SUPPORTING INFORMATION

Relationship between molecular structures and thermogravimetric of gallium-amidinate based compounds

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1. Synthesis and structural characterization of molecular compounds

1.1 Materials and Methods

Unless otherwise stated, all reactions were performed under controlled atmosphere conditions (N_2 or Ar), using Schlenk techniques or an MBraun glove box. Glassware was stored in an incubator at 120°C overnight before use.

The gallium precursor $GaCl_3$ was purchased from Strem Chemicals and used without further purification. Deuterated solvents were purchased from Eurisotop. All other chemicals (carbodiimides, solvents, etc.) were purchased from Sigma Aldrich.

The synthesis and deuterated solvents were degassed, dried over Na/benzophenone, and cold distilled before being stored in an MBraun glove box under Ar (H_2O/O_2 <1 ppm). Solvents used for washing, such as pentane, are dried on an MBraun MB-SPS 800 solvent purification system. Tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene are degassed, dried over sodium and stored in an MBraun glove box under argon (H_2O/O_2<1ppm).

Synthesis details of the **L^6Li**, **$(L^6)GaCl_2$** and **$(L^6)GaMe_2$** complexes was previously published by our group.[1] The experimental procedure and characterization for the other complexes are reported below, even for the ones that can be found in literature.[2–6]

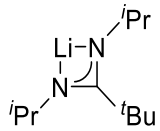
Mass spectrometry experiments were performed on a Tims-TOF mass spectrometer (Bruker, France) equipped with atmospheric pressure chemical ionization (APCI) source with one direct probe to introduce solid compounds. Few μg of sample were deposited into glass capillary. All mass spectra were produced in positive mode. Capillary and end plate voltages were set at 4.2 kV and 0.5 kV for experiments, Corona for APCI was set at 4000nA. Nitrogen was used as the nebuliser and drying gas at 3 bar and 2 L min^{-1}, respectively, with a drying temperature of 250 °C. APCI heater was set at 300°C. Tuning mix (Agilent, France) was used for calibration. The elemental compositions of all ions were determined with the instrument software Data Analysis, the precision of mass measurement was less than 5 ppm.

X-ray crystallography data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo-κ (λ = 0.71069Å) X-ray source and a graphite monochromator. The crystal structures were solved using Shelxt33[7] or olex[8] and refined using Shelxl-97 or Shelxl-2014.[7] ORTEP drawings were made using ORTEP III[9] for Windows. Details of crystal data Details of crystal data and structure refinements are summarized in Tables S1-S6.

1.2 Lithium amidinate compounds

General: A solution of carbodiimide (up to 40 mmol) in diethyl ether (0.8 mol/L) was cooled at 0 °C. One equivalent of organolithium was added dropwise to the solution, which is let back to room temperature. After 30 min of stirring, the solvent is evaporated under vacuum, resulting in a solid. The solid is washed (if needed) with pentane and let dry under vacuum overnight ($5 \cdot 10^{-2}$ mbar).

(^{i}PrNC^{t}BuN^{i}Pr)Li (**L^{1}Li**),[2]



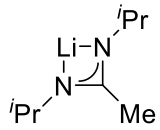
$C_{11}H_{23}LiN_2$ MM = 190.26 g/mol

The general protocol is applied using di*iso*propyl carboddiimide (2.5 mL in 20 mL Et_2O ; 15.8 mmol ; 1,0 equiv.) and *tert*-butyllithium (9.4 mL ; 16.0 mmol ; 1.0 equiv.). After washing with pentane, a yellow solid is isolated (2.56 g ; 85%).

^{1}H-NMR (THF-d$_8$): δ 3.88 (m, $^{3}J_{H-H}$ = 5.9 Hz, 2H, N*H*CMe$_2$); 1.11 (s, 9H, C^{t}*Bu*); 0.93 (d, $^{3}J_{H-H}$ = 6.0 Hz, 12H, HC*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 167.95 (s, N*C*^{t}BuN); 46.57 (s, H*C*Me$_2$); 39.40 (s, *C*Me$_3$); 31.05 (s, HC*Me$_2$*); 26.38 (s, C*Me$_3$*)

(^{i}PrNCMeN^{i}Pr)Li (**L^{2}Li**)



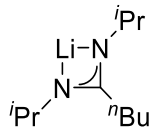
$C_8H_{17}LiN_2$ MM = 148.18 g/mol

The general protocol is applied using di*iso*propyl carbodiimide (1.6 mL in 12 mL Et_2O; 10.3 mmol ; 1.0 equiv.) and methyllithium (10.0 mL ; 16.0 mmol ; 1.5 equiv.). After washing with pentane, a white solid is isolated (1.42 g ; 93%).

^{1}H-NMR (THF-d_8): δ 3.43 (m, $^3J_{H-H}$ = 6.2 Hz, 2H, N*H*CMe_2); 1.73 (s, 3H, C*Me*); 0.92 (d, $^3J_{H-H}$ = 6.1 Hz, 12H, HC*Me_2*)

^{13}C-NMR (THF-d_8): δ 168.64 (s, N*C*MeN); 47.71 (s, H*C*Me_2); 27.54 (s, HC*Me_2*); 10.51 (s, C*Me*)

(^{i}PrNC^{n}BuN^{i}Pr)Li (**L^{3}Li**)



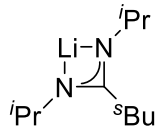
$C_{11}H_{23}LiN_2$ MM = 190.26 g/mol

The general protocol is applied using di*iso*propyl carbodiimide (2.5 mL in 20 mL Et_2O ; 16.1 mmol ; 1.0 equiv.) and *n*-butyllithium (10.1 mL ; 16.2 mmol ; 1,0 equiv.). After washing with pentane, a white solid is isolated (1.80 g ; 59%).

^{1}H-NMR (THF-d_8): δ 3.46 (m, $^3J_{H-H}$ = 6.1 Hz, 2H, NC*H*Me_2); 2.21 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, CC*H_2*CH_2); 1.40 (m, 4H, CH_2C*H_2*C*H_2*Me); 0.96 (dt, 15H, HC*Me_2*, H_2C*Me*)

^{13}C-NMR (THF-d_8): δ 172.11 (s, NC^{n}BuN); 47.41 (s, NH*C*Me_2); 32.44 (s, C*C*$H_2$$CH_2$Et); 27.73 (s, HC*$Me_2$*); 25.84 (s, CH_2*CH_2*Et); 24.36 (s, CH_2*CH_2*Me); 14.38 (s, CH_2*Me*)

(^{i}PrNC^{s}BuN^{i}Pr)Li (**L^{4}Li**)



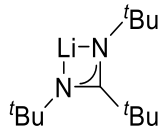
$C_{11}H_{23}LiN_2$ MM = 190.26 g/mol

The general protocol is applied using di*iso*propyl carbodiimide (2.5 mL in 20 mL Et_2O ; 16.1 mmol ; 1.0 equiv.) and *sec*-butyl lithium (9.5 mL ; 15.2 mmol ; 0.9 equiv.). After washing with pentane, a yellow solid is isolated (2.24 g ; 73%).

^{1}H-NMR (THF-d_8): δ 3.87 (s br, 1H); 3.36 (s br, 1H); 2.82 (sext, $^3J_{H-H}$ = 7.5 Hz, 1H, C*H*C(Me)CH_2); 1.69 (m, 1H, HC(Me)C*H_2*Me); 1.55 (m, 1H, HC(Me)C*H_2*Me); 1.20 (d, $^3J_{H-H}$ = 7.3 Hz, 3H, HC*Me_2*); 0.91 (m, 15H, HC*Me_2*, CH_2*Me*)

^{13}C-NMR (THF-d_8): δ 173.44 (s, N*C*^{s}BuN); 47.59 (br s, H*C*Me$_2$); 45.89 (br s, HC*Me$_2$*); 35.45 (s, HC*Me$_2$*); 29.07 (s, HC*Me$_2$*); 28.22 (br s, C*C*(Me)Et); 27.75 (s, C*Me*); 19.43 (s, C*C*H$_2$Me); 13.78 (s, CH$_2$*Me*)

(^{t}BuNC^{t}BuN^{t}Bu)Li (**L^{5}Li**),[2]



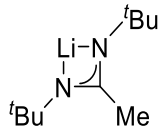
$C_{13}H_{27}LiN_2$ MM = 218.31 g/mol

The general protocol is applied using di*tert*butyl carbodiimide (2.5 mL in 20 mL Et_2O ; 13.0 mmol ; 1.0 equiv.) and *tert*-butyllithium (7.6 mL ; 12.9 mmol ; 1.0 equiv.). A white solid is isolated (1.39 g ; 49%).

^{1}H-NMR (THF-d_8): δ 1.29 (s, 18H, N^{t}*Bu*), 1.15 (s, 9H, C^{t}*Bu*)

^{13}C-NMR (THF-d_8): δ 163.16 (s, N*C*^{t}BuN); 52.50 (s, C*C*Me$_3$); 39.04 (s, N*C*Me$_3$); 33.28 (s, NC*Me$_3$*); 31.87 (s, CC*Me$_3$*)

(^{t}BuNCMeN^{t}Bu)Li (**L^{6}Li**),[1]



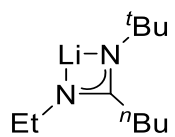
$C_{10}H_{27}LiN_2$ MM = 176.23 g/mol

The general protocol is applied using di*tert*butyl carbodiimide (2.5 mL in 20 mL Et_2O ; 13.0 mmol ; 1.0 equiv.) and methyllithium (8.1 mL ; 13.0 mmol ; 1.0 equiv.). After washing with pentane, a white solid is isolated (1.38 g ; 60%).

^{1}H-NMR (THF-d_8): δ 1.94 (s, 3H, C*Me*), 1.11 (s, 18H, N^{t}*Bu*)

^{13}C-NMR (THF-d_8): δ 169.01 (s, N*C*MeN); 50.36 (s, N*C*Me$_3$); 34.16 (s, NC*Me$_3$*); 19.15 (s, C*Me*)

(^{t}BuNC^{n}BuNEt)Li (**L^{7}Li**)



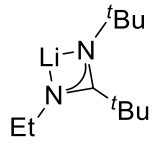
$C_{11}H_{23}LiN_2$ MM = 190.26 g/mol

The general protocol is applied using 1-*tert*-butyl-3-ethylcarbodiimide (2 mL dans 16 mL Et_2O ; 12.9 mmol ; 1.0 equiv.) and *n*-butyllithium (5.2 mL ; 13.0 mmol ; 1.0 equiv.). A yellow solid is isolated (2.01 g ; 82%).

^{1}H-NMR (THF-d_8): δ 3.08 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, NC*H*$_2$Me); 2.29 (t, 2H, CC*H*$_2$CH$_2$); 1.52 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 1.36 (m, $^3J_{H-H}$ = 7.6 Hz, 2H, CH$_2$C*H*$_2$Me); 1.14 (s, 9H, N^t*Bu*); 0.95 (tt, $^3J_{H-H}$ = 7.2 Hz, 6H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 174.54 (s, NC^{n}BuN); 50.87 (s, NCMe$_3$); 41.87 (s, NCH$_2$Me); 34.35 (s, C*Me*$_3$); 31.82 (s, CCH$_2$CH$_2$); 29.77 (s, CH$_2$CH$_2$CH$_2$); 24.73 (s, CH$_2$CH$_2$Me); 20.65 (s, NCH$_2$*Me*); 14.38 (s, CH$_2$*Me*)

(^{t}BuNC^{t}BuNEt)Li (**L^{8}Li**)



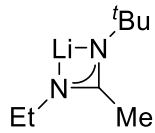
$C_{11}H_{23}LiN_2$ MM = 190.26 g/mol

The general protocol is applied using 1-*tert*-butyl-3-ethylcarbodiimide (0.9 mL in 10 mL Et_2O ; 5.8 mmol ; 1.0 equiv.) and *tert*-butyllithium (3.6 mL ; 6.1 mmol ; 1.1 equiv.). After washing with pentane, a white solid is isolated (0.97 g ; 88%).

^{1}H-NMR (THF-d_8): δ 3.52 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, NC*H*$_2$Me); 1.30 (s, 9H, N^t*Bu*); 1.11 (s, 9H, C^t*Bu*); 1.01 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 158.14 (s, NCtBuN); 50.83 (s, NCMe$_3$); 43.58 (s, NCH$_2$Me); 38.54 (s, CCMe$_3$); 29.18 (s, NC*Me*$_3$); 28.93 (s, CC*Me*$_3$); 18.86 (s, CH$_2$*Me*)

(^{t}BuNCMeNEt)Li (**L^{9}Li**)



$C_8H_{17}LiN_2$ MM = 148.18 g/mol

The general protocol is applied using 1-*tert*-butyl-3-ethylcarbodiimide (4.95 g in 50 mL Et_2O ; 39.2 mmol ; 1.0 equiv.) and methyllithium (24.5 mL ; 39.2 mmol ; 1.0 equiv.). After washing with pentane, a white solid is isolated (5.18 g ; 89%).

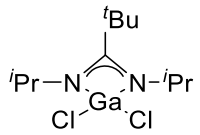
^{1}H-NMR (THF-d_8): δ 3.05 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, NC*H_2*Me); 1.85 (s, 3H, C*Me*); 1.14 (s, 9H, N^t*Bu*); 0.94 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, CH_2*Me*)

^{13}C-NMR (THF-d_8): δ 170.75 (s, N*C*MeN); 50.63 (s, N*C*Me_3); 42.52 (s, N*C*H_2Me); 33.77 (s, C*Me*$_3$); 19.65 (s, C*Me*); 15.24 (s, CH_2*Me*)

1.3 Gallium amidinate chlorinated complexes

General: A solution of the lithium amidinate (up to 4 mmol) in THF or Et_2O (0.20 mmol/L) was cooled down to -78 °C. A cold solution of $GaCl_3$ in the same solvent was slowly added to the first one by cannula. The mixture is stirred and let back to room temperature overnight. The solvent is removed by evaporation under vacuum and the chlorinated gallium amidinate complex with the lithium salt are dried under vacuum. The gallium complex is purified either by sublimation/distillation or by extraction with toluene.

(^{i}PrNC^{t}BuN^{i}Pr)GaCl$_2$ (**(L^1)GaCl$_2$**),[2,6] CAS: 213386-20-0



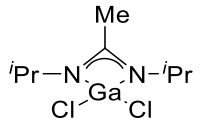
$C_{11}H_{23}Cl_2GaN_2$ MM = 323.94 g/mol

The general protocol is followed using (^{i}PrNC^{t}BuN^{i}Pr)Li lithium amidinate complex (**L^{1}Li**) (652 mg in 10 mL Et_2O ; 3.4 mmol ; 0.9 equiv.) and $GaCl_3$ (701 mg in 10 mL of Et_2O 3.7 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by sublimation (100 °C, $5\cdot10^{-2}$ mbar) to yield a white solid (1.00 g ; 90%).

^{1}H-NMR (THF-d$_8$): δ 4.26 (m, $^3J_{H-H}$ = 6.2 Hz, 2H, N*H*CMe$_2$); 1.44 (s, 9H, C^t*Bu*); 1.17 (d, $^3J_{H-H}$ = 6.2 Hz, 12H, HC*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 180.66 (s, N*C*^{t}BuN); 48.08 (s, NH*C*Me$_2$); 39.49 (s, C*C*Me$_3$); 28.97 (s, C*Me$_3$*); 25.90 (s, HC*Me$_2$*)

(^{i}PrNCMeN^{i}Pr)GaCl$_2$ (**(L^2)GaCl$_2$**),[5] CAS: 1533452-80-0



$C_8H_{17}Cl_2GaN_2$ MM = 281.87 g/mol

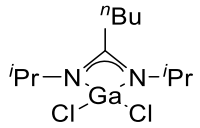
The general protocol is followed using (^{i}PrNCMeN^{i}Pr)Li lithium amidinate complex (**L^{2}Li**) (400.8 mg in 10 mL THF ; 2.6 mmol ; 1.0 equiv.) and $GaCl_3$ (481.3 mg in 10 mL THF ; 2.7 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by sublimation (50 °C, $5\cdot10^{-2}$ mbar) to yield a white solid (0.38 g ; 55%).

^{1}H-NMR (THF-d_8): δ 3.70 (m, $^3J_{H\text{-}H}$ = 6.4 Hz, 2H, N*H*CMe$_2$); 2.08 (s, 3H, C*Me*); 1.12 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 12H, HC*Me$_2$*)

^{13}C-NMR (THF-d_8): δ 174.53 (s, N*C*MeN); 46.89 (s, NH*C*Me$_2$); 24.84 (s, HC*Me$_2$*); 11.23 (s, C*Me*)

HR-MS Pos (APCI): $[L^2GaCl_2H]^+$ calcd *m/z* 281.0097 for $C_8H_{17}Cl_2GaN_2H^+$; found *m/z* 281.0087.

(^{i}PrNC^{n}BuN^{i}Pr)GaCl$_2$ (**(L^3)GaCl$_2$**)



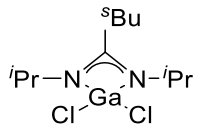
$C_{11}H_{23}Cl_2GaN_2$ MM = 323.94 g/mol

The general protocol is followed using (^{i}PrNC^{n}BuN^{i}Pr)Li lithium amidinate complex (**L^{3}Li**) (444.0 mg in 15 mL THF ; 2.3 mmol ; 1.0 equiv.) and $GaCl_3$ (411.5 mg in 10 mL THF ; 2.3 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by sublimation (80 °C, $5\cdot10^{-2}$ mbar) to yield a white solid (375.0 mg ; 50%).

^{1}H-NMR (THF-d_8): δ 3.73 (m, $^3J_{H\text{-}H}$ = 6.2 Hz, 2H, N*H*CMe$_2$); 2.44 (t, 2H, CC*H$_2$*CH$_2$); 1.58 (m, 2H, CH$_2$C*H$_2$*CH$_2$), 1.47 (m, 2H, CH$_2$C*H$_2$*Me); 1.13 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 12H, HC*Me$_2$*); 0.98 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 176.90 (s, N*C*^{n}BuN); 46.94 (NH*C*Me$_2$); 30.07 (s, C*C*H$_2$CH$_2$); 25.79 (s, HC*Me$_2$*); 25.27 (s, CH$_2$*C*H$_2$CH$_2$); 23.72 (s, CH$_2$*C*H$_2$Me); 14.04 (s, CH$_2$*Me*)

(^{i}PrNC^{s}BuN^{i}Pr)GaCl$_2$ (**(L^4)GaCl$_2$**)



$C_{11}H_{23}Cl_2GaN_2$ MM = 323.94 g/mol

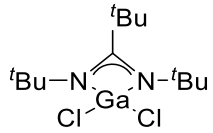
The general protocol is followed using (^{i}PrNC^{s}BuN^{i}Pr)Li lithium amidinate complex (**L^{4}Li**) (400.3 mg in 15 mL THF ; 2.1 mmol ; 1.0 equiv.) and $GaCl_3$ (377.1 mg in 7 mL THF ; 2.1 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by toluene extraction to yield a white solid (560.3 mg ; 82%).

^{1}H-NMR (THF-d_8): δ 3.87 (m, $^3J_{H-H}$ = 6.1 Hz, 2H, N*H*CMe$_2$); 2.83 (m, $^3J_{H-H}$ = 7.5 Hz, C*H*C(Me)CH$_2$, 1H); 1.73 (m, 2H, CCH(Me)C*H$_2$*Me); 1.33 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, CCH(*Me*)CH$_2$); 1.13 (m, 12H, HC*Me$_2$*); 1.01 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 179.21 (s, NC^{s}BuN); 47.27 (s, NH*C*Me$_2$); 35.66 (s, C*C*H(Me)CH$_2$); 27.37 (s, CCH(Me)C*H$_2$*Me); 25.45 (s, HC*Me$_2$*), 25.39 (s, HC*Me$_2$*); 17.12 (s, CCH*(Me)*CH$_2$); 12.77 (s, H$_2$C*Me*)

HR-MS Pos (APCI): [(L^4)GaCl$_2$H]$^+$ calcd *m/z* 323.0567 for $C_{11}H_{23}Cl_2GaN_2H^+$; found *m/z* 323.0554.

(^{t}BuNC^{t}BuN^{t}Bu)GaCl$_2$(**(L^5)GaCl$_2$**),[2] CAS : 213386-25-5



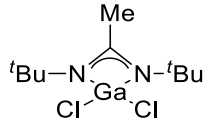
$C_{13}H_{27}Cl_2GaN_2$ MM = 352.00 g/mol

The general protocol is followed using (^{t}BuNC^{t}BuN^{t}Bu)Li lithium amidinate complex (**L^{5}Li**) (499.3 mg in 10 mL THF ; 2.3 mmol ; 1.0 equiv.) and GaCl$_3$ (426.8 mg in 5 mL THF ; 2.4 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by sublimation (100 °C, 5·10^{-2} mbar) to yield a white solid (78.5 mg). The rest is extracted with toluene (233.3 mg ; 68%).

^{1}H-NMR (THF-d_8): δ 1.52 (s, 4,5H); 1.51 (s, 9H); 1.48 (s, 4,5H); 1.45 (s, 9H)

^{13}C-NMR (THF-d_8): δ 184.92 (s, NC^{t}BuN); 57.44 (s, NCMe$_3$); 56.98 (s, NCMe$_3$); 56.75 (s, CNCMe$_3$); 34.42 (s, NC*Me$_3$C*^{t}Bu); 31.81 (s, CC*Me$_3$*); 31.39 (s, NC*Me$_3$*); 31.19 (s, CC*Me$_3$*)

(^{t}BuNCMeN^{t}Bu)GaCl$_2$ (**(L^6)GaCl$_2$**),[1]



$C_{10}H_{21}Cl_2GaN_2$ MM = 309.92 g/mol

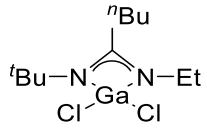
The general protocol is followed using (^{t}BuNCMeN^{t}Bu)Li lithium amidinate complex (**L^{6}Li**) (800.4 mg in 20 mL THF ; 4.5 mmol ; 1.0 equiv.) and GaCl$_3$ (815.4 mg in 20 mL THF ; 4.6 mmol ; 1.0 equiv.). The solvent was evaporated under vacuum and the solid was purified by sublimation at 85 °C and 5 × 10^{-2} mbar, yielding a white solid (0.96 g; 68%).

^{1}H-NMR (THF-d_8): δ 2.38 (s, 3H, C*Me*); 1.34 (s, 18H, N*tBu*)

^{13}C-NMR (THF-d_8): δ 176.0 (s, NCMeN); 53.2 (s, NCMe$_3$); 31.4 (s, C*Me$_3$*); 17.0 (s, C*Me*)

HR-MS Pos (APCI): $[(L^6)GaClH]^+$ calcd *m/z* 273.0644 for $C_{10}H_{21}ClGaN_2^+$; found *m/z* 273.0655.

(^{t}BuNC^{n}BuNEt)$GaCl_2$ (**(L^7)$GaCl_2$**)



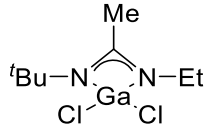
$C_{11}H_{23}Cl_2GaN_2$ MM = 323.94 g/mol

The general protocol is followed using (^{t}BuNC^{n}BuNEt)Li lithium amidinate complex (**L^7Li**) (310.7 mg in 14 mL toluene ; 1.6 mmol ; 1.0 equiv.) and $GaCl_3$ (299.6 mg in 7 mL toluene ; 1.7 mmol ; 1.0 equiv). The chlorinated gallium amidinate complex is purified by sublimation (50 °C, $5{\cdot}10^{-2}$ mbar) to yield a colourless oil (155.5 mg ; 29%).

^{1}H-NMR (THF-d_8): δ 3.18 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, N*H*$_2$CMe); 2.41 (t, 2H, CC*H*$_2$CH$_2$); 1.57 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 1.46 (m, 2H, H$_2$CC*H*$_2$Me); 1.31 (s, 9H, C*Me*$_3$); 1.04 (t, 3H, H$_2$C*Me*); 0.96 (t, $^3J_{H\text{-}H}$ = 6.2 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 174.17 (s, N*C*^{n}BuN); 52.10 (s, N*C*Me$_3$); 39.55 (s, C*C*H$_2$CH$_2$); 32.11 (s, C*Me*$_3$); 30.55 (s, C*C*H$_2$CH$_2$); 28.15 (s, CH$_2$*C*H$_2$CH$_2$); 24.20 (s, CH$_2$*C*H$_2$Me); 18.47 s, (H$_2$C*Me*); 14.02 (s, CH$_2$CH$_2$*Me*)

(^{t}BuNCMeNEt)$GaCl_2$ (**(L^9)$GaCl_2$**)



$C_8H_{17}Cl_2GaN_2$ MM = 281.86 g/mol

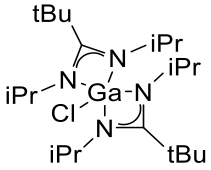
The general protocol is followed using (^{t}BuNCMeNEt)Li lithium amidinate complex (**L^9Li**) (337.8 mg in 20 mL THF ; 2.3 mmol, 1.0 equiv.) and $GaCl_3$ (400.6 mg in 8 mL THF ; 2.3 mmol ; 1.0 equiv.). The chlorinated gallium amidinate complex is purified by sublimation (70 °C, $5{\cdot}10^{-2}$ mbar) to yield a white solid (403.0 mg ; 63%).

^{1}H-NMR (THF-d_8): δ 3.14 (q, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, NC*H*$_2$Me); 2.12 (s, 3H, C*Me*); 1.29 (s, 9H, N^t*Bu*); 1.06 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d_8): δ 173.29 (s, N*C*MeN); 52.75 (s, N*C*Me$_3$); 39.42 (s, N*C*H$_2$Me); 31.30 (s, C*Me*$_3$), 17.50 (s, CH$_2$*Me*); 13.66 (s, C*Me*)

HR-MS Pos (APCI): $[(L^9)GaCl_2H]^+$ calcd *m/z* 281.0097 for $C_8H_{17}Cl_2GaN_2H^+$; found *m/z* 281.0089.

$(iPrNCtBuNiPr)_2GaCl$ (**$(L^1)_2GaCl$**)



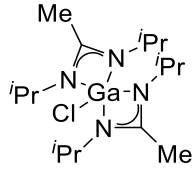
$C_{22}H_{46}ClGaN_4$ MM = 471.81 g/mol

The general protocol is followed using (^{i}PrNC^{t}BuN^{i}Pr)Li lithium amidinate complex (**L^1Li**) (1036.8 mg in 20 mL THF ; 5.4 mmol ; 1.0 equiv.) and $GaCl_3$ (479.9 mg in 10 mL THF ; 2.7 mmol ; 0.5 equiv.). The chlorinated gallium bis-amidinate complex is purified by sublimation (120 °C, $5\cdot10^{-2}$ mbar) to yield a white solid (480.9 mg ; 37%). ^{1}H-NMR analysis shows few unknown peaks after sublimation.

^{1}H-NMR (THF-d_8): δ 4.29 (m, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H, N*H*CMe$_2$); 1.41 (s, 18H, C^t*Bu*); 1.28 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 24H, HC*Me$_2$*)

^{13}C-NMR (THF-d_8): δ 175.97 (s, N*C*^{t}BuN); 46.52 (s, NH*C*Me$_2$); 38.33 (s, C*C*Me$_3$), 29.12 (s, HC*Me$_2$*); 24.33 (s, C*Me$_3$*)

$(^i$PrNCMeN^{i}Pr)$_2$GaCl (**$(L^2)_2GaCl$**),[4] CAS: 954501-63-4



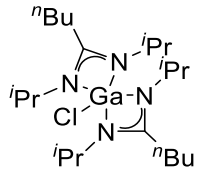
$C_{16}H_{34}ClGaN_4$ MM = 387.65 g/mol

The general protocol is followed using (^{i}PrNCMeN^{i}Pr)Li lithium amidinate complex (**L^2Li**) (367.5 mg in 20 mL THF ; 2.5 mmol ; 1.0 equiv.) and $GaCl_3$ (218.6 mg in 9 mL THF ; 1.2 mmol ; 0.5 equiv.). The chlorinated gallium bis-amidinate complex is purified by sublimation (115 °C, $5\cdot10^{-2}$ mbar) to yield a white solid (300.0 mg ; 62%).

^{1}H-NMR (C_6D_6): δ 3.43 (m, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, N*H*CMe$_2$); 1.40 (s, 6H, C*Me*); 1.26 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 24H, HC*Me$_2$*)

^{13}C-NMR (THF-d_8): δ 170.15 (s, N*C*MeN); 47.28 (s, NH*C*Me$_2$); 24.79 (s, HC*Me$_2$*); 11.51 (s, C*Me*)

(^{i}PrNC^{n}BuN^{i}Pr)$_2$GaCl (($\mathbf{L^3}$)$_2$GaCl)



$C_{22}H_{46}ClGaN_4$ MM = 471.81 g/mol

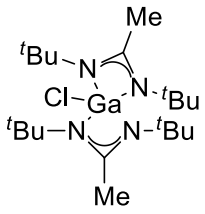
The general protocol is followed using (^{i}PrNC^{n}BuN^{i}Pr)Li lithium amidinate complex (**L^{3}Li**) (297.6 mg in 15 mL THF; 1.6 mmol ; 1.0 equiv.) and $GaCl_3$ (139.2 mg in 6 mL THF ; 0.8 mmol ; 0.5 equiv.). The chlorinated gallium bis-amidinate complex is purified by extraction to yield a yellow oil (232.5 mg ; 62%).

^{1}H-NMR (THF-d$_8$): δ 3.66 (m, $^{3}J_{H-H}$ = 6.7 Hz, 4H, N*H*CMe$_2$); 2.31 (t, 3H, CC*H*$_2$CH$_2$) ; 1.47 (m, 8H, CH$_2$C*H*$_2$C*H*$_2$Me); 1.20 (d, $^{3}J_{H-H}$ = 6.5 Hz, 24H, HC*Me*$_2$); 0.95 (t, $^{3}J_{H-H}$ = 7.0 Hz, 3H, CH$_2$*Me*)

^{13}C-NMR (THF-d$_8$): δ 172.96 (s, N*C*^{n}BuN); 47.21 (s, NH*C*Me$_2$); 30.27 (s, C*C*H$_2$CH$_2$); 25.79 (s, CH$_2$*C*H$_2$CH$_2$); 25.15 (s, HC*Me*$_2$); 23.91 (s, CH$_2$*C*H$_2$Me); 14.07 (s, CH$_2$*Me*)

HR-MS Pos (APCI): [(L^3)$_2$Ga]$^+$ calcd *m/z* 435.2973 for $C_{22}H_{46}GaN_4^+$; found *m/z* 435.2975.

(tBuNCMeNtBu)$_2$GaCl (($\mathbf{L^6}$)$_2$GaCl)



$C_{20}H_{42}ClGaN_4$ MM = 443.76 g/mol

The general protocol is followed using (^{t}BuNCMeN^{t}Bu)Li lithium amidinate complex (**L^{6}Li**) (401.1 mg in 18 mL THF ; 2.3 mmol ; 1.0 equiv.) and $GaCl_3$ (203.5 mg in 6 mL THF ; 1.2 mmol ; 0.5 equiv.). The chlorinated gallium bis-amidinate complex is purified by sublimation (120 °C, 5.10^{-2} mbar) to yield a white solid (162.4 mg ; 32%). The mono-amidinate complex is the main impurity in the reaction.

^{1}H-NMR (THF-d$_8$): δ 2.35 (s, 6H, C*Me*); 1.30 (s, 36H, N^{t}*Bu*)

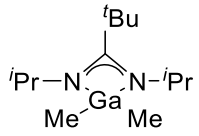
^{13}C-NMR (THF-d$_8$): δ 170.38 (s, N*C*MeN); 52.77 (s, N*C*Me$_3$); 31.86 (s, C*Me*$_3$); 18.93 (s, C*Me*)

1.4 Gallium amidinate methylated complexes

Protocol A: A solution of the purified chlorinated gallium amidinate in THF or Et_2O (0.20 mmol/L) was cooled down to -78 °C. Methyllithium solution (1.6 M in Et_2O; 1 or 2 equivalents) was added dropwise with a syringe. The mixture is stirred and let back to room temperature overnight. The solvent is removed by evaporation under vacuum at room temperature or at -40 °C. The desired methylated gallium amidinate complex is distilled directly or after under vacuum drying to then purify either by sublimation/distillation or by extraction.

Protocol B: The chlorinated gallium amidinate complex not separated from the lithium salt is placed in solution (Et_2O or THF; 0.20 mmol/L) and cooled down to -78 °C. Methyllithium solution (1.6 M in Et_2O; 1 or 2 equivalents) was added dropwise with a syringe. The mixture is stirred and let back to room temperature overnight. The solvent is removed by evaporation under vacuum at -40 °C. The methylated gallium amidinate complex is finally directly distilled.

(^{i}PrNC^{t}BuN^{i}Pr)GaMe$_2$ (**(L^1)GaMe$_2$**),[3] CAS: 213386-22-2



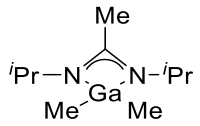
$C_{13}H_{29}GaN_2$ MM = 283.11 g/mol

General protocol A is followed using the chlorinated gallium amidinate complex (^{i}PrNC^{t}BuN^{i}Pr)GaCl$_2$ (**(L^1)GaCl$_2$**) (467.5 mg in 10 mL THF ; 1.4 mmol ; 1.0 equiv.) and methyllithium (1.9 mL ; 3.0 mmol ; 2.1 equiv.). The methylated gallium amidinate complex is dried before sublimation (50 °C, $5 \cdot 10^{-2}$ mbar) to yield a white solid (140.5 mg ; 34%).

^{1}H-NMR (THF-d$_8$): δ 4.17 (m, $^3J_{H\text{-}H}$ = 6.1 Hz, 2H, N*H*CMe$_2$); 1.38 (s, 9H, *CMe$_3$*); 1.02 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 12H, HC*Me$_2$*); -0.33(s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 174.83 (s, N*C*^{t}BuN); 46.94 (s, NH*C*Me$_2$); 40.09 (s, C*C*Me$_3$); 29.93 (s, HC*Me$_2$*); 26.48 (s, C*Me$_3$*); -5.07 (s, Ga*Me$_2$*)

(^{i}PrNCMeN^{i}Pr)GaMe$_2$ (**(L^2)GaMe$_2$**),[3,10] CAS: 135389-74-1



$C_{10}H_{23}GaN_2$ MM = 241.03 g/mol

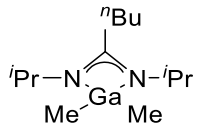
General protocol A is followed using the chlorinated gallium amidinate complex (^{i}PrNCMeN^{i}Pr)GaCl$_2$ (**(L^2)GaCl$_2$**) (209.4 mg in 10 mL Et_2O ; 0.7 mmol, 1.0 equiv.) and methyllithium (1.6 mL ; 1.6 mmol ; 2.2 equiv.). Diethylether is evaporated under vacuum at -40 °C and the methylated gallium amidinate complex is isolated by distillation to yield a colourless oil (98.0 mg ; 55%).

