# Supporting Information

## Dialumenes – Aryl vs. Silyl Stabilization for Small Molecule Activation and Catalysis.

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## Contents

# 1. Experimental

## 1.1 General Experimental procedures

All experiments and manipulations were carried out under argon atmosphere using standard Schlenk or glovebox techniques. Glassware was heat dried under vacuum prior to use. Ground glass joints were coated with the polytetrafluoroethylene (PTFE)-based grease Merkel Triboflon III.

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or ABCR and used as received. n-Hexane, THF and toluene were refluxed over sodium/benzophenone, distilled and deoxygenated prior to use. Deuterated benzene ($C_6D_6$) and THF-$d_8$ were obtained from Deutero Deutschland GmbH and were dried over 4 Å molecular sieves. Carbon dioxide (5.0), Hydrogen (5.0) nitrogen monoxide (5.0) and oxygen gas (5.0) were purchased from Westfalen AG and used as received.

The following compounds were prepared according to literature procedures; $I^iPr_2Me_2$ (1,3-di-*iso*-propyl-4,5dimethyl-imidazolin-2-ylidene),[S1] $Me_3N{\cdot}AlH_3$,[S2] $I^iPr_2Me_2AlH_3$,[S3] and $TippLi{\cdot}OEt_2$.[S4]

NMR spectra were recorded on a Bruker AV400US, DRX400, AVHD300 or AV500cr at ambient temperature (300 K). $^1H$ and $^{13}C$ NMR spectra were calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as internal standard.

Elemental analyses (EA) were conducted with a EURO EA (HEKA tech) instrument equipped with a CHNS combustion analyser.

Melting Points (M.P.) were determined in sealed glass capillaries under inert gas with a Büchi M-565 melting point apparatus.

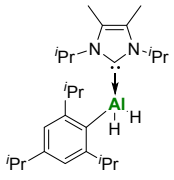
ATR-FTIR spectra were recorded on a Perkin Elmer FTIR spectrometer (diamond ATR, Spectrum Two; located inside an argon-filled glovebox) in a range of 400 – 4000 $cm^{-1}$.

LIFDI-ESI Mass spectrometry data were acquired using an Exactive Plus Orbitrap system (ionization method: LIFDI) by Thermo Fisher Scientific.

UV/vis spectra were recorded on a Agilent, Cary 60, UV-Vis Spectrophotometer in the range 200-1100 nm.

## 1.2 Synthesis & Characterisation Data of Novel Compounds

### Compound 1 – $I^iPr_2Me_2Al(Tipp)H_2$



TippLi·$OEt_2$ (2.70 g, 9.51 mmol) in 50 mL of $Et_2O$ was added via a dropping funnel over a period of 1 hour to a $Et_2O$ stirring solution of $I^iPr_2Me_2AlH_3$ (2.00g, 9.51 mmol) at -78 °C. After complete addition the reaction mixture was kept at -78 °C for an additional hour and then slowly allowed to warm to room temperature overnight. After stirring for an additional 24 hours at room temperature, the solvent was removed and the crude product was then extracted with hexanes several times. Colourless crystalline material of **1** was obtained from the concentrated hexane solution at -30 °C. Yield = 2.57 g, 66%. **$^1$H NMR** (400 MHz, $C_6D_6$, δ ppm): 7.23 (2H, s, *m-H* Tipp), 5.59 (2H, sept, $J_{HH}$ = 7.1 Hz NC*H*$(CH_3)_2$), 5.11 (2H, br. s. Al$H_2$), 4.02 (2H, sept, $J_{HH}$= 6.8 Hz, *o*-iPr C*H*$(CH_3)_2$), 2.96 (1H, sept, $J_{HH}$= 6.9 Hz, *p*-iPr C*H*$(CH_3)_2$), 1.48 (6H, s, CC$H_3$), 1.42 (12H, d, $J_{HH}$ = 6.8 Hz, *o*-iPr CH(C$H_3)_2$), 1.38 (6H, d, $J_{HH}$ = 6.9 Hz, *p*-iPr CH(C$H_3)_2$), 1.03 (12H, d, $J_{HH}$ = 7.0 Hz, NCH(C$H_3)_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, δ ppm): 175.44 (N*C*N – assigned HMBC), 158.02 (*o-C* Tipp), 147.88 (*p-C* Tipp), 145.6 (*ipso-C* Tipp – assigned HMBC), 125.73 (*C*$CH_3$), 119.77 (*m-C* Tipp), 52.45 (N*C*H$(CH_3)_2$), 36.70 (*o*-iPr *C*H$(CH_3)_2$), 35.08 (*p*-iPr *C*H$(CH_3)_2$), 25.53 (*o*-iPr CH(*C*$H_3)_2$), 24.67 (*p*-iPr CH(*C*$H_3)_2$), 21.27 (NCH(*C*$H_3)_2$), 9.83 (C*C*$H_3$). **$^{27}$Al NMR** (78.2 MHz, $C_6D_6$, δ ppm): 112.9 (br. s.). **IR:** 1712 $cm^{-1}$ (Al-H). **LIFDI-ESI:** $C_{26}H_{45}N_2Al$ calculated (found): 412.34 (411.3839 m/z)

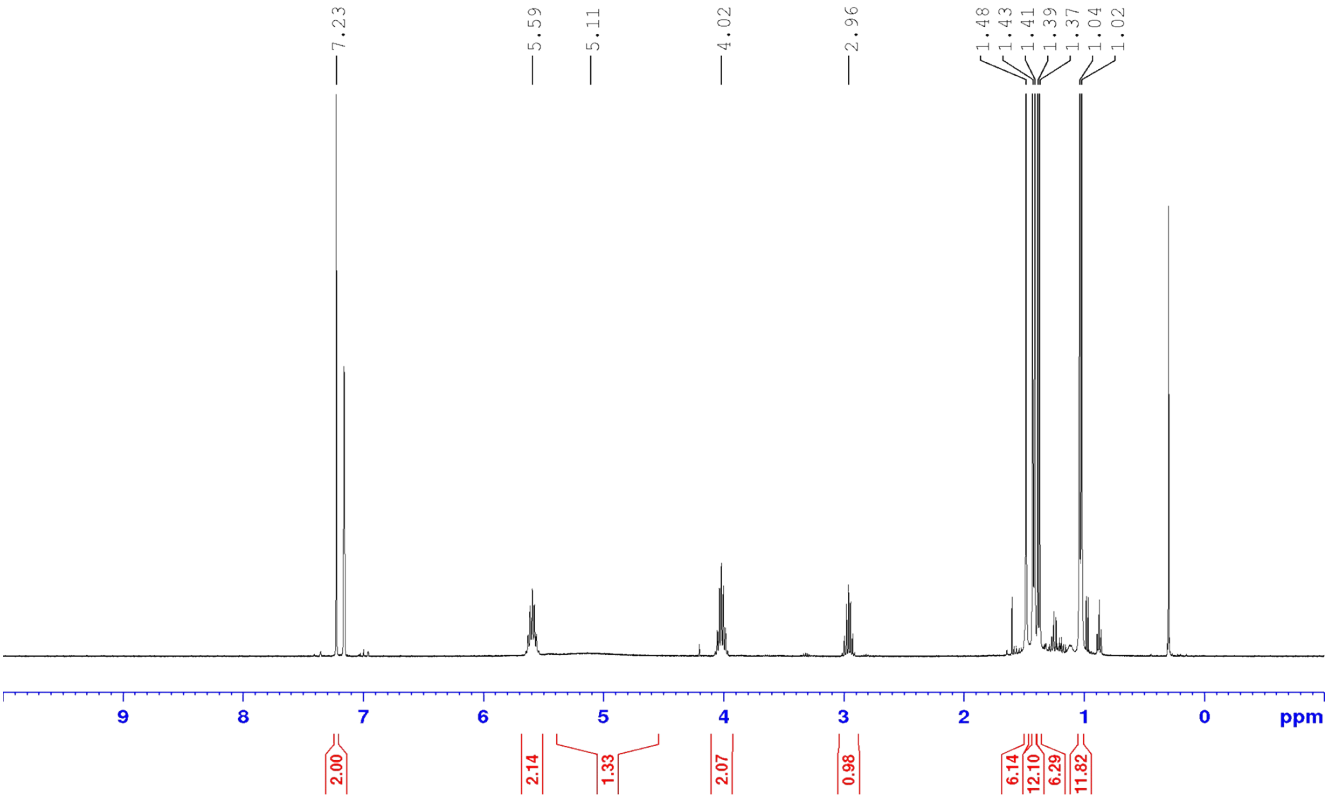



**Figure S 1.** $^1$H NMR spectrum of Compound **1** - $I^iPr_2Me_2Al(Tipp)H_2$, in $C_6D_6$.

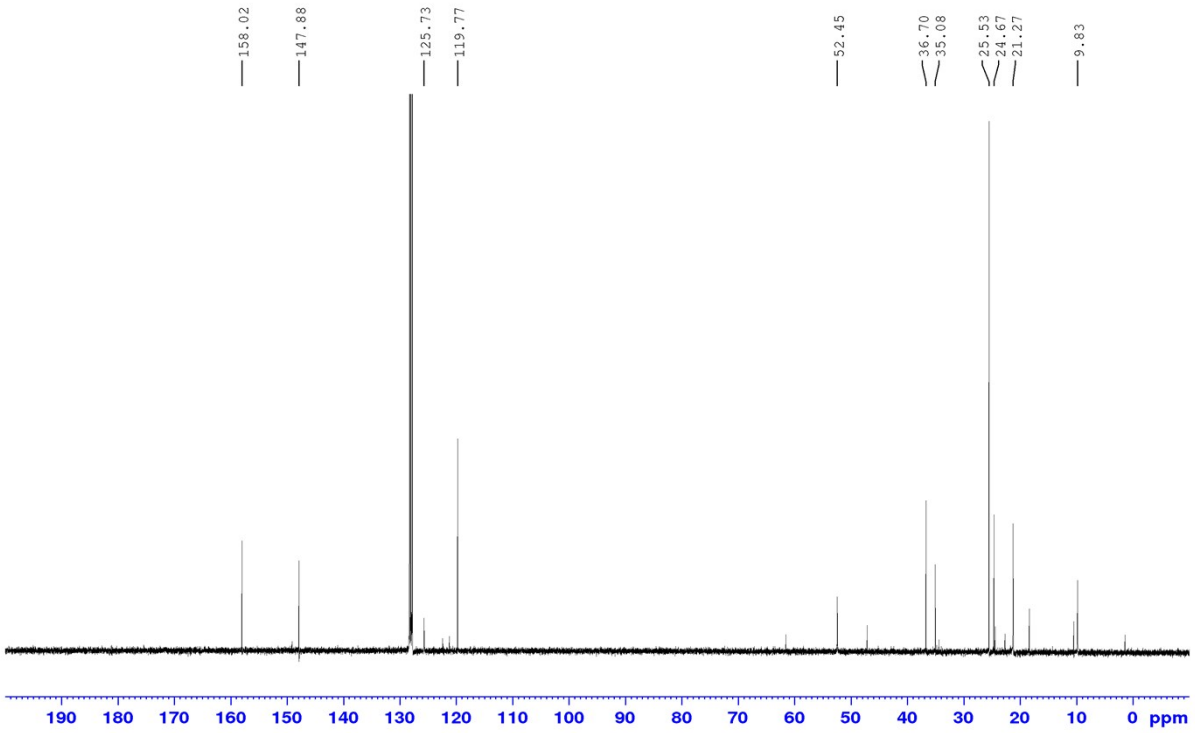



**Figure S 2.** $^{13}C\{^{1}H\}$ NMR spectrum of Compound **1** - $I^{i}Pr_2Me_2Al(Tipp)H_2$, in $C_6D_6$.

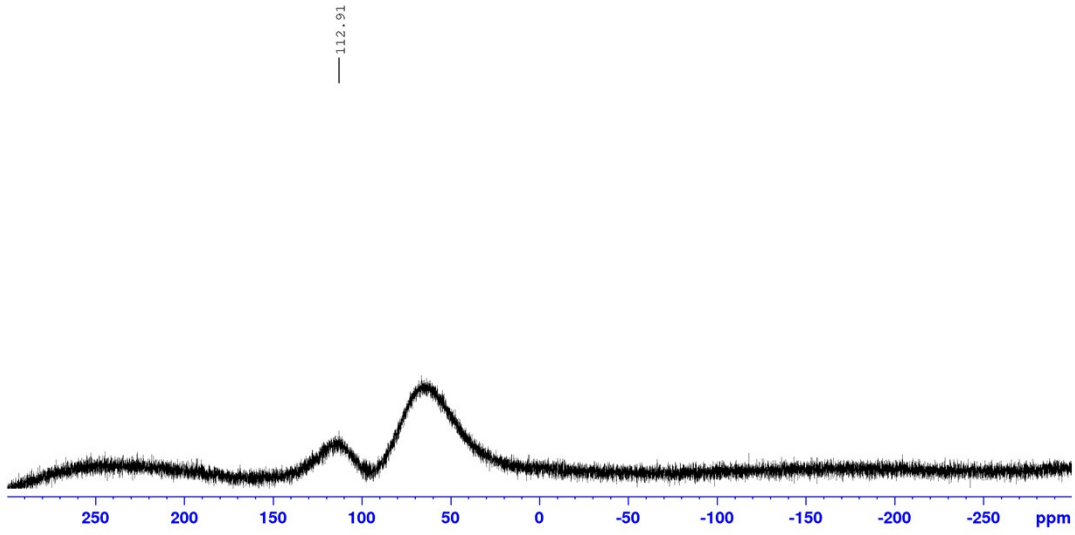



**Figure S 3**. $^{27}Al$ NMR spectrum of Compound **1** - $I^{i}Pr_2Me_2Al(Tipp)H_2$, in $C_6D_6$

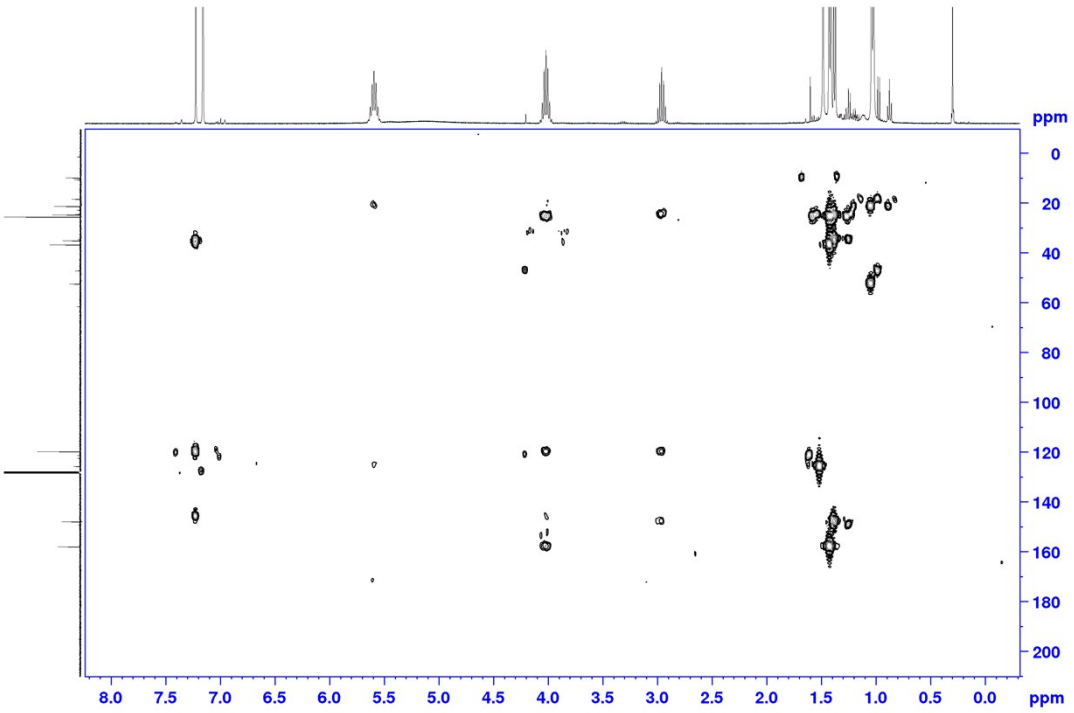



**Figure S 4**. $^{1}H$-$^{13}C$ HMBC for compound **1** - $I^{i}Pr_2Me_2Al(Tipp)H_2$, in $C_6D_6$

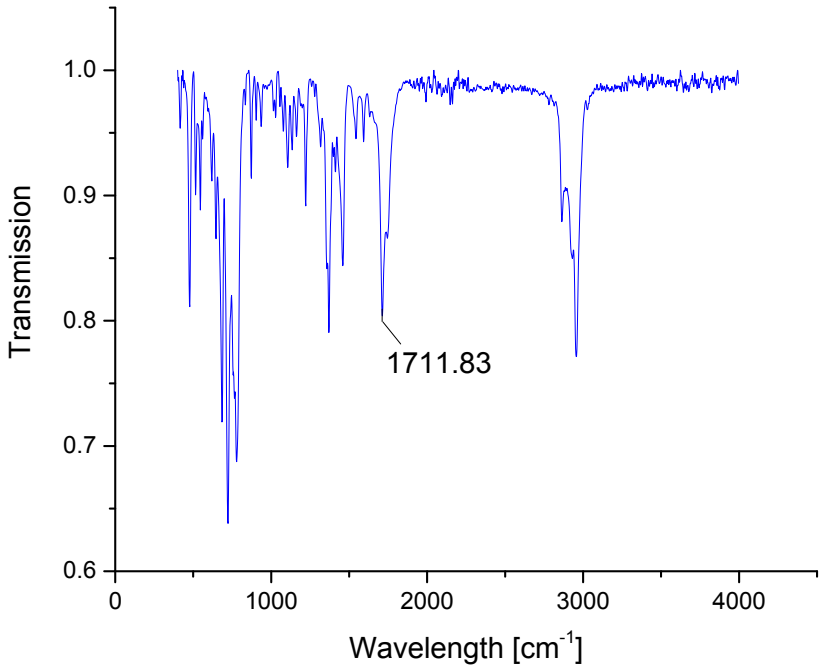
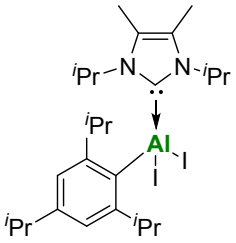



**Figure S 5.** IR data of compound **1 -** $I^{i}Pr_2Me_2Al(Tipp)H_2$

**Compound 2 – $I^iPr_2Me_2Al(Tipp)I_2$**



Iodomethane (5 eq., 3.44 g, 1.51 mL, 24.2 mmol) was added dropwise via syringe to a toluene solution of $I^iPr_2Me_2Al(H)_2Tipp$ (**1**) (2.00 g, 4.85 mmol) at 0 °C. After complete addition, an oil bubbler was fitted to the top of the Schlenk flask and the reaction mixture was allowed to stir at room temperature overnight. Volatiles were removed under reduced pressure, the crude compound was washed with hexane and subsequently extracted with toluene. Colourless crystalline material of **2** was obtained from the concentrated toluene solution at -30 °C. Yield = 1.70 g, 52%. **$^1$H NMR** (400 MHz, $C_6D_6$, δ ppm): 7.08 (2H, s, *m-H* Tipp), 5.77 (2H, sept, $J_{HH}$ = 7.0 Hz NC*H*$(CH_3)_2$), 4.10 (2H, sept, $J_{HH}$= 6.6 Hz, *o*-iPr C*H*$(CH_3)_2$), 2.84 (1H, sept, $J_{HH}$= 6.9 Hz, *p*-iPr C*H*$(CH_3)_2$), 1.46 (6H, s, CC$H_3$), 1.29 (12H, d, $J_{HH}$ = 6.7 Hz, *o*-iPr CH(C$H_3)_2$), 1.28 (6H, d, $J_{HH}$ = 6.9 Hz, *p*-iPr CH(C$H_3)_2$), 1.01 (12H, d, $J_{HH}$ = 7.0 Hz, NCH(C$H_3)_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, δ p pm): 161.44 (N*C*N – assigned HMBC), 156.42 (*o-C* Tipp), 149.69 (*p-C* Tipp), 140.2 (*ipso-C* Tipp – assigned HMBC), 126.54 (*C*$CH_3$), 121.25 (*m-C* Tipp), 53.15 (N*C*H$(CH_3)_2$), 37.02 (*o*-iPr *C*H$(CH_3)_2$), 34.86 (*p*-iPr *C*H$(CH_3)_2$), 25.18 (*o*-iPr CH(*C*$H_3)_2$), 24.41 (*p*-iPr CH(*C*$H_3)_2$), 20.61 (NCH(*C*$H_3)_2$), 9.82 (C*C*$H_3$). **$^{27}$Al NMR** (78.2 MHz, $C_6D_6$, δ ppm): no signal found. **LIFDI-ESI:** $C_{26}H_{43}N_2AlI_2$ calculated (found): 664.13 (663.8990 m/z).

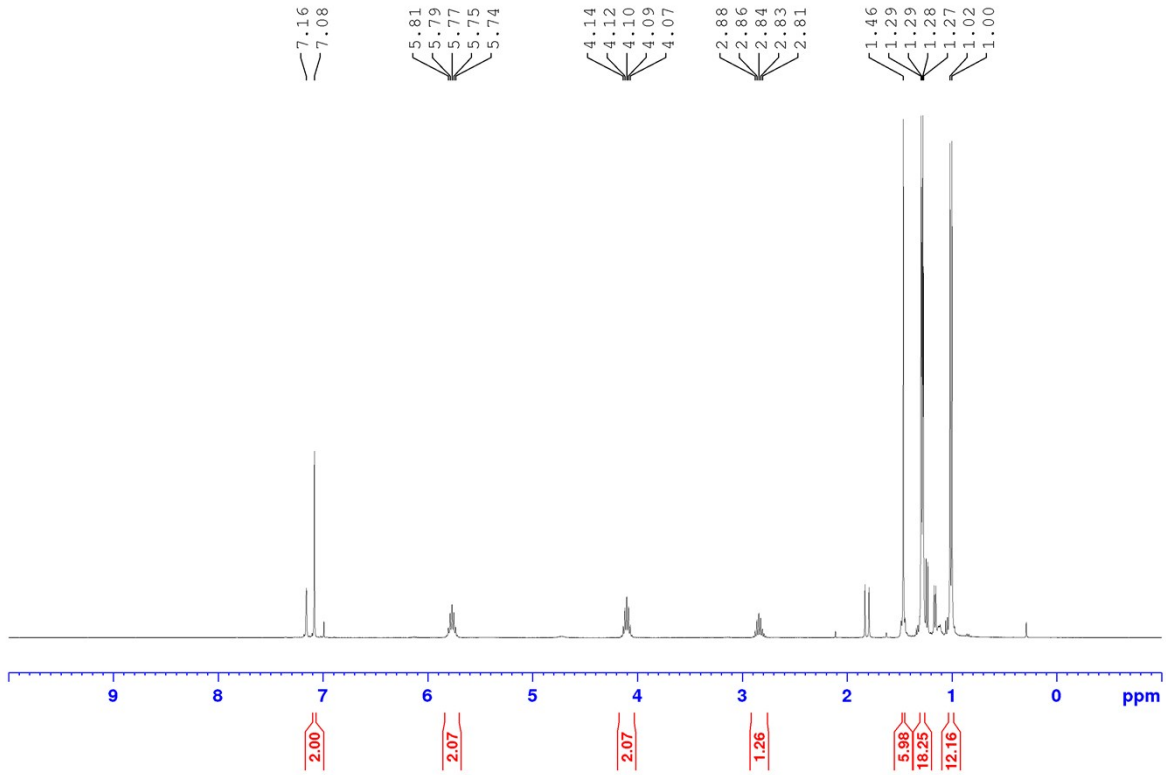



**Figure S 6.** $^1$H NMR Spectrum of Compound **2 -** $I^iPr_2Me_2Al(Tipp)I_2$, in $C_6D_6$.

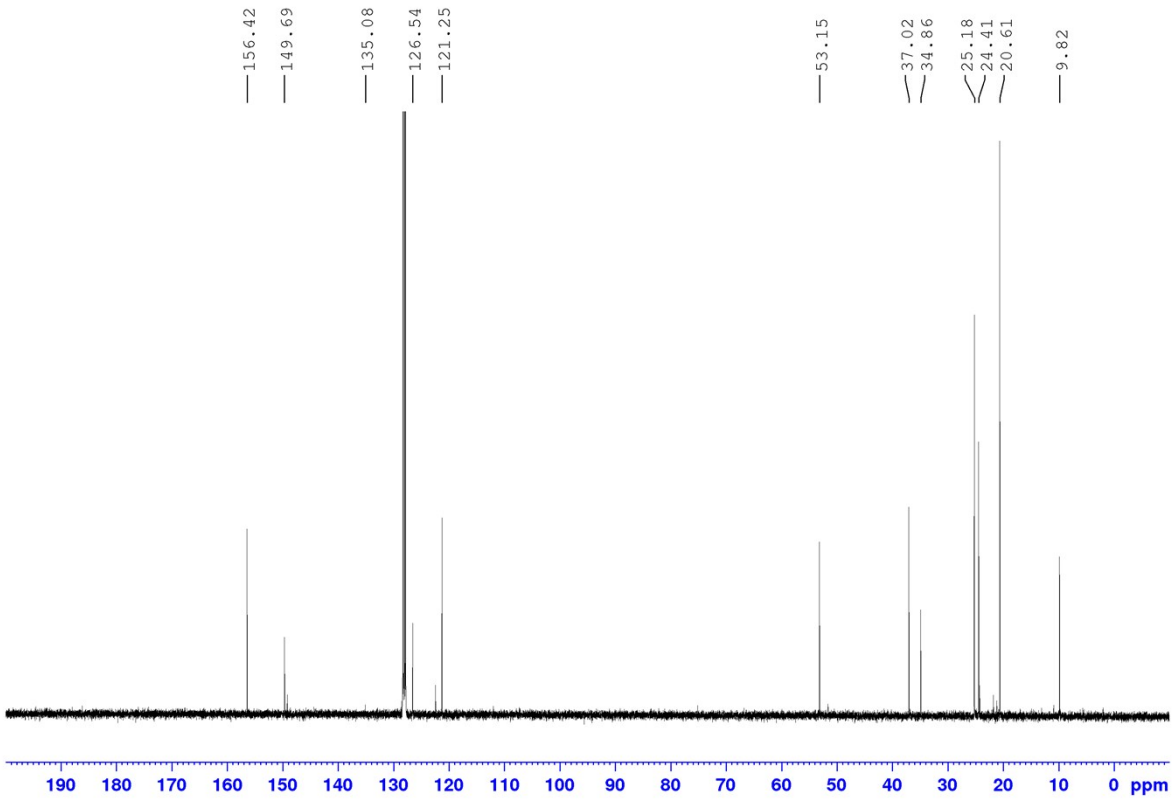



**Figure S 7.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **2** - $I^{i}Pr_2Me_2Al(Tipp)I_2$, in $C_6D_6$.

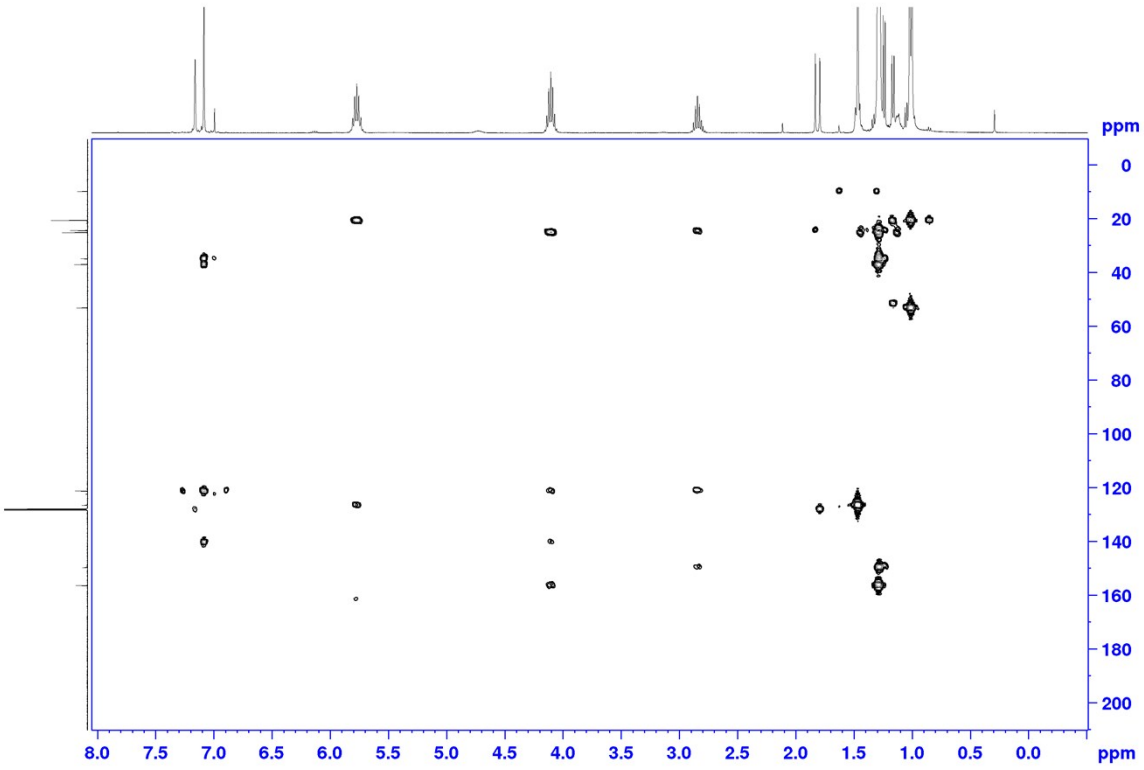



Figure S 8. $^{1}H$-$^{13}C$ HMBC for compound **2** - $I^{i}Pr_2Me_2Al(Tipp)I_2$, in $C_6D_6$

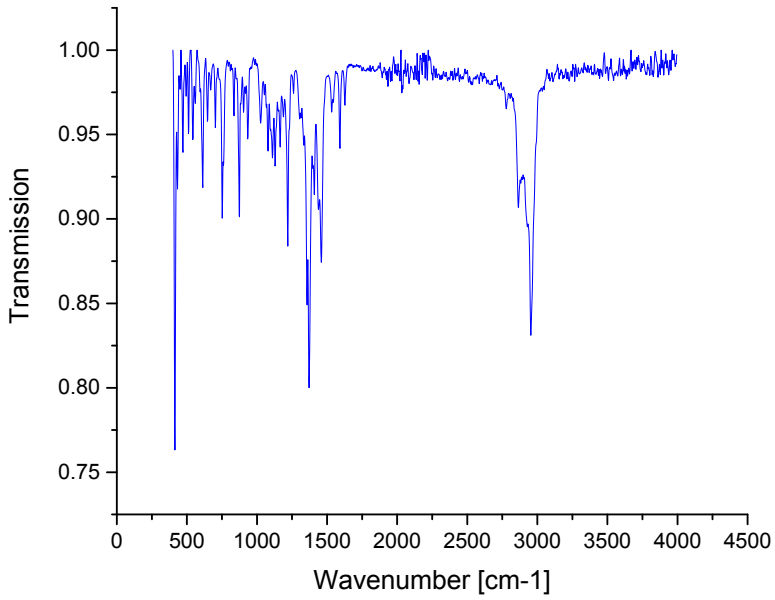
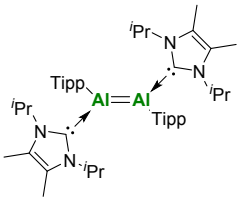



**Figure S 9.** IR spectrum of Compound **2** - $I^iPr_2Me_2Al(Tipp)I_2$, loss of Al-H at 1711 $cm^{-1}$

**Compound 3 – [I$^{i}$Pr$_2$Me$_2$Al(Tipp)]$_2$**




1.5 mL of benzene was added to a Schlenk flask containing I$^{i}$Pr$_2$Me$_2$Al(I)$_2$Tipp (**2**) (0.25 g, 0.37 mmol) and $KC_8$ (3 eq, 152 mg, 1.13 mmol) at room temperature. The solution was stirred vigorously for 72 hours upon which the solution became dark black in colour. Volatiles were removed under reduced pressure. The product was then extracted with hexane until the supernatant became colourless. The hexane solution was concentrated to the point of crystallisation and placed at 5 °C to yield black crystalline material of **3**. Yield = 0.15 g, 48%. **$^{1}$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.21 (2H, br.s. *m-H* Tipp), 7.18 (2H, br.s. *m-H* Tipp), 6.75 (2H, br.s, NC*H*$(CH_3)_2$), 5.66 (2H, br.s, NC*H*$(CH_3)_2$), 5.31 (2H, br.s, *o*-iPr C*H*$(CH_3)_2$), 4.72 (2H, br.s, *o*-iPr C*H*$(CH_3)_2$), 2.93 (1H, br.s, *p*-iPr C*H*$(CH_3)_2$), 1.67 (6H, s, CC*H*$_3$), 1.59 (6H, s, CC*H*$_3$), 1.51 (12H, br. s., iPr CH(C*H*$_3)_2$), 1.37 (24H, br. s., iPr CH(C*H*$_3)_2$), 1.20 (12H, br. s., iPr CH(C*H*$_3)_2$), 0.77 (12H, br. s., iPr CH(C*H*$_3)_2$). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 180.34 (N*C*N), 156.74 (*o-C* Tipp), 156.05 (*o-C* Tipp), 153.79 (*ipso-C* Tipp), 146.29 (*p-C* Tipp), 125.68 (*C*CH$_3$), 120.00 (*m-C* Tipp), 118.73 (*m-C* Tipp), 53.70 (N*C*H$(CH_3)_2$), 39.99 (*o*-iPr *C*H$(CH_3)_2$), 39.40 (*o*-iPr *C*H$(CH_3)_2$), 35.05 (*p*-iPr *C*H$(CH_3)_2$), 32.19 (N*C*H$(CH_3)_2$), 26.72 (*o*-iPr CH(*C*H$_3)_2$), 25.67 (*o*-iPr CH(*C*H$_3)_2$), 24.84 (*p*-iPr CH(*C*H$_3)_2$), 23.26 (NCH(*C*H$_3)_2$), 14.58 (NCH(*C*H$_3)_2$), 10.09 (C*C*H$_3$), 9.85 (C*C*H$_3$). **$^{27}$Al NMR** (78.2 MHz, $C_6D_6$, δ ppm): no signal found. **Elemental Analysis:** $C_{52}H_{86}N_4Al_2$ calculated (found) %: C 76.05 (73.86); H 10.56 (10.37); N 6.82 (6.38). **Melting point**: 122-126 °C, black solid to orange oil. **LIFDI-ESI:** $C_{52}H_{86}N_4Al_2$ calculated (found): 820.65 (821.1934 m/z).**UV/vis:** 479 nm (Ɛ = 6045 L mol$^{-1}$ cm$^{-1}$), 833 nm (Ɛ = 6273 L mol$^{-1}$ cm$^{-1}$).

