backbone C), 121.6 (imidazolylidene backbone C), 173.7 (carbenic $\underline{\text{NCN}}$). ^{119}Sn NMR (186 MHz, benzene- d_6 , 298K): $\delta_{\text{Sn}} -51.7$. Elemental microanalysis: calc. for $\text{C}_{13}\text{H}_{24}\text{BrSnN}_3$: C 37.09 % H 5.75 % N 9.98 %; meas. C 36.91% H 5.55% N 9.89%. Crystallographic data: $\text{C}_{13}\text{H}_{24}\text{BrSnN}_3$ ($M_r = 420.97$): monoclinic, $P2_1/c$, $a = 9.8651(2)$, $b = 17.9521(5)$, $c = 11.5150(3)$ Å, $\beta = 100.350(3)^\circ$, $V = 1969.51(9)$ Å³, $Z = 4$, $\rho_c = 1.565$ g cm⁻³, $T = 150$ K, $\mu(\text{Cu K}\alpha) = 12.669$ mm⁻¹, $\lambda = 1.54180$ Å. $R_1 = 0.0303$ for

3492 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.0783$ for 4055 all unique reflections. Max. and min. residual electron densities 1.23, $-0.61 \text{ e } \text{\AA}^{-3}$.

(L^{tBu})PbBr (3): To a mixture of [(L^{tBu})H₂]Br (200 mg, 0.657 mmol) and Pb{N(SiMe₃)₂}₂ (347 mg, 0.657 mmol) was added toluene (10 mL) at -78°C . The reaction mixture was warmed to room temperature and stirred for 3 h, over which time a green solution was formed. Volatiles were removed in vacuo, and the product isolated as a green powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated toluene solution and stored at -30°C . Yield: 162 mg, 48%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298K): δ_{H} 1.20 (9H, s, ^tBu C(CH₃)₃), 1.43 (9H, s, ^tBu C(CH₃)₃), 3.82 (2H, br dt, ²J_{HH} = 1.4 Hz, ³J_{HH} = 3.7 Hz, ethylene CH₂), 4.86 (2H, br dt, ²J_{HH} = 1.4 Hz, ³J_{HH} = 3.7 Hz, ethylene CH₂), 6.14 (1H, d, ³J_{HH} = 1.6 Hz, imidazolylidene backbone CH), 6.38 (1H, d, ³J_{HH} = 1.6 Hz, imidazolylidene backbone CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298K): δ_{C} 31.1 (^tBu C(CH₃)₃), 32.1 (^tBu C(CH₃)₃), 49.2 (ethylene C), 57.4 (^tBu C(CH₃)₃), 58.9 (ethylene C), 59.1 (^tBu C(CH₃)₃), 118.3 (imidazolylidene backbone C), 122.7 (imidazolylidene backbone C), 204.0 (carbenic NCN). ²⁰⁷Pb NMR (104 MHz, benzene-d₆, 298K): δ_{Pb} 2093 (s, br). Elemental microanalysis: calc. for C₁₃H₂₄BrPbN₃: C 30.65% H 4.75% N 8.25%; meas. C 30.53% H 4.91% N 8.09%. Crystallographic data: C₁₃H₂₄BrPbN₃ (M_r = 509.46): monoclinic, $P2_1$, $a = 9.4653(3)$, $b = 18.0137(4)$, $c = 11.4577(3) \text{ \AA}$, $\beta = 98.587(3)^\circ$, $V = 1931.70(9) \text{ \AA}^3$, $Z = 4$, $\rho_c = 1.910 \text{ g cm}^{-3}$, $T = 150 \text{ K}$, $\mu(\text{Mo K}\alpha) = 10.802 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$. $R_1 = 0.0408$ for 7843 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.0710$ for all 9103 unique reflections. Max. and min. residual electron densities 1.600, $-1.149 \text{ e } \text{\AA}^{-3}$.

(L^{Mes})GeBr (4): To a mixture of [(L^{Mes})H₂]Br (600 mg, 1.64 mmol) and Ge{N(SiMe₃)₂}₂ (644 mg, 1.64 mmol) was added toluene (15 mL) at -78°C . The reaction mixture was warmed to room temperature and then heated to 80°C for 2 d, over which time a colourless solution was formed. Volatiles were removed in vacuo, and the product isolated as a pale yellow powder. Single

crystals suitable for X-ray crystallography were obtained from a concentrated solution in THF layered with hexane and stored at room temperature. Yield: 709 mg, 99%. Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 1.42 (9H, s, ^tBu C(CH $_3$) $_3$), 2.00 (3H, s, Mes *para* CH $_3$), 2.06 (6H, br s, Mes *ortho* CH $_3$), 3.43 (4H, br m, ethylene CH $_2$), 5.89 (1H, br m, imidazolylidene backbone CH), 6.12 (1H, br m, imidazolylidene backbone CH), 6.68 (2H, s, Mes *meta* CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_{C} 18.5 (Mes *ortho* C(CH $_3$)), 21.1 (Mes *para* C(CH $_3$)), 30.7 (^tBu C(CH $_3$) $_3$), 43.8 (^tBu C(CH $_3$) $_3$), 52.5 (ethylene C), 56.5 (ethylene C), 121.3 (imidazolylidene backbone C), 121.3 (imidazolylidene backbone C), 128.4 (Mes *para* C(CH $_3$)), 129.7 (Mes *meta* C), 133.0 (Mes *ortho* C(CH $_3$)), 140.0 (Mes *ipso* C), 169.5 (carbenic NCN). Elemental microanalysis: calc. for $\text{C}_{18}\text{H}_{26}\text{BrGeN}_3$: C 49.48% H 6.00% N 9.62%; meas. C 49.54% H 5.82% N 9.53%. Crystallographic data: $\text{C}_{18}\text{H}_{26}\text{BrGeN}_3$ (M_r = 436.92): orthorhombic, $Pbca$, a = 13.8454(3), b = 13.2083(3), c = 21.4808(7) Å, V = 13928.28(18) Å 3 , Z = 8, ρ_c = 1.478 g cm $^{-3}$, T = 150 K, $\mu(\text{Cu K}\alpha)$ = 4.510 mm $^{-1}$, λ = 1.54184 Å. R_1 = 0.0406 for 3229 observed unique reflections [$I > 2\sigma(I)$], wR_2 = 0.0983 for all 4070 unique reflections. Max. and min. residual electron densities 0.94, -0.43 e Å $^{-3}$.

(L^{Mes})SnBr (5): To a mixture of [(L^{Mes})H $_2$]Br (200 mg, 0.546 mmol) and Sn{N(SiMe $_3$) $_2$ } $_2$ (238 mg, 0.546 mmol) was added toluene (10 mL) at room temperature. The reaction mixture was stirred overnight, over which time a yellow solution was formed. Volatiles were removed in vacuo, and the product isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution of benzene at room temperature. Yield: 170 mg, 65%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 1.37 (9H, s, ^tBu C(CH $_3$) $_3$), 1.98 (3H, s, Mes *para* CH $_3$), 2.00 (6H, br s, Mes *ortho* CH $_3$), 3.45 (4H, br m, ethylene CH $_2$), 5.85 (1H, br d, imidazolylidene backbone CH), 5.97 (1H, br d, imidazolylidene backbone CH), 6.65 (2H, s, Mes *meta* CH). ^1H NMR (400 MHz, toluene- d_8 , 198K): δ_{H} 1.31 (9H, s, ^tBu C(CH $_3$) $_3$), 1.57 (3H, s, Mes *ortho* CH $_3$), 1.85 (3H, s, Mes *para* CH $_3$), 2.19 (3H, s, Mes *ortho* CH $_3$), 3.19

(1H, br m, ethylene CH₂), 3.26 (1H, br d, ethylene CH₂), 3.44 (1H, br t, ethylene CH₂), 4.22 (1H, br t, ethylene CH₂), 5.30 (1H, br m, imidazolylidene backbone CH), 6.02 (1H, br d, imidazolylidene backbone CH), 6.36 (1H, br s, Mes *meta* CH), 6.46 (1H, br s, Mes *meta* CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298K): δ_C 18.4 (Mes *ortho* C(CH₃)), 21.0 (Mes *para* C(CH₃)), 31.8 (^tBu C(CH₃)₃), 45.7 (^tBu C(CH₃)₃), 54.7 (ethylene C), 56.4 (ethylene C), 121.2 (imidazolylidene backbone C), 122.4 (imidazolylidene backbone C), 129.7 (Mes *para* C(CH₃)), 129.7 (Mes *meta* C), 133.6 (Mes *ortho* C(CH₃)), 140.1 (Mes *ipso* C), 174.7 (carbenic NCN). ¹¹⁹Sn NMR (186 MHz, benzene-d₆, 298K): δ_{Sn} -67.8. Elemental microanalysis: calc. for C₁₈H₂₆BrSnN₃: C 44.76% H 5.43% N 8.70%; meas. C 44.62% H 5.60% N 8.51%. Crystallographic data: C₁₈H₂₆BrSnN₃ (*M*_r = 483.04): monoclinic, *P*2₁/*c*, *a* = 12.0118(5), *b* = 11.7611(5), *c* = 14.2461(6) Å, β = 95.161(4)°, *V* = 2004.42(15) Å³, *Z* = 4, ρ_c = 1.601 g cm⁻³, *T* = 150 K, μ(Mo Kα) = 3.271 mm⁻¹, λ = 0.71073 Å. *R*₁ = 0.0399 for 3646 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.0848 for all 4633 unique reflections. Max. and min. residual electron densities 0.807, -0.872 e Å⁻³.

{(L^{Mes})PbBr}₄ (6): To a mixture of [(L^{Mes})H₂]Br (200 mg, 0.546 mmol) and Pb{N(SiMe₃)₂}₂ (288 mg, 0.545 mmol) was added toluene (15 mL) at -78°C. The reaction mixture was warmed to room temperature and stirred for 3 h, over which time a yellow green solution was formed. Volatiles were removed in vacuo, and the product isolated as a yellow green powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated toluene solution and stored at -30°C. Yield: 140 mg, 45%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298K): δ_H 0.77 (9H, s, ^tBu C(CH₃)₃), 1.84 (3H, s, Mes *para* CH₃), 2.08 (3H, s, Mes *ortho* CH₃), 2.14 (3H, s, Mes *ortho* CH₃), 2.83 (1H, br m, ethylene CH), 3.43 (1H, br m, ethylene CH), 4.05 (1H, br m, ethylene CH), 4.60 (1H, br m, ethylene CH), 6.62 (1H, s, Mes *meta* CH), 6.69 (1H, s, Mes *meta* CH), 6.71 (1H, s, imidazolylidene backbone CH), 7.66 (1H, s, NH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298K): δ_C 17.2 (Mes *para* C(CH₃)), 18.3 (Mes *ortho* C(CH₃)), 21.0 (Mes *ortho* C(CH₃)), 28.6 (^tBu

C(CH₃)₃), 46.1 (ethylene C), 53.8 (^tBu C(CH₃)₃), 57.3 (ethylene C), 128.2 (imidazolylidene backbone C), 129.3 (Mes *meta* C), 130.7 (Mes *meta* C), 133.5 (imidazolylidene backbone C), 136.2 (Mes *para* C(CH₃)), 136.6 (Mes *ortho* C(CH₃)), 137.9 (Mes *ortho* C(CH₃)), 139.8 (Mes *ipso* C), 201.8 (carbenic NCN). ²⁰⁷Pb NMR (186 MHz, benzene-d₆, 298K): δ_{Pb} 1358 (s, br). Elemental microanalysis: calc. for C₇₂H₁₀₄Br₄PbN₁₂: C 37.83% H 4.59% N 7.35%; meas. C 37.55% H 4.94% N 7.22%. Crystallographic data: C₇₂H₁₀₄Br₄PbN₁₂ (*M_r* = 2286.12): orthorhombic, *P*2₁2₁2₁, *a* = 18.3855(2), *b* = 18.7475(2), 35.3673(3) Å, β = 90°, *V* = 12190.5(2) Å³, *Z* = 4, ρ_c = 1.522 g cm⁻³, *T* = 150 K, μ(Cu Kα) = 12.420 mm⁻¹, λ = 1.54184 Å. *R*₁ = 0.0424 for 22966 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.1072 for all 25147 unique reflections. Max. and min. residual electron densities 1.518, -0.788 e Å⁻³.

{{(L^{tBu})Ge}₂ (7): In a glovebox, **1** (20 mg, 0.0533 mmol) and 1 equiv. of KC₈ (7.21 mg, 0.0533 mmol) in benzene-d₆ were mixed in a J Young's NMR tube. The reaction mixture turned from colourless to dark purple instantly. Small crystals for X-ray crystallography were obtained by slow evaporation of a concentrated solution in diethyl ether at room temperature.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298K): δ_H 1.41 (9H, s, ^tBu C(CH₃)₃), 1.58 (9H, s, ^tBu C(CH₃)₃), 3.15 (1H, br m, ethylene CH), 3.54 (1H, br m, ethylene CH), 3.81 (1H, br m, ethylene CH), 5.88 (1H, br m, ethylene CH), 6.27 (1H, br m, imidazolylidene backbone CH), 6.40 (1H, br m, imidazolylidene backbone CH). ¹³C{¹H} NMR δ_C 29.7 (^tBu C(CH₃)₃), 30.9 (^tBu C(CH₃)₃), 49.0 (ethylene C), 52.5 (ethylene C), 54.8 (^tBu C(CH₃)₃), 58.6 (^tBu C(CH₃)₃), 116.2 (imidazolylidene backbone C), 120.1 (imidazolylidene backbone C), 185.1 (carbenic NCN).

Crystallographic data: C₂₆H₄₈Ge₂N₆ (*M_r* = 589.88): triclinic, *P*-1, *a* = 7.6374(8), *b* = 10.4822(7), *c* = 19.8989(17) Å, α = 89.931(7), β = 92.983(9), γ = 111.037(8)°, *V* = 1484.6(2) Å³, *Z* = 2, ρ_c = 1.320 g cm⁻³, *T* = 173(2) K, μ(synchrotron radiation, 0.6889 Å) = 2.049 mm⁻¹, λ = 0.6889 Å. *R*₁ = 0.1860 for 2353 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.4080 for all 3737 unique reflections. Max. and min. residual electron densities 4.763, -1.161 e Å⁻³.

$\{(L^{\text{Mes}})\text{Ge}\}_2$ (**8**): In a glovebox, **2** (20 mg, 0.0458 mmol) and 1 equiv. of KC_8 (6.19 mg, 0.0458 mmol) in benzene- d_6 were mixed in a J Young's NMR tube. The reaction mixture turned from colourless to dark purple instantly. The product was not isolated due to the highly reactive nature of the compound.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 1.49 (9H, s, $^t\text{Bu C}(\underline{\text{CH}_3})_3$), 2.11 (3H, s, Mes *para* CH_3), 2.13 (3H, br s, Mes *ortho* CH_3), 2.25 (3H, br s, Mes *ortho* CH_3), 3.31 (1H, br ddd, $^2J_{\text{HH}} = 2.1$ Hz, $^3J_{\text{HH}} = 8.1$ Hz, $^3J_{\text{HH}} = 12.6$ Hz, ethylene CH), 3.56 (1H, br ddd, $^2J_{\text{HH}} = 2.1$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 12.4$ Hz, ethylene CH), 4.22 (1H, br ddd, $^2J_{\text{HH}} = 1.6$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 12.6$ Hz, ethylene CH), 5.19 (1H, br ddd, $^2J_{\text{HH}} = 1.6$ Hz, $^3J_{\text{HH}} = 8.1$ Hz, $^3J_{\text{HH}} = 12.4$ Hz, ethylene CH), 5.94 (1H, d, $^2J_{\text{HH}} = 1.5$ Hz, imidazolylidene backbone CH), 6.25 (1H, br d, $^2J_{\text{HH}} = 1.5$ Hz, imidazolylidene backbone CH), 6.48 (1H, s, Mes *meta* CH), 6.62 (1H, s, Mes *meta* CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_{C} 19.1 (Mes *ortho* $\text{C}(\underline{\text{CH}_3})$), 19.6 (Mes *ortho* $\text{C}(\underline{\text{CH}_3})$), 21.2 (Mes *para* $\text{C}(\underline{\text{CH}_3})$), 30.9 ($^t\text{Bu C}(\underline{\text{CH}_3})_3$), 48.5 (ethylene C), 51.8 (ethylene C), 55.1 ($^t\text{Bu C}(\underline{\text{CH}_3})_3$), 119.6 (imidazolylidene backbone C), 121.5 (imidazolylidene backbone C), 129.1 (Mes *meta* C), 129.1 (Mes *meta* C), 134.8 (Mes *para* $\text{C}(\underline{\text{CH}_3})$), 135.1 (Mes *ortho* $\text{C}(\underline{\text{CH}_3})$), 136.1 (Mes *ortho* $\text{C}(\underline{\text{CH}_3})$), 137.7 (Mes *ipso* C), 186.7 (carbenic NCN).

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Chapter IV

Synthesis and Reactivity of Germylium-ylidene Cations

Incorporating a N_{amido}⁺C_{NHC} Chelating Ligand System

4.1 Introduction

Oxidative addition and reductive elimination of σ -bonds are fundamental steps involved in small molecule activation and catalysis.¹ In 2007, Bertrand et al. reported two singlet (alkyl)(amino)carbenes capable of facile H₂ and NH₃ activation.² Since then, E-H bond activation by carbenes and their heavier group 14 analogues R₂E (tetrelenes) has been studied extensively.^{1,3–12} Spurred by studies from Power et al. on neutral germylenes and stannylenes,⁸ intensive research has shown that kinetically, the ability for such compounds to activate E-H bonds (such as that in H₂) is inversely related to the HOMO-LUMO energy gap. This reflects the fact that both donation from the H-H bonding σ orbital to the vacant p orbital and back-donation from the lone pair on the metal centre to the anti-bonding H-H σ^* orbital are important in the bond activation process. The choice of ligand is therefore crucial in terms of tuning the HOMO-LUMO gap and the consequent reactivity of the compound. In short, σ -donating ligands should reduce the gap by elevating the HOMO, while π -donor ligands and/or narrow angles around the metal centre should widen the gap by elevating the LUMO and lowering the HOMO, respectively.¹³

In contrast to well-studied neutral tetrelenes, the reactivity of cationic tetrylium-ylidenes (RE:⁺) is underexplored.^{14,15} These compounds feature a divalent centre with six valence electrons. They are also ambiphilic in nature - being both nucleophilic at the lone pair and electrophilic due to the vacant p_π orbital and net electron deficiency. The positive charge is considered to enhance the electrophilicity of the metal centre, leading to higher reactivity.¹⁴ The synthesis and isolation of such species usually requires a strongly electron donating ligand to stabilise

the highly electrophilic metal centre in the form of a complex of the type $R(L)E^+$. However, although an authentic one-coordinate germylium-ylidene still remains elusive, various kinetic and/or electronic stabilisation strategies have been employed to facilitate the isolation of higher coordinate cations.^{15–26} These usually involve using either bulky or additional neutral/anionic donor ligands, which elevate the energy of the p_π orbital of Ge(II) centre, widen the HOMO-LUMO gap and hence as a consequence hinder the E-H bond activation by such cations. Only in recent years have a few examples of acyclic germylium-ylidenes (**I–V**) capable of oxidatively adding E-H/C-X bonds been reported (**Figure 4.1.1**).^{28–32} Reversible bond activation (i.e. oxidative addition followed by reductive elimination) is relatively rare; only **I**, which contains a transition metal fragment has shown reversible activation of Si-H and B-H bonds at elevated temperatures.

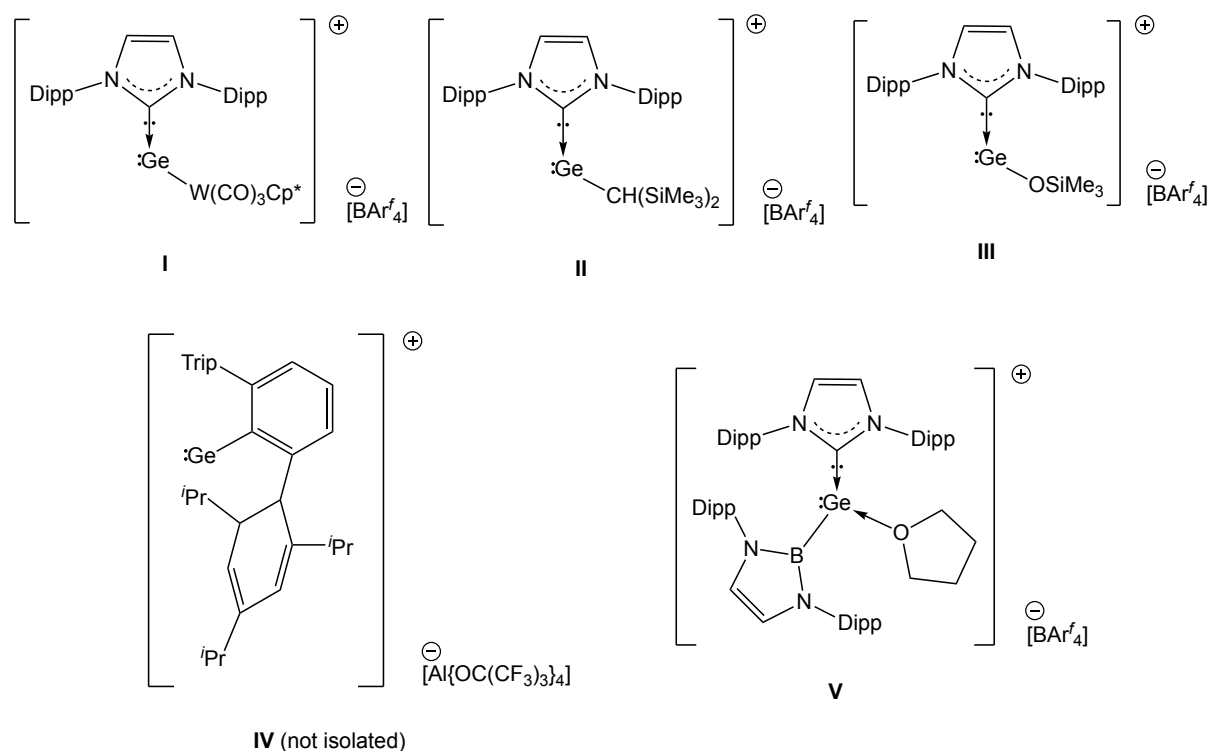
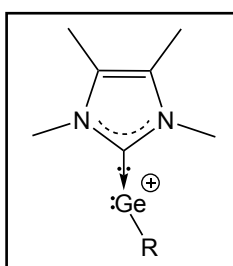


Figure 4.1.1: Reported germylium-ylidenes capable of the oxidative addition of E-H/C-X bonds.

With an interest in developing cationic systems that are able to reversibly activate E-H bonds, DFT calculations have been conducted in our group to investigate the effect of the R substituent in NHC-stabilised germylium-ylidenes of the type $[(NHC)GeR]^+$ on the free energy

ΔG° of hydrogen activation (**Table 4.1.1**). The value of ΔG° reflects the degree of thermodynamic reversibility of the reaction. On this basis it was discovered that ΔG° becomes more negative (i.e. the oxidative addition of H_2 becomes less reversible) when R becomes more σ -donating, and is closest to 0 kcal mol⁻¹ (i.e. most reversible) when R is a π -donating amino group (**Table 4.1.1**, red). Presumably this reflects stabilisation of the higher oxidation state by stronger σ donation and of the Ge(II) state (with its formally vacant p_π orbital) by π -donor substituents.



R	N(Ph)(Me)	Ph	H	Me	Bpin	SiMe ₃
ΔG° (kcal mol ⁻¹)	-9.28	-21.79	-23.54	-26.14	-29.99	-30.89

Table 4.1.1: DFT calculations of ΔG° for the oxidative addition of H_2 at a range of NHC-stabilised germylium-ylidenes.

On the basis of previous research in this field and these computational results, it was therefore thought interesting to explore the potential for (reversible) E-H bond activation by germylium-ylidenes incorporating both a strongly σ -donating ligand (e.g. N-heterocyclic carbene) and a π -donor ligand (e.g. N_{amido}). Such a compound has no precedent, although a recent publication from Hahn et al.³³ did report in situ NMR data proposed to be for cation **VI** in benzene-d₆. Unfortunately, this compound could not be isolated, and no structural evidence (from X-ray crystallography) was obtained; reactivity studies also did not give conclusive results.

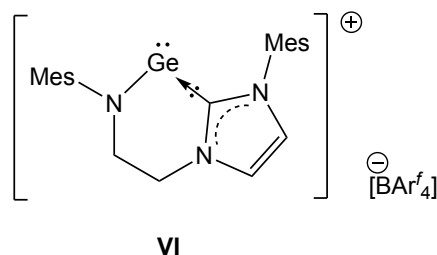


Figure 4.1.2: Structure of a proposed germylium-ylidene incorporating a $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand.

4.2 Project aims

The aim of this project is to utilise the halo-germylene compounds **1** and **4** reported in Chapter 3 as precursors for the preparation and characterisation of novel two-coordinate germylium-ylidenes employing an $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand scaffold (**Figure 4.2.1**). These germylium-ylidenes would ideally be characterised by X-ray crystallography in order to establish unambiguously their monomeric structures in the solid state. Subsequently, computational studies as well as experimental data were to be used to probe potential reactivity in small molecule activation, including dihydrogen as well as protic/hydridic E-H bonds. It was hoped that these results could then be compared to previously reported NHC-stabilised, two-coordinate germylium-ylidenes and plausible reaction mechanisms proposed accordingly.

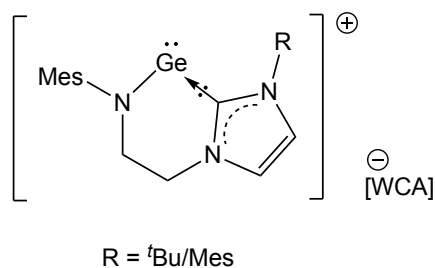


Figure 4.2.1: Target germylium-ylidene cations.

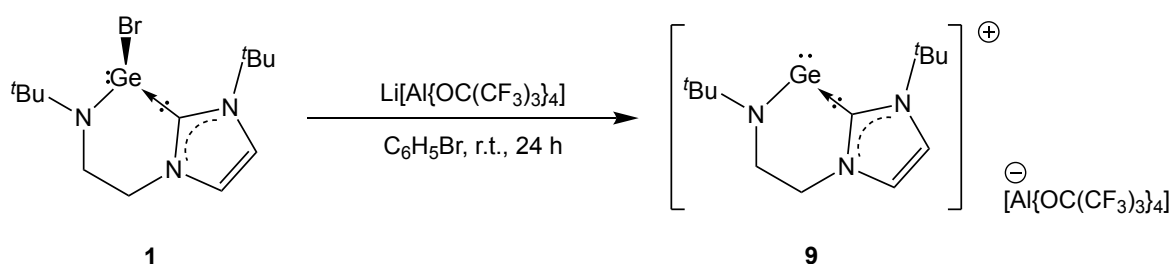
4.3 Results and discussion

4.3.1 Synthesis and characterisation of $[(L^{t\text{Bu}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **9**

Cationic germylium-ylidene **9** was synthesised via halide abstraction from the previously prepared bromogermylene **1** using a source of a weakly coordinating anion (WCA).^{14,34} In this

work, $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ was chosen due to the fact that it can be easily and safely prepared on a relatively large scale (ca. 4-5 g) using a published procedure.³⁵ The $[\text{Al}(\text{OR}^f)_4]^-$ anion is also stable and very weakly coordinating due to the sterically shielded nature of the oxygen atoms (by the four bulky $\text{C}(\text{CF}_3)_3$ groups) and the electronic stabilisation derived from perfluorination.³⁶

Vigorous stirring of a solution of **1** in bromobenzene with one equivalent of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ at room temperature overnight afforded the cationic germylium-ylidene **9** (**Scheme 4.3.1**). The reaction mixture turned from a white suspension to a yellow solution with accompanying formation of a precipitate. $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ gradually goes into solution as the reaction proceeds to form the product which has a higher solubility in bromobenzene.



Scheme 4.3.1: Synthesis of germylium-ylidene, **9**, from bromogermylene precursor **1**.

Compound **9** was fully characterised in the solution state by ^1H , ^{13}C , ^{19}F and ^{27}Al NMR spectroscopy in bromobenzene- d_5 . The ^1H NMR spectrum of precursor **1** was also measured in bromobenzene- d_5 in order to directly compare the chemical shifts. Upon halide abstraction, the ^1H NMR spectrum shows complete conversion to a new species. The two singlets (each integrating to 9H) corresponding to the two $t\text{Bu}$ groups, shift upfield from $\delta_{\text{H}} = 1.29$ and 1.42 ppm to $\delta_{\text{H}} = 1.04$ and 1.27 ppm. The ethylene backbone protons appear as two broad triplets (integrating to 2H), shifted upfield from $\delta_{\text{H}} = 3.40$ and 3.60 ppm to $\delta_{\text{H}} = 3.05$ and 3.41 ppm. The imidazolyliidene backbone protons shift downfield slightly from $\delta_{\text{H}} = 6.23$ and 6.48 ppm to $\delta_{\text{H}} = 6.42$ and 6.66 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (measured in bromobenzene- d_5) features a carbenic carbon resonance features at $\delta_{\text{C}} = 164.5$ ppm. It is comparable to the ^{13}C resonance

reported for the carbenic carbon of putative germylium-ylidene **VI** in Hahn's paper.³³ Notably, however their spectrum was measured in benzene- d_6 , whereas compound **9** is only very slightly soluble in benzene. In our system, performing the dehalogenation reaction in benzene leads to the rapid precipitation from solution of product formed as a yellow oil. In addition, the ^{13}C NMR shift of carbenic carbon of **9** is also close to other reported examples of NHC-stabilised germylium-ylidenes with di-/tri-coordination (**Figure 4.3.1**).^{27,33,37}

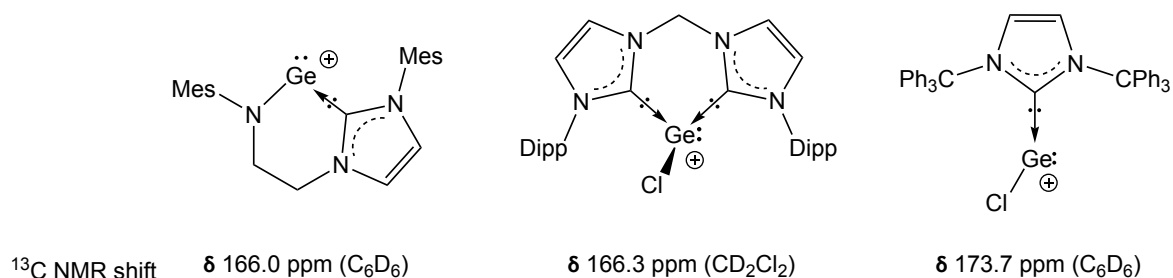


Figure 4.3.1: Previously reported mono-/bis-NHC stabilised germylium-ylidenes and their ^{13}C NMR chemical shifts for the carbenic carbon.

In contrast to the lack of solid-state structures reported by Hahn et al.,³³ single crystals of **9** can be obtained by slowly concentrating a solution in bromobenzene. When the solution becomes concentrated enough, thin acicular crystals are formed from the solution at room temperature; storage at -30°C leads to the formation of more crystals. X-ray crystallography unambiguously reveals a monomeric, two-coordinate structure for **9** in the solid state (**Figure 4.3.2**).

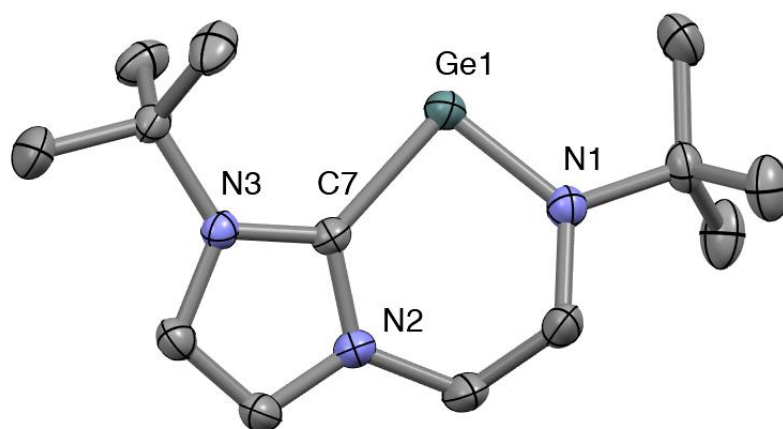


Figure 4.3.2: Molecular structure of the cationic component of compound **9** as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Ge(1)-N(1) 1.822(4), Ge(1)-C(7) 2.049(4), C(7)-Ge(1)-N(1) 93.13(15).

Compound **9** crystallises in a triclinic space group (*P*-1) and the asymmetric unit contains one cationic germylium-ylidene fragment and one $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ anion. As expected, the cationic fragment engages in a very low degree of interaction with the counter-ion (closest Ge-O contact = 8.341 Å). Cation formation is signalled by shortening of the Ge-N_{amido} and Ge-C_{NHC} bond lengths from 1.856(11) to 1.822(4) Å and 2.062(13) to 2.049(4) Å respectively (compared to bromogermylene **1**). This can be rationalised by the increasing degree of σ and π donation from the NHC and amido group respectively to a more Lewis acidic Ge(II) centre. The C_{NHC}-Ge-N_{amido} chelate angle measured for **9** is 93.13(15)°, indicating a low degree of *s/p* orbital hybridisation at Ge. This angle is much narrower than those found for acyclic, two-coordinate, NHC-stabilised germylium-ylidenes (e.g. 105.3(1)° for **V** and 102.7(1)° for **II**)^{29,32} presumably due to the constraints of the chelating backbone in **9**. This structural feature has an underlying influence on the bond activation capabilities of compound **9** (vide infra).

4.3.2 Computational and experimental studies of $[(\text{L}^{\text{tBu}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **9**

In order to gain insight into potential bond activation reactivity by compound **9**, DFT calculations (PBE1PBE, Def-TZVP level of theory) were performed to probe the electronic properties of the frontier molecular orbitals of **9**.*

* This part was performed by Dr Petra Vasko from the Aldridge group.

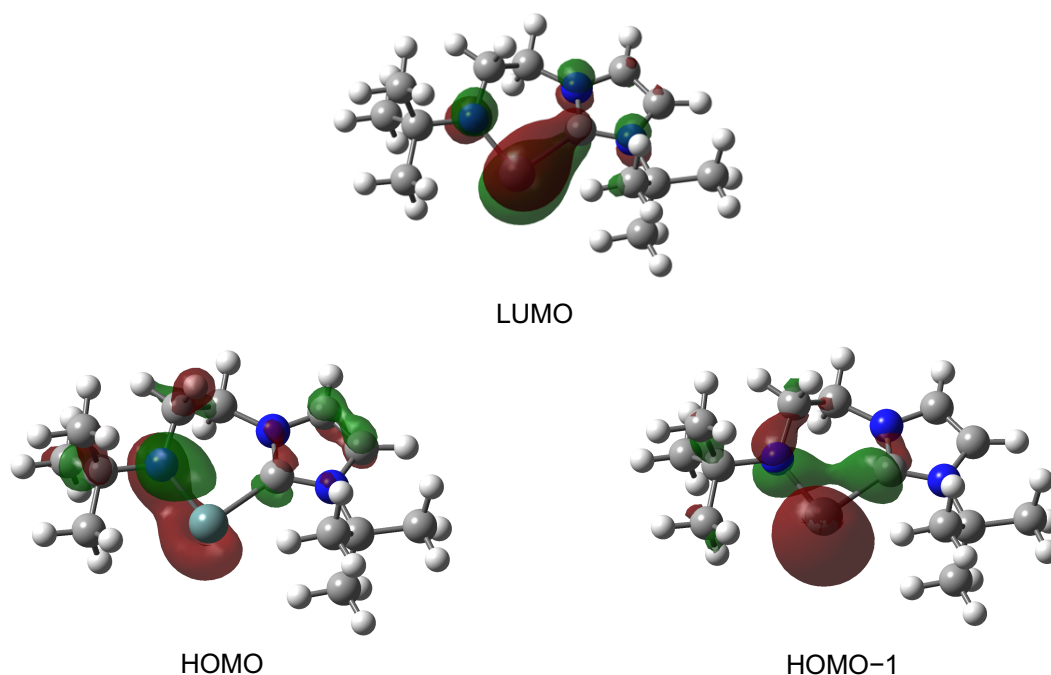


Figure 4.3.3: Selected frontier orbitals of the cationic fragment of germylium-ylidene **9**.

As shown in **Figure 4.3.3**, the LUMO of germylium-ylidene **9** consists mainly of an empty p_π orbital at the germanium centre with an anti-bonding phase relationship with the $N_{\text{amido}} p_\pi$ orbital. The HOMO however, is not the germanium lone pair; this is featured in the HOMO-1 with a significant lower energy ($E = -10.50 \text{ eV} / -1013 \text{ kJ mol}^{-1}$). The calculated HOMO-LUMO gap of **9** is 457 kJ mol^{-1} and energy gap between the two key frontier orbitals (i.e. LUMO and HOMO-1) is 477 kJ mol^{-1} . This is significantly wider than that determined for boryl (**V**, 132 kJ mol^{-1}) or alkyl substituted (**II**, 187 kJ mol^{-1}) NHC-stabilised germylium-ylidenes.^{29,32} The enlarged energy gap of **9** can be rationalised due to π electron donation from the N_{amido} lone pair to Ge(II). This elevates the energy of the formally vacant p_π orbital, hence increasing the LUMO to HOMO-1 energy gap. The narrow $C_{\text{HNC}}\text{-Ge-}N_{\text{amido}}$ angle also indicates a high degree of 4s character of the lone pair, which would also lead to a wide energy gap between the frontier orbitals (HOMO stabilisation).³⁸

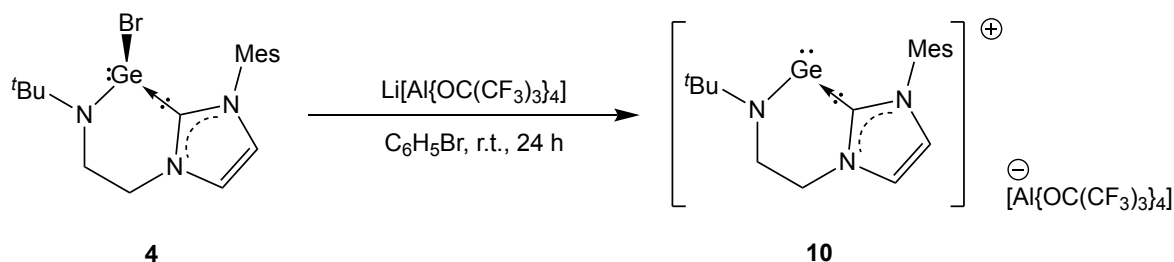
Based on the relatively large frontier orbital energy gap, germylium-ylidene **9** was thought unlikely to effect oxidative addition of relatively non-polar bonds (such as that in H_2). To prove

this experimentally, isolated **9** was exposed (separately) to dihydrogen and a range of small molecules containing hydridic E-H bonds. We firstly tested its activity towards the apolar molecule H₂. Isolated crystals of **9** were dissolved in bromobenzene-d₅ in a J Young's NMR tube and subjected to H₂ (ca. 2 bar pressure) after freeze-pump-thaw degassing. The ¹H NMR spectrum measured at this point suggests that **9** shows no reaction with excess H₂ under these conditions. After 12 h at room temperature, all signals in the ¹H NMR spectrum remained the same, with the dissolved H₂ signal observed as a singlet at $\delta_{\text{H}} = 4.42$ ppm. The sample was heated at 80°C for 6 h but the spectra showed no obvious differences. The reactivity of **9** towards other more polar hydridic reagents was then probed using the same method. No reaction was detected of **9** with PhSiH₃, Et₃SiH₃ or Me₃N·BH₃ at ambient or elevated temperatures.

The experimental data in conjunction with DFT calculations are consistent with the idea that germylium-ylidene **9** is not able to undergo oxidative addition of apolar or hydridic E-H bonds. This is presumably due to a high kinetic barrier for more-or-less concerted bond activation resulting from a large HOMO–1-LUMO gap. This in turn can be rationalised due to the presence of a π -donating N_{amido} ligand and a small chelating angle around the Ge(II) centre.

4.3.3 Synthesis and characterisation of [(L^{Mes})Ge][Al{OC(CF₃)₃}₄], **10** and [(L^{Mes})Ge]₂(μ -Br)[Al{OC(CF₃)₃}₄], **11**

In Chapter 3 we reported that the related bromogermylene **4** can be prepared in good yield and purity. We therefore sought to synthesise and examine the subsequent reactivity of the corresponding germylium-ylidene **10**, accessed from **4** via halide abstraction. The synthesis was carried out using similar reaction conditions as in the case of compound **9** (**Scheme 4.3.2**).



Scheme 4.3.2: Synthesis of germylium-ylidene, **10**, from bromogermylene precursor **4**.

Halide abstraction appeared to be effective, and complete conversion of **4** to compound **10** was achieved after stirring vigorously with $\text{Li[Al\{OC(CF}_3\)_3\}_4]$ in bromobenzene at room temperature overnight. In a similar fashion to **9**, **10** was characterised in the solution state by ^1H , ^{13}C , ^{19}F and ^{27}Al NMR spectroscopy in bromobenzene- d_5 . In the ^1H NMR spectrum, a 9H singlet at $\delta_{\text{H}} = 0.98$ ppm corresponds to the amido $t\text{Bu}$ group and two singlets integrating to 6H and 3H (at $\delta_{\text{H}} = 1.72$ and 2.80 ppm, respectively) can be assigned to the *ortho* and *para* methyl groups of the mesityl substituent. This contrasts with the bromogermylene precursor **4**, for which the *ortho* methyl signal is broad, possibly due to slightly more hindered rotation of the mesityl group. In addition, the ethylene backbone signals for **10** appear as two well resolved multiplets at $\delta_{\text{H}} = 3.20$ and 3.60 ppm (integrating to 2H each), instead of one broad signal as observed for precursor **4**. This pattern is analogous to the signals measured for ethylene backbone protons of germylium-ylidene **9**, and further supports the formation of cationic species **10**. After stirring overnight the reaction mixture was filtered and concentrated. Instead of direct crystallisation by concentrating the solution (as in the case of **9**), compound **10** was obtained as a yellow oil after removing the solvent. Nonetheless, single crystals suitable for X-ray crystallography could be obtained by layering a concentrated bromobenzene solution with hexane. The solid-state structure so obtained confirmed the product to be monomeric germylium-ylidene **10** (Figure 4.3.4).

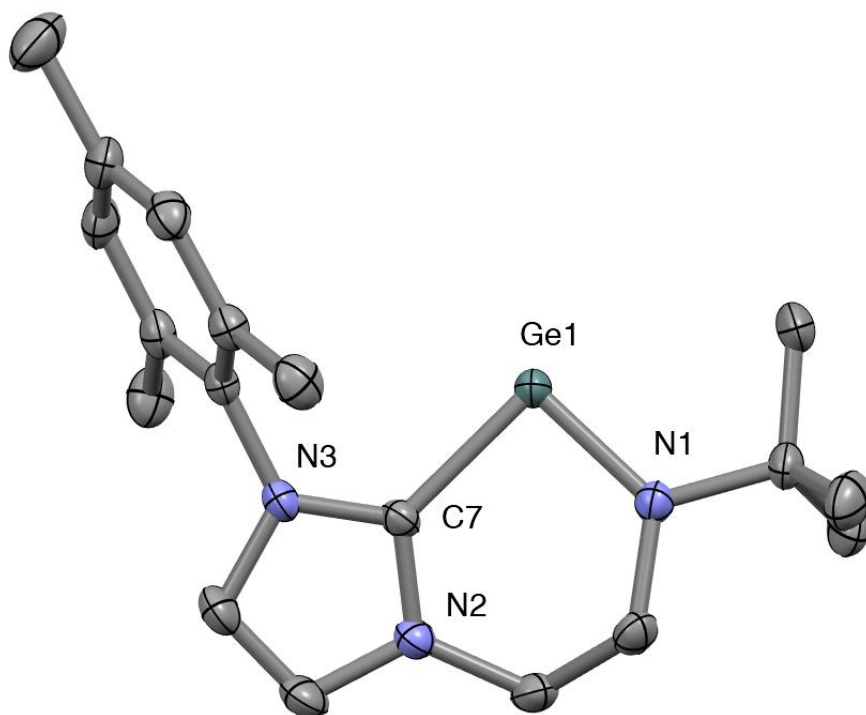
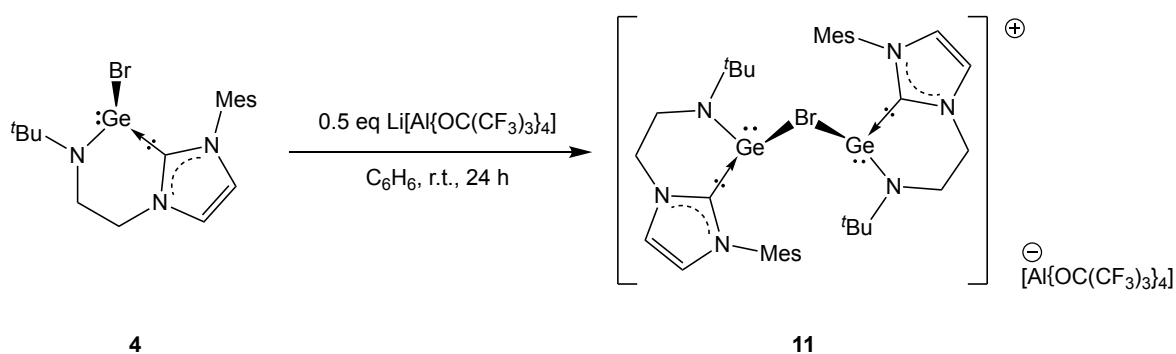


Figure 4.3.4: Molecular structure of the cationic component of compound **10** as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 1.830(4), Ge(1)-C(7) 2.040(4), C(7)-Ge(1)-N(1) 91.84(19).

Compound **10** crystallises in a monoclinic space group ($P2_1/n$). As with compound **9**, it is shown to be monomeric in the solid state with a closest Ge-O contact of 8.421 Å. The Ge- N_{amido} bond length (1.830(4) Å) is comparable to that of **9** (1.822(4) Å) and is significantly shortened from the precursor **4** (1.891(3) Å), in line with the formation of a two-coordinate cationic germanium centre. The measured $C_{\text{NHC}}\text{-Ge-}N_{\text{amido}}$ chelate angle is 91.84(19)° (cf. 93.13(15)° for **9**), which also implies a relatively large frontier orbital energy gap.

We also investigated the importance of the stoichiometry of the halide abstraction agent (in this case $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$) in the formation of germylium-ylidene **10**. With this in mind, half an equivalent of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ was combined with one equivalent of **4** in benzene- d_6 at room temperature (**Scheme 4.3.3**).



Scheme 4.3.3: Synthesis of bromide bridging digermanylene, **11**, from the bromogermanylene precursor **4**.

A new species was formed in the reaction mixture according to the ^1H NMR spectrum measured in situ in benzene- d_6 . Knowing that compound **10** is not soluble in benzene, the spectrum was compared with the bromogermanylene precursor **4**. A significantly shifted set of signals was observed in the aliphatic region - the $t\text{Bu}$ group is shifted from $\delta_{\text{H}} = 1.42$ to 1.09 ppm, the *ortho* methyl group of mesityl substituent from $\delta_{\text{H}} = 2.06$ to 1.78 ppm and the *para* methyl signal from $\delta_{\text{H}} = 2.00$ to 2.11 ppm. Moreover, the ethylene backbone protons are observed as two distinct multiplets (2H each), rather than a broad singlet for **4**. In the aromatic region, the signals for imidazolyliidene backbone protons and mesityl *meta* CH also show clear changes with respect to precursor. It therefore seems likely that a new species (i.e. not compound **4** or **10**) has been formed.

Intrigued by the structure of the product, single crystals were successfully obtained by layering a concentrated solution in dichloromethane with hexane stored at -30°C . X-ray crystallography allows the solid-state structure to be confirmed as a bromide-bridged digermanium cation, **11** (**Figure 4.3.5**).

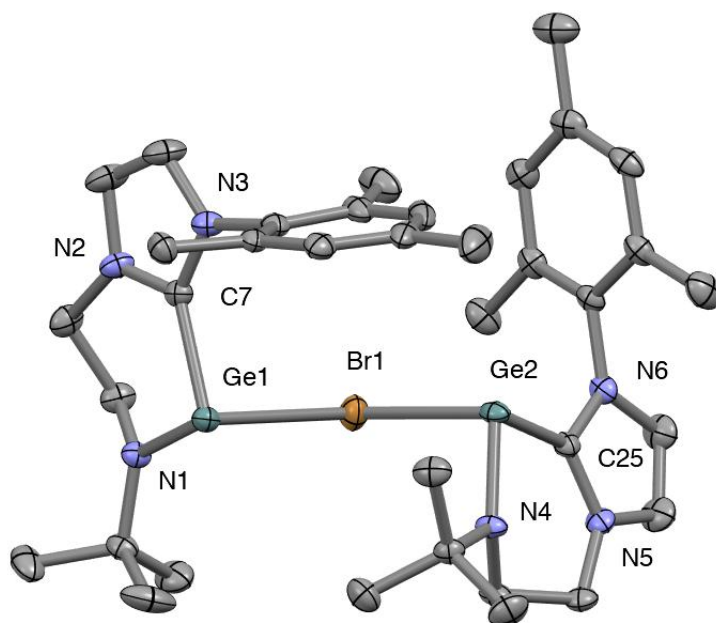


Figure 4.3.5: Molecular structure of the cationic component of bromide bridging germylene **11** as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 1.8538(13), Ge(1)-C(7) 2.0624(16), Ge(1)-Br(1) 2.7682(3), Ge(2)-N(4) 1.8574(14), Ge(2)-C(25) 2.0568(15), Ge(2)-Br(1) 2.7289(3), C(7)-Ge(1)-Br(1) 91.68(4), N(1)-Ge(1)-Br(1) 95.64(4), C(7)-Ge(1)-N(1) 90.99(6), C(25)-Ge(2)-Br(1) 88.62(4), N(4)-Ge(2)-Br(1) 97.92(4), C(25)-Ge(2)-N(4), 90.20(6).

Compound **11** crystallises in a triclinic space group (*P*-1). In the solid-state structure, the asymmetric unit contains a cationic species with a central Ge-Br-Ge unit, partnered by a single $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ anion. The mean Ge- N_{amido} bond length is 1.856 Å, which is shorter than the bromogermylene **4** (1.891(3) Å), but longer than germylium-ylidene **10** (1.830(4) Å). This is presumably due to a lower degree of π -donation from amido nitrogen to Ge(II), resulting from partial retention of the bridging bromide compared to compound **10**. The mean Ge- C_{NHC} distance is 2.060 Å, which is very similar to that found in **4** (2.059(3) Å) and significantly longer than found in **10** (2.040(4) Å). The mean distance of Ge-Br bridging bonds is 2.749 Å, which is longer than the sum of the covalent radii of Ge and Br (2.40 Å)³⁹ and the Ge-Br distance in the bromogermylene **4** (2.611(2) Å). This is in accordance with the presence of partial dative character between the bromide and two Ge(II) centres. The average bond angles measured for the $\text{C}_{\text{NHC}}\text{-Ge-Br}$, $\text{N}_{\text{amido}}\text{-Ge-Br}$ and chelating $\text{C}_{\text{NHC}}\text{-Ge-N}_{\text{amido}}$ units are 90.15, 96.78 and 90.60° respectively, which confirms a low degree of *s/p* hybridisation at the germanium centre as in the case of compound **4**.

Compound **11** is presumably formed by the trapping of in situ generated germylium-ylidene **10** by unreacted bromogermylene **4**. This result demonstrates the importance of the solvent choice and the stoichiometry of reagents when performing halide abstraction chemistry targeting germylium-ylidenes.

4.3.4 Computational and experimental studies of $[(L^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **10**

DFT calculations were also performed on the cationic component of **10** and the energies of its frontier orbitals calculated.* As shown in **Figure 4.3.6** (and analogous to compound **9**), the LUMO of **10** mainly consists of the vacant p_π orbital at germanium, with an antibonding phase relationship with the corresponding $N_{\text{amido}} p_\pi$ orbital. The HOMO is a π bonding orbital centred in the mesityl group. The lone pair on Ge is found in the HOMO-3 with a very low energy ($-10.49 \text{ eV}/-1012 \text{ kJ mol}^{-1}$). The energy gap between the frontier orbitals HOMO-3 and LUMO is 480 kJ mol^{-1} , which is comparable to that found for compound **9** (477 kJ mol^{-1}). Again, the wide energy gap is presumably caused by the presence of the π -donating N_{amido} ligand and the narrow angle at the germanium centre.

* This part was performed by Dr Petra Vasko from the Aldridge group.

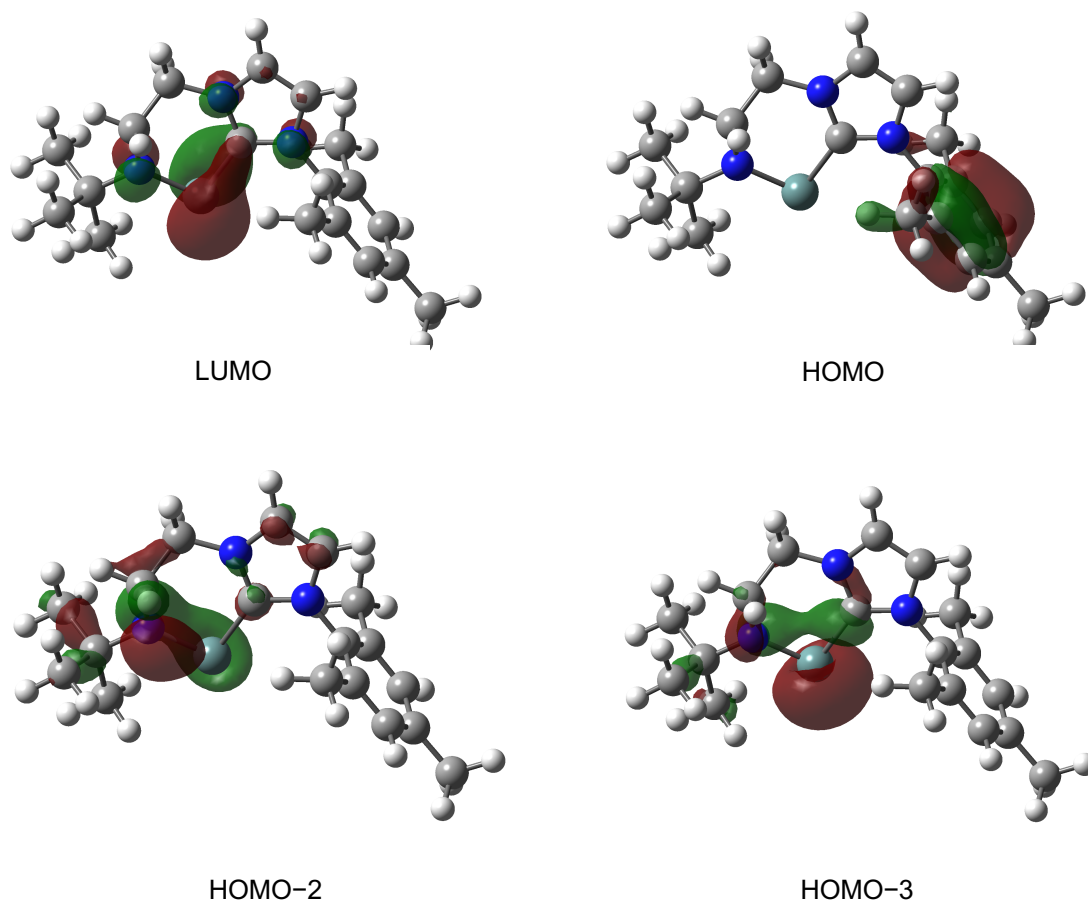
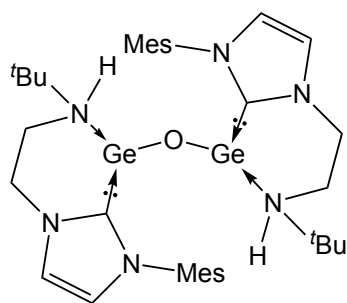


Figure 4.3.6: Selected frontier orbitals of the cationic fragment of germylium-ylidene, **10**.

Experimentally, due to the wide frontier energy gap of **10**, facile oxidative addition of E-H bonds is not likely to take place on the Ge(II) centre. In addition, compound **9** shows no reactivity towards H_2 or hydridic substrates. Therefore we did not test its reactivity towards common small molecules such as dihydrogen, silanes or boranes. Interestingly, however, during early attempts to crystallise compound **10**, a solid-state structure of the water activation product $[\{(\text{L}^{\text{Mes}}\text{H})\text{Ge}\}_2(\mu\text{-O})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]_2$ was obtained due to the presence of adventitious moisture (potentially from the bromobenzene used) (**Figure 4.3.7**).



(12)

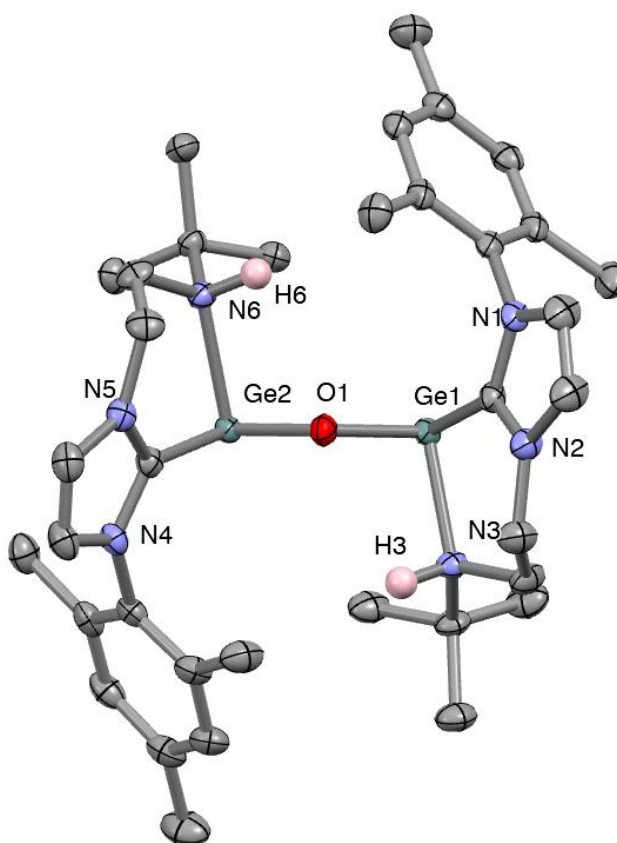


Figure 4.3.7: Molecular structure of the dicationic component of oxo-bridged compound, **12**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(3) 2.189(3), Ge(1)-C(1) 2.064(3), Ge(1)-O(1) 1.830(2), Ge(2)-N(6) 2.189(3), Ge(2)-C(19) 2.050(3), Ge(2)-O(1) 1.838(2), Ge(1)-O(1)-Ge(2) 117.57(14).

The product **12** is an oxo-bridged dinuclear compound which crystallises in a triclinic space group (*P*-1). Based on the solid-state structure, **12** is presumably formed by double O-H bond activation of a H₂O molecule by two compound **10**. The mean Ge-O distance within the Ge-

O-Ge linkage is 1.834 Å, which is comparable to the sum of the covalent radii of the two atoms (1.86 Å).³⁹ The most striking feature of this structure is that the nitrogen atom of each of the amido groups is in a distorted trigonal pyramidal geometry with a sum of the angle of 339.75° around the N3 and 342.09° around N6, instead of the expected trigonal planar (sum of the angles is ca. 360°) if the O-H bond was oxidatively added to the Ge(II) centre. As a comparison, the sum of the angles around N1 in compound **10** is 359.76°, which reflects a trigonal planar geometry. Therefore, as an alternative to formal oxidative addition of H₂O at the Ge centre, we considered the hypothesis that the O-H linkage might have been formally added across the Ge-N_{amido} bond, leading to the formation of a new N-H bond and dative bonding between N and Ge. This idea is further supported by the significantly elongated Ge-N bond length (mean = 2.189 Å, cf. 1.830(4) Å for **10**) due to the change from a X type N_{amido} ligand to a L type neutral N donor ligand.

On this basis it became apparent that instead of formal oxidative addition of E-H bonds at the Ge(II) centre, compounds **9** and **10** may be able to effect small molecule activation in a cooperative manner (i.e. by formally adding the E-H bond across the Ge-N_{amido} covalent bond). This proposal is consolidated further by a serendipitous finding relating to one of the bromogermylene compounds described in Chapter 3. When trying to crystallise the bromogermylene **4** from THF, a related hydrolysis product [(L^{Mes}H)Ge(OH)]Br, **13** was obtained (**Figure 4.3.8**). In this case, presumably one equivalent of water reacts with **4**, affording the O-H activation product **13**, with ejection of the bromide anion.

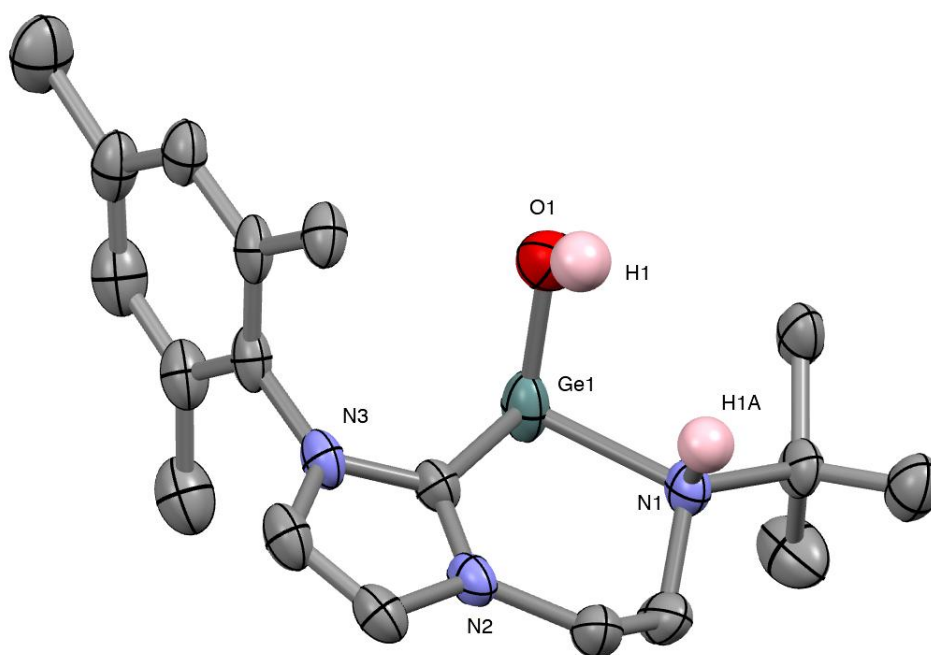


Figure 4.3.8: Molecular structure of the cationic component of compound **13**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 2.113(7), Ge(1)-C(7) 2.051(9), Ge(1)-O(1) 1.770(8), C(7)-Ge(1)-N(1) 91.84(19).

Compound **13** crystallises in a monoclinic space group ($P2_1/n$). There is only one monomeric Ge-containing cation in the asymmetric unit and intermolecular hydrogen bonding is observed between the bromide anion and the Ge-OH and N-H fragments. Again, the trigonal pyramidal geometry at N(1) with a sum of angles of 339.01° indicates that H_2O has been added across the Ge-N bond to give Ge-OH and NH moieties, rather than forming a Ge(H)OH unit via oxidative addition. The Ge-N(1) bond length of **13** is accordingly much longer than in **4** (2.113(7) Å vs. 1.891(3) Å).

In order to further confirm the identity of the product, compound **13** can be independently synthesised by reacting bromogermylene **4** with one equivalent of degassed water and isolated as a white powder. It can then be fully characterised by 1H , ^{13}C NMR spectroscopy, IR spectroscopy and elemental analysis. In the 1H NMR spectrum, in addition to the ligand backbone signals, a singlet (1H) at $\delta_H = 6.24$ ppm can be assigned to the N-H proton and a singlet (1H) at $\delta_H = 11.01$ ppm can be assigned to the O-H proton. Moreover, the IR spectrum

of **13** shows a sharp signal at 3272 cm^{-1} which can be assigned to the O-H stretching band. This feature is comparable to those reported by Roesky et al. (3571 cm^{-1})⁴⁰ and Driess et al. (3643 cm^{-1}) (**Figure 4.3.9**).⁴¹

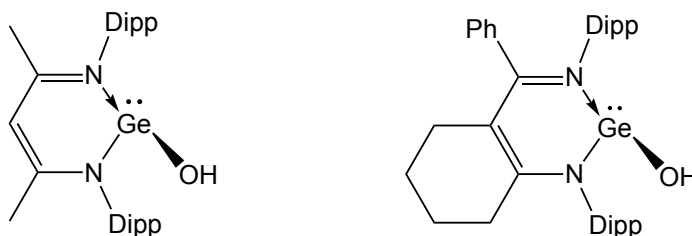
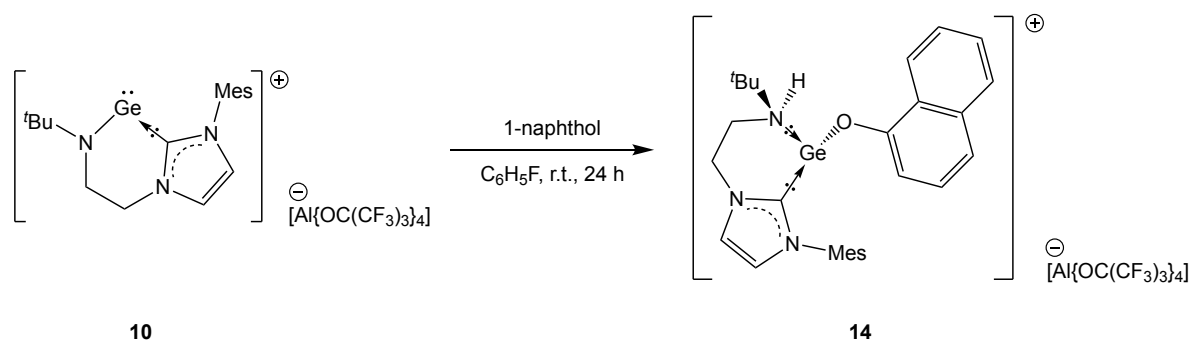


Figure 4.3.9: Previously reported examples of three-coordinate Ge(II) hydroxide.

The water activation results (resulting in compounds **12** and **13**) show that it is possible for germylium-ylidenes **9** and **10** to activate E-H bonds in a similar (cooperative) manner, as might be expected for the increased Lewis acidity of the cationic Ge(II) centre compared to the neutral bromogermylene **4**. We therefore sought to investigate cooperative (1,2-) bond activation by compound **10** towards O-H and N-H bonds in a more controlled fashion.

We firstly tested the reactivity of **10** towards O-H bonds. Attempts to add water in controlled (stoichiometric) manner were not successful, 1-naphthol was chosen as a more convenient source of the O-H bond because (i) it can more easily be weighed; and (ii) its flat naphthyl fragment might enable the crystallisation of the activation product. Accordingly, combining compound **10** with one equivalent of 1-naphthol affords the OH activation product, $[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7-1)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **14**, in 58% yield (**Scheme 4.3.4**).



Scheme 4.3.4: Synthesis of O-H activation product, **14**, from the germylium-ylidene **10**.

A 1-naphthol solution in fluorobenzene was titrated into an in situ prepared solution of **10**, and the progress of the reaction monitored via the ^1H NMR spectra of reaction aliquots. In the ^1H NMR spectrum of the product, the signal due to the ^tBu group is shifted upfield from $\delta_{\text{H}} = 0.98$ to 0.76 ppm compared to precursor **10**. The four ethylene backbone protons change from two multiplets to four broad multiplets integrating to 1H each. The NH signal was found at $\delta_{\text{H}} = 2.74$ ppm. The imidazolyliene backbone protons shift downfield from $\delta_{\text{H}} = 6.36$ and 6.55 ppm to $\delta_{\text{H}} = 6.43$ and 6.66 ppm. Notably, the mesityl group of **14** shows two distinct signals for the two *ortho* methyl and two *meta* CH groups, rather than one signal for each for compound **10**. The carbenic carbon signal is observed at 165.8 ppm in the ^{13}C spectrum.

Single crystals of **14** were obtained by layering a concentrated solution in fluorobenzene with hexane at room temperature over a period of several days (**Figure 4.3.10**).