^{1}H-NMR (THF-d$_8$): δ 3.57 (m, $^3J_{H\text{-}H}$ = 6.3 Hz, 2H, N*H*CMe$_2$); 1.86 (s, 3H, C*Me*); 0.99 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 12H, HC*Me$_2$*); -0.33 (s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 169.09 (s, N*C*MeN); 46.20 (s, NH*C*Me$_2$); 25.60 (s, HC*Me$_2$*); 10.52 (s, C*Me*); -5.61 (s, Ga*Me$_2$*)

HR-MS Pos (APCI): [(L^2)GaMe$_2$H]$^+$ calcd *m/z* 241.1190 for $C_{10}H_{23}GaN_2H^+$; found *m/z* 241.1183.

(^{i}PrNC^{n}BuN^{i}Pr)GaMe$_2$ (**(L^3)GaMe$_2$**)



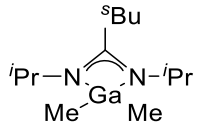
$C_{13}H_{29}GaN_2$ MM = 283.11 g/mol

General protocol A is followed using the chlorinated gallium amidinate complex (^{i}PrNC^{n}BuN^{i}Pr)GaCl$_2$ (**(L^3)GaCl$_2$**) (298.6 mg in 10 mL THF ; 0.7 mmol ; 1.0 equiv.) and methyllithium (1.2 mL ; 1.9 mmol ; 2.1 equiv.). The methylated gallium amidinate complex is dried before distillation (50 °C, 5·10^{-2} mbar) to yield a colourless oil (83.0 mg ; 29%).

^{1}H-NMR (THF-d$_8$): δ 3.62 (m, $^3J_{H\text{-}H}$ = 6.3 Hz, 2H, N*H*CMe$_2$); 2.26 (t, 2H, CC*H$_2$*CH$_2$); 1.53 (m, 2H, CH$_2$C*H$_2$*CH$_2$); 1.43 (m, 2H, CH$_2$C*H$_2$*Me); 1.00 (d, 12H, HC*Me$_2$*); 0.95 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH$_2$*Me*); -0.33 (s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 172.00 (s, N*C*^{n}BuN); 46.16 (s, NH*C*Me$_2$); 30.68 (s, C*C*H$_2$CH$_2$); 26.05 (s, HC*Me$_2$*); 25.37 (s, CH$_2$*C*H$_2$CH$_2$); 23.80 (s, CH$_2$*C*H$_2$Me); 14.17 (s, CH$_2$*Me*); -5.43 (s, Ga*Me$_2$*)

(^{i}PrNC^{s}BuN^{i}Pr)GaMe$_2$ (**(L^4)GaMe$_2$**)



$C_{13}H_{29}GaN_2$ MM = 283.11 g/mol

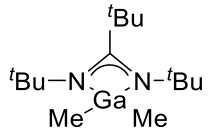
General protocol B is followed using the lithium amidinate (^{i}PrNC^{s}BuN^{i}Pr)Li (**L^{4}Li**) (403.0 mg in 10 mL THF ; 2.1 mmol ; 1.0 equiv.), gallium trichloride (381.4 mg in 10 mL THF ; 2.2 mmol ; 1.0 equiv.) and methyllithium (2.1 mL ; 3.4 mmol ; 1.6 equiv.). Diethylether was evaporated under vacuum at -40°C, the methylated gallium amidinate complex was isolated by distillation (25 °C, 5·10^{-2} mbar) to yield a colourless oil (358.4 mg ; 58%).

^{1}H-NMR (THF-d$_8$): δ 3.76 (m, $^3J_{H-H}$ = 6.2 Hz, 2H, N*H*CMe$_2$); 2.70 (m, $^3J_{H-H}$ = 7.7 Hz, C*H*C(Me)CH$_2$, 1H); 1.61 (m, 2H, CCH(Me)C*H$_2$*Me); 1.26 (d, $^3J_{H-H}$ = 7.3 Hz, 3H, CCH(*Me*)CH$_2$); 1.01 (m, 15H, HC*Me$_2$*, *CH$_2$*Me); -0.32 (s, 6H, GaMe$_2$)

^{13}C-NMR (THF-d$_8$): δ 173.89 (s, N*C*^{s}BuN); 46.31 (s, NH*C*Me$_2$); 35.27 (s, C*C*H(Me)CH$_2$); 27.87 (s, CCH(Me)C*H$_2$*Me); 26.14 (s, HC*Me$_2$*), 26.01 (s, HC*Me$_2$*); 17.90 (s, CCH*(Me)*CH$_2$); 13.04 (s, H$_2$C*Me*); -5.30 (s, GaMe$_2$)

HR-MS Pos (APCI): [(L^4)GaMe$_2$H]$^+$ calcd *m/z* 283.1659 for $C_{13}H_{29}GaN_2H^+$; found *m/z* 283.1649.

(^{t}BuNC^{t}BuN^{t}Bu)GaMe$_2$ (**(L^5)GaMe$_2$**),[2] CAS: 251292-88-3



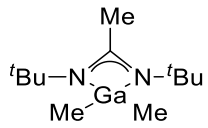
$C_{15}H_{33}GaN_2$ MM = 311.17 g/mol

General protocol A is followed using the chlorinated gallium amidinate complex (^{t}BuNC^{t}BuN^{t}Bu)GaCl$_2$ (**(L^5)GaCl$_2$**) (233.3 mg in 10 mL THF ; 0.7 mmol ; 1.0 equiv.) and methyllithium (0.9 mL ; 1.4 mmol ; 2.2 equiv.). The methylated gallium amidinate complex is dried before distillation (75 °C, 5·10^{-2} mbar) to yield a colourless oil (85.0 mg ; 41%).

^{1}H-NMR (THF-d$_8$): δ 1.45 (s, 9H, C^{t}*Bu*); 1.37 (s, 18H, N^{t}*Bu*); -0.32 (s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 177.86 (s, N*C*^{t}BuN); 54.30 (s, N*C*Me$_3$); 38.02 (s, C*C*Me$_3$); 34.54 (s, NC*Me$_3$*); 32.32 (s, CC*Me$_3$*); -3.91 (s, Ga*Me$_3$*)

(^{t}BuNCMeN^{t}Bu)GaMe$_2$ (**(L^6)GaMe$_2$**),[1]



$C_{12}H_{27}GaN_2$ MM = 269.09 g/mol

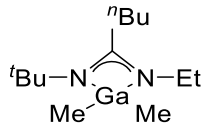
General protocol A is followed using the chlorinated gallium amidinate complex (^{t}BuNCMeN^{t}Bu)GaCl$_2$ (**(L^6)GaCl$_2$**) (230.6 mg in 10 mL THF ; 0.7 mmol ; 1.0 equiv.) and methyllithium (1.6 mL ; 1.6 mmol ; 2.2 equiv.). The solvent was then evaporated under vacuum at −40 °C and the final complex was purified by distillation, yielding a transparent oil (98.0 mg; 49%).

^{1}H-NMR (THF-d$_8$): δ 2.12 (s, 3H, C*Me*); 1.19 (s, 18H, N*tBu*) ; -0.34 (s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 169.6 (s, N*C*MeN); 51.4 (s, N*C*Me$_3$); 31.9 (s, C*Me$_3$*); 17.9 (s, C*Me*); -6.0 (s, Ga*Me$_2$*)

HR-MS Pos (APCI): [(L^6)GaMe$_2$]$^+$ calcd *m/z* 269.1503 for $C_{12}H_{29}GaN_2^+$; found *m/z* 269.1510.

(^{t}BuNC^{n}BuNEt)GaMe$_2$ **(L^7)GaMe$_2$)**



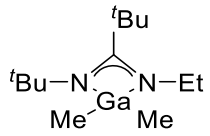
$C_{13}H_{29}GaN_2$ MM = 283.11 g/mol

General protocol A is followed using the chlorinated gallium amidinate complex (^{t}BuNC^{n}BuNEt)GaCl$_2$ (**(L^7)GaCl$_2$**) (244.7 mg in 7 mL THF ; 0.8 mmol, 1.0 equiv.) and methyllithium (1.0 mL ; 1.6 mmol ; 2.1 equiv.). The methylated gallium amidinate complex is dried before distillation (40 °C, 5·10^{-2} mbar) to yield a colourless oil (63.2 mg ; 30%).

^{1}H-NMR (THF-d$_8$): δ 3.14 (m, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, NC*H$_2$*Me); 2.35 (t, 2H, CC*H$_2$*CH$_2$); 1.56 (m, 2H; CH$_2$C*H$_2$*CH$_2$); 1.44 (m, 2H, CH$_2$C*H$_2$*Me); 1.20 (s, 9H, N*^{t}Bu*); 1.01 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, NCH$_2$*Me*); 0.96 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH$_2$*Me*); -0.35 (s, 6H, Ga*Me$_2$*)

^{13}C-NMR (THF-d$_8$): δ 173.75 (s, N*C*^{n}BuN); 51.44 (s, N*C*Me$_3$); 39.76 (s, NCH$_2$Me); 32.44 (s, C*Me$_3$*); 29.93 (s, C*C*H$_2$CH$_2$); 28.93 (s, CH$_2$*C*H$_2$CH$_2$); 24.09 (s, CH$_2$*C*H$_2$Me); 17.46 (s, NCH$_2$*Me*); 14.04 (s, CH$_2$*Me*); -6.22 (s, Ga*Me$_2$*)

(^{t}BuNC^{t}BuNEt)GaMe$_2$ (**(L^8)GaMe$_2$**)



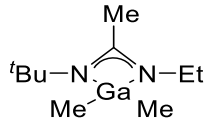
$C_{13}H_{29}GaN_2$ MM = 283.11 g/mol

General protocol B is followed using the lithium amidinate (^{t}BuNC^{t}BuNEt)Li (**L^{8}Li**) (400.4 mg in 10 mL THF ; 2.1 mmol ; 1.0 equiv.), gallium trichloride (378.5 mg in 10 mL THF ; 2.1 mmol ; 1.0 equiv.) and methyllithium (2.1 mL ; 3.3 mmol ; 1.5 equiv.). Diethylether was evaporated under vacuum at -40°C, the methylated gallium amidinate complex was isolated by distillation (25 °C, $5\cdot10^{-2}$ mbar) to yield a colourless oil (158.0 mg ; 27%).

^{1}H-NMR (THF-d$_8$): δ 3.44 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, NC*H*$_2$Me); 1.39 (s, 9H, N^t*Bu*); 1.34 (s, 9H, C^t*Bu*); 1.01 (t, 3H, CH$_2$*Me*); -0.35 (s, 6H, Ga*Me*$_2$)

^{13}C-NMR (THF-d$_8$): δ 177.28 (s, N*C*^{t}BuN); 53.15 (s, N*C*Me$_3$); 43.18 (s, N*C*H$_2$Me); 38.76 (s, C*C*Me$_3$); 34.44 (s, NC*Me*$_3$); 30.74 (s, CC*Me*$_3$); 17.91 (s, CH$_2$*Me*); -5.40 (s, Ga*Me*$_2$)

(^{t}BuNCMeNEt)GaMe$_2$ (**(L^9)GaMe$_2$**)



$C_{10}H_{23}GaN_2$ MM = 241.03 g/mol

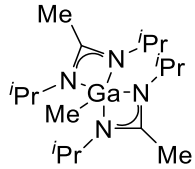
General protocol B is followed using the lithium amidinate (^{t}BuNCMeNEt)Li (**L^{9}Li**) (412.0 mg in 10 mL THF ; 2.8 mmol ; 1.0 equiv.), gallium trichloride (490.1 mg in 10 mL THF ; 2.8 mmol ; 1.0 equiv.) and methyllithium (2.7 mL ; 4.3 mmol ; 1.6 equiv.). Diethylether was evaporated under vacuum at -40°C, the methylated gallium amidinate complex was isolated by distillation (25 °C, $5\cdot10^{-2}$ mbar) to yield a colourless oil (392.7 mg ; 50%).

^{1}H-NMR (THF-d$_8$): δ 3.11 (q, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, NC*H*$_2$Me); 1.97 (s, 3H, C*Me*); 1.19 (s, 9H, N^t*Bu*); 1.00 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH$_2$*Me*); -0.35 (s, 6H, Ga*Me*$_2$)

^{13}C-NMR (THF-d$_8$): δ 170.25 (s, N*C*MeN); 51.22 (s, N*C*Me$_3$); 39.93 (s, N*C*H$_2$Me); 31.93 (s, N*C*Me$_3$); 17.16 (s, C*Me*); 14.23 (s, CH$_2$*Me*); -6.25 (s, Ga*Me*$_2$)

HR-MS Pos (APCI): [(L^9)GaMe$_2$H]$^+$ calcd *m/z* 241.1190 for $C_{10}H_{23}GaN_2H^+$; found *m/z* 241.1187.

(^{i}PrNCMeN^{i}Pr)$_2$GaMe (**(L^2)$_2$GaMe**),[10] CAS: 2931449-49-7



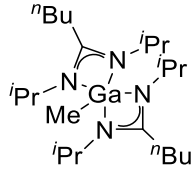
$C_{17}H_{37}GaN_4$ MM = 367.23 g/mol

General protocol A is followed using the bis-amidinate chlorinated gallium complex (^{i}PrNCMeN^{i}Pr)$_2$GaCl (**(L^2)$_2$GaCl**) (195.0 mg in 9 mL THF ; 0.5 mmol ; 1.0 equiv.) and methyllithium (0.3 mL ; 0.5 mmol ; 1.0 equiv.). The methylated gallium bis-amidinate complex is dried before sublimation (150 °C, $5 \cdot 10^{-2}$ mbar) to yield a white solid (100.0 mg ; 54%).

^{1}H-NMR (C$_6$D$_6$): δ 3.53 (m, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, N*H*CMe$_2$); 1.52 (s, 6H, C*Me*); 1.25 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 24H, HC*Me$_2$*); 0.33 (s, 3H, Ga*Me*)

^{13}C-NMR (THF-d$_8$): δ 167.25 (s, N*C*MeN); 47.35 (s, NH*C*Me$_2$); 25.35 (s, HC*Me$_2$*); 11.37 (s, C*Me*); -1.10 (s, Ga*Me*)

(^{i}PrNC^{n}BuN^{i}Pr)$_2$GaMe (**(L^3)$_2$GaMe**)



$C_{23}H_{49}GaN_4$ MM = 451.40 g/mol

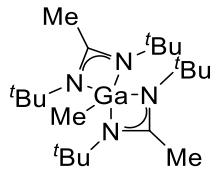
General protocol A is followed using the bis-amidinate chlorinated gallium complex (^{i}PrNC^{n}BuN^{i}Pr)$_2$GaCl (**(L^3)$_2$GaCl**) (656.4 mg in 10 mL THF ; 1.4 mmol ; 1.0 equiv.) and methyllithium (1.0 mL ; 1.6 mmol ; 1.1 equiv.). The methylated gallium bis-amidinate complex is dried before extraction with toluene to yield a yellow oil (509.4 mg ; 81%).

^{1}H-NMR (THF-d$_8$): δ 3.63 (m, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, N*H*CMe$_2$); 2.26 (t, 4H, CC*H$_2$*CH$_2$); 1.44 (m, 8H, CH$_2$C*H$_2$*CH$_2$, CH$_2$C*H$_2$*Me); 1.15 (d, 24H, HC*Me$_2$*); 0.95 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 6H, CH$_2$*Me*); -0.22 (s, 3H, Ga*Me*)

^{13}C-NMR (THF-d$_8$): δ 170.20 (s, N*C*^{n}BuN); 47.29 (s, NH*C*Me$_2$); 30.68 (s, C*C*H$_2$CH$_2$); 25.73 (s, HC*Me$_2$*); 25.66 (s, CH$_2$*C*H$_2$CH$_2$); 23.92 (s, CH$_2$*C*H$_2$Me); 14.20 (s, CH$_2$*Me*); -0.75 (s, Ga*Me*)

HR-MS Pos (APCI): $[(L^3)_2GaMeH]^+$ calcd *m/z* 451.3286 for $C_{23}H_{49}GaN_4H^+$; found *m/z* 451.3280.

(^{t}BuNCMeN^{t}Bu)$_2$GaMe (**(L^6)$_2$GaMe**)



$C_{21}H_{45}GaN_4$ MM = 423.34 g/mol

General protocol B is followed using the lithium amidinate (^{t}BuNCMeN^{t}Bu)Li (**L^{6}Li**) (503.2 mg in 15 mL THF ; 2.9 mmol ; 1.0 equiv.), gallium trichloride (256.3 mg in 10 mL THF ; 1.5 mmol ; 0.5 equiv.) and methyllithium (0.9 mL ; 1.4 mmol ; 0.5 equiv.). After evaporation of the solvent, the methylated gallium bis-amidinate complex was purified by sublimation (90 °C, $5 \cdot 10^{-2}$ mbar) to yield a colourless solid (81.0 mg ; 13%). The low yield is due to the formation of mono-amidinate species.

^{1}H-NMR (THF-d$_8$): δ 2.10 (s, 6H, C*Me*); 1.30 (s, 36H, N^t*Bu*); -0.18 (s, 3H, Ga*Me*)

^{13}C-NMR (THF-d$_8$): δ 167.04 (s, N*C*MeN); 52.31 (s, N*C*Me$_3$); 32.32 (s, C*Me$_3$*); 19.53 (s, C*Me*); 2.32 (s, Ga*Me*)

L[1]Li

Figure S1-1 - ^{1}H-NMR of **L[1]Li** in THF-d_8, 300 MHz

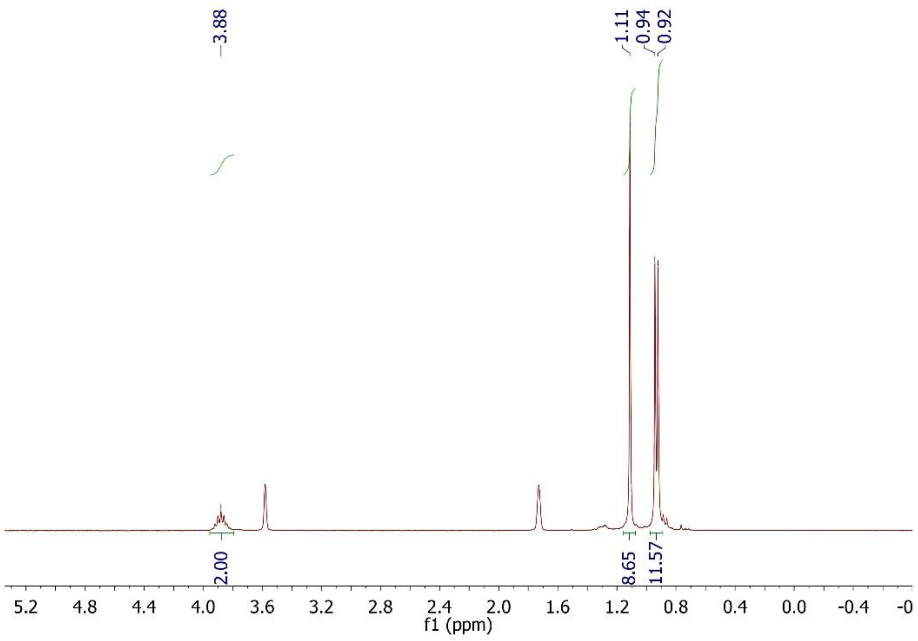
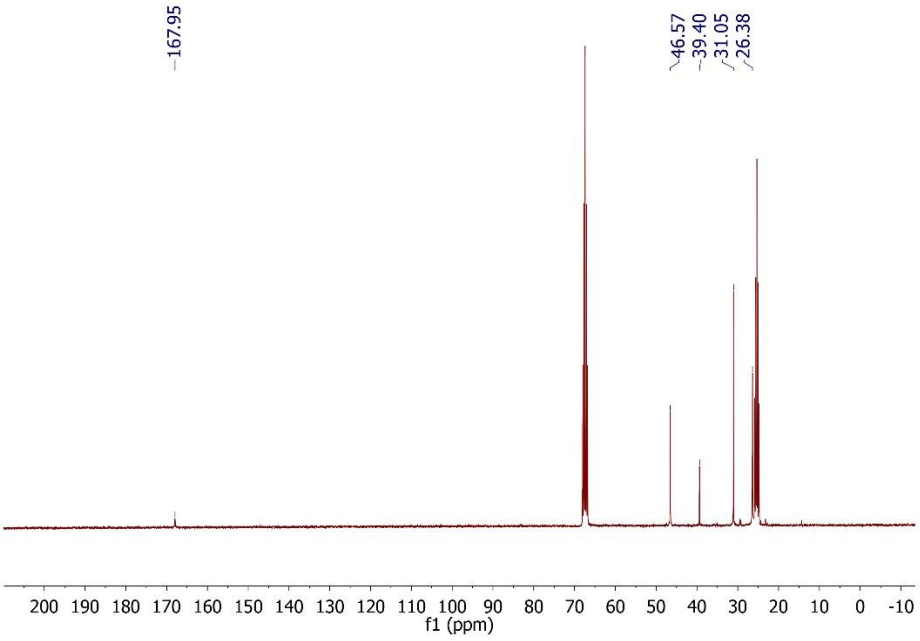


Figure S1-2 - ^{13}C-NMR of **L[1]Li** in THF-d_8, 300 MHz



L²Li

Figure S1-3 - ^{1}H-NMR of **L²Li** in THF-d_8, 300 MHz

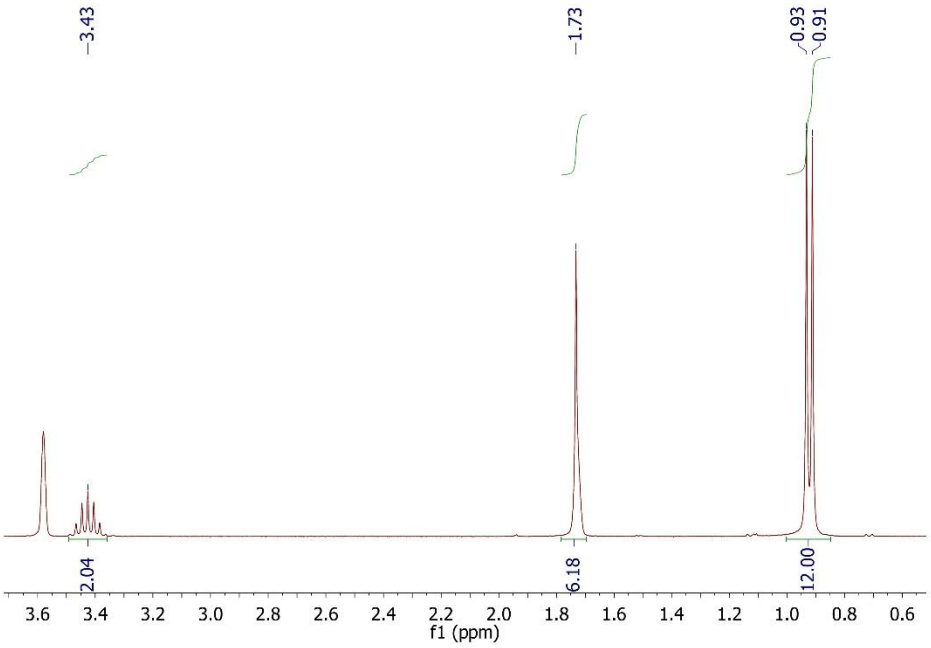
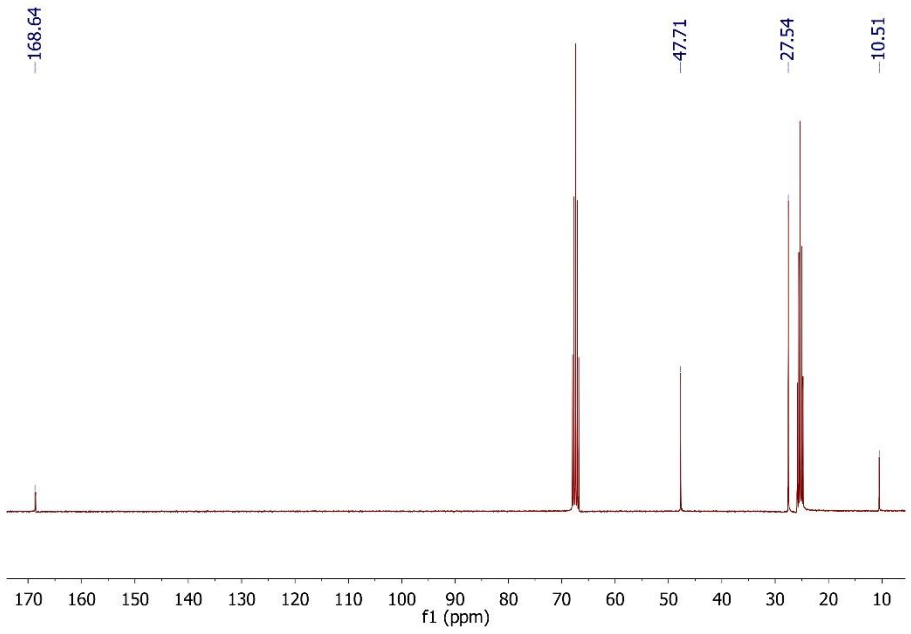


Figure S1-4 - ^{13}C-NMR of **L²Li** in THF-d_8, 300 MHz



L^{3}Li

Figure S1-5 - ^{1}H-NMR of **L^{3}Li** in THF-d_8, 300 MHz

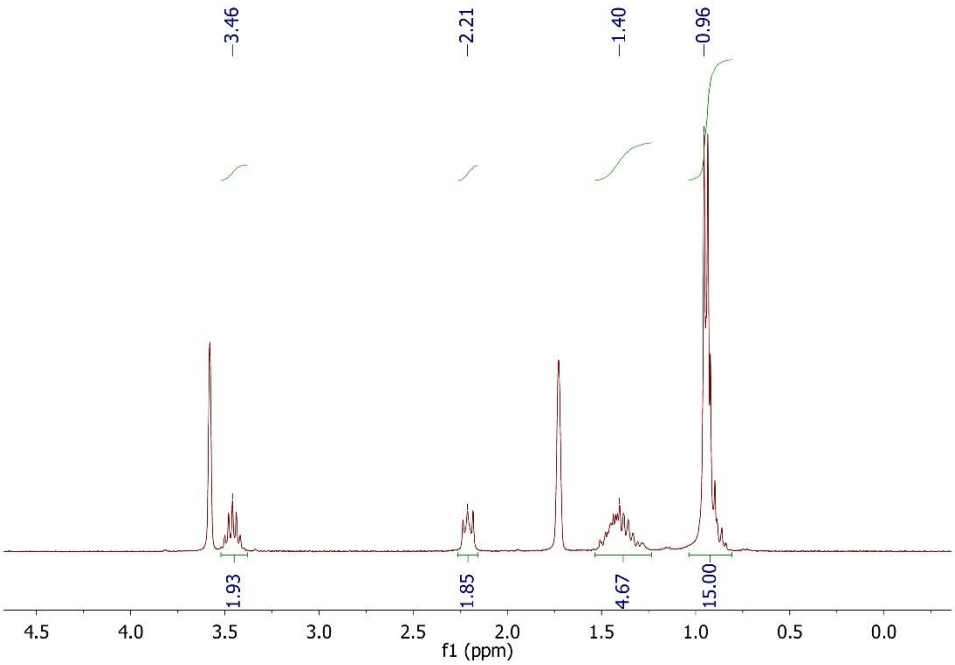
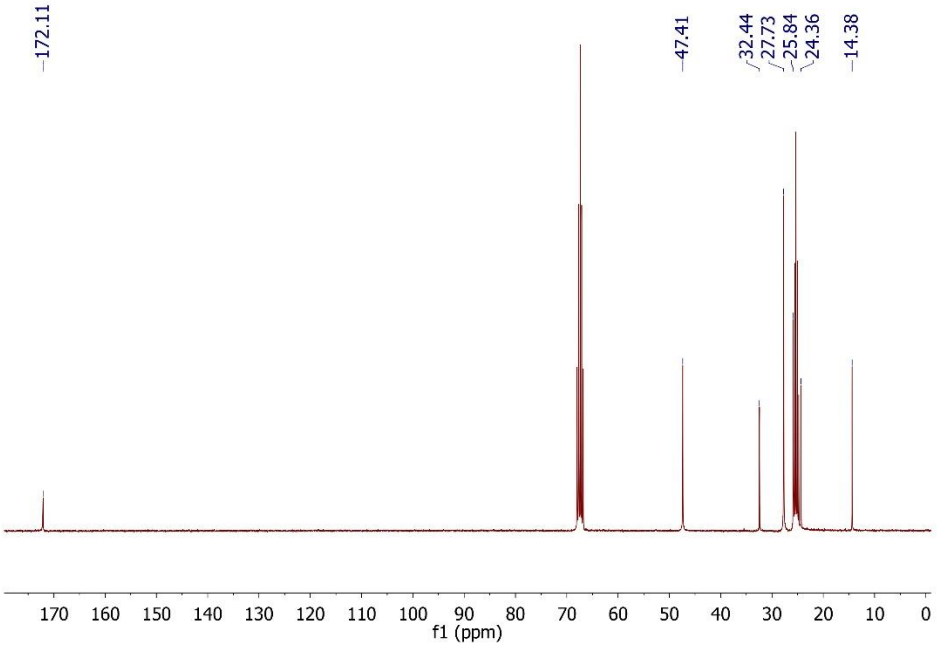


Figure S1-6 - ^{13}C-NMR of **L^{3}Li** in THF-d_8, 300 MHz



L^{4}Li

Figure S1-7 - ^{1}H-NMR of **L^{4}Li** in THF-d_8, 300 MHz.

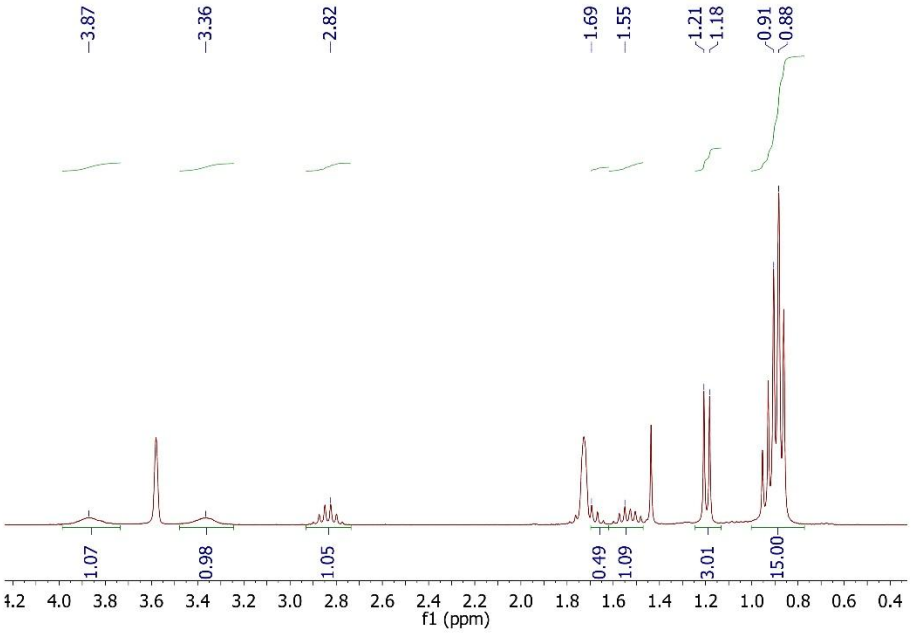
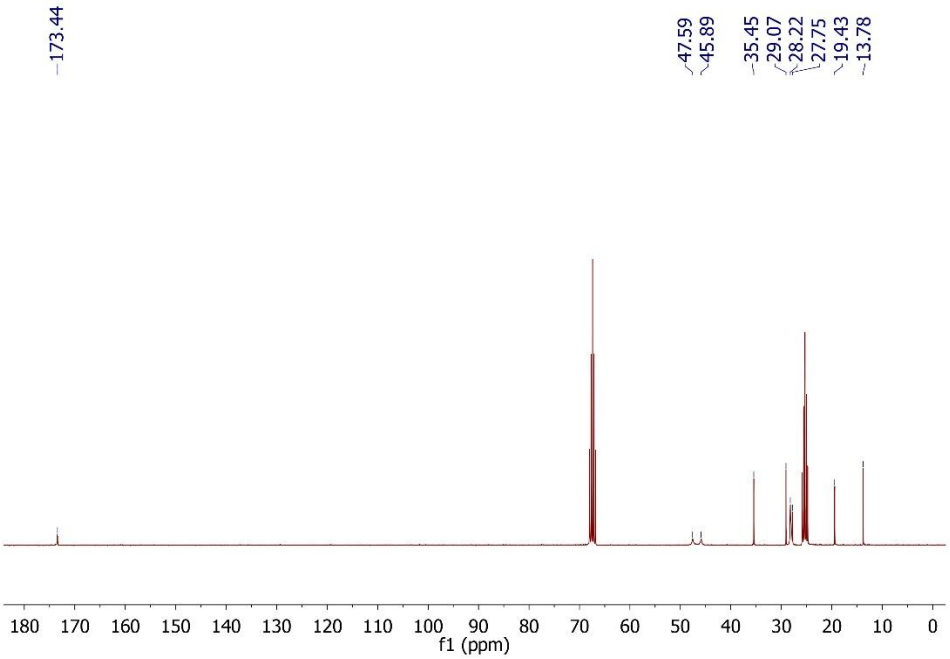


