# Electronic Supporting Information

## Reductive elimination of $[AlH_2]^+$ from a cationic Ga-Al dihydride

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# 1 General remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line and glovebox techniques. THF-$d_8$, $C_6D_6$, toluene, THF, and diethylether were distilled under argon from sodium/benzophenone ketyl before use. n-pentane was distilled under argon from sodium before use. Commercially available TMEDA, $CD_2Cl_2$, and $C_6D_5Br$ were dried over $CaH_2$ and distilled before use. $[Et_3NH]Cl$ was purchased from TCI and purified by sublimation before use. $LiAlH_4$ was purchased from Sigma Aldrich and recrystallised from diethylether. All other commercially available materials were used as received. $Et_3N{\cdot}AlH_3$ was prepared from $[Et_3NH]Cl$ and an excess of $LiAlH_4$ in *n*-pentane by a procedure analogous to that reported in the literature for $Me_3N{\cdot}AlH_3$.[1] It was distilled as a liquid at room temperature, and stored at -40°C. $[Et_3NH][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$,[2] [{BDI}Al] (**I$^{Al}$**, {BDI} = {HC(C(CH$_3$)Ndipp)$_2$}; dipp = 2,6-*i*Pr$_2$-C$_6$H$_3$),[3] [{BDI}Ga] (**I$^{Ga}$**),[3] 1,3,4,5-tetramethyl-imidazol-2-ylidene ($IMe_4$)**[4]** were prepared according to literature procedures. NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer in J. Young's NMR tubes at 25°C unless stated otherwise. Chemical shifts for $^1H$ and $^{13}C\{^1H\}$ were referenced internally to residual solvent peaks, reported relative to tetramethylsilane. $^{11}B\{^1H\}$ and $^{27}Al$ were referenced externally to $BF_3(OEt_2)$ and aqueous $Al(NO_3)_3$, respectively. IR spectra were recorded in KBr pellets using an AVATAR 360 FT-IR spectrometer. Elemental analysis were performed on an elementar vario EL instrument.

# 2 Synthetic procedures and characterisation

## 2.1 Synthesis of $[(TMEDA){\cdot}AlH_3]_n$

$[(TMEDA){\cdot}AlH_3]_n$ was prepared according to modified literature procedures.[5, 6] A Schlenk tube was charged with 400 mg $Et_3N{\cdot}AlH_3$ (3.05 mmol), 2 ml pentane was added via cannula and the solution cooled to -20°C in a salt-ice bath. A 5 ml pentane solution of 1.28 g TMEDA (11.01 mmol) was added dropwise by cannula with stirring. A colourless precipitate formed immediately, and the reaction mixture was allowed to warm to room temperature over the course of 1 hour. The reaction mixture was cooled again to -20°C, the precipitate was collected by cannula filtration, and washed with two portions of pentane. The product was isolated as a colourless powder in a yield of 311 mg (70%), after thorough drying under vacuum.

$[(TMEDA){\cdot}AlH_3]_n$ is highly soluble in THF, benzene, and toluene, but insoluble in diethylether and aliphatic hydrocarbons. It has been previously characterised by NMR spectroscopy[6] and single crystal X-ray diffraction.[5, 6] Here, we additionally include the NMR spectra recorded in THF-$d_8$. We note that the $^{27}Al$ chemical shift in $C_6D_6$ was similar to those of other amine adducts of $AlH_3$, but differed significantly to that reported previously for $[(TMEDA){\cdot}AlH_3]_n$.[6]

$^{1}$H NMR (400 MHz, THF-$d_8$) δ 3.50-2.70 (br, 3H, Al*H*), 2.46 (s, 4H, C*H*$_2$), 2.20 (s, 12H, C*H*$_3$).

$^{13}$C{$^{1}$H} NMR (101 MHz, THF-$d_8$) δ 57.85 (*C*H$_2$), 46.05 (*C*H$_3$).

$^{27}$Al NMR (104 MHz, THF-$d_8$) δ 113.78 (br).

$^{1}$H NMR (400 MHz, $C_6D_6$) δ 4.05 (3H, br, Al*H*$_3$), 2.44 (s, 4H, C*H*$_2$), 2.03 (s, 12H, C*H*$_3$).

$^{13}$C{$^{1}$H} NMR (101 MHz, $C_6D_6$) δ 55.81 (*C*H$_2$), 45.58 (*C*H$_3$).

$^{27}$Al NMR (104 MHz, $C_6D_6$) δ 136.88 (br).

IR spectroscopy (KBr pellet): ν = 1713 cm$^{-1}$ (br, Al-H)

Elemental analysis calculated for $C_6H_{19}AlN_2$: C 49.29, H 13.10, N 19.16%. Found: C 48.22, H 12.69, N 19.46%. Despite repeated attempts, we were unable to obtain more accurate elemental analysis for this compound. This may result from partial hydrolysis of the compound when handled outside of the glovebox immediately prior to analysis.

## 2.2 NMR spectra of [(TMEDA)·$AlH_3$]$_n$

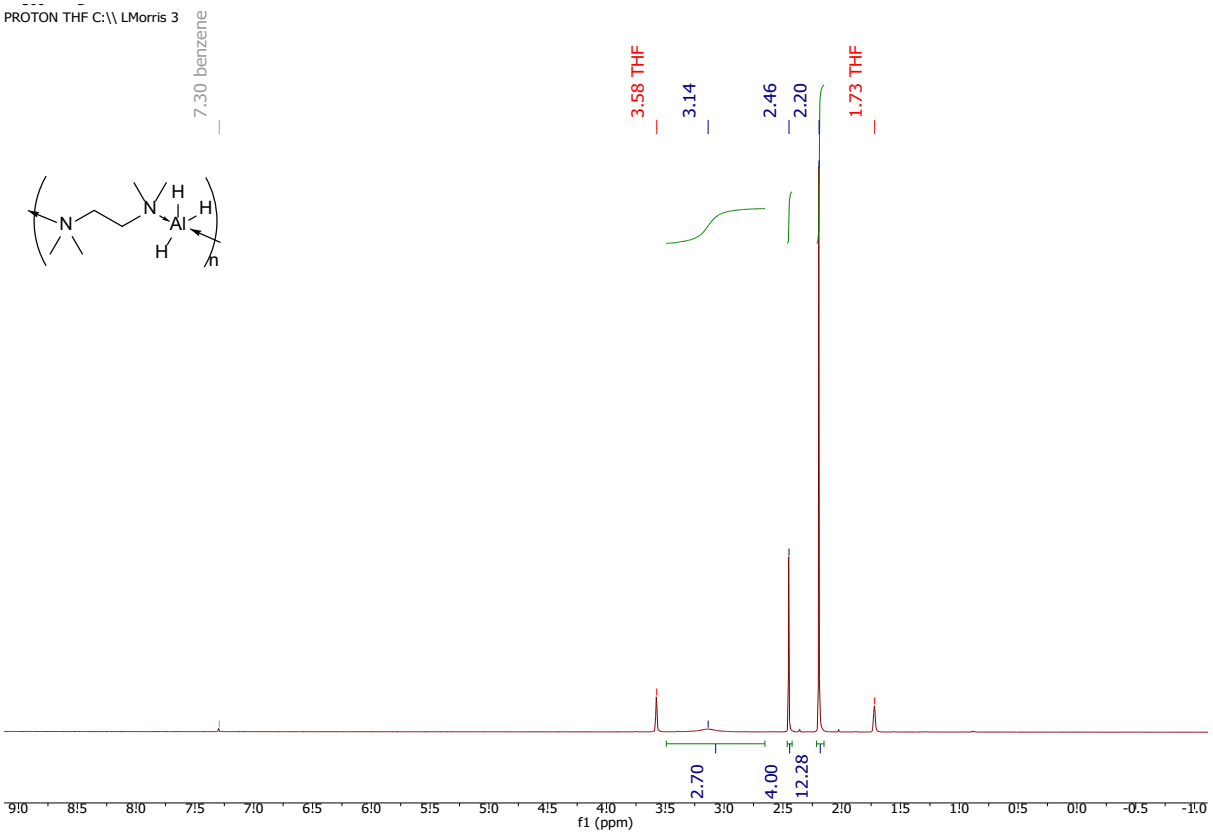



Figure S 1: $^{1}$H NMR (400 MHz, THF-$d_8$).

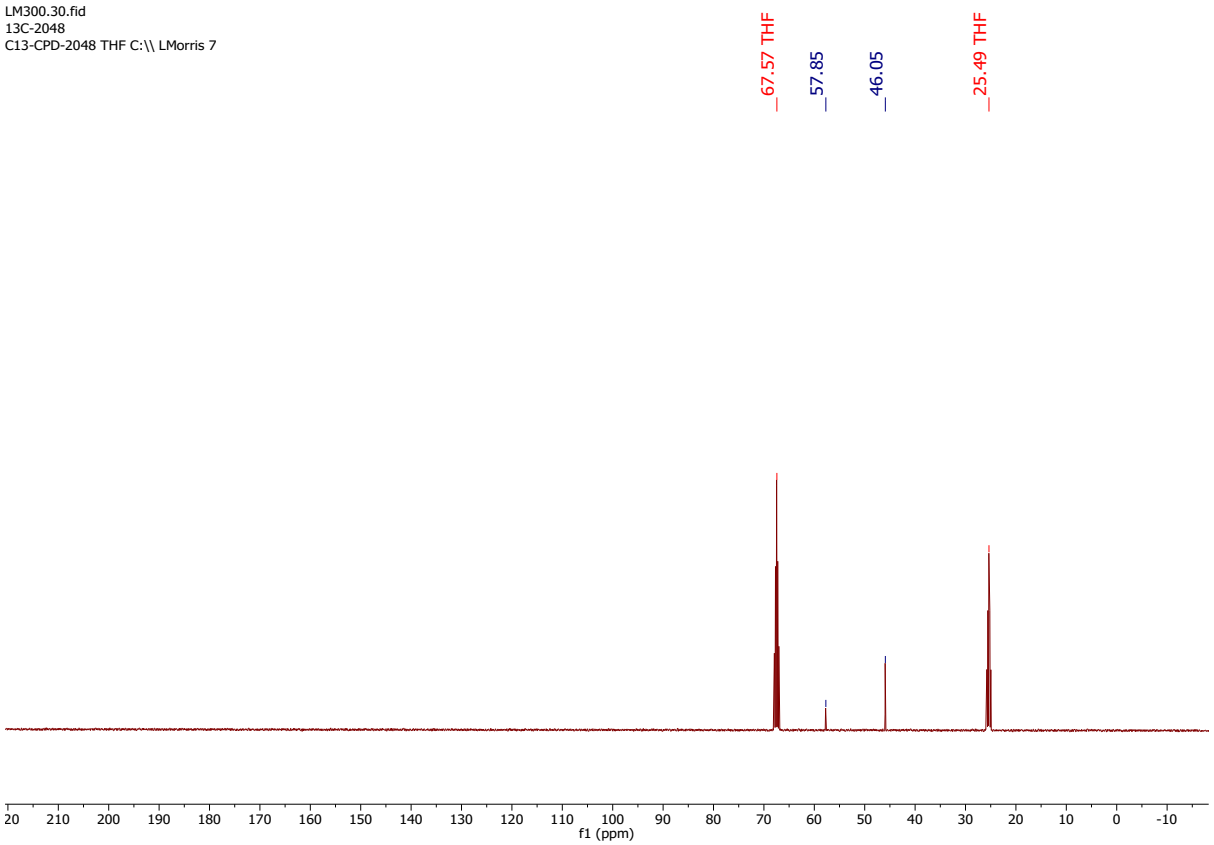



Figure S 2: $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-$d_8$).

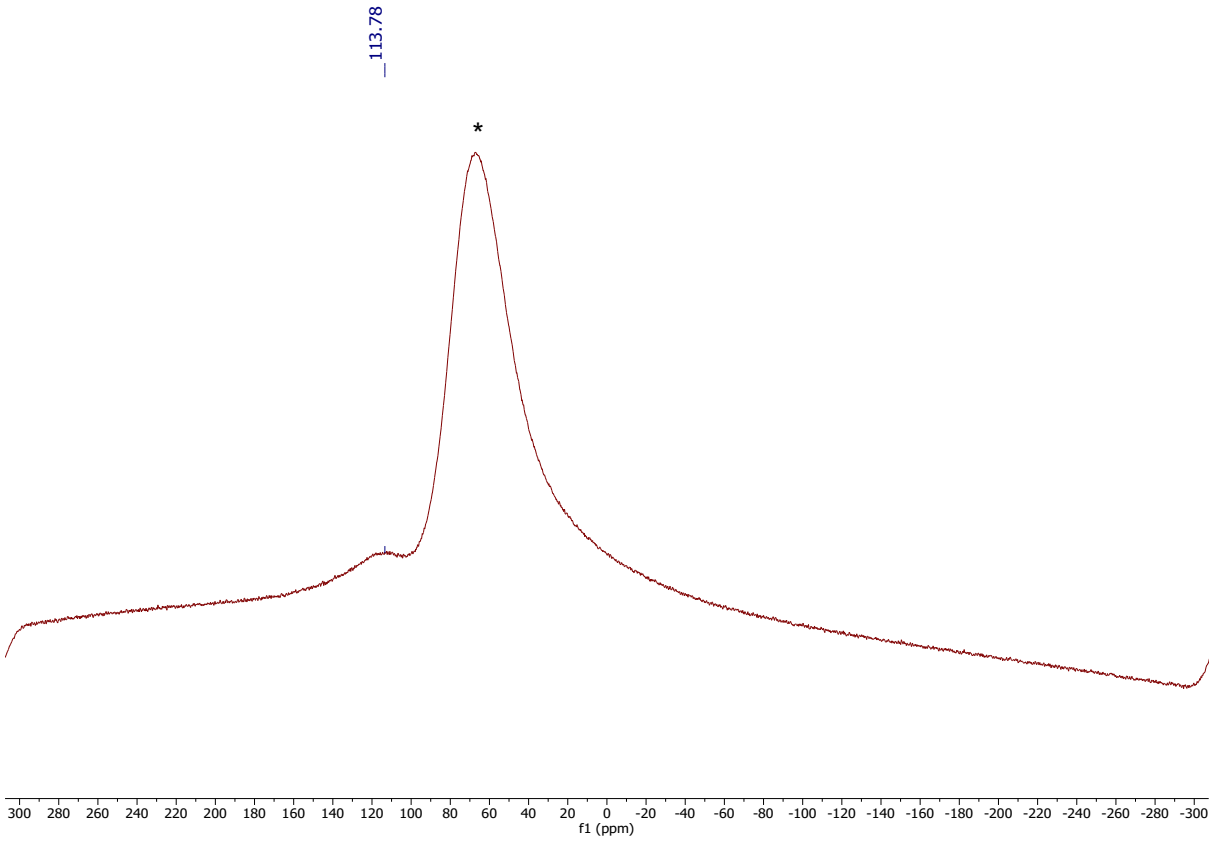



Figure S 3: $^{27}Al$ NMR (104 MHz, THF-$d_8$). * background signal from spectrometer probe.

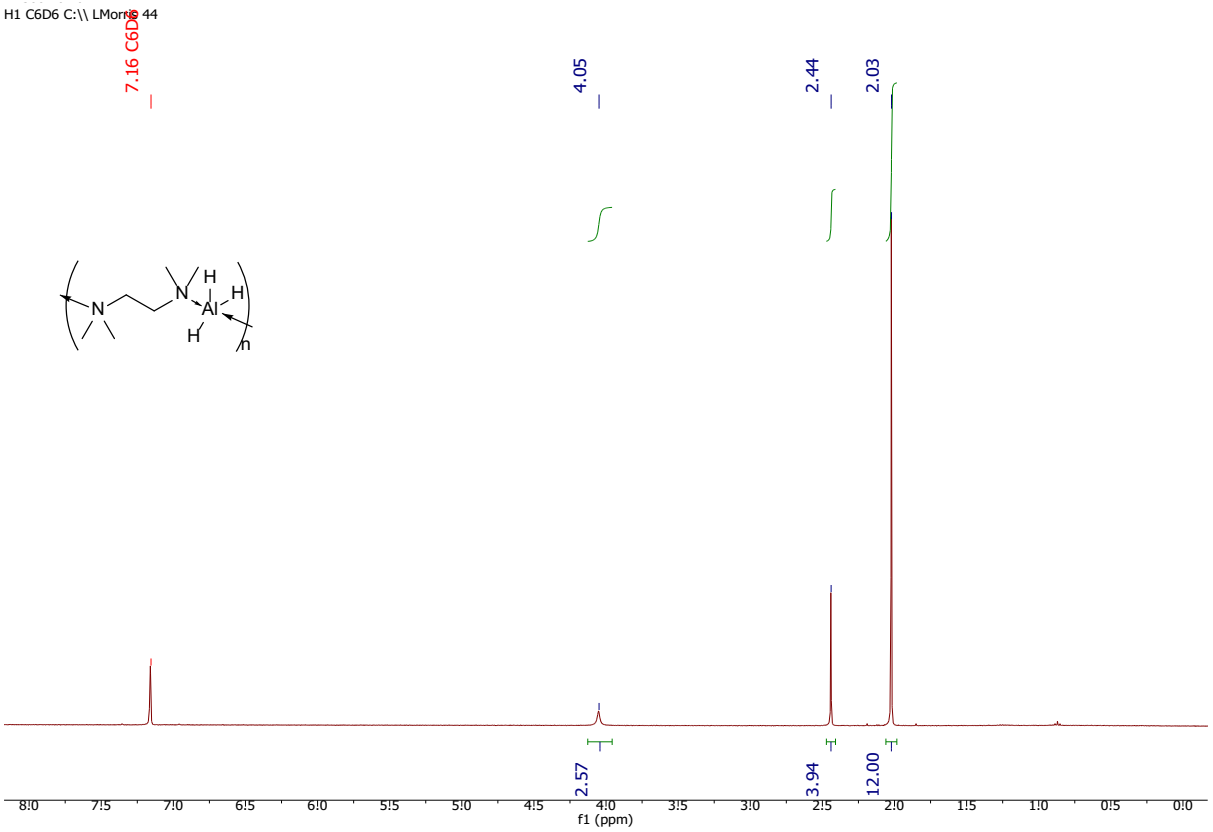



Figure S 4: $^{1}H$ NMR (400 MHz, $C_6D_6$).

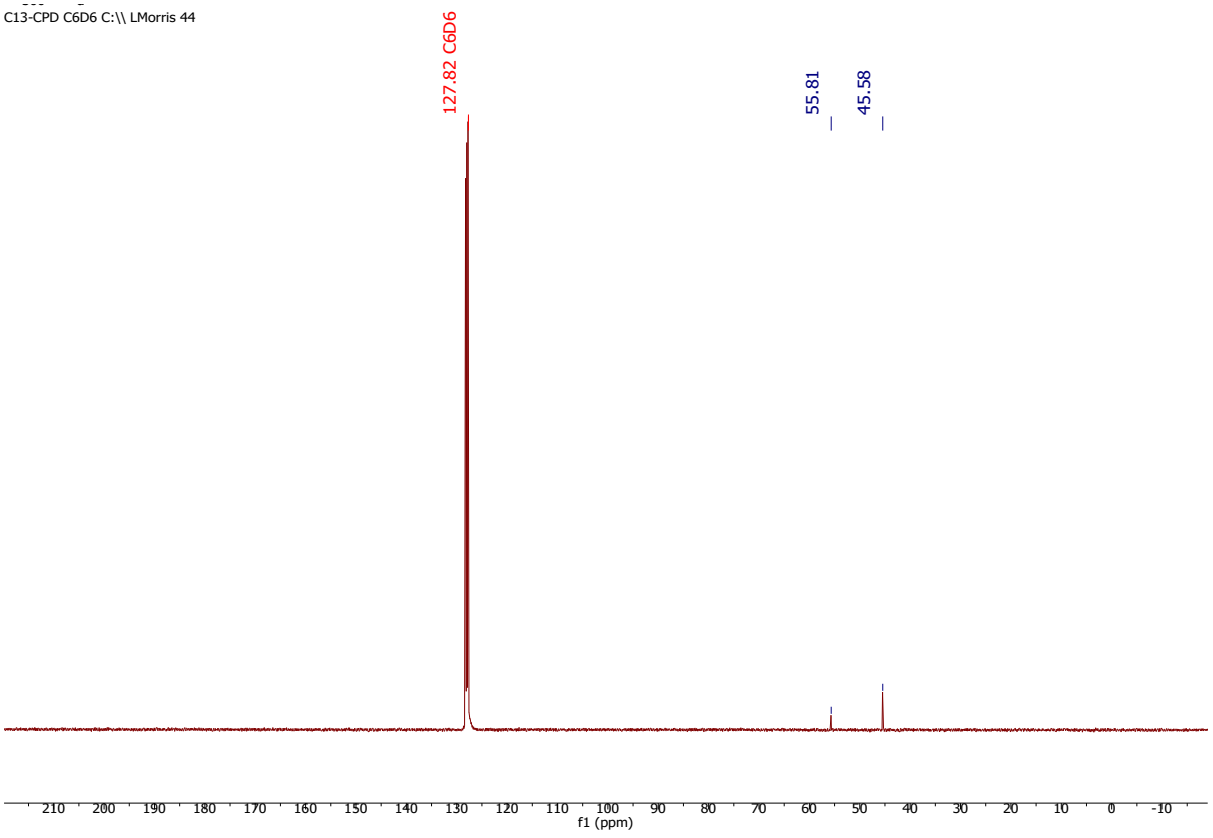



Figure S 5: $^{13}C\{^{1}H\}$ NMR (101 MHz, $C_6D_6$).

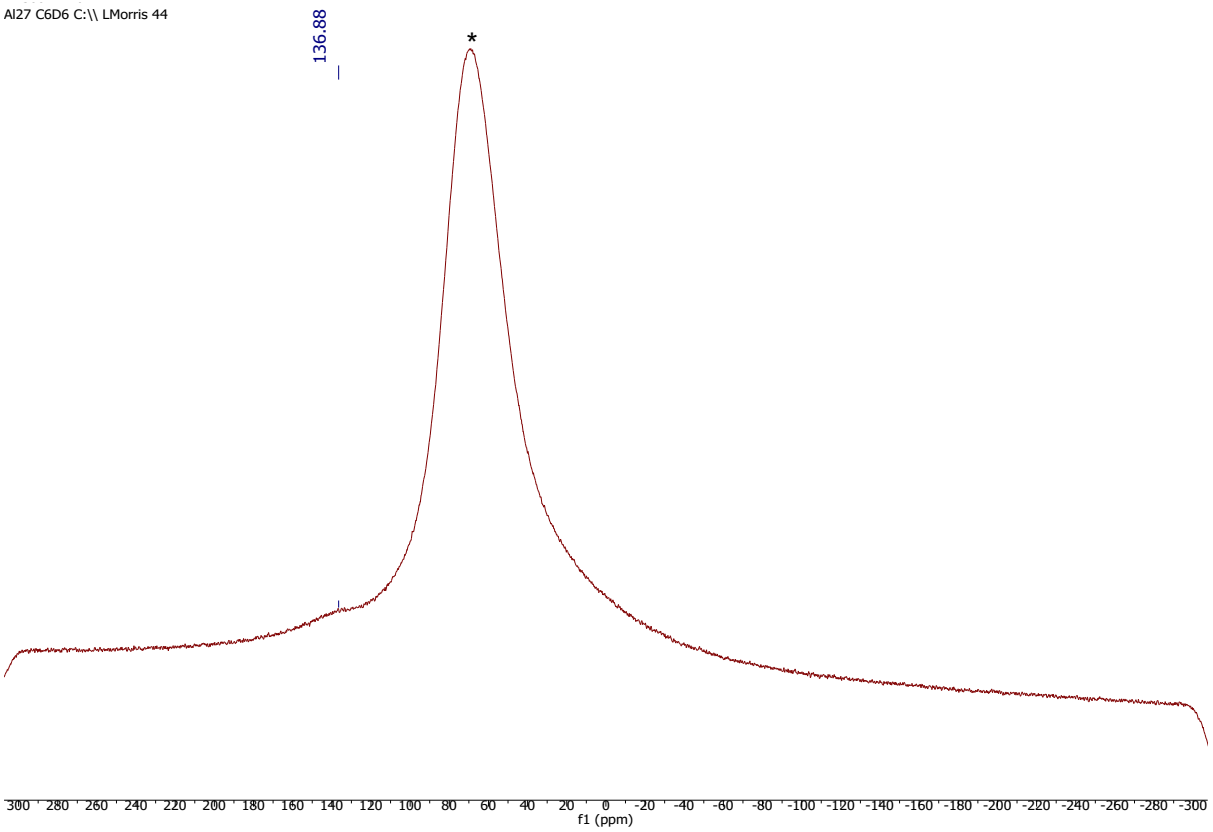



Figure S 6: $^{27}$Al NMR (104 MHz, $C_6D_6$). * background signal from spectrometer probe.

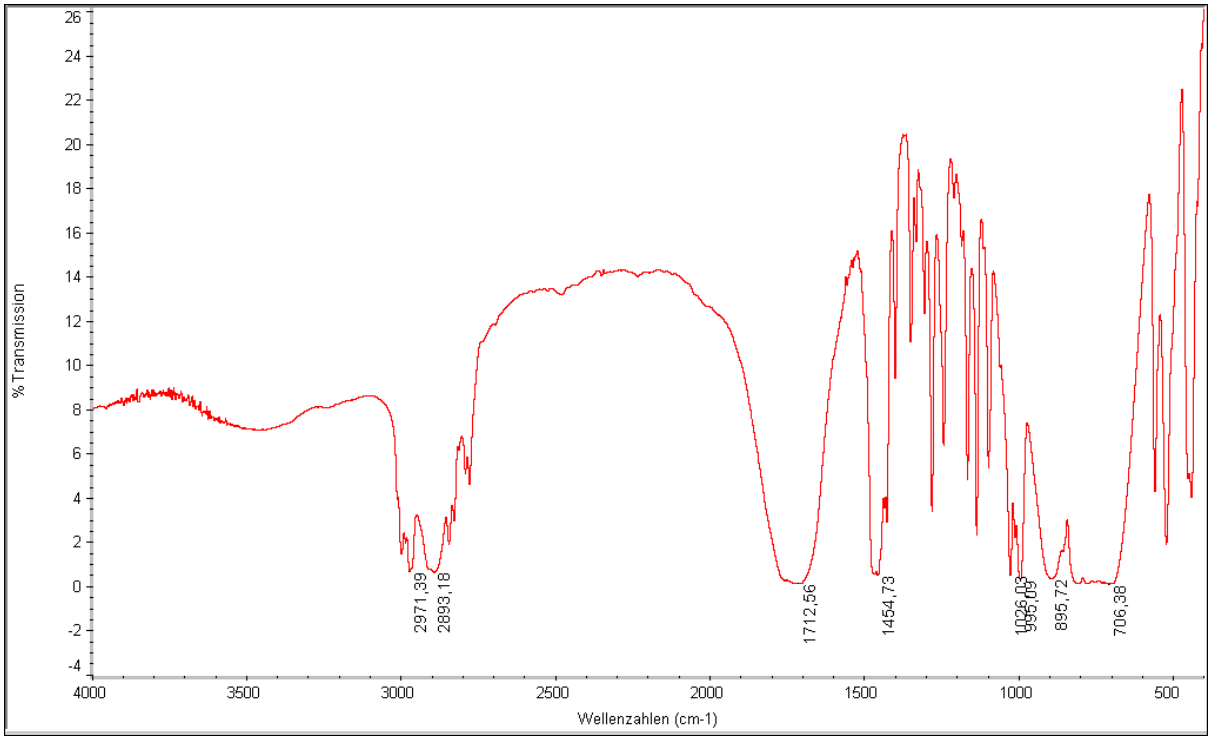



Figure S 7: IR spectrum (KBr pellet) of $[(tmeda)\cdot AlH_3]_n$.

## 2.3 Synthesis of [(TMEDA)$AlH_2$·($OEt_2$)][B($C_6H_3$-3,5-$Me_2$)$_4$] **1** and [(TMEDA)$AlH_2$·(thf)$_2$][B($C_6H_3$-3,5-$Me_2$)$_4$] **1·thf$_2$**

A Schlenk flask was charged with 100 mg [(TMEDA)·$AlH_3$]$_n$ (0.6$_8$4 mmol) and 364 mg [$Et_3NH$][B($C_6H_3$-3,5-$Me_2$)$_4$] (0.684 mmol). Diethylether (5 ml) was added to the stirring mixture by cannula, resulting in the evolution hydrogen gas. The resulting colourless suspension was stirred for 4 hours. The product was isolated by cannula filtration, washed with pentane, and vacuum dried to obtain **1** as a colourless powder. Yield 367 mg, 82%. Partial loss of diethylether occurs when exposed to high vacuum for several hours.

$^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.10 (t, *J* = 2.8 Hz, 8H, *ortho*-$C_6\underline{H_3}$), 6.52 (m,4H, *para*- $C_6\underline{H_3}$), 3.65 (q, *J* = 7.0 Hz, 4H, O$C\underline{H_2}$), 3.60-3.05 (br, 2H, Al-$\underline{H}$), 2.29 (s, 12H, N$C\underline{H_3}$), 2.18 (s, 24H, $C_6H_3C\underline{H_3}$), 2.05 (s, 4H, N$C\underline{H_2}$), 1.21 (t, *J* = 7.0 Hz, 6H, $OCH_2C\underline{H_3}$).

$^1$H NMR (400 MHz, THF-$d_8$) δ 6.96 (s, 8H, *ortho*-$C_6\underline{H_3}$), 6.34 (s, 4H, *para*- $C_6\underline{H_3}$), 3.39 (q, *J* = 7.0 Hz, 4H, O$C\underline{H_2}$), 2.36 (s, 4H, N$C\underline{H_2}$), 2.24 (s, 12H, N$C\underline{H_3}$), 2.08 (s, 24H, $C_6H_3C\underline{H_3}$), 1.12 (t, *J* = 7.0 Hz, 6H $OCH_2C\underline{H_3}$).

$^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$) δ 165.34 (q, $^1J_{(B\text{-}C)}$ = 49.0 Hz, *ipso*-B$\underline{C}_6H_3$), 134.60 (q, $^3J_{(B\text{-}C)}$ = 2.8 Hz, *meta*-B$\underline{C}_6H_3$), 134.48 (d, *J* = 1.0 Hz, *ortho*-B$\underline{C}_6H_3$), 123.82 (*para*-B$\underline{C}_6H_3$),), 66.02 (O$\underline{C}H_2CH_3$), 56.44 (N$\underline{C}H_2$), 47.66 (N$CH_3$), 22.09 ($C_6H_3\underline{C}H_3$), 14.72 ($OCH_2\underline{C}H_3$).

$^{27}$Al NMR (104 MHz, $CD_2Cl_2$) δ 147.76 (br).

$^{11}$B{$^1$H} NMR (128 MHz, $CD_2Cl_2$) δ -6.73.

IR (KBr pellet): v = 1852 cm$^{-1}$ (Al-H).

Analysis calculated for $C_{42}H_{64}AlBN_2O$: C 77.52, H 9.91, N 4.30%. Found: C 76.33, H 9.92, N 5.03%. Despite repeated attempts, we were unable to obtain more accurate elemental analysis of this compound. This may be due to traces of [(tmeda)$_2AlH_2$][$BAr_4$] or other impurities which could not be separated by washing. Attempts to further purify the compound by crystallisation were unsuccessful and the as obtained material was suitable for further use.

Colourless needle-like single crystals suitable for X-ray diffraction analysis of the bis-THF complex, **1·thf$_2$** were obtained by slow diffusion of pentane into a THF solution of 90 mg **1** (0.1383 mmol) at -40°C. The mother liquor was decanted, the crystals washed with cold THF and *n*-pentane, then vacuum dried to yield 81 mg of **1·thf$_2$**, 81%.

$^1$H NMR (400 MHz, THF-$d_8$) δ 7.01 – 6.94 (m, 8H, 2,6-Ar), 6.34 (s, 4H, 4-Ar), 3.68 – 3.59 (m, 8H, 2,5-THF), 2.33 (s, 4H, C$\underline{H_2}$), 2.22 (s, 12H, N$C\underline{H_3}$), 2.09 (s, 24H, Ar-C$\underline{H_3}$), 1.83 – 1.75 (m, 8H, 3,4-THF).

$^{13}C\{^{1}H\}$ NMR (101 MHz, THF-$d_8$) δ 165.77 (q, $^{1}J(^{11}B)$ = 49.3 Hz, 1-Ar), 135.62 (2,6-Ar), 132.96 (q, $^{3}J(^{11}B)$ = 2.8 Hz, 3,5-Ar), 123.62 (4-Ar), 68.39 (2,5-THF), 56.18 ($\underline{C}H_2$), 46.84 (N$\underline{C}H_3$), 26.55 (3,4-THF), 22.46 (Ar-$\underline{C}H_3$).

$^{11}B\{^{1}H\}$ NMR (128 MHz, THF-$d_8$) δ -6.92.

No signal could be observed in the $^{27}Al$ NMR spectrum.

IR (KBr pellet): v = 1731 $cm^{-1}$ (Al-H).

Elemental analysis calculated for $C_{46}H_{70}AlBN_2O_2$: C 76.64, H 9.79, N 3.89%. Found: C 75.48, H 9.75, N 3.89%. Despite repeated attempts, we were unable to obtain more accurate elemental analysis for this compound. This is tentatively ascribed to residual non-coordinating THF in the crystal lattice.

## 2.4 NMR and IR spectra of [(TMEDA)$AlH_2$·($OEt_2$)][B($C_6H_3$-3,5-$Me_2$)$_4$] **1**.

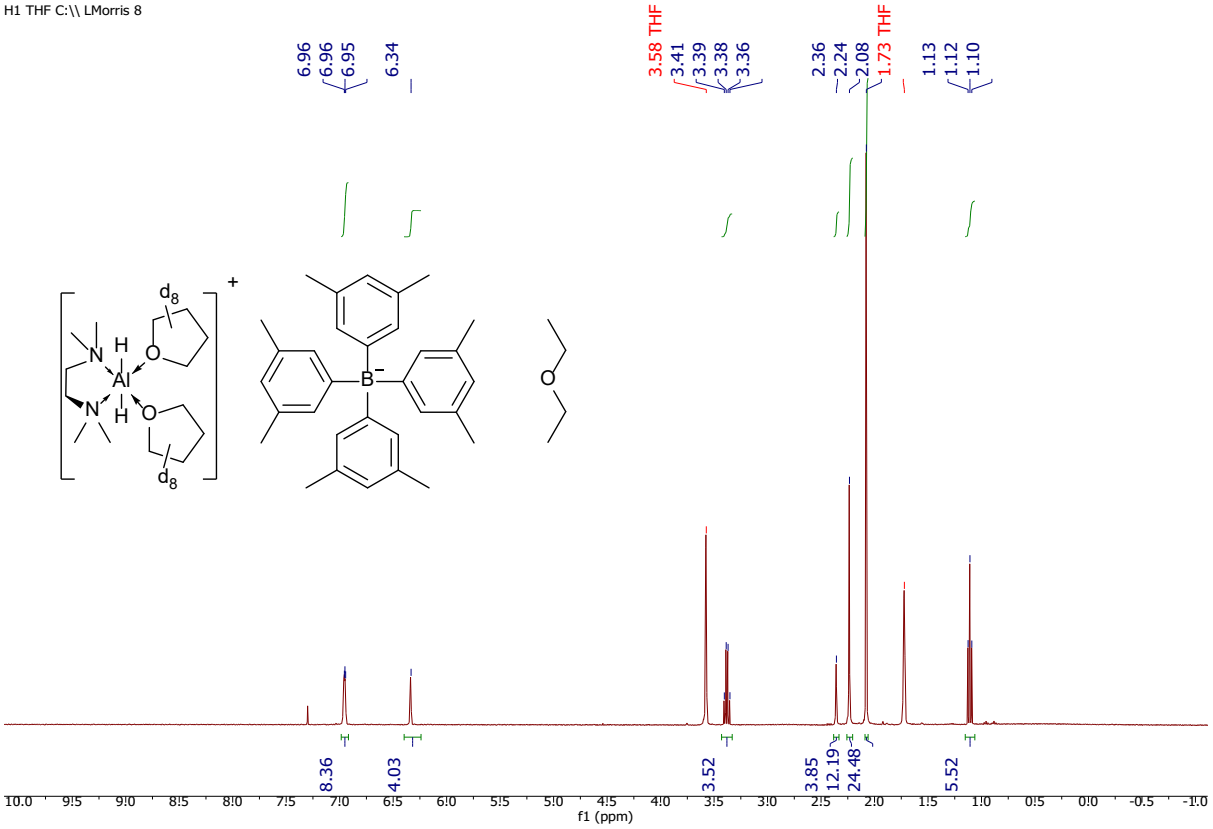



Figure S 8: $^{1}H$ NMR spectrum (400 MHz, THF-$d_8$).

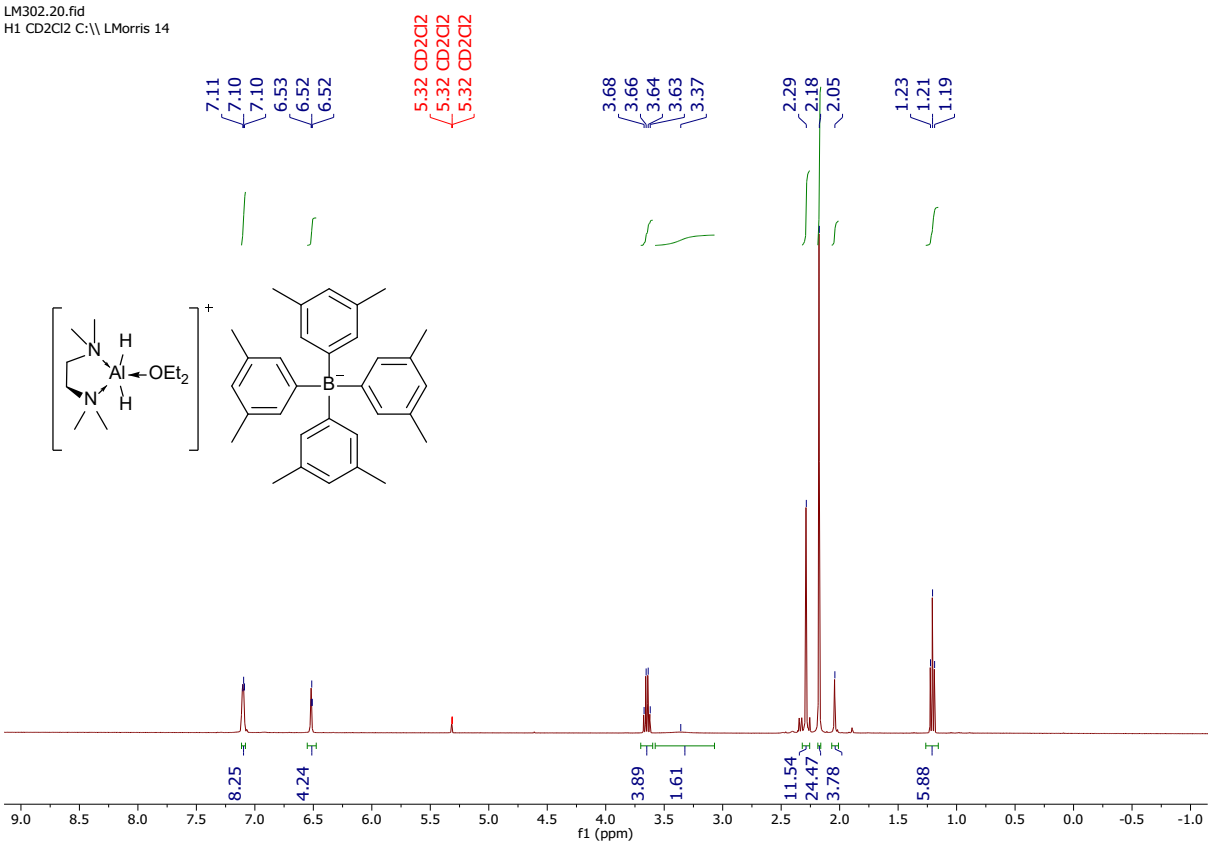



Figure S 9: $^{1}H$ NMR (400 MHz, $CD_2Cl_2$).

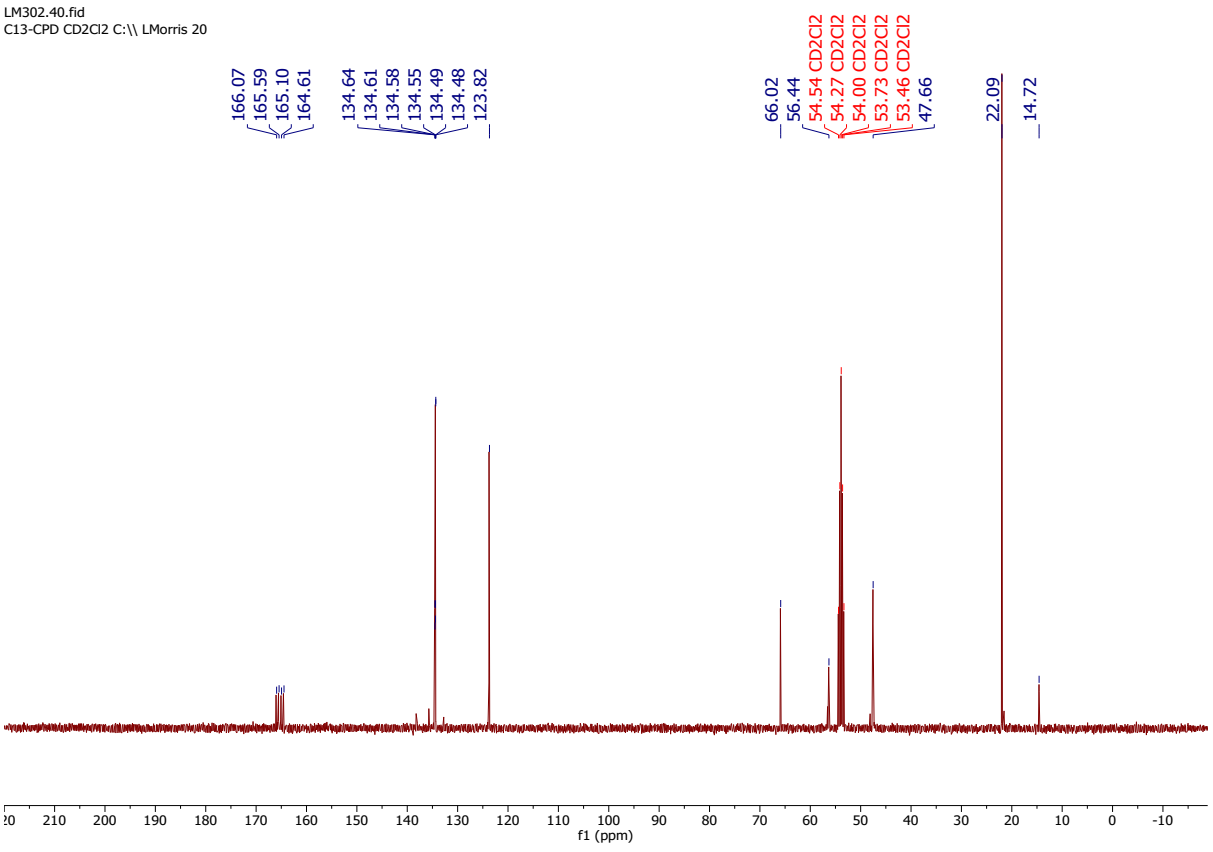



Figure S 10: $^{13}C\{^{1}H\}$ NMR (101 MHz, $CD_2Cl_2$).