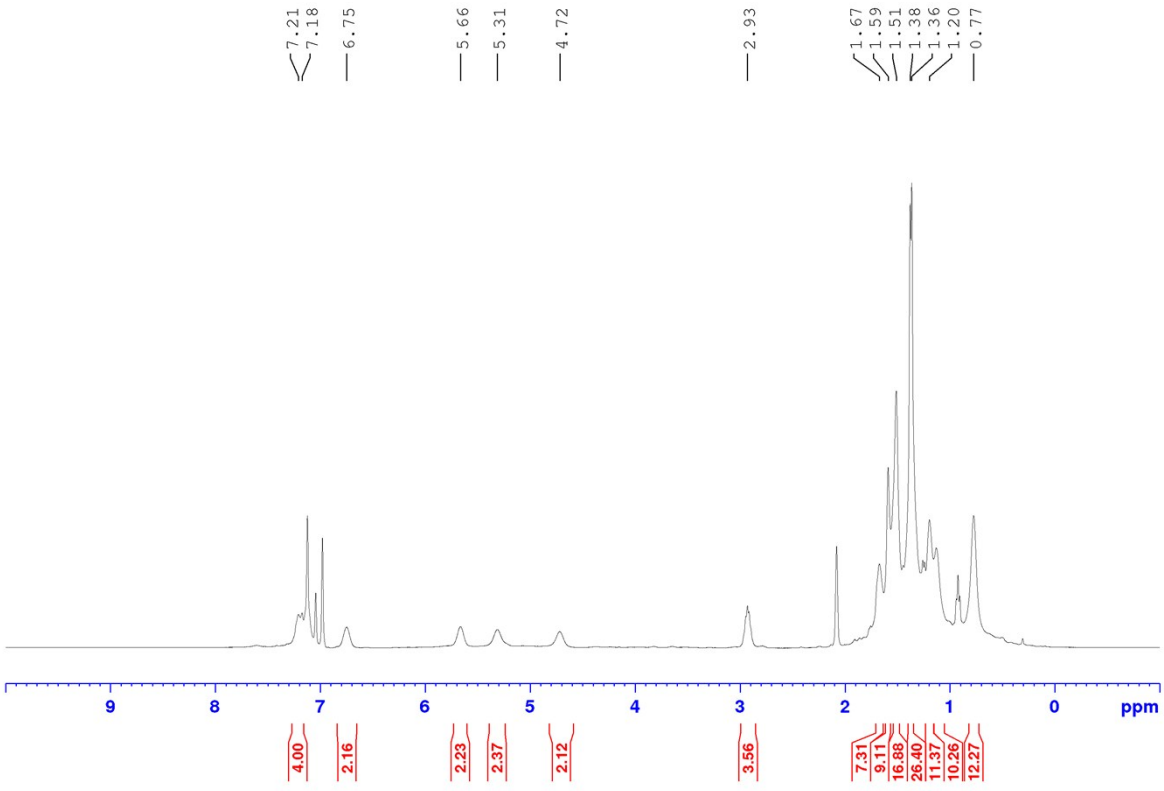



**Figure S 10.** $^{1}$H NMR Spectrum of Compound **3** – [I$^{i}$Pr$_2$Me$_2$Al(Tipp)]$_2$, in $d_8$-Toluene at 228K.

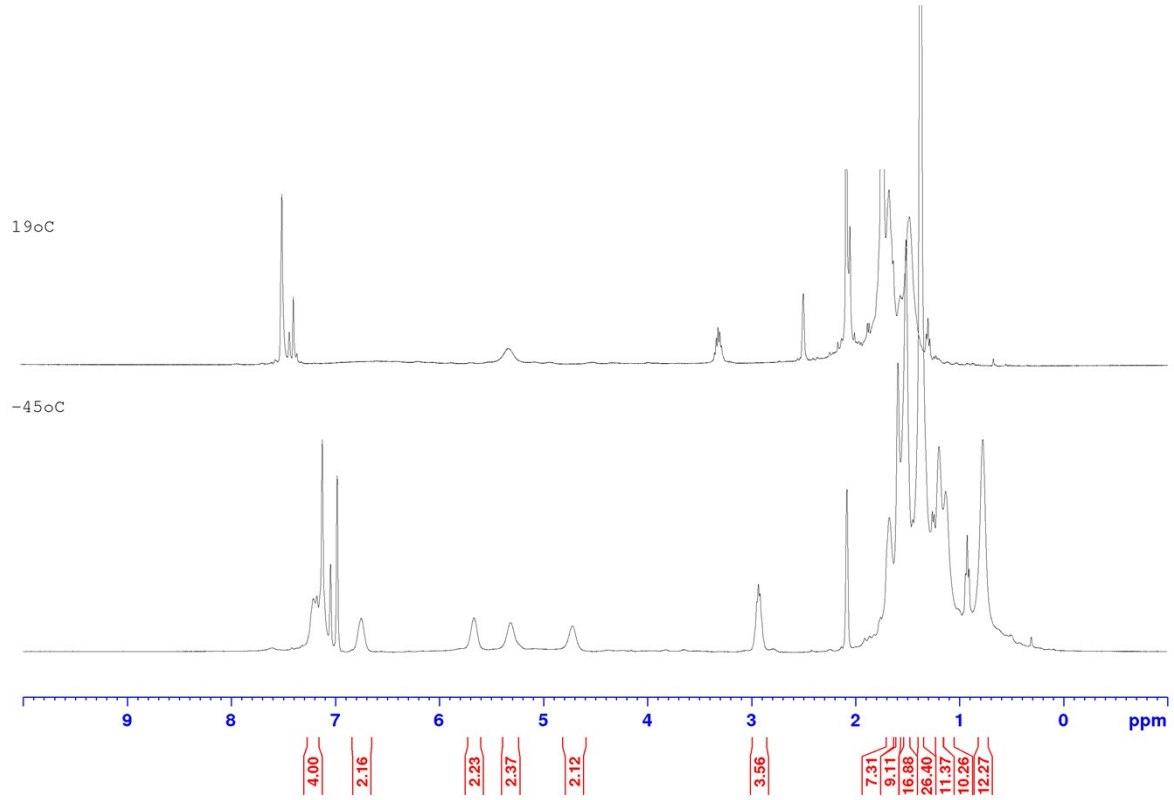



**Figure S 11.** Stacked VT $^{1}$H NMR Spectrum of Compound **3** – [$^{i}$Pr$_2$Me$_2$Al(Tipp)]$_2$, in d$_8$-Toluene.

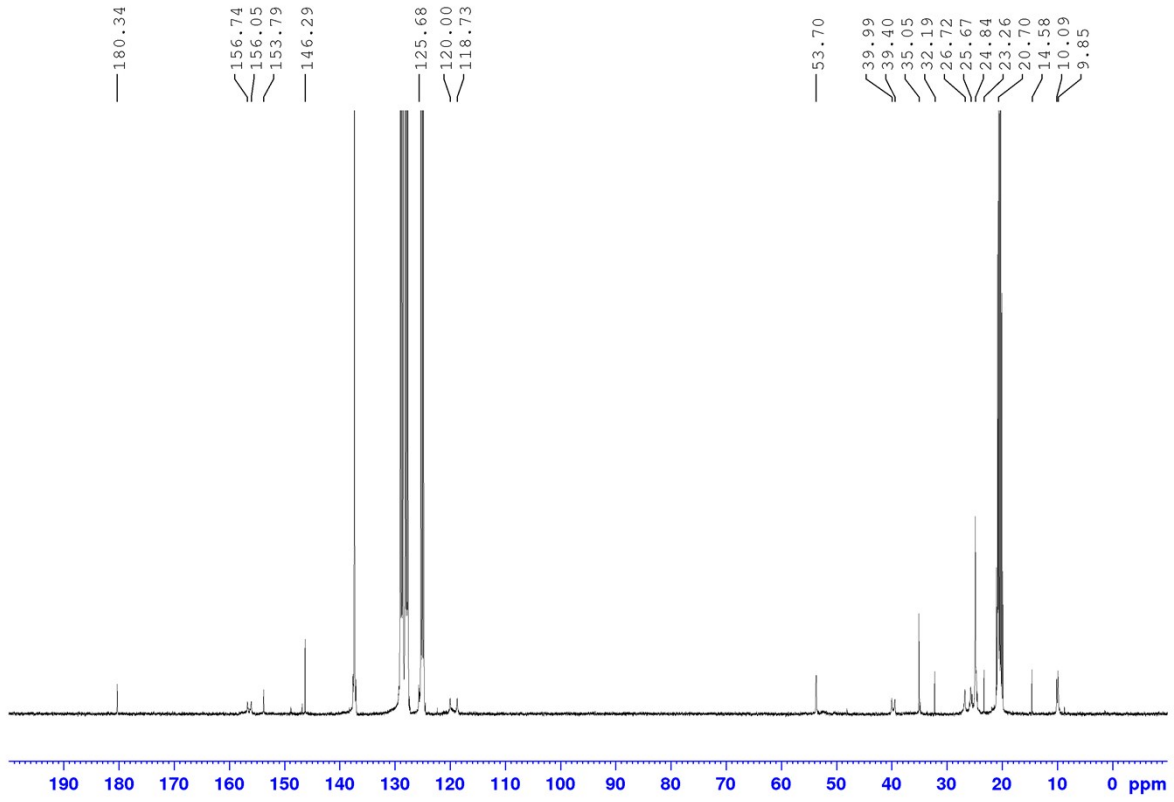



**Figure S 12.** $^{13}$C{$^{1}$H} NMR Spectrum of Compound **3** – [$^{i}$Pr$_2$Me$_2$Al(Tipp)]$_2$, in d$_8$-Toluene at 228K.

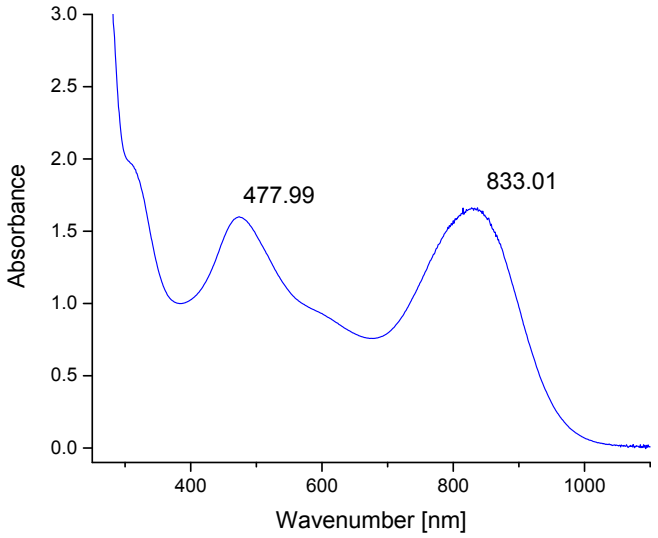
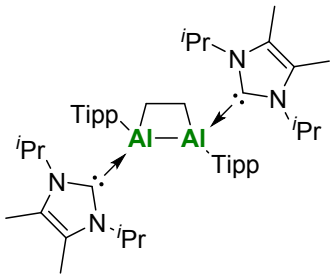



**Figure S 13.** UV/vis of compound **3** – $[I^iPr_2Me_2Al(Tipp)]_2$, in pentane

**Compound 4 –AlAl$^{(Tipp)}$ + $CH_2CH_2$**




Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, then freeze-pump-thawed degassed three times before the schlenk flask was backfilled with ethylene (1 atm) at room temperature. The reaction mixture instantly changed from the black colour of **3** to orange-yellow and was stirred for a further 4 hours. Volatiles were removed under reduced pressure. The product was then extracted with 3 x 3 mL of pentane and concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, orange-yellow crystalline powder of **4** was isolated. Yield = 36 mg, 70%. **$^1$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.18 (2H, s, *m-H* Tipp), 7.14 (2H, s, *m-H* Tipp), 5.88 (2H, m, NC*H*$(CH_3)_2$), 4.34 (1H, m, *o*-C*H*$(CH_3)_2$), 4.13 (2H, m, *o*-C*H*$(CH_3)_2$), 3.92 (1H, m, *o*-C*H*$(CH_3)_2$), 2.95 (2H, m, *p*-C*H*$(CH_3)_2$), 1.64 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C*H*$_3)_2$), 1.57 (12H, s, CC*H*$_3$), 1.40 (4H, s, AlC*H*$_2$), 1.38 (6H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.37 (12H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.25 (18H, overlapping d, CH(C*H*$_3)_2$), 0.97, (3H, d, $J_{HH}$ = 6.7 Hz, CH(C*H*$_3)_2$), 0.90 (6H, d, $J_{HH}$ = 6.7 Hz, CH(C*H*$_3)_2$), 0.88 (6H, d, $J_{HH}$ = 7.0 Hz, CH(C*H*$_3)_2$). **$^{13}$C{$^1$H} NMR** (125 MHz, $C_6D_6$, 228 K, δ ppm): 177.44 (N*C*N), 157.6 (*o-C*), 156.5 (*o*-C), 155.9 (*ipso-C*), 146.3 (*p*-C), 124.9 (*C*CH$_3$), 121.2 (*m-C*), 120.1 (*m-C*), 119.2 (*m-C*), 61.6 (N*C*H$(CH_3)_2$), 52.2 (*o-C*H$(CH_3)_2$), 47.1 (*o-C*H$(CH_3)_2$), 36.6 (*p-C*H$(CH_3)_2$), 35.0 (CH(*C*H$_3)_2$), 34.8 (CH(*C*H$_3)_2$), 32.0 (CH(*C*H$_3)_2$), 27.2 (CH(*C*H$_3)_2$), 26.9 (CH(*C*H$_3)_2$), 24.8 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 21.1 (CH(*C*H$_3)_2$), 18.4 (CH(*C*H$_3)_2$), 14.4 (Al*C*H$_2$), 10.0 (C*C*H$_3$).

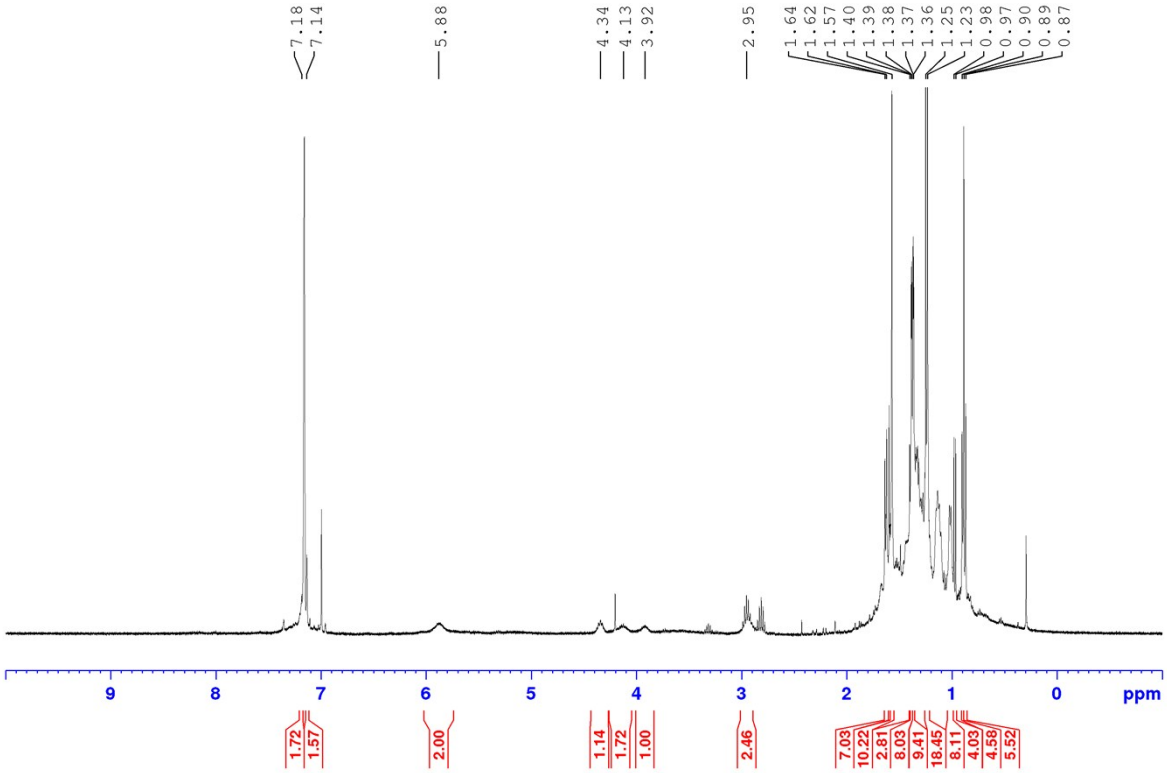



**Figure S 14**. $^1$H NMR Spectrum of Compound **4** – AlAl$^{(Tipp)}$ + $CH_2CH_2$, in $C_6D_6$

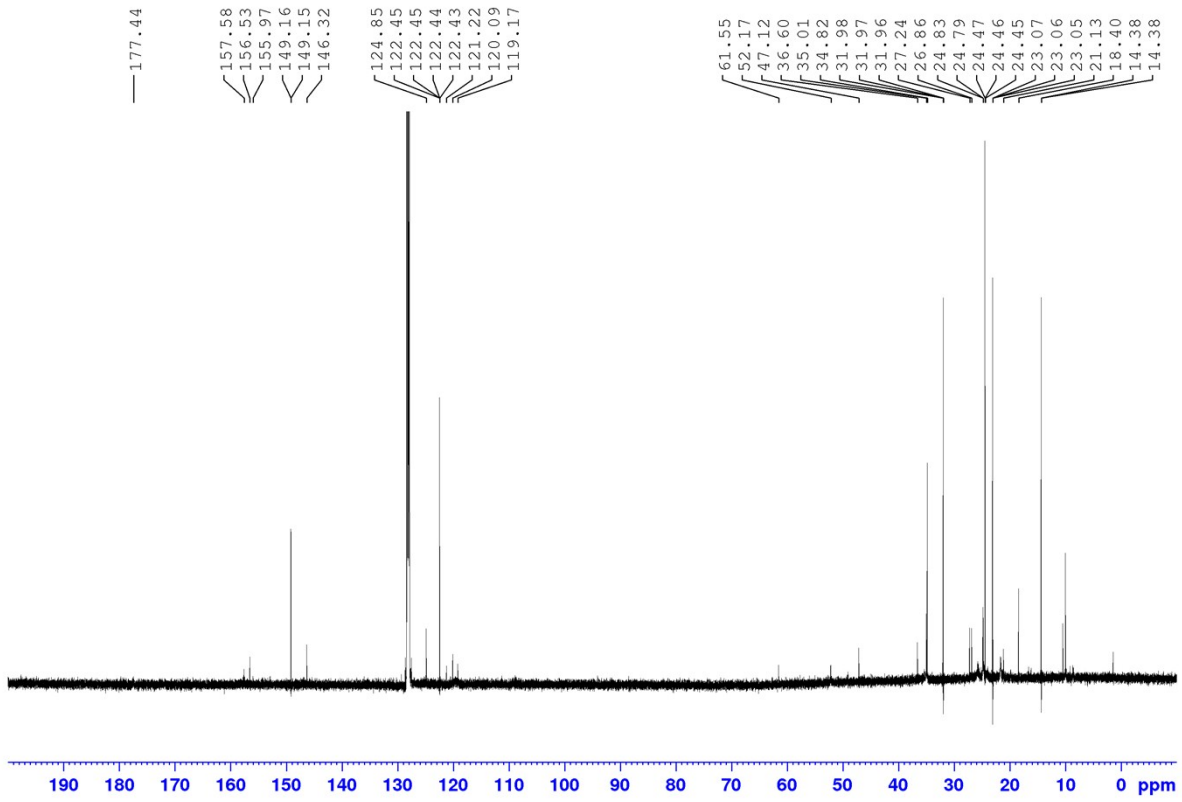
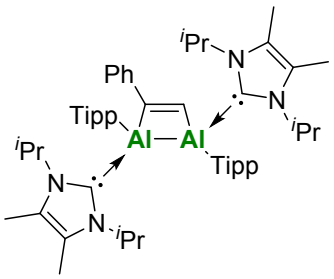



**Figure S 15**. $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4** – $AlAl^{(Tipp)}$ + $CH_2CH_2$, in $C_6D_6$

**Compound 5 –AlAl$^{(Tipp)}$ + PhCCH**




Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, PhCCH (6.7 µL, 0.061 mmol) was added via syringe at room temperature. The reaction mixture instantly changed from the black colour of **3** to yellow. The solution was stirred for 4 hours before volatiles were removed under reduced pressure. The product was then extracted with 3 x 3 mL of pentane and concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, yellow crystalline material of **5** was isolated. Yield = 28 mg, 50%. **$^{1}$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 8.54 (1H, s, C*H*), 7.36-7.25 (4H, m, Ar-*H*), 7.21 (1H, s, *m*-Ar-*H* Tipp), 7.14 (1H, s, *m*-Ar-*H* Tipp), 7.12 (2H, s, *m*-Ar-*H* Tipp), 7.05 (1H, m, Ar-H), 5.95 (2H, m, NC*H*$(CH_3)_2$), 5.08 (2H, br.s., NC*H*$(CH_3)_2$), 4.23 (1H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 4.02 (1H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 3.89 (1H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 3.75 (1H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 2.96 (2H, (1H, m, C*H*$(CH_3)_2$ *p*-iPr Tipp), 1.60 (6H, s, CC*H*$_3$), 1.57 (6H, s, CC*H*$_3$) 1.53 – 0.86 (60H, br. d, overlapping, CH(C*H*$_3$)$_2$). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 193.54 (Al*C*=CH), 179.61 (Al*C*H), 176.53, (N*C*N), 176.34 (N*C*N), 159.56 (ipso-*C* PhCCH), 157.54 (*o*-*C* Tipp), 156.72 (*o*-*C* Tipp), 156.01 (ipso-*C* Tipp), 146.63 (*p*-*C* Tipp), 146.27 (*p*-*C* Tipp), 127.56 (*o*-*C* PhCCH), 125.67 (*p*-*C* PhCCH), 125.02 (*C*CH$_3$), 122.44 (*m*-*C* PhCCH), 120.40 (*C*CH$_3$), 120.28 (*m*-C Tipp), 119.34 (*m*-C Tipp), 118.55 (*m*-C Tipp), 61.53 (*m*-*C*H$(CH_3)_2$), 52.59 (NCH$(CH_3)_2$), 52.51 (NCH$(CH_3)_2$), 47.11 (*m*-*C*H$(CH_3)_2$), 35.05 (*p*-*C*H$(CH_3)_2$), 34.82 (*p*-*C*H$(CH_3)_2$), 27.49, 27.41, 27.38, 25.89, 25.56, 25.29, 25.06, 24.90, 24.83, 24.47, 24.43, 22.74, 22.09, 21.87, 21.67, 18.39, 14.30, 10.51 (CH(*C*H$_3$)$_2$ signals from 27.49-10.51), 10.11 (C*C*H$_3$), 10.10 (C*C*H$_3$). **IR:** 2778 cm$^{-1}$ (C-H). **LIFDI-ESI:** $C_{60}H_{92}N_4Al_2$ calculated (found): 922.70 (922.0497 m/z).

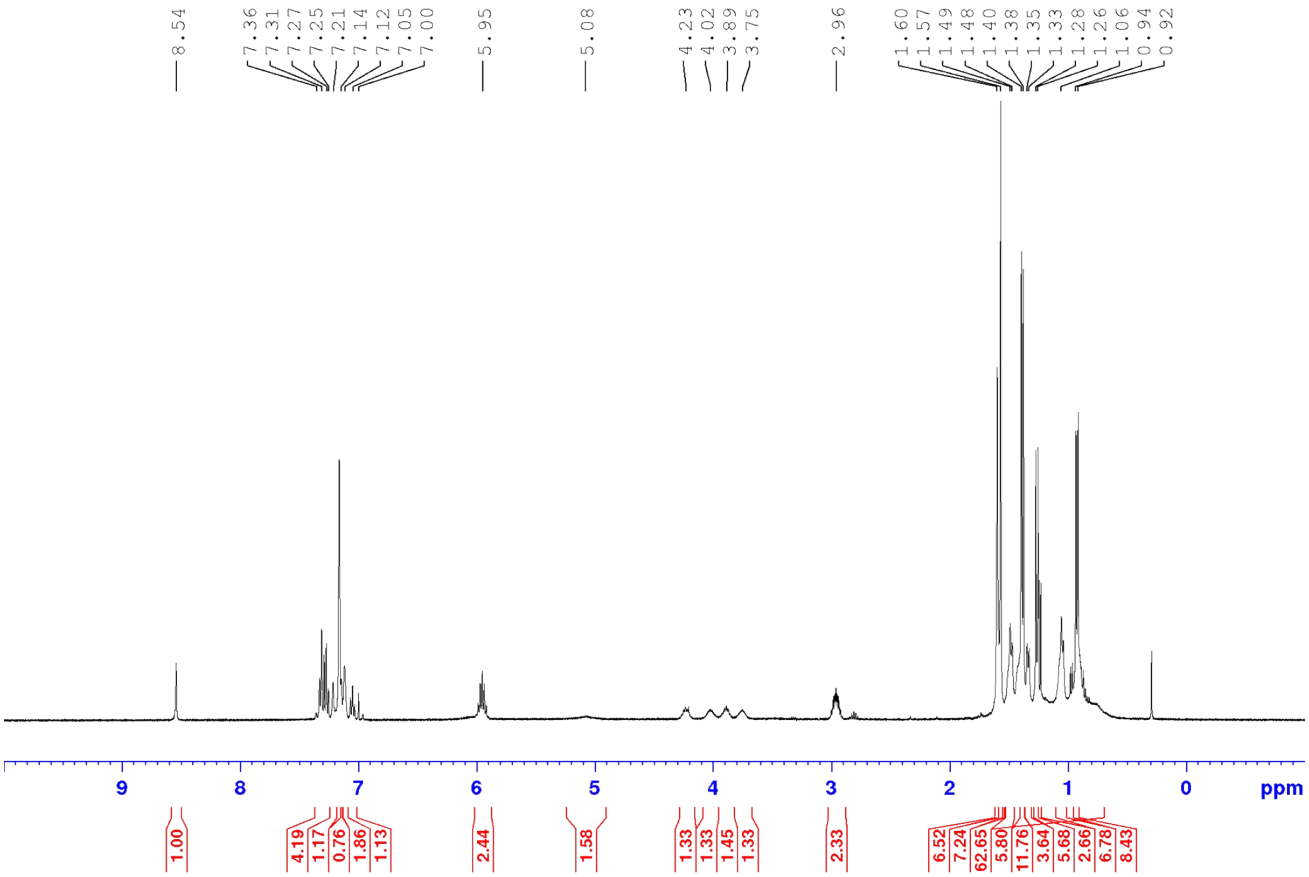



**Figure S 16.** $^{1}$H NMR Spectrum of Compound **5** – AlAl$^{(Tipp)}$ + PhCCH, in $C_6D_6$

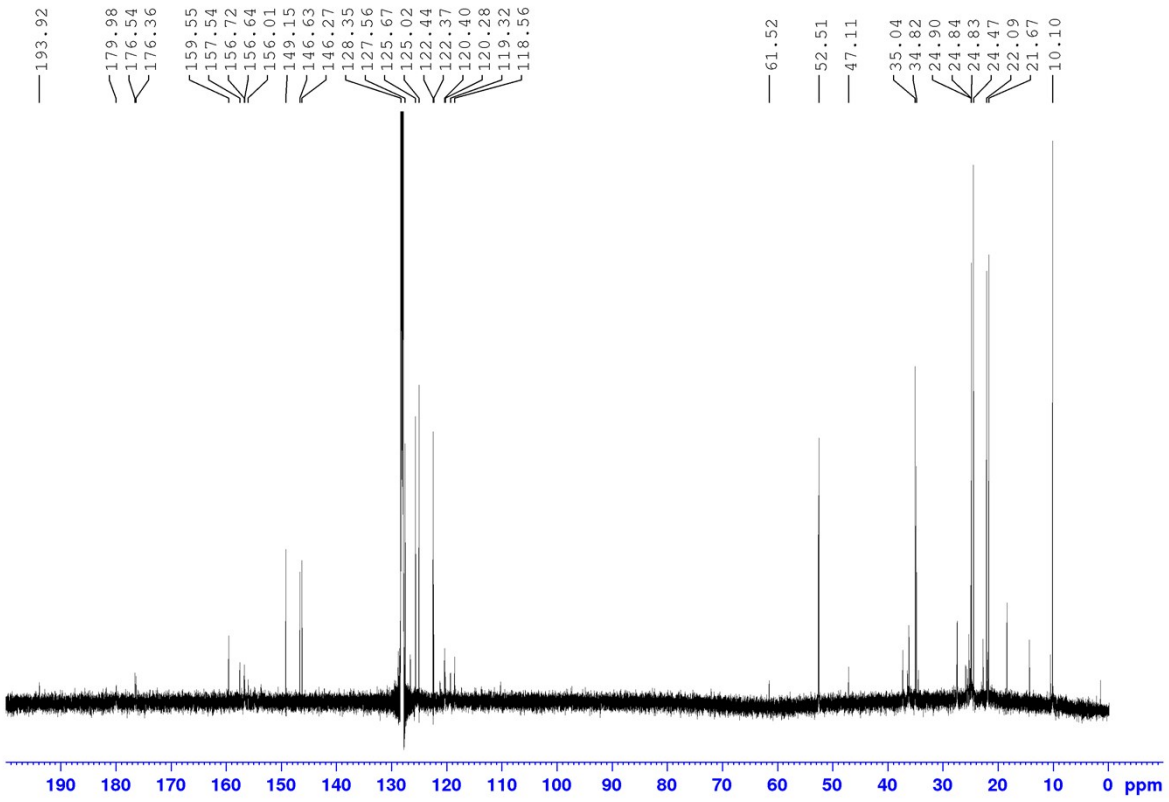



**Figure S 17.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5** – $AlAl^{(Tipp)}$ + PhCCH, in $C_6D_6$

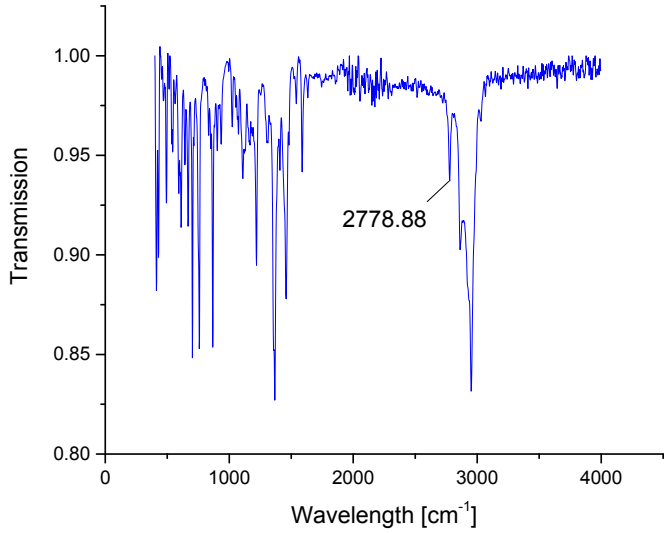
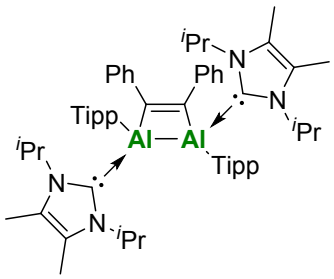



**Figure S 18.** IR Spectrum of Compound **5** – $AlAl^{(Tipp)}$ + PhCCH

**Compound 6 –AlAl$^{(Tipp)}$ + PhCCPh**




Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, PhCCPh (10 mg, 0.061 mmol) was added via syringe at room temperature. The reaction mixture instantly changed from the black colour of **3** to yellow, and was stirred for a further 4 hours. Volatiles were removed under reduced pressure. The product was then extracted with 3 x 3 mL of pentane and concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, yellow crystalline material of **5** was isolated. Yield = 36 mg, 59%. **$^{1}$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.19 (2H, s, *m*-Ar-*H* Tipp), 7.10 (2H, s, *m*-Ar-*H* Tipp), 7.08 (4H, m, *o*-Ar-H PhCCPh), 6.89 (2H, m, *p*-Ar-H PhCCPh), 6.81 (4H, m, *m*-Ar-H PhCCPh), 6.06 (2H, m, NC*H*$(CH_3)_2$), 5.04 (2H, m, NC*H*$(CH_3)_2$), 3.83 (2H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 3.72 (2H, m, C*H*$(CH_3)_2$ *o*-iPr Tipp), 2.99 (2H, m, C*H*$(CH_3)_2$ *p*-iPr Tipp), 1.68-1.23 (36H, m, CH(C*H*$_3)_2$), 1.62 (6H, s, C*H*$_3$ NHC), 1.54 (6H, s, C*H*$_3$ NHC), 0.99 (6H, d, $J_{HH}$ = 7.47 Hz, CH(C*H*$_3)_2$), 0.76 (12H, m, CH(C*H*$_3)_2$), 0.55 (6H, m, CH(C*H*$_3)_2$). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 187.55 (Al*C*), 175.48 (N*C*N), 158.26 (*ipso*-*C* Tipp), 156.65 (*ipso*-*C* Tipp), 156.10 (*o*-*C* Tipp), 155.96 (*o*-*C* Tipp), 153.68 (*ipso*-*C* PhCCPh), 146.28 (*p*-*C* Tipp), 127.09 (*o*-*C* PhCCPh), 125.22 (*C*CH$_3$), 122.44 (*p*-*C* PhCCPh), 121.57 (*m*-*C* PhCCPh), 121.45 (*C*CH$_3$), 120.39 (*m*-*C* Tipp), 119.89 (*m*-*C* Tipp), 119.02 (*m*-*C* Tipp), 53.13 (N*C*H$(CH_3)_2$), 52.77 (N*C*H$(CH_3)_2$), 48.50 (*o*-*C*H$(CH_3)_2$), 37.62 (*o*-*C*H$(CH_3)_2$), 36.42 (*o*-*C*H$(CH_3)_2$), 35.03 (*p*-*C*H$(CH_3)_2$), 28.2, 26.6, 25.3, 25.1, 25.0, 24.8, 24.7, 24.6, 24.5, 23.5, 22.5, 21.3, 21.1, 21.0, (CH(*C*H$_3)_2$ signals from 28.2-21.0), 10.3 (C*C*H$_3$), 10.1 (C*C*H$_3$). **IR:** 1544 cm$^{-1}$ (C=C). **LIFDI-ESI:** $C_{66}H_{96}N_4Al_2$ calculated (found): 998.73 (997.9891 m/z).