Figure S1-8 - ^{13}C-NMR of **L^{4}Li** in THF-d_8, 300 MHz



L^{5}Li

Figure S1-9 - ^{1}H-NMR of **L^{5}Li** in THF-d_8, 300 MHz

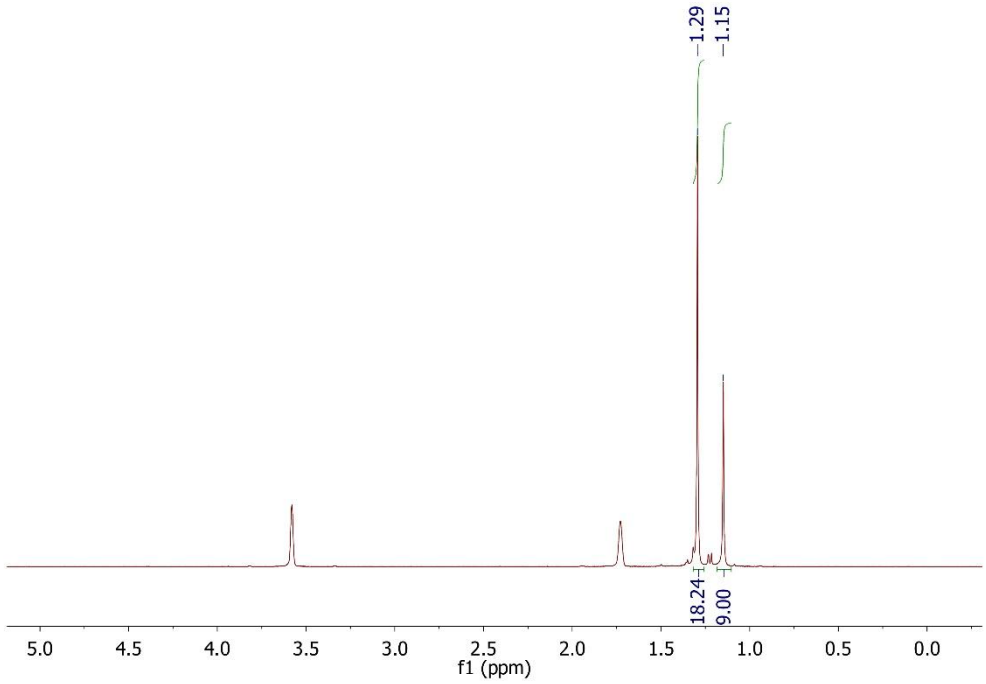
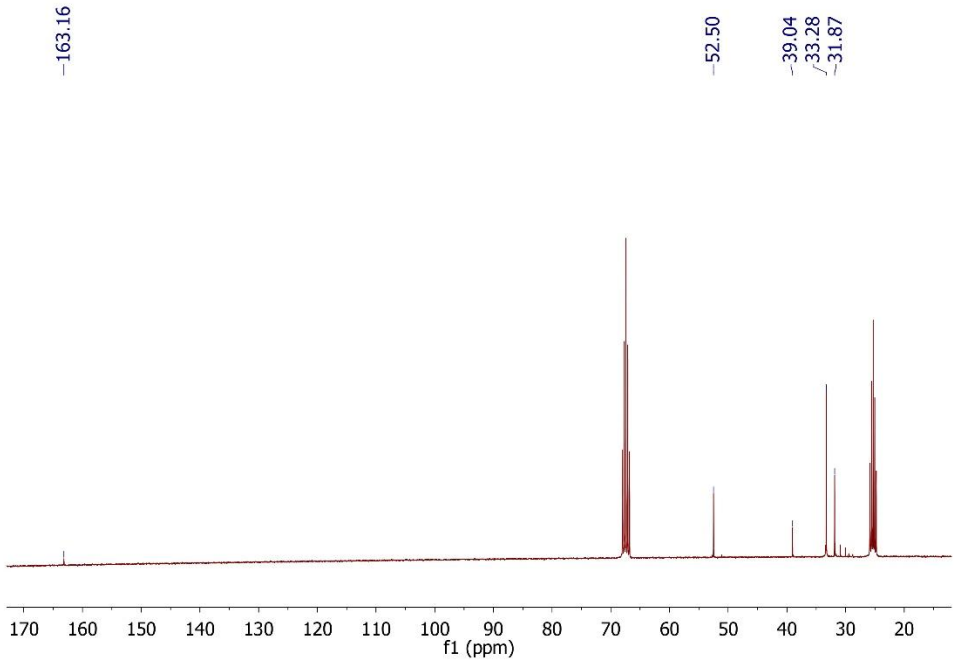
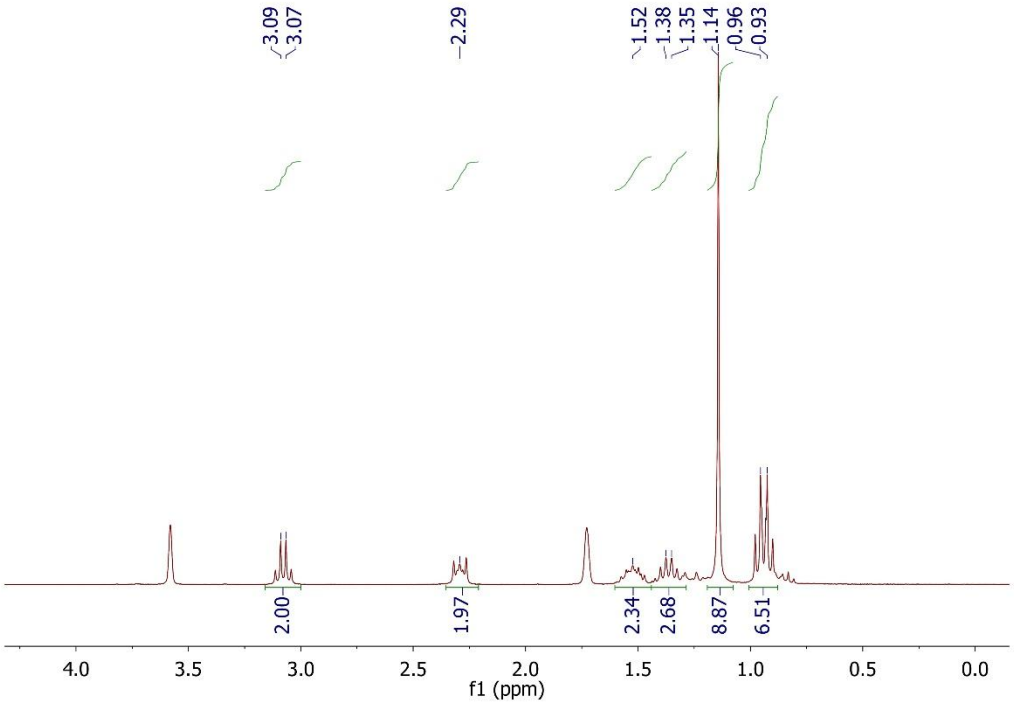


Figure S1-10 - ^{13}C-NMR of **L^{5}Li** in THF-d_8, 300 MHz



L^{7}Li

Figure S1-11 - ^{1}H-NMR of **L^{7}Li** in THF-d_8, 300 MHz



L^{8}Li

Figure S1-12 - ^{1}H-NMR of **L^{8}Li** in THF-d_8, 300 MHz

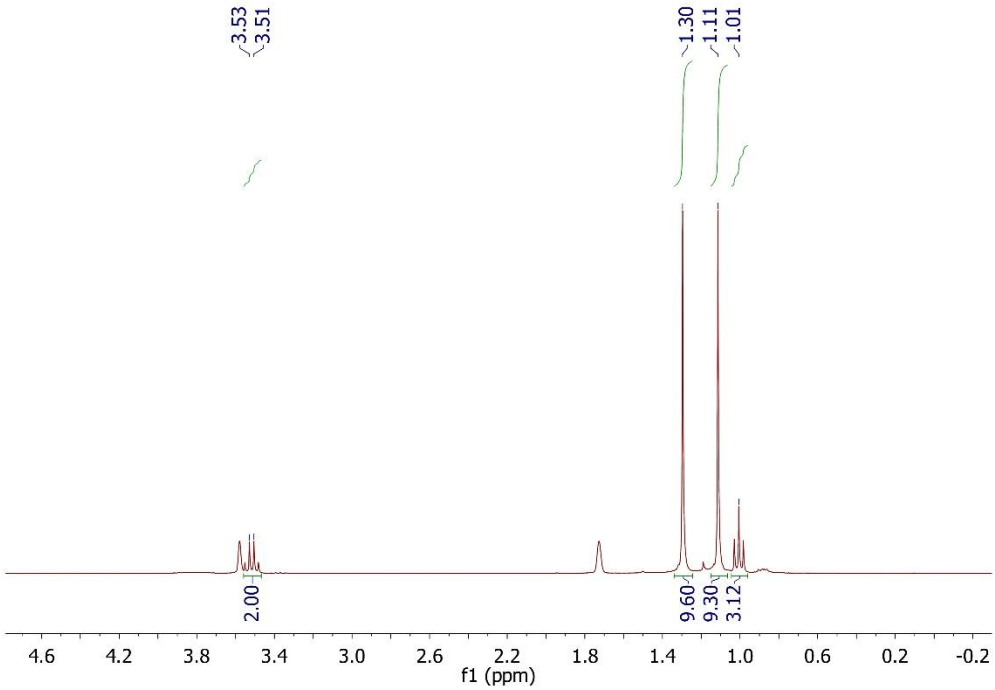
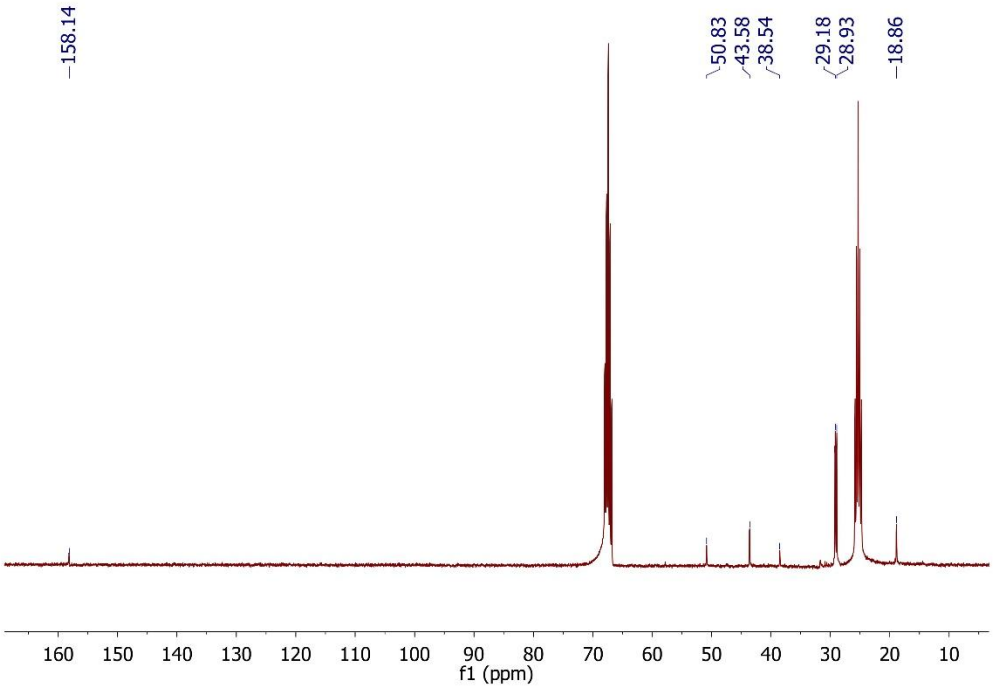


Figure S1-13 - ^{13}C-NMR of **L^{8}Li** in THF-d_8, 300 MHz



L^{9}Li

Figure S1-14 - ^{1}H-NMR of **L^{9}Li** in THF-d_8, 300 MHz

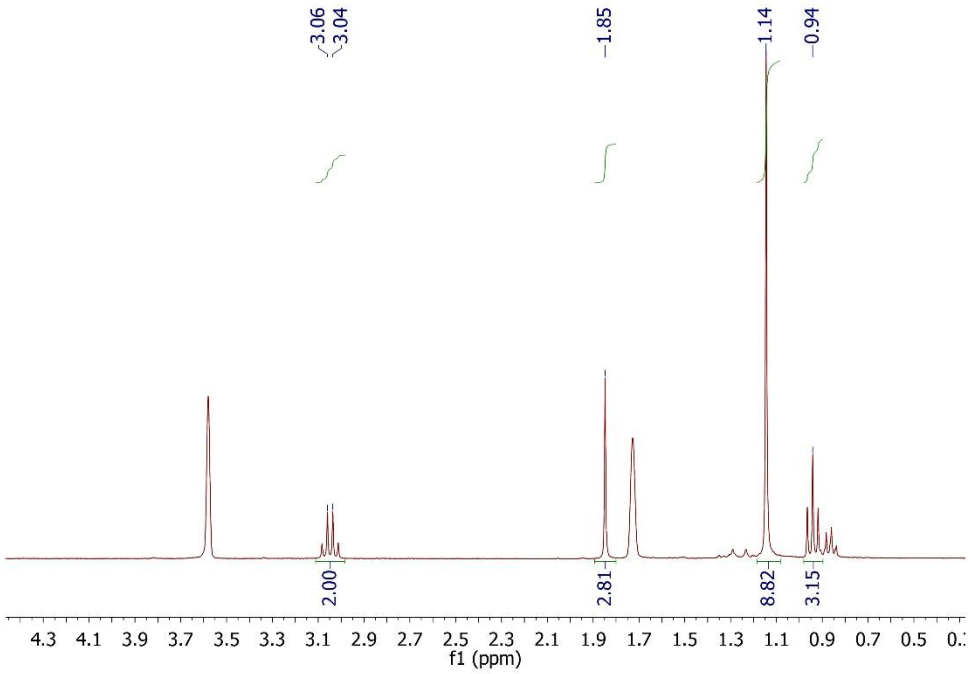
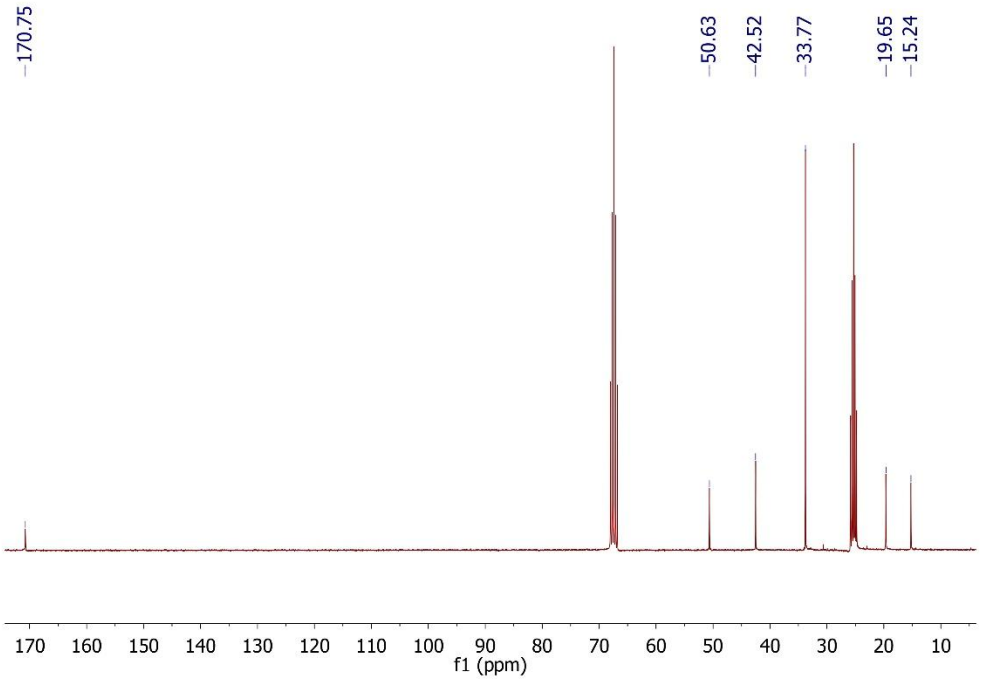


Figure S1-15 - ^{13}C-NMR of **L^{9}Li** in THF-d_8, 300 MHz



(L^{1})GaCl$_2$

Figure S1-16 - ^{1}H-NMR of **(L^{1})GaCl$_2$** in THF-d_8, 300 MHz

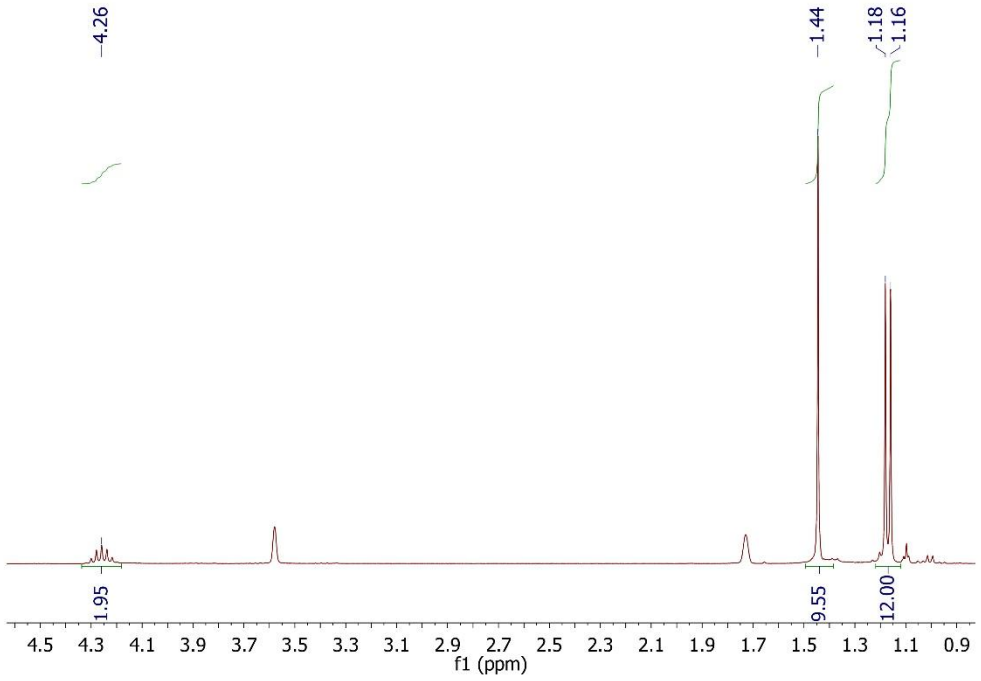
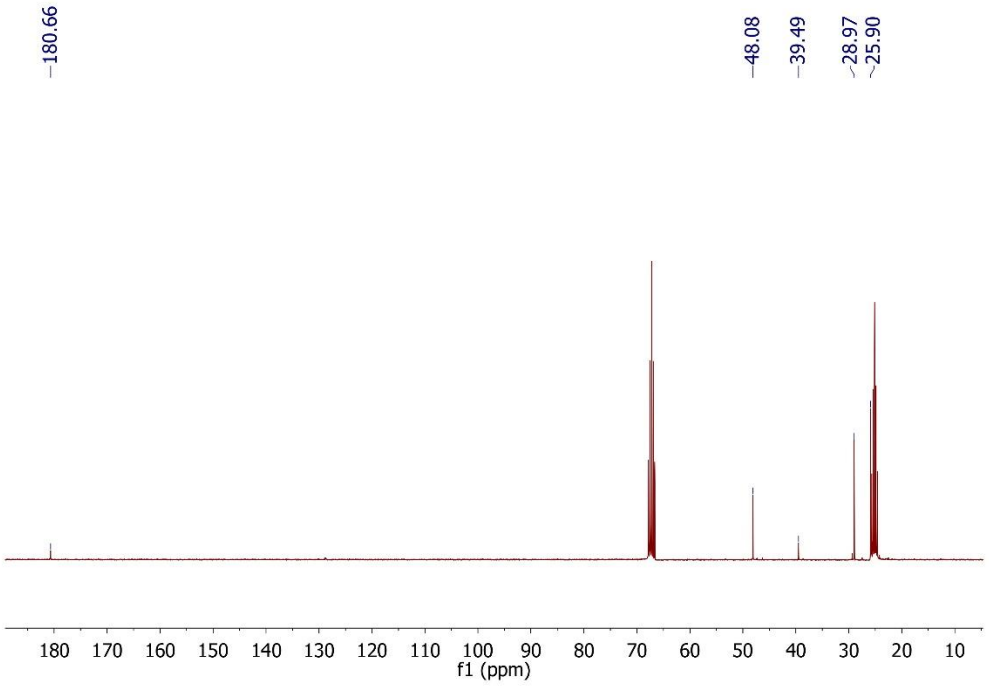


Figure S1-17 - ^{13}C-NMR of **(L^1)GaCl$_2$** in THF-d$_8$, 300 MHz



(L^2)GaCl$_2$

Figure S1-18 - ^{1}H-NMR of **(L^2)GaCl$_2$** in THF-d$_8$, 300 MHz

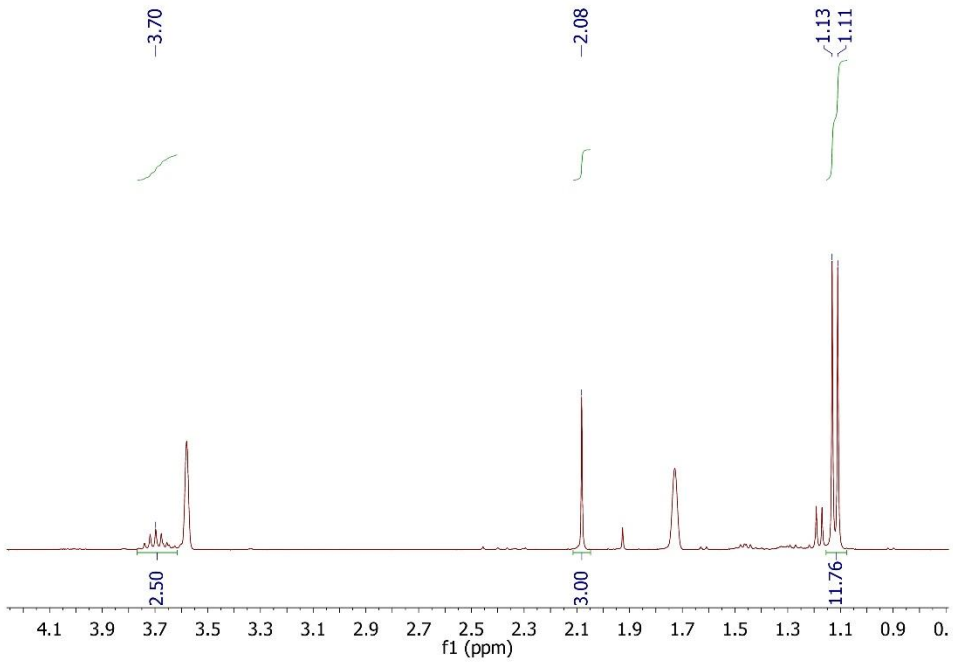
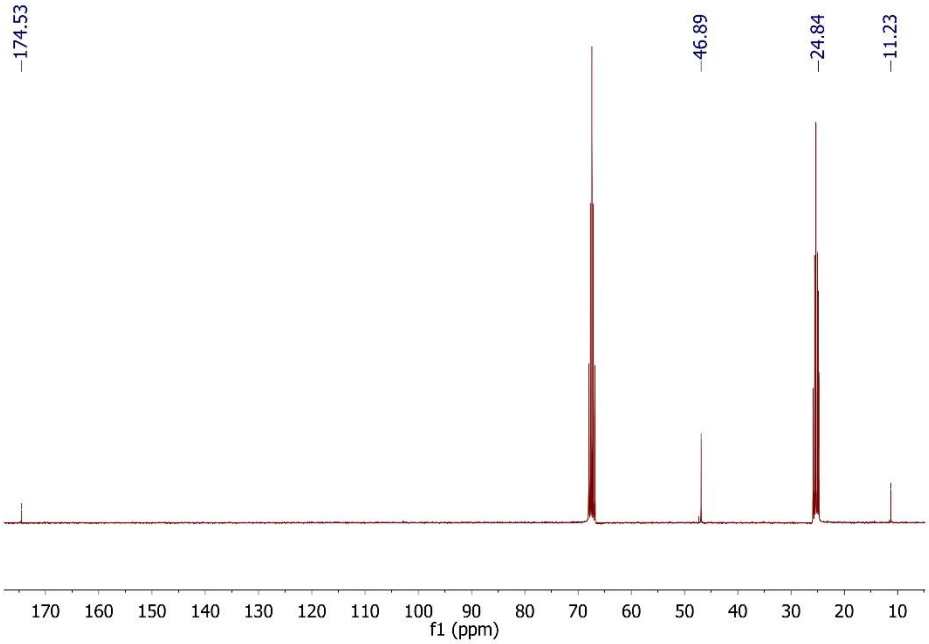


Figure S1-19 - ^{13}C-NMR of **(L^2)GaCl$_2$** in THF-d$_8$, 300 MHz



(L^3)GaCl$_2$

Figure S1-20 - ^{1}H-NMR of **(L^3)GaCl$_2$** in THF-d$_8$, 300 MHz

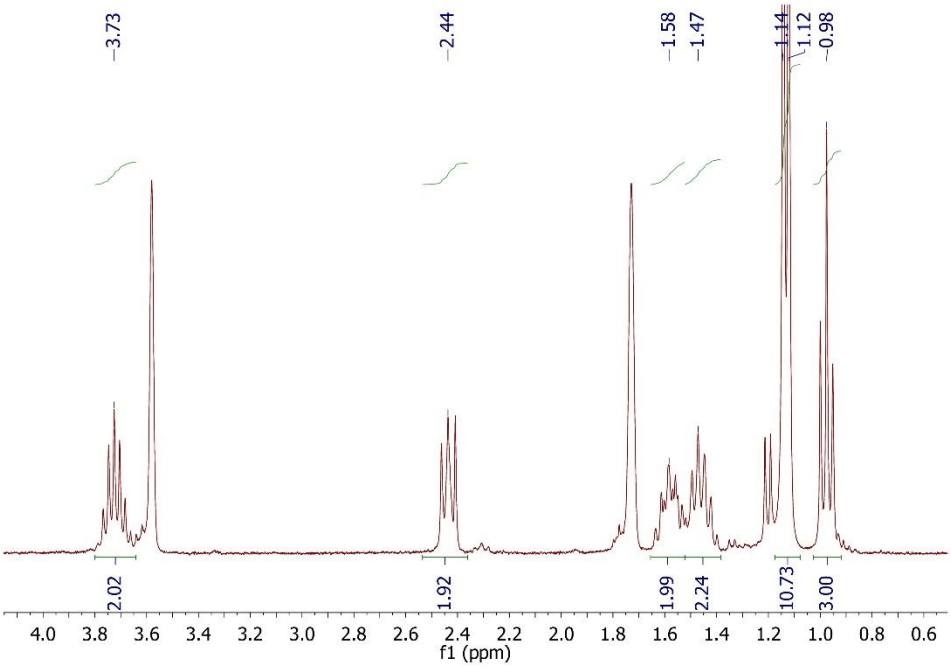
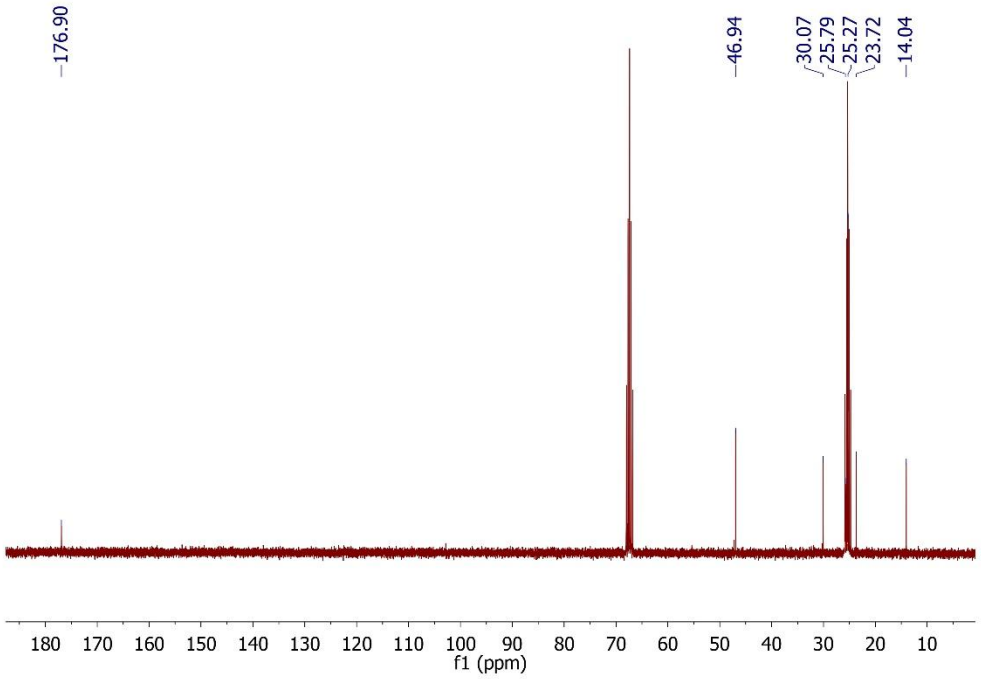


Figure S1-21 - ^{13}C-NMR of **(L^3)GaCl$_2$** in THF-d$_8$, 300 MHz



(L^4)GaCl$_2$

Figure S1-22 - ^{1}H-NMR of **(L^4)GaCl$_2$** in THF-d$_8$, 300 MHz

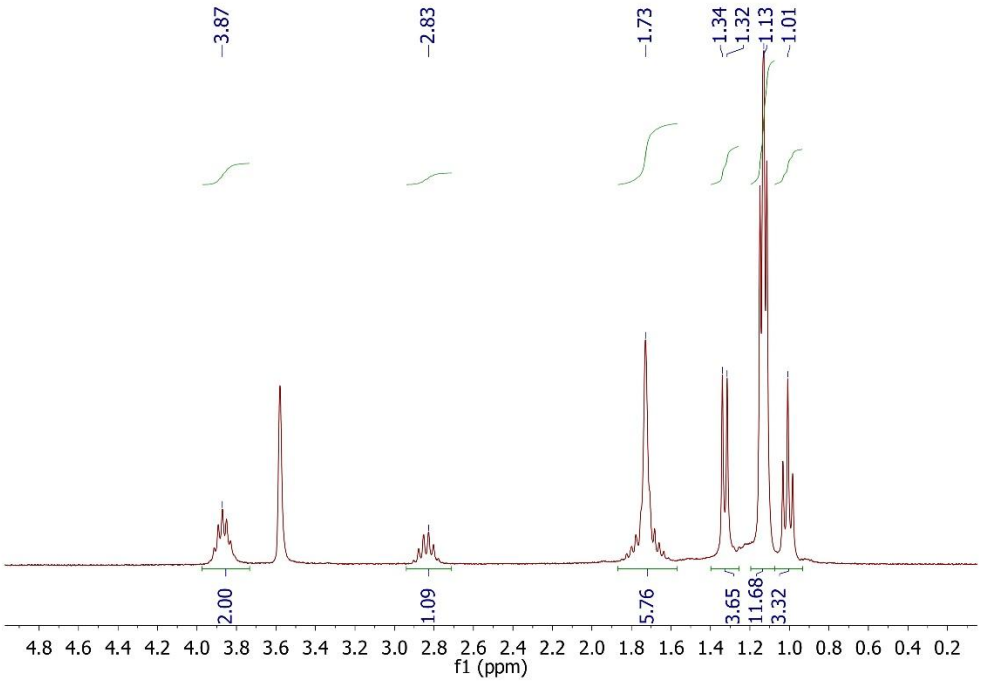
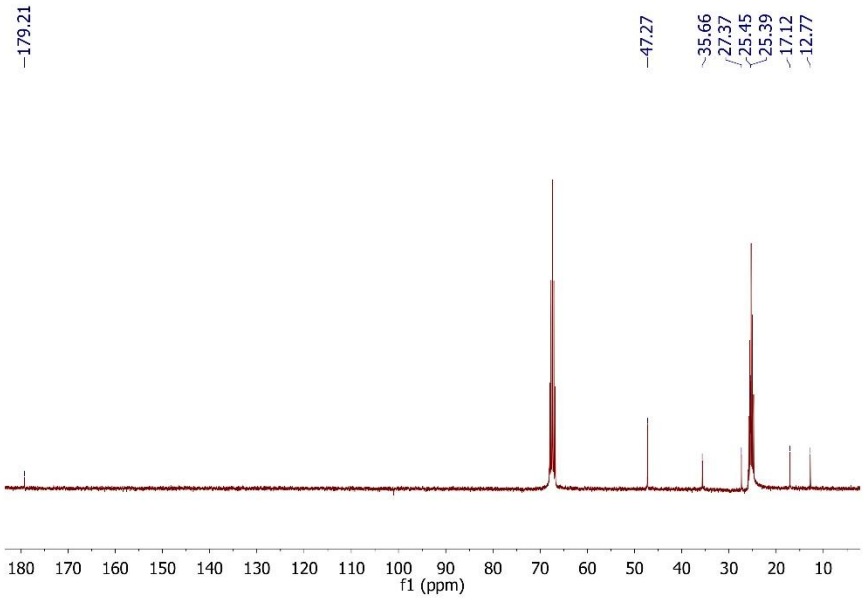


Figure S1-23 - ^{13}C-NMR of **(L^4)GaCl$_2$** in THF-d$_8$, 300 MHz



(L^5)GaCl$_2$

Figure S1-24 - ^{1}H-NMR of **(L^5)GaCl$_2$** in THF-d$_8$, 300

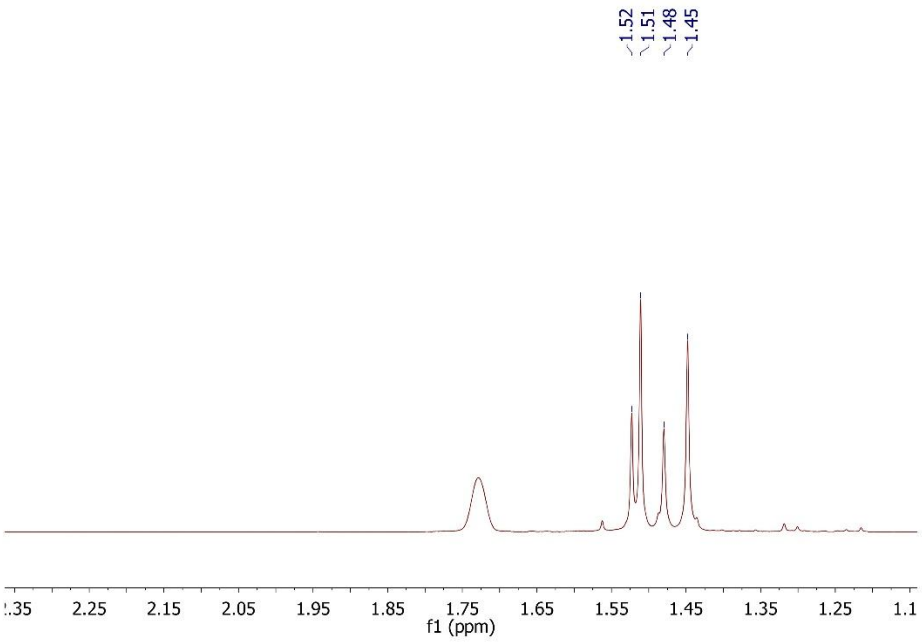
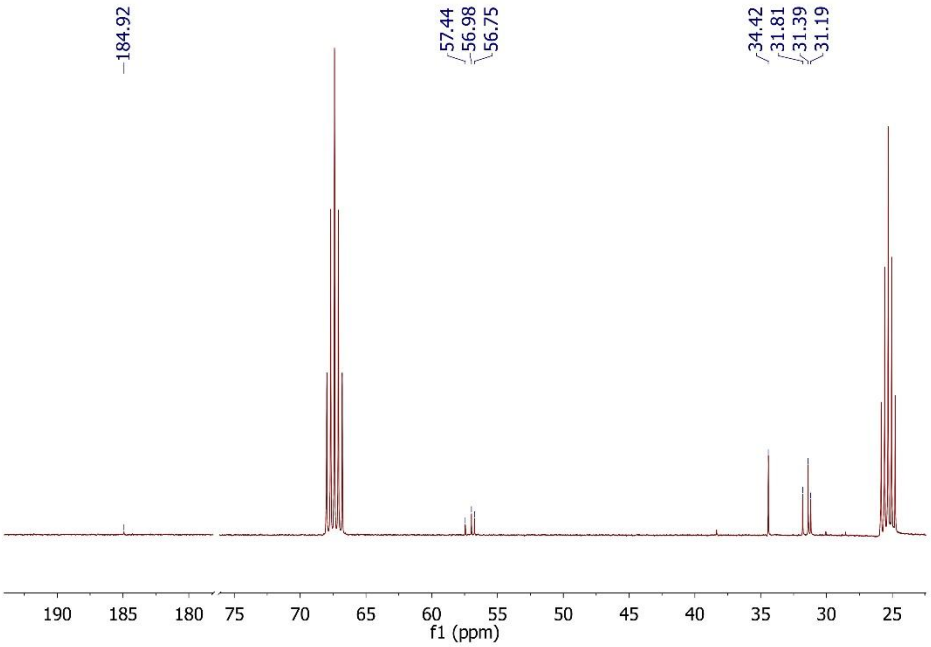