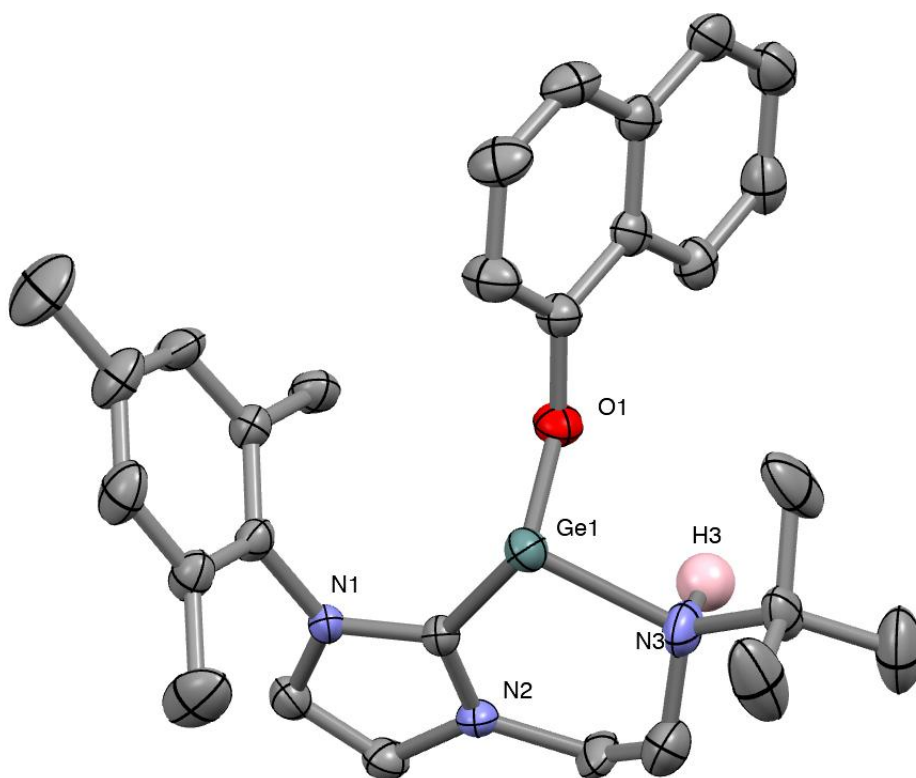
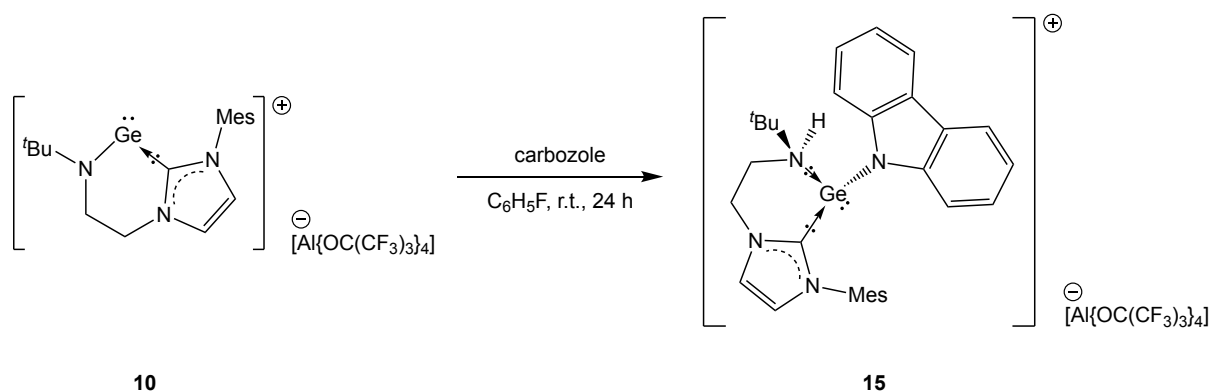


Figure 4.3.10: Molecular structure of the cationic component of 1-naphthol activation product, **14**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(3) 2.154(5), Ge(1)-C(1) 2.057(5), C(7)-Ge(1)-N(3) 86.9(2).

Compound **14** crystallises in an orthorhombic space group (*Fdd2*) with one monomer in the asymmetric unit. The structure in the solid state confirms activation of the O-H bond in naphthol in 1,2 fashion. While the Ge-C_{NHC} bond length of **14** (2.057(5) Å) is only slightly longer than that of **10** (2.040(4) Å), the Ge(1)-N(3) distance (2.154(5) Å) appears to be much longer than the Ge(1)-N(1) distance in **10** (1.830(4) Å) and in fact close to the Ge(1)-N(3) distance in compound **12** (2.189(3) Å). This is consistent with the conversion of an anionic amido ligand to a neutral N donor amine ligand. In addition, in the solid-state structure, the naphthoxy fragment and H3 are shown to be added on the same face of the chelate ring, consistent with the idea of a 1,2-*syn*-addition pathway. This geometry gives important insights into the potential mechanism of the bond activation (*vide infra*).

In light of these O-H bond activation results, we began to investigate N-H bond activation by **10** using the same method (**Scheme 4.3.5**). The reaction with ammonia was tested first. However, it is difficult to control the stoichiometry of the ammonia added as in the case of O-H activation and it leads to the formation of protio-ligand. After trying various reagents containing N-H bonds such as *p*-toluidine and 1-naphthylamine, carbazole was chosen due to its crystalline nature (easy to weigh out stoichiometrically) as well as the potential advantages of crystallisation of the product. One equivalent of carbazole was added to in situ generated **10** in fluorobenzene. Stirring at room temperature overnight yielded the N-H activation product $[(L^{Mes}H)Ge(NC_{12}H_8)][Al\{OC(CF_3)_3\}_4]$, **15**, in 60% yield.



Scheme 4.3.5: Synthesis of the N-H activation product, **15**, from the germylium-ylidene **10**.

Compound **15** has been characterised by multinuclear NMR spectroscopy, X-ray crystallography and elemental analysis. The ^1H NMR spectrum shows a similar ligand pattern to compound **14**, featuring a N-H resonance at $\delta_{\text{H}} = 3.72$ ppm. The $t\text{Bu}$ resonance is particularly shielded at $\delta_{\text{H}} = 0.33$ ppm compared to the O-H activation product **14** ($\delta_{\text{H}} = 0.76$ ppm). This is potentially due to positioning above the carbazole aromatic π system.

Single crystals of compound **15** were obtained by layering a concentrated solution in fluorobenzene with hexane (**Figure 4.3.11**). **15** crystallises in the same space group as the 1-naphthol activation product, **14**. The solid-state structure displays very similar features as **14**, with an elongated Ge-N distance (2.134(6) Å) compared to **10** (1.830(4) Å) and an overall geometry reflecting *syn*-addition of the carbazolyl fragment and H1.

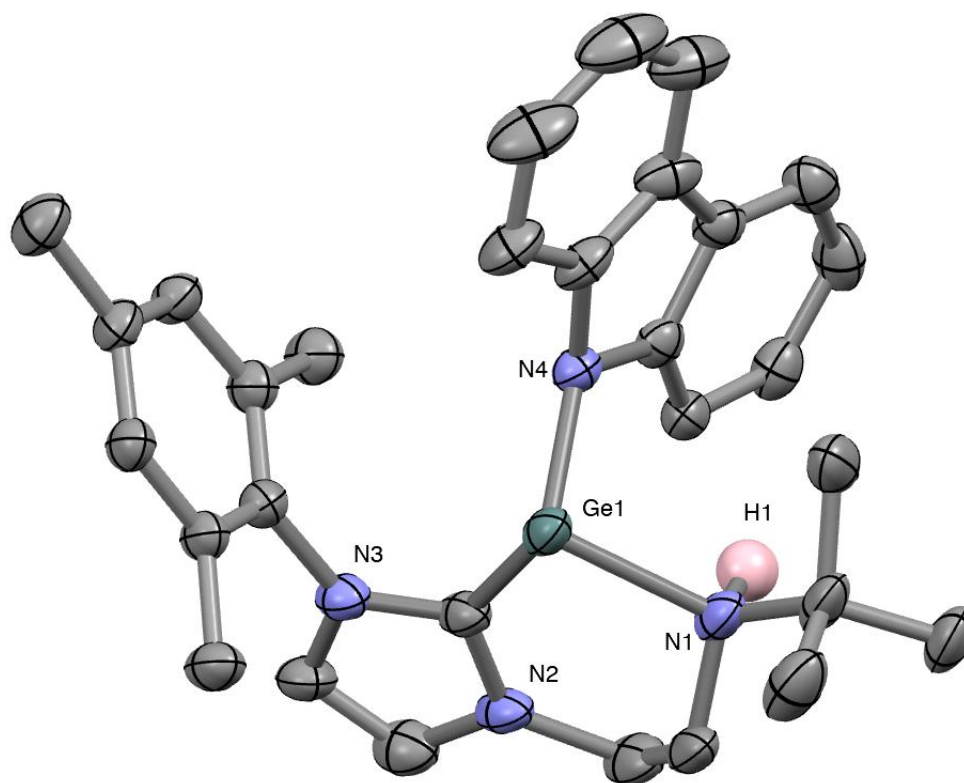


Figure 4.3.11: Molecular structure of the cationic component of carbazole activation product, **15**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 2.134(6), Ge(1)-C(7) 2.030(9), C(7)-Ge(1)-N(1) 87.6(3).

Reactivity proceeding via cooperative addition of an E-H bond across the metal centre and ligand backbone was previously reported for a neutral germylene stabilised by a modified β -diketiminato ligand scaffold (**Figure 4.3.12**).^{41–43} Reaction with excess ammonia gas leads to the formation of the 1,4-addition product, while the silylene analogue affords the 1,1-addition product.⁴⁴ DFT calculations reveal that in the case of germylene, the 1,4-addition product is more favourable both kinetically and thermodynamically, reflecting relative stabilities of Ge(II) and Si(II).⁴⁵

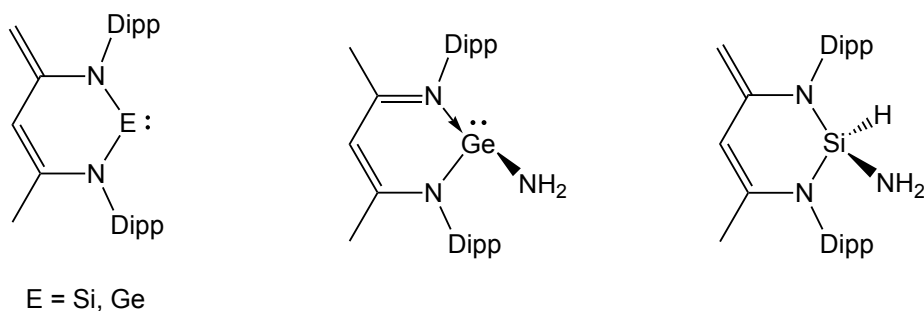
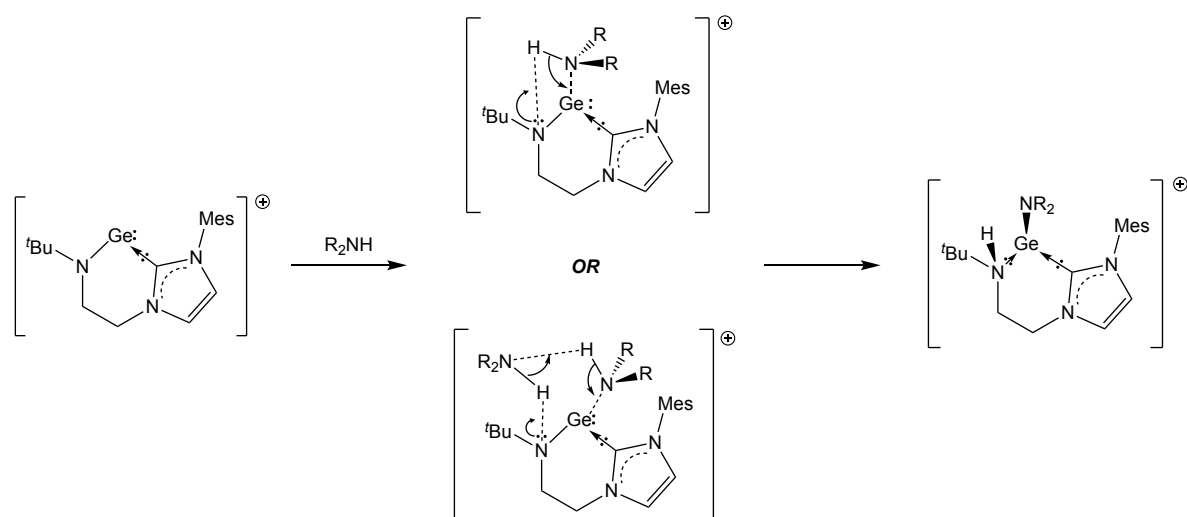


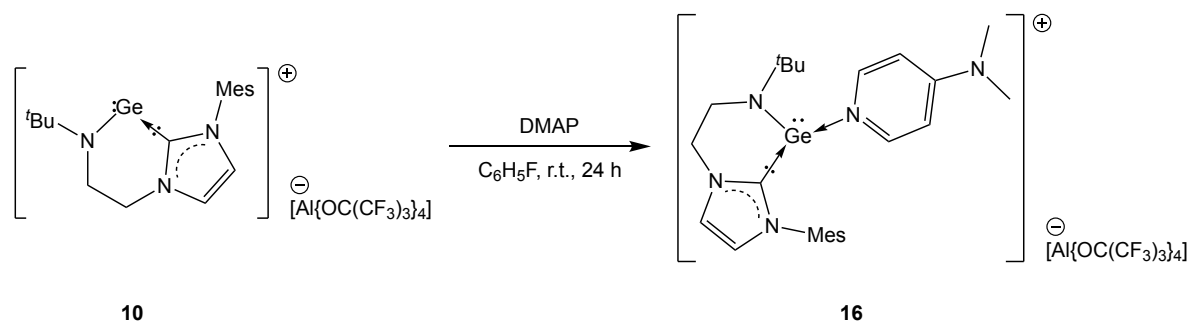
Figure 4.3.12: 1,1-addition vs. 1,4-addition products of ammonia activation by a germylene (left) and a silylene (right) stabilised by a modified β -diketiminato ligand.

Based on these results (and literature precedent) we postulate a potential reaction mechanism for formation of compounds **14** and **15**. As mentioned earlier, the reactivities of neutral tetrelenes towards E-H bonds (E = N or O) have been extensively studied since an initial report from Power et al. in 2009.⁸ In these studies, it was postulated that, in contrast with H_2 , the first step in reactions with H_2O or NH_3 involves the coordination of the substrate to the vacant p_π orbital of the metal centre, forming a Lewis acid-base adduct.⁵ This is followed by a intermolecular proton transfer presumably aided by a second molecule of the substrate, resulting in a 1,1-addition product with a net oxidation state change of +2.⁴⁶ We propose that the pathway for the 1,2-addition of E-H bonds at compound **10** involves initial coordination of one molecule of R_2NH , followed by proton transfer potentially mediated by a second substrate molecule, as analogous to the neutral tetrelenes, as illustrated on **Scheme 4.3.6**.



Scheme 4.3.6: Proposed mechanisms for N-H bond activation of **10** (anions omitted for clarity).

In order to gain more evidence of the initial step in the bond activation process (i.e. coordination at Ge), a non-protic N donor ligand was used. In this case, one equivalent of *N,N*-dimethylpyridin-4-amine (DMAP) was combined with in situ generated **10** in fluorobenzene at room temperature. After stirring overnight, the adduct **16** was formed.



Scheme 4.3.7: Synthesis of DMAP coordination product $[(L^{\text{Mes}})\text{Ge}(\text{DMAP})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **16**, from the germylium-ylidene **10**.

Although multiple attempts at recrystallising compound **16** were made, they were not successful due to its oily nature. The ^1H NMR spectrum of **16**, however, confirms the formation of a Lewis acid adduct. A downfield shift of the $t\text{Bu}$ and mesityl *ortho* CH_3 groups upon coordination to **10**. The NMe_2 group of coordinated DMAP resonances from $\delta_{\text{H}} = 2.43$ (free DMAP) to 1.48 ppm upon coordination. The aromatic protons feature at $\delta_{\text{H}} = 6.34$ (1H), 6.64 (1H) and 7.32 (2H) ppm. The integration of the DMAP signals in relation to the ligand backbone

signals suggests the formation of a 1:1 adduct. Moreover, in the ^{13}C NMR spectrum, the carbenic carbon resonance can be found at $\delta_{\text{C}} = 166.1$ ppm. The formation of **16** is consistent with the Lewis acidic nature of the Ge(II) centre of **10**, which facilitates coordination of carbazole to Ge(II) centre in the formation of compound **15**. Previous examples of germylium-ylidenes forming an adduct with DMAP include a quasi mono-coordinate Ge cation (**Figure 4.3.13**, left)⁴⁷ and a two-coordinate $[\text{LGeCl}]^+$ (L = a carbodiphosphorane ligand) (**Figure 4.3.13**, right).⁴⁸

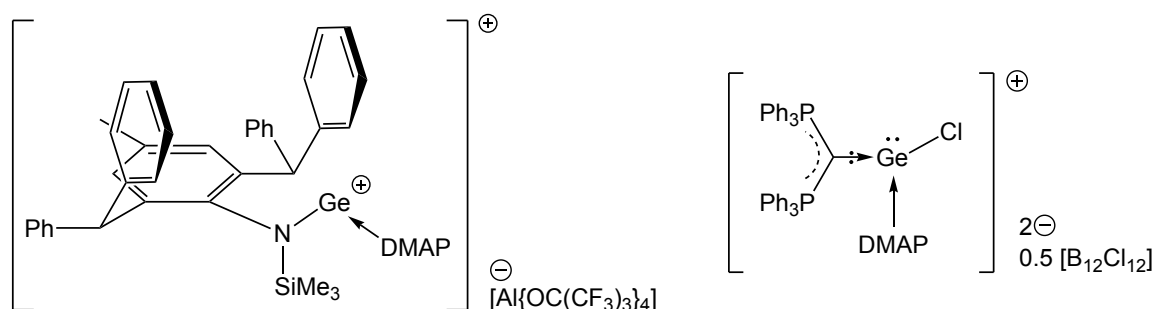
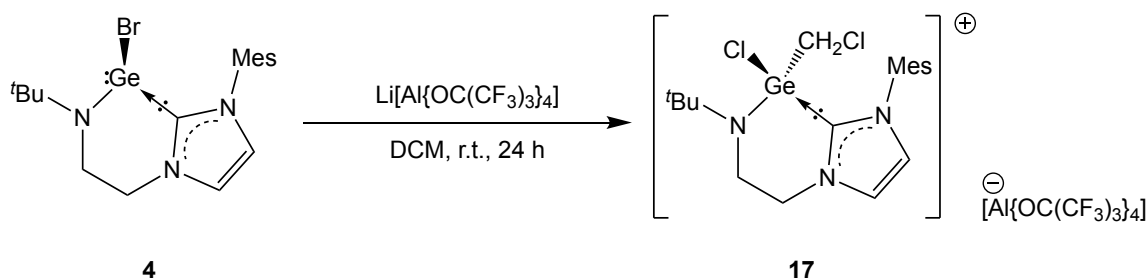


Figure 4.3.13: Previous examples of DMAP adducts of Ge(II) cations.

In addition to the cooperative activation of N-H and O-H bonds across the Ge-N linkage, we also discovered that compound **10** is capable of the oxidative addition of the C-Cl bond in dichloromethane under ambient conditions. Originally, bromogermylene **4** was combined with one equivalent of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ in dichloromethane as an attempt to synthesise the germylium-ylidene **10**. Instead of **10**, however, the dichloromethane activation product $[(\text{L}^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **17** was formed (**Scheme 4.3.8**). Interestingly, compound **9**, by contrast, can be synthesised under the same conditions without activating dichloromethane, as shown by in situ ^1H NMR monitoring, suggesting a subtle influence by the N-bond imidazolyliidene substituent.



Scheme 4.3.8: Synthesis of dichloromethane activation product, **17**, from the bromogermylene **4**.

To our knowledge, compound **17** represents the third example of the oxidative addition of dichloromethane by a germylium-ylidene (and the first for a cyclic system). Two other dichloromethane activation products generated from acyclic NHC-stabilised germylium-ylidenes have been reported by our group (**II**, **Figure 4.3.14**, left)²⁹ and by Rivard et al. (**III**, **Figure 4.3.14**, right).³⁰

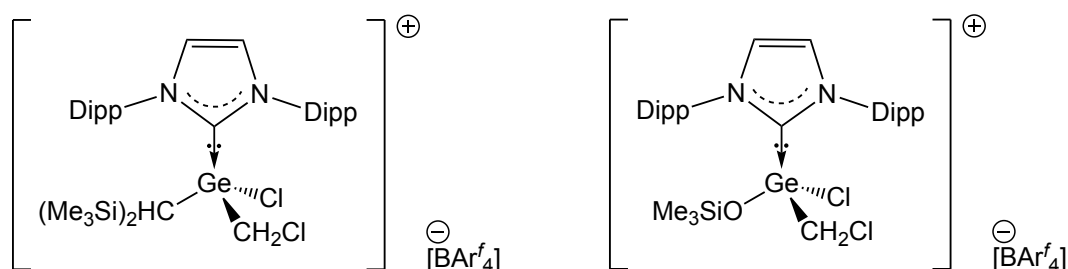


Figure 4.3.14: Previous examples of dichloromethane activation products.

The NMR spectra of **17** were measured in bromobenzene- d_5 and can be compared with those of the germylium-ylidene **10**. In the ^1H NMR spectrum (**Figure 4.3.15**), the resonances for the $t\text{Bu}$ and mesityl *para* CH_3 group are comparable to **10**. In similar fashion to the E-H bond activation products **14** and **15**, the two *ortho* mesityl groups give rise to two distinct signals (3H each) rather than a 6H singlet. A pair of doublets (1H each) at $\delta_{\text{H}} = 2.50$ and 2.79 ppm that displays a clear roofing effect provides evidence for the formation of a species containing the CH_2Cl fragment. The $^2J_{\text{HH}}$ coupling constant 13.2 Hz is comparable to the two previous examples shown above with 12.0 Hz (**II**)²⁹ and 12.6 Hz (**III**).³⁰ The four ethylene backbone protons appear as two multiplets integrating to 2H each in the region of $\delta_{\text{H}} = 3.0\text{--}4.0$ ppm. In

the aromatic region, the imidazolylidene backbone signals shift downfield from $\delta_{\text{H}} = 6.36$ and 6.55 ppm to $\delta_{\text{H}} = 6.57$ and 6.75 ppm. Correspondingly, the two *meta* CH groups of the mesityl substituent give rise to two (1H) singlets at $\delta_{\text{H}} = 6.67$ and 6.69 ppm, instead of one singlet for **10**. The changes in the chemical shift suggest the formation of a new species.

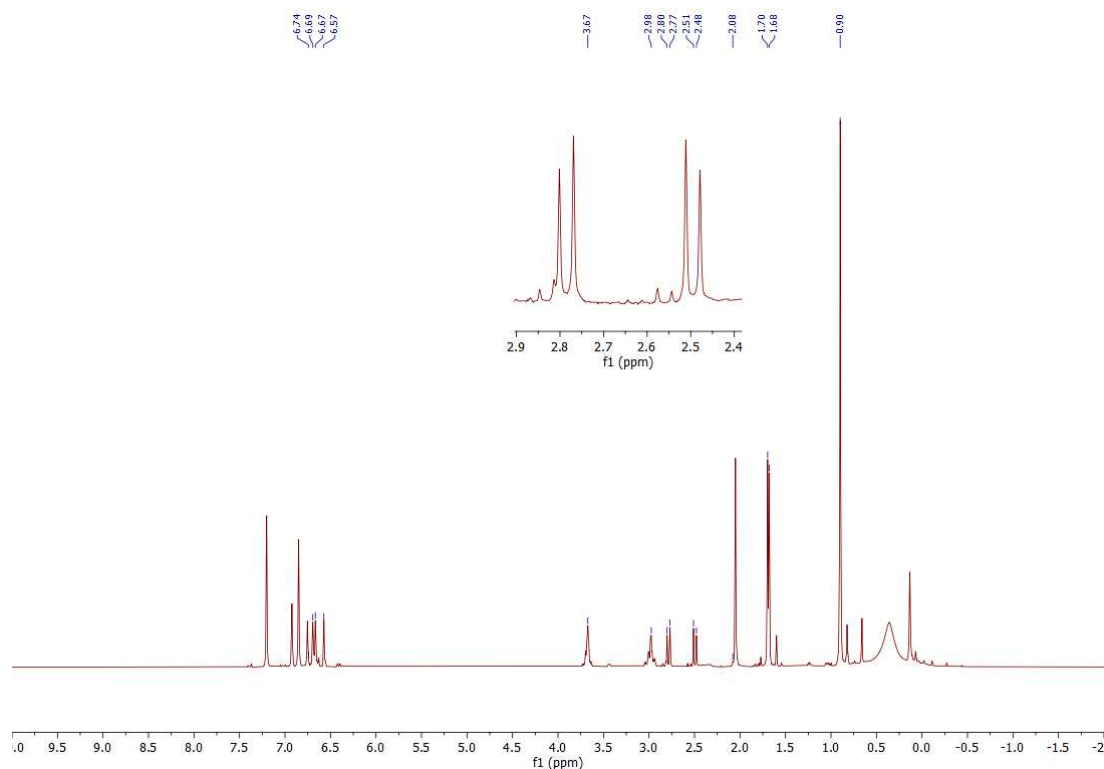


Figure 4.3.15: ^1H NMR spectrum of compound **17**.

Single crystals of **17** could be obtained by layering a concentrated solution in dichloromethane with hexane. Pale yellow crystals could be isolated in a relatively high yield at 85%. The compound crystallises in a monoclinic space group ($P2_1/c$). The solid-state structure reveals that **17** is in fact the CH_2Cl_2 1,1 activation product (**Figure 4.3.16**).

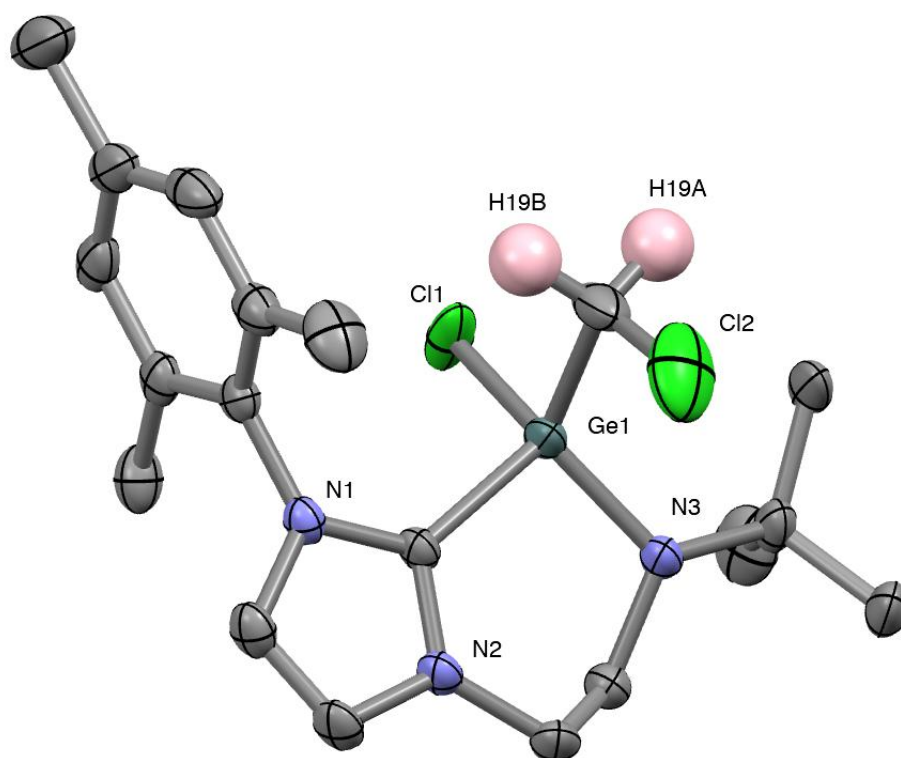


Figure 4.3.16: Molecular structure of the cationic component of dichloromethane activation product, **17**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(3) 1.808(2), Ge(1)-C(1) 1.968(3), C(1)-Ge(1)-N(3) 99.30(11).

The solid-state structure confirms that the C-Cl bond has been cleaved at the Ge(II) centre to generate a Ge(IV) product in which the metal centre adopts a distorted tetrahedral geometry. Compared to the molecular structure of **10**, the Ge(1)-N(3) and Ge(1)-C(1) bond lengths are both shortened from 1.830(4) to 1.808(2) Å and 2.040(4) to 1.968(3) Å respectively, presumably due to the smaller size of the Ge(IV) centre compared to Ge(II). The C(1)-Ge(1)-N(3) chelate angle is significantly wider than that of **10**. This presumably results from the smaller Ge(IV) centre which is drawn closer into the chelate ring.

The formation of compound **17** presumably results from the high polarity of the C-Cl bond in dichloromethane and a highly electrophilic carbon, which is attacked by the germanium lone pair in a S_N2 -like nucleophilic substitution process that eventually leads to the activation product **17** (despite the low-lying nature of the Ge-centred lone pair in **10**).

4.4 Conclusions

This chapter describes the synthesis and characterisation of two novel germylium-ylidene cations **9** and **10** incorporating a $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand system. Both compounds have been characterised by multinuclear NMR spectroscopy and X-ray crystallography. DFT calculations were carried out to predict the potential reactivity of the compounds and show that both cations possess a relatively large frontier orbital energy gap. As such, a high kinetic barrier to the concerted oxidative addition of E-H bonds at the metal centre is observed in both cases. The experimental data is in accordance with DFT calculations - compound **9** shows no reactivity towards H_2 or hydridic E-H bonds even under forcing conditions. However, compound **10** is shown to be capable of activating both O-H and N-H bonds in cooperative fashion across the Ge-N linkage. Reactions with 1-naphthol or carbazole lead to the formation of tethered amine stabilised Ge(II) aryloxide/amide products respectively. In addition, **10** undergoes oxidative addition of the C-Cl bond in dichloromethane with an accompanying Ge(II) to Ge(IV) redox transformation. The mechanism of E-H bond activation is postulated to be a 1,2-addition of which the pathway involves either a single or an additional molecule of the substrate. The accessibility of the first step of this proposed mechanism is suggested by the ready coordination of DMAP to compound **10** under ambient conditions.

4.5 Experimental details

[(L^{tBu})Ge][Al{OC(CF₃)₃}₄] (9**):** To a suspension of Li[Al{OC(CF₃)₃}₄] (390 mg, 0.40 mmol) in bromobenzene (5 mL) was added a solution of compound **1** (150 mg, 0.40 mmol) at room temperature. The reaction mixture was stirred for 12 h, over which time a yellow solution and a white precipitate were formed. Volatiles were removed in *vacuo* and compound **9** was isolated as an oily yellow solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in bromobenzene stored at -30°C. Yield: 200 mg, 40%.

Spectroscopic data: ¹H NMR (400 MHz, bromobenzene-d₅, 298K): δ_H 1.04 (9H, s, ^tBu C(CH₃)₃), 1.27 (9H, s, ^tBu C(CH₃)₃), 3.05 (2H, br m, ethylene CH₂), 3.41 (2H, br m, ethylene CH₂), 6.42

(1H, s, imidazolylidene backbone CH), 6.66 (1H, s, imidazolylidene backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene- d_5 , 298K): δ_{C} 30.5 (^tBu C($\underline{\text{CH}_3}$)₃), 31.7 (^tBu C($\underline{\text{CH}_3}$)₃), 45.0 (ethylene C), 51.8 (ethylene C), 61.0 (^tBu C($\underline{\text{CH}_3}$)₃), 61.2 (^tBu C($\underline{\text{CH}_3}$)₃), 79.5 (C($\underline{\text{CF}_3}$)₃), 120.1 (imidazolylidene backbone C), 121.0 (imidazolylidene backbone C), 121.9 (q, $^1J_{\text{CF}} = 292.5$ Hz, C($\underline{\text{CF}_3}$)₃), 164.5 (carbenic N $\underline{\text{CN}}$). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, bromobenzene- d_5 , 298K): $\delta_{\text{F}} -74.6$. $^{27}\text{Al}\{^1\text{H}\}$ NMR (104 MHz, bromobenzene- d_5 , 298K): δ_{Al} 35.4. Elemental microanalysis: calc. for $\text{C}_{29}\text{H}_{24}\text{AlF}_{36}\text{GeN}_3\text{O}_4$: C 27.60% H 1.92% N 3.33% meas. C 27.51% H 2.02% N 3.38%. Crystallographic data: $\text{C}_{29}\text{H}_{24}\text{AlF}_{36}\text{GeN}_3\text{O}_4$ ($M_r = 1262.08$): triclinic, $P-1$, $a = 10.2433(6)$, $b = 14.4020(8)$, $c = 16.1962(9)$ Å, $\alpha = 95.690(5)^\circ$, $\beta = 107.389(5)^\circ$, $\gamma = 100.633(5)^\circ$, $V = 2210.4(2)$ Å³, $Z = 2$, $\rho_{\text{c}} = 1.896$ g cm⁻³, $T = 150$ K, $\lambda = 1.54184$ Å. $R_1 = 0.0778$ for 7732 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.2304$ for all 9104 unique reflections. Max. and min. residual electron densities 1.67, -1.17 e Å⁻³.

$[(\text{L}^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (10**)**: To a suspension of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (334 mg, 0.34 mmol) in bromobenzene (5 mL) was added a solution of compound **4** (150 mg, 0.34 mmol) at room temperature. The reaction mixture was stirred for 12 h, over which time a yellow solution and a white precipitate were formed. Volatiles were removed in *vacuo* and compound **10** was isolated as a yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in bromobenzene layered with hexane and stored at room temperature. Yield: 193 mg, 42%.

Spectroscopic data: ^1H NMR (400 MHz, bromobenzene- d_5 , 298K): δ_{H} 0.98 (9H, s, ^tBu C($\underline{\text{CH}_3}$)₃), 1.72 (6H, s, Mes *ortho* CH₃), 2.08 (3H, s, Mes *para* CH₃), 3.20 (2H, m, ethylene CH₂), 3.60 (2H, m, ethylene CH₂), 6.36 (1H, d, $^3J_{\text{HH}} = 1.7$ Hz, imidazolylidene backbone CH), 6.55 (1H, d, $^3J_{\text{HH}} = 1.7$ Hz, imidazolylidene backbone CH), 6.64 (2H, s, Mes *meta* CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene- d_5 , 298K): δ_{C} 17.5 (Mes *ortho* C($\underline{\text{CH}_3}$)), 21.1 (Mes *para* C($\underline{\text{CH}_3}$)), 30.4 (^tBu C($\underline{\text{CH}_3}$)₃), 46.0 (ethylene C), 51.5 (ethylene C), 61.3 (^tBu C($\underline{\text{CH}_3}$)₃), 79.5 (C($\underline{\text{CF}_3}$)₃), 121.9 (q, $^1J_{\text{CF}} = 292.0$ Hz, C($\underline{\text{CF}_3}$)₃), 122.2 (imidazolylidene backbone C), 122.7 (imidazolylidene

backbone C), 123.9 (Mes *para* C(CH₃)), 130.1 (Mes *meta* C), 134.1 (Mes *ortho* C(CH₃)), 141.7 (Mes *ipso* C), 165.6 (carbenic N $\overline{\text{C}}\text{N}$). ¹⁹F{¹H} NMR (376 MHz, bromobenzene-d₅, 298K): δ_{F} -74.6. ²⁷Al{¹H} NMR (104 MHz, bromobenzene-d₅, 298K): δ_{Al} 35.4. Crystallographic data: C₃₄H₂₆AlF₃₆GeN₃O₄ (*M*_r = 1324.15): monoclinic, *P*2₁/*n*, *a* = 10.5246(1), *b* = 18.4838(3), *c* = 24.2497(3) Å, β = 98.747(1)°, *V* = 4662.54(11) Å³, *Z* = 4, ρ_{c} = 1.886 g cm⁻³, *T* = 150 K, λ = 1.54184 Å. *R*₁ = 0.0938, for 7840 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.2713 for all 9656 unique reflections. Max. and min. residual electron densities 2.035, -1.517 e Å⁻³.

[(**L**^{Mes})Ge]₂(μ-Br)][Al{OC(CF₃)₃}]₄ (**11**): To a mixture of **4** (200 mg, 0.46 mmol) and Li[Al{OC(CF₃)₃}]₄ (223 mg, 0.23 mmol) was added benzene (10 mL) at room temperature. The reaction mixture was stirred overnight, over which time a yellow solution and a white precipitate were formed. Volatiles were removed in *vacuo* and compound **11** was isolated as a yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in dichloromethane layered with hexane and stored at -30°C. Yield: 276 mg, 68%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298K): δ_{H} 1.09 (9H, s, ^{*t*}Bu C(CH₃)₃), 1.78 (6H, s, Mes *ortho* CH₃), 2.11 (3H, s, Mes *para* C(CH₃)), 3.19 (2H, m, ethylene CH₂), 3.33 (2H, m, ethylene CH₂), 5.84 (1H, d, ³*J*_{HH} = 1.9 Hz, imidazolylidene backbone CH), 6.12 (1H, d, ³*J*_{HH} = 1.9 Hz, imidazolylidene backbone CH), 6.67 (2H, s, Mes *meta* CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298K): δ_{C} 17.9 (Mes *ortho* C(CH₃)), 20.9 (Mes *para* C(CH₃)), 30.3 (^{*t*}Bu C(CH₃)₃), 44.5 (ethylene C), 51.6 (ethylene C), 57.6 (^{*t*}Bu C(CH₃)₃), 86.7 (C(CF₃)₃), 121.9 (imidazolylidene backbone C), 122.3 (q, ¹*J*_{CF} = 292.7 Hz, C(CF₃)₃), 122.5 (imidazolylidene backbone C), 129.8 (Mes *para* C(CH₃)), 132.4 (Mes *meta* CH), 134.8 (Mes *ortho* C(CH₃)), 140.5 (Mes *ipso* C), 166.0 (carbenic N $\overline{\text{C}}\text{N}$). ¹⁹F{¹H} NMR (376 MHz, benzene-d₆, 298K): δ_{F} -75.7. ²⁷Al{¹H} NMR (104 MHz, benzene-d₆, 298K): δ_{Al} 34.7. Elemental microanalysis: calc. for C₅₁H₄₉AlBrF₄₆Ge₂N₆O₄: C 35.08% H 2.83% N 4.81% meas. C 35.19% H 2.97% N 4.46%. Crystallographic data: C₅₁H₄₉AlBrF₃₆Ge₂N₆O₄ (*M*_r = 1761.06): triclinic, *P*-1, *a* = 11.0633(1), *b*

= 18.7791(2), $c = 18.8201(2)$ Å, $\alpha = 61.968(1)$, $\beta = 80.591(1)$, $\gamma = 80.424(1)^\circ$, $V = 3386.38(7)$ Å³, $Z = 2$, $\rho_c = 1.727$ g cm⁻³, $T = 150$ K, $\lambda = 1.54184$ Å. $R_1 = 0.0265$, for 13008 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.0681$ for all 14100 unique reflections. Max. and min. residual electron densities 0.66, -0.51 e Å⁻³.

[(L^{Mes}H)Ge]₂(μ-O)][Al{OC(CF₃)₃}₄] (12): Due to the adventitious formation of the compound, no experimental procedure or spectroscopic data are reported. Crystallographic data: C₆₈H₅₄Al₂F₇₂BrGe₂N₆O₉ ($M_r = 2666.32$): triclinic, $P-1$, $a = 16.4333(3)$, $b = 16.7339(3)$, $c = 20.3938(3)$ Å, $\alpha = 76.708(2)^\circ$, $\beta = 69.453(2)^\circ$, $\gamma = 77.456(2)^\circ$, $V = 5053.06(17)$ Å³, $Z = 2$, $\rho_c = 1.856$ g cm⁻³, $T = 150$ K, $\lambda = 1.54184$ Å. $R_1 = 0.0682$ for 18808 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.1977$ for all 21002 unique reflections. Max. and min. residual electron densities 1.640, -1.360 e Å⁻³.

[(L^{Mes}H)Ge(OH)]Br (13): To a solution of **4** (50 mg, 0.114 mmol) in benzene was added a saturated solution of H₂O in benzene (3.247 mL, 0.114 mmol) using a microsyringe. The reaction mixture was stirred at room temperature 2 h, over which time a white suspension was formed. Volatiles were removed in *vacuo*, and the product isolated as a white powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in THF layered with hexane and stored at -30°C . Yield: 33 mg, 63 %.

Spectroscopic data: ¹H NMR (400 MHz, bromobenzene-*d*₅, 298K): δ_H 0.81 (9H, s, ^{*t*}Bu C(CH₃)₃), 1.75 (6H, s, Mes *ortho* CH₃), 2.01 (6H, s, Mes *para* CH₃), 2.57 (2H, br m, ethylene CH₂), 4.60 (2H, br m, ethylene CH₂), 6.24 (1H, s, NH), 6.49 (2H, s, Mes *meta* CH), 7.04 (1H, br m, imidazolylidene backbone CH), 7.05 (1H, br m, imidazolylidene backbone CH), 11.01 (1H, s, OH). ¹³C{¹H} NMR (126 MHz, bromobenzene-*d*₅, 298K): δ_C 17.8 (Mes *ortho* C(CH₃)), 21.3 (Mes *para* C(CH₃)), 29.1 (^{*t*}Bu C(CH₃)₃), 42.3 (ethylene C), 49.9 (ethylene C), 49.9 (^{*t*}Bu C(CH₃)₃), 128.3 (imidazolylidene backbone C), 128.5 (imidazolylidene backbone C), 130.0 (Mes *meta* C), 134.1 (Mes *ortho* C(CH₃)), 137.7 (Mes *ipso* C), 140.6 (Mes *para* C(CH₃)), 187.1

(carbenic NCN). Elemental microanalysis: calc. for $\text{C}_{18}\text{H}_{28}\text{BrGeN}_3\text{O}$: C 47.52% H 6.20% N 9.24%; meas. C 47.39% H 6.06% N 9.17%.

$[(\text{L}^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7\text{-1})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (14**)**: To a solution of **10** (generated in situ from **4** (200 mg, 0.46 mmol) and $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (446 mg, 0.46 mmol) in fluorobenzene (5 mL)) was titrated a solution of 1-naphthol (66 mg, 0.46 mmol) in fluorobenzene (3 mL) at room temperature until complete conversion was reached. After stirring for 12 h at room temperature, the reaction mixture was filtered and volatiles removed in *vacuo* to obtain compound **14** as a pale yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in fluorobenzene layered with hexane and stored at room temperature. Yield: 390 mg, 58%.

Spectroscopic data: ^1H NMR (400 MHz, bromobenzene- d_5 , 298K): δ_{H} 0.76 (9H, s, $^t\text{Bu C}(\text{CH}_3)_3$), 1.36 (3H, s, Mes *para* CH_3), 1.81 (3H, s, Mes *ortho* CH_3), 2.05 (3H, s, Mes *ortho* CH_3), 2.61 (1H, br m, ethylene CH), 2.74 (1H, m, NH), 3.03 (1H, br m, ethylene CH), 3.77 (1H, br m, ethylene CH), 4.08 (1H, br m, ethylene CH), 5.97 (1H, br d, $^3J_{\text{HH}} = 8.0$ Hz, naph), 6.33 (1H, s, Mes *meta* CH), 6.43 (1H, d, $^3J_{\text{HH}} = 1.6$ Hz, imidazolylidene backbone CH), 6.66 (1H, d, $^3J_{\text{HH}} = 1.6$ Hz, imidazolylidene backbone CH), 6.72 (1H, s, Mes *meta* CH), 6.99 (2H, overlapping m, naph), 7.30 (2H, overlapping m, naph), 7.61 (1H, br d, $^3J_{\text{HH}} = 8.0$ Hz, naph), 7.85 (1H, br dd, $^3J_{\text{HH}} = 8.0$ Hz, naph). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene- d_5 , 298K): δ_{C} 17.0 (Mes *para* $\text{C}(\text{CH}_3)$), 17.5 (Mes *ortho* $\text{C}(\text{CH}_3)$), 21.2 (Mes *ortho* $\text{C}(\text{CH}_3)$), 26.7 ($^t\text{Bu C}(\text{CH}_3)_3$), 42.6 (ethylene C), 47.8 (ethylene C), 58.2 ($^t\text{Bu C}(\text{CH}_3)_3$), 79.5 ($\text{C}(\text{CF}_3)_3$), 110.1 (naph), 120.7 (naph), 121.8 (naph), 121.9 (q, $^1J_{\text{CF}} = 292.7$ Hz, $\text{C}(\text{CF}_3)_3$), 122.5 (imidazolylidene backbone C), 123.6 (imidazolylidene backbone C), 126.0 (naph), 126.5 (naph), 127.4 (naph), 128.5 (naph), 130.2 (Mes *meta* C), 130.5 (Mes *meta* C), 130.7 (Mes *para* $\text{C}(\text{CH}_3)$), 133.7 (Mes *ortho* $\text{C}(\text{CH}_3)$), 133.8 (Mes *ortho* $\text{C}(\text{CH}_3)$), 135.4 (naph), 135.6 (naph), 141.7 (Mes *ipso* C), 154.6 (naph), 165.8 (carbenic NCN). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, bromobenzene- d_5 , 298K): δ_{F} -74.6. $^{27}\text{Al}\{^1\text{H}\}$ NMR (104 MHz, bromobenzene- d_5 , 298K): δ_{Al} 35.5. Crystallographic data (for fluorobenzene

hemisolvate): $\text{C}_{47}\text{H}_{36.5}\text{AlF}_{36.5}\text{GeN}_3\text{O}_5$ ($M_r = 1516.36$): orthorhombic, $Fdd2$, $a = 85.6035(17)$, $b = 27.8903(7)$, $c = 9.72344(19)$ Å, $V = 23214.8(9)$ Å³, $Z = 16$, $\rho_c = 1.735$ g cm⁻³, $T = 150$ K, $\lambda = 1.54184$ Å. $R_1 = 0.0540$ for 10524 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.1493$ for all 10863 unique reflections. Max. and min. residual electron densities 0.96, -0.73 e Å⁻³.

[(L^{Mes}H)Ge(NC₁₂H₈)] [Al{OC(CF₃)₃}]₄ (15): To a solution of **10** (generated in situ from **4** (200 mg, 0.46 mmol) and Li[Al{OC(CF₃)₃}]₄ (446 mg, 0.46 mmol) in fluorobenzene (5 mL)) was titrated a solution of carbazole (7.7 mg, 0.46 mmol) in fluorobenzene (3 mL) at room temperature until complete conversion was reached. After stirring for 12 h at room temperature, the reaction mixture was filtered and volatiles removed in *vacuo* to obtain **15** as a white solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in fluorobenzene layered with hexane and stored at room temperature. Yield: 410 mg, 60%. Spectroscopic data: ¹H NMR (400 MHz, bromobenzene-d₅, 298K): δ_{H} 0.33 (9H, s, ^tBu C(CH₃)₃), 0.69 (3H, s, Mes *para* CH₃), 1.83 (3H, s, Mes *ortho* CH₃), 1.87 (3H, s, Mes *ortho* CH₃), 2.83 (1H, br m, ethylene CH), 3.02 (1H, br m, ethylene CH), 3.72 (1H, m, NH), 3.98 (1H, br m, ethylene CH), 4.28 (1H, br m, ethylene CH), 5.80 (1H, s, Mes *meta* CH), 6.46 (1H, d, ³J_{HH} = 1.8 Hz, imidazolylidene backbone CH), 6.64 (1H, s, Mes *meta* CH), 6.76 (1H, d, ³J_{HH} = 1.8 Hz, imidazolylidene backbone CH), 7.08 (4H, overlapping m, carbazoyl), 7.88 (4H, overlapping m, carbazoyl). ¹³C{¹H} NMR (126 MHz, bromobenzene-d₅, 298K): δ_{C} 16.5 (Mes *para* C(CH₃)), 17.8 (Mes *ortho* C(CH₃)), 21.0 (Mes *ortho* C(CH₃)), 25.4 (^tBu C(CH₃)₃), 42.6 (ethylene C), 48.2 (ethylene C), 59.0 (^tBu C(CH₃)₃), 78.4 (C(CF₃)₃), 119.7 (carbazoyl), 120.5 (carbazoyl), 120.6 (carbazoyl), 121.8 (q, ¹J_{CF} = 292.2 Hz, C(F₃)₃), 122.7 (imidazolylidene backbone C), 124.8 (imidazolylidene backbone C), 126.0 (carbazoyl), 126.4 (carbazoyl), 126.4 (carbazoyl), 129.2 (Mes *meta* C), 129.3 (Mes *meta* C), 130.8 (Mes *ortho* C(CH₃)), 133.2 (Mes *ortho* C(CH₃)), 135.4 (Mes *para* C(CH₃)), 141.5 (Mes *ipso* C), 164.7 (carbenic NCN). ¹⁹F{¹H} NMR (376 MHz, bromobenzene-d₅, 298K): δ_{F} -74.6. ²⁷Al{¹H} NMR (104 MHz, bromobenzene-d₅, 298K): δ_{Al} 35.4. Elemental microanalysis: calc. for C₄₆H₃₅AlF₃₆GeN₄O₄: C 37.05% H 2.37% N

3.76% meas. C 36.94% H 2.55% N 3.69%. Crystallographic data (for fluorobenzene hemisolvate): $C_{49}H_{37.5}AlF_{36.5}GeN_4O_4$ ($M_r = 1539.40$): orthorhombic, $Fdd2$, $a = 80.2560(12)$, $b = 29.4338(5)$, $c = 10.7141(2)$ Å, $V = 25309.3(7)$ Å³, $Z = 16$, $\rho_c = 1.616$ g cm⁻³, $T = 150$ K, $\lambda = 1.54184$ Å. $R_1 = 0.1155$ for 12751 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.3316$ for all 13230 unique reflections. Max. and min. residual electron densities 0.63, -0.39 e Å⁻³.

[(L^{Mes})Ge(DMAP)][Al{OC(CF₃)₃}]₄ (16): To a solution of **10** (generated in situ from **4** (200 mg, 0.46 mmol) and Li[Al{OC(CF₃)₃}]₄ (446 mg, 0.46 mmol) in fluorobenzene (5 mL)) was added dropwise at room temperature a solution of *N,N*-dimethylpyridin-4-amine (56 mg, 0.46 mmol) in fluorobenzene (3 mL), and the reaction mixture warmed to room temperature. After stirring for 12 h, the reaction mixture was filtered and volatiles removed in *vacuo* to obtain **16** as a yellow oil.

Spectroscopic data: ¹H NMR showed complete conversion to compound **16**. ¹H NMR (400 MHz, bromobenzene-d₅, 298K): δ_H 1.08 (9H, s, ^tBu C(CH₃)₃), 1.48 (6H, br s, N(CH₃)₂), 2.13 (3H, s, Mes *para* CH₃), 2.42 (6H, s, Mes *ortho* CH₃), 3.25 (2H, br m, ethylene CH₂), 3.60 (2H, t, ³J_{HH} = 4.57 Hz, ethylene CH₂), 5.95 (1H, br m, imidazolylidene backbone CH), 5.96 (1H, br m, imidazolylidene backbone CH), 6.34 (1H, d, ³J_{HH} = 1.6 Hz, DMAP *meta* CH), 6.63 (2H, s, Mes *meta* CH₂), 6.64 (1H, d, ³J_{HH} = 1.6 Hz, DMAP *meta* CH), 7.32 (2H, br s, DMAP *ortho* CH). ¹³C{¹H} NMR (126 MHz, bromobenzene-d₅, 298K): δ_C 17.4 (DMAP NCH₃), 21.2 (Mes *para* C(CH₃)), 31.1 (Mes *ortho* C(CH₃)), 38.7 (^tBu C(CH₃)₃), 43.7 (ethylene C), 53.4 (ethylene C), 56.2 (^tBu C(CH₃)₃), 79.5 (^tBu C(CH₃)₃), 106.8 (imidazolylidene backbone C), 106.8 (imidazolylidene backbone C), 121.9 (q, ¹J_{CF} = 291.7 Hz, C(CF₃)₃), 122.8 (DMAP *meta* C), 130.2 (Mes *meta* C), 132.5 (Mes *ipso* C), 140.7 (Mes *para* C(CH₃)), 145.3 (DMAP *ortho* C), 155.3 (Mes *ortho* C(CH₃)), 166.1 (carbenic NCN), DMAP *ipso* C resonance was not observed. ¹⁹F{¹H} NMR (376 MHz, bromobenzene-d₅, 298K): δ_F -74.6. ²⁷Al{¹H} NMR (104 MHz, bromobenzene-d₅, 298K): δ_{Al} 35.4.

$[(L^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**17**): To a mixture of compound **4** (200 mg, 0.46 mmol) and $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (446 mg, 0.46 mmol) was added dichloromethane (5 mL) at -78°C and the reaction mixture warmed to room temperature and stirred for 12 h, over which time a pale yellow solution and a white precipitate were formed. The reaction was filtered and the volatiles were removed in *vacuo*. Compound **17** was obtained as an off-white solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution of compound **17** in dichloromethane layered with hexane and stored at room temperature. Yield: 544 mg, 85%. Spectroscopic data: ^1H NMR (400 MHz, bromobenzene- d_5 , 298K): δ_{H} 0.90 (9H, s, $t\text{Bu C}(\text{CH}_3)_3$), 1.68 (3H, s, Mes *ortho* CH₃), 1.70 (3H, s, Mes *ortho* CH₃), 2.05 (3H, s, Mes CH₃ *para*), 2.50 (1H, d, $^2J_{\text{HH}} = 13.2$ Hz, CHCl), 2.79 (1H, d, $^2J_{\text{HH}} = 13.2$ Hz, CHCl), 2.97 (2H, m, ethylene CH₂), 3.67 (2H, m, ethylene CH₂), 6.57 (1H, br d, $^3J_{\text{HH}} = 1.1$ Hz, imidazolylidene backbone CH), 6.67 (1H, s, Mes *meta* CH), 6.69 (1H, s, Mes *meta* CH), 6.75 (1H, br d, $^3J_{\text{HH}} = 1.1$ Hz, imidazolylidene backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene- d_5 , 298K): δ_{C} 17.1 (Mes *ortho* C(CH₃)), 17.7 (Mes *ortho* C(CH₃)), 21.2 (Mes *para* C(CH₃)), 28.4 ($t\text{Bu C}(\text{CH}_3)_3$), 32.8 (CH₂Cl), 42.9 (ethylene C), 52.5 (ethylene C), 57.7 ($t\text{Bu C}(\text{CH}_3)_3$), 79.6 (C(CF₃)₃), 121.9 (q, $^1J_{\text{CF}} = 292.8$ Hz, C(CF₃)₃), 122.8 (imidazolylidene backbone C), 125.4 (imidazolylidene backbone C), 130.6 (Mes *para* C(CH₃)), 130.7 (Mes *meta* C), 130.8 (Mes *meta* C), 131.7 (Mes *ortho* C(CH₃)), 134.3 (Mes *ortho* C(CH₃)), 135.5 (Mes *ipso* C), 143.1 (carbenic NCN). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, bromobenzene- d_5 , 298K): δ_{F} -74.6. $^{27}\text{Al}\{^1\text{H}\}$ NMR (104 MHz, bromobenzene- d_5 , 298K): δ_{Al} 35.4. Elemental microanalysis: calc. for $\text{C}_{35}\text{H}_{28}\text{AlCl}_2\text{F}_{36}\text{GeN}_3\text{O}_4$: C 29.83% H 2.00% N 2.98% meas. C 29.75% H 2.15% N 2.94%. Crystallographic data: $\text{C}_{35}\text{H}_{28}\text{AlCl}_2\text{F}_{36}\text{GeN}_3\text{O}_4$ ($M_r = 1409.08$): monoclinic, $P2_1/c$, $a = 14.74170(10)$, $b = 13.18170(10)$, $c = 26.3043(2)$ Å, $\beta = 96.6750(10)^\circ$, $V = 5076.82(7)$ Å³, $Z = 4$, $\rho_c = 1.844$ g cm⁻³, $T = 150$ K, $\mu(\text{Cu K}\alpha) = 0.712$ mm⁻¹, $\lambda = 1.54184$ Å. $R_1 = 0.0588$ for 9782 observed unique reflections [$I > 2\sigma(I)$] and $wR_2 = 0.1574$ for all 10561 unique reflections. Max. and min. residual electron densities 1.006, -0.552 e Å⁻³.

4.6 References

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Chapter V

Synthesis and Reactivity of Group 14 Metallylene Compounds

Incorporating a N^{amido}P^{phosphino} Chelate Ligand System

5.1 Introduction

The last decade saw rapid development in main group element based catalysis, especially for the hydroboration of aldehydes and ketones.^{1,2} Low-valent germanium compounds have been shown to act as effective catalysts that rival the efficiency of transition metal complexes in this transformation (**Figure 5.1.1**).^{3–10} A major breakthrough in this field was made by Jones et al. in 2014, in which two-coordinate germanium (I) and tin (II) hydrides were synthesised by making use of extremely bulky amido ligands, and shown to exhibit high catalytic activity in the hydroboration of a wide range of aldehydes and ketones.¹¹ A plausible reaction mechanism was proposed and the rate-determining step was shown to be the σ -bond metathesis of HBpin with the germanium/tin alkoxide formed by hydrometallation of the carbonyl compound. The ability to effect this reaction in catalytic fashion (which has not been reported for other group 14 metal hydrides)^{12–14} and the high turnover frequency (TOF) were mainly attributed to the availability of the empty *p* orbital on the metal(II) centre of the hydrometallated intermediates.

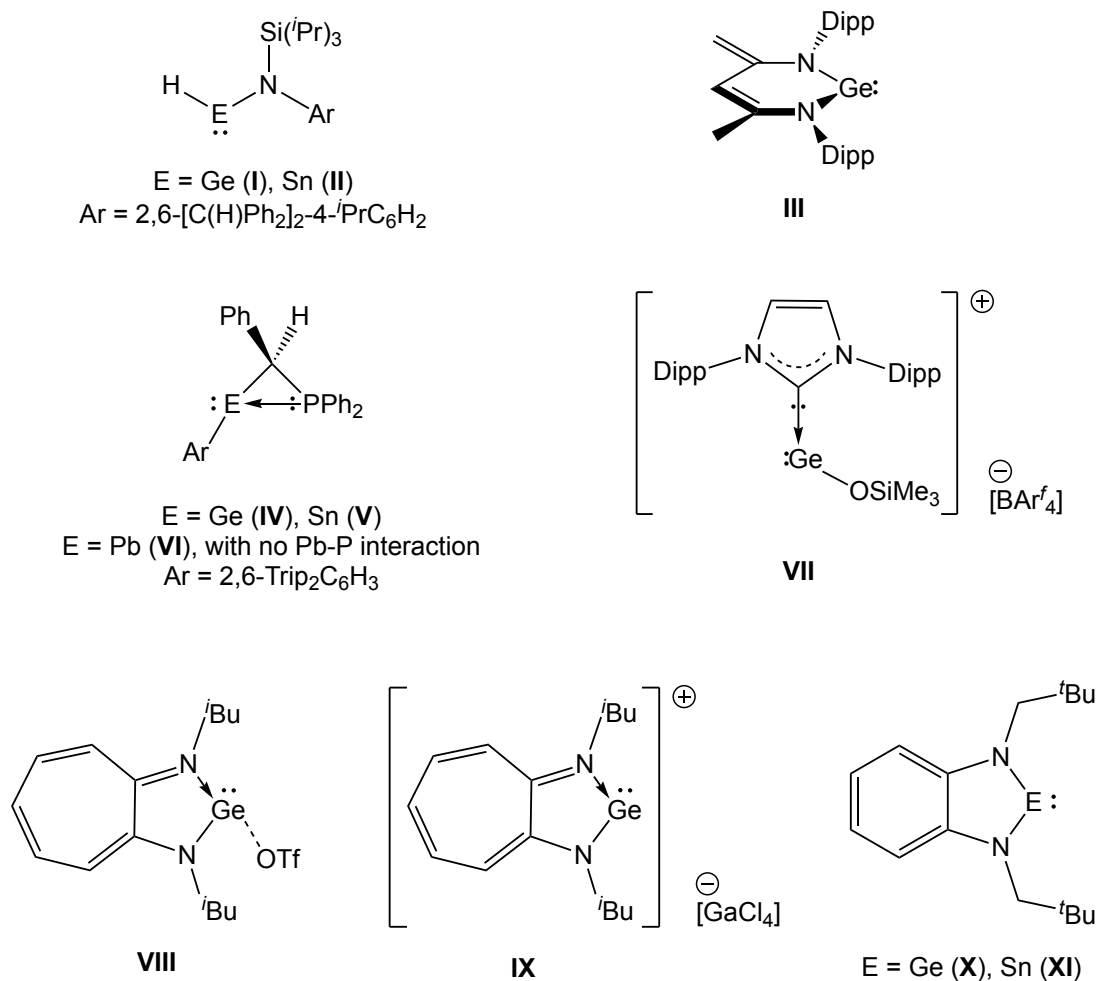


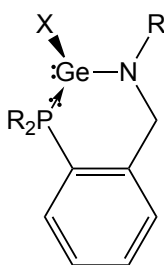
Figure 5.1.1: Previously reported Ge(II) and Sn(II) compounds which have been employed as catalysts for the hydroboration of carbonyl compounds.

Subsequently, the first example of an N-heterocyclic germylene (III) that effects catalytic turnover was reported by Zhao et al.¹⁵ Interestingly, the reaction mechanism was proposed to involve cooperative activation of the carbonyl function between the ligand and the Ge(II) centre. Wesemann et al. have also investigated the reactions between Lewis pairs featuring heavier group 14 element centres (Ge, IV; Sn, V; Pb, VI; **Figure 5.1.1**) and HBpin/carbonyl compounds.^{16,17} These tetrelene systems are stabilised by a tethered intramolecular phosphine donor as part of a three-membered ring. While all three Lewis pairs exhibit highly active catalytic performance, the reaction pathways and the actual catalytically active species vary in each case. *Cationic* germanium compounds have also been shown to promote the hydroboration of aldehydes and ketones. Rivard et al. reported the first siloxygermylium-

ylidene (**VII**) that is able to catalyse this transformation for sterically hindered ketone substrates.¹⁸ Shortly thereafter Nagendran et al. reported two Ge(II) cations (**VIII** and **IX**) stabilised by aminotropoiminate (ATI) ligands which are capable of catalysing the hydroboration of a variety of ketones and aldehydes.¹⁹ Around the same time Khan et al. also studied the catalytic performance of previously reported N-heterocyclic germylene (**X**) and stannylene species (**XI**) in cyanosilylation and hydroboration reactions.^{20–22} Encouraged by these results, we thought that it would be of interest to develop novel low-valent germanium compounds and apply these systems in catalysis. Ideally they would have a low coordination number around the metal centre in order to promote high reactivity, and potentially give better catalytic performance compared to the existing systems.

5.2 Project aims

At the outset, the aim of this part of the project was to synthesise and characterise novel low-valent germanium(II) compounds incorporating a $N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ chelateing ligand system (**Figure 5.2.1**) and study their reactivity towards small molecules. This type of compound might also be described as a Ge(II)-P Lewis pair. Replacement of the strongly σ -donating NHC in the $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligands described in Chapters 3 and 4 with a more weakly donating, potentially hemi-labile phosphine donor could potentially lead to novel and/or higher reactivities in bond activation and ultimately catalysis. The resulting germylenes might also form interesting heterometallic complexes with transition metals, which themselves might be of interest in cooperative bond activation processes. The target ligand scaffold was chosen to have a six-membered P-Ge-N chelating ring analogous to the $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised tetrelenes studied in previous parts of the project. The ligand system and its phosphorus oxide form have previously been applied in the synthesis of transition metal complexes but not in main group coordination chemistry.^{23–29}



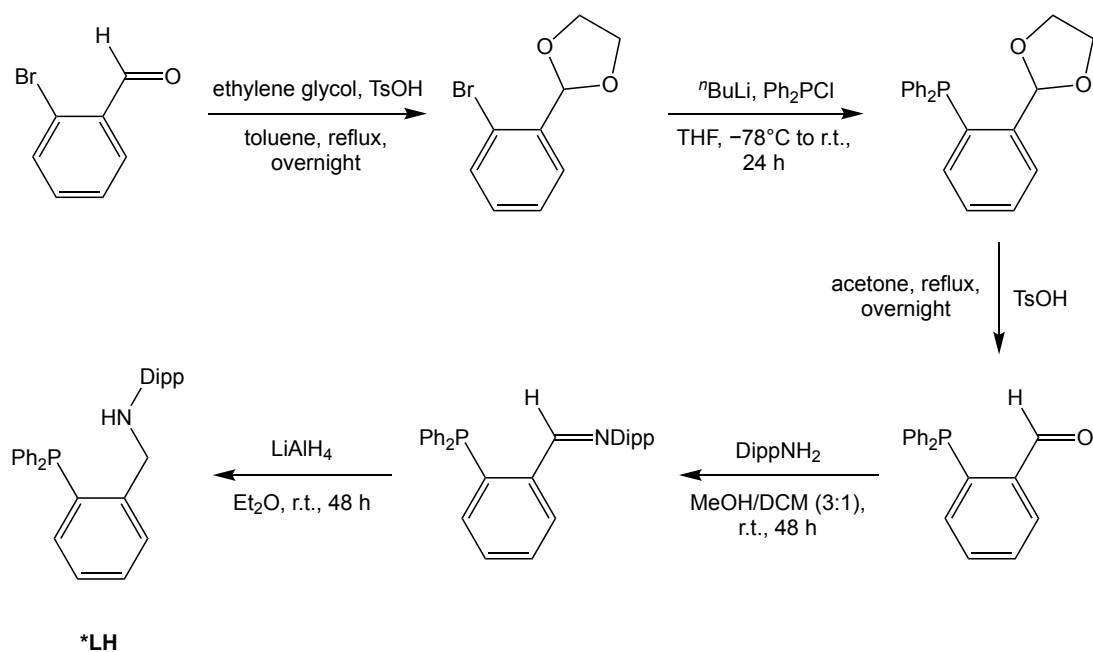
X = halide/alkyl/aryl, R = alkyl/aryl

Figure 5.2.1: Generic form of a germylene incorporating the target N^{amido}P^{phosphino} chelate ligand.

5.3 Results and discussion

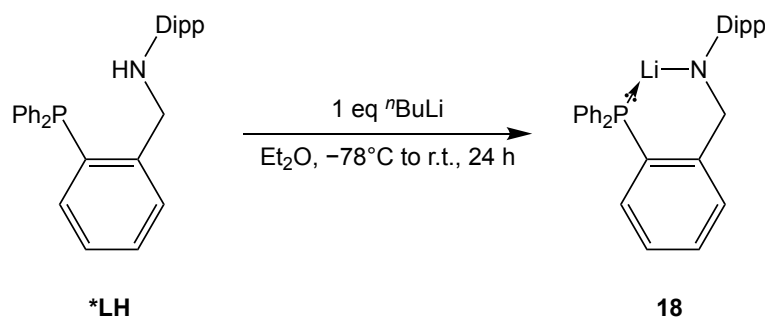
5.3.1 Synthesis of *LLi, **18** and *LGeCl, **19**

The protio-ligand *LH (*L = *ortho*-Ph₂P(C₆H₄)CH₂NDipp) was synthesised in five steps following literature procedures (**Scheme 5.3.1**).^{27,29} The final product is air and moisture stable and can be recrystallised from diethyl ether and isolated as colourless crystals in ca. 31% overall yield.



Scheme 5.3.1: Synthetic route to *LH.

Attempts were made to lithiate ***LH** to generate the novel lithiated ligand ***LLi**, **18** (**Scheme 5.3.2**). Dissolving ***LH** in the minimal amount of diethyl ether followed by dropwise addition of 1.2 equivalents of $n\text{BuLi}$ at -78°C gave a bright yellow solution, which generated a white suspension once warmed to room temperature. The suspension was filtered, and the residue washed with hexane before drying in vacuo and isolated as a white powder in 74% yield.

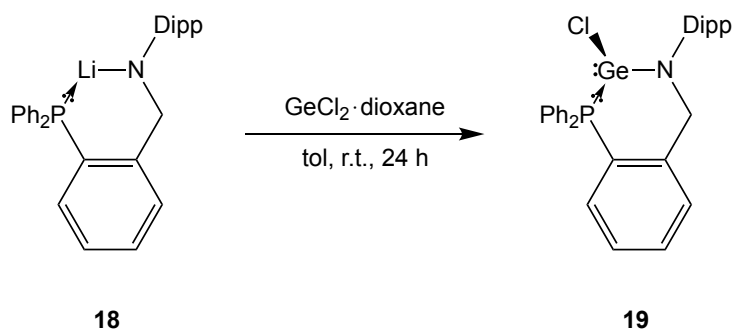


Scheme 5.3.2: Lithiation of ***LH** to give ***LLi**, **18**.