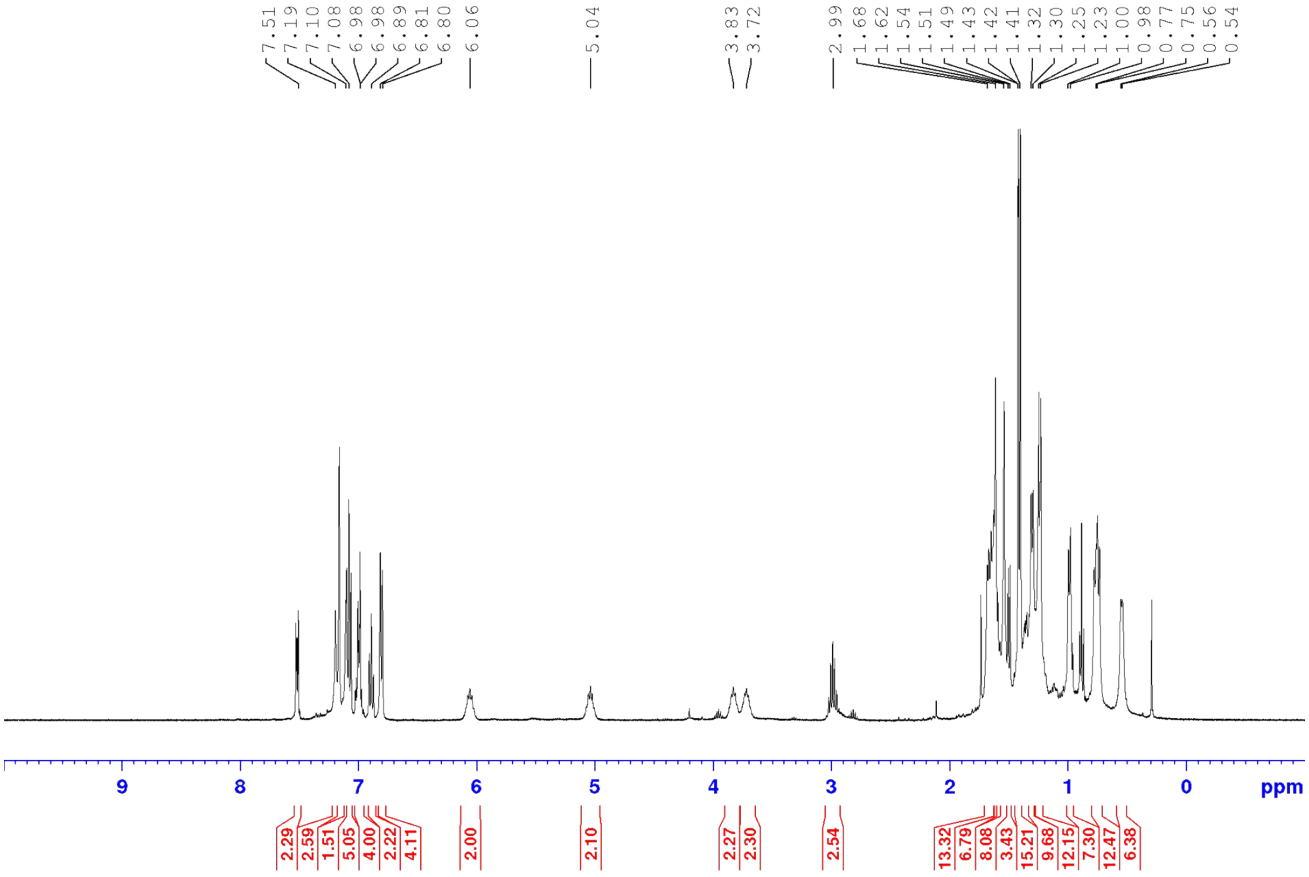



**Figure S 19.** $^{1}$H NMR spectrum of compound **6 -** AlAl$^{(Tipp)}$ + PhCCPh, in $C_6D_6$.

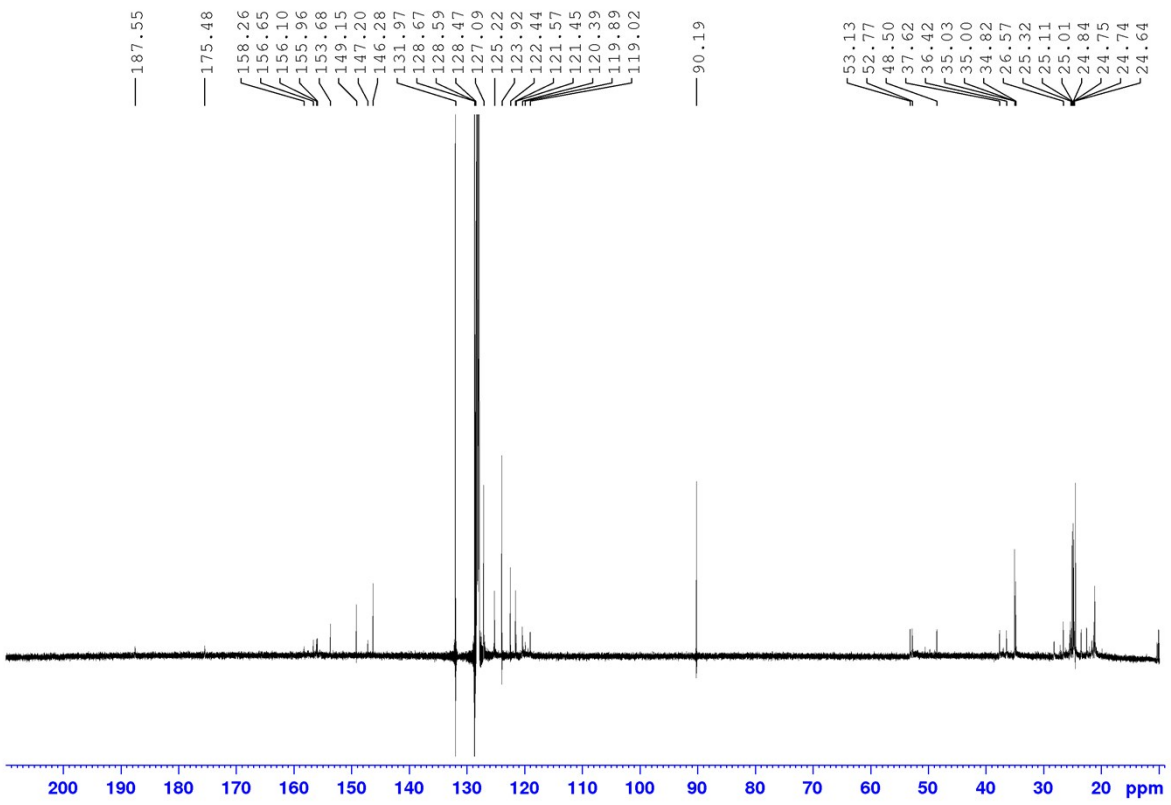



**Figure S 20.** $^{13}C\{^{1}H\}$ NMR spectrum of compound **6 -** $AlAl^{(Tipp)}$ + PhCCPh, in $C_6D_6$. Contains unreacted PhCCPh (132.0, 128.7, 123.9, 90.2 ppm).

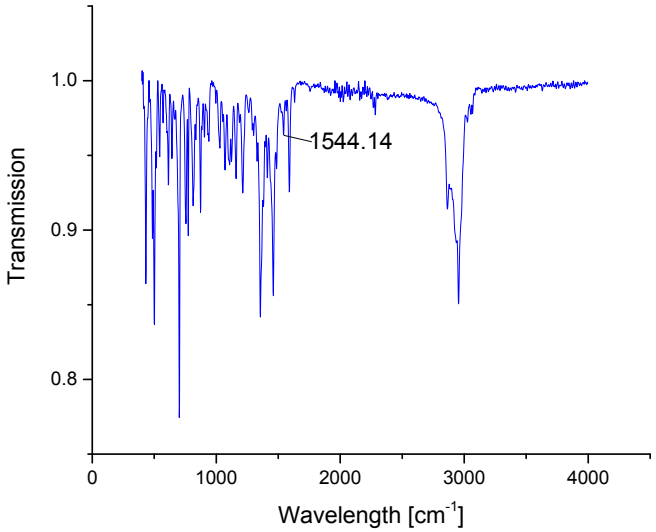
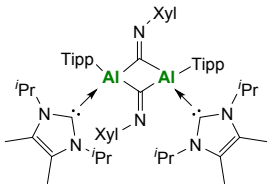



**Figure S 21.** IR Spectrum of Compound **6 –** $AlAl^{(Tipp)}$ + PhCCPh

**Compound 7 –AlAl$^{(Tipp)}$ + XylNC**




Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, 2,6-dimethylphenyl isocyanate (XylNC) (16.10 mg, 2 eq. 0.121 mmol) was dissolved in 1 mL of Toluene and added via syringe at room temperature. The reaction mixture instantly changed from the black colour of **3** to dark red, and was stirred for a further 4 hours. Volatiles were removed under reduced pressure. The product was then extracted with 3 x 3 mL of pentane and concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, red crystalline material of **7** was isolated. Yield = 31 mg, 52%. **$^{1}$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.12 (2H, d, $J_{HH}$ = 6.9 Hz, *m*-H Xyl), 7.06 (2H, s, *m-H* Tipp), 7.04 (2H, s, *m-H* Tipp), 6.89 (2H, d, $J_{HH}$ = 7.2 Hz, *m-H* Xyl), 6.77 (2H, t, $J_{HH}$ = 7.4 Hz, *p-H* Xyl), 6.43 (2H, m, NC*H*$(CH_3)_2$), 4.35 (2H, m, NC*H*$(CH_3)_2$), 3.94 (2H, m, *o*-C*H*$(CH_3)_2$), 3.40 (2H, m, *o*-C*H*$(CH_3)_2$), 3.27 (2H, m, *p*-C*H*$(CH_3)_2$), 2.63 (6H, s, o-C$H_3$ Xyl), 2.07 (6H, s, o-C$H_3$ Xyl), 1.73 (6H, s, CC$H_3$ NHC), 1.69 (6H, d, $J_{HH}$ = 6.5 Hz, CH(C$H_3)_2$), 1.61 (6H, s, CC$H_3$ NHC), 1.48 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C$H_3)_2$), 1.32 (6H, d, $J_{HH}$ = 6.8 Hz, CH(C$H_3)_2$), 1.27 (6H, d, $J_{HH}$ = 6.9 Hz, CH(C$H_3)_2$), 1.24 (6H, d, $J_{HH}$ = 7.0 Hz, CH(C$H_3)_2$), 0.89 (12H, d, $J_{HH}$ = 6.5 Hz, CH(C$H_3)_2$), 0.74 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C$H_3)_2$), 0.53 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C$H_3)_2$), 0.36 (6H, d, $J_{HH}$ = 7.1 Hz, CH(C$H_3)_2$), 0.18 (6H, d, $J_{HH}$ = 6.8 Hz, CH(C$H_3)_2$). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 303.4 (Al*C*=N), 172.0 (N*C*N), 171.8 (N*C*N), 161.6 (*ipso-C* Xyl), 158.1 (*o-C* Tipp), 156.4 (*o-C* Tipp), 155.9 (*ipso-C* Tipp), 155.6 (*ipso-C* Tipp), 147.6 (*p-C* Tipp), 134.9 (*o-C* Xyl), 126.9 (*p-C* Xyl), 126.2 (*C*$CH_3$ NHC), 125.9 (*C*$CH_3$ NHC), 121.7 (*m-C* Xyl), 120.3 (*m-C* Tipp), 119.9 (*m-C* Tipp), 118.1 (*m-C* Tipp), 61.5 (N*C*H$(CH_3)_2$), 59.7 (NC*H*$(CH_3)_2$), 54.6 (*o-C*H$(CH_3)_2$), 51.6 (*o-C*H$(CH_3)_2$), 48.5 (*p-C*H$(CH_3)_2$), 37.2, 36.9, 34.8, 27.3, 26.7, 25.9, 25.5, 24.8, 22.4, 22.1 (*o-C*$H_3$ Xyl), 20.95 (*o-C*$H_3$ Xyl), 19.9, 19.7, 18.7 (CH(*C*$H_3)_2$ signals from 37.2 -18.7), 10.2 (*C*C$H_3$ NHC), 10.0 (C*C*$H_3$ NHC). **IR:** 1594, 1544 cm$^{-1}$ (C=N). **LIFDI-ESI:** $C_{70}H_{104}N_6Al_2$ calculated (found): 1082.80 (1081.8679 m/z).

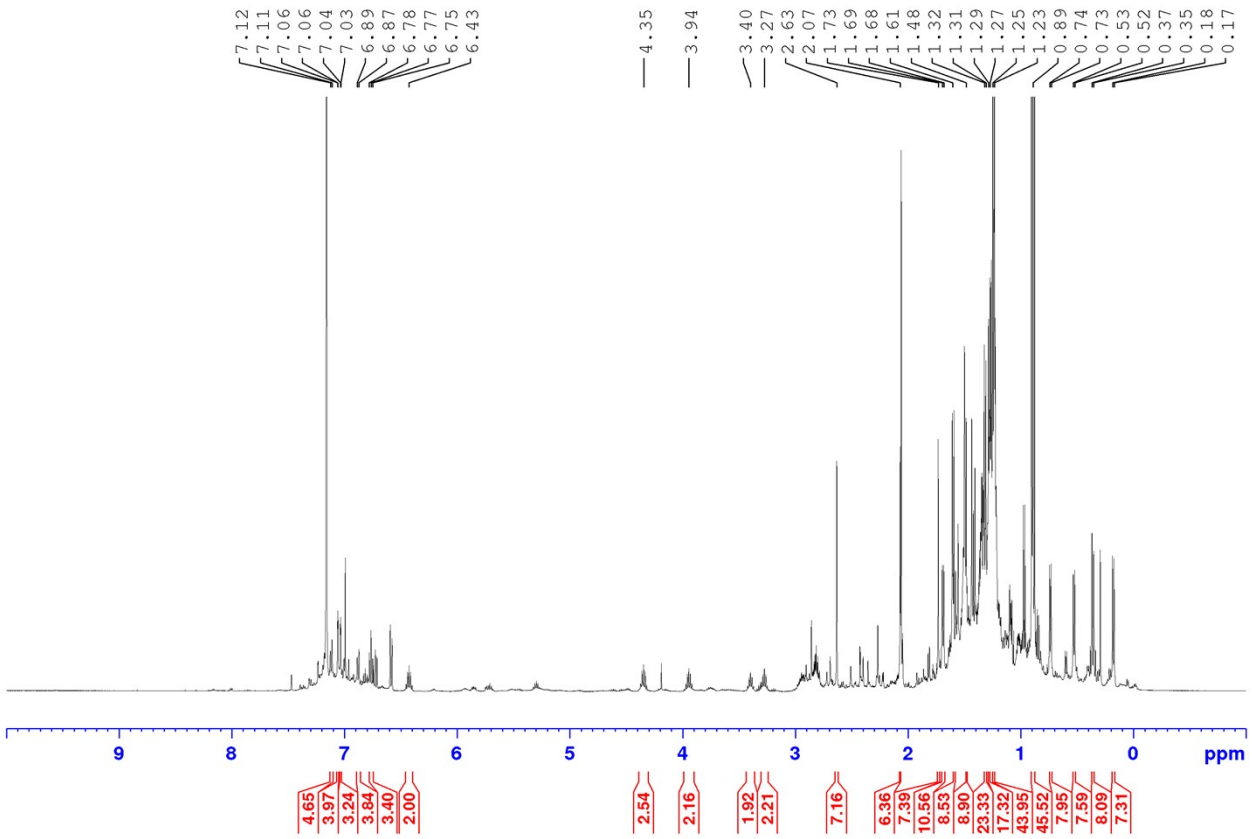



**Figure S 22.** $^{1}$H NMR Spectrum of Compound **7** – AlAl$^{(Tipp)}$ + XylNC, in $C_6D_6$

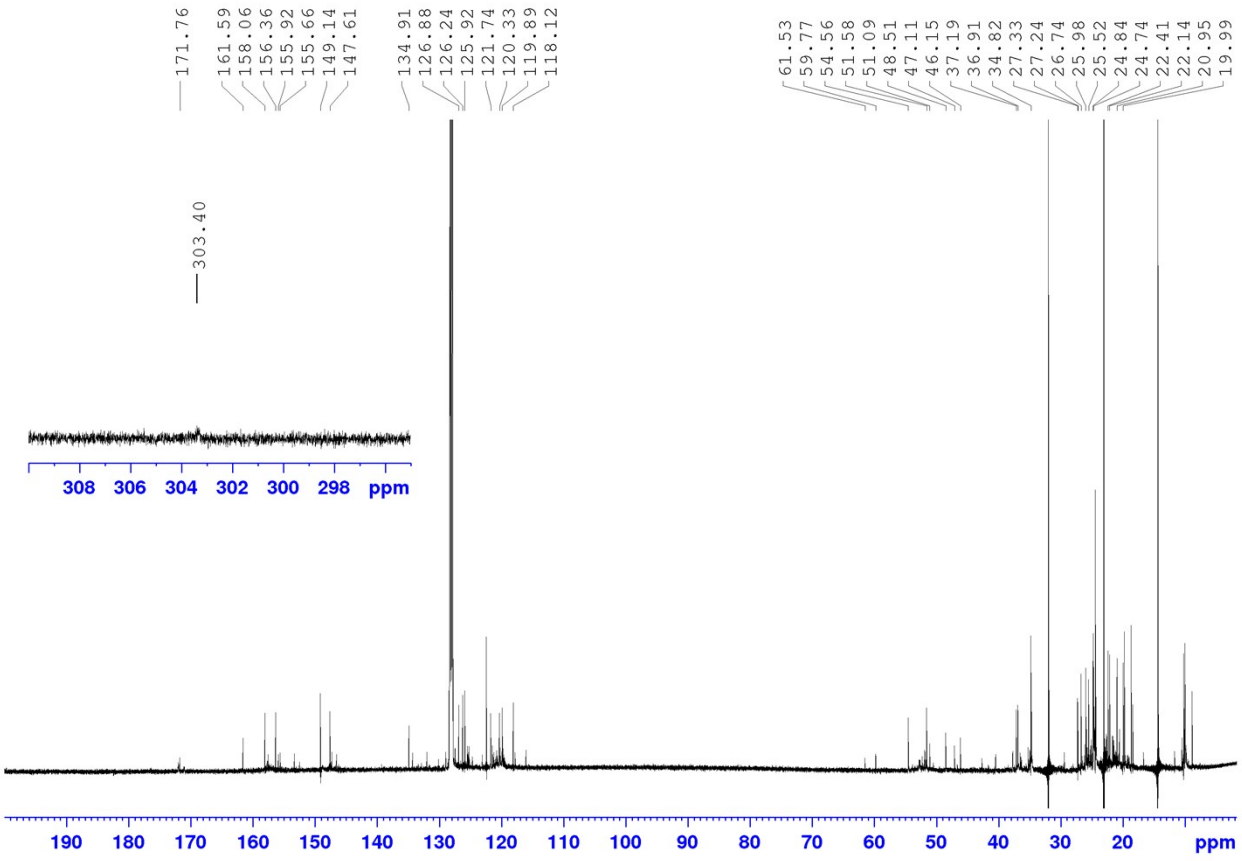



**Figure S 23.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **7** – $AlAl^{(Tipp)}$ + XylNC, in $C_6D_6$

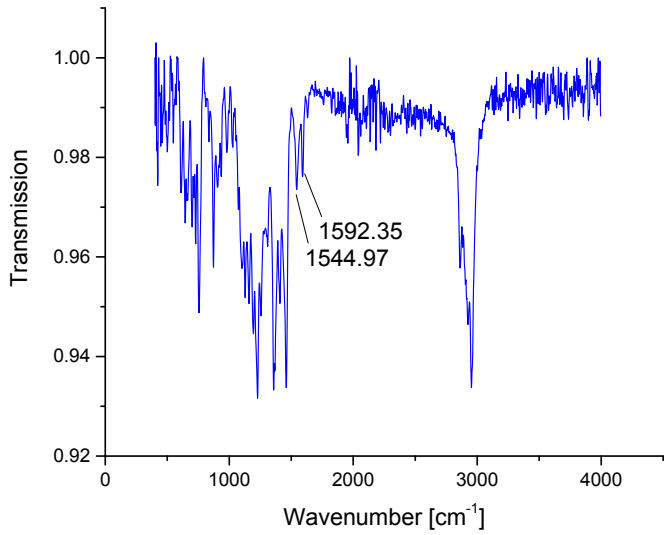
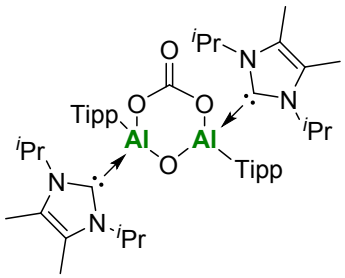



**Figure S 24**. IR Spectrum of compound **7** – $AlAl^{(Tipp)}$ + XylNC

**Compound 9 - AlAl$^{(Tipp)}$ + $CO_2$**



Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, then freeze-pump-thawed degassed three times before the schlenk flask was backfilled with $CO_2$ (1 atm) at room temperature. The reaction mixture instantly changed from the black colour of **3** to pale yellow, and was stirred for a further 4 hours at room temperature. Volatiles were removed under reduced pressure. The product was then washed with 3 x 5 mL of hexane and extracted with toluene. The toluene solution was then concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, colourless crystals of **9** were isolated. Yield = 52 mg, 86%. **$^1$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.32 (2H, s, *m*-Ar-*H* Tipp), 7.19 (2H, s, *m*-Ar-*H* Tipp), 4.69 (2H, m, NC*H*$(CH_3)_2$), 4.01 (4H, m, *o*-C*H*$(CH_3)_2$), 3.60 (2H, m, NC*H*$(CH_3)_2$), 2.89 (2H, m, *p*-C*H*$(CH_3)_2$), 1.50 (12H, s, CC$H_3$), 1.35-1.31 (72H, br. overlapping doublet), CH(C$H_3)_2$), 1.22 (12H, d, $J_{HH}$ = 6.87 Hz, CH(C$H_3)_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 185.20 (N*C*N), 159.12 (*C*$O_3$), 156.85 (*ipso-C*), 156.07 (*o-C*), 148.47 (*p-C*), 147.34 (*o-C*), 125.64 (*C*$CH_3$), 122.49 (*C*$CH_3$), 119.57 (*m-C*), 51.20 (N*C*H$(CH_3)_2$), 51.11 (N*C*H$(CH_3)_2$), 36.72 (*C*H$(CH_3)_2$), 35.03 (*C*H$(CH_3)_2$), 31.97 (*C*H$(CH_3)_2$), 26.33 (CH(*C*$H_3)_2$), 24.54 (CH(*C*$H_3)_2$), 22.36 (CH(*C*$H_3)_2$), 21.05 (CH(*C*$H_3)_2$), 14.37 (CH(*C*$H_3)_2$), 8.88 (C*C*$H_3$), 8.07 (C*C*$H_3$). **IR:** 1658 cm$^{-1}$ ($CO_3$).

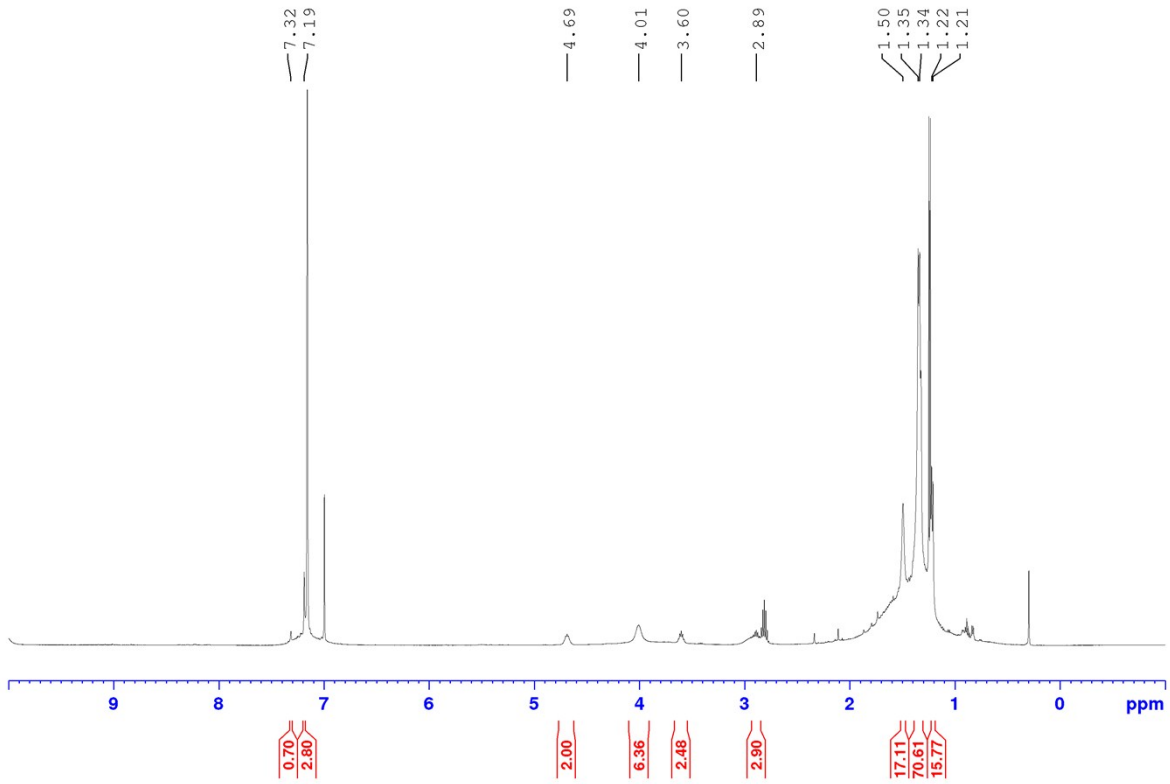



**Figure S 25.** $^1$H NMR Spectrum of Compound **9** – AlAl$^{(Tipp)}$ + $CO_2$, in $C_6D_6$

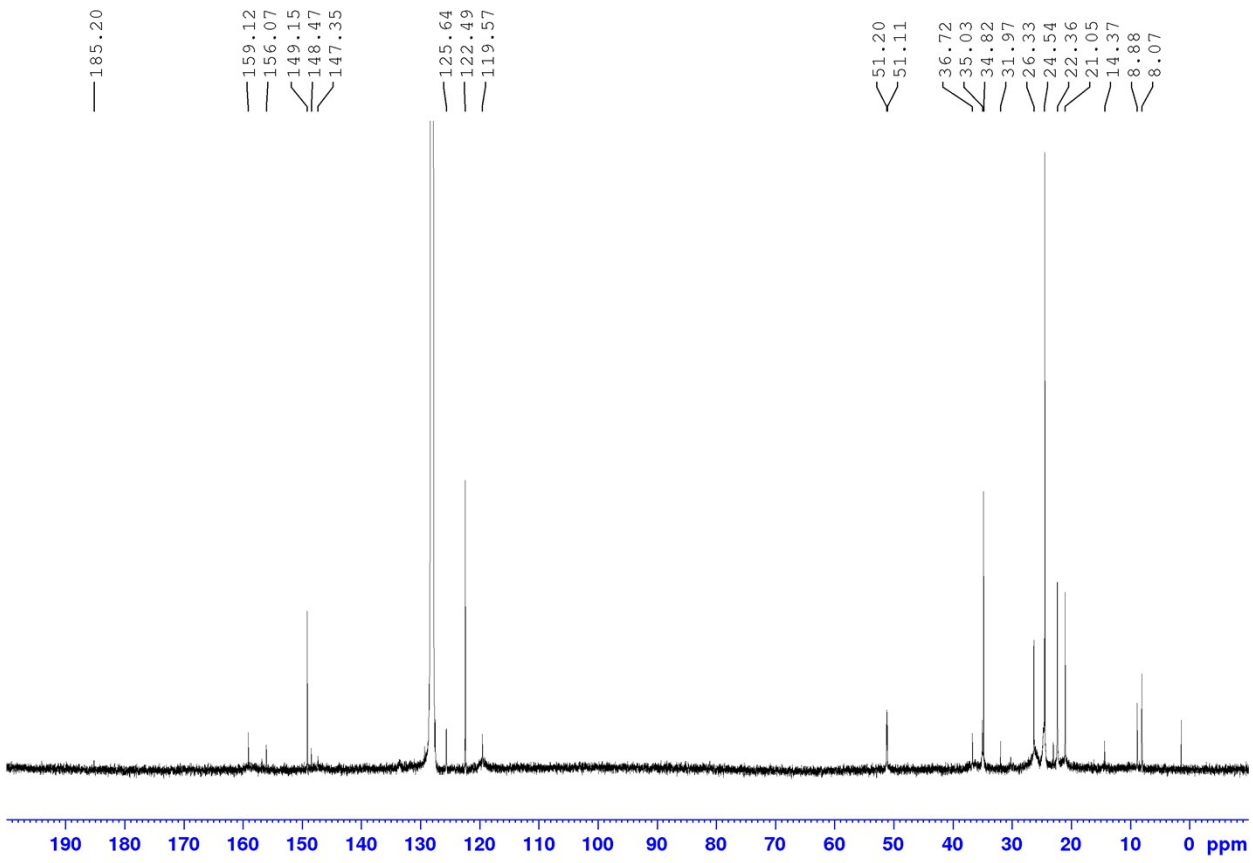



**Figure S 26.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **9** – $AlAl^{(Tipp)}$ + $CO_2$, in $C_6D_6$

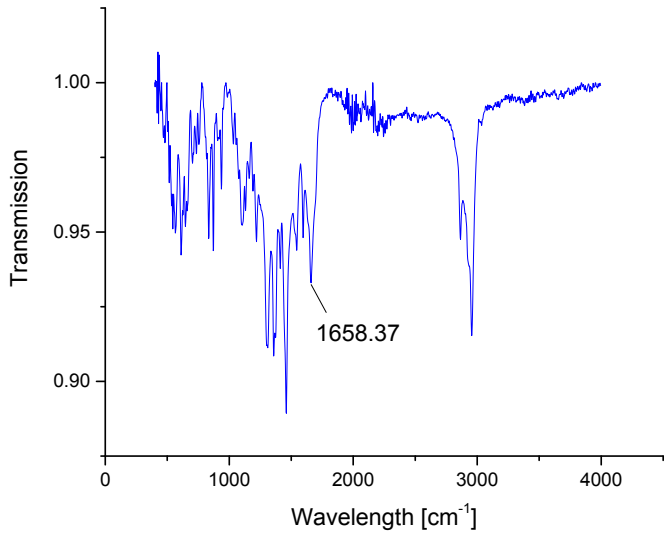
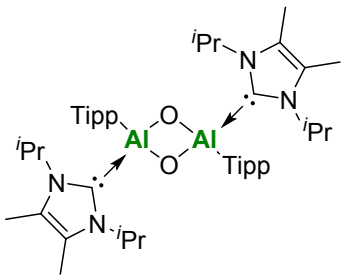



**Figure S 27.** IR Spectrum of Compound **9** - $AlAl^{(Tipp)}$ + $CO_2$

**Compound 10 –AlAl$^{(Tipp)}$ + $O_2$**




Compound **3** (42 mg, 0.051 mmol) was dissolved in 2 mL of Toluene, then freeze-pump-thawed degassed three times before the schlenk flask was backfilled with $O_2$ (1 atm) at room temperature. The reaction mixture instantly changed from the black colour of **3** to pale yellow then colourless and was stirred for a further 4 hours at room temperature. Volatiles were removed under reduced pressure. The product was then washed with 3 x 5 mL of hexane and extracted with toluene. The toluene solution was then concentrated to the point of crystallisation. After storage at -30 °C for 48 hours, colourless crystals of **10** were isolated. Yield = 36 mg, 83%. **$^1$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.58 (2H, m, C*H*$(CH_3)_2$), 7.24 (2H, s, *m-H* Tipp), 7.15 (2H, s, *m-H* Tipp), 5.31 (2H, m, C*H*$(CH_3)_2$), 5.21 (2H, m, *o*-C*H*$(CH_3)_2$), 3.65 (2H, m, *o*-C*H*$(CH_3)_2$), 2.93 (2H, m, *p*-C*H*$(CH_3)_2$), 1.74 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.61 (6H, s, CC*H*$_3$), 1.53 (6, s, CC*H*$_3$), 1.34 (12H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.20 (6H, d, $J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.13 (6H, d, $J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.97 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 0.81 (6H, d, $J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 177.7 (N*C*N), 157.5 (*o-C* Tipp), 154.5 (*ipso-C* Tipp), 147.5 (*p-C* Tipp), 125.3 (*C*CH$_3$), 124.1 (*C*CH$_3$), 119.9 (*m-C* Tipp), 118.8 (*m-C* Tipp), 52.7 (N*C*H$(CH_3)_2$), 50.5 (N*C*H$(CH_3)_2$), 35.1 (*o*-*C*H$(CH_3)_2$), 34.8 (*o*-*C*H$(CH_3)_2$), 32.0 (*p*-*C*H$(CH_3)_2$), 26.8 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 22.0 (CH(*C*H$_3$)$_2$), 21.7 (CH(*C*H$_3$)$_2$), 21.5 (CH(*C*H$_3$)$_2$), 21.3 (CH(*C*H$_3$)$_2$), 18.4 (CH(*C*H$_3$)$_2$), 14.3 (CH(*C*H$_3$)$_2$), 10.0 (*C*CH$_3$), 9.8 (*C*CH$_3$).