Figure S1-25 - ^{13}C-NMR of **(L^5)GaCl$_2$** in THF-d$_8$, 300 MHz



(L^7)GaCl$_2$

Figure S1-26 - ^{1}H-NMR of **(L^7)GaCl$_2$** in THF-d$_8$, 300 MHz

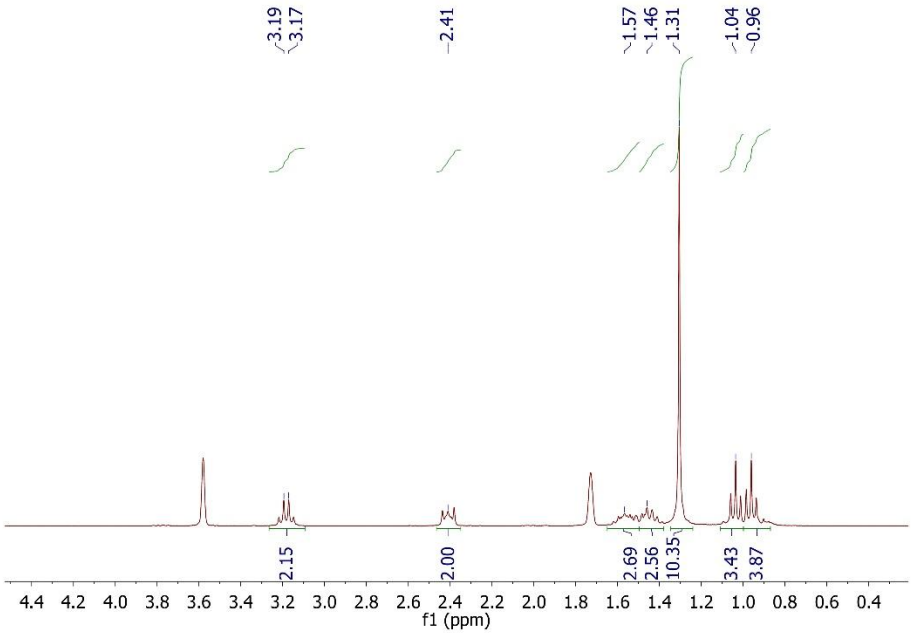
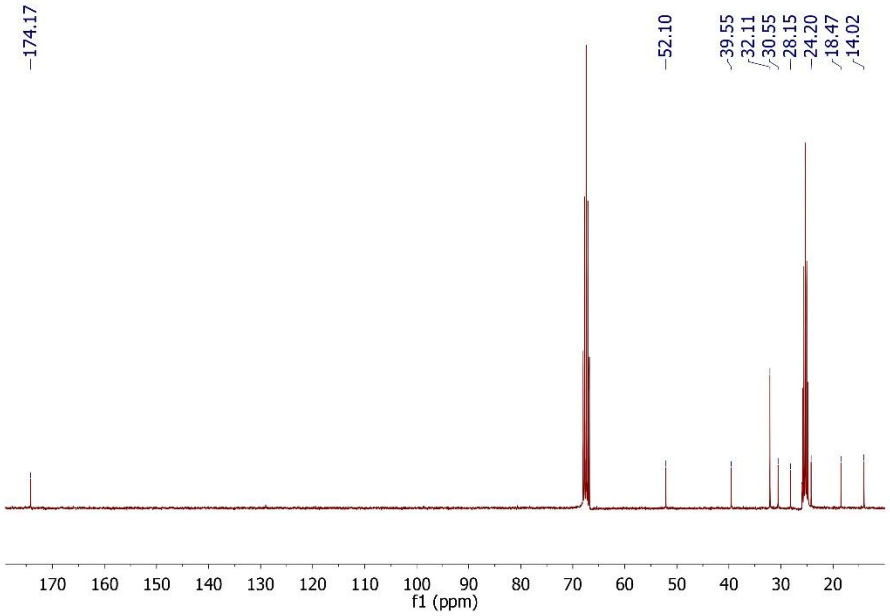


Figure S1-27 - ^{13}C-NMR of **(L^{7})GaCl$_2$** in THF-d$_8$, 300 MHz



(L^{9})GaCl$_2$

Figure S1-28 - ^{1}H-NMR of **(L^{9})GaCl$_2$** in THF-d$_8$, 300 MHz

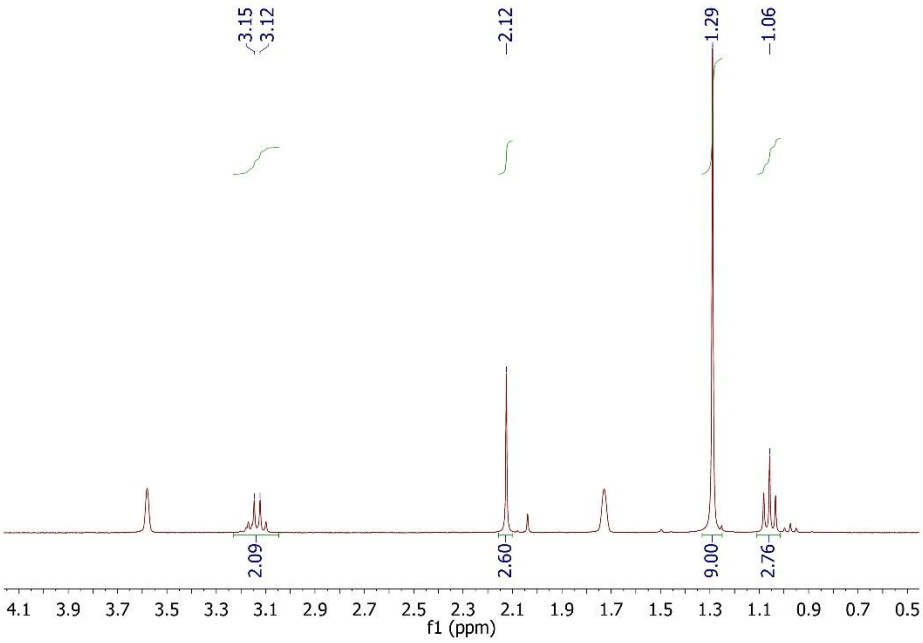
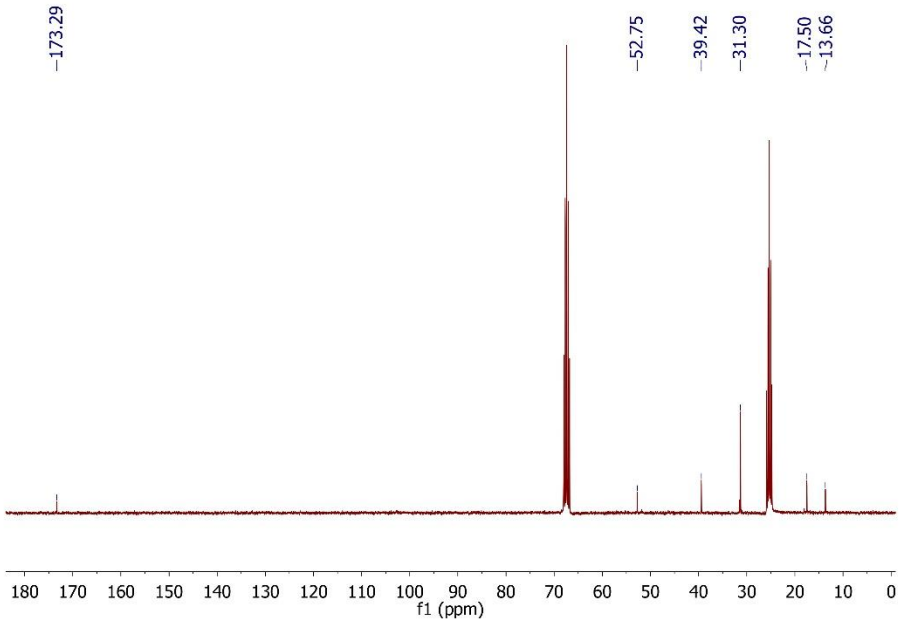
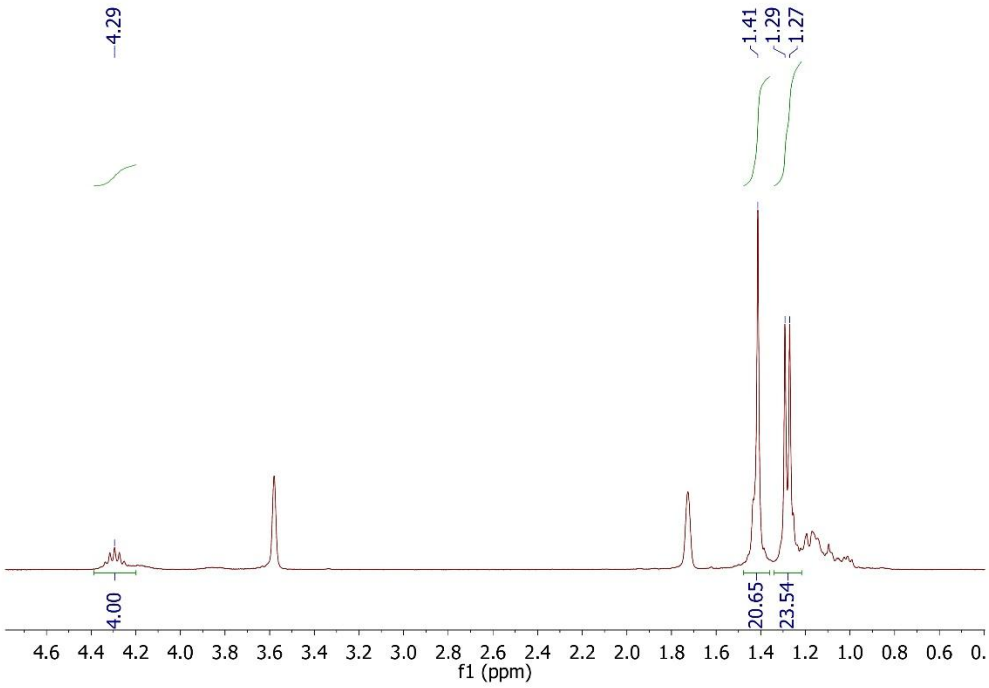


Figure S1-29 - ^{13}C-NMR of **(L^{9})GaCl$_2$** in THF-d$_8$, 300 MHz



$(L^1)_2$GaCl

Figure S1-30 - ^{1}H-NMR of **$(L^1)_2$GaCl** in THF-d_8, 300 MHz



(L^2)$_2$GaCl

Figure S1-31 - ^{1}H-NMR of **(L^2)$_2$GaCl** in C_6D_6, 300 MHz

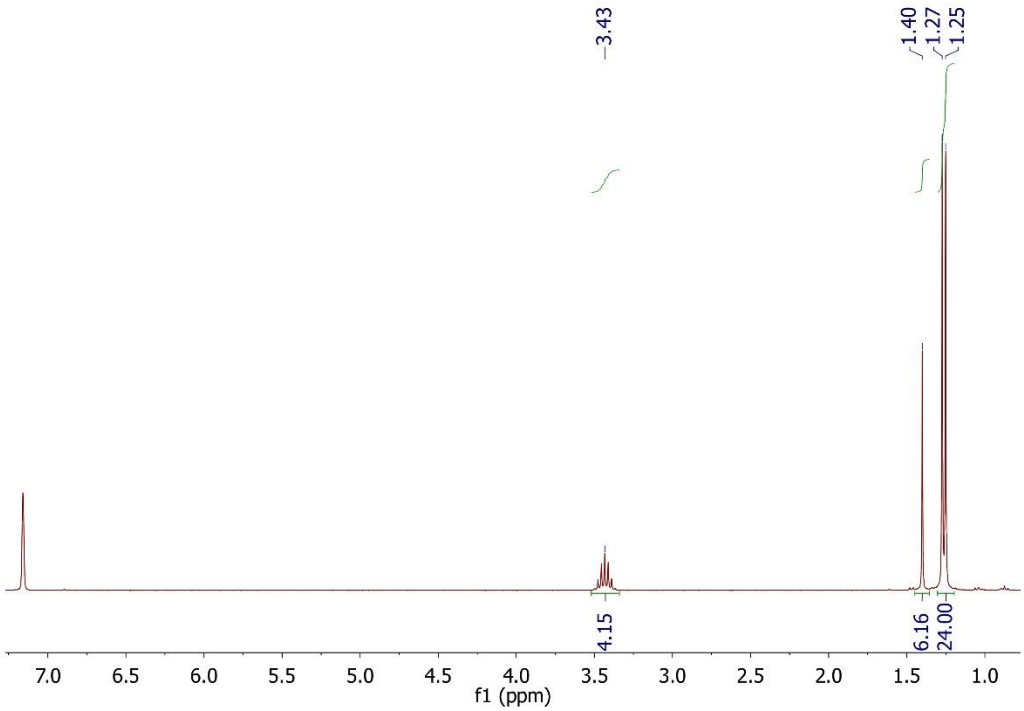
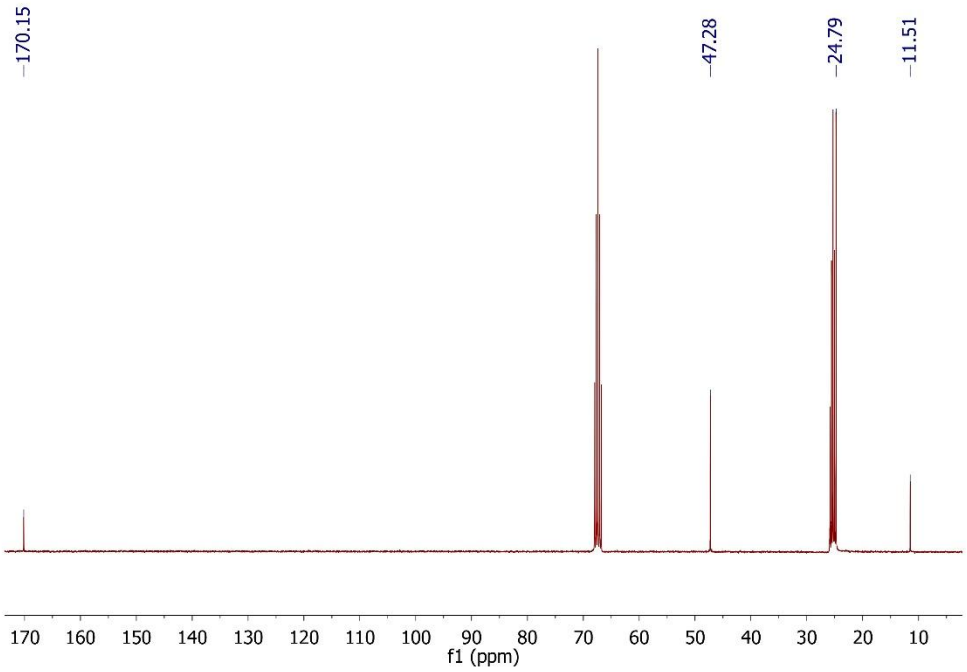


Figure S1-32 - ^{13}C-NMR of **(L^2)$_2$GaCl** in THF-d_8, 300 MHz



$(L^3)_2GaCl$

Figure S1-33 -1 ^{1}H-NMR of **$(L^3)_2GaCl$** in THF-d_8, 300 MHz

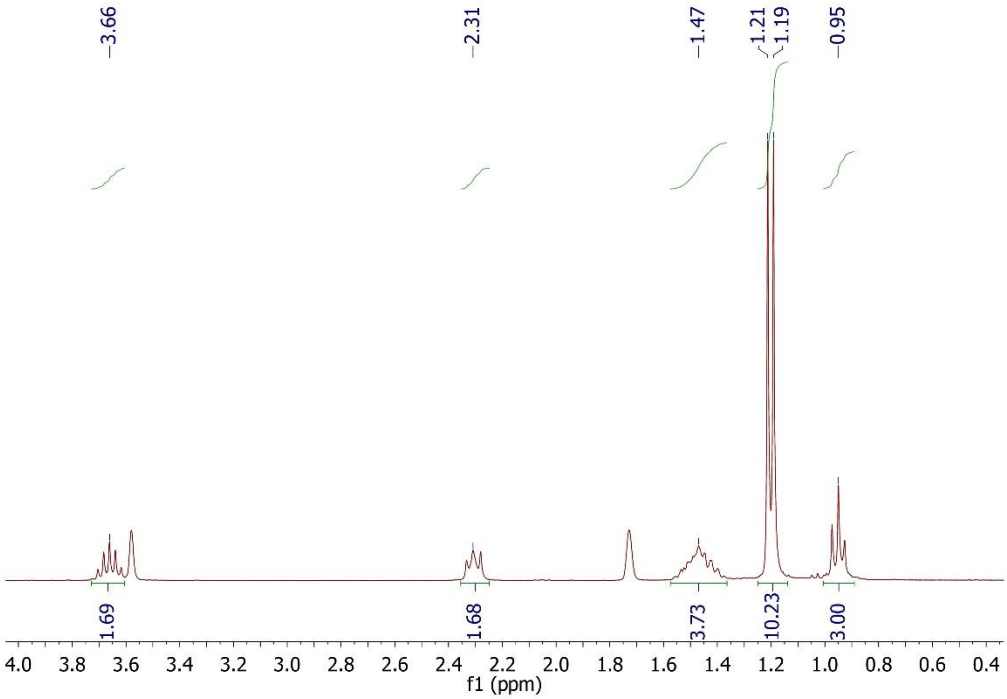
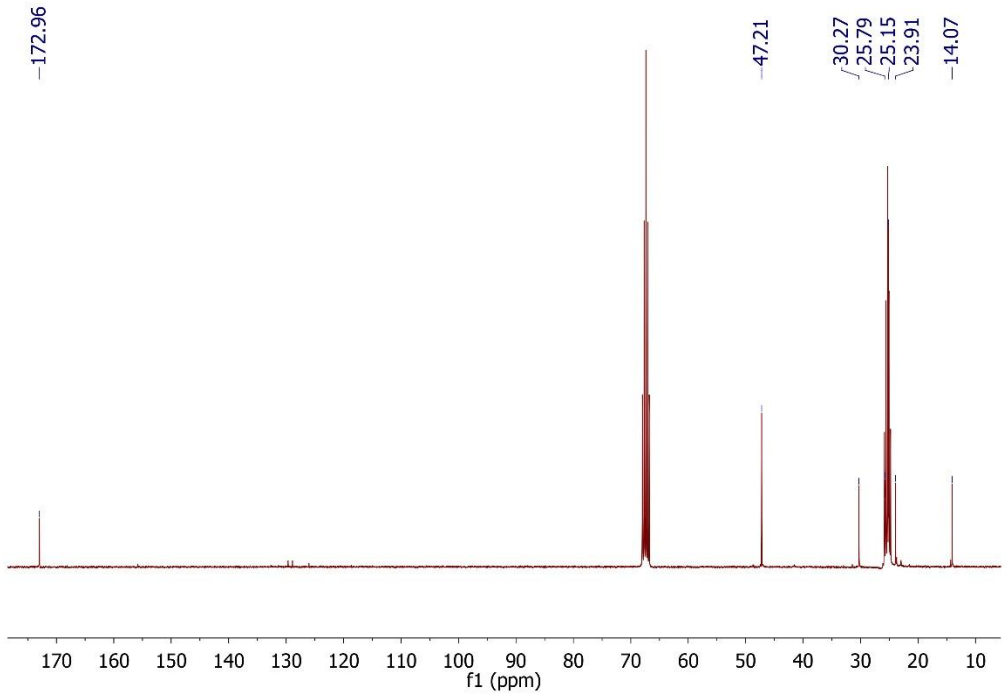


Figure S1-34 - ^{13}C-NMR of **$(L^3)_2GaCl$** in THF-d_8, 300 MHz



$(L^6)_2GaCl$

Figure S1-35 - ^{1}H-NMR of **$(L^6)_2GaCl$** in THF-d_8, 300 MHz

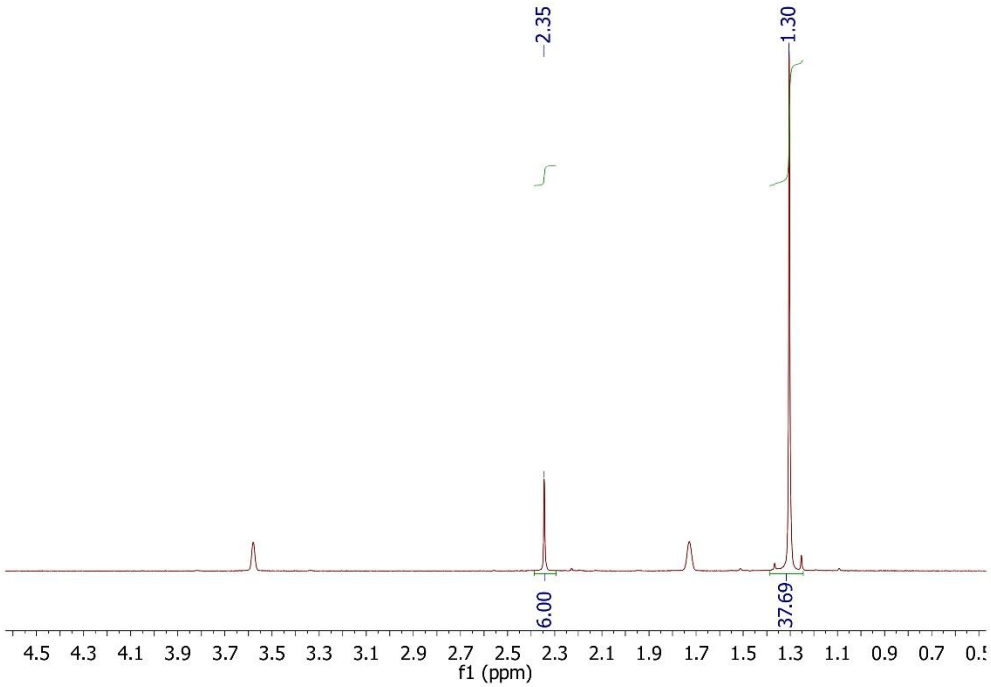
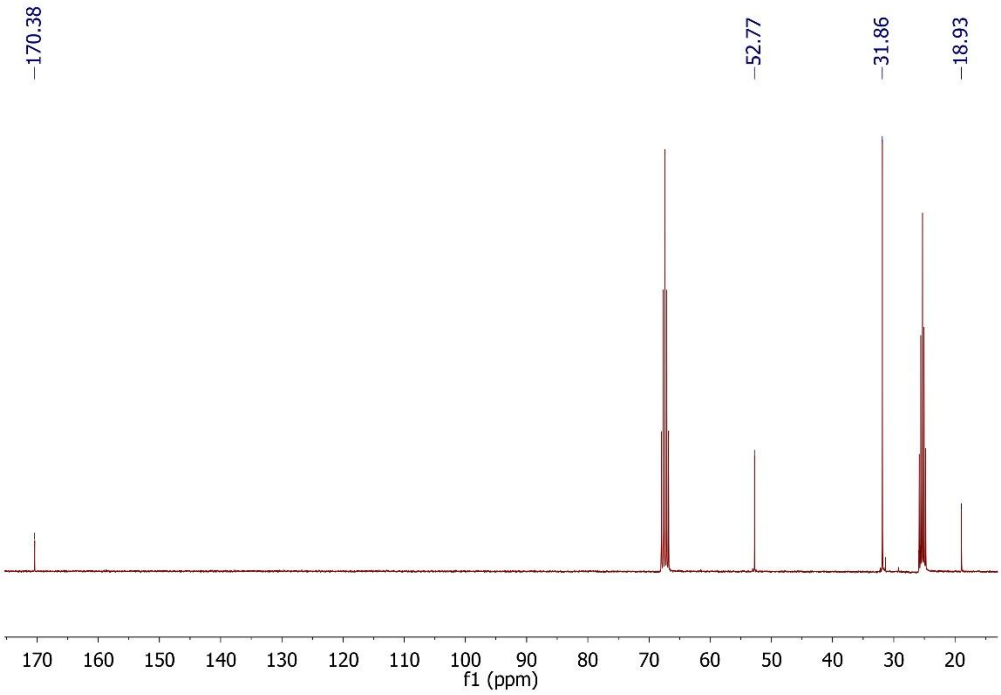


Figure S1-36 - ^{13}C-NMR of **$(L^6)_2GaCl$** in THF-d_8, 300 MHz



(L[1])GaMe$_2$

Figure S1-37 - ^{1}H-NMR of **(L[1])GaMe$_2$** in THF-d$_8$, 300 MHz

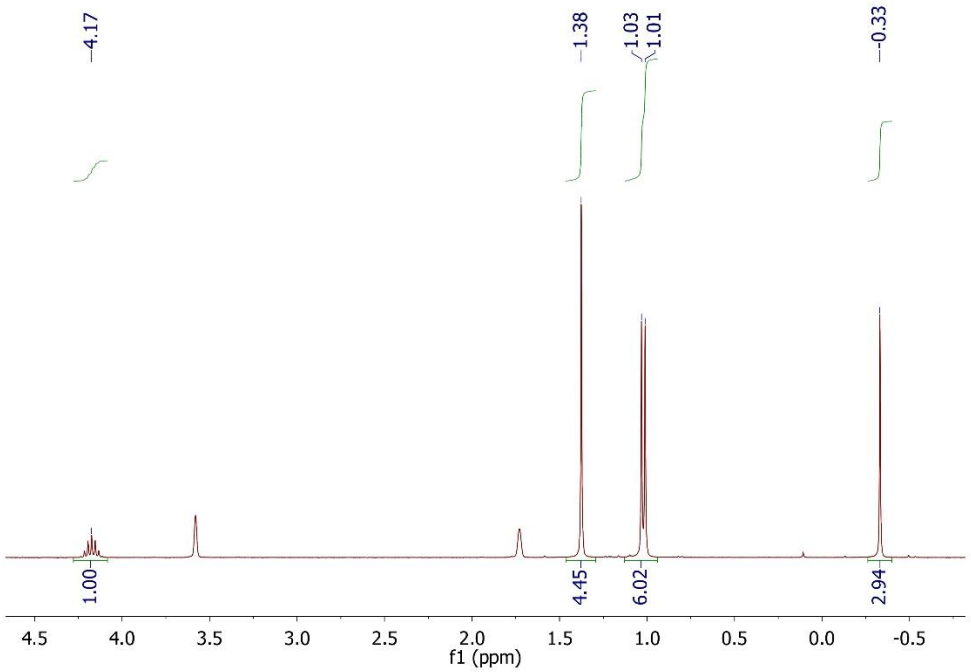
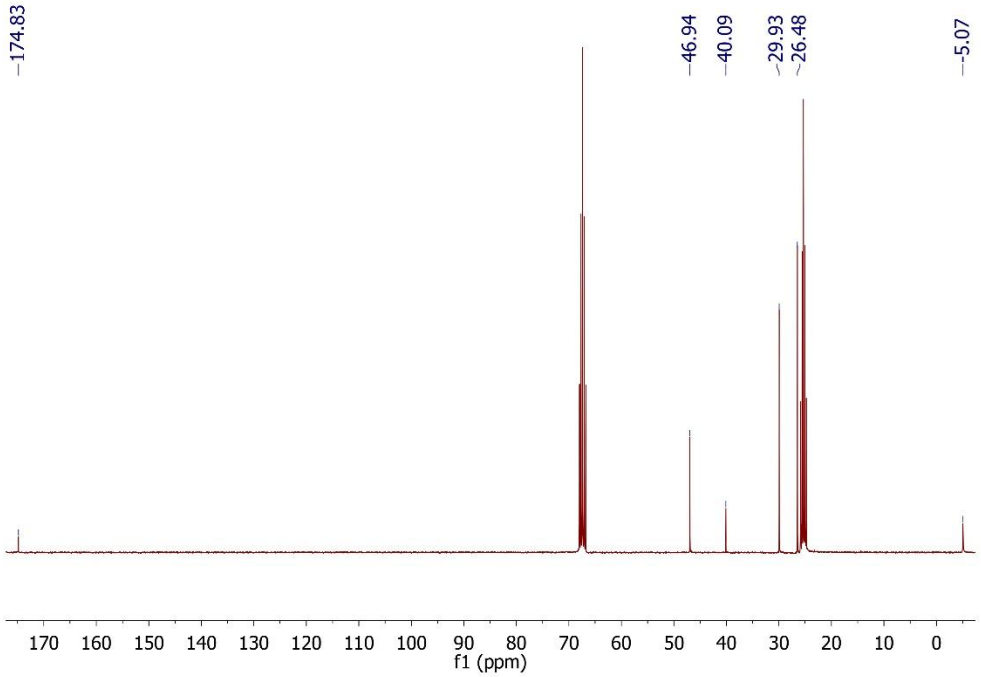


Figure S1-38 - ^{13}C-NMR of **(L[1])GaMe$_2$** in THF-d$_8$, 300 MHz



(L^2)GaMe$_2$

Figure S1-39 - ^{1}H-NMR of **(L^2)GaMe$_2$** in THF-d$_8$, 300 MHz

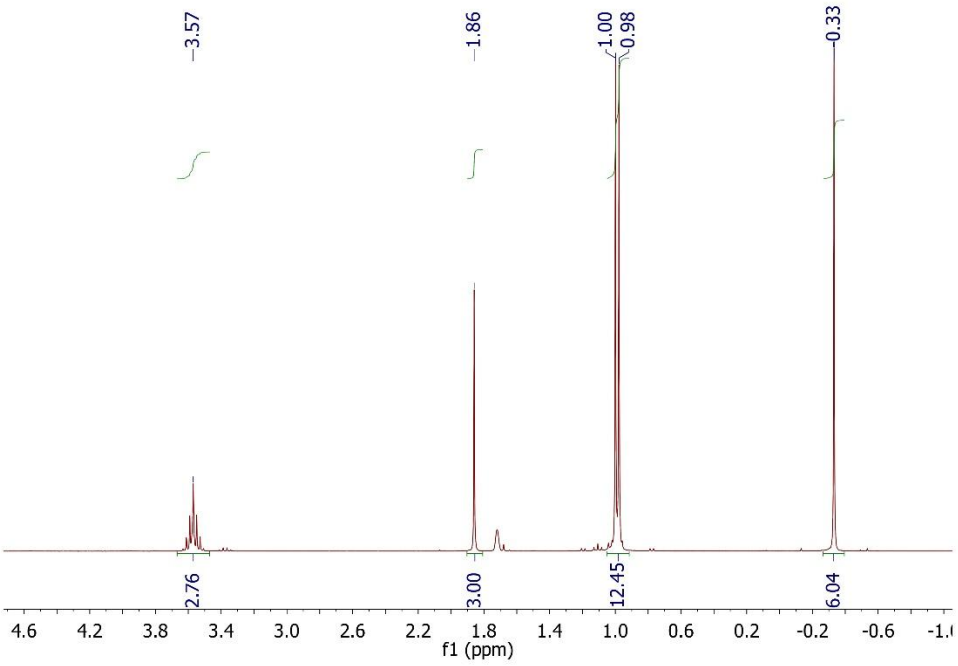
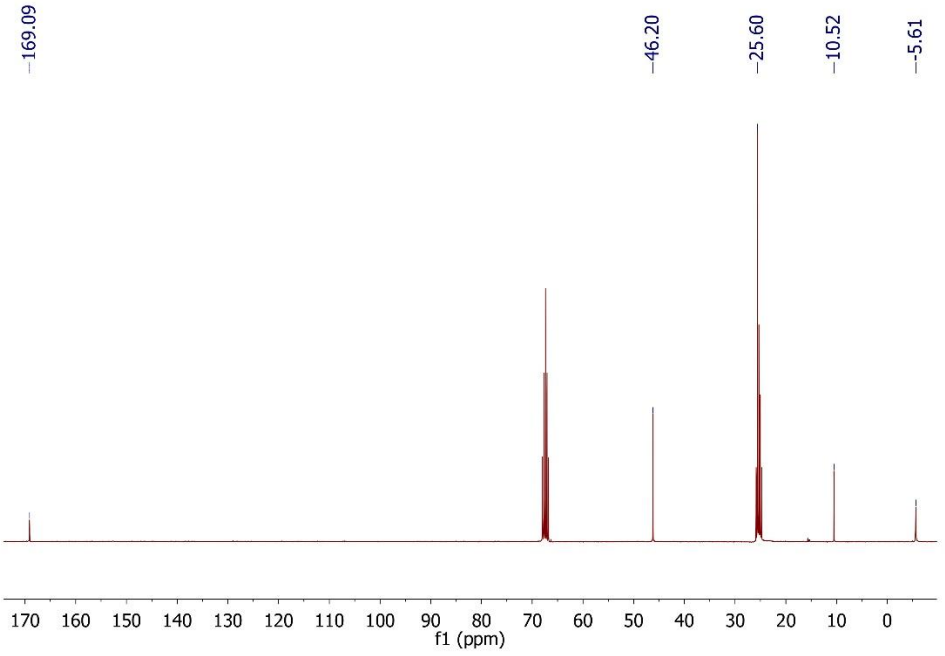


Figure S1-40 - ^{13}C-NMR of **(L^2)GaMe$_2$** in THF-d$_8$, 300 MHz



(L^3)GaMe$_2$

Figure S1-41 - ^{1}H-NMR of **(L^3)GaMe$_2$** in THF-d$_8$, 300 MHz

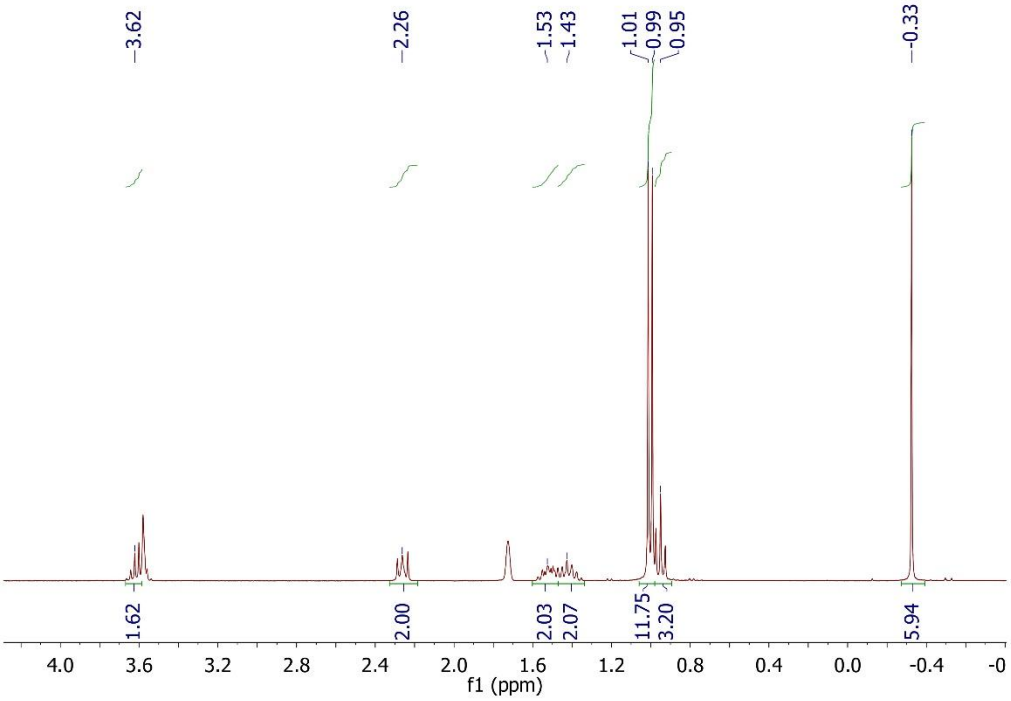
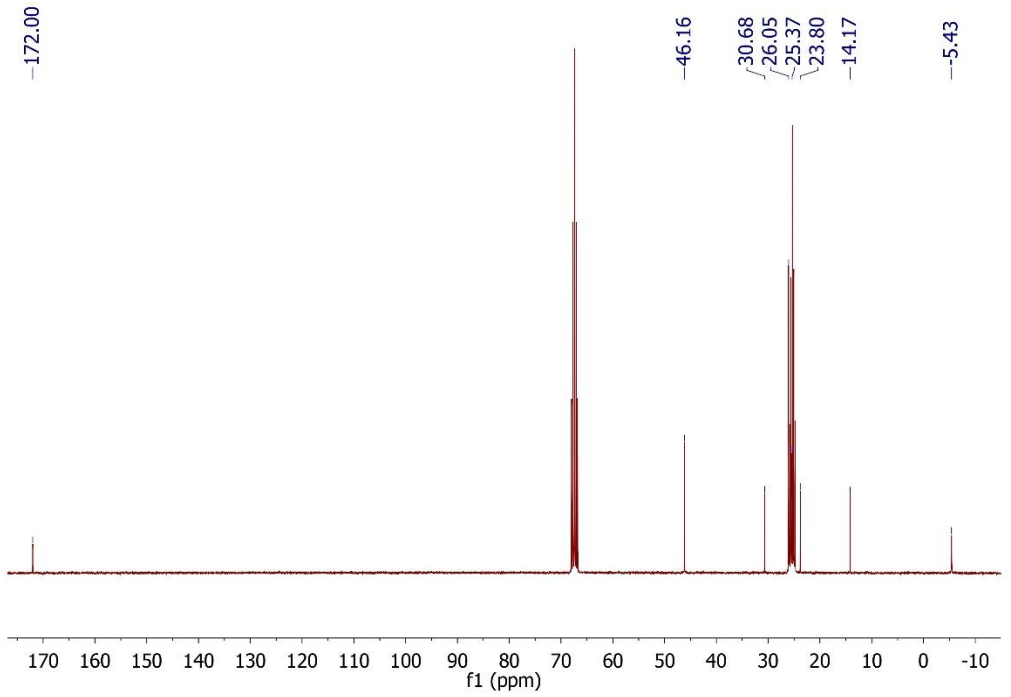