18 has been characterised by multinuclear NMR spectroscopy and was used for further reactivity without additional purification. Due to its low solubility in hydrocarbon solvents such as benzene and toluene, NMR measurements were carried out in THF- d_8 , in which it dissolves to give a bright orange solution. In the ^1H NMR spectrum, the Dipp $i\text{Pr}$ groups give rise to signals at $\delta_{\text{H}} = 1.03$ (12H, s) and 3.84 (2H, sep). Two broad doublets at $\delta_{\text{H}} = 4.67$ and 4.68 ppm can be assigned to the inequivalent methylene protons. The state of aggregation of **18** - in the absence of crystallographic data - cannot be definitively ascertained. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a broad singlet can be found at $\delta_{\text{P}} = -15.9$ ppm, which is close to the value measured for ***LH** (-15.6 ppm). Although the lithiated ligand **18** is very air- and moisture-sensitive and turns yellow instantly when exposed to air, it is stable under a nitrogen atmosphere for several months without decomposition.

***LLi** (**18**) can be shown to undergo a salt metathesis reaction with $\text{GeCl}_2 \cdot \text{dioxane}$ in toluene to afford the corresponding chlorogermylene ***LGeCl**, **19** (**Scheme 5.3.3**). The reaction at room temperature initially forms a white suspension, which gradually becomes clearer and

forms a pale green solution with precipitate within one hour. Removal of the solvent after filtration gives an oily solid of low purity as shown in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Compound **19** could be crystallised by dissolving a crude sample in a mixture of toluene and hexane and storing at -30°C overnight. Using this approach, a pale yellow green crystalline solid was isolated in good yield (67%), and in good purity (on the basis of ^1H NMR spectroscopic measurements).



Scheme 5.3.3: Synthesis of chlorogermylene, **19**, from $^*\text{LLi}$, **18**.

The formation of compound **19** was “hinted” at by the enhanced solubility in the reaction solvent (i.e. toluene or benzene). It has been fully characterised by multinuclear NMR spectroscopy and elemental microanalysis. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, **19** is characterised by a singlet at $\delta_{\text{P}} = -24.4$ ppm. This chemical shift is comparable to previously reported phosphine-stabilised germylenes as outlined in **Figure 5.3.1**.^{16,30,31}

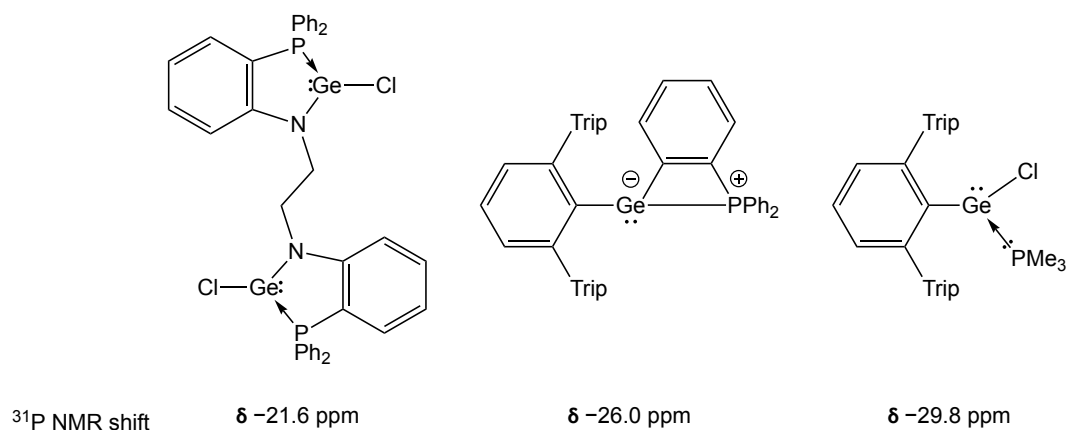
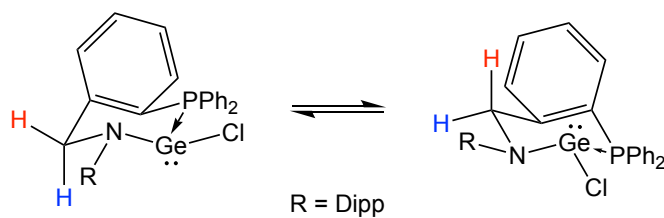


Figure 5.3.1: Previously reported phosphine stabilised germylenes and their $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts.

In the ^1H NMR spectrum of **19** at 298K, the signals for the Dipp $i\text{Pr}$ groups and methylene CH_2 unit are broad, presumably due to fluxional processes occurring under ambient conditions. The observed fluxionality presumably results from the interconversion of the chair conformation (ring flip) of compound **19** (**Scheme 5.3.4**), as postulated for compound **5** (Chapter 3).



Scheme 5.3.4: Ring flip of **19**.

The kinetics of this phenomenon were studied by VT ^1H NMR spectra measured in toluene- d_8 at five different temperatures in the range 193 to 298K (**Figure 5.3.2**).

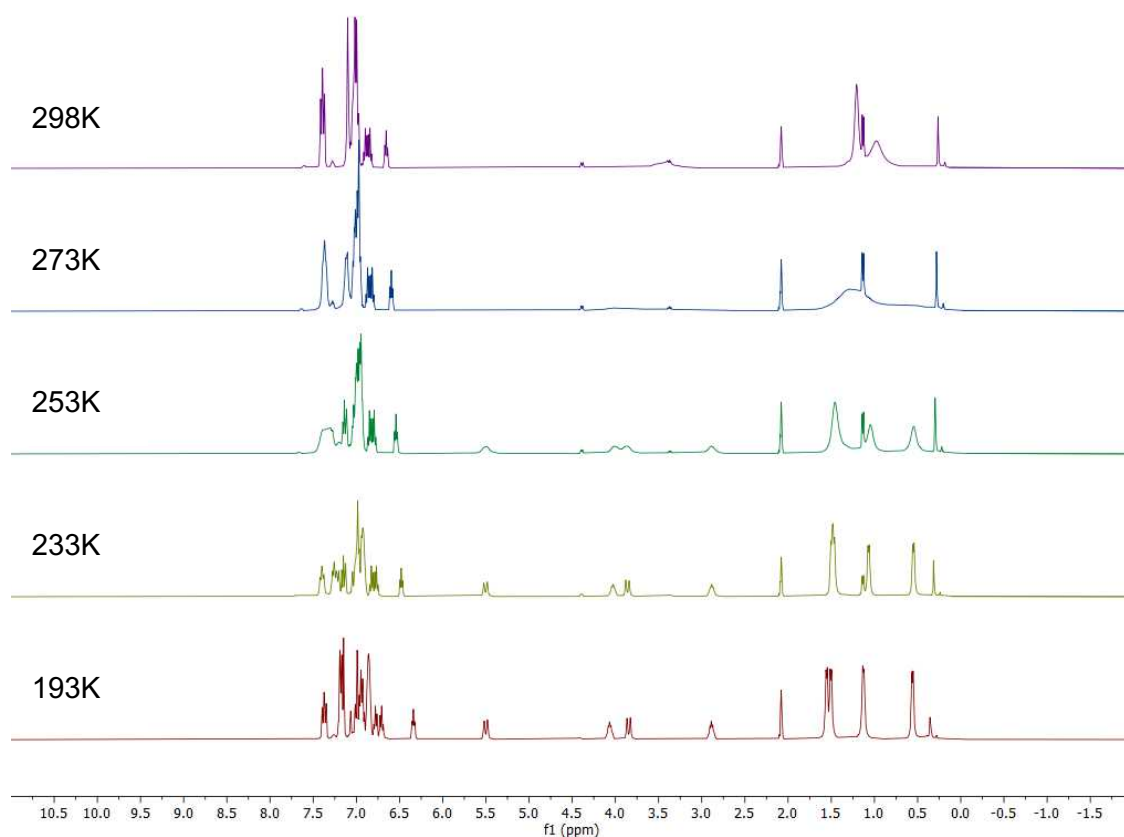


Figure 5.3.2: ^1H NMR spectra at various temperatures of compound **19** in toluene- d_8 .

From these data, the activation energy ($\Delta G^\ddagger$) for the exchange process can be estimated from the signals for the methylene CH_2 protons (via the Eyring equation) as 46.3 kJ mol^{-1} at the coalescence temperature T_c (ca. 253K). This energy barrier is comparable to the value calculated for the fluxional process in compound **5** which incorporates a $\text{N}_{\text{amido}}^{\wedge}\text{C}_{\text{NHC}}$ ligand ($\Delta G^\ddagger = 49(1) \text{ kJ mol}^{-1}$; Chapter 3). The relative insensitivity to the nature of the donor implies that the phosphine (or NHC) group does not dissociate from the Ge(II) centre during the fluxional processes. Such a dissociative event would presumably involve a higher activation barrier for the system incorporating the stronger NHC donor.

Single crystals of **19** suitable for X-ray crystallography can be obtained by layering a concentrated toluene solution with hexane and storage at -30°C . Compound **19** crystallises in the triclinic $P-1$ space group and the asymmetric unit consists of a single monomeric germylene species (**Figure 5.3.3**).

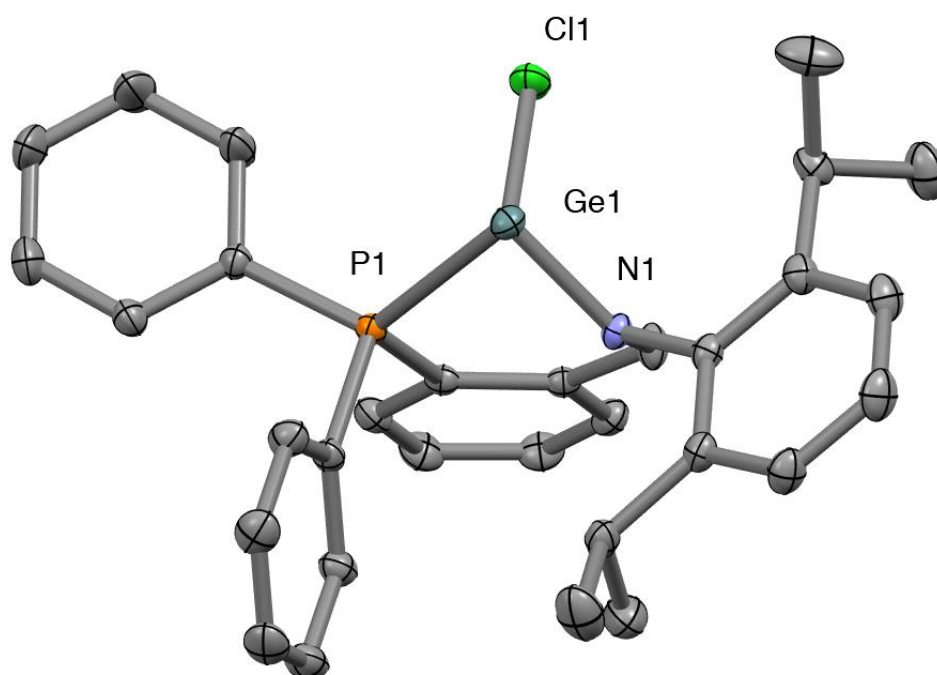
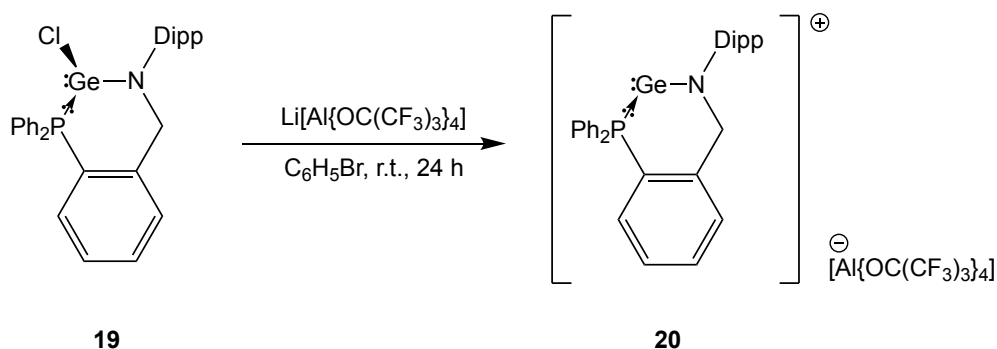


Figure 5.3.3: Molecular structure of $^*\text{LGeCl}$, **19**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Cl(1)-Ge(1) 2.3330(4), Ge(1)-N(1) 1.8894(12), Ge(1)-P(1) 2.4659(4), Cl(1)-Ge(1)-N(1) 98.96(4), Cl(1)-Ge(1)-P(1) 90.494(14), P(1)-Ge(1)-N(1) 84.39(4).

The Ge-Cl bond length (2.3330(4) Å) is in accordance with those measured for previously reported chlorogermylene incorporating a $N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ ligand (e.g. 2.2934(8) Å for $\text{Ph}_2\text{PC}\{\text{C}(\text{Me})\text{N}(\text{Dipp})\}_2\text{GeCl}$ reported by Roesky et al.).^{32,33} The Ge-N distance (1.8894(12) Å) is towards the shorter end of the range (ca. 1.9-2.0 Å) reported for literature examples.^{30,32-35} The Ge-P distance (2.4659(4) Å) is longer than typical Ge-P covalent bonds (2.33-2.37 Å)^{16,36-38} but comparable to reported phosphine-stabilised germynes (e.g. 2.4437(12) Å for the digermylene $(\text{PNNP})(\text{GeCl})_2$ ($\text{PNNP} = \{\text{PPh}_2(2\text{-C}_6\text{H}_4)\text{NH}(\text{CH}_2)\}_2$) reported by Goicoechea et al.).^{30,32,34,35,37,39-42} indicating that a description as a dative interaction between the phosphine and the metal centre is most appropriate. As is typical for chlorogermynes, the chloride group in **19** is aligned almost perpendicular to the P(1)-Ge(1)-N(1) plane with a mean angle of 94.7°, which reflects a low degree of *s/p* orbital hybridisation at the germanium(II) centre. Once synthesised, compound **19** serves as a versatile precursor for the subsequent synthesis of more reactive derivatives such as germylium-ylidenes and alkoxo/aryloxo/amido-substituted germynes as outlined below.

5.3.2 Synthesis and reactivity of germylium-ylidene $[(*\text{L})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **20**

Following the same method as employed for the synthesis of germylium-ylidenes **9** and **10** which employ a $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ ligand system (see Chapters 3 and 4), the N,P-stabilised system **20** could also be accessed. Accordingly, combining chlorogermylene **19** with one equivalent of $\text{Li}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (as the weakly coordinating anion source) in bromobenzene leads to the formation of the halide abstraction product $[(*\text{L})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, **20** (**Scheme 5.3.5**).



Scheme 5.3.5: Synthesis of germylium-ylidene, **20**, from chlorogermylene precursor **19**.

The ^1H NMR spectrum of **20** can be compared to that of its precursor compound **19** (both measured in bromobenzene- d_5). On chloride abstraction, the signals associated with the Dipp ^iPr groups become sharper and shift upfield from $\delta_{\text{H}} = 0.91$ (6H), 1.12 (6H) and 3.33 (2H) ppm to 0.81 (6H), 0.91 (6H) and 2.30 (2H) ppm. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the singlet signal shifts significantly downfield from $\delta_{\text{P}} = -24.4$ to -2.4 ppm compared to the chlorogermylene **19**. This change is consistent with the formation of a more electron deficient Ge(II) centre.

Single crystals for X-ray crystallography were obtained by layering a concentrated solution in fluorobenzene with hexane at storage at -30°C . Compound **20** crystallises in the triclinic $P-1$ space group, and the asymmetric unit contains a monomeric Ge cation and an aluminate counteranion (**Figure 5.3.4**). There are no close contacts between anion and cation. To the best of our knowledge, it represents the first example of a cyclic $\text{N}_{\text{amido}}^{\wedge}\text{P}_{\text{phosphino}}$ chelate stabilised germylium-ylidene.

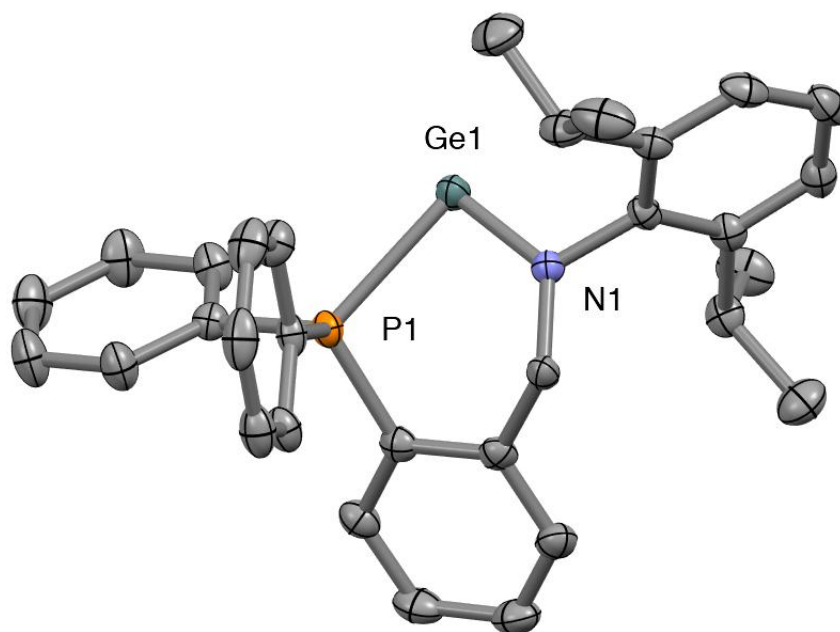
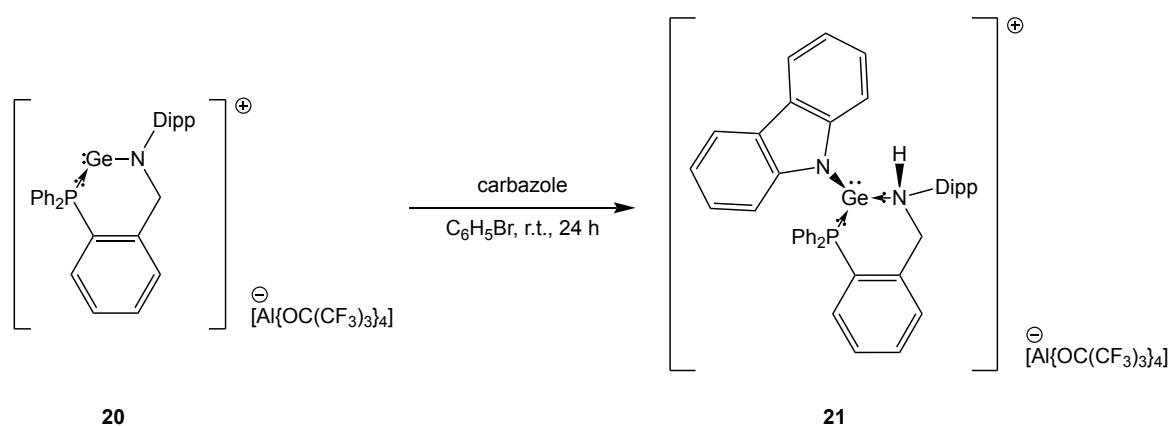


Figure 5.3.4: Molecular structure of the cationic component of compound **20**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ge(1)-N(1) 1.815(3), Ge(1)-P(1) 2.4418(10), P(1)-Ge(1)-N(1) 88.61(11).

Compared to the chlorogermylene **19**, both Ge-N and Ge-P bond lengths are shortened significantly - from 1.8894(12) to 1.815(3) Å for the former and 2.4659(4) to 2.4418(10) Å for the latter. This observation is in line with the decrease in coordination number around Ge(II) from three to two. The P-Ge-N chelate angle 88.61(11)° is even smaller than that measured for Ge cations **9** (93.13(15)°) and **10** (91.84(19)°). This, together with the presence of π donors, potentially indicates a relatively large HOMO-LUMO gap for **20**, and consequently low reactivity towards concerted E-H bond activation processes.

As shown in Chapter 4, the reactivity of germylium-ylidenes towards protic E-H bonds is more strongly correlated with LUMO energy than with the HOMO-LUMO gap. As such, we tested the reactivity of **20** towards polar protic N-H bonds by reacting it with one equivalent of carbazole in fluorobenzene. Similar reaction conditions to those employed in the synthesis of compound **15** (described in Chapter 4) were also used here (**Scheme 5.3.6**). Upon addition of carbazole, the colour of the reaction mixture changed from bright yellow to pale yellow and the in situ product was characterised by multinuclear NMR spectroscopy. The isolated compound **15** from recrystallisation was also characterised by ^1H NMR and display the same set of resonances as the in situ characterised product despite having relatively low solubility in bromobenzene- d_5 .



Scheme 5.3.6: Synthesis of N-H activation product, **21**, from the germylium-ylidene **20**.

In the ^1H NMR spectrum, four doublets of 3H each are observed for the Dipp ^iPr groups with the most shielded signal found at $\delta_{\text{H}} = 0.03$ ppm. The N-H signal was measured at $\delta_{\text{H}} = 6.02$ ppm with a $^3J_{\text{HP}}$ coupling of 11.1 Hz. In the $^{31}\text{P}\{^1\text{H}\}$ NMR a singlet is observed at $\delta_{\text{P}} = -9.4$ ppm, representing an upfield shift from the germylium-ylidene precursor **20** (-2.4 ppm).

Single crystals suitable for X-ray diffraction were obtained by layering a concentrated solution in fluorobenzene with hexane stored at -30°C . Compound **21** crystallises in a monoclinic $C2/c$ space group and the asymmetric unit contains a monomeric cation, partnered with an aluminate counterion (**Figure 5.3.5**). This provides further evidence for the formation of an N-H activation product via cleavage of the N-H bond in carbazole across the germanium centre and the N_{amido} ligand.

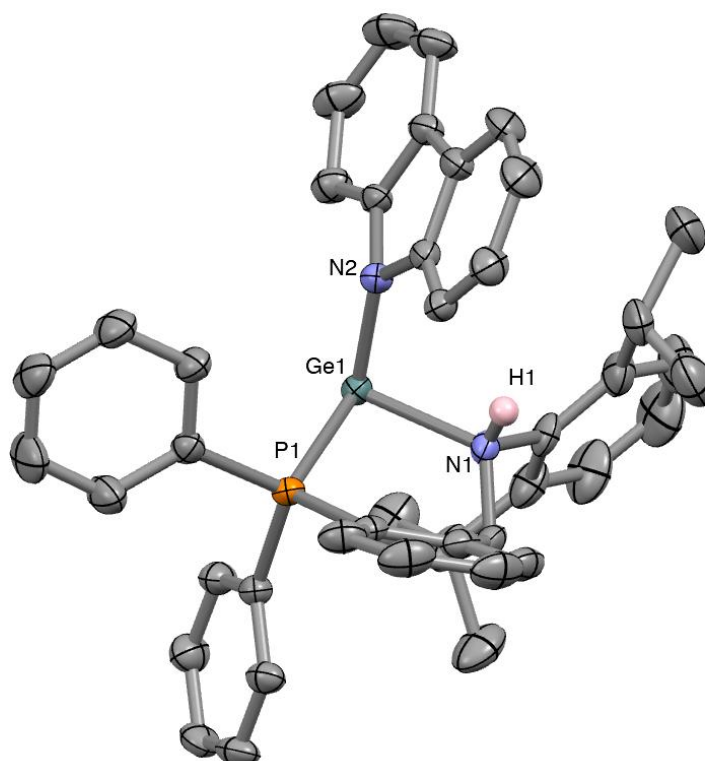


Figure 5.3.5: Molecular structure of the cationic component of the carbazole activation product, **21**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ge(1)-N(1) 1.923(3), Ge(1)-P(1) 2.4815(10), P(1)-Ge(1)-N(1) 86.80(9).

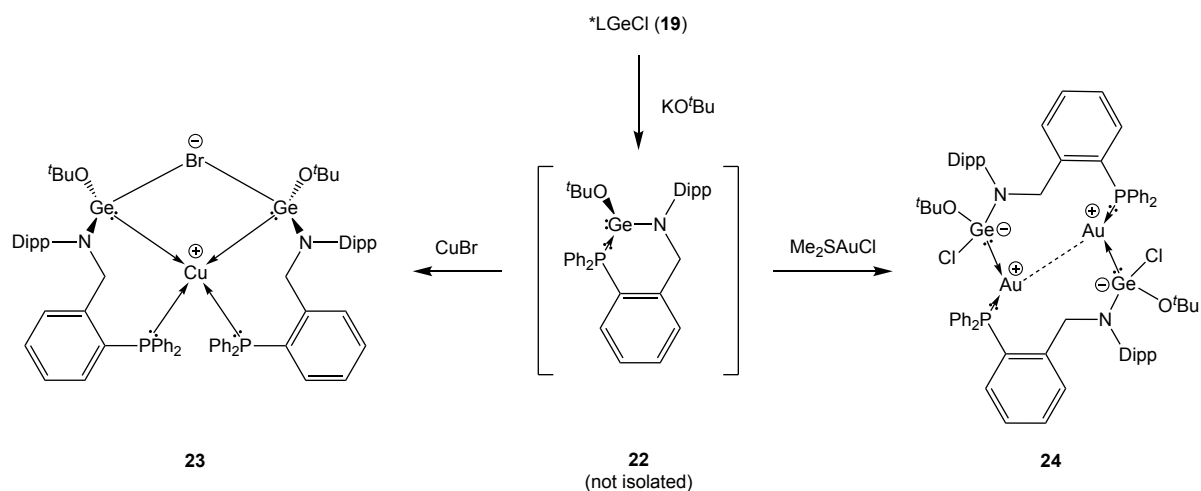
The Ge-N distance is elongated from 1.815(3) (in precursor **20**) to 1.923(3) Å, and the geometry at N(1) changes from trigonal planar to non-planar in **21**. Both features imply that the N-H bond has been cleaved across the Ge-N linkage and that the anionic amido group has been converted to a neutral secondary amine donor, as is also observed in the cases of germylium-ylidenes **9** and **10**. The Ge-P distance (2.4815(10) Å) and P-Ge-N angle (86.80(9)°) remain similar to cation **20** (2.4418(10) Å and 88.61(11)° respectively). As shown previously, it is evident that H1 and the carbazole fragment are added to the same side of the Ge1-N1-P1 unit, implying a 1,2-*syn*-addition mechanism. The cooperative activation of N-H bond by compound **20** can be rationalised in the same way as cations **9** and **10** (see Chapter 4 for detailed discussion).

5.3.3 Synthesis of *LGeO^tBu, **22**, and its characterisation through the formation of heterometallic complexes featuring copper (**23**) and gold (**24**)

In the catalytic hydroboration studies reported by Jones et al.,¹¹ the catalytically active 2-coordinate tin(II) hydride was generated in situ from the related tin(II) *tert*-butoxide, which acts as a convenient pre-catalyst. This compound is reported to be significantly more thermally stable and air-/moisture tolerant than the hydride species. Therefore, another interesting synthetic target from the chlorogermylene **19** precursor would be an alkoxy/aryloxy germylene, which can potentially be accessed from chloride substitution via salt metathesis with the corresponding alkali metal alkoxide/aryloxide. We first tried to substitute the chloride for a *tert*-butoxide group using one equivalent of the commercially available KO^tBu in both benzene and toluene. Although attempts to crystallise the product (compound **22**) have not been successful due to its oily nature, spectroscopic data can be obtained from in situ NMR spectra to provide evidence for the formation of an alkoxo-germylene product. In the ¹H NMR spectrum, a 9H singlet at $\delta_{\text{H}} = 1.30$ ppm can be assigned to the *tert*-butoxide fragment. The resonances assigned to the Dipp ⁱPr groups are shifted slightly from the precursor **19**, being two sharp doublets at 0.99 (6H) and 1.29 (6H) ppm and a broad septet at 3.42 (2H) ppm. The methylene

CH₂ signal is shifted from 4.76 to 4.93 ppm. The ³¹P{¹H} NMR signal is also shifted slightly from δ_P = -24.4 to -22.8 ppm.

Divalent germanium compounds have been investigated as electron donating ligands when combined with group 11 transition metals (Cu, Ag, Au).^{30,43–53} In order to confirm the formation of compound **19** (given the lack of crystallographic authentication) samples were synthesised in situ and reacted with the group 11 metal halides, CuBr and Me₂SAuCl (**Scheme 5.3.7**) with the aim of generating crystalline bimetallic systems, from which the prior formation of **19** could then be inferred. The corresponding reaction with AgCl under the same conditions led to complete decomposition to *LH. Interestingly, for both reactions one equivalent of transition metal reagent was added, yet **19** forms a 2:1 adduct with Cu and 1:1 adduct with Au under the same reaction conditions, as illustrated by the solid-state structures of the products **23** and **24** (vide infra).



Scheme 5.3.7: In situ synthesis of $^*LGeO^tBu$ and its reactivity towards copper and gold halides.

The reaction of **19** with one equivalent of $CuBr$ yielded the tetrahedral $Cu(I)$ adduct **23**. Single crystals suitable for X-ray crystallography were obtained from a concentrated hexane solution (**Figure 5.3.6**). Unfortunately no satisfactory NMR data could be obtained even from crystalline samples of **23** - due to the low solubility of the crystalline material in common NMR solvents (e.g. benzene- d_6 , THF- d_8 or bromobenzene- d_5). Moreover **23** decomposes on

exposure to halogenated solvents such as dichloromethane so attempts to obtain NMR spectra in these media were also unsuccessful. Nonetheless, the connectivity revealed for **23** by the crystallographic study does provide evidence for the proposed formulation of the *tert*-butoxygermylene system **19**.

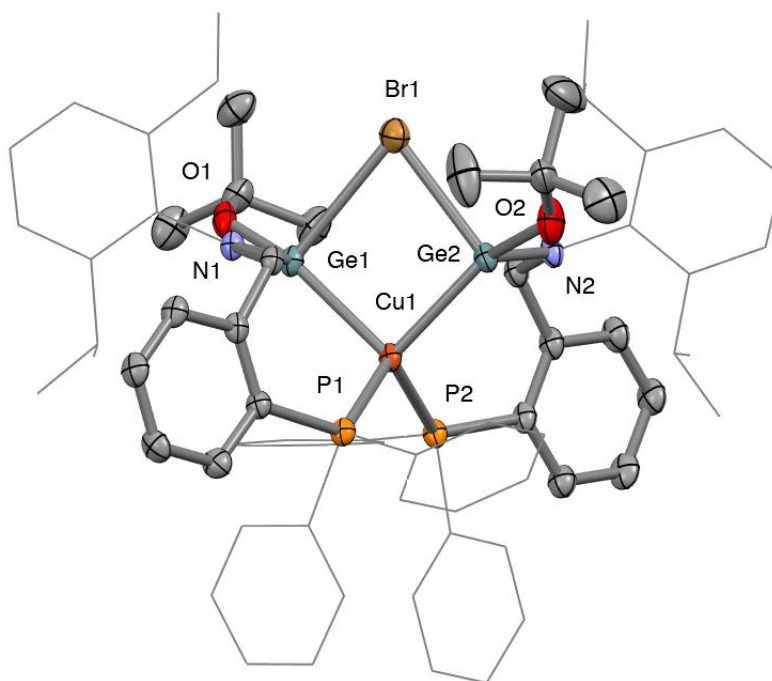


Figure 5.3.6: Molecular structure of compound **23**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. The Dipp and phenyl groups are shown in wireframe format. Selected bond lengths (Å) and angles (°): Ge(1)-O(1) 1.850(3), Ge(1)-N(1) 1.841(3), Ge(1)-Br(1) 2.8221(6), Ge(1)-Cu(1) 2.4426(6), P(1)-Cu(1) 2.3387(9), Ge(2)-O(2) 1.814(3), Ge(2)-N(2) 1.845(3), Ge(2)-Br(1) 2.7082(6), Ge(2)-Cu(1) 2.4208(6), P(2)-Cu(1) 2.3318(9), Ge(1)-Cu(1)-Ge(2) 90.95(2), Ge(1)-Cu(1)-P(1) 106.78(3), Ge(2)-Cu(1)-P(2) 106.26(3), P(1)-Cu(1)-P(2) 112.09(3).

Complex **23** crystallises in the triclinic *P*-1 space group and the asymmetric unit contains a CuBr unit ligated by two molecules of **19**: each germanium atom is covalently bonded to a *tert*-butoxide and a N_{amido} group, as well as acting as a σ donor ligand to the copper atom. The copper centre features a slightly distorted tetrahedral geometry, with coordination from two germylene donors and two PPh₂ groups. Whilst the mean P-Cu bond length (2.335 Å) is comparable to literature examples (e.g. 2.320 Å (mean) for the Cu(I) PGeP pincer complex [Cu{ κ^3 P,Ge,*P*-GeCl(pyrmP^{*i*}Pr₂)₂CMe₂}(PPh₃)]; (HpyrmP^{*i*}Pr₂)₂CMe₂ = 5,5-dimethyl-1,9-bis(di-isopropylphosphanylmethyl)dipyrromethane reported by Cabeza et al.),^{30,52} the

average Ge-Cu distance (2.432 Å) is exceptionally long for a donor-acceptor bond. The reported Ge-Cu distances for all germyl, base-stabilised and non-base-stabilised copper(I) complexes fall in the range 2.21–2.38 Å.^{30,45–48,50–56} As such, the long bond length in complex **23** indicates a weak Ge(II)-Cu(I) interaction.

With respect to the chemistry with Me₂SAuCl, an in situ ¹H NMR spectrum of compound **24** within the reaction mixture features a doublet (12H) at 1.21 ppm and a septet (2H) at 3.27 ppm for the Dipp ⁱPr group, a doublet (2H) at 4.53 ppm for the methylene CH₂ as well as a singlet (9H) at 1.62 ppm. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated solution in toluene with hexane and stored at room temperature for 1 h and confirmed to be a dimeric Ge(II)-Au complex (**Figure 5.3.7**).

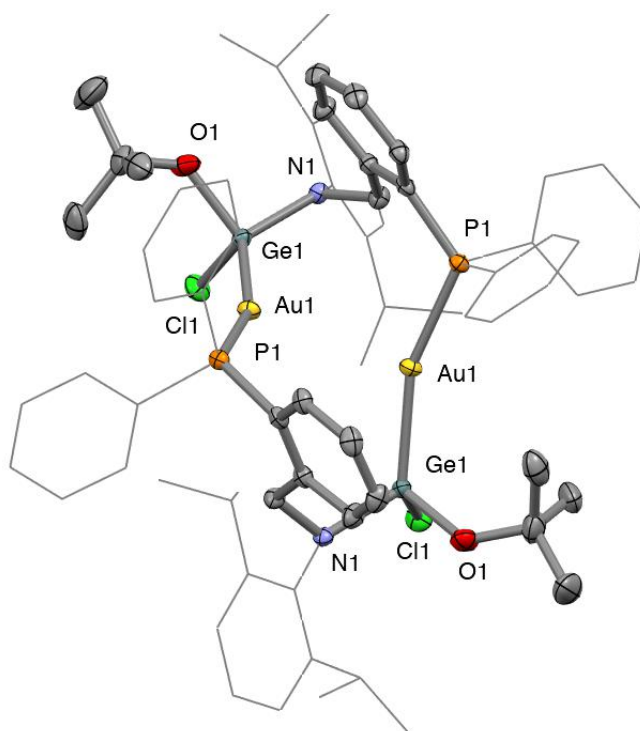


Figure 5.3.7: Molecular structure of compound, **24**, as determined by X-ray crystallography. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. The Dipp and phenyl groups are shown in wireframe format. Selected bond lengths (Å) and angles (°): Ge(1)-Au(1) 2.4101(4), Ge(1)-N(1) 1.856(3), Ge(1)-Cl(1) 2.2086(9), Ge(1)-O(1) 1.803(3), P(1)-Au(1) 2.3357(8), Au(1)-Au(1) 3.3434(2), O(1)-Ge(1)-N(1) 98.77(12), O(1)-Ge(1)-Cl(1) 101.13(11), Cl(1)-Ge(1)-Au(1) 115.05(3), N(1)-Ge(1)-Au(1) 120.58(8), Ge(1)-Au(1)-P(1) 159.36(2).

Compound **24** is dimeric and crystallises in the monoclinic $I2/a$ space group. The asymmetric unit contains one monomeric fragment and the other half of the dimer is generated by a C_2 rotational axis. The solid-state structure reveals that the Au-Cl bond essentially inserts into the Ge-P Lewis pair of the pre-formed $^*LGeO^tBu$. The Ge-Au distances (2.4101(4) Å) are in line with reported germyl gold complexes.^{30,43,56–60} The Au-Au distance (3.3434(2) Å) is shorter than the van der Waals radii of gold (3.7 Å) and the Ge-Au-P fragment is not linear (159.36(2)°), both suggesting the presence of a (weak) aurophilic interaction and the potential cause of aggregation.^{57,61}

5.3.4 Syntheses of $^*LGe\{N(SiMe_3)_2\}$, **25**, and $^*LGe\{O(C_{10}H_7-1)\}$, **26**

In search of a germylene derivative that might act as a facile source of a germanium hydride, and that could be isolated cleanly (and characterised crystallographically), we reacted crystalline samples of compound **19** with one equivalent of each of the $Li[N(SiMe_3)_2]$ and $Li[O(C_{10}H_7-1)]$ (**Scheme 5.3.8**).⁶²



Scheme 5.3.8: Reaction of *LGeCl , **19** with $Li[N(SiMe_3)_2]$ and $Li[O(C_{10}H_7-1)]$ to afford compounds **25** and **26**.

In the case of $^*LGe\{N(SiMe_3)_2\}$ (**25**), in situ 1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were shown to be relatively clean, containing only a trace amount of *LH (less than 1%). In the 1H spectrum, a singlet (18H) corresponding to the trimethylsilyl groups is found at $\delta_H = 0.38$ ppm, while the Dipp iPr groups give rise to two doublets and a septet (6H, 6H and 2H) at $\delta_H = 1.04$, 1.22 and 3.42 ppm, respectively. The methylene CH_2 group is seen as two broad

overlapping doublets at $\delta_{\text{H}} = 5.58$ ppm. The ^{31}P signal is slightly shifted downfield to $\delta_{\text{P}} = -18.5$ ppm from **19** (-24.4 ppm). Despite being 99% spectroscopically pure, multiple attempts to crystallise this compound were unsuccessful. Therefore we chose to react **19** with the lithium 1-naphthoxide $\text{Li}[\text{O}(\text{C}_{10}\text{H}_7-1)]$ in order to obtain a crystalline product; in this case the naphthoxy-germylene $^*\text{LGe}\{\text{O}(\text{C}_{10}\text{H}_7-1)\}$, **26** could be obtained and in this case structurally characterised by X-ray crystallography. Again, the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR of the isolated, crystalline compound **26** were relatively clean with ca. 6% of $^*\text{LH}$ and other impurities. The ^1H NMR spectrum features two doublets (6H each) at 0.97 and 1.13 ppm and a septet (2H) at 3.53 ppm, corresponding to the Dipp ^iPr groups. The methylene CH_2 group comes at 4.93 ppm as a doublet. The $^{31}\text{P}\{^1\text{H}\}$ NMR signal is slightly shifted upfield to -26.1 ppm compared to **19** (-24.4 ppm). Single crystals of **26** suitable for X-ray crystallographic studies were obtained from a concentrated solution in benzene (**Figure 5.3.8**).

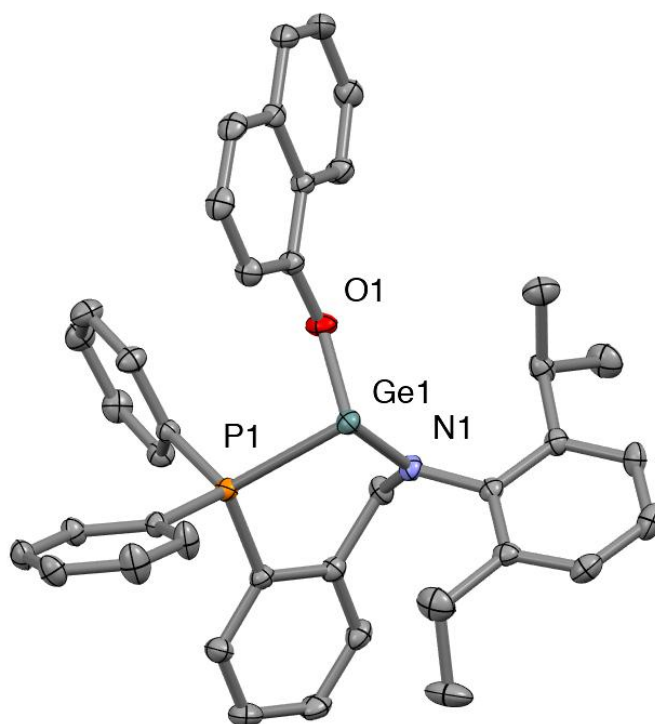
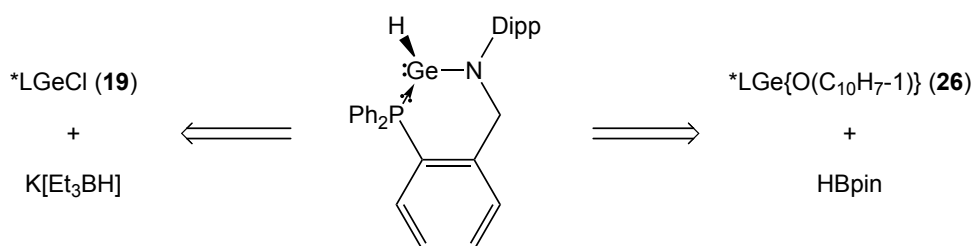


Figure 5.3.8: Molecular structure as determined by X-ray crystallography and a picture of crystals of $^*\text{LGe}\{\text{O}(\text{C}_{10}\text{H}_7-1)\}$, **26**. Thermal ellipsoids set at 40% possibility level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ge(1)-N(1) 1.8811(14), Ge(1)-P(1) 2.5277(5), Ge(1)-O(1) 1.8946(14), P(1)-Ge(1)-N(1) 87.63(5), O(1)-Ge(1)-N(1) 97.01(6), O(1)-Ge(1)-P(1) 89.48(5).

Compound **26** crystallises in a monoclinic $P2_1/n$ space group and the asymmetric unit contains a monomeric three-coordinate germanium species. The Ge-N bond length (1.8811(14) Å) is comparable to that of compound **19** (1.8894(12) Å) and the Ge-P distance is slightly lengthened (2.4659(4) to 2.5277(5) Å), implying an even weaker interaction within the phosphine/Ge(II) Lewis pair than in compound **19**. Compound **26** can be crystallised and isolated relatively cleanly (less than 10% *LH) with a moderate yield (60%). The small amount of *LH present in the crystalline **26** might come from protonation in the reaction mixture which leads to co-crystallisation of *LH with the product **26**. With the isolated **26** in hand, we sought to examine its reactivity as a pre-catalyst for catalytic hydroboration reactions.

5.3.5 Catalytic hydroboration reactions using compound **26** as a pre-catalyst

Intrigued by the reports of hydridogermynes (e.g. **1**) capable of catalysing hydroboration reactions with efficiencies that rival transition metal catalysts,^{10,11} we were interested to probe the possibility of synthesising *LGeH, i.e. a Ge(II) hydride stabilised by the chelating N-amido[^]P-phosphino ligand (*L) and to investigate its catalytic reactivity in organic reactions. Our hypothesis was that the weakly bound nature of the phosphine ligand in such a system (hinted at by the long Ge-P distances in related systems) might render it hemi-labile under catalytic conditions, thereby generating a low-coordinate amidogermanium hydride (similar to Jones' systems), which would prove to be highly reactive towards ketone/aldehyde substrates. *LGeH could potentially be accessed via two different routes - either by reacting *LGeCl (**19**) with a relatively ionic hydride source (e.g. K[Et₃BH]), or by taking *LGe{O(C₁₀H₇-1)} (**26**) with HBpin in a manner similar to the chemistry reported by Jones (**Scheme 5.3.9**).



Scheme 5.3.9: Two synthetic methods to access the germylene hydride *LGeH.

In both cases the reaction mixture underwent a rapid colour change from colourless to yellow upon mixing the two reagents together; in situ ^1H , ^{31}P and ^{11}B NMR spectroscopy were used to monitor for the formation of the target Ge(II) hydride. Promisingly, the ^1H NMR spectrum of both reaction mixtures is consistent with the formation of the hydridogermylene, $^*\text{LGeH}$. The signature Ge-H signal appears as a doublet at $\delta_{\text{H}} = 5.68$ ppm, with a $^2J_{\text{HP}}$ coupling constant of 6.4 Hz. Although no phosphine stabilised germylene hydride has been reported previously, the chemical shift and coupling constant of the Ge-H hydride signal can be compared to previously reported germylphosphines, summarised in **Table 5.3.1**. In addition, the aliphatic region features four doublets for the Dipp ^iPr groups at 1.11, 1.17, 1.25 and 1.28 ppm integrating to 2H each and two septets at 3.85 and 3.53 ppm ($^3J_{\text{HH}} = 6.8$ Hz). The methylene CH_2 group gives rise to two broad doublets at 4.61 and 4.81 ppm. In the ^{11}B NMR spectrum a peak appears at 22.5 ppm which can be assigned to the co-product, $(\text{C}_{10}\text{H}_7-1)\text{OBpin}$.

	Ge-H chemical shift (ppm)	$^2J_{\text{HP}}$ coupling constant (Hz)
$^t\text{BuH}_2\text{Ge-PHPPh}$	3.71	Not reported
$\text{Ph}_2\text{HGe-PHPPh}$	5.46	18
$^t\text{BuH}_2\text{Ge-PHCy}$	5.73	12
$\text{Ph}_2\text{HGe-PHCy}$	4.47	Not reported

Table 5.3.1: Summary of the ^1H NMR chemical shifts and the $^2J_{\text{HP}}$ coupling constant for previously reported germylphosphines.⁶³

Although the in situ formation of the hydridogermylene hydride $^*\text{LGeH}$ is suggested, this species appears to be unstable over extended periods of time, and decomposes in solution to $^*\text{LH}$ and unidentified products under ambient conditions overnight. Therefore it was thought that it would be challenging to isolate and structurally characterise this hydride compound and (for example) utilise it as a catalyst. Naphthoxide compound **26** instead was therefore used as a pre-catalyst for hydroboration reactions, as it is relatively more stable in solution and can be isolated in a decent yield and purity (and converted to the hydride in situ by pinacolborane).

HBpin and benzaldehyde were chosen to be the substrates, to allow direct comparison with other reported germanium(II) catalysts.^{11,15,19} A summary of the results of catalytic experiments using *LH or **26** at various catalytic loadings (together with control experiments) is outlined in **Table 5.3.2**.

$$\text{Ph}-\text{CHO} + \text{H-Bpin} \xrightarrow[\text{C}_6\text{D}_6, \text{ r.t.}]{\text{Cat.}} \text{Ph}-\text{CH}_2-\text{OBpin}$$

Entry	Cat.	Cat. Loading (mol%)	Time (h)	Yield (%)	TOF (h ⁻¹)
1	-	-	21	6.1	-
2	*LH	10	8	6.6	0.08
3	26	3	1.0	>99	169
4	26	1	1.9	>99	113

Table 5.3.2: Results of catalytic experiments of hydroboration of benzaldehyde.

For all of the catalytic experiments except entry **1**, a slight excess of HBpin (3.45×10^{-4} mol, 1.2 equiv.) and benzaldehyde (2.87×10^{-4} mol, 1.0 equiv.) were used in a fixed amount of solvent (benzene-d₆, 0.45 mL), at room temperature.* The catalyst loading was calculated with respect to the stoichiometry of benzaldehyde. The catalytic runs were monitored in situ by ¹H NMR spectroscopy. The consumption of benzaldehyde and the formation of the borate ester PhCH₂OBpin (% yield is given in each case in **Table 5.3.2**) were monitored by the relative integration of the multiplets at $\delta_{\text{H}} = 7.51$ and 7.32 ppm, which correspond respectively to the *ortho* aromatic protons of the two compounds.⁶⁴ For entries **3** and **4**, the two substrates were combined in the solvent before being added to the pre-catalyst **26**, due to the observed decomposition of (a catalytic amount of) **26** in the sole presence of benzaldehyde. This is potentially caused by a trace amount of benzoic acid resulting from the auto-oxidation of

* This will be referred to as the “typical” reaction conditions in the following discussion.

benzaldehyde upon exposure to air (which can then be removed by pre-mixing benzaldehyde/HBpin).⁶⁵

In order to assess and minimise the conversion represented by the background reaction (i.e. the reaction occurring in the presence of no added catalyst), we assessed the “blank” reaction as shown by entry **1**. HBpin and benzaldehyde (6.89×10^{-5} mol of each) were combined in 0.45 mL of benzene- d_6 at a lower concentration than the typical reaction conditions for entries **2-5**. The reaction shows ca. 6% of conversion after 21 h at room temperature. This value is comparable to the similar “blank” reactions reported in recent studies of main group catalysts.^{11,15,64,66–68} In addition, since samples of compound **26** typically contain traces of the protio-ligand *LH (and the presence of benzoic acid impurity in the benzaldehyde substrate would offer a source of the same), a second control reaction was run using 10 mol% of crystalline *LH with the same substrate under typical conditions (entry **2**). The reaction shows ca. 7% of conversion after 8 h at room temperature. This result confirms that the protio-ligand does itself not act as an effective catalyst for the hydroboration reaction.

We then tested the catalytic performance of **26** at 3 mol% loading relative to benzaldehyde. The reaction was monitored by multi-scan ^1H NMR spectroscopy (one spectrum per minute) from the earliest possible time until the conversion reached ca. 99% in each case. The time taken from mixing the reagents to the first NMR scan was calculated by combining the time recorded by a stopwatch and half of the ^1H NMR spectrum running time (51 s). This process usually takes 2.5-5.5 minutes. Therefore on the kinetic profile plots, the x-axis does not start at 0 s and 0 concentration, as the first scan was taken at 354 s after the reagents were mixed together. The concentration of borate ester $\text{PhCH}_2\text{OBpin}$ was plotted against time in seconds (**Figure 5.3.9**). As shown in the temporal plot - the first scan (after 354 s) shows that the reaction has already reached nearly 50% conversion of the benzaldehyde starting material. The reaction reached >99% conversion after ca. 3400 s and the TOF (i.e. number of turnovers per mole of catalyst per hour) is estimated to be 169 h^{-1} .

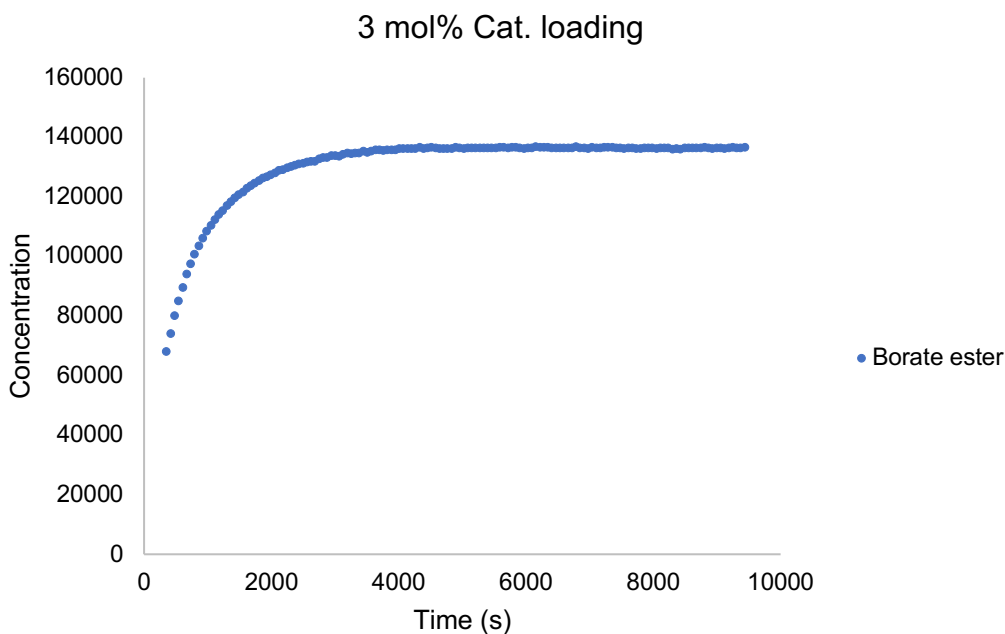


Figure 5.3.9: Plot of the concentration of the borate ester versus time at 3 mol% catalyst loading.

Since at 3 mol% catalyst loading, the hydroboration reaction proceeded too fast to allow data to be measured up to 50% conversion, the reaction was repeated with 1 mol% loading (**Figure 5.3.10**). The first NMR scan was acquired at 200 s after the reagents were mixed together. The reaction reaches 50% conversion after ca. 1600 s and >99% after 7000 s. The TOF is estimated to be 113 h^{-1} . The turnover frequencies per hour calculated for catalyst **26** at both 1 mol% and 3 mol% are based on the initial reaction periods from 0 to 50 % conversion. However, in order to compare these values with the efficiencies of the other reported Ge/Sn based catalysts for the same reaction, a TOF of the average value for complete reaction at 52 h^{-1} (at 1 mol% of **26**) was used here instead. Our catalyst is therefore more efficient than the reported N-heterocyclic germylene (**III**) which has a TOF of ca. 2 h^{-1} .¹⁵ Although this value is lower than the reported TOF (i.e. 800 h^{-1}) for the same reaction catalysed by the in situ generated tin(II) hydride (**II**) (from the tin(II) *t*Bu oxide pre-catalyst) reported by Jones et al., it is comparable to the reported TOF (67 h^{-1}) of Jones' germanium(II) hydride (**I**).¹¹ The contrast in reactivity between Ge(II) and Sn(II) compounds as catalysts has been rationalised in terms of a more polar Sn(II)-O bond in the intermediate and therefore higher reactivity towards HBpin

than the germanium analogue. The average TOF for complete reaction of **26** at 1 mol% was higher than the same reaction catalysed by two germylene cations, (**VIII**) and (**IX**), with TOF of 42.5 and 36.5 h⁻¹ respectively.¹⁹ Moreover, the “blank” reaction reported for these catalytic studies showed 95% conversion after 8 h at room temperature, which is higher than the value we observed in the reference catalytic runs.

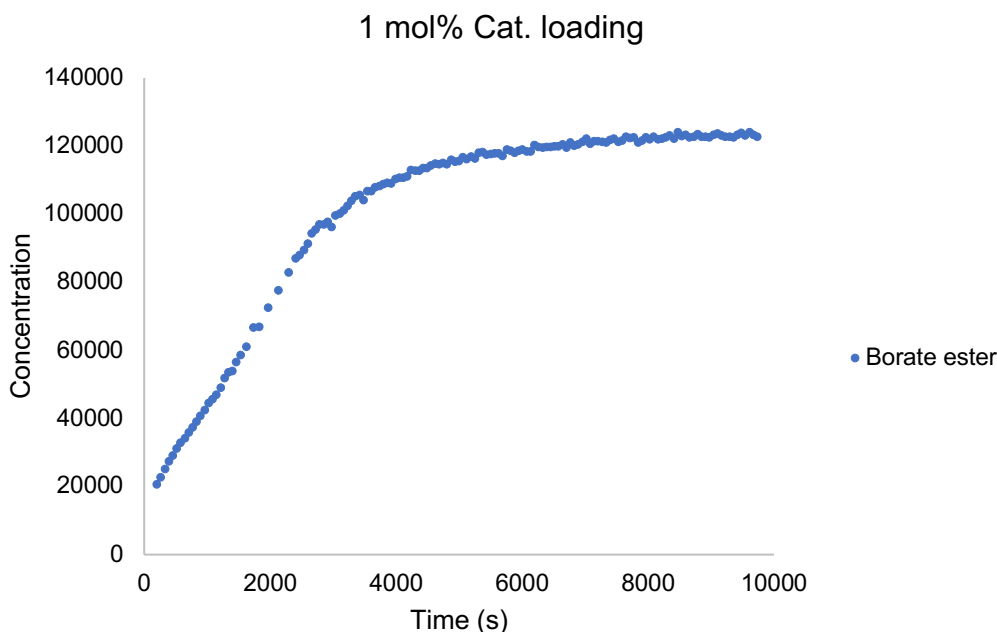


Figure 5.3.10: Plot of the concentration of the borate ester (y-axis) versus time (x-axis) at 1 mol% Cat. loading.

From the temporal data obtained at 1 and 3 mol% catalyst loadings, we next attempted to study the reaction profile and ascertain the order in catalyst. Instead of using the initial rates (k_{obs}) method reported in the work of Jones et al., Burés’ technique of utilising a normalised time scale $t[\text{cat}]_T^n$ was adopted.^{69,70} This graphical analysis method does not require any rate data and allows direct comparison between the entire reaction profiles. It is also highly tolerant of relatively large human errors or outliers in the datasets. Therefore it is best suited for the data analysis in this study. In this method, the concentration of a reagent (in this case benzaldehyde was chosen due to the clear separation of the ¹H NMR signal at $\delta_H = 7.51$ ppm) was plotted against a normalised time scale $t[\text{cat}]_T^n$ with n equal to 0, 0.5, 1 and 2 for each catalyst loading (**Figure 5.3.11**). The order in catalyst (n) was then determined graphically by

identifying when the plots most closely overlay each other. As shown in the four plots, the two curves clearly overlay best when $n = 1$. Therefore it can be concluded that the order in catalyst is one. This is consistent with the order in catalyst for hydroboration of 4-ethylacetophenone with HBpin catalysed by Ge(II) hydride (I) reported by Jones et al.¹¹

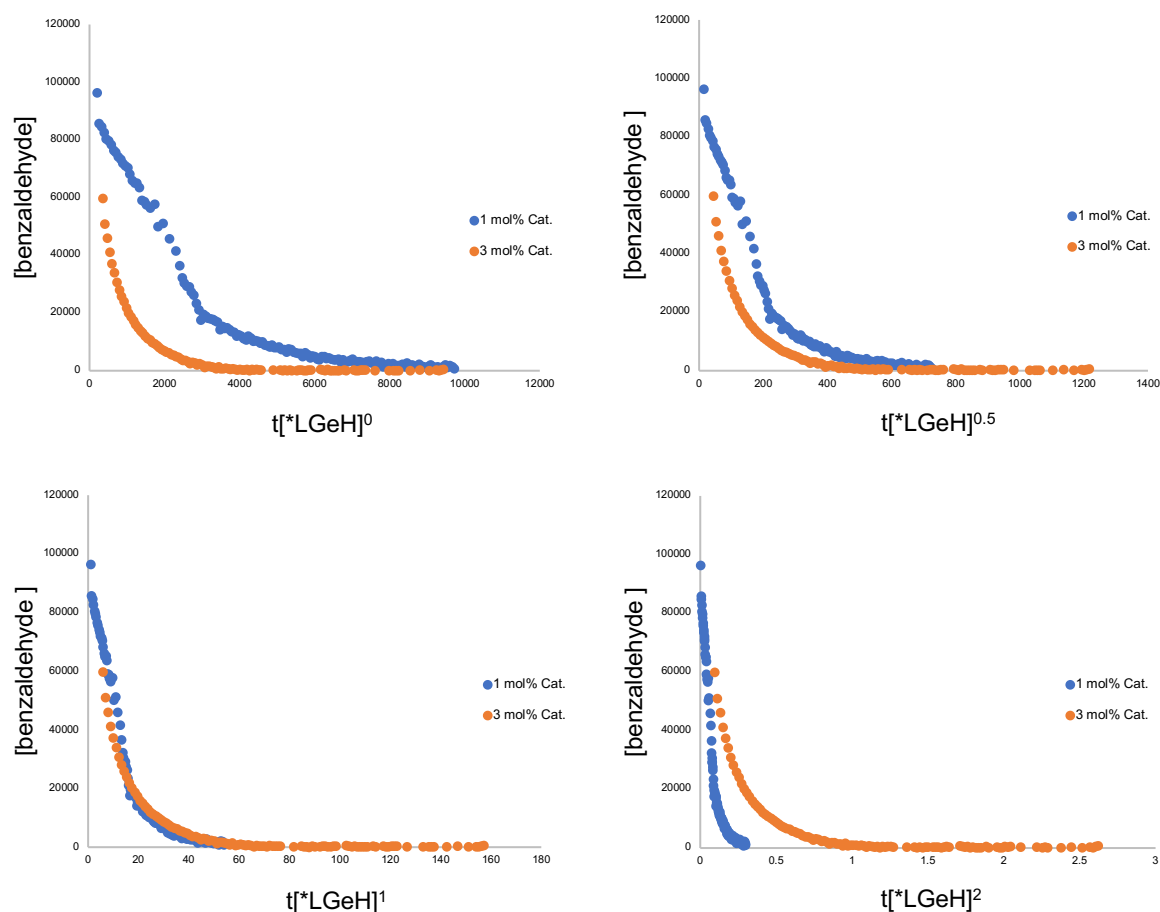


Figure 5.3.11: Plots of concentration of borate ester against $t[\text{cat}]_T^n$ with $n = 0, 0.5, 1$ and 2 .

One of the limitations of this method is that it assumes that the concentration of catalyst remains constant throughout the reaction course. Since we have tested that our catalyst, $^*\text{LGeH}$ remains stable in solution for at least 5 h under ambient conditions and both the catalytic runs finished within 3 h, it is reasonable to assume that $[\text{cat}]$ did not change significantly in both reaction profiles.

In order to gain further understanding of the reaction mechanism of the hydroboration catalysis by $^*\text{LGeH}$ and compare it to other Ge(II)/Sn(II) systems reported as effective catalysts, the order in each of the reagents (HBpin and benzaldehyde) was investigated using the method described in a subsequent paper by Burés.⁷⁰ In Burés' study, a simple graphical method was developed to approximate the order of reagents utilising the concept of the trapezoid rule, which enables visual comparison as in the case of the order of catalyst. In contrast to the method used to determine the order in catalyst (constant concentration), the quantity plotted on the x-axis here is the normalised time scale for each reagent (concentration changing with time).

Experimentally, this was performed by altering the concentration of the reagent in question while keeping the concentrations of the other reagent and the catalyst constant. In all of the catalytic runs, the amount of catalyst added was approximately 4 mg (2 mol%). A "reference" experiment was run first with slight excess of HBpin (1.1 equiv.) and benzaldehyde (1 equiv.). In the second run the concentration of HBpin was increased to 1.6 equiv., with the other parameters unchanged. In the third run, the concentration of benzaldehyde was increased to 1.7 equiv., with the other parameters unchanged. The data obtained from the multi-scan ^1H NMR spectra were then plotted with the assumption of 0, 0.5, 1, 1.5 order in HBpin or benzaldehyde to give the results below.

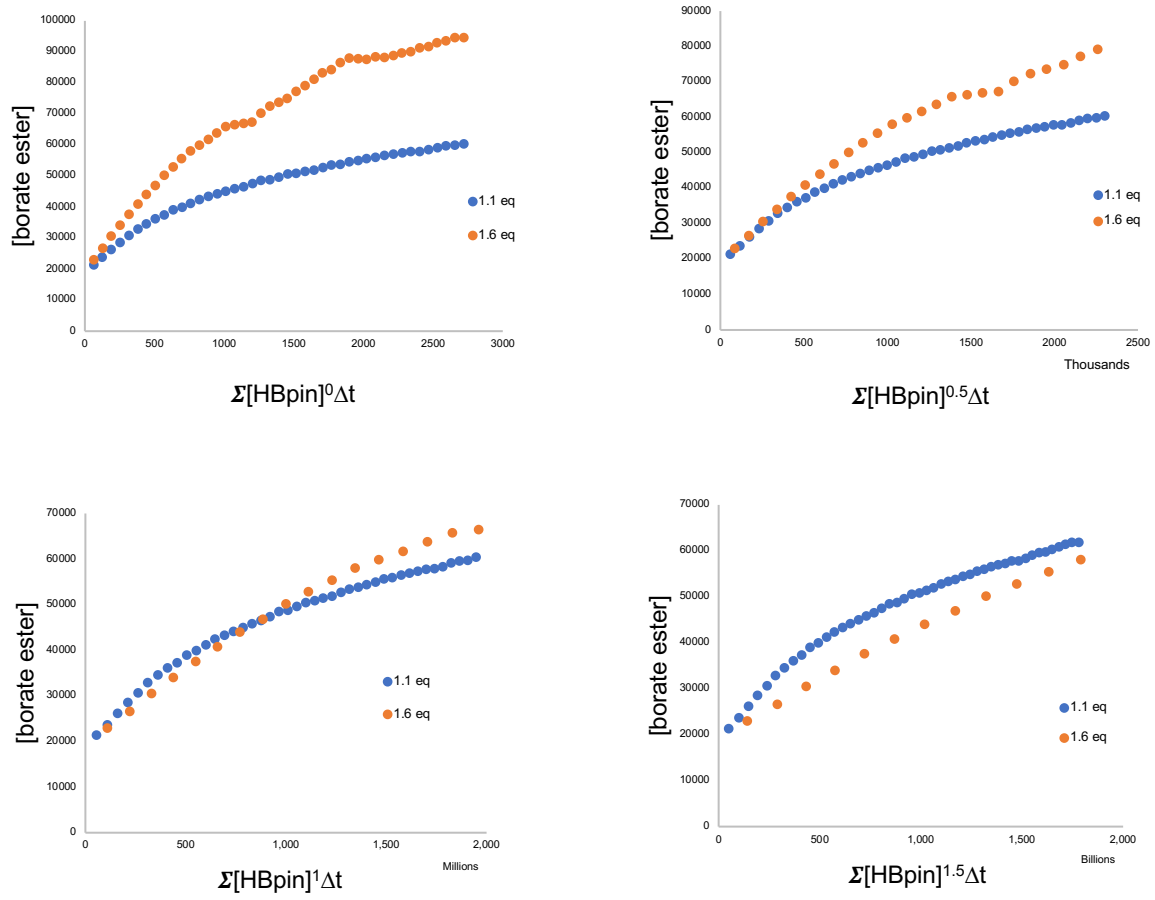


Figure 5.3.12: Plots of concentration of borate ester against $\Sigma[\text{HBpin}]^n \Delta t$ with $n = 0, 0.5, 1$ and 1.5 .