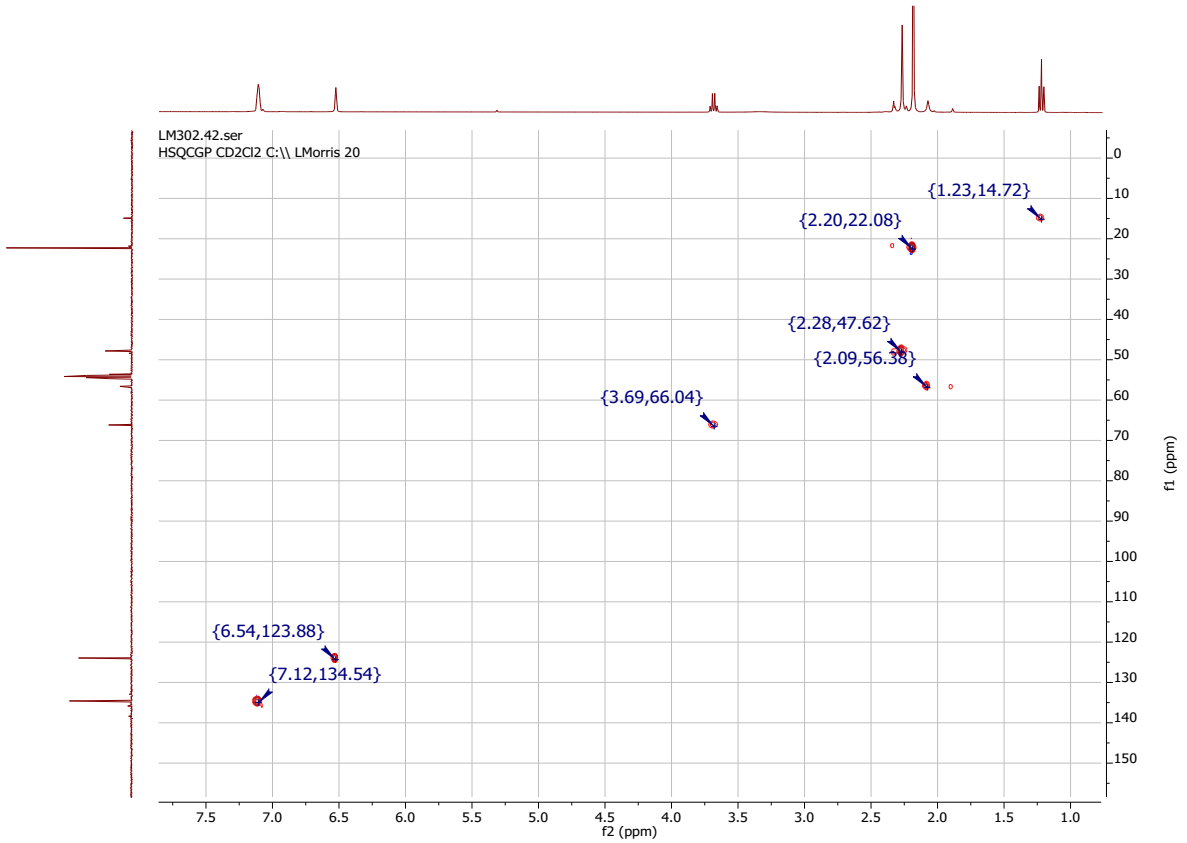



Figure S 11: $^{13}C$-$^{1}H$ HSQC spectrum ($CD_2Cl_2$).

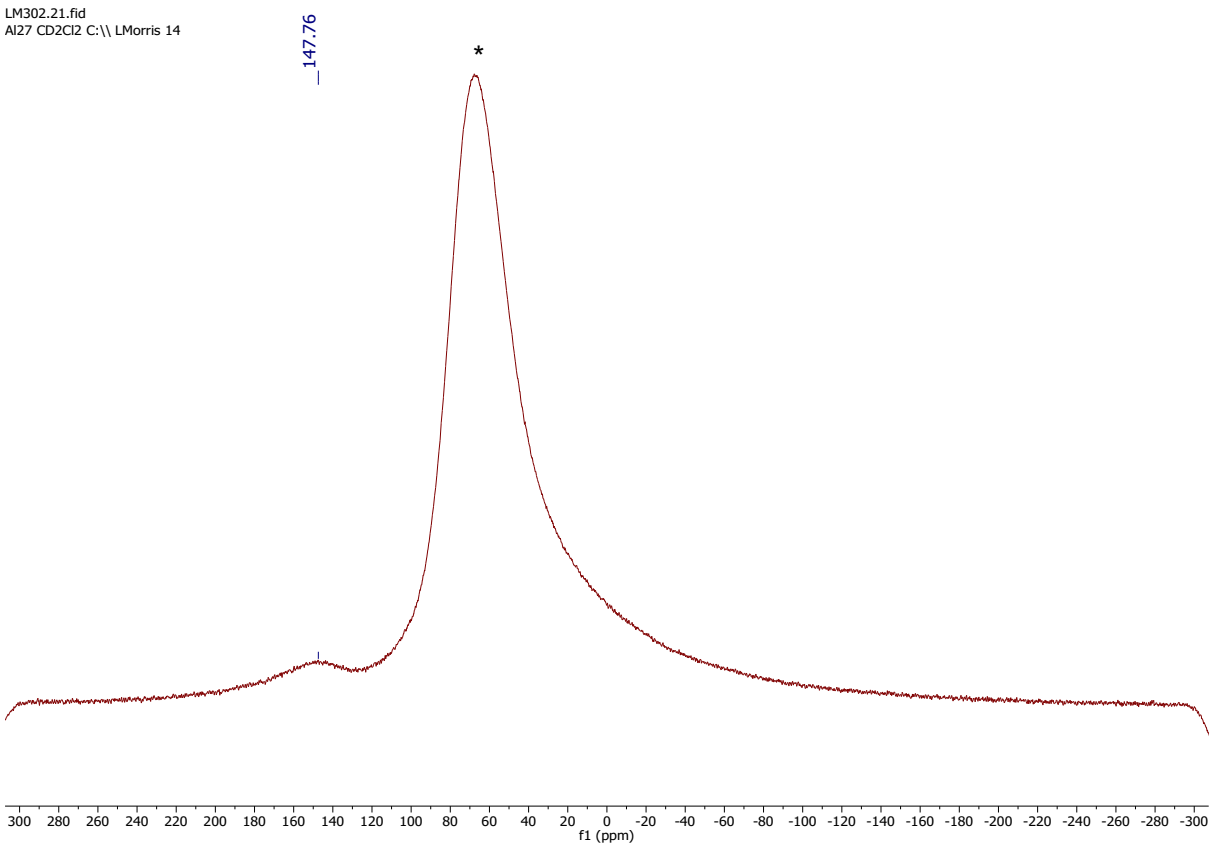



Figure S 12: $^{27}Al$ NMR (104 MHz, $CD_2Cl_2$). * background signal from spectrometer probe.

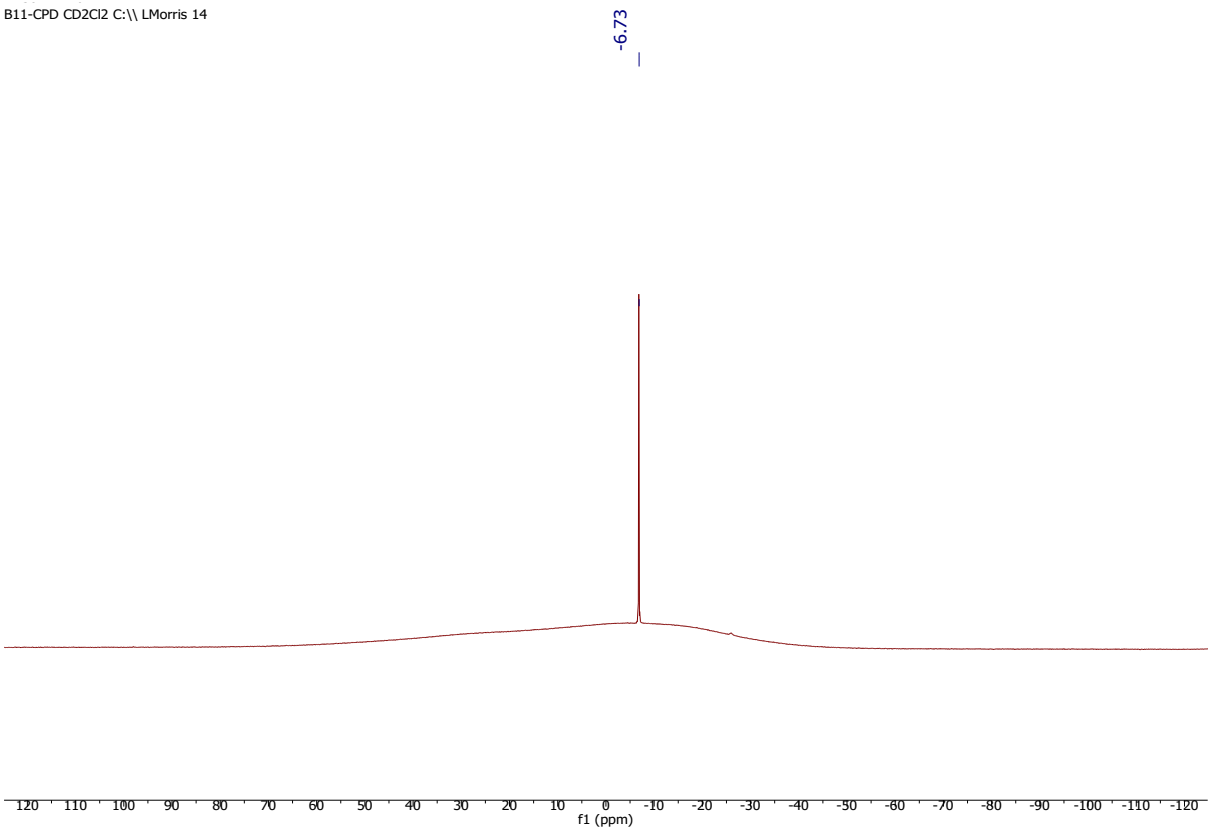



Figure S 13: $^{11}B\{^{1}H\}$ NMR (128 MHz, $CD_2Cl_2$).

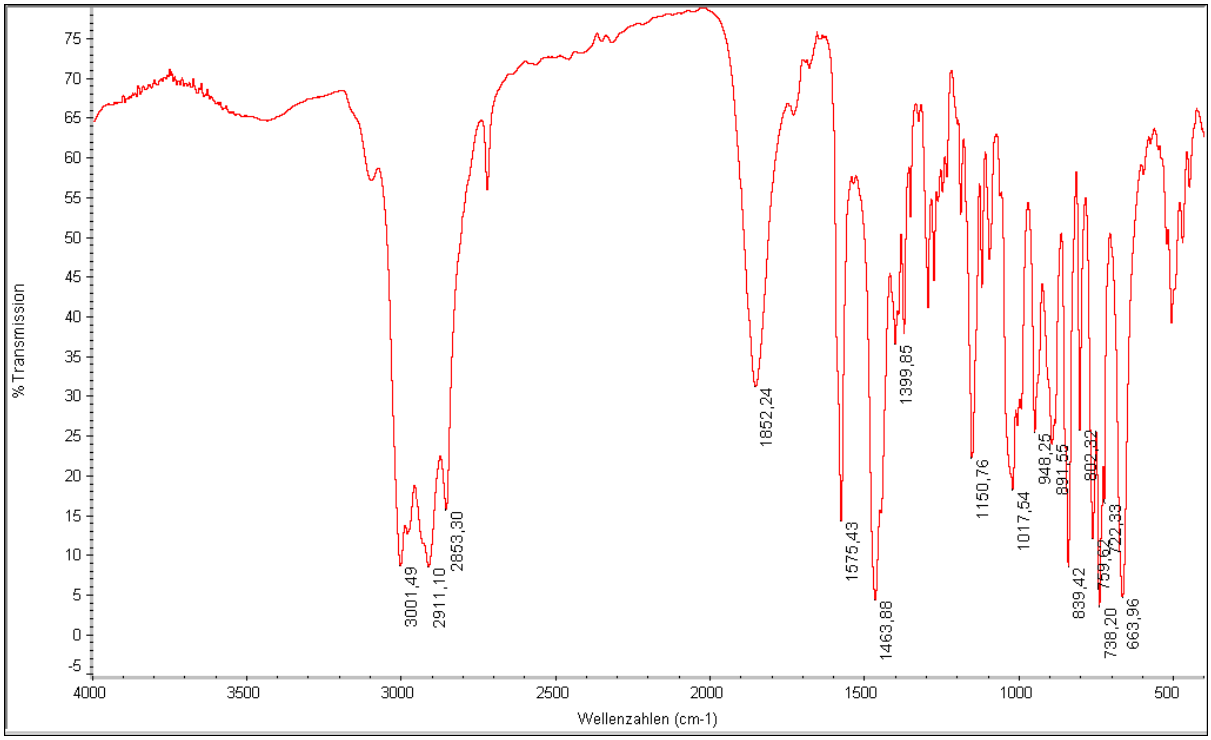



Figure S 14: IR spectrum (KBr pellet) of **1**.

## 2.5 NMR and IR spectra of [(TMEDA)$AlH_2$·$(thf)_2$][$B(C_6H_3$-3,5-$Me_2)_4$] **1·thf₂**

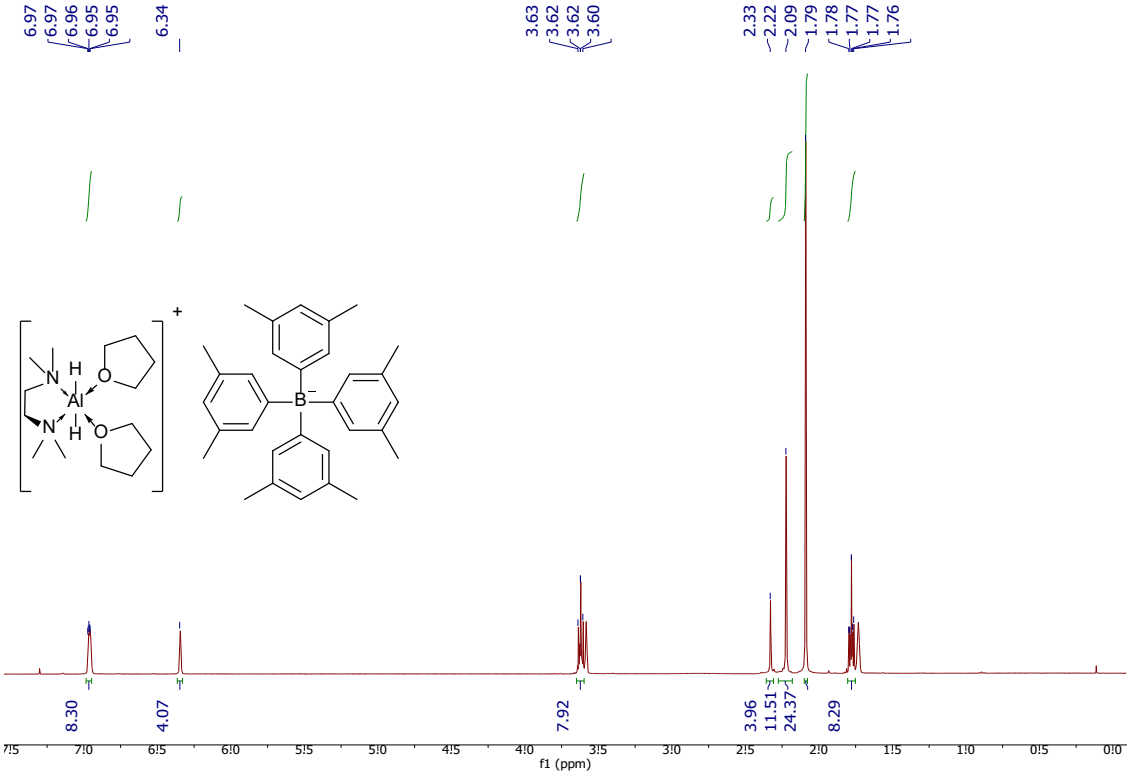



Figure S 15: $^1H$ NMR (400 MHz, THF-$d_8$).

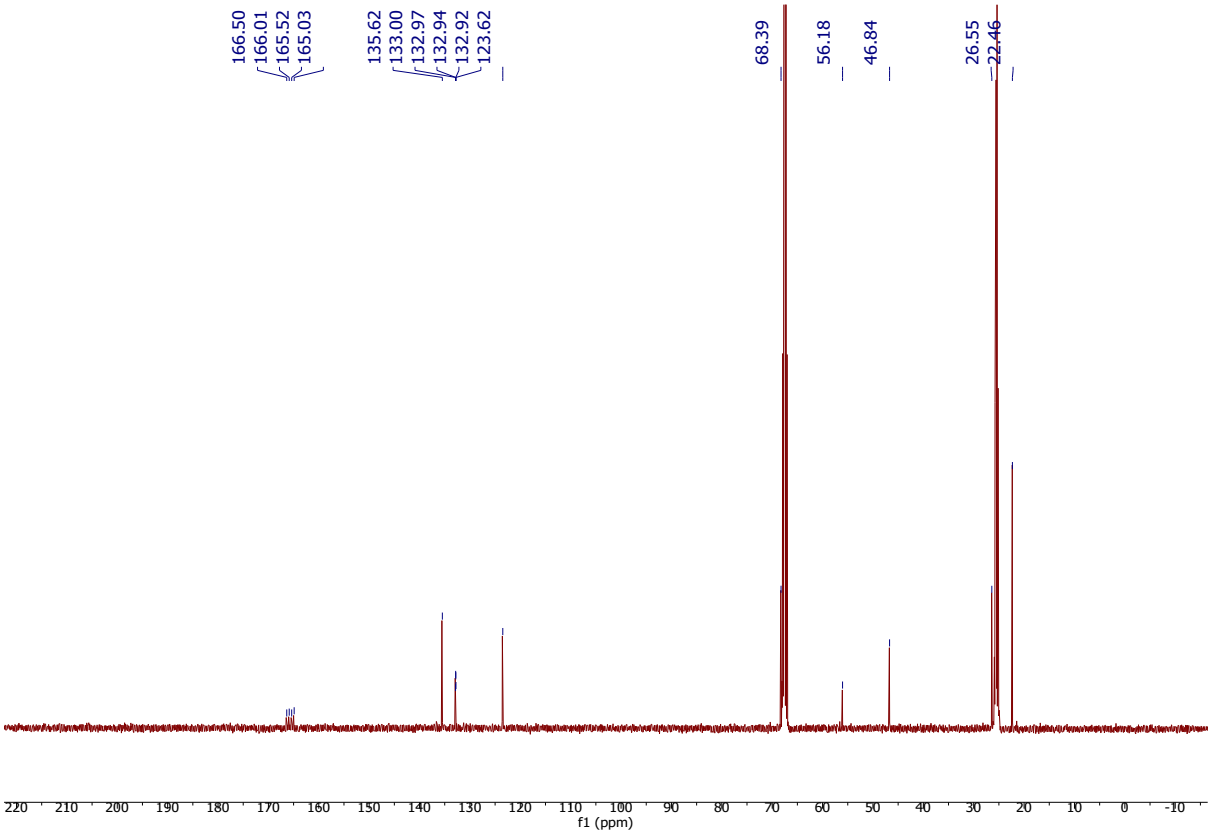



Figure S 16: $^{13}C\{^1H\}$ NMR (101 MHz, THF-$d_8$)

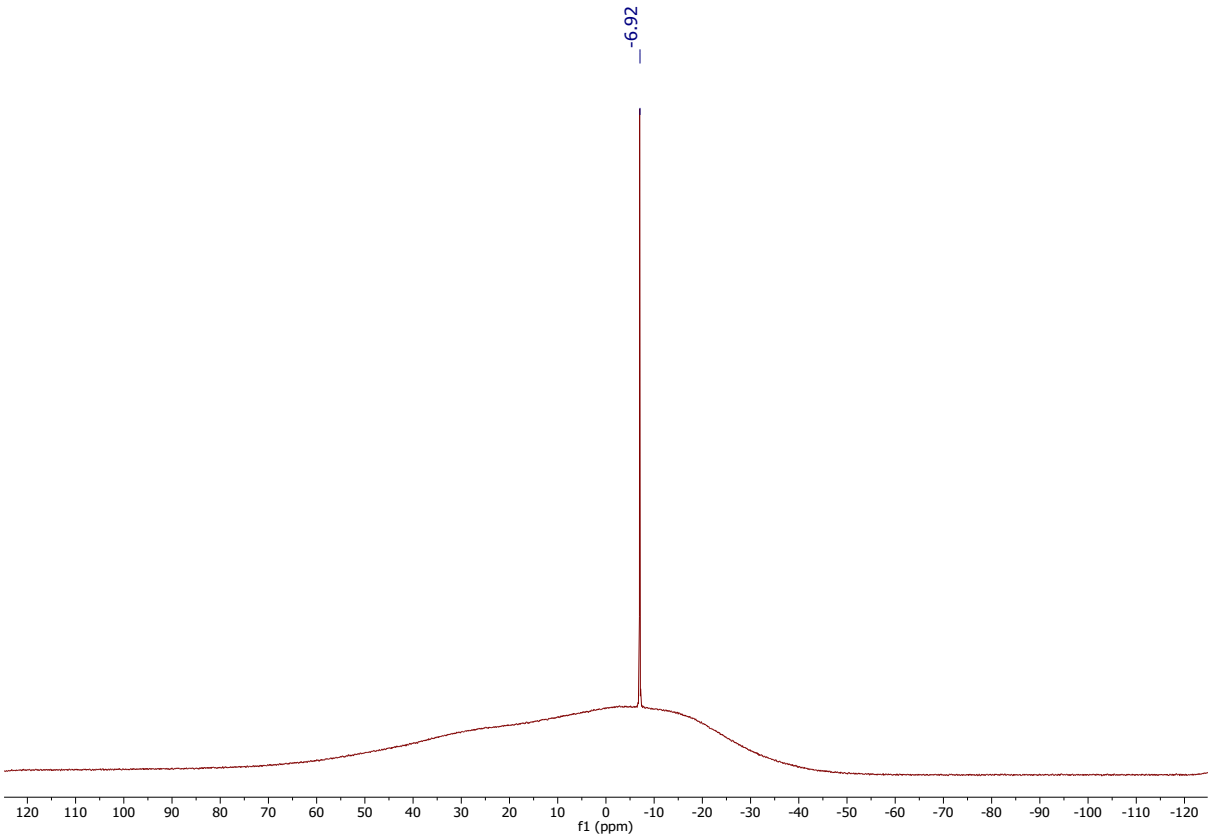



Figure S 17: $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-$d_8$)

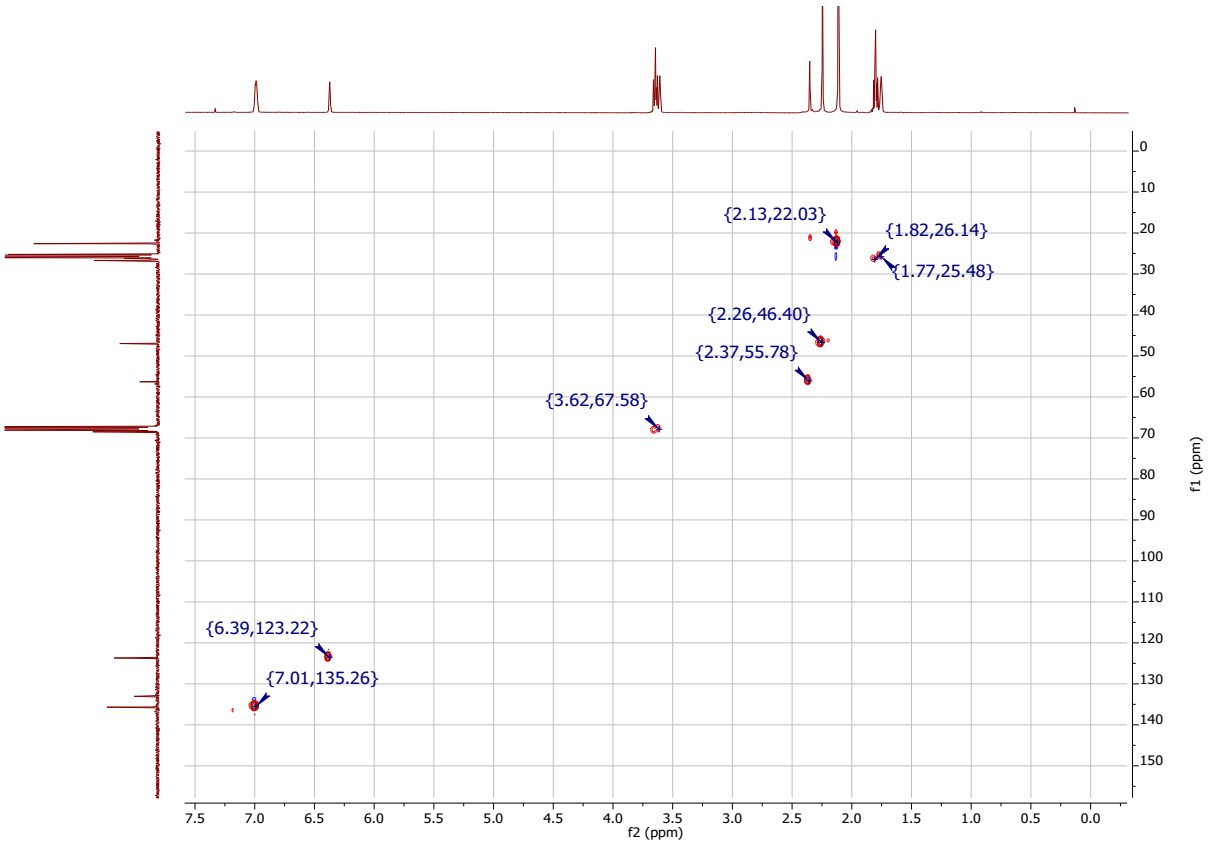



Figure S 18: $^{13}C$-$^{1}H$ HSQC spectrum (THF-$d_8$).

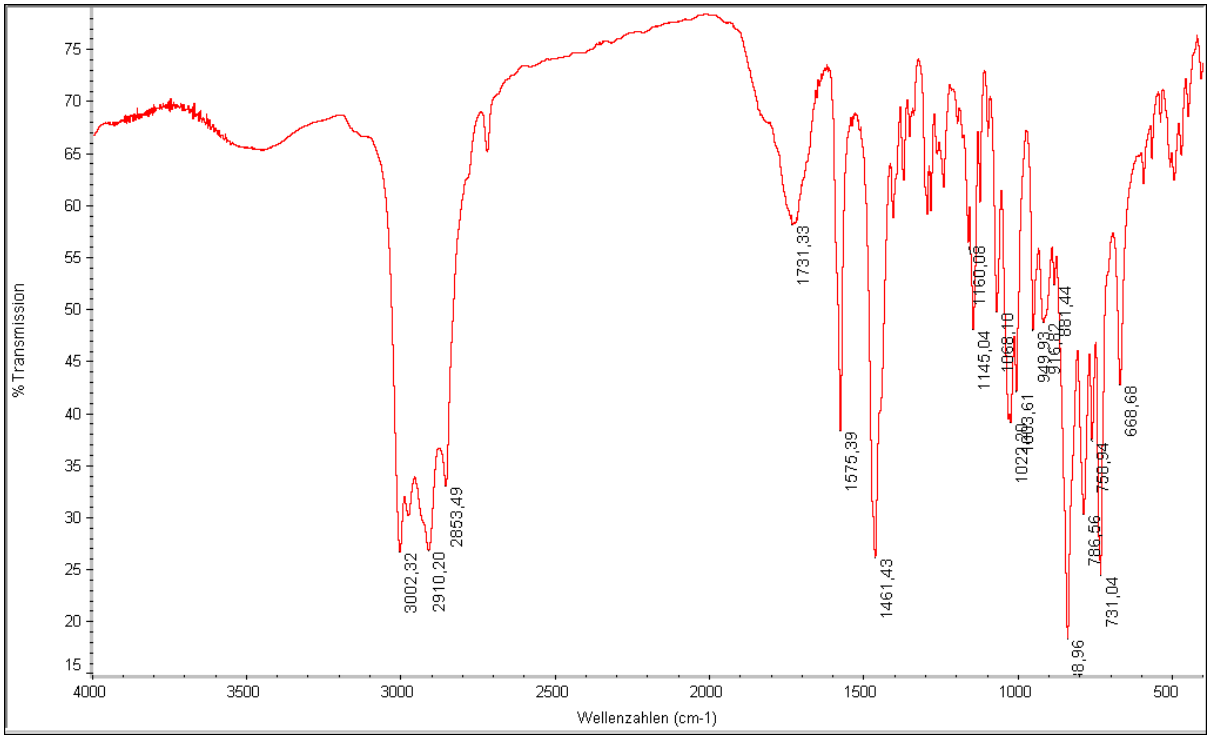



Figure S 19: IR spectrum (KBr pellet).

## 2.6 X-ray crystal structure of $[(TMEDA)AlH_2{\cdot}(thf)_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ **1·thf₂**

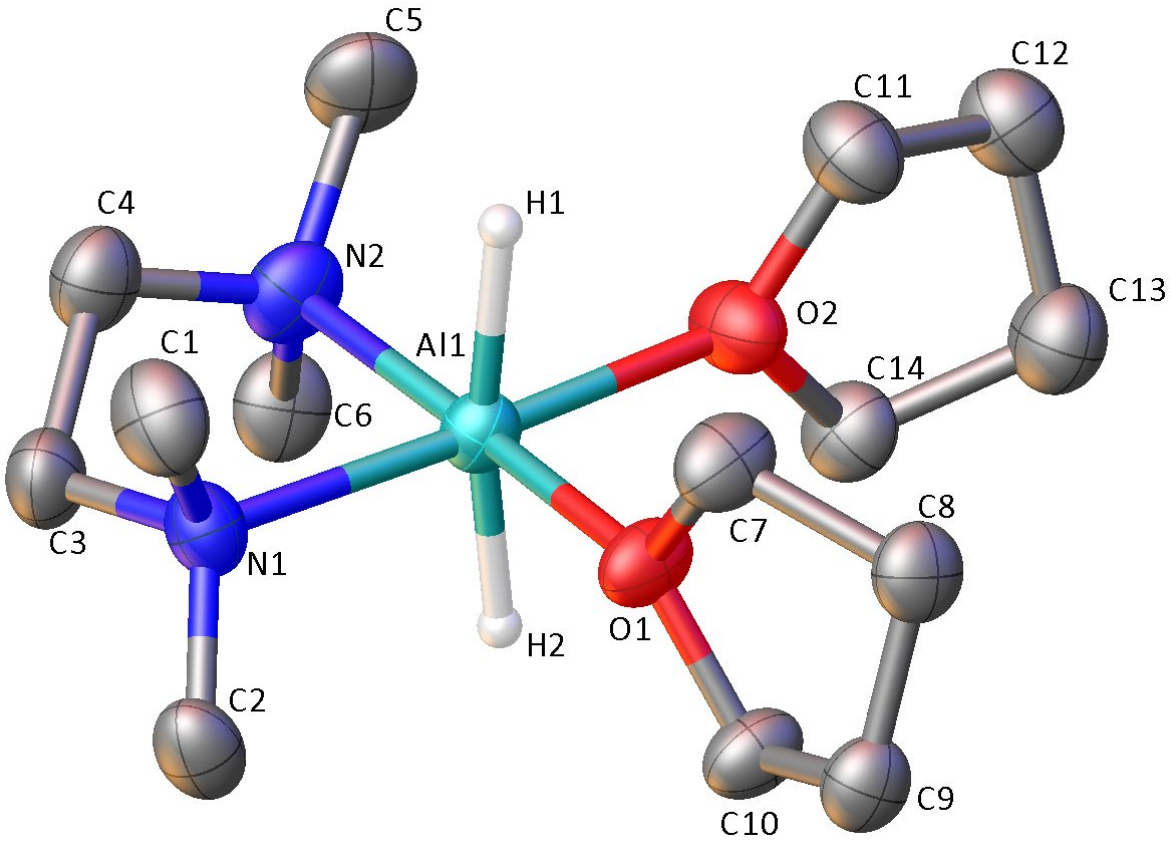



Figure S 20: X-ray crystal structure of the cationic part of **1·thf₂.** Thermal ellipsoids are shown at the 50% level and hydrogen atoms are omitted for clarity, except for those bound to aluminium.

## 2.7 Synthesis of $[(IMe_4)_2AlH_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ **2**

To a Schlenk flask containing 200 mg **IMe$_4$** (1.61 mmol), was added a 10 ml diethylether solution of 106 mg $Et_3N{\cdot}AlH_3$ (0.805 mmol). The stirring reaction mixture was cooled to -78°C, and 430 mg $[Et_3NH][BAr_4]$ (0.805 mmol) was added portion-wise as a solid by means of a bent glass joint. The reaction was removed from the cold bath, and after 2 hours, a colourless precipitate was collected by canula filtration and washed twice with *n*-pentane to yield 420 mg **2** as a colourless powder in 74% yield. Single crystals suitable for X-ray diffraction analysis were obtained directly from the reaction of **3$^{Ga}$** with $IMe_4$ in $C_6D_6$, see section 2.20.

Although **2** could be straightforwardly recrystallised from a THF/pentane mixture at -40°C, complete removal of lattice-THF from these samples under vacuum proved difficult, and given the known reactivity of **I$^{Al}$** towards THF,[7] the precipitate from diethylether was used without further purification.

The chemical shifts and FWHM for the NHC resonances (particularly the *N*-methyl protons) of **2** were found to be concentration dependent in THF-$d_8$, a characteristic which we tentatively assign to an equilibrium between the $[(\mathbf{IMe_4})_2AlH_2]^+$ cation and $[AlH_2{\cdot}(thf)_4]^+$ [8] and free-carbene. This accounts for the variation in NMR spectra between those of crystals isolated from the reaction of **3$^{Ga}$** and **IMe$_4$** (7 mg/ml), and those shown below (25 mg/ml). Although we did not investigate this phenomenon in detail, the NMR, IR, and elemental analysis are consistent with the crystallographically determined structure regardless of synthetic route (i.e. preparative scale from $Et_3N{\cdot}AlH_3$ or NMR-scale from **3$^{Ga}$**).

$^1$H NMR (400 MHz, THF-$d_8$) δ 6.96 (m, 8H, *ortho*-$C_6H_3$), 6.29 (s, 4H, *para*-$C_6H_3$)), 3.45 (s, 12H, N$CH_3$), 2.01 (s, 24H, $C_6H_3(CH_3)_2$), 1.93 (s, 12H, $CCH_3^{NHC}$).

$^{13}$C{$^1$H} NMR (101 MHz, THF-$d_8$) δ 165.73 (q, $^1J_{(C\text{-}B)}$ = 49 Hz, *ipso*-$C_6H_3$), 161.91 (br, Al-*C*), 135.53 (s, *ortho*-$C_6H_3$), 133.19 (q, $^3J_{(C\text{-}B)}$ = 2.9 Hz), 128.93 ($H_3CC{=}CCH_3$), 123.57 (*para*-$C_6H_3$), 34.47 ($NCH_3$), 22.30 ($C_6H_3(CH_3)_2$), 8.41 ($H_3CC{=}CCH_3$).

$^{11}$B{$^1$H} NMR (128 MHz, THF-$d_8$) δ -6.81.

$^{27}$Al NMR (104 MHz, THF-$d_8$) δ 108.12 (very broad).

IR spectroscopy (KBr pellet): ν = 1812 cm$^{-1}$ (Al-H).

Elemental analysis calculated for $C_{46}H_{62}AlBN_4$: C 77.95, H 8.82, N 7.90%. Found: C 76.50, H 8.90, N 8.04%. Despite repeated attempts, we were unable to obtain more accurate elemental analysis for this compound. This is tentatively ascribed to traces of additional non-coordinated $IMe_4$ in the precipitated and washed product, or to residual lattice THF after recrystallisation from THF/pentane.

## 2.8 NMR and IR spectra of $[(IMe_4)_2AlH_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ **2**

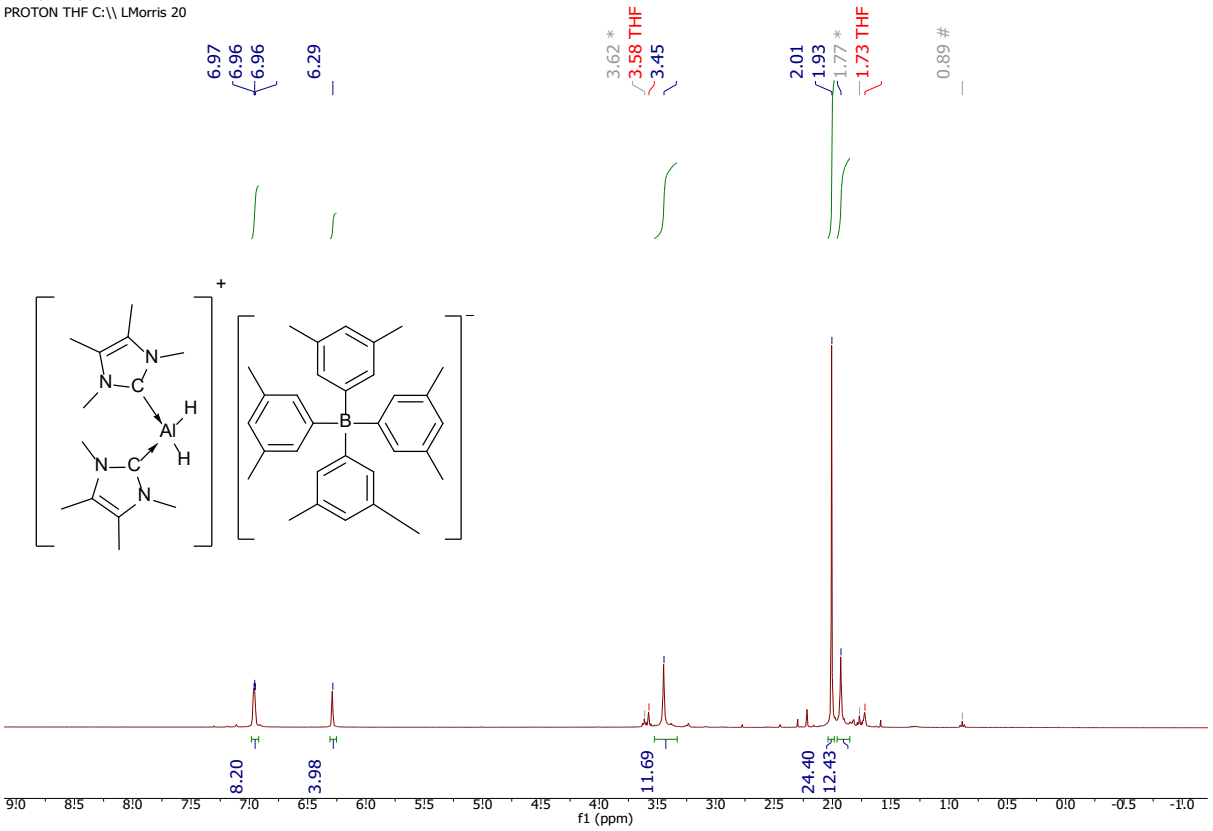



Figure S 21: $^1$H NMR (400 MHz, THF-$d_8$, 25 mg/ml).*residual THF from crystallisation, # n-pentane.

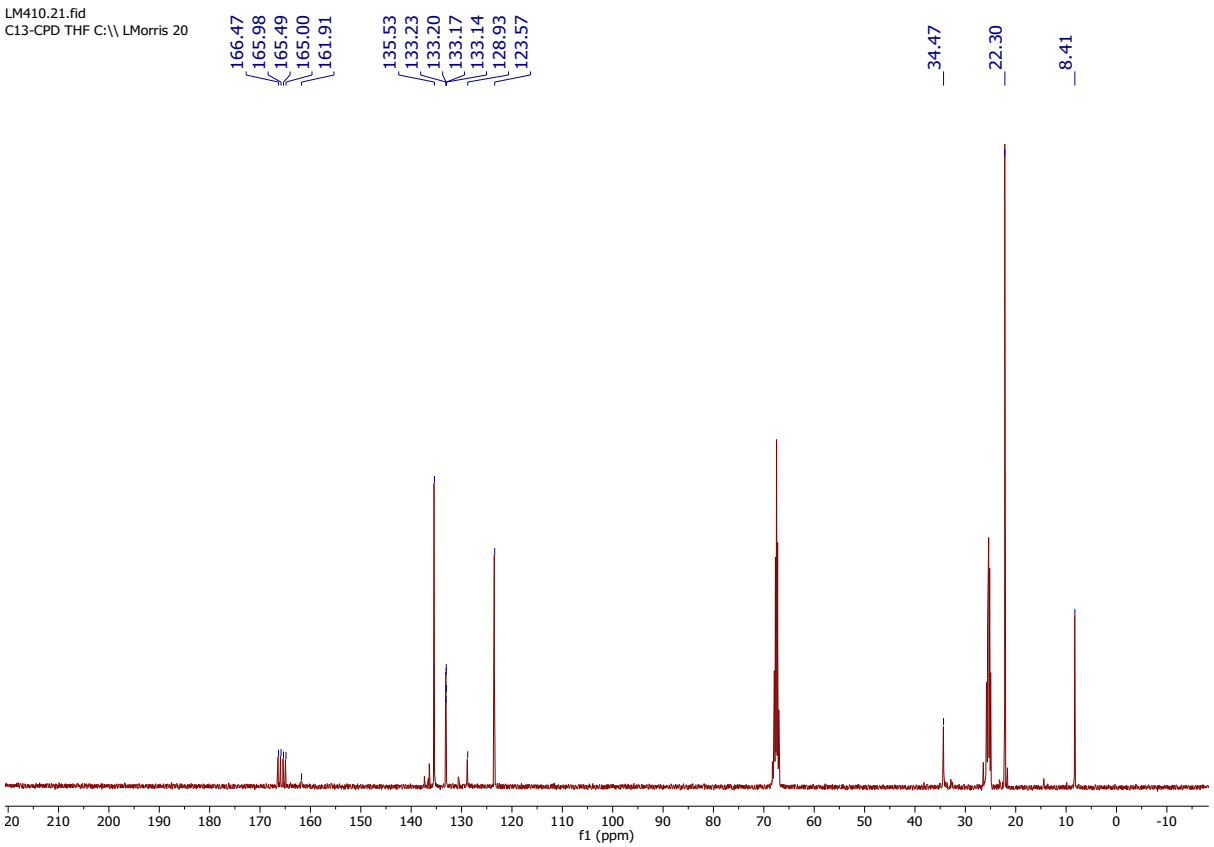



Figure S 22: $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-$d_8$)

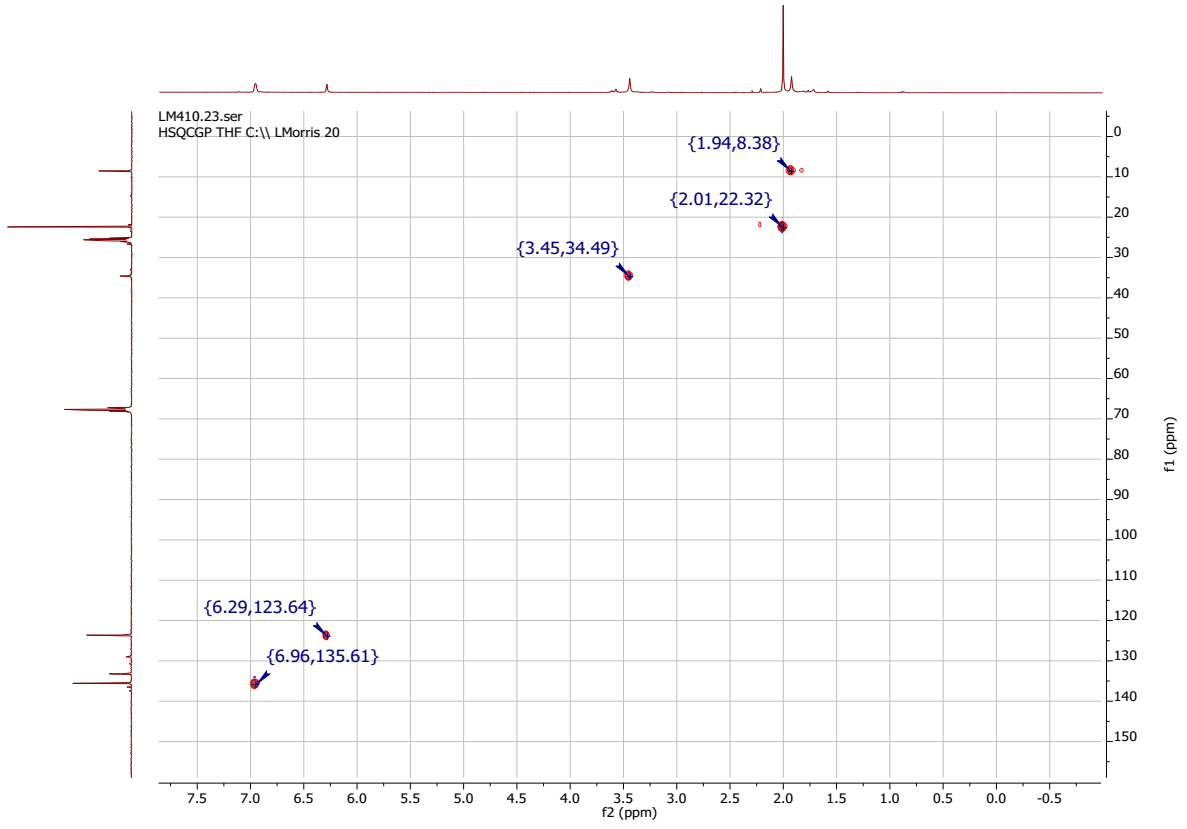



Figure S 23: $^{13}C$-$^{1}H$ HSQC spectrum (THF-$d_8$).