Figure S1-42 - ^{13}C-NMR of **(L^3)GaMe$_2$** in THF-d$_8$, 300 MHz



(L^4)GaMe$_2$

Figure S1-43 - ^{1}H-NMR of **(L^4)GaMe$_2$** in THF-d$_8$, 300 MHz

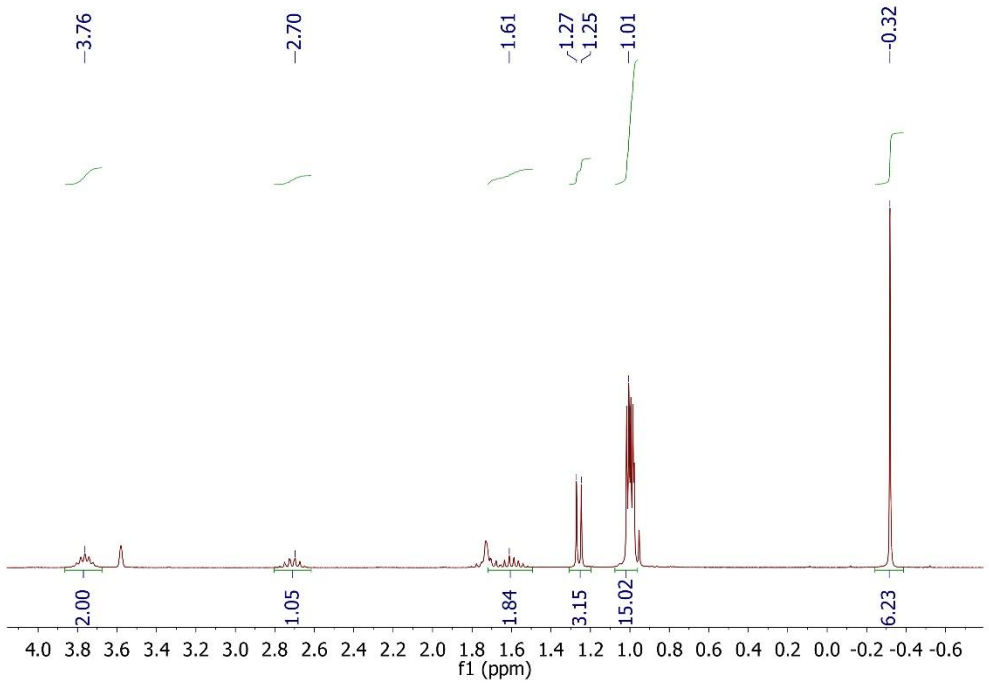
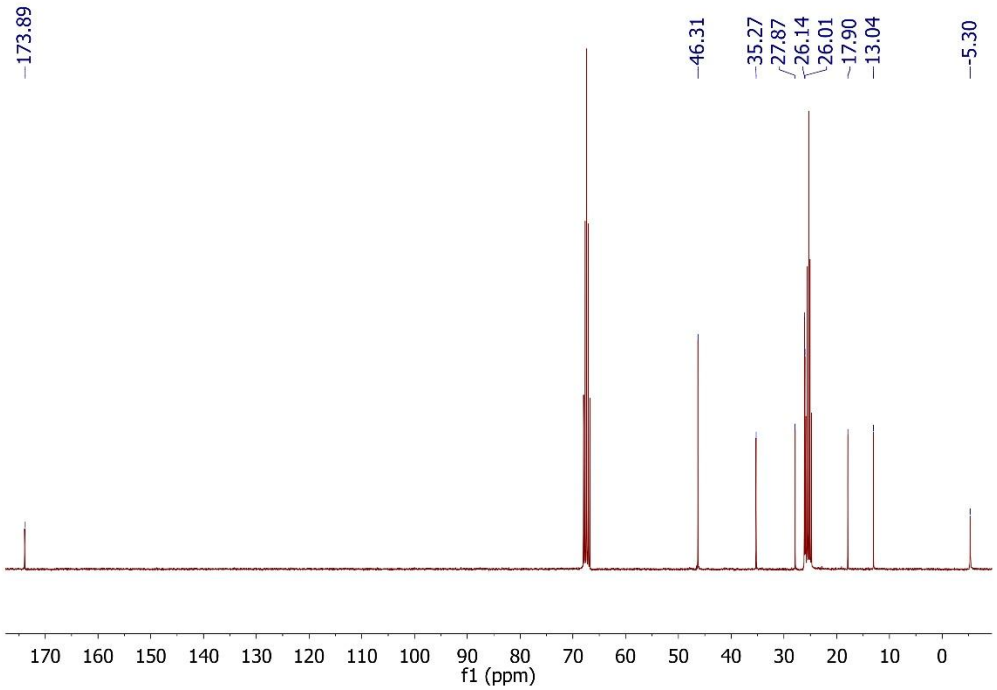


Figure S1-44 - ^{13}C-NMR of **(L^4)GaMe$_2$** in THF-d$_8$, 300 MHz



(L^5)GaMe$_2$

Figure S1-45 - ^{1}H-NMR of **(L^5)GaMe$_2$** in THF-d$_8$, 300 MHz.

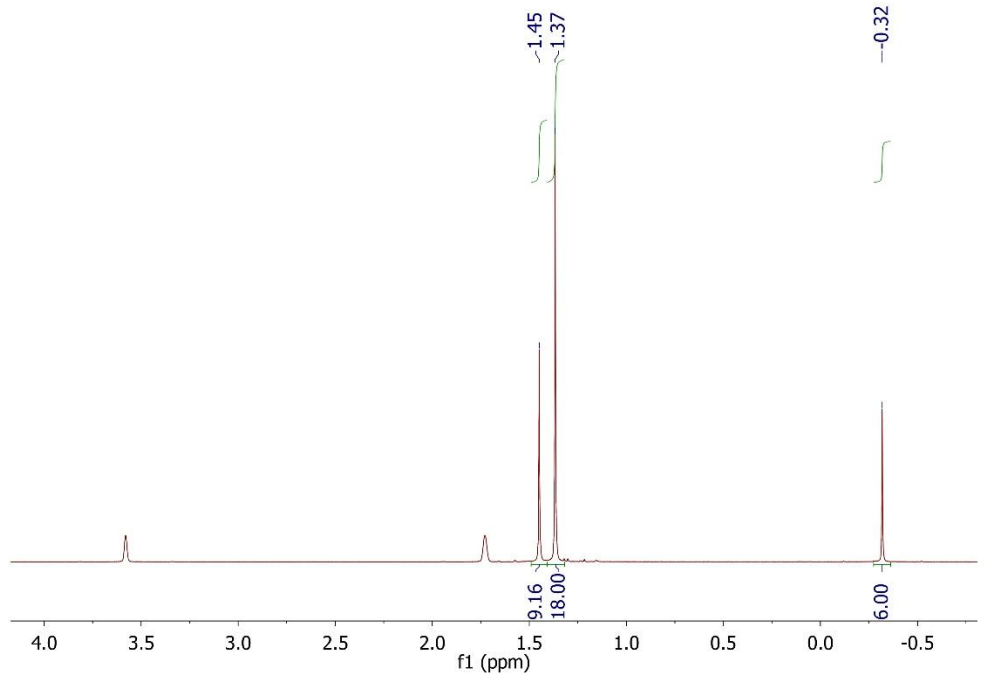
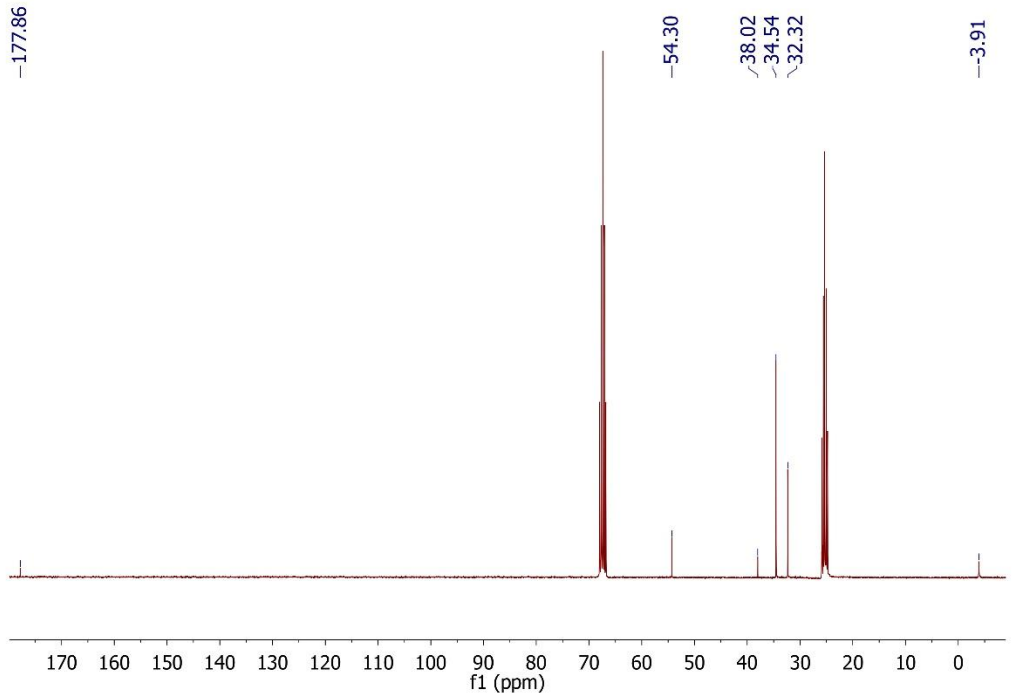


Figure S1-46 - ^{13}C-NMR of **(L^5)GaMe$_2$** in THF-d$_8$, 300 MHz



(L^7)GaMe$_2$

Figure S1-47 - ^{1}H-NMR of **(L^7)GaMe$_2$** in THF-d$_8$, 300 MHz.

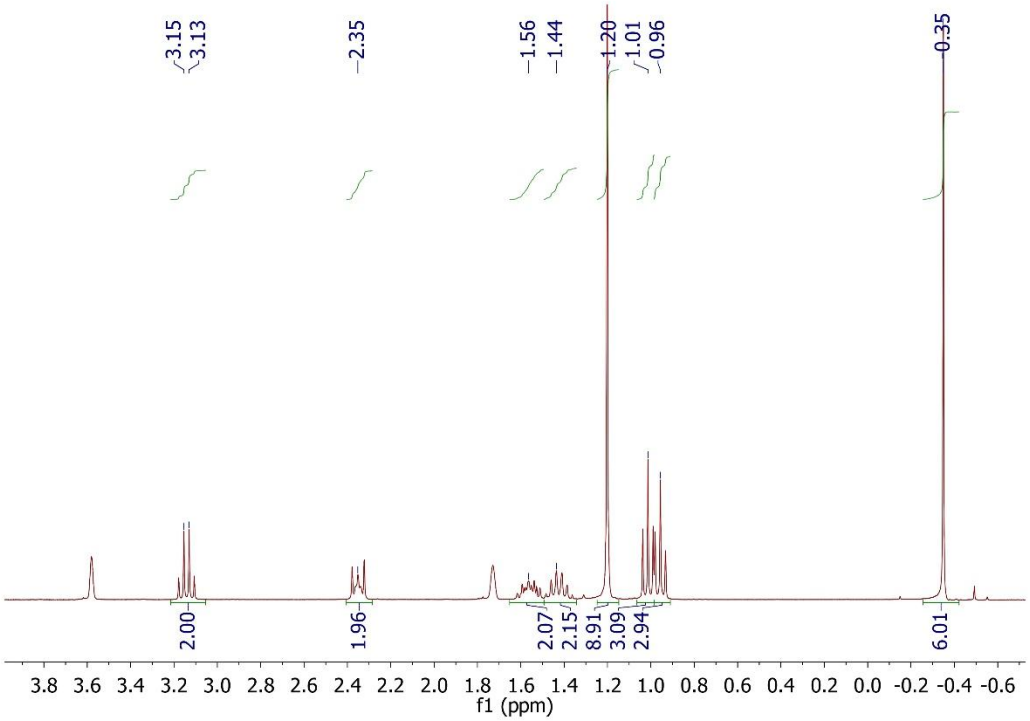
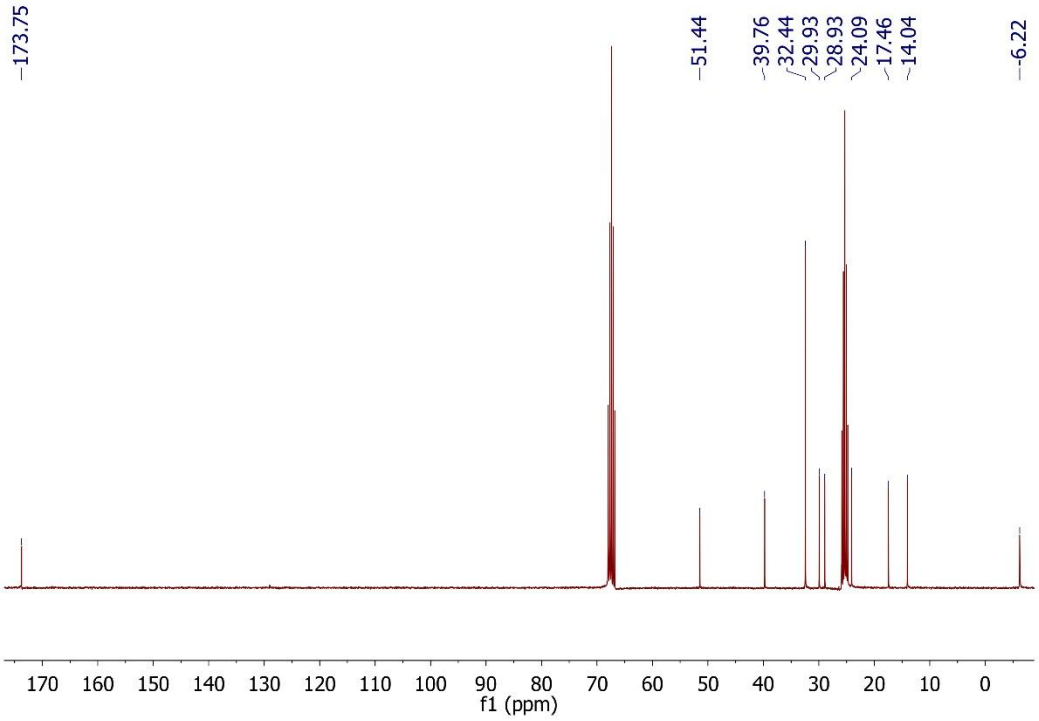


Figure S1-48 - ^{13}C-NMR of **(L^7)GaMe$_2$** in THF-d$_8$, 300 MHz



(L[8])GaMe$_2$

Figure S1-49 - ^{1}H-NMR of **(L[8])GaMe$_2$** in THF-d$_8$, 300 MHz

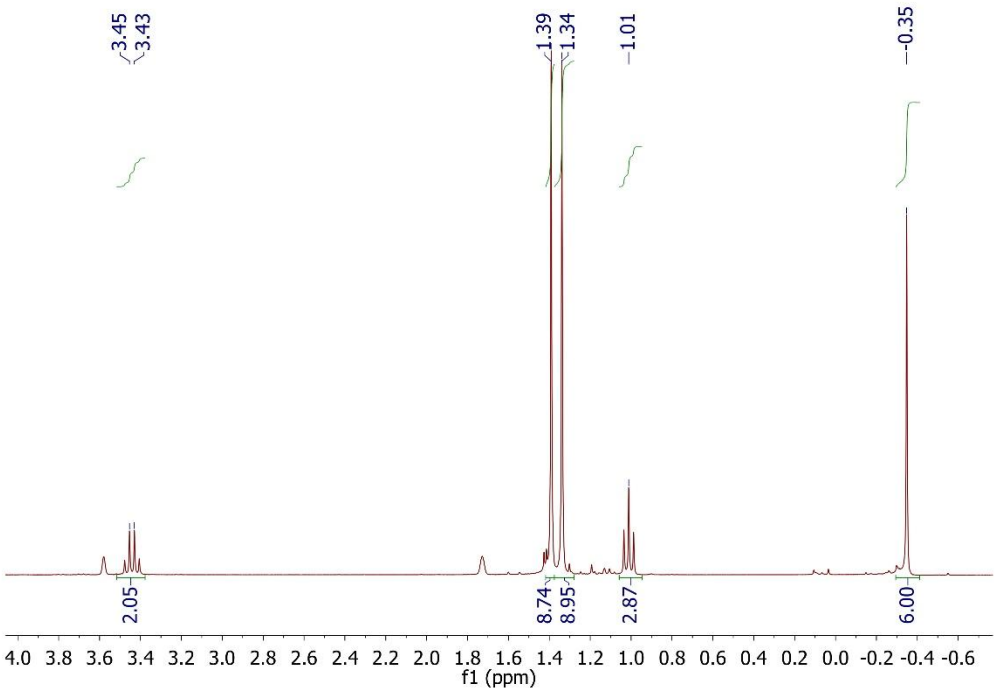
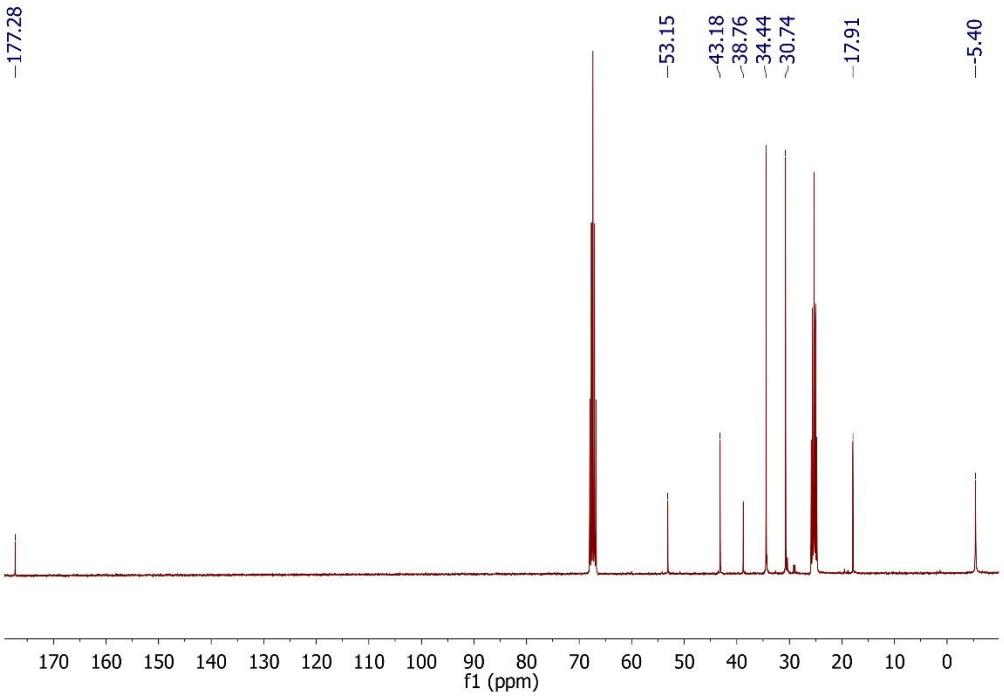


Figure S1-50 - ^{13}C-NMR of **(L[8])GaMe$_2$** in THF-d$_8$, 300 MHz



(L^9)GaMe$_2$

Figure S1-51 - ^{1}H-NMR of **(L^9)GaMe$_2$** in THF-d$_8$, 300 MHz

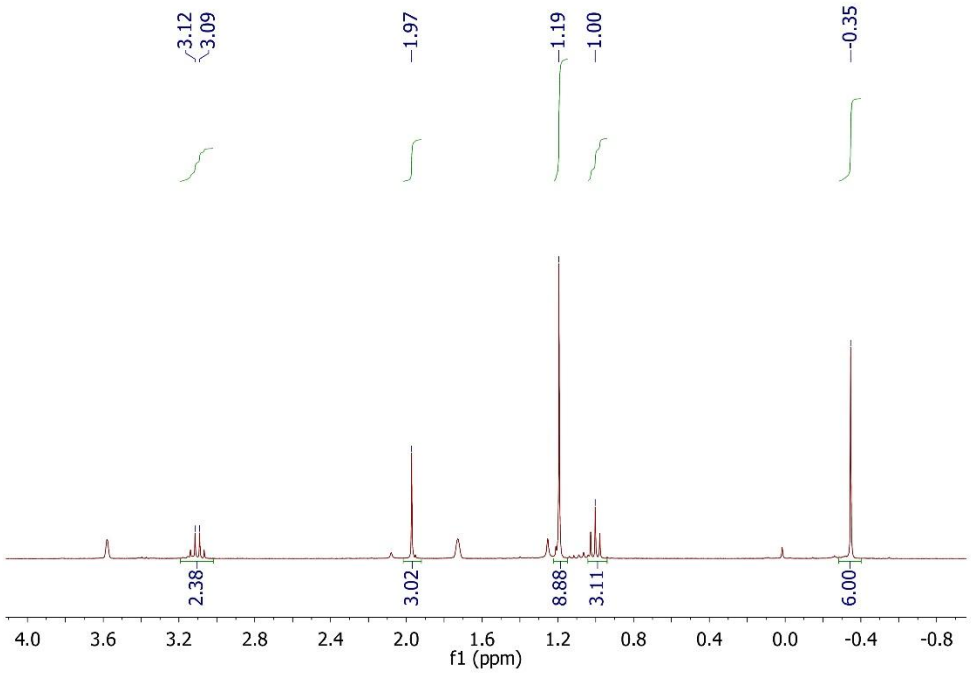
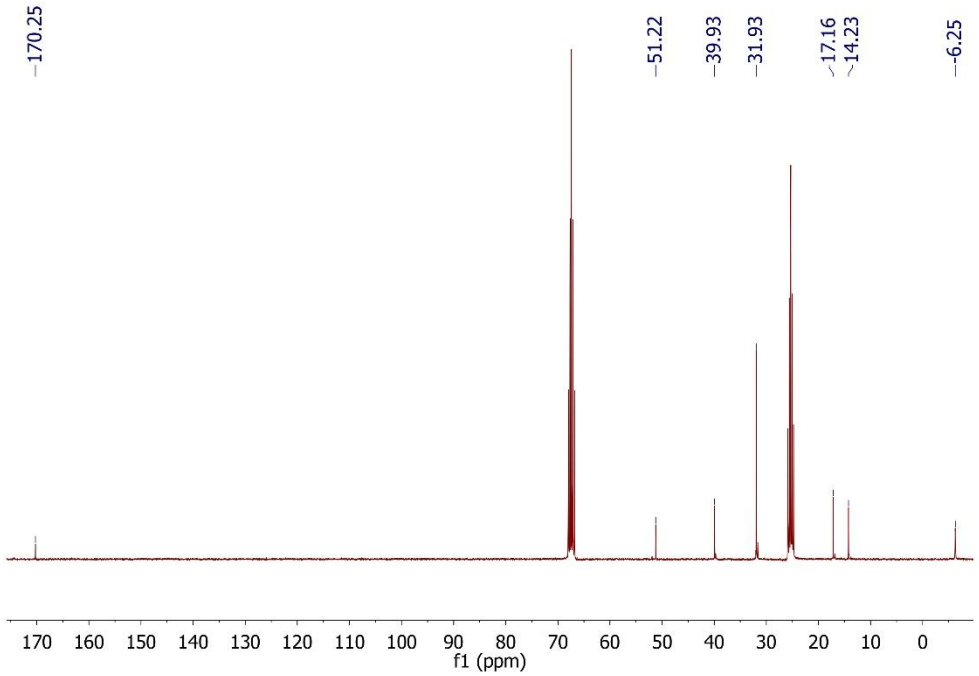


Figure S1-52 - ^{13}C-NMR of **(L^9)GaMe$_2$** in THF-d$_8$, 300 MHz



$(L^2)_2$GaMe

Figure S1-53 - ^{1}H-NMR of **$(L^2)_2$GaMe** in C_6D_6, 300 MHz

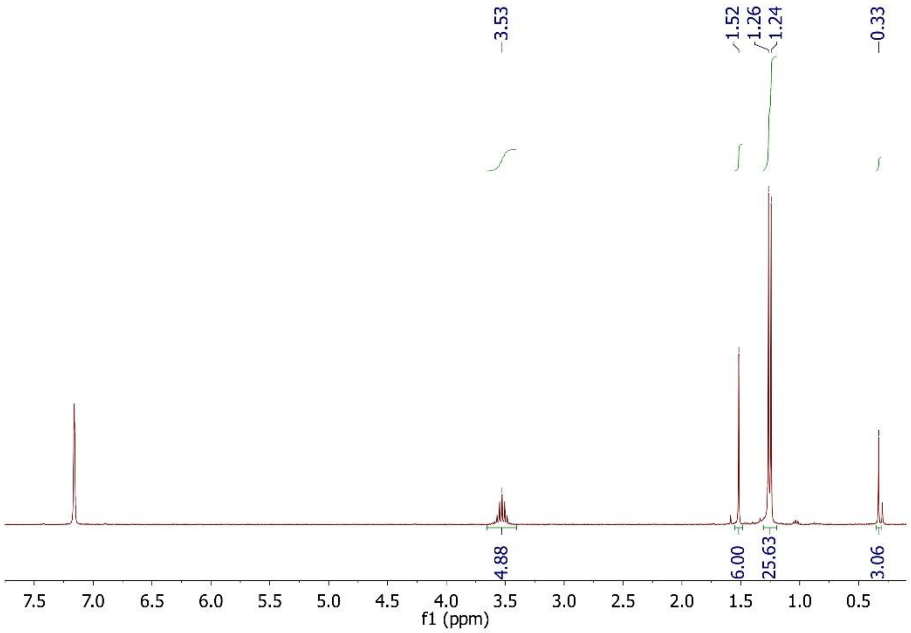
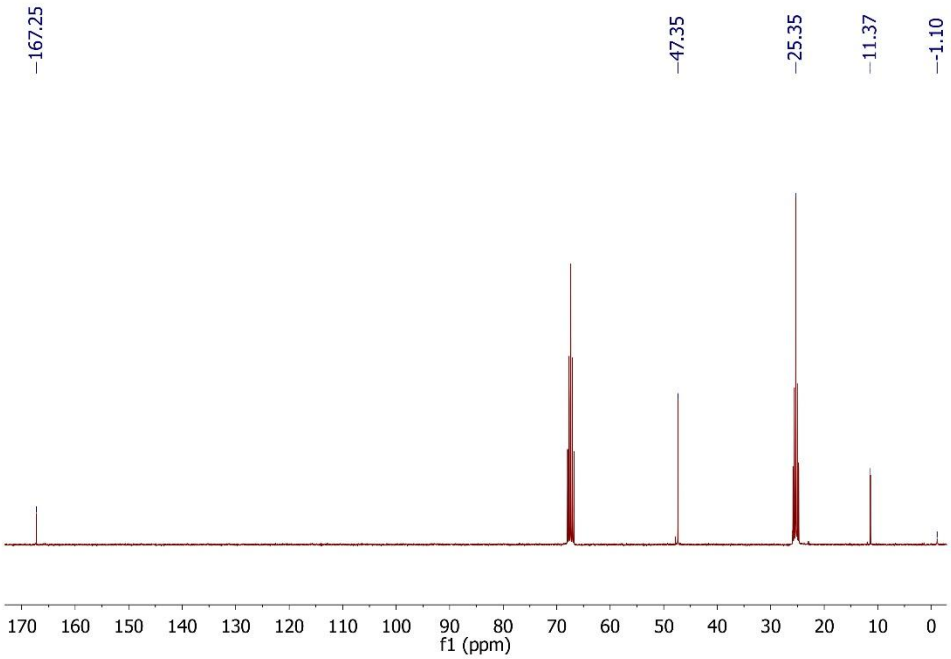


Figure S1-54 - ^{13}C-NMR of **$(L^2)_2$GaMe** in THF-d_8, 300 MHz



$(L^3)_2$GaMe

Figure S1-55 - ^{1}H-NMR of **$(L^3)_2$GaMe** in THF-d_8, 300 MHz

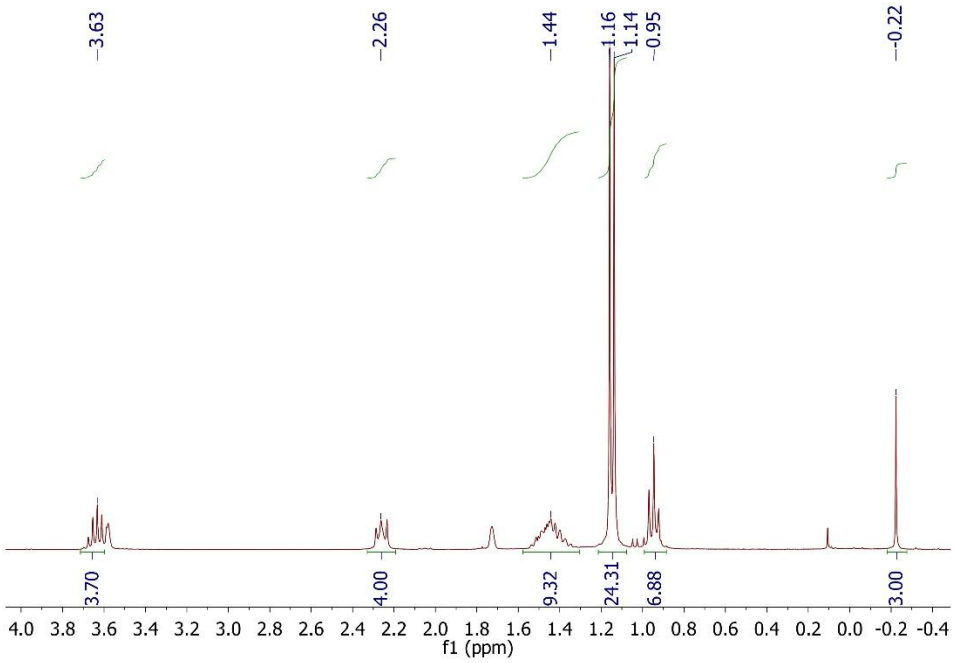
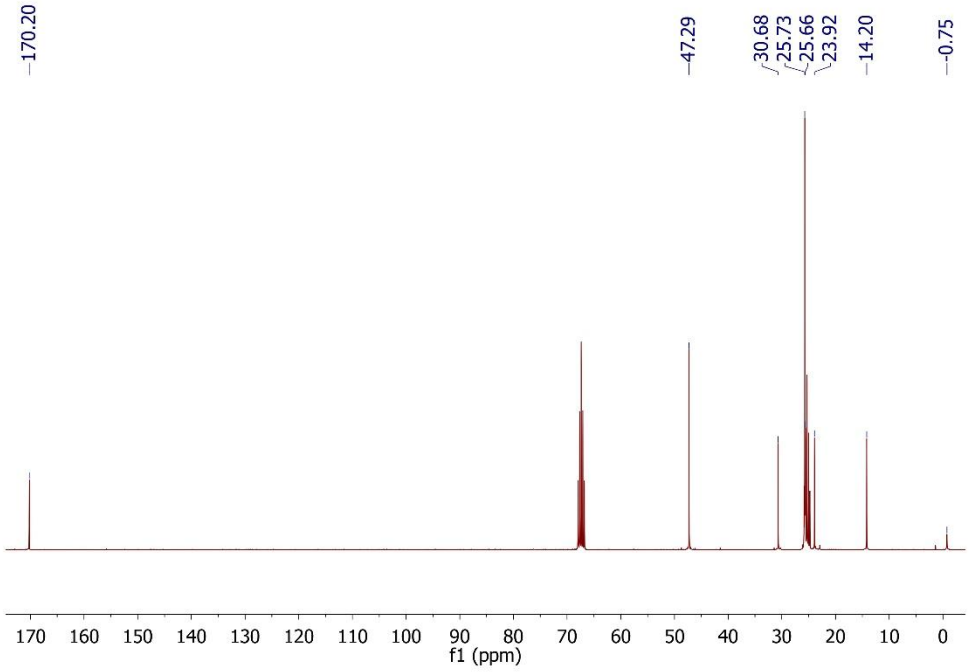


Figure S1-56 - ^{13}C-NMR of **$(L^3)_2$GaMe** in THF-d_8, 300 MHz



$(L^6)_2GaMe$

Figure S1-57 - ^{1}H-NMR of **$(L^6)_2GaMe$** in THF-d_8, 300 MHz

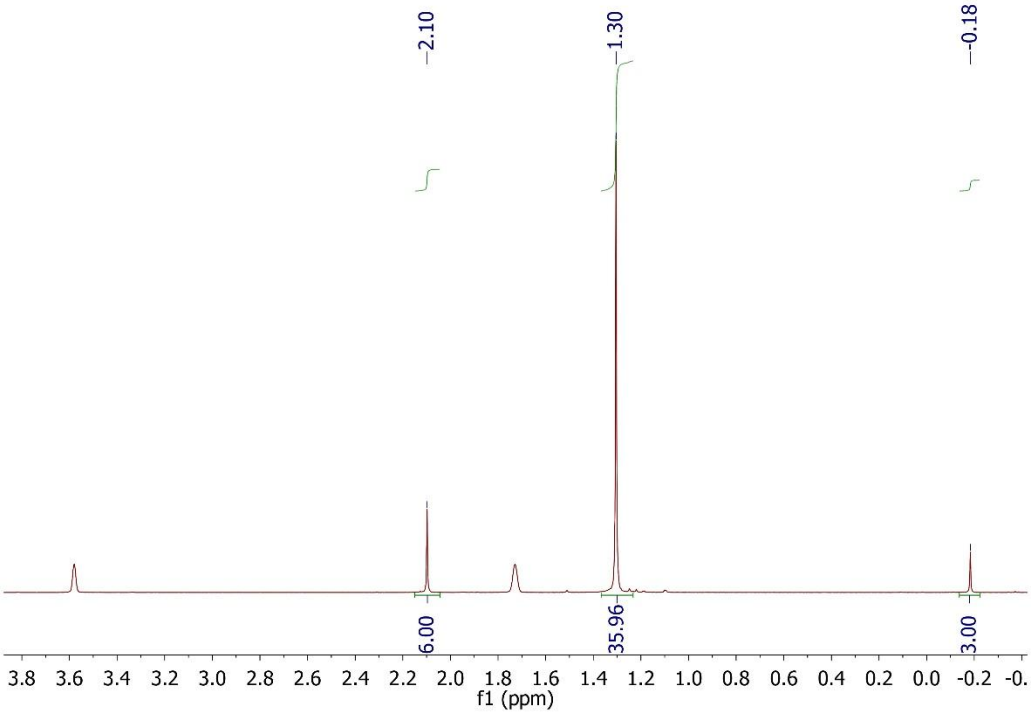
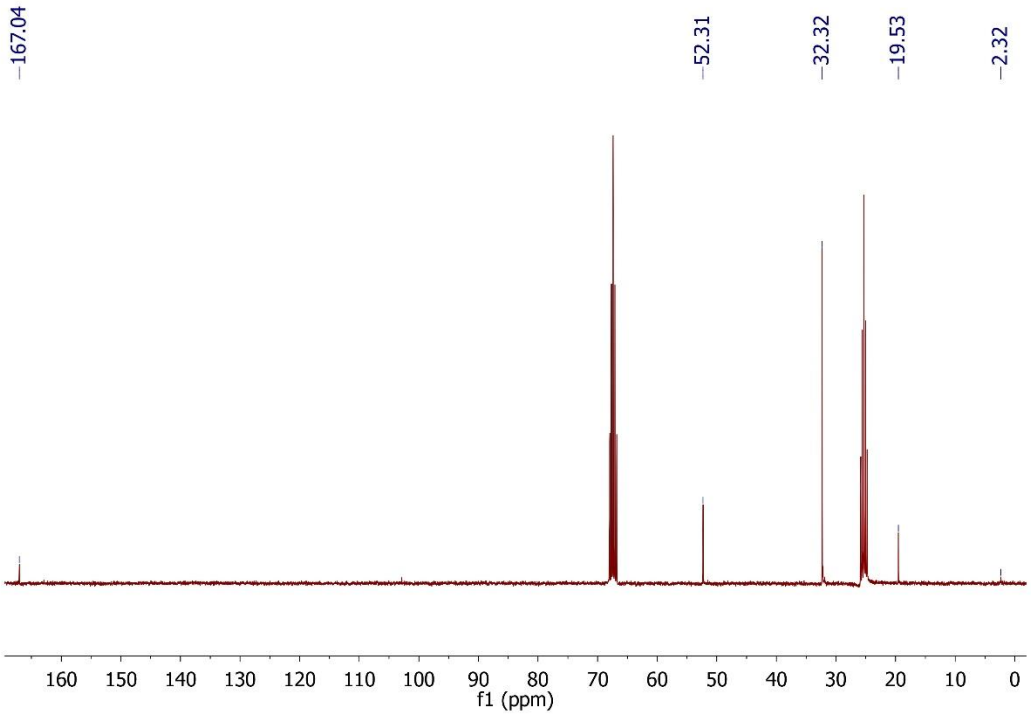


Figure S1-58 - ^{13}C-NMR of **$(L^6)_2GaMe$** in THF-d_8, 300 MHz



2. X-ray crystallography of molecular compounds

Table S1 - Crystal data and structure refinement of **$(L^4)GaCl_2$** and **$(L^1)GaCl_2$**.