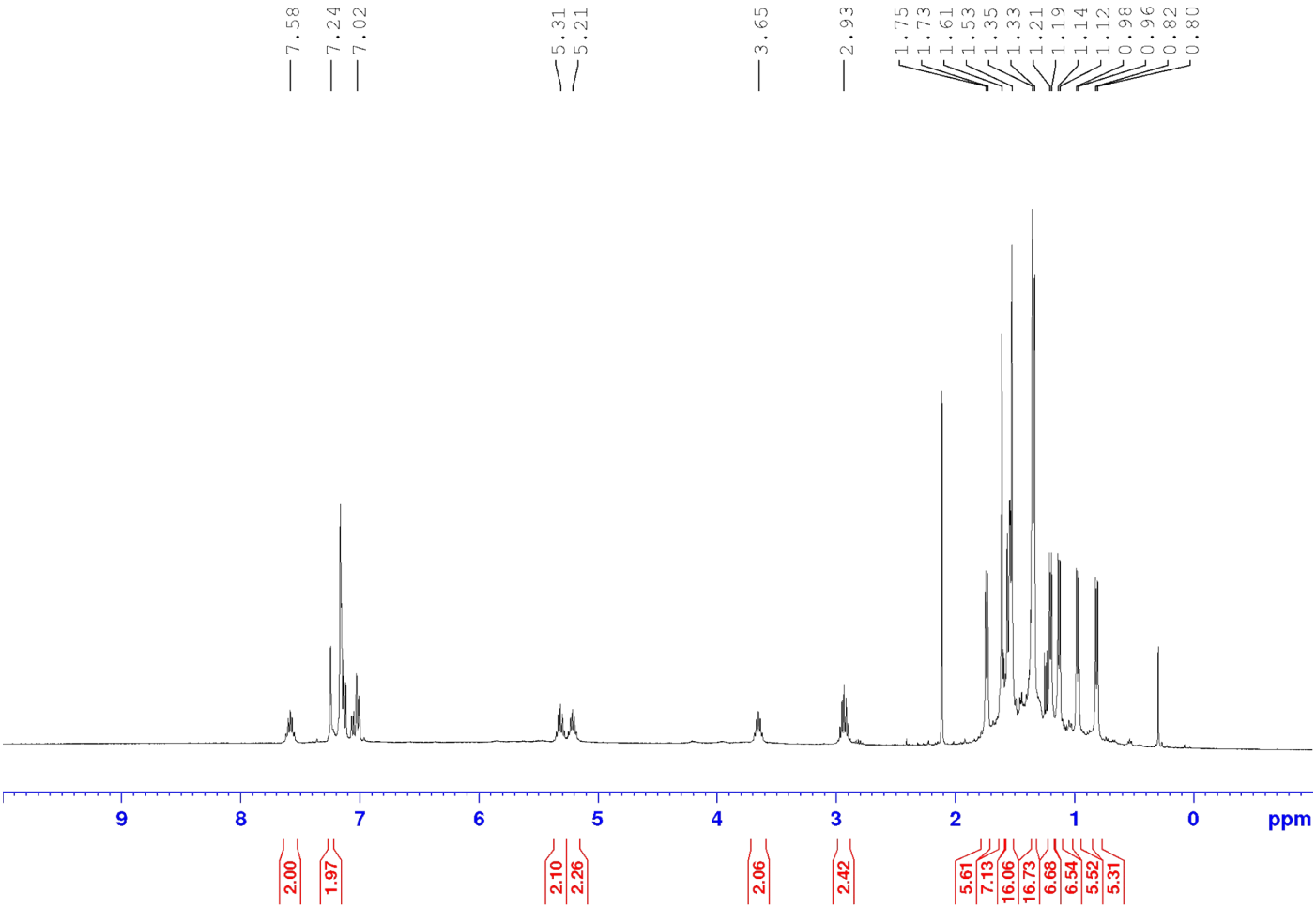



Figure S 28. $^1$H NMR Spectrum of Compound **10** – AlAl$^{(Tipp)}$ + $O_2$, in $C_6D_6$

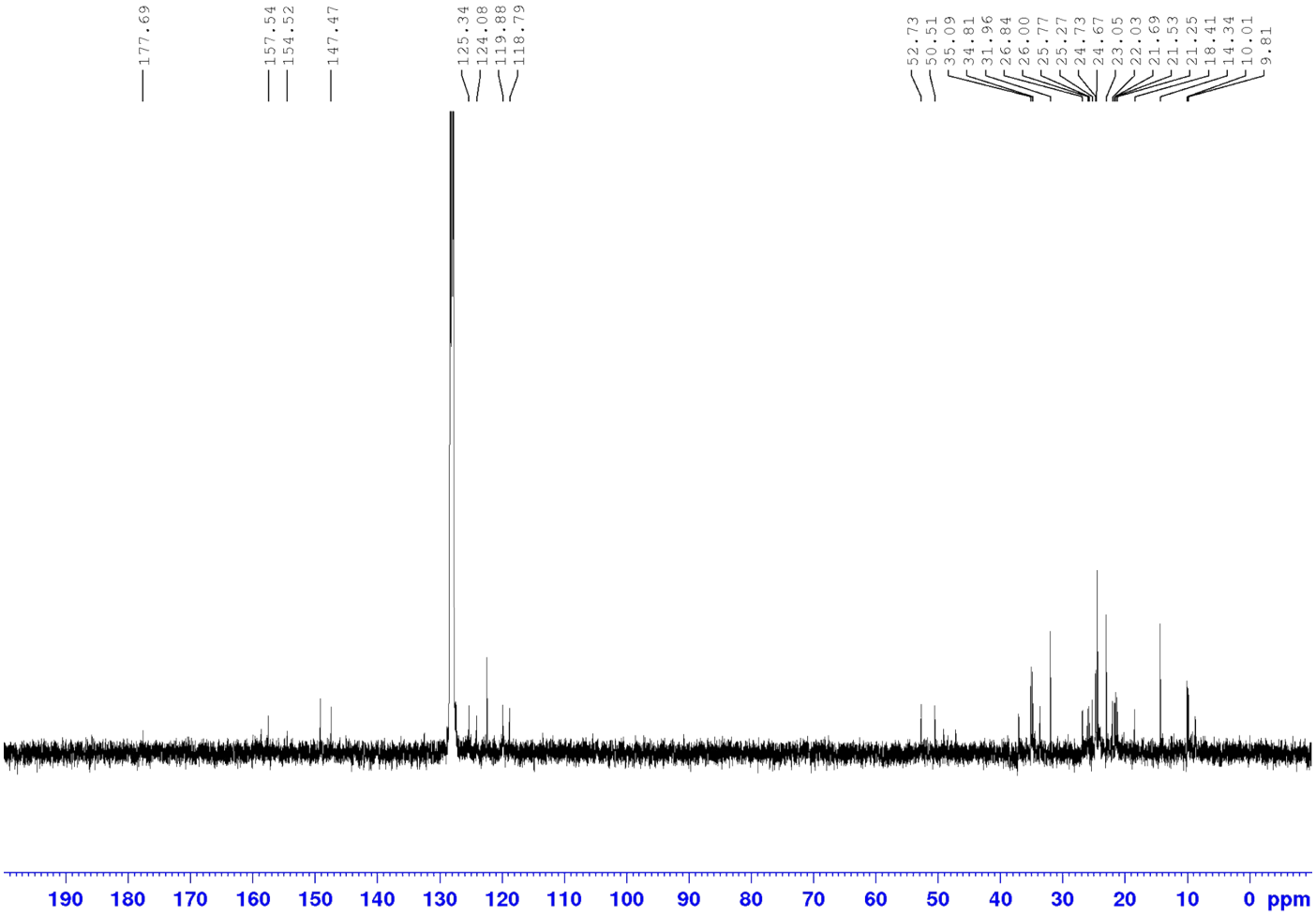
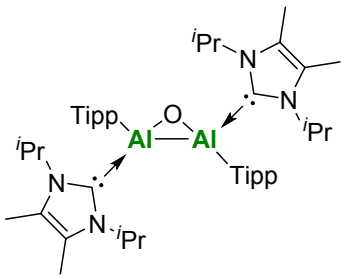



Figure S 29. $^{1}H$ NMR Spectrum of Compound **10** – $AlAl^{(Tipp)}$ + $O_2$, in $C_6D_6$

**Compound 11 –AlAl$^{(Tipp)}$ + $N_2O$ / N-Methylmorpholine-N-Oxide**




Compound **3** (50 mg, 0.061 mmol) was dissolved in 2 mL of Toluene, followed by the addition of *N*-methylmorpholine-*N*-Oxide (7mg, 0.061 mmol) at room temperature. The reaction mixture instantly changed from the black colour of **3** to red, and was stirred for a further 4 hours at room temperature. Volatiles were removed under reduced pressure. The product was then extracted with 3 x 5 mL of hexane and then concentrated to the point of crystallisation (approximately 0.3 mL). After storage at -30 °C for 24 hours, red crystals of **10** were isolated. Yield = 37 mg, 73%. **$^1$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.58 (2H, m, C*H*$(CH_3)_2$), 7.24 (2H, s, *m-H* Tipp), 7.15 (2H, s, *m-H* Tipp), 5.31 (2H, m, C*H*$(CH_3)_2$), 5.21 (2H, m, *o*-C*H*$(CH_3)_2$), 3.65 (2H, m, *o*-C*H*$(CH_3)_2$), 2.93 (2H, m, *p*-C*H*$(CH_3)_2$), 1.74 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C*H*$_3)_2$), 1.61 (6H, s, CC*H*$_3$), 1.53 (6, s, CC*H*$_3$), 1.34 (12H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.25 (12H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.20 (6H, d, $J_{HH}$ = 6.5 Hz, CH(C*H*$_3)_2$), 1.13 (6H, d, $J_{HH}$ = 6.7 Hz, CH(C*H*$_3)_2$), 0.97 (6H, d, $J_{HH}$ = 6.6 Hz, CH(C*H*$_3)_2$), 0.81 (6H, d, $J_{HH}$ = 6.9 Hz, CH(C*H*$_3)_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 177.7 (N*C*N), 157.5 (*o-C* Tipp), 154.5 (*ipso-C* Tipp), 147.5 (*p-C* Tipp), 125.3 (*C*CH$_3$), 124.1 (*C*CH$_3$), 119.9 (*m-C* Tipp), 118.8 (*m-C* Tipp), 52.7 (NCH$(CH_3)_2$), 50.5 (NC*H*$(CH_3)_2$), 35.1 (*o*-*C*H$(CH_3)_2$), 34.8 (*o*-*C*H$(CH_3)_2$), 32.0 (*p*-*C*H$(CH_3)_2$), 26.8 (CH(*C*H$_3)_2$), 26.0 (CH(*C*H$_3)_2$), 25.8 (CH(*C*H$_3)_2$), 25.3 (CH(*C*H$_3)_2$), 24.7 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 22.0 (CH(*C*H$_3)_2$), 21.7 (CH(*C*H$_3)_2$), 21.5 (CH(*C*H$_3)_2$), 21.3 (CH(*C*H$_3)_2$), 18.4 (CH(*C*H$_3)_2$), 14.3 (CH(*C*H$_3)_2$), 10.0 (C*C*H$_3$), 9.8 (C*C*H$_3$). **UV/vis:** 314 nm (Ɛ = 1952 L mol$^{-1}$ cm$^{-1}$), 512 nm (Ɛ = 1155 L mol$^{-1}$ cm$^{-1}$).

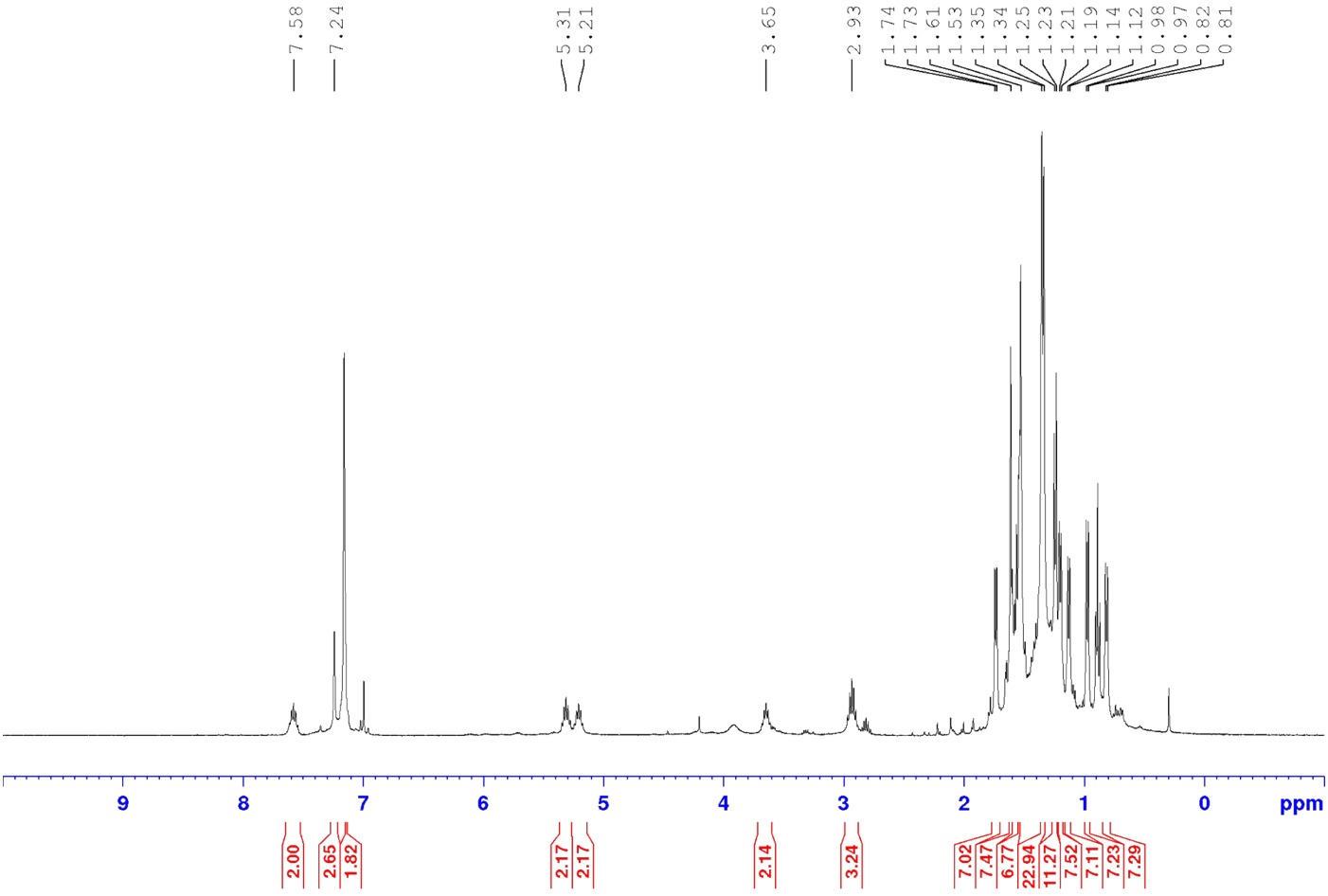



**Figure S 30.** $^1$H NMR Spectrum of Compound **11** – AlAl$^{(Tipp)}$ + $N_2O$, in $C_6D_6$

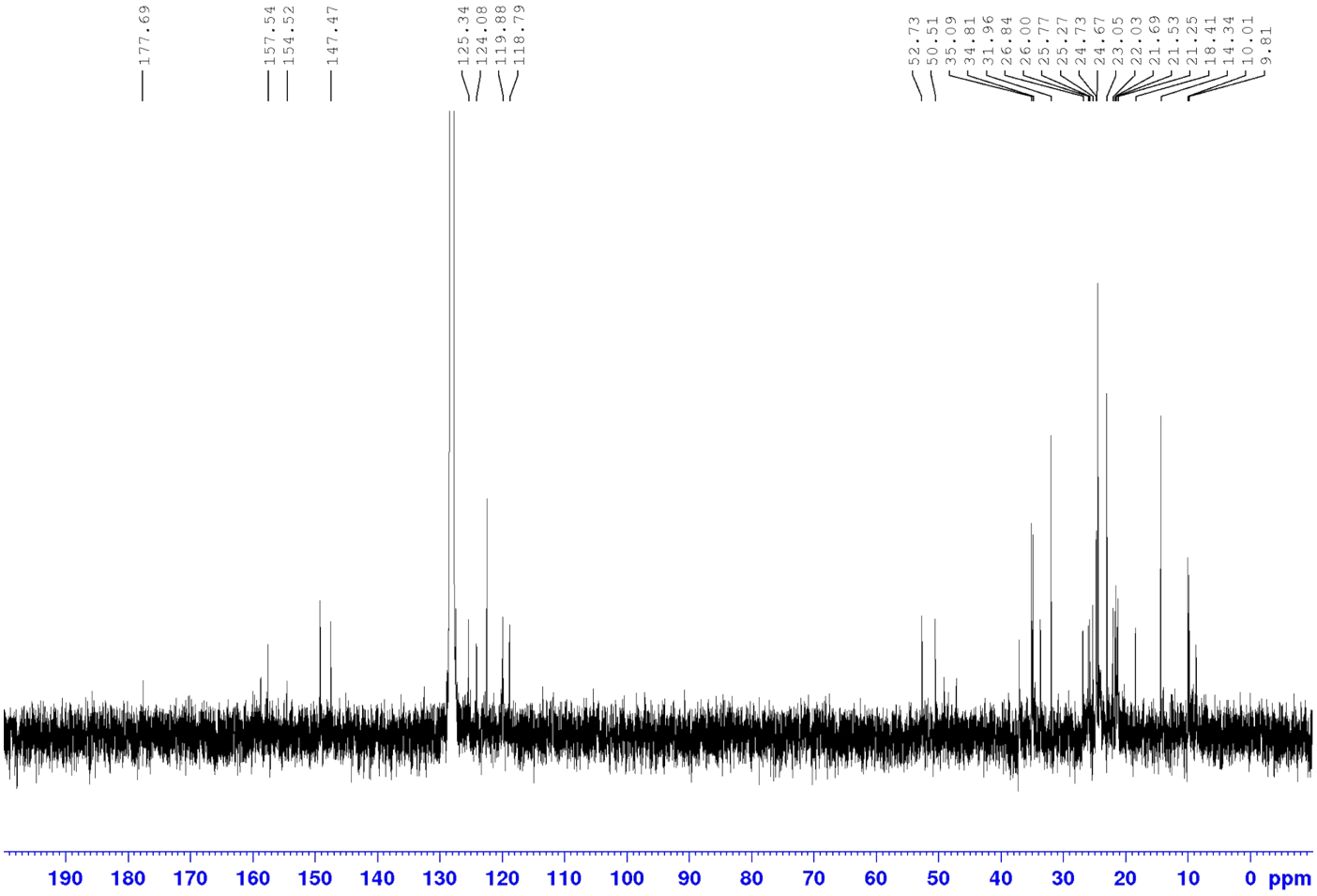



**Figure S 31.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **11** – $AlAl^{(Tipp)}$ + $N_2O$, in $C_6D_6$

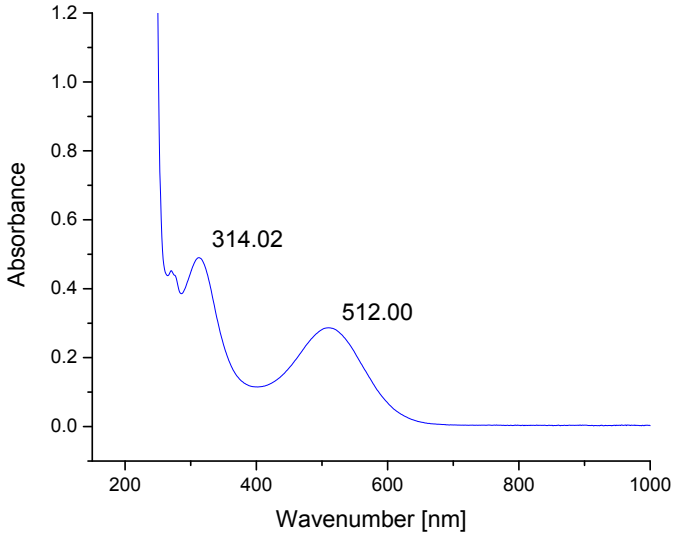
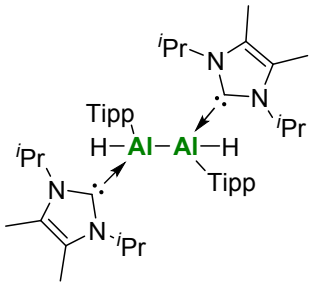



**Figure S 32.** UV/Vis spectra of Compound **11** – $AlAl^{(Tipp)}$ + $N_2O$, in pentane

**Compound 12 –AlAl$^{(Tipp)}$ + $H_2$**




Compound **3** (75 mg, 0.079 mmol) was dissolved in 2 mL of Hexane, then freeze-pump-thawed degassed three times before the schlenk flask was backfilled with $H_2$ (1 atm) at room temperature. The reaction was heated in an oil bath to 50 °C for 16 hrs. Volatiles were removed under reduced pressure, to leave a yellow solid. The solid was extracted with 3 x 5 mL of hexane and concentrated to the point of crystallisation, after 1 week at -30 °C yellow microcrystalline material of **12** was isolated. Yield = 64 mg, 85%. **$^1$H NMR** (400 MHz, $C_6D_6$, 228 K, δ ppm): 7.23 (2H, s, *m-H* Tipp), 5.85 (2H, m, C*H*$(CH_3)_2$), 4.20 (2H, m, C*H*$(CH_3)_2$), 2.94 (1H, m, C*H*$(CH_3)_2$), 1.62 (6H, s, C(C*H*$_3$)), 1.60 (6H, s, C(C*H*$_3$)), 1.51 (12H, d, $J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.45 (6H, d, $J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.36 (12H, d, $J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.24 (12H, d, $J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.20 (6H, d, $J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.03 (6H, d, $J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$, 228 K, δ ppm): 177.00 (N*C*N), 157.68 (*ipso-C*), 157.31 (*o-C*), 146.22 (*p-C*), 125.32 (*C*$(CH_3)$), 119.65 (*m-C*), 61.54 (N*C*H$(CH_3)_2$), 52.66 (*C*H$(CH_3)_2$), 47.12 (*C*H$(CH_3)_2$), 34.82 (*C*H$(CH_3)_2$), 25.99 (CH(*C*H$_3$)$_2$), 22.74 (CH(*C*H$_3$)$_2$), 21.16 (CH(*C*H$_3$)$_2$), 18.40 (CH(*C*H$_3$)$_2$), 14.29 (CH(*C*H$_3$)$_2$), 10.51 (C(*C*H$_3$)), 10.09 (C(*C*H$_3$)). **$^{27}$Al NMR** (78.2 MHz, $C_6D_6$, δ ppm): no signal found. **IR:** 1593, 1634 cm$^{-1}$ (Al-H). **UV/vis:** 297 nm (Ɛ = 65,284 L mol$^{-1}$ cm$^{-1}$), 331 nm (Ɛ = 60,621 L mol$^{-1}$ cm$^{-1}$).

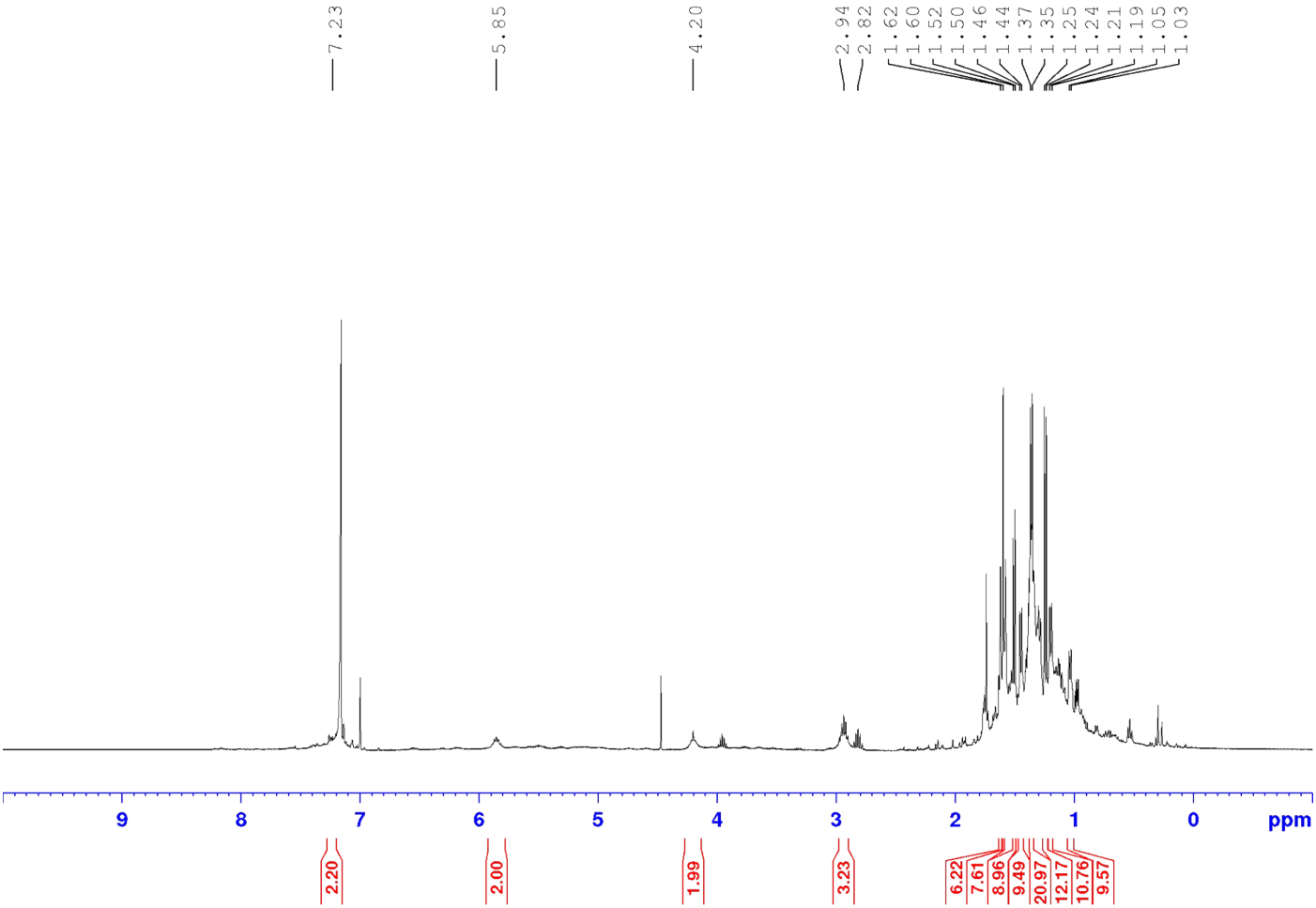



**Figure S 33**. $^1$H NMR Spectrum of Compound **12** – AlAl$^{(Tipp)}$ + $H_2$, in $C_6D_6$

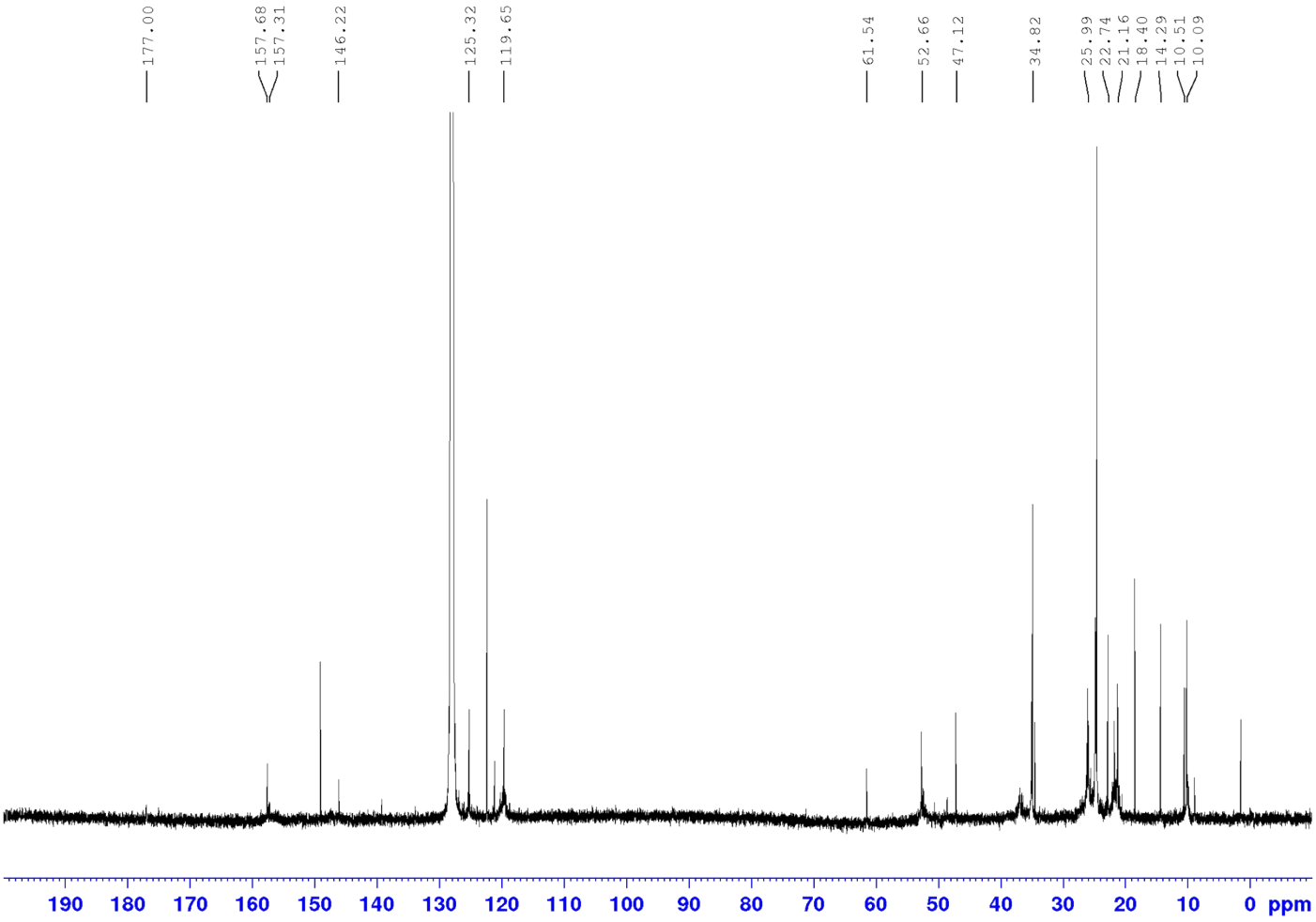



**Figure S 34.** $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **12** – $AlAl^{(Tipp)}$ + $H_2$, in $C_6D_6$

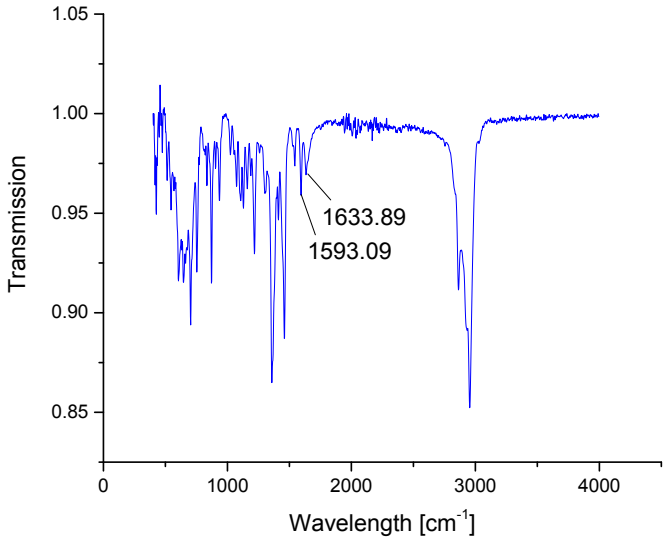



**Figure S 35.** IR Spectrum of Compound **12** – $AlAl^{(Tipp)}$ + $H_2$

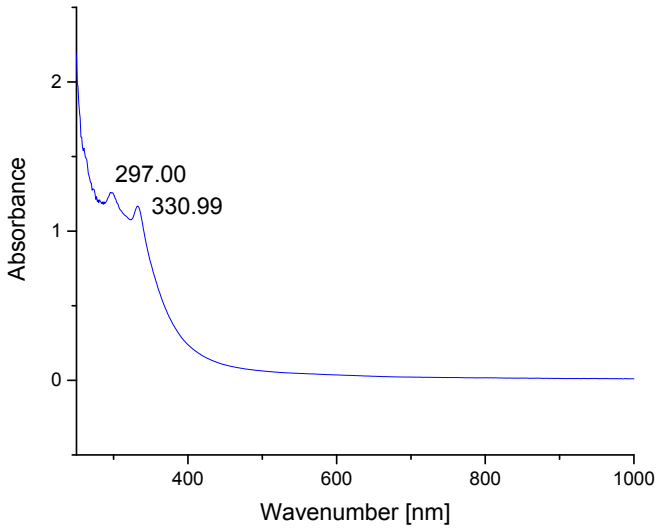



**Figure S 36.** UV/vis of Compound **11 –** $AlAl^{(Tipp)}$ + $H_2$, in pentane

## 1.3 Supporting Spectra for Reactivity

**Rearrangement of Al=Al$^{(Tipp)}$ + PhCCH**

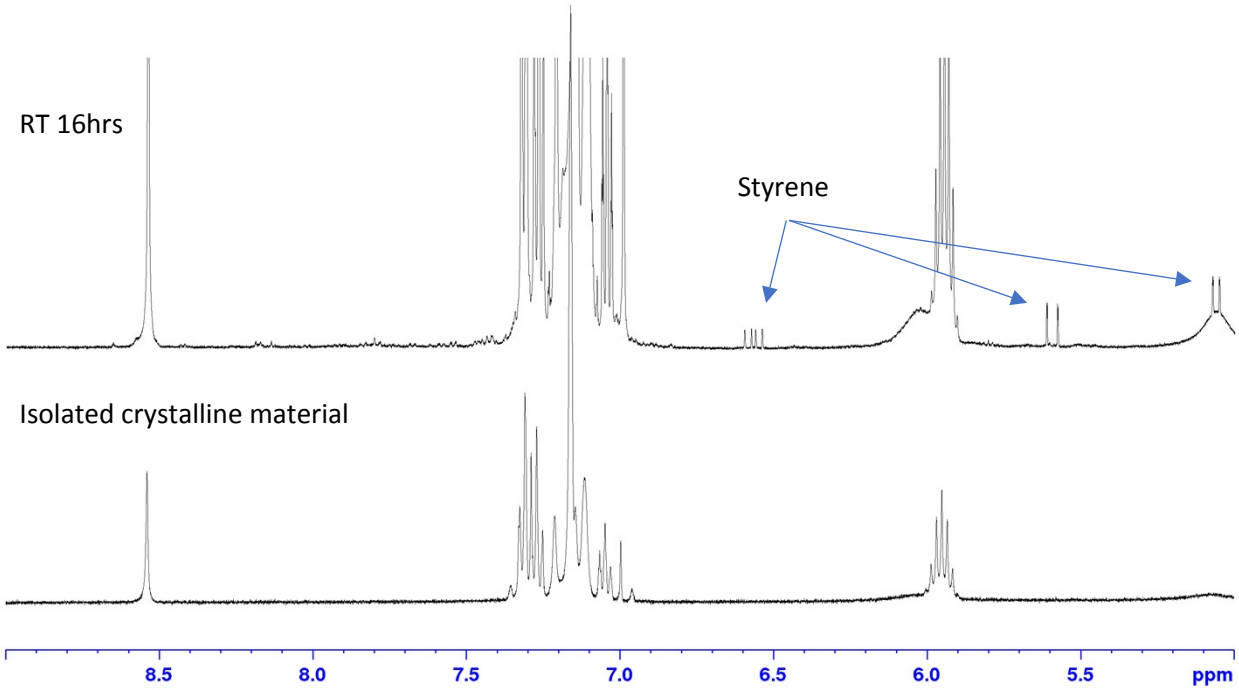



**Figure S 37.** $^{1}$H NMR Stack plot (9.0 – 5.0 ppm) for rearrangement of Compound **5** – AlAl$^{(Tipp)}$ + PhCCH, in $C_6D_6$ from isolated crystalline material

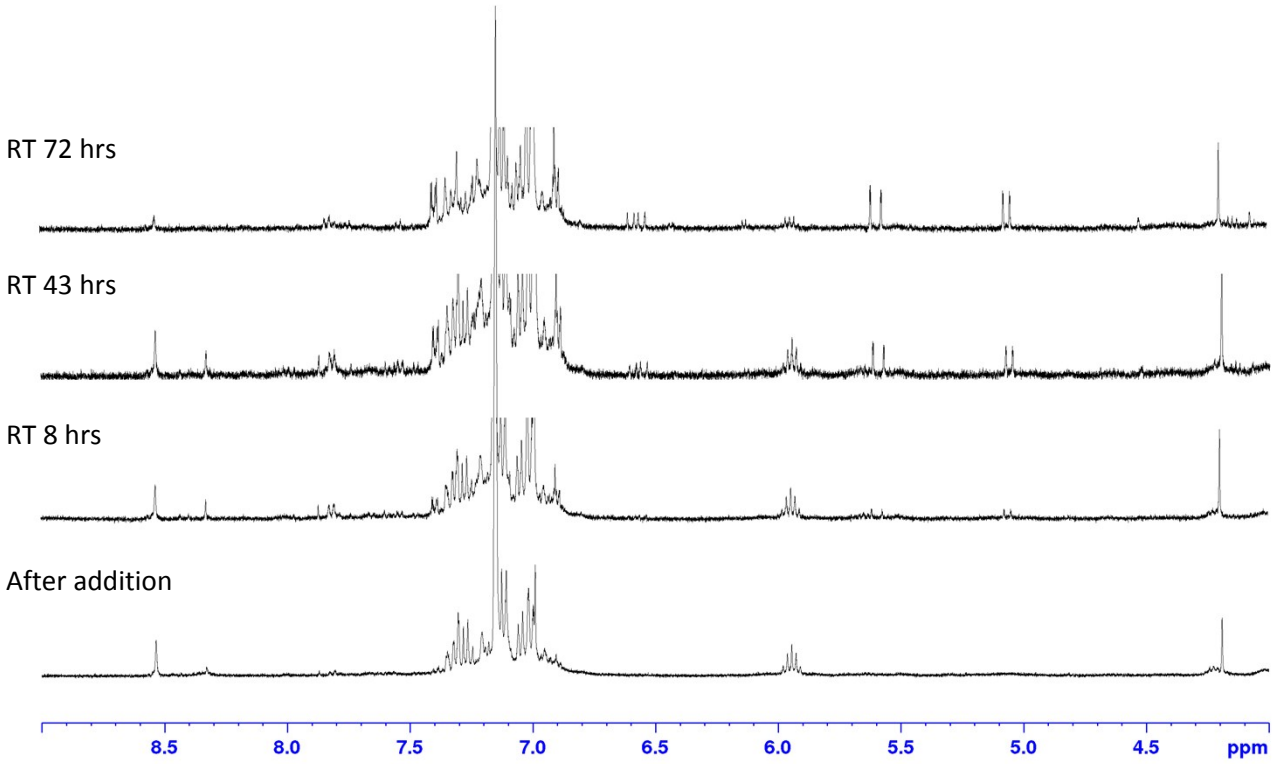



**Figure S 38.** $^{1}$H NMR Stack plot (9.0 – 4.0 ppm) for rearrangement of Compound **5** – AlAl$^{(Tipp)}$ + PhCCH, in $C_6D_6$, from reaction mixture. Compound **3** (15 mg, 18.2 µmol) was dissolved in 0.5 mL of $C_6D_6$, PhCCH (2.0 µL, 18.2 µmol) was

added via syringe at room temperature. The reaction mixture instantly changed from the black colour of **3** to yellow and was monitored at regular intervals by $^{1}$H NMR.