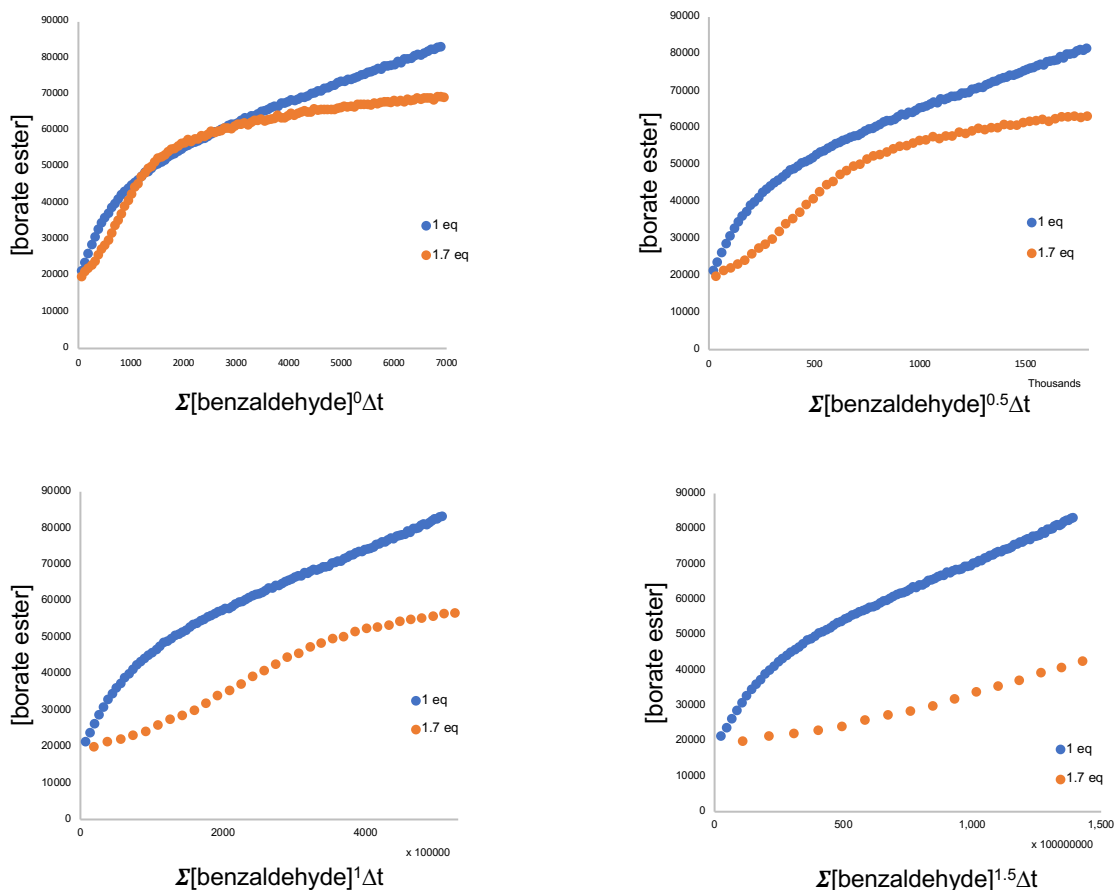
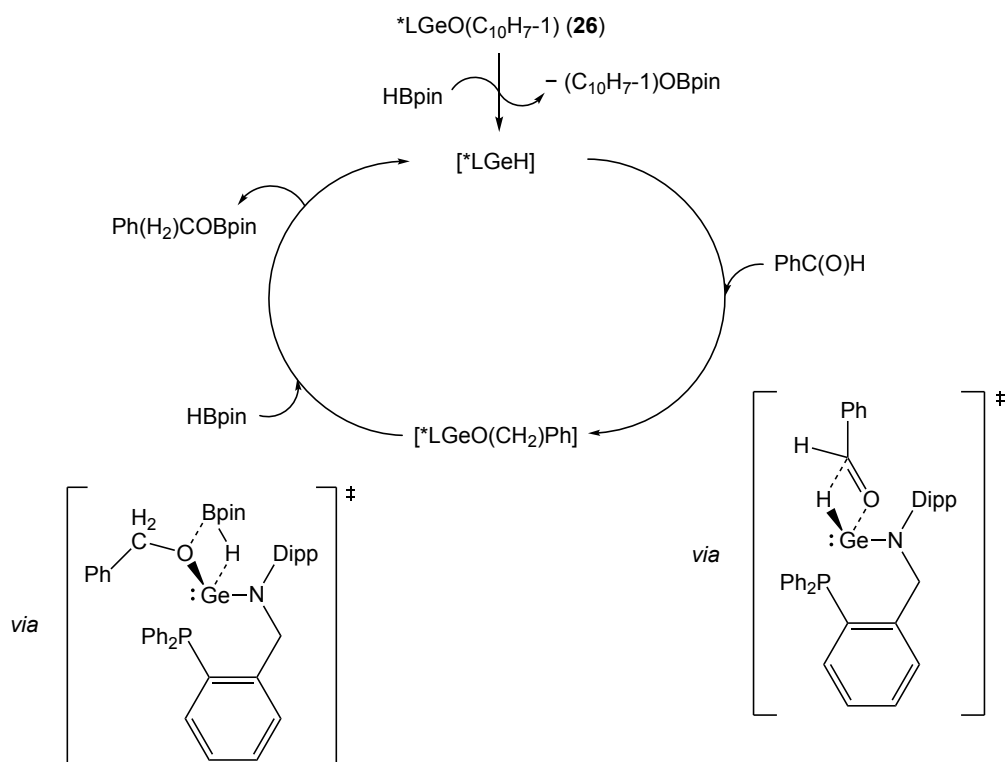


Figure 5.3.13: Plots of concentration of borate ester against $\Sigma[\text{benzaldehyde}]^n \Delta t$ with $n = 0, 0.5, 1$ and 1.5 .

From the plots, it can be concluded visually that the reaction has first-order dependence in HBpin and (most likely) a zero-order dependence in benzaldehyde. These results are in accordance with those reported in Jones' study in which the initial rates method was used to work out the order in catalyst and reagents. Interestingly in our studies, an induction period can be seen on the plots where the ratio of concentration of HBpin and benzaldehyde is 1.1:1.7. We postulate that this might be due to the presence of excess benzaldehyde which hinders the formation of the active species $^*\text{LGeH}$ from the pre-catalyst $^*\text{LGeO}^t\text{Bu}$ by coordinating to the vacant p orbital at the germanium(II) centre. Attempts to obtain additional data were prevented by the COVID shutdown.

It has been shown that compound **26** can act as an effective pre-catalyst for the hydroboration reaction and does not react with benzaldehyde. The formation of germylene hydride $^*\text{LGeH}$ is also observed when combining **26** with one equivalent of HBpin. Hence the first step of the reaction is likely to be the formation of $^*\text{LGeH}$. Based on the order of HBpin (one) and benzaldehyde (zero), the rate determining step is presumably the reaction between the intermediate $^*\text{LGeOCH}_2\text{Ph}$ and HBpin. A plausible mechanism can therefore be proposed for the catalytic cycle based on the experimental data and the relevant literature precedent (**Scheme 5.3.10**).^{11,19} Compound **26** reacts with HBpin to give the catalytically active species $^*\text{LGeH}$ in situ, which undergoes σ -bond metathesis with benzaldehyde to form the hydrogermylated intermediate via a four-membered ring transition state. The intermediate then reacts with HBpin and afford the hydroboration product $\text{PhCH}_2\text{OBpin}$ and regenerate the active Ge(II) hydride catalyst. Assuming this is the rate-determining step, the hemi-labile nature of the phosphine group in the intermediate allows for the generation of an empty p orbital at the Ge(II) centre as well as an empty coordination site, which is key for the facile reaction with HBpin and therefore a high TOF.



Scheme 5.3.10: Proposed catalytic cycle for the hydroboration of HBpin, catalysed by compound **26** as a pre-catalyst.

5.4 Conclusions

This chapter describes the synthesis and characterisation of a chlorogermylene system stabilised by an $\text{N}_{\text{amido}}\wedge\text{P}_{\text{phosphino}}$ chelate ligand (**19**), accessed via lithiation of the corresponding protio-ligand followed by salt metathesis with $\text{GeCl}_2 \cdot \text{dioxane}$. This compound could subsequently be utilised as the precursor to a number of reactive molecular species. These include a two-coordinate germylium-ylidene cation (**20**), which displays a similar cooperative (1,2) mode of N-H activation with carbazole (**21**), as do the $\text{N}_{\text{amido}}\wedge\text{C}_{\text{NHC}}$ -stabilised cations **9** and **10** described in Chapter 4. The chloride substituent in **19** could also be substituted by various alkoxo (**22**), amido (**25**) or aryloxo (**26**) groups. The *tert*-butoxy germylene proved to be challenging to crystallise, therefore it was synthesised in situ and combined with transition metal halides (CuCl and Me_2SAuCl) to afford two heterometallic complexes (**23** and **24**) which could be structurally characterised by X-ray crystallography. While the bis(trimethylsilyl)amino germylene could also not be isolated in pure form, the

naphthoxy derivative was recrystallised and isolated in a decent yield and purity and its reactivity as a pre-catalyst for the hydroboration of benzaldehyde was studied. Stoichiometric reactions showed that the corresponding germylene hydride $^*\text{LGeH}$ can be formed (via two routes) but the compound is unstable and decomposes in solution overnight at room temperature. After optimisation of the reaction method and conditions, **26** was tested as a pre-catalyst and turnover frequencies of ca. 113 h^{-1} achieved. The order in catalyst was shown to be one using a normalised time scale graphic analysis method. The catalytic performance of $^*\text{LGeH}$ can be compared to other Ge(II) systems for this reaction and a potential mechanism of the catalytic cycle was proposed. The fact that $^*\text{LGeH}$ is capable of catalysing the hydroboration reactions reflects the hemi-lability of the phosphine group and the potentially enhanced reactivity comparing to the previously studied NHC group.

5.5 Experimental details

***LLi (18):** To a solution of $^*\text{LH}$ (1 g, 2.21 mmol) in diethyl ether (20 mL) was added dropwise at -78°C , 1.2 equivalents of $^n\text{BuLi}$ (1.66 mL of a 1.6 M solution in hexane, 2.66 mmol). The colour of solution instantly changed from colourless to yellow. The reaction mixture was slowly warmed to room temperature and stirred overnight, over which time an off-white suspension was formed. The resulting white solid was isolated by filtration, washed with hexane (15 mL) and dried in vacuo. It was used for subsequent chemistry without further purification. Yield: 750 mg, 74%.

Spectroscopic data: ^1H NMR (400 MHz, THF-d_8 , 298K): δ_{H} 1.03 (12H, d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, Dipp $^i\text{Pr CH}(\text{CH}_3)_2$), 3.84 (2H, sep, $^3J_{\text{HH}} = 6.8\text{ Hz}$, Dipp $^i\text{Pr CH}(\text{CH}_3)_2$), 4.67 (1H, br m, methylene CH), 4.68 (1H, br m, methylene CH), 6.20 (1H, t, $^3J_{\text{HH}} = 7.4\text{ Hz}$, Dipp *para* CH), 6.62 (1H, br m, phenyl CH), 6.64 (2H, d, $^3J_{\text{HH}} = 7.4\text{ Hz}$, Dipp *meta* CH), 6.89 (1H, br m, phenyl backbone CH), 7.16-7.26 (11H, overlapping m, PPh_2 and phenyl backbone CH), 8.10 (1H, br m, phenyl backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF-d_8 , 298K): δ_{C} 25.3 (Dipp $^i\text{Pr CH}(\text{CH}_3)_2$), 28.0 (CH_3 of ^tBu), 60.8 (d, $^3J_{\text{CP}} = 25.1\text{ Hz}$, methylene C), 113.2 (Dipp *para* C), 122.9 (Dipp *meta* C),

125.0 (phenyl backbone C), 128.2 (PPh₂), 128.9 (br d, $^3J_{CP}$ = 3.9 Hz, phenyl backbone C), 129.5 (m, phenyl backbone C), 132.1 (m, phenyl backbone C), 133.2 (phenyl backbone C), 133.9 (PPh₂), 134.6 (br d, $^1J_{CP}$ = 19.5 Hz, PPh₂), 139.0 (PPh₂), 141.5 (Dipp ^{*i*}Pr CH(CH₃)₂), 155.7 (d, $^1J_{CP}$ = 21.9 Hz, phenyl backbone C), 162.7 (Dipp *ipso* C). $^7\text{Li}\{^1\text{H}\}$ NMR (104 MHz, THF-d₈, 298K): δ_{Li} 0.2 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, THF-d₈, 298K): δ_{P} -15.9 (s).

***LGeCl (19):** To a mixture of *LLi (750 mg, 1.64 mmol) and GeCl₂·dioxane (379 mg, 1.64 mmol) was added toluene (15 mL) at -78°C. The reaction mixture was warmed to room temperature and stirred overnight, over which time a light green suspension was formed. The resulting mixture was filtered, and the filtrate concentrated in vacuo. A small portion of hexane (1 mL) was added and the solution stored at -30°C to give **19** as a pale yellow crystalline solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene layered with hexane and stored at -30°C. Yield: 610 mg, 67%.

Spectroscopic data: ^1H NMR (400 MHz, benzene-d₆, 298K): δ_{H} 1.01 (6H, br m, Dipp ^{*i*}Pr CH(CH₃)₂), 1.25 (6H, br m, Dipp ^{*i*}Pr CH(CH₃)₂), 3.50 (2H, br sep, Dipp ^{*i*}Pr CH(CH₃)₂), 4.76 (2H, br m, methylene CH₂), 6.66 (1H, br m, phenyl backbone CH), 6.84 (1H, br m, phenyl backbone CH), 6.89 (1H, br m, phenyl backbone CH), 6.95-7.15 (10H, m, aromatic H of PPh₂, phenyl CH and Dipp CH), 7.42 (4H, br m, PPh₂). ^1H NMR (400 MHz, toluene-d₈, 193K): δ_{H} 0.56 (3H, d, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 1.13 (3H, d, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 1.51 (3H, d, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 1.56 (3H, d, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 2.89 (1H, sep, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 3.85 (1H, d, $^2J_{\text{HH}}$ = 15.5 Hz, methylene CH₂), 4.07 (1H, sep, $^3J_{\text{HH}}$ = 6.2 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 5.50 (1H, d, $^2J_{\text{HH}}$ = 15.5 Hz, methylene CH₂), 6.34 (1H, br m, phenyl backbone CH), 6.71 (1H, br m, phenyl backbone CH), 6.78 (1H, br m, phenyl backbone CH), 6.83 – 7.01 (10H, overlapping m, PPh₂, phenyl CH and Dipp CH), 7.17 (2H, br m, PPh₂), 7.37 (2H, br m, PPh₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene-d₆, 298K): δ_{C} 24.6 (Dipp ^{*i*}Pr CH(CH₃)₂), 26.3 (Dipp ^{*i*}Pr CH(CH₃)₂), 28.9 (Dipp ^{*i*}Pr CH(CH₃)₂), 59.8 (d, $^3J_{CP}$ = 10.6 Hz, methylene C), 124.0 (Dipp *para* C), 124.3 (Dipp *ortho* C), 124.3 (phenyl backbone C), 126.3

(Dipp *meta* C), 127.7 (d, $^3J_{\text{CP}} = 5.6$ Hz, phenyl backbone C), 129.3 (d, $^2J_{\text{CP}} = 9.8$ Hz, PPh₂), 129.6 (d, $^2J_{\text{CP}} = 8.9$ Hz, phenyl backbone C), 131.3 (d, $^3J_{\text{CP}} = 2.0$ Hz, PPh₂), 131.4 (d, $^4J_{\text{CP}} = 1.8$ Hz, PPh₂), 134.4 (d, $^1J_{\text{CP}} = 10.3$ Hz, PPh₂), 135.4 (d, $^4J_{\text{CP}} = 1.8$ Hz, phenyl backbone C), 147.6 (d, $^2J_{\text{CP}} = 8.2$ Hz, phenyl backbone C), 148.9 (d, $^1J_{\text{CP}} = 12.8$ Hz, phenyl backbone C), 149.1 (Dipp *ipso* C). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, benzene-*d*₆, 298K): $\delta_{\text{P}} -24.4$ (s). Elemental microanalysis: calc. for C₃₁H₃₃ClGeNP: C 66.65% H 5.95% N 2.51%; meas. C 66.47% H 5.75% N 2.43%. Crystallographic data: C₃₁H₃₃ClGeNP, $M_r = 558.67$, triclinic, *P*-1, $a = 9.1837(3)$, $b = 11.0396(4)$, $c = 14.5439(5)$ Å, $\alpha = 111.357(3)^\circ$, $\beta = 90.475(3)^\circ$, $\gamma = 90.475(3)^\circ$, $V = 1371.34(9)$ Å³, $Z = 2$, $\rho_{\text{c}} = 1.353$ g cm⁻³, $T = 150$ K, $\mu(\text{CuK}\alpha) = 3.105$ mm⁻¹, $\lambda = 1.54184$ Å. $R_1 = 0.0250$ for 5273 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.0672$ for all 5691 unique reflections. Max. and min. residual electron densities 0.503, -0.248 e Å⁻³.

[(*L)Ge][Al{OC(CF₃)₃}]₄ (20): To a mixture of *LGeCl (**19**) (200 mg, 0.358 mmol) and Li[Al{OC(CF₃)₃}]₄ (474 mg, 0.358 mmol) was added bromobenzene (15 mL) at room temperature. The reaction mixture was stirred at room temperature for 12 h, over which time a yellow solution and a white precipitate were formed. The resulting mixture was filtered and volatiles removed in vacuo to obtain compound **19** as a yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in bromobenzene layered with hexane and stored at -30°C for 20 days. Yield: 153 mg, 29%.

Spectroscopic data: ^1H NMR (400 MHz, bromobenzene-*d*₅, 298K): δ_{H} 0.81 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, Dipp *i*Pr CH(CH₃)₂), 0.91 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, Dipp *i*Pr CH(CH₃)₂), 2.30 (2H, sep, $^3J_{\text{HH}} = 6.8$ Hz, Dipp *i*Pr CH(CH₃)₂), 4.17 (2H, br m, methylene CH₂), 6.91-6.94 (2H, m, phenyl backbone CH), 6.96-6.99 (2H, m, phenyl backbone CH), 7.03-7.19 (10H, m, aromatic H of PPh₂), 7.28-7.36 (3H, br m, Dipp *meta/para* CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene-*d*₅, 298K): δ_{C} 24.4 (Dipp *i*Pr CH(CH₃)₂), 25.9 (Dipp *i*Pr CH(CH₃)₂), 28.4 (Dipp *i*Pr CH(CH₃)₂), 65.1 (d, $^3J_{\text{CP}} = 13.4$ Hz, methylene C), 79.9 (C(CF₃)₃), 117.3 (d, $^1J_{\text{CP}} = 44.4$ Hz, phenyl backbone C), 119.0 (d, $^1J_{\text{CP}} = 52.3$ Hz, PPh₂), 121.9 (q, $^1J_{\text{CF}} = 292.7$ Hz, C(CF₃)₃), 125.1 (phenyl

backbone C), 126.9 (phenyl backbone C), 130.1 (PPh₂), 130.4 (PPh₂), 130.7 (d, ²J_{CP} = 11.6 Hz, phenyl backbone CH), 133.7 (d, ²J_{CP} = 11.3 Hz, PPh₂), 134.0 (Dipp C), 134.2 (d, ⁴J_{CP} = 2.6 Hz, phenyl backbone C), 134.5 (Dipp C), 141.6 (d, ³J_{CP} = 11.1 Hz, phenyl backbone C), 142.6 (d, ¹J_{CP} = 27.7 Hz, Dipp C), 145.6 (Dipp *ipso* C). ¹⁹F{¹H} NMR (376 MHz, bromobenzene-d₅, 298K): δ_F -74.9. ²⁷Al{¹H} NMR (104 MHz, bromobenzene-d₅, 298K): δ_{Al} 35.1. ³¹P{¹H} NMR (104 MHz, bromobenzene-d₅, 298K): δ_P -2.4 (s). Elemental microanalysis: calc. for C₄₇AlF₃₆O₄H₃₃BrGeNP: C 37.88% H 2.23% N 0.94%; meas. C 37.87% H 2.61% N 0.90%. Crystallographic data: C₄₇AlF₃₆O₄H₃₃BrGeNP, *M*_r = 1490.28, triclinic, *P*-1, *a* = 12.1911(3), *b* = 15.3762(6), *c* = 29.9659(10) Å, α = 83.214(3)°, β = 88.694(2)°, γ = 87.381(2)°, *V* = 5571.2(3) Å³, *Z* = 4, ρ_c = 1.777 g cm⁻³, *T* = 150 K, μ(CuKα) = 2.718 mm⁻¹, λ = 1.54184 Å. *R*₁ = 0.0647 for 19220 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.1824 for all 24700 unique reflections. Max. and min. residual electron densities 1.843, -0.859 e Å⁻³.

[(*LH)Ge(NC₁₂H₈)] [Al{OC(CF₃)₃]₄] (21): To a mixture of *LGeCl (**19**) (200 mg, 0.358 mmol) and Li[Al{OC(CF₃)₃]₄] (474 mg, 0.358 mmol) was added fluorobenzene (15 mL) at room temperature. An orange solution and a white precipitate were formed. The reaction mixture was stirred overnight before being filtered onto solid carbazole (59.9 mg, 0.358 mmol). On stirring at room temperature overnight, the colour of the reaction mixture changed from orange to yellow. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in fluorobenzene layered with hexane and stored at -30°C. Yield: 387 mg, 43%. Spectroscopic data: ¹H NMR (400 MHz, bromobenzene-d₅, 298K): δ_H 0.03 (3H, d, ³J_{HH} = 6.3 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 0.60 (3H, d, ³J_{HH} = 6.8 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 0.65 (3H, d, ³J_{HH} = 6.62 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 1.18 (3H, d, ³J_{HH} = 6.6 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 2.41 (1H, sep, ³J_{HH} = 7.1 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 2.43 (1H, sep, ³J_{HH} = 6.5 Hz, Dipp ^{*i*}Pr CH(CH₃)₂), 3.88 (1H, br m, methylene CH), 4.59 (1H, br m, methylene CH), 6.02 (1H, d, ³J_{HP} = 11.1 Hz, NH), 6.55 (1H, dd, ³J_{HH} = 6.6 Hz, ⁴J_{HH} = 2.5 Hz, Dipp *meta* CH), 6.87-6.91 (2H, m, Dipp *meta/para* CH), 7.08-7.37 (13H, m, PPh₂ and phenyl backbone CH), 7.42-7.54 (8H, br m, carbazole aromatic

H), 7.97 (1H, m, phenyl backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, bromobenzene- d_5 , 298K): δ_{C} 21.7 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 23.5 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 24.1 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 24.3 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 31.8 (Dipp ^iPr $\underline{\text{CH}}$ (CH_3) $_2$), 58.3 (d, $^3J_{\text{CP}} = 6.3$ Hz, methylene C), 79.9 ($\underline{\text{C}}$ (CF_3) $_3$), 110.9 (PPh $_2$), 119.7 (PPh $_2$), 120.5 (phenyl backbone CH), 121.6 (PPh $_2$), 121.8 (carbazolyl), 121.9 (q, $^1J_{\text{CF}} = 292.3$ Hz, C($\underline{\text{C}}$ F $_3$) $_3$), 123.6 (phenyl backbone CH), 124.2 (carbazolyl), 127.4 (Dipp C), 130.8 (Dipp C), 131.7 (carbazolyl), 133.5 (carbazolyl), 133.6 (phenyl backbone C), 133.7 (phenyl backbone C), 134.1 (carbazolyl), 134.5 (carbazolyl), 134.6 (phenyl backbone C), 134.8 (Dipp *ipso* C), 136.8 (d, $^1J_{\text{CP}} = 14.7$ Hz, PPh $_2$), 139.6 (phenyl backbone C), 140.9 (Dipp *ortho* C). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, bromobenzene- d , 298K): δ_{P} -9.4 (s). Crystallographic data: $\text{C}_{59}\text{H}_{42}\text{F}_{36}\text{AlGeN}_2\text{O}_4$, $M_r = 1657.48$, monoclinic, $\text{C}2/c$, $a = 28.6853(7)$, $b = 18.4131(3)$, $c = 29.1049(8)$ Å, $\beta = 120.236(4)^\circ$, $V = 13281.4(7)$ Å 3 , $Z = 8$, $\rho_c = 1.658$ g cm $^{-3}$, $T = 150$ K, $\mu(\text{CuK}\alpha) = 2.356$ mm $^{-1}$, $\lambda = 1.54184$ Å. $R_1 = 0.0669$ for 10222 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.1958$ for all 13689 unique reflections. Max. and min. residual electron densities 0.737, -0.595 e Å $^{-3}$.

***LGeO t Bu (22):** To a mixture of *LGeCl (200 mg, 0.358 mmol) and KO t Bu (40 mg, 0.358 mmol) was added toluene (15 mL) at -78°C. The reaction mixture was warmed to room temperature and stirred for 12 h, over which time a light green solution was formed. Volatiles were removed in vacuo and the product isolated as a pale green oil. In situ ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show near 100% conversion to **22**.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 0.99 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 1.29 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 1.30 (9H, s, ^tBu C($\underline{\text{CH}_3}$) $_3$), 3.42 (2H, sep, $^3J_{\text{HH}} = 6.65$ Hz, Dipp ^iPr $\underline{\text{CH}}$ (CH_3) $_2$), 4.93 (2H, br m, methylene CH $_2$), 6.87 (1H, br m, phenyl backbone CH), 6.92 (1H, br m, phenyl backbone CH), 7.02-7.14 (11H, overlapping m, PPh $_2$, Dipp CH and phenyl backbone CH), 7.38 (4H, br m, PPh $_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_{C} 24.2 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 26.6 (Dipp ^iPr CH($\underline{\text{CH}_3}$) $_2$), 28.7 (Dipp ^iPr $\underline{\text{CH}}$ (CH_3) $_2$), 34.3 (^tBu C($\underline{\text{CH}_3}$) $_3$), 56.2 (d, $^3J_{\text{CP}} = 15.3$ Hz, methylene C), 72.4 (^tBu

$\underline{\text{C}}(\text{CH}_3)_3$, 123.8 (Dipp C), 126.0 (Dipp C), 128.0 (phenyl backbone C), 128.9 (d, $^2J_{\text{CP}} = 7.2$ Hz, PPh_2), 129.3 (PPh_2), 129.6 (phenyl backbone C), 131.3 (d, $^2J_{\text{CP}} = 6.2$ Hz, phenyl backbone C), 134.3 (d, $^1J_{\text{CP}} = 17.1$ Hz, PPh_2), 134.5 (d, $^4J_{\text{CP}} = 1.3$ Hz, phenyl backbone C), 134.7 (d, $^3J_{\text{CP}} = 5.1$ Hz, phenyl backbone C), 135.6 (d, $^3J_{\text{CP}} = 2.1$ Hz, PPh_2), 144.3 (Dipp *ipso* C), 145.5 (d, $^1J_{\text{CP}} = 21.1$ Hz, phenyl backbone C), 147.4 (Dipp *ortho* C). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, benzene- d_6 , 298K): $\delta_{\text{P}} -22.8$ (s).

$\{(*\text{L})\text{Ge}\}_2(\mu\text{-Cu})(\mu\text{-Br})$ (23): $*\text{LGeCl}$ (**19**) (200 mg, 0.358 mmol) and KO^tBu (40 mg, 0.358 mmol) were added to a Schlenk tube (15 mL) and dissolved in toluene (10 mL) at -78°C . The reaction mixture was warmed to room temperature and stirred overnight, over which time a yellow-green solution formed, which was then filtered onto one equivalent of solid CuBr (51 mg, 0.358 mmol). The resulting mixture was stirred at room temperature overnight. After filtration, all volatiles were removed in vacuo, and the product was isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in a mixed toluene/hexane solvent at room temperature. Yield: 172 mg, 36%.

Spectroscopic data: No satisfactory NMR data could be obtained due to the low solubility of the isolated, crystalline compound **23** in common NMR solvents. Crystallographic data: $\text{C}_{73}\text{H}_{91}\text{BrCuGe}_2\text{N}_3\text{O}_2\text{P}_2$, $M_r = 1379.04$, triclinic, $P-1$, $a = 13.3336(6)$, $b = 15.2998(5)$, $c = 18.3315(7)$ Å, $\alpha = 82.661(3)^\circ$, $\beta = 72.046(4)^\circ$, $\gamma = 75.329(3)^\circ$, $V = 3436.5(2)$ Å³, $Z = 2$, $\rho_c = 1.333$ g cm⁻³, $T = 150$ K, $\mu(\text{Cu K}\alpha) = 2.851$ mm⁻¹, $\lambda = 1.54184$ Å. $R_1 = 0.0498$ for 11190 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.1607$ for all 14256 unique reflections. Max. and min. residual electron densities 0.925, -1.693 e Å⁻³.

$\{*\text{LGe}(\text{O}^t\text{Bu})\text{ClAu}\}_2$ (24): $*\text{LGeCl}$ (**19**) (200 mg, 0.358 mmol) and KO^tBu (40 mg, 0.358 mmol) were dissolved in toluene (10 mL) at -78°C . The resulting mixture was warmed to room temperature and stirred overnight, over which time a yellow-green solution formed, which was then filtered to one equivalent of solid Me_2SAuCl (105 mg, 0.358 mmol). The resulting mixture

was stirred at room temperature overnight. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene layered with hexane and stored at room temperature. In situ ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show near 100% conversion to **24**. The isolated yield was not determined.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 1.21 (12H, d, $^3J_{\text{HH}} = 6.84$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 1.62 (9H, s, ^tBu $\text{C}(\text{CH}_3)_3$), 3.27 (2H, sep, $^3J_{\text{HH}} = 6.83$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 4.53 (1H, br m, methylene CH), 4.54 (1H, br m, methylene CH), 6.78 (1H, br m, phenyl backbone CH), 6.87 (1H, br m, phenyl backbone CH), 7.00-7.14 (10H, m, aromatic H of PPh_2), 7.15-7.22 (4H, br m, overlap of Dipp CH and phenyl backbone CH), 8.08 (1H, br m, phenyl backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_{C} 24.7 (Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 28.1 (Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 33.7 (^tBu $\text{C}(\text{CH}_3)_3$), 53.9 (d, $^3J_{\text{CP}} = 13.4$ Hz, methylene C), 74.3 (^tBu $\text{C}(\text{CH}_3)_3$), 124.1 (Dipp C), 125.2 (PPh_2), 125.7 (Dipp C), 127.4 (phenyl backbone C), 128.6 (PPh_2), 129.3 (phenyl backbone C), 129.5 (d, $^1J_{\text{CP}} = 19.1$ Hz, PPh_2), 131.8 (phenyl backbone C), 132.0 (phenyl backbone C), 133.2 (d, $^2J_{\text{CP}} = 7.6$ Hz, phenyl backbone C), 134.7 (d, $^1J_{\text{CP}} = 14.2$ Hz, phenyl backbone C), 143.5 (Dipp *ipso* C), 144.7 (d, $^2J_{\text{CP}} = 10.5$ Hz, PPh_2), 149.3 (Dipp *ortho* C). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, benzene- d_6 , 298K): δ_{P} 24.8 (s). Crystallographic data: $\text{C}_{98}\text{H}_{116}\text{Au}_2\text{Cl}_2\text{Ge}_2\text{N}_2\text{O}_2\text{P}_2$, $M_r = 2025.87$, monoclinic, $I2/a$, $a = 27.2503(3)$, $b = 11.85700(10)$, $c = 30.4248(4)$ Å, $\beta = 114.986(2)^\circ$, $V = 8910.4(2)$ Å³, $Z = 4$, $\rho_c = 1.510$ g cm⁻³, $T = 150$ K, $\mu(\text{CuK}\alpha) = 8.092$ mm⁻¹, $\lambda = 1.54184$ Å. $R_1 = 0.0296$ for 8004 observed unique reflections [$I > 2\sigma(I)$], $wR_2 = 0.3312$ for all 9168 unique reflections. Max. and min. residual electron densities 1.132, -0.969 e Å⁻³.

The experimental details for $\text{Li}[\text{O}(\text{C}_{10}\text{H}_7-1)]$ are described in Chapter 2.

***LGe{N(SiMe₃)₂} (25)**: To a mixture of *LGeCl (200 mg, 0.358 mmol) and $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (59.8 mg, 0.358 mmol) was added toluene (15 mL) at -78°C . The reaction mixture was warmed to room temperature and then stirred for 12 h, over which time a light green solution was formed.

Volatiles were removed in vacuo and the product isolated as a pale yellow oil. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show near 100% conversion to **25**.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 0.38 (18H, s, $\text{N}(\text{Si}(\text{CH}_3)_3)_2$), 1.04 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 1.22 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 3.42 (2H, sep, $^3J_{\text{HH}} = 6.8$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 5.58 (1H, br m, methylene CH), 5.58 (1H, br m, methylene CH), 6.83 (1H, t, $^3J_{\text{HH}} = 7.5$ Hz, Dipp *para* CH), 6.95-7.21 (13H, overlapping m, PPh_2 , Dipp *meta* CH and phenyl backbone CH), 7.79 (1H, dd, $^3J_{\text{HP}} = 7.7$ Hz, $^3J_{\text{HH}} = 4.7$ Hz, phenyl CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene- d_6 , 298K): δ_{C} 4.79 ($\text{Si}(\text{CH}_3)_3$), 23.1 (Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 28.0 (Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 28.6 (Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 54.4 (d, $^3J_{\text{CP}} = 22.5$ Hz, methylene C), 124.0 (Dipp *meta* C), 127.4 (phenyl backbone C), 128.5 (Dipp *para* C), 128.7 (d, $^2J_{\text{CP}} = 6.2$ Hz, phenyl backbone C), 129.3 (PPh_2), 132.3 (d, $^3J_{\text{CP}} = 4.9$ Hz, PPh_2), 133.8 (d, $^1J_{\text{CP}} = 19.1$ Hz, PPh_2), 134.1 (s, phenyl backbone C), 135.1 (s, phenyl backbone C), 137.2 (d, $^2J_{\text{CP}} = 14.8$ Hz, phenyl backbone C), 138.1 (d, $^2J_{\text{CP}} = 13.5$ Hz, PPh_2), 141.2 (Dipp *ipso* C), 145.0 (d, $^1J_{\text{CP}} = 27.7$ Hz, phenyl backbone C), 148.4 (Dipp *ortho* C). $^{31}\text{P}\{^1\text{H}\}$ NMR (104 MHz, benzene- d_6 , 298K): $\delta_{\text{P}} -18.5$ (s).

***LGe{O(C₁₀H₇-1)} (26)**: To a mixture of ***LGeCl (19)** (200 mg, 0.358 mmol) and $\text{Li}[\text{O}(\text{C}_{10}\text{H}_7-1)]$ (53.8 mg, 0.358 mmol) was added benzene (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 h, over which time a yellow-green solution was formed. The resulting mixture was concentrated and filtered into a Y-tube for crystallisation via slow evaporation, affording **26** as a yellow crystalline solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in benzene at room temperature. Yield: 145 mg, 60%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298K): δ_{H} 0.97 (6H, d, $^3J_{\text{HH}} = 6.5$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 1.13 (6H, d, $^3J_{\text{HH}} = 6.5$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 3.53 (2H, sep, $^3J_{\text{HH}} = 6.5$ Hz, Dipp ^iPr $\text{CH}(\text{CH}_3)_2$), 4.93 (2H, br m, methylene CH_2), 6.74 (1H, m, Dipp CH), 6.86 - 6.96 (8H, overlapping m, PPh_2 and Dipp CH), 7.07 - 7.31 (9H, m, phenyl backbone CH and naph),

7.39-7.43 (4H, m, PPh₂), 7.70 (1H, d, ³J_{HH} = 8.0 Hz, naph), 8.10 (1H, d, ³J_{HH} = 8.1 Hz, naph). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298K): δ_C 24.4 (Dipp ⁱPr CH(CH₃)₂), 26.2 (Dipp ⁱPr CH(CH₃)₂), 29.0 (Dipp ⁱPr CH(CH₃)₂), 59.1 (d, ³J_{CP} = 12.4 Hz, methylene C), 110.8 (naph), 117.9 (naph), 123.9 (naph), 124.2 (Dipp *meta* C), 125.8 (naph), 125.9 (naph), 126.4 (naph), 126.6 (phenyl backbone C), 127.0 (naph), 127.7 (naph), 128.5 (Dipp *para* C), 128.8 (phenyl backbone C), 129.2 (d, ²J_{CP} = 9.4 Hz, phenyl backbone C), 129.6 (PPh₂), 129.9 (d, ²J_{CP} = 8.3 Hz, phenyl backbone C), 130.9 (br d, PPh₂), 131.1 (br d, PPh₂), 134.2 (d, ¹J_{CP} = 11.7 Hz, PPh₂), 134.8 (d, ³J_{CP} = 2.0 Hz, phenyl backbone C), 136.1 (naph), 147.2 (d, ³J_{CP} = 6.5 Hz, Dipp *ipso* C), 148.0 (d, ¹J_{CP} = 13.1 Hz, phenyl backbone C), 148.7 (d, ⁴J_{CP} = 2.3 Hz, Dipp *ortho* C), 158.8 (d, ³J_{CP} = 5.0 Hz, naph). ³¹P{¹H} NMR (104 MHz, benzene-d₆, 298K): δ_P -26.1 (s). Crystallographic data: C₄₇H₄₆GeNOP, *M*_r = 744.41, monoclinic, *P*2₁/*n*, *a* = 14.1468(3), *b* = 9.5287(2), *c* = 29.8485(5) Å, β = 102.646(2)°, *V* = 3925.99(14) Å³, *Z* = 4, ρ_c = 1.259 g cm⁻³, *T* = 150 K, μ(CuKα) = 1.712 mm⁻¹, λ = 1.54184 Å. *R*₁ = 0.0357 for 6689 observed unique reflections [*I* > 2σ(*I*)], *wR*₂ = 0.0906 for all 8192 unique reflections. Max. and min. residual electron densities 0.441, -0.500 e Å⁻³.

Catalysis studies

General procedure. To a J. Young's NMR tube was added the required amount of the pre-catalyst **26** as a crystalline solid. To the pre-catalyst was added distilled and degassed benzene-d₆ (0.45 mL) which was stored over molecular sieves. The tube was gently shaken until all pre-catalyst was dissolved. To another J. Young's NMR tube was added the calculated amount of HBpin and benzaldehyde using two micro-syringes. The resultant mixture was quickly transferred into the pre-catalyst solution using a thin cannular. The resulting mixture was shaken with the concomitant start of the stopwatch. All of the catalysed reactions were clean with traces of by-products observed spectroscopically. Isolated yields were not determined.

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Chapter VI

Conclusions and Future Work

6.1 Conclusions and suggestions for future research

The thesis has explored the synthesis and reactivity of low-valent germanium compounds featuring tethered $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ and $N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ ligand systems. In Chapter 3 and 4, $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised halo-metallylenes (Ge, Sn and Pb analogues of carbenes) were synthesised and the germylenes utilised for the formation of cationic germylium-ylidenes. Metal-ligand cooperativity in the activation of E-H (E = N and O) bonds was subsequently demonstrated by these systems. Preliminary studies were also conducted towards generating metal-metal bonded Ge(I) species via reduction of halo-germylene precursors. In Chapter 5, similar studies were carried out using a related $N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ ligand, with the resulting germylium-ylidene demonstrating comparable reactivity towards E-H bonds. In addition, an isolable alkoxo-germylene featuring this ligand framework was shown to act as an effective pre-catalyst for the hydroboration reaction between benzaldehyde and HBpin. The catalytic applications of group 14 compounds stabilised by these two ligand scaffolds in the hydroboration of carbonyls (or of other organic transformations such as hydrosilylation) together with an in-depth investigation their reaction mechanisms, offers an extension of this work which might be targeted in future research.

Jones' two-coordinate Ge(II) and Sn(II) hydrides have been shown to display high catalytic activity in hydroboration of aldehydes and ketones,¹ whereas Roesky's $\text{Nacnac}^{\text{Dipp}}\text{E(II)H}$ (E = Ge, Sn) hydrides show no catalytic reactivity.²⁻⁴ Our studies imply that the phosphino group might act as a hemi-labile donor that allows for facile coordination of the aldehyde and ready approach of the HBpin reductant in the catalytic hydroboration reaction. The contrast in reactivity between these three systems lends further evidence to the idea that the vacant *p* orbital on the metal centre is key to its catalytic performance. Therefore it would be interesting

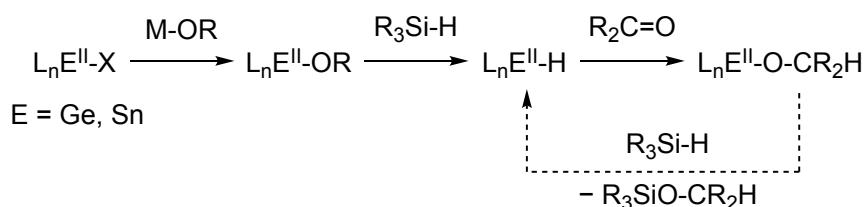
to investigate the effect of a less labile, more σ -donating NHC group on the effectiveness of the Ge(II) compound as a (pre-)catalyst in the same reaction. A $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised Ge(II) hydride might be achieved by combining the chlorogermylene precursor with a hydride source. For a more stable and easier to handle system, $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised Ge(II) alkoxide can be generated instead via salt metathesis. Their catalytic performance and TOF could then be compared with the $^*L\text{Ge}(\text{OC}_{10}\text{H}_7-1)$ ($^*L = N_{\text{amido}}^{\wedge}P_{\text{phosphino}}$ ligand) system. Preliminary experiments were carried out where $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised Ge(II) *tert*-butoxide was utilised in situ as a pre-catalyst, with the finding that it is indeed less catalytically active.



Figure 6.1.1: $N_{\text{amido}}^{\wedge}C_{\text{NHC}}$ stabilised Ge(II) hydride and Ge(II) alkoxide.

As described in Chapter 5, we deduced from the kinetic data obtained from the NMR experiments that the order of reaction in benzaldehyde is zero and HBpin is one, hence the rate-determining step of the catalytic cycle is likely to be the σ -bond metathesis between HBpin and the $^*L\text{GeOCH}_2\text{Ph}$ intermediate. This could further be probed by replacing benzaldehyde with other aliphatic/aromatic aldehyde substrates. Alkyl R groups would - in theory - increase the Lewis basicity of the alkoxide $\text{O}^{\delta-}$ in the intermediate and make it more reactive towards HBpin, accelerating the rate-determining step and leading to a higher TOF. In addition, aromatic aldehydes with an electron-donating *para* substituent (such as NR_2 or OR) on the phenyl ring would increase the Lewis basicity of $\text{O}^{\delta-}$ and increase the TOF. Moreover, the tin analogue of the pre-catalyst $^*L\text{Ge}(\text{OC}_{10}\text{H}_7-1)$ (**26**) or even the $^*L\text{Sn}(\text{II})\text{H}$ might be synthesised and applied as catalyst in the hydroboration reactions. Compared to its germanium counterpart, the Sn-O bond would be expected to be more polarised and therefore the $^*L\text{SnOCR}_3$ intermediate would be more reactive towards HBpin, which might lead to a higher TOF.

Hydrosilylation of carbonyl compounds is an important transformation since it generates silyl-protected alcohols in one step. Since the report of the Wilkinson's catalyst acting as an effective catalyst of this reaction,⁵ a wide range of transition metal complexes have been shown to effect the catalytic hydrosilylation of aldehydes and ketones.⁶ In more recent years, main group compounds such as borohydrides⁷ and NHCs⁸ were developed to mediate this transformation.⁹ However there have not been examples of low valent group 14 hydrides as catalysts for this transformation. Analogous to transition metal hydrides, group 14 metal hydrides might be able to follow a similar catalytic mechanism as shown in **Scheme 6.1.1**.



Scheme 6.1.1: A typical synthetic route of group 14 metal hydrides and the proposed mechanism for hydrosilylation of carbonyls.

Therefore, in addition to the catalytic hydroboration of aldehydes, it would be interesting to investigate whether $^*\text{LGe}(\text{OC}_{10}\text{H}_7\text{-1})$ (**26**) might also act as an effective pre-catalyst in hydrosilylation as the enhanced lability of the phosphine ligand (compared to NHCs) would presumably facilitate coordination of the carbonyl/silane substrates.

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Appendix

Name	Purity	Supplier	Purification procedure and storage
Aqueous ammonia	35%	Fisher Scientific	
Benzaldehyde	99.5%	Sigma-Aldrich	Stored in an ampoule at 5 °C.
2-Bromobenzaldehyde	97%	Acros Organics	Stored at 5 °C.
Carbazole	95%	Sigma-Aldrich	
2-Chloroethanol	99%	Sigma-Aldrich	
CuBr	98%	Sigma-Aldrich	
Diisopropylamine	99.5%	Sigma-Aldrich	
2-Dimethylaminobenzaldehyde	99%	Sigma-Aldrich	Stored in glove box.
DMAP	99%	Sigma-Aldrich	Stored in glove box.
Ethylene glycerol	99.8%	Sigma-Aldrich	
Et ₃ SiH	99%	Sigma-Aldrich	Stored over molecular sieves in an ampoule by Dr. Robert Mangan.
Formaldehyde	37%	Sigma-Aldrich	
GeCl ₂ ·dioxane	unknown	ABCR	Stored in glove box.
Glyoxal	40 wt% in water	Sigma-Aldrich	
HBpin	97%	Sigma-Aldrich	Stored in an ampoule at 5 °C.
HBr	48%	Fisher Scientific	
H ₃ PO ₄	85%	Fisher Scientific	
K ₂ CO ₃ (anhydrous)	99%	Fisher Scientific	
KOH	85%	Sigma-Aldrich	
KO ^t Bu	98%	Sigma-Aldrich	
LiAlH ₄	97%	Alfa Aesar	A suspension of LiAlH ₄ in Et ₂ O is stirred overnight before filtered; the filtrate is concentrated in vacuo. ¹
Li[N(SiMe ₃) ₂]	97%	Sigma-Aldrich	Stored in glove box.
Me ₃ NBH ₃	97%	Sigma-Aldrich	Stored in glove box.
MgSO ₄ (anhydrous)	99.5%	Sigma-Aldrich	
1-Naphthol	99%	Sigma-Aldrich	
ⁿ BuLi	1.6M in hexane	Sigma-Aldrich	Stored in an ampoule at 5 °C.
NH ₃ BH ₃	98%	Sigma-Aldrich	Stored in glove box.
NH ₄ Cl	99%	Fluorochem	

PbCl ₂	98%	Sigma-Aldrich	Stored in glove box.
Perfluoro- <i>tert</i> -butanol	97%	Fluorochem	Distilled and stored over molecular sieves in an ampoule.
Ph ₂ PCI	99%	Sigma-Aldrich	
PhSiH ₃	97%	Sigma-Aldrich	Distilled and stored in an ampoule by Dr. Robert Mangan.
Potassium chunks in mineral oil	99.5%	Sigma-Aldrich	
SnBr ₂	99.2%	Alfa Aesar	Stored in glove box.
SOBr ₂	97%	Sigma-Aldrich	Stored in an ampoule.
<i>tert</i> -Butylamine	98%	Sigma-Aldrich	
2- <i>tert</i> -Butylaminoethanol	99%	Sigma-Aldrich	
2,4,6-Trimethylaniline	98%	Alfa Aesar	
TsOH	98.5%	Sigma-Aldrich	

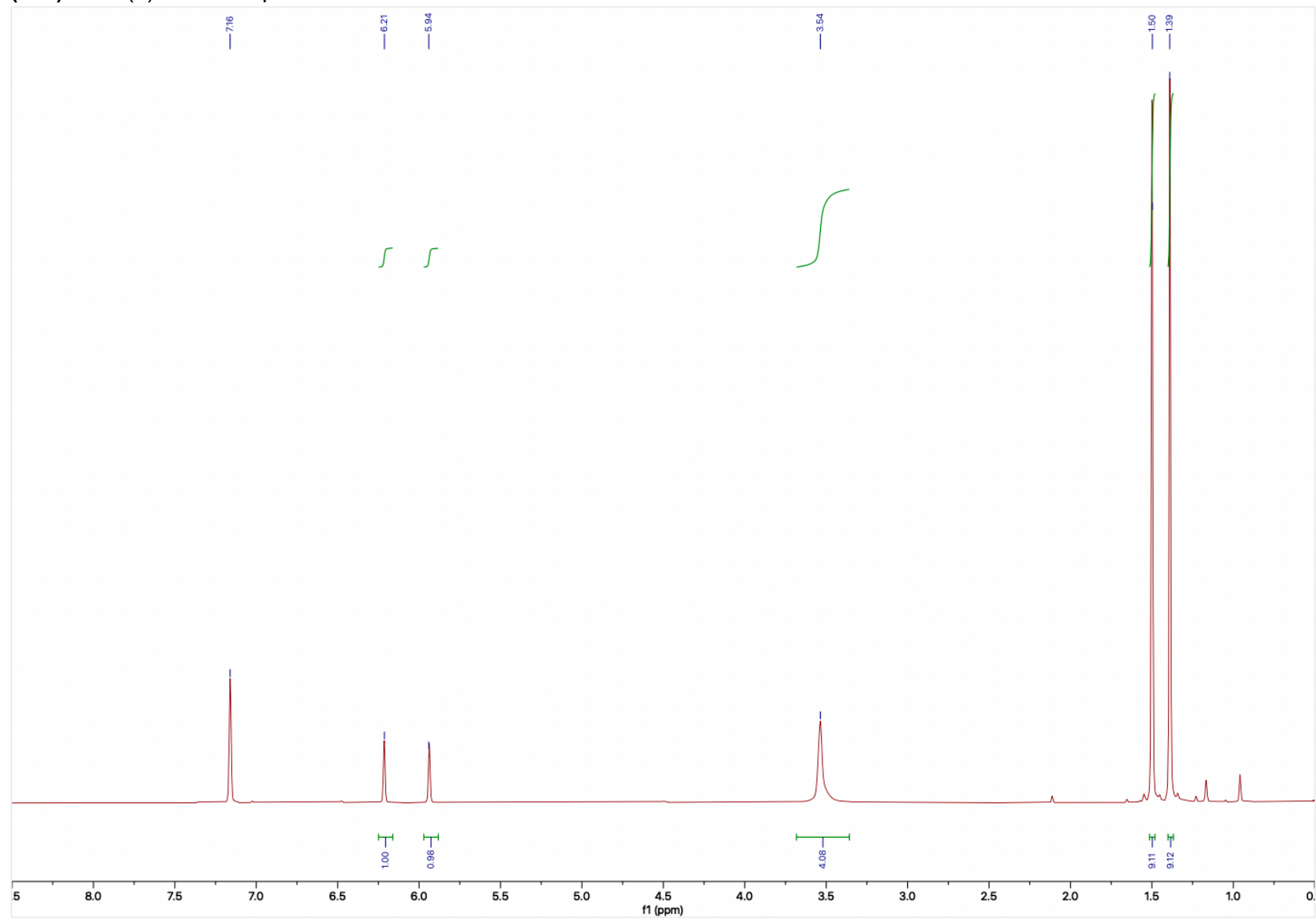
1 I. Krossing, *Chem. - A Eur. J.*, 2001, **7**, 490–502.

Name	Purity	Supplier	Drying/purification procedure if applicable
Acetone	99.9%	Sigma-Aldrich	Used as supplied.
Acetonitrile	99.9%	Sigma-Aldrich	Used as supplied.
Benzene	unknown	Rathburn Chemicals	Dried using Braun SPS system, degassed and stored over a potassium mirror.
Bromobenzene	99%	Alfa Aesar	Dried by stirring over CaH ₂ overnight, distilled, degassed and stored over molecular sieves.
Chloroform	99.8%	Sigma-Aldrich	Used as supplied.
Dichloromethane	99.8%	Sigma-Aldrich/Fisher Scientific	Dried using Braun SPS system, degassed and stored over molecular sieves.
Distilled water	N/A	N/A	Purified by Elix water purification system.
Ethanol	99.8%	Sigma-Aldrich	Used as supplied.
Et ₂ O	99.8%	Sigma-Aldrich	Distilled from sodium wire and benzophenone, degassed and stored over a potassium mirror.
Fluorobenzene	99%	Sigma-Aldrich	Dried by stirring over CaH ₂ overnight, distilled, degassed and stored over molecular sieves.
Hexane	97%	Sigma-Aldrich	Dried using Braun SPS system, degassed and stored over a potassium mirror.
Isopropanol	99.5%	Sigma-Aldrich	Used as supplied.
Methanol	99.9%	Sigma-Aldrich	Used as supplied.
Pentane	99%	Sigma-Aldrich	Dried using Braun SPS system, degassed and stored over a potassium mirror.
THF	99.9%	Sigma-Aldrich	Distilled from sodium wire and benzophenone, degassed and stored over a sodium mirror.
Toluene	99.9%	Sigma-Aldrich	Dried using Braun SPS system, degassed and stored over a potassium mirror.

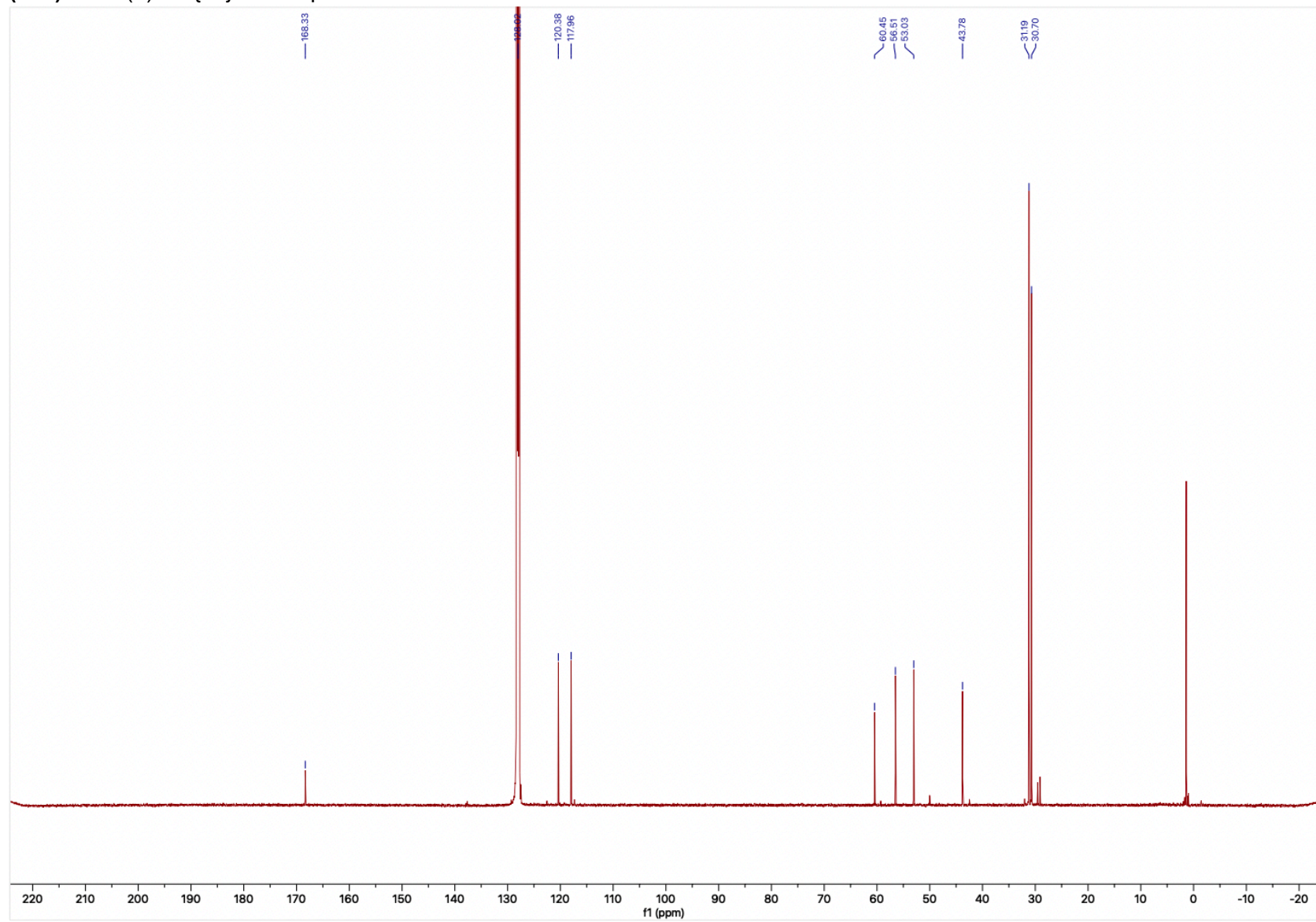
Name	Purity	Supplier	Drying procedure if applicable
C ₆ D ₆	99.5%	Cambridge Isotope Laboratories	Stirred over CaH ₂ , distilled, degassed, and stored over a potassium mirror. For catalytic reactions, distilled C ₆ D ₆ is stored over molecular sieves.
C ₆ D ₅ Br	99%	Cambridge Isotope Laboratories	Stirred over CaH ₂ , distilled, degassed, and stored over molecular sieves.
CDCl ₃	99.8%	Sigma-Aldrich	Used as supplied.
THF-d ₈	99.5%	Cambridge Isotope Laboratories	Stirred over Li[AlH ₄], distilled, degassed, and stored over molecular sieves.
Toluene-d ₈	99.5%	Cambridge Isotope Laboratories	Stirred over CaH ₂ , distilled, degassed, and stored over molecular sieves.

Name	Supplier	Drying procedure if applicable
Ar	BOC	Used as supplied.
N ₂	BOC	Used as supplied.
H ₂	BOC	Used as supplied.
NH ₃	-	Dried and stored in an ampoule by Dr Andrey Protchenko.

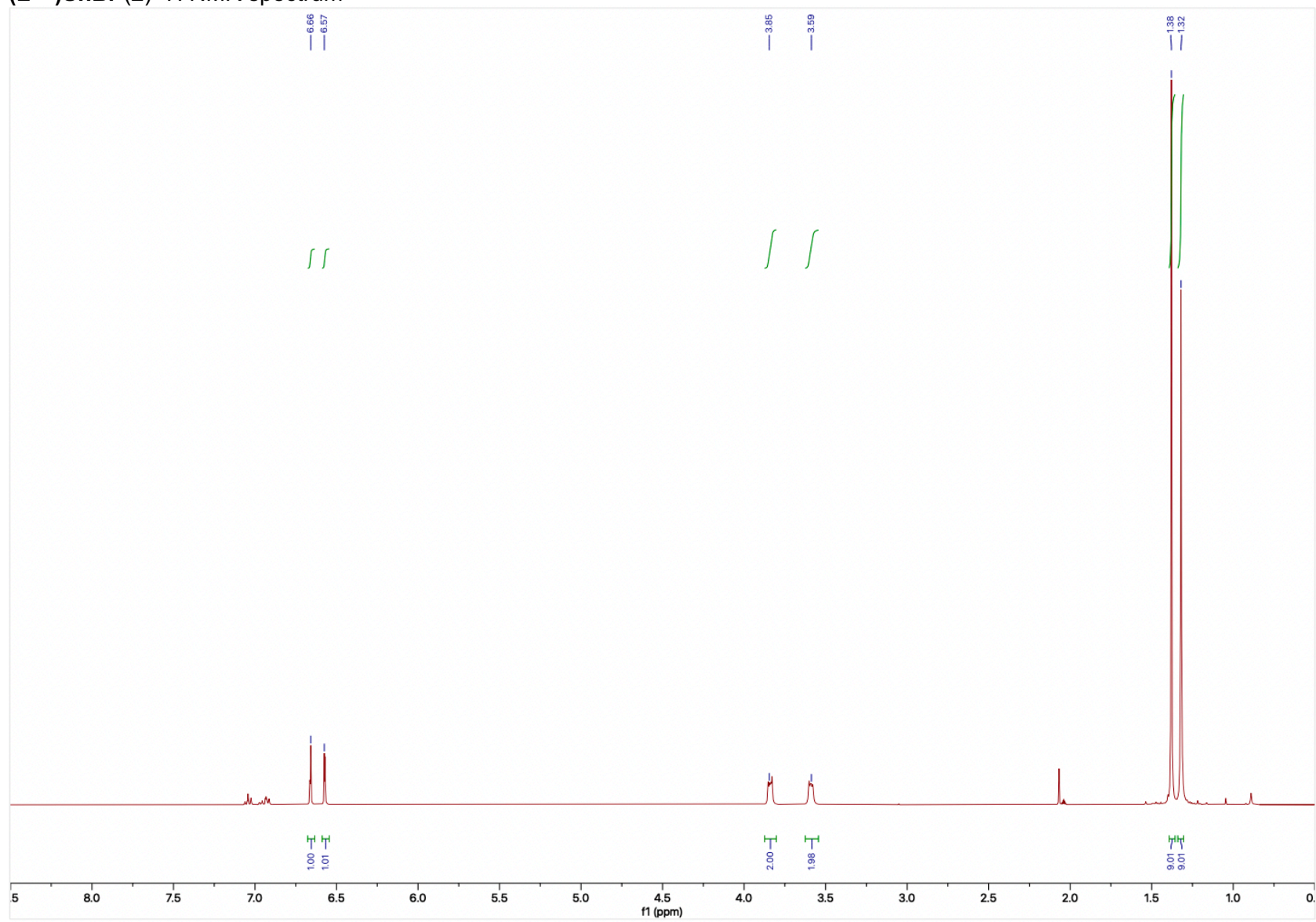
(L^{tBu})GeBr (1) ¹H NMR spectrum



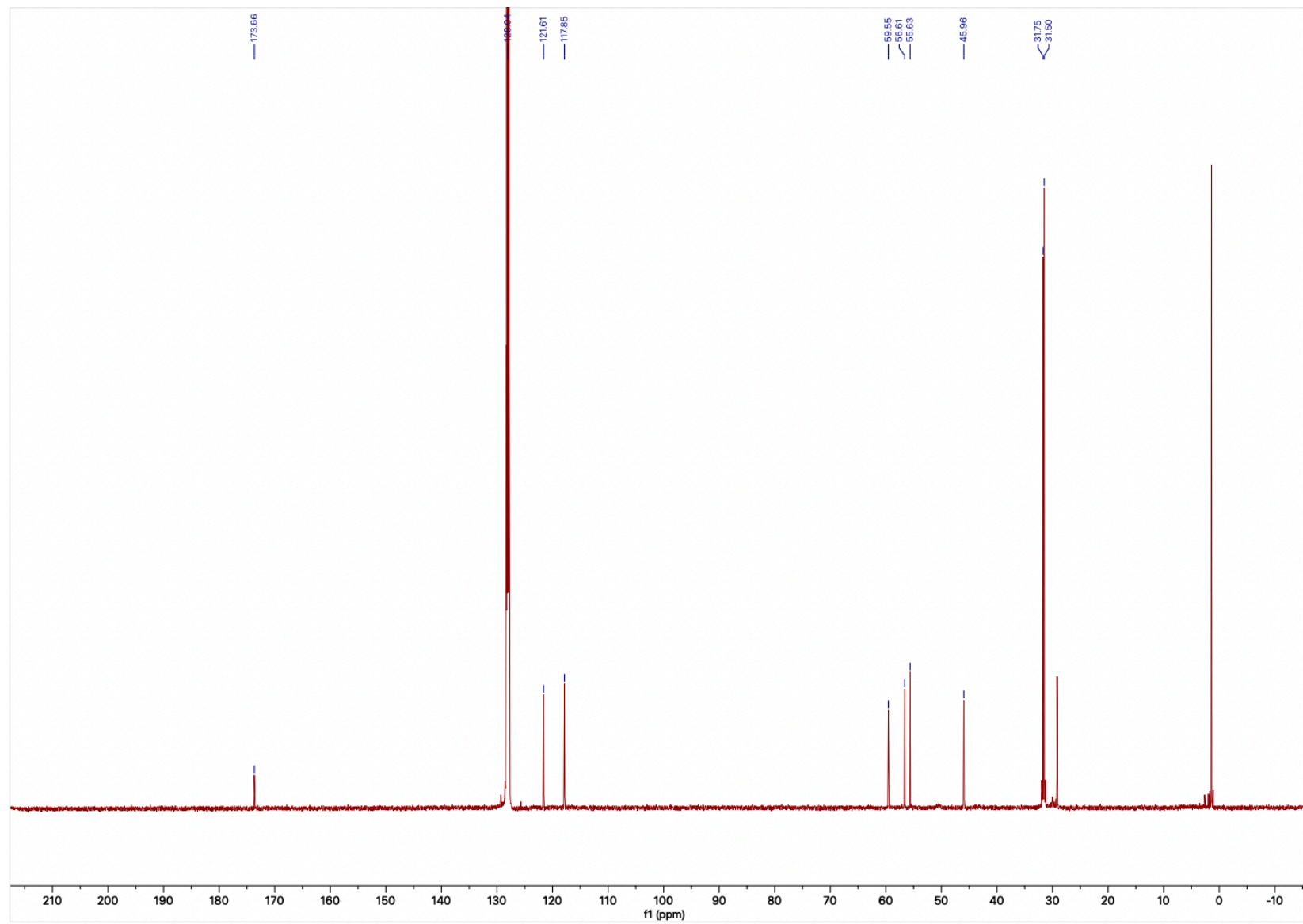
(L^{tBu})GeBr (1) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



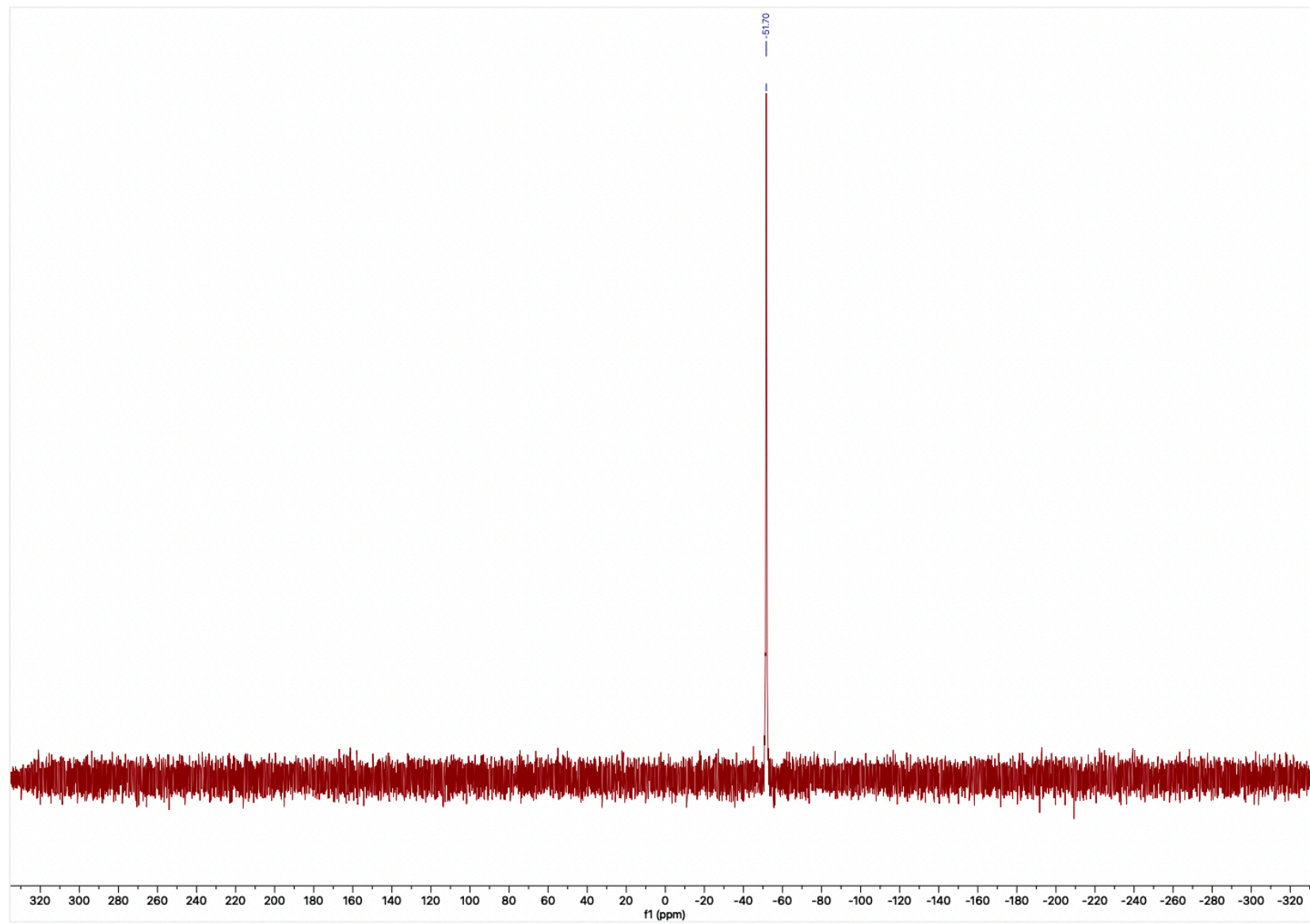
(L^{tBu})SnBr (2) ¹H NMR spectrum



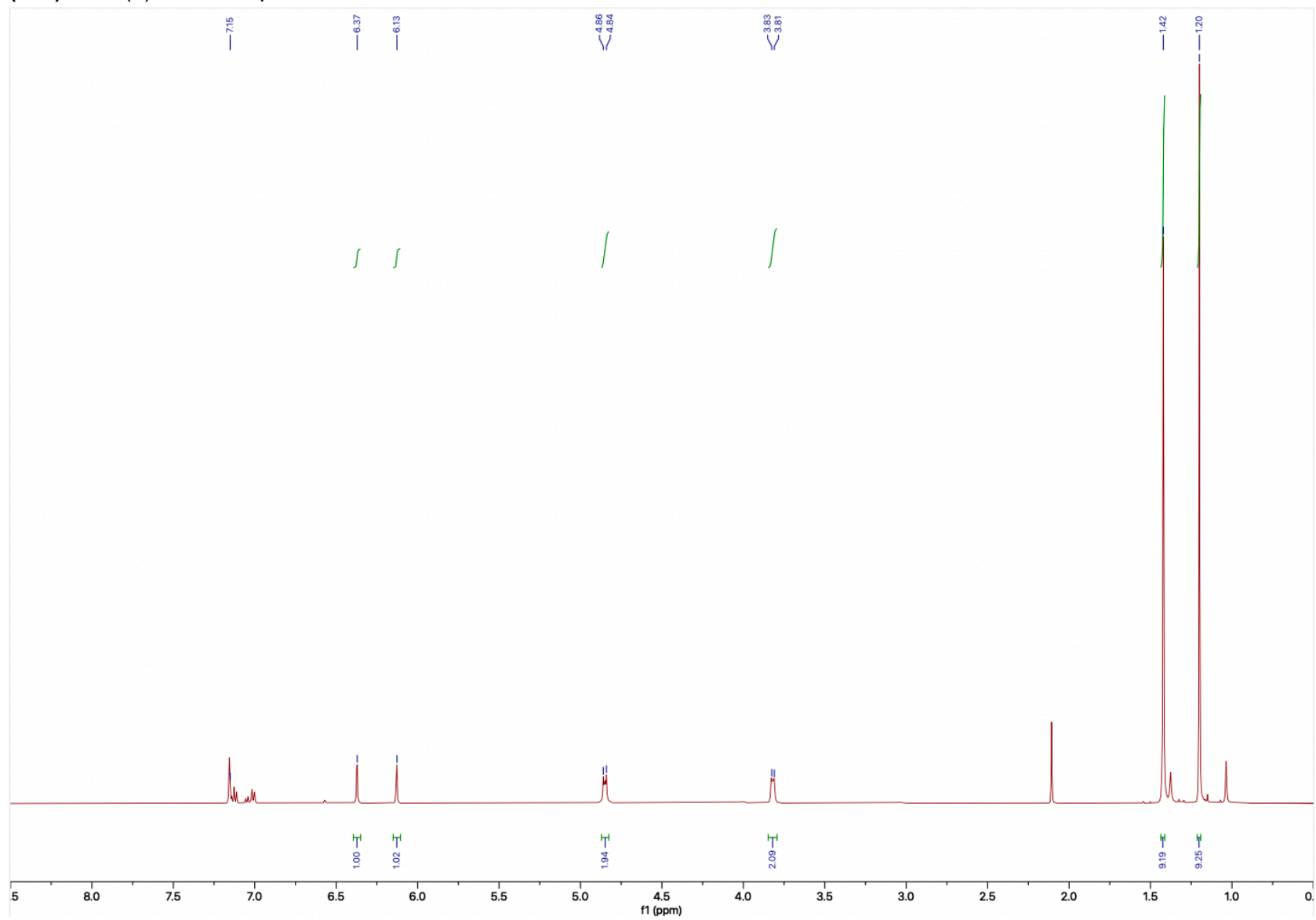
(L^{tBu})SnBr (2) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