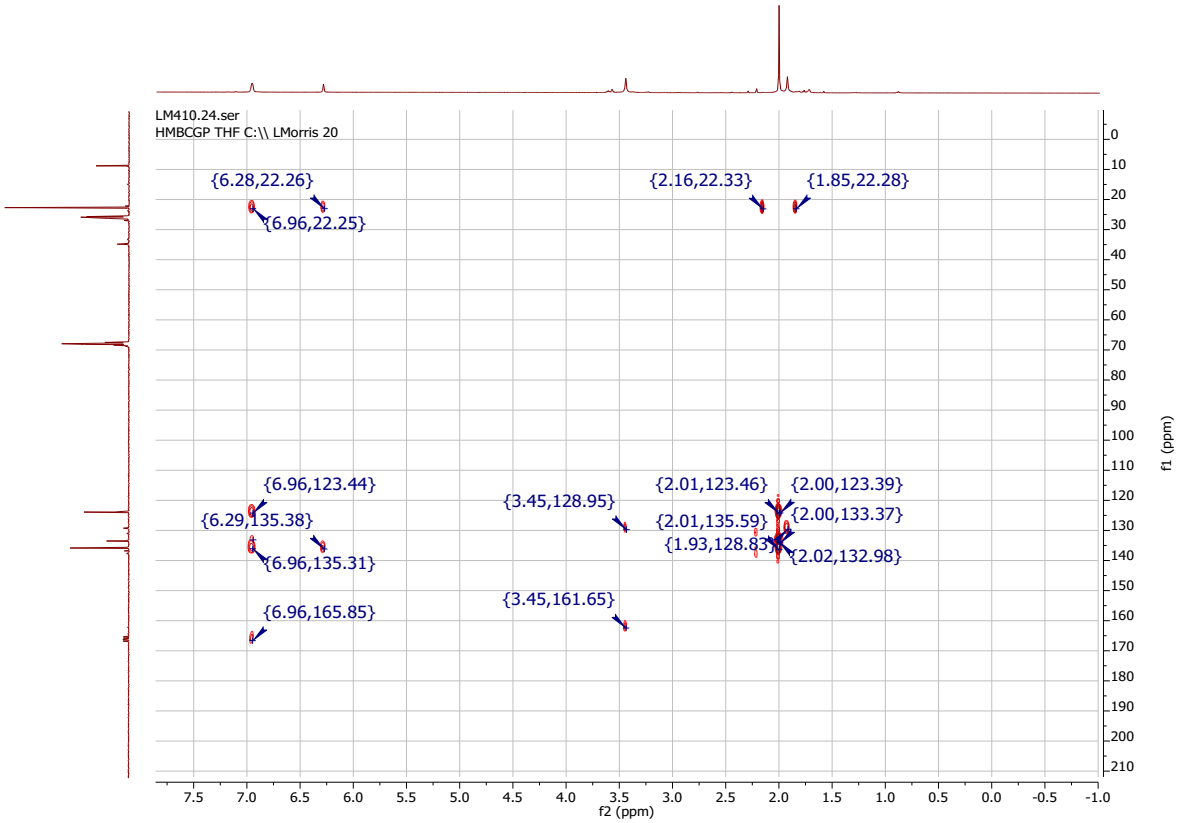



Figure S 24: $^{13}C$-$^{1}H$ HMBC spectrum (THF-$d_8$).

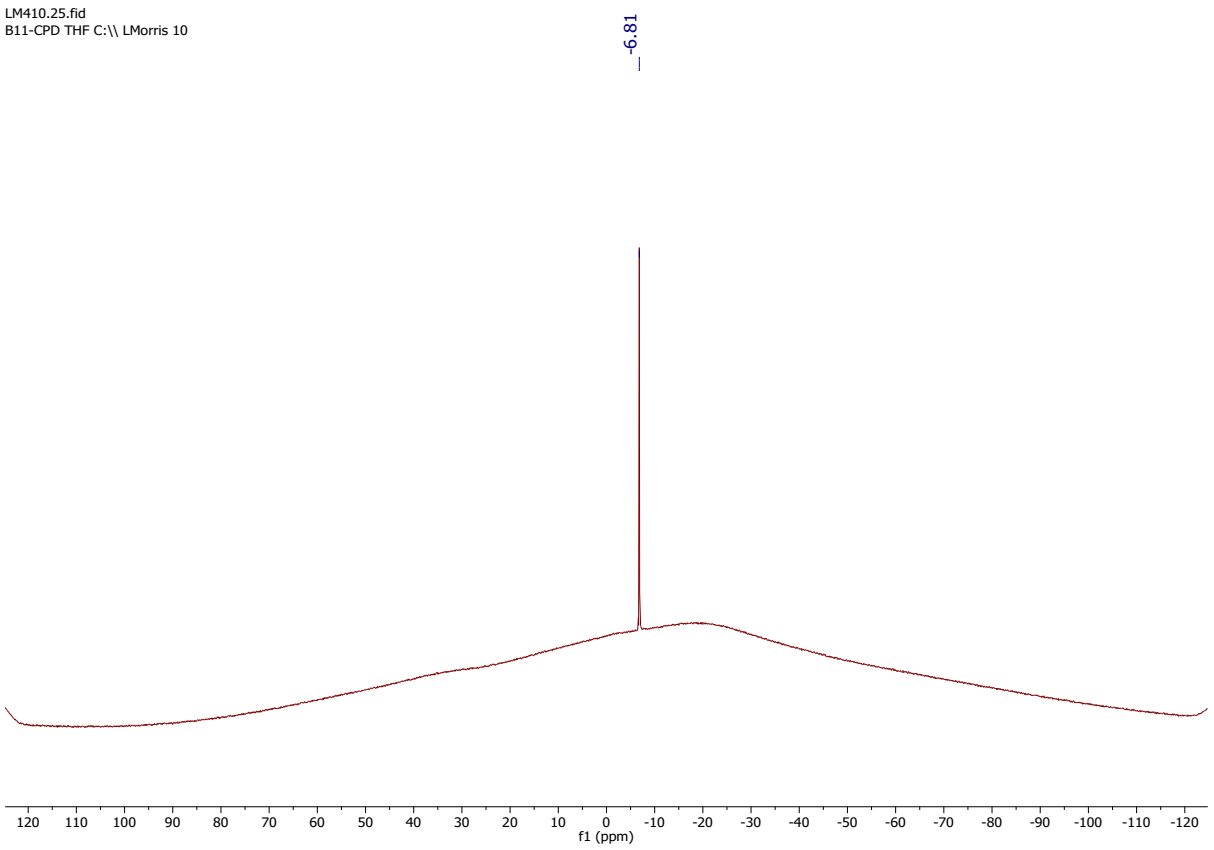



Figure S 25: $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-$d_8$)

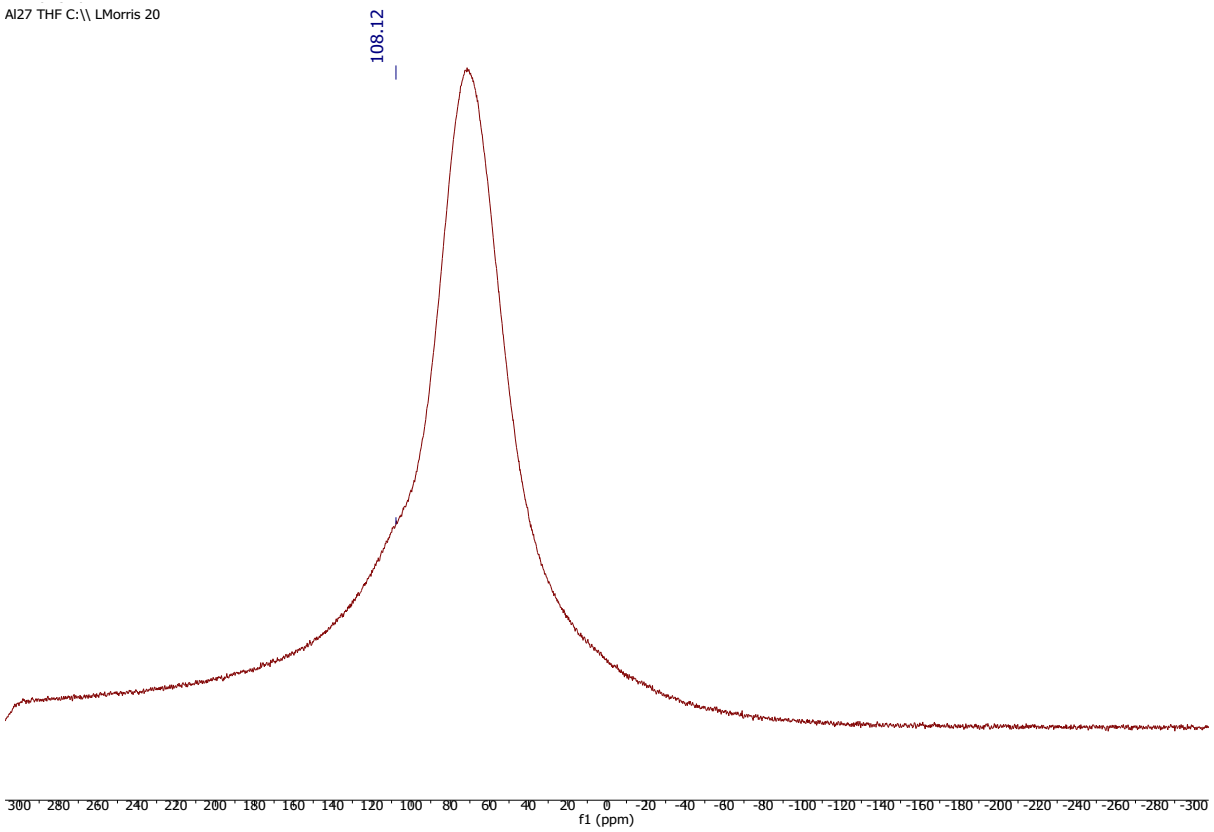



Figure S 26: $^{27}$Al NMR (104 MHz, THF-$d_8$)

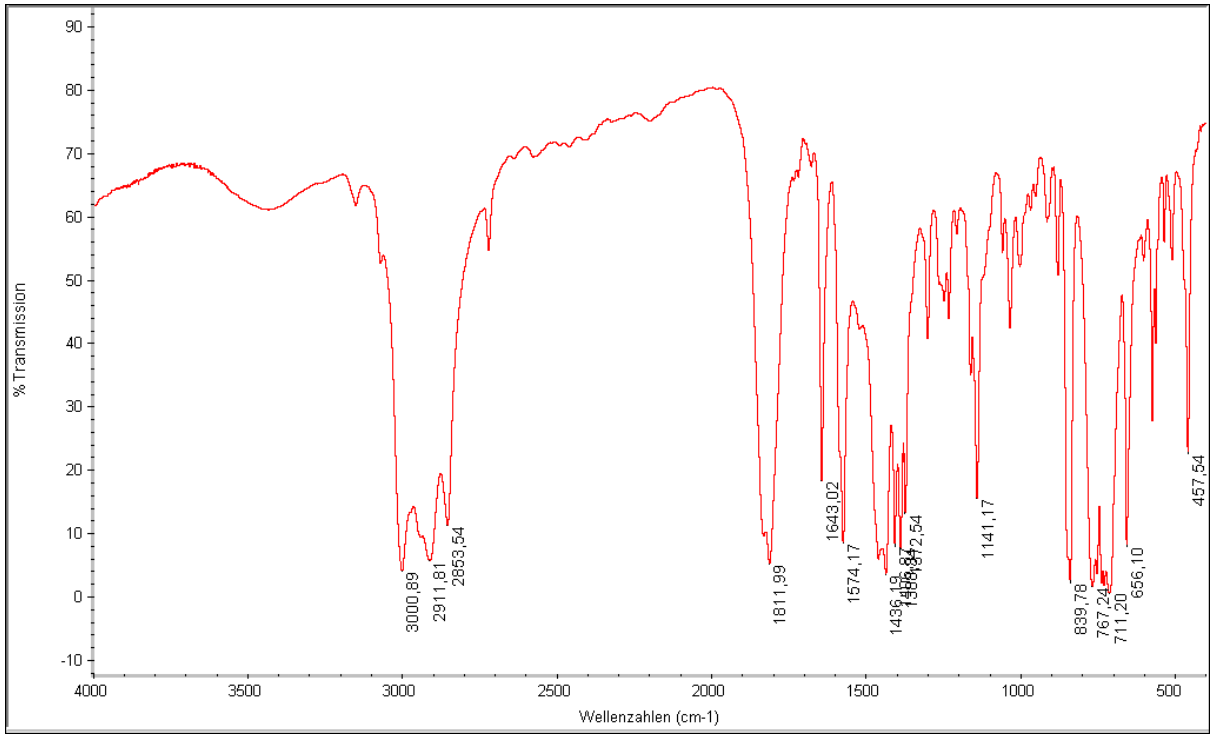



Figure S 27: IR spectrum (KBr pellet) of **2**.

## 2.9 X-ray crystal structure of $[(IMe_4)_2AlH_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ **2**.

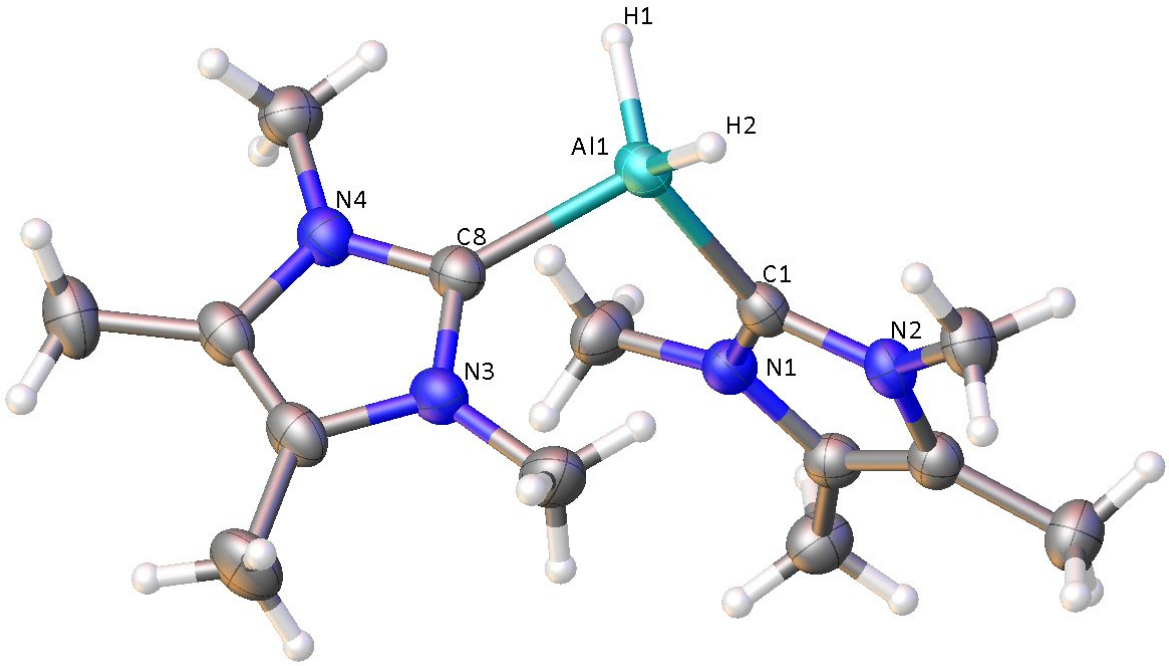



Figure S 28: X-ray crystal structure of the cationic part of compound **2**. Thermal ellipsoids are shown at the 50% probability level. Selected distances (Å) and angles (°): Al1-C1 2.0283(17), Al1-C8 2.0203(16), Al1-H1 1.490(18), Al1-H2 1.50(2), N2-C1 1.357(2), N2-C5 1.385(2), C3-C5 1.360(2), N1-C3 1.389(2), N1-C1 1.346(2), N3-C8 1.352(2), N3-C10 1.389(2), C10-C12 1.350(2), C12-N4 1.3831(19), C4-C8 1.353(2), C1-Al1-C8 102.92(7), C1-Al1-H1 110.8(7), C1-Al1-H2 108.5(7), H1-Al1-H2 115.6(10), C8-Al1-H1 107.9(7), C8-Al1-H2 110.3(7), N1-C1-Al1 128.84(11), N2-C1-Al1 129.75(12), N3-C8-Al1 1.352(2), N4-C8-Al1 130.13(11).

## 2.10 Synthesis of $[\{TMEDA\}Al(H)(H)Al\{BDI\}][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ $\mathbf{3^{Al}}$

A Schlenk tube was charged with 53 mg $\mathbf{I^{Al}}$ (0.117 mmol),* 76 mg **1** (0.117 mmol) and 5 ml toluene. The initially red-orange suspension rapidly decoloured to yellow, and the reaction mixture was stirred at room temperature for 20 hours. The product was isolated by cannula filtration and washed twice with toluene (2x 5 ml), and once with pentane (5 ml), to obtain 88 mg $\mathbf{3^{Al}}$ as a pale-cream coloured powder in 74% isolated yield after drying under vacuum. *In our hands, $\mathbf{I^{Al}}$ prepared from $[Cp^*Al]_4$ by the reported literature procedure[3] was often found to contain residual $[Cp^*Al]_4$ (approx. 5%) following crystallisation of the BDI-complex from the crude product mixture. $[Cp^*Al]_4$ is unreactive towards **1** and the minor impurity could be straightforwardly removed from the product by washing with excess toluene.

Single crystals suitable for X-ray diffraction analysis were obtained by layering a 0.6 ml toluene solution of $\mathbf{I^{Al}}$ (30 mg, 0.099 mmol) above a heterogeneous mixture of poorly soluble **1** (64 mg, 0.099 mmol) and 0.6 ml toluene in a 5 mm diameter NMR tube. The mixture was left to stand for seven days, upon which most of the insoluble powder was replaced by very large colourless block-like single crystals of $\mathbf{3^{Al}}$.

**3$^{Al}$** is insoluble in aliphatic hydrocarbons, very poorly soluble in benzene and toluene, moderately soluble in THF and fluorobenzene, and readily soluble in bromobenzene.

$^{1}$H NMR (400 MHz, $C_6D_5Br$) δ 7.45 (br, 8H, *ortho*-$BC_6H_3$),7.17-7.10 (m, 2H, *para*-$NC_6H_3$), 7.10 – 7.02 (m, 4H, *meta*-$NC_6H_3$), 6.50 (br, 4H, *para*-$BC_6H_3$), 4.96 (s, 1H, *H*C{C($CH_3$)Ndipp}$_2$), 4.45 (br, 1H, (BDI)Al*H*), 3.36 (br, 1H, (TMEDA)Al*H*), 3.21 (hept, *J* = 6.6 Hz, 2H, *H*C($CH_3$)$_2$), 3.01 (hept, *J* = 6.4 Hz, 2H, *H*C($CH_3$)$_2$), 2.13 (s, 24H, BAr-C$H_3$), 1.58 (s, 6H, HC{C(C$H_3$)Ndipp}$_2$), 1.51 (s, 6H, NC$H_3$), 1.48 – 1.36 (m, 4H, NC$H_2$), 1.30 (d, *J* = 6.8 Hz, 6H, HC(C$H_3$)$_2$), 1.23 (s, 6H, NC$H_3$), 1.10 (d, *J* = 6.7 Hz, 6H, HC(C$H_3$)$_2$), 1.05 (d, *J* = 6.9 Hz, 6H, HC(C$H_3$)$_2$), 1.00 (d, *J* = 6.7 Hz, 6H, HC(C$H_3$)$_2$).

$^{13}$C{$^{1}$H} NMR (101 MHz, $C_6D_5Br$) δ 170.73 (HC{*C*($CH_3$)Ndipp}$_2$), 165.21 (q, *J* = 49.0, 48.5 Hz, *ipso*-B*C*$_6H_3$), 145.85 (*ortho*-N*C*$_6H_3$), 142.35 (*ortho*-N*C*$_6H_3$), 140.70 (*ipso*-N*C*$_6H_3$), 134.82 (*ortho*-B*C*$_6H_3$), 133.34 (m, *meta*-B*C*$_6H_3$), 127.62 (*para*-N*C*$_6H_3$), 125.64 (*meta*- N*C*$_6H_3$), 124.46 (*meta*- N*C*$_6H_3$), 123.86 (*para*-B*C*$_6H_3$), 97.01 (H*C*{C($CH_3$)Ndipp}$_2$), 56.62 (N*C*H$_2$), 47.52 (N*C*H$_3$), 47.44 (N*C*H$_3$), 29.62 (H*C*($CH_3$)$_2$), 27.65 (H*C*($CH_3$)$_2$), 25.91 (HC(*C*H$_3$)$_2$), 24.71 (HC(*C*H$_3$)$_2$), 24.62 (HC(*C*H$_3$)$_2$), 23.90 (HC(*C*H$_3$)$_2$), 23.19 (HC{C(*C*H$_3$)Ndipp}$_2$), 22.23 (BC$_6$H$_3$*C*H$_3$).

$^{11}$B NMR (128 MHz, $C_6D_5Br$) δ -6.27.

$^{1}$H NMR (400 MHz, THF-$d_8$) δ 7.31 (m, 6H, N$C_6H_3$), 7.11 – 6.88 (m, 8H, *ortho*-$BC_6H_3$), 6.32 (s, 4H, *para*-$BC_6H_3$), 5.27 (s, 1H, *H*C{C($CH_3$)Ndipp}$_2$), 4.44 (br, 1H, (BDI)Al*H*), 3.51 (br, 1H, (TMEDA)Al*H*), 3.39 (hept, *J* = 6.8 Hz, 2H, *H*C($CH_3$)$_2$), 3.13 (hept, *J* = 6.8 Hz, 2H, *H*C($CH_3$)$_2$), 2.05 (s, 26H, BAr-C$H_3$), 1.89 (m, 4H, NC$H_2$), 1.83 (s, 6H, HC{C(C$H_3$)Ndipp}$_2$), 1.76 (s, 6H, NC$H_3$),* 1.54 (s, 6H, NC$H_3$), 1.42 (d, *J* = 6.8 Hz, 6H, HC(C$H_3$)$_2$), 1.25 (d, *J* = 6.9 Hz, 6H, HC(C$H_3$)$_2$), 1.21 (d, *J* = 6.7 Hz, 6H, HC(C$H_3$)$_2$), 1.13 (d, *J* = 6.8 Hz, 6H, HC(C$H_3$)$_2$).*this resonance overlaps with that of the residual solvent peak.

$^{13}$C{$^{1}$H} NMR (101 MHz, THF-d8) δ 172.08 (HC{*C*($CH_3$)Ndipp}$_2$), 165.00 (*ipso*-B*C*$_6H_3$), 147.05 (*ortho*-N*C*$_6H_3$), 143.68 (*ortho*-N*C*$_6H_3$), 142.07 (*ipso* -N*C*$_6H_3$), 135.54 (*ortho*-B*C*$_6H_3$), 133.22 (q, $^{3}J_{(B-C)}$ = 2.9 Hz, *meta*-B*C*$_6H_3$), 128.55 (*meta/para*-N*C*$_6H_3$), 126.67 (*meta/para*-N*C*$_6H_3$), 125.63 (*meta/para*-N*C*$_6H_3$), 123.78 (*para*-B*C*$_6H_3$), 97.87 (H*C*{C($CH_3$)Ndipp}$_2$), 57.66 (N*C*H$_2$), 48.35 (N*C*H$_3$), 48.30 (N*C*H$_3$), 30.72 (H*C*($CH_3$)$_2$), 28.73 (H*C*($CH_3$)$_2$), 26.46 ((HC(*C*H$_3$)$_2$), 24.37 ((HC(*C*H$_3$)$_2$), 23.74 (HC{C(*C*H$_3$)Ndipp}$_2$), 22.38 (BC$_6$H$_3$*C*H$_3$).* two of the resonances corresponding to HC(*C*H$_3$)$_2$ were obscured by that of THF-d8.

$^{11}$B{$^{1}$H} NMR (128 MHz, THF-d8) δ -7.02.

Elemental analysis calculated for $C_{67}H_{95}Al_2BN_4$: C 78.80, H 9.38, N 5.49. Found: C 78.98, H 8.90, N 5.10%.

IR spectroscopy (KBr pellet): v = 1822, 1728 $cm^{-1}$ (Al-H)

## 2.11 NMR and IR spectra of [{TMEDA}Al(H)(H)Al{BDI}][B($C_6H_3$-3,5-$Me_2$)$_4$] **3$^{Al}$**

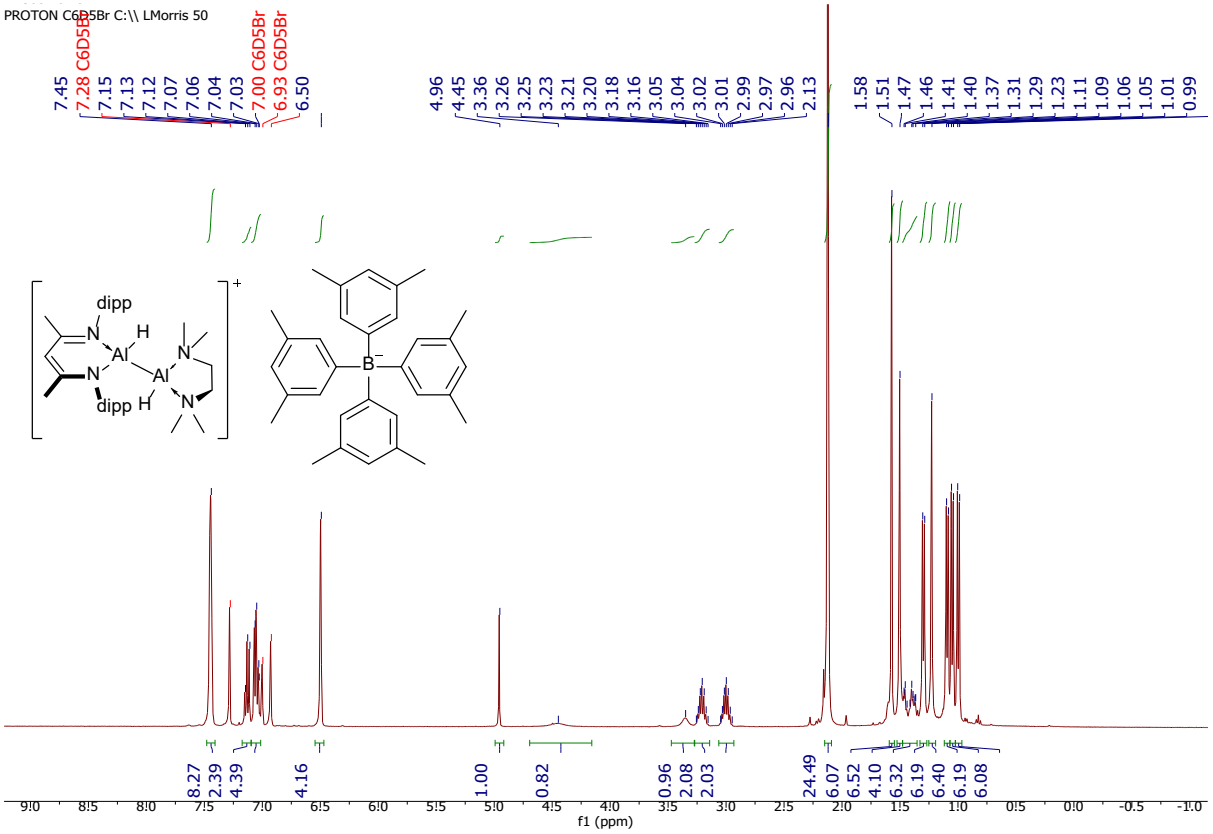



Figure S 29: $^1$H NMR (400 MHz, $C_6D_5Br$).

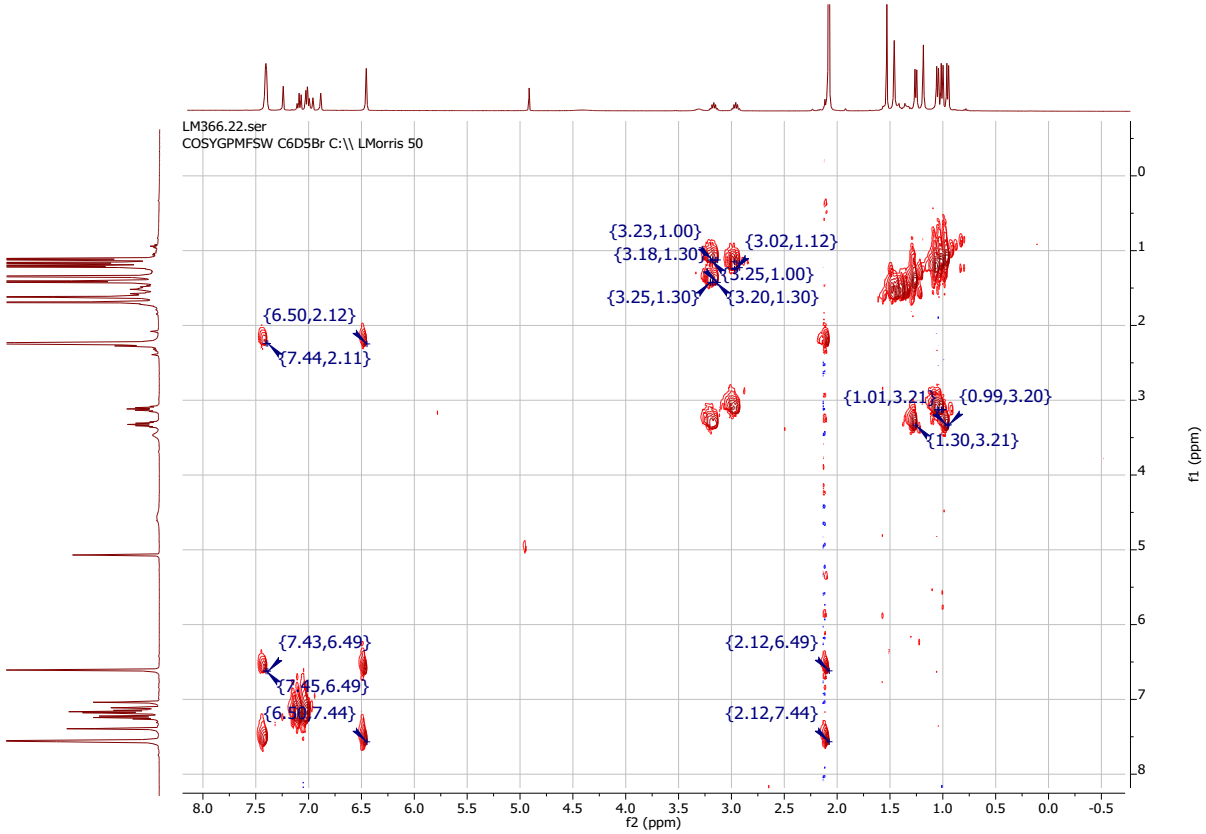



Figure S 30: $^{1}$H-$^{1}$H COSY spectrum ($C_6D_5Br$).

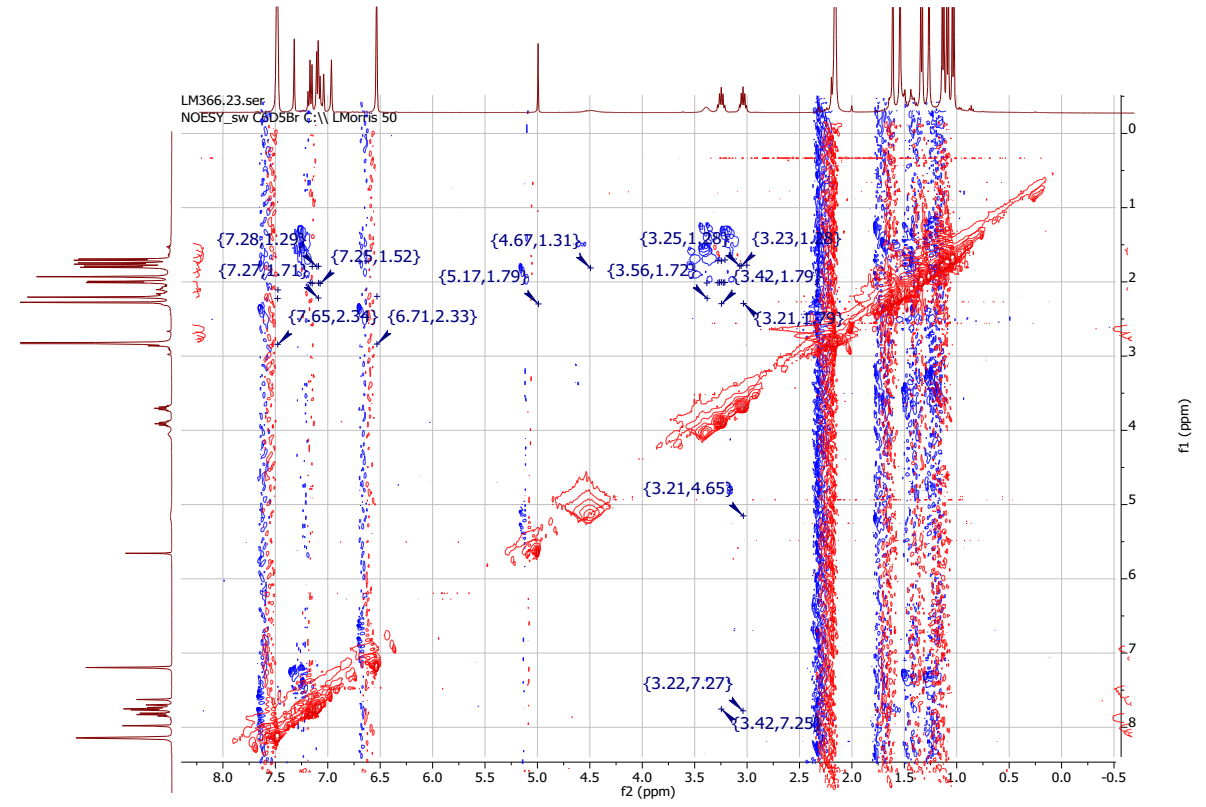



Figure S 31: $^{1}$H-$^{1}$H NOESY spectrum ($C_6D_5Br$).

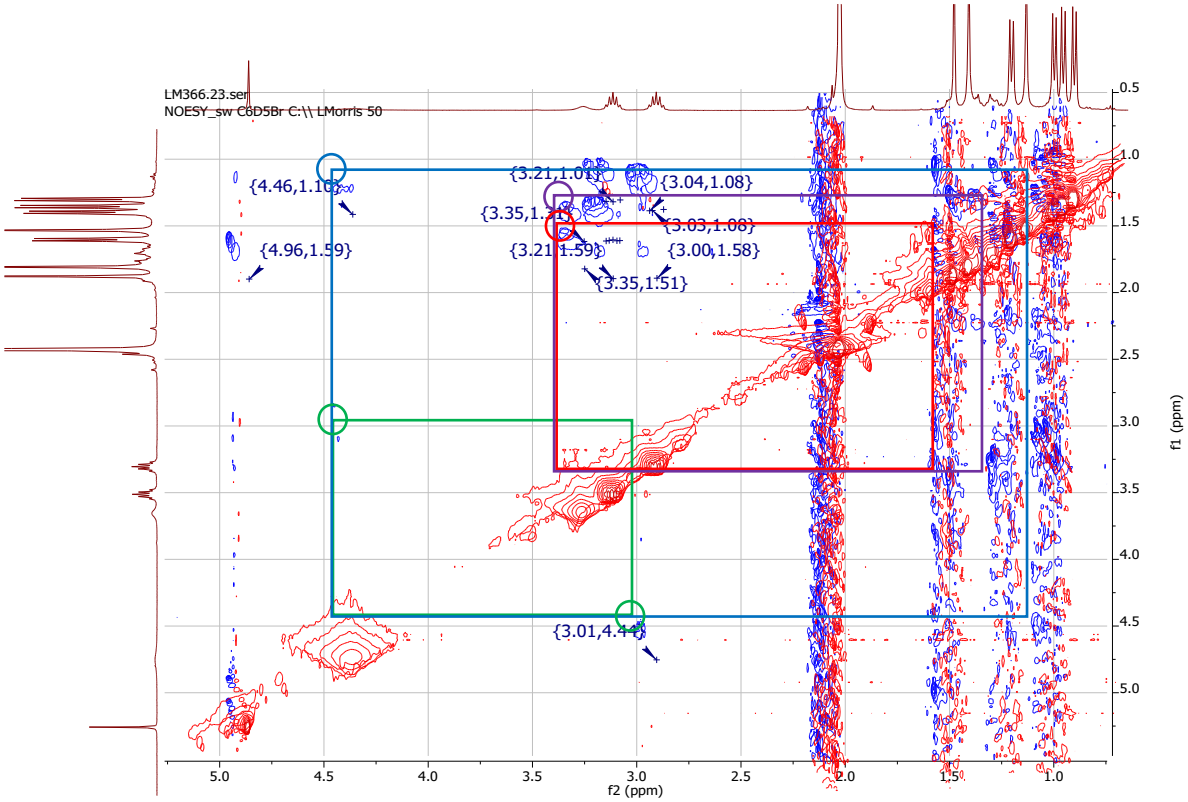



Figure S 32: Expanded $^{1}$H-$^{1}$H NOESY spectrum ($C_6D_5Br$). Relevant coupling relationships are highlighted according to the following scheme: Green = (BDI)Al*H*↔*H*C$(CH_3)_2^{(dipp)}$. Blue = (BDI)Al*H*↔*H*$_3$C$^{(Dipp)}$. Red = (TMEDA)Al*H*↔*H*$_3$C$^{(TMEDA)}$. Purple = (TMEDA)Al*H*↔*H*$_3$C$^{(dipp)}$.

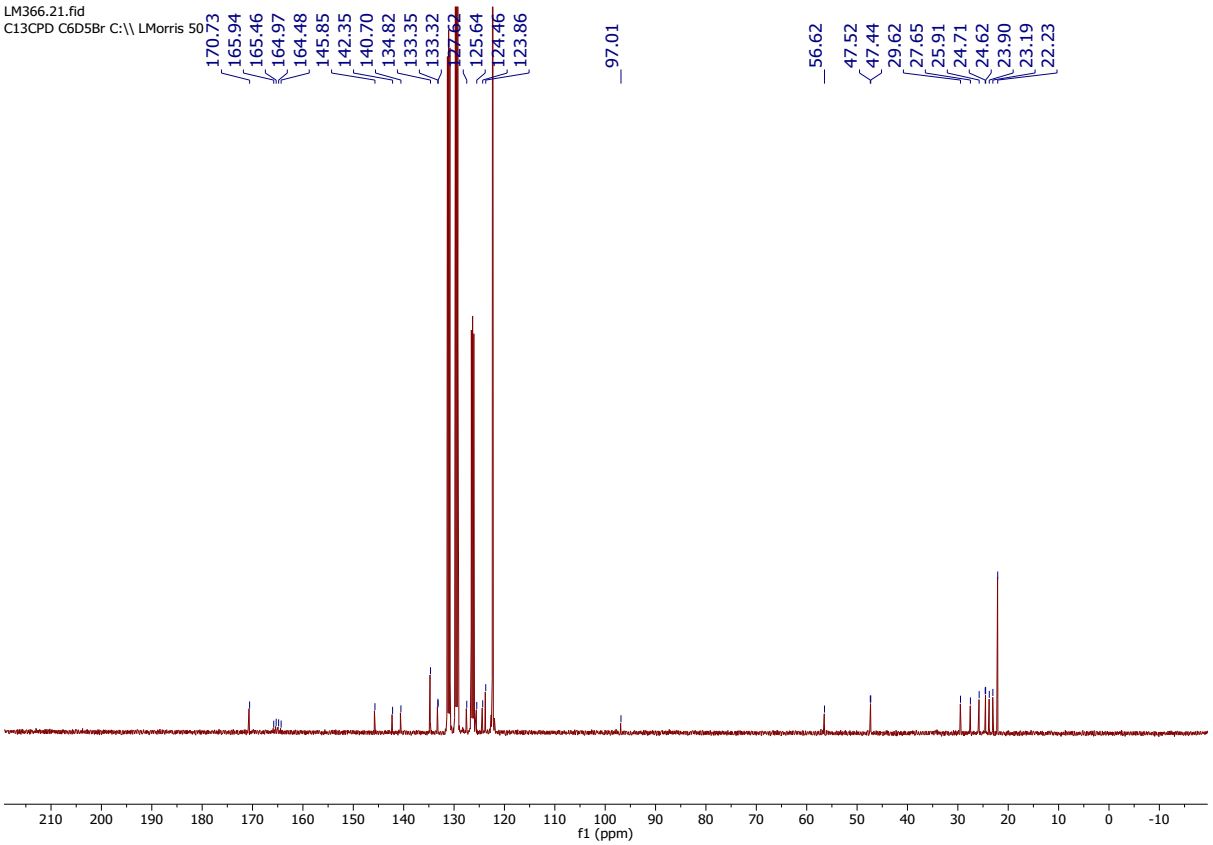



Figure S 33: $^{13}C\{^{1}H\}$ NMR (101 MHz, $C_6D_5Br$)

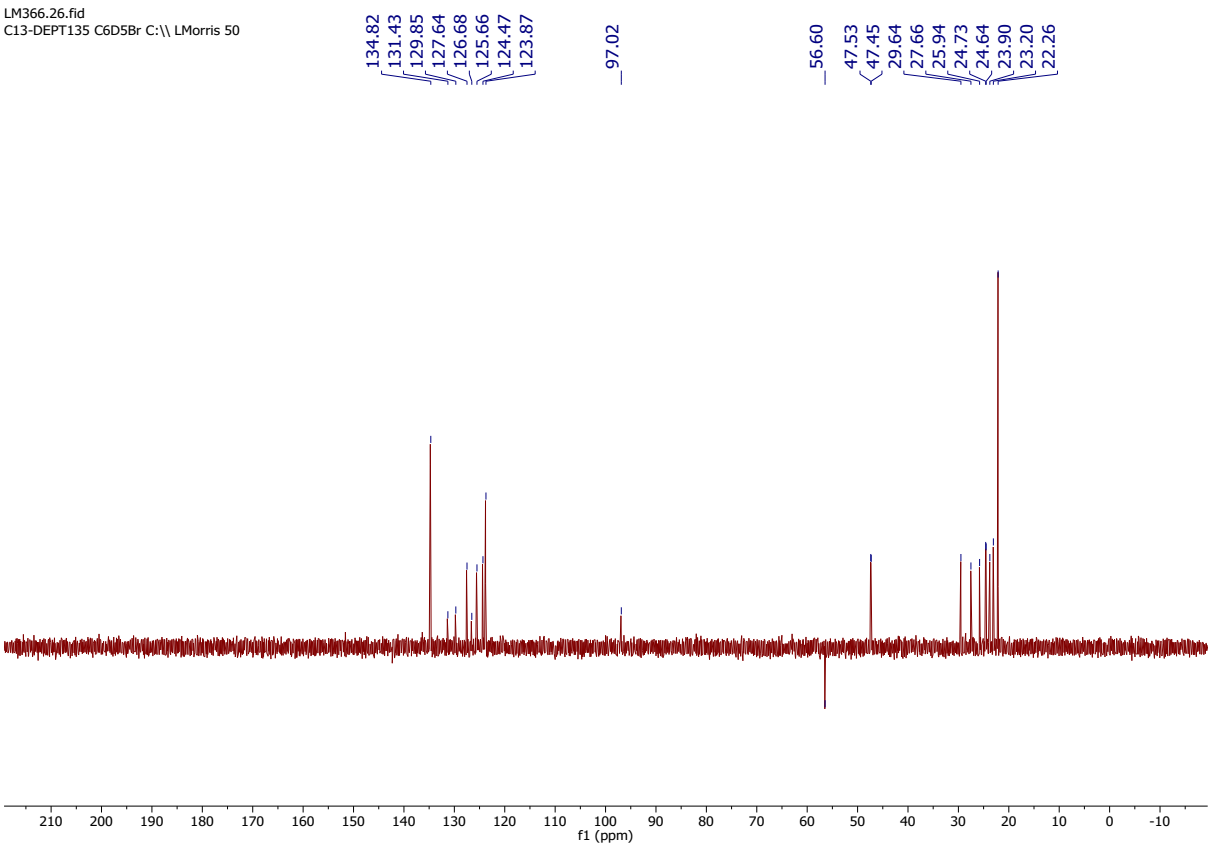



Figure S 34: $^{13}C$ DEPT 135 NMR spectrum (101 MHz, $C_6D_5Br$).