**Small Molecule Activation Reactions**

Dialumene **3** (30 mg, 37 µmol) in 0.5 mL $C_6D_6$ and N-Methylmorpholine N-oxide (4 mg, 37 µmol) were added to a Teflon tapped NMR tube, instant colour change from black to red (formation of compound **11**) was observed and 1H NMR was taken. To the NMR tube containing the *insitu* generated compound **11** a further equivalent of N-Methylmorpholine N-oxide (4 mg, 37 µmol) was added, colour change from red to yellow which then further faded to colourless was observed (formation of compound **10**) and $^{1}$H NMR was taken.

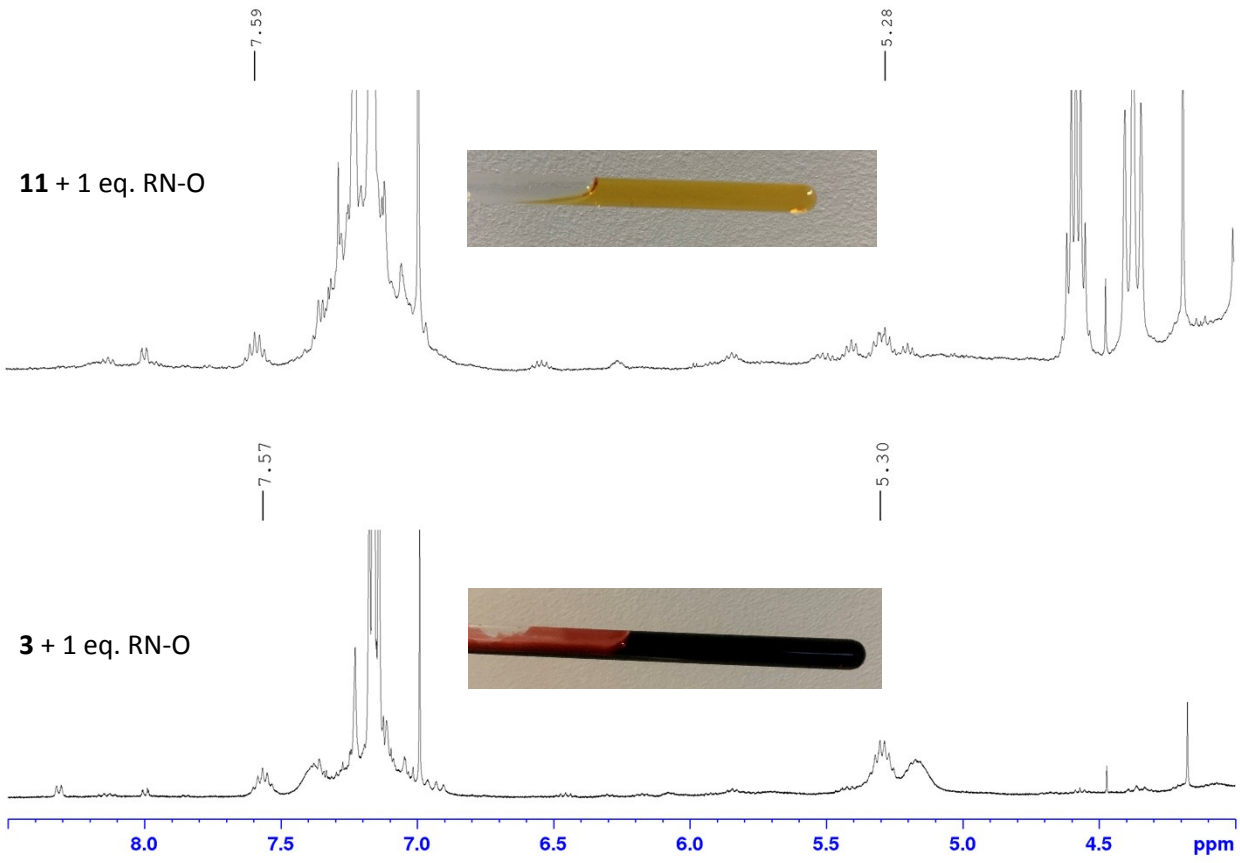



**Figure S 39.** Stacked $^{1}$H NMR spectra for sequential N-Methylmorpholine N-oxide addition to **3**, in $C_6D_6$.

## 1.4 Catalysis

### $CO_2$ Hydroboration

*General Procedure:* Dialumene **3** (10 mg, 5 mol%) in 0.5 mL $C_6D_6$ and Pinacol borane (34 µL 0.24 mmol) were added to a Teflon tapped NMR tube. The solution was freeze–pump– thaw degassed three times before being refilled with 1 bar of $CO_2$. The $^{1}H$ and $^{11}B$ NMR spectra were recorded and then regularly monitored by NMR spectroscopy until >80% consumption of HBpin.

Dialumene **3** (2 mg, 1 mol%) in 0.5 mL $C_6D_6$ and Pinacol borane (34 µL, 0.24 mmol) were added to a Teflon tapped NMR tube. The solution was freeze–pump– thaw degassed three times before being refilled with 1 bar of $CO_2$. The $^{1}H$ and $^{11}B$ NMR spectra were recorded and then placed in an oil bath at 60 °C and regularly monitored by NMR spectroscopy until >80% consumption of HBpin.

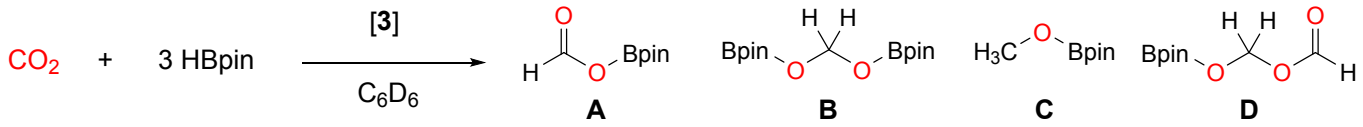



**Table S 1.** Product distribution across the 3 catalytic reactions. Yields calculated based on relative NMR integrals

| Entry | Catalyst Loading/ mol % | Time/ hr | Temperature/ °C | HBpin consumed/ % | Product distribution/ % | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | A | B | C | D |
| 1 | 5 | 58 | 20 | 81 | 39 | 27 | 34 | 0 |
| 2 | 5 | 24 | 20 | 66 | 65 | 15 | 17 | 3 |
| 3 | 1 | 24 | 60 | 62 | 49 | 7 | 41 | 3 |

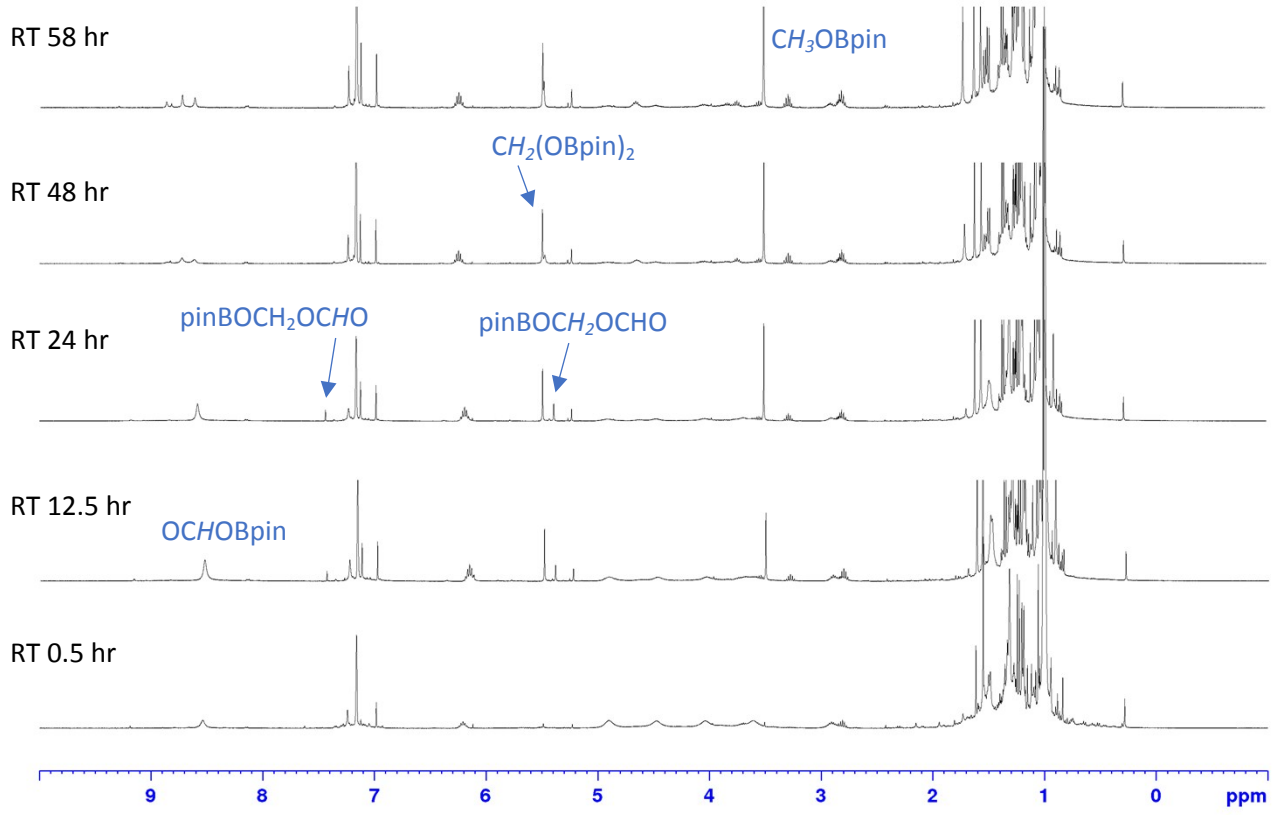



**Figure S 40.** Stacked $^{1}H$ NMR spectra for 5 mol% **3** with HBpin and 1 atm of $CO_2$ at Room Temperature in $C_6D_6$

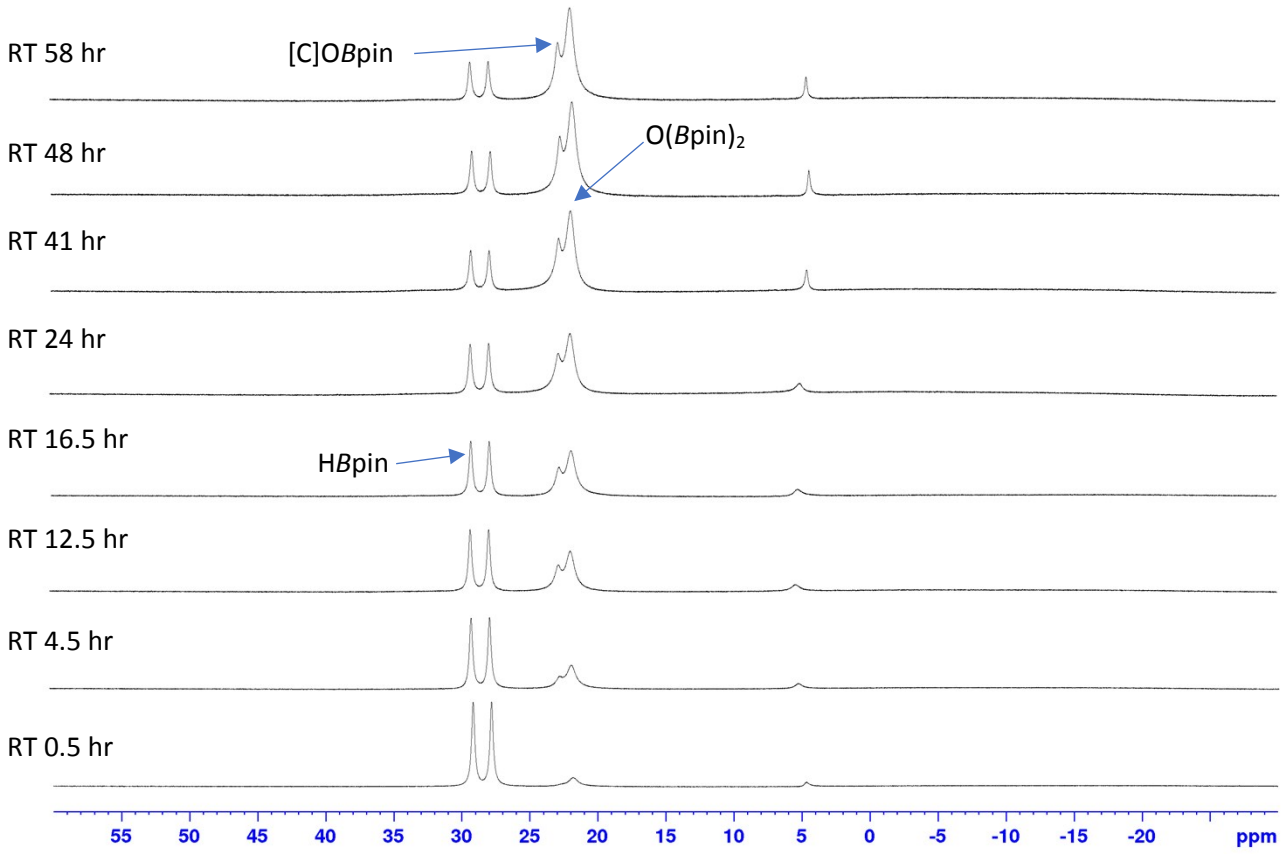



**Figure S 41.** Stacked $^{11}$B NMR spectra for 5 mol% **3** with HBpin and 1 atm of $CO_2$ at Room Temperature in $C_6D_6$

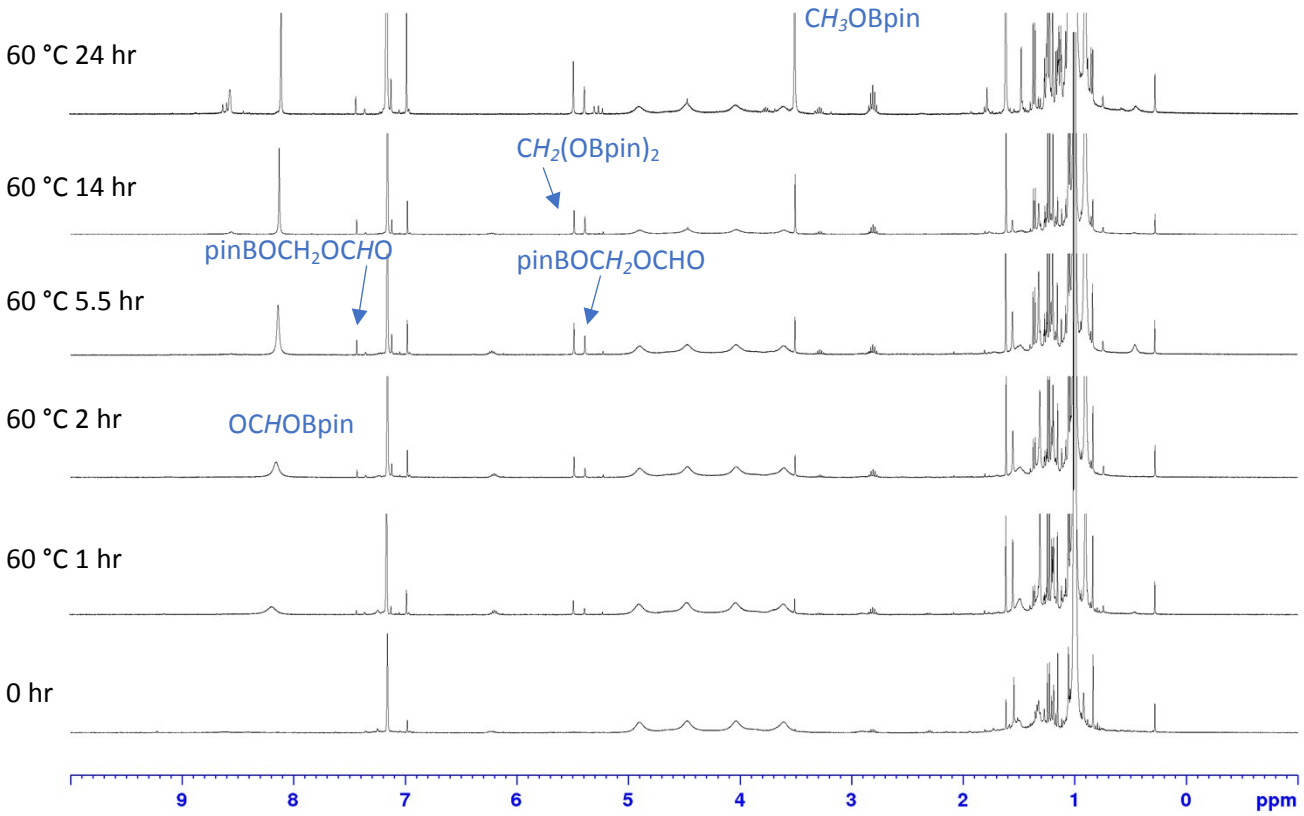



**Figure S 42.** Stacked $^{1}$H NMR spectra for 1 mol% **3** with HBpin and 1 atm of $CO_2$ at 60 °C in $C_6D_6$

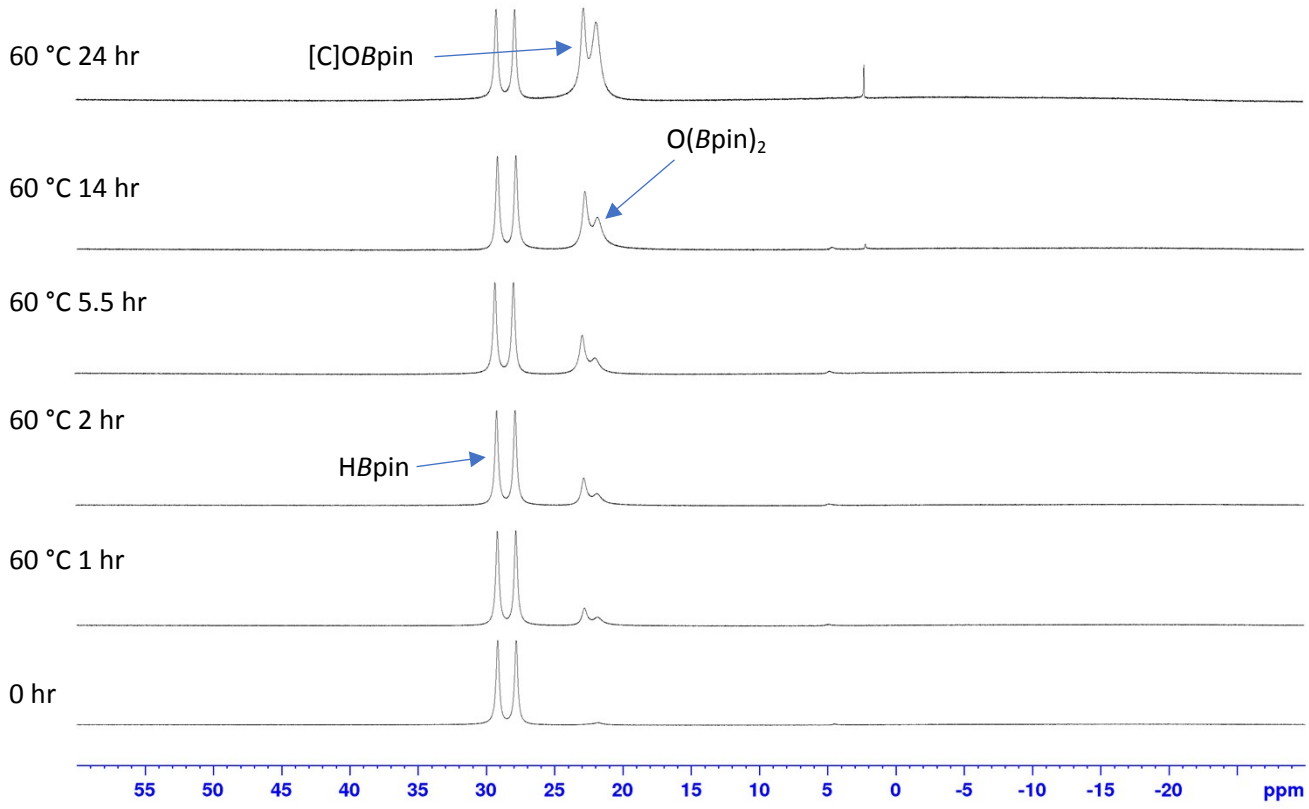



**Figure S 43.** Stacked $^{11}$B NMR spectra for 1 mol% **3** with HBpin and 1 atm of $CO_2$ at 60 °C in $C_6D_6$

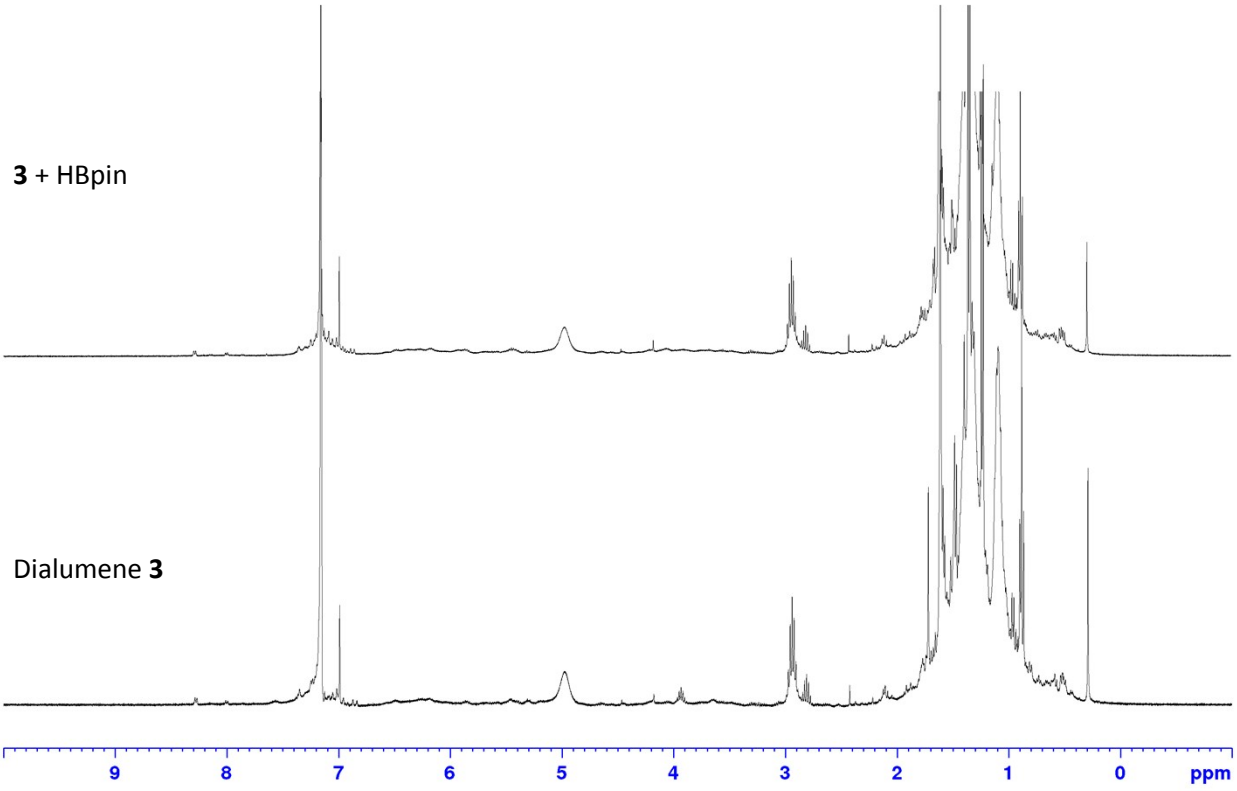



**Figure S 44.** Stacked $^{1}$H NMR spectrum for reaction of 1 eq. of HBpin (1.6 µL, 24 µmol) and dialumene **3** (20 mg, 24 µmol). No apparent change via $^{1}$H spectroscopy.

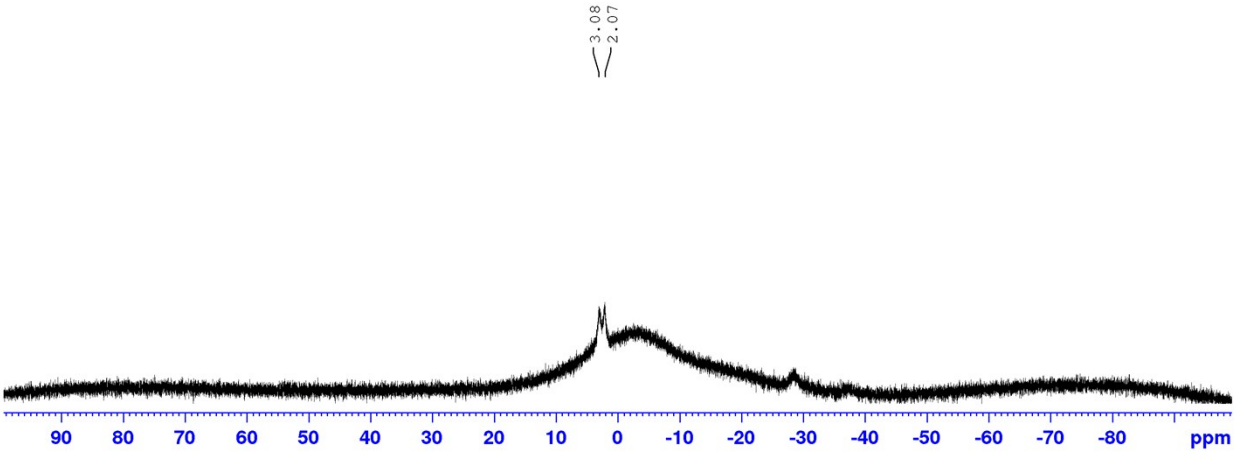



**Figure S 45.** $^{11}$B NMR spectrum for reaction of 1 eq. of HBpin (1.6 µL, 24 µmol) and dialumene **3** (20 mg, 24 µmol). Complete consumption of HBpin and formation of new 4-coordinate boron species (δ 2.57 ppm $J_{HB}$ = 129.8 Hz).

### Amine Borane Dehydrogenation

*General Procedure:* Aluminium catalyst (5 mol%) in 0.5 mL $C_6D_6$ and dimethylaminoborane (21 mg, 0.35 mmol) were added to a Teflon tapped NMR tube. The $^1$H and $^{11}$B NMR spectra were recorded and then regularly monitored by NMR spectroscopy until >80% consumption of $Me_2NHBH_3$.

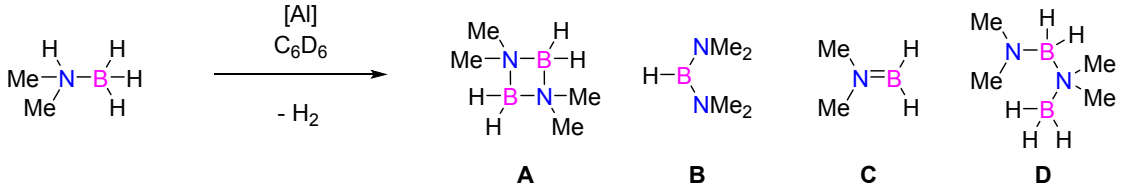



**Table S 2.** Product distribution across the 4 catalytic reactions. Yields calculated based on relative NMR integrals

| Entry | Catalyst | Catalyst loading / mol % | Temp/ °C | Time/ hr | Conversion / % | Product distribution | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | A | B | C | D | Others |
| 1 | **1** | 5 | 60 | 24 | 31 | 11 | - | - | 15 | 5 |
| 2 | **3** | 5 | 20 | 44 | 78 | 35 | 5 | - | 23 | - |
| 3 | **3** | 1 | 20 | 16.5 | 60 | 45 | 1 | <1 | 14 | - |
| 4 | **3$^{Si}$** | 5 | 20 | 16.5 | 17 | 5 | 1 | - | 11 | - |

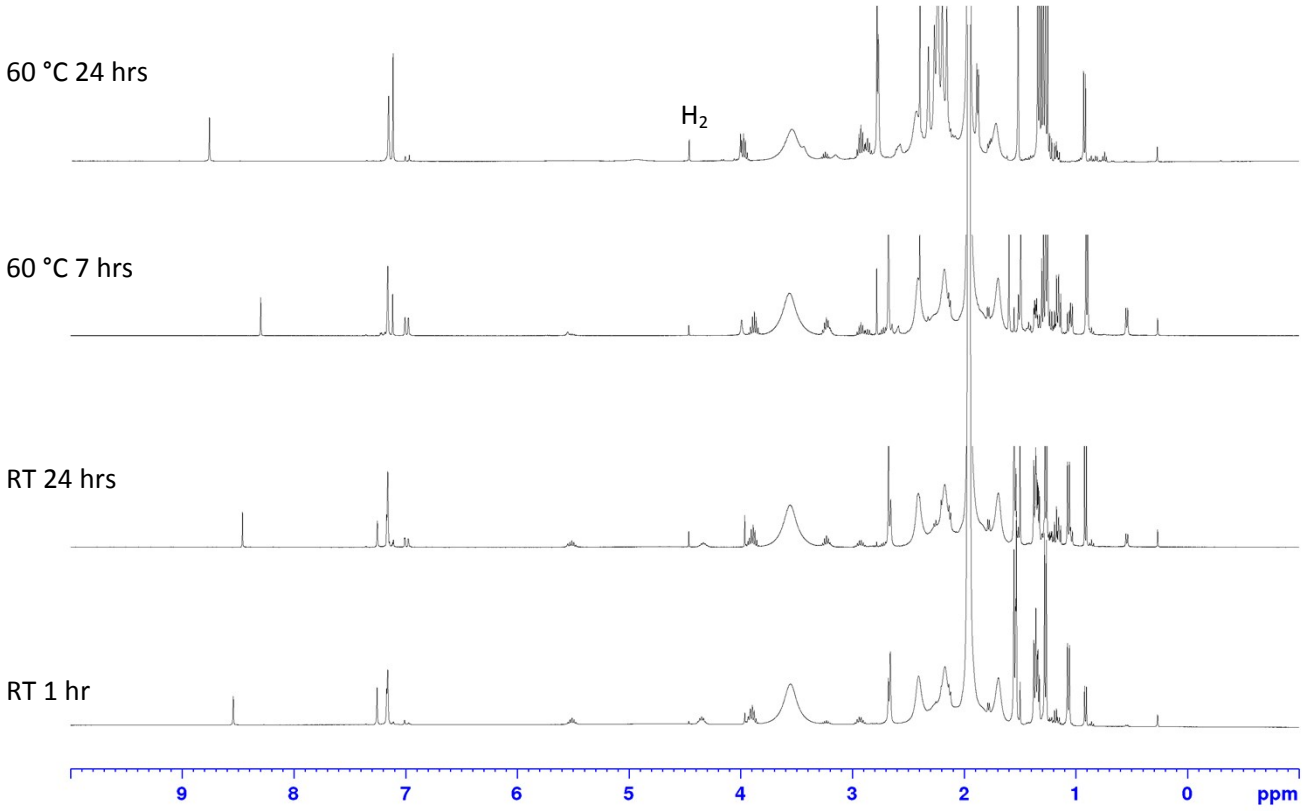



**Figure S 46.** Stacked $^{1}H$ NMR spectra for 5 mol% **1** (7 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature then 60 °C in $C_6D_6$ (Entry 1).