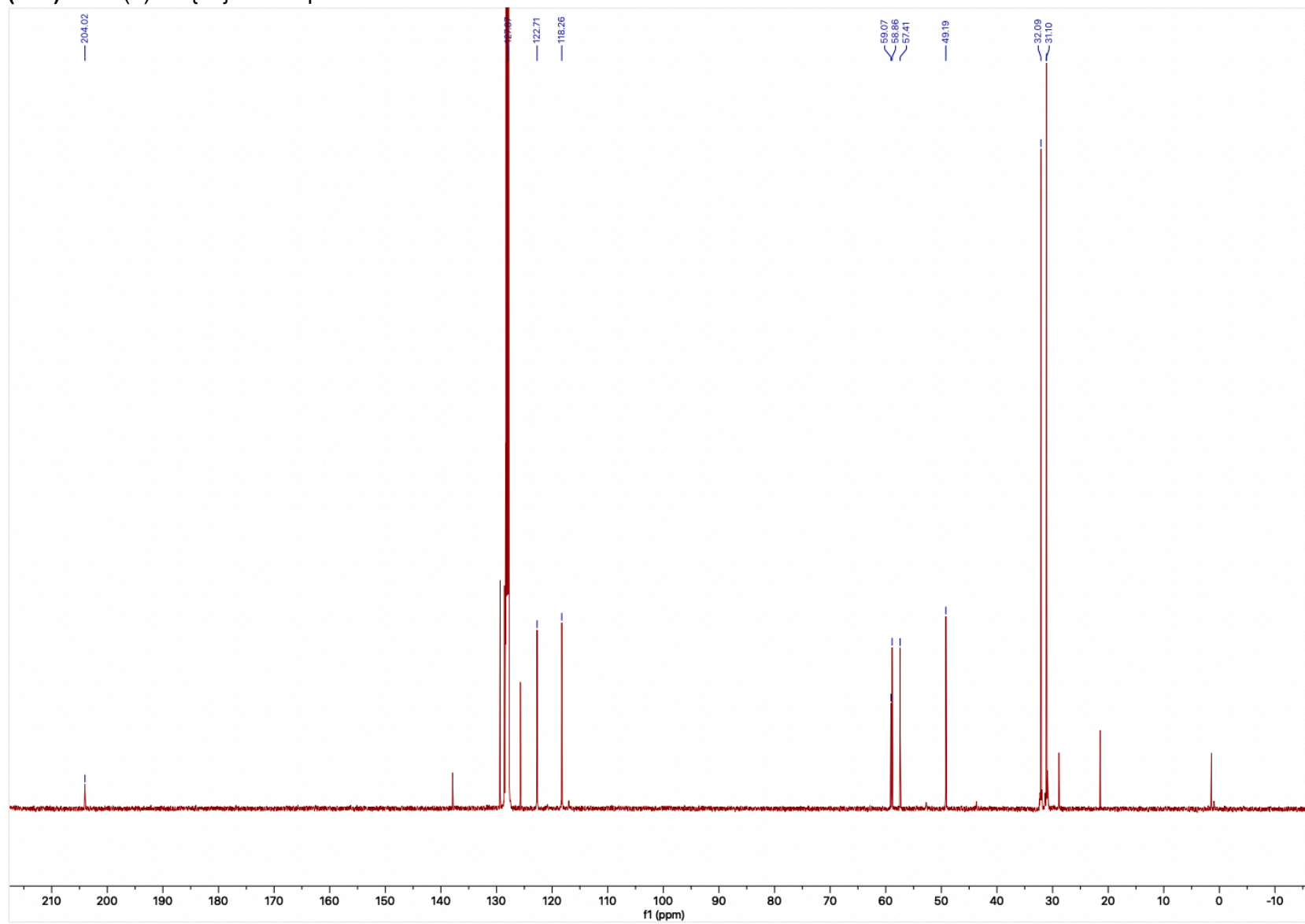
(L^{tBu})SnBr (2) ¹¹⁹Sn NMR spectrum



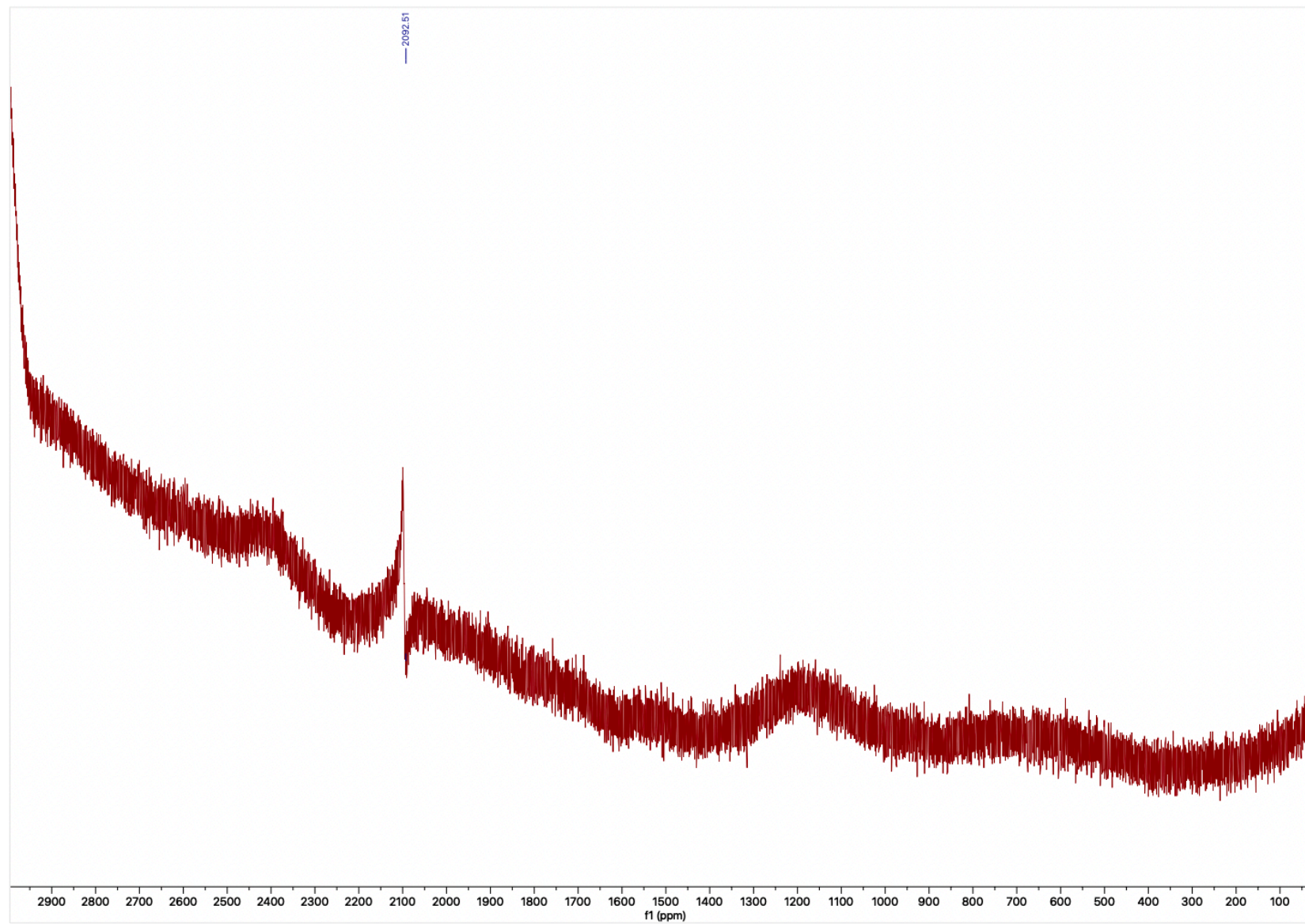
(L^{tBu})PbBr (3) ¹H NMR spectrum



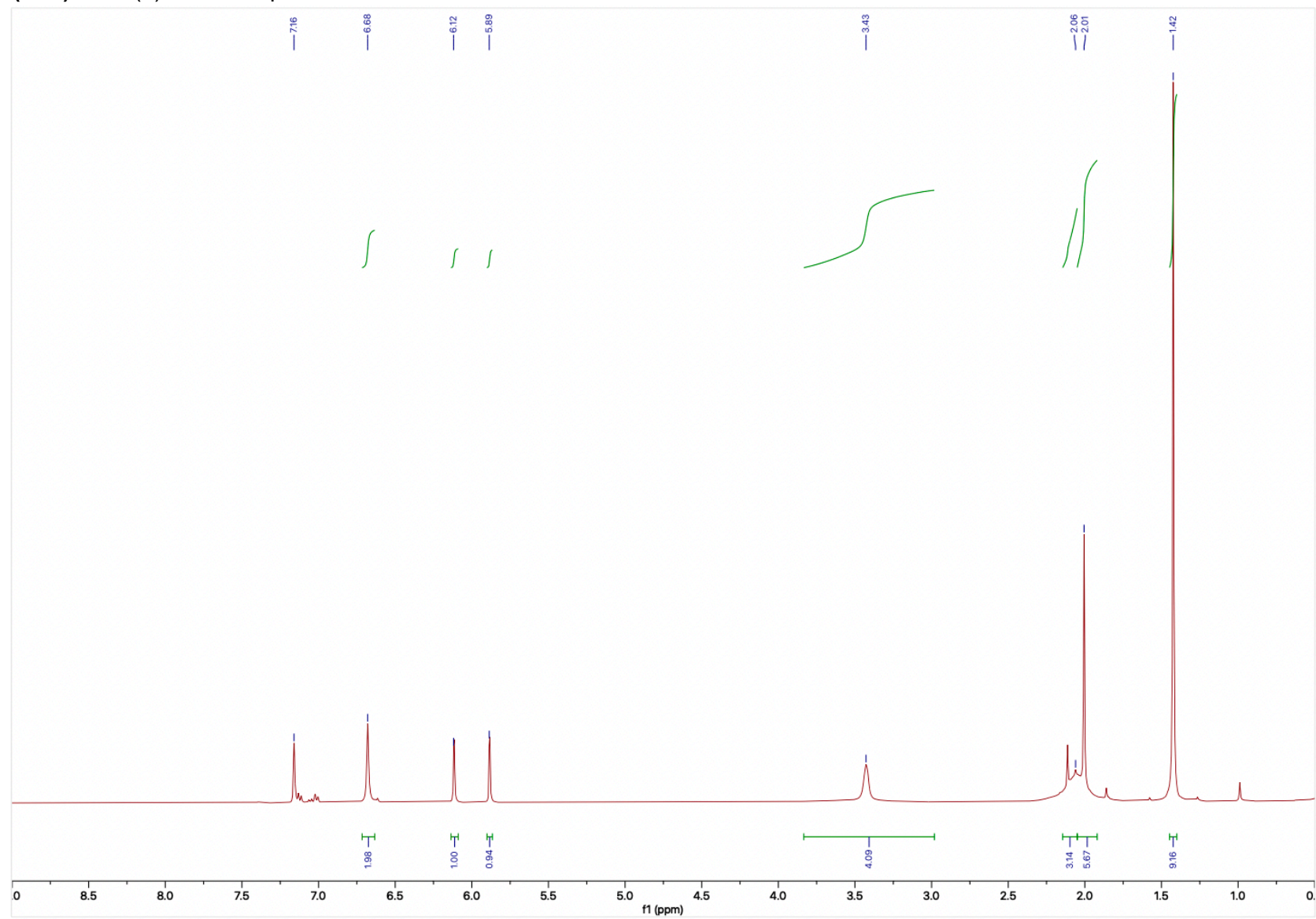
(L^{tBu})PbBr (3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



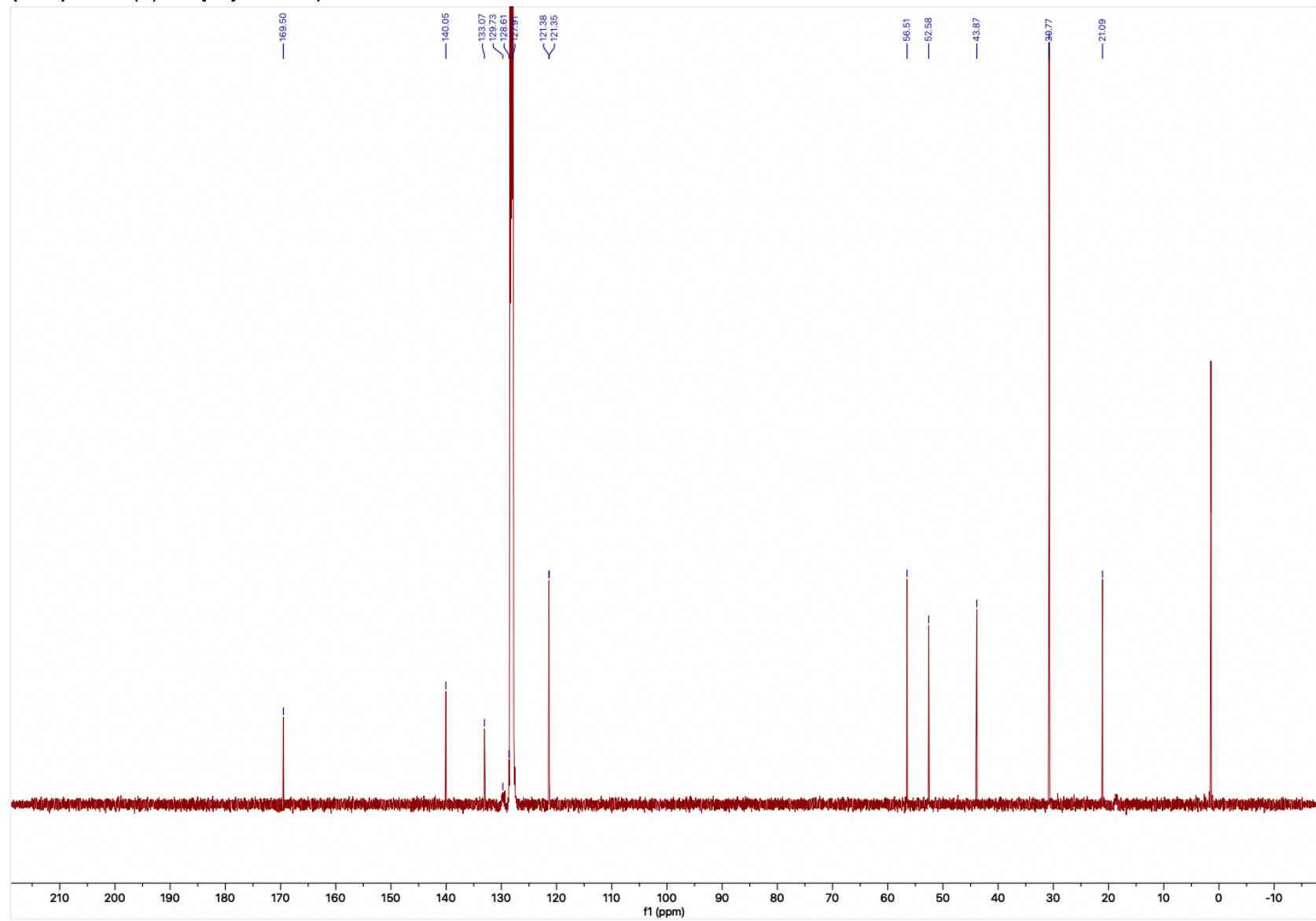
(L^{tBu})PbBr (3) ²⁰⁷Pb NMR spectrum



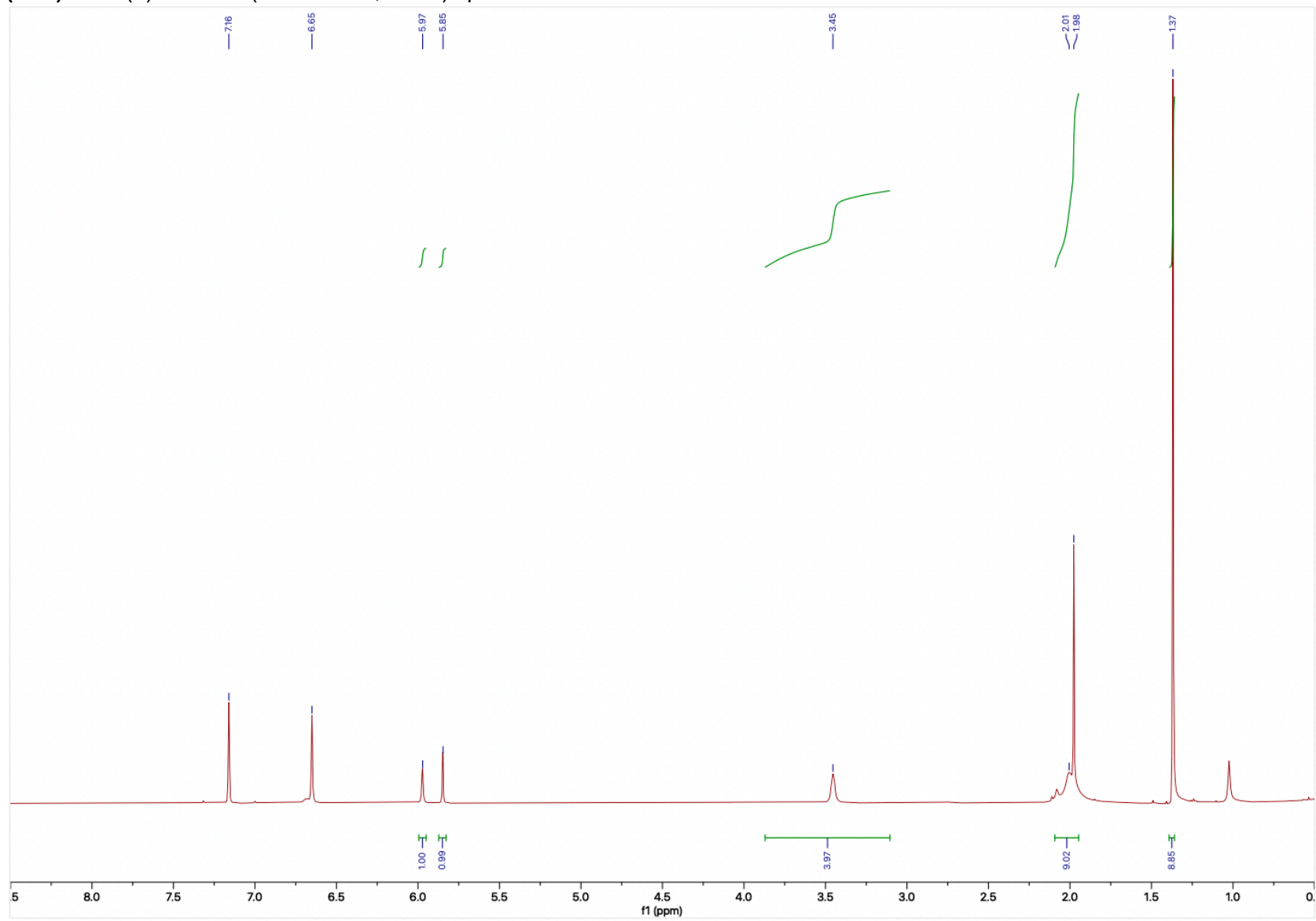
(L^{Mes})GeBr (4) ¹H NMR spectrum



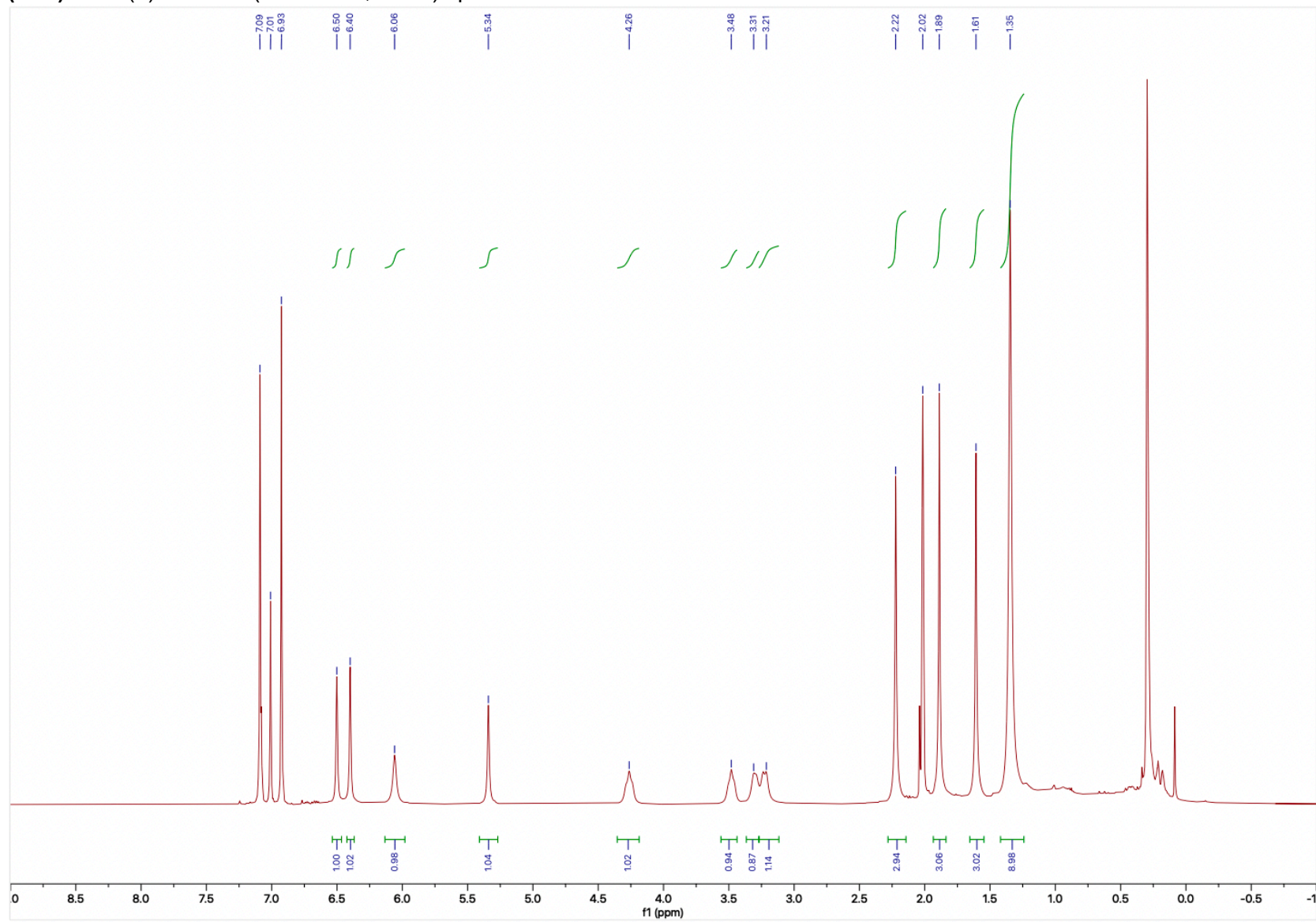
(L^{Mes})GeBr (4) ¹³C{¹H} NMR spectrum



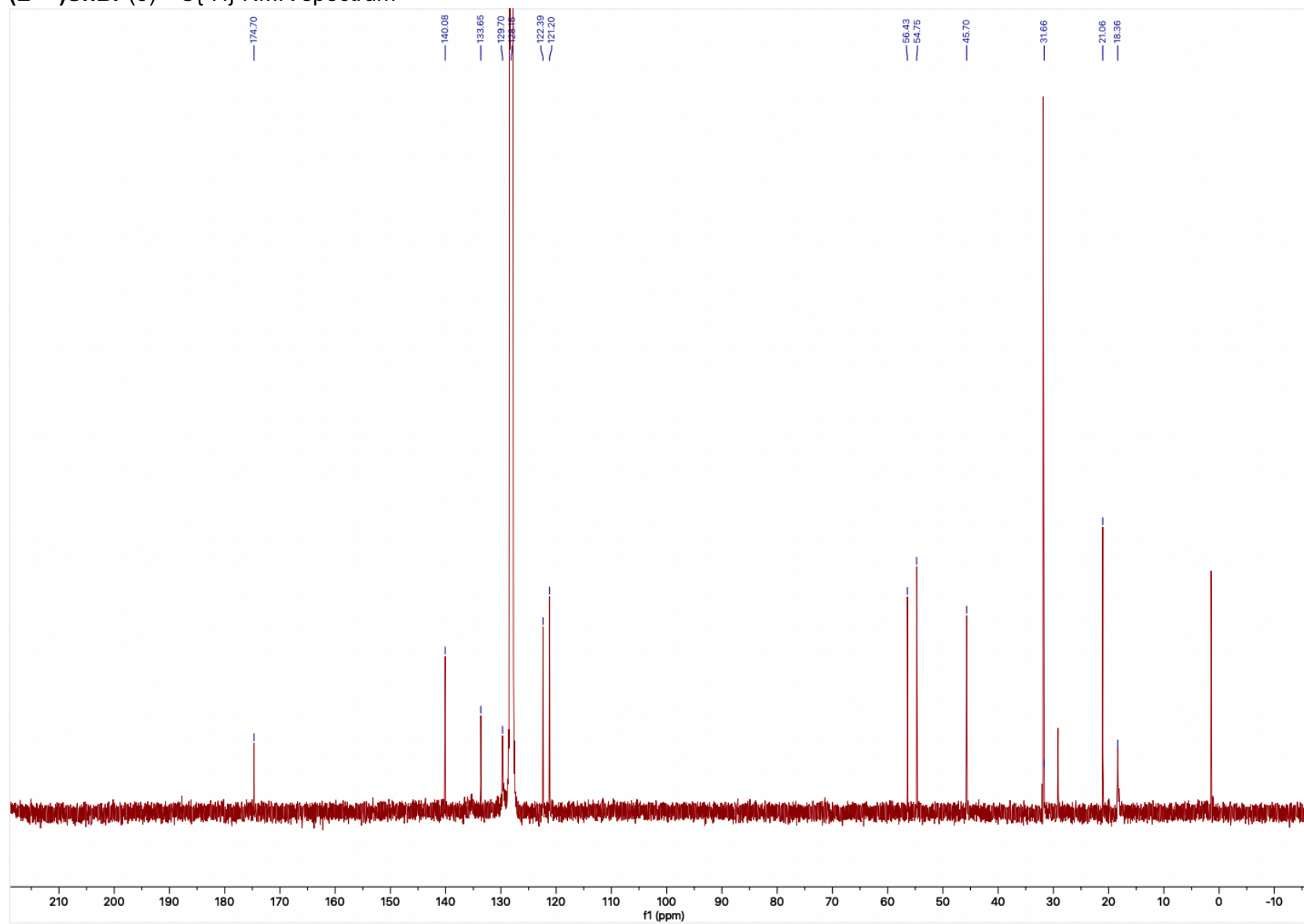
(L^{Mes})SnBr (5) ¹H NMR (benzene-d₆, 298K) spectrum



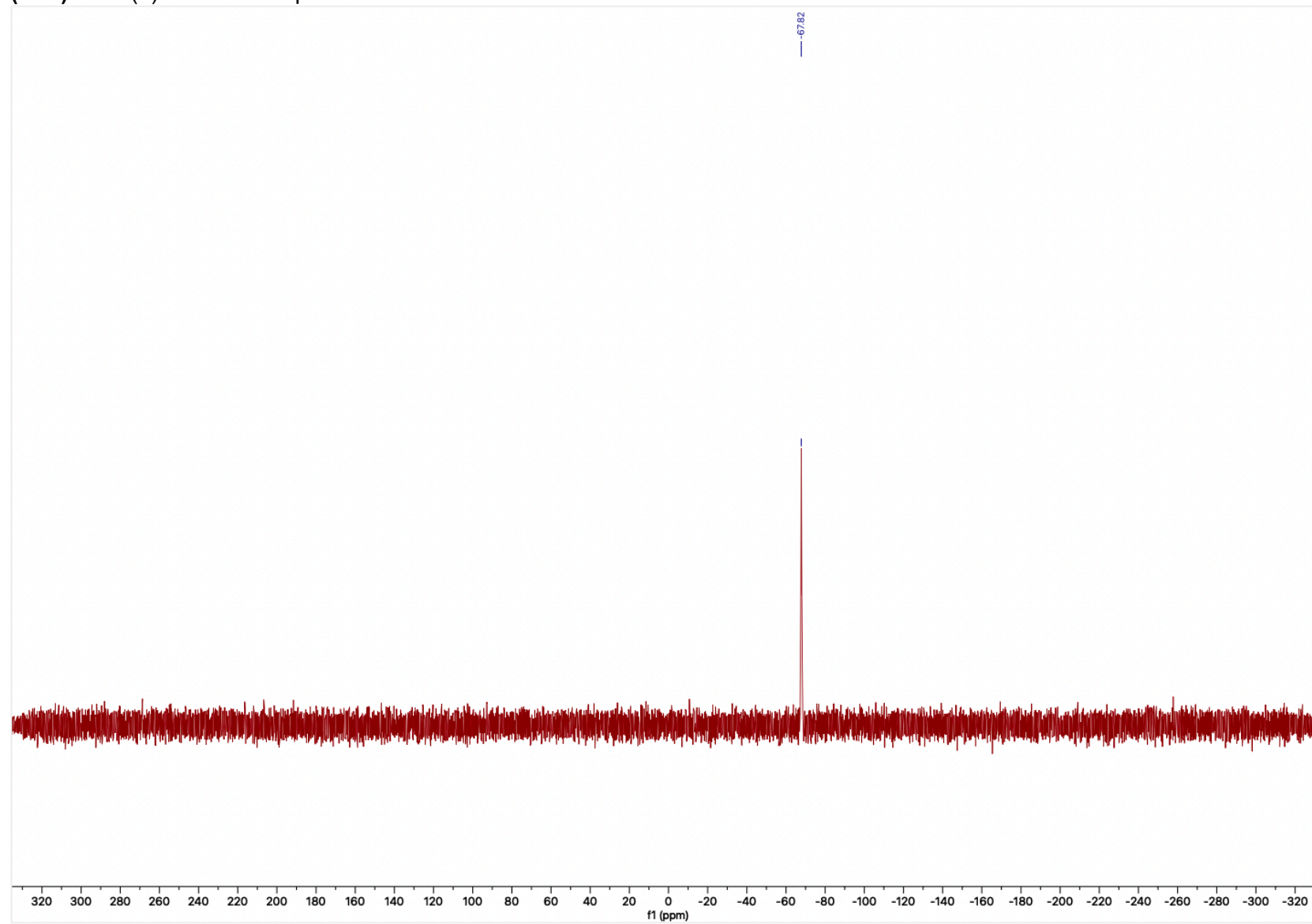
(L^{Mes})SnBr (5) ¹H NMR (toluene-d₈, 198K) spectrum



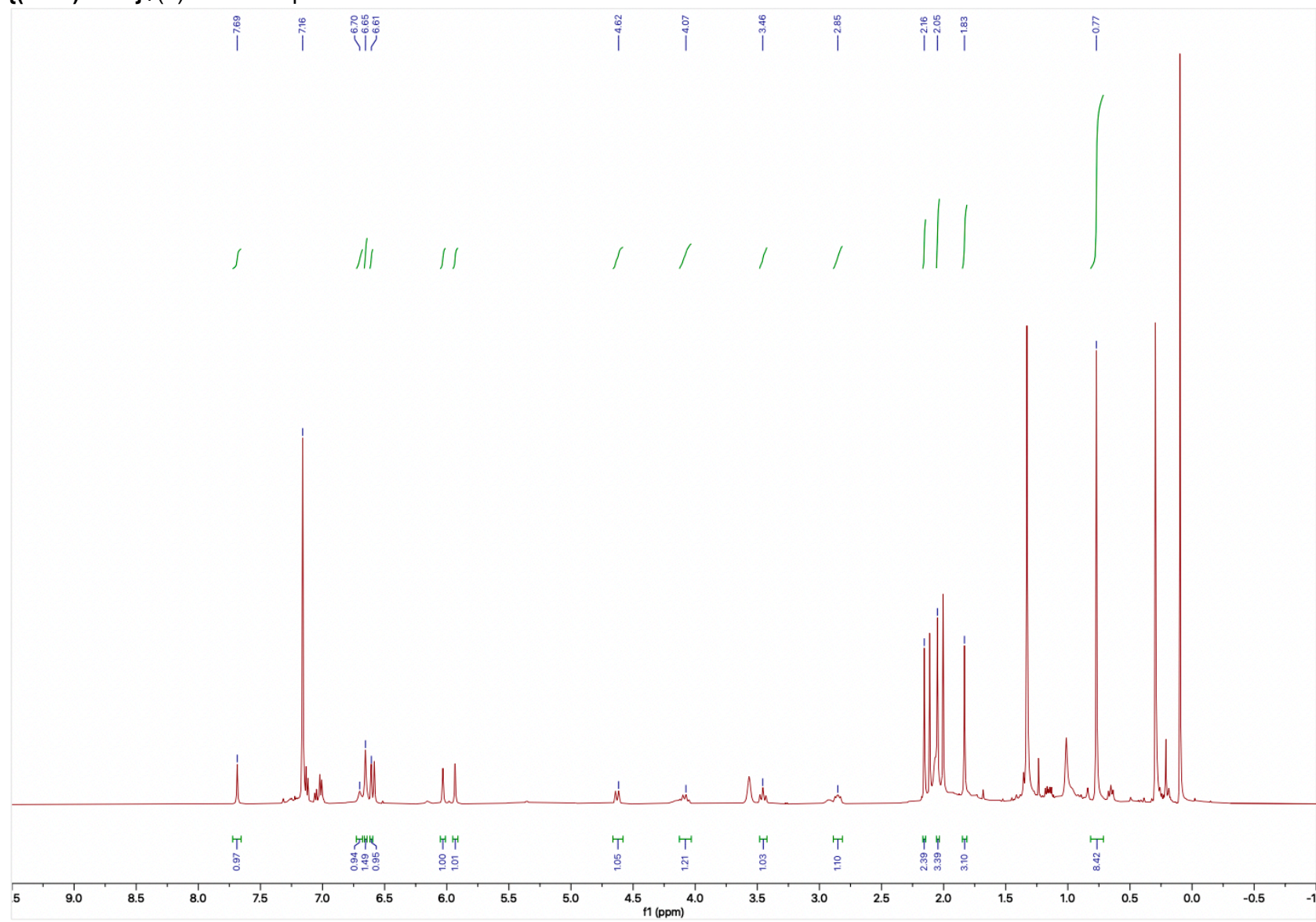
(L^{Mes})SnBr (5) ¹³C{¹H} NMR spectrum



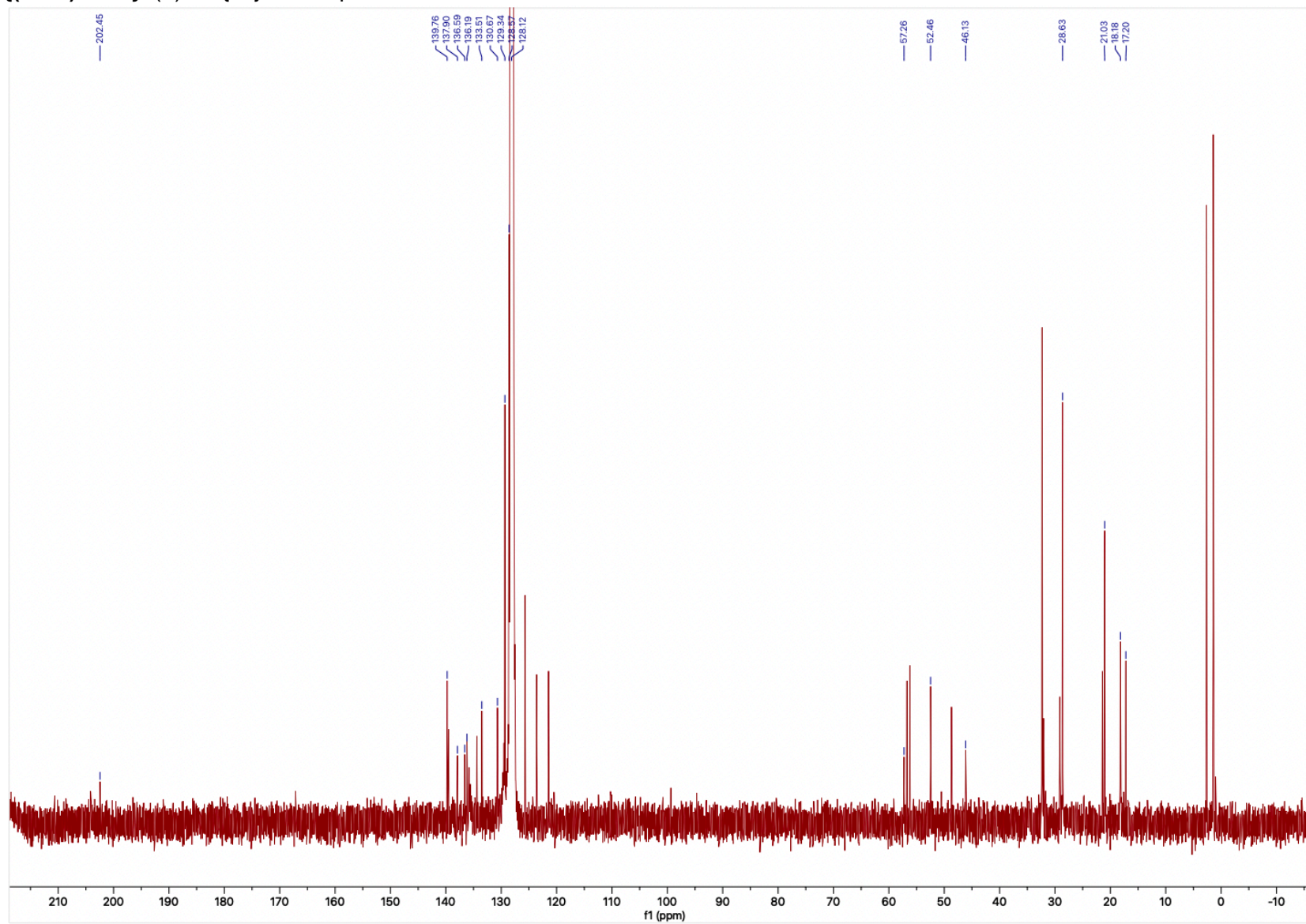
(L^{Mes})SnBr (5) ¹¹⁹Sn NMR spectrum



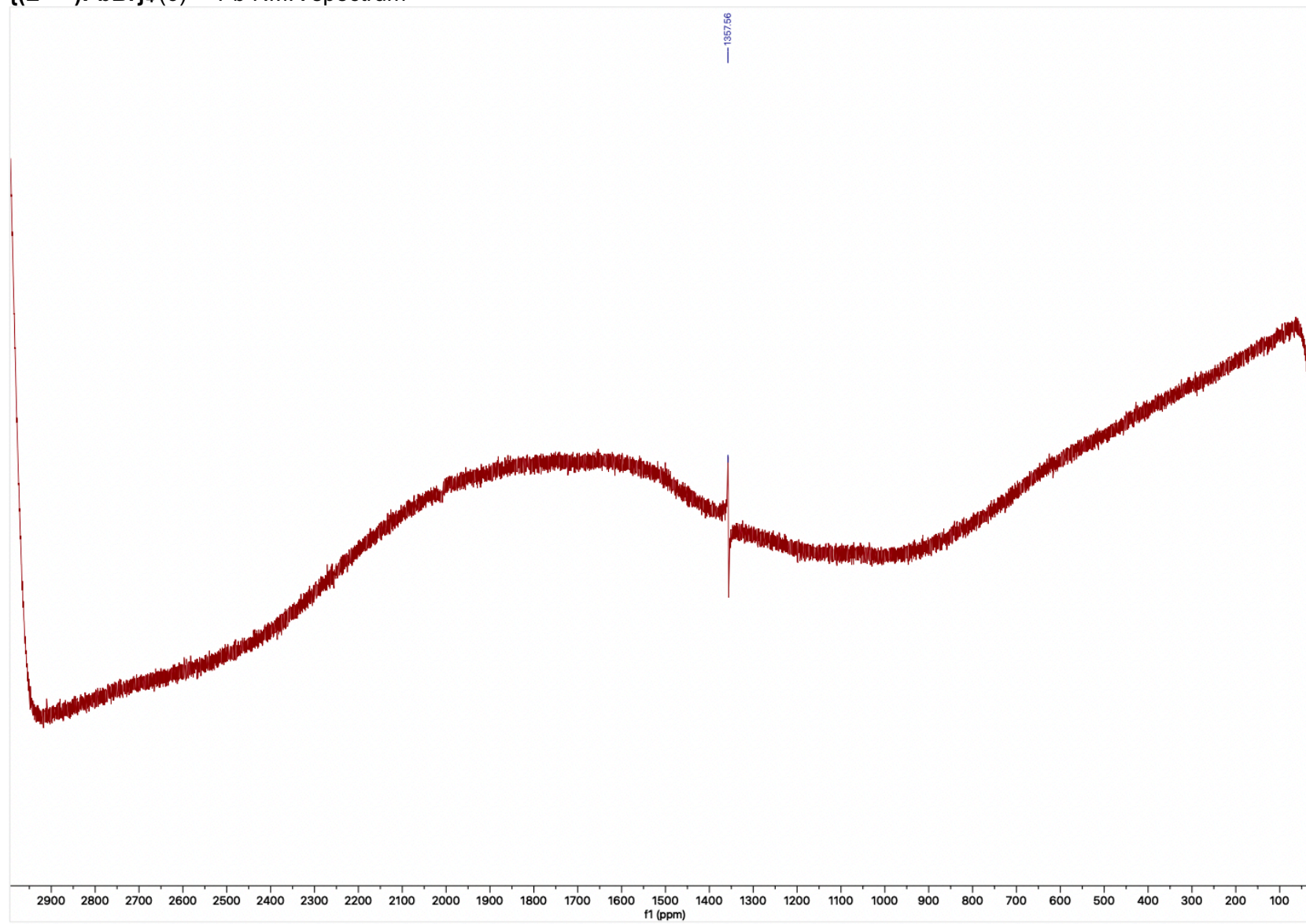
$\{(L^{\text{Mes}})_4\text{PbBr}\}_4$ (6) ^1H NMR spectrum



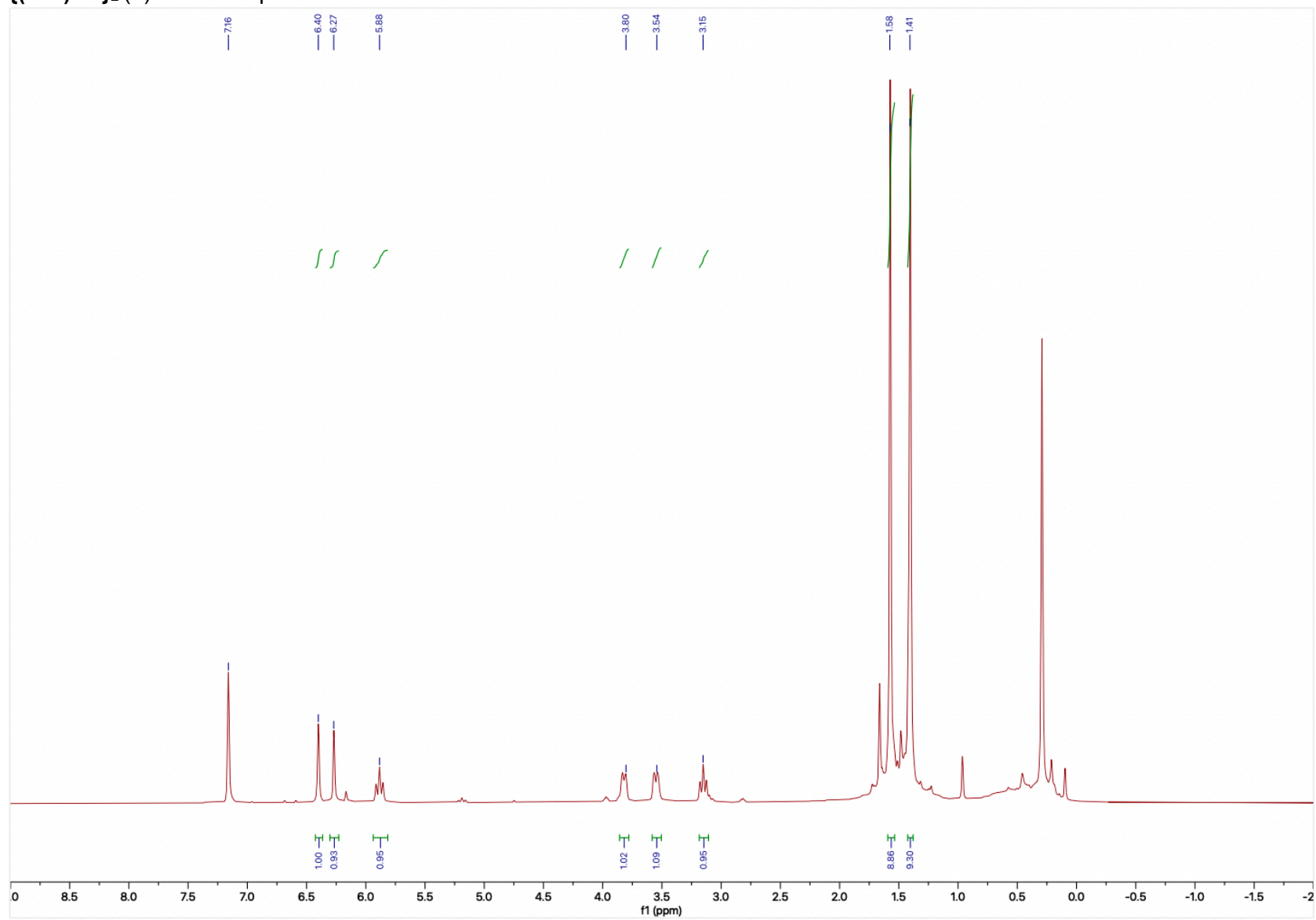
$\{(\text{L}^{\text{Mes}})\text{PbBr}\}_4$ (6) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

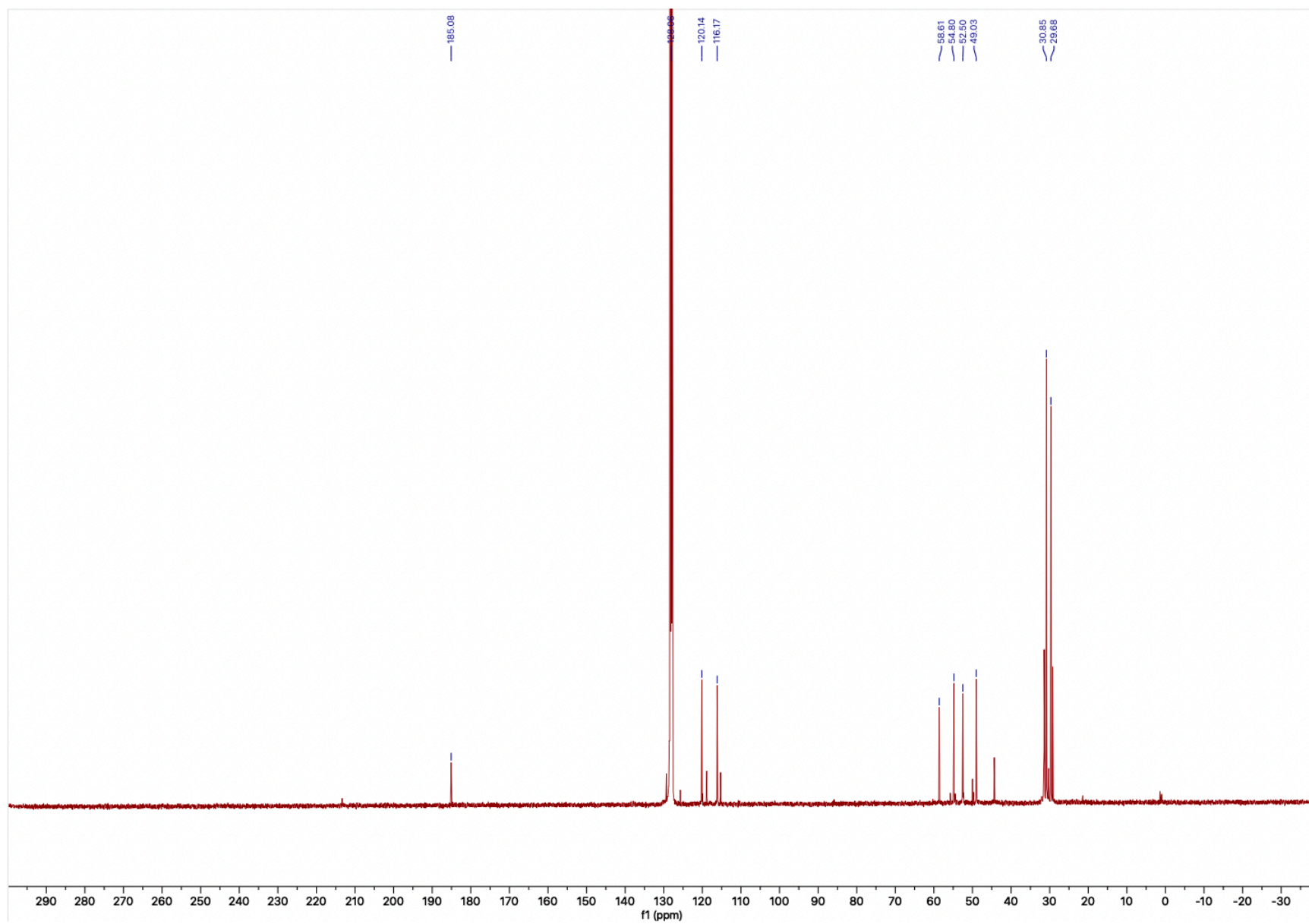


$\{(\text{L}^{\text{Mes}})\text{PbBr}\}_4$ (6) ^{207}Pb NMR spectrum

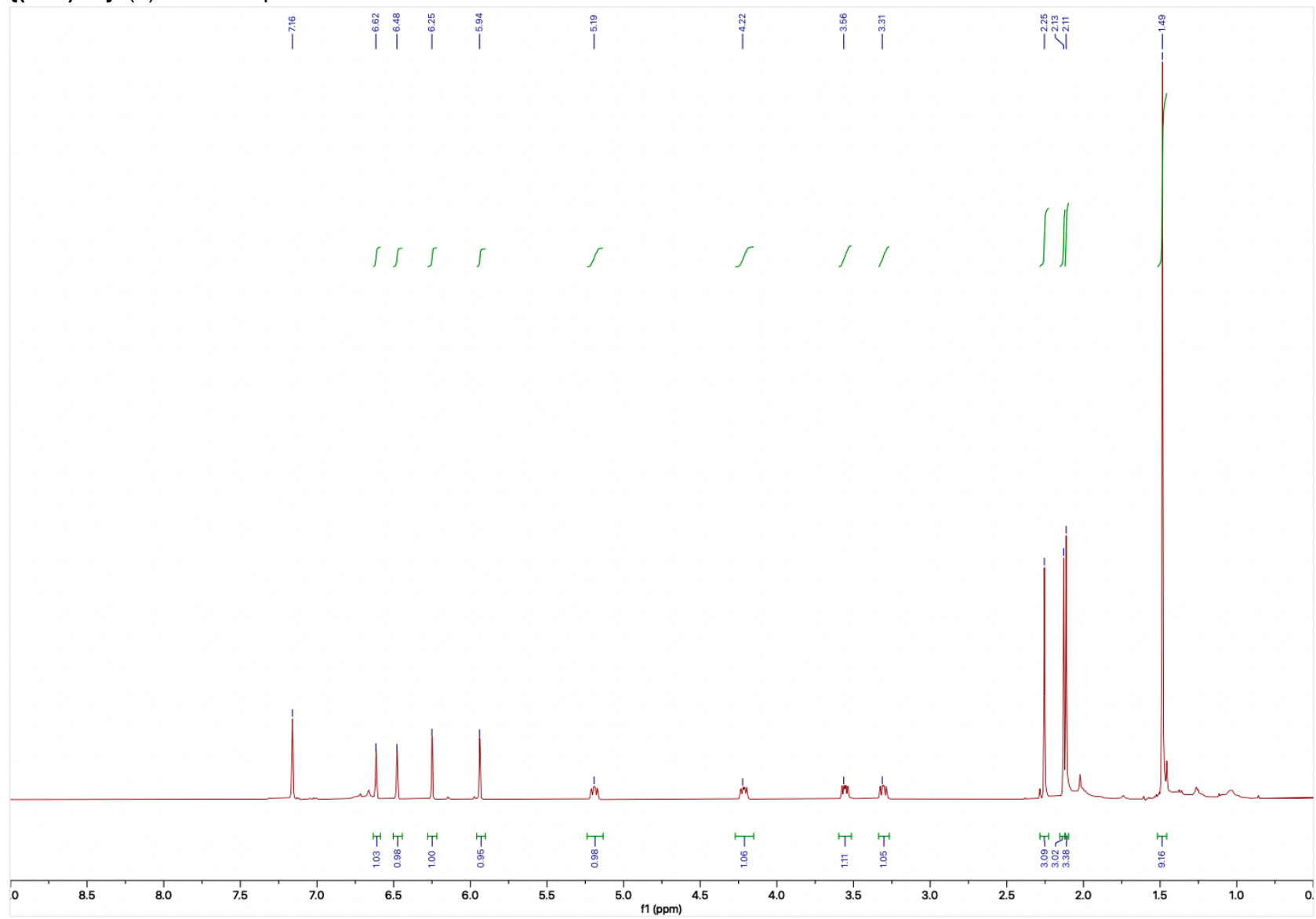


$\{(L^{tBu})Ge\}_2$ (7) 1H NMR spectrum

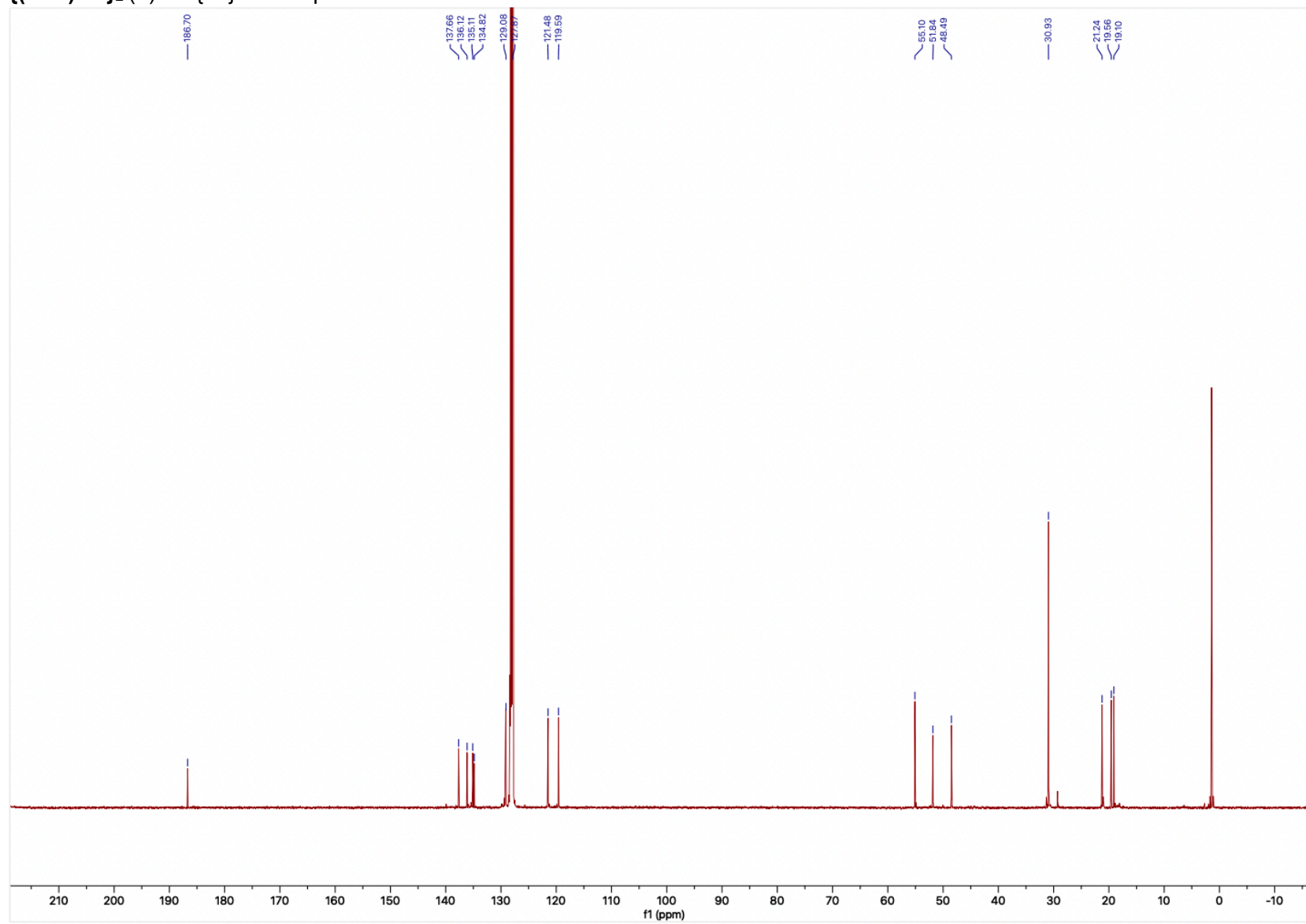




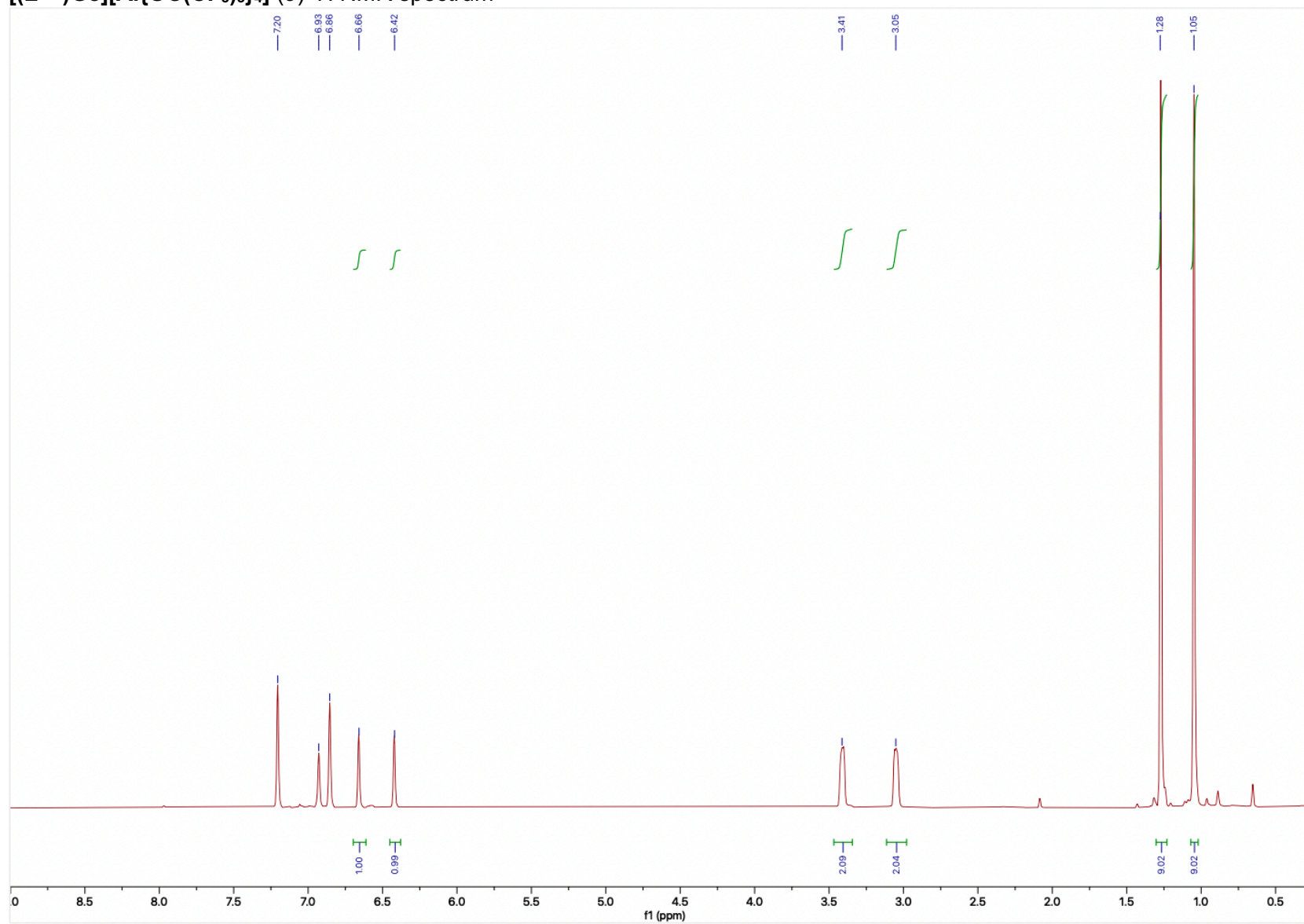
$\{(\text{L}^{\text{Mes}})\text{Ge}\}_2$ (**8**) ^1H NMR spectrum



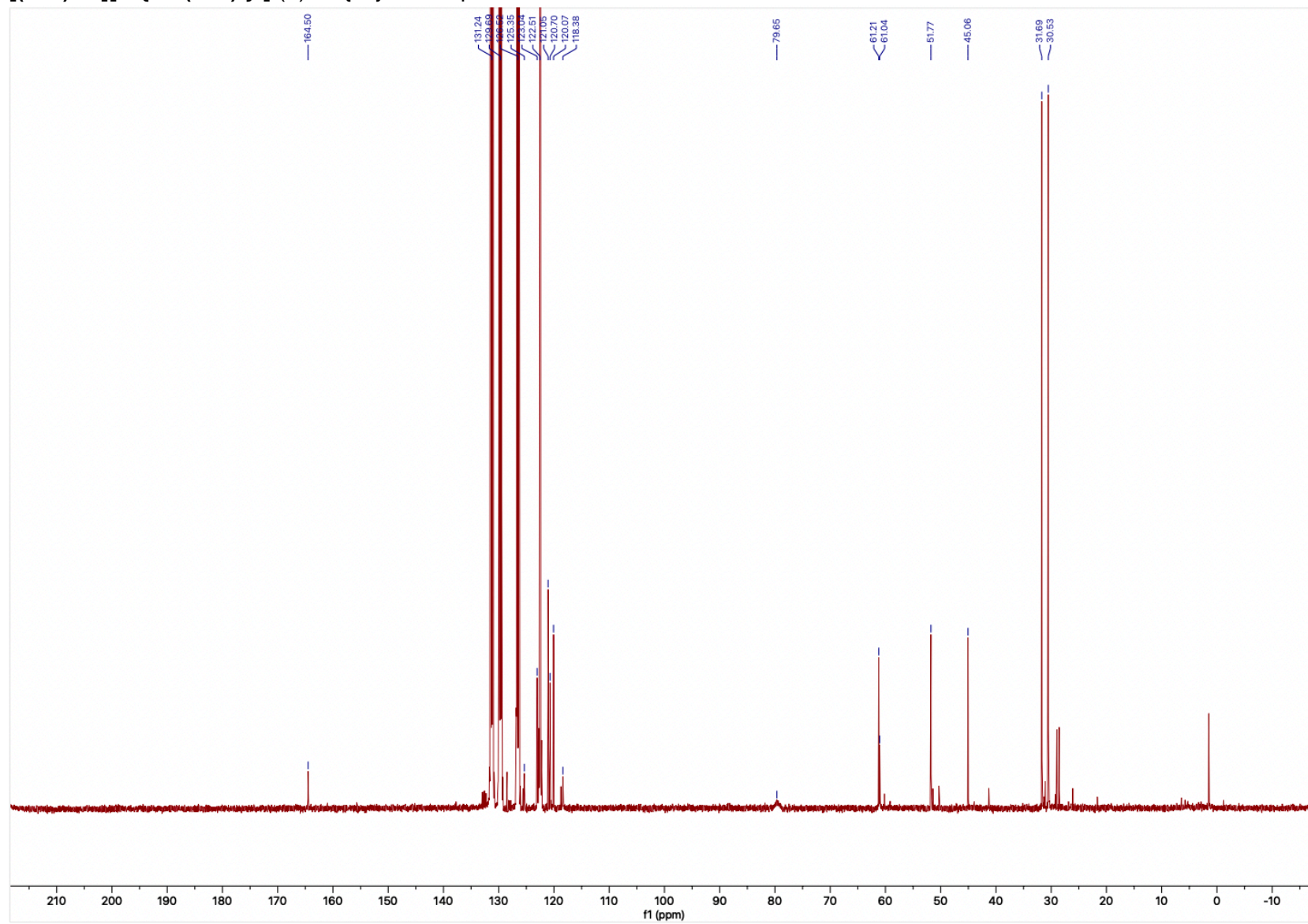
$\{(L^{\text{Mes}})\text{Ge}\}_2$ (**8**) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