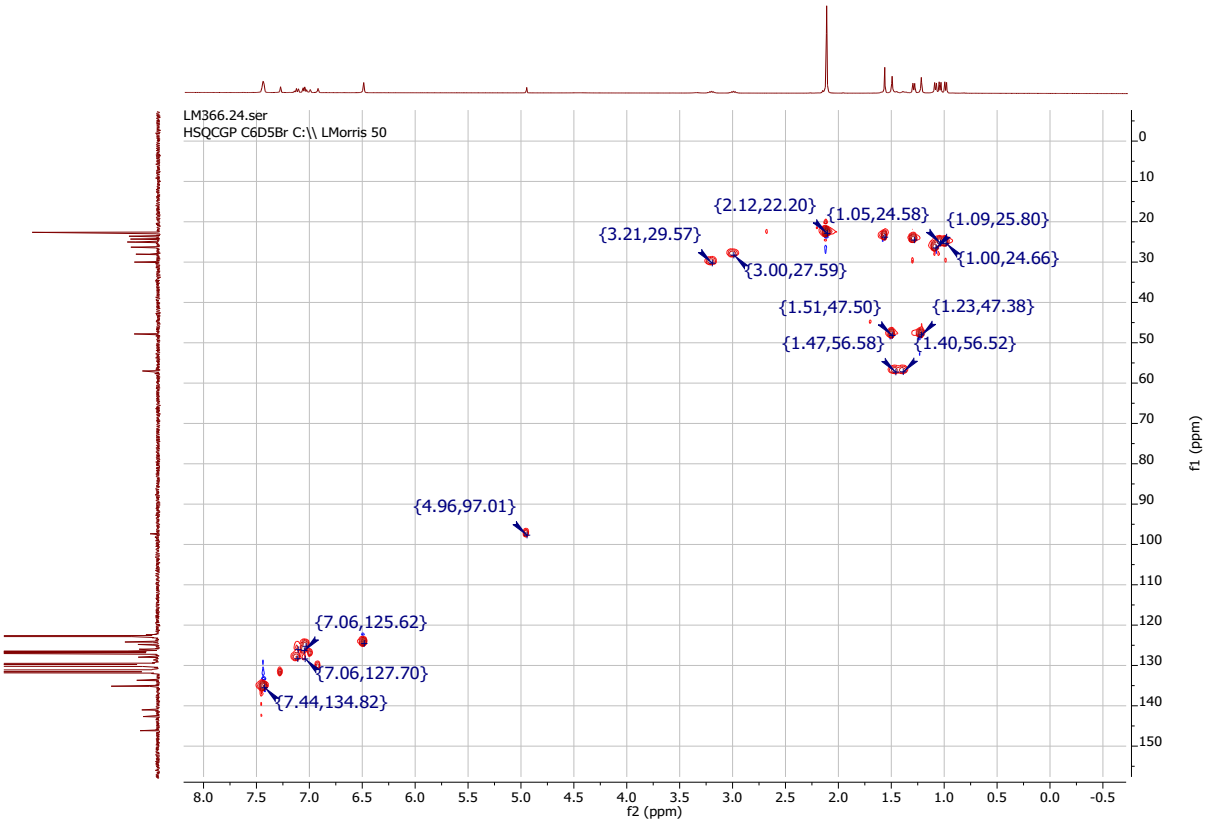



Figure S 35: $^{13}C$-$^{1}H$ HSQC spectrum ($C_6D_5Br$).

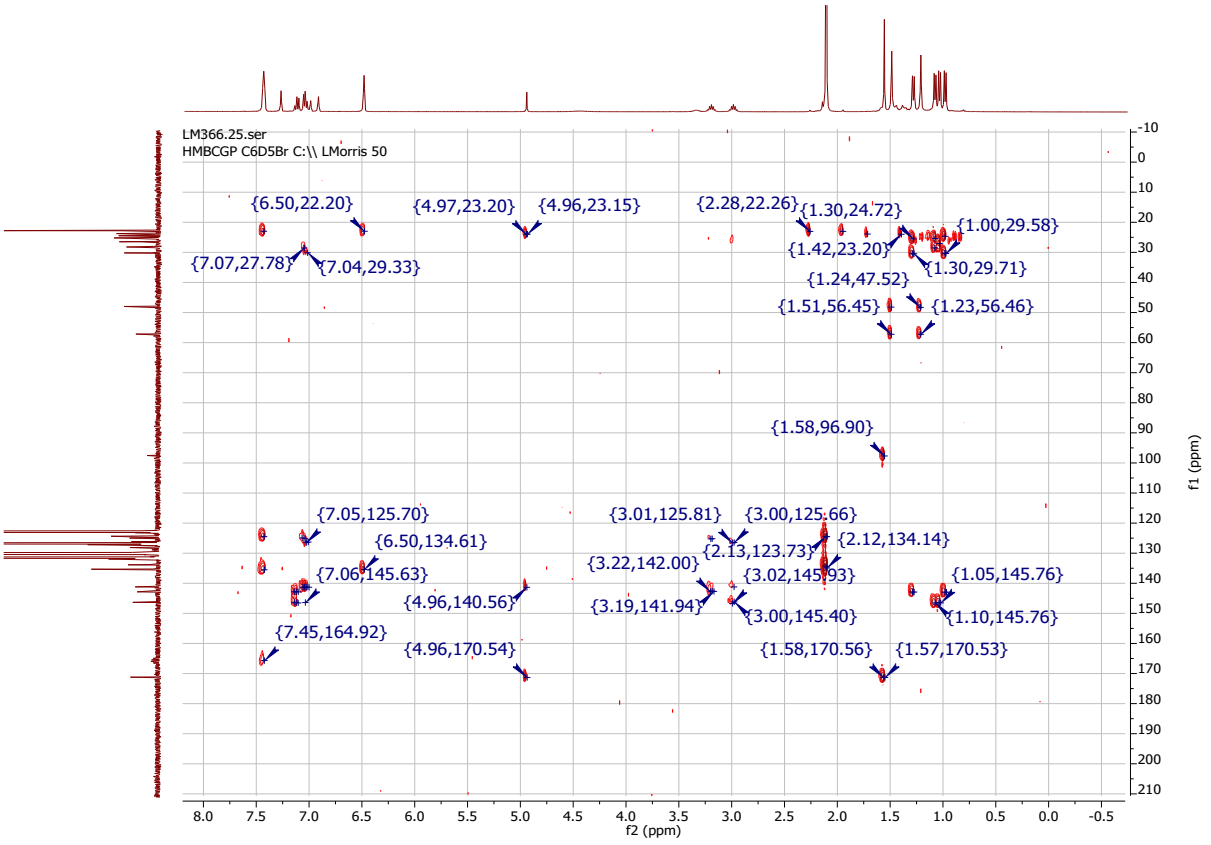



Figure S 36: $^{13}C$-$^{1}H$ HMBC spectrum ($C_6D_5Br$).

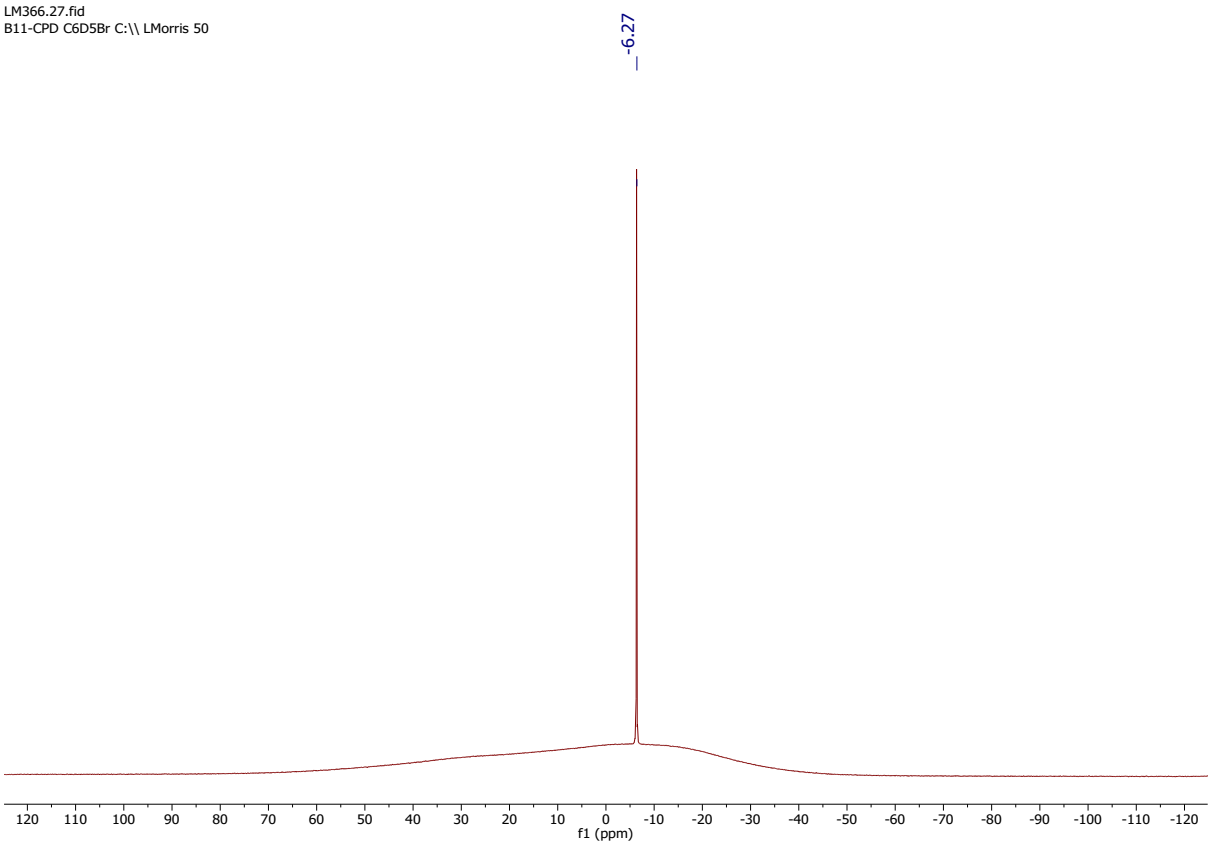



Figure S 37: $^{11}B\{^{1}H\}$ NMR (128 MHz, $C_6D_5Br$).

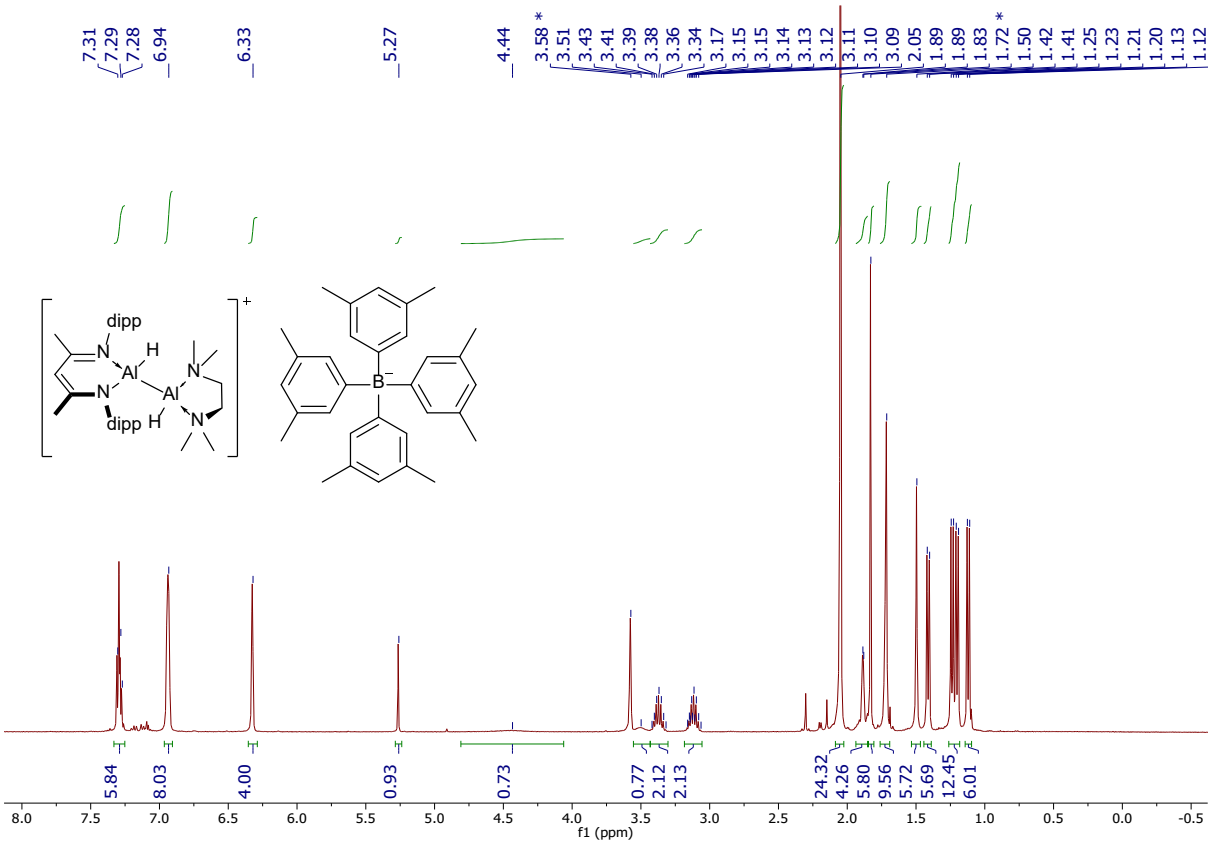



Figure S 38: $^{1}H$ NMR (400 MHz, THF-$d_8$ (*)).


Figure S 39: $^{1}$H-$^{1}$H COSY spectrum (THF-$d_8$)

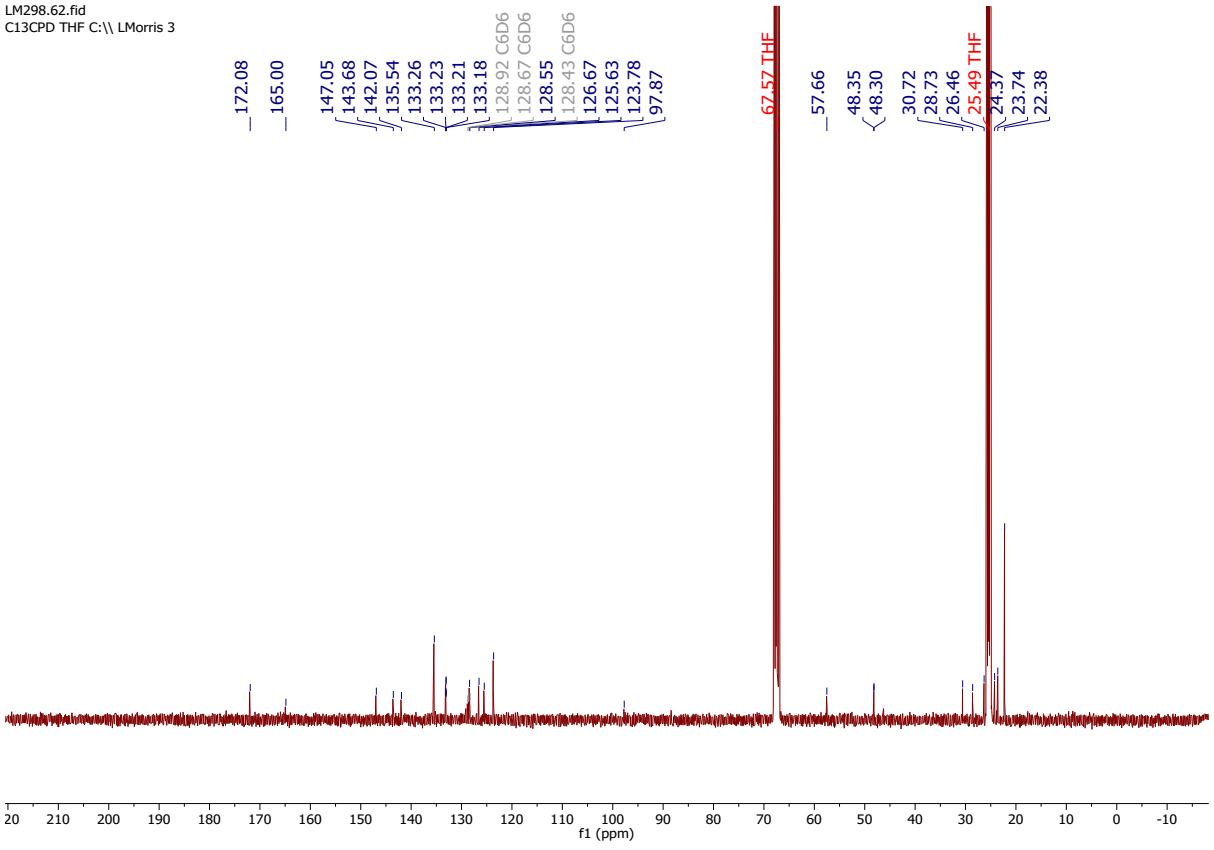



Figure S 40: $^{13}$C{$^{1}$H} NMR (101 MHz, THF-$d_8$).


Figure S 41: $^{13}C$-$^{1}H$ HSQC spectrum (THF-$d_8$).


Figure S 42: $^{13}C$-$^{1}H$ HMBC spectrum (THF-$d_8$).


Figure S 43: $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-$d_8$).

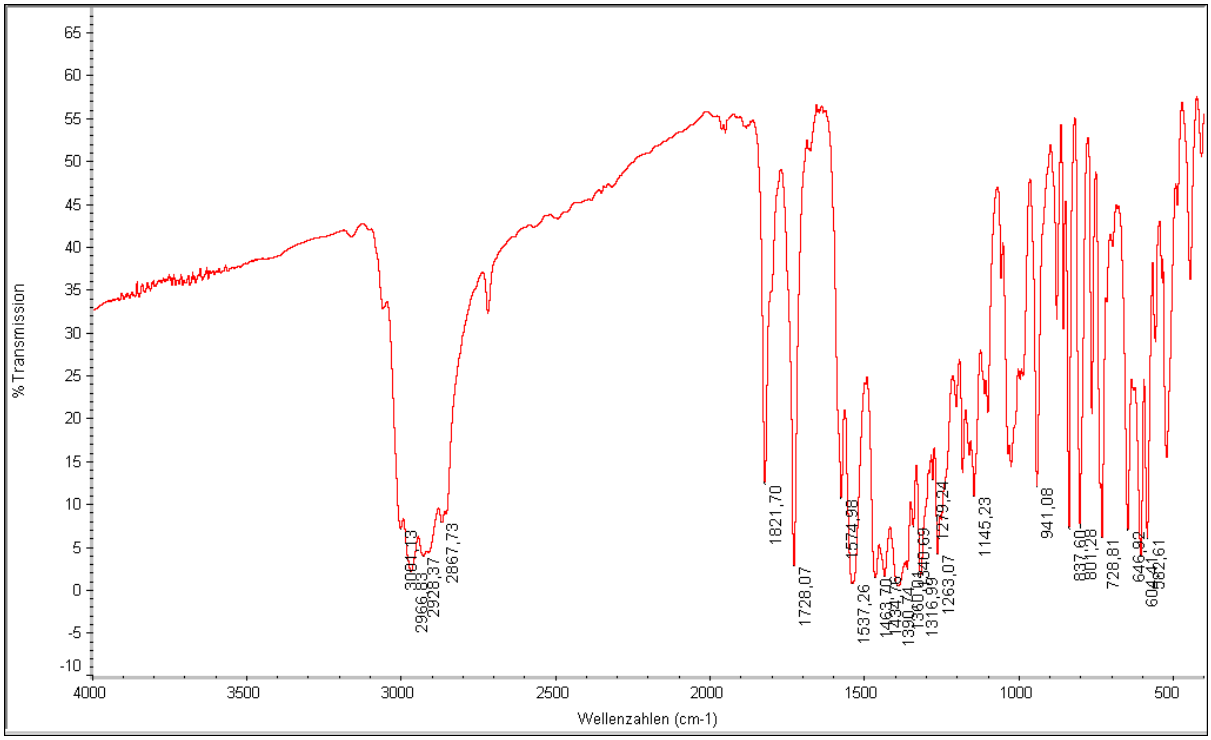



Figure S 44: IR spectrum (KBr pellet) of **3$^{Al}$**

## 2.12 X-ray crystal structure of $\mathbf{3^{Al}}$

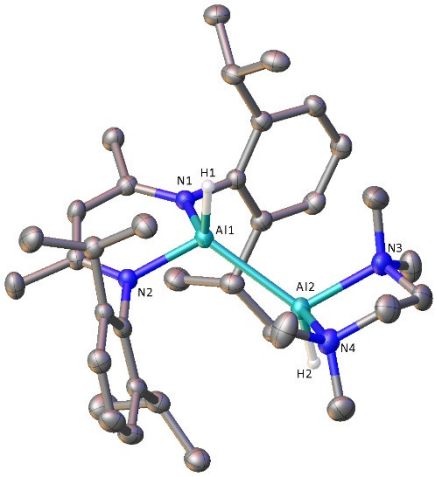



Figure S 45: Selected distances (Å) and angles (°) for $\mathbf{3^{A}}$: Al1-Al2 2.6117(10), Al1-N1 1.9127(11), Al1-N2 1.9070(11), Al2-N3 2.0272(12), Al2-N4 2.0579(12), Al1-H1 1.565(17), Al2-H2 1.491(16), N1-Al1-Al2 115.03(4), N2-Al1-Al2 115.17(4), N2-Al1-N1 95.43(5), N3-Al2-Al1 114.73(4), N3-Al2-N4 87.43(5), N4-Al2-Al1 116.22(4), C2-N1-Al1 121.11(9), C2-N1-C6 121.05(10), C6-N1-Al1 117.09(8), C4-N2-Al1 121.85(9), C4-N2-C18 118.68(8).

## 2.13 Synthesis of [{TMEDA}Al(H)(H)Ga{BDI}][B($C_6H_3$-3,5-$Me_2$)$_4$] $\mathbf{3^{Ga}}$

A Schlenk flask was charged with 100 mg [(TMEDA)$AlH_2$·$OEt_2$][$BAr_4^{Me2}$] (**1**, 0.154 mmol) and 75 mg BDIGa ($\mathbf{I^{Ga}}$) (0.154 mmol) and 3 ml toluene was added via cannula. The pale-yellow suspension was stirred at room temperature for 48 hours. The resulting colourless precipitate was isolated by cannula filtration, washed with toluene and pentane, and dried under vacuum to provide 127 mg of [(BDI)Ga(H)-(H)Al(TMEDA)][$BAr_4^{Me2}$], 76% yield.

Single crystals suitable for X-ray diffraction analysis were obtained by layering a 0.5 ml toluene solution of $\mathbf{I^{Ga}}$ (15 mg, 0.0308 mmol) on a heterogeneous mixture of **1** (20 mg, 0.0308 mmol) and 0.4 ml toluene in a 5 mm diameter NMR tube. The mixture was left to stand for seven days, upon which most of the insoluble powder was replaced by very large colourless block-like single crystals of $\mathbf{3^{Ga}}$.

$\mathbf{3^{Ga}}$ is insoluble in hydrocarbon solvents and diethylether, but readily soluble in fluorobenzene and bromobenzene. When dissolved in THF, it decomposes to give $\mathbf{I^{Ga}}$ and **1·thf$_2$**.

$^1$H NMR (400 MHz, $C_6D_5Br$) δ 7.45 (s, 8H, 2,6-$BC_6H_3$), 7.13 – 7.01 (m, 6H, $NC_6H_3$), 6.50 (s, 4H, , 4-$BC_6H_3$), 5.39 (d, br, $^3J_{(H-H)}$ = 11.0 Hz, 1H, Ga*H*), 4.80 (s, 1H, *H*C{C($CH_3$)Ndipp}$_2$), 3.50-3.30 (br, 1H, Al*H*), 3.28 (hept, *J* = 6.1 Hz, 2H, *H*C($CH_3$)$_2$), 3.01 (hept, *J* = 6.7, Hz, 2H, *H*C($CH_3$)$_2$), 2.13 (s, 24H, BAr-C$H_3$), 1.57 (s, 6H, HC{C(C$H_3$)Ndipp}$_2$), 1.49 (s, 6H, NC$H_3$), 1.46-1.31 (m, 4H, N$CH_2$), 1.28 (d, *J* = 6.8 Hz, 6H, HC(C$H_3$)$_2$), 1.19 (s, 6H, NC$H_3$), 1.11 – 0.98 (three overlapping doublets, *J* = 6.2, 6.8, 7.0 Hz, 18H, HC(C$H_3$)$_2$).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $C_6D_5Br$) δ 168.39 (HC{*C*($CH_3$)Ndipp}$_2$), 165.27 (q, $^{1}J_{C\text{-}B}$ = 49.1 Hz, *ipso*-B*C*$_6H_3$), 145.36 (*ortho*-N*C*$_6H_3$), 143.03 (*ipso*-N*C*$_6H_3$), 141.78 (*ortho*-N*C*$_6H_3$), 134.84 (*ortho*-B*C*$_6H_3$), 133.38 (q, unresolved, $^{3}J_{C\text{-}B}$ = 3.2 Hz, *meta*-B*C*$_6H_3$), 127.01 (*para*-N*C*$_6H_3$), 125.46 (*meta*-N*C*$_6H_3$), 124.27 (*meta*-N*C*$_6H_3$), 123.88 (*para*-B*C*$_6H_3$), 95.09 (HC{C($CH_3$)Ndipp}$_2$), 56.50 (N*C*H$_2$), 47.40 (N*C*H$_3$), 29.39 (H*C*($CH_3$)$_2$), 27.51 (H*C*($CH_3$)$_2$), 25.99 (HC(*C*H$_3$)$_2$), 24.79 (HC(*C*H$_3$)$_2$), 24.52 (HC(*C*H$_3$)$_2$), 23.74 (HC(*C*H$_3$)$_2$), 23.13 HC{C(*C*H$_3$)Ndipp}$_2$, 22.27 (B$C_6H_3$*C*H$_3$).

$^{11}B\{^{1}H\}$ NMR (128 MHz, $C_6D_5Br$) δ -6.27.

Analysis calculated for $C_{44}H_{64}BGaN_4$: C 72.44, H 8.84, N 7.68%. Found: C 72.34, H 9.06, N 8.01%.

IR spectroscopy (KBr pellet): v = 1850 cm$^{-1}$ (Al-H), 1748 cm$^{-1}$ (Ga-H).

## 2.14 NMR and IR spectra of [{TMEDA}Al(H)(H)Ga{BDI}][B($C_6H_3$-3,5-$Me_2$)$_4$] **3$^{Ga}$**

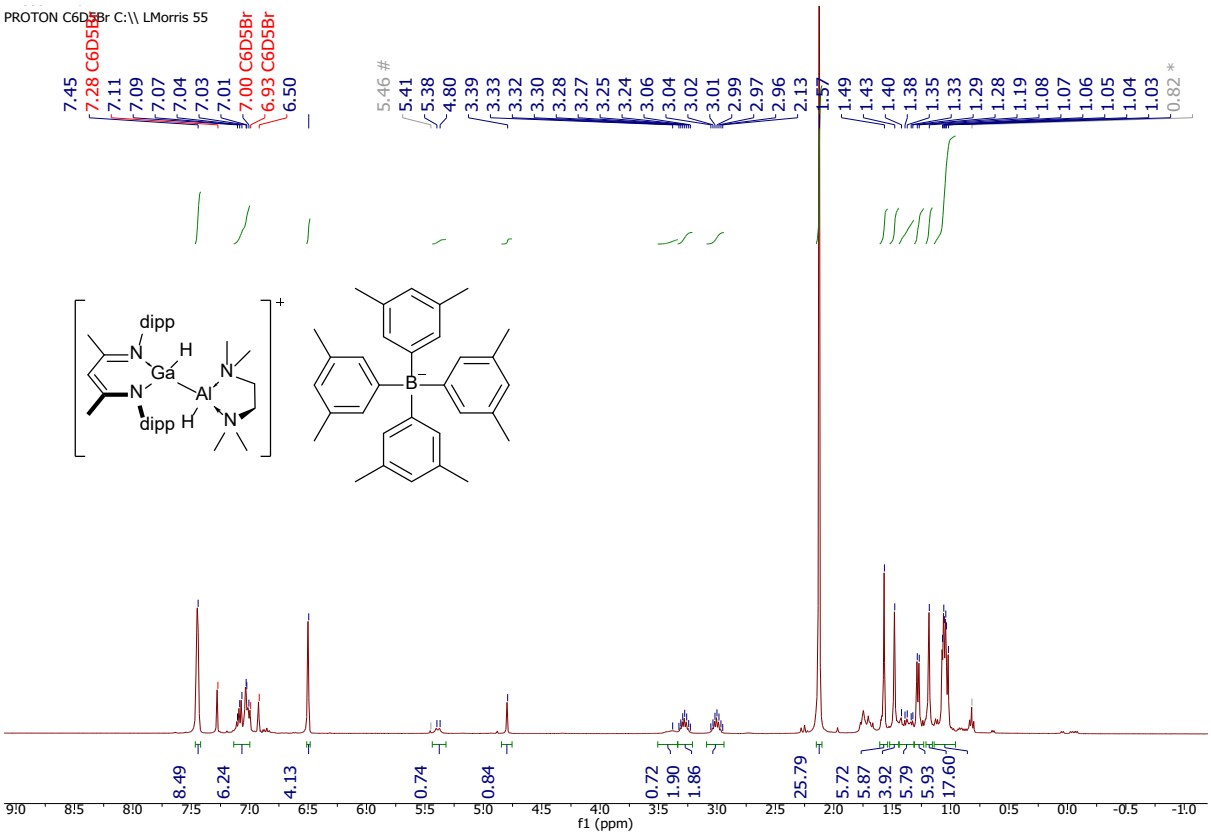



Figure S 46: $^{1}H$ NMR (400 MHz, $C_6D_5Br$). # unidentified impurity. * pentane.

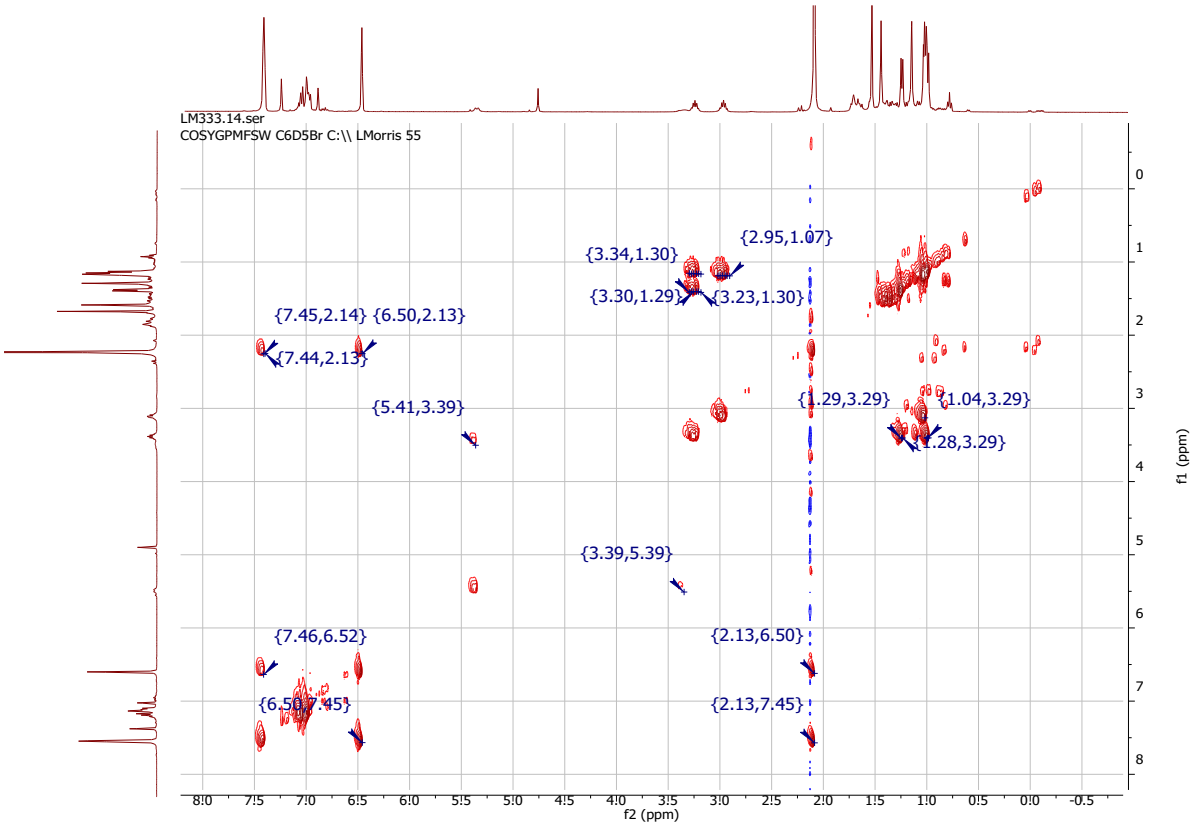



Figure S 47: $^{1}$H-$^{1}$H COSY spectrum ($C_6D_5Br$).

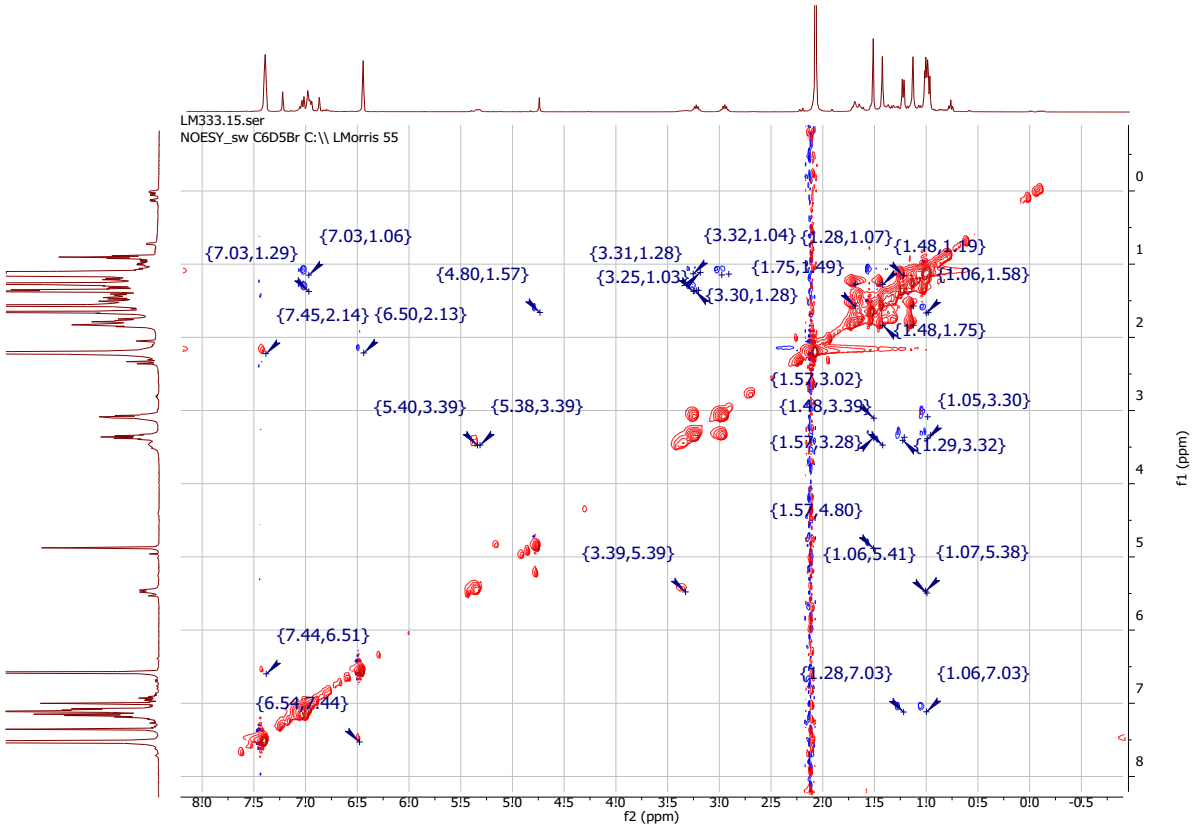



Figure S 48: $^{1}$H-$^{1}$H NOESY spectrum ($C_6D_5Br$).

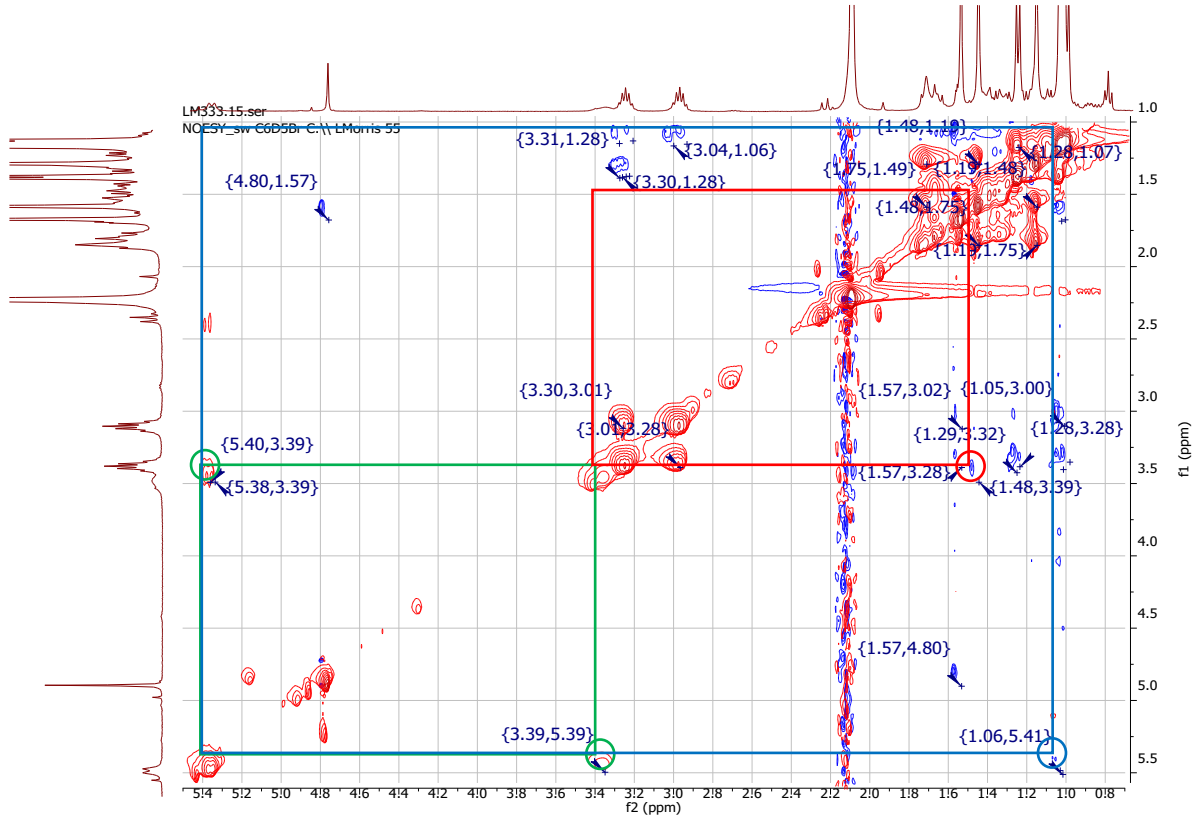



Figure S 49: Expanded $^{1}$H-$^{1}$H NOESY spectrum with NOE couplings highlighted according to the following scheme: Green = Ga*H*↔*H*Al. Blue = Ga*H*↔ $H_3C^{(Dipp)}$ Red = Al*H*↔$H_3C^{(TMEDA)}$.

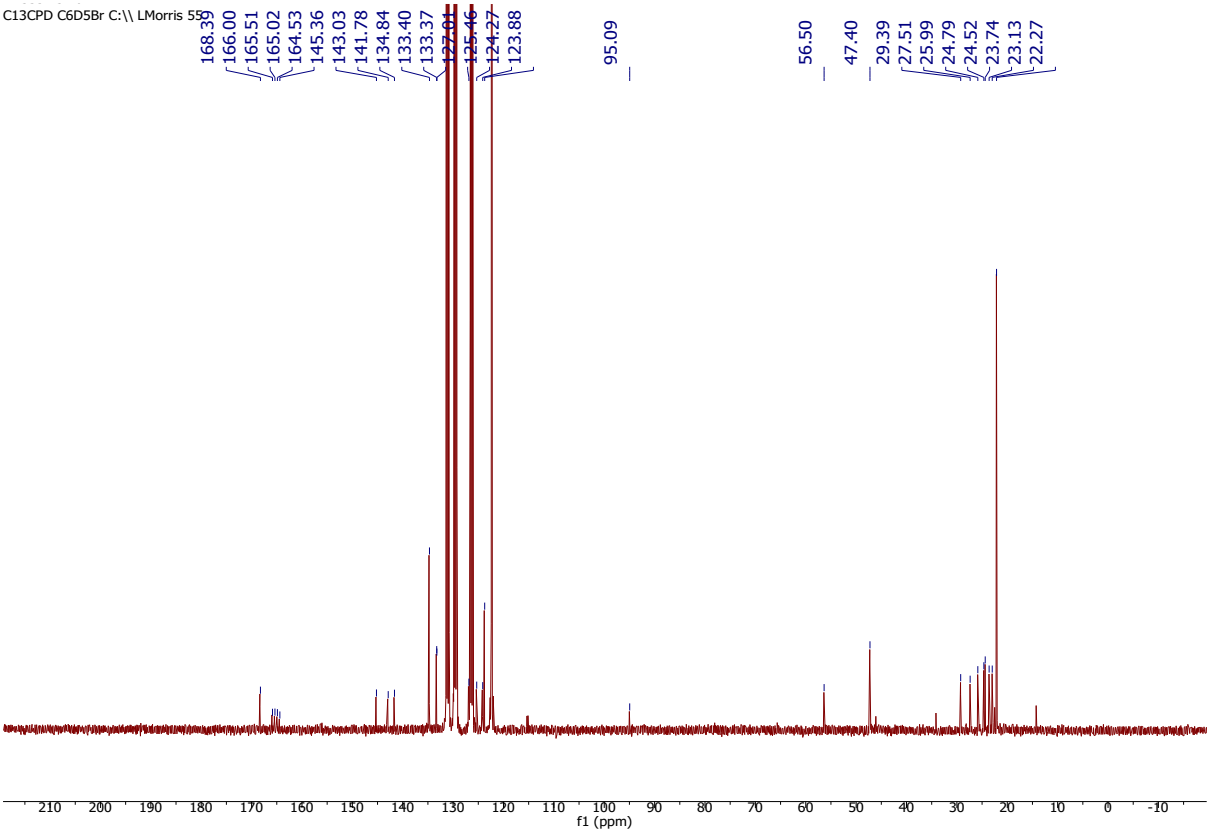



Figure S 50: $^{13}C\{^{1}H\}$ NMR (101 MHz, $C_6D_5Br$).