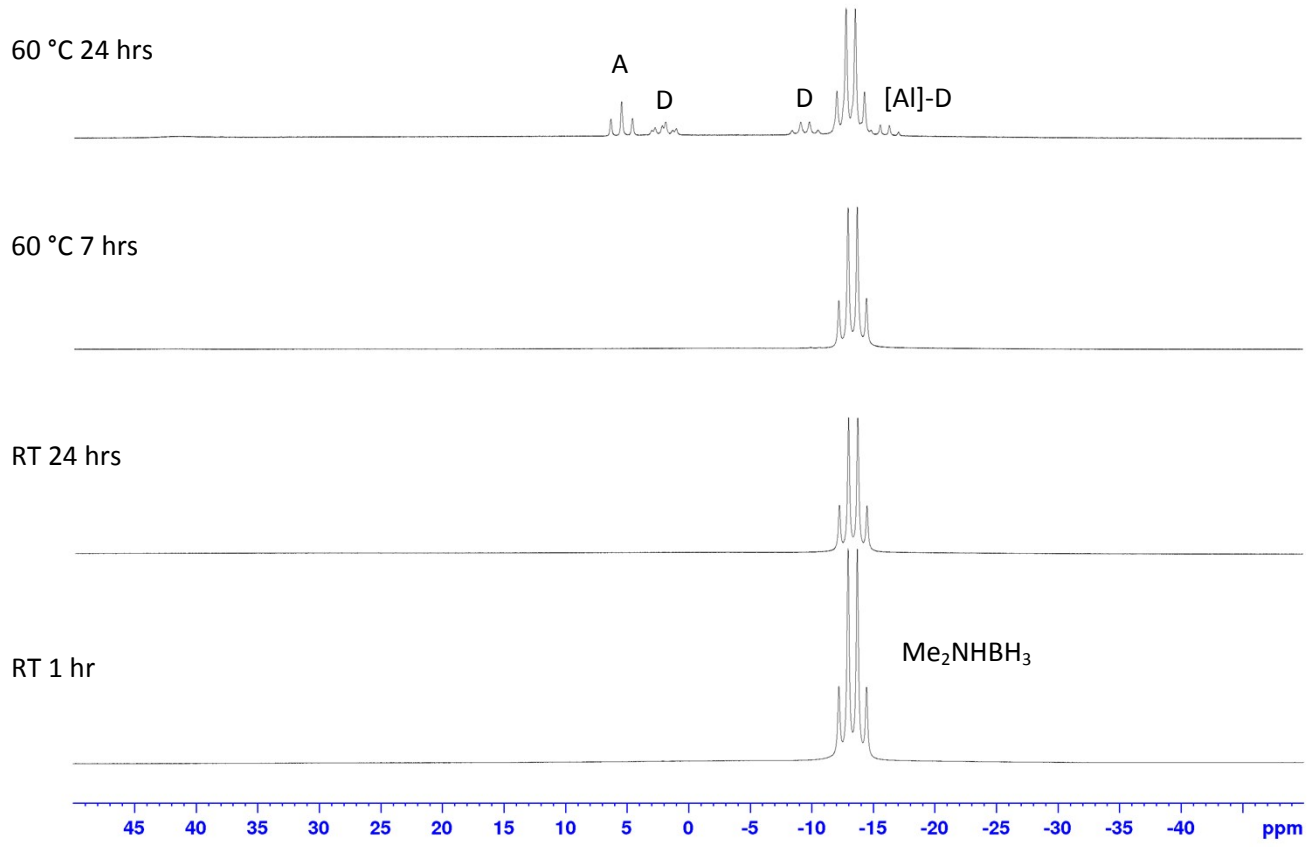



**Figure S 47.** Stacked $^{11}B$ NMR spectra for 5 mol% **1** (7 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature then 60 °C in $C_6D_6$ (Entry 1).

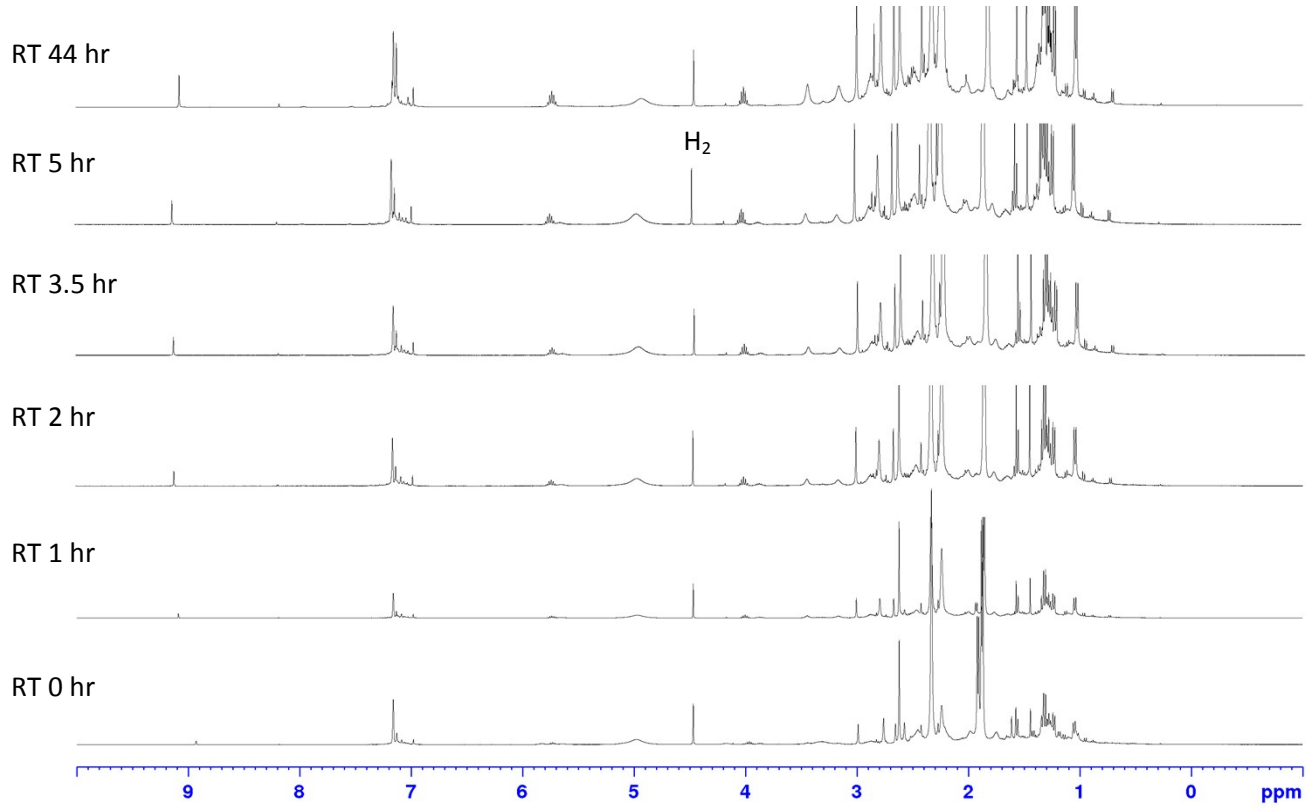



**Figure S 48.** Stacked $^{1}H$ NMR spectra for 5 mol% **3** (14 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 2).

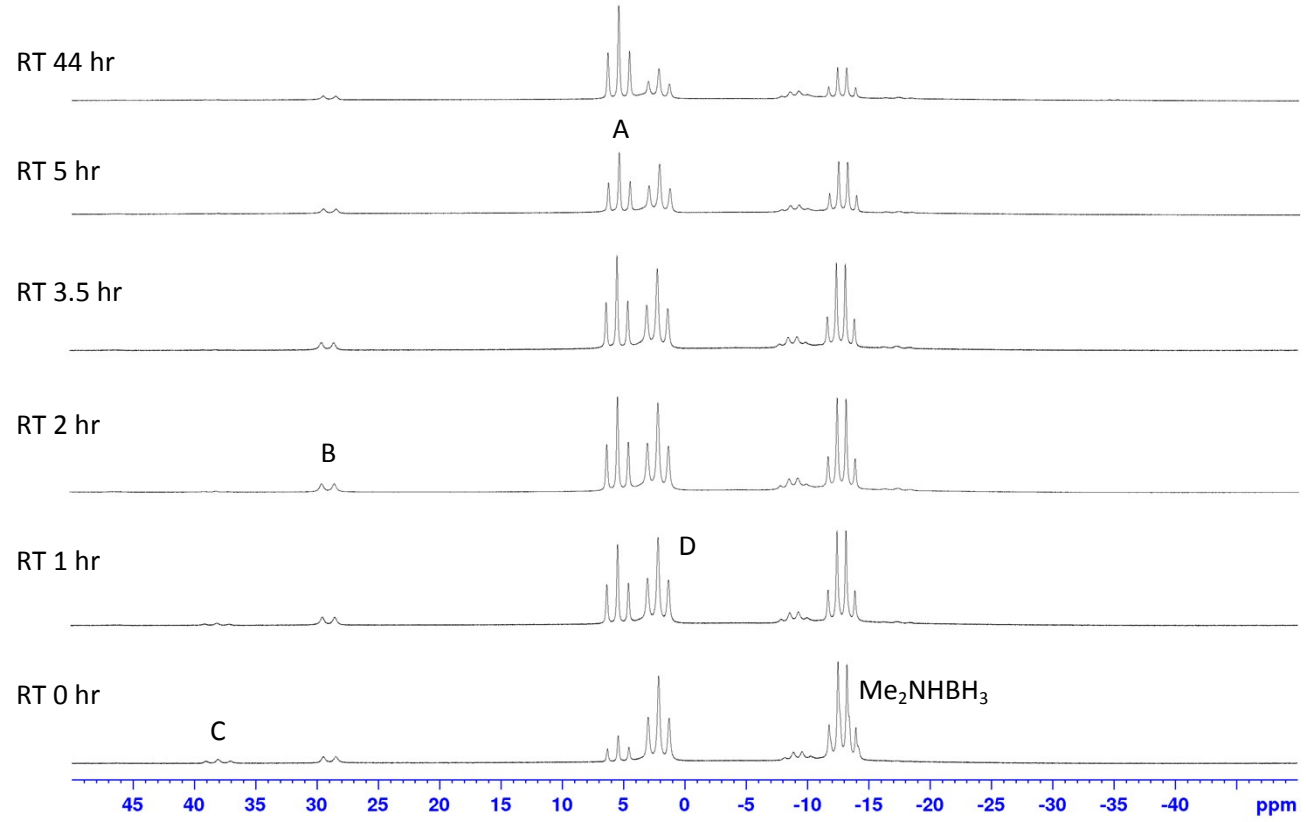



**Figure S 49.** Stacked $^{11}B$ NMR spectra for 5 mol% **3** (14 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 2).

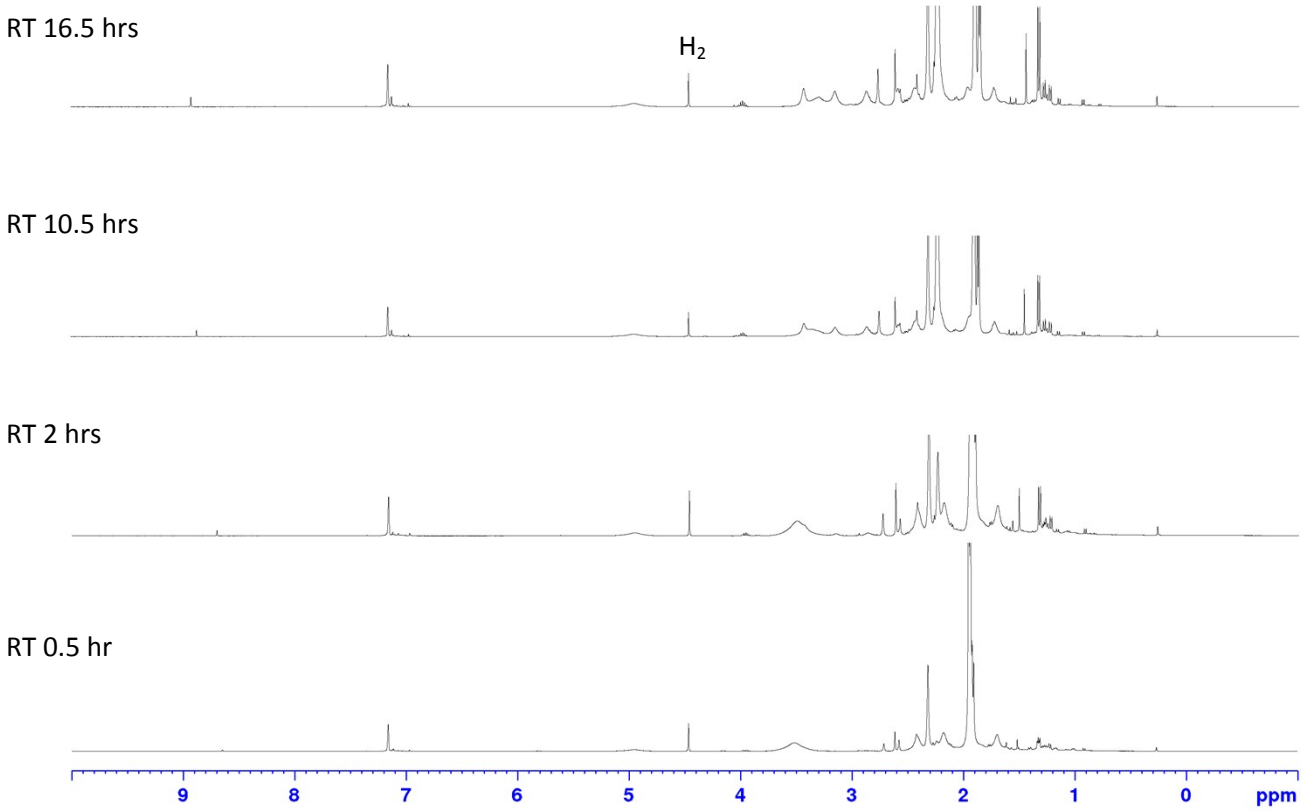



**Figure S 50.** Stacked $^{1}H$ NMR spectra for 1 mol% **3** (3 mg, 1 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 3).

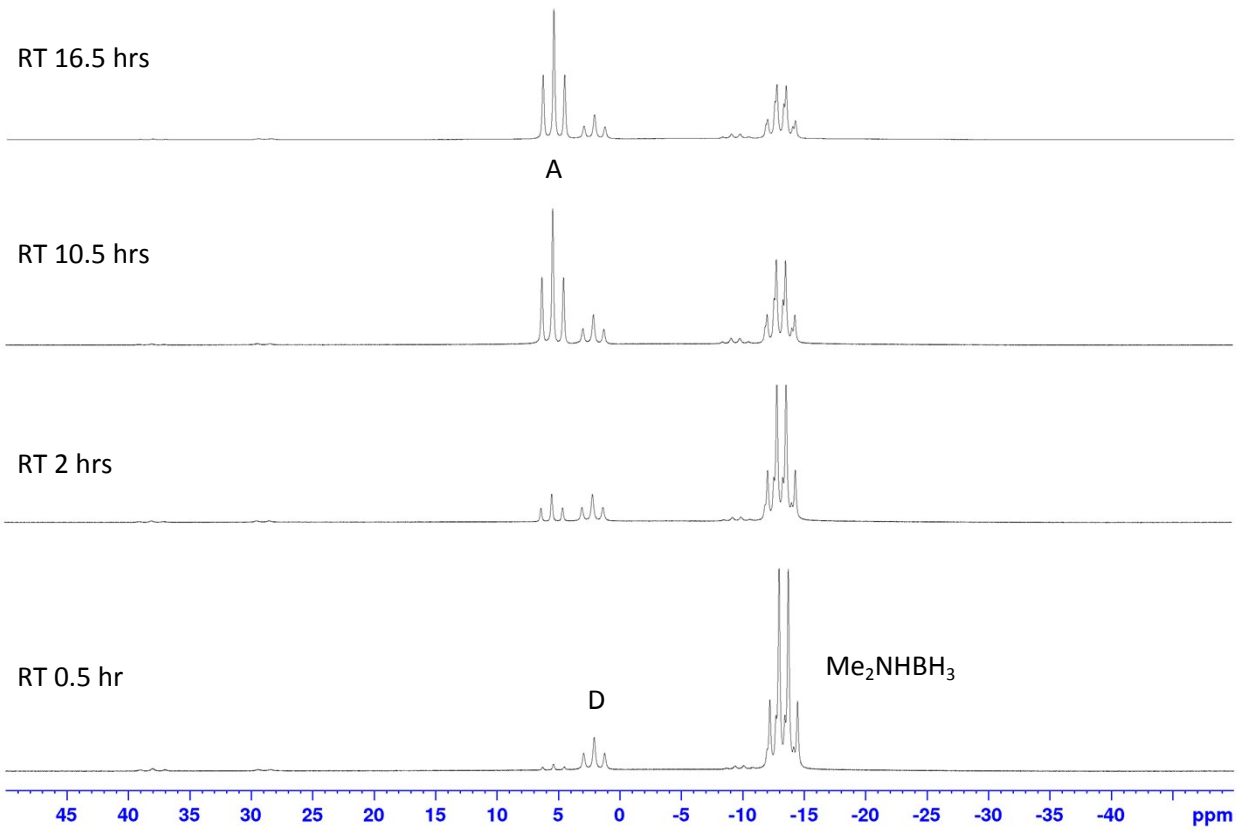



**Figure S 51.** Stacked $^{11}B$ NMR spectra for 1 mol% **3** (3 mg, 1 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 3).

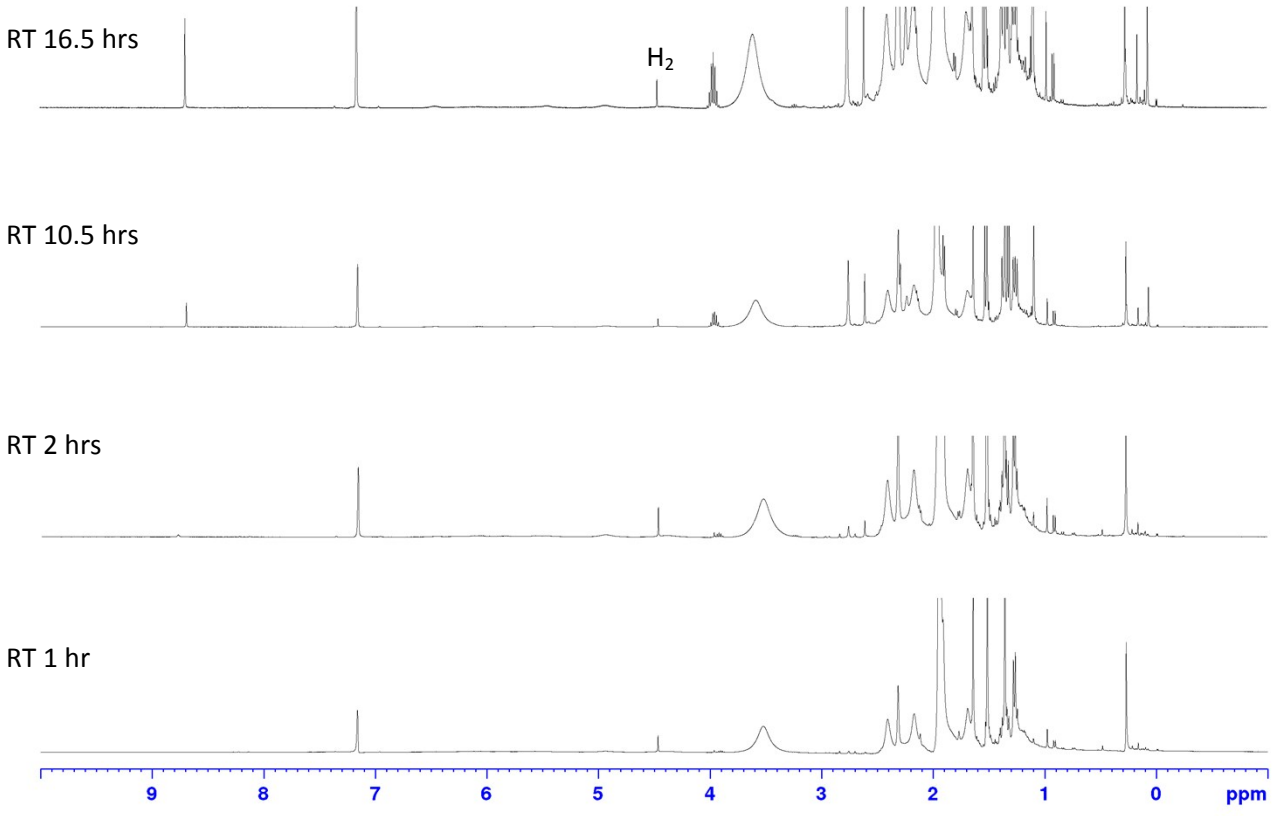



**Figure S 52.** Stacked $^{1}H$ NMR spectra for 5 mol% $\mathbf{3^{Si}}$ (13 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 4).

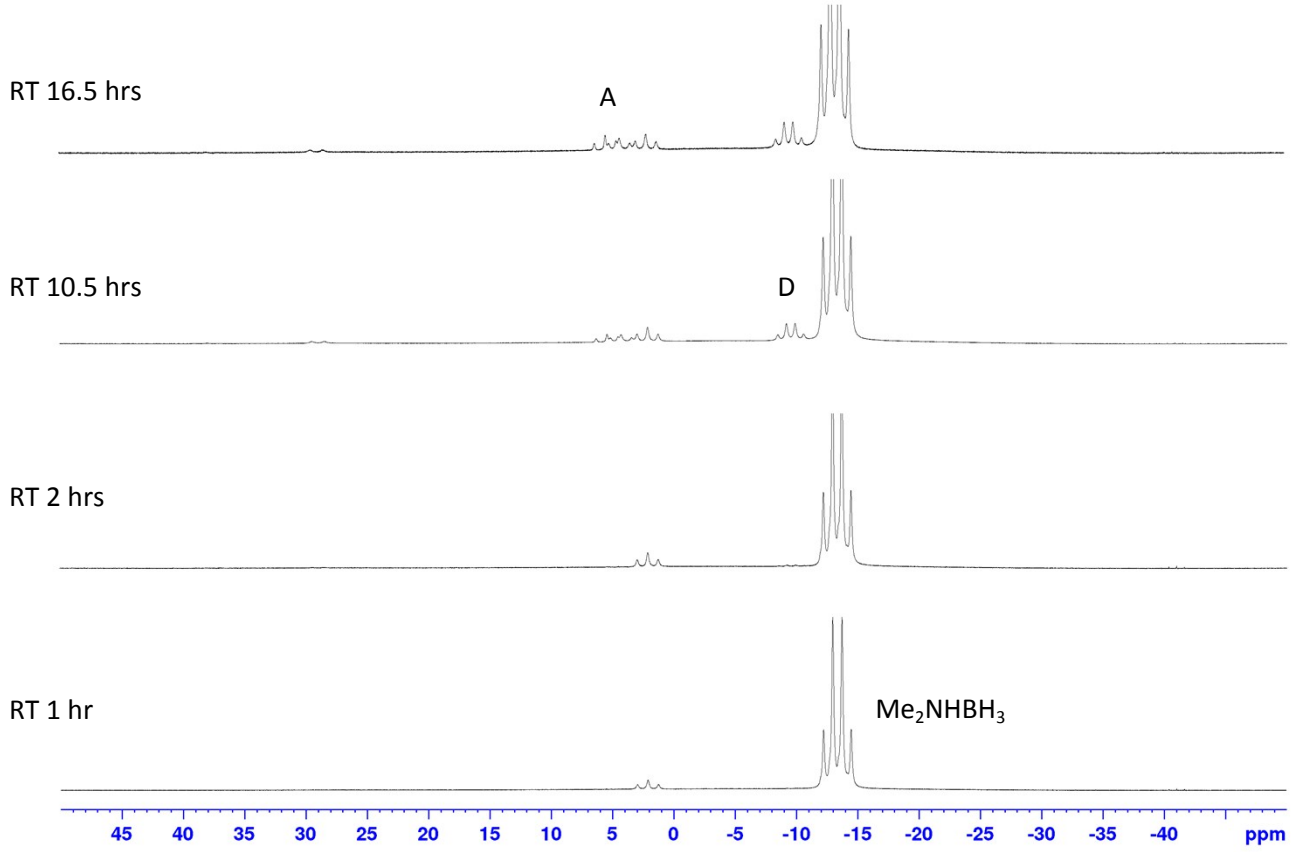



**Figure S 53.** Stacked $^{11}B$ NMR spectra for 5 mol% **3$^{Si}$** (13 mg, 5 mol%) with $Me_2NHBH_3$ at Room temperature in $C_6D_6$ (Entry 4).

## 2. X-Ray Crystallography

### 2.1 General Procedures

Crystallographic data were collected on the single crystal X-ray diffractometers “Apex II CCD” equipped with a fine-focus sealed tube source, a Triumph monochromator and a CCD detector (7), “Bruker Photon CMOS” equipped with a IMS microsource, a Helios optic monochromator and a CMOS plate detector (2, 4, 6) and a “Bruker Photon CMOS” equipped with a TXS rotating anode source, a Helios optic monochromator and a CMOS plate detector (3, 11). The data collection was performed, using the APEX II[S5] and APEX III[S6] software package on single crystals coated with Fomblin® Y as perfluorinated ether. The crystals were fixed on the top of a kapton micro sampler with perfluorinated ether, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[S7] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[S7] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved using direct methods with the aid of successive difference Fourier maps, and were refined against all data using the APEX II and APEX III software in conjunction with SHELXL-2014[S8] and SHELXLE.[S9] Hydrogen atoms were calculated in ideal positions as follows: methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and Uiso(H) = 1.5·Ueq(C). Methylene, aromatic and other H atoms were placed in calculated positions and refined using a riding model with C–H distances of 0.99 Å, 0.95 Å and 1.00 Å, respectively, and Uiso(H) = 1.2Ueq(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing Σw(Fo2-Fc2)2 with the SHELXL weighting scheme.[S10] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S11] A split layer refinement was used for disordered groups and SIMU, DELU and SAME restraints were employed to stabilize the refinement of the layers. All images were created using mercury.[S12]

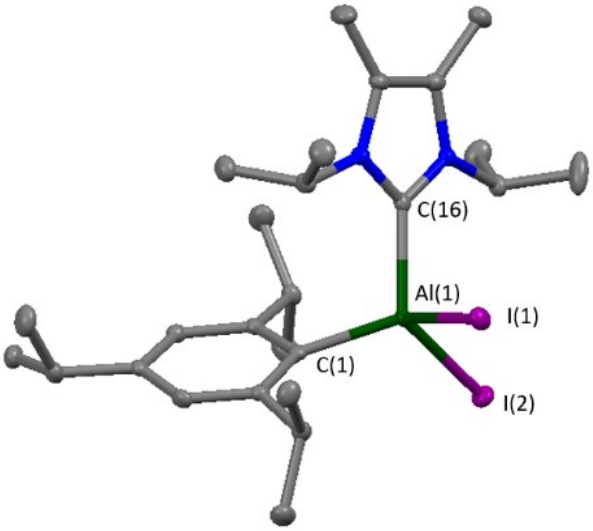



**Figure S 54.** Molecular structure of compound **2** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles(°): Al(1)-C(1) 1.9887(19), Al(1)-C(16) 2.0645(18), Al(1)-I(1) 2.5968(9), Al(1)-I(2) 2.5762(8), C(1)-Al(1)-(C16) 107.86(7), I(1)-Al(1)-I(2) 102.93(2).

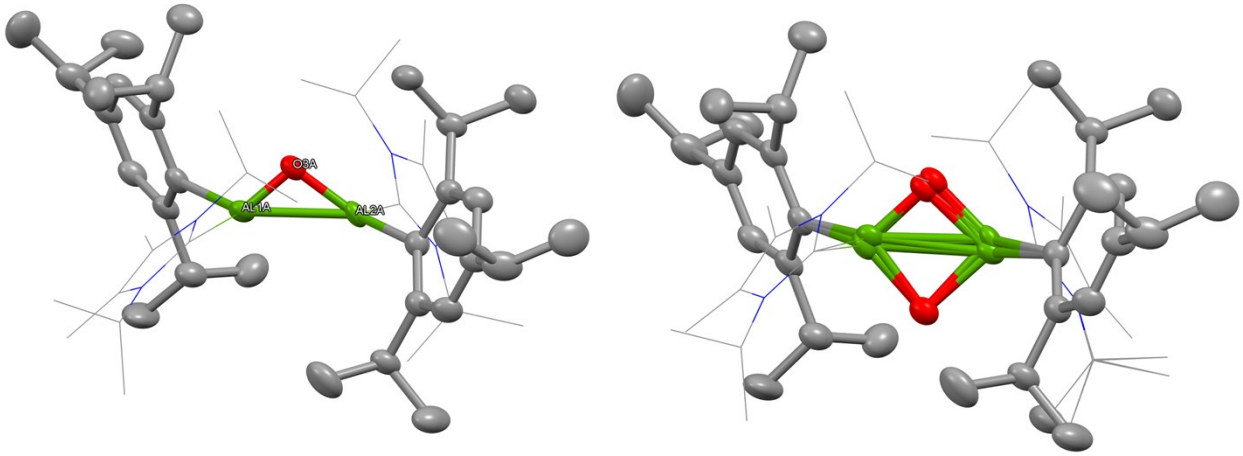



**Figure S 55.** Molecular structure of compound **11** in the solid state. Ellipsoids are set at the 50% probability level; NHC ligands are depicted in wire frame and hydrogen atoms are omitted for clarity. Part A disorder (left); Full structure (right). Due to presence of disorder around the central Al-O core, key bond lengths and angles are not discussed.

## 2.2 X-ray Crystallographic Table

| Compound (CCDC code) | 2 (1989167) | 3 (1989168) | 4 (1989169) | 6 (1989170) | 7 (1989171) | 11 (1989172) |
|---|---|---|---|---|---|---|
| **Molecular formula** | $C_{26}H_{43}Al_1N_2I_2$ | $C_{55}H_{93}Al_2N_4$ | $C_{54}H_{90}Al_2N_4$ | $C_{72}H_{102}Al_2N_4$ | $C_{70}H_{104}Al_2N_6$ | $C_{58}H_{100}Al_2N_4O_{1.79}$ |
| **Molecular weight** | 664.40 | 864.29 | 849.26 | 1077.54 | 1083.55 | 936.20 |
| **Space group** | P21/n | C2/c | P21/c | P2/c | C2/c | C2/c |
| **a (Å)** | 10.145(2) | 35.126(3) | 12.4062(10) | 13.5339(6) | 21.6994(18) | 36.035(2) |
| **b (Å)** | 17.053(4) | 15.4352(11) | 18.1378(16) | 13.5131(6) | 15.8898(18) | 15.3951(8) |
| **c (Å)** | 17.044(3) | 21.8147(17) | 24.620(2) | 18.1559(6) | 20.777(2) | 21.8876(12) |
| **α °** | 90 | 90 | 90 | 90 | 90 | 90 |
| ***β* °** | 102.029(8) | 109.512(4) | 101.846(3) | 100.481(2) | 90.177(8) | 104.190(3) |
| **γ °** | 90 | 90 | 90 | 90 | 90 | 90 |
| **Volume (Å$^3$)** | 2883.9(10) | 11148.2(15) | 5422.0(8) | 3265.0(2) | 7163.9(12) | 11771.9(11) |
| **$D_C$ (g cm$^{-3}$)** | 1.530 | 1.030 | 1.040 | 1.096 | 1.005 | 1.056 |
| **μ (mm$^{-1}$)** | 2.227 | 0.088 | 0.090 | 0.087 | 0.081 | 0.090 |
| **Reflections collected** | 80760 | 226432 | 73016 | 95226 | 101077 | 85121 |
| **Unique reflections** | 5252 | 10196 | 9874 | 5992 | 6569 | 10794 |
| **Parameters varied** | 292 | 605 | 581 | 395 | 510 | 766 |
| **$R_{int}$** | 0.0330 | 0.0431 | 0.0693 | 0.0563 | 0.0552 | 0.0443 |
| **$R_1$** | 0.0151 (I>2σ(I))<br>0.0174 (all data) | 0.0471 (I>2σ(I))<br>0.0536 (all data) | 0.0645 (I>2σ(I))<br>0.0949 (all data) | 0.0406 (I>2σ(I))<br>0.0460 (all data) | 0.0747 (I>2σ(I))<br>0.0884 (all data) | 0.0582 (I>2σ(I))<br>0.0845 (all data) |
| **$wR_2$** | 0.0367 (I>2σ(I))<br>0.0385 (all data) | 0.1268 (I>2σ(I))<br>0.1328 (all data) | 0.1672 (I>2σ(I))<br>0.1923 (all data) | 0.0962 (I>2σ(I))<br>0.0997 (all data) | 0.1843 (I>2σ(I))<br>0.1924 (all data) | 0.1440 (I>2σ(I))<br>0.1602 (all data) |

## 3. DFT Calculations

### 3.1 General Information

Geometry optimizations and harmonic frequency calculations were performed using *Gaussian09*[S13] employing the B3LYP-D3[S14-18]/6-311G(d)[S19,20] level of density functional theory. The SMD polarizable continuum model was used to account for solvent effects of benzene.[S21] Stationary points are characterized as minima by analysis of computed Hessians. Optimization of the small model systems were performed retaining $C_i$ symmetry. For improved energies, single point calculations were conducted at the SMD-B3LYP-D3/6-311G(2d,2p) [S19,20] level. Natural Bond Orbital (NBO) analysis were performed on the B3LYP-D3/6-311G(2d,2p)[S19,20] level of theory using the *NBO 6.0* program,[S22] interfaced with *Gaussian09*.[S23,24] Pictures of molecular structures were generated with the ChemCraft[S25], Mercury[S26] or GaussView[S27] programs.