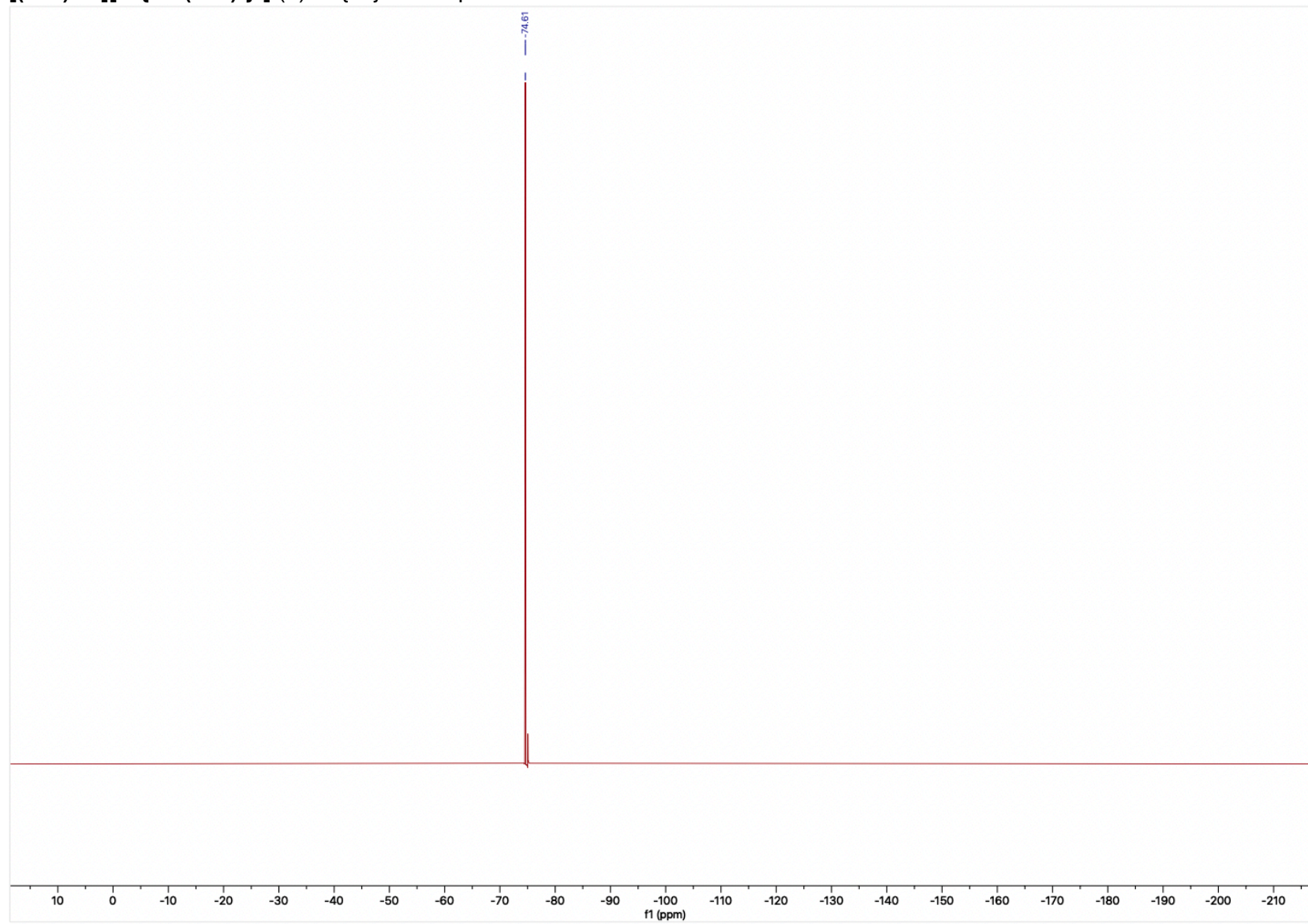
$[(L^{tBu})Ge][Al\{OC(CF_3)_3\}_4]$ (**9**) 1H NMR spectrum



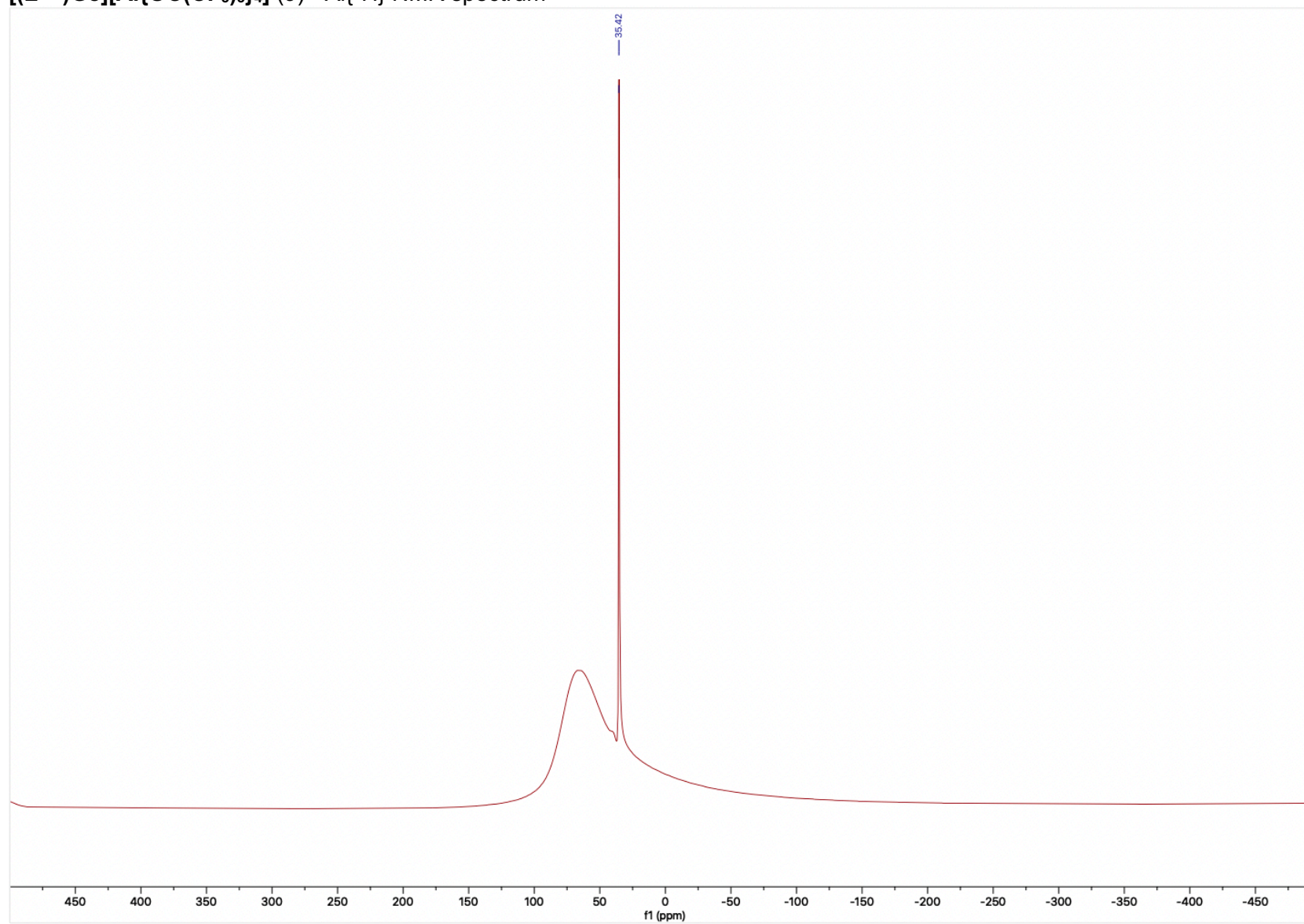
$[(L^{tBu})Ge][Al\{OC(CF_3)_3\}_4]$ (**9**) $^{13}C\{^1H\}$ NMR spectrum



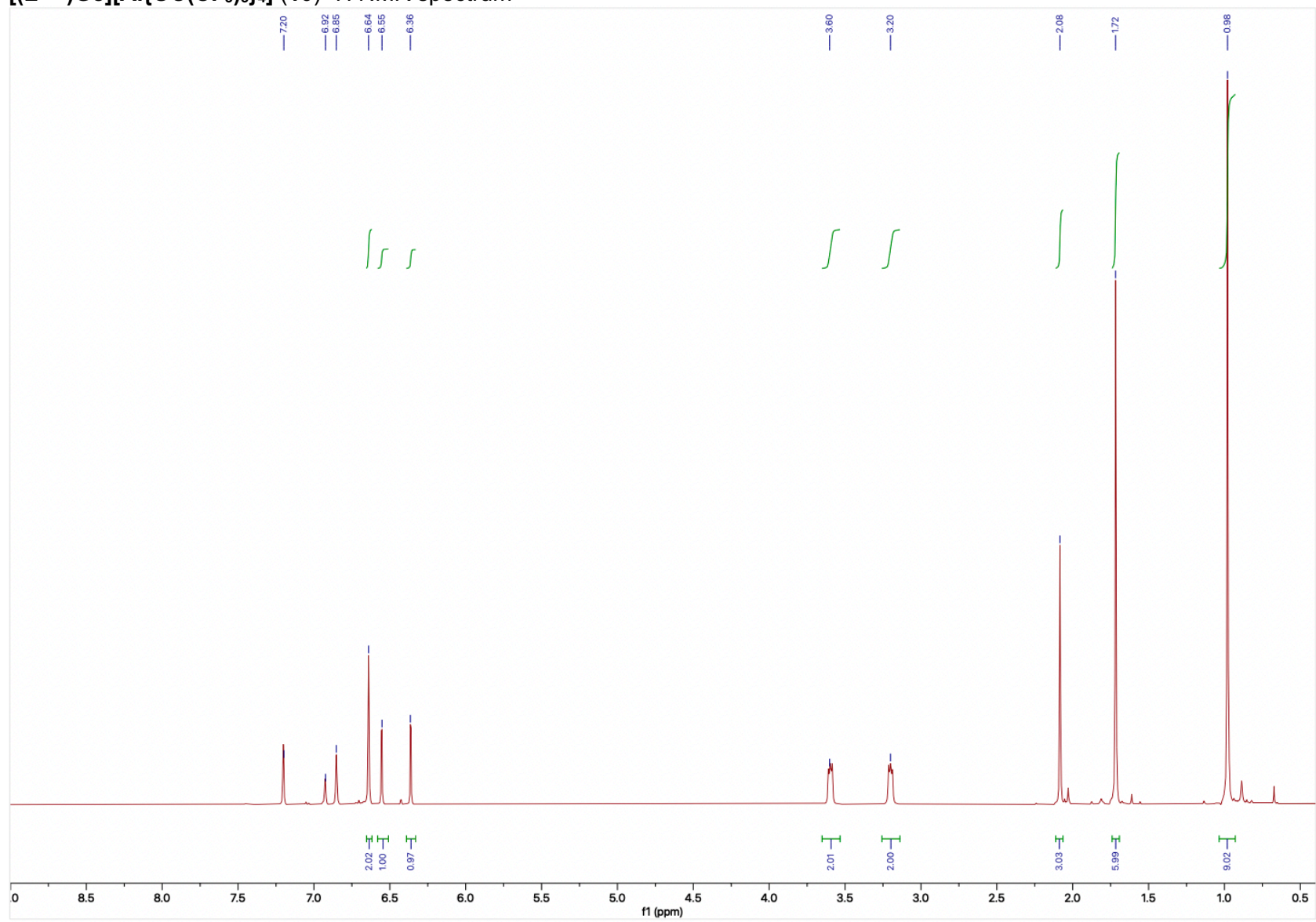
$[(L^{tBu})Ge][Al\{OC(CF_3)_3\}_4]$ (**9**) $^{19}F\{^1H\}$ NMR spectrum



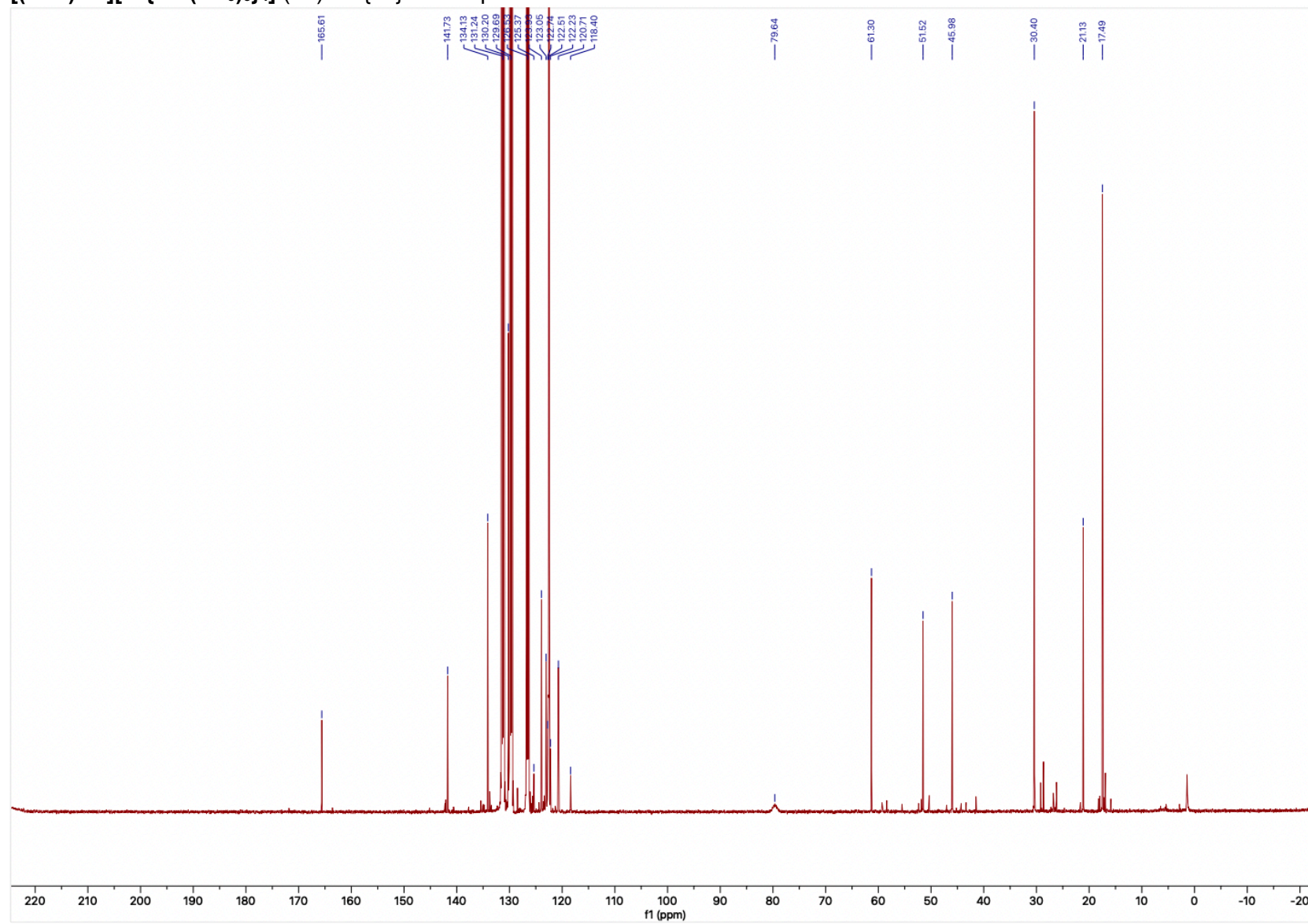
$[(L^{tBu})Ge][Al\{OC(CF_3)_3\}_4]$ (**9**) $^{27}Al\{^1H\}$ NMR spectrum



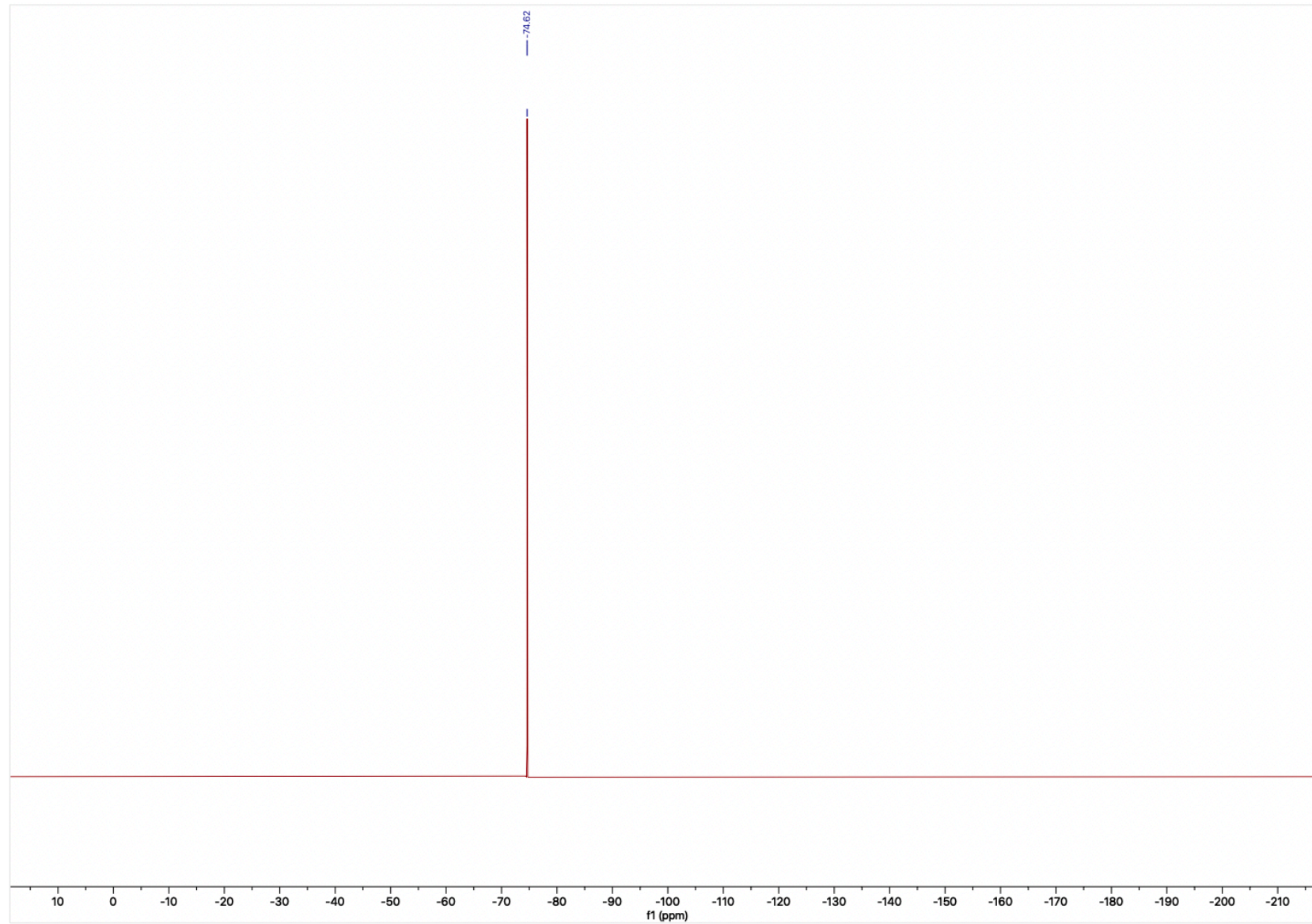
$[(L^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**10**) ^1H NMR spectrum



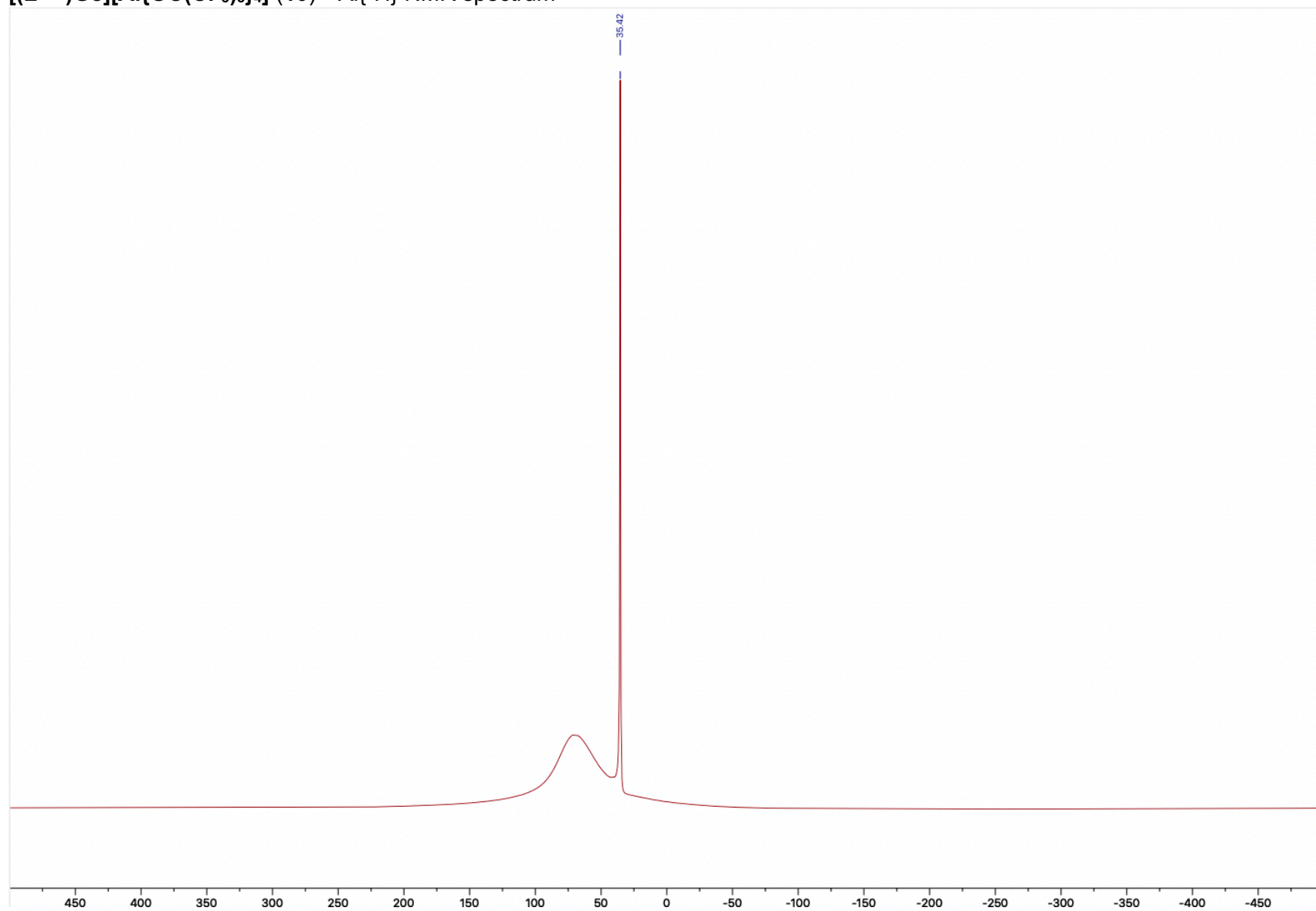
$[(L^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**10**) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



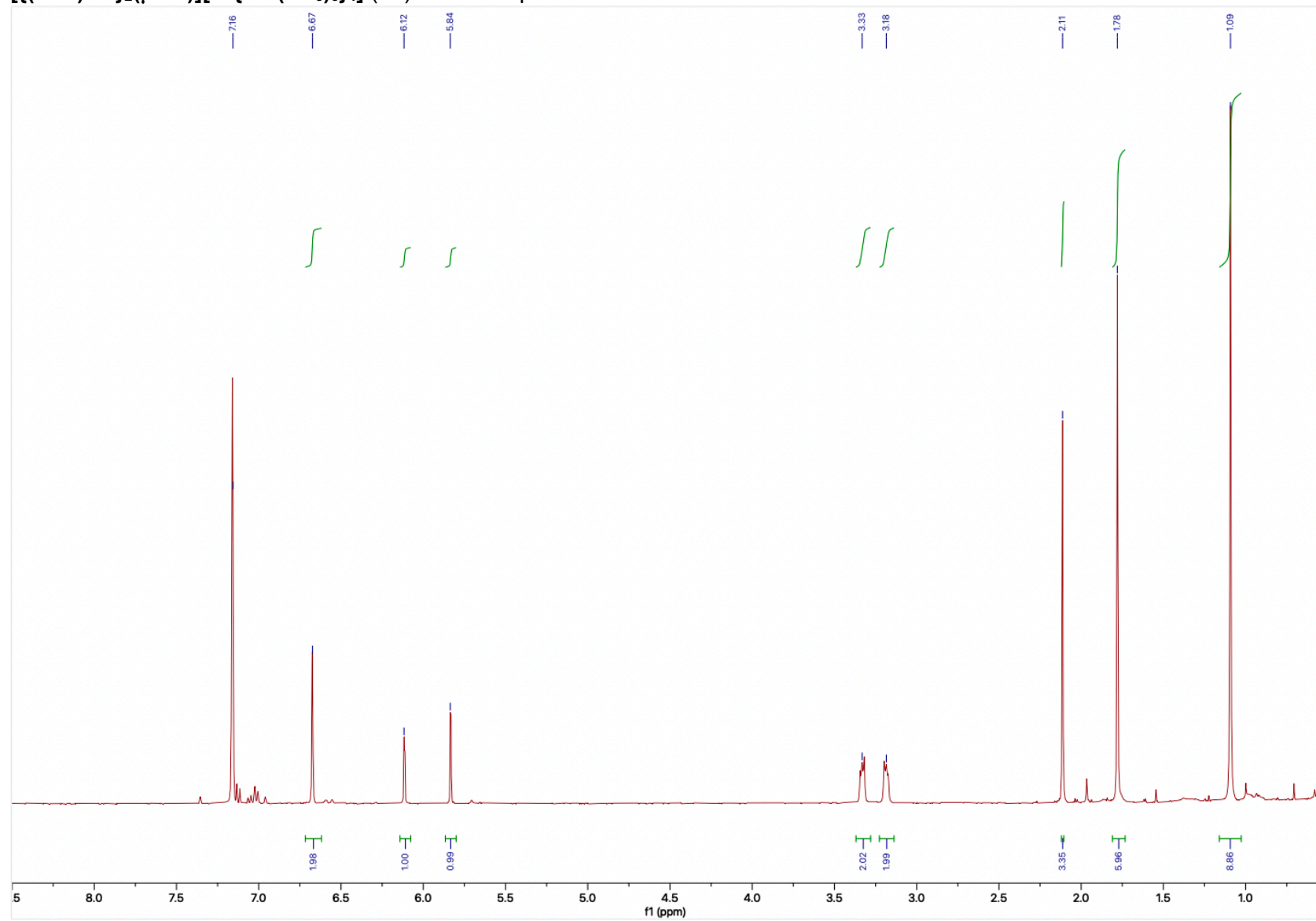
$[(L^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**10**) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



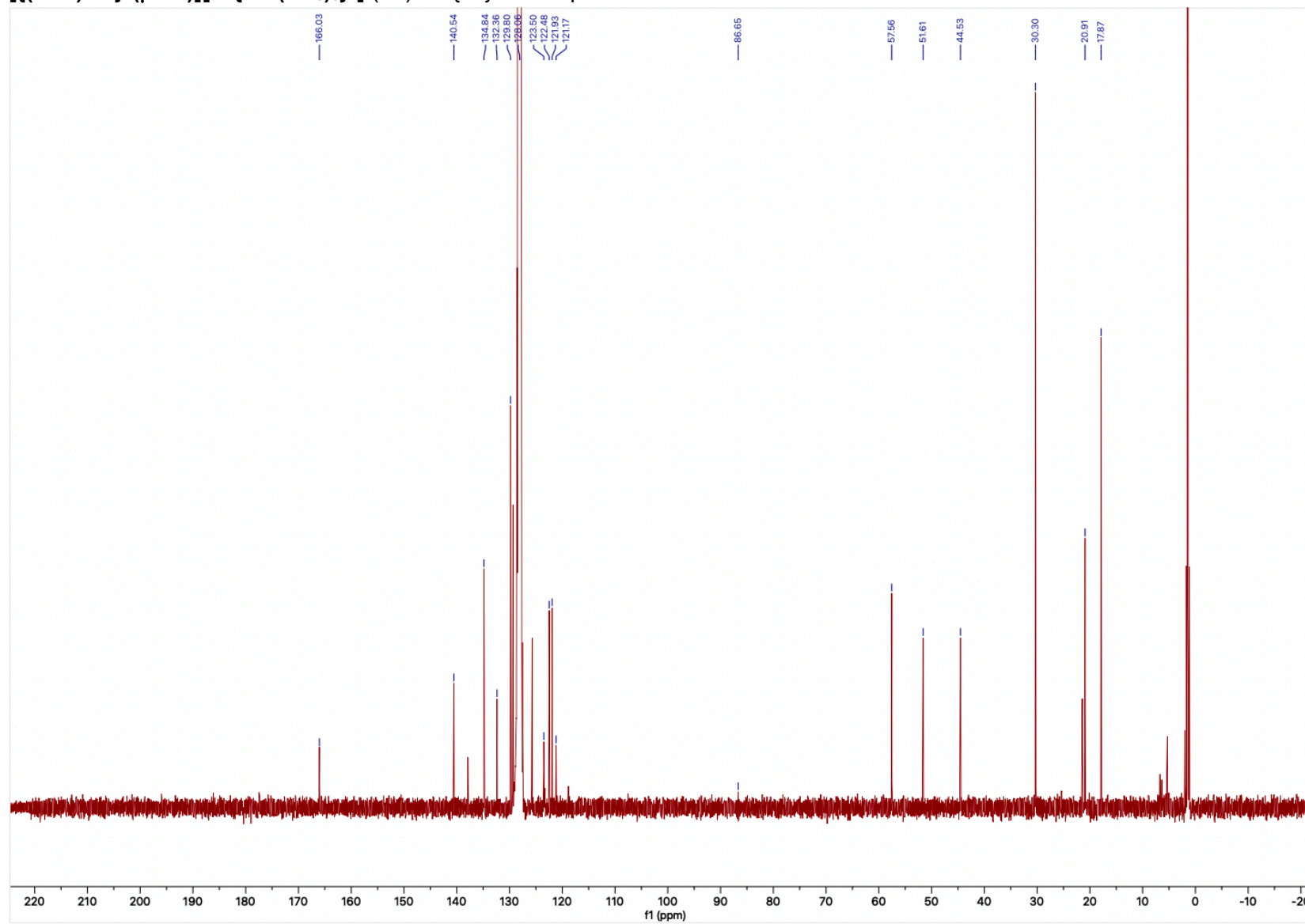
$[(L^{\text{Mes}})\text{Ge}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**10**) $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum



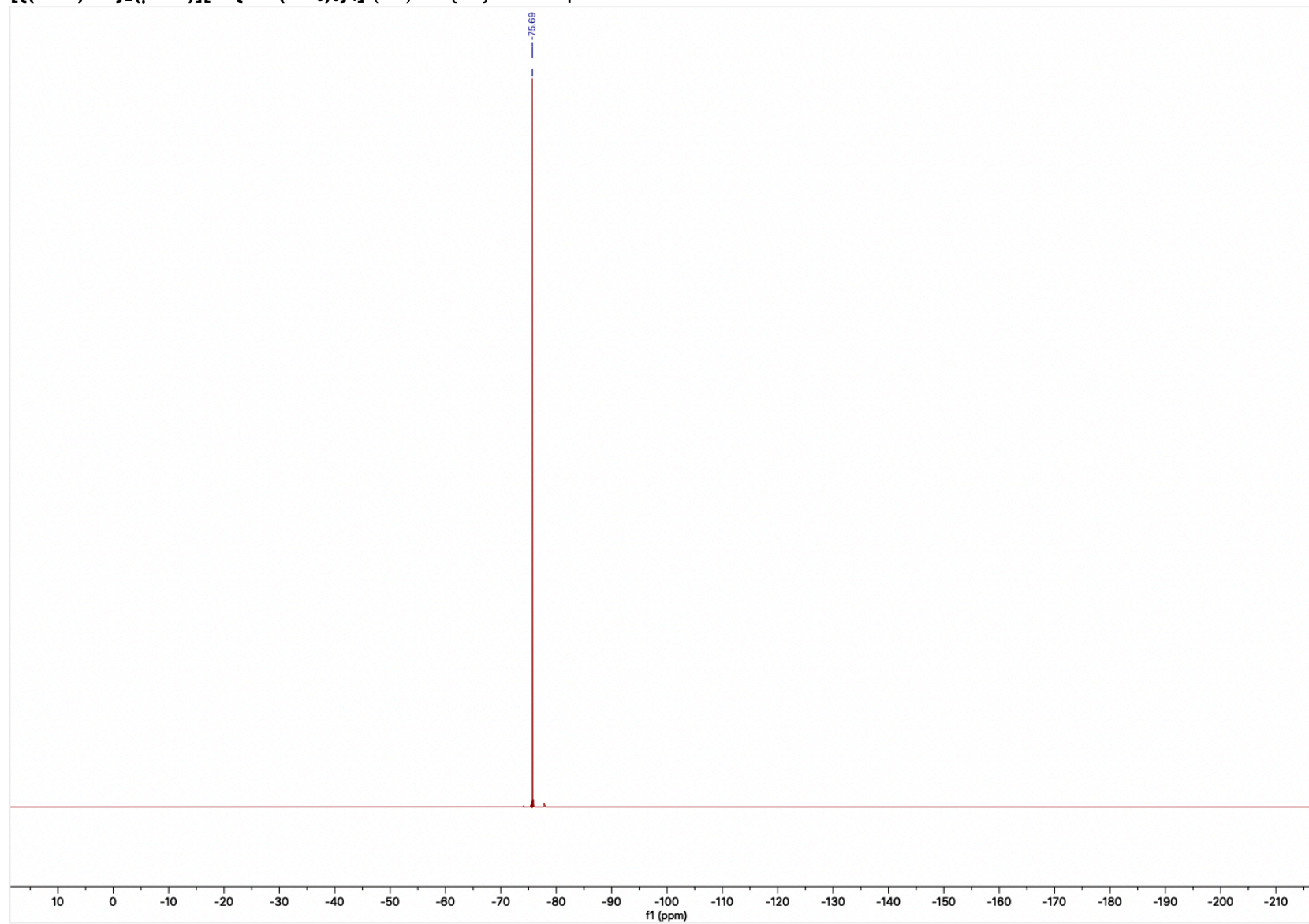
$[(L^{\text{Mes}})\text{Ge}]_2(\mu\text{-Br})[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (11) ^1H NMR spectrum



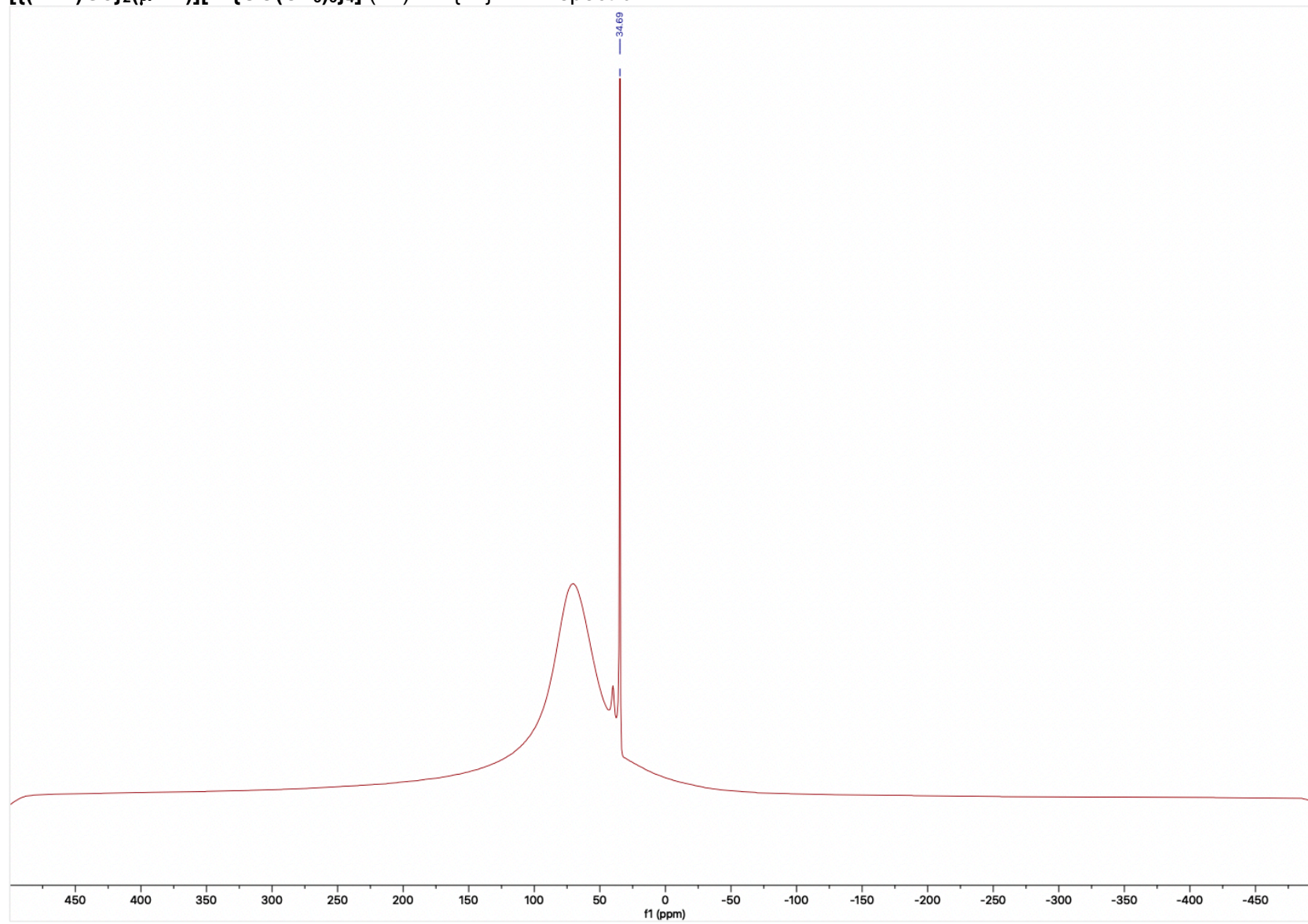
$[(L^{\text{Mes}})\text{Ge}]_2(\mu\text{-Br})[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (11) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



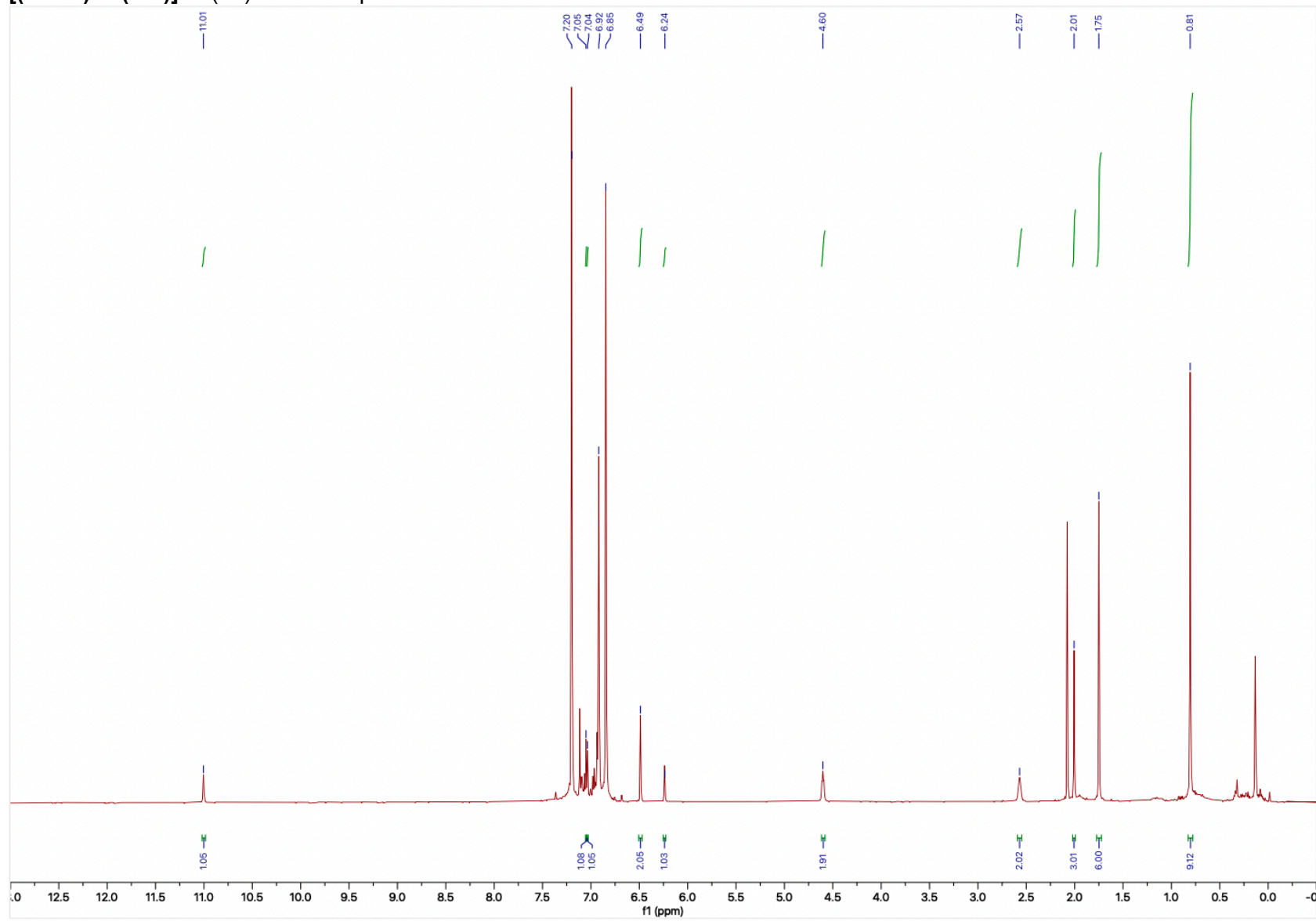
$[(L^{\text{Mes}})\text{Ge}]_2(\mu\text{-Br})[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (11) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



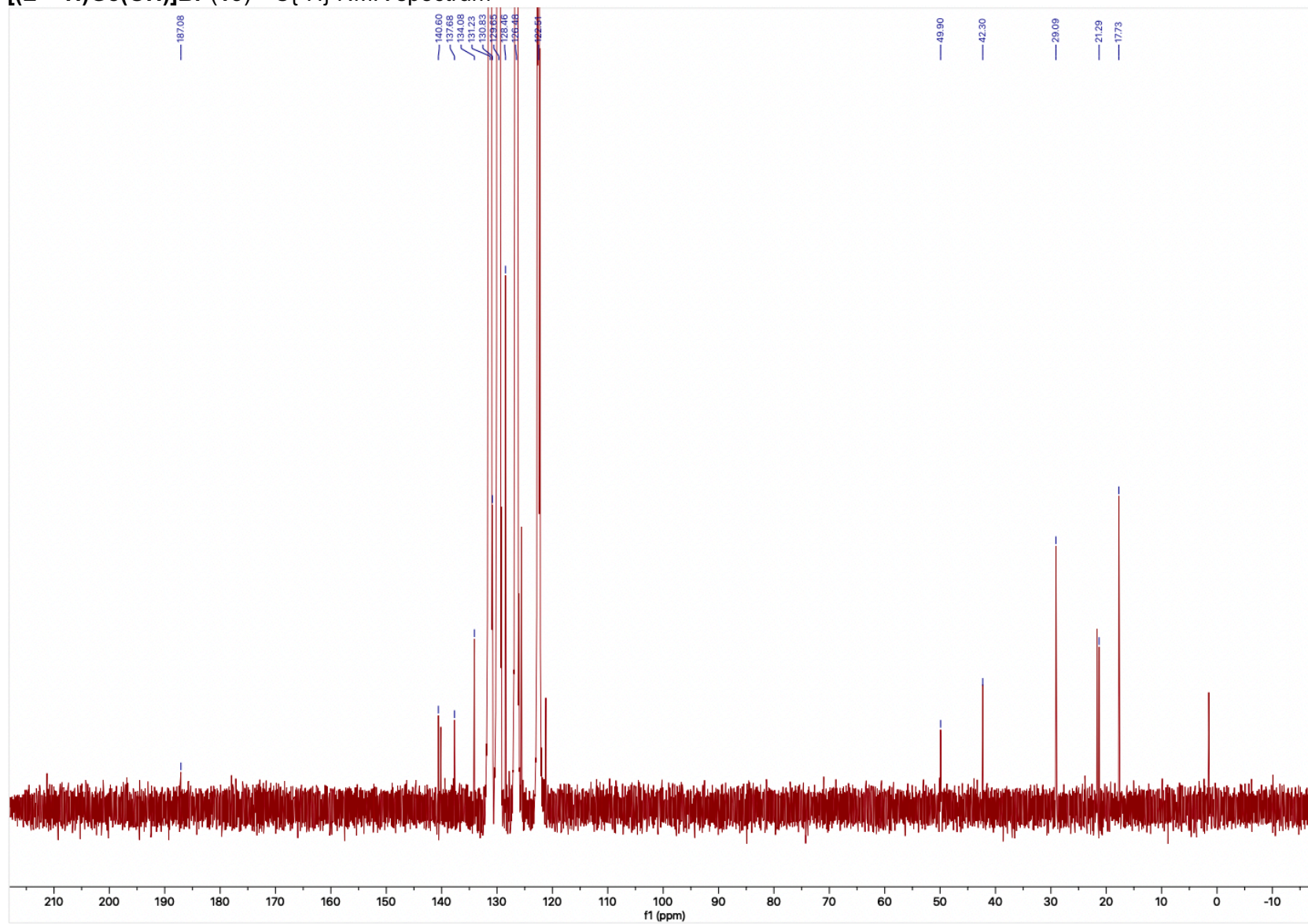
$[(L^{\text{Mes}})\text{Ge}]_2(\mu\text{-Br})[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**11**) $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum



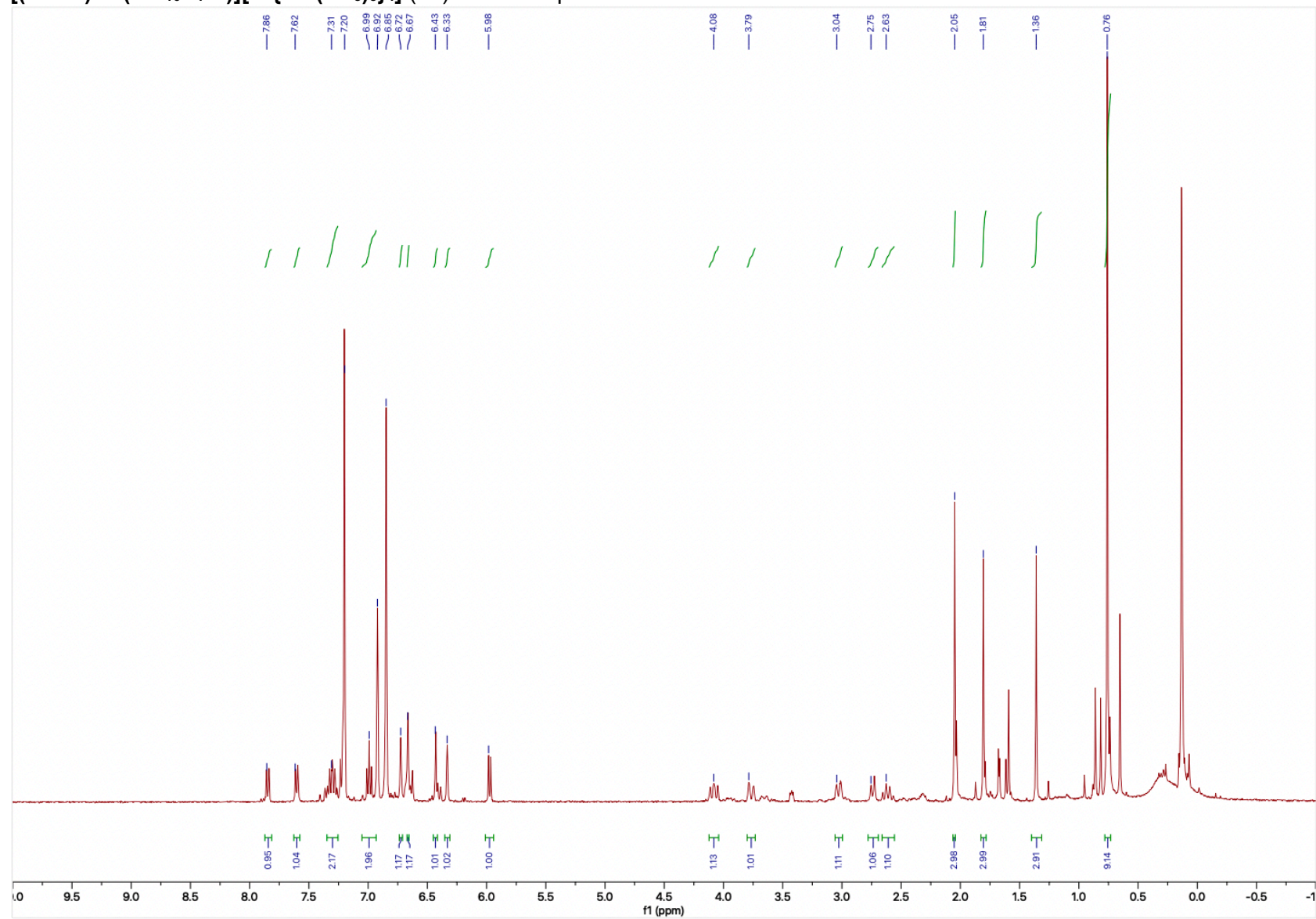
$[(L^{Me_3H})Ge(OH)]Br$ (13) 1H NMR spectrum



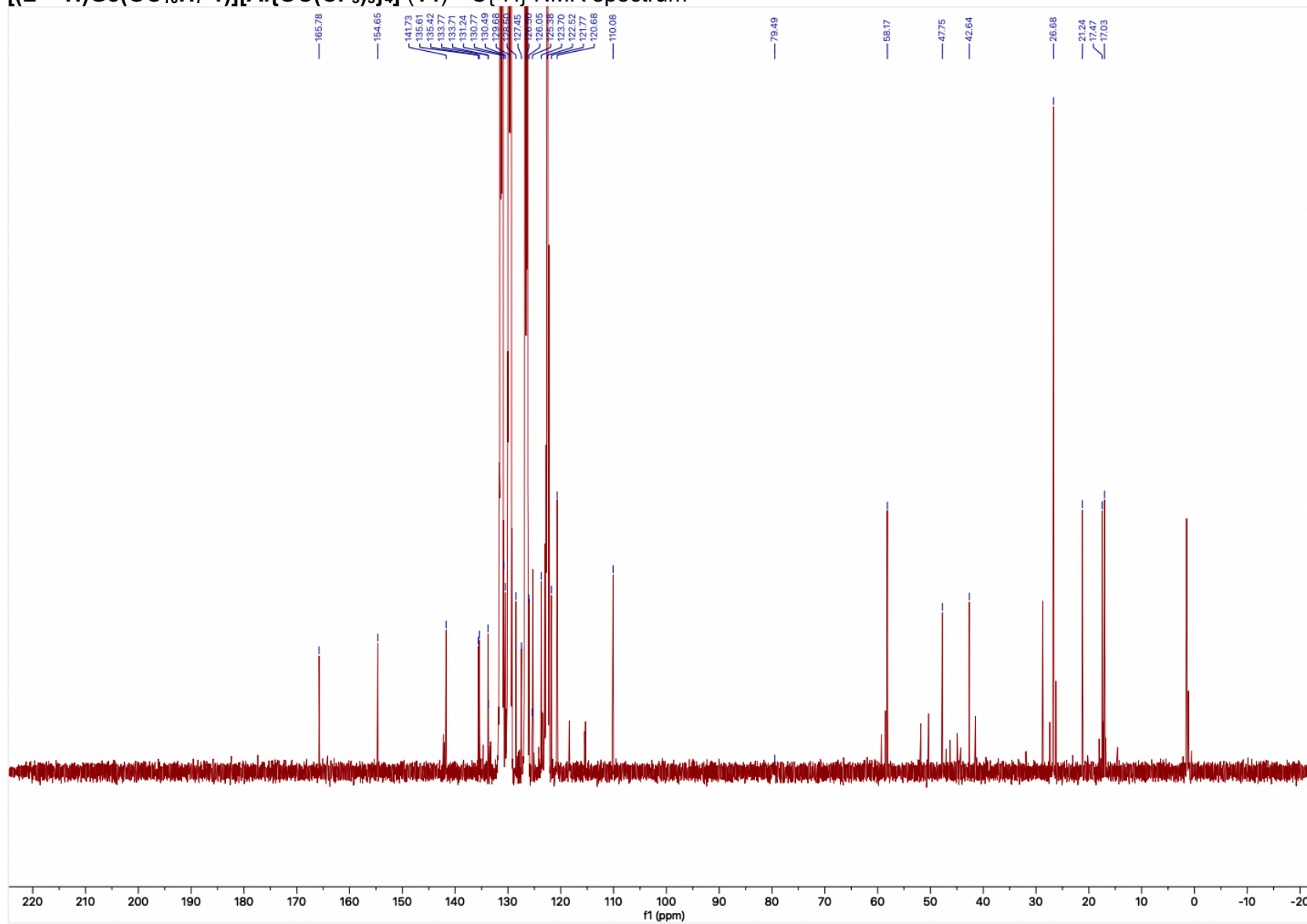
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OH})]\text{Br}$ (13) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



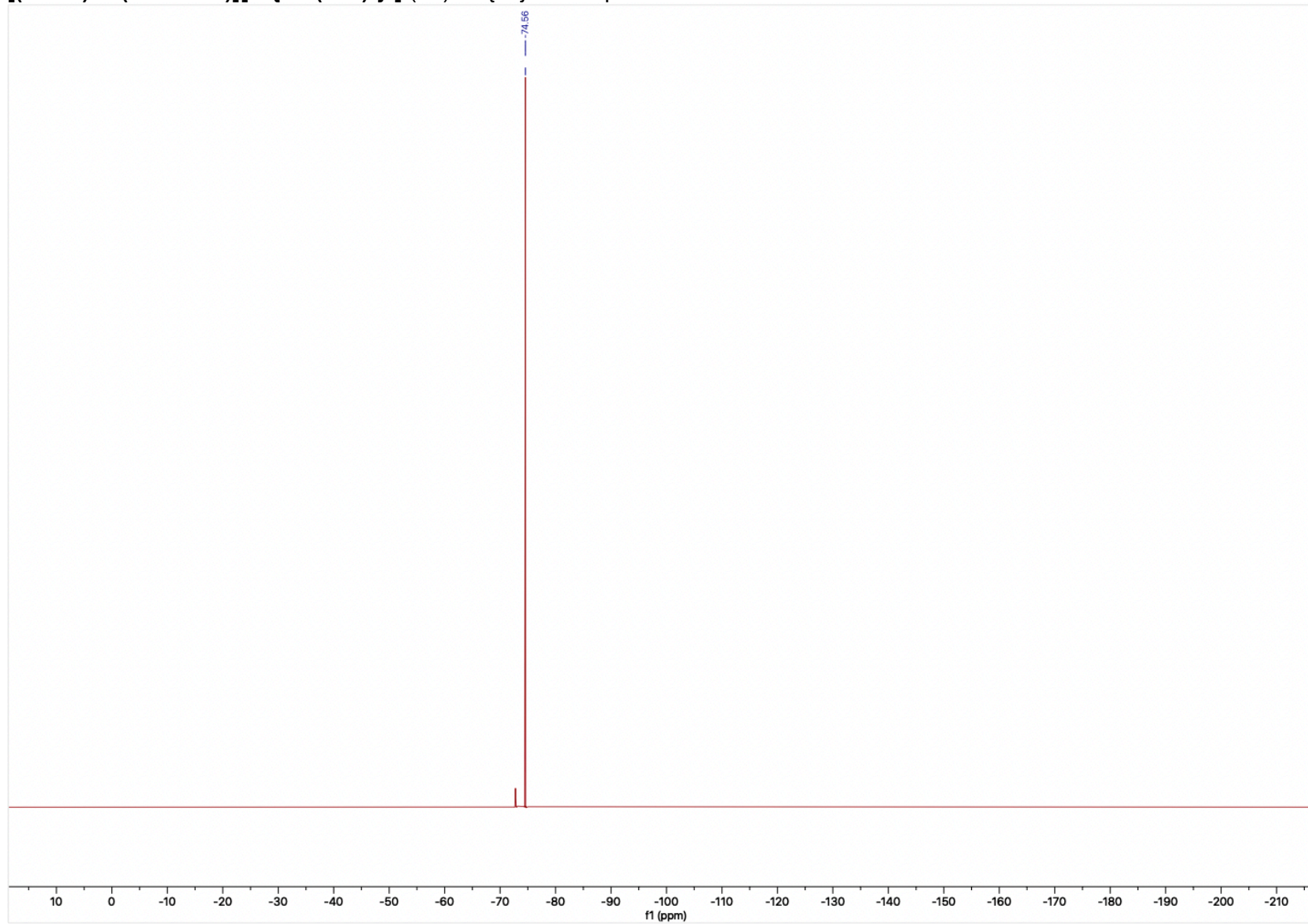
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7-1)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**14**) ^1H NMR spectrum



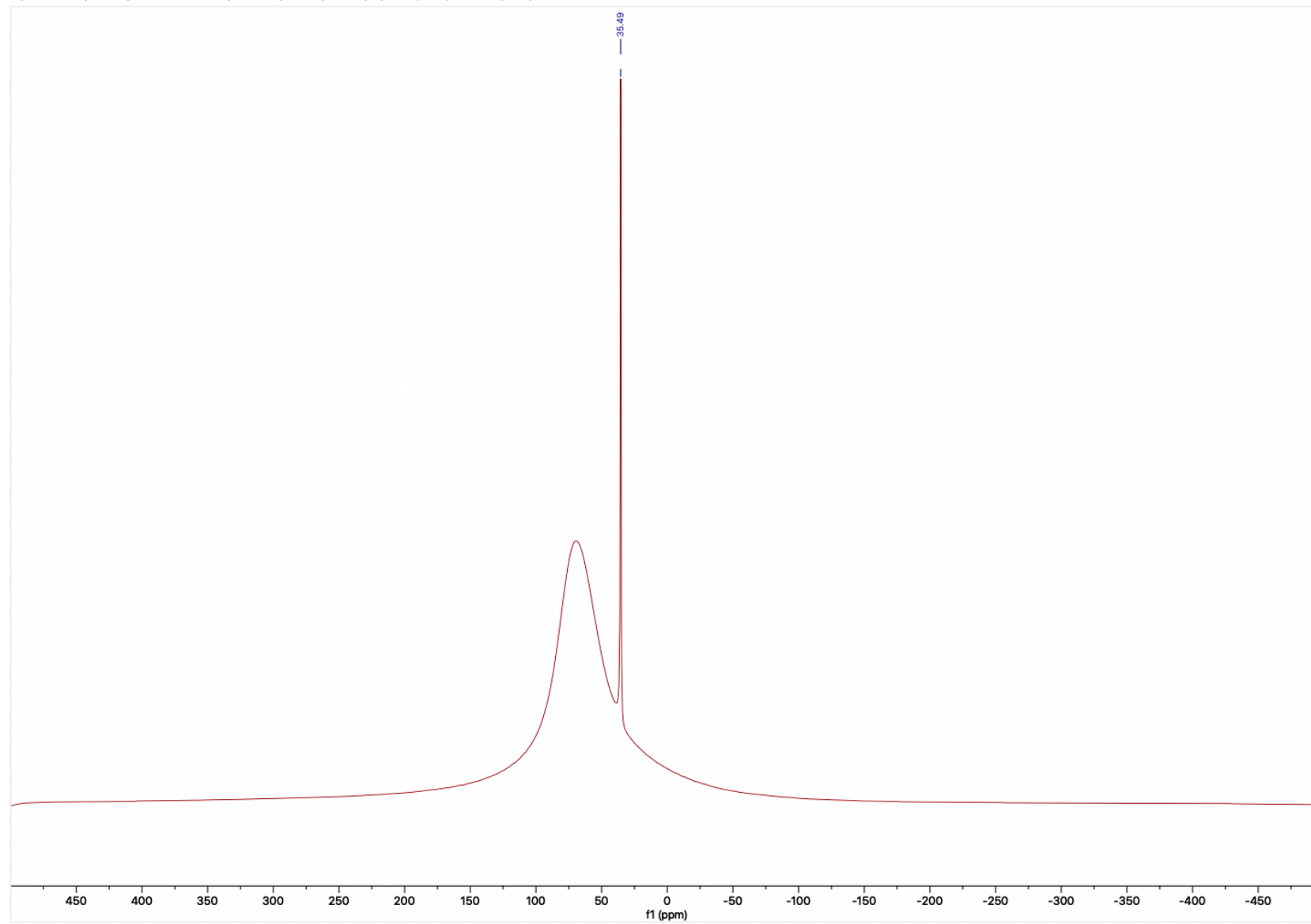
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7-1)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**14**) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



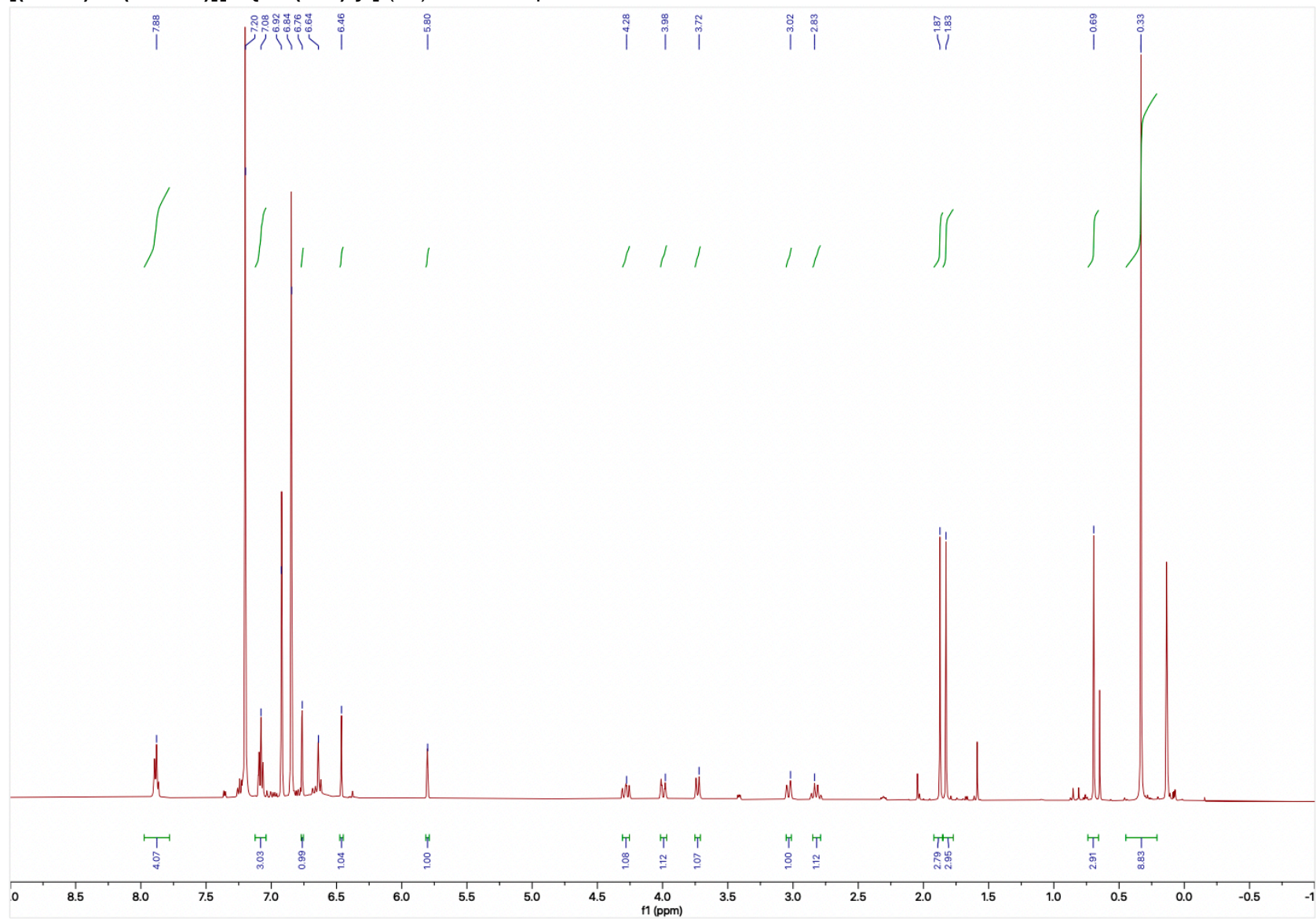
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7-1)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**14**) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



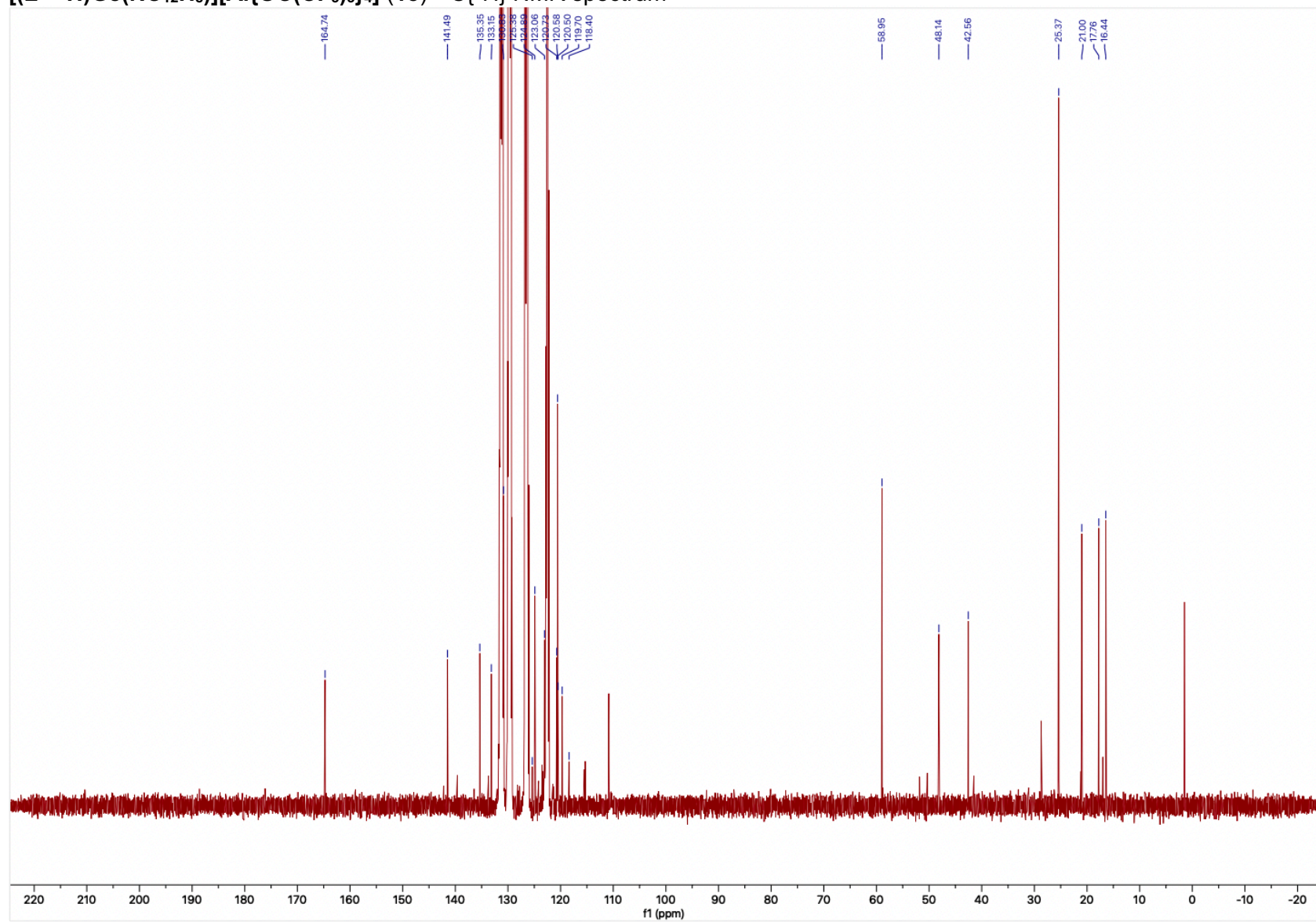
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{OC}_{10}\text{H}_7-1)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**14**) $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum



