Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information for:

Investigations into the structure, reactivity, and AACVD of aluminium and gallium amidoenoate complexes

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A. Thin film analysis

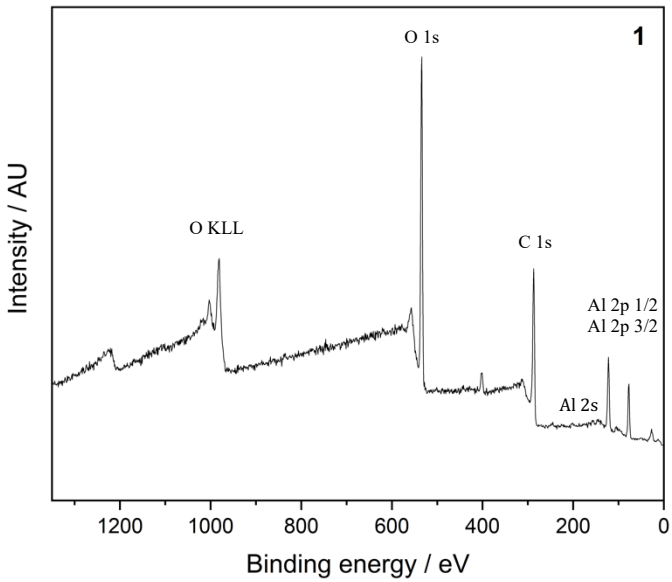

Fig 1: Survey scan of thin film deposited by complex [AlCl(AME^{Dip})$_2$] (**3-Al**). No Cl present in survey scan (Cl 2p$_{3/2}$ = 200 eV; 2p$_{1/2}$ = 202 eV; Cl 2s = 270 eV).

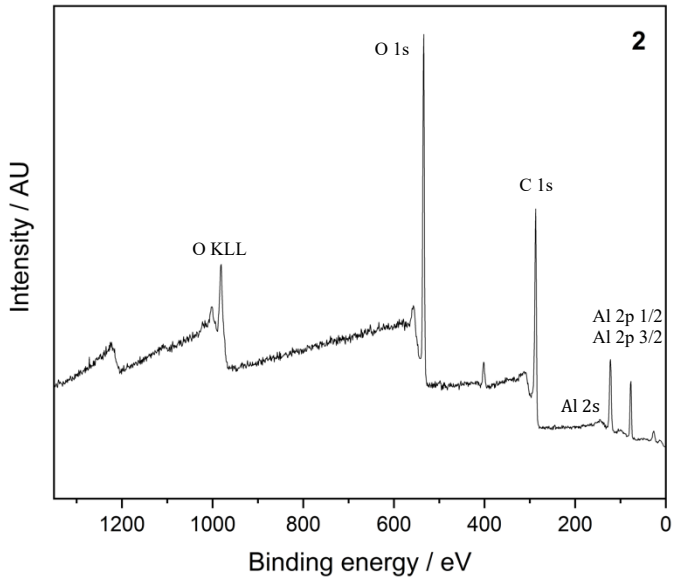

Fig 2: Survey scan of thin film deposited by complex [AlH(AME^{Dip})$_2$] (**4-Al**). No Cl present in survey scan (Cl 2p$_{3/2}$ = 200 eV; 2p$_{1/2}$ = 202 eV; Cl 2s = 270 eV).

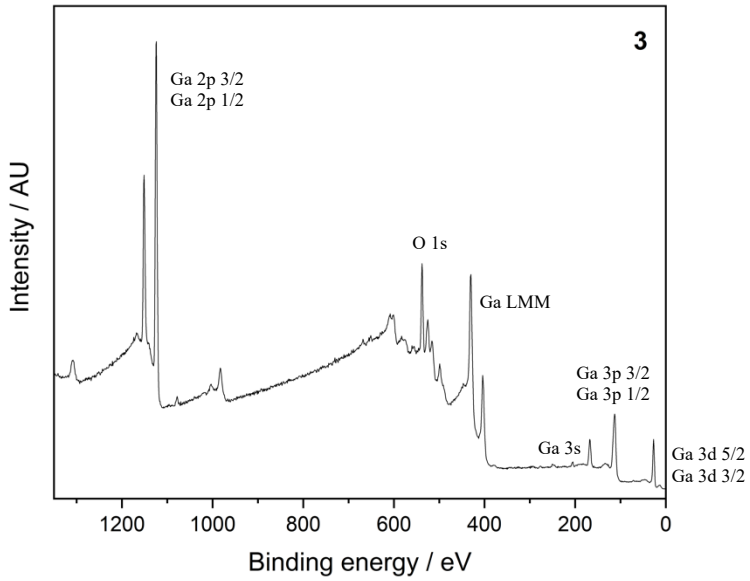

Fig 3: Survey scan of thin film deposited by complex [$GaCl_2(AME^{iPr})$] (**1-Ga**). No Cl present in survey scan (Cl $2p_{3/2}$ = 200 eV; $2p_{1/2}$ = 202 eV; Cl 2s = 270 eV).

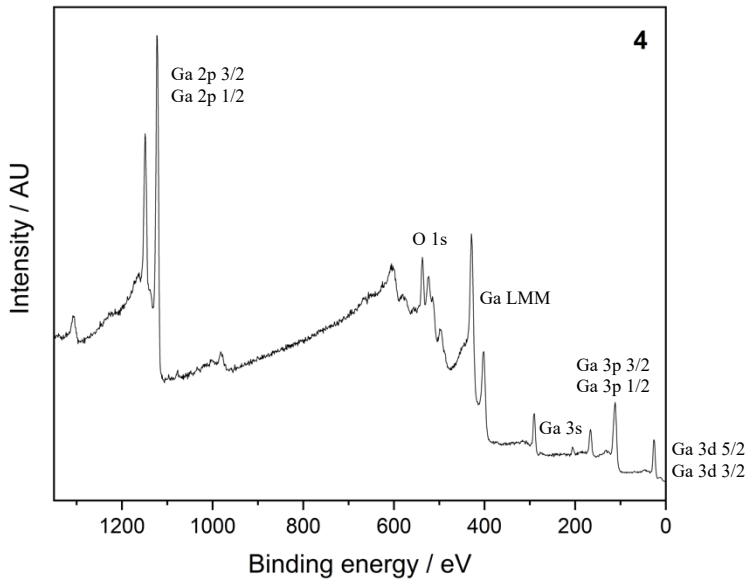

Fig 4: Survey scan of thin film deposited by complex [$GaCl(AME^{Dip})_2$] (**3-Ga**). No Cl present in survey scan (Cl $2p_{3/2}$ = 200 eV; $2p_{1/2}$ = 202 eV; Cl 2s = 270 eV).

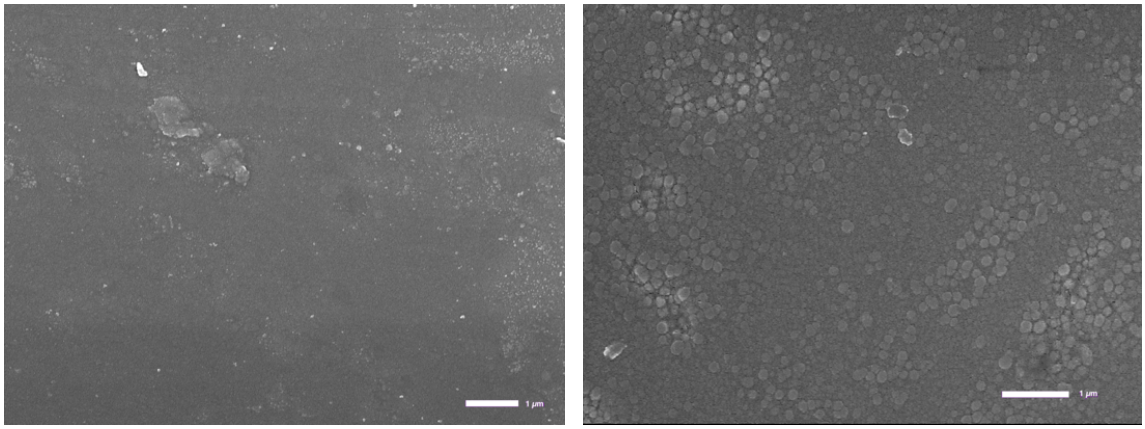

Fig 5. SEM images of Ga_2O_3 on glass (left) and on quartz after annealing treatment (1000 °C in air for 12 hours) deposited from [GaCl(AME^{Dip})$_2$], (**3-Ga**). 1µm scale bar inset.

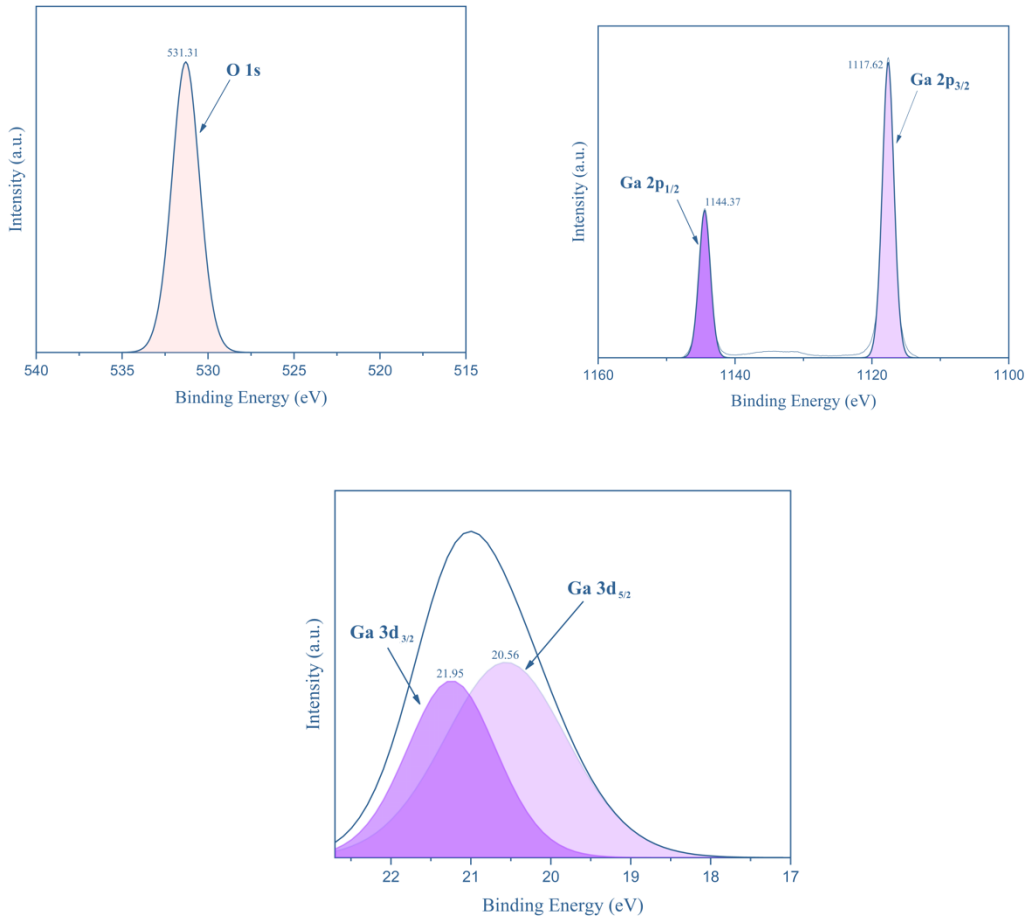

Fig 6. XPS analysis of Ga_2O_3 showing the Ga $3d_{5/2}$, $3d_{3/2}$, $2p_{3/2}$ and $2p_{1/2}$ states, including the O 1s state, deposited from [GaCl(AME^{Dip})$_2$], (**3-Ga**).

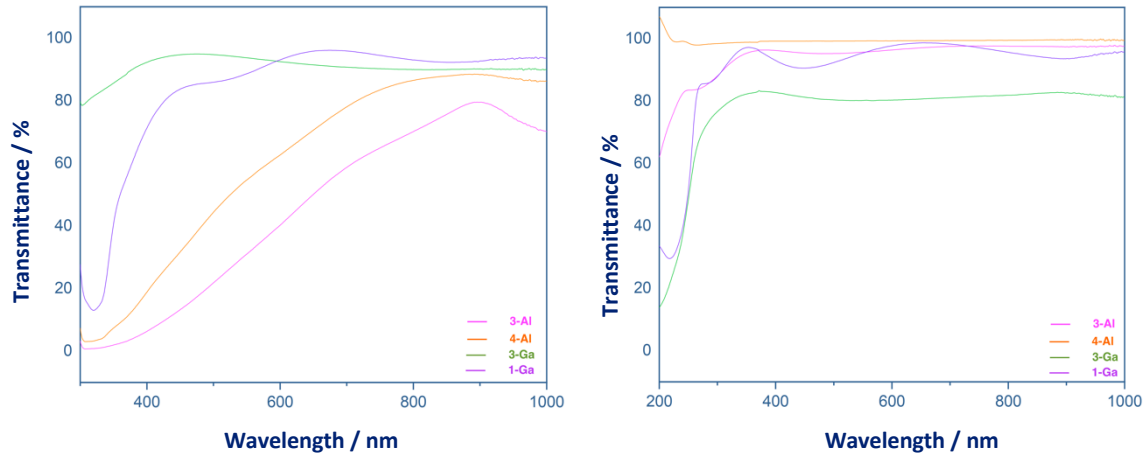

Fig 7. UV-vis (transmittance) plots generated for each of the precursors deposited on glass (left) and on quartz (right) after annealing treatment (1000 °C in air for 12 hours showing improved transmission and transparency after the post-annealing treatment.