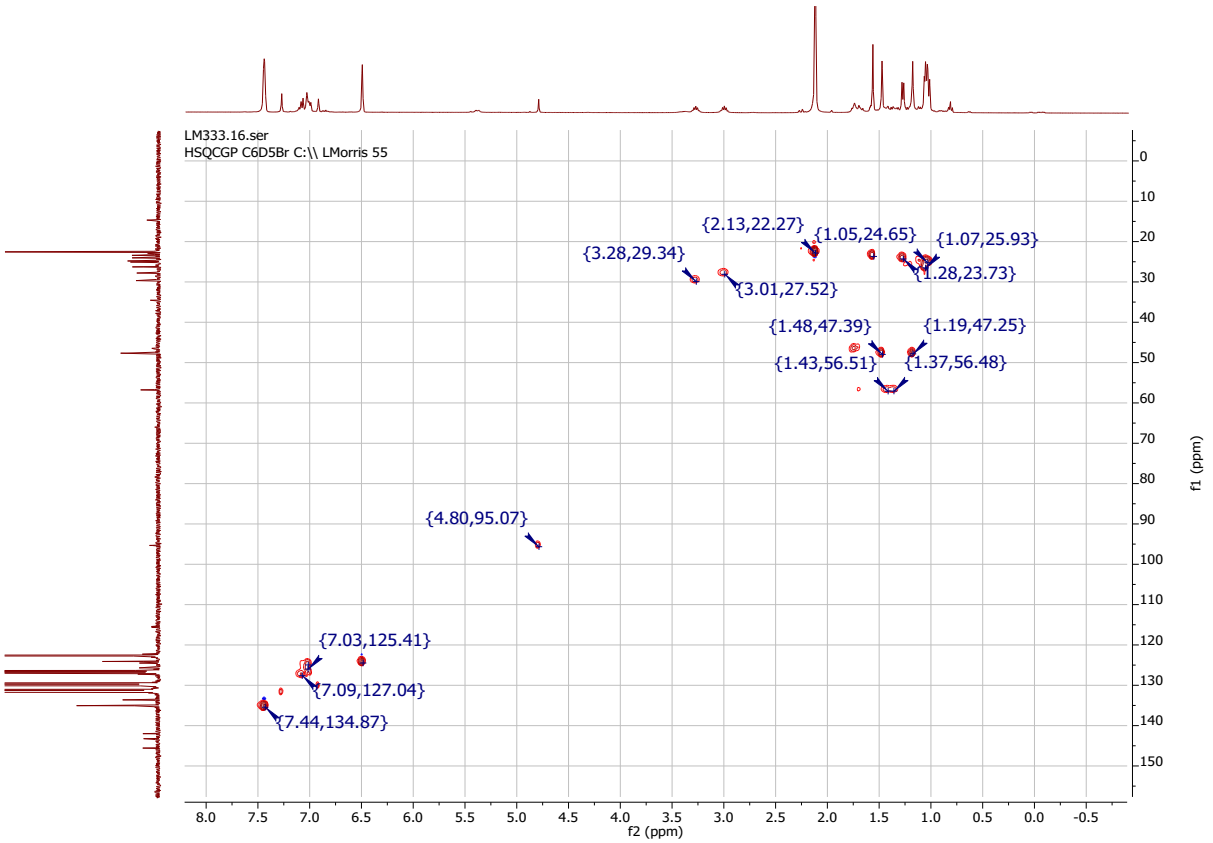



Figure S 51: $^{13}C$-$^{1}H$ HSQC spectrum ($C_6D_5Br$).

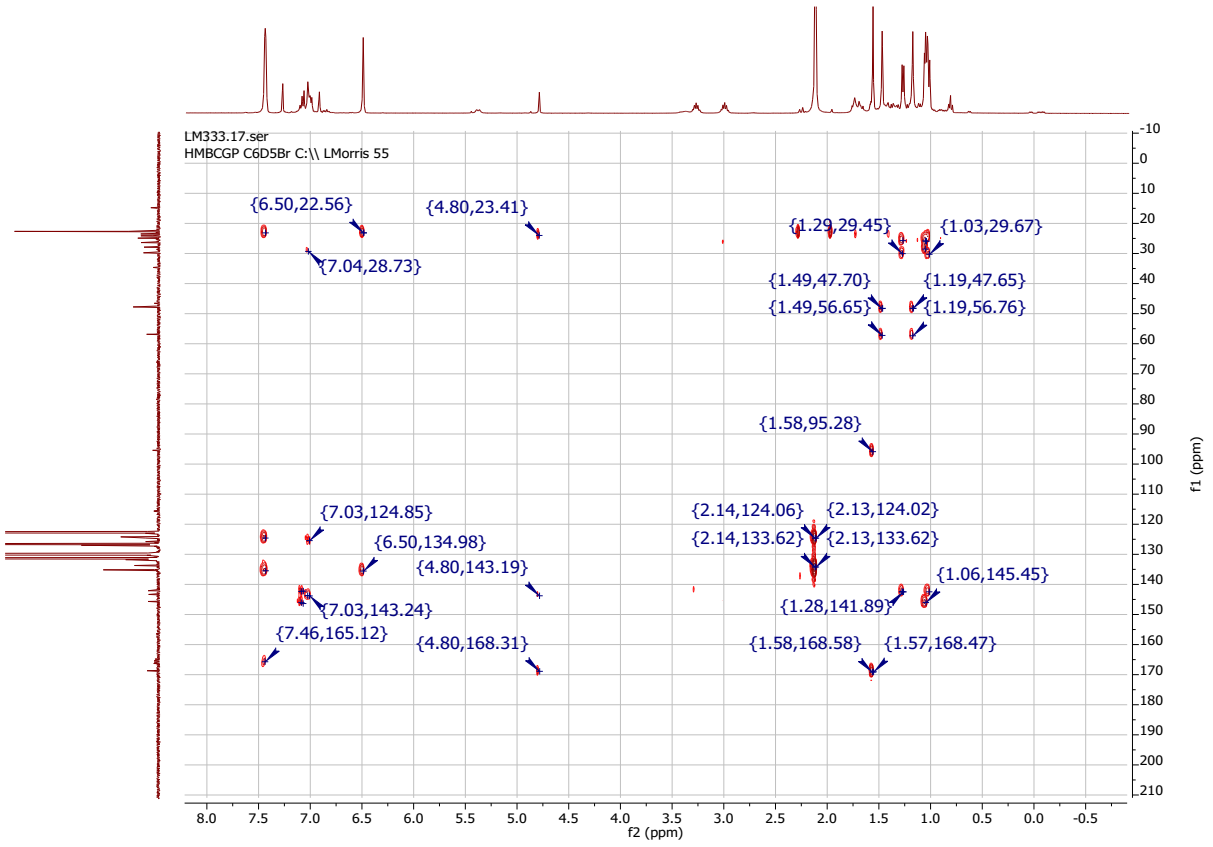



Figure S 52: $^{13}C$-$^{1}H$ HMBC spectrum ($C_6D_5Br$).

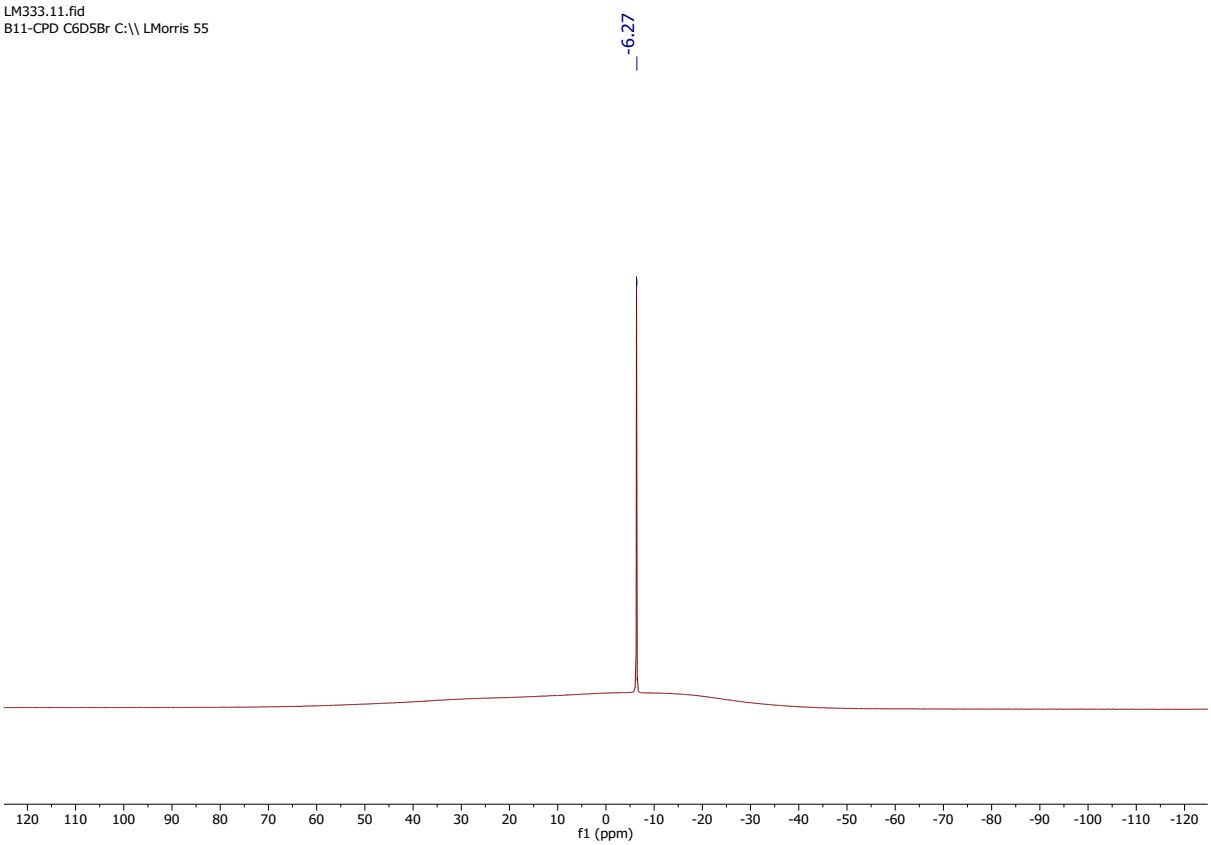



Figure S 53: $^{11}B\{^{1}H\}$ NMR (128 MHz, $C_6D_5Br$).

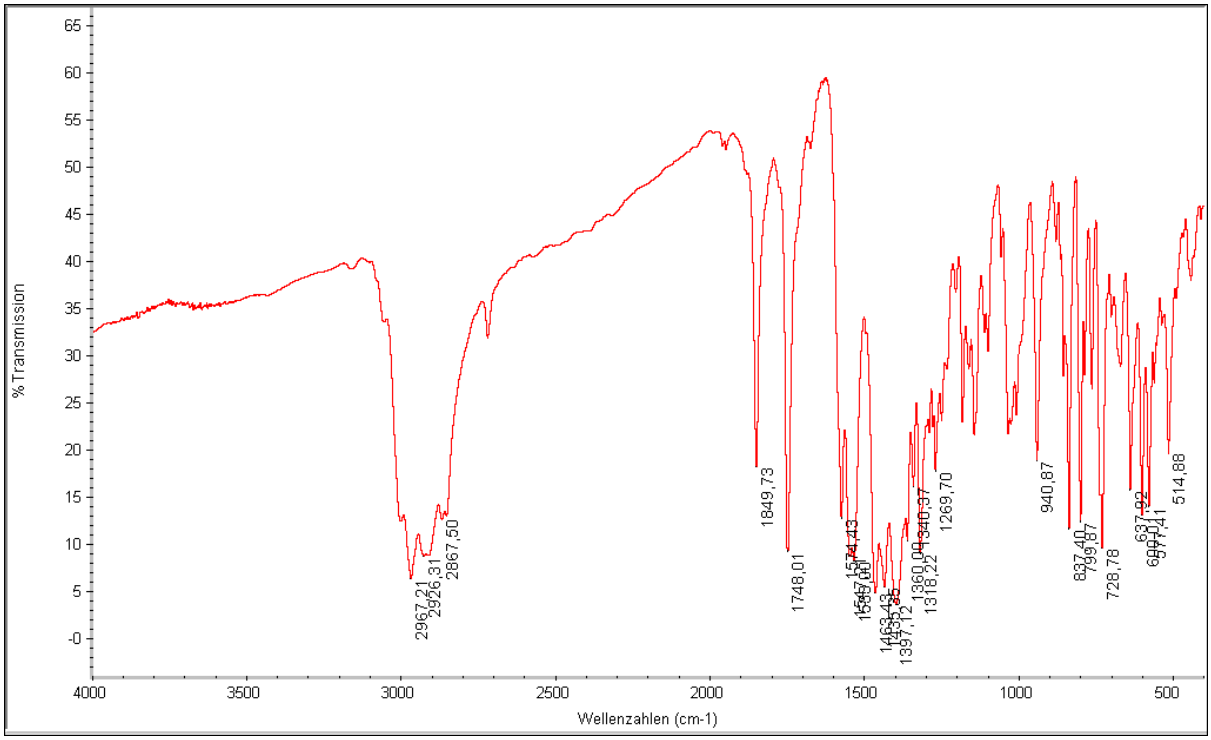



Figure S 54: IR spectrum (KBr pellet) of **3**$^{Ga}$.

## 2.15 In situ NMR spectra of the reaction of **3**$^{Ga}$ with THF-d$_8$

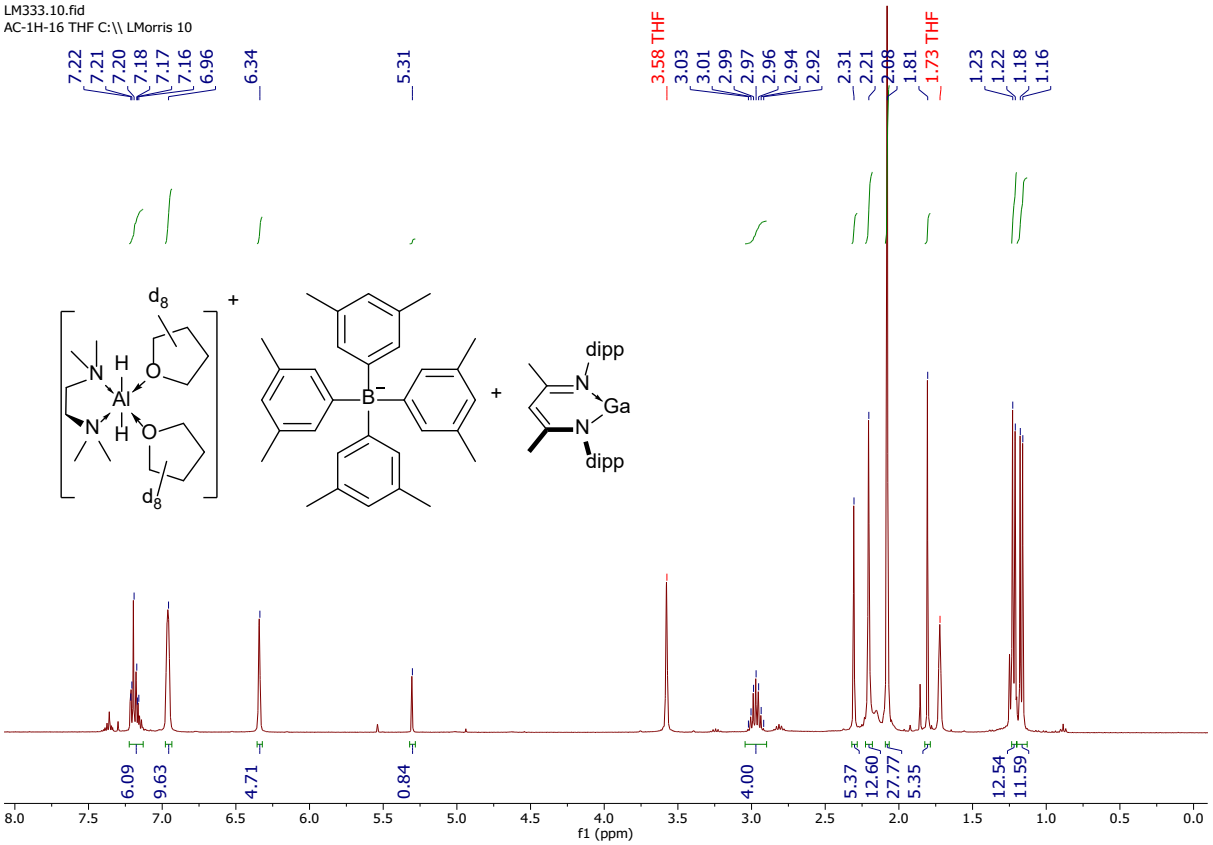



Figure S 55: $^1$H NMR (400 MHz, THF-d$_8$) of the reaction mixture.

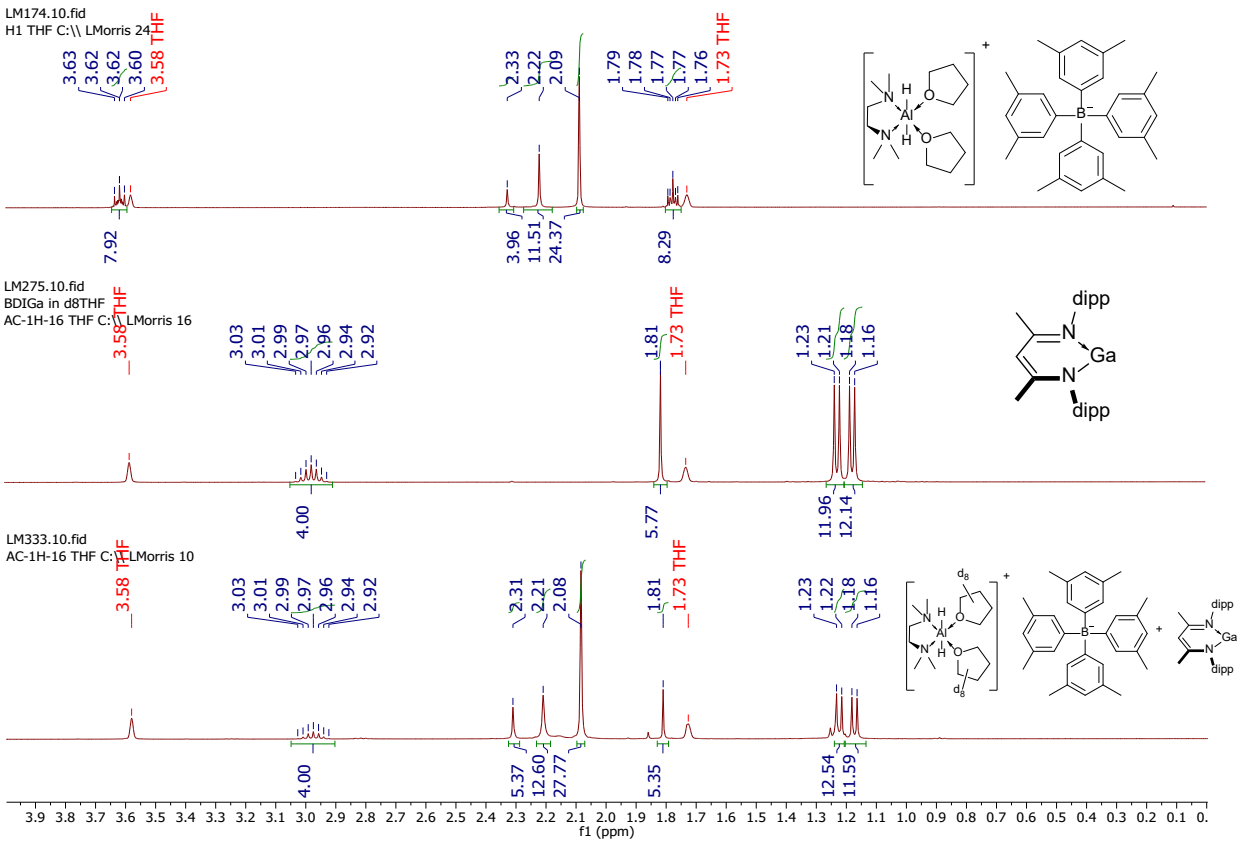



Figure S 56: Stacked expanded $^{1}$H NMR spectra (400 MHz, THF-$d_8$) of **1·thf$_2$** (top), **I$^{Ga}$** (centre), and **3$^{Ga}$** (bottom).

## 2.16 Synthesis of [(IMe$_4$)$_2$Al(H)(H)Al{BDI}][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] **4$^{Al}$**

NMR scale reaction: A J. Young's NMR tube was charged with 20 mg **3$^{Al}$** (0.0196 mmol) and 5 mg **IMe$_4$** (0.0392 mmol) and 0.6 ml of THF-$d_8$ was added. Analysis of the resulting yellow solution by $^{1}$H NMR spectroscopy showed quantitative conversion of the starting compounds to **4$^{Al}$** and uncomplexed TMEDA.

From **3$^{Al}$**: THF (0.6 ml) was added to a mixture of 40 mg **3$^{Al}$** (0.0392 mmol) and 10 mg **IMe$_4$** (0.0804 mmol) and the resulting bright yellow solution stirred for 30 minutes. Solvent was removed under vacuum, yielding a yellow residue, which was washed with two portions of *n*-pentane and recrystallised by slowly cooling a saturated toluene solution from 65°C to room temperature. Yellow block-like single crystals were suitable for X-ray diffraction analysis were collected by decantation, washed with *n*-pentane, and vacuum dried to obtain the title compound. Yield 16 mg, 56%.

From **2**: In the glovebox, 3 ml toluene was added to a mixture of 147 mg **2** (0.206 mmol) and 100 mg **I$^{Al}$** (0.217 mmol*) in a screw-cap vial. The reaction mixture was shaken vigorously for one minute, upon which a clear yellow solution was formed. The sample was transferred to the freezer, and cooled to -40°C overnight. A thick, bright yellow slurry of microcrystalline **4$^{Al}$** in toluene was obtained, and washed with 5 ml cold toluene over a filter-frit, followed by 1 ml

*n*-pentane, and vacuum dried to obtain pure **4$^{Al}$** as a yellow powder. Yield 144 mg, 61%.*In our hands, **I$^{Al}$** prepared from $[Cp^*Al]_4$ by the reported literature procedure[3] was often found to contain residual $[Cp^*Al]_4$ (approx. 5%) following crystallisation of the BDI-complex from the crude product mixture. $[Cp^*Al]_4$ is unreactive towards **2** and the minor impurity could be straightforwardly removed from the product during the workup procedure.

$^1$H NMR (400 MHz, THF-$d_8$) δ 7.33 – 7.01 (m, 6H, $NC_6H_3$), 6.91 (m, 8H, *ortho*-$BC_6H_3$), 6.28 (s, 4H *para*-$BC_6H_3$), 5.27 (s, 1H, $HC\{C(CH_3)Ndipp\}_2$), 4.75 (s, br, 1H, (BDI)Al*H*), 3.86 (s, br, 1H, $(NHC)_2AlH$), 3.48 (hept, *J* = 6.5 Hz, 2H, $HC(CH_3)_2$), 3.19 (hept, *J* = 6.7 Hz, 2H, $HC(CH_3)_2$), 3.08 (s, 12H, $NCH_3^{NHC}$), 2.00 (s, 24H, BAr-$CH_3$), 1.82 (s, 12H $CCH_3^{NHC}$), 1.74 (s, 6H, $HC\{C(CH_3)Ndipp\}_2$), 1.22 (d, *J* = 6.8 Hz, 12H, $HC(CH_3)_2$), 1.10 (d, *J* = 6.7 Hz, 6H, $HC(CH_3)_2$), 0.89 (d, *J* = 6.7 Hz, 6H, $HC(CH_3)_2$).

$^{13}$C{$^1$H} NMR (101 MHz, THF-$d_8$) δ 171.49 ($HC\{C(CH_3)Ndipp\}_2$), 166.18 (*br*, $C^{carbene}$), 165.73 (q, *J* = 49.2 Hz, *ipso*-$BC_6H_3$), 146.67 (*ortho*-$NC_6H_3$), 144.37 (*ortho*-$NC_6H_3$), 143.38 (*ipso* -$NC_6H_3$), 135.57 (m (partially resolved), *J* = 1.0 Hz, *ortho*-$BC_6H_3$), 132.94 (q, *J* = 2.9 Hz, *meta*-$BC_6H_3$), 127.93 ($C{=}C^{NHC}$), 127.79 (*para*-$NC_6H_3$), 125.39 (*meta*-$NC_6H_3$), 125.07 (*meta*-$NC_6H_3$), 123.49 (*para*-$BC_6H_3$), 98.65 ($HC\{C(CH_3)Ndipp\}_2$), 34.65 ($NCH_3$), 30.38 ($HC(CH_3)_2$), 28.66 ($HC(CH_3)_2$), 26.10 ($HC(CH_3)_2$), 25.06 ($HC(CH_3)_2$), 24.39 ($HC(CH_3)_2$), 24.00 ($HC(CH_3)_2$), 23.85 ($HC\{C(CH_3)Ndipp\}_2$), 22.36 ($BC_6H_3CH_3$), 8.45 ($CCH_3^{NHC}$).

$^{11}$B{$^1$H} NMR (128 MHz, THF-$d_8$) δ -6.90.

IR spectroscopy (KBr pellet): ν = 1777, 1702 cm$^{-1}$ (Al-H).

Elemental analysis calculated for $C_{75}H_{103}Al_2BN_6$: C 78.10, H 9.00, N 7.29%. Found: C 78.27, H 8.95, N 6.89%.

2.17 In situ $^{1}$H NMR spectrum (400 MHz, THF-$d_8$) of the reaction between **3$^{Al}$** and **IMe$_4$**

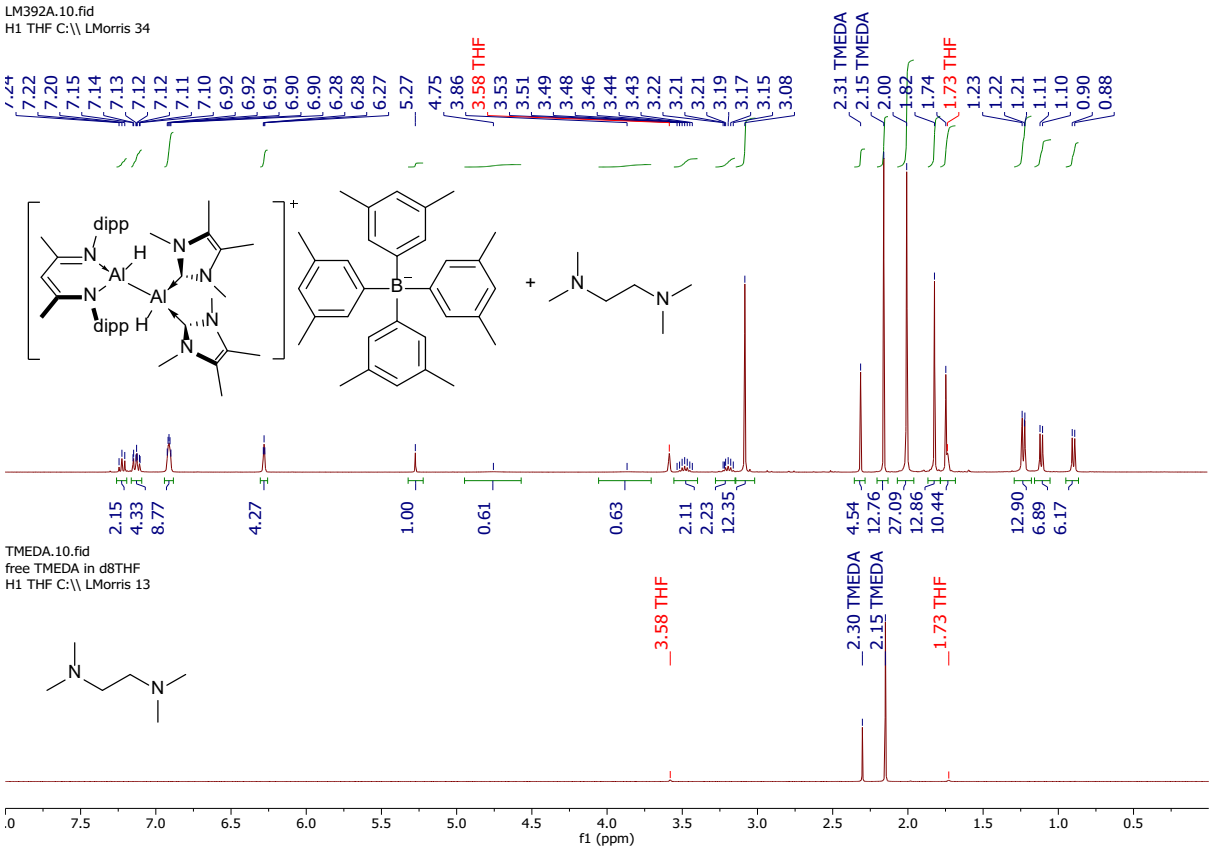



Figure S 57: In situ $^{1}$H NMR spectrum (400 MHz, THF-$d_8$) of the reaction between **3$^{Al}$** and **IMe$_4$** to give **4$^{Al}$** and TMEDA stacked above the NMR spectrum of pure TMEDA in the same solvent.

## 2.18 NMR and IR spectra of $[(IMe_4)_2Al(H)(H)Al\{BDI\}][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ **4$^{Al}$**

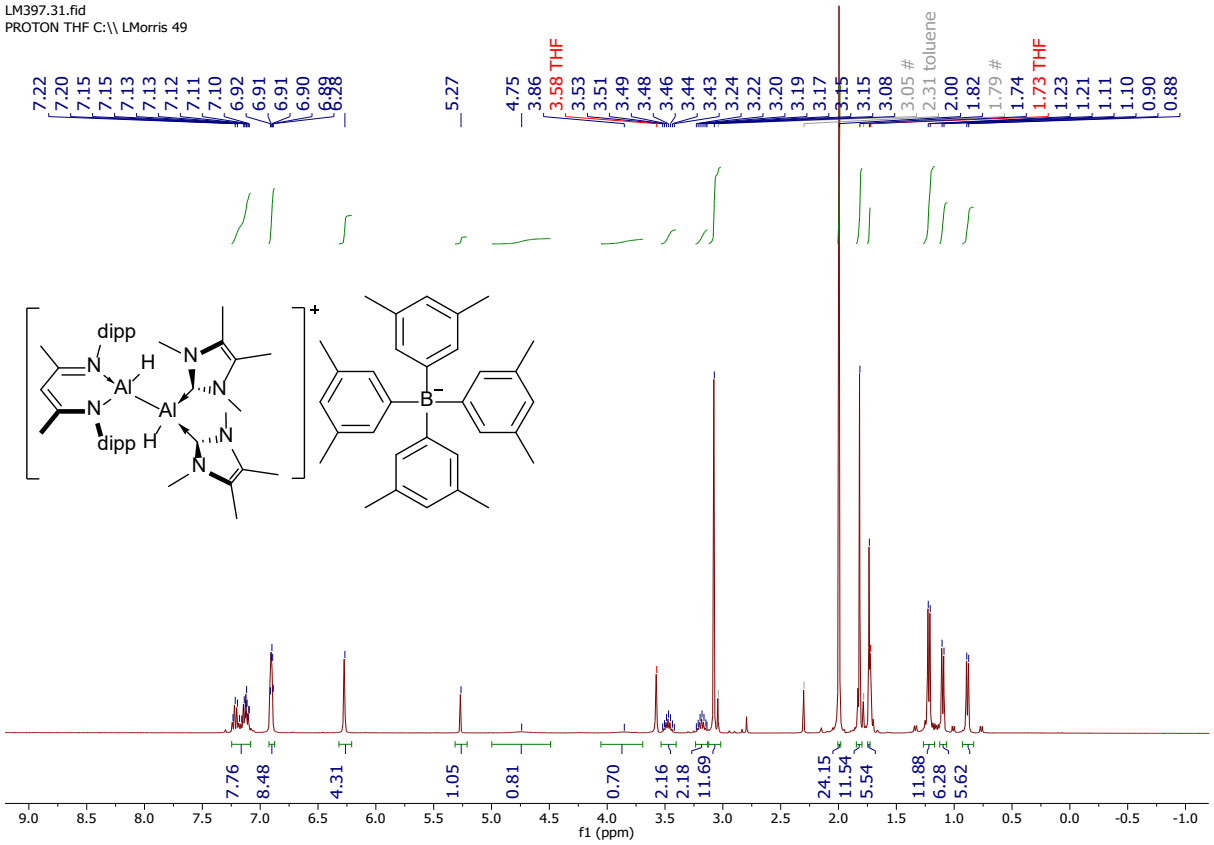



Figure S 58: $^1$H NMR spectrum of **3$^{Al}$** (THF-$d_8$, 400 MHz).* Residual toluene of crystallisation. # unidentified impurity.

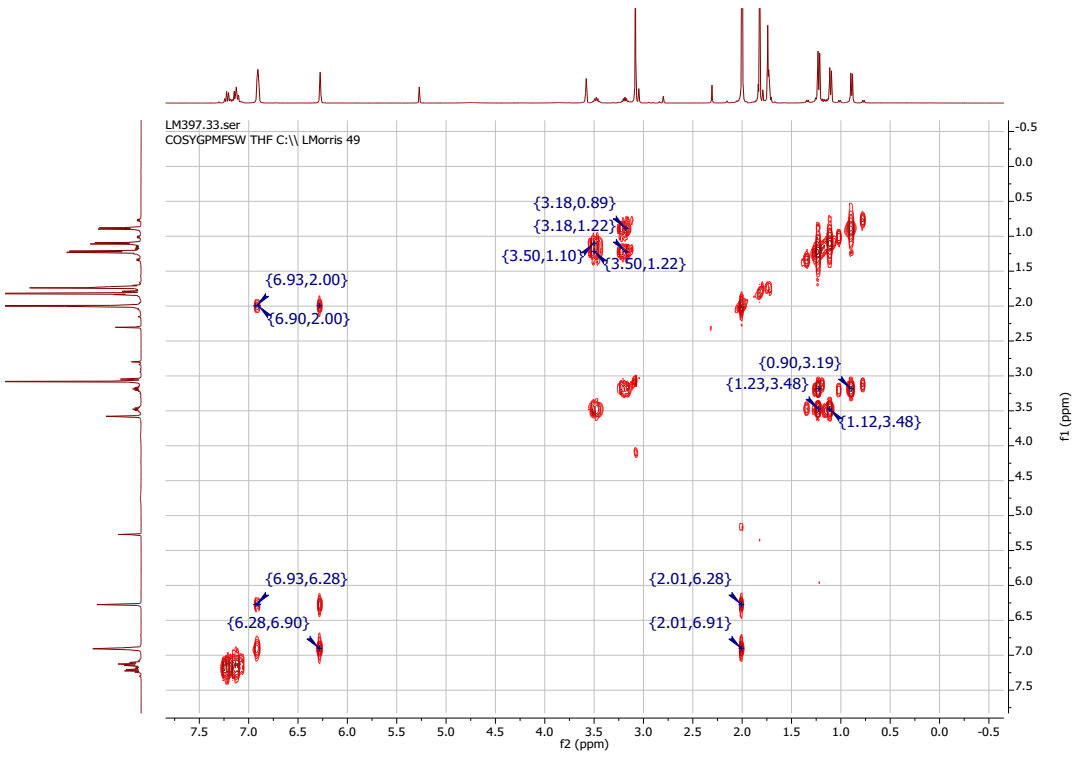



Figure S 59: $^1$H-$^1$H COSY NMR spectrum (THF-$d_8$).

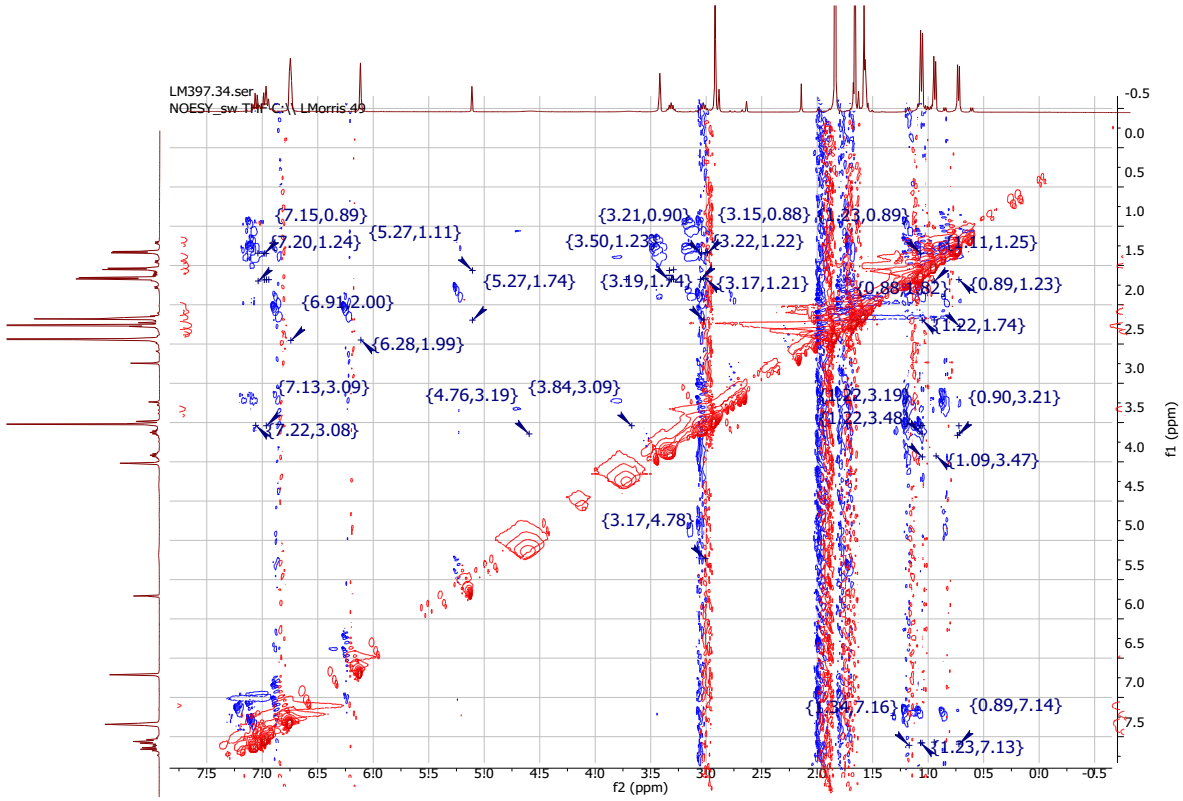



Figure S 60: $^{1}$H-$^{1}$H NOESY NMR spectrum (THF-$d_8$).

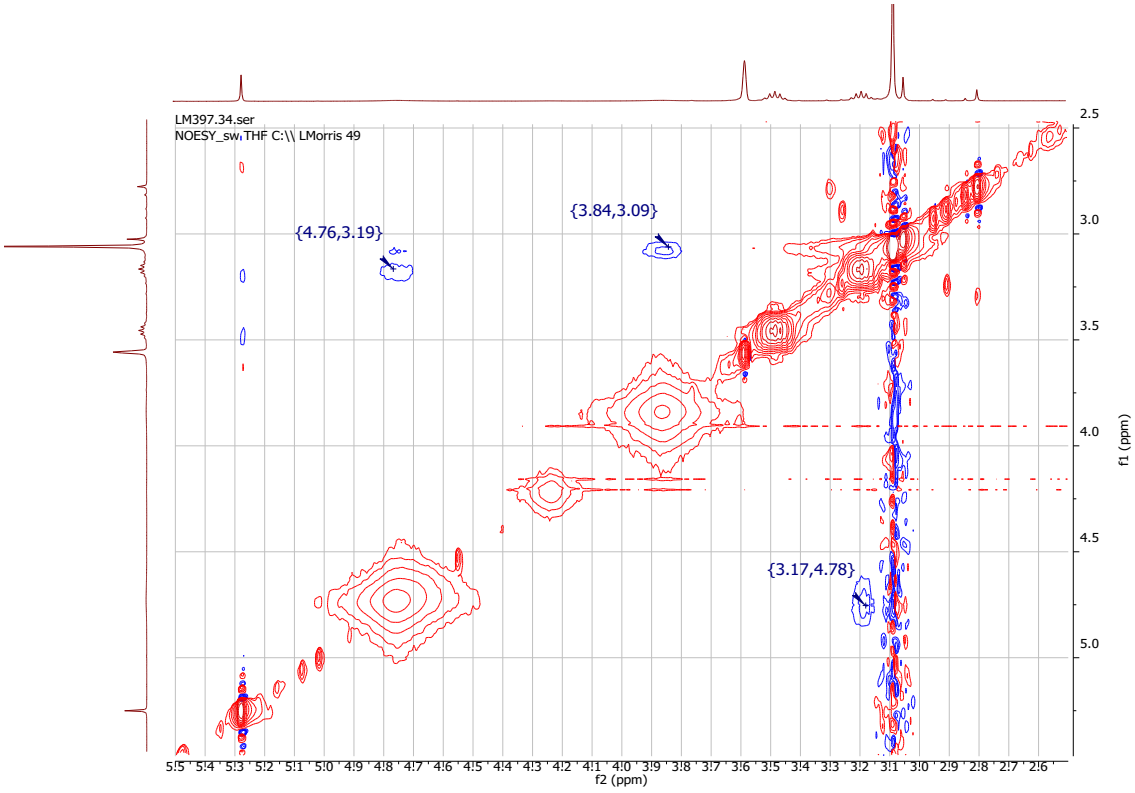



Figure S 61: Expanded $^{1}$H-$^{1}$H NOESY NMR spectrum (THF-$d_8$), showing ligand-hydride through-space couplings.