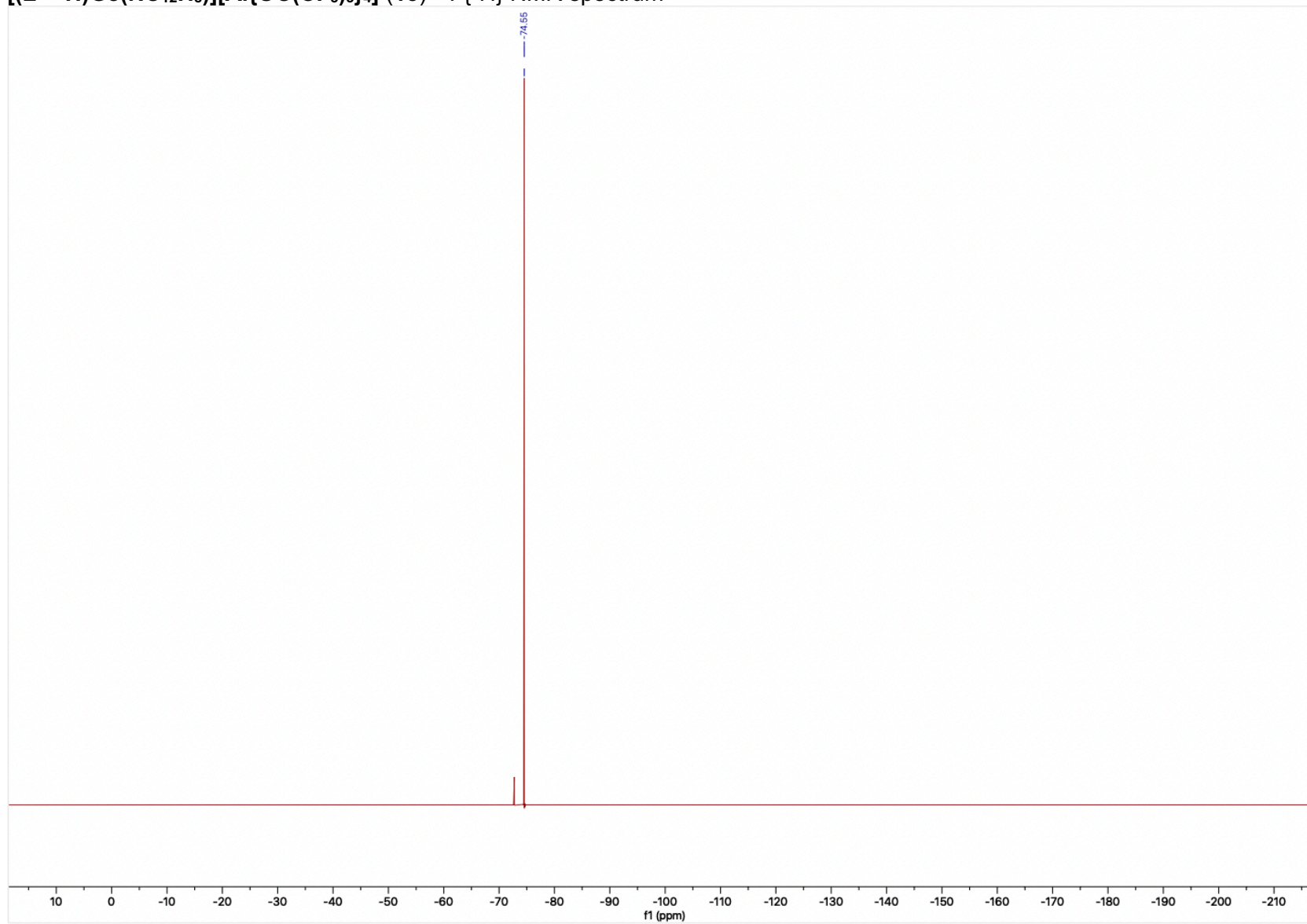
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{NC}_{12}\text{H}_8)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**15**) ^1H NMR spectrum



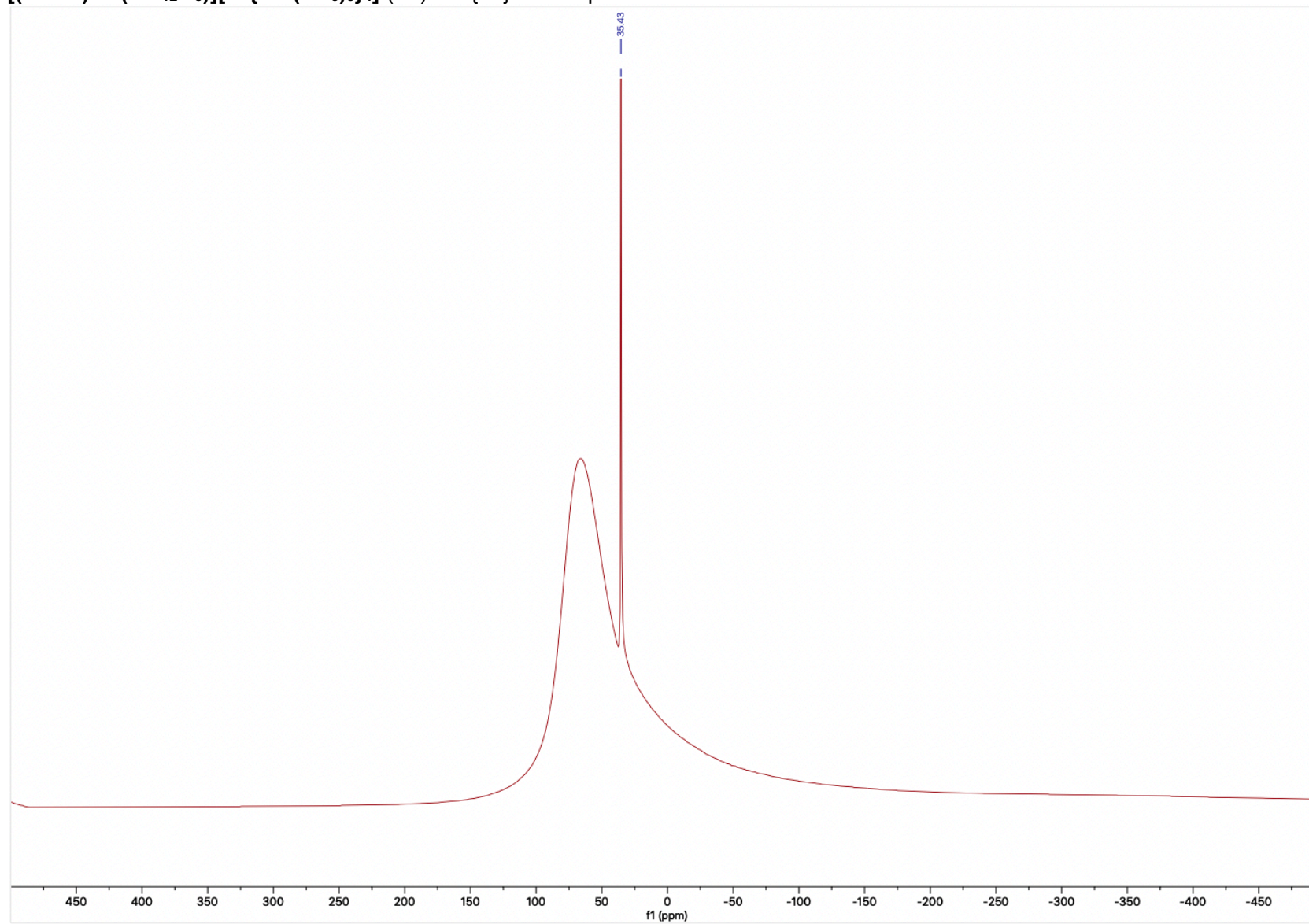
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{NC}_{12}\text{H}_8)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**15**) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



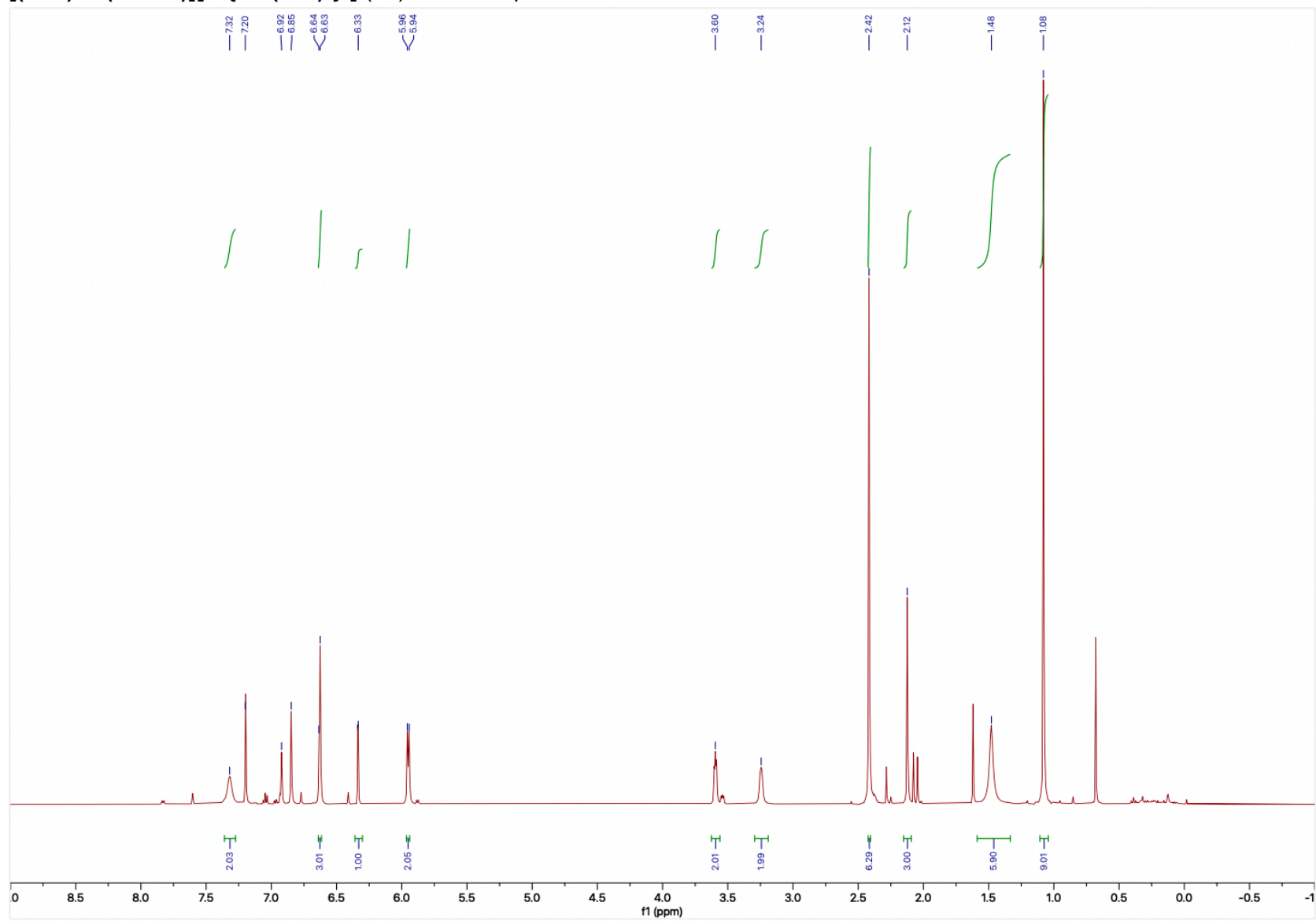
$[(L^{\text{Mes}}\text{H})\text{Ge}(\text{NC}_{12}\text{H}_8)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**15**) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



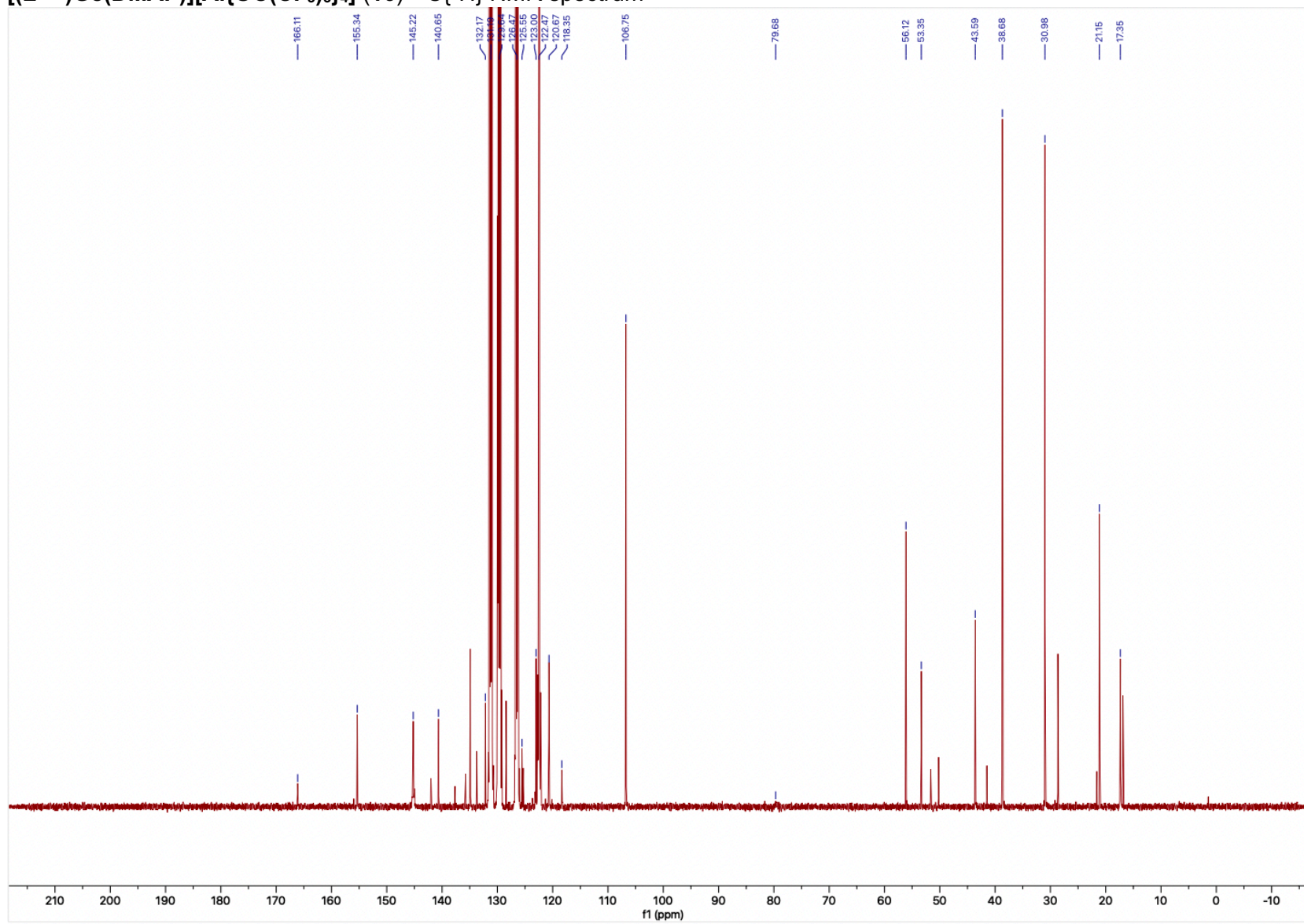
$[(L^{Mes}H)Ge(NC_{12}H_8)][Al\{OC(CF_3)_3\}_4]$ (**15**) $^{27}Al\{^1H\}$ NMR spectrum



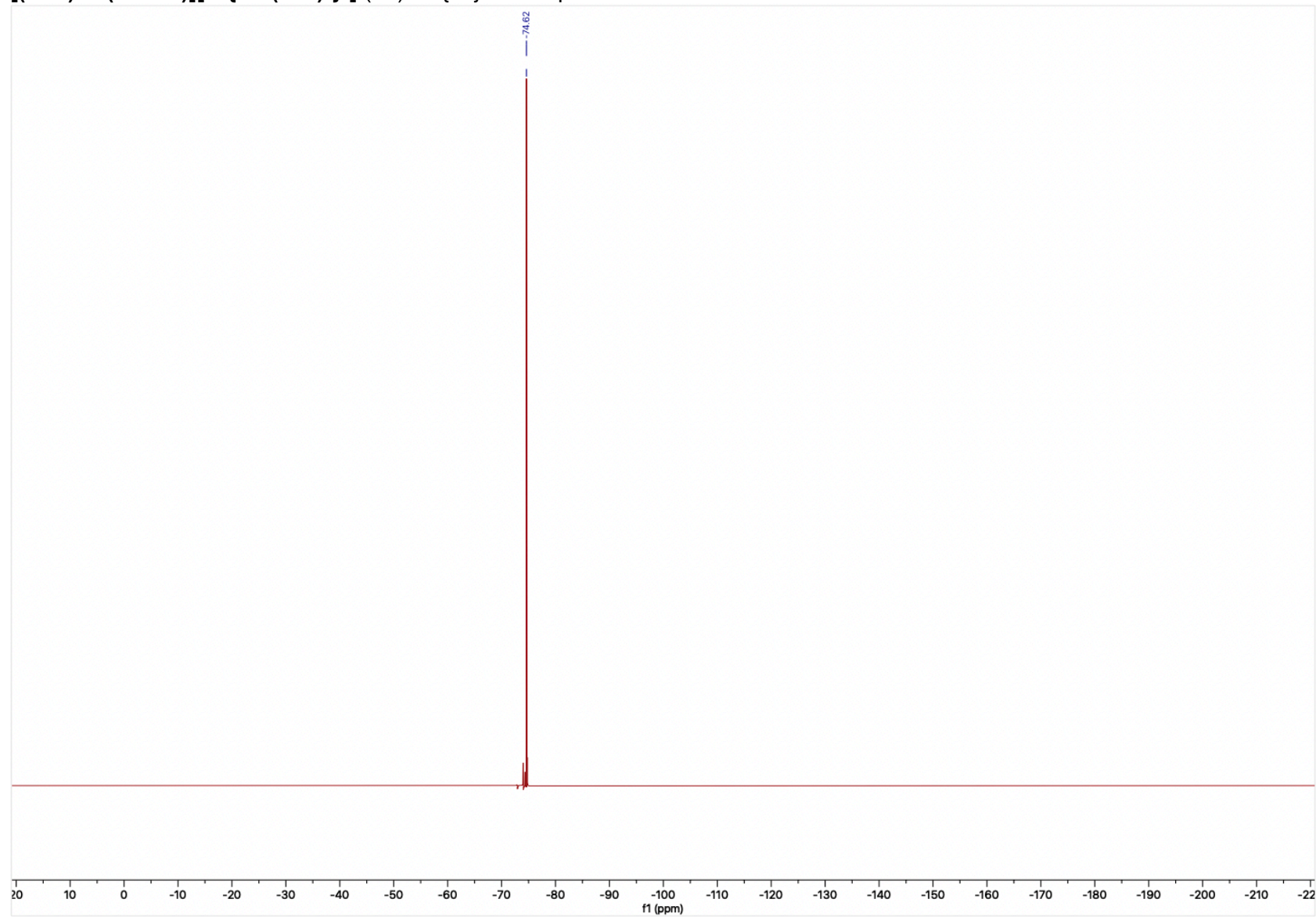
$[(L^{\text{Mes}})\text{Ge}(\text{DMAP})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (16) ^1H NMR spectrum



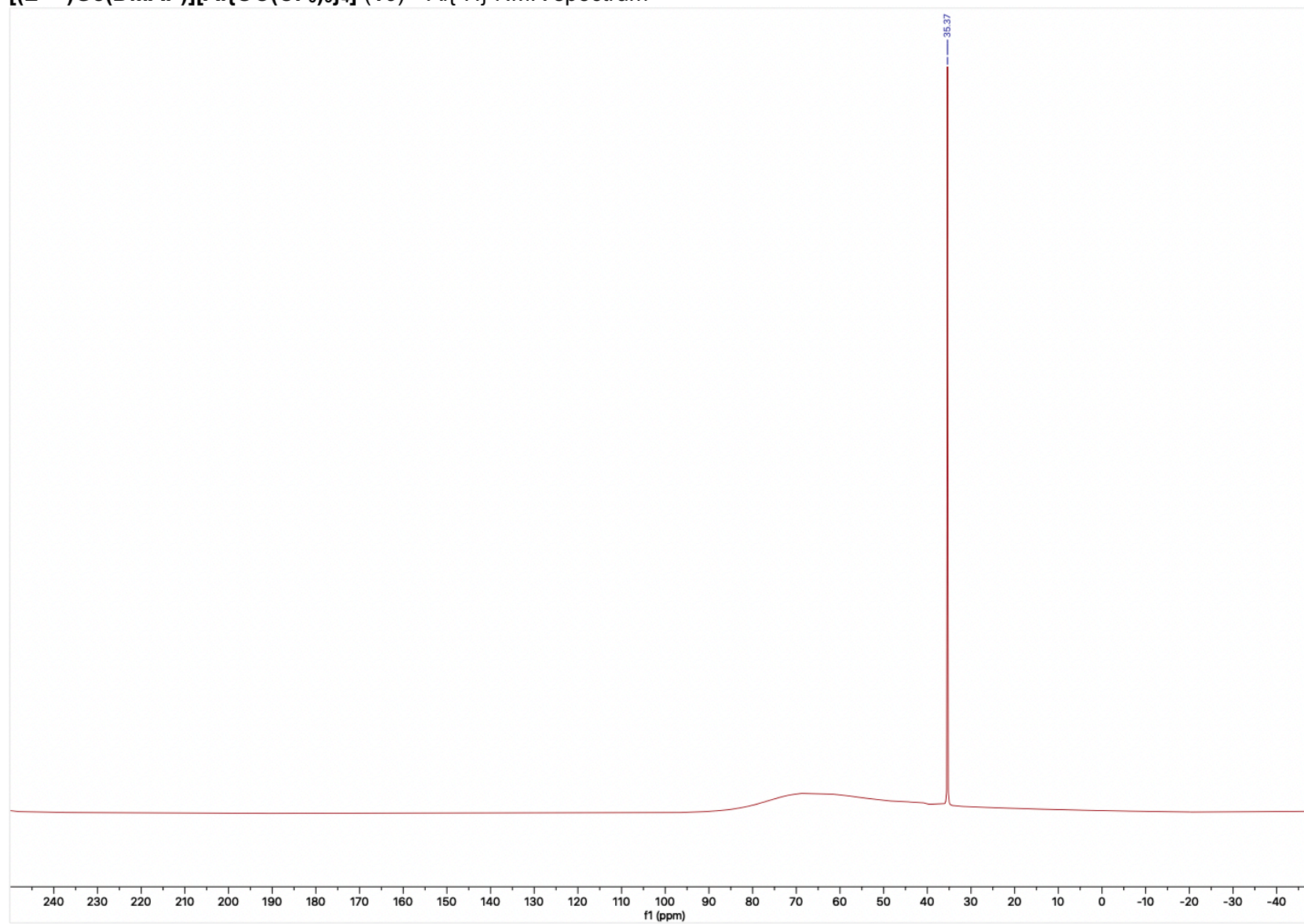
$[(L^{\text{Mes}})\text{Ge}(\text{DMAP})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (16) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



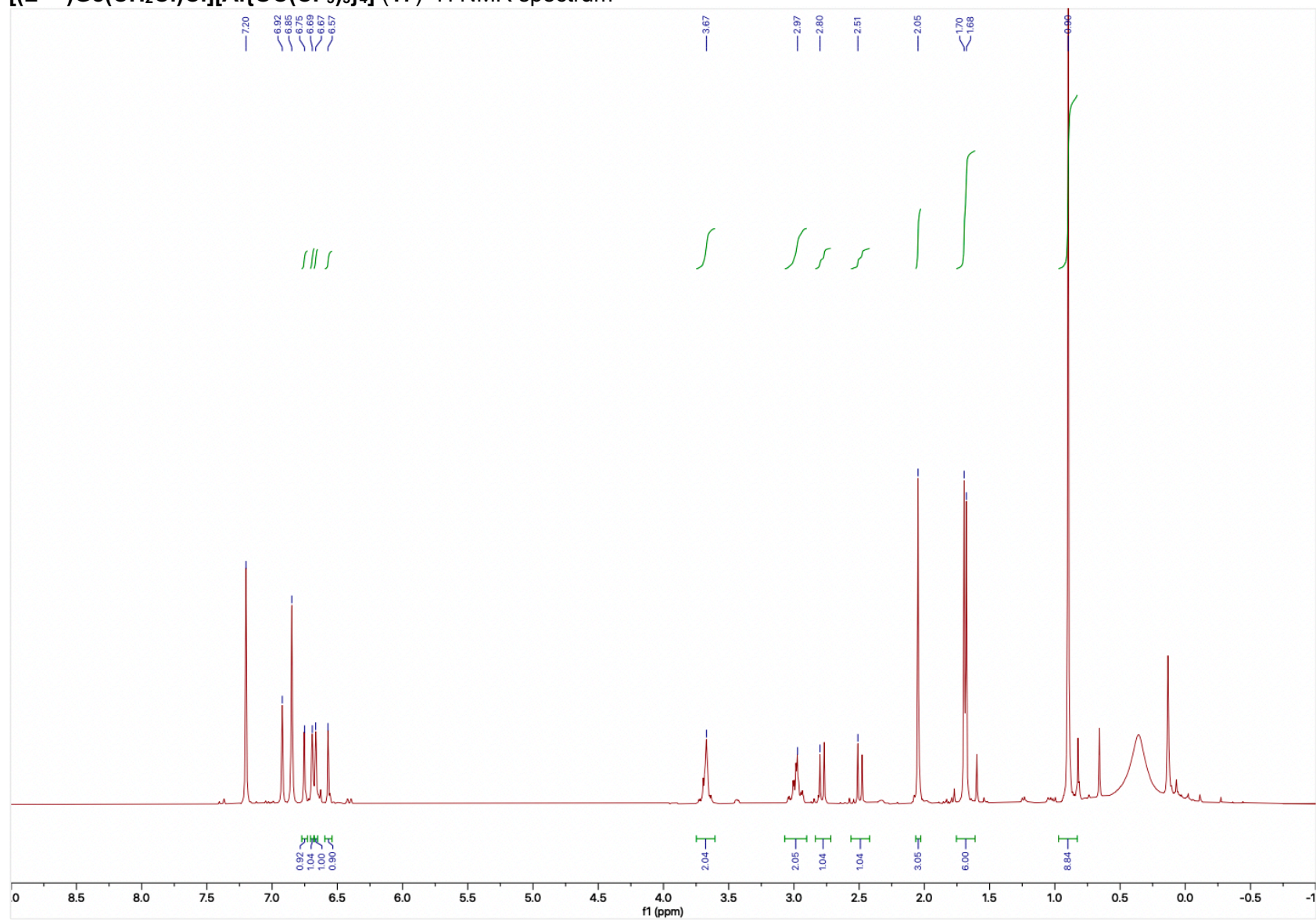
$[(L^{\text{Mes}})\text{Ge}(\text{DMAP})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**16**) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



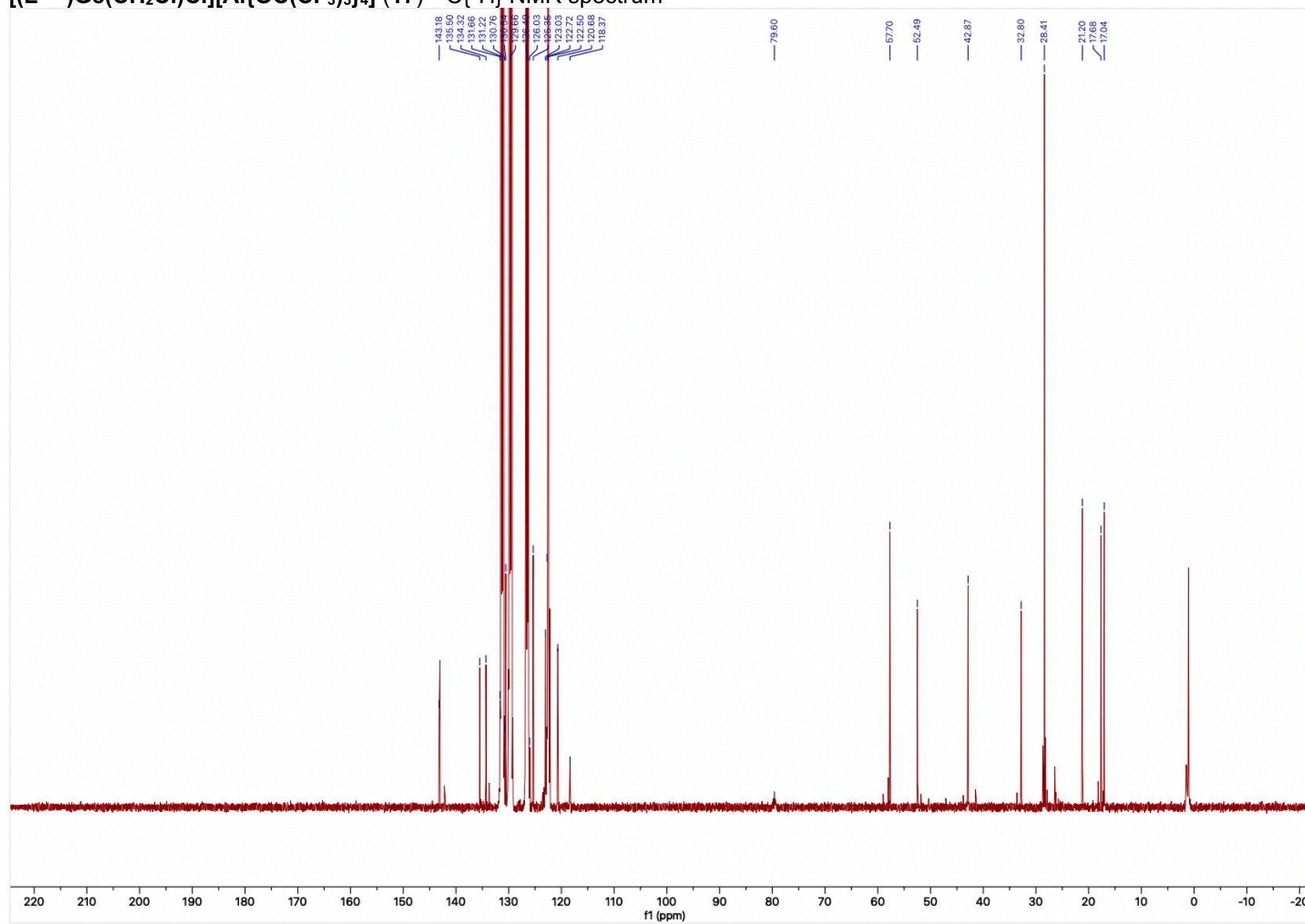
$[(L^{\text{Mes}})\text{Ge}(\text{DMAP})][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (16**) $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum**



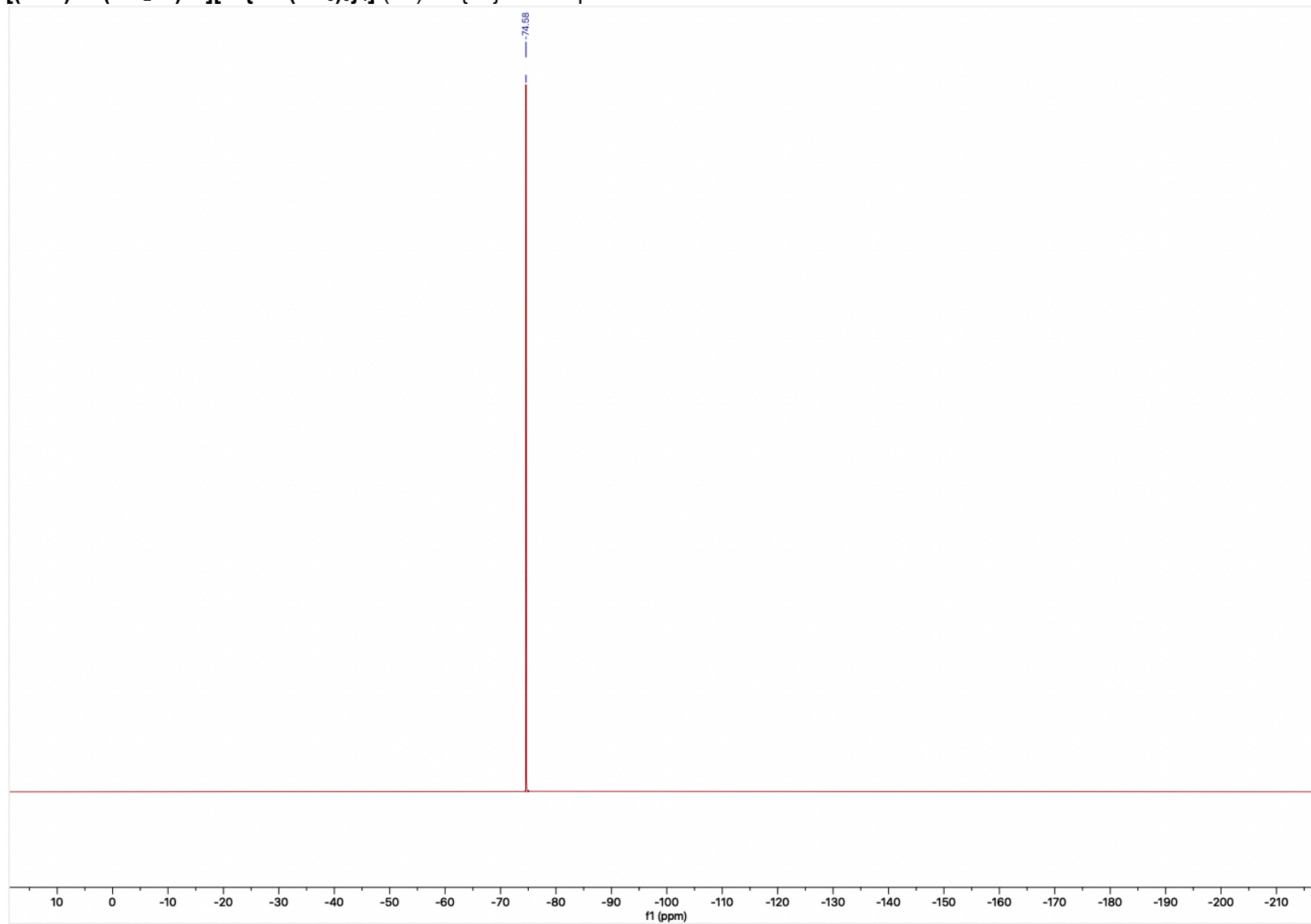
$[(L^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (17) ^1H NMR spectrum



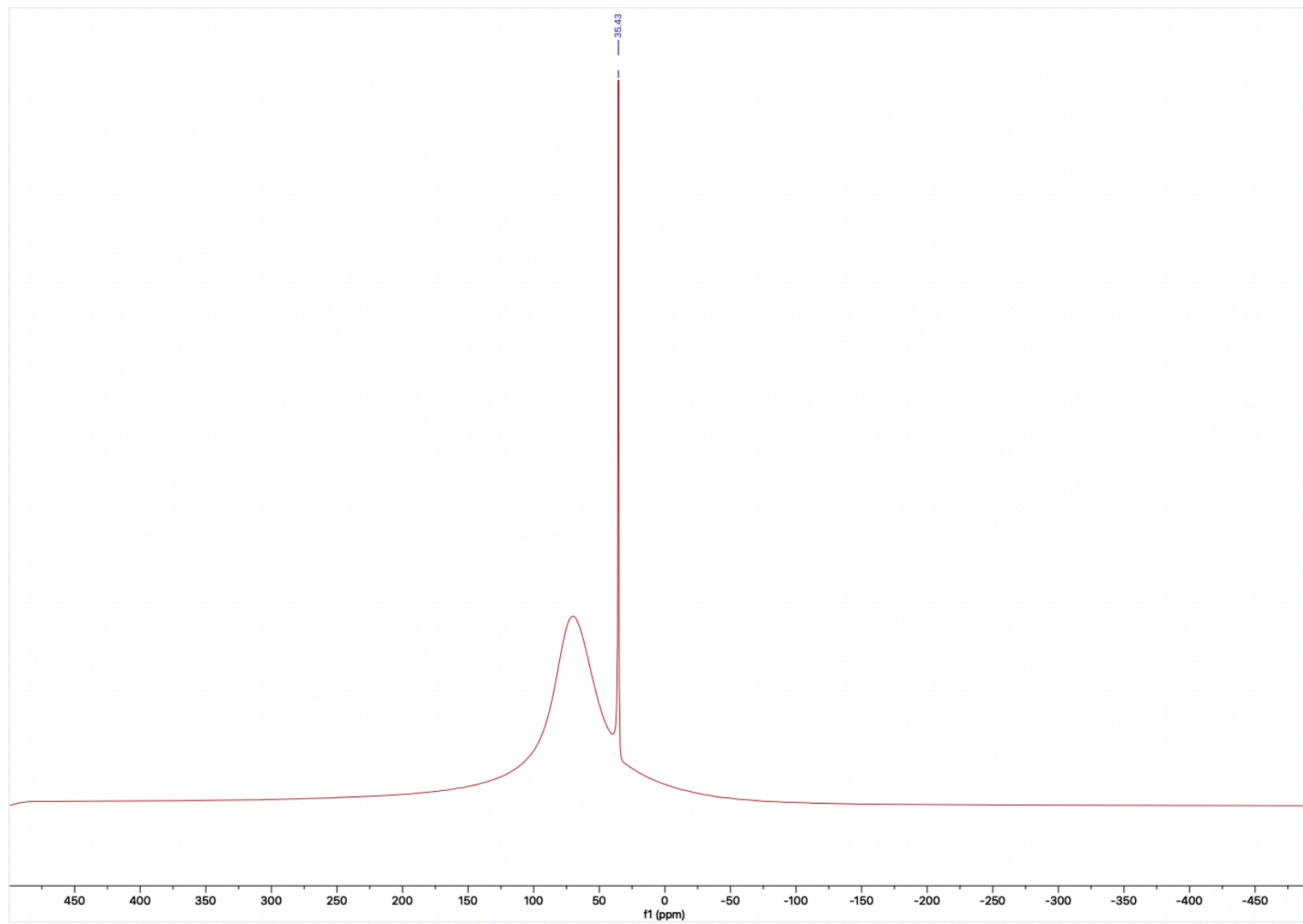
$[(L^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (17) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



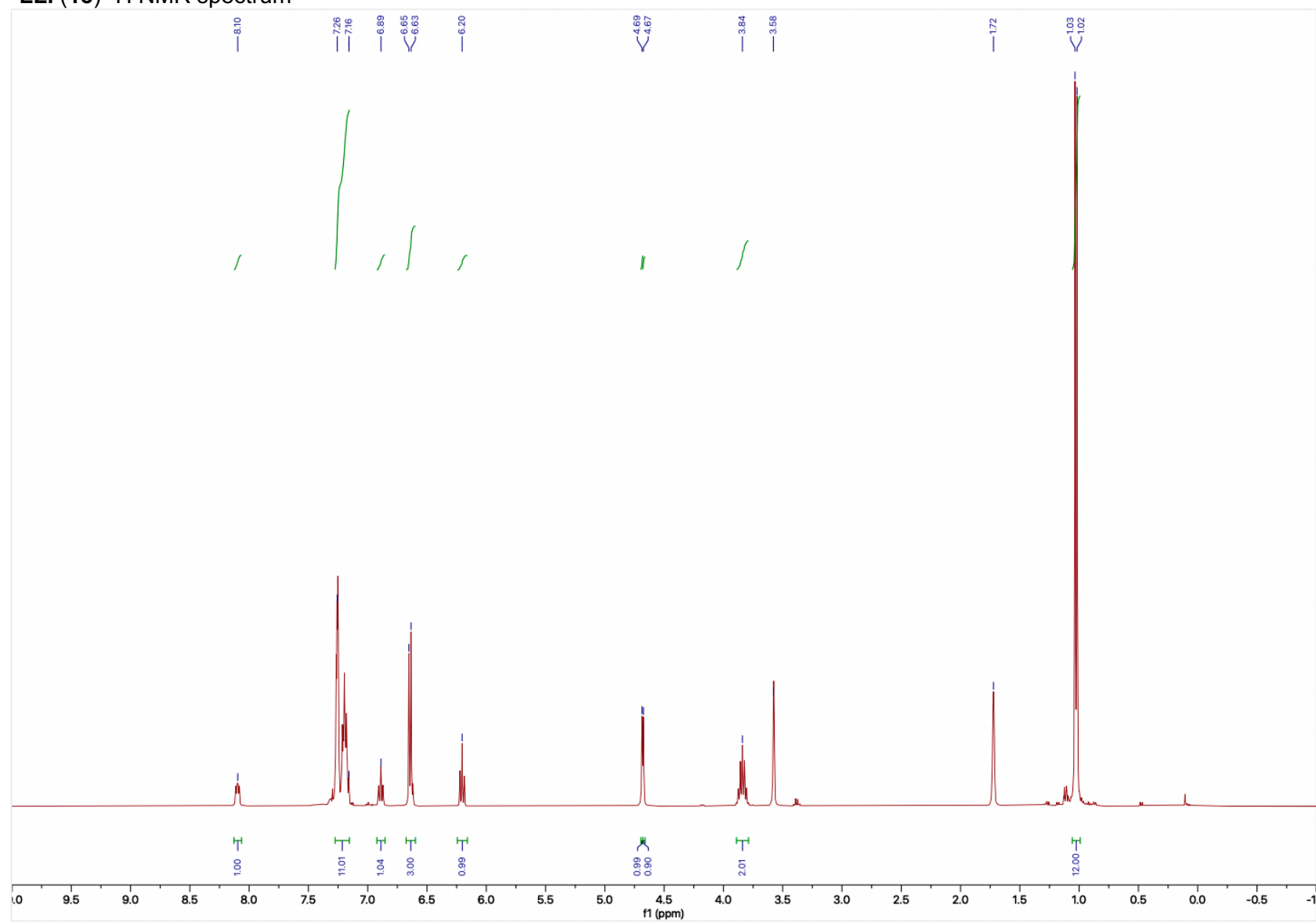
$[(L^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (17) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum



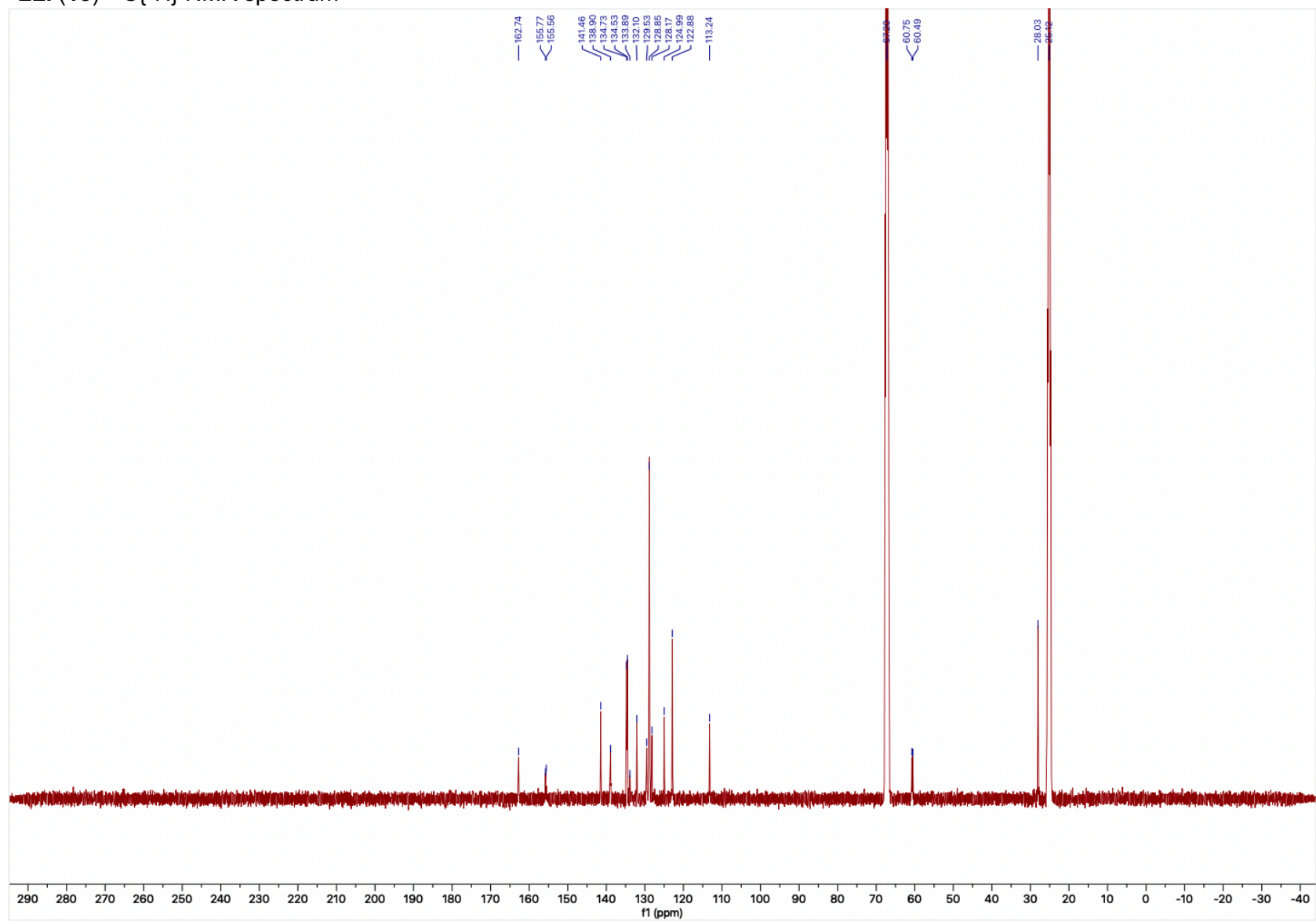
$[(L^{\text{Mes}})\text{Ge}(\text{CH}_2\text{Cl})\text{Cl}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**17**) $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum



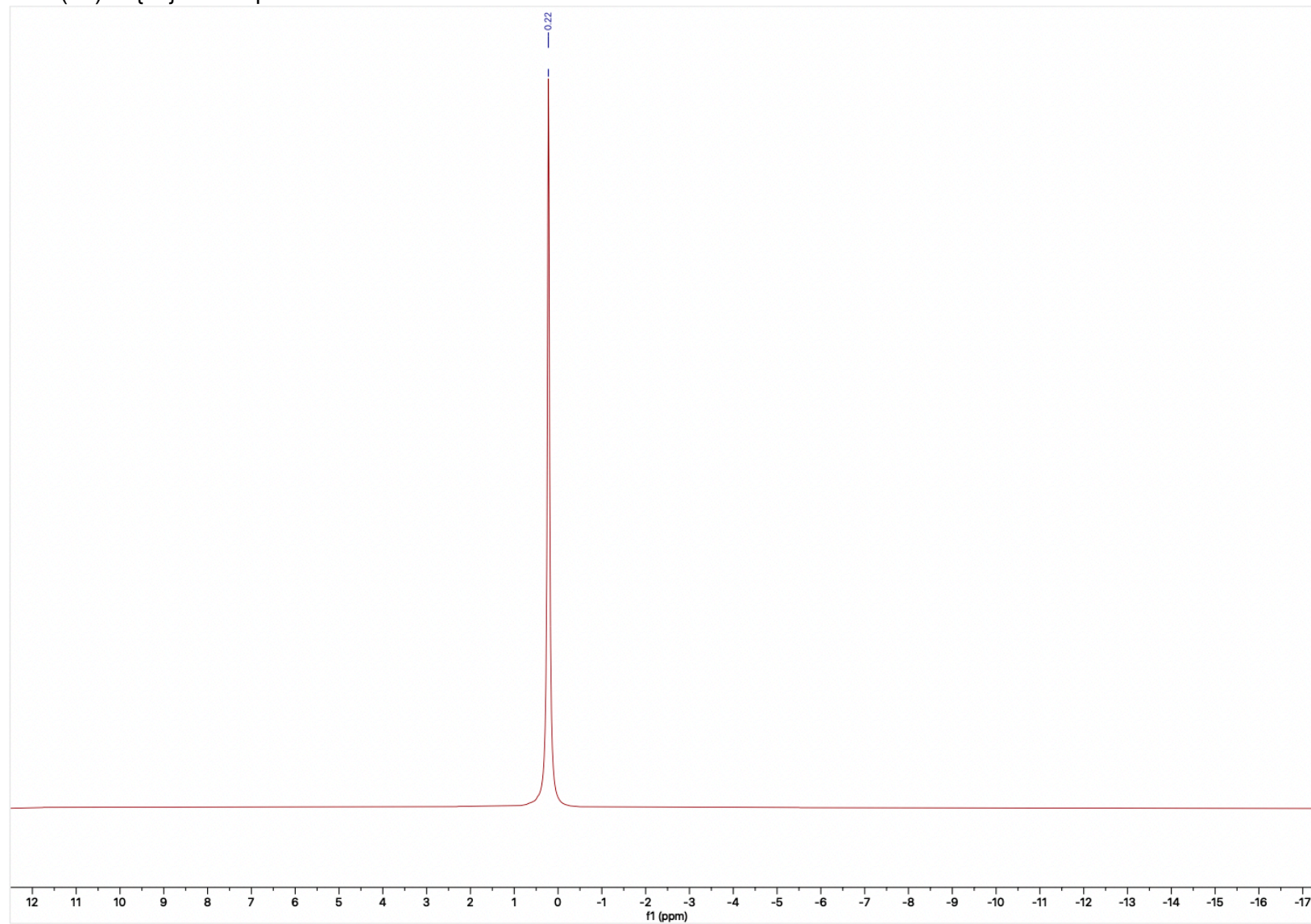
*LLi (18) ^1H NMR spectrum



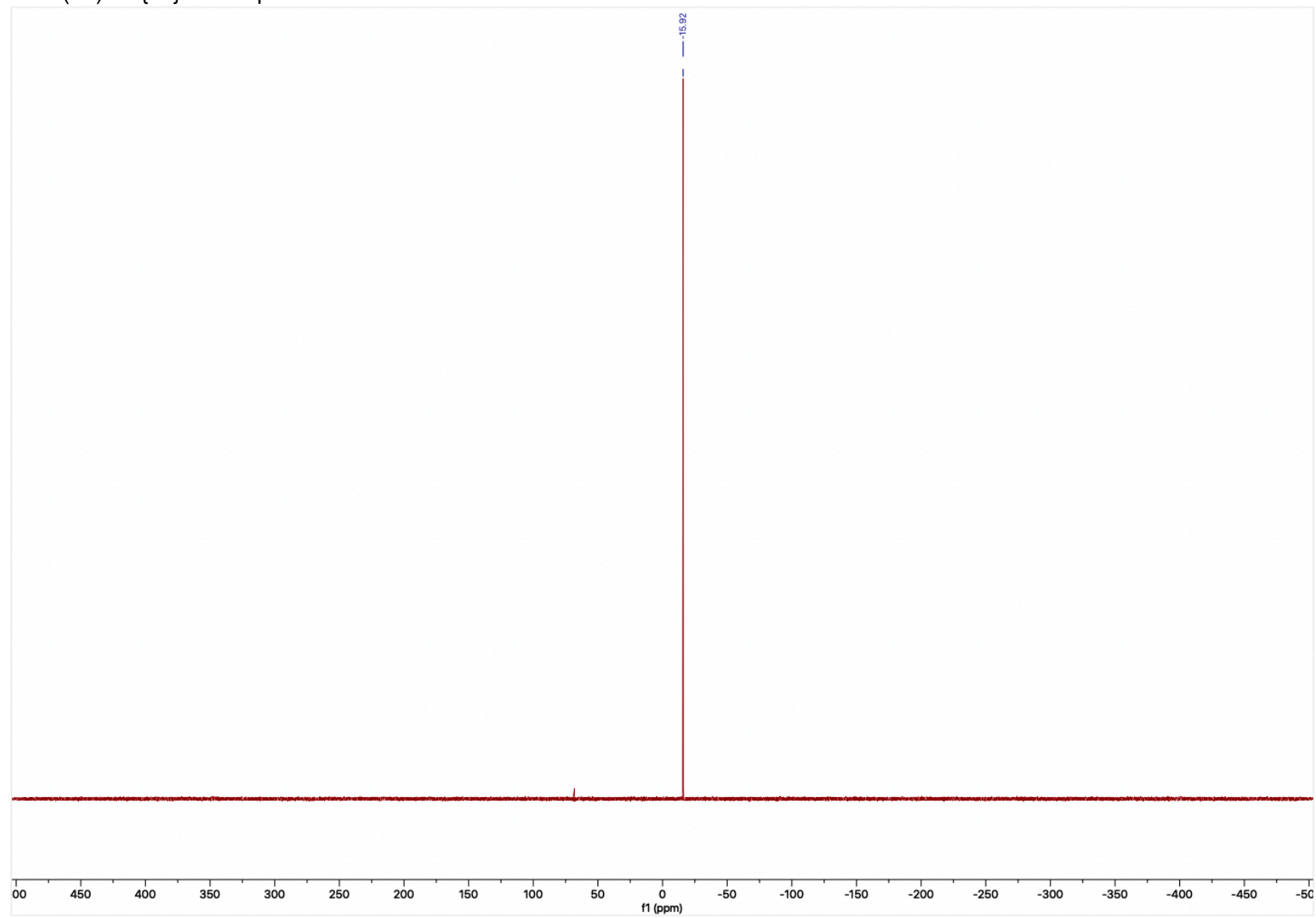
*LLi (18) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



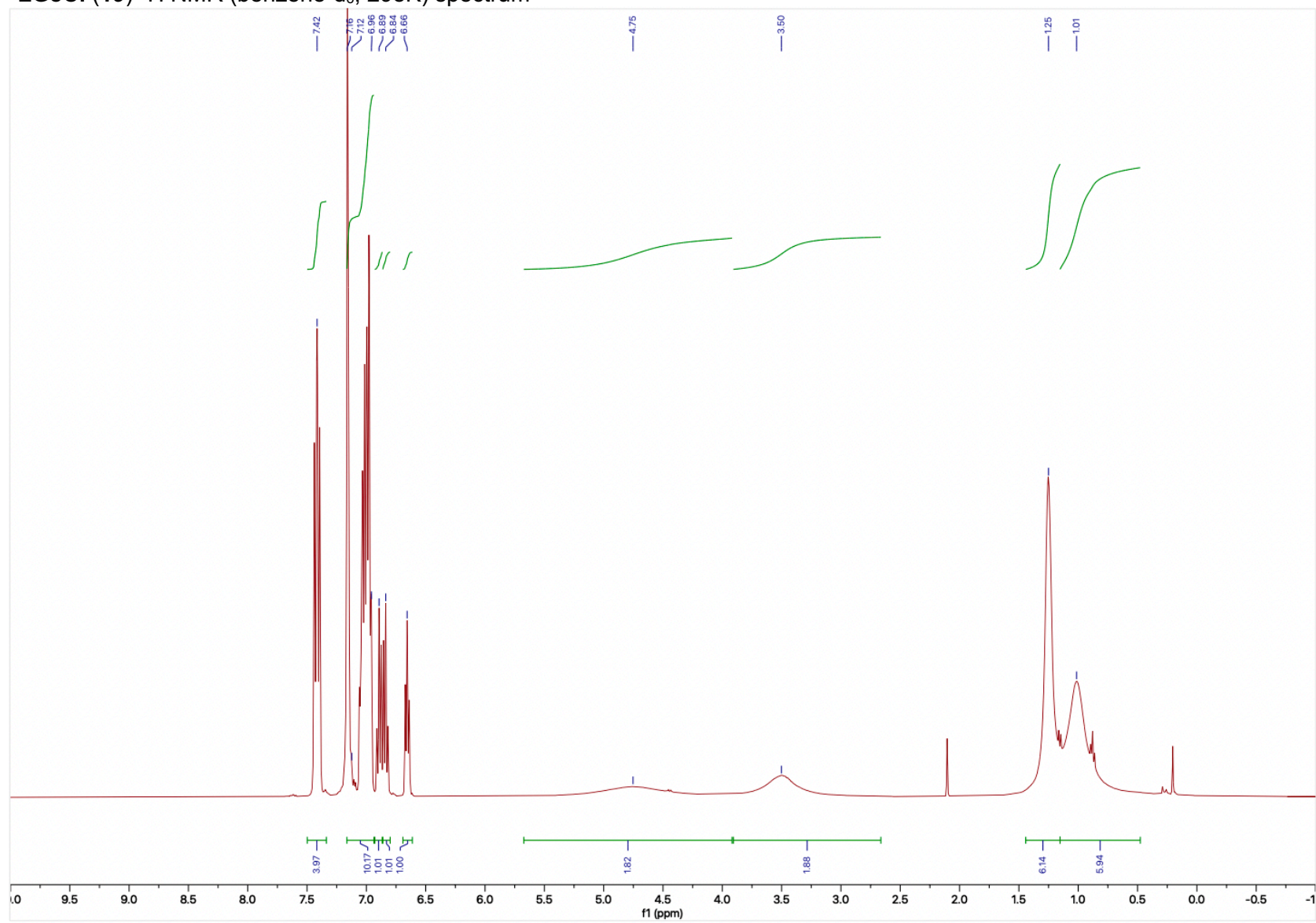
***LLi (18)** $^7\text{Li}\{^1\text{H}\}$ NMR spectrum



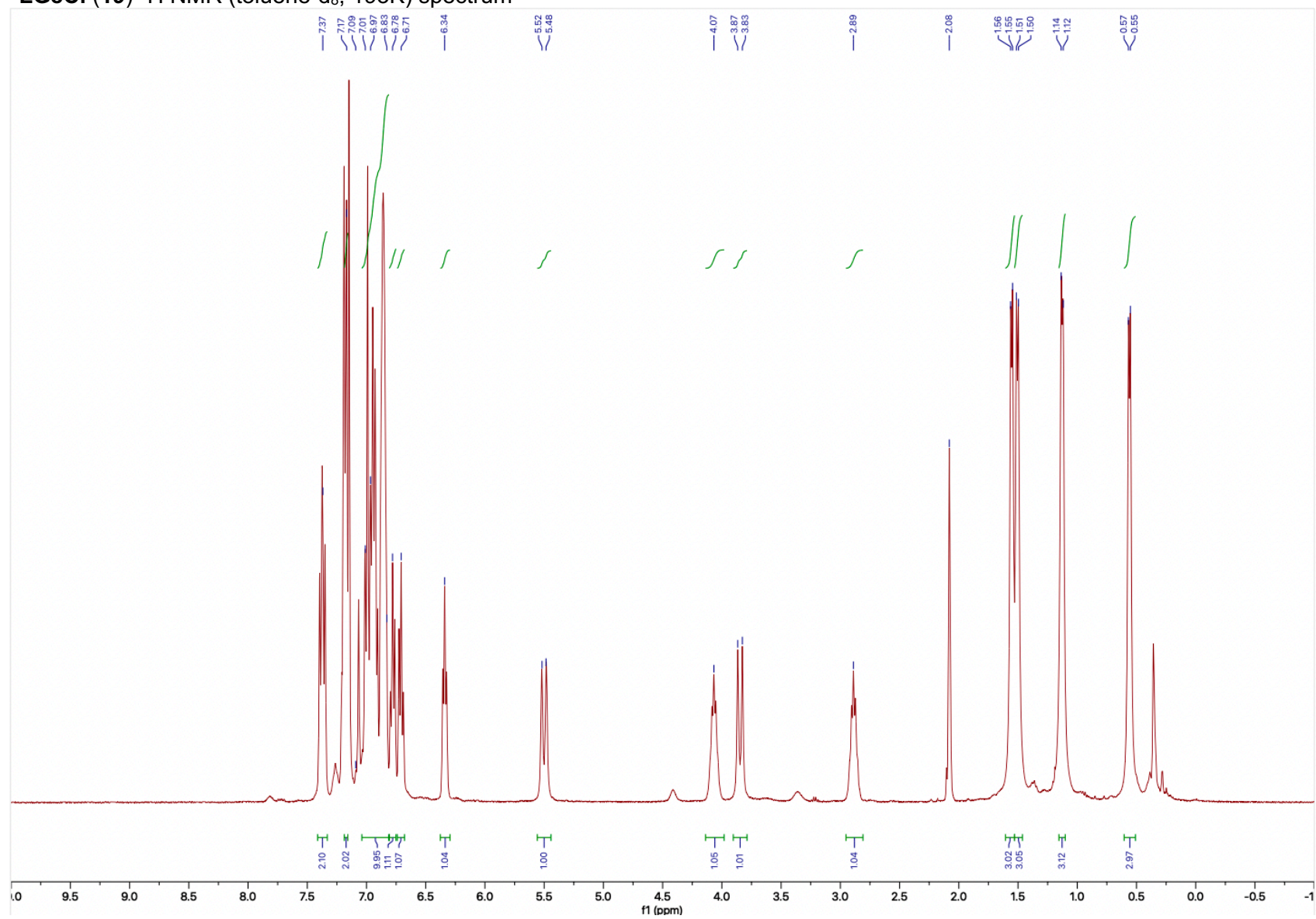
*LLi (18) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



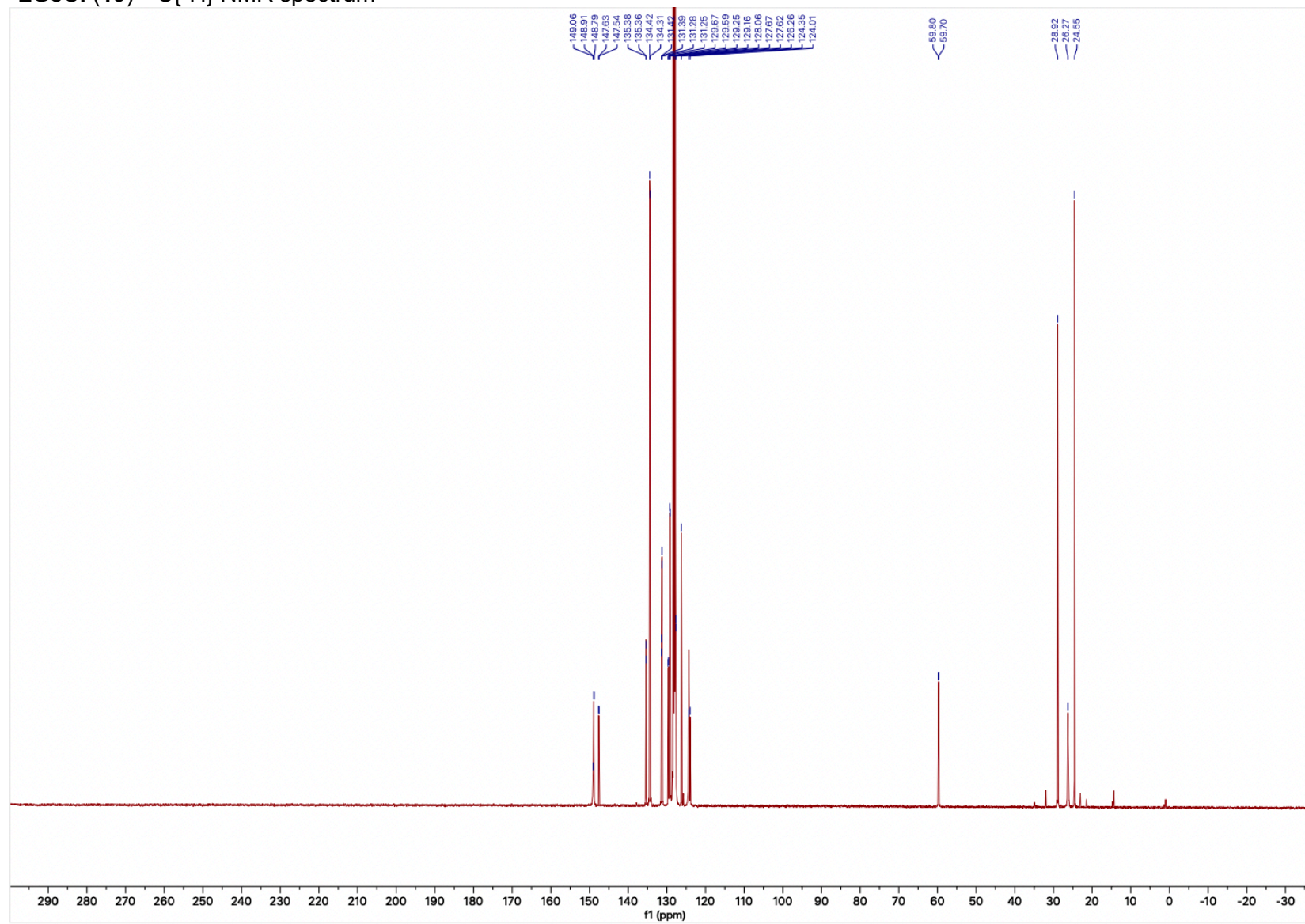
*LGeCl (19) ^1H NMR (benzene- d_6 , 298K) spectrum



*LGeCl (19) ^1H NMR (toluene- d_8 , 193K) spectrum



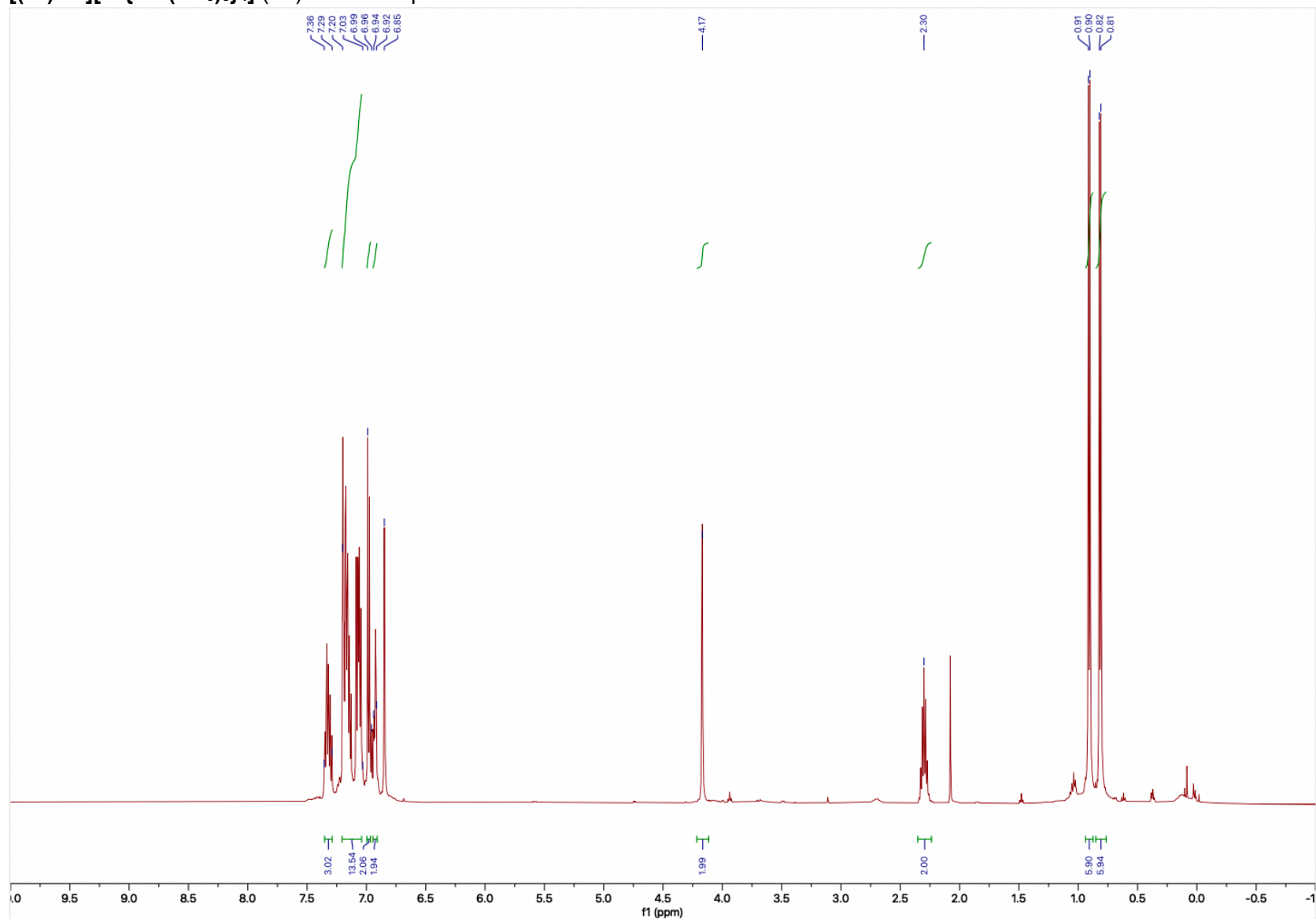
*LGeCl (19) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