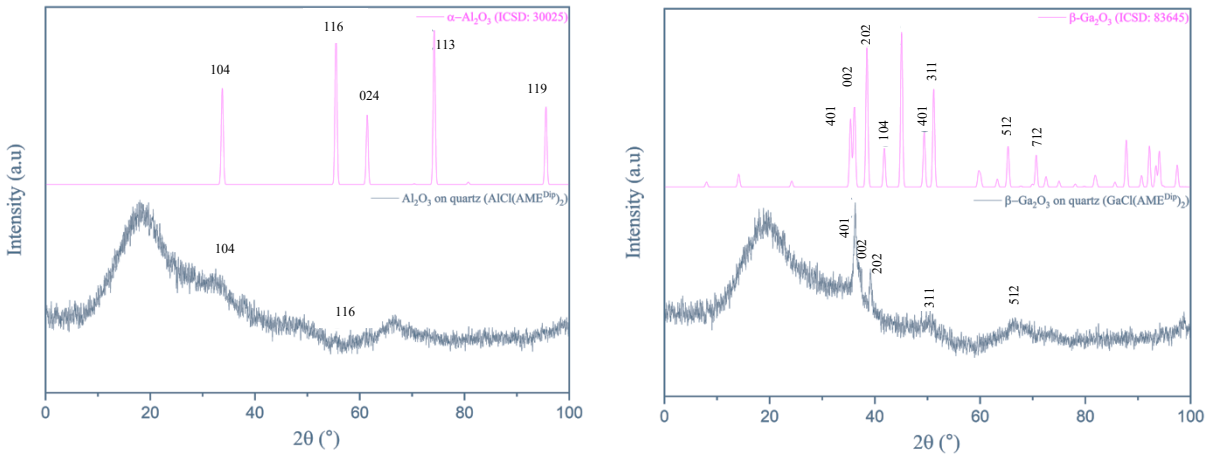

Fig 8. XRD patterns of Al_2O_3 (left) and Ga_2O_3 (right) thin films on quartz with improved crystallinity after annealing treatment (1000 °C in air for 12 hours), deposited from [AlCl(AME^{Dip})$_2$], (**3-Al**) and [GaCl(AME^{Dip})$_2$], (**3-Ga**) respectively (0.2 g of precursor).

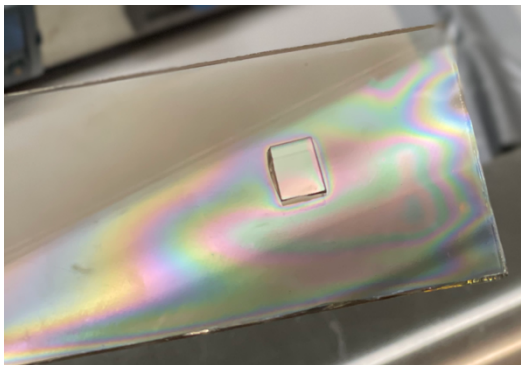

Fig 9. Photograph of a thin film deposited on glass and quartz (pre-anneal) from precursor **3-Ga** (0.2 g of precursor).

B. NMR spectra from reactivity studies

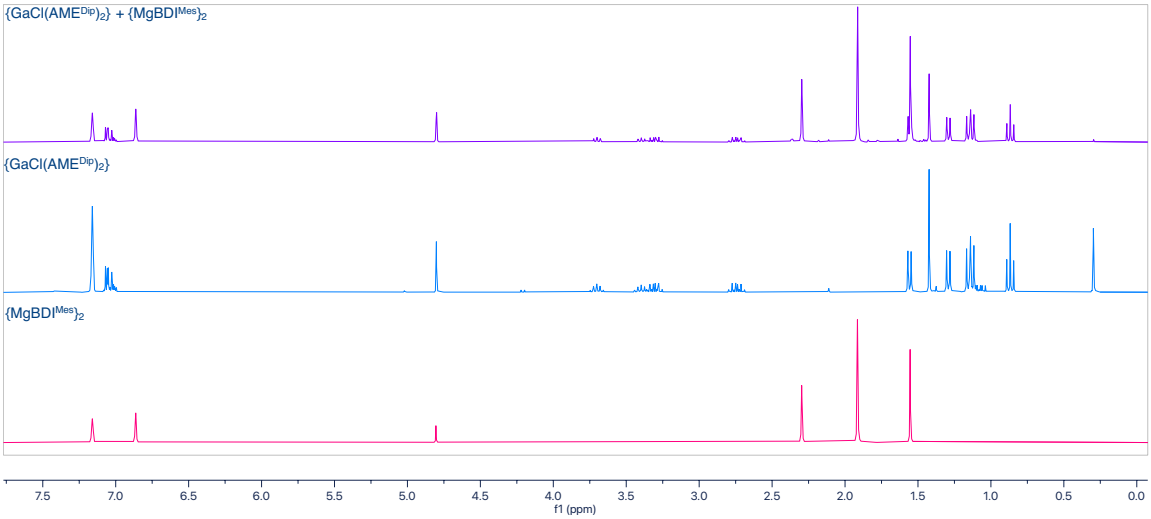

Fig 10. Stacked ^{1}H NMR spectra of magnesium(I) dimers, [Mg(BDI^{Mes})] (bottom), [GaCl(AME^{Dip})$_2$], **3-Ga** (middle) and the product of their addition at ambient temperature (top).

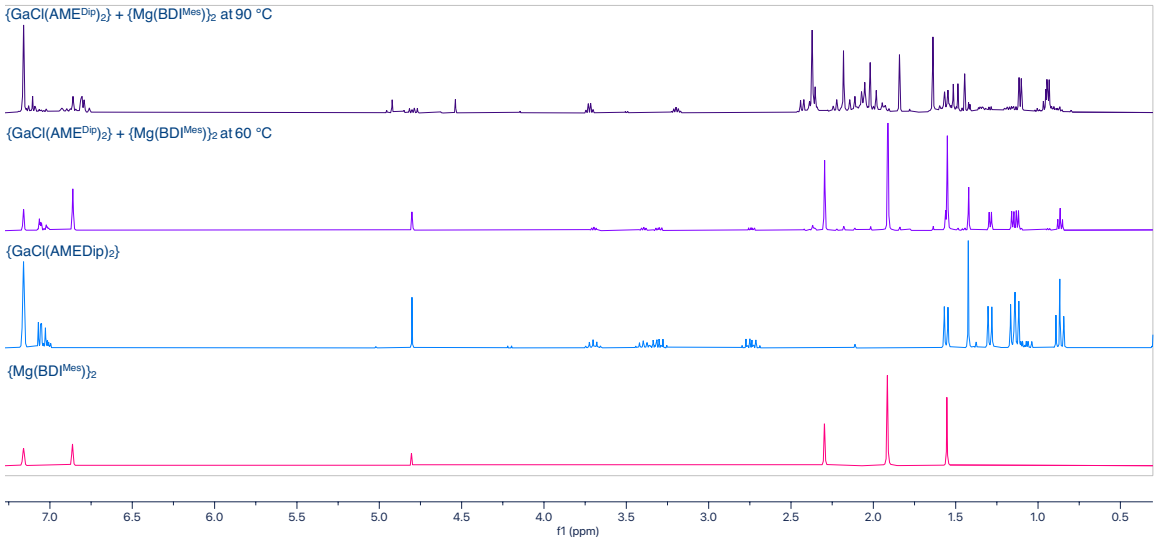

Fig 11. Stacked ^{1}H NMR spectra of magnesium(I) dimers, [Mg(BDI^{Mes})] (bottom), [GaCl(AME^{Dip})$_2$], **3-Ga** (lower middle), the product of their addition after stirring at 60 °C (upper middle) and after stirring at 90 °C (top).