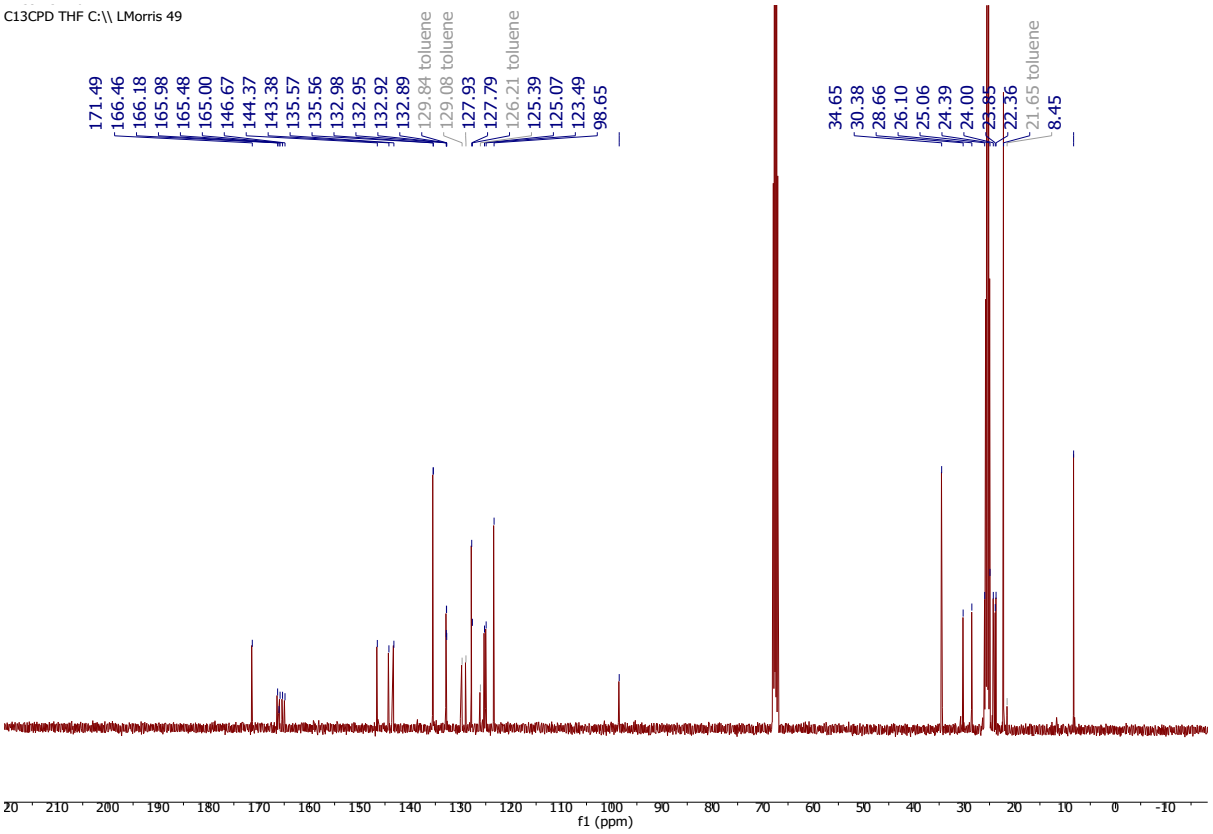



Figure S 62: $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-$d_8$).

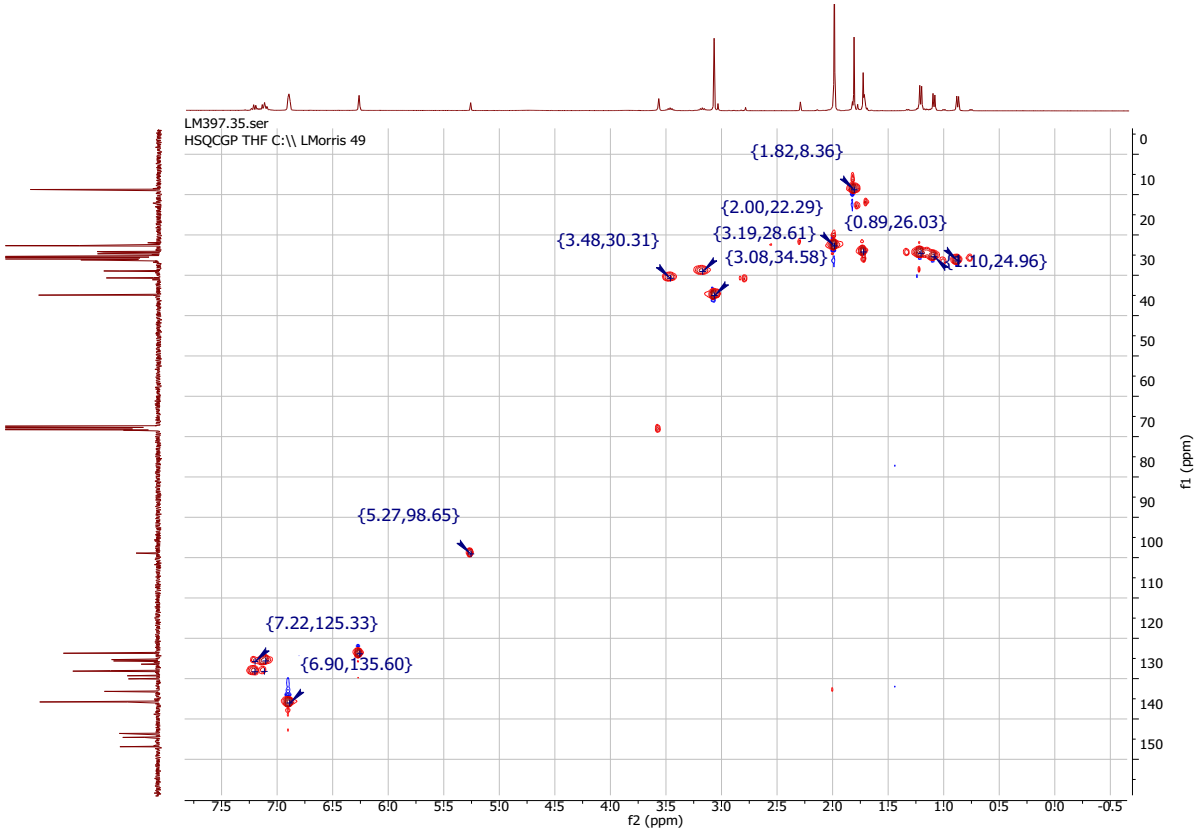



Figure S 63: $^{13}C$-$^{1}H$ HSQC NMR spectrum (THF-$d_8$).

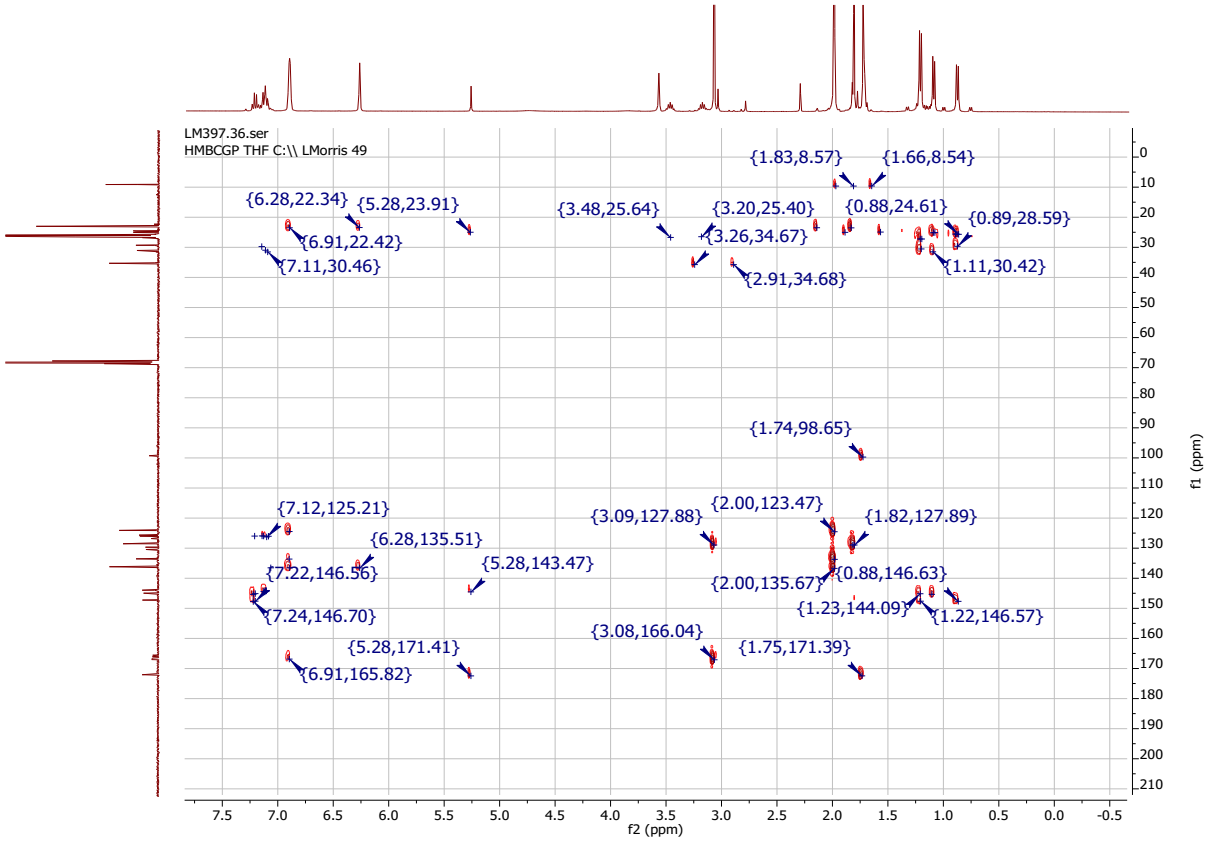



Figure S 64: $^{13}C$-$^{1}H$ HMCC NMR spectrum (THF-$d_8$).

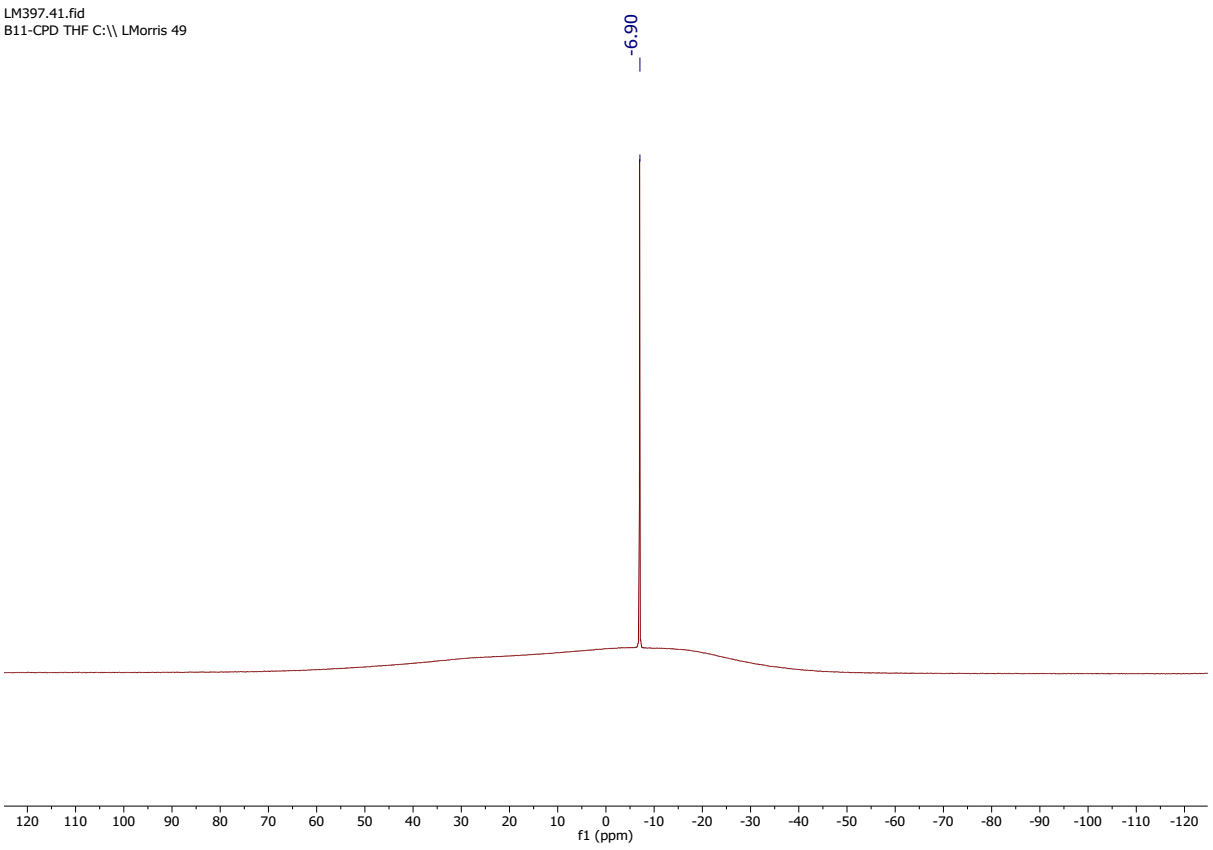



Figure S 65: $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-$d_8$)

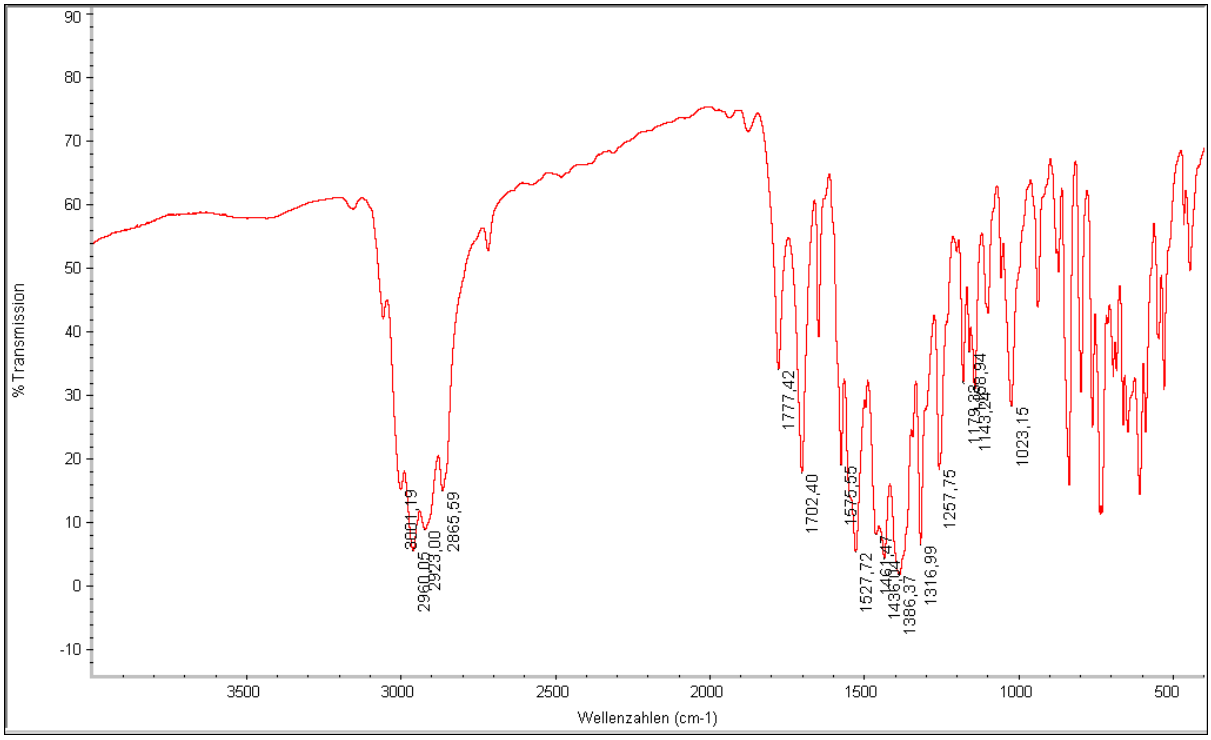



Figure S 66: IR spectrum (KBr pellet) of $\mathbf{4^{Al}}$.

## 2.19 Reaction of $\mathbf{3^{Ga}}$ with **IMe$_4$**: *in situ* NMR analysis of $[(IMe_4)_2Al(H)(H)Ga\{BDI\}][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ $\mathbf{4^{Ga}}$ and crystallisation of **2**.

A J. Young's NMR tube was charged with 20 mg $\mathbf{3^{Ga}}$ (0.0188 mmol) and 5 mg **IMe$_4$** (0.0402 mmol) and 0.6 ml $C_6D_6$ was added. On mixing, all solid dissolved, and a pale-yellow solution formed. The reaction was monitored by $^1$H NMR spectroscopy, showing a 2:3 mixture of $\mathbf{I^{Ga}}$ and $\mathbf{4^{Ga}}$ with quantitative release of TMEDA after 15 minutes at room temperature, a 2:1 mixture after 24 hours at room temperature, and quantitative conversion to $\mathbf{I^{Ga}}$ after a further 60 minutes at 60°C. On cooling the solution back to room temperature, colourless plate-like single crystals of **2** suitable for X-ray diffraction analysis were deposited from the reaction mixture, and could be isolated in 30% crystalline yield (4 mg) following decantation and vacuum drying.

$^1$H NMR characterisation of $\mathbf{4^{Ga}}$ from *in situ* analysis of reaction mixture. Resonances corresponding to decomposition products **2** and $\mathbf{I^{Ga}}$ are labelled as such. Integration for resonances corresponding to the borate anion refer to the total borate in solution, as the mixture includes the cations of both $\mathbf{4^{Ga}}$ and **2**.$^1$H NMR (400 MHz, $C_6D_6$) δ 7.64 (s, 18H, *ortho*-$BC_6H_3$), 7.17 (s, 4H, $NC_6H_3$, overlaps with $C_6D_5H$), 7.04-6.86 (m, 7H, $NC_6H_3$), 6.63 (*para*-$BC_6H_3$), 5.96 (d, $^3J$ = 5.7 Hz, 1H, Ga*H*), 5.20 (s, 1H, $\mathbf{I^{Ga}}$), 4.86 (s, 1H, *H*C{C(CH$_3$)Ndipp}$_2$), 4.29 (br, 1H, Al*H*), 3.99 (br, 1H, Al*H*, **2**), 3.53 (hept, *J* = 6.8 Hz, 2H, *H*C(CH$_3$)$_2$), 3.24 (hept, *J* = 6.8 Hz, 2H, *H*C(CH$_3$)$_2$), 3.15 (hept, *J* = 6.8 Hz, 3H, $\mathbf{I^{Ga}}$), 2.82 (s, 8H, **2**), 2.80 (s, 3H, free-NHC), 2.72 (s, 12H, NC$H_3^{NHC}$), 2.35 (s, 9H, TMEDA), 2.20 (s, 55H, BAr-C$H_3$), 2.12 (s, 28H,

TMEDA), 1.72 (s, 4H, **I$^{Ga}$**), 1.53 (s, 6H, HC{C(C$H_3$)Ndipp}$_2$), 1.35-1.25 (overlapped CC$H_3^{NHC}$, **I$^{Ga}$**, **2**), 1.23 (d, *J* = 6.8 Hz, 6H, HC(C$H_3$)$_2$), 1.17-1.10 (overlapped doublets, **I$^{Ga}$**, HC(C$H_3$)$_2$), 0.84 (d, *J* = 6.7 Hz, 6H, HC(C$H_3$)$_2$).

$^{13}$C NMR characterisation of **4$^{Ga}$** from *in situ* analysis of reaction mixture. $^{13}$C NMR (101 MHz, $C_6D_6$) δ 168.22 (HC{*C*(CH$_3$)Ndipp}$_2$), 165.62 (q, $^3J_{(C\text{-}B)}$ = 49.3 Hz, *ipso*-BC$_6H_3$), 163.64 (**I$^{Ga}$**), 162.77 (Al*C*$^{NHC}$), 159.97 (**2**), 145.43 (*ortho*-Ndipp), 144.56 (*ipso*-Ndipp), 143.76 (**I$^{Ga}$**), 143.22 (*ortho*-Ndipp), 143.04 (**I$^{Ga}$**), 135.37 (*ortho*-BC$_6H_3$), 133.42 (q, unresolved, $^2J_{(B\text{-}C)}$ = 3.1 Hz, *ortho*-BC$_6H_3$) 127.45 (*C*=*C*$^{NHC}$), 126.54 (Ndipp), 126.30 (Ndipp), 124.39 (Ndipp), 124.01 (**I$^{Ga}$**), 123.75 (*para*-BC$_6H_3$), 99.57 (**I$^{Ga}$**), 96.15 (H*C*{C(CH$_3$)Ndipp}$_2$), 58.37 (TMEDA), 46.05 (TMEDA), 33.95 (N*C*H$_3^{NHC}$), 33.55 (**2**), 29.40 (H*C*(CH$_3$)$_2$), 28.65 (**I$^{Ga}$**), 27.78 (H*C*(CH$_3$)$_2$), 25.58 (HC(*C*H$_3$)$_2$), 24.78 (HC(*C*H$_3$)$_2$), 23.93 (**I$^{Ga}$**), 23.87 (**I$^{Ga}$**), 23.72 (HC(*C*H$_3$)$_2$), 23.37 (HC{C(*C*H$_3$)Ndipp}$_2$), 22.30 (BAr-C$H_3$), 7.95 (NC$H_3^{NHC}$ **4$^{Ga}$** or **2**), 7.80 (NC$H_3^{NHC}$ **4$^{Ga}$** or **2**).

$^{11}$B{$^1$H} NMR (128 MHz, $C_6D_6$) δ -6.17.

## 2.20 *In situ* NMR spectra from reaction of **3$^{Ga}$** with **IMe$_4$** and isolated crystals of **2** thereof.

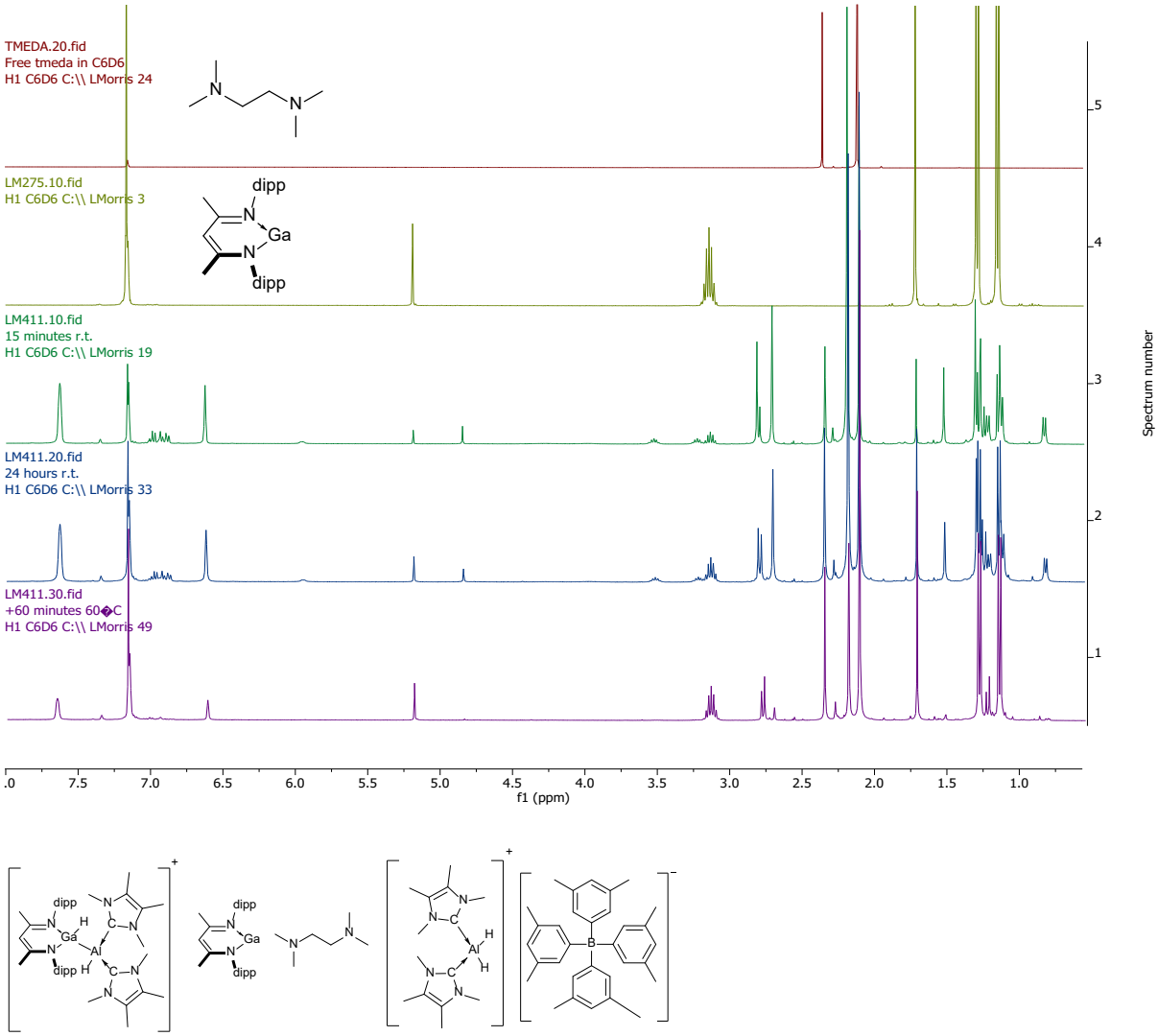



Figure S 67: Stacked $^1$H NMR spectra (400 MHz, $C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** after 15 minutes and 24 hours at room temperature and after a further 60 minutes at 60°C, with spectra of pure TMEDA and **I$^{Ga}$** in the same solvent for comparison.

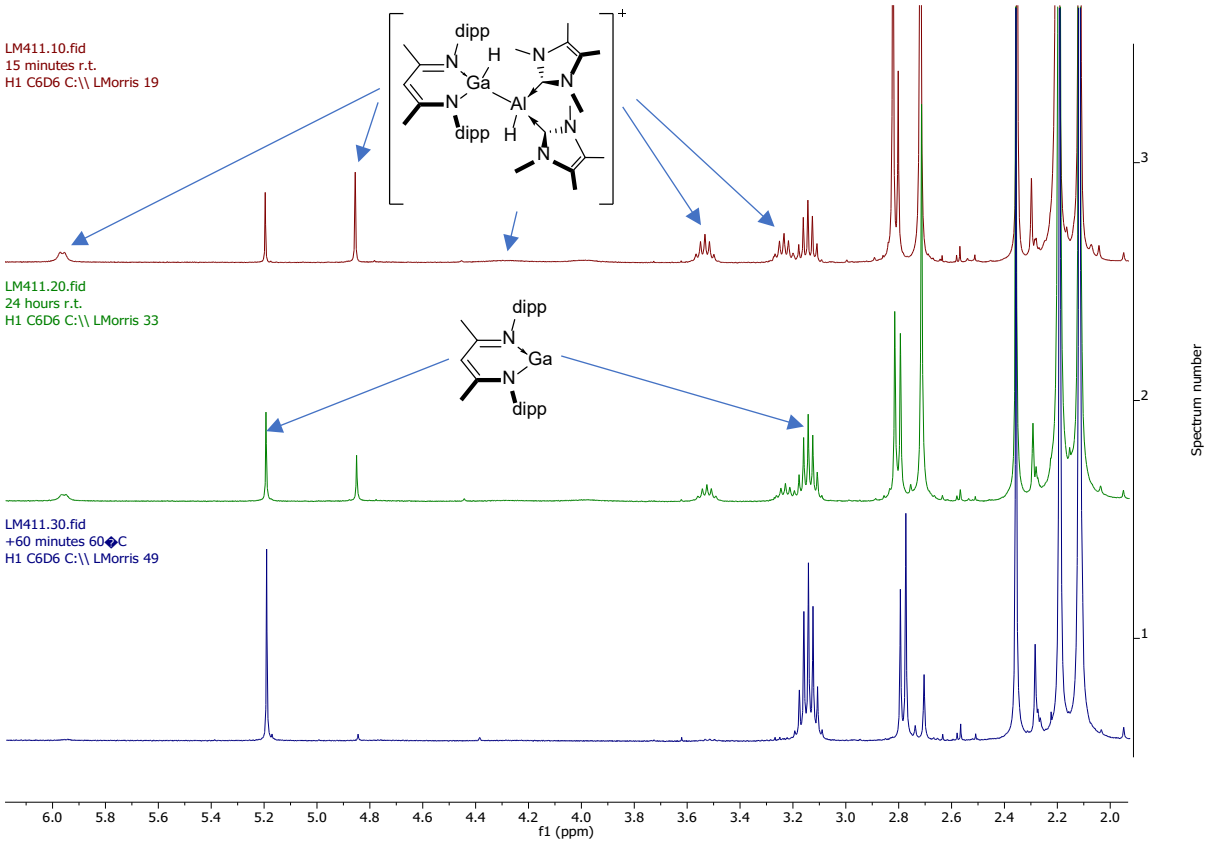



Figure S 68: Expanded stacked *in situ* $^{1}$H NMR spectra (400 MHz, $C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** after 15 minutes and 24 hours at room temperature and after a further 60 minutes at 60°C (top to bottom respectively).

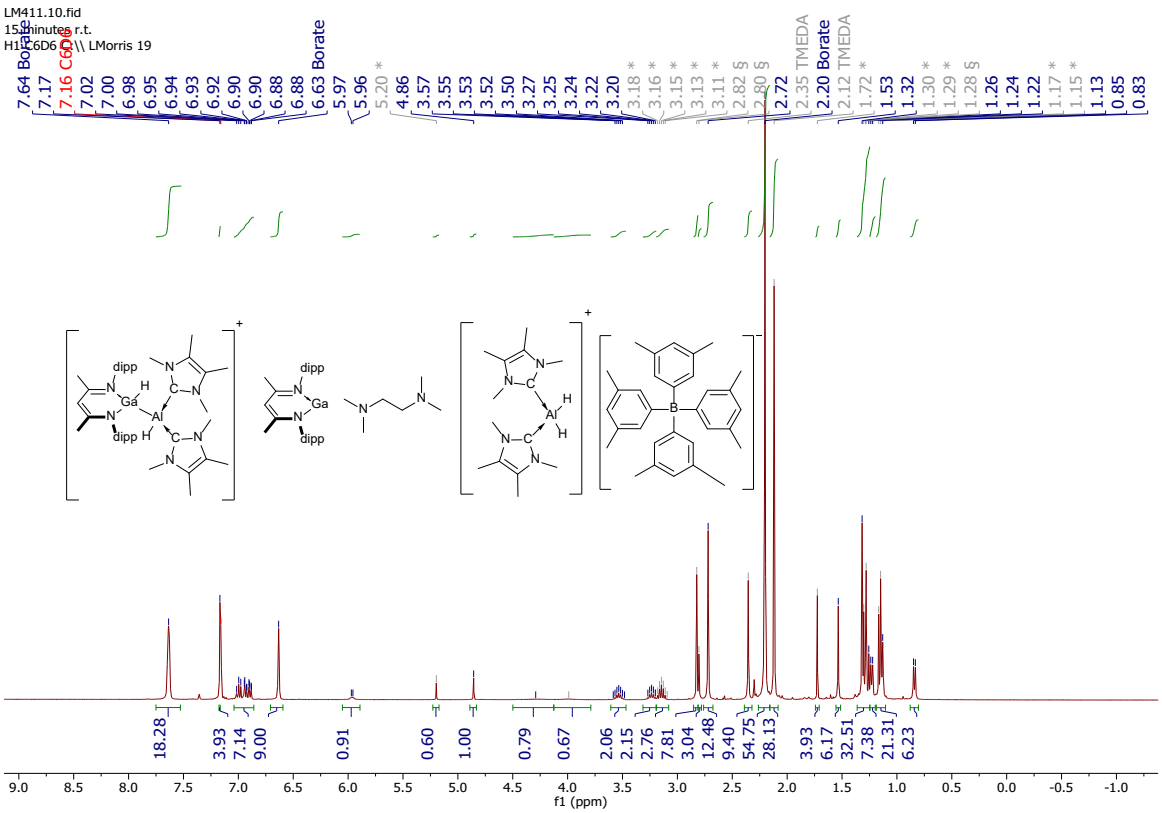



Figure S 69: *in situ* $^{1}$H NMR spectrum (400 MHz, $C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**, **I$^{Ga}$** (*), TMEDA (labelled), and **2** (§).

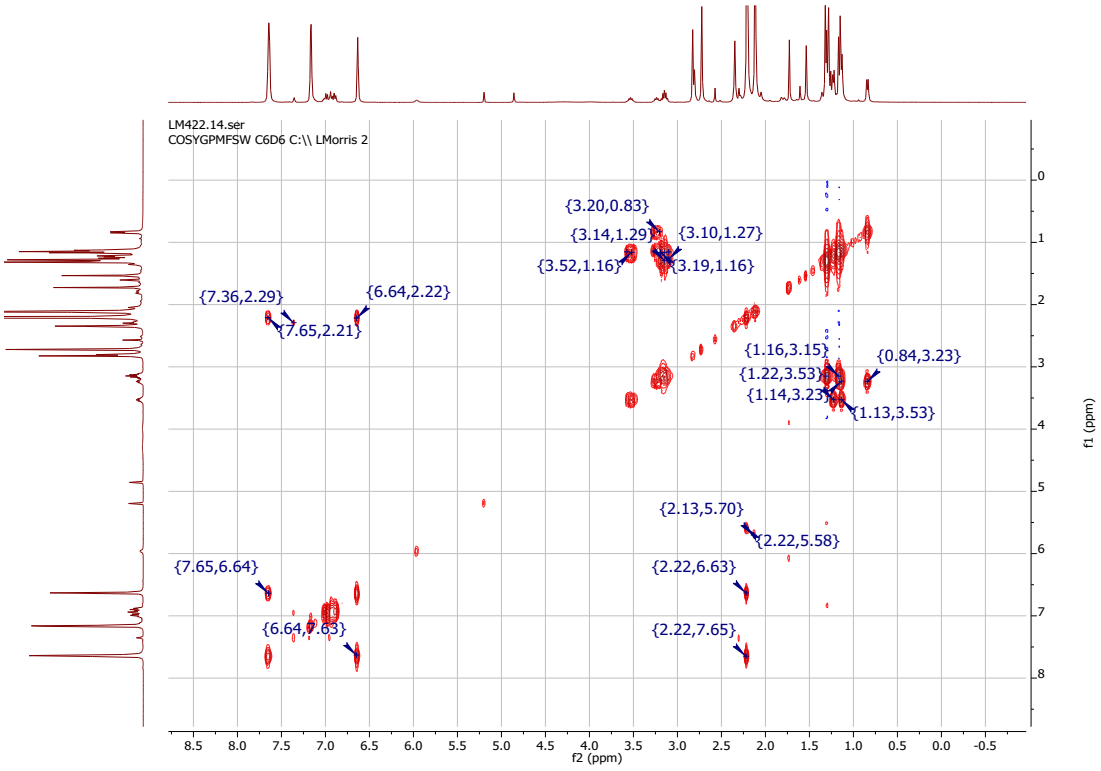



Figure S 70: *in situ* $^{1}$H-$^{1}$H COSY NMR spectrum ($C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**.

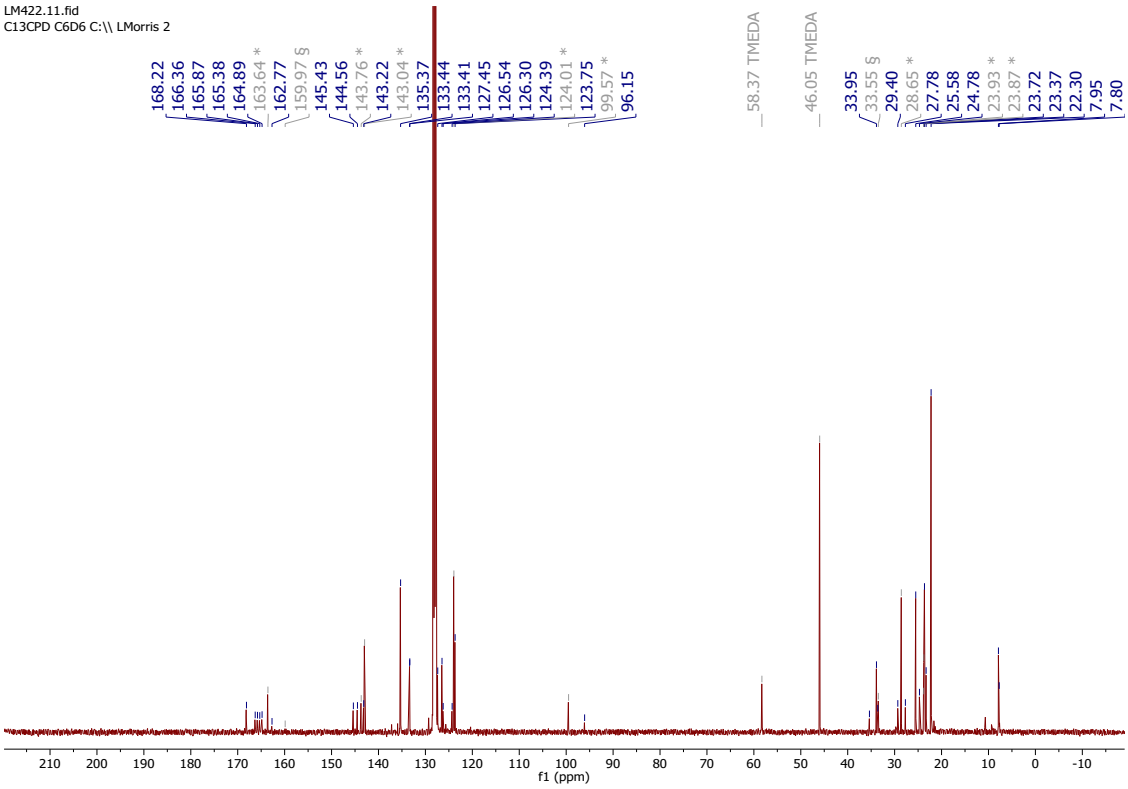



Figure S 71: Figure S 72: *in situ* $^{1}$H NMR spectrum (400 MHz, $C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**, **I$^{Ga}$** (*), TMEDA (labelled), and **2** (§).

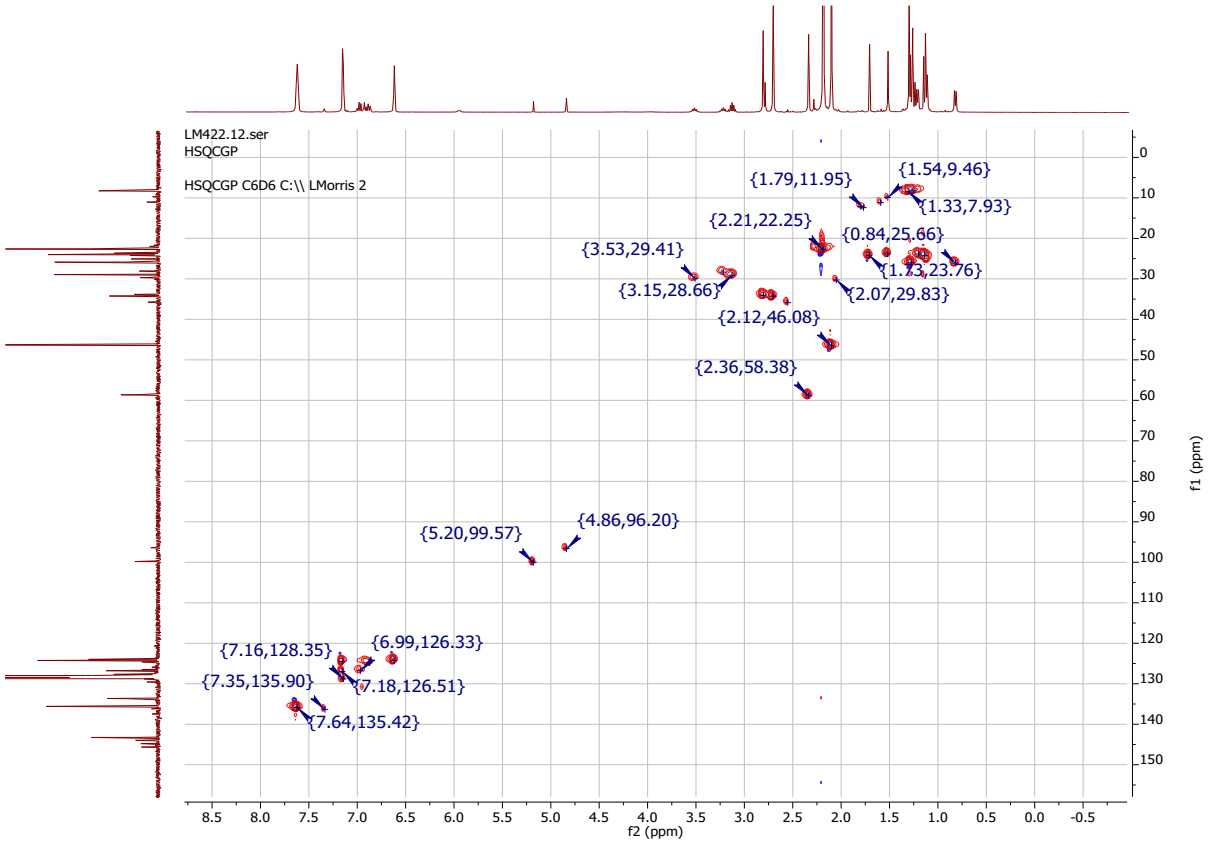



Figure S 73: *in situ* $^{13}$C-$^{1}$H HSQC NMR spectrum ($C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**.

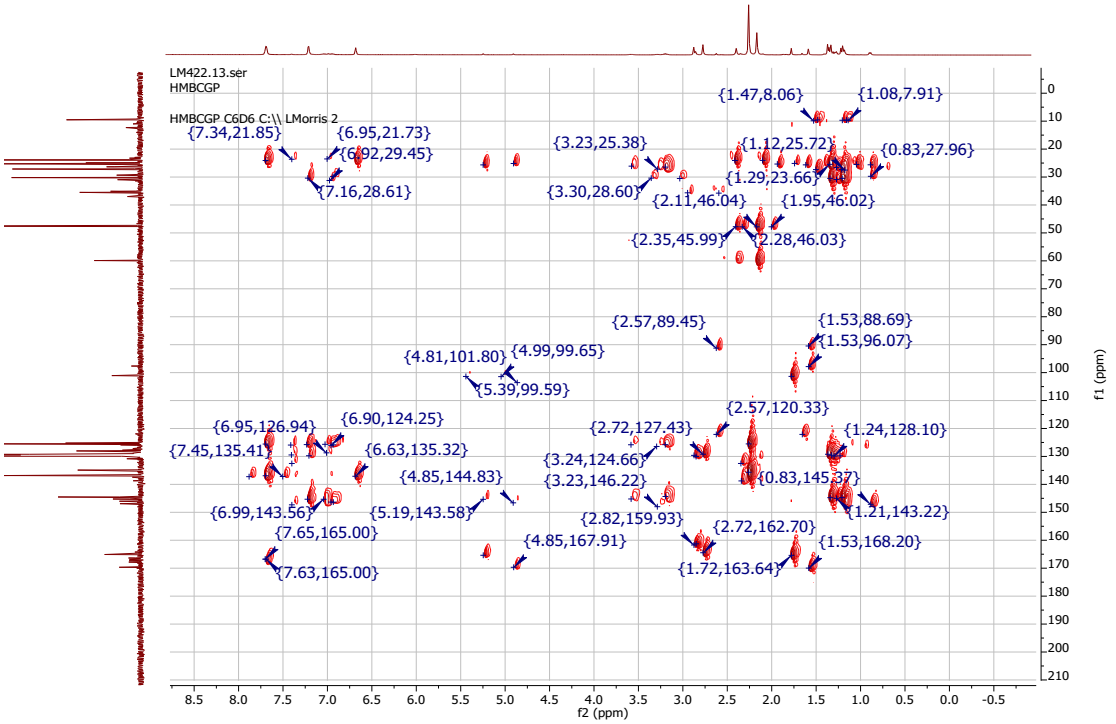



Figure S 74: *in situ* $^{13}C$-$^{1}H$ HSQC NMR spectrum ($C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**.