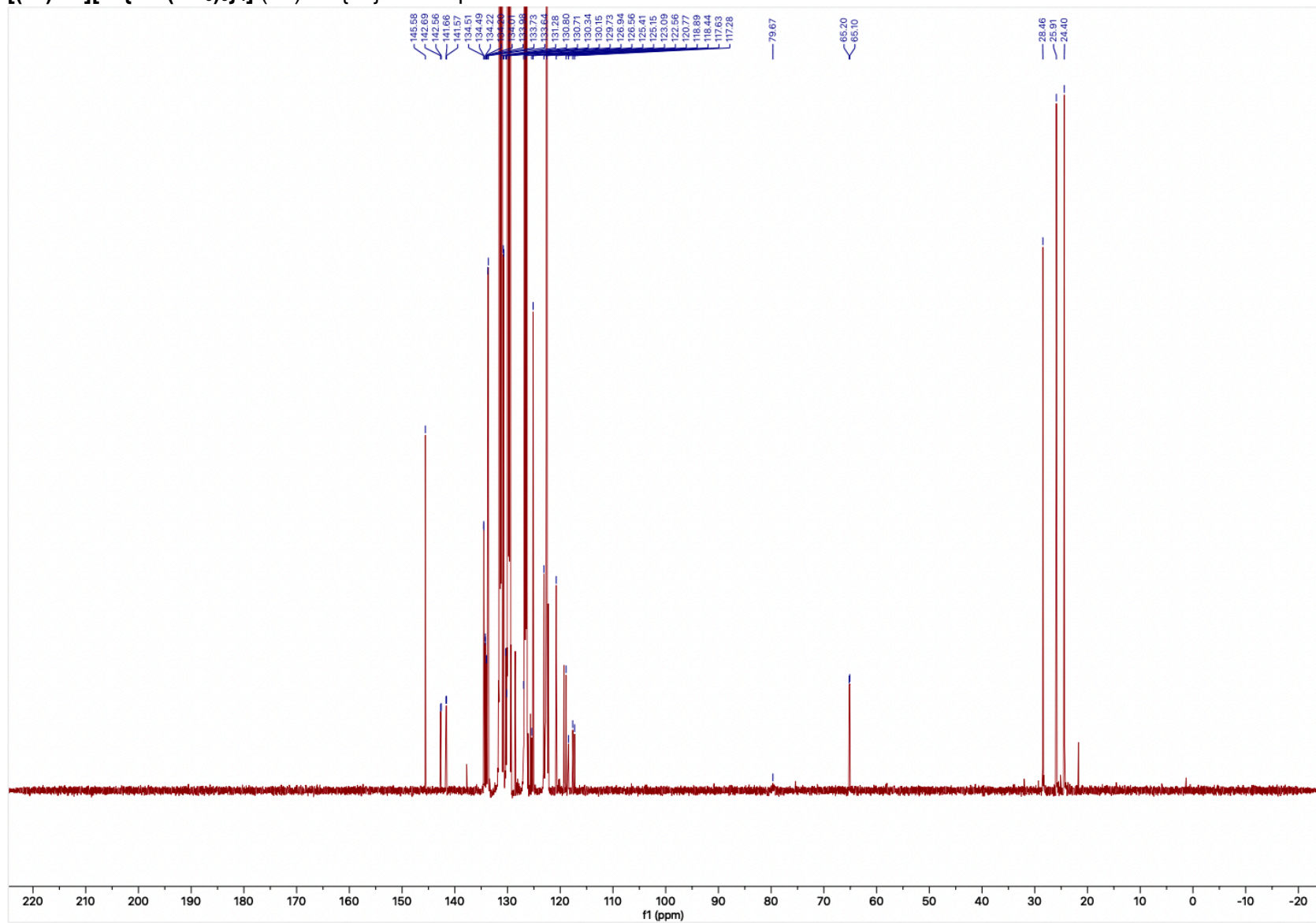
***LGeCl (19)** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



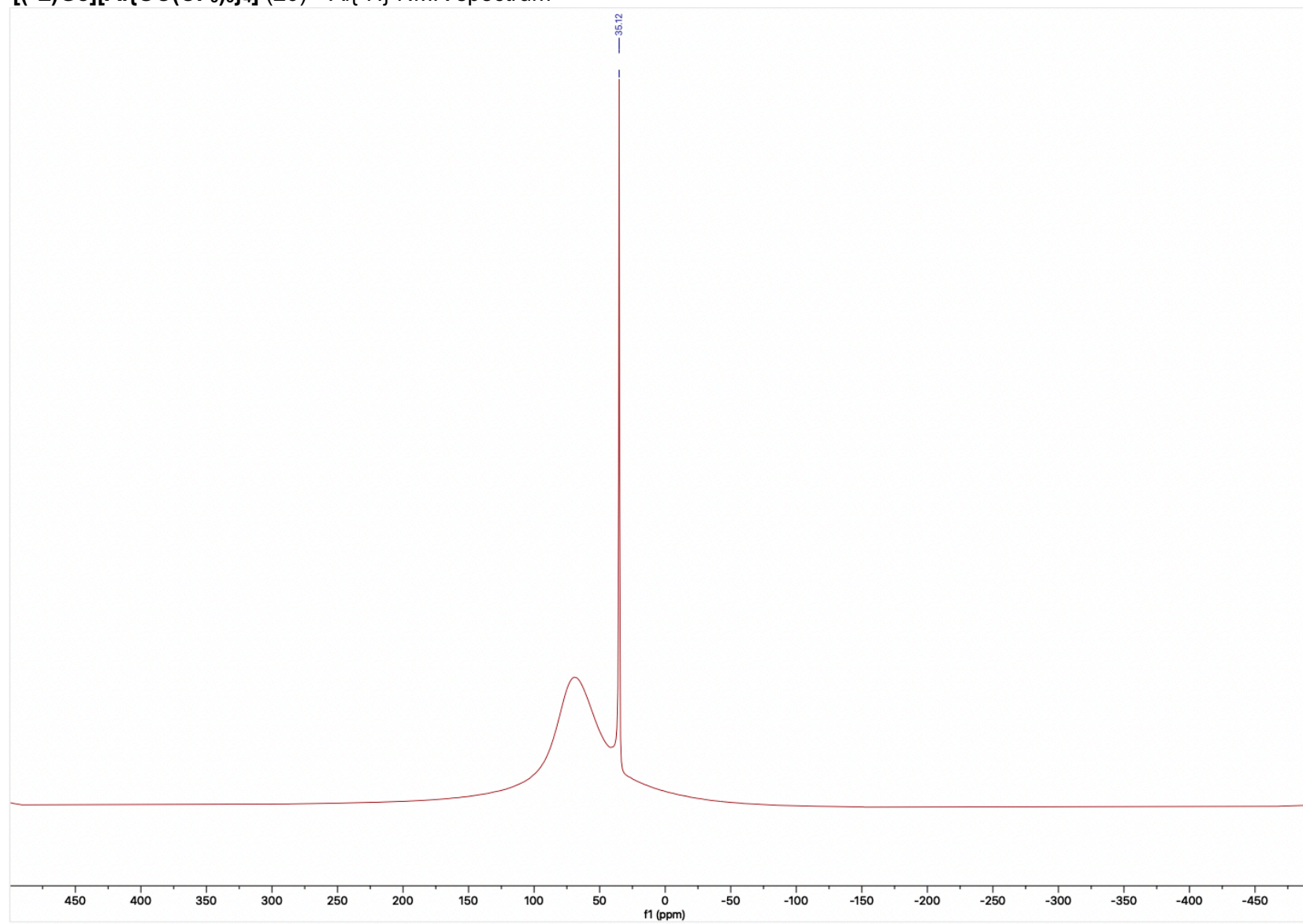
$[(^*L)Ge][Al\{OC(CF_3)_3\}_4]$ (20) 1H NMR spectrum



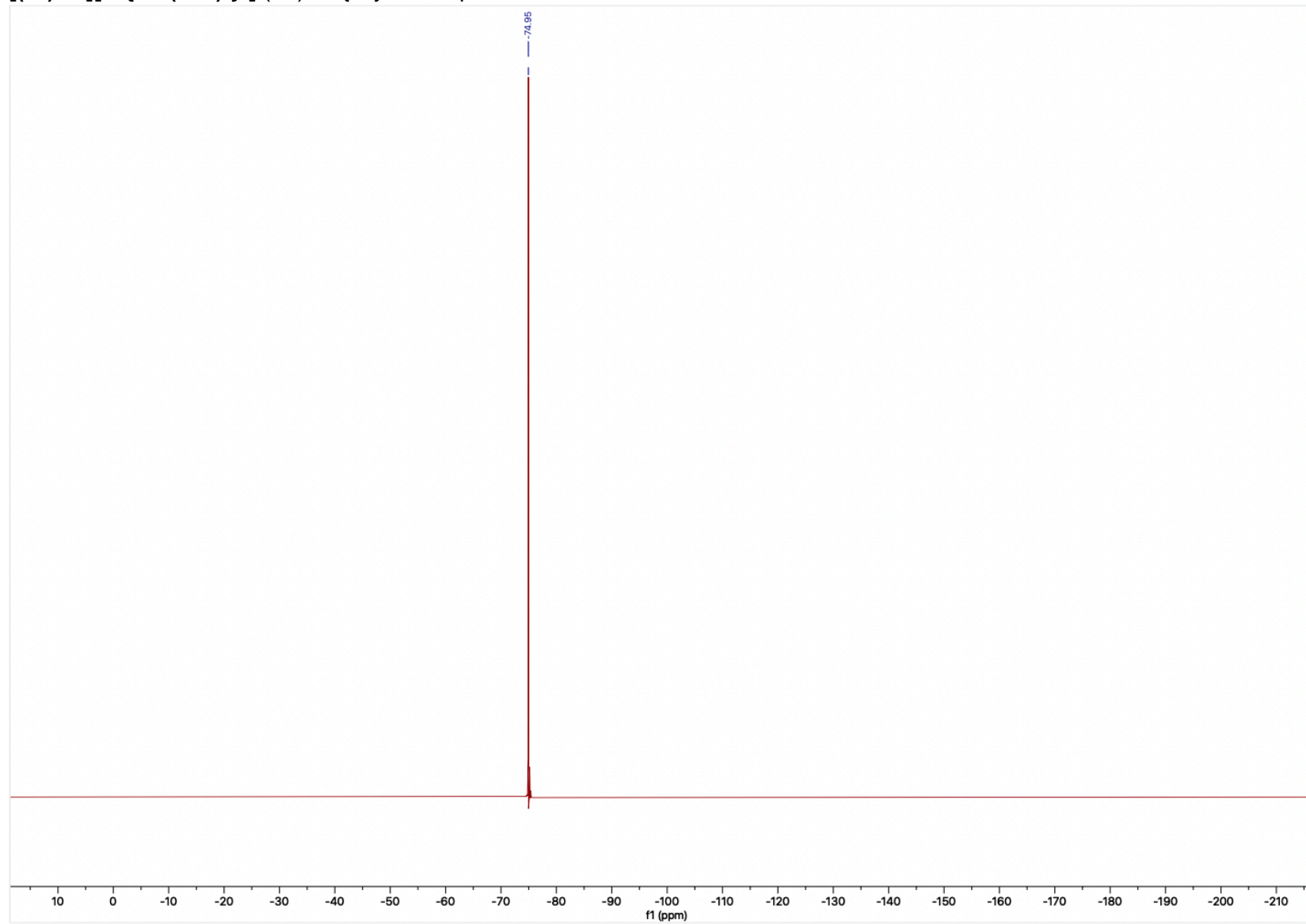
$[(^*L)Ge][Al\{OC(CF_3)_3\}_4]$ (20) $^{13}C\{^1H\}$ NMR spectrum



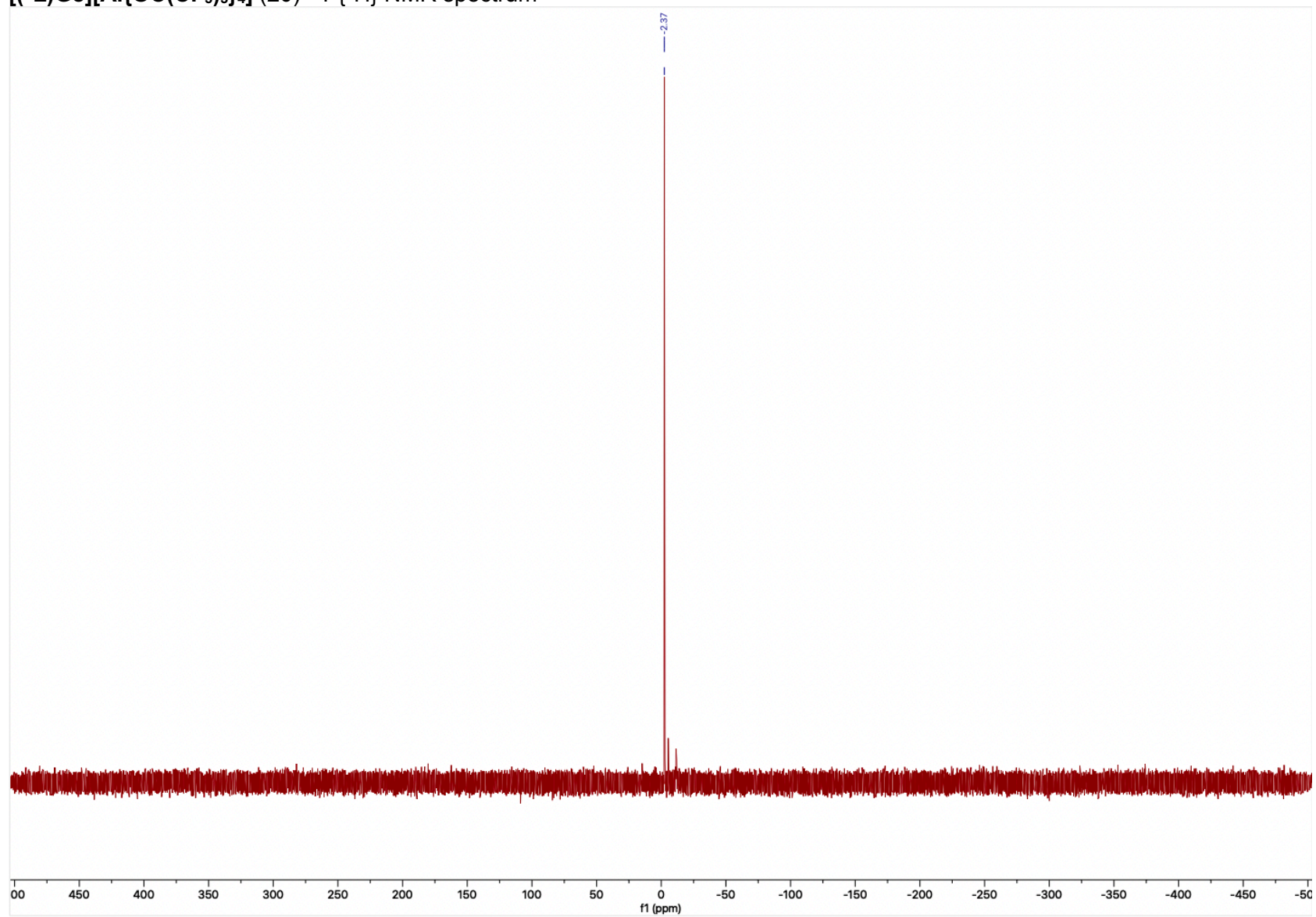
$[(^*L)Ge][Al\{OC(CF_3)_3\}_4]$ (20**) $^{27}Al\{^1H\}$ NMR spectrum**



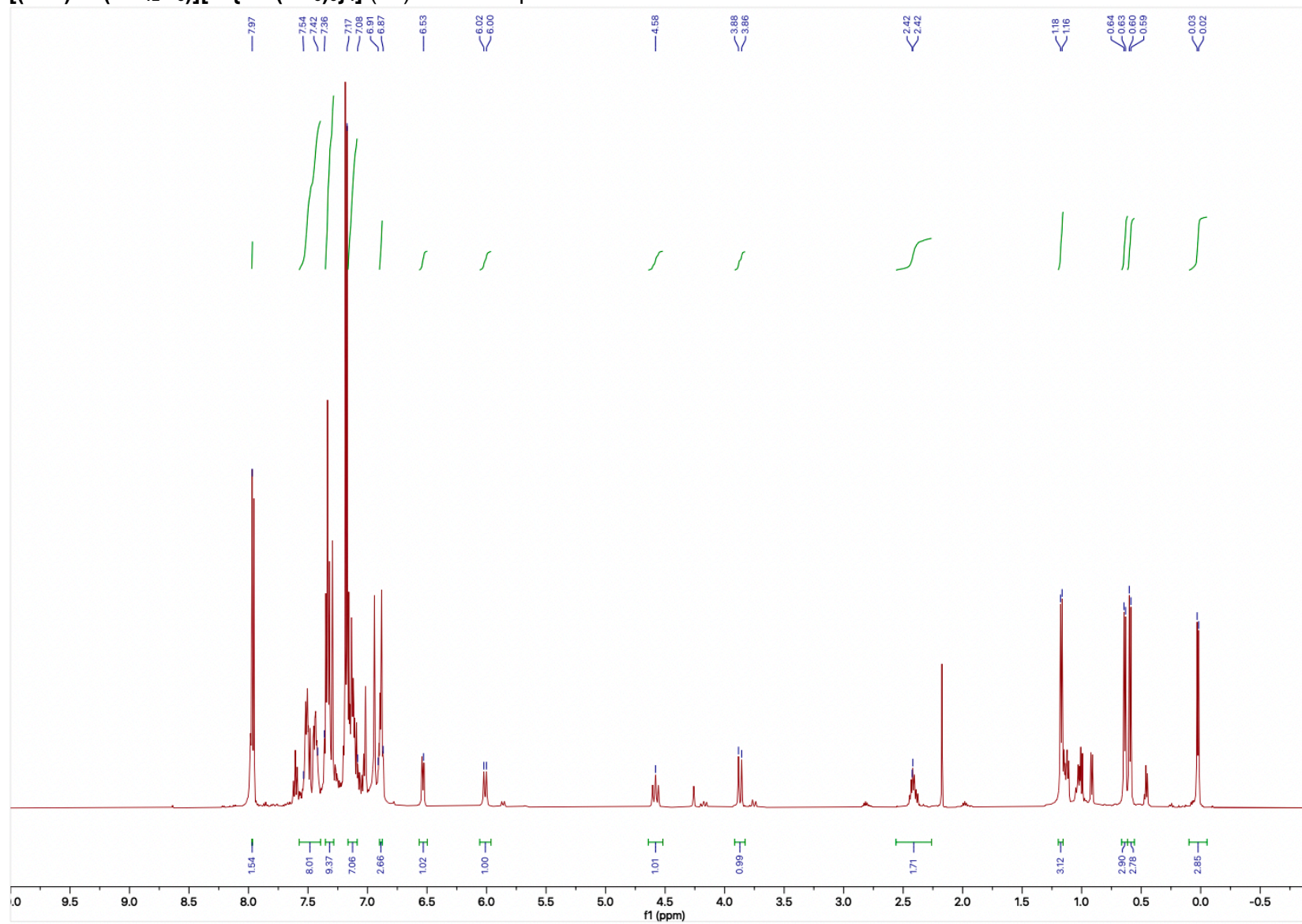
$[(^*L)Ge][Al\{OC(CF_3)_3\}_4]$ (20**) $^{19}F\{^1H\}$ NMR spectrum**



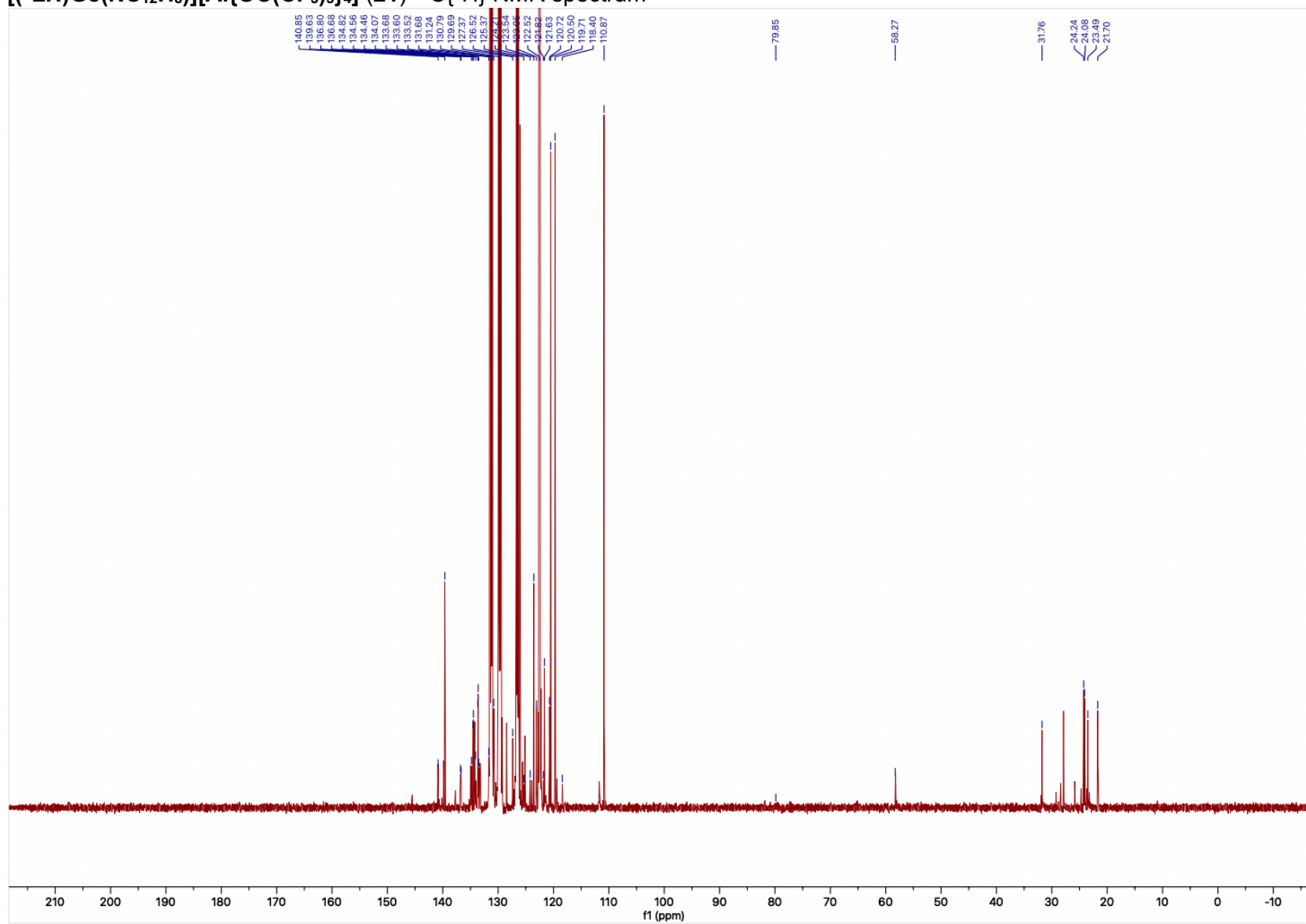
$[(^*L)Ge][Al\{OC(CF_3)_3\}_4]$ (20**) $^{31}P\{^1H\}$ NMR spectrum**



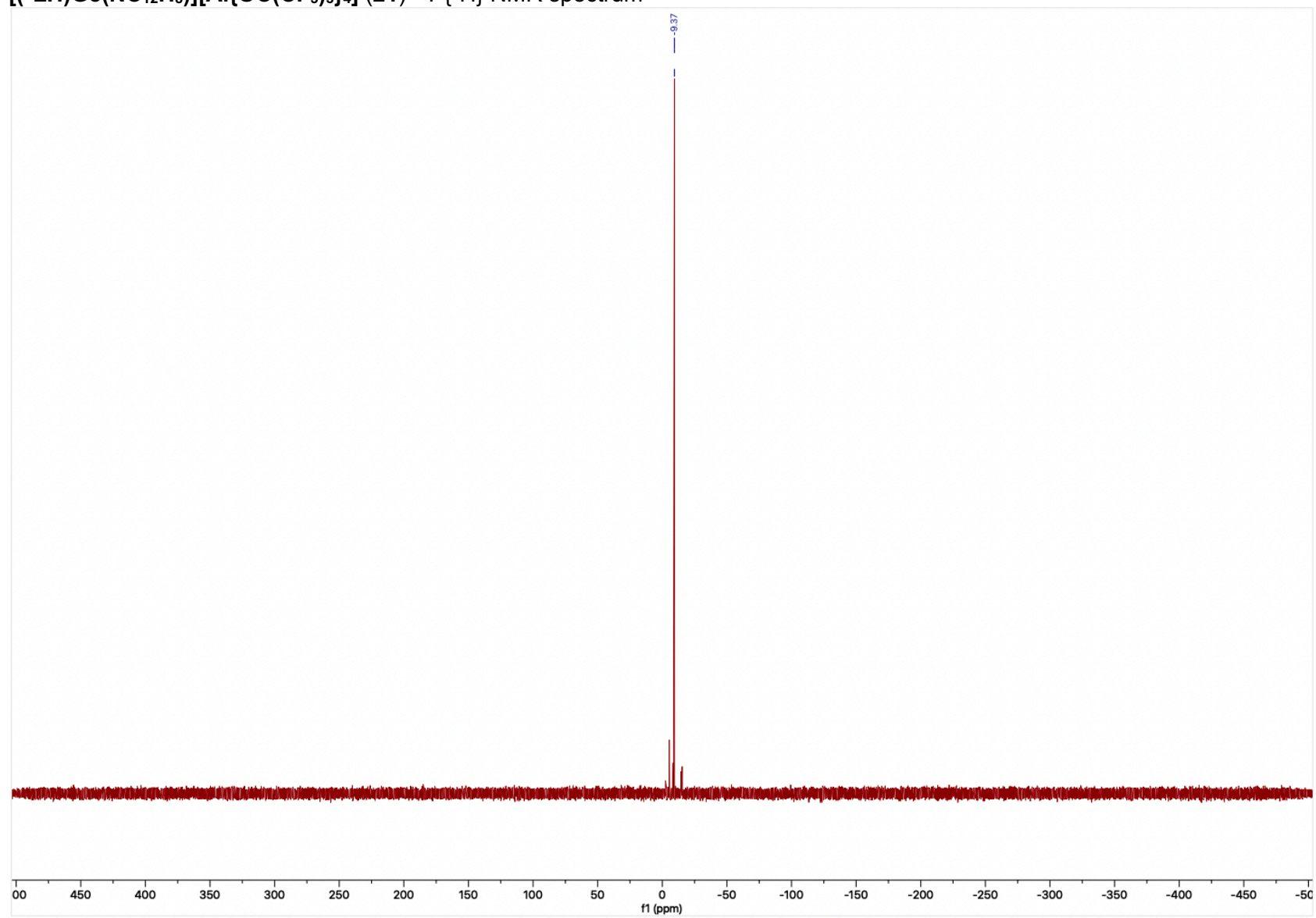
$[(^*LH)Ge(NC_{12}H_8)][Al\{OC(CF_3)_3\}_4]$ (21) 1H NMR spectrum



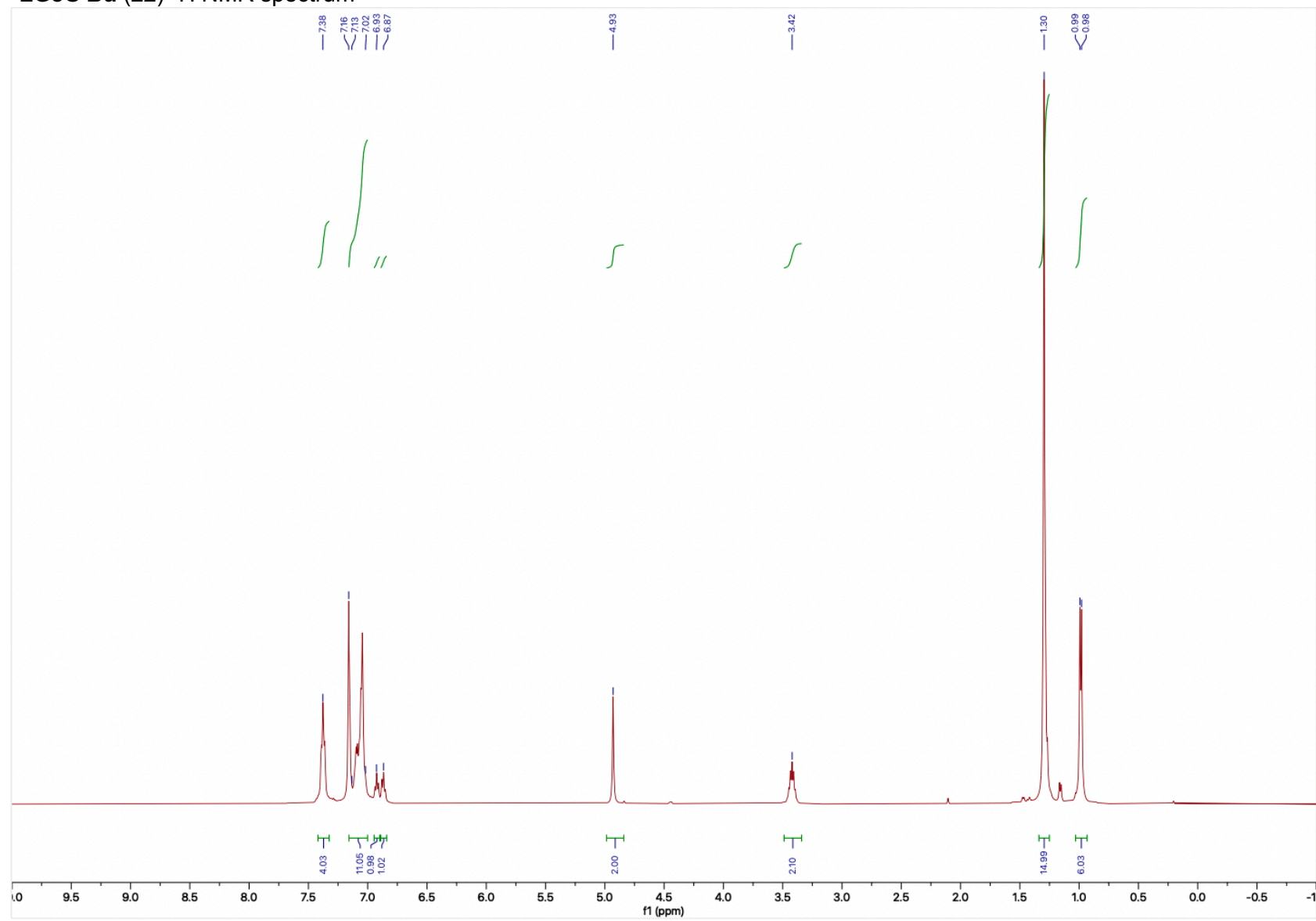
[(*LH)Ge(NC₁₂H₈)] [Al{OC(CF₃)₃}₄] (21) ¹³C{¹H} NMR spectrum



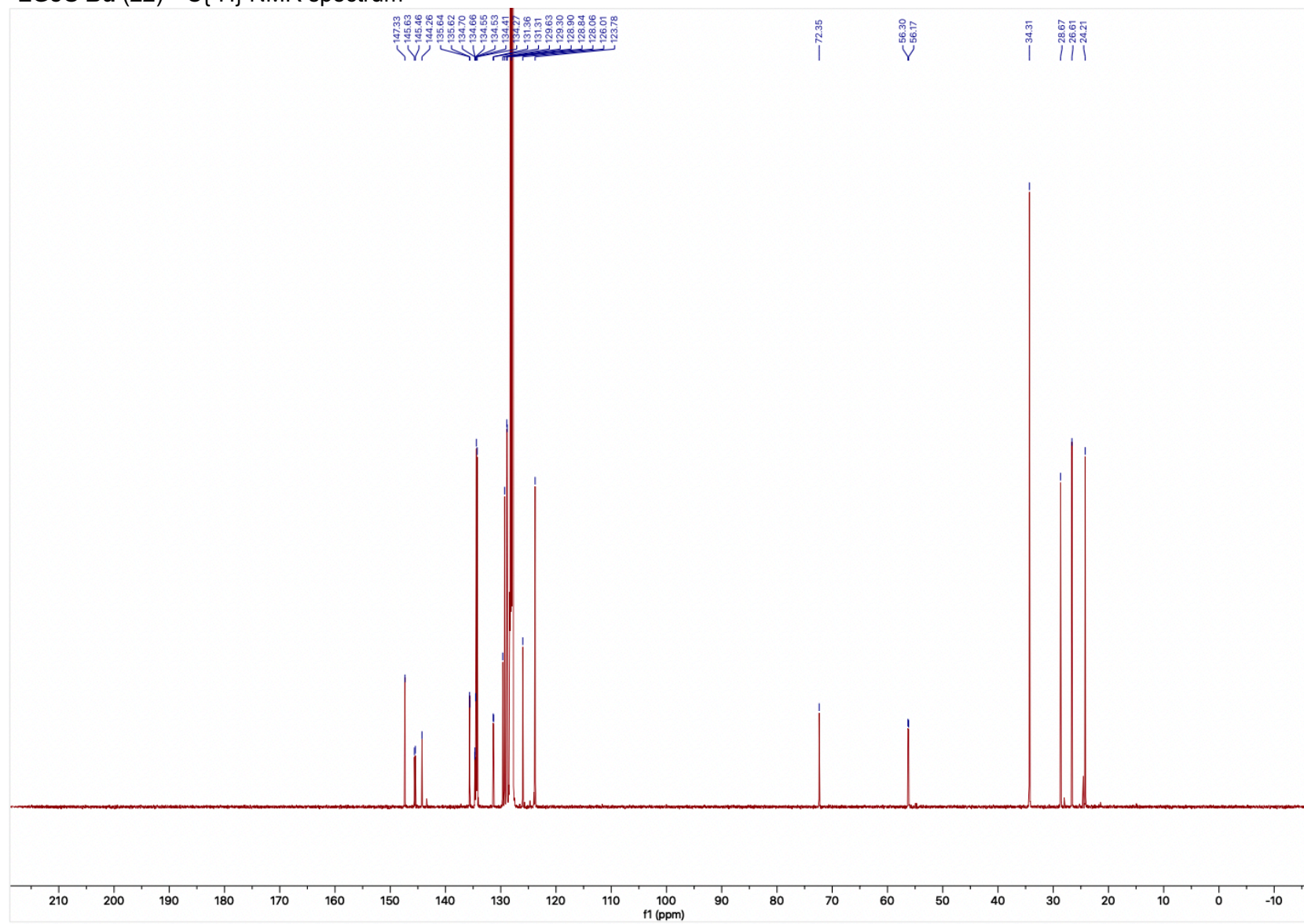
$[(^*\text{LH})\text{Ge}(\text{NC}_{12}\text{H}_8)][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (21) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



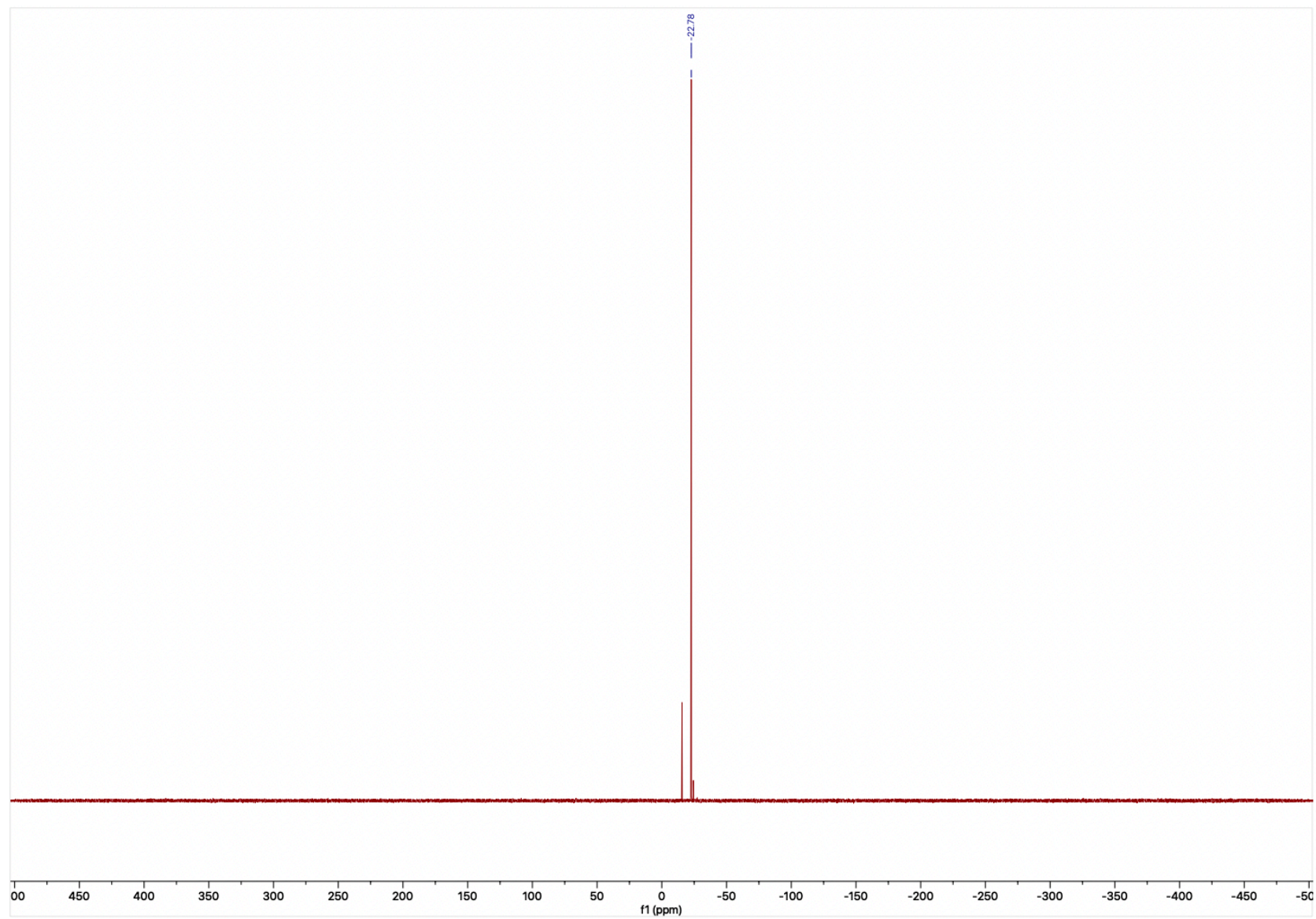
*LGeO^tBu (22) ¹H NMR spectrum



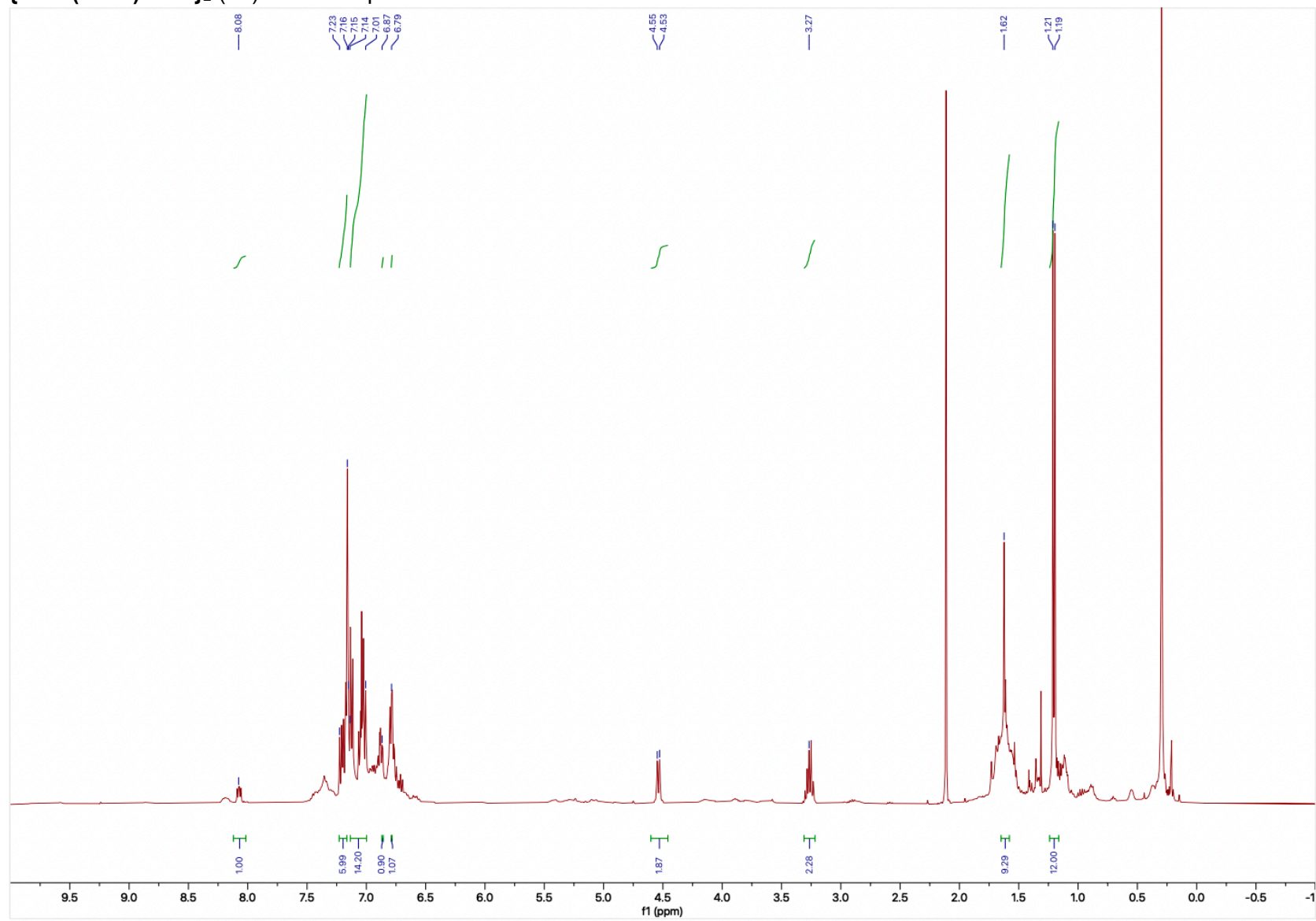
*LGeO^tBu (22) ¹³C{¹H} NMR spectrum



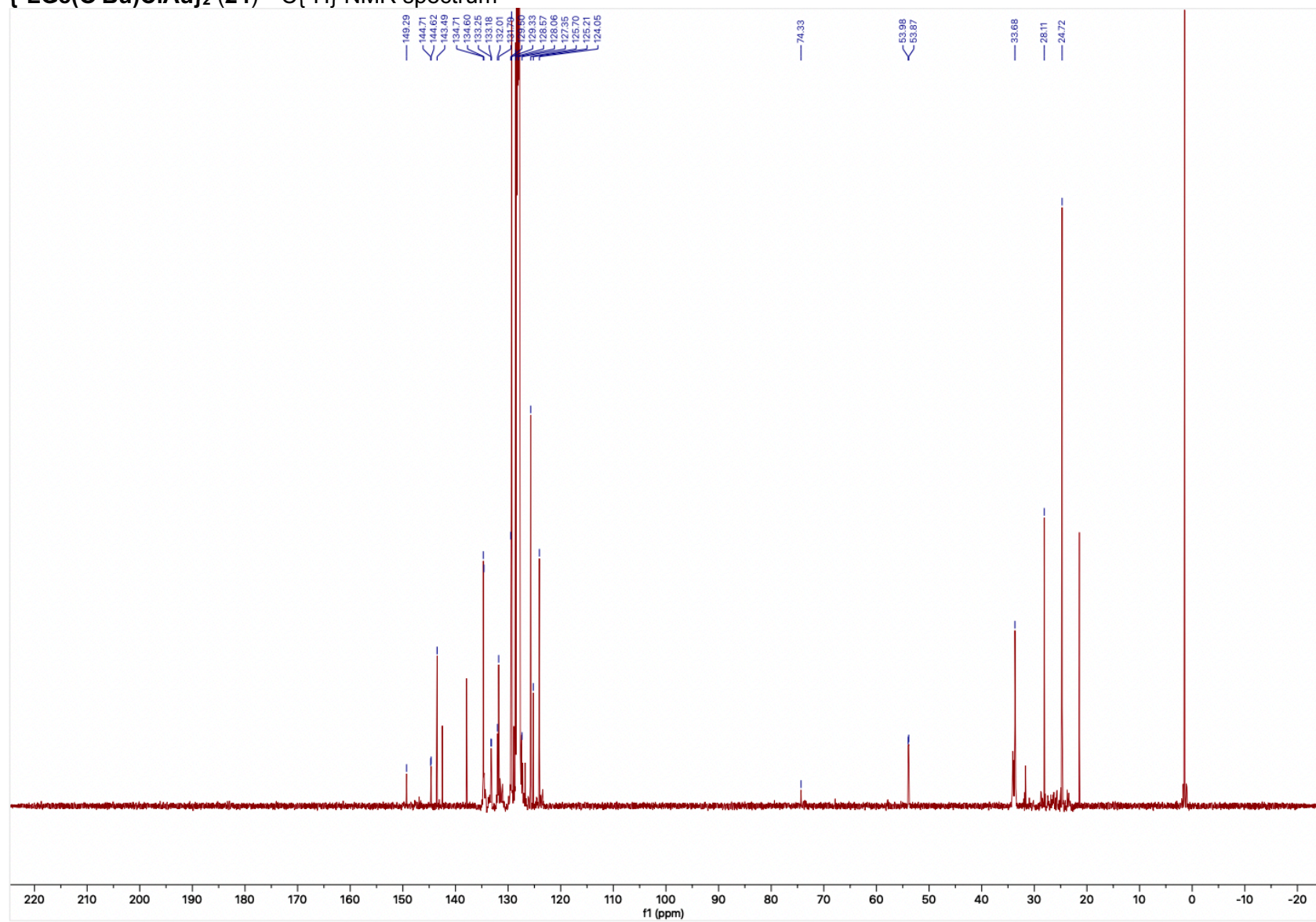
*LGeO^tBu (22) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



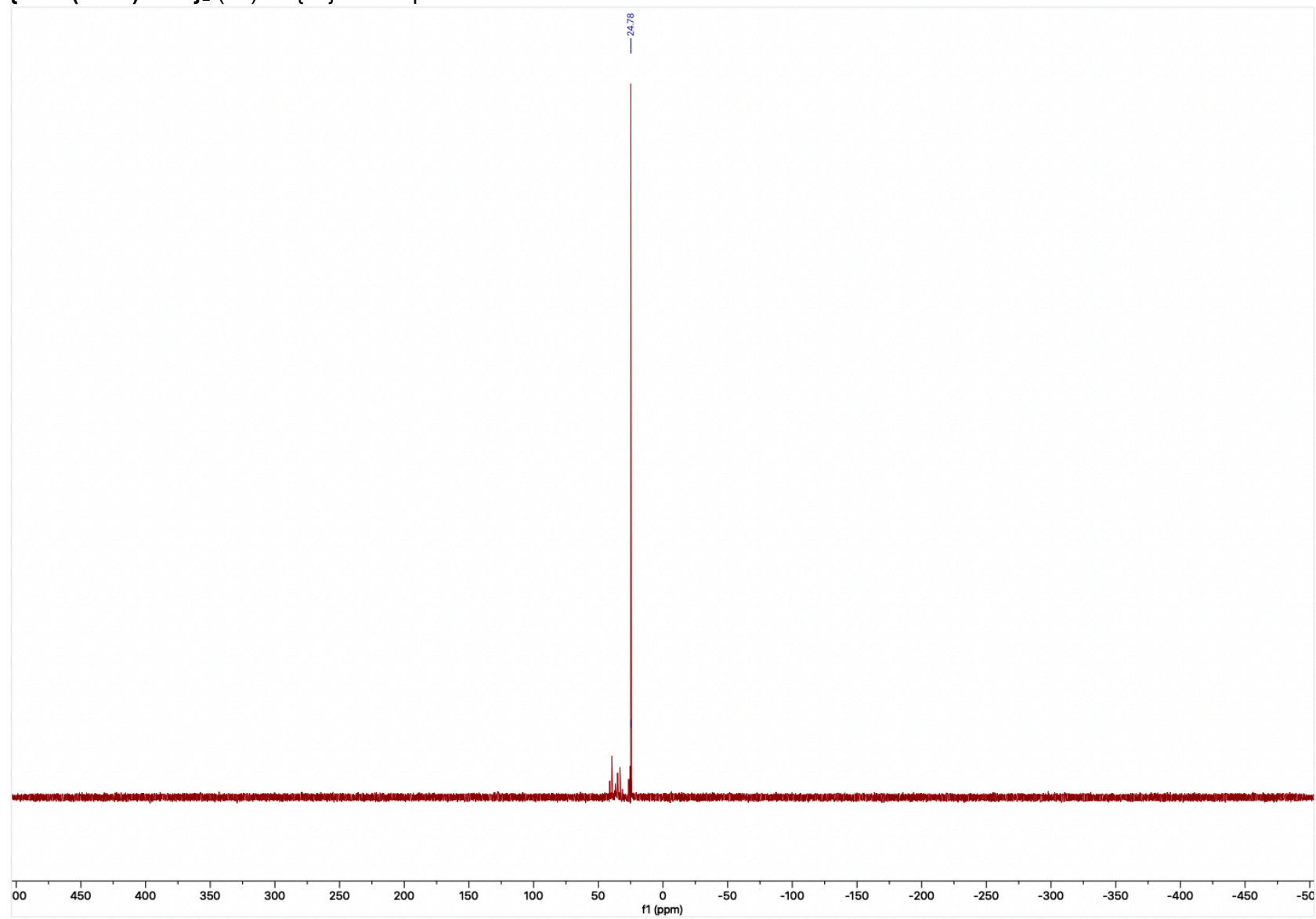
$\{^*\text{LGe}(\text{O}^t\text{Bu})\text{ClAu}\}_2$ (24) ^1H NMR spectrum



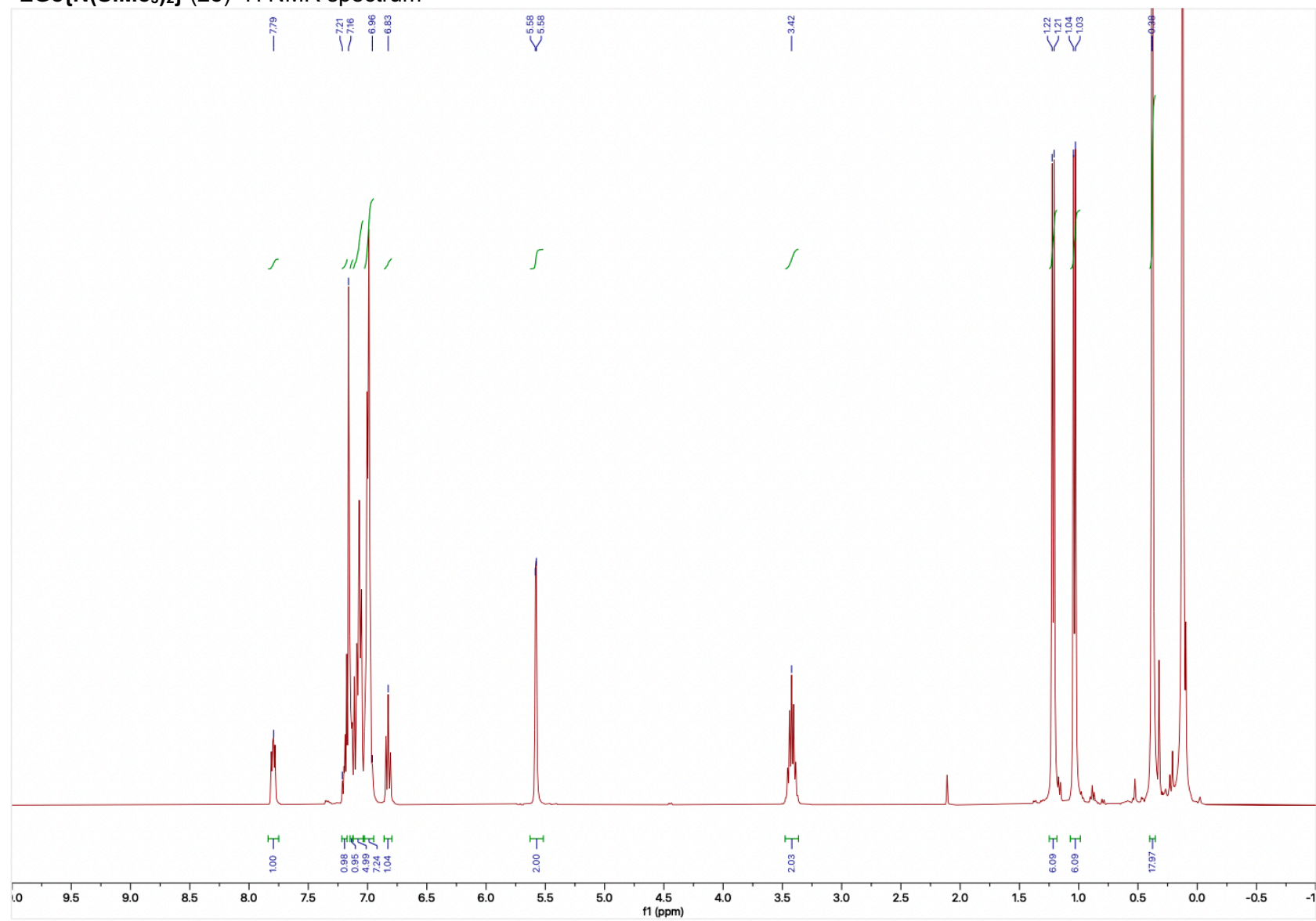
$\{^*\text{LGe}(\text{O}^t\text{Bu})\text{ClAu}\}_2$ (24) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



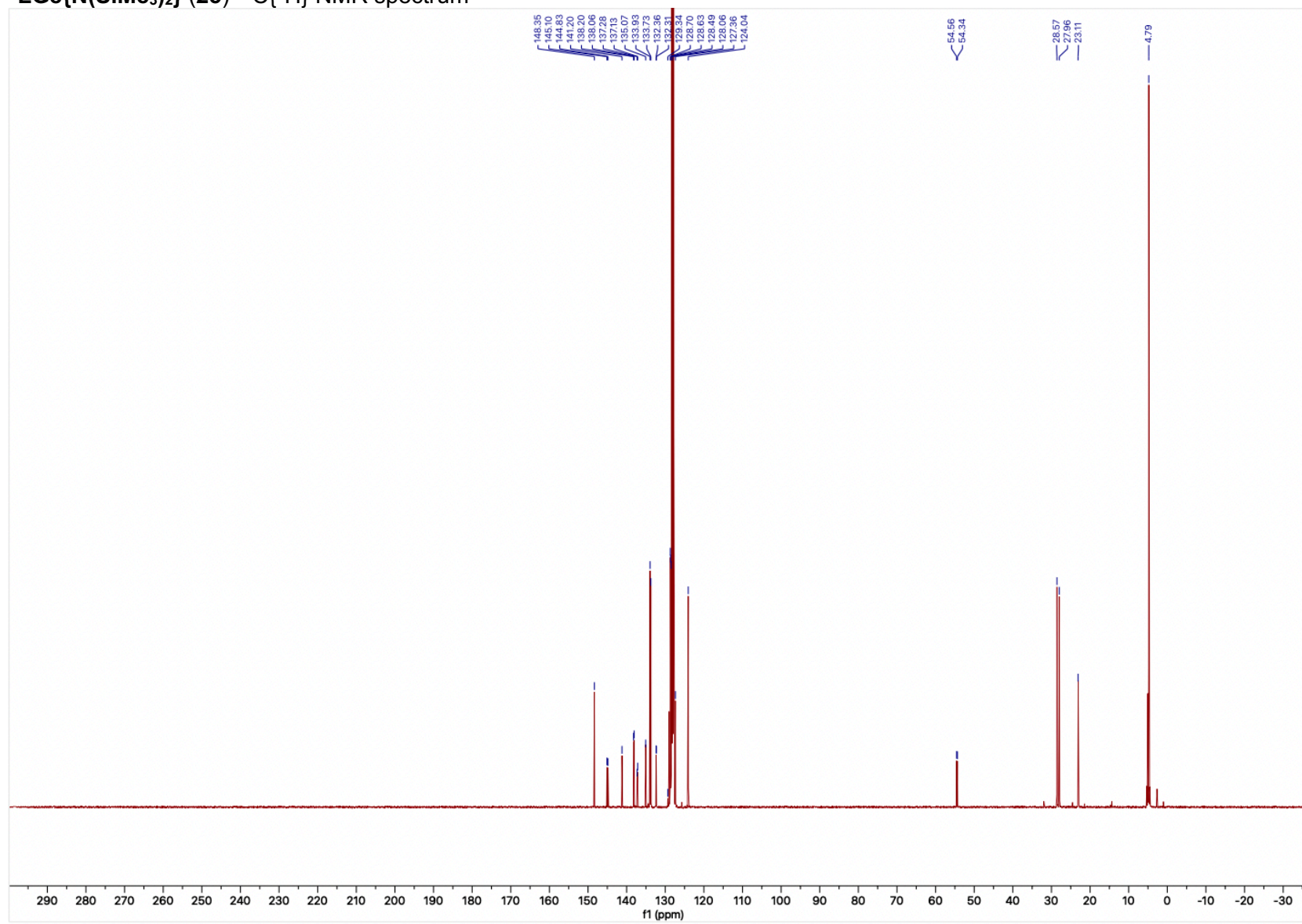
$\{^*\text{LGe}(\text{O}^t\text{Bu})\text{ClAu}\}_2$ (**24**) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



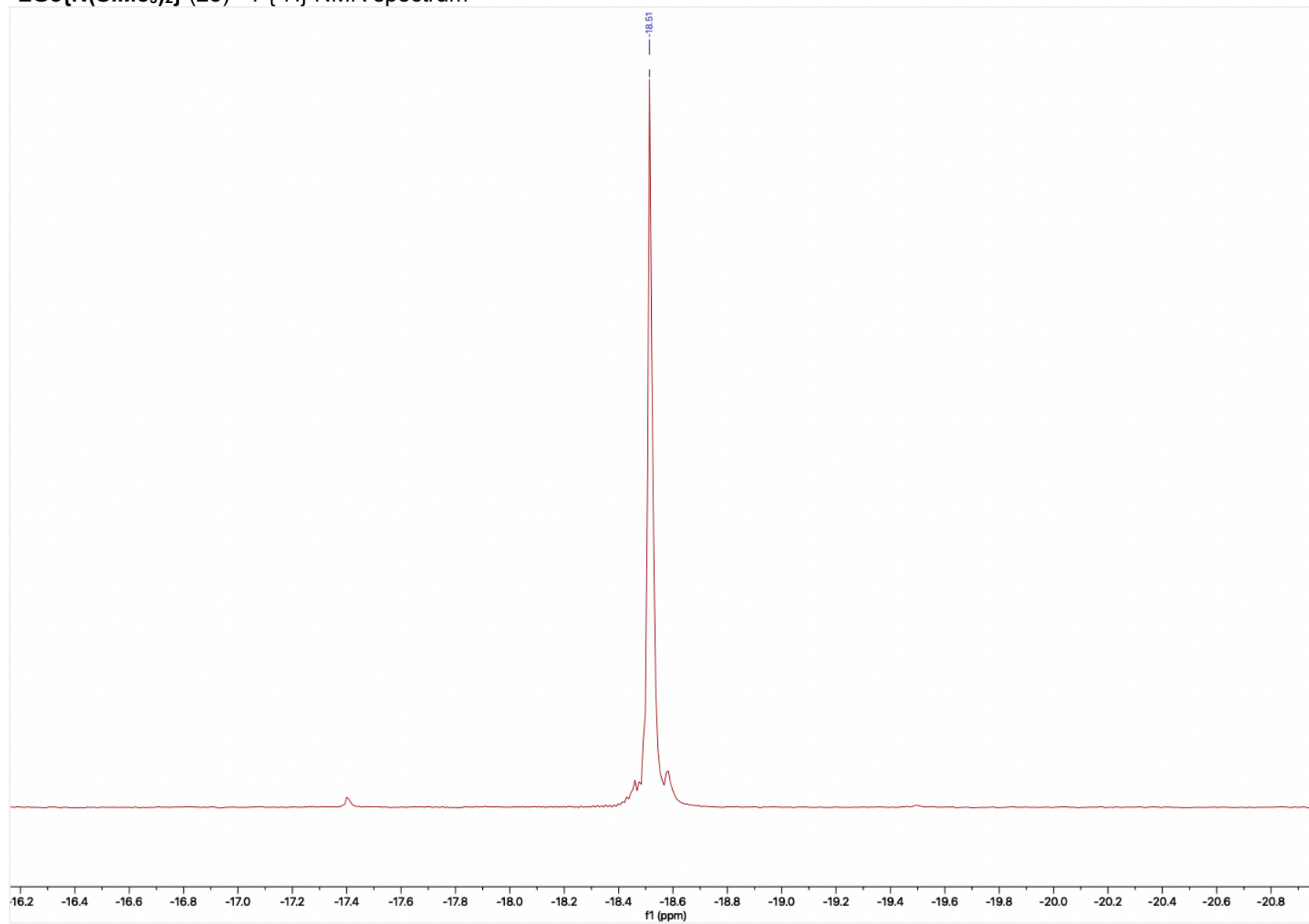
*LGe{N(SiMe₃)₂} (25) ¹H NMR spectrum



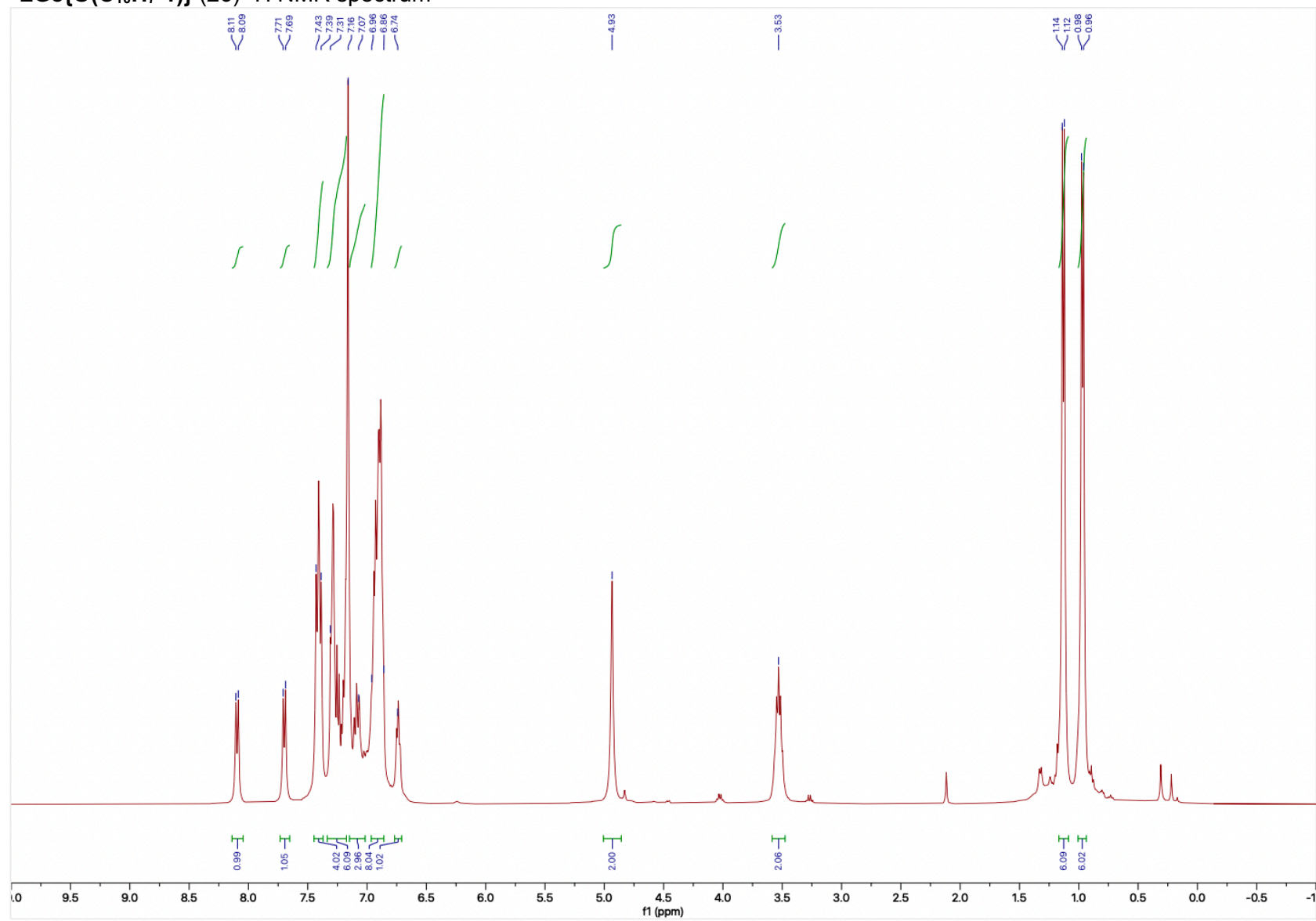
*LGe{N(SiMe₃)₂} (25) ¹³C{¹H} NMR spectrum



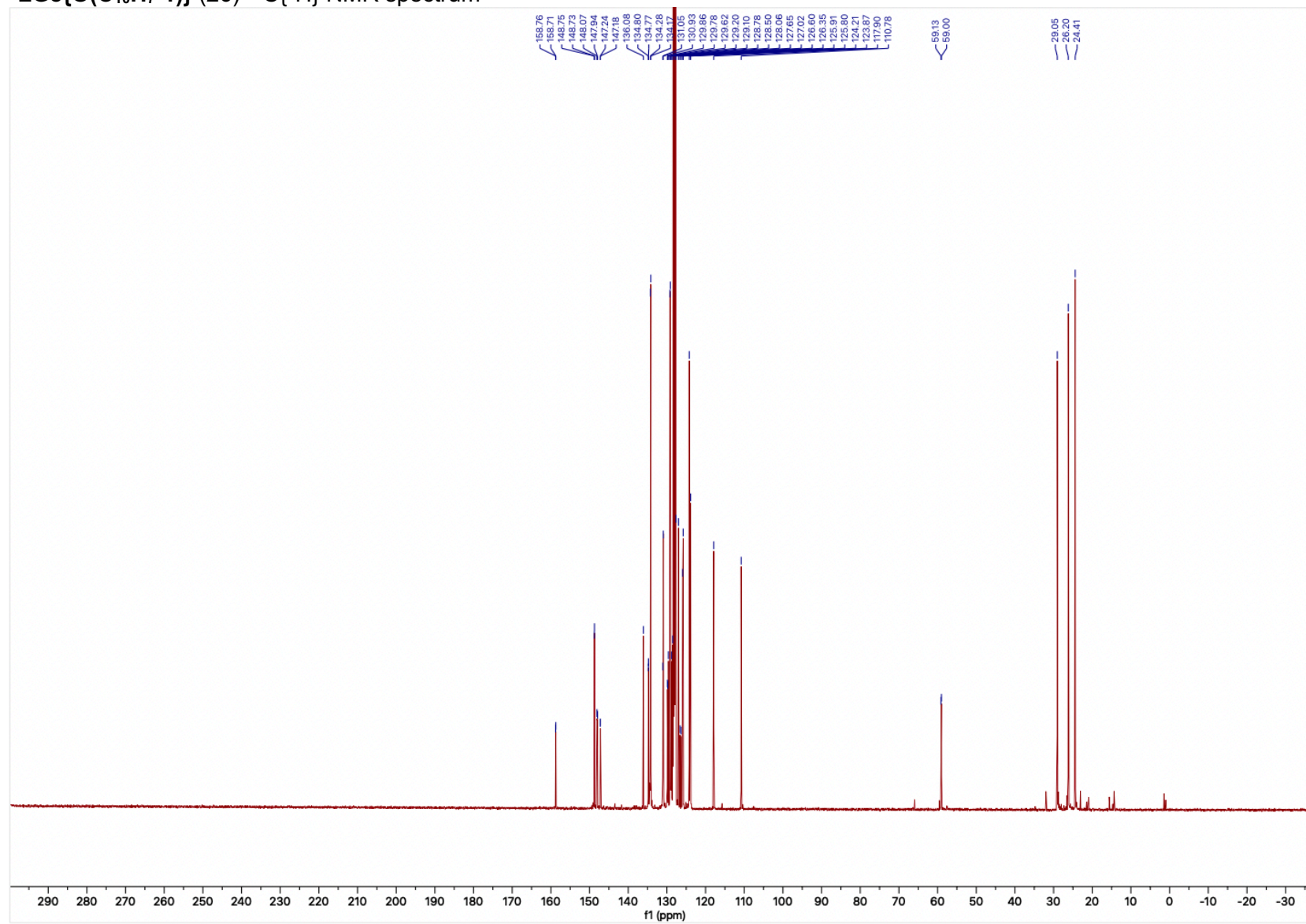
***LGe{N(SiMe₃)₂} (25)** ³¹P{¹H} NMR spectrum



*LGe{O(C₁₀H₇-1)} (26) ¹H NMR spectrum



*LGe{O(C₁₀H₇-1)} (26) ¹³C{¹H} NMR spectrum



*LGe{O(C₁₀H₇-1)} (26) ³¹P{¹H} NMR spectrum