C. NMR spectra of complexes

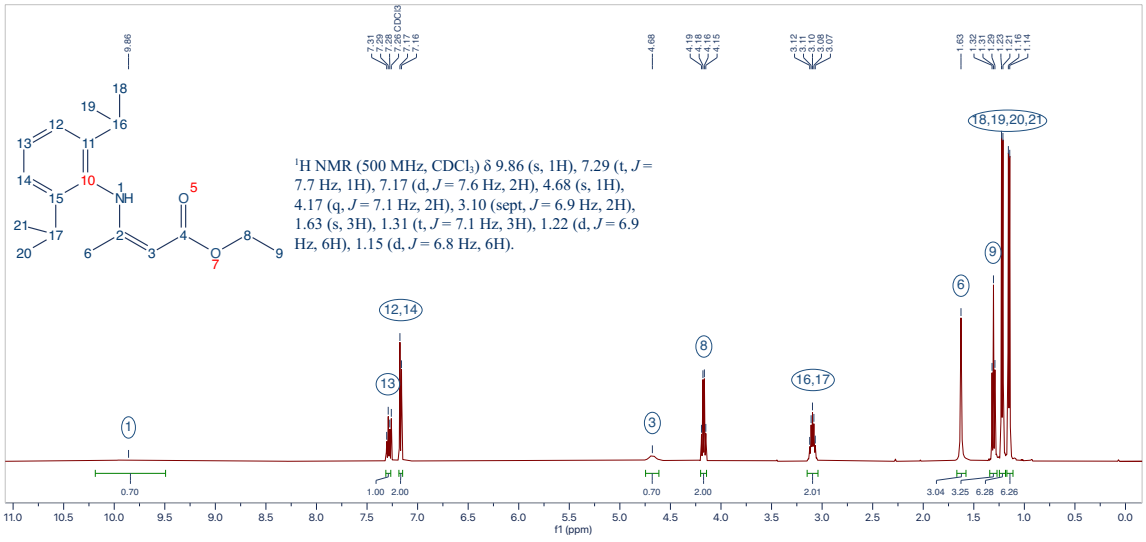

Fig 12. ^{1}H NMR of HAME^{Dip}

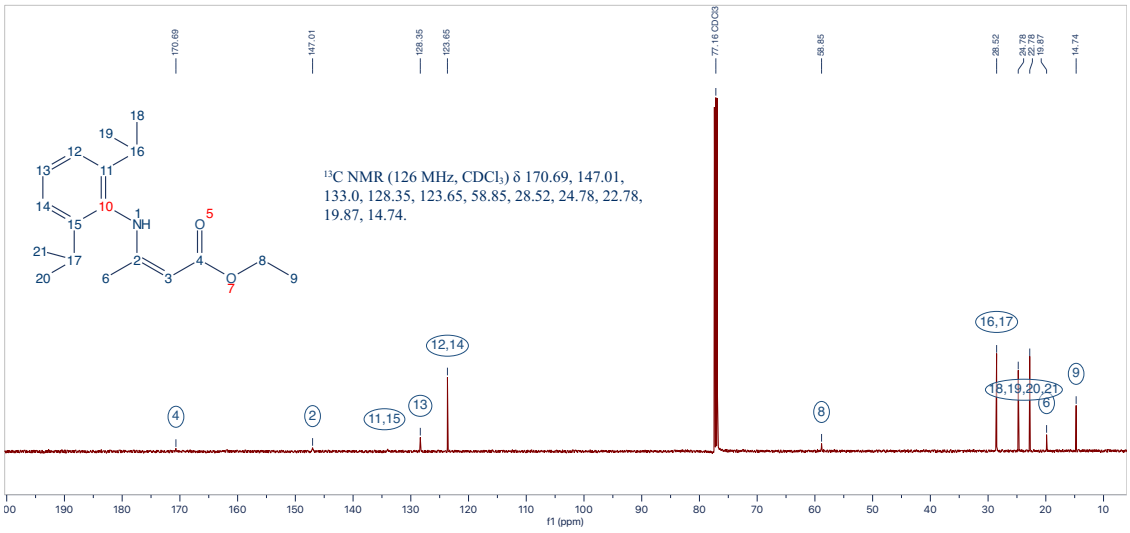

Fig 13. $^{13}C\{^{1}H\}$ NMR of HAME^{Dip}

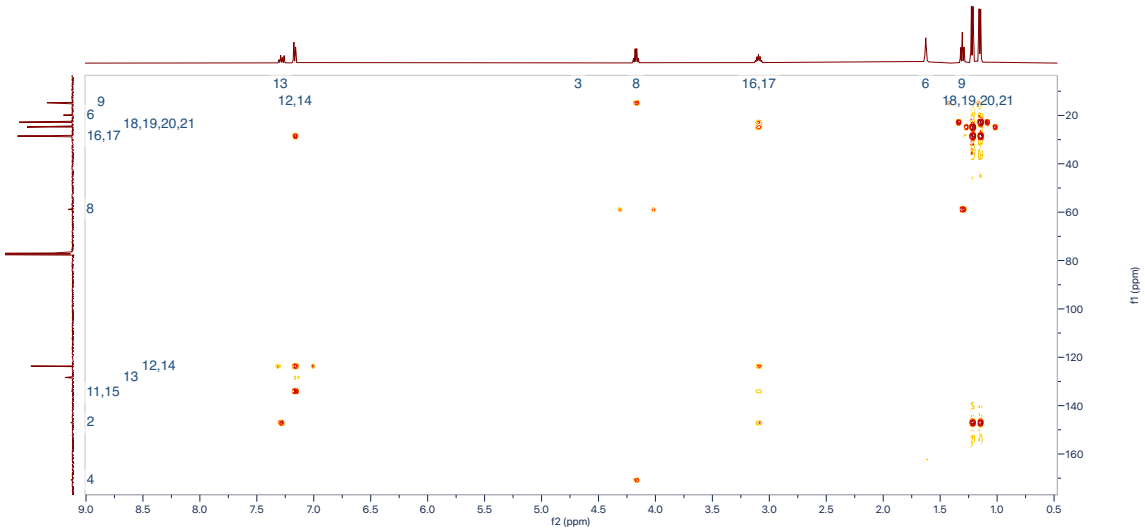

Fig 14. $^{1}H–^{1}H$ COSY NMR of HAME^{Dip}

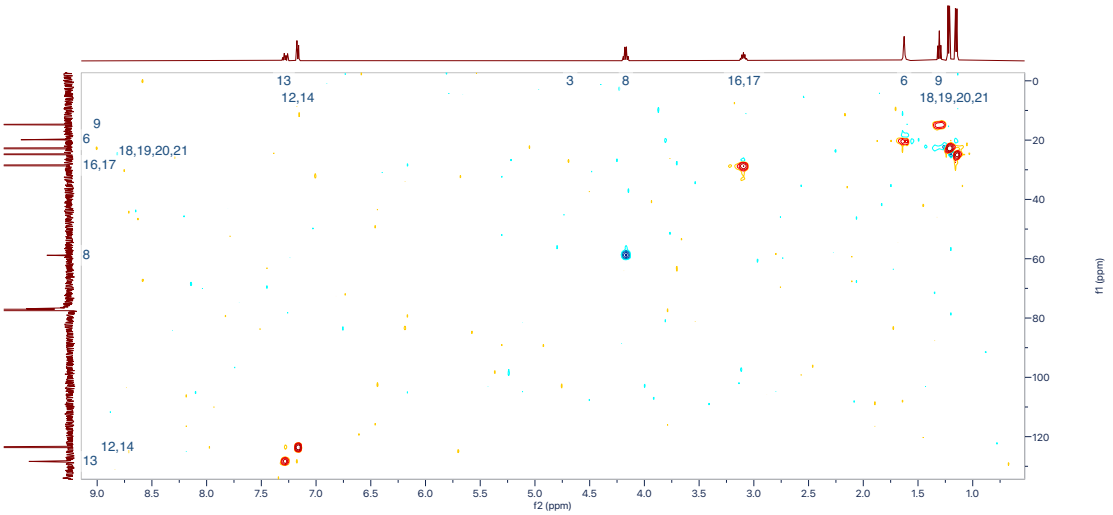

Fig 15. $^{1}H–^{13}C$ HSQC NMR of HAME^{Dip}

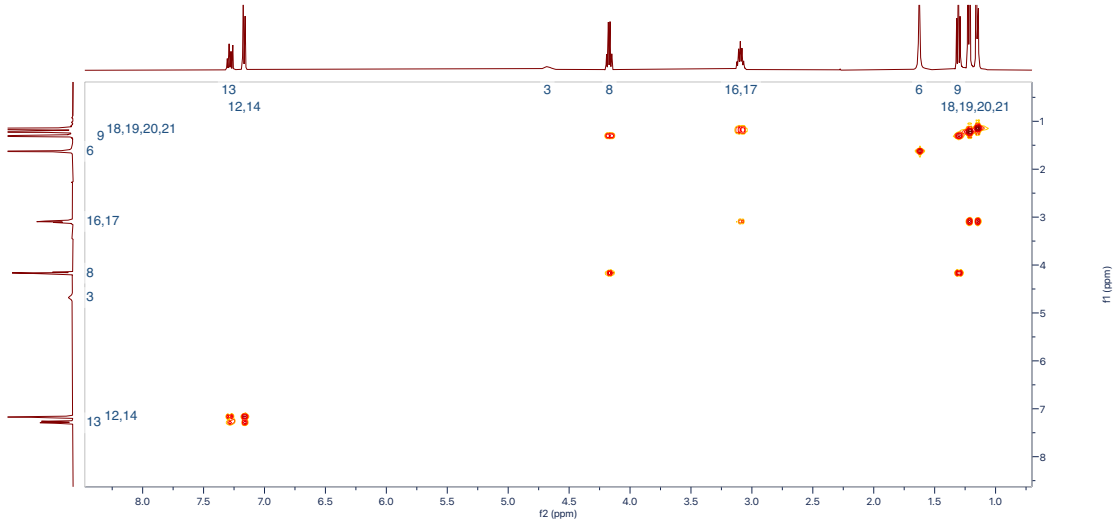

Fig 16. $^{1}H–^{13}C$ HMBC NMR of HAME^{Dip}

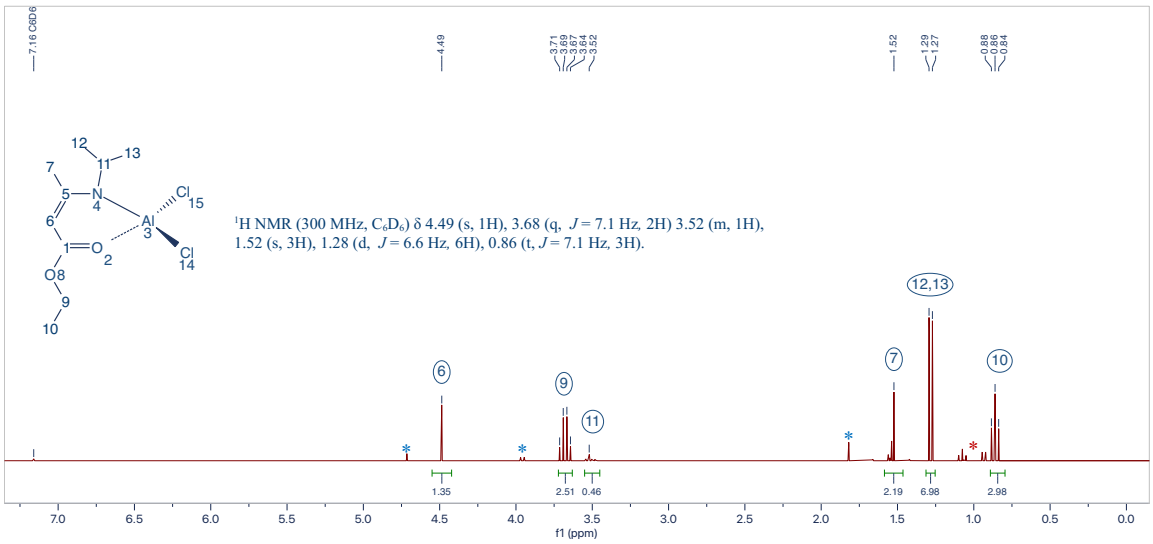

Fig 17. ^{1}H NMR of [$AlCl_2$(AME^{iPr})] (**1-Al**), solvents (hexane and diethyl ether), marked with an asterisk (red) and small quantities of unidentified decomposition product (blue)

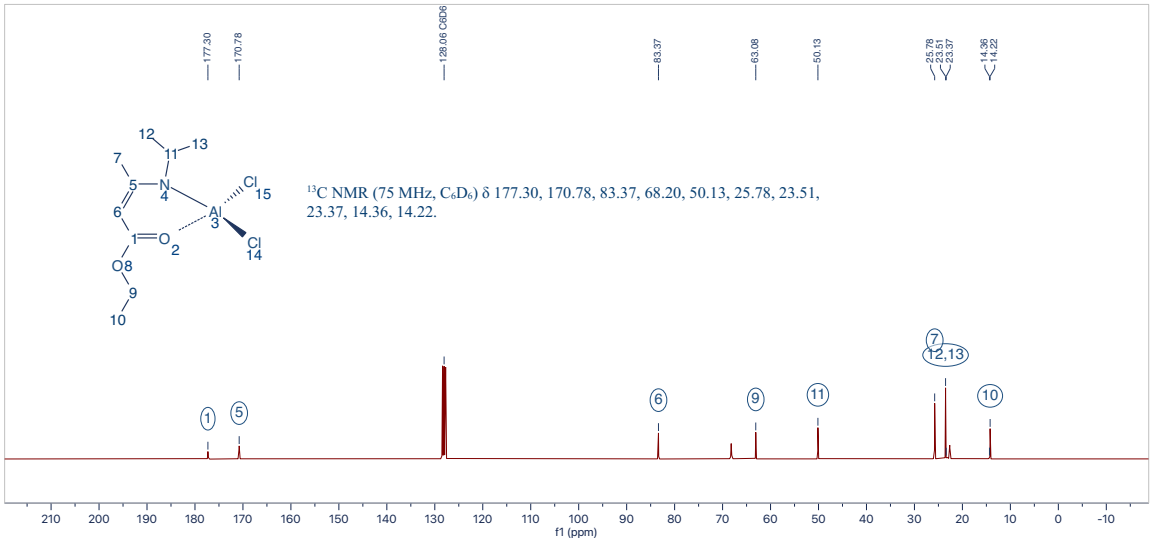

Fig 18. $^{13}C\{^1H\}$ NMR of [$AlCl_2$(AME^{iPr})], (**1-Al**)

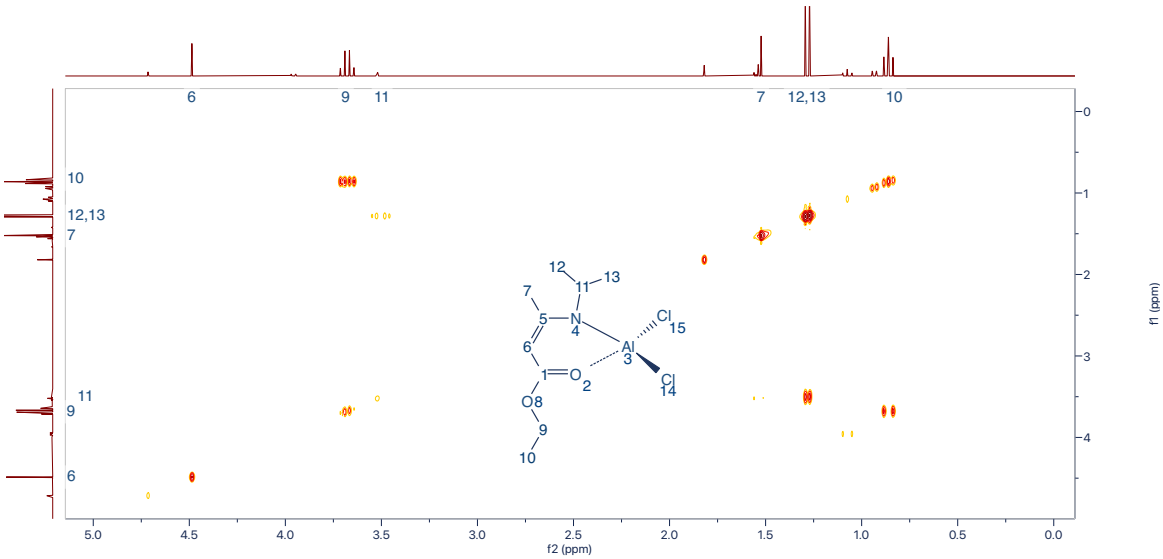

Fig 19. $^{1}H–^{1}H$ COSY NMR of $[AlCl_2(AME^{iPr})]$ (**1-Al**)

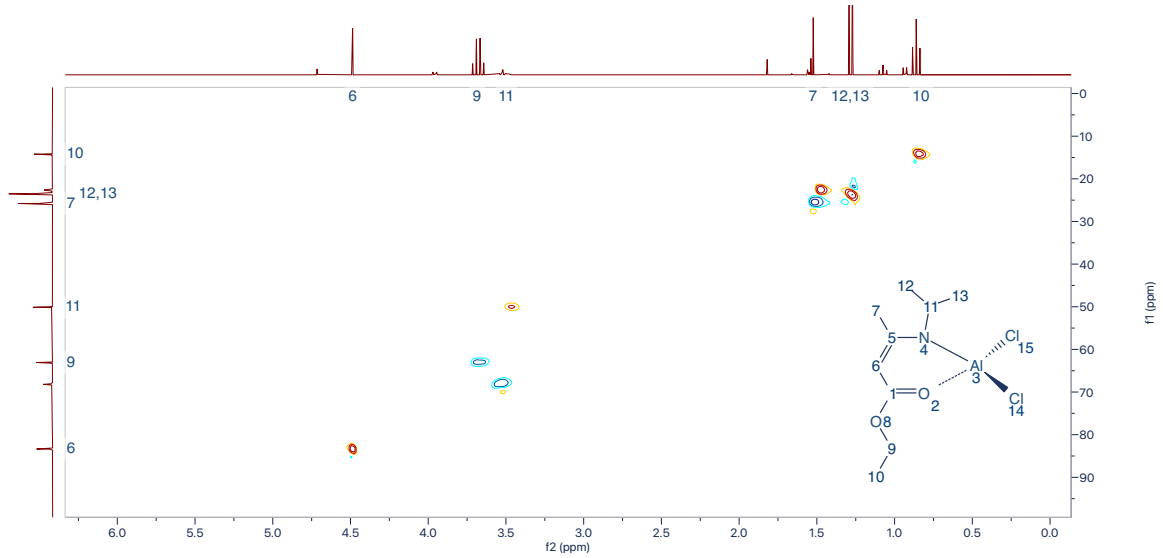

Fig 20. $^{1}H–^{13}C$ HSQC NMR of $[AlCl_2(AME^{iPr})]$ (**1-Al**)