### 3.2 Results

**Table S 3.** Comparison of selected bond length [Å], angles, dihedral, trans-bent and twisted angles [°] for the calculated and experimental structures of **3**, **3$^{Si}$** and **7**. Geometries are calculated at the B3LYP-D3/6-311G(d) level of theory. Experimental data are taken from SC-XRD analysis. θ represents the *trans*-bent angle and τ the twist angle.

| Compound | bond/angle/dihedral | exp. | calc. | Δ(calc.-exp.) |
|---|---|---|---|---|
| **3** | r($Al^1Al^2$) | 2.4039(8) | 2.38 | 0.02 |
| | r($Al^{1/2}C^{1/C27}$) | 2.029(2)/2.018(2) | 2.02/2.02 | 0.01/0.00 |
| | r($Al^{1/2}C^{16/C42}$) | 2.060(2)/2.042(2) | 2.05/2.04 | 0.01/0.00 |
| | a($C^{1/27}Al^{1/2}C^{16/42}$) | 110.27(7)/112.84(7) | 107.5/113.4 | 2.8/0.6 |
| | d($C^1Al^1Al^2C^{27}$) | -167.04(9) | -172.1 | 5.1 |
| | d($C^{16}Al^1Al^2C^{42}$) | -175.54(8) | -177.5 | 2.0 |
| | d($C^1Al^1Al^2C^{42}$) | 35.81(9) | 32.6 | 3.2 |
| | d($C^{16}Al^1Al^2C^{27}$) | -18.39(9) | -22.2 | 3.8 |
| | θ | 17.25/23.70 | 19.0/21.5 | 1.8/2.2 |
| | τ | 12.06 | 7.2 | 4.9 |
| **3$^{Si}$*** | r($Al^1Al^{1'}$) | 2.394(1) | 2.39 | 0.00 |
| | r($Al^1Si^1$) | 2.494(1) | 2.47 | 0.02 |
| | r($Al^1C^1$) | 2.072(3) | 2.08 | 0.01 |
| | a($Si^1Al^1C^1$) | 116.21(9) | 114.7 | 1.5 |
| | d($Si^1Al^1Al^{1'}Si^{1'}$) | 180.00(7) | 171.3 | 8.7 |
| | d($C^1Al^1Al^{1'}C^{1'}$) | 180.0(1) | 173.3 | 6.7 |
| | d($Si^1Al^1Al^{1'}C^{1'}$) | 1.2(1) | 7.7 | 6.5 |
| | θ | 0.71 | 0.7 | 0.0 |
| | τ | 0.00 | 7.4 | 7.4 |
| **7** | r($Al^1C^1$) | 2.042(7) | 2.04 | 0.00 |
| | r($Al^1C^{16}$) | 2.109(3) | 2.11 | 0.00 |
| | r($Al^1C^{27}$) | 2.059(3) | 2.05 | 0.01 |
| | r($C^{27}$-$N^3$) | 1.292(4) | 1.29 | 0.00 |
| | r($Al^1Al^{1'}$) | 2.948(1) | 2.93 | 0.02 |
| | r($C^{27}C^{27'}$) | 2.718(4) | 2.70 | 0.02 |
| | a($Al^1C^{27}Al^{1'}$) | 91.6(1) | 91.0 | 0.6 |
| | a($C^{27}Al^1C^{27'}$) | 82.7(1) | 82.2 | 0.5 |
| | a($C^{27}N^1C^{28}$) | 126.3(2) | 127.2 | 0.9 |

*in the original publication the calculations on **3$^{Si}$** were performed without dispersion, which is however important in the Tipp-substituted case **3** and was thus also applied to **3$^{Si}$** for comparative reasons.

**Calculated properties**

**Table S 4.** Calculated transitions and UV-Vis absorption bands using TD-DFT (time-dependent-DFT) for **3**.

| Wavelength [nm] | MO contributions | f | Contribution |
|---|---|---|---|
| 794 | HOMO→LUMO | 0.1977 | 96.4% |
| 661 | HOMO→LUMO+1 | 0.0296 | 95.4% |
| 634 | HOMO→LUMO+2 | 0.0107 | 98.5% |
| 592 | HOMO→LUMO+3<br>HOMO→LUMO+4 | 0.0271 | 89.5%<br>4.6% |
| 518 | HOMO→LUMO+5 | 0.0262 | 95.34% |
| 448 | HOMO→LUMO+10 | 0.0925 | 89.5% |

**Table S 5**. Monomerisation energies of dialumenes **3** and **3$^{Si}$**.

| Compound | $\Delta G_{298}$ [kcal/mol] | $D^0(0)$ [kcal/mol] | $\Delta G_{298}{}^{03}$ [kcal/mol] | $D^0(0)^{03}$ [kcal/mol] |
|---|---|---|---|---|
| **3** | 22.1 | 37.2 | 60.6 | 79.9 |
| **3$^{Si}$** | 22.5 | 38.5 | 53.1 | 70.1 |

**Table S 6**. NHC Dissociation energies for dialumenes **3** and **3$^{Si}$**.

| Compound | $\Delta G_{298}{}^{NHC}$[kcal/mol] | $D^0(0)^{NHC}$[kcal/mol] |
|---|---|---|
| **3** | 26.0 | 41.9 |
| **3$^{Si}$** | 16.9 | 33.9 |

**Calculated properties**

**Table S 4.** Calculated transitions and UV-Vis absorption bands using TD-DFT (time-dependent-DFT) for **3**.

| Wavelength [nm] | MO contributions | f | Contribution |
|---|---|---|---|
| 794 | HOMO→LUMO | 0.1977 | 96.4% |
| 661 | HOMO→LUMO+1 | 0.0296 | 95.4% |
| 634 | HOMO→LUMO+2 | 0.0107 | 98.5% |
| 592 | HOMO→LUMO+3<br>HOMO→LUMO+4 | 0.0271 | 89.5%<br>4.6% |
| 518 | HOMO→LUMO+5 | 0.0262 | 95.34% |
| 448 | HOMO→LUMO+10 | 0.0925 | 89.5% |

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|---|---|---|---|---|
| **3** | 22.1 | 37.2 | 60.6 | 79.9 |
| **3$^{Si}$** | 22.5 | 38.5 | 53.1 | 70.1 |

**Table S 6**. NHC Dissociation energies for dialumenes **3** and **3$^{Si}$**.

| Compound | $\Delta G_{298}{}^{NHC}$[kcal/mol] | $D^0(0)^{NHC}$[kcal/mol] |
|---|---|---|
| **3** | 26.0 | 41.9 |
| **3$^{Si}$** | 16.9 | 33.9 |

**Molecular Orbitals**

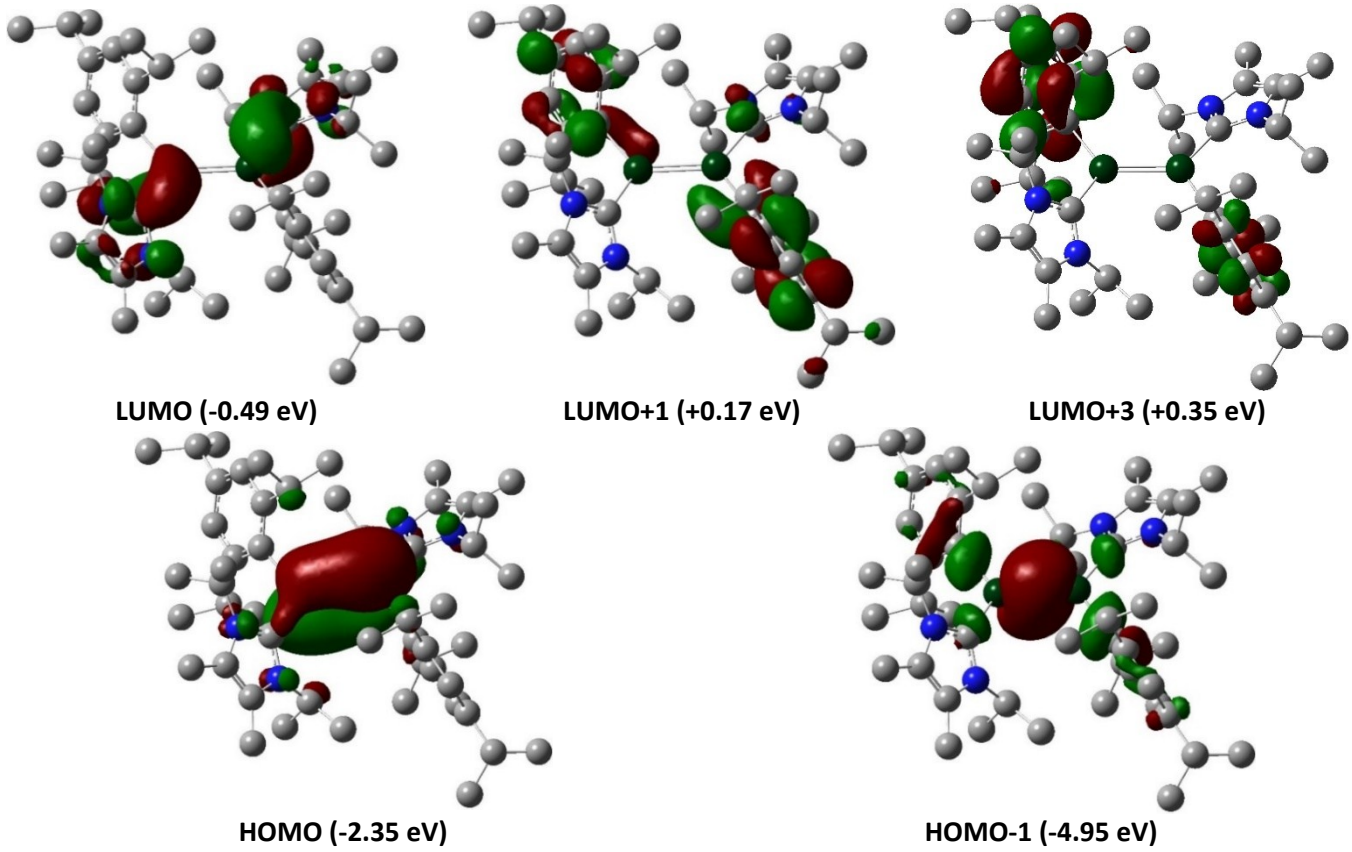



**Figure S 56:** Frontier orbitals of Tipp substituted dialumene, **3.**

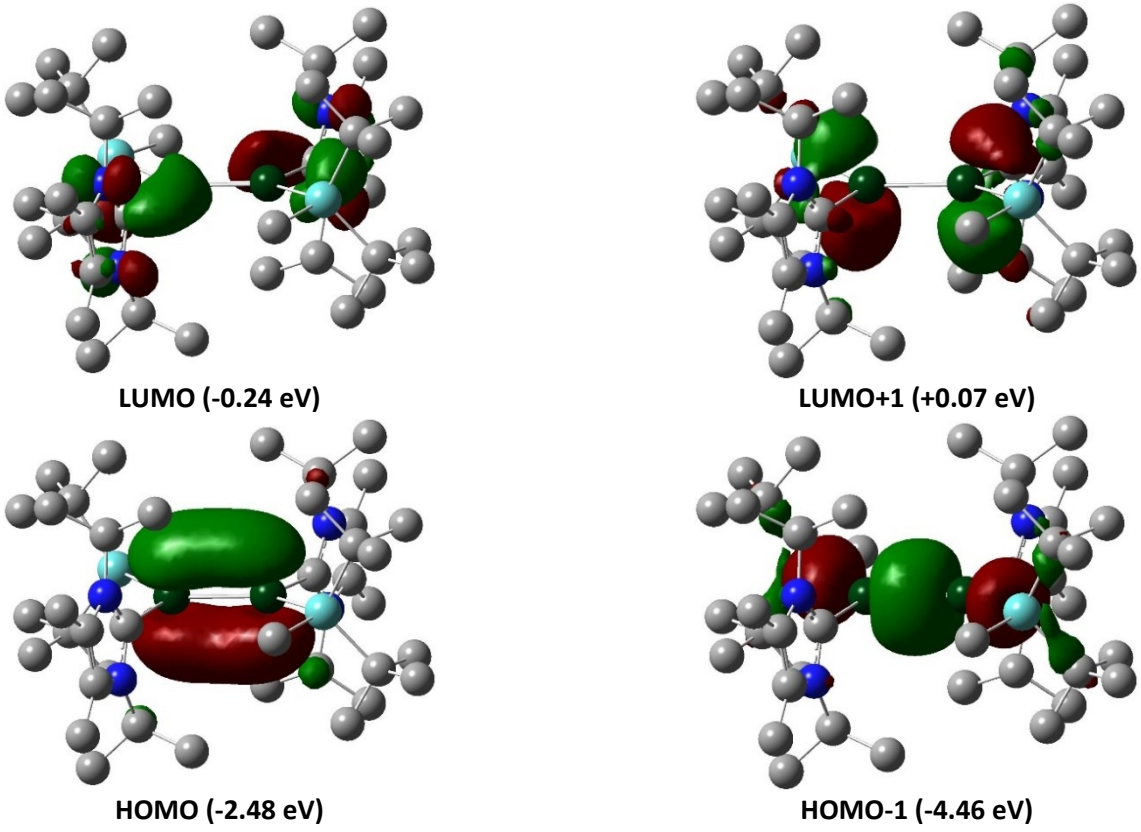
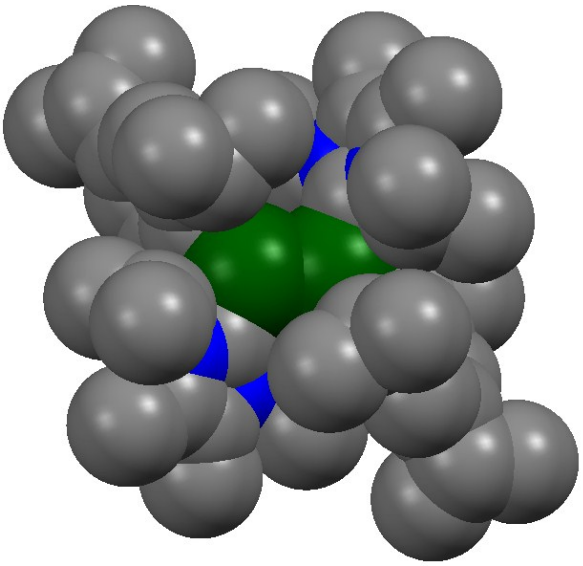
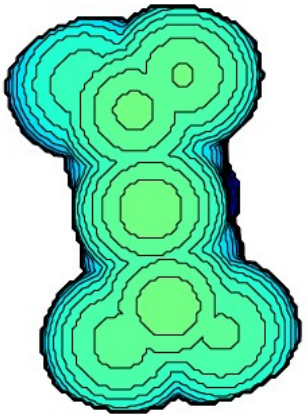



**Figure S 57:** Frontier orbitals of Silyl substituted dialumene, **3$^{Si}$.**

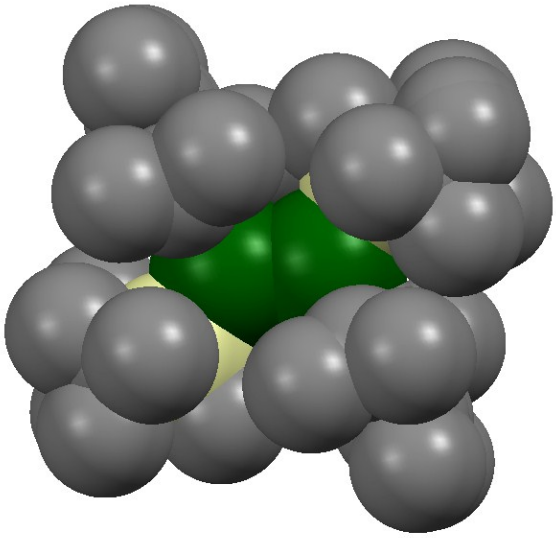
**Steric effects: space filling diagrams of the dialumenes with %$V_{bur}$ and steric maps of the ligands**

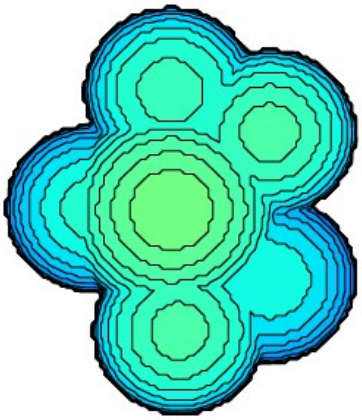




$\%V_{bur}$ = 29.9%

**Figure S 58.** Space filling diagram (left) for dialumene **3**, steric map of the Tipp ligand and $\%V_{bur}$ (right) calculated with the SambVca 2.1 web tool using default parameters with H atoms omitted from the calculation.[S28-30]

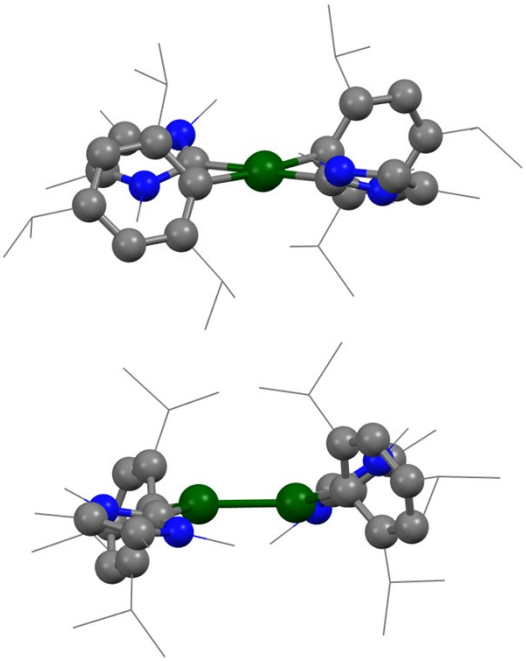
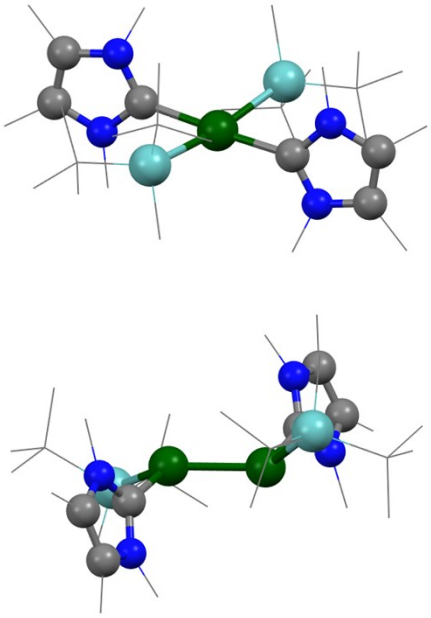
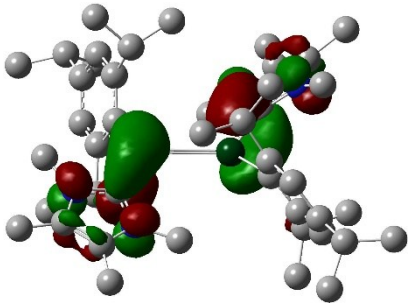
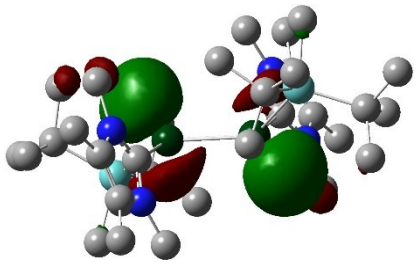
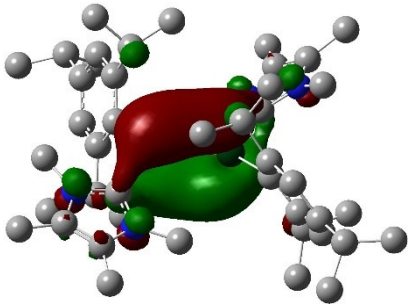
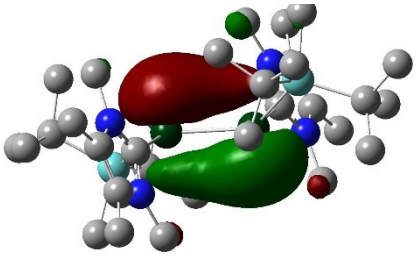




$\%V_{bur}$ = 30.7%

**Figure S 59.** Space filling diagram (left) for dialumene **3$^{Si}$**, steric map of the Tipp ligand and $\%V_{bur}$ (right) with the SambVca 2.1 web tool using default parameters with H atoms omitted from the calculation.[S28-30]

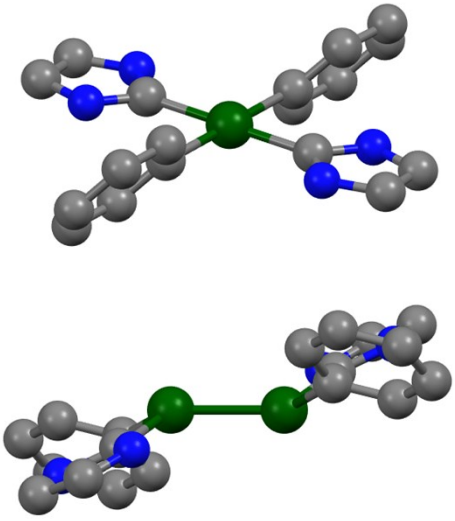
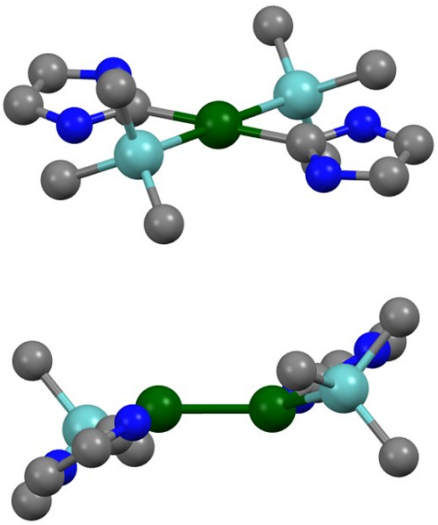
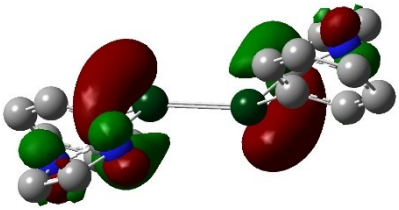
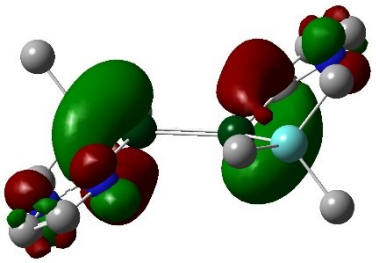
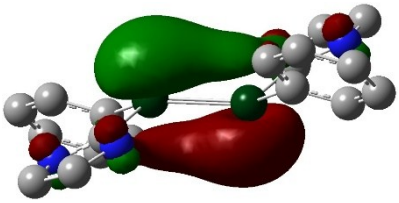
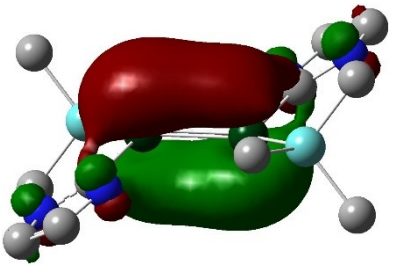
**Steric effects: Replacement of the NHC by $IMe_4$**

| $^{IMe4}$**3** | $^{IMe4}$**3**$^{Si*}$ |
|---|---|
|  |  |
| r(AlAl) = 2.40, θ = 11.3/15.3 °, τ = 4.2 ° | r(AlAl) = 2.43, θ = 30.4/42.1 °, τ = 11.7 ° |
|  |  |
| **LUMO (-0.68 eV)** | **LUMO (-0.40 eV)** |
|  |  |
| **HOMO (-2.45 eV)** | **HOMO (-2.75 eV)** |

*a planar isomer located 4.4 kcal/mol higher in energy

**Figure S 60:** Calculated structures for $^{IMe4}$**3** and $^{IMe4}$**3**$^{Si}$ in two different views (Me, $^{i}$Pr and $^{t}$Bu groups shown as wireframe for clarity) and their frontier orbitals.

Smallest possible model systems: Reduction of the steric demand of the ligands (TMS instead of Si$^t$Bu$_2$Me/Ph instead of Tipp) and replacement of the NHC by $IH_4$

| $^S$**3** | $^S$**3**$^{Si}$ |
|---|---|
|  |  |
| r(AlAl) = 2.43, θ = 31.8 °, τ = 0.0 ° | r(AlAl) = 2.41, θ = 21.2 °, τ = 0.0 ° |
|  |  |
| **LUMO (-1.00 eV)** | **LUMO (-0.97 eV)** |
|  |  |
| **HOMO (-2.78 eV)** | **HOMO (-2.86 eV)** |

*small imaginary frequency, which couldn't be removed maintaining symmetry

**Figure S 61:** Calculated structures for $^S$**3** and $^S$**3**$^{Si}$ in two different views and frontier orbitals.

**Monomers $^{M}$3 and $^{M}$3$^{Si}$**

Summary:

The Gibbs free energy to break the Al-Al bonds is similar in both cases (22.1 kcal/mol in **3** vs. 22.5 kcal/mol in **3$^{Si}$**) with corresponding singlet-triplet gaps of the monomers being slightly decreased for the electropositive silyl substituted **3$^{Si}$** ($\Delta E_{S\text{-}T}$(**$^{M}$3**) = 38.5 kcal/mol, $\Delta E_{S\text{-}T}$(**$^{M}$3$^{Si}$**) = 30.6 kcal/mol). The structures of the monomers however differ, with the factors discussed above revisited: the LUMO of Tipp-substituted **$^{M}$3** shows partial conjugation of the empty *p*-orbital at the Al center to the empty *p*-orbital of $C^{NHC}$. In contrast, **$^{M}$3$^{Si}$** is not capable of this as the NHC plane is orientated nearly perpendicular to the $C^{NHC}$-Al-Si plane (84 ° vs. 48 ° for **$^{M}$3**), thus preventing effective π-interactions. As presumed, the HOMO-LUMO gap in the monomers is smaller for the silyl version (**$^{M}$3** = 2.82 eV; **$^{M}$3$^{Si}$** = 2.50 eV) yielding an increased overlap in its planar dimeric configuration and thus lowering the occupied orbitals in energy in **3$^{Si}$**. This also elucidates the reduced HOMO-LUMO gap in **3** of 1.86 eV vs. 2.24 eV in **3$^{Si}$**, respectively.

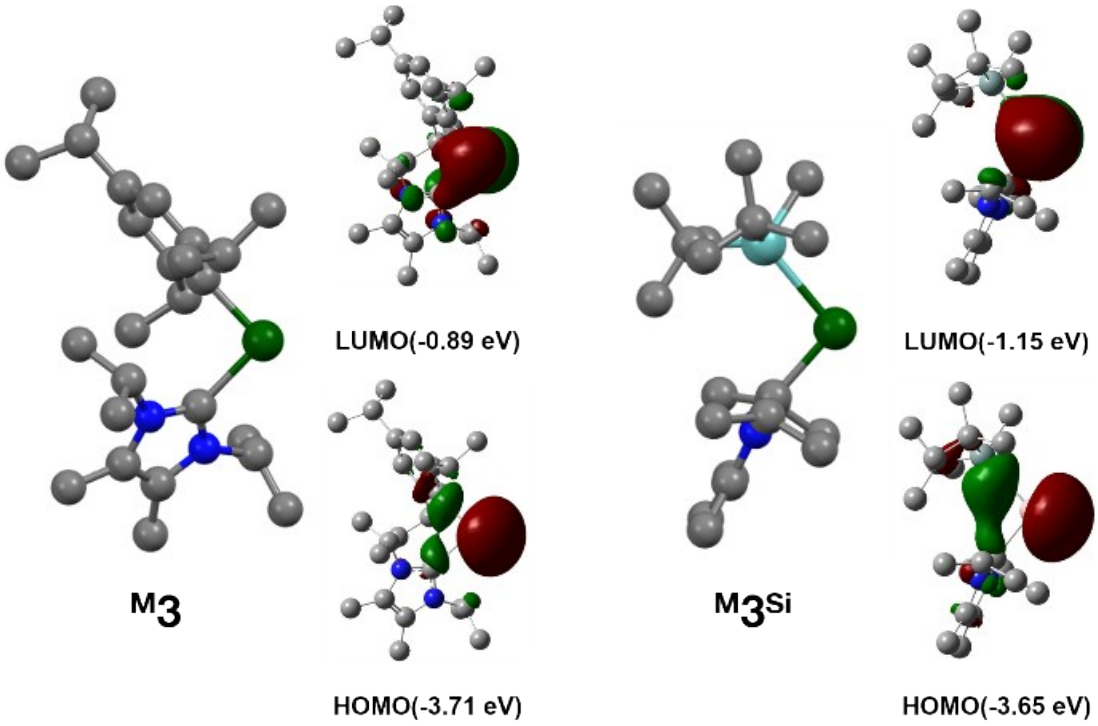



**Figure S 62.** Calculated molecular structure of monomers **$^{M}$3** and **$^{M}$3$^{Si}$** including their frontier orbitals

**NBO Analysis for dialumenes 3, $3^{Si}$ and the corresponding monomers**

**Table S 7.** Selected results of the NBO analysis of compound **3**.

| Bond in 3 | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| $Al^1$–$Al^2$ | 0.49($Al^1$) | 1.92 | 49% ($Al^1$)<br>51% ($Al^2$) | $sp^{1.09}$($Al^1$)<br>$sp^{1.04}$($Al^2$) | 1.53 |
| $Al^1$–$Al^2$ | 0.48($Al^2$) | 1.61 | 51% ($Al^1$)<br>49% ($Al^2$) | $sp^{23.15}$($Al^1$)<br>$sp^{52.27}$ ($Al^2$) | 1.53 |
| $Al^1$–$C^1$ | -0.55($C^1$) | 1.93 | 17% ($Al^1$)<br>83% ($C^1$) | $sp^{2.58}$($Al^1$)<br>$sp^{2.31}$($C^1$) | 0.52 |
| $Al^2$–$C^{27}$ | -0.56($C^{27}$) | 1.92 | 17% ($Al^2$)<br>83% ($C^{27}$) | $sp^{2.47}$($Al^2$)<br>$sp^{2.34}$($C^{27}$) | 0.54 |
| $Al^1$–$C^{16}$ | 0.01($C^{16}$) | 1.95 | 14% ($Al^1$)<br>86% ($C^{16}$) | $sp^{3.93}$($Al^1$)<br>$sp^{1.24}$($C^{16}$) | 0.55 |
| $Al^2$–$C^{42}$ | 0.01($C^{42}$) | 1.94 | 15% ($Al^2$)<br>85% ($C^{42}$) | $sp^{3.86}$($Al^2$)<br>$sp^{1.25}$($C^{42}$) | 0.55 |

**Table S 8.** Selected results of the second order perturbation theory analysis of compound **3**.

| Donor NBO (Occupancy) | Acceptor NBO (Occupancy) |
|---|---|
| π ($Al^1$–$Al^2$) (1.61) | π*($C^{16}$–$N^1$) (0.55) |
| π ($Al^1$–$Al^2$) (1.61) | π*($C^{27}$–$N^3$) (0.54) |

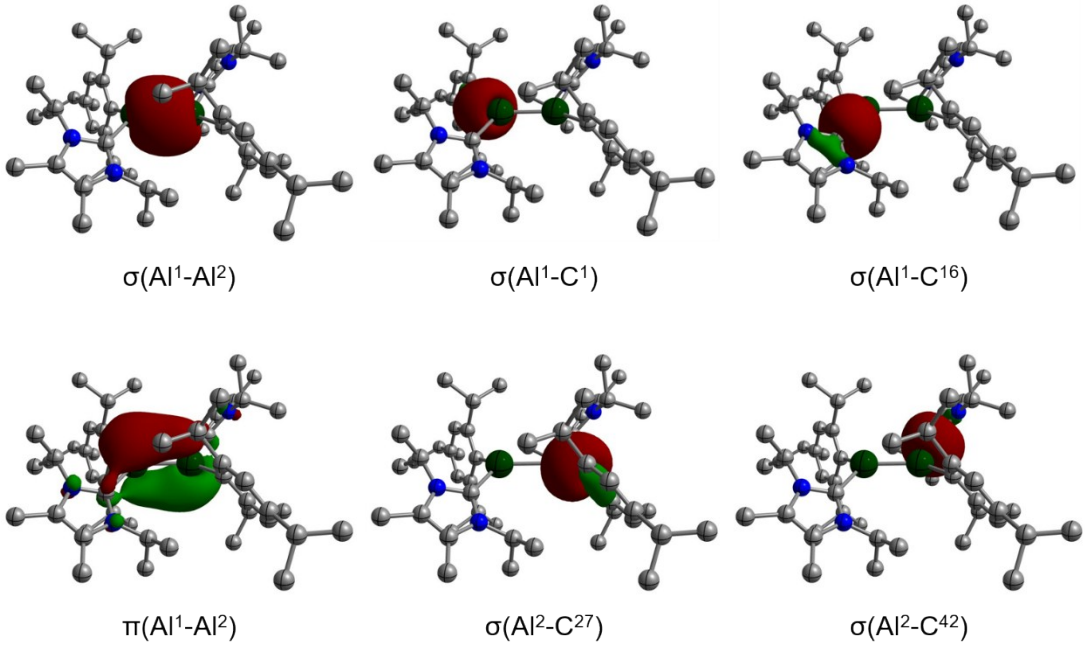



**Figure S 63.** Selected NLMOs of dialumene **3**.

**Table S 9**. Fragment charges obtained from NPA analysis for **3, $3^{Si}$** and the corresponding monomers $^{M}$**3**/$^{M}$**$3^{Si}$**.

| Compound | NPA fragment charge | | |
|---|---|---|---|
| | $Al^1/Al^2$ | NHC | Tipp/Si$^t$Bu$_2$Me |
| **3** | 0.49/0.48 | 0.16/0.15 | -0.64 |
| **$3^{Si}$** | 0.08 | 0.22 | -0.30 |
| **$^{M}$3** | 0.55 | 0.15 | -0.70 |
| **$^{M}3^{Si}$** | 0.40 | 0.05 | -0.45 |

**Table S 10.** Selected results of the NBO analysis of the **$3^{Si}$**.

| Bond in $3^{Si}$ | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| $Al^1$–$Al^{1'}$ | 0.08($Al^1$) | 1.92 | 50% ($Al^1$)<br>50% ($Al^{1'}$) | $sp^{1.12}$($Al^1$)<br>$sp^{1.12}$($Al^{1'}$) | 1.67 |
| $Al^1$–$Al^{1'}$ | 0.08($Al^{1a}$) | 1.76 | 50% ($Al^1$)<br>50% ($Al^{1'}$) | $sp^{99.99}$($Al^1$)<br>$sp^{99.99}$ ($Al^{1'}$) | 1.67 |
| $Al^1$–$Si^1$ | 1.15($Si^1$) | 1.93 | 36% ($Al^1$)<br>64% ($Si^1$) | $sp^{1.78}$($Al^1$)<br>$sp^{1.97}$($Si^1$) | 0.88 |
| $Al^1$–$C^1$ | 0.06($C^1$) | 1.94 | 14% ($Al^1$)<br>86% ($C^1$) | $sp^{4.87}$($Al^1$)<br>$sp^{1.24}$($C^1$) | 0.49 |