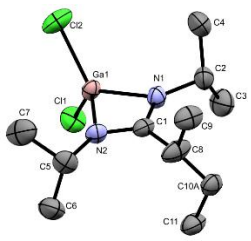
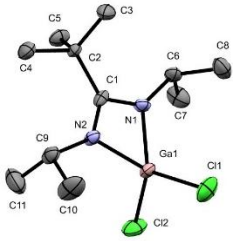
			
		$(L^4)GaCl_2$	**$(L^1)GaCl_2$**
Crystallised from		pentane	Et_2O
Empirical formula		$C_{11}H_{23}Cl_2GaN_2$	$C_{11}H_{23}GaN_2$
Formula weight [g mol^{-1}]		323.93	323.93
Crystal colour, habit		colourless, plate	colourless, plate
Crystal dimensions [mm^3]		0.38 × 0.32 × 0.1	1.2 × 0.6 × 0.4
Temperature [K]		150.01	150(2)
Crystal system		orthorhombic	monoclinic
Space group		$P2_12_12_1$	$P2_1/n$
Z		4	8
2θ range for cell determination [°]		5.574 to 56.564	2.802 to 60.248
Unit cell parameters	a [Å]	8.3253(4)	17.4120(7)
	b [Å]	12.4177(7)	11.1790(12)
	c [Å]	15.2544(7)	17.4180(12)
	α [°]	90	90
	β [°]	90	113.100(2)
	γ [°]	90	90
	V [Å^3]	1577.02(14)	3118.6(4)
D_x [g cm^{-3}]		1.364	1.380
F(000)		672.0	1344.0
μ [mm^{-1}]		2.064	2.087
Radiation		MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected		7902	9174
Symmetry-independent reflections		3905	9174
Data/restraints/parameters		3905/4/167	9174/0/304
Goodness of fit		1.042	1.149
Final R indexes [I>=2σ (I)]		R_1 = 0.0309	R_1 = 0.0371
		wR_2 = 0.0745	wR_2 = 0.0779
Final R indexes [all data]		R_1 = 0.0365	R_1 = 0.0558
		wR_2 = 0.0776	wR_2 = 0.0881
$\Delta\rho$ (max; min) [e Å^{-3}]		0.34; -0.30	0.88; -0.68
CCDC number		2444176	2444177

Table S2 - Crystal data and structure refinement of **$(L^3)GaCl_2$** and **$(L^5)GaCl_2$**.

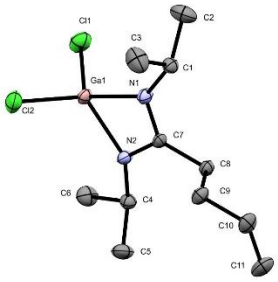
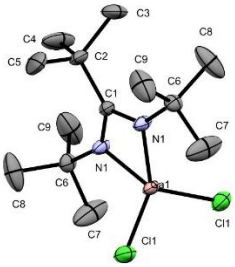
		 **$(L^3)GaCl_2$**	 **$(L^5)GaCl_2$**
Crystallised from		pentane	pentane
Empirical formula		$C_{11}H_{23}Cl_2GaN_2$	$C_{13}H_{27}Cl_2GaN_2$
Formula weight [g mol^{-1}]		323.93	351.98
Crystal colour, habit		colourless, plate	colourless, plate
Crystal dimensions [mm^3]		0.8 × 0.6 × 0.08	0.24 × 0.14 × 0.14
Temperature [K]		149.99	149.99
Crystal system		monoclinic	trigonal
Space group		*P2$_1$/c*	*P3$_2$21*
Z		4	3
2θ range for cell determination [°]		5.286 to 60.068	5.59 to 60.27
Unit cell parameters	*a* [Å]	11.1300(14)	9.3037(7)
	b [Å]	8.8553(11)	9.3037(7)
	c [Å]	15.859(2)	17.0719(14)
	α [°]	90	90
	β [°]	99.543(4)	90
	γ [°]	90	120
	V [Å3]	1541.5(3)	1279.7(2)
D_x [g cm^{-3}]		1.396	1.370
F(000)		672.0	552.0
μ [mm^{-1}]		2.111	1.913
Radiation		MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected		24162	48766
Symmetry-independent reflections		4515	2516
Data/restraints/parameters		4515/0/150	2516/0/104
Goodness of fit		1.105	1.064
Final R indexes [I>=2σ (I)]		R_1 = 0.0483, wR_2 = 0.0839	R_1 = 0.0197; wR_2 = 0.0496
Final R indexes [all data]		R_1 = 0.0768 wR_2 = 0.0960	R_1 = 0.0209 wR_2 = 0.0501
$\Delta\rho$ (max; min) [e Å^{-3}]		1.42; -1.01	0.44; -0.31
CCDC number		2444178	2444179

Table S3 - Crystal data and structure refinement of **$(L^2)_2GaCl$** and **$(L^2)GaCl_2$**.

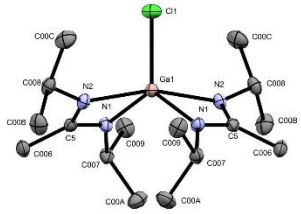
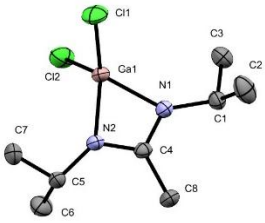
		 **$(L^2)_2GaCl$**	 **$(L^2)GaCl_2$**
Crystallised from		pentane	pentane
Empirical formula		$C_{16}H_{34}ClGaN_4$	$C_8H_{17}Cl_2GaN_2$
Formula weight [g mol^{-1}]		387.64	281.85
Crystal colour, habit		colourless, plate	colourless, plate
Crystal dimensions [mm^3]		0.56 × 0.28 × 0.14	0.6 × 0.36 × 0.3
Temperature [K]		150.01	150.01
Crystal system		monoclinic	triclinic
Space group		*C2/c*	*P-1*
Z		4	2
2θ range for cell determination [°]		4.896 to 74.684	
Unit cell parameters	*a* [Å]	11.5212(7)	7.6891(8)
	b [Å]	12.8021(8)	8.1001(9)
	c [Å]	14.1052(9)	10.6545(11)
	α [°]	90	94.218(4)
	β [°]	108.129(2)	90.509(3)
	γ [°]	90	102.564(4)
	V [Å^3]	1977.2(2)	645.73(12)
D_x [g cm^{-3}]		1.302	1.450
F(000)		824.0	288.0
μ [mm^{-1}]		1.530	2.508
Radiation		MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected		30070	3336
Symmetry-independent reflections		5114	3336
Data/restraints/parameters		5114/0/106	3336/0/124
Goodness of fit		1.028	1.081
Final R indexes [I>=2σ (I)]		R_1 = 0.0241	R_1 = 0.0384
		wR_2 = 0.0598	wR_2 = 0.0982
Final R indexes [all data]		R_1 = 0.0302	R_1 = 0.0493
		wR_2 = 0.0625	wR_2 = 0.1031
$\Delta\rho$ (max; min) [e Å^{-3}]		0.51; -0.30	0.75; -0.54
CCDC number		2444180	2444181

Table S4 - Crystal data and structure refinement of **$(L^6)_2GaCl$** and **$(L^1)_2GaCl$**.

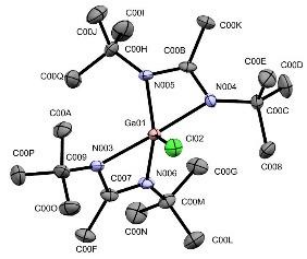
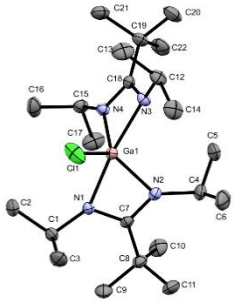
		 **$(L^6)_2GaCl$**	 **$(L^1)_2GaCl$**
Crystallised from		pentane	pentane
Empirical formula		$C_{20}H_{42}ClGaN_4$	$C_{22}H_{46}ClGaN_4$
Formula weight [g mol^{-1}]		443.74	471.80
Crystal colour, habit		colourless, plate	colourless, plate
Crystal dimensions [mm^3]		0.48 × 0.4 × 0.28	0.42 × 0.4 × 0.1
Temperature [K]		150.0	150.01
Crystal system		monoclinic	monoclinic
Space group		*Pn*	*P2$_1$/c*
Z		2	4
2θ range for cell determination [°]		2.702 to 56.564	4.902 to 65.154
Unit cell parameters	*a* [Å]	8.8449(17)	19.8594(15)
	b [Å]	15.075(3)	9.2733(7)
	c [Å]	9.2168(18)	15.2312(12)
	α [°]	90	90
	β [°]	96.248(6)	109.454(2)
	γ [°]	90	90
	V [Å3]	1221.6(4)	2644.9(4)
D_x [g cm^{-3}]		1.206	1.185
F(000)		476.0	1016.0
μ [mm^{-1}]		1.246	1.155
Radiation		MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected		6601	52487
Symmetry-independent reflections		5934	9615
Data/restraints/parameters		5934/2/250	9615/38/288
Goodness of fit		1.106	1.004
Final R indexes [I>=2σ (I)]		R_1 = 0.0680	R_1 = 0.0325
		wR_2 = 0.1656	wR_2 = 0.0721
Final R indexes [all data]		R_1 = 0.0828	R_1 = 0.0582
		wR_2 = 0.1750	wR_2 = 0.0811
$\Delta\rho$ (max; min) [e Å^{-3}]		2.48; -0.87	0.46; -0.34
CCDC number		2444182	2444183

Table S5 - Crystal data and structure refinement of **$(L^5)GaMe_2$** and **$(L^2)_2GaMe$**.

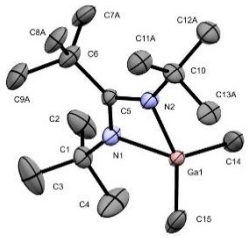
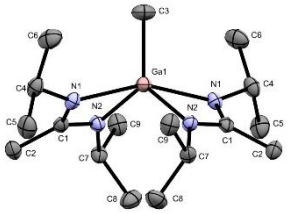
		 **$(L^5)GaMe_2$**	 **$(L^2)_2GaMe$**
Crystallised from		pentane	pentane
Empirical formula		$C_{15}H_{33}GaN_2$	$C_{17}H_{37}GaN_4$
Formula weight [g mol^{-1}]		311.15	367.22
Crystal colour, habit		colourless, plate	colourless, plate
Crystal dimensions [mm^3]		0.3 × 0.2 × 0.08	0.18 × 0.14 × 0.11
Temperature [K]		150.01	150.01
Crystal system		trigonal	monoclinic
Space group		*P3$_2$21*	*C2/c*
Z		6	4
2θ range for cell determination [°]		3.502 to 52.738	6.298 to 66.258
Unit cell parameters	*a* [Å]	9.3337(3)	11.6007(7)
	b [Å]	9.3337(3)	12.7308(9)
	c [Å]	34.8997(14)	14.2351(8)
	α [°]	90	90
	β [°]	90	107.820(4)
	γ [°]	120	90
	V [Å3]	2633.1(2)	2001.5(2)
D_x [g cm^{-3}]		1.177	1.219
F(000)		1008.0	792.0
μ [mm^{-1}]		1.557	1.378
Radiation		MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected		17865	10774
Symmetry-independent reflections		3590	3816
Data/restraints/parameters		3590/144/236	3816/0/107
Goodness of fit		1.095	1.004
Final R indexes [I>=2σ (I)]		R_1 = 0.0501	R_1 = 0.0451
		wR_2 = 0.1023	wR_2 = 0.0963
Final R indexes [all data]		R_1 = 0.0672	R_1 = 0.0786
		wR_2 = 0.1096	wR_2 = 0.1101
$\Delta\rho$ (max; min) [e Å^{-3}]		0.42; -0.85	0.51; -0.68
CCDC number		2444184	2444185

Table S6 - Summary of the bond lengths Ga-N/Ga-X (where X=Cl or Me) and N-C are reported (in Å), as well as the chelation angle (NCN) and the τ_5 parameter for penta-coordinated complexes.

	$(L^1)GaCl_2$	**$(L^1)_2GaCl$**	**$(L^5)GaCl_2$**	**$(L^6)GaCl_2$**	**$(L^6)_2GaCl$**	**$(L^3)GaCl_2$**	**$(L^4)GaCl_2$**	**$(L^5)GaMe_2$**
τ_5		0.895			0.941			
$\widehat{NCN}$ (°)	108.1(4)	109.06(10)	107.3(2)	109.5(2)	110.1(6); 111.8(6)	109.5(2)	109.4(3)	106.8(5)
Ga—X (Å)	2.1556(10) ; 2.1562(10)	2.2399(5)	2.1640(5)	2.1546(7) ; 2.1550(8)	2.253(2)	2.1491(8); 2.1535(9)	2.1509(10); 2.1481(11)	1.975(7); 1.974(7)
Ga—N (Å)	1.927(5); 1.942(4)	2.0592(10) ; 1.9947(10)	1.9295(15)	1.943(2) ; 1.938(2)	2.090(6); 2.068(6); 1.977(6); 1.968(6)	1.939(2); 1.945(2)	1.934(3); 1.944(3)	1.982(5); 1.980(5)
N—C (Å)	1.354(7); 1.320(7)	1.3384(16) ; 1.3431(15)	1.357(2)	1.331(3) ; 1.341(3)	1.332(10); 1.354(10); 1.310(10); 1.330(10)	1.331(3); 1.338(4)	1.327(5); 1.331(5)	1.339(8); 1.336(8)

3. Thermal analyses

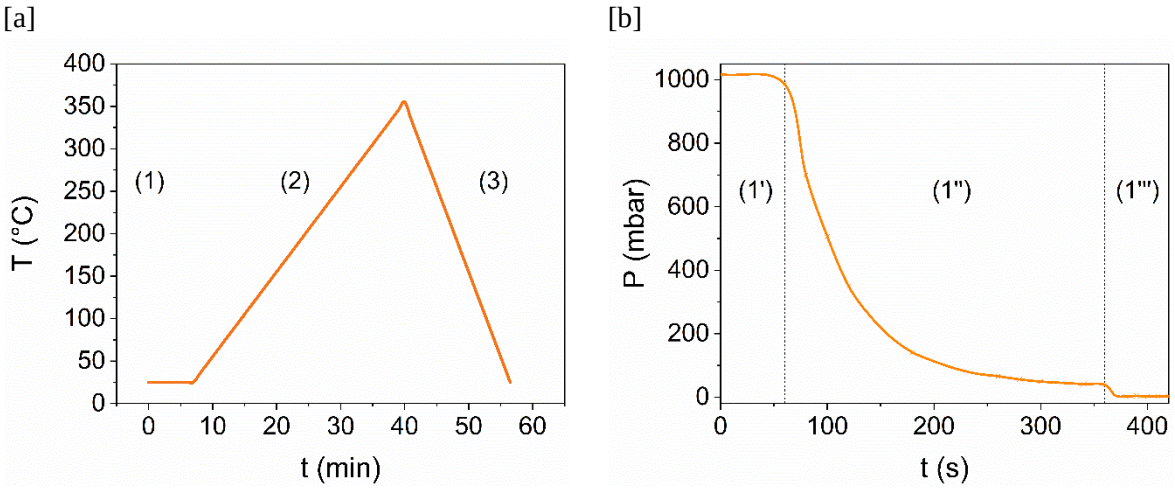
Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analyses were conducted under atmospheric pressure and under vacuum using a Setsys Evolution ATG 16/18 easy fit (KEP Technologies, France), combining both TG and DSC analyses. Calisto software provided by Setaram was used for acquisition and treatment.

3.1 Data acquisition

For each measurement, 10-20 mg of the molecular compound was weighed inside a glove box and placed in a 70 µL uncovered alumina crucible. To minimize air exposure, the crucible was stored in a sealed chamber before being transferred to the platinum rod inside the furnace, where it was continuously purged with N_2.

TG and DSC analyses were conducted following a three-step temperature program. The sample was first maintained at 25°C under a continuous nitrogen (N_2, Air Liquide, U quality, purity>99.995) flow for stabilization. This stabilization phase depends on the pressure conditions: in case of atmospheric pressure, the sample was stabilized under a constant N_2 flow (Figure S2[a], 1). In case of reduced pressure, the stabilization phase included an initial step under atmospheric pressure for 1 min (Figure S2[b], part 1'), followed by a gradual vacuum application over 5 min (Figure S2[b], part 1''), and a final rapid vacuum step reaching ~1 mbar within 1 min (Figure S2 [b], part 1'''). The total stabilization time was standardized to 7 min for all measurements. Then the sample was heated at a constant rate of 10°C/min to a maximum temperature (T_{max}) in the range 205-450°C, depending on the estimated volatility of the compound and the analysis pressure (Figure S2[a], part 2). Upon reaching T_{max}, a cooling program was initiated (Figure S2[a], part 3).

Figure S2 - [a] Typical temperature program for TG/DSC analysis, including (1) the stabilization phase before analysis, (2) the heating ramp at 10 °C/min, and (3) the cooling phase at the end of the analysis. [b] Stabilization steps for TG/DSC analysis under reduced pressure, comprising (1') an initial stabilization at atmospheric pressure, followed by (1'') a gradual vacuum application, and concluding with (1''') a rapid vacuum step reaching 1 mbar.



3.2 Data treatment

Determination of Evaporation and Fusion Temperatures - The onset (T_{onset}) and offset (T_{offset}) temperatures of a thermal event are determined using the tangent method, as described by Vyazovkin.[11] This method involves identifying the intersection points between the tangents to the DSC peak and the baseline of the DSC curve. The area (S_{peak}) between the DSC curve and its baseline also provides access to the energy associated with the thermal event. As an example, the fusion and vaporization temperatures of the commercial compound $[Ga(NMe_2)_3]_2$ were determined using this approach (Figure S3a).

Evaluation of Residual Mass Percentages After TG/DSC Analysis - The residual mass ($\%_{res}$) of a compound after TG/DSC analysis corresponds to the mass difference measured by the analyzer's internal balance between the start and end of heating. This method provides high precision (±10 µg) but may overestimate residues, as early volatilization during stabilization at room temperature under reduced pressure is not recorded. To improve accuracy of the characterization, the crucible was weighed before and after analysis using two separate balances—one inside a glove box and another under a fume hood. While this approach accounts for early volatilization, it introduces greater uncertainty due to the use of different instruments, with a precision in the milligram range. For a ~20 mg sample, a 5–10% residual mass difference corresponds to 1 mg, which falls within the measurement error. TG curves were

corrected by subtracting a blank experiment (empty crucible) acquired in the same conditions in terms of atmosphere, flow rate and temperature program.

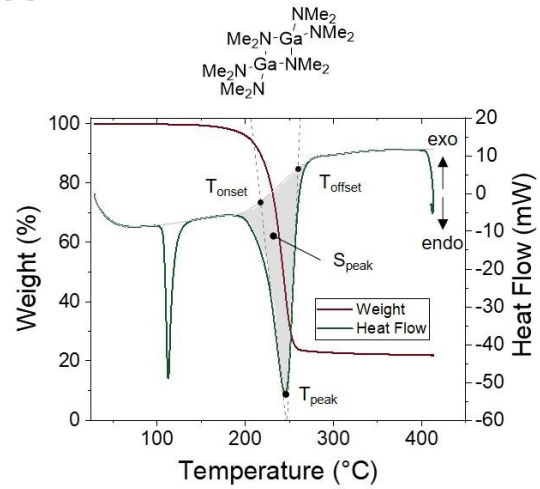
Evaluation of the Mass Loss Profile - TG curves were differentiated with respect to temperature to determine whether a compound vaporizes as a single species (indicated by a single peak) or as multiple species (evidenced by multiple peaks). As an illustrative example, the dimer $[Ga(NMe_2)_3]_2$ exhibited a single-step mass loss profile, as shown in the TG/DSC curves (Figure S3b).

Deconvolution of DSC Signal Peaks - Multiple thermal events may overlap within a narrow temperature range, particularly due to the rapid heating rate (10 °C/min), making peak separation difficult. To resolve these events, Calisto software including AKTS contribution was used for complexes exhibiting multi-step mass loss profiles in DTG curves.

Methodology Validation - To validate the methodology, repeatability tests were conducted on the complexes **$(L^5)GaCl_2$** (under reduced pressure) and **$(L^6)GaCl_2$** (at atmospheric pressure). The resulting superimposed TG/DSC curves and identical residual mass percentages confirmed the reproducibility of the measurements.

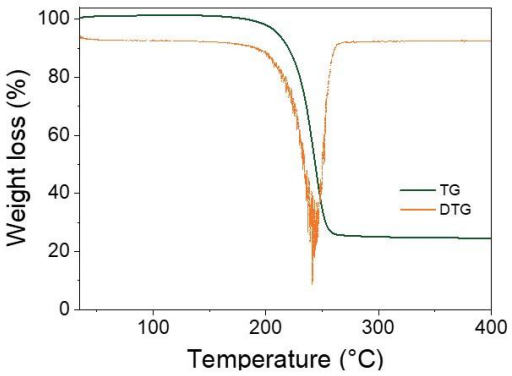
Figure S3 – [a] TG/DSC curves of the commercial compound $[Ga(NMe_2)_3]_2$ at atmospheric pressure as a function of temperature, illustrating the application of the tangent method for estimating the onset temperatures of thermal events under both atmospheric and reduced pressure conditions. [b] TG and DTG curves of the commercial compound $[Ga(NMe_2)_3]_2$ under atmospheric pressure (N_2), showing a single-step mass loss profile

[a]



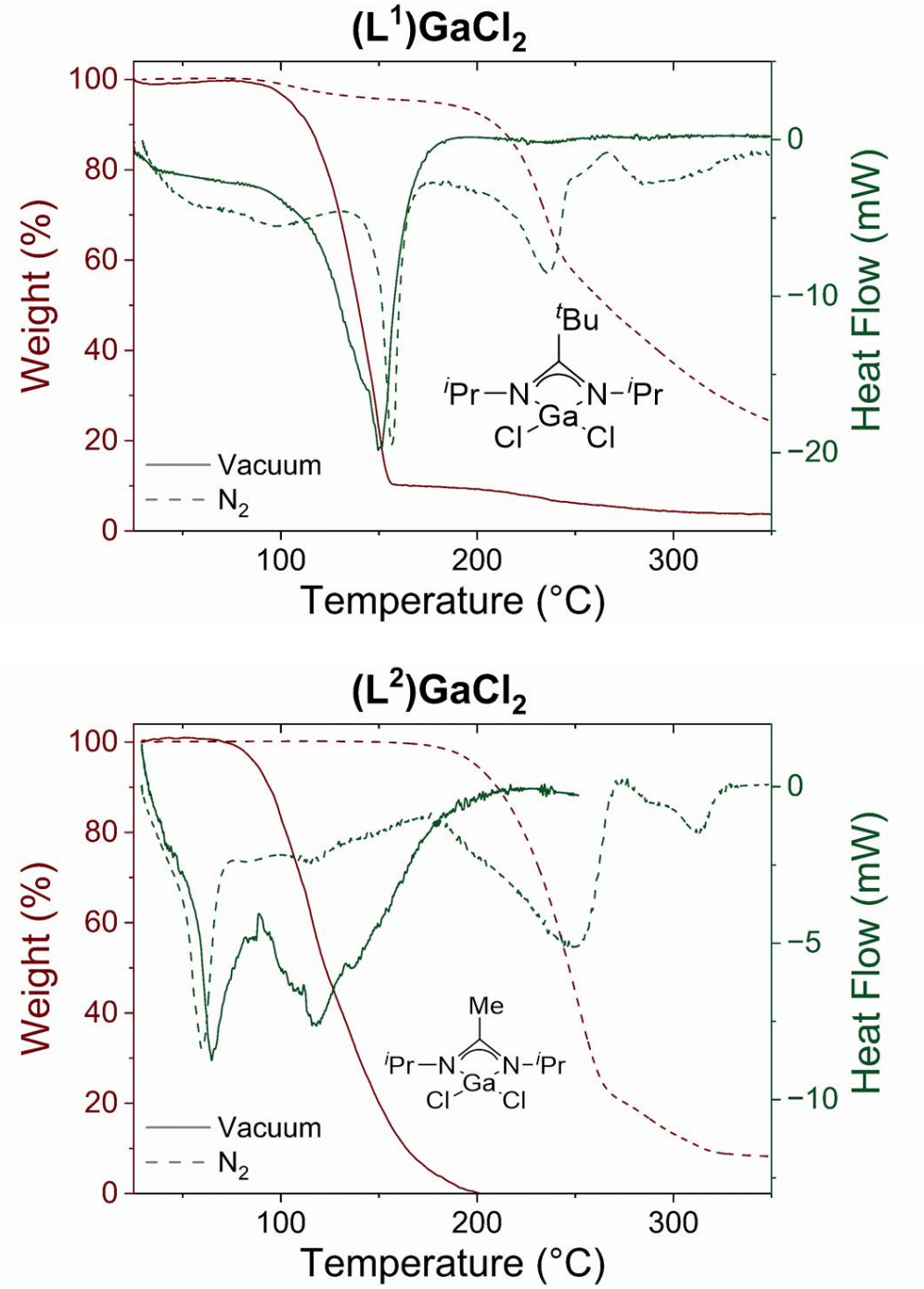
(°C)	Fusion	Evaporation
T_{onset}	109	217
T_{peak}	113	245
T_{offset}	117	260

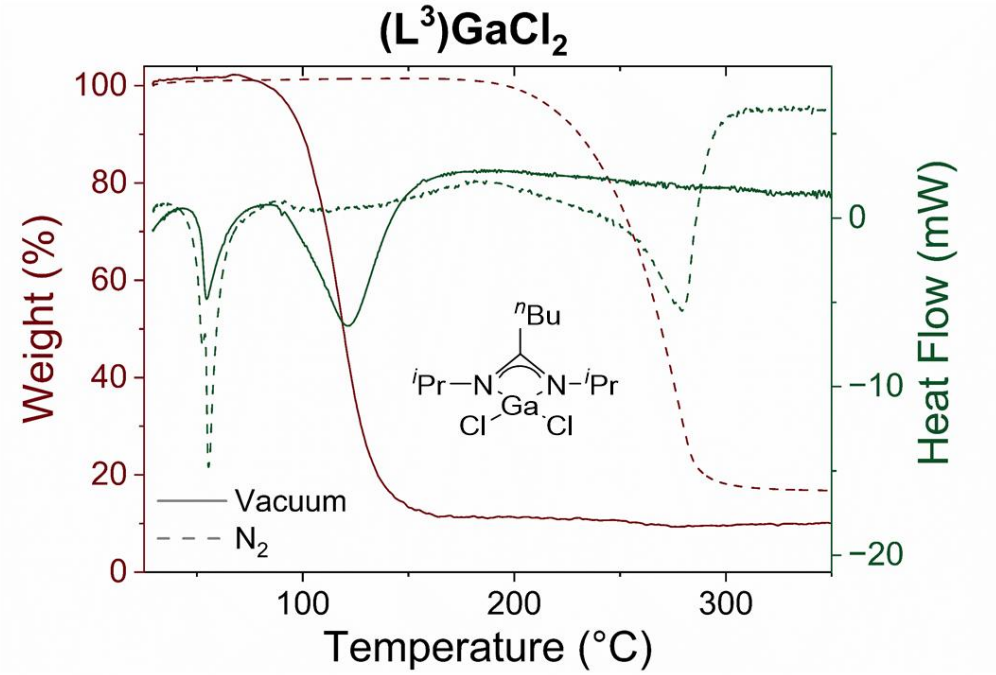
[b]

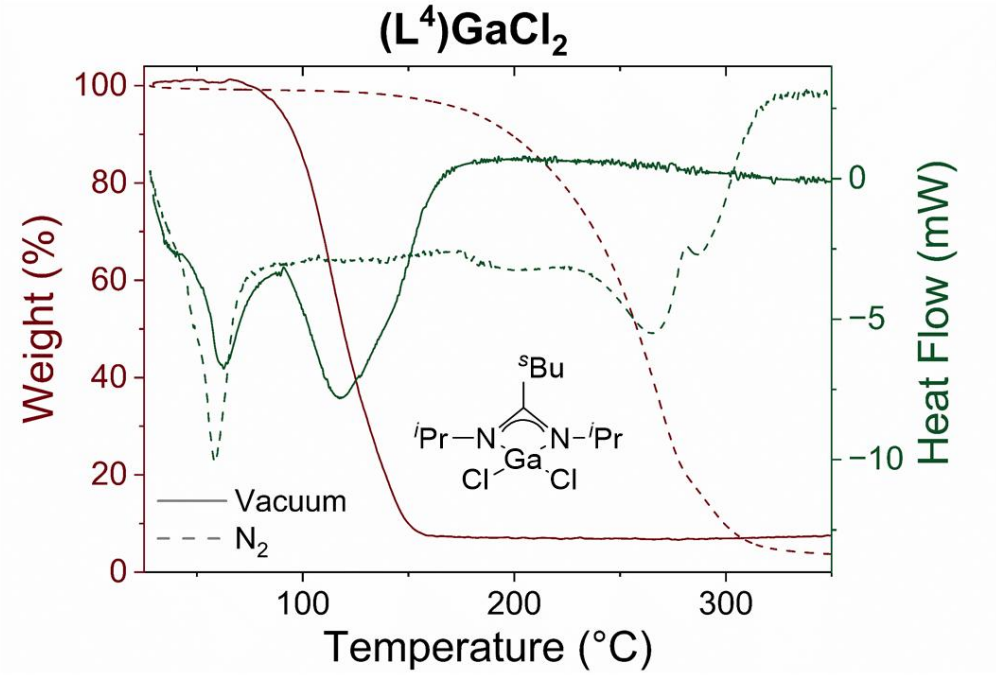


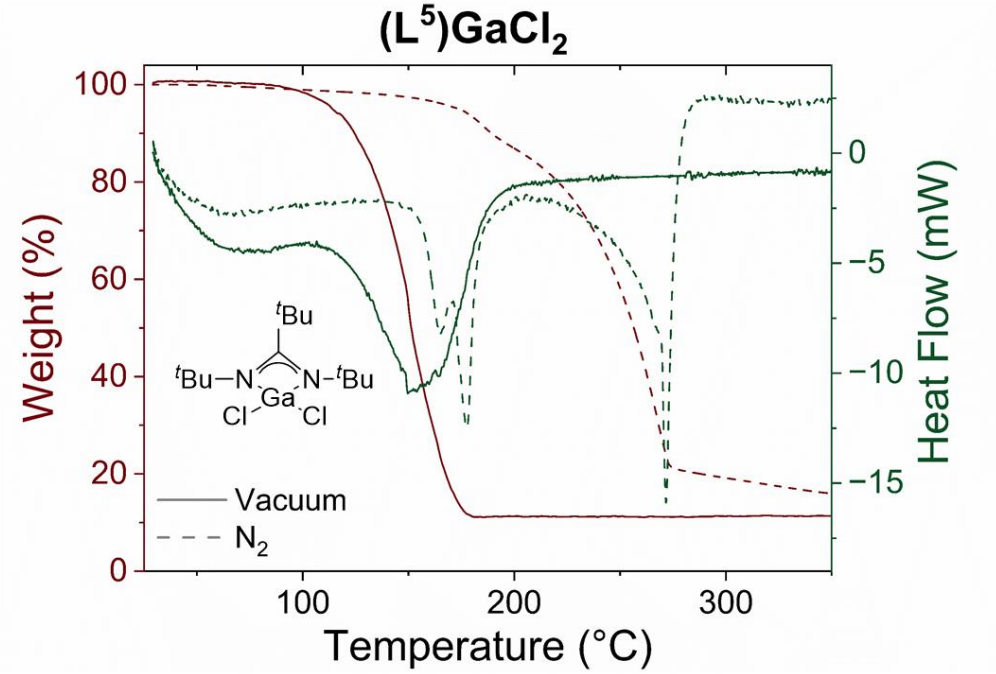
3.3 TG/DSC curves

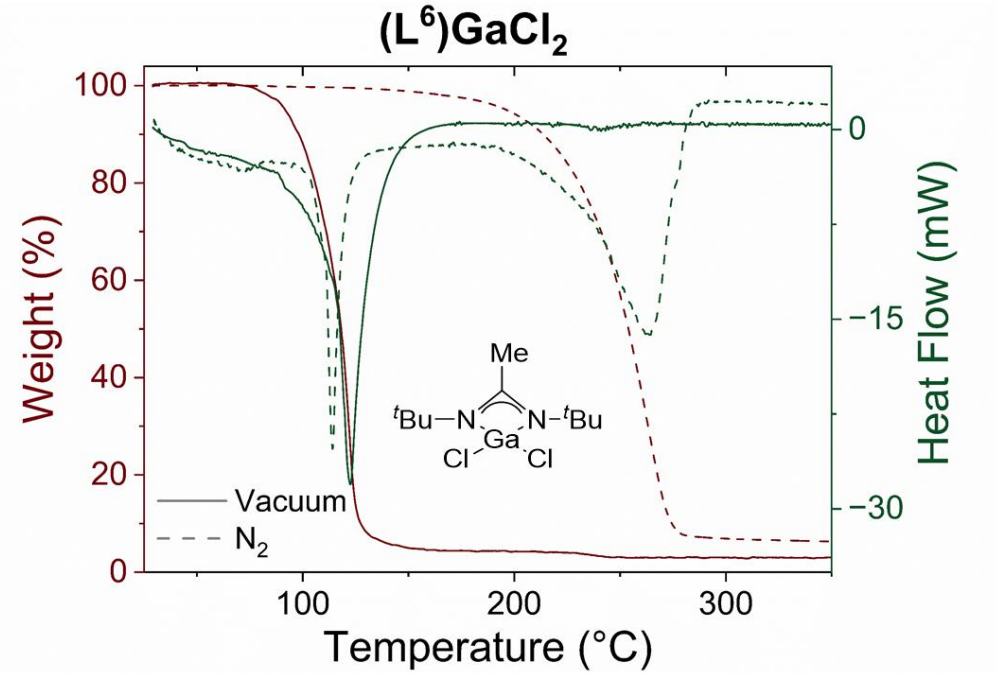
Figure S4 1 – TG/DSC curves of gallium-amidinate chloride complexes.