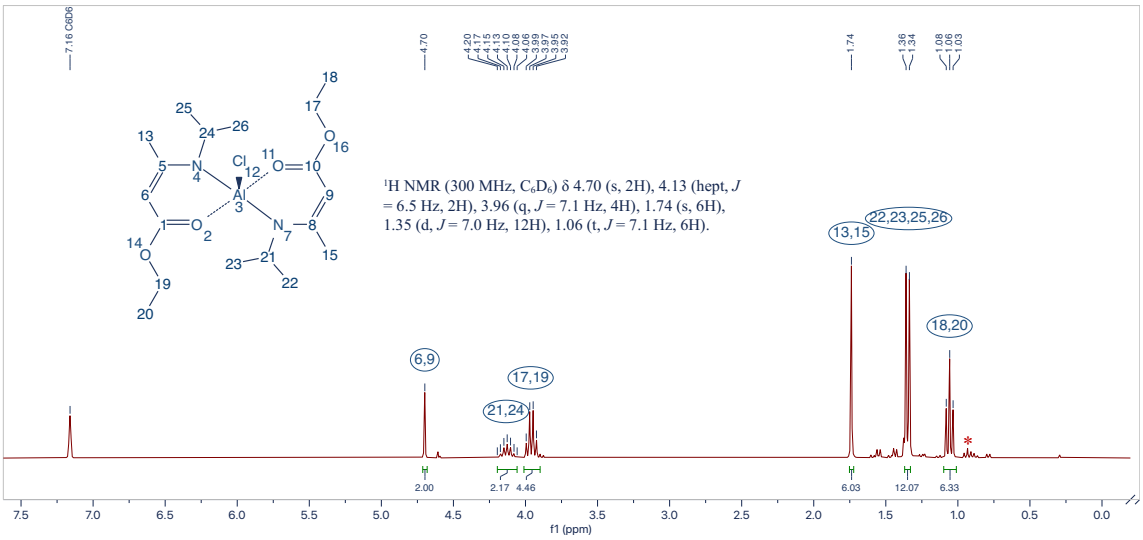

Fig 21. ^{1}H NMR of [AlCl(AME^{iPr})$_2$] (**2-Al**), solvents (hexane and diethyl ether), marked with a red asterisk

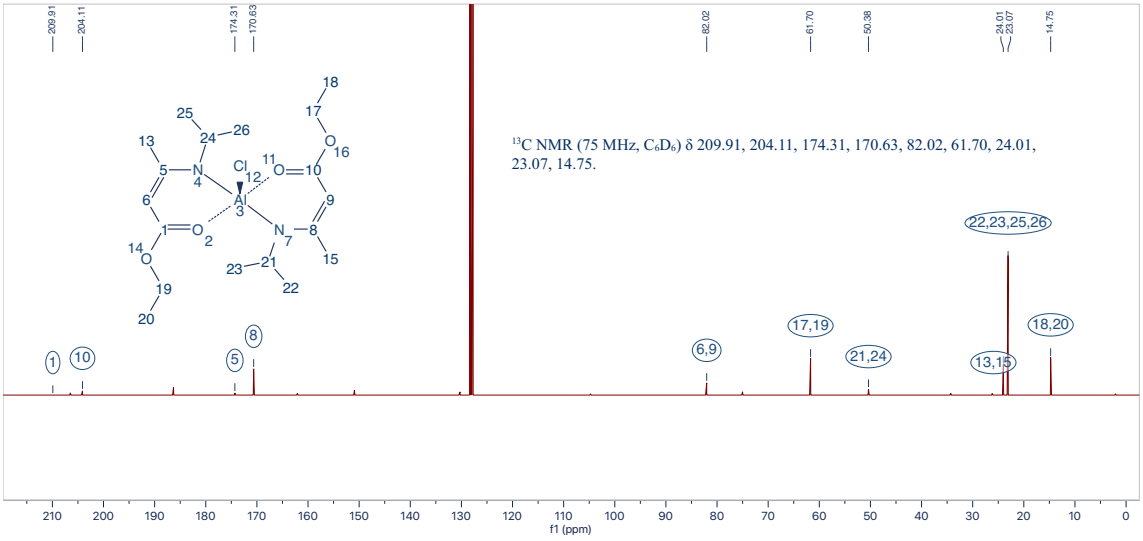

Fig 22. ^{13}C{^{1}H} NMR of [AlCl(AME^{iPr})$_2$] (**2-Al**),

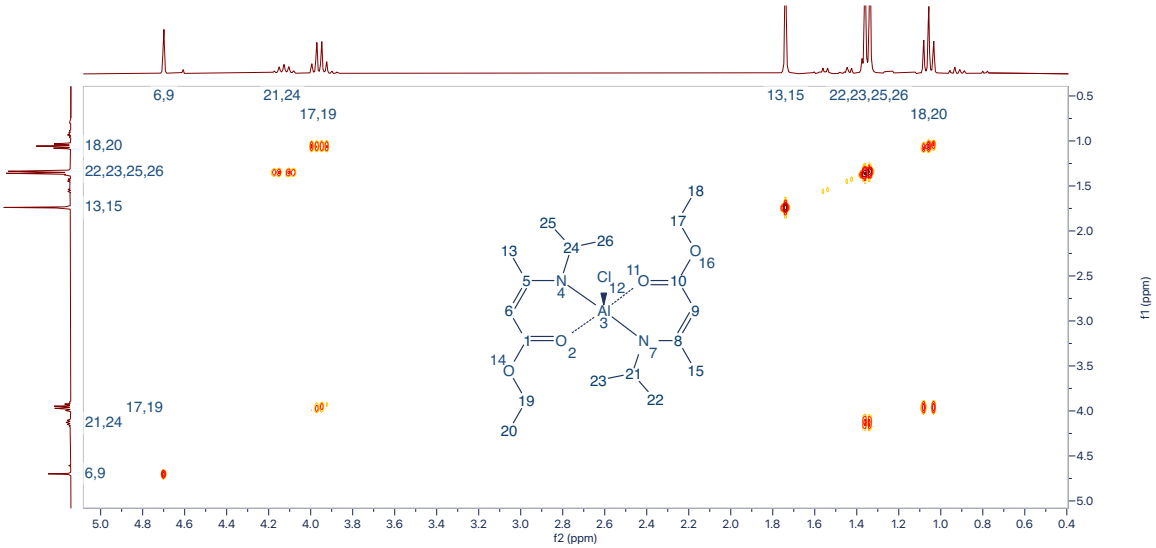

Fig 23. ^{1}H–^{1}H COSY NMR of [AlCl(AME^{iPr})$_2$] (**2-Al**)

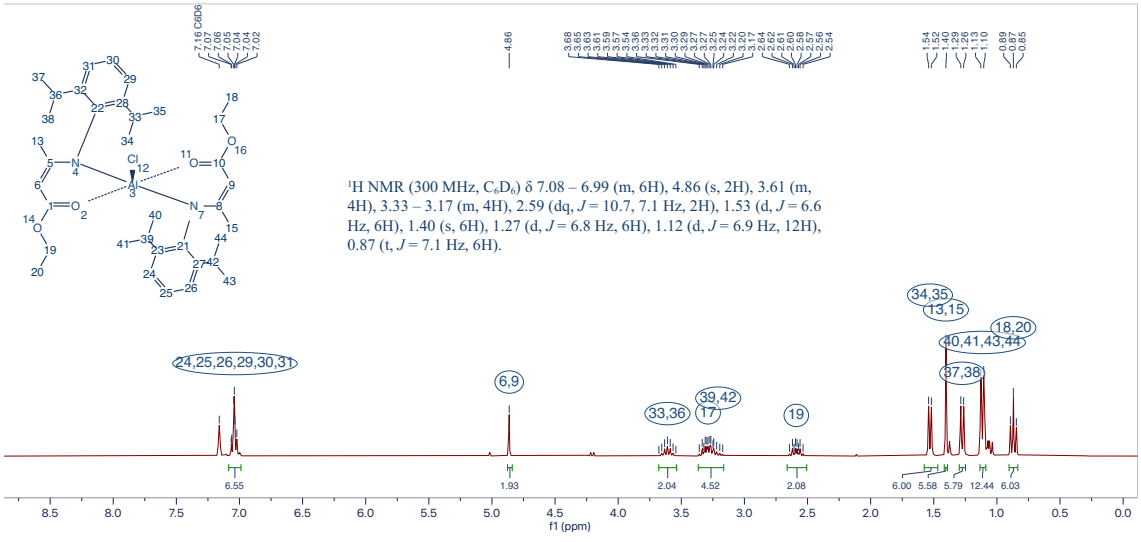

Fig 24. ^{1}H NMR of [AlCl(AME^{Dip})$_2$] (**3-Al**)

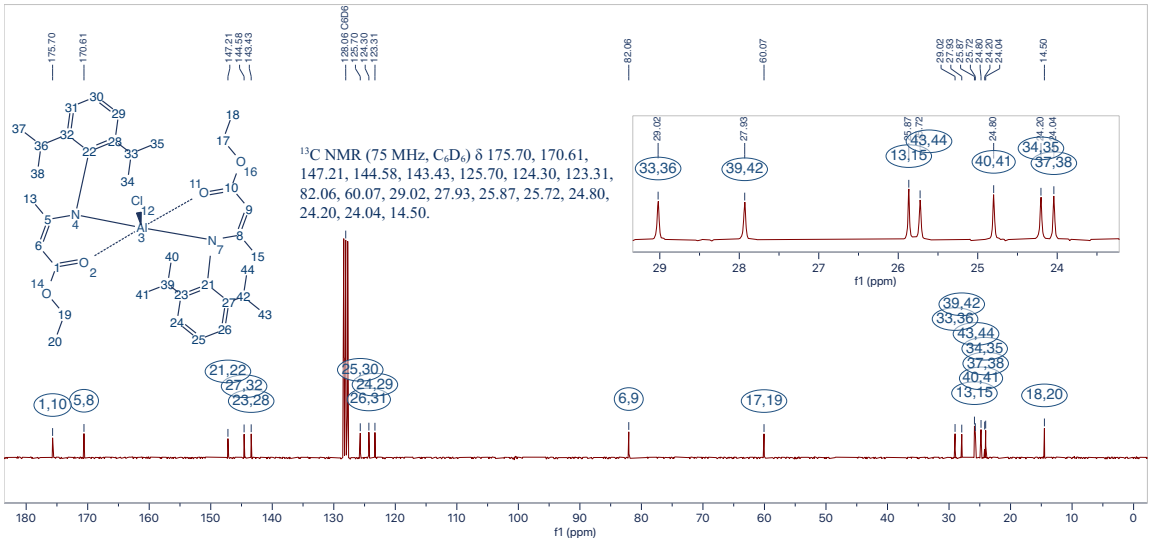

Fig 25. $^{13}C\{^{1}H\}$ NMR of $[AlCl(AME^{Dip})_2]$ (**3-Al**)

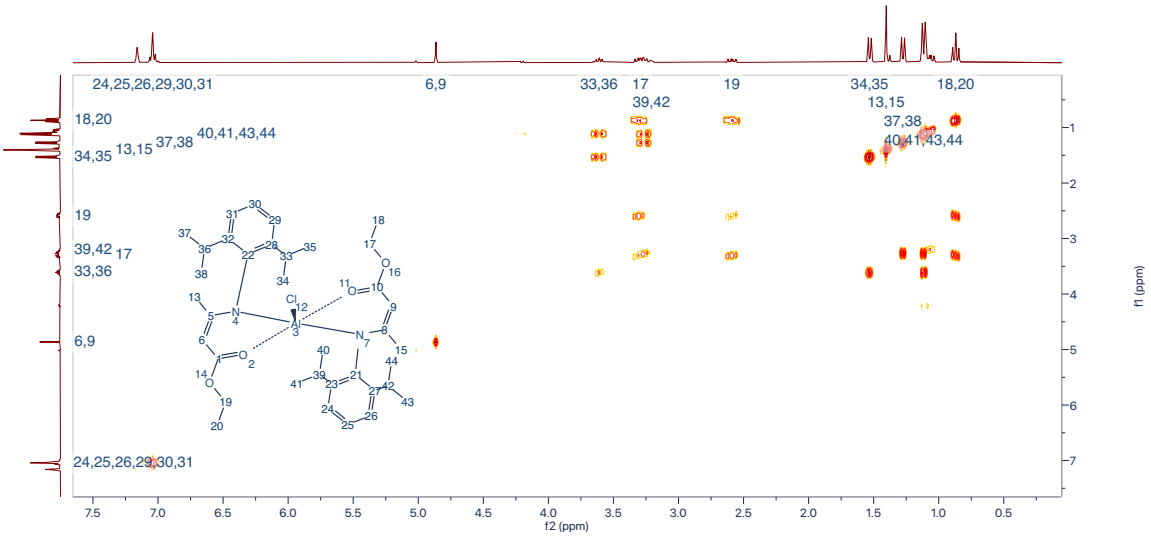

Fig 26. $^{1}H–^{1}H$ COSY NMR of $[AlCl(AME^{Dip})_2]$ (**3-Al**)