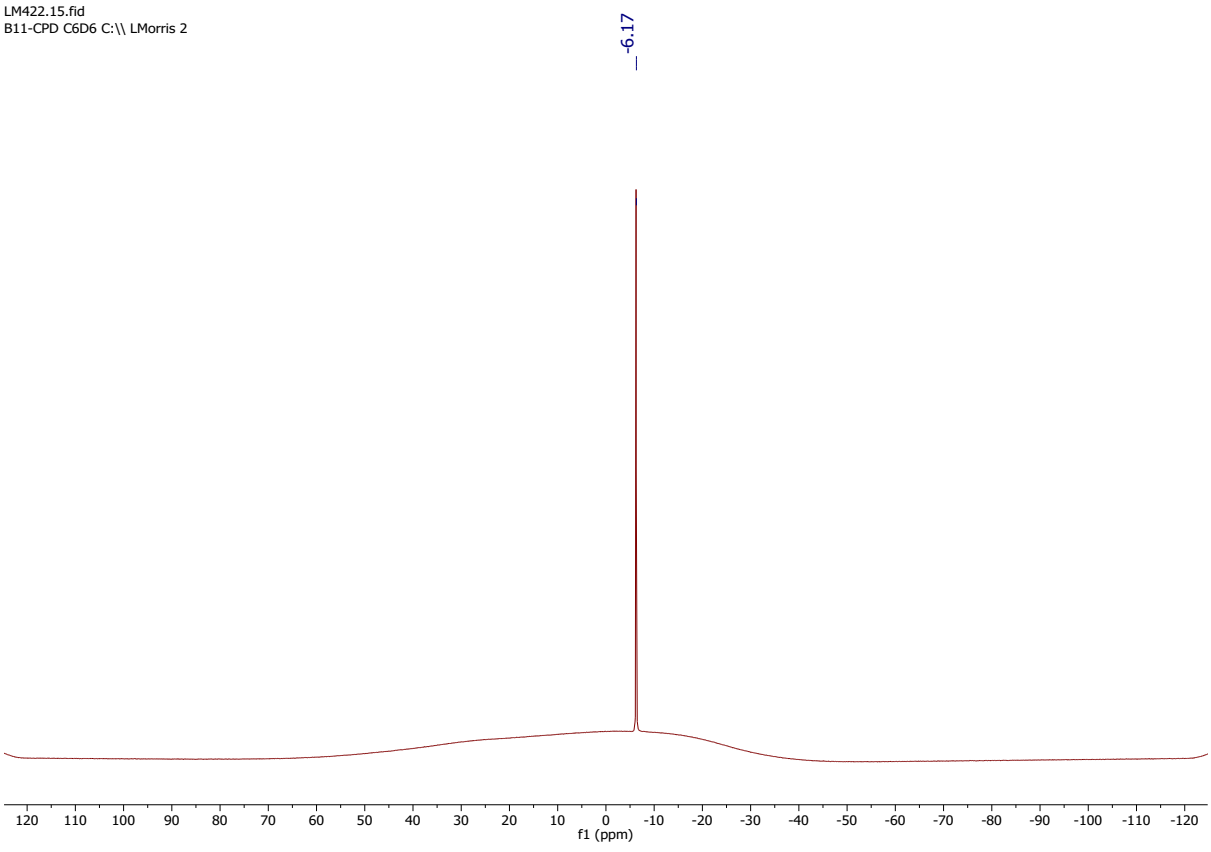



Figure S 75: *in situ* $^{11}B$ NMR spectrum (128 MHz, $C_6D_6$) of the reaction between **3$^{Ga}$** and **IMe$_4$** to give compound **4$^{Ga}$**.

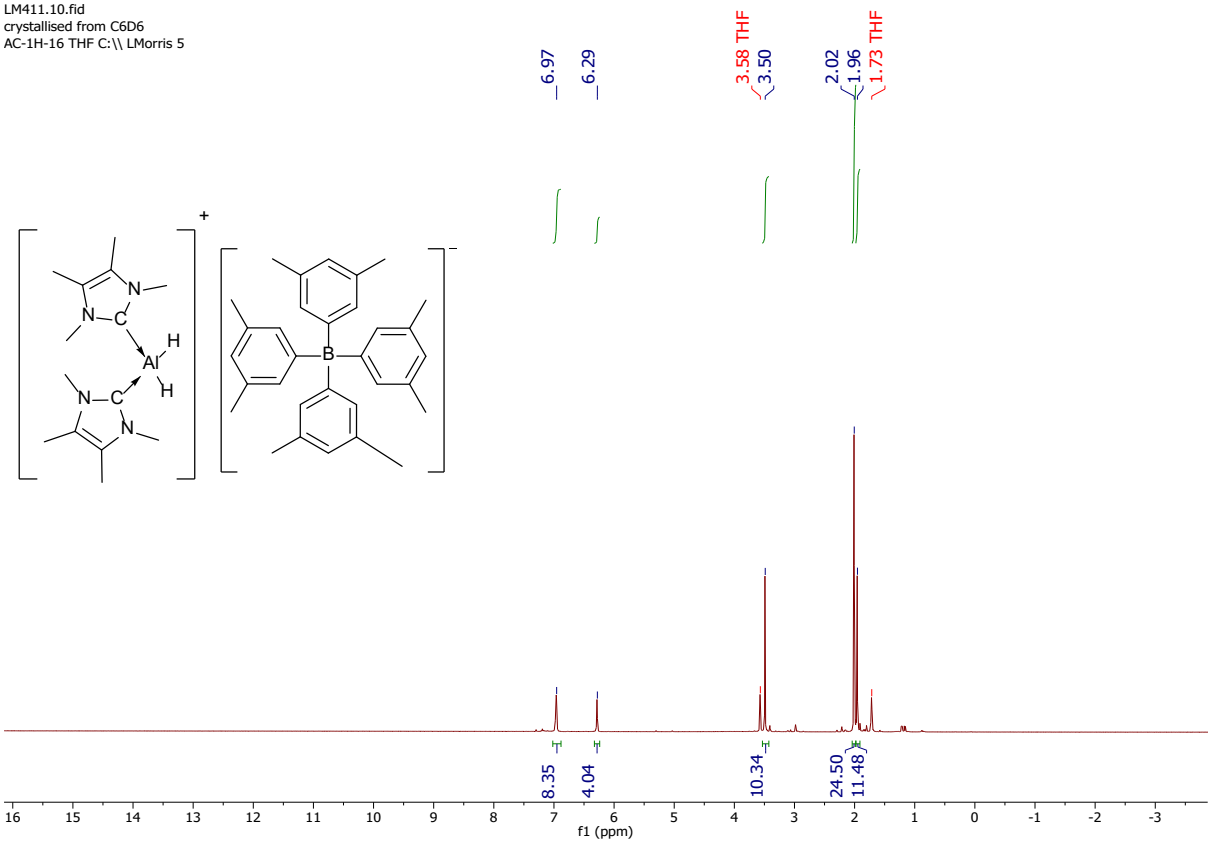



Figure S 76: $^{1}$H NMR spectrum (400 MHz, THF-$d_8$, 6.5 mg/ml) from crystals of compound **2** isolated from the reaction between $\mathbf{3^{Ga}}$ and $\mathbf{IMe_4}$.

# 3 X-ray crystallography

X-ray diffraction data were collected on an Eulerian 4-circle diffractometer STOE STADIVARI in ω-scan mode with Cu-Kα radiation at 100 K, with the exception of compound $\mathbf{4^{Al}}$, which was collected at 150 K due to a phase transition below this temperature. The structures were solved by direct methods using SHELXT.[9] All refinements were carried out against F 2 with ShelXL[10] as implemented in the program system Olex2.[11] In all cases, metal-bound hydrides were located from the Fourier difference map and refined freely. The hydrogen atoms bound to C3 in compounds $\mathbf{3^{Al}}$, $\mathbf{3^{Ga}}$, and $\mathbf{4^{Al}}$ were also located in the Fourier difference map and freely refined. Each crystal structure contained one cationic metal-complex and one borate anion per asymmetric unit. In addition, the crystal structure of $\mathbf{1{\cdot}thf_2}$ also contained one THF molecule, for which the C49A/C49B carbon atom was modelled account for a 0.278:0.722 disorder. The crystal structure of $\mathbf{4^{Al}}$ additionally contained half a molecule of toluene per asymmetric unit, which was disordered with 0.5:0.5 occupancy across a symmetry element and modelled using the Fragment DB plugin available in Olex2.

Table S 1: Crystal data and structure refinement.

| Identification code | **1·thf$_2$** | **2** | **3$^{Al}$** | **3$^{Ga}$** | **4$^{Al}$** |
|---|---|---|---|---|---|
| Empirical formula | $C_{50}H_{78}AlBN_2O_3$ | $C_{46}H_{62}AlBN_4$ | $C_{67}H_{95}Al_2BN_4$ | $C_{67}H_{95}AlBGaN_4$ | $C_{157}H_{214}Al_4B_2N_{12}$ |
| Formula weight | 792.93 | 708.78 | 1021.23 | 1063.97 | 2398.93 |
| Temperature/K | 100(2) | 100(2) | 100 (2) | 100(2) | 150(2) |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | $P2_1$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | P-1 |
| a/Å | 12.966(3) | 16.068(3) | 16.022(3) | 15.996(3) | 12.130(2) |
| b/Å | 15.946(3) | 12.667(3) | 20.090(4) | 20.151(4) | 16.522(3) |
| c/Å | 12.986(3) | 22.560(5) | 19.443(4) | 19.375(4) | 20.716(4) |
| α/° | 90 | 90 | 90 | 90 | 96.05(3) |
| β/° | 117.09(3) | 109.03(3) | 98.52(3) | 98.43(3) | 102.03(3) |
| γ/° | 90 | 90 | 90 | 90 | 108.20(3) |
| Volume/Å$^3$ | 2390.6(10) | 4340.8(17) | 6189(2) | 6178(2) | 3791.8(15) |
| Z | 2 | 4 | 4 | 4 | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.102 | 1.085 | 1.096 | 1.144 | 1.051 |
| μ/mm$^{-1}$ | 0.675 | 0.657 | 0.728 | 1.051 | 0.667 |
| F(000) | 868.0 | 1536.0 | 2224.0 | 2296.0 | 1302.0 |
| Crystal size/mm$^3$ | 0.54 × 0.1 × 0.05 | 0.2 × 0.15 × 0.06 | 0.38 × 0.38 × 0.29 | 0.41 × 0.35 × 0.34 | 0.47 × 0.297 × 0.2 |
| Radiation | CuKα (λ = 1.54178) | Cu Kα (λ = 1.54178) | CuKα (λ = 1.54178) | CuKα (λ = 1.54178) | Cu Kα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.646 to 144.242 | 8.118 to 143.998 | 5.578 to 144.184 | 6.364 to 144.998 | 4.436 to 144.268 |
| Index ranges | -15 ≤ h ≤ 15, -18 ≤ k ≤ 13, -15 ≤ l ≤ 15 | -18 ≤ h ≤ 19, -7 ≤ k ≤ 15, -27 ≤ l ≤ 26 | -11 ≤ h ≤ 19, -24 ≤ k ≤ 20, -22 ≤ l ≤ 23 | -16 ≤ h ≤ 19, -24 ≤ k ≤ 22, -23 ≤ l ≤ 13 | -14 ≤ h ≤ 14, -19 ≤ k ≤ 13, -24 ≤ l ≤ 25 |
| Reflections collected | 58430 | 60757 | 78881 | 75886 | 94792 |
| Independent reflections | 6155 [$R_{int}$ = 0.0580, $R_{sigma}$ = 0.0436] | 8449 [$R_{int}$ = 0.0490, $R_{sigma}$ = 0.0360] | 12065 [$R_{int}$ = 0.0248, $R_{sigma}$ = 0.0157] | 12068 [$R_{int}$ = 0.0235, $R_{sigma}$ = 0.0158] | 14496 [$R_{int}$ = 0.0420, $R_{sigma}$ = 0.0322] |
| Data/restraints/parameters | 6155/367/545 | 8449/0/493 | 12065/0/698 | 12068/0/698 | 14496/136/860 |
| Goodness-of-fit on F$^2$ | 1.004 | 0.972 | 1.013 | 1.039 | 0.979 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0454, $wR_2$ = 0.1080 | $R_1$ = 0.0380, $wR_2$ = 0.0959 | $R_1$ = 0.0364, $wR_2$ = 0.0936 | $R_1$ = 0.0372, $wR_2$ = 0.0965 | $R_1$ = 0.0481, $wR_2$ = 0.1304 |
| Final R indexes [all data] | $R_1$ = 0.0522, $wR_2$ = 0.1103 | $R_1$ = 0.0605, $wR_2$ = 0.1033 | $R_1$ = 0.0433, $wR_2$ = 0.0976 | $R_1$ = 0.0419, $wR_2$ = 0.0994 | $R_1$ = 0.0668, $wR_2$ = 0.1402 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.17 | 0.21/-0.31 | 0.25/-0.23 | 0.48/-0.59 | 0.27/-0.30 |
| Flack parameter | -0.01(4) | | | | |

# 4 Computational analysis

## 4.1 Computational details

Calculations were carried out with Gaussian09 at DFT level,[12] using the hybrid functional B3PW91.[13] Aluminium and gallium atoms were treated with small-core Stuttgart Dresden relativistic effective pseudopotentials (SDDALL) with additional polarization orbitals.[14] Carbon, hydrogen and nitrogen were treated using the extended all electron Gaussian-Type 6-31G** Pople basis set.[15] Geometry optimizations were computed without symmetry constraints. Bonding were studied using the Natural Bonding Orbital (NBO) analysis.[16]

## 4.2 NBO information for compound $\mathbf{3^{Al}}$

Wiberg Bond Indexes (WBI) show that Al-Al interaction as well as the two aluminium-hydride are single bonds, with a value of 0.92 for Al-Al and around 0.7 for the two Al-H. Bond analyses revealed a strong polarisation of the Al-H bond toward the hydride (72 %), shown by the HOMO-7 and -8. A covalent interaction between the two metals (almost 50 % contribution on each aluminium) is observed. The associated σ molecular orbital is the HOMO-1 while the LUMO+1 represent the π interaction between the two metals.

Table S 2: NBO information for compound $\mathbf{3^{Al}}$

| **Complexes** | **Natural Charges** | | **NBO** | | | | **WBI** | |
|---|---|---|---|---|---|---|---|---|
| | | | **Bond** | **Occupancy** | **Center (contribution)** | **Hybridation (contribution%)** | | |
| **3Al** | $Al_1$<br>$Al_3$<br>$H_2$<br>$H_4$ | 1.11<br>1.09<br>-0.44<br>-0.49 | $Al_1$-$H_2$ | 1.96 | $Al_1$ (28%) ; $H_2$ (72%) | $Al_1$ (s39 p60 d1) ; $H_2$ (s100) | $Al_1$-$Al_3$<br>$Al_1$-$H_2$<br>$Al_3$-$H_4$ | 0.92<br>0.73<br>0.67 |
| | | | $Al_3$-$H_4$ | 1.97 | $Al_3$ (25%) ; $H_4$ (74%) | $Al_3$ (s43 p56 d1) ; $H_4$ (s100) | | |
| | | | $Al_1$- $Al_3$ | 1.92 | $Al_1$ (47%) ; $Al_3$ (53%) | $Al_1$ (s37 p63) ; $Al_3$ (s49 p51) | | |
| | | | **Second Order** | | | | | |
| | | | **Donor** | **Acceptor** | | **Total Energy (kcal.mol$^{-1}$)** | $Al_1$<br>$Al_3$<br>$H_2$<br>$H_4$ | 2.47<br>2.25<br>0.81<br>0.76 |
| | | | x | x | | x | | |

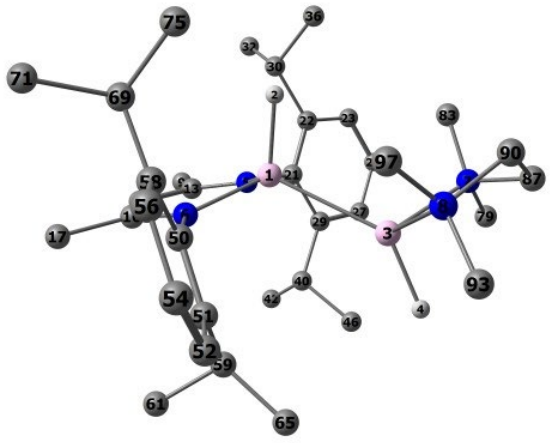
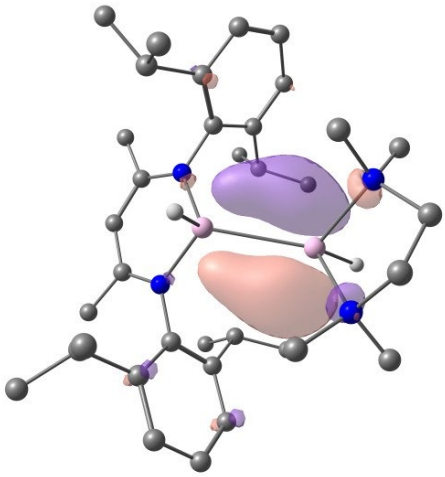
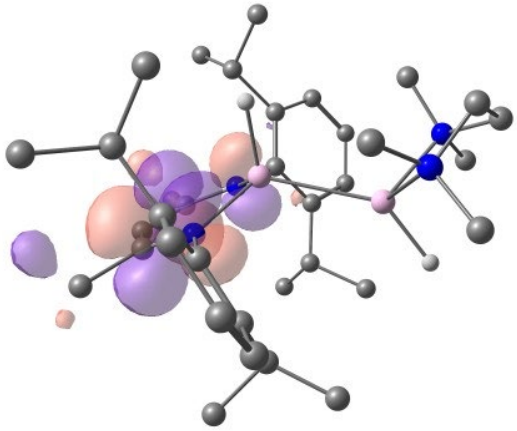


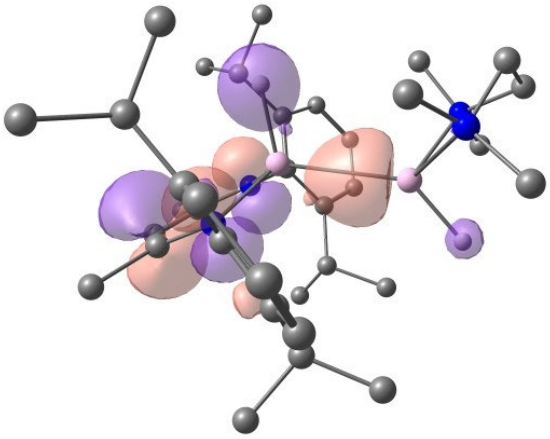

Figure S 77: Atomic labels for $\mathbf{3^{Al}}$



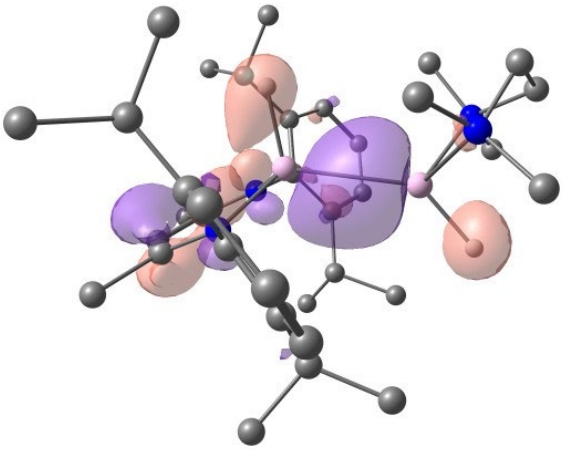
LUMO+1 (153)



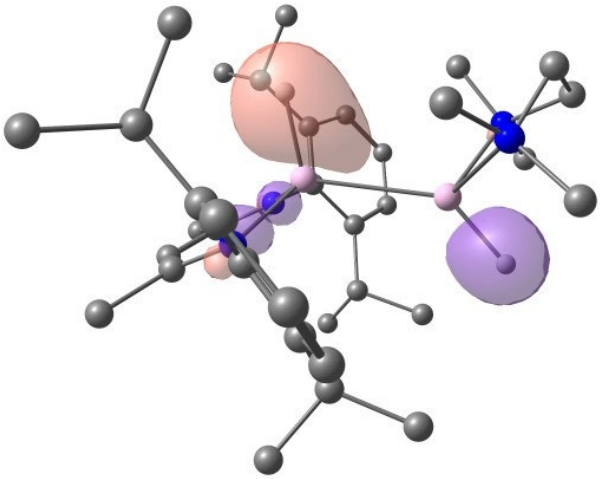
LUMO (152)



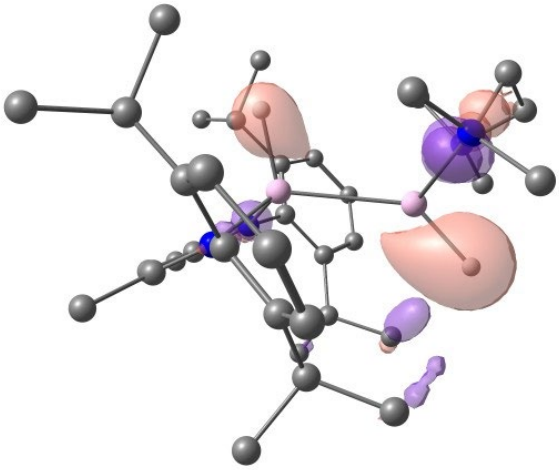
HOMO (151)



HOMO-1 (150)



HOMO-7 (144)



HOMO-8 (143)

Figure S 78: Selected orbitals for **3**$^{Al}$

## 4.3 NBO information for compound $\mathbf{3^{Ga}}$

Wiberg Bond Indexes (WBI) show that Al-Ga interaction as well as the two aluminium-hydride are single bonds, with a value of 0.9 for Al-Al and 0.80 and 0.68 respectively for the Ga-H and Al-H. Bond analyses revealed that the metal-hydride bonding is polarised toward the hydride. In the case of aluminium, the polarisation is higher (74 % against 67 % with the Ga). The associated molecular orbitals for these two bonds are the HOMO 7 and -11. A covalent interaction between the two metals (almost 50 % contribution on each center) is observed. The associated σ molecular orbital is the HOMO-2 while the LUMO+1 represent the π bonding between the two metals.

Table S 3: NBO information for compound $\mathbf{3^{Ga}}$

<table>
<tr><th rowspan="2">Complexes</th><th colspan="2" rowspan="2">Natural Charges</th><th colspan="4">NBO</th><th colspan="2" rowspan="2">WBI</th></tr>
<tr><th>Bond</th><th>Occupancy</th><th>Center (contribution)</th><th>Hybridation (contribution%)</th></tr>
<tr><td rowspan="15">3Ga</td><td rowspan="15">Ga1<br>Al3<br>H2<br>H4</td><td rowspan="15">0.79<br>1.21<br>-0.34<br>-0.48</td><td>Ga1-H2</td><td>1.96</td><td>Ga1 (33%) ; H2 (67%)</td><td>Ga1 (s40 p60) ; H2 (s100)</td><td rowspan="15">Ga1-Al3<br>Ga1-H2<br>Al3-H4<br><br>Ga1<br>Al3<br>H2<br>H4</td><td rowspan="15">0.91<br>0.80<br>0.68<br><br>2.66<br>2.26<br>0.89<br>0.77</td></tr>
<tr><td>Al3-H4</td><td>1.97</td><td>Al3 (26%) ; H4 (74%)</td><td>Al3 (s44 p55 d1) ; H4 (s100)</td></tr>
<tr><td>Ga1- Al3</td><td>1.93</td><td>Ga1 (53%) ; Al3 (47%)</td><td>Ga1 (s40 p59 d1) ; Al3 (s47 p53)</td></tr>
<tr><td colspan="4">Second Order</td></tr>
<tr><td>Donor</td><td colspan="2">Acceptor</td><td>Total Energy (kcal.mol-1)</td></tr>
<tr><td>x</td><td colspan="2">x</td><td>x</td></tr>
</table>

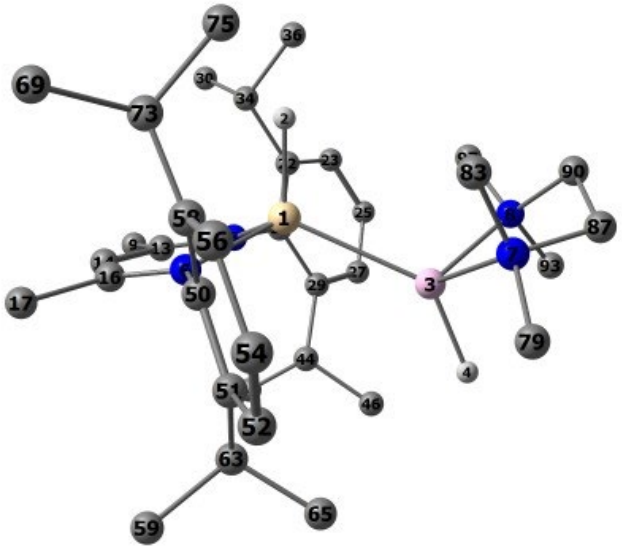
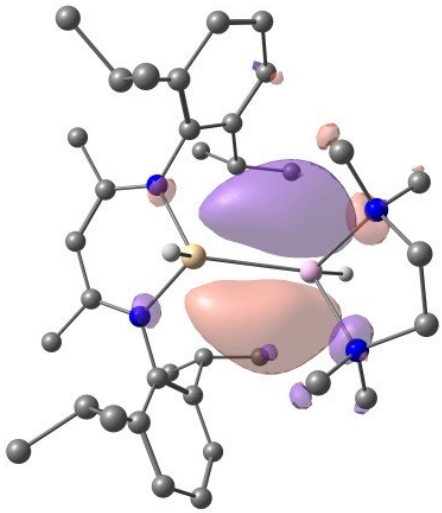
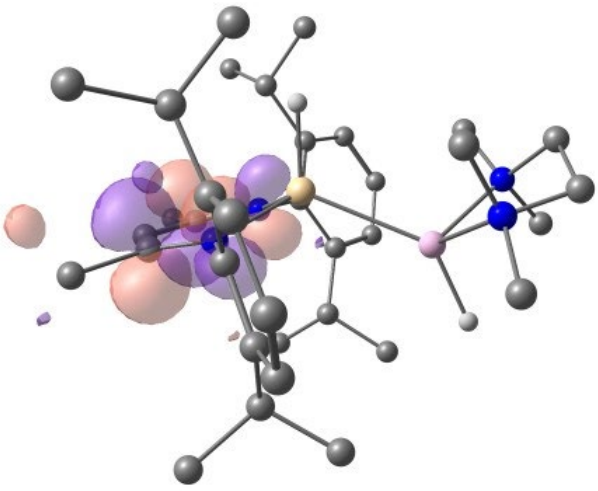


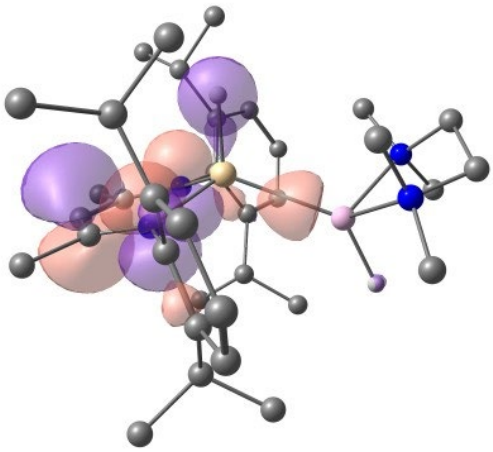

Figure S 79: Atomic labels for $\mathbf{3^{Ga}}$



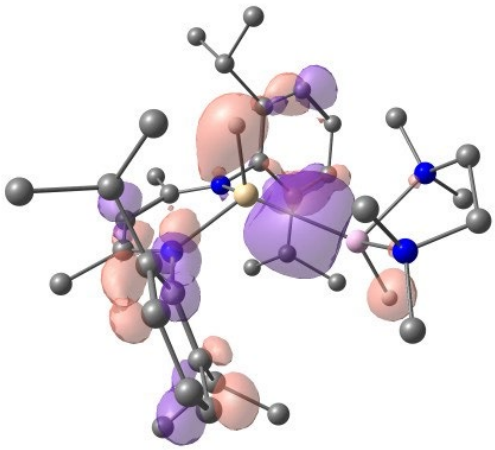
LUMO+1 (153)



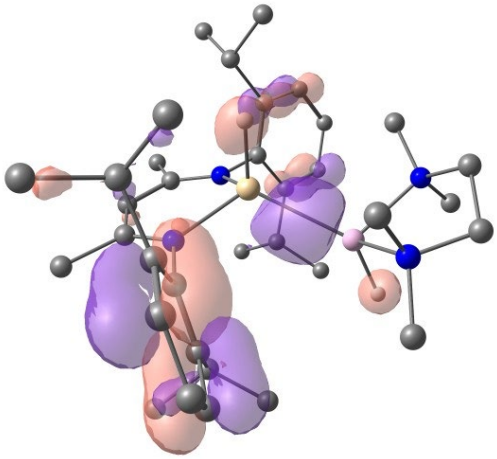
LUMO (152)



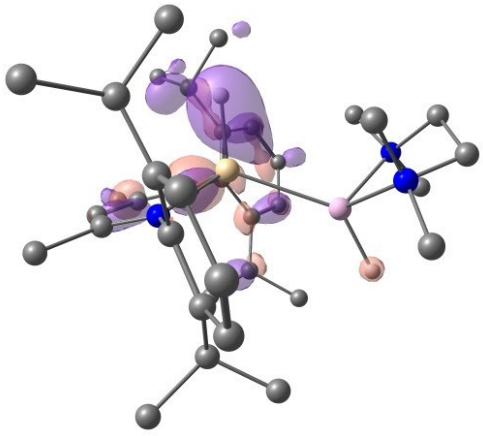
HOMO (151)



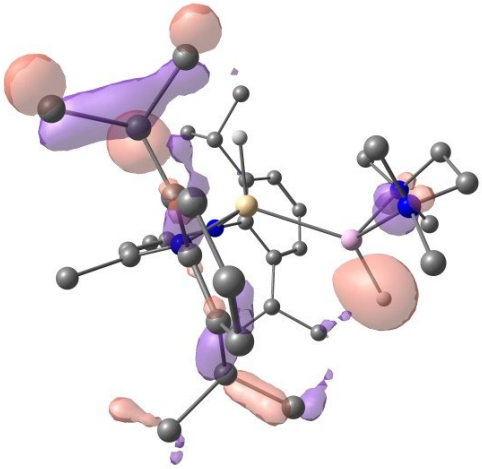
HOMO-2 (149)



HOMO-4 (147)



HOMO-7 (144)



HOMO-11 (140)

Figure S 80: Selected orbitals for **3**$^{Ga}$

## 4.4 NBO information for compound $\mathbf{4^{Al}}$

Wiberg Bond Indexes (WBI) shows a value of 0.91 for the interaction between the two aluminium atoms suggesting a single bond, that is corroborate by a bond analysis. The Al-Al bonding is covalent with a participation of approximately 50% of each center. The HOMO and HOMO-1 allow to show this σ bonding. Both aluminium-hydride interactions are single bonds strongly polarised on the hydride, that is consistent with lower WBI (0.72 and 0.75). These participations of the hydride can be observed with the HOMO-7 to -10.

| Complexes | Natural Charges | | NBO | | | | WBI | |
|---|---|---|---|---|---|---|---|---|
| | | | Bond | Occupancy | Center (contribution) | Hybridation (contribution%) | | |
| **4Al** | $Al_1$<br>$Al_3$<br>$H_2$<br>$H_4$ | 1.17<br>0.69<br>-0.45<br>-0.41 | $Al_1$-$H_2$ | 1.97 | $Al_1$ (27%) ; $H_2$ (73%) | $Al_1$ (s38 p61 d1) ; $H_2$ (s100) | $Al_1$-$Al_3$<br>$Al_1$-$H_2$<br>$Al_3$-$H_4$ | 0.91<br>0.72<br>0.75 |
| | | | $Al_3$-$H_4$ | 1.96 | $Al_3$ (29%) ; $H_4$ (71%) | $Al_3$ (s35 p64 d1) ; $H_4$ (s100) | | |
| | | | $Al_1$- $Al_3$ | 1.93 | $Al_1$ (45%) ; $Al_3$ (55%) | $Al_1$ (s41 p59) ; $Al_3$ (s44 p56) | | |
| | | | **Second Order** | | | | $Al_1$<br>$Al_3$<br>$H_2$<br>$H_4$ | 2.44<br>2.88<br>0.80<br>0.84 |
| | | | **Donor** | **Acceptor** | | **Total Energy (kcal.mol$^{-1}$)** | | |
| | | | x | x | | x | | |

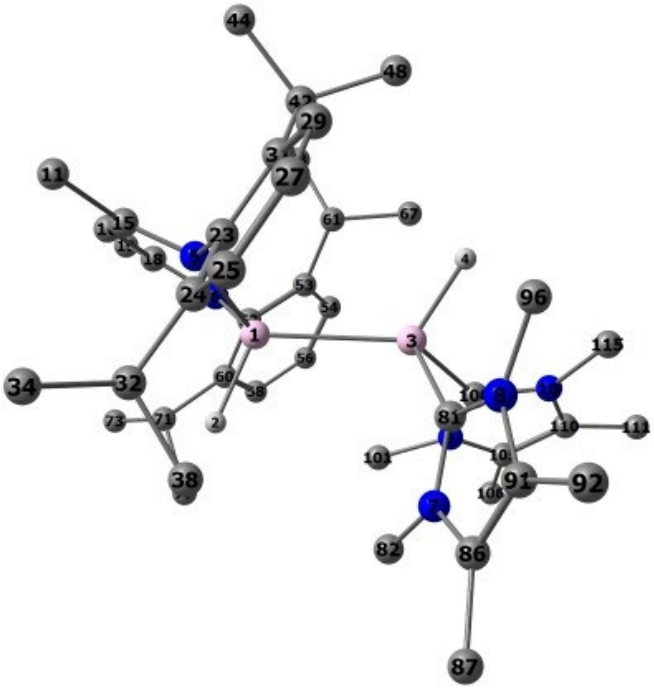
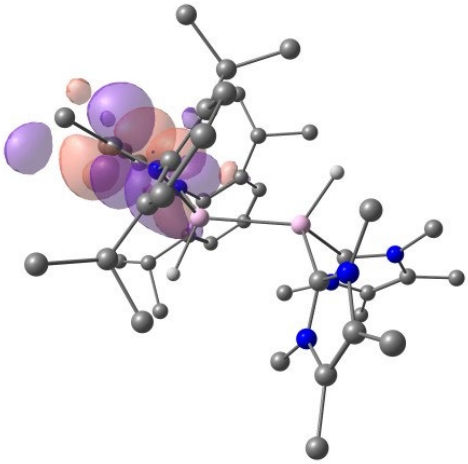
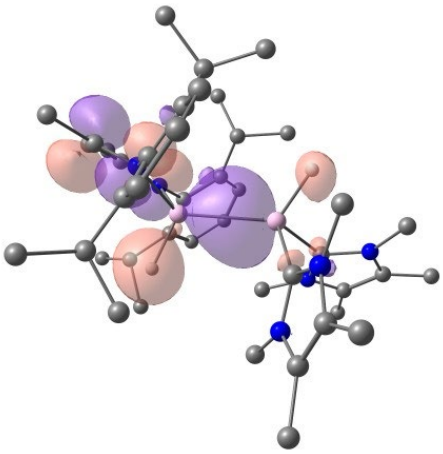


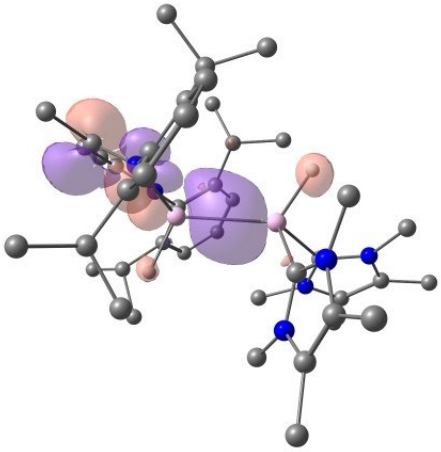

Figure S 81: Atomic labels for $\mathbf{4^{Al}}$



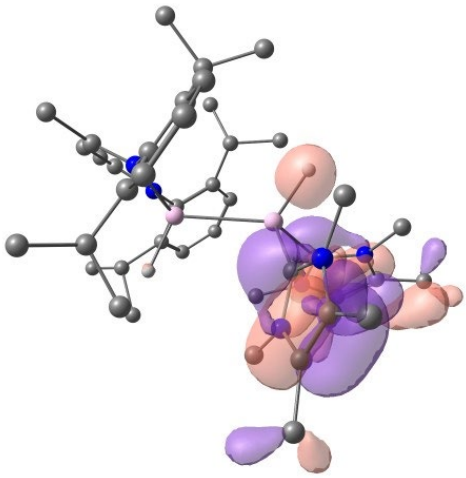
LUMO (187)



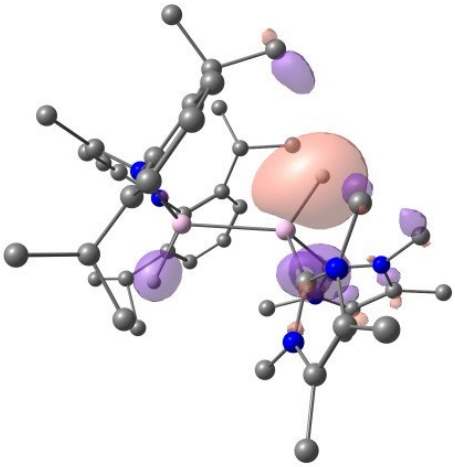
HOMO (186)



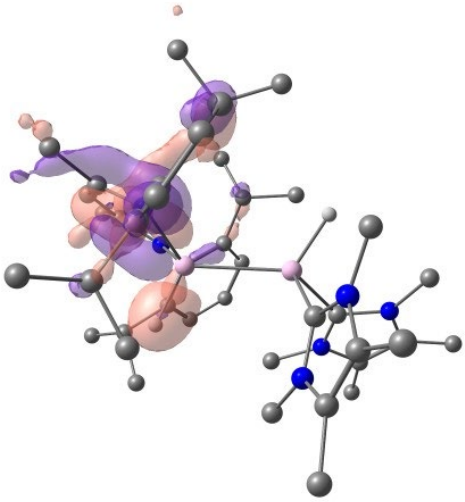
HOMO-1 (185)



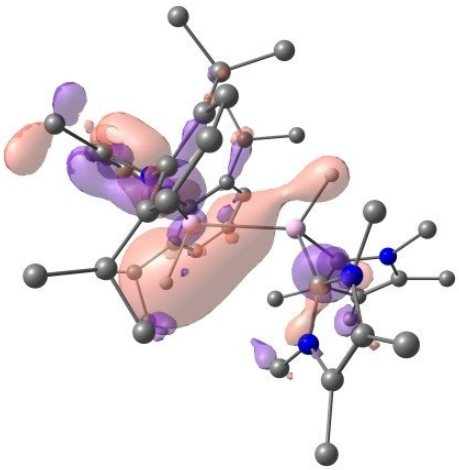
HOMO-7 (179)



HOMO-8 (178)



HOMO-9 (177)



HOMO-10 (176)

Figure S 82: Selected orbitals for **4**$^{Al}$

## 4.5 NBO information for compound $\mathbf{4^{Ga}}$

Wiberg Bond Indexes (WBI) suggest a single bond between the two metal centers with a value of 0.92. Bond analysis revealed a covalent bond with a participation of 50% of each center. The HOMO and HOMO-1 show this σ bonding. Aluminium-hydride and gallium-hydride interactions are single bonds strongly polarised on the hydride. In the case of Ga-H bond the polarisation on the hydride is less important than in the case of the Al-H (68% compared to 71%). This is consistent with the WBI (0.76 and 0.80). These participations of the hydride can be observed with the HOMO-7, -9 and -10.

| **Complexes** | **Natural Charges** | | **NBO** | | | | **WBI** | |
|---|---|---|---|---|---|---|---|---|
| | | | **Bond** | **Occupancy** | **Center (contribution)** | **Hybridation (contribution%)** | | |
| **4Ga** | Al<br>Ga<br>$H_{52}$<br>$H_{53}$ | 0.80<br>0.86<br>-0.36<br>-0.40 | Al-$H_{53}$ | 1.96 | Al (29%) ; $H_{53}$ (71%) | $Al_1$ (s36 p63 d1) ; $H_{53}$ (s100) | Al- Ga<br>Al-$H_{53}$<br>Ga-$H_{52}$ | 0.92<br>0.76<br>0.80 |
| | | | Ga-$H_{52}$ | 1.97 | Ga (32%) ; $H_{52}$ (68%) | Ga (s39 p61) ; $H_{52}$ (s100) | | |
| | | | Al- Ga | 1.93 | Al (49%) ; $Al_3$ (51%) | Al (s41 p59) ; Ga (s45 p55) | | |
| | | | **Second Order** | | | | Al<br>Ga<br>$H_{52}$<br>$H_{53}$ | 2.89<br>2.62<br>0.88<br>0.84 |
| | | | **Donor** | **Acceptor** | | **Total Energy (kcal.mol$^{-1}$)** | | |
| | | | x | x | | x | | |

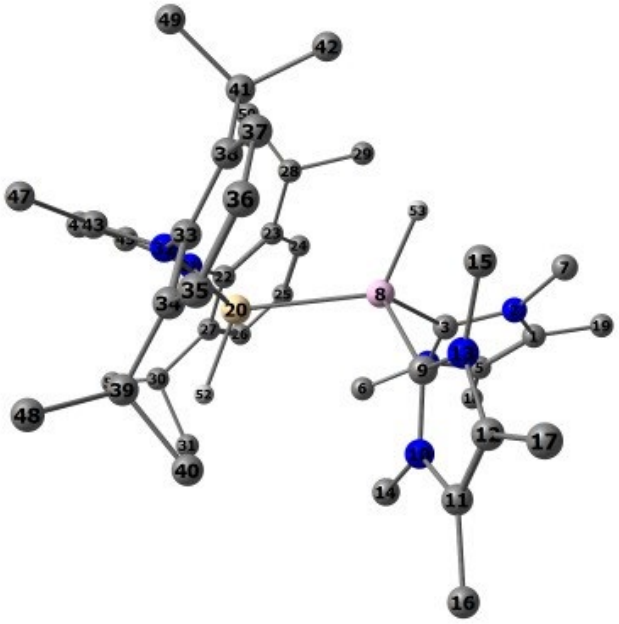



Figure S 83: Atomic labels for $\mathbf{4^{Ga}}$

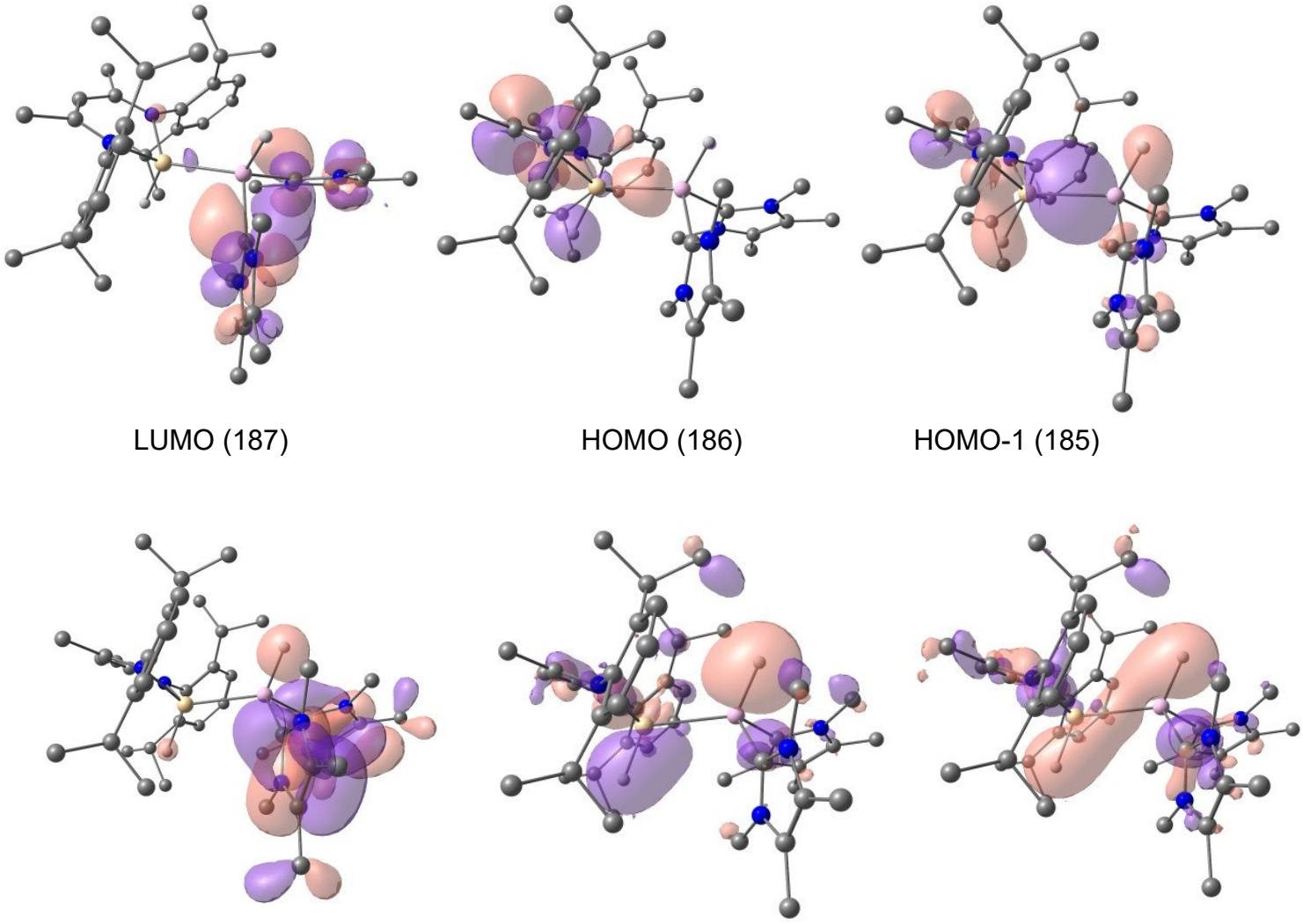



Figure S 84: Selected orbitals for $\mathbf{4^{Ga}}$

## 4.6 Calculated energies

Table S 4: Calculated energies for compounds $\mathbf{3^M}$, $\mathbf{4^M}$, and the products of disproportionation of $\mathbf{4^M}$: **2** and $\mathbf{I^M}$. (M = Al, Ga)

| | H (Hartree) | H (kcal.mol-1) | G (Hartree) | G (kcal.mol-1) |
|---|---|---|---|---|
| 3Al | -1590.79 | -998223.47 | -1590.92 | -998303.99 |
| 3Ga | -1590.83 | -998246.11 | -1590.96 | -998328.17 |
| 4Al | -2009.68 | -1261076.73 | -2009.84 | -1261175.61 |
| 4Ga | -2009.72 | -1261101.48 | -2009.88 | -1261201.06 |
| Product-4Al | -2009.66 | 15.30 | -2009.82 | 11.26 |
| Product-4Ga | -2009.73 | -2.08 | -2009.90 | -8.86 |