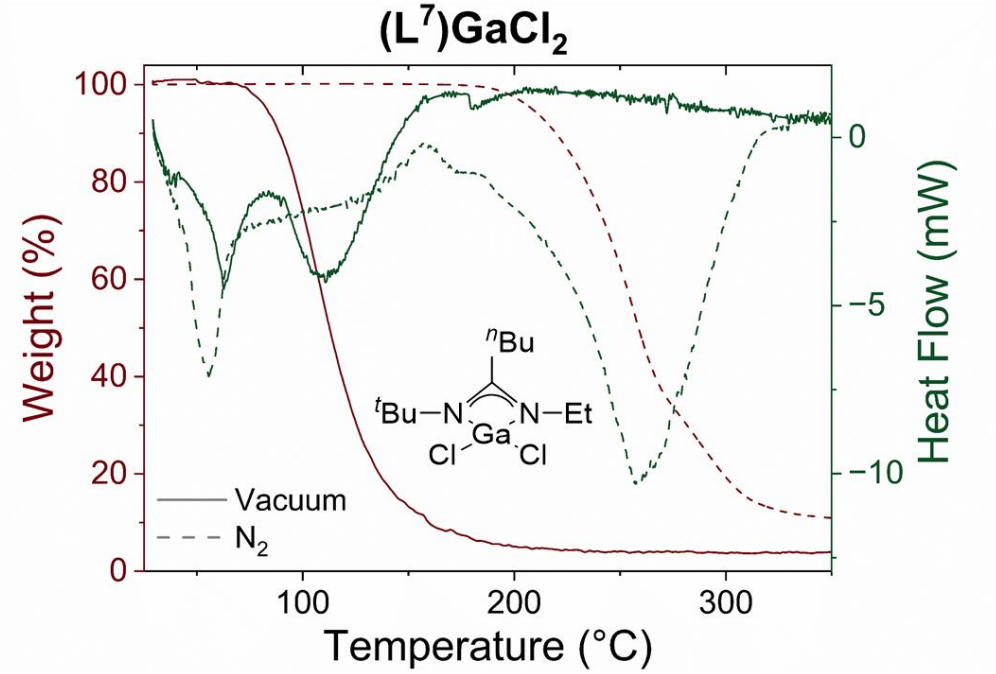



(L3)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
nBu
iPr—N
N–iPr
Ga
Cl
Cl


(L4)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
sBu
iPr—N
N–iPr
Ga
Cl
Cl


(L5)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
tBu
tBu–N
N–tBu
Ga
Cl
Cl


(L6)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
Me
tBu–N
N–tBu
Ga
Cl
Cl


(L7)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
nBu
tBu–N
N–Et
Ga
Cl
Cl

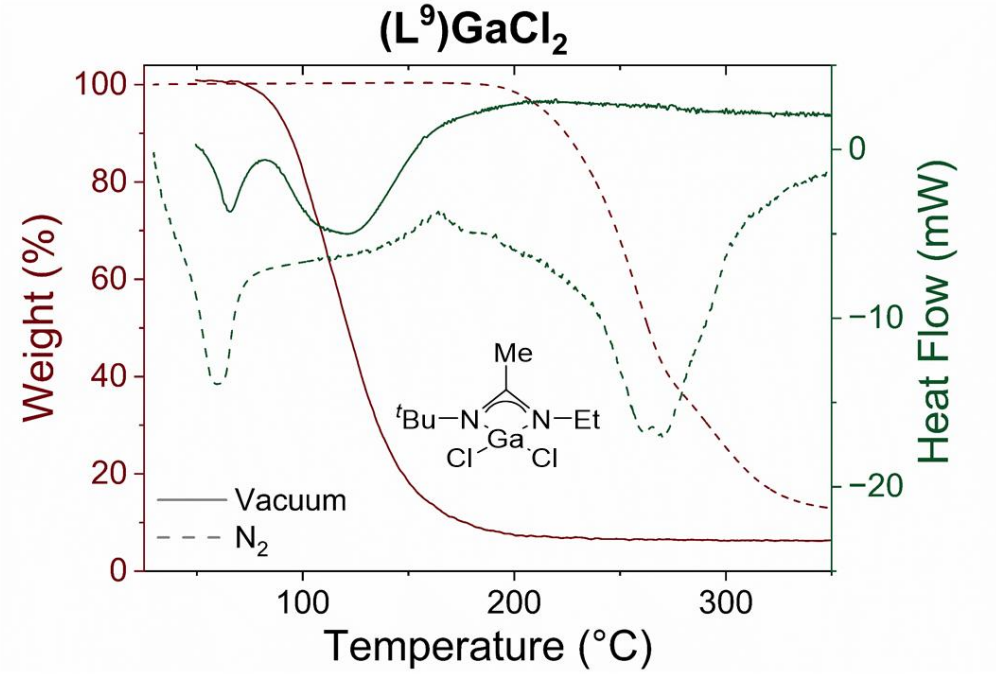
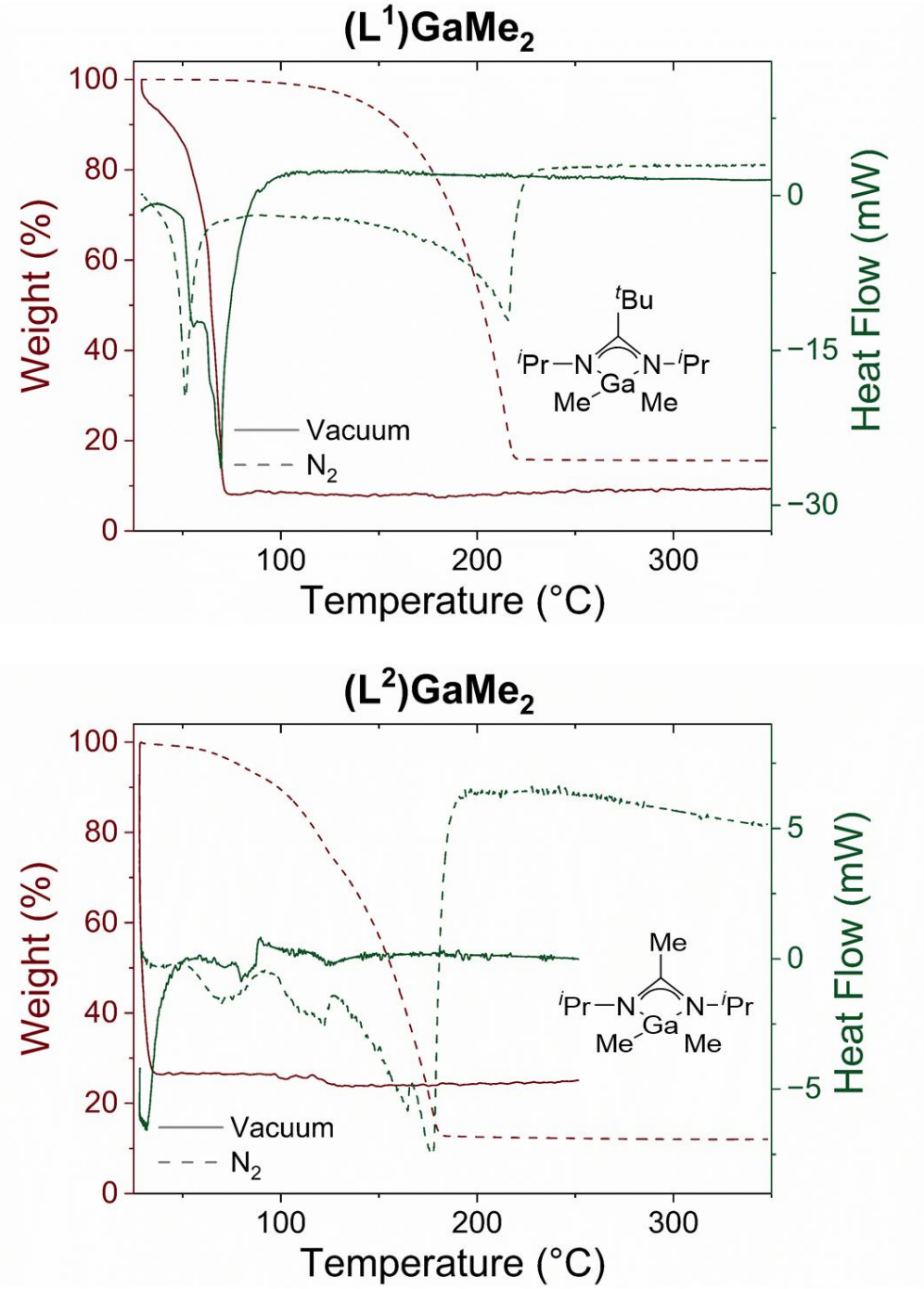
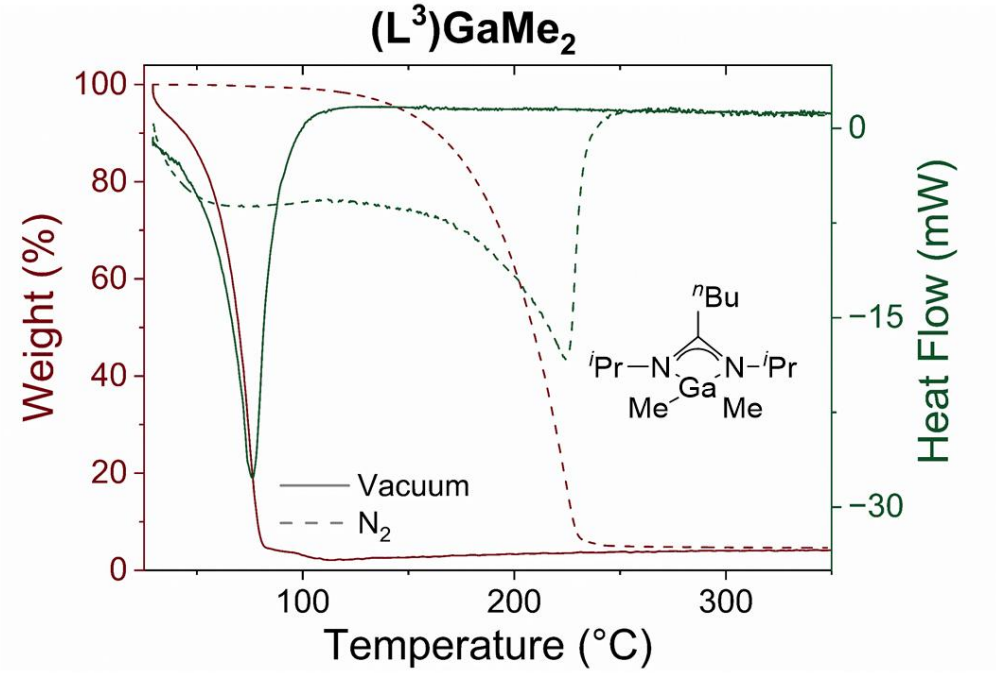
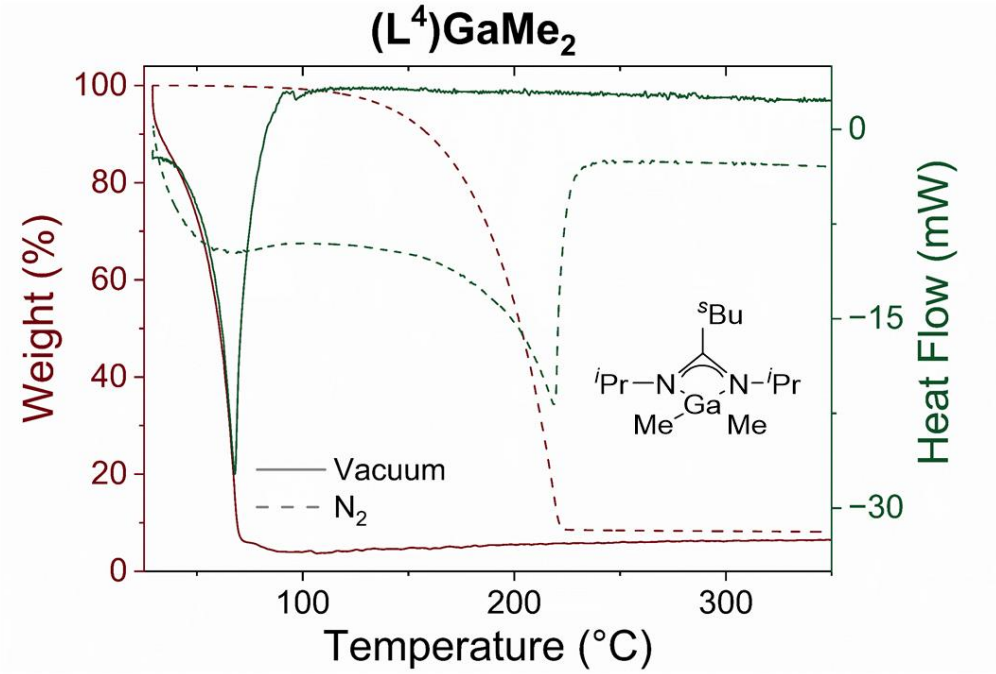
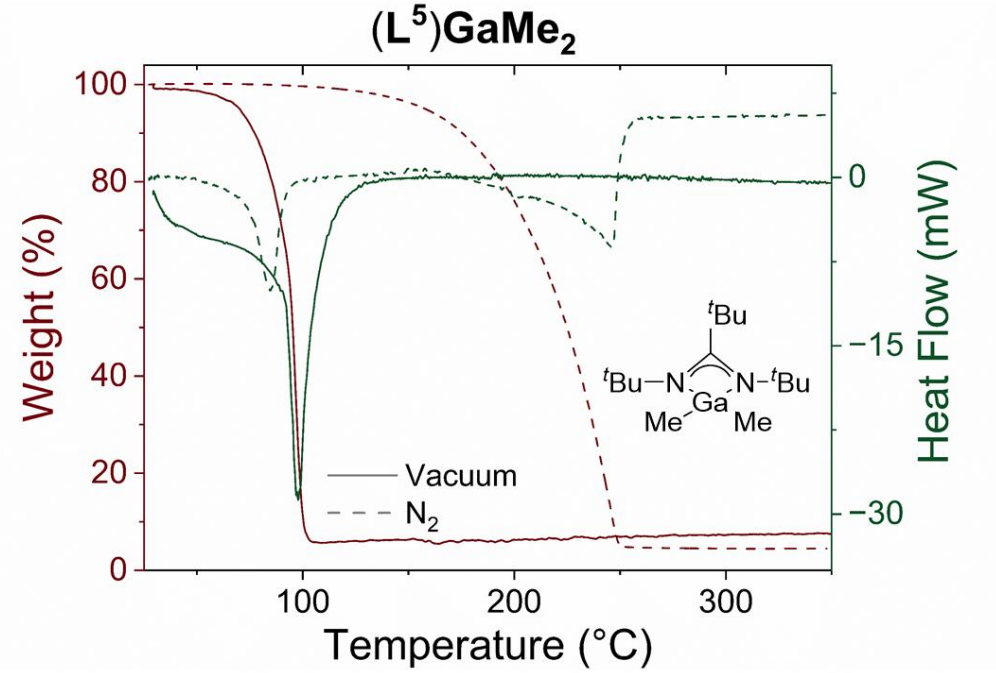

(L9)GaCl2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
Me
tBu–N
N–Et
Ga
Cl
Cl

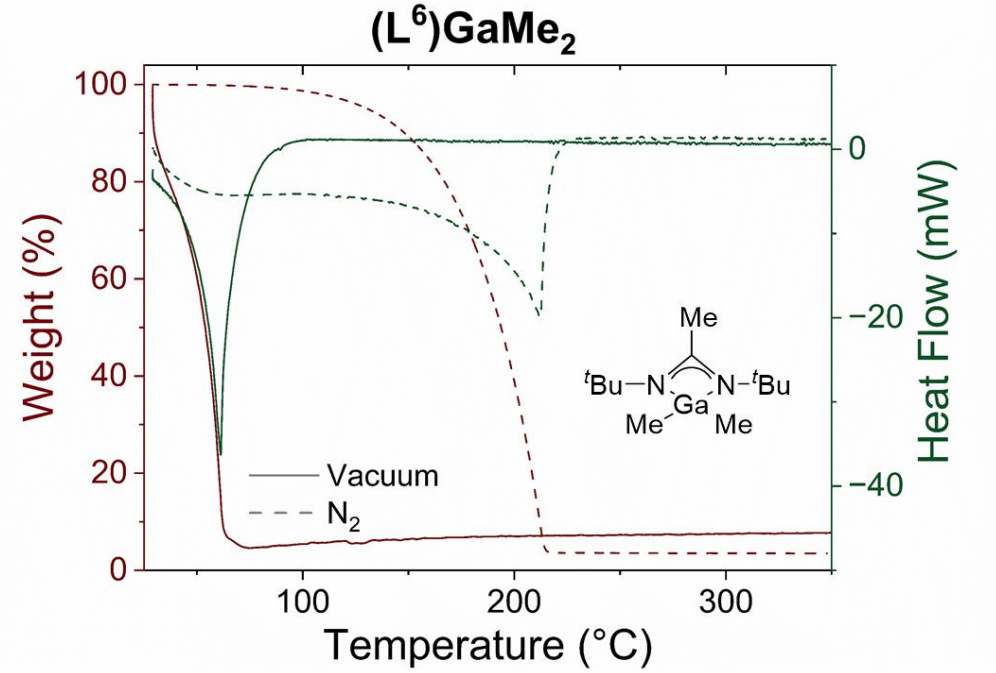
Figure S4-2 - TG/DSC curves of gallium-amidinate methyl complexes.

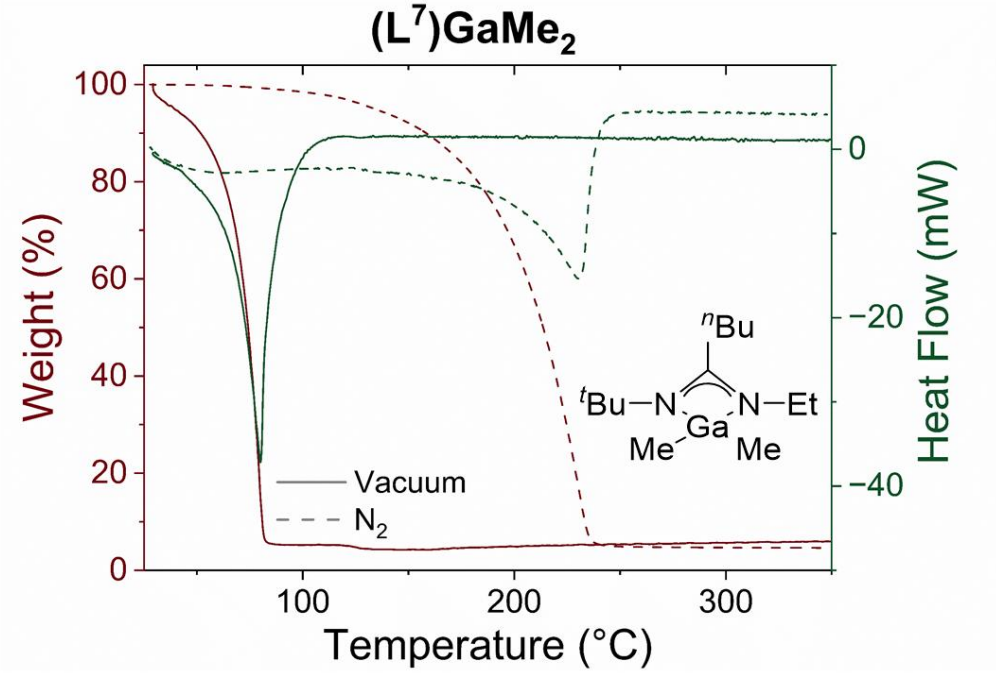


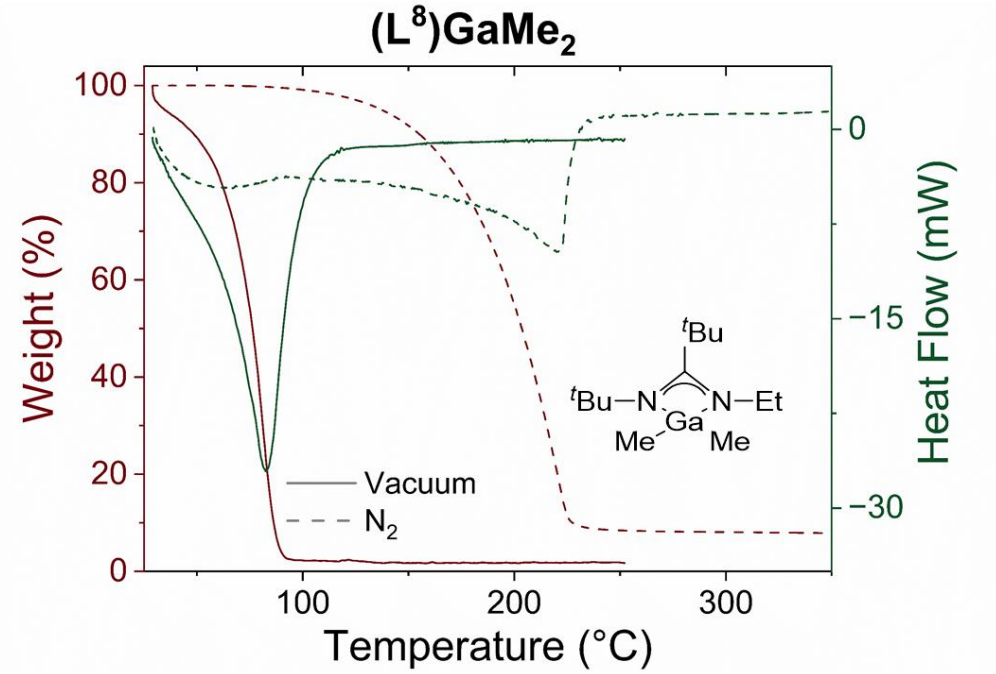

(L3)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
nBu
iPr—N
N–iPr
Ga
Me
Me


(L4)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
sBu
iPr—N
N–iPr
Ga
Me
Me


(L5)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
tBu
tBu–N
N–tBu
Ga
Me
Me


(L6)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
Me
tBu–N
N–tBu
Ga
Me
Me


(L7)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
nBu
tBu–N
N–Et
Ga
Me
Me


(L8)GaMe2
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
tBu
tBu–N
N–Et
Ga
Me
Me

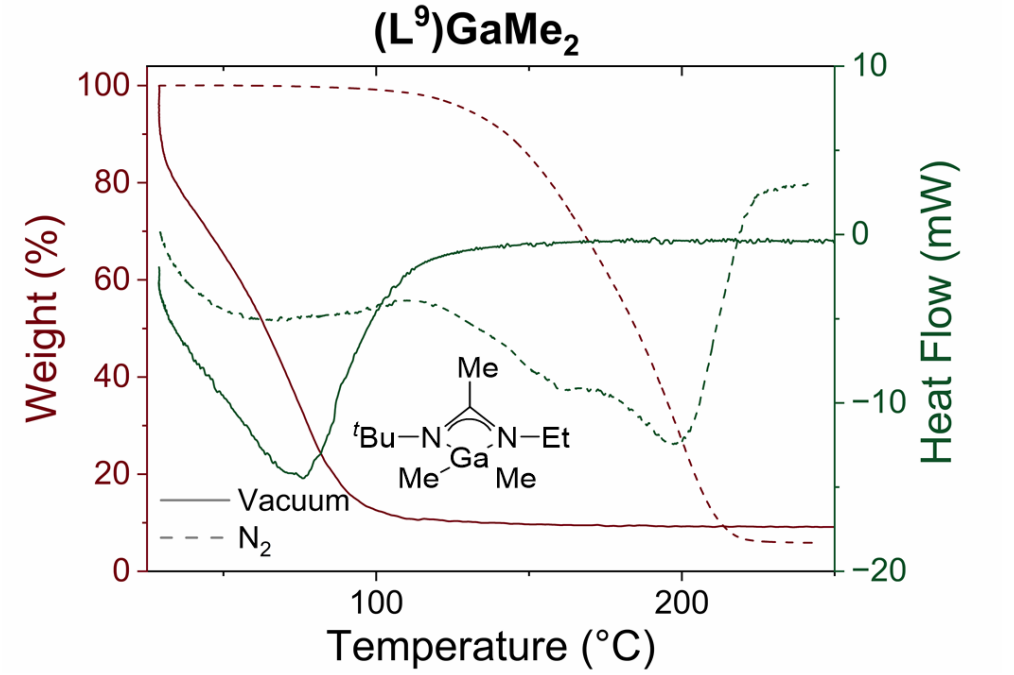
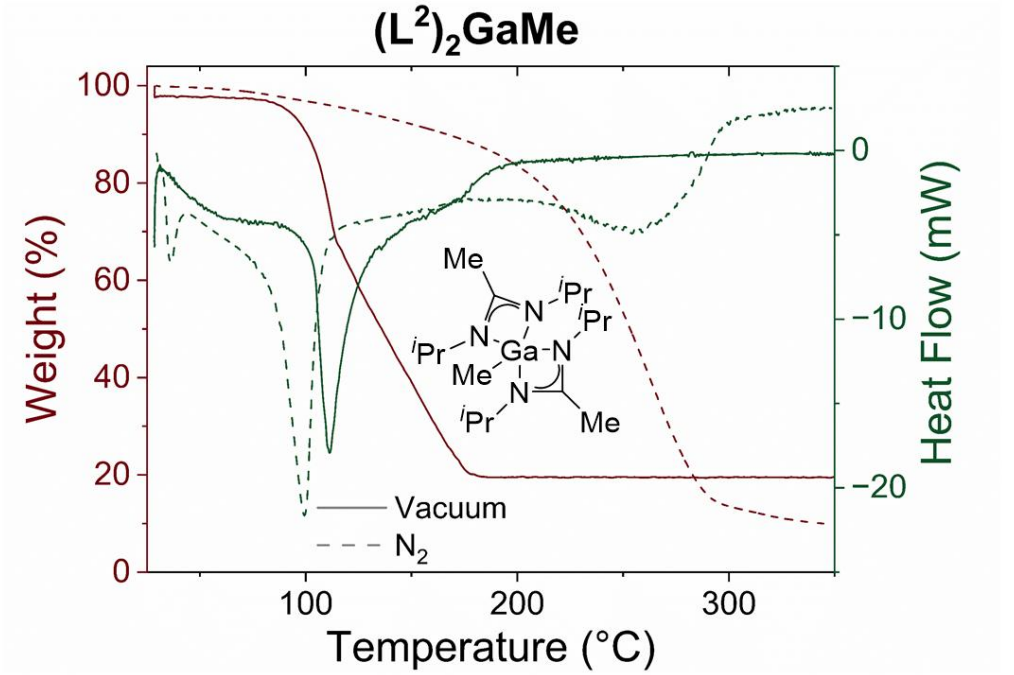
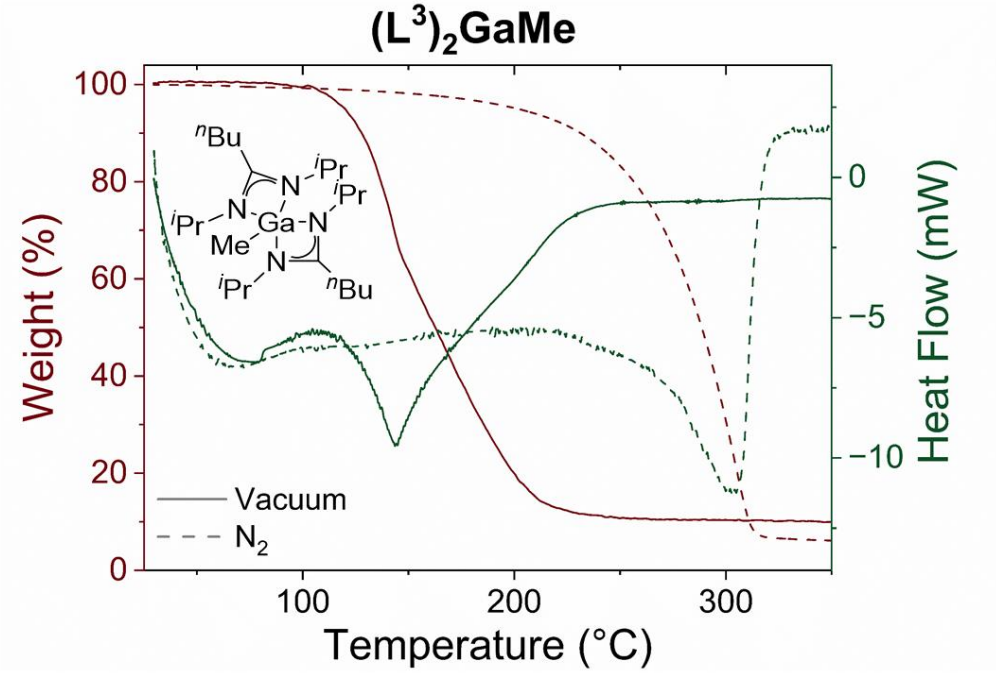


Figure S4-3 - TG/DSC curves of gallium-bisamidinate methyl complexes.