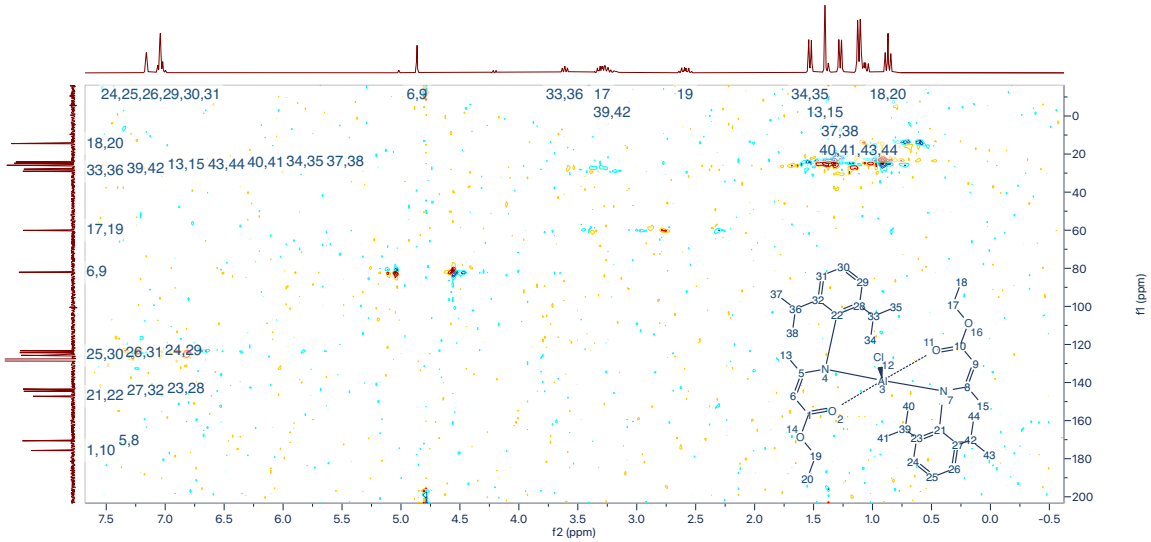

Fig 27. $^{1}H–^{13}C$ HSQC NMR of $[AlCl(AME^{Dip})_2]$ (**3-Al**)

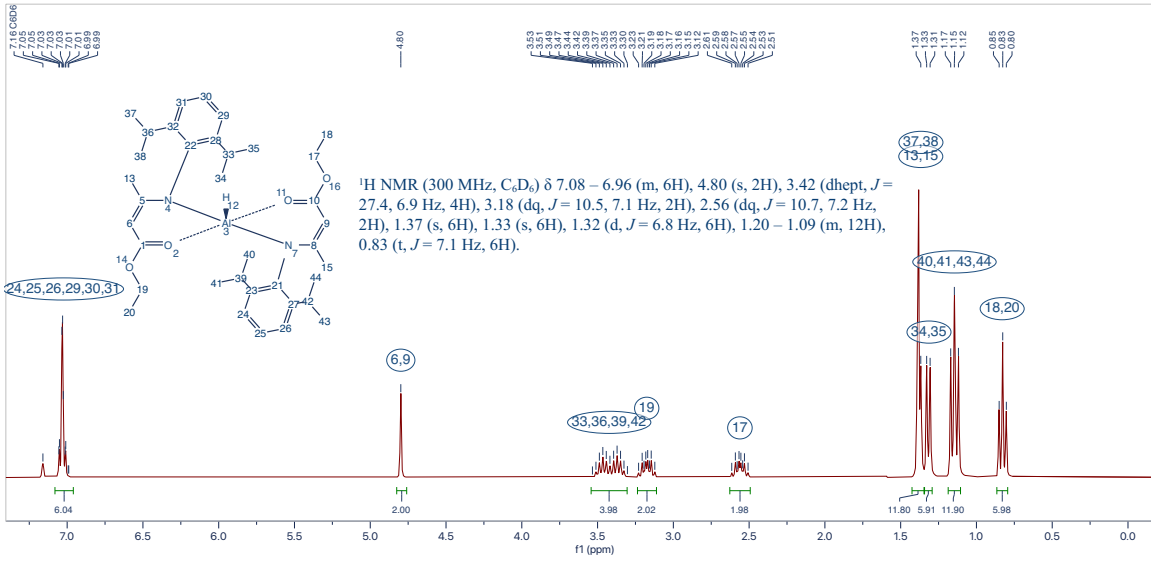

Fig 28. ^{1}H NMR of $[AlH(AME^{Dip})_2]$ (**4-Al**)

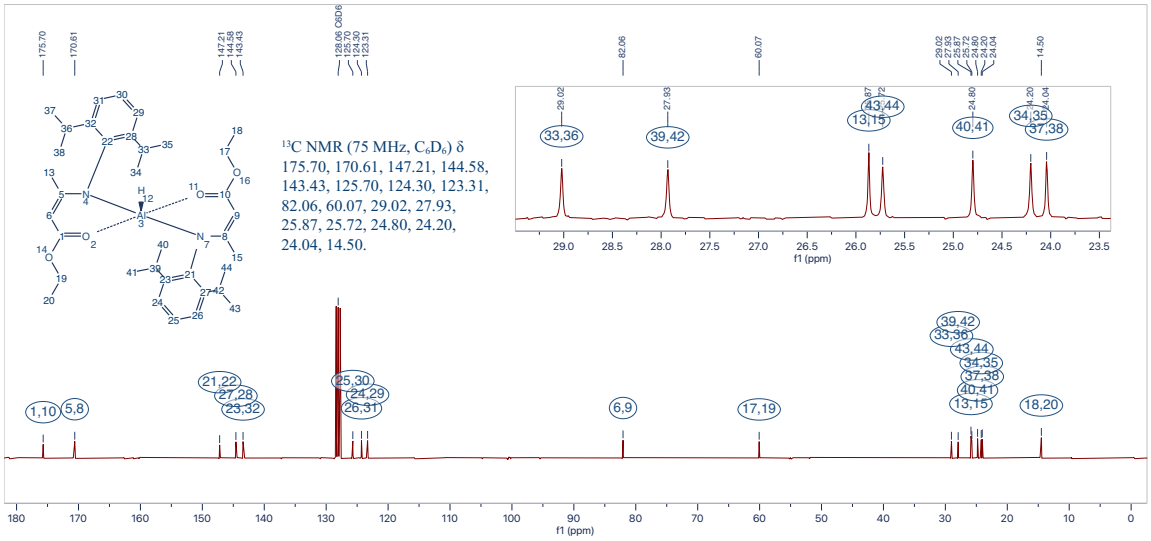

Fig 29. $^{13}C\{^{1}H\}$ NMR of $[AlH(AME^{Dip})_2]$ (**4-Al**)

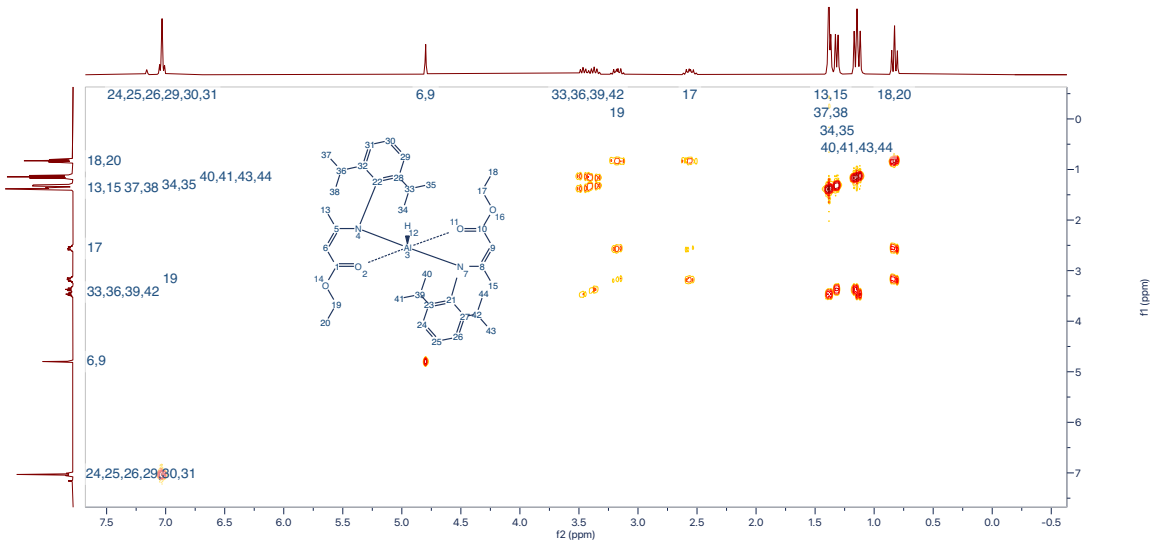

Fig 30. $^{1}H–^{1}H$ COSY NMR of $[AlH(AME^{Dip})_2]$ (**4-Al**)

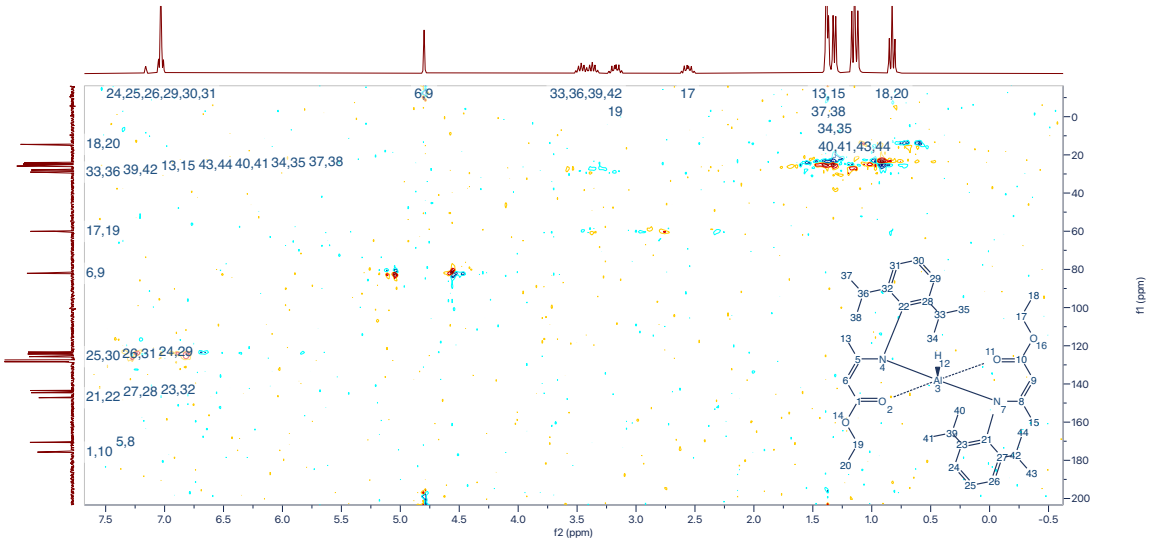

Fig 31. $^{1}H–^{13}C$ HSQC NMR of $[AlH(AME^{Dip})_2]$ (**4-Al**)

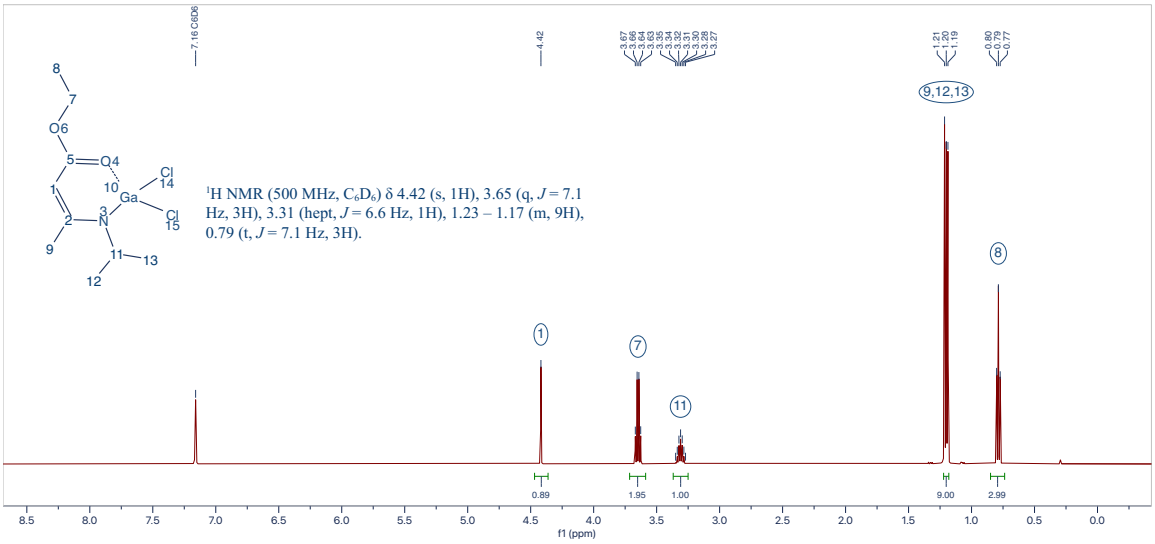

Fig 32. ^{1}H NMR of $[GaCl_2(AME^{iPr})_2]$ (**1-Ga**)