## 4.7 Coordinates of calculated structures

**3Al**

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| | | | |
|---|---|---|---|
| Al | 0.567125 | 13.947900 | 15.033460 |
| H | 1.151036 | 14.175833 | 13.546915 |
| Al | 2.643785 | 13.488341 | 16.592994 |
| H | 2.917164 | 13.255122 | 18.154449 |
| N | -0.823483 | 12.617967 | 15.005208 |
| N | -0.557087 | 15.433928 | 15.518542 |
| N | 3.928293 | 11.989261 | 15.899978 |
| N | 4.249769 | 14.815843 | 16.216229 |
| C | -3.152564 | 11.879719 | 14.606715 |
| H | -3.438529 | 11.933860 | 13.550223 |
| H | -4.056245 | 12.057046 | 15.194469 |
| H | -2.787359 | 10.872121 | 14.803646 |
| C | -2.119750 | 12.940102 | 14.891702 |
| C | -2.596392 | 14.253535 | 15.003364 |
| H | -3.665113 | 14.378698 | 14.872249 |
| C | -1.884182 | 15.414795 | 15.338913 |
| C | -2.697104 | 16.678102 | 15.467673 |
| H | -2.169074 | 17.466036 | 16.004507 |
| H | -3.646047 | 16.472998 | 15.968635 |
| H | -2.936079 | 17.054586 | 14.466754 |
| C | -0.389470 | 11.246844 | 14.979427 |
| C | -0.040200 | 10.641202 | 13.749369 |
| C | 0.473871 | 9.338423 | 13.778319 |

| | | | |
|---|---|---|---|
| H | 0.740530 | 8.854007 | 12.842757 |
| C | 0.623760 | 8.643855 | 14.972675 |
| H | 1.010709 | 7.628629 | 14.968610 |
| C | 0.246322 | 9.242942 | 16.170792 |
| H | 0.328597 | 8.680362 | 17.096747 |
| C | -0.261461 | 10.546696 | 16.204801 |
| C | -0.260888 | 11.317903 | 12.402089 |
| H | -0.661963 | 12.318826 | 12.589948 |
| C | -1.290584 | 10.542880 | 11.562999 |
| H | -1.516721 | 11.088547 | 10.641190 |
| H | -2.227684 | 10.389152 | 12.105263 |
| H | -0.911263 | 9.556196 | 11.276726 |
| C | 1.041494 | 11.494209 | 11.610328 |
| H | 1.527502 | 10.533210 | 11.408763 |
| H | 1.745504 | 12.137045 | 12.145554 |
| H | 0.834077 | 11.965800 | 10.644402 |
| C | -0.737189 | 11.133721 | 17.527804 |
| H | -0.905559 | 12.204962 | 17.373253 |
| C | -2.076368 | 10.504933 | 17.949279 |
| H | -1.963307 | 9.430758 | 18.132018 |
| H | -2.847645 | 10.631063 | 17.185266 |
| H | -2.440251 | 10.964640 | 18.874058 |
| C | 0.285046 | 10.985662 | 18.661145 |
| H | -0.091594 | 11.466627 | 19.569544 |
| H | 1.242005 | 11.456492 | 18.415572 |
| H | 0.474447 | 9.936101 | 18.909864 |

| | | | |
|---|---|---|---|
| C | 0.127340 | 16.634886 | 15.916820 |
| C | 0.457229 | 16.803716 | 17.285973 |
| C | 1.201127 | 17.931330 | 17.650693 |
| H | 1.451232 | 18.090586 | 18.695133 |
| C | 1.607518 | 18.867787 | 16.703855 |
| H | 2.177803 | 19.740152 | 17.010768 |
| C | 1.263461 | 18.692955 | 15.369657 |
| H | 1.568487 | 19.436242 | 14.638049 |
| C | 0.518939 | 17.584716 | 14.945193 |
| C | -0.046221 | 15.839141 | 18.353276 |
| H | -0.186336 | 14.862847 | 17.872170 |
| C | -1.414693 | 16.287187 | 18.894912 |
| H | -1.771013 | 15.585846 | 19.656628 |
| H | -2.172063 | 16.339568 | 18.109944 |
| H | -1.342121 | 17.277418 | 19.357476 |
| C | 0.925037 | 15.646180 | 19.522714 |
| H | 1.024363 | 16.552085 | 20.129715 |
| H | 1.922483 | 15.345708 | 19.188376 |
| H | 0.553697 | 14.859209 | 20.186235 |
| C | 0.137019 | 17.478360 | 13.474052 |
| H | -0.476221 | 16.580812 | 13.346682 |
| C | -0.695193 | 18.690847 | 13.025353 |
| H | -0.101517 | 19.610946 | 13.036765 |
| H | -1.563714 | 18.853431 | 13.669690 |
| H | -1.053048 | 18.545803 | 12.000973 |
| C | 1.364560 | 17.316004 | 12.566363 |

| | | | |
|---|---|---|---|
| H | 1.054687 | 17.266316 | 11.517351 |
| H | 1.904506 | 16.392815 | 12.793846 |
| H | 2.055145 | 18.160786 | 12.666186 |
| C | 3.812041 | 10.759233 | 16.722257 |
| H | 3.959682 | 11.009248 | 17.774333 |
| H | 4.559746 | 10.020661 | 16.408789 |
| H | 2.816031 | 10.330675 | 16.592239 |
| C | 3.667635 | 11.639112 | 14.481952 |
| H | 2.674427 | 11.193193 | 14.402157 |
| H | 4.414915 | 10.921448 | 14.121584 |
| H | 3.688071 | 12.529835 | 13.852347 |
| C | 5.283667 | 12.576516 | 16.069875 |
| H | 6.035012 | 11.965873 | 15.551674 |
| H | 5.518760 | 12.553365 | 17.138285 |
| C | 5.306666 | 14.003548 | 15.550281 |
| H | 5.117317 | 14.021289 | 14.473506 |
| H | 6.293658 | 14.455152 | 15.710130 |
| C | 4.752006 | 15.360522 | 17.503250 |
| H | 3.947674 | 15.908055 | 17.997632 |
| H | 5.591896 | 16.042636 | 17.322285 |
| H | 5.068443 | 14.551683 | 18.162310 |
| C | 3.858739 | 15.951181 | 15.343218 |
| H | 3.435650 | 15.570899 | 14.411799 |
| H | 4.729660 | 16.579087 | 15.118998 |
| H | 3.103731 | 16.557530 | 15.847168 |

**3Ga**

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| | | | |
|---|---|---|---|
| Ga | 0.678623 | 6.175278 | 14.955195 |
| H | 1.130004 | 5.936735 | 13.430539 |
| Al | 2.682903 | 6.625646 | 16.532956 |
| H | 2.888097 | 6.857702 | 18.098478 |
| N | -0.536146 | 4.641013 | 15.476116 |
| N | -0.803261 | 7.553135 | 14.959588 |
| N | 3.955044 | 8.117598 | 15.837062 |
| N | 4.269380 | 5.292315 | 16.177122 |
| C | -2.700585 | 3.456627 | 15.409400 |
| H | -2.971087 | 3.106995 | 14.406820 |
| H | -3.632660 | 3.674965 | 15.936060 |
| H | -2.181523 | 2.645000 | 15.919288 |
| C | -1.855546 | 4.702793 | 15.288088 |
| C | -2.549038 | 5.877899 | 14.953755 |
| H | -3.618176 | 5.756180 | 14.819717 |
| C | -2.085937 | 7.199249 | 14.852068 |
| C | -3.143167 | 8.244340 | 14.585324 |
| H | -2.780141 | 9.259853 | 14.742530 |
| H | -4.017935 | 8.074159 | 15.217697 |
| H | -3.476047 | 8.160513 | 13.544767 |
| C | 0.128425 | 3.434238 | 15.867891 |
| C | 0.518499 | 2.487339 | 14.892086 |
| C | 1.260894 | 1.374920 | 15.308594 |
| H | 1.562418 | 0.634533 | 14.572347 |

| | | | |
|---|---|---|---|
| C | 1.607878 | 1.191973 | 16.641169 |
| H | 2.176645 | 0.316641 | 16.942443 |
| C | 1.204826 | 2.124702 | 17.593200 |
| H | 1.456314 | 1.959527 | 18.636558 |
| C | 0.462544 | 3.255607 | 17.235184 |
| C | -0.712285 | 1.409000 | 12.967494 |
| H | -0.133365 | 0.479509 | 12.980936 |
| H | -1.064181 | 1.560713 | 11.941946 |
| H | -1.585712 | 1.260966 | 13.608611 |
| C | 0.136426 | 2.607383 | 13.422327 |
| H | -0.466207 | 3.513031 | 13.302571 |
| C | 1.364986 | 2.759978 | 12.514259 |
| H | 1.922201 | 3.671003 | 12.751141 |
| H | 1.055607 | 2.827141 | 11.466071 |
| H | 2.042861 | 1.903808 | 12.603432 |
| C | -1.400090 | 3.765719 | 18.855086 |
| H | -2.158570 | 3.706302 | 18.071723 |
| H | -1.758014 | 4.468169 | 19.615116 |
| H | -1.320939 | 2.777458 | 19.320873 |
| C | -0.035840 | 4.217966 | 18.306383 |
| H | -0.182610 | 5.193521 | 17.826222 |
| C | 0.941739 | 4.411556 | 19.470489 |
| H | 1.047680 | 3.504931 | 20.075263 |
| H | 0.573545 | 5.196819 | 20.137888 |
| H | 1.937193 | 4.713616 | 19.130684 |
| C | -0.379024 | 8.920906 | 14.936025 |

| | | | |
|---|---|---|---|
| C | -0.236820 | 9.618558 | 16.161690 |
| C | 0.281098 | 10.918515 | 16.128541 |
| H | 0.372886 | 11.477871 | 17.055687 |
| C | 0.655624 | 11.518857 | 14.930050 |
| H | 1.049803 | 12.531312 | 14.926415 |
| C | 0.491542 | 10.828786 | 13.734644 |
| H | 0.754449 | 11.314275 | 12.798416 |
| C | -0.031609 | 9.529867 | 13.706281 |
| C | -2.049010 | 9.658543 | 17.907463 |
| H | -2.414849 | 9.196202 | 18.830216 |
| H | -2.818743 | 9.535796 | 17.141448 |
| H | -1.934584 | 10.732059 | 18.093560 |
| C | -0.710511 | 9.029649 | 17.484283 |
| H | -0.879999 | 7.959152 | 17.326330 |
| C | 0.312079 | 9.174999 | 18.617633 |
| H | 0.500949 | 10.223839 | 18.869928 |
| H | 1.269764 | 8.706314 | 18.370147 |
| H | -0.063095 | 8.690514 | 19.524802 |
| C | -1.305263 | 9.629341 | 11.533777 |
| H | -2.238215 | 9.773522 | 12.085620 |
| H | -1.536813 | 9.088160 | 10.610582 |
| H | -0.933610 | 10.619987 | 11.250965 |
| C | -0.265393 | 8.854866 | 12.360451 |
| H | -0.665398 | 7.854459 | 12.552775 |
| C | 1.028432 | 8.680014 | 11.554373 |
| H | 1.511526 | 9.641274 | 11.347332 |

| | | | |
|---|---|---|---|
| H | 0.812152 | 8.207600 | 10.590765 |
| H | 1.741225 | 8.039267 | 12.081380 |
| C | 3.846383 | 9.347811 | 16.662655 |
| H | 2.849915 | 9.777886 | 16.539819 |
| H | 4.593061 | 10.084704 | 16.343838 |
| H | 4.001455 | 9.097313 | 17.713563 |
| C | 3.683064 | 8.472169 | 14.421064 |
| H | 3.699203 | 7.583193 | 13.788713 |
| H | 4.428973 | 9.189668 | 14.058479 |
| H | 2.690409 | 8.921108 | 14.350041 |
| C | 5.311775 | 7.526038 | 15.992767 |
| H | 5.564443 | 7.560214 | 17.056893 |
| H | 6.056704 | 8.128560 | 15.456842 |
| C | 5.321565 | 6.092882 | 15.487579 |
| H | 5.117191 | 6.063733 | 14.413734 |
| H | 6.308223 | 5.638255 | 15.639645 |
| C | 4.780120 | 4.774170 | 17.473101 |
| H | 5.096971 | 5.596009 | 18.115893 |
| H | 5.622034 | 4.092998 | 17.300115 |
| H | 3.980539 | 4.232540 | 17.981173 |
| C | 3.872451 | 4.136987 | 15.331145 |
| H | 3.113163 | 3.546907 | 15.848335 |
| H | 4.740936 | 3.500372 | 15.124455 |
| H | 3.454655 | 4.495913 | 14.389014 |

**4Al**

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| | | | |
|---|---|---|---|
| Al | 3.071885 | 5.514548 | 5.857724 |
| H | 1.596113 | 5.075362 | 6.373140 |
| Al | 4.255465 | 3.498543 | 4.615372 |
| H | 5.844302 | 3.509007 | 4.340552 |
| N | 4.090775 | 6.184717 | 7.368151 |
| N | 2.815715 | 7.250108 | 5.005991 |
| N | 2.816516 | 1.154114 | 6.023239 |
| N | 4.919878 | 1.025172 | 6.399265 |
| N | 2.412510 | 3.007332 | 2.119191 |
| N | 4.255050 | 1.932585 | 1.948802 |
| C | 4.406810 | 7.838032 | 9.179192 |
| H | 3.636355 | 7.553396 | 9.904969 |
| H | 4.552625 | 8.916689 | 9.254022 |
| H | 5.325970 | 7.329899 | 9.473018 |
| C | 3.944722 | 7.448496 | 7.797218 |
| C | 3.352693 | 8.457166 | 7.028382 |
| H | 3.312172 | 9.437942 | 7.486814 |
| C | 2.902345 | 8.390843 | 5.699379 |
| C | 2.491537 | 9.704223 | 5.080319 |
| H | 2.551995 | 9.691628 | 3.991900 |
| H | 3.112716 | 10.515206 | 5.466014 |
| H | 1.454684 | 9.930599 | 5.351703 |
| C | 4.908652 | 5.281933 | 8.134522 |
| C | 4.332372 | 4.486754 | 9.149475 |

| | | | |
|---|---|---|---|
| C | 5.166371 | 3.625559 | 9.872318 |
| H | 4.739510 | 3.015427 | 10.663911 |
| C | 6.531254 | 3.561484 | 9.620635 |
| H | 7.167233 | 2.911083 | 10.215691 |
| C | 7.084512 | 4.351030 | 8.616788 |
| H | 8.154046 | 4.305222 | 8.433046 |
| C | 6.295268 | 5.213632 | 7.849358 |
| C | 2.853063 | 4.554200 | 9.503440 |
| H | 2.401543 | 5.356619 | 8.910923 |
| C | 2.626927 | 4.875754 | 10.988514 |
| H | 2.964417 | 4.059312 | 11.635915 |
| H | 1.560612 | 5.028221 | 11.184819 |
| H | 3.160549 | 5.779156 | 11.297891 |
| C | 2.129162 | 3.255216 | 9.125208 |
| H | 2.219969 | 3.059331 | 8.053542 |
| H | 1.063535 | 3.327576 | 9.368118 |
| H | 2.541849 | 2.397948 | 9.669210 |
| C | 6.945749 | 6.087551 | 6.782883 |
| H | 6.150272 | 6.412233 | 6.102982 |
| C | 7.580796 | 7.346863 | 7.396424 |
| H | 6.846767 | 7.978065 | 7.902378 |
| H | 8.055325 | 7.951426 | 6.616282 |
| H | 8.352432 | 7.077128 | 8.126042 |
| C | 7.992179 | 5.340918 | 5.947060 |
| H | 8.870769 | 5.061597 | 6.538585 |
| H | 8.348070 | 5.987361 | 5.137994 |

| | | | |
|---|---|---|---|
| H | 7.574382 | 4.438908 | 5.492749 |
| C | 2.319192 | 7.274496 | 3.657113 |
| C | 3.244877 | 7.187779 | 2.589419 |
| C | 2.752819 | 7.206043 | 1.280698 |
| H | 3.450070 | 7.161915 | 0.449445 |
| C | 1.388724 | 7.303038 | 1.022307 |
| H | 1.028103 | 7.336477 | -0.002345 |
| C | 0.491527 | 7.371638 | 2.081619 |
| H | -0.572600 | 7.449809 | 1.875565 |
| C | 0.927609 | 7.356772 | 3.412497 |
| C | 4.745728 | 7.148886 | 2.839890 |
| H | 4.896395 | 6.758955 | 3.853281 |
| C | 5.346558 | 8.562997 | 2.794637 |
| H | 5.201308 | 9.017633 | 1.808388 |
| H | 6.422910 | 8.528836 | 2.993798 |
| H | 4.890405 | 9.222478 | 3.537591 |
| C | 5.497868 | 6.222518 | 1.878275 |
| H | 5.064396 | 5.217656 | 1.863436 |
| H | 6.542600 | 6.131676 | 2.190915 |
| H | 5.501713 | 6.606474 | 0.852412 |
| C | -0.112531 | 7.438353 | 4.523923 |
| H | 0.415541 | 7.530699 | 5.477809 |
| C | -1.032257 | 8.659606 | 4.365757 |
| H | -1.684857 | 8.563176 | 3.491540 |
| H | -0.468713 | 9.589836 | 4.250174 |
| H | -1.678976 | 8.760645 | 5.243267 |

| | | | |
|---|---|---|---|
| C | -0.954939 | 6.156232 | 4.602080 |
| H | -1.706195 | 6.243616 | 5.394160 |
| H | -0.330869 | 5.289003 | 4.834581 |
| H | -1.485010 | 5.970166 | 3.660888 |
| C | 3.994216 | 1.769623 | 5.747779 |
| C | 1.528333 | 1.611435 | 5.531252 |
| H | 1.561772 | 2.696126 | 5.409520 |
| H | 0.752534 | 1.379012 | 6.261624 |
| H | 1.278669 | 1.132935 | 4.579699 |
| C | 2.995986 | 0.036688 | 6.827014 |
| C | 1.874929 | -0.829940 | 7.282144 |
| H | 1.175822 | -0.288510 | 7.929448 |
| H | 2.262275 | -1.673949 | 7.855504 |
| H | 1.305185 | -1.238485 | 6.440479 |
| C | 4.338431 | -0.040135 | 7.072654 |
| C | 5.127938 | -1.003604 | 7.886400 |
| H | 5.857743 | -1.551698 | 7.279996 |
| H | 4.468404 | -1.738716 | 8.350855 |
| H | 5.676441 | -0.497431 | 8.688172 |
| C | 6.343059 | 1.321067 | 6.452234 |
| H | 6.919860 | 0.431590 | 6.187153 |
| H | 6.620855 | 1.656097 | 7.454368 |
| H | 6.553692 | 2.120524 | 5.742590 |
| C | 3.571930 | 2.764793 | 2.778243 |
| C | 1.351379 | 3.878835 | 2.592399 |
| H | 0.418536 | 3.319540 | 2.702328 |

| | | | |
|---|---|---|---|
| H | 1.201106 | 4.709156 | 1.899598 |
| H | 1.644471 | 4.290517 | 3.557244 |
| C | 2.362649 | 2.346773 | 0.900698 |
| C | 1.206780 | 2.457372 | -0.029698 |
| H | 0.274544 | 2.115155 | 0.433183 |
| H | 1.376148 | 1.847653 | -0.918795 |
| H | 1.052342 | 3.490079 | -0.361051 |
| C | 3.538161 | 1.657228 | 0.793468 |
| C | 4.054419 | 0.773874 | -0.286878 |
| H | 4.309492 | -0.222733 | 0.089229 |
| H | 4.950590 | 1.189585 | -0.761238 |
| H | 3.300407 | 0.648299 | -1.065816 |
| C | 5.564598 | 1.364446 | 2.225704 |
| H | 6.212632 | 1.483687 | 1.354765 |
| H | 5.478530 | 0.300477 | 2.464877 |
| H | 6.000032 | 1.903113 | 3.067468 |

**Producst-4Al**

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| | | | |
|---|---|---|---|
| C | -1.266155 | -3.404269 | -4.261375 |
| N | -0.109470 | -3.991105 | -3.773320 |
| C | 0.760025 | -3.061793 | -3.305703 |
| N | 0.138933 | -1.877548 | -3.514498 |
| C | -1.106583 | -2.054667 | -4.096173 |
| C | 0.683168 | -0.569403 | -3.169557 |
| C | 0.134111 | -5.423840 | -3.768460 |

| | | | |
|---|---|---|---|
| Al | 2.628386 | -3.425616 | -2.527586 |
| C | 2.315306 | -4.287226 | -0.684456 |
| N | 1.704262 | -3.710530 | 0.376372 |
| C | 1.674665 | -4.560263 | 1.470634 |
| C | 2.303069 | -5.711020 | 1.077474 |
| N | 2.682655 | -5.514857 | -0.242360 |
| C | 1.154453 | -2.360894 | 0.380568 |
| C | 3.423510 | -6.499814 | -1.016825 |
| C | 1.046196 | -4.185701 | 2.765294 |
| C | 2.588168 | -6.968395 | 1.820096 |
| C | -1.997965 | -0.918239 | -4.451417 |
| C | -2.388880 | -4.188238 | -4.843402 |
| Al | -0.327185 | 1.497212 | 0.553774 |
| N | -1.056554 | 3.252660 | -0.003426 |
| C | -1.400200 | 3.290767 | -1.401912 |
| C | -0.428521 | 3.693520 | -2.346406 |
| C | -0.758012 | 3.635063 | -3.704580 |
| C | -2.009849 | 3.202922 | -4.127370 |
| C | -2.958861 | 2.821190 | -3.185934 |
| C | -2.679407 | 2.855415 | -1.815350 |
| C | 0.954525 | 4.180213 | -1.935222 |
| C | 2.032549 | 3.141992 | -2.279411 |
| C | -3.756470 | 2.429945 | -0.826670 |
| C | -4.046872 | 0.925717 | -0.932346 |
| N | -0.089905 | 2.170976 | 2.402588 |
| C | 0.473036 | 1.184915 | 3.288104 |

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| C | -0.386073 | 0.307722 | 3.988484 |
| C | 0.187550 | -0.688466 | 4.785268 |
| C | 1.567530 | -0.823170 | 4.892915 |
| C | 2.399676 | 0.046291 | 4.196613 |
| C | 1.877719 | 1.063540 | 3.390000 |
| C | -1.902867 | 0.407444 | 3.897290 |
| C | -2.482502 | -0.755664 | 3.078399 |
| C | 2.834040 | 1.995212 | 2.657348 |
| C | 3.568881 | 1.255418 | 1.529927 |
| C | -0.384944 | 3.385185 | 2.891374 |
| C | -0.936376 | 4.404403 | 2.105525 |
| C | -1.252800 | 4.349886 | 0.742378 |
| C | -1.830454 | 5.590854 | 0.113178 |
| C | -0.125564 | 3.693058 | 4.343408 |
| C | -2.570400 | 0.483134 | 5.277543 |
| C | 3.835912 | 2.666071 | 3.607753 |
| C | 1.301559 | 5.543406 | -2.550773 |
| C | -5.049012 | 3.242623 | -0.990535 |
| H | 3.356539 | -2.026285 | -2.293172 |
| H | 3.300237 | -4.541235 | -3.457550 |
| H | -0.393173 | 4.723346 | 4.581087 |
| H | 0.928025 | 3.537345 | 4.593549 |
| H | -0.700558 | 3.024525 | 4.991408 |
| H | -1.137348 | 5.342461 | 2.607708 |
| H | -1.176210 | 5.962809 | -0.681208 |
| H | -1.964151 | 6.381753 | 0.852283 |

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| H | -2.796221 | 5.378777 | -0.354591 |
| H | -0.459492 | -1.362355 | 5.340651 |
| H | 1.993612 | -1.591415 | 5.533000 |
| H | 3.477540 | -0.055591 | 4.291152 |
| H | -2.144769 | 1.332499 | 3.364289 |
| H | -2.443716 | -0.446124 | 5.842840 |
| H | -3.646437 | 0.653113 | 5.168417 |
| H | -2.160939 | 1.296458 | 5.884566 |
| H | -2.059792 | -0.774137 | 2.067456 |
| H | -3.570602 | -0.663662 | 2.991940 |
| H | -2.266200 | -1.718343 | 3.555806 |
| H | 2.238221 | 2.788719 | 2.194666 |
| H | 3.334001 | 3.190426 | 4.426828 |
| H | 4.442977 | 3.396506 | 3.062998 |
| H | 4.523205 | 1.939251 | 4.053305 |
| H | 4.172201 | 0.430722 | 1.925923 |
| H | 4.242013 | 1.934386 | 0.995950 |
| H | 2.860045 | 0.839180 | 0.805864 |
| H | -0.023504 | 3.946168 | -4.442658 |
| H | -2.250602 | 3.179910 | -5.186833 |
| H | -3.942905 | 2.501371 | -3.518794 |
| H | 0.955087 | 4.301515 | -0.847200 |
| H | 1.406880 | 5.484360 | -3.639127 |
| H | 2.253953 | 5.907344 | -2.151699 |
| H | 0.536584 | 6.295694 | -2.334662 |
| H | 1.830022 | 2.185132 | -1.785627 |

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| H | 3.020508 | 3.487738 | -1.957111 |
| H | 2.078320 | 2.964499 | -3.359867 |
| H | -3.375396 | 2.618456 | 0.182218 |
| H | -5.523132 | 3.059715 | -1.960687 |
| H | -4.866944 | 4.318742 | -0.911575 |
| H | -5.771732 | 2.966639 | -0.215657 |
| H | -4.792186 | 0.623192 | -0.188794 |
| H | -3.138257 | 0.337159 | -0.763789 |
| H | -4.442741 | 0.667956 | -1.921387 |
| H | 0.062323 | -2.379058 | 0.359122 |
| H | 1.523494 | -1.822109 | -0.491015 |
| H | 1.479909 | -1.824070 | 1.272839 |
| H | 1.501500 | -3.288725 | 3.198424 |
| H | 1.155272 | -4.997174 | 3.486942 |
| H | -0.024394 | -3.984154 | 2.649962 |
| H | 2.131288 | -7.840244 | 1.338962 |
| H | 2.189779 | -6.906460 | 2.834115 |
| H | 3.664125 | -7.159083 | 1.900167 |
| H | 2.857905 | -7.432827 | -1.083604 |
| H | 4.388286 | -6.701554 | -0.544459 |
| H | 3.593752 | -6.103267 | -2.017390 |
| H | 0.175809 | -0.157177 | -2.289838 |
| H | 0.556337 | 0.113983 | -4.010892 |
| H | 1.745551 | -0.679148 | -2.954015 |
| H | -2.167314 | -0.250912 | -3.600849 |
| H | -2.968358 | -1.289746 | -4.785836 |

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| H | -1.577914 | -0.314325 | -5.263669 |
| H | -2.764189 | -4.944244 | -4.145174 |
| H | -2.094284 | -4.702157 | -5.765498 |
| H | -3.221043 | -3.526986 | -5.090579 |
| H | -0.106449 | -5.846202 | -4.746348 |
| H | -0.473812 | -5.918580 | -3.005558 |
| H | 1.191828 | -5.598026 | -3.569224 |

**4Ga**

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| | | | |
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| C | 3.526287 | 1.687688 | 0.762873 |
| N | 4.234101 | 1.930179 | 1.930572 |
| C | 3.551861 | 2.754191 | 2.768333 |
| N | 2.402734 | 3.025432 | 2.103794 |
| C | 2.358148 | 2.390288 | 0.872168 |
| C | 1.346671 | 3.900868 | 2.583059 |
| C | 5.534798 | 1.342720 | 2.210212 |
| Al | 4.243730 | 3.444140 | 4.606670 |
| C | 3.988927 | 1.736281 | 5.756911 |
| N | 2.818416 | 1.106818 | 6.030824 |
| C | 3.008174 | 0.008436 | 6.857426 |
| C | 4.349504 | -0.040886 | 7.118314 |
| N | 4.920260 | 1.020377 | 6.430919 |
| C | 1.526982 | 1.532675 | 5.519469 |
| C | 6.337155 | 1.345409 | 6.498914 |
| C | 1.897009 | -0.868566 | 7.316754 |

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|---|---|---|---|
| C | 5.145675 | -0.974851 | 7.959432 |
| C | 1.214246 | 2.535687 | -0.068061 |
| C | 4.042785 | 0.820980 | -0.330721 |
| Ga | 3.035619 | 5.397916 | 5.832382 |
| N | 2.791448 | 7.246901 | 4.955815 |
| C | 2.295480 | 7.284419 | 3.614811 |
| C | 3.217557 | 7.183944 | 2.544097 |
| C | 2.724605 | 7.197576 | 1.235777 |
| C | 1.360557 | 7.301870 | 0.977831 |
| C | 0.465597 | 7.383604 | 2.038433 |
| C | 0.903998 | 7.373662 | 3.368517 |
| C | 4.717402 | 7.133587 | 2.798426 |
| C | 5.472281 | 6.227915 | 1.819375 |
| C | -0.131609 | 7.463594 | 4.483105 |
| C | -0.976476 | 6.183645 | 4.572056 |
| N | 4.120280 | 6.157420 | 7.396995 |
| C | 4.939437 | 5.272062 | 8.169585 |
| C | 4.364716 | 4.472309 | 9.183012 |
| C | 5.198008 | 3.613035 | 9.908326 |
| C | 6.564210 | 3.551889 | 9.660322 |
| C | 7.117250 | 4.343422 | 8.657680 |
| C | 6.327268 | 5.203851 | 7.888388 |
| C | 2.884632 | 4.541008 | 9.531962 |
| C | 2.163277 | 3.235513 | 9.171488 |
| C | 6.975995 | 6.080283 | 6.823745 |
| C | 8.014017 | 5.333598 | 5.977542 |

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| C | 3.951781 | 7.424871 | 7.787489 |
| C | 3.342920 | 8.416437 | 7.005437 |
| C | 2.888229 | 8.364580 | 5.675614 |
| C | 2.481440 | 9.694187 | 5.080975 |
| C | 4.407102 | 7.858399 | 9.162397 |
| C | 2.655953 | 4.887636 | 11.010768 |
| C | 7.618540 | 7.332013 | 7.444396 |
| C | 5.323763 | 8.546077 | 2.787989 |
| C | -1.047922 | 8.686827 | 4.323338 |
| H | 1.557538 | 5.083474 | 6.420959 |
| H | 5.827341 | 3.509348 | 4.344271 |
| H | 3.587906 | 7.697249 | 9.873127 |
| H | 4.650762 | 8.922210 | 9.177519 |
| H | 5.264650 | 7.288917 | 9.521195 |
| H | 3.296375 | 9.397564 | 7.463658 |
| H | 2.520587 | 9.695106 | 3.991351 |
| H | 3.121503 | 10.492270 | 5.462868 |
| H | 1.453542 | 9.931098 | 5.376617 |
| H | 4.770494 | 3.003230 | 10.700109 |
| H | 7.200638 | 2.904030 | 10.257733 |
| H | 8.187630 | 4.301390 | 8.476884 |
| H | 2.435337 | 5.335036 | 8.927015 |
| H | 3.004224 | 4.087988 | 11.673411 |
| H | 1.588324 | 5.032584 | 11.206306 |
| H | 3.180303 | 5.803347 | 11.298692 |
| H | 2.259905 | 3.020685 | 8.103389 |

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| H | 1.096250 | 3.309928 | 9.407809 |
| H | 2.573399 | 2.386917 | 9.730825 |
| H | 6.177945 | 6.413296 | 6.151168 |
| H | 6.889408 | 7.952825 | 7.969933 |
| H | 8.081022 | 7.948620 | 6.666387 |
| H | 8.400271 | 7.053949 | 8.160102 |
| H | 8.891967 | 5.040612 | 6.563433 |
| H | 8.372781 | 5.983965 | 5.172857 |
| H | 7.588413 | 4.438275 | 5.516544 |
| H | 3.420630 | 7.143760 | 0.403940 |
| H | 0.998805 | 7.331992 | -0.046567 |
| H | -0.598425 | 7.467653 | 1.833446 |
| H | 4.861279 | 6.722384 | 3.804430 |
| H | 5.184189 | 9.023339 | 1.811601 |
| H | 6.399148 | 8.503739 | 2.991219 |
| H | 4.866290 | 9.189223 | 3.544022 |
| H | 5.032902 | 5.226364 | 1.772601 |
| H | 6.513880 | 6.122557 | 2.138213 |
| H | 5.487981 | 6.638670 | 0.803998 |
| H | 0.401598 | 7.560456 | 5.433539 |
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| H | -0.479582 | 9.613977 | 4.207026 |
| H | -1.694411 | 8.791959 | 5.200627 |
| H | -1.724138 | 6.275451 | 5.367096 |
| H | -0.353825 | 5.315037 | 4.805061 |
| H | -1.510975 | 5.992909 | 3.634282 |

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| H | 1.546943 | 2.612932 | 5.364908 |
| H | 0.750826 | 1.312856 | 6.253321 |
| H | 1.287507 | 1.023542 | 4.581357 |
| H | 1.182509 | -0.327540 | 7.947291 |
| H | 2.292458 | -1.695462 | 7.909088 |
| H | 1.343117 | -1.301724 | 6.476864 |
| H | 5.891028 | -1.522332 | 7.371765 |
| H | 4.493057 | -1.711561 | 8.430914 |
| H | 5.676206 | -0.443384 | 8.756786 |
| H | 6.934286 | 0.460292 | 6.267080 |
| H | 6.590489 | 1.712893 | 7.496177 |
| H | 6.546336 | 2.129800 | 5.772532 |
| H | 0.409174 | 3.347576 | 2.682950 |
| H | 1.206559 | 4.740170 | 1.898970 |
| H | 1.638824 | 4.301147 | 3.552679 |
| H | 0.273181 | 2.193939 | 0.376794 |
| H | 1.386475 | 1.944752 | -0.969156 |
| H | 1.076136 | 3.577701 | -0.376350 |
| H | 4.275780 | -0.188541 | 0.024737 |
| H | 4.951967 | 1.232790 | -0.783180 |
| H | 3.297549 | 0.726920 | -1.122339 |
| H | 6.189899 | 1.463626 | 1.345006 |
| H | 5.434441 | 0.277473 | 2.437411 |
| H | 5.973945 | 1.866092 | 3.059599 |

**Product-4Ga**

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| C | -1.345784 | -3.433398 | -4.245511 |
| N | -0.236619 | -4.084706 | -3.728984 |
| C | 0.708638 | -3.205766 | -3.315037 |
| N | 0.182662 | -1.988062 | -3.585465 |
| C | -1.076714 | -2.094268 | -4.155388 |
| C | 0.834018 | -0.711242 | -3.321340 |
| C | -0.110115 | -5.530181 | -3.647504 |
| Al | 2.564157 | -3.678917 | -2.564124 |
| C | 2.260052 | -4.492235 | -0.697569 |
| N | 1.717516 | -3.867165 | 0.373608 |
| C | 1.699156 | -4.690071 | 1.488719 |
| C | 2.262646 | -5.874521 | 1.097367 |
| N | 2.593899 | -5.724018 | -0.241392 |
| C | 1.220230 | -2.498551 | 0.367017 |
| C | 3.260306 | -6.757040 | -1.021336 |
| C | 1.142072 | -4.261291 | 2.799214 |
| C | 2.526697 | -7.125745 | 1.857794 |
| C | -1.873255 | -0.909270 | -4.572002 |
| C | -2.532906 | -4.154767 | -4.778678 |
| Ga | -0.204691 | 1.355851 | 0.398476 |
| N | -0.999216 | 3.245986 | -0.123040 |
| C | -1.358401 | 3.310766 | -1.507899 |
| C | -0.400336 | 3.731905 | -2.459924 |
| C | -0.739522 | 3.680613 | -3.815720 |

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| C | -1.988945 | 3.235951 | -4.233246 |
| C | -2.925194 | 2.834320 | -3.286988 |
| C | -2.634866 | 2.861321 | -1.918532 |
| C | 0.980185 | 4.227583 | -2.051794 |
| C | 2.063159 | 3.192572 | -2.390427 |
| C | -3.695620 | 2.414309 | -0.922109 |
| C | -3.963760 | 0.906055 | -1.030710 |
| N | 0.031605 | 2.106956 | 2.363521 |
| C | 0.601673 | 1.136225 | 3.247571 |
| C | -0.245954 | 0.255613 | 3.960160 |
| C | 0.337485 | -0.739247 | 4.750999 |
| C | 1.719038 | -0.874520 | 4.841421 |
| C | 2.541220 | -0.007188 | 4.130461 |
| C | 2.008291 | 1.008599 | 3.329230 |
| C | -1.763236 | 0.352281 | 3.878761 |
| C | -2.343427 | -0.805514 | 3.052518 |
| C | 2.952776 | 1.938247 | 2.579491 |
| C | 3.696188 | 1.190763 | 1.462585 |
| C | -0.286142 | 3.321472 | 2.822515 |
| C | -0.850884 | 4.332085 | 2.029868 |
| C | -1.182684 | 4.307885 | 0.666417 |
| C | -1.772780 | 5.569946 | 0.084173 |
| C | -0.040183 | 3.652733 | 4.275277 |
| C | -2.426224 | 0.412979 | 5.261631 |
| C | 3.948561 | 2.634479 | 3.518105 |
| C | 1.322189 | 5.588812 | -2.673872 |

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| C | -5.002838 | 3.206011 | -1.070488 |
| H | 3.379215 | -2.322216 | -2.364720 |
| H | 3.138480 | -4.846104 | -3.494961 |
| H | -0.293304 | 4.691148 | 4.492591 |
| H | 1.006341 | 3.482717 | 4.544629 |
| H | -0.637972 | 3.006843 | 4.926194 |
| H | -1.057038 | 5.263939 | 2.541803 |
| H | -1.127486 | 5.970008 | -0.704100 |
| H | -1.901704 | 6.336905 | 0.848931 |
| H | -2.743138 | 5.370120 | -0.379901 |
| H | -0.302563 | -1.411876 | 5.316236 |
| H | 2.153520 | -1.640319 | 5.478826 |
| H | 3.620534 | -0.108841 | 4.210005 |
| H | -2.009015 | 1.280918 | 3.354339 |
| H | -2.296240 | -0.521313 | 5.818084 |
| H | -3.502951 | 0.582795 | 5.158621 |
| H | -2.014795 | 1.221138 | 5.873990 |
| H | -1.920484 | -0.822138 | 2.041560 |
| H | -3.431326 | -0.713135 | 2.963972 |
| H | -2.128102 | -1.771195 | 3.524540 |
| H | 2.345955 | 2.717208 | 2.107017 |
| H | 3.439720 | 3.170048 | 4.325362 |
| H | 4.551522 | 3.359581 | 2.961621 |
| H | 4.639444 | 1.920708 | 3.979255 |
| H | 4.314139 | 0.382466 | 1.869697 |
| H | 4.356946 | 1.870683 | 0.914536 |

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| H | 2.995765 | 0.748443 | 0.745612 |
| H | -0.014389 | 4.006173 | -4.556978 |
| H | -2.237468 | 3.218173 | -5.290998 |
| H | -3.908106 | 2.505030 | -3.614522 |
| H | 0.979320 | 4.354062 | -0.964557 |
| H | 1.430974 | 5.525434 | -3.761722 |
| H | 2.271283 | 5.960531 | -2.273952 |
| H | 0.551595 | 6.336692 | -2.462953 |
| H | 1.868614 | 2.236394 | -1.891555 |
| H | 3.050299 | 3.544425 | -2.072137 |
| H | 2.107198 | 3.007355 | -3.469722 |
| H | -3.307160 | 2.606176 | 0.083119 |
| H | -5.484650 | 3.017949 | -2.035966 |
| H | -4.835004 | 4.284324 | -0.991319 |
| H | -5.713133 | 2.918160 | -0.288338 |
| H | -4.696963 | 0.587922 | -0.281613 |
| H | -3.046189 | 0.327512 | -0.875018 |
| H | -4.364069 | 0.645661 | -2.017347 |
| H | 0.127963 | -2.478864 | 0.391549 |
| H | 1.571489 | -1.997078 | -0.533994 |
| H | 1.603525 | -1.954611 | 1.231964 |
| H | 1.648830 | -3.372955 | 3.190903 |
| H | 1.252265 | -5.059447 | 3.535335 |
| H | 0.075644 | -4.021776 | 2.725372 |
| H | 2.002463 | -7.985510 | 1.426143 |
| H | 2.187901 | -7.018912 | 2.889577 |

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| H | 3.594944 | -7.367258 | 1.885379 |
| H | 2.658686 | -7.669512 | -1.032546 |
| H | 4.239415 | -6.981169 | -0.590394 |
| H | 3.395067 | -6.395164 | -2.040292 |
| H | 0.318351 | -0.177945 | -2.516760 |
| H | 0.823522 | -0.097741 | -4.224347 |
| H | 1.866702 | -0.899242 | -3.029338 |
| H | -2.007215 | -0.195569 | -3.753141 |
| H | -2.863395 | -1.219784 | -4.910443 |
| H | -1.395297 | -0.373090 | -5.399637 |
| H | -2.967520 | -4.831026 | -4.034560 |
| H | -2.286030 | -4.748535 | -5.666126 |
| H | -3.307343 | -3.442442 | -5.067780 |
| H | -0.386690 | -5.982771 | -4.602025 |
| H | -0.754032 | -5.932685 | -2.860355 |
| H | 0.930224 | -5.779555 | -3.437522 |

# 5 References


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