(L3)2GaMe
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
nBu
iPr
Me
Ga
N

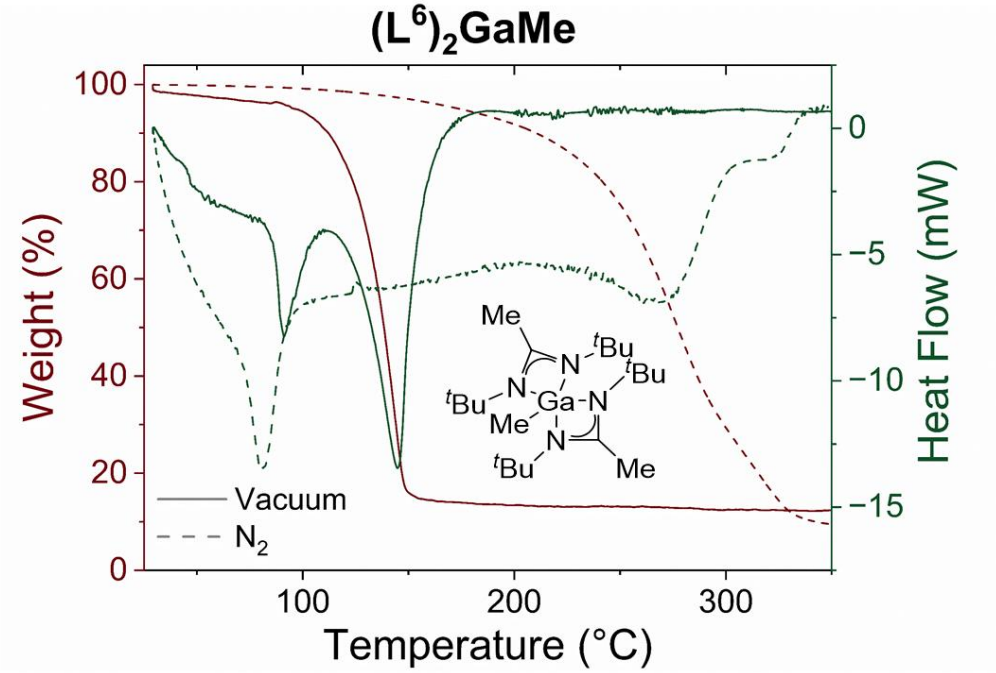

(L6)2GaMe
Weight (%)
Heat Flow (mW)
Temperature (°C)
Vacuum
N2
Me
tBu
Ga
N

Figure S5 – Evaluation of relative vaporization energy values by determination of the areas under the vaporization peaks of gallium-amidinate compounds based on TGA/DSC under atmospheric and reduced pressure

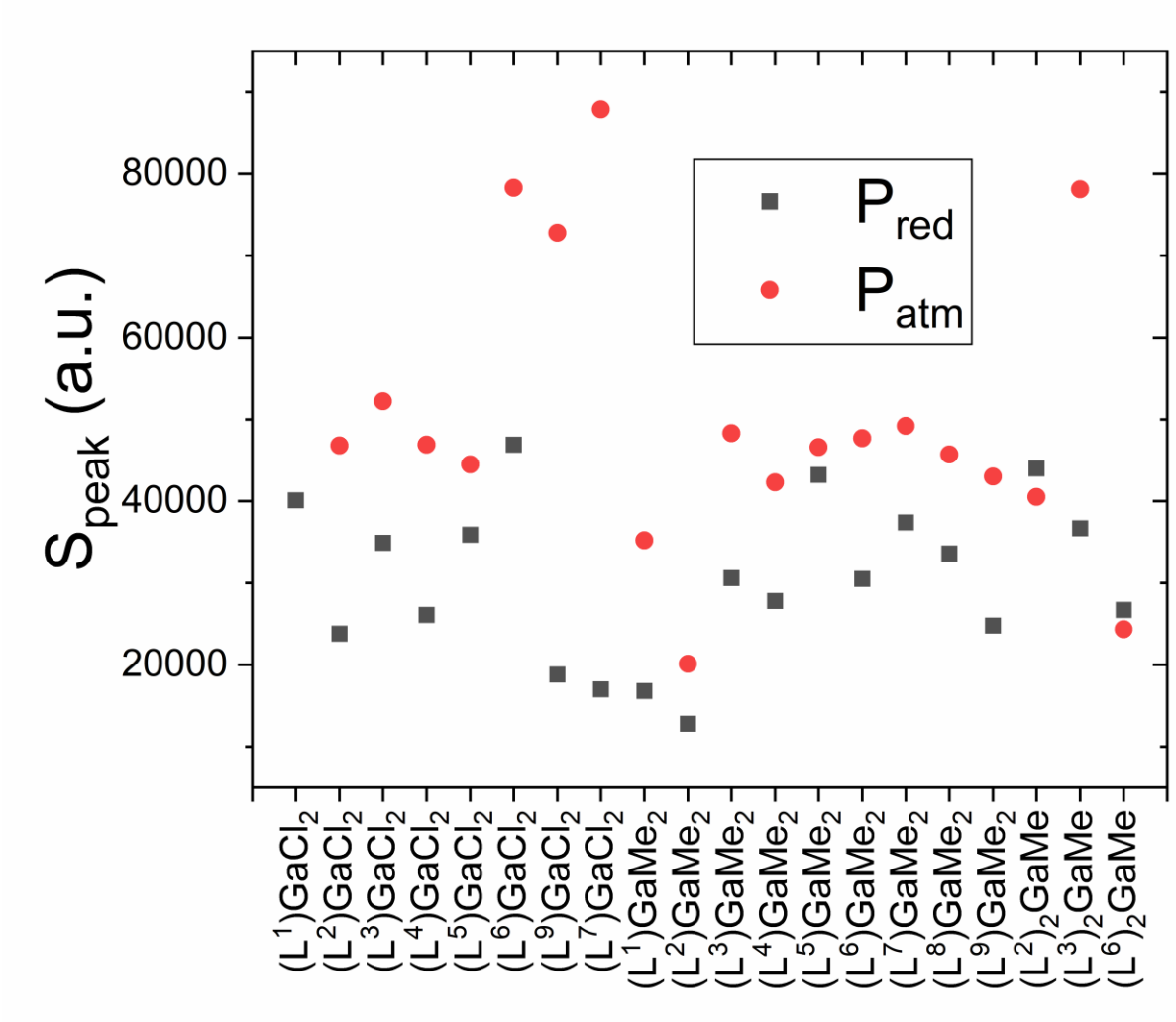
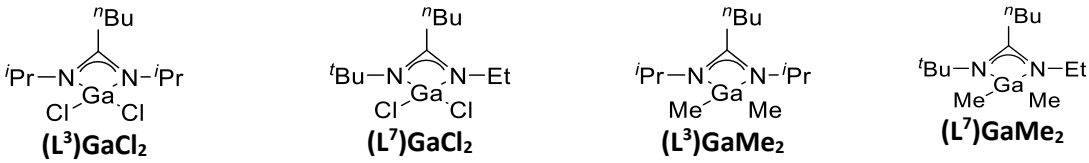
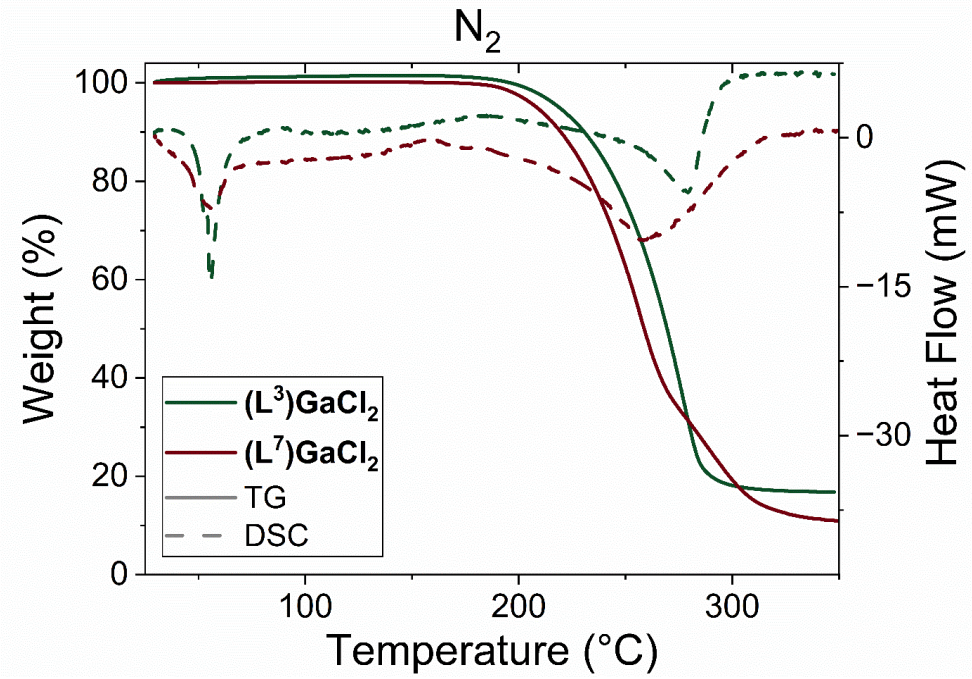
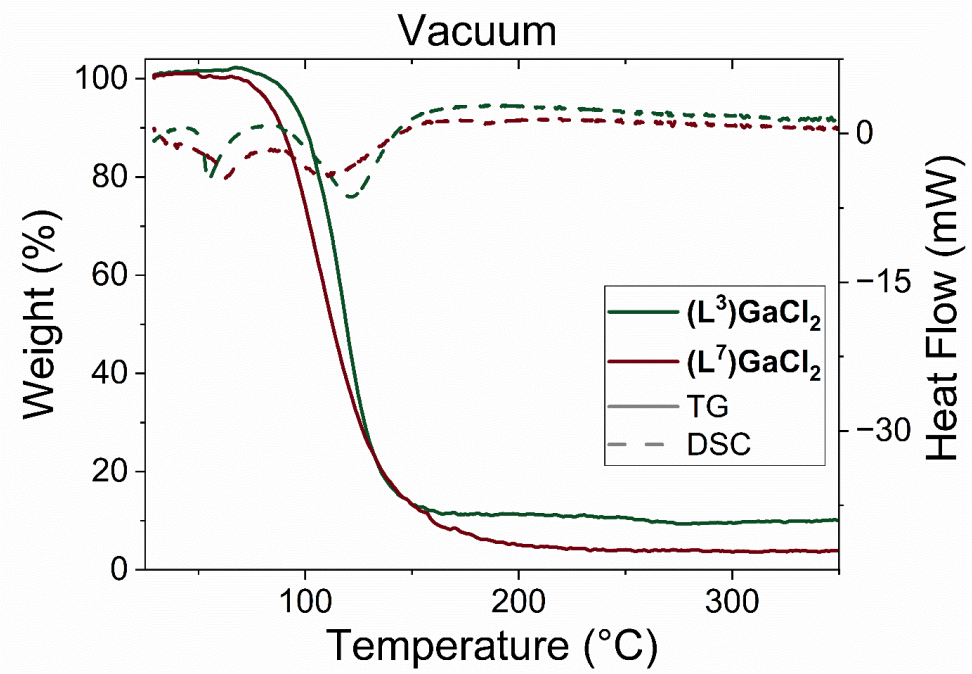
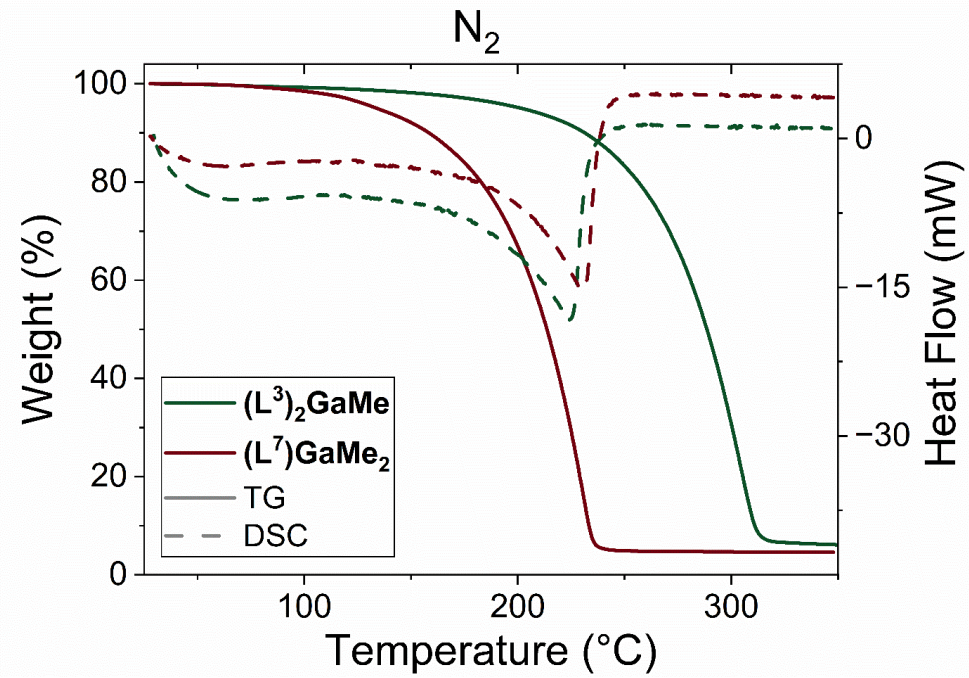


Figure S6 – Impact of symmetry on the thermal properties, evaluated by TG/DSC curves of compounds with same molecular weight but different substituents on the N atoms (^{i}Pr/^{i}Pr vs Et/^{t}Bu)








N2
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L3)2GaMe
(L7)GaMe2
TG
DSC

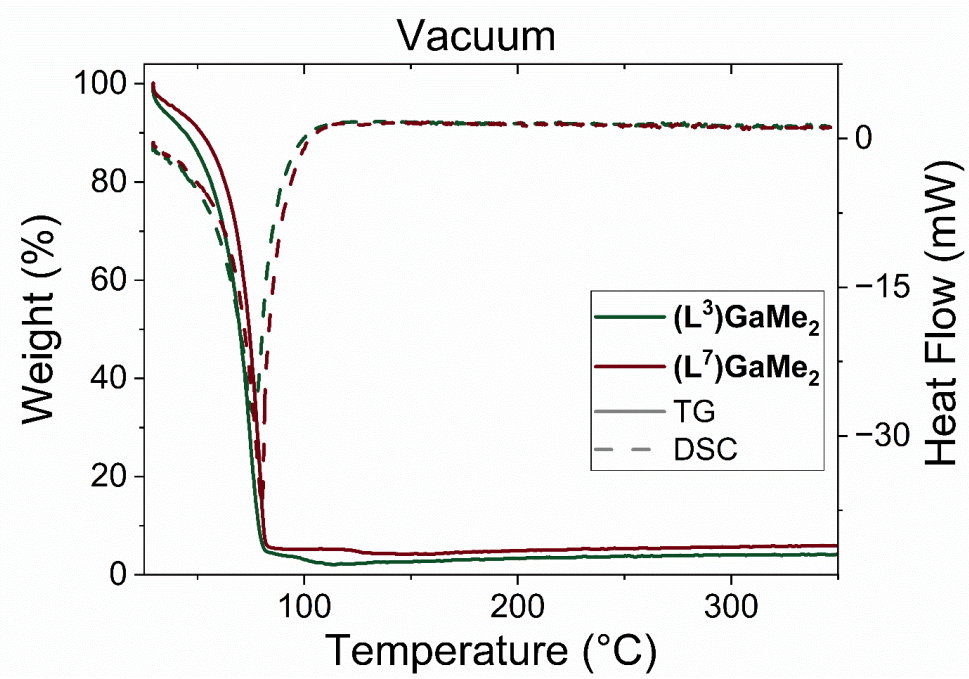
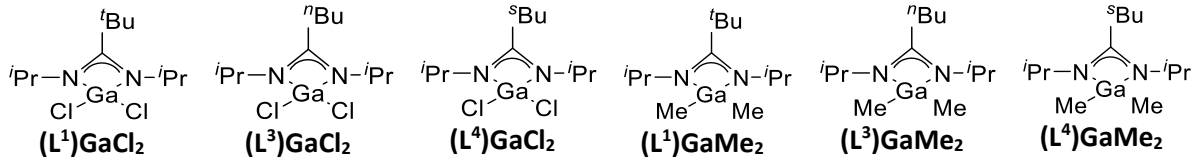
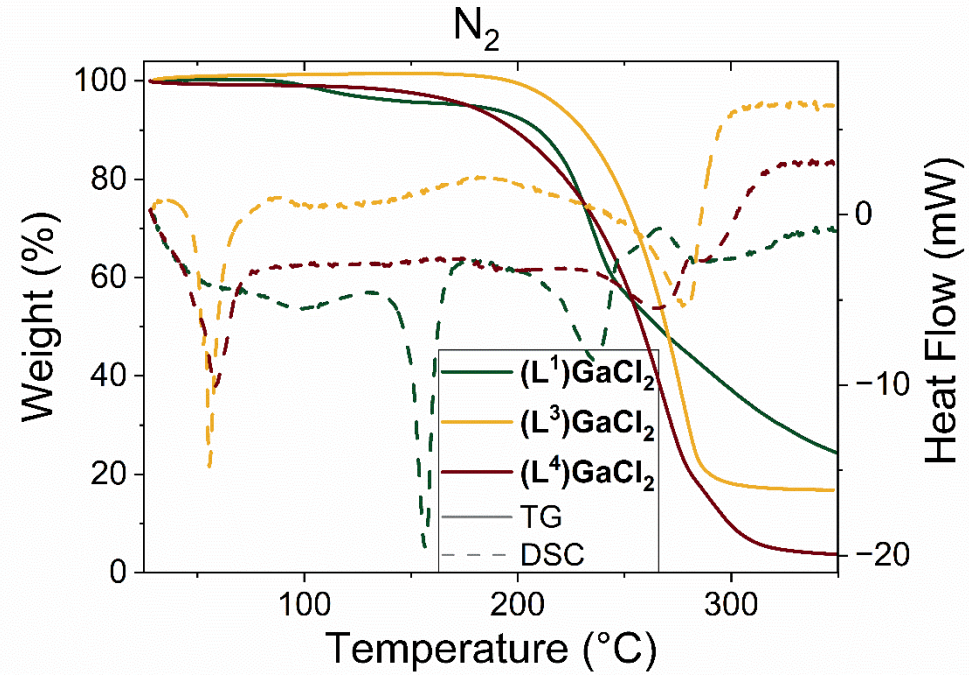
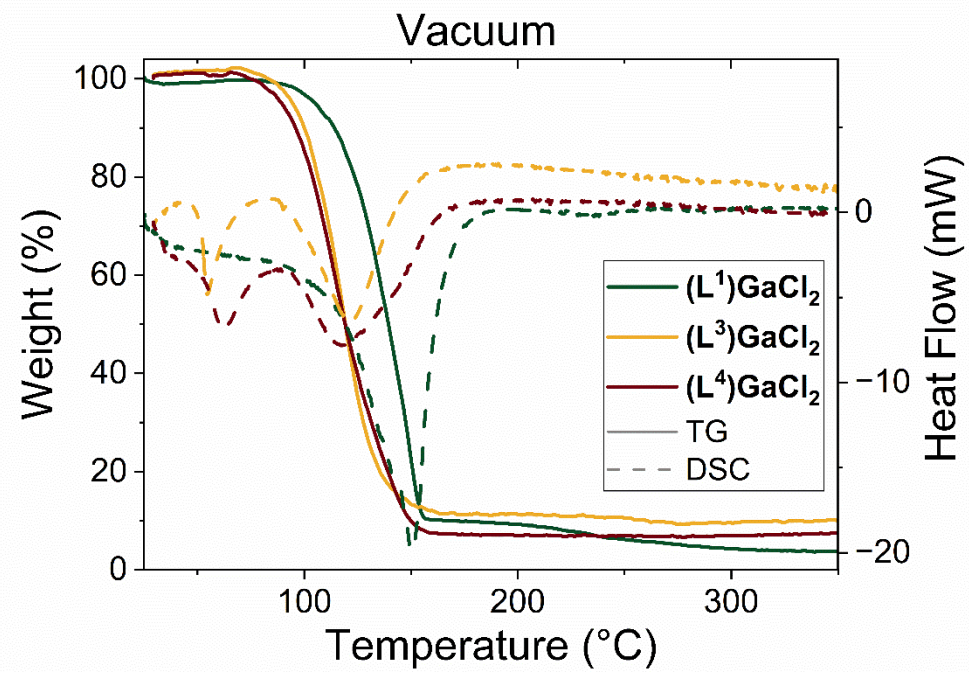
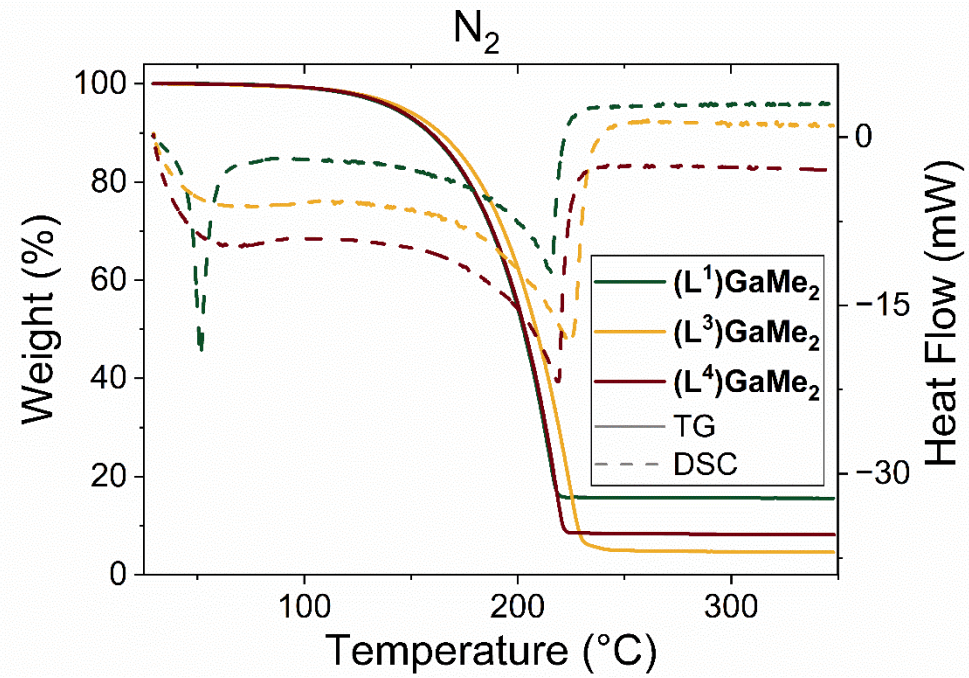

Vacuum
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L3)GaMe2
(L7)GaMe2
TG
DSC

Figure S7 - Impact of branching on the thermal properties, evaluated by TG/DSC curves of compounds with same molecular weight but different substituents on the endocylic position (^{t}Bu, ^{n}Bu, ^{s}Bu)








N2
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L1)GaMe2
(L3)GaMe2
(L4)GaMe2
TG
DSC

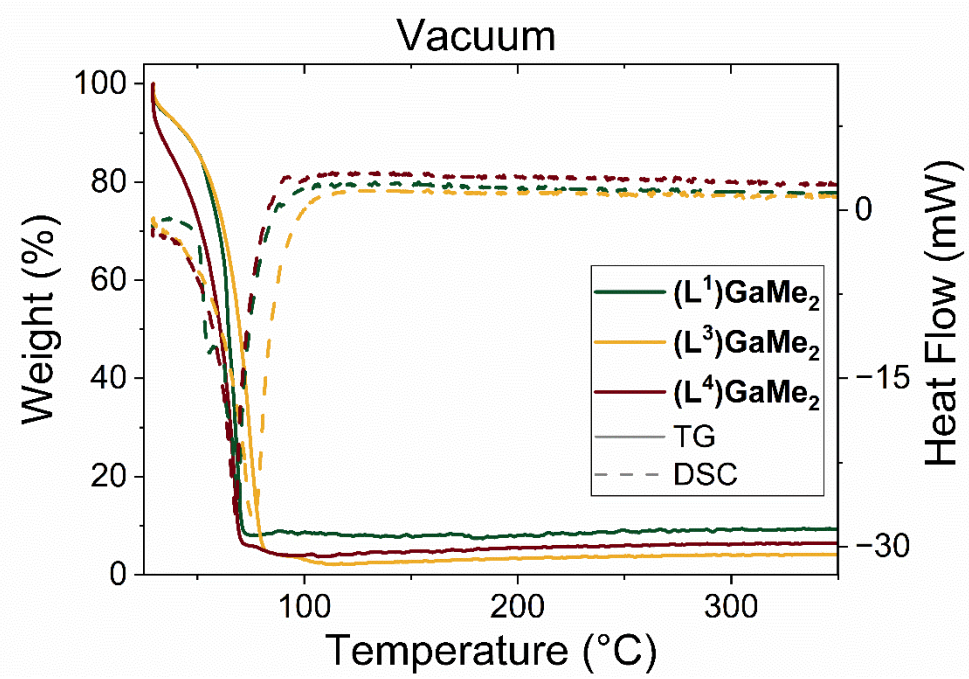

Vacuum
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L1)GaMe2
(L3)GaMe2
(L4)GaMe2
TG
DSC

Figure S8- Impact of branching and symmetry on the thermal properties, evaluated by TG/DSC curves of compounds with same molecular weight but different substituent on the endocylic carbon and N atoms

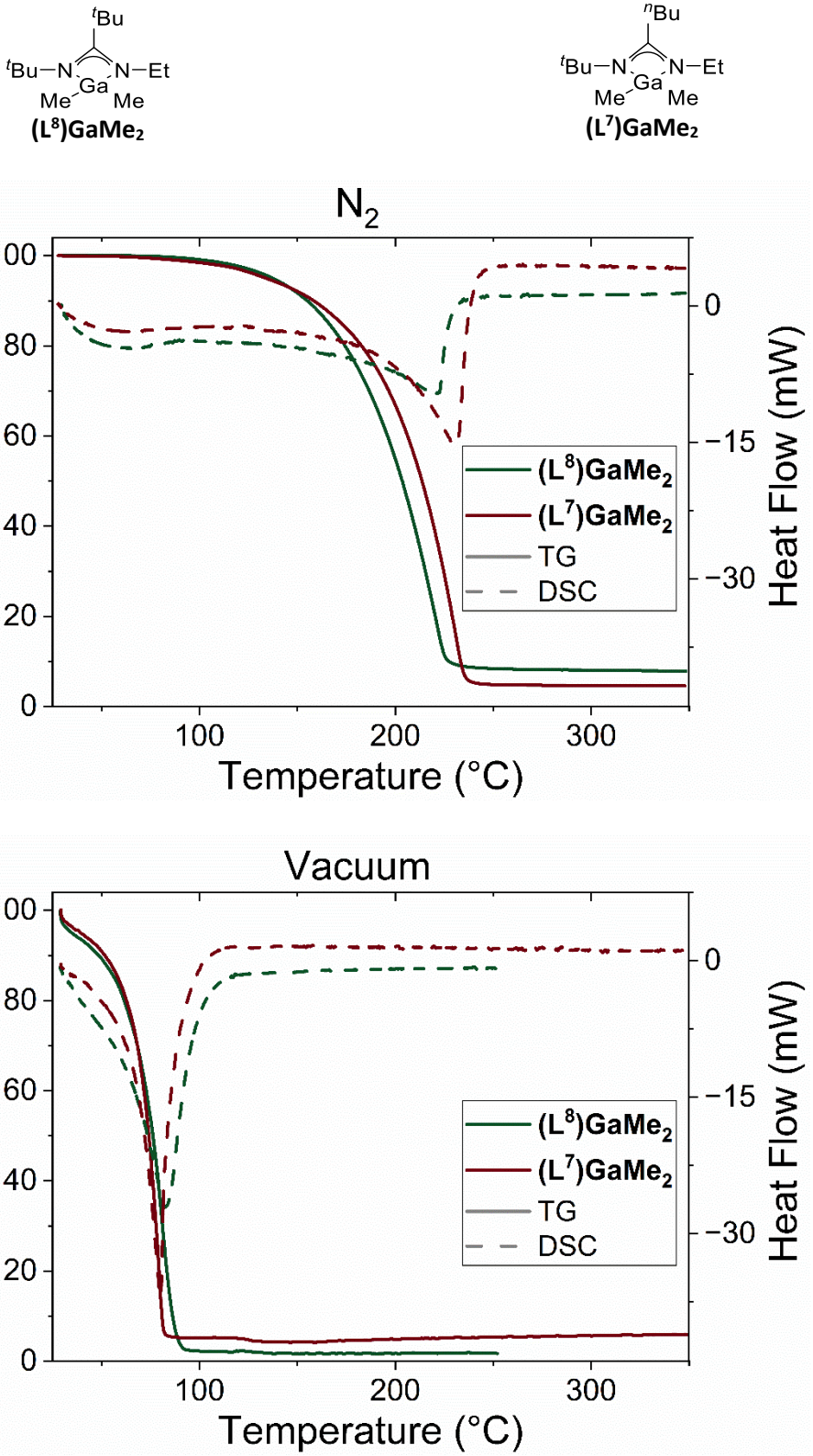
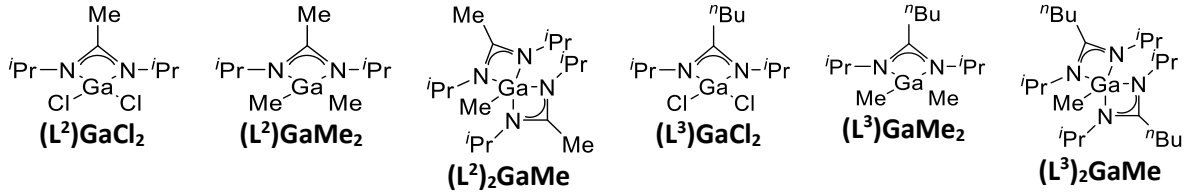
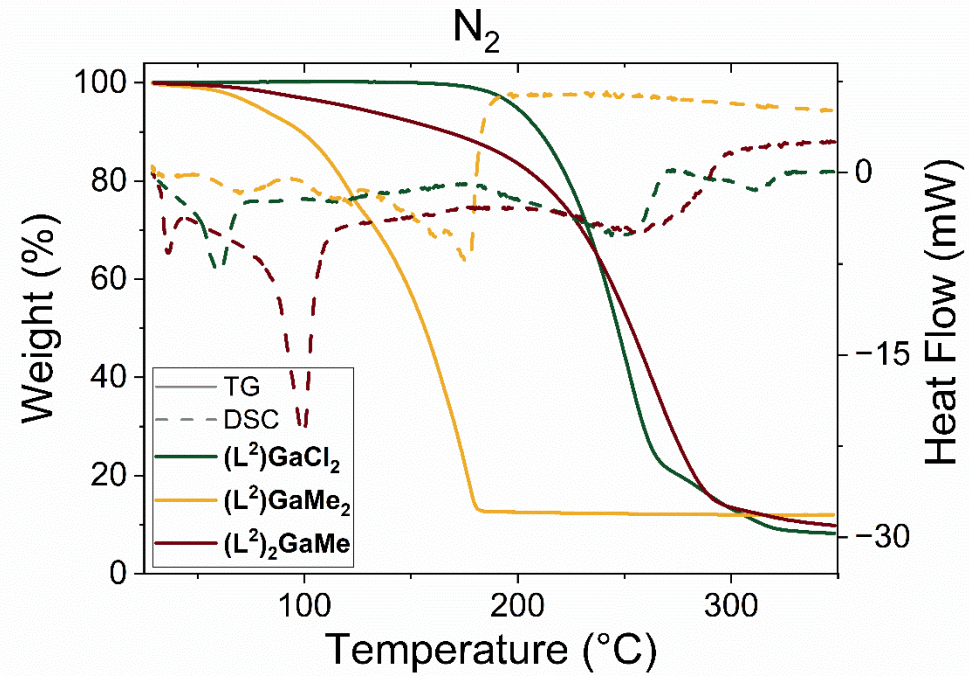
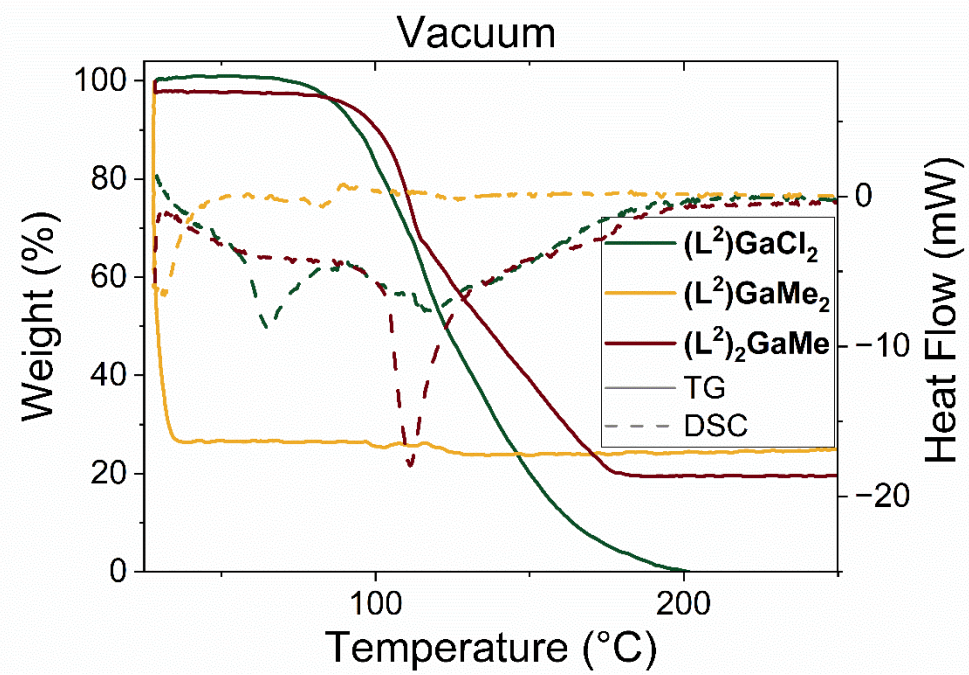
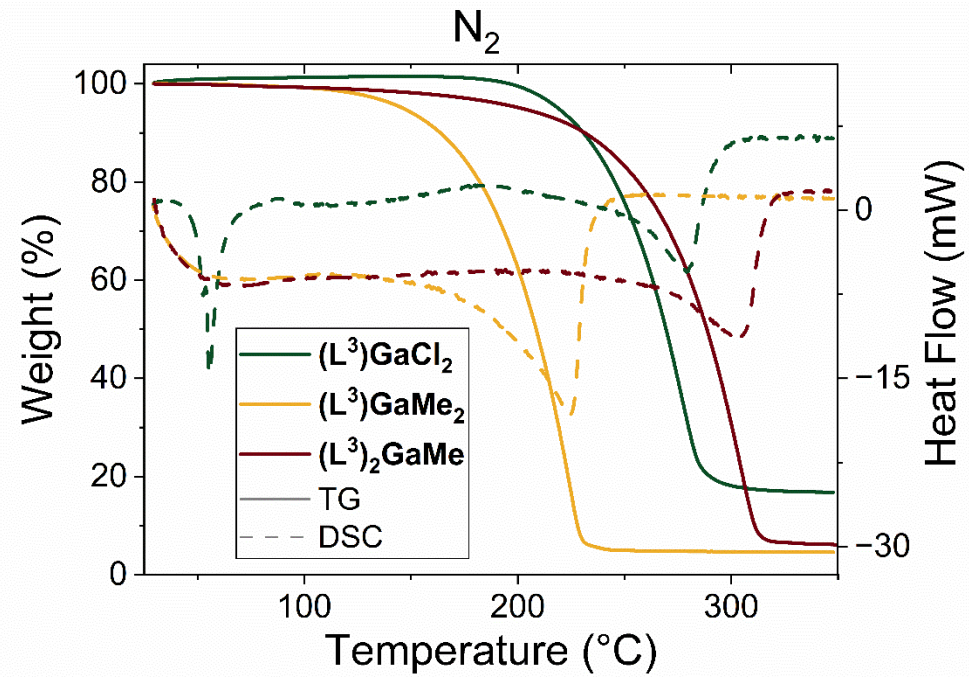


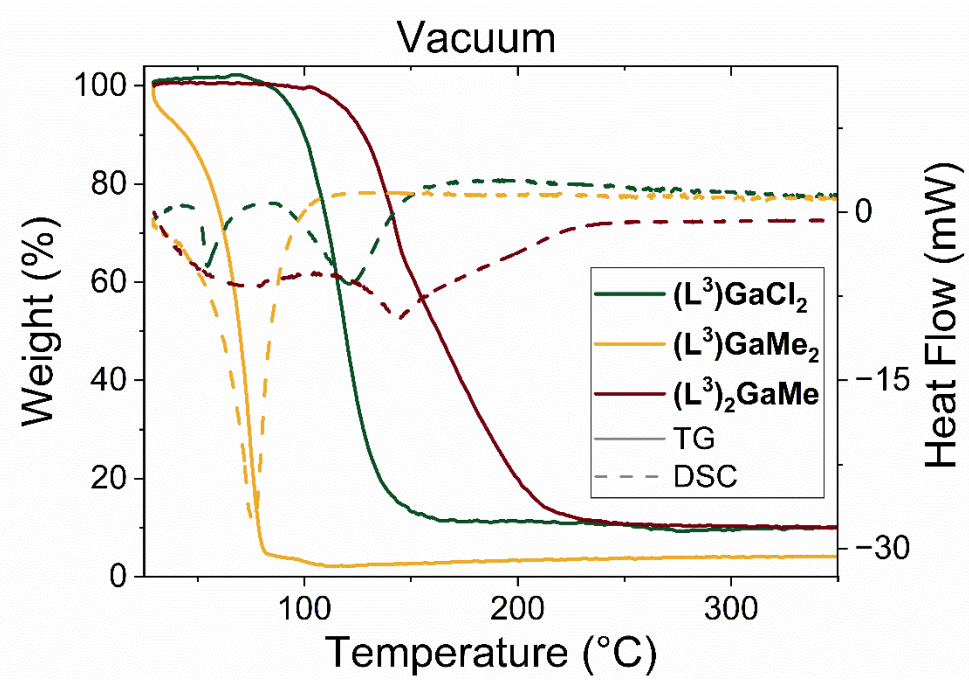
Figure S9 – Evolution of thermal properties of amidinate-based complex, evaluated by TG/DSC curves of compounds with the same amidinate ligand but different stoechiometries








N2
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L3)GaCl2
(L3)GaMe2
(L3)2GaMe
TG
DSC


Vacuum
Weight (%)
Heat Flow (mW)
Temperature (°C)
(L3)GaCl2
(L3)GaMe2
(L3)2GaMe
TG
DSC

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