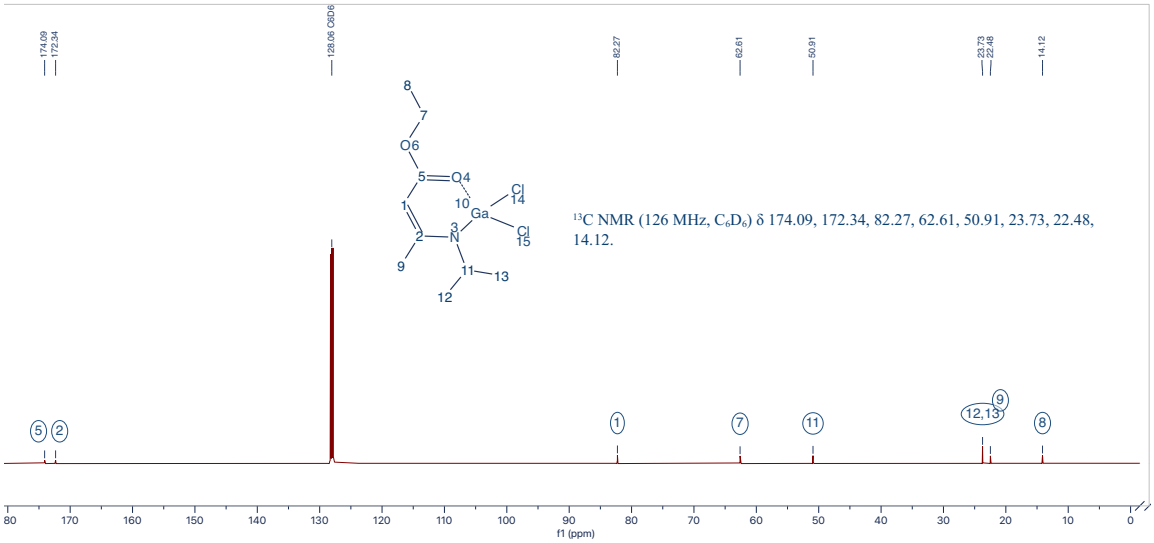

Fig 33. $^{13}C\{^{1}H\}$ NMR of $[GaCl_2(AME^{iPr})_2]$ (**1-Ga**)

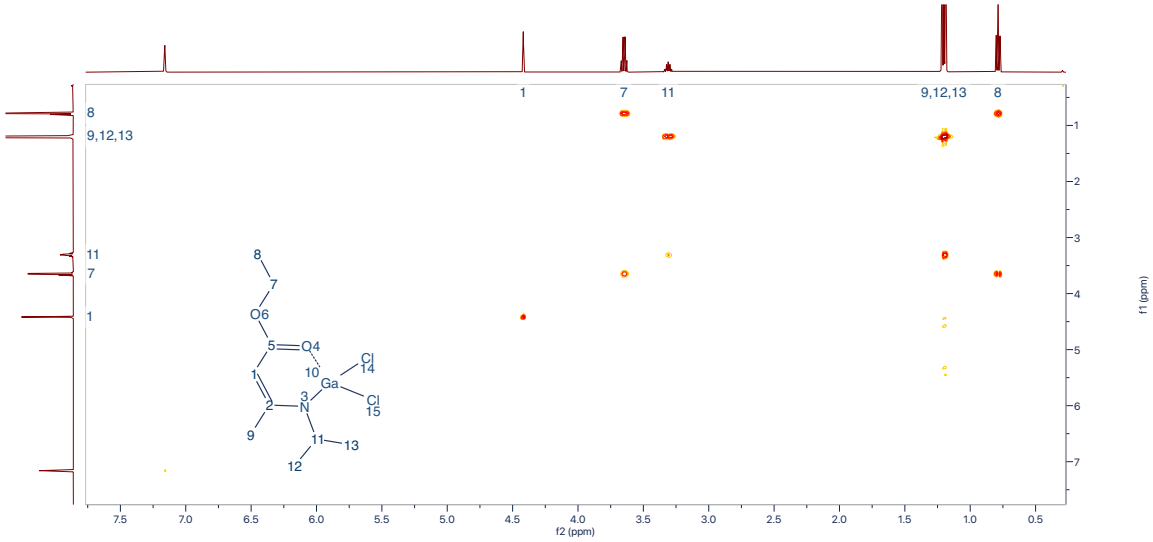

Fig 34. $^{1}H–^{1}H$ COSY NMR of $[GaCl_2(AME^{iPr})_2]$ (**1-Ga**)

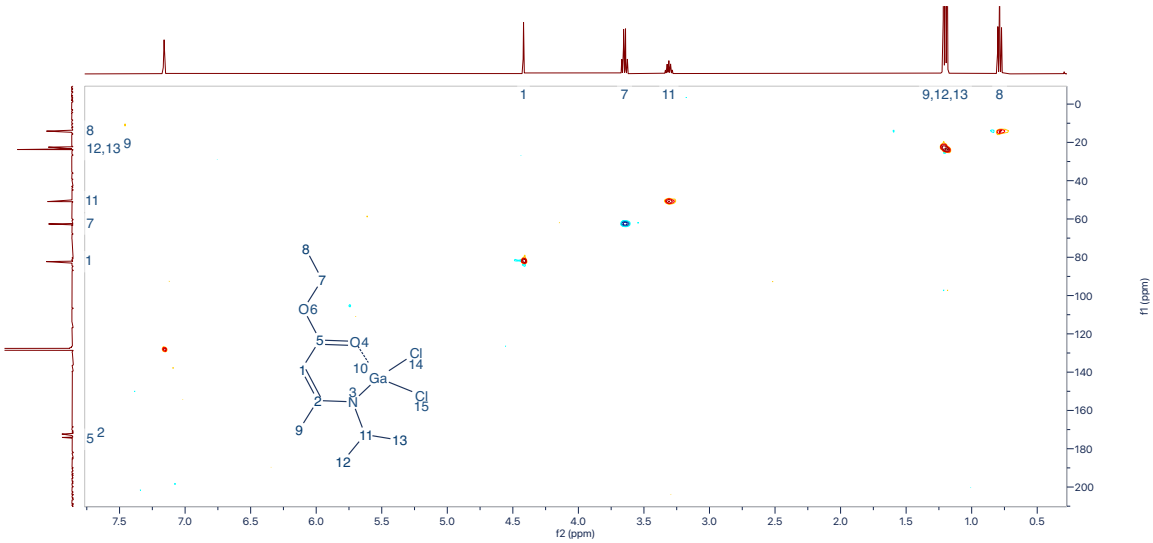

Fig 35. $^{1}H–^{13}C$ HSQC NMR of $[GaCl_2(AME^{iPr})_2]$ (**1-Ga**)

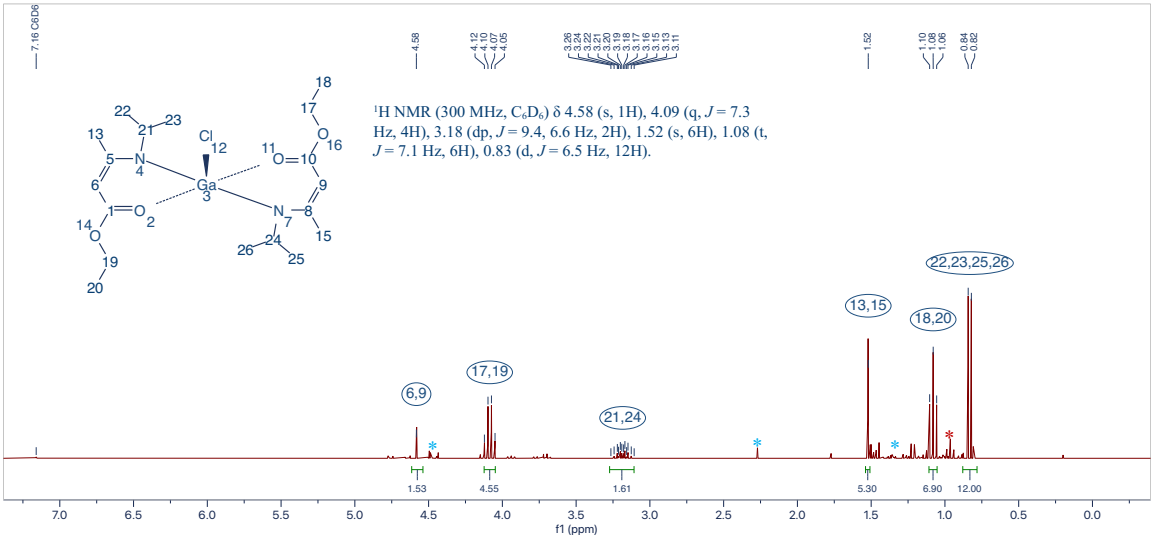

Fig 36. ^{1}H NMR of [GaCl(AME^{iPr})$_2$] (**2-Ga**), solvents (hexane and diethyl ether), marked with an asterisk (red) and small quantities of unidentified decomposition product (blue)

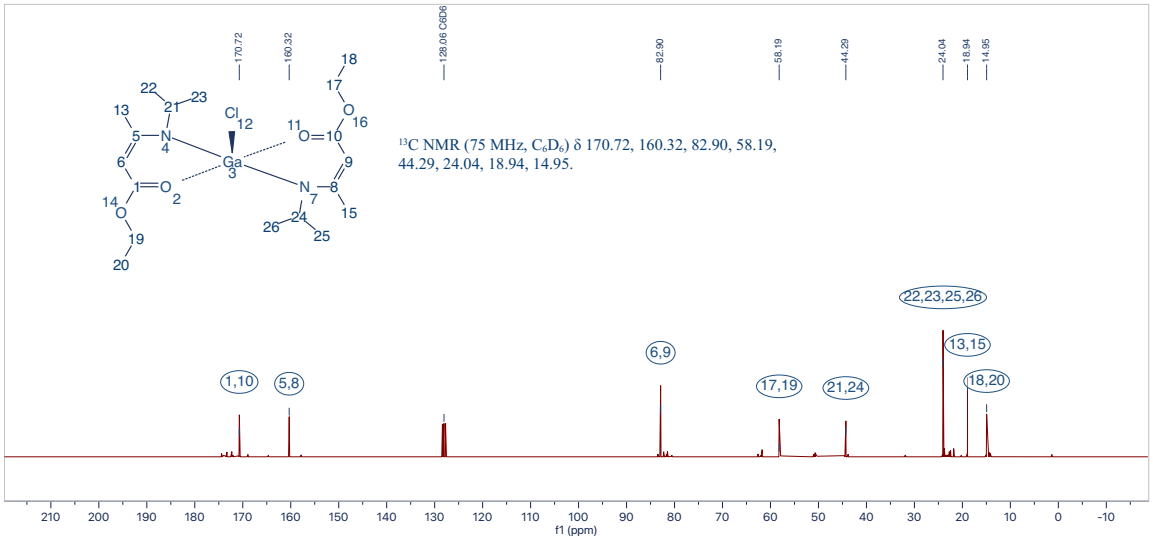

Fig 37. ^{13}C{^{1}H} NMR of [GaCl(AME^{iPr})$_2$] (**2-Ga**)

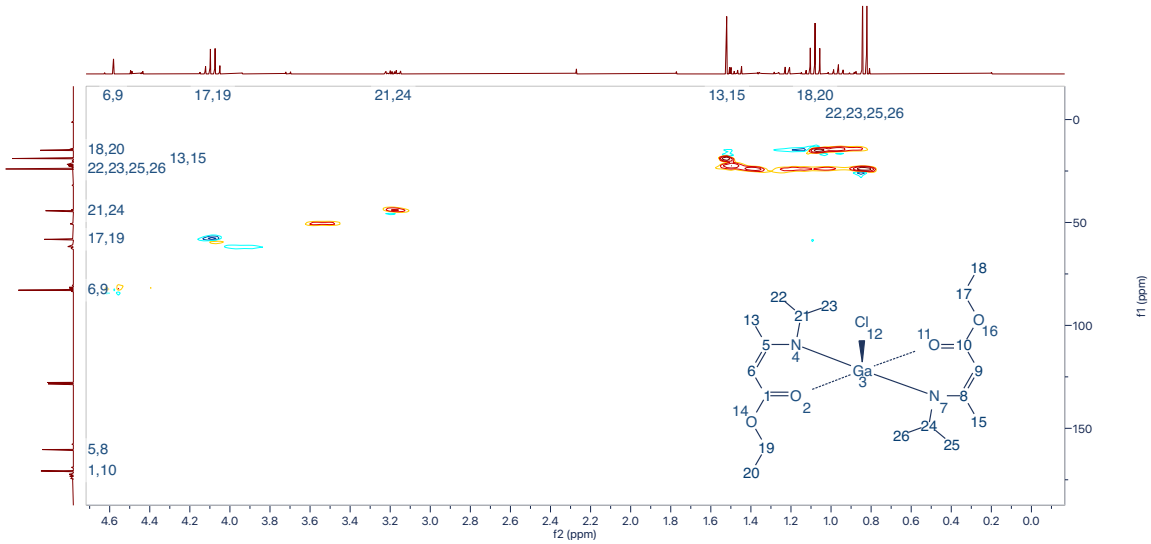

Fig 38. $^{1}H–^{13}C$ HSQC NMR of $[GaCl(AME^{iPr})_2]$ (**2-Ga**)

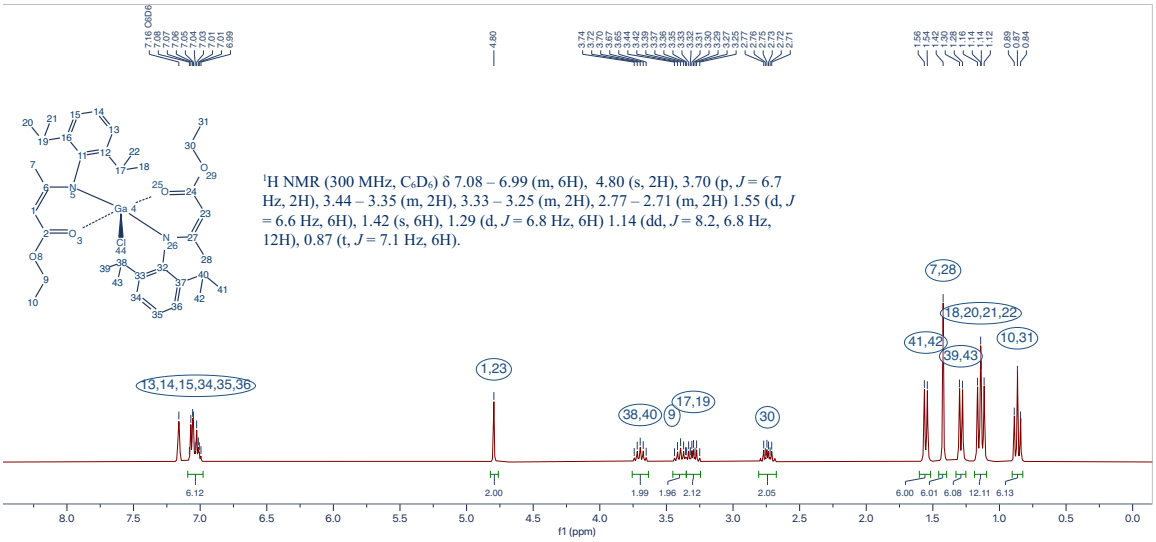

Fig 39. ^{1}H NMR of $[GaCl(AME^{Dip})_2]$ (**3-Ga**)

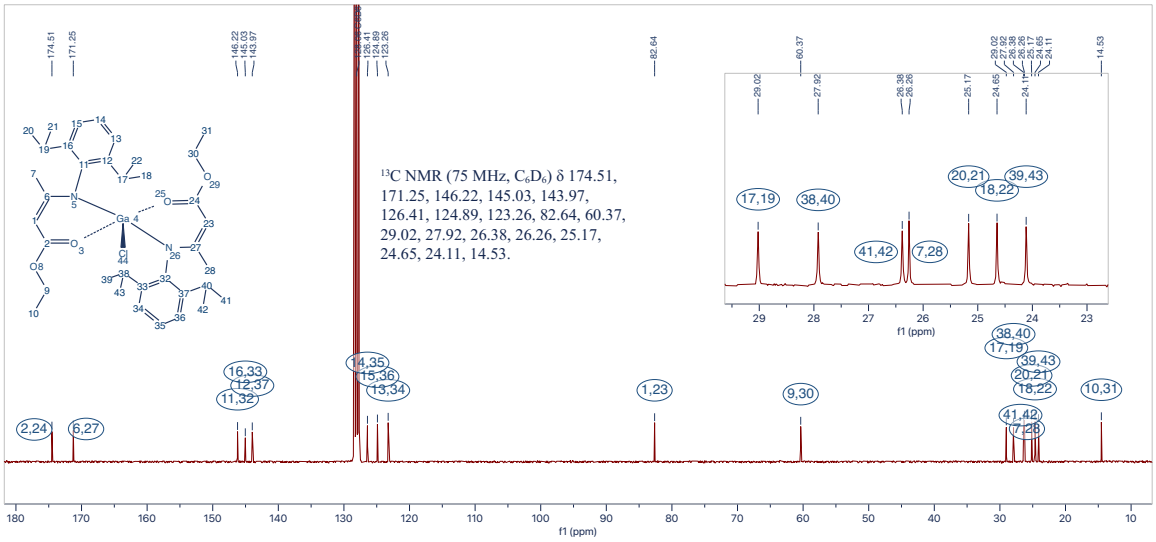

Fig 40. $^{13}C\{^{1}H\}$ NMR of [GaCl(AME^{Dip})$_2$] (**3-Ga**)

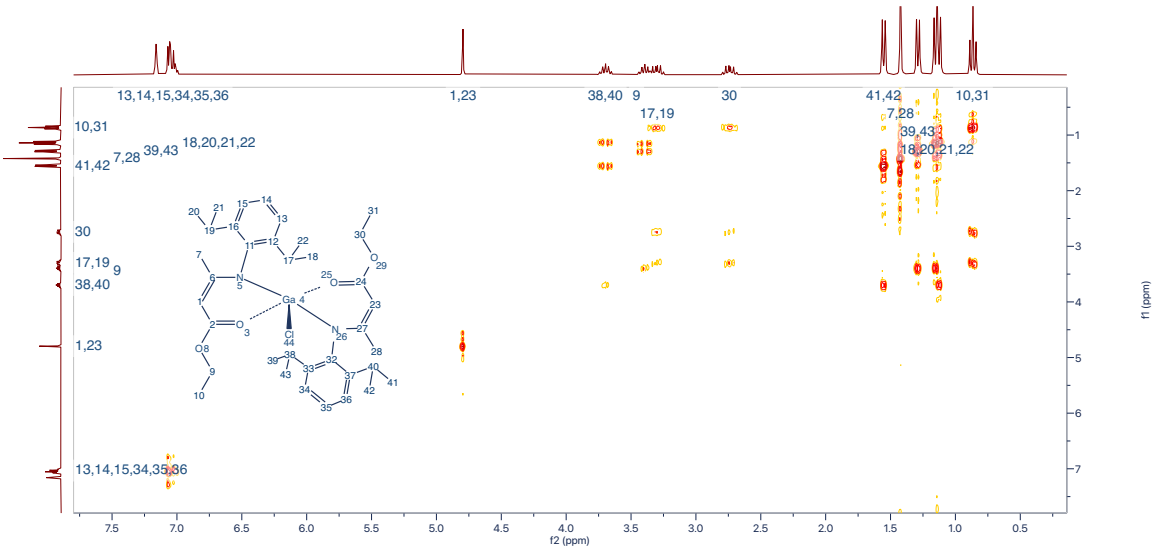

Fig 41. $^{1}H–^{1}H$ COSY NMR of [GaCl(AME^{Dip})$_2$] (**3-Ga**)

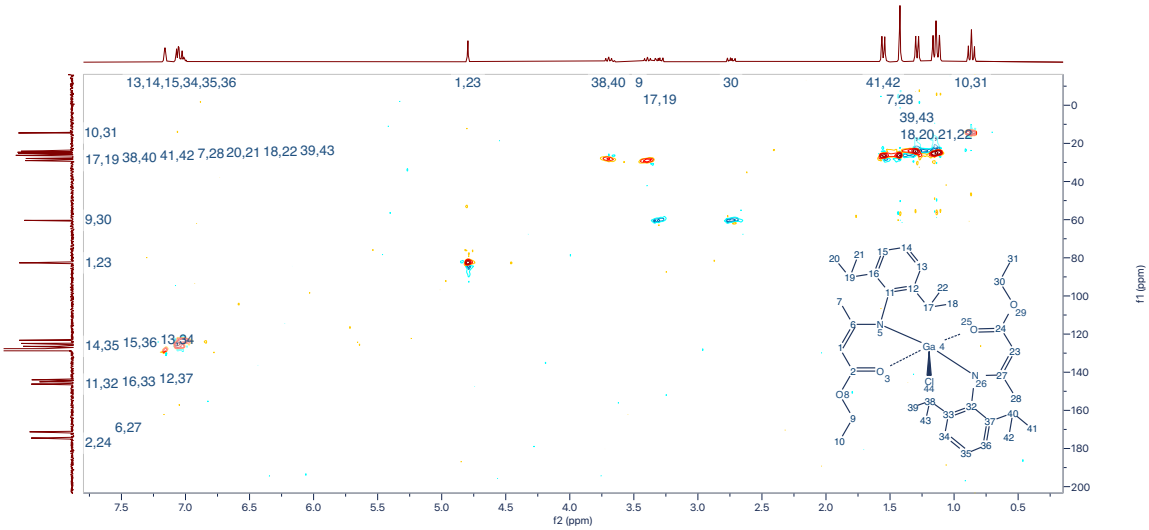

Fig 42. $^{1}H–^{13}C$ HSQC NMR of [GaCl(AME^{Dip})$_2$] (**3-Ga**)

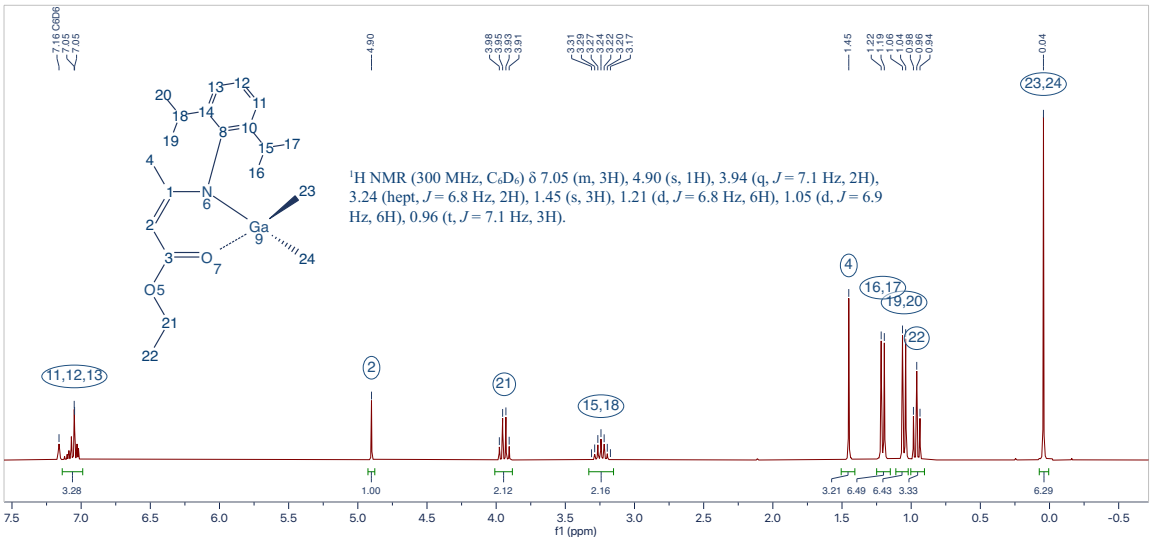

Fig 43. ^{1}H NMR of [GaMe$_2$(AME^{Dip})] (**4-Ga**)

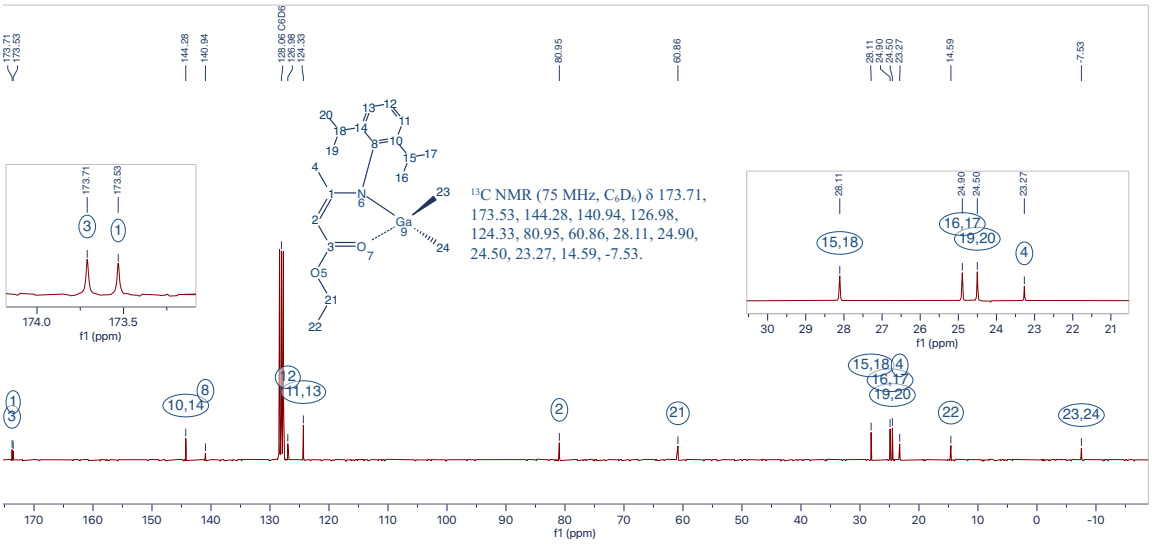

Fig 44. $^{13}C\{^{1}H\}$ NMR of [GaMe$_2$(AME^{Dip})] (**4-Ga**)

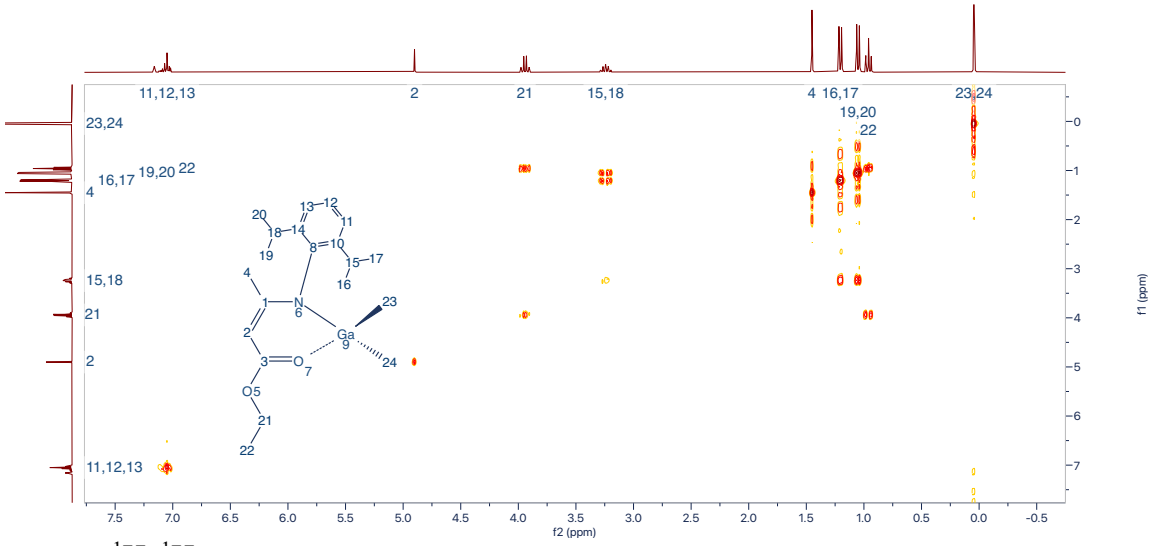

Fig 45. $^{1}H–^{1}H$ COSY NMR of [$GaMe_2$(AME^{Dip})] (**4-Ga**)

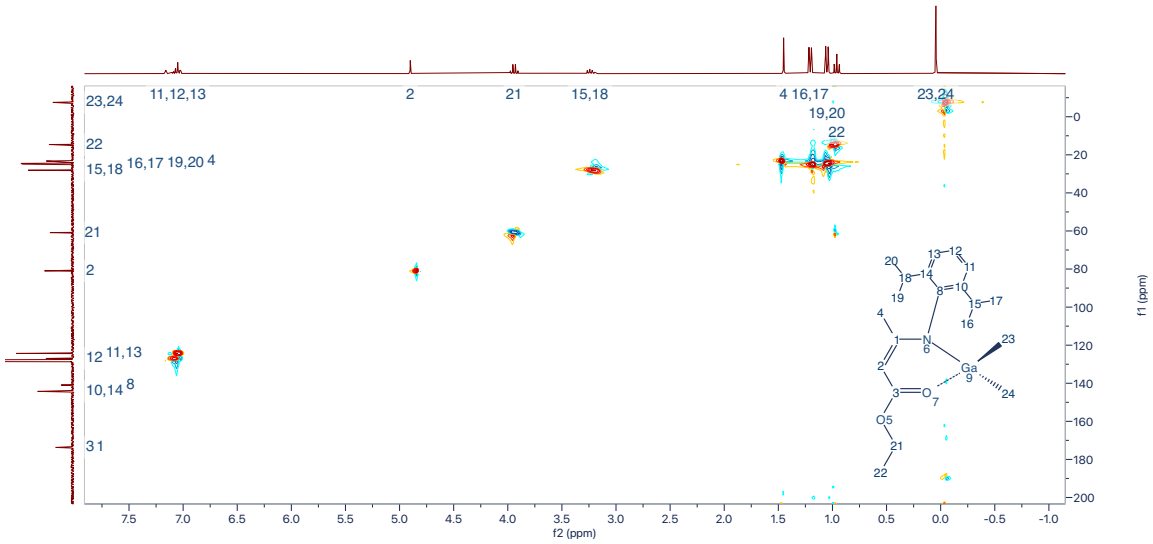

Fig 46. $^{1}H–^{13}C$ HSQC NMR of [$GaMe_2$(AME^{Dip})] (**4-Ga**)

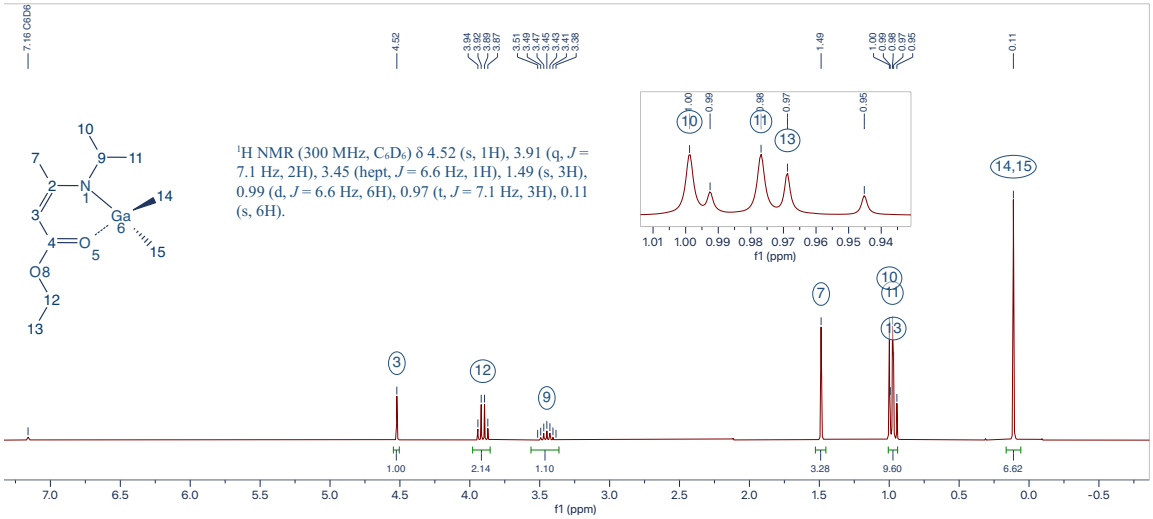

Fig 47. ^{1}H NMR of [$GaMe_2$(AME^{iPr})] (**5-Ga**)

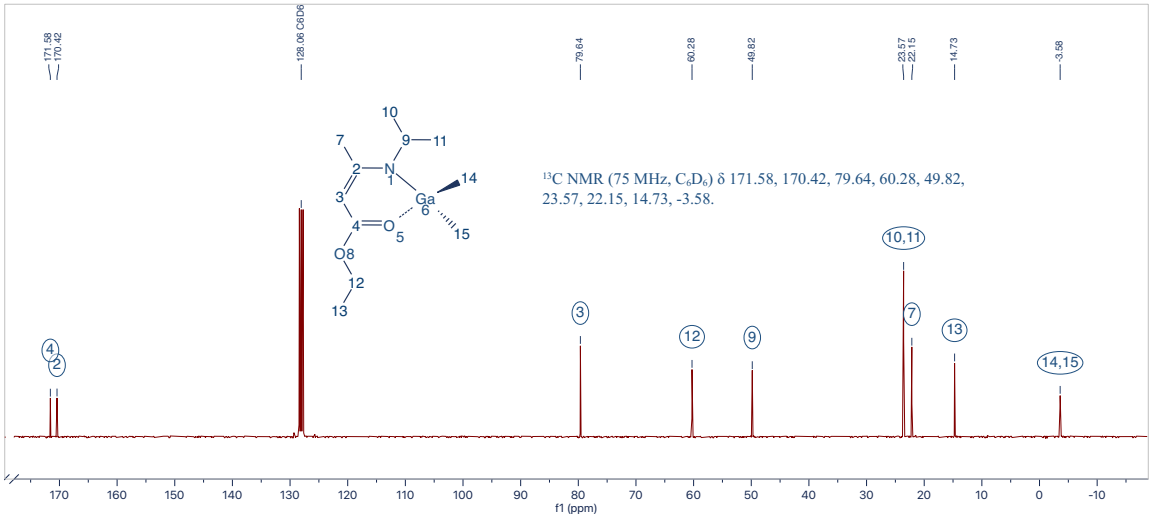

Fig 48. $^{13}C\{^{1}H\}$ NMR of $[GaMe_2(AME^{iPr})]$ (**5-Ga**)

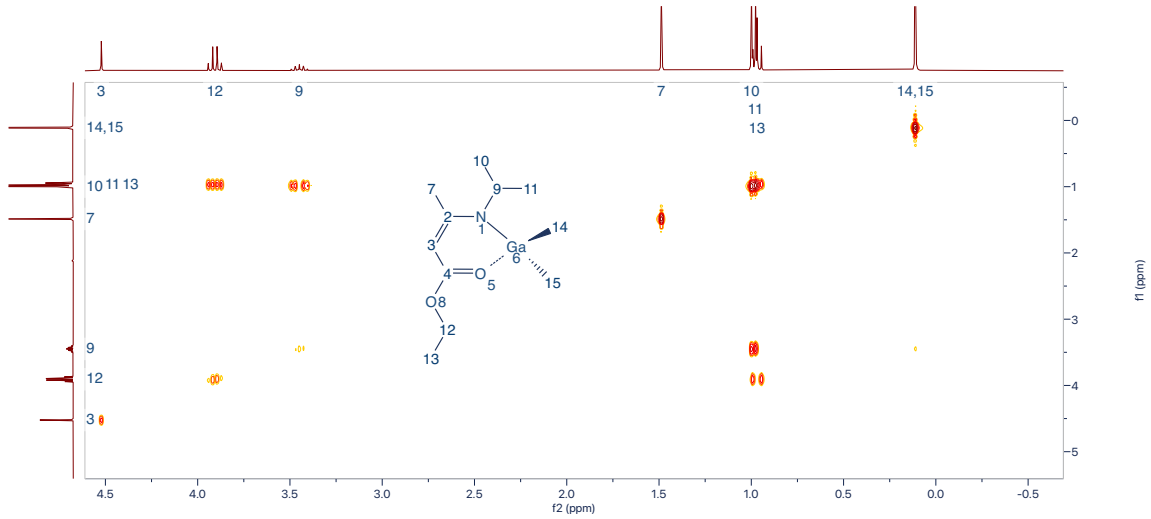

Fig 49. $^{1}H–^{1}H$ COSY NMR of $[GaMe_2(AME^{iPr})]$ (**5-Ga**)

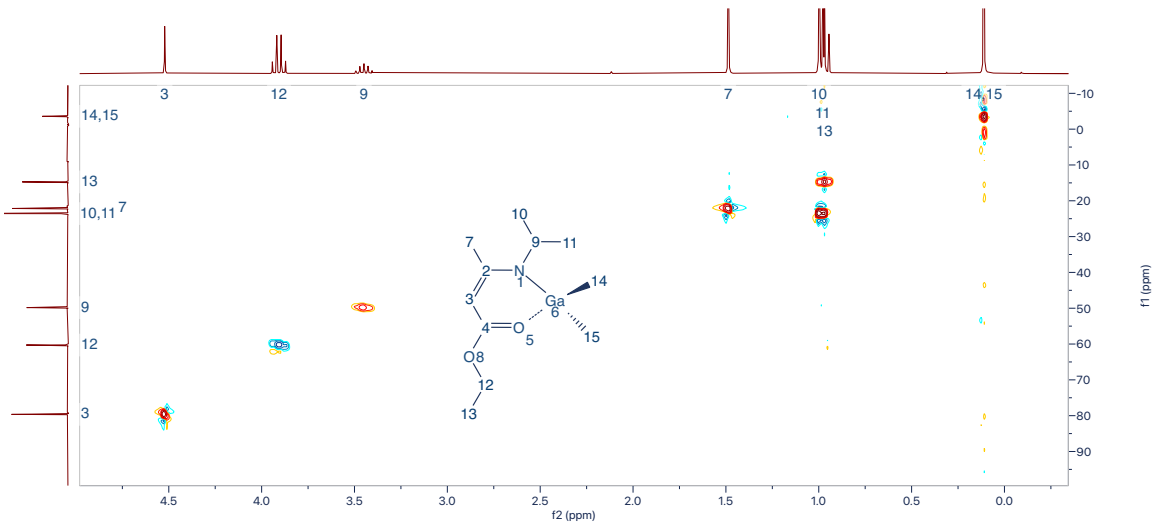

Fig 50. $^{1}H–^{13}C$ HSQC NMR of $[GaMe_2(AME^{iPr})]$ (**5-Ga**)

D. Crystallographic data

Complex	**1-Al**	**2-Al**	**3-Al**	**1-Ga**	**2-Ga**	**3-Ga**	**4-Al**
Chemical formula	$C_9H_{16}Cl_2AlNO_2$	$C_{18}H_{32}ClAlN_2O_4$	$C_{36}H_{52}ClAlN_2O_4$	$C_9H_{16}Cl_2GaNO_2$	$C_{18}H_{32}ClGaN_2O_4$	$C_{36}H_{52}ClGaN_2O_4$	$C_{36}H_{53}AlN_2O_4$
Fw (g mol^{-1})	268.11	402.88	639.22	310.85	445.62	658.49	619.49
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal
a (Å)	9.04510(10)	12.1273(2)	8.90810(10)	9.08077(15)	12.1961(2)	8.97530(10)	21.07670(10)
b (Å)	8.10630(10)	12.6240(2)	23.8108(2)	8.02118(10)	12.6013(2)	23.7494(2)	21.07670(10)
c (Å)	18.2392(2)	14.5316(3)	16.8695(2)	18.3319(3)	14.5825(2)	16.86750(10)	16.37980(10)
a (deg)	90	90	90	90	90	90	90
b (deg)	98.3700(10)	103.938(2)	96.8650(10)	98.2836(16)	103.144(2)	96.4410(10)	90
g (deg)	90	90	90	90	90	90	90
V (Å^3)	1321.10(3)	2159.21(7)	3552.52(7)	1321.34(3)	2182.42(6)	3572.75(5)	7276.35(8)
Z	4	4	4	4	4	4	8
r_{calcd} (g cm^{-3})	1.346	1.239	1.195	1.563	1.356	1.268	1.129
m (mm^{-1})	1.346	2.160	1.497	6.439	3.048	2.045	0.816
Reflns collected	19678	34653	61929	44799	32986	60788	65063
Unique reflns	2633	4257	7384	2646	4359	7039	7178
R_{int}	0.0292	0.0429	0.0404	0.0514	0.0240	0.0454	0.0545
R_1 and wR_2 [*All data*]	0.0255, 0.0692	0.0442, 0.1031	0.0440, 0.1072	0.0256, 0.0614	0.0315, 0.0802	0.0320, 0.0848	0.0402, 0.1055