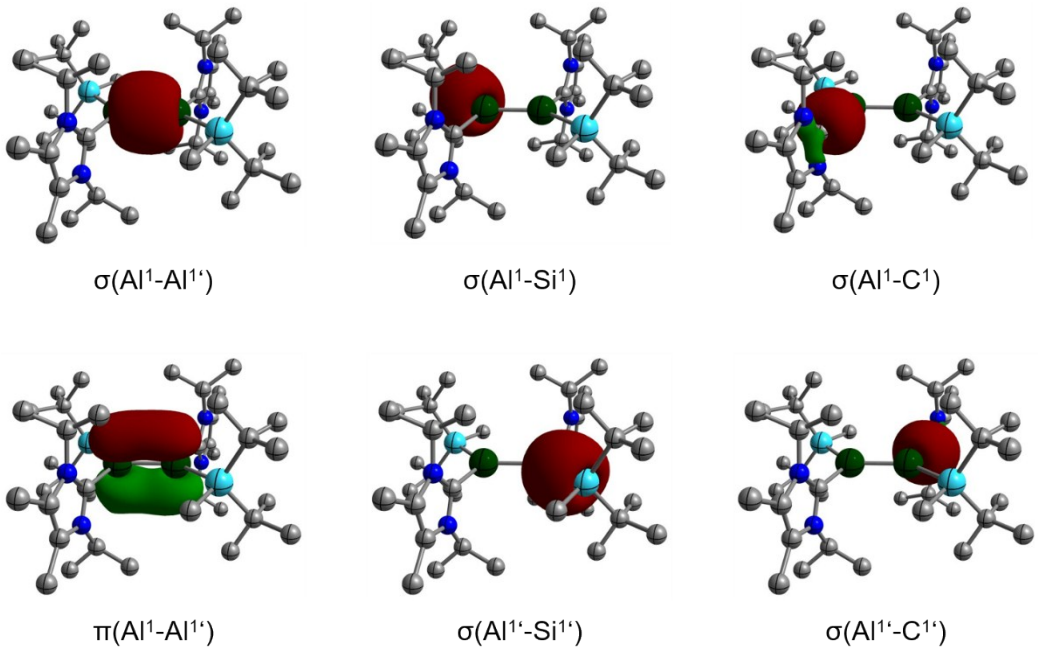



**Figure S 64.** Selected NLMOs of dialumene **$3^{Si}$**.

**Table S 11.** Selected results of the NBO analysis of the monomer $^{M}$**3**.

| Bond in $^{M}$3 | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| LP $Al^1$ | 0.55($Al^1$) | 1.91 | – | $sp^{0.19}$($Al^1$) | – |
| $Al^1$–$C^1_{Tipp}$ | -0.58($C^1$) | 1.92 | 13% ($Al^1$)<br>87% ($C^1$) | $sp^{8.11}$($Al^1$)<br>$sp^{2.63}$($C^1$) | 0.45 |
| $Al^1$–$C^2_{NHC}$ | 0.04($C^2$) | 1.94 | 10% ($Al^1$)<br>90% ($C^2$) | $sp^{15.87}$($Al^1$)<br>$sp^{1.37}$($C^2$) | 0.40 |

**Table S 12.** Selected results of the NBO analysis of the monomer $^{M}$**3**$^{Si}$.

| Bond in $^{M}$3$^{Si}$ | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| LP $Al^1$ | 0.40 ($Al^1$) | 1.86 | – | $sp^{0.18}$($Al^1$) | – |
| $Al^1$–$Si^1$ | 1.02($Si^1$) | 1.86 | 26% ($Al^1$)<br>74% ($Si^1$) | $sp^{8.76}$($Al^1$)<br>$sp^{2.01}$($Si^1$) | 0.72 |
| $Al^1$–$C^1$ | -0.04($C^1$) | 1.94 | 10% ($Al^1$)<br>90% ($C^1$) | $sp^{15.72}$($Al^1$)<br>$sp^{1.35}$($C^1$) | 0.46 |

**NBO Analysis for the small model dialumenes $^{S}$3 and $^{S}$3$^{Si}$**

**Table S 13.** Selected results of the NBO analysis of compound $^{S}$**3**.

| Bond in $^{S}$3 | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| $Al^1$–$Al^2$ | 0.52($Al^1$) | 1.93 | 50% ($Al^1$)<br>50% ($Al^2$) | $sp^{1.18}$($Al^1$)<br>$sp^{1.18}$($Al^2$) | 1.47 |
| $Al^1$–$Al^2$ | 0.52($Al^2$) | 1.55 | 50% ($Al^1$)<br>50% ($Al^2$) | $sp^{16.6}$($Al^1$)<br>$sp^{16.6}$($Al^2$) | 1.47 |
| $Al^1$–$C^1_{Tipp}$ | -0.52($C^1$) | 1.81 | 18% ($Al^1$)<br>82% ($C^1$) | $sp^{2.64}$($Al^1$)<br>$sp^{2.83}$($C^1$) | 0.58 |
| $Al^1$–$C^2_{NHC}$ | 0.01($C^2$) | 1.95 | 15% ($Al^1$)<br>85% ($C^2$) | $sp^{4.03}$($Al^1$)<br>$sp^{1.24}$($C^2$) | 0.61 |

**Table S 14**. Selected results of the second order perturbation theory analysis of compound $^{S}$**3**.

| Donor NBO (Occupancy) | Acceptor NBO (Occupancy) |
|---|---|
| π ($Al^1$–$Al^2$) (1.55) | π*($C^2$–$N^1$) (0.54) |
| π ($Al^1$–$Al^2$) (1.55) | π*($C^4$–$N^3$) (0.54) |

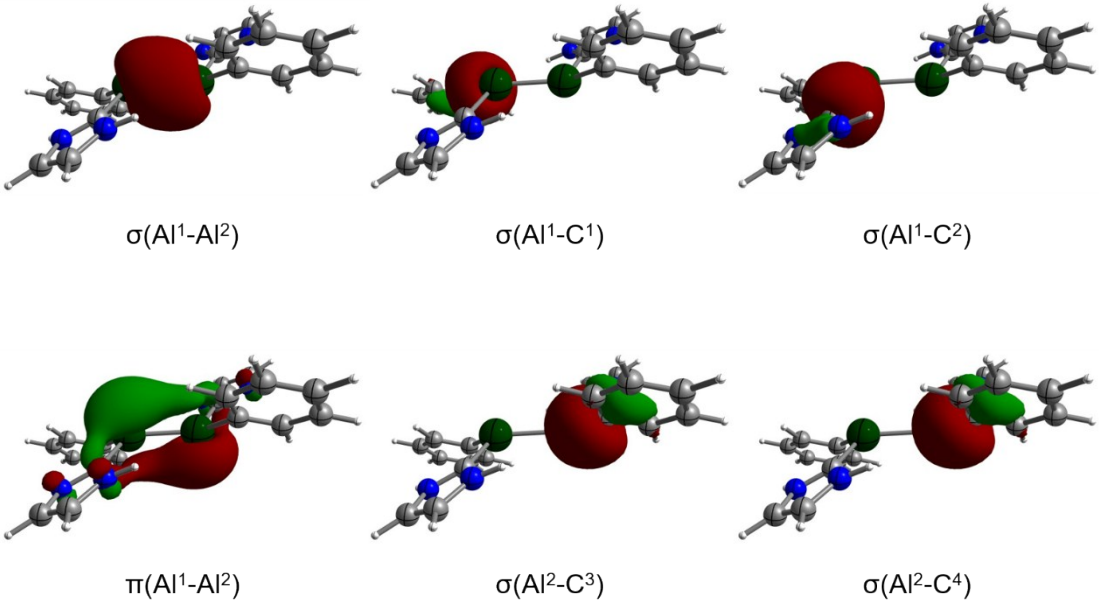



**Figure S 65.** Selected NLMOs of dialumene $^{S}$**3**.

**Table S 15.** Selected results of the NBO analysis of the $^{S}\mathbf{3}^{Si}$.

| Bond in $^{S}\mathbf{3}^{Si}$ | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| $Al^1$–$Al^2$ | 0.09($Al^1$) | 1.95 | 50% ($Al^1$)<br>50% ($Al^2$) | $sp^{1.23}$($Al^1$)<br>$sp^{1.23}$($Al^2$) | 1.56 |
| $Al^1$–$Al^2$ | 0.09($Al^2$) | 1.61 | 50% ($Al^1$)<br>50% ($Al^2$) | $sp^{46.22}$($Al^1$)<br>$sp^{46.22}$($Al^2$) | 1.56 |
| $Al^1$–$Si^1$ | 1.02($Si^1$) | 1.94 | 39% ($Al^1$)<br>61% ($Si^1$) | $sp^{1.92}$($Al^1$)<br>$sp^{2.09}$($Si^1$) | 0.90 |
| $Al^1$–$C^1$ | 0.03($C^1$) | 1.95 | 16% ($Al^1$)<br>84% ($C^1$) | $sp^{4.27}$($Al^1$)<br>$sp^{1.21}$($C^1$) | 0.62 |

**Table S 16**. Selected results of the second order perturbation theory analysis of compound $^{S}\mathbf{3}^{Si}$.

| Donor NBO (Occupancy) | Acceptor NBO (Occupancy) |
|---|---|
| π ($Al^1$–$Al^2$) (1.61) | π*($C^1$–$N^1$) (0.53) |
| π ($Al^1$–$Al^2$) (1.61) | π*($C^2$–$N^3$) (0.53) |

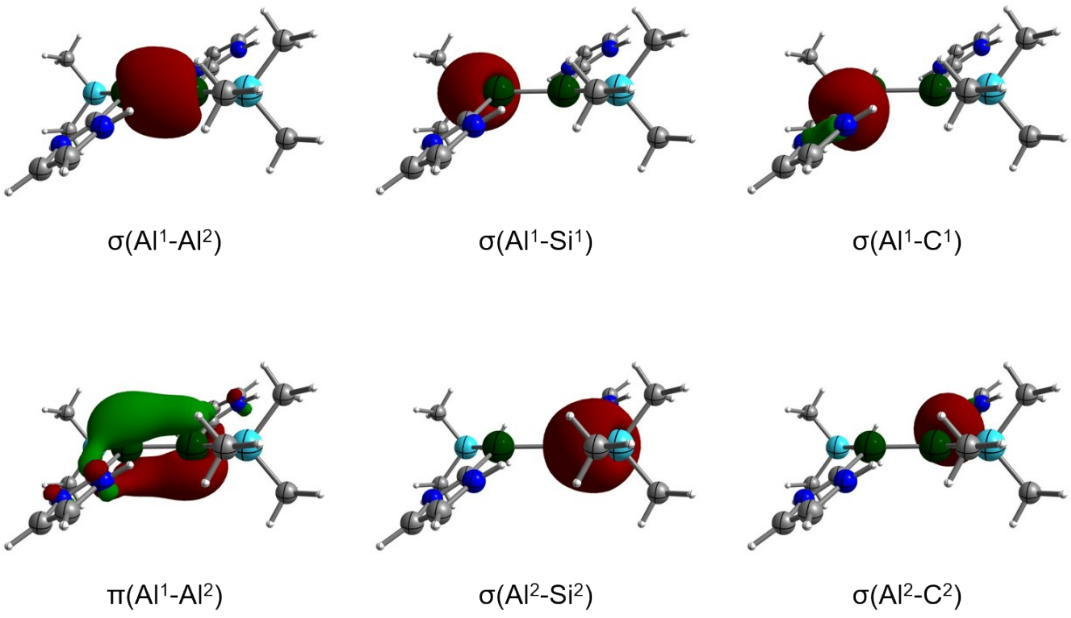



**Figure S 66.** Selected NLMOs of $^{S}\mathbf{3}^{Si}$.

**Table S 17.** Fragment charges obtained from NPA analysis for $^{S}\mathbf{3}$ and $^{S}\mathbf{3}^{Si}$.

| Compound | NPA fragment charge | | |
|---|---|---|---|
| | $Al^1/Al^2$ | NHC | Tipp/Si$^t$Bu$_2$Me |
| $^{S}\mathbf{3}$ | 0.52 | 0.13 | -0.65 |
| $^{S}\mathbf{3}^{Si}$ | 0.09 | 0.15 | -0.24 |

**Compound 7 –AlAl$^{(Tipp)}$ + XylNC**

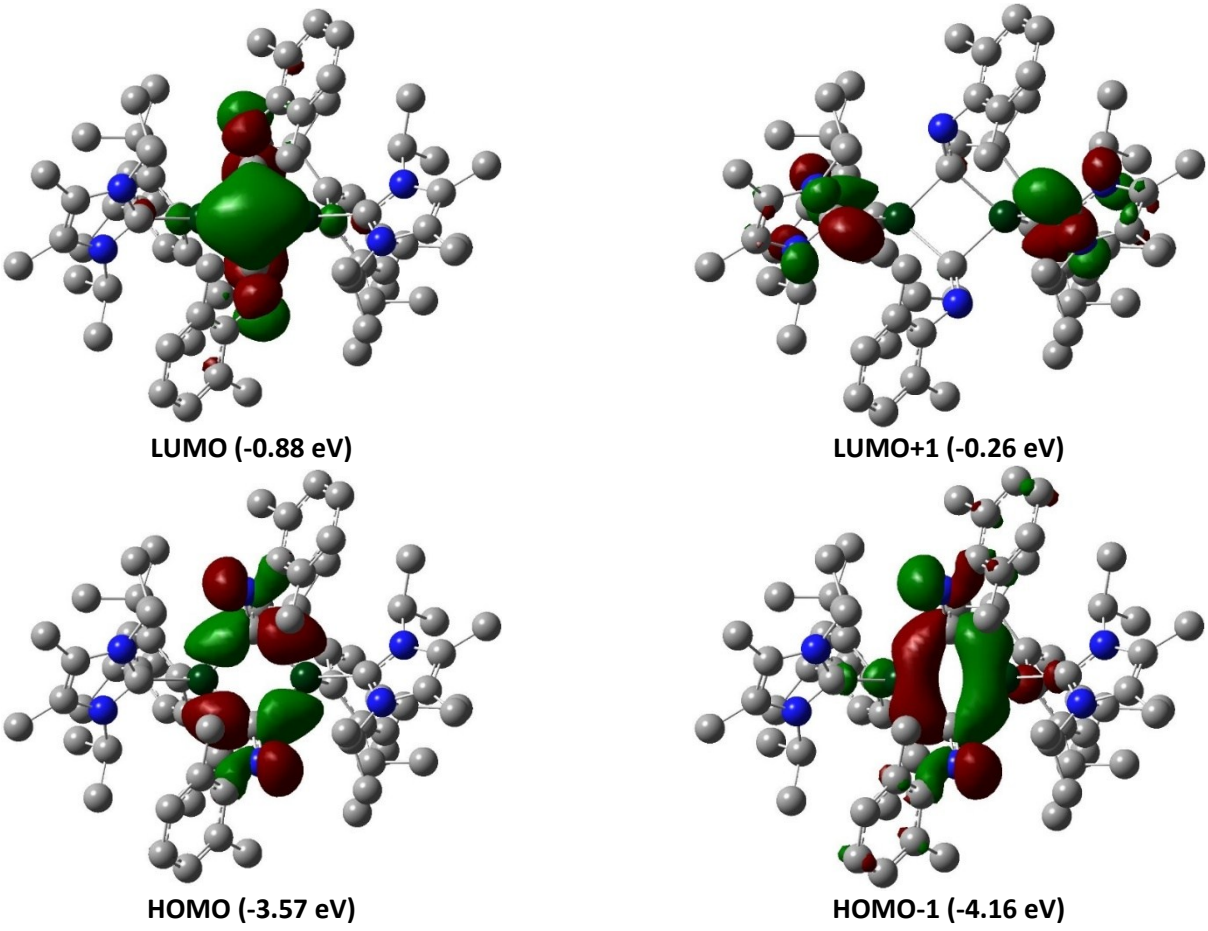



**Figure S 67.** Frontier orbitals of **7.**

**Table S 18.** Selected results of the NBO analysis of **7**.

| Bond in 7 | NBO analysis (NLMOs) | | | | |
|---|---|---|---|---|---|
| | NPA charge | Occupancy | pol. | hybr. | WBI |
| $Al^1$–$Al^{1'}$ | –1.60($Al^{1/1'}$) | – | – | – | 0.04 |
| $Al^1$–$C^1{}_{Tipp}$ | -0.59($C^1$) | 1.91 | 15% ($Al^1$)<br>85% ($C^1$) | $sp^{2.57}$($Al^1$)<br>$sp^{2.39}$($C^1$) | 0.46 |
| $Al^1$–$C^{16}{}_{NHC}$ | -0.59($C^{16}$) | 1.94 | 13% ($Al^1$)<br>87% ($C^{16}$) | $sp^{3.77}$($Al^1$)<br>$sp^{1.32}$($C^{16}$) | 0.43 |
| $Al^1$–$C^{27}{}_{CNXyl}$ | -0.73($C^{27}$) | 1.91 | 17% ($Al^1$)<br>83% ($C^{27}$) | $sp^{2.79}$($Al^1$)<br>$sp^{1.96}$($C^{27}$) | 0.52 |
| $Al^1$–$C^{27'}{}_{CNXyl}$ | -0.73($C^{27'}$) | 1.89 | 15% ($Al^1$)<br>85% ($C^{27'}$) | $sp^{2.94}$($Al^1$)<br>$sp^{2.08}$($C^{27'}$) | 0.48 |
| $C^{27}$–$N^3$ | -0.55($N^3$) | 1.98 | 37% ($C^{27}$)<br>63% ($N^3$) | $sp^{1.29}$($C^{27}$)<br>$sp^{2.07}$($N^3$) | 1.82 |
| $C^{27}$–$N^3$ | – | 1.95 | 36% ($C^{27}$)<br>64% ($N^3$) | $sp^{99.99}$($C^{27}$)<br>$sp^{99.99}$($N^3$) | 1.82 |
| LP $N^3$ | – | 1.82 | – | $sp^{3.22}$($N^3$) | – |
| $C^{27}$–$C^{27'}$ | – | – | – | – | 0.06 |

**Table S 19**. Fragment charges obtained from NPA analysis for **7**.

| Compound | NPA fragment charge | | | |
|---|---|---|---|---|
| | $Al^1/Al^2$ | NHC | Tipp | CNXyl |
| **7** | 1.60/1.60 | 0.24/0.24 | -0.63 | -1.21 |

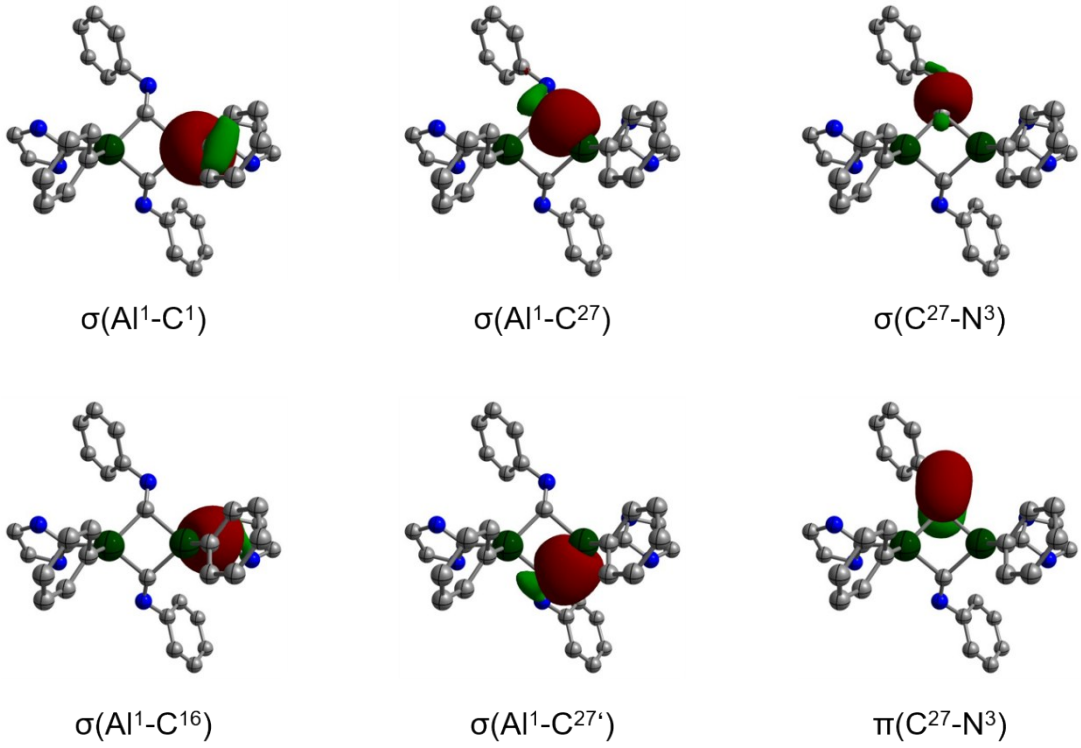



**Figure S 68.** Selected NLMOs of **7** (symmetric NLMOs only shown once), Me and $^i$Pr groups removed for clarity.

**Table S 20.** Selected experimental and calculated IR frequencies for **7**.

| Compound | Mode | Exp. $\tilde{\nu}$ [$cm^{-1}$] | Calc. $\tilde{\nu}$ [$cm^{-1}$]* |
|---|---|---|---|
| **7** | C=N asymm | 1544 | 1568 |

* calculated wavenumbers for the CN stretching mode are scaled by a factor 0.969, being the ratio of the calculated stretching mode of free CNXyl (2187 $cm^{-1}$) to the experimental value (2119 $cm^{-1}$)

**Compound 10 –AlAl$^{(Tipp)}$ + $O_2$**

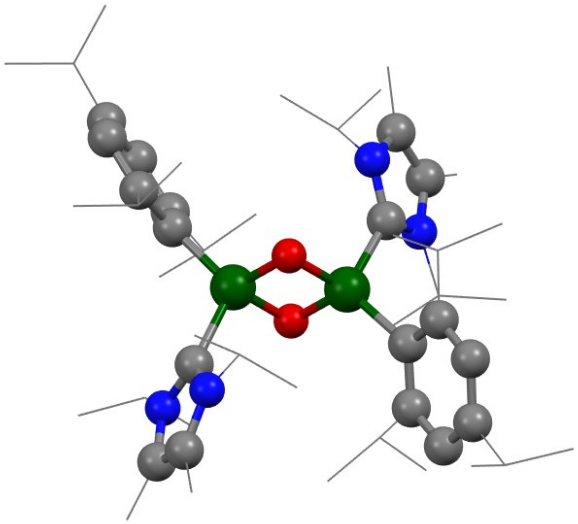


**Table S 21.** Calculated bond radii for **10**.

| Bond | Calc. value |
|---|---|
| r($Al^1Al^2$) | 2.47 |
| r($Al^1O^1$) | 1.79 |
| r($Al^2O^1$) | 1.79 |
| r($Al^1O^2$) | 1.79 |
| r($Al^2O^2$) | 1.79 |
| r($Al^1C^{NHC}$) | 2.07 |
| r($Al^1C^{Tipp}$) | 1.99 |
| r($Al^2C^{NHC}$) | 2.07 |
| r($Al^2C^{Tipp}$) | 1.99 |
| r($O^1O^2$) | 2.58 |

**Figure S 69.** Calculated structure of **10**.

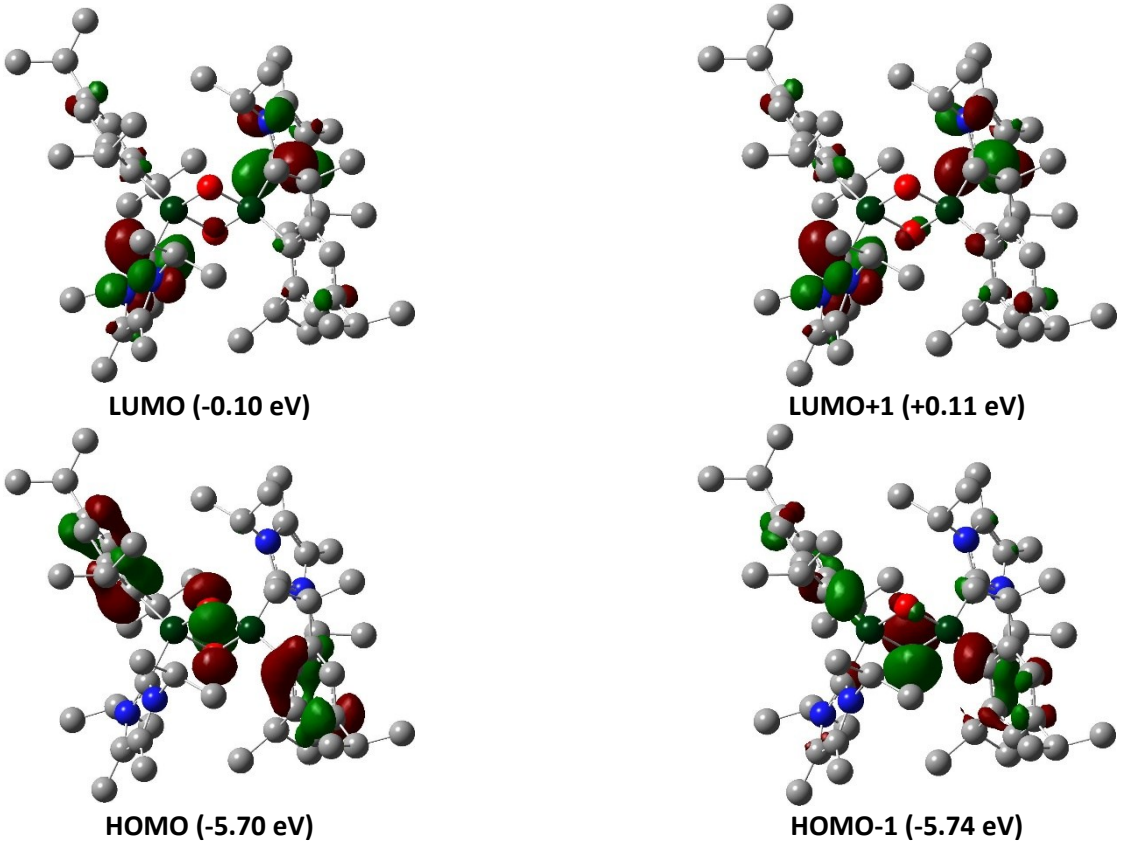



**Figure S 70.** Frontier orbitals of **10**.

**Table S 23.** Calculated transitions and UV-Vis absorption bands using TD-DFT (time-dependent-DFT) for **10**.

| Wavelength [nm] | MO contributions | f | Contribution |
|---|---|---|---|
| 259 | HOMO-1→LUMO<br>HOMO→LUMO | 0.0259 | 54.2%<br>41.0% |

**Compound 11 –AlAl$^{(Tipp)}$ + $N_2O$/*N*-methylmorpholine-*N*-oxide**

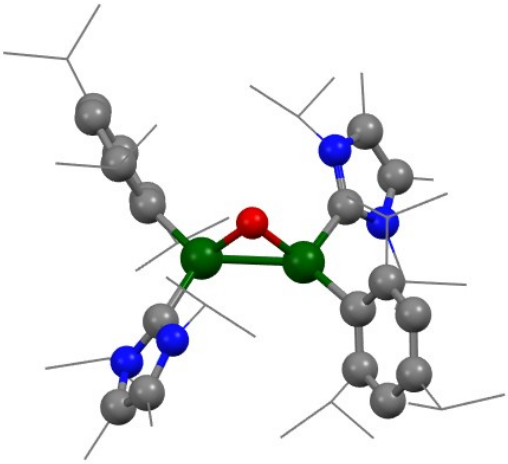


**Figure S 71.** Calculated structure of **11**.

**Table S 22.** Calculated bond radii for **11**.

| Bond | Calc. value |
|---|---|
| r($Al^1Al^2$) | 2.40 |
| r($Al^1O^1$) | 1.80 |
| r($Al^2O^1$) | 1.79 |
| r($Al^1C^{NHC}$) | 2.06 |
| r($Al^1C^{Tipp}$) | 2.00 |
| r($Al^2C^{NHC}$) | 2.06 |
| r($Al^2C^{Tipp}$) | 2.01 |

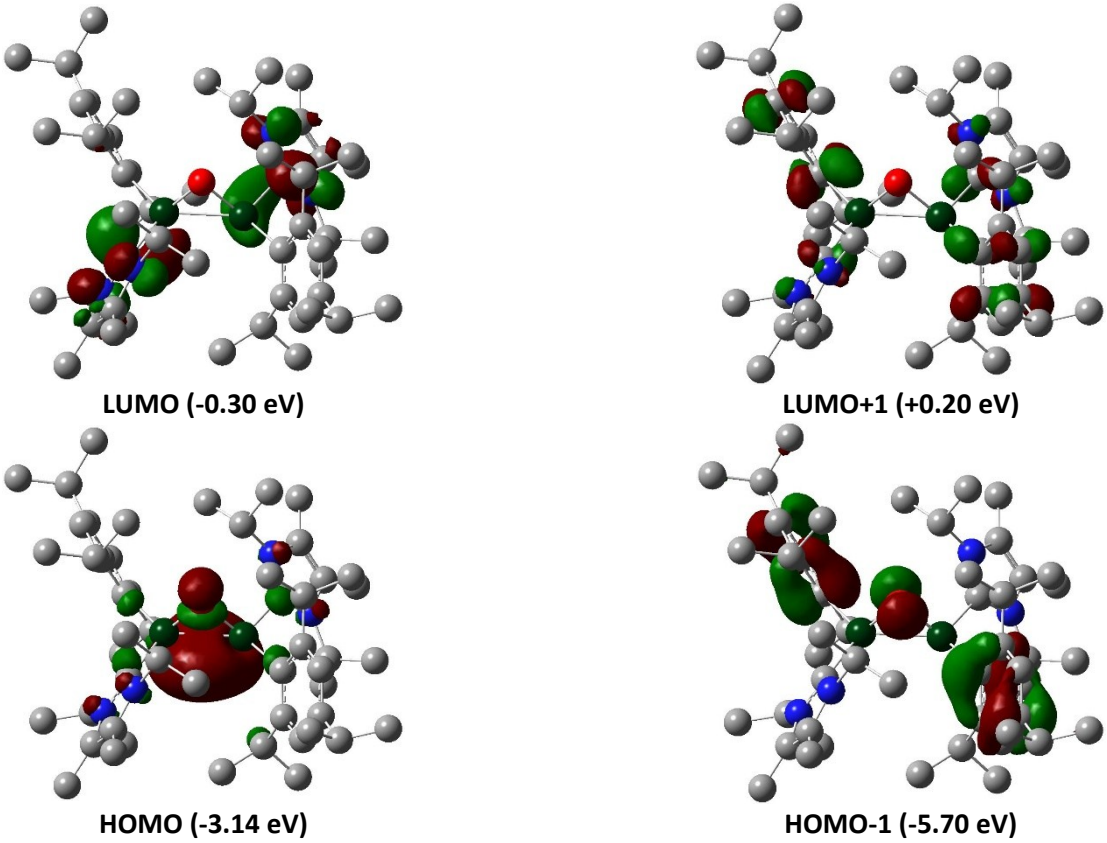



**Figure S 72.** Frontier orbitals of **11**.

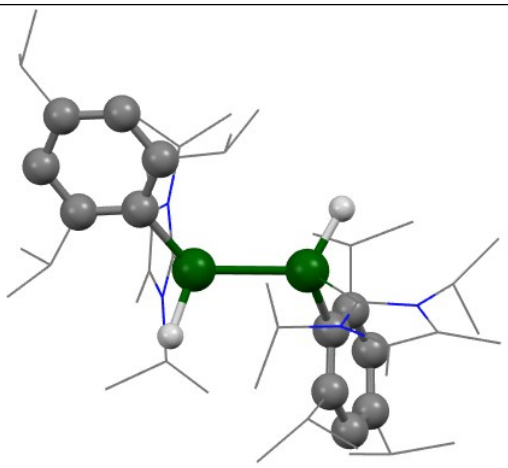
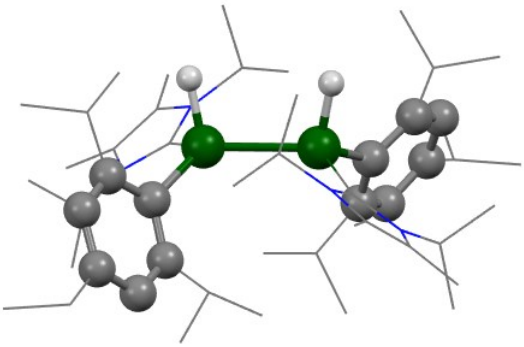
**Table S 23.** Calculated transitions and UV-Vis absorption bands using TD-DFT (time-dependent-DFT) for **11**.

| Wavelength [nm] | MO contributions | f | Contribution |
|---|---|---|---|
| 519 | HOMO→LUMO | 0.2696 | 99.0% |
| 343 | HOMO→LUMO+10 | 0.0249 | 97.9% |
| 337 | HOMO→LUMO+10 | 0.0228 | 97.5% |
| 316 | HOMO→LUMO+12<br>HOMO→LUMO+13<br>HOMO→LUMO+15 | 0.0246 | 75.4%<br>16.8%<br>2.7% |

**Compound 12 - AlAl$^{(Tipp)}$ + $H_2$**

Since no molecular structure of the reaction of **3** and $H_2$ could be obtained (Compound **12**), we calculated several possible isomeric products of this reaction (terminal or bridging hydrides, orientation H: cis or trans; orientation NHC and Tipp ligands cis or trans). The two isomers **12$^{trans}$** and **12$^{cis}$**, given in Table S 19, are most preferred in energy. Each of them possesses two Al-H stretching frequencies, separated only a few cm$^{-1}$. The measured IR spectrum of **12** bears two distinct peaks at 1593 and 1634 cm$^{-1}$ with a determined full-width at half-height (FWHH) of 14 cm$^{-1}$. Thus the experimental band width is too big to detect the two calculated peaks separately for each isomer, which gives rise to a mixture of **12$^{trans}$**/**12$^{cis}$** nicely reproducing the experimentally observed shifts (Figure S 72). Calculations concerning the mechanism of this reaction are concern of a follow up publication, as the increased temperature of 50°C needed to run the reaction, might also enable reaction pathways via the monomeric $^{M}$**3** to proceed. Thus, a ratio of **12$^{trans}$**/**12$^{cis}$** cannot be determined and is presumed 1:1 for the convoluted IR spectrum in Figure S 72.

**Table S 24**. Calculated structures, IR shifts and energies for the two products **12$^{trans}$** and **12$^{cis}$**.

| | **12$^{trans}$** | **12$^{cis}$** |
|---|---|---|
| **Molecular structure** |  |  |
| **Calc. Al-H $\tilde{\nu}$ [cm$^{-1}$]**[a] | 1634 cm$^{-1}$ (s)<br>1648 cm$^{-1}$ (w) | 1660 cm$^{-1}$ (w)<br>1676 cm$^{-1}$ (s) |
| **$\Delta G_{298}$**[b] | -35.3 kcal/mol | -27.5 kcal/mol |

[a] calculated wavenumbers for the Al-H stretching mode are scaled by a factor of 0.944 being the ratio of the calculated Al-H stretching mode of **1** ($^{i}Pr_2Me_2Al(Tipp)H_2$, 1812 cm$^{-1}$) to the experimental value (1711 cm$^{-1}$); [b] referenced to dialumene **3** and $H_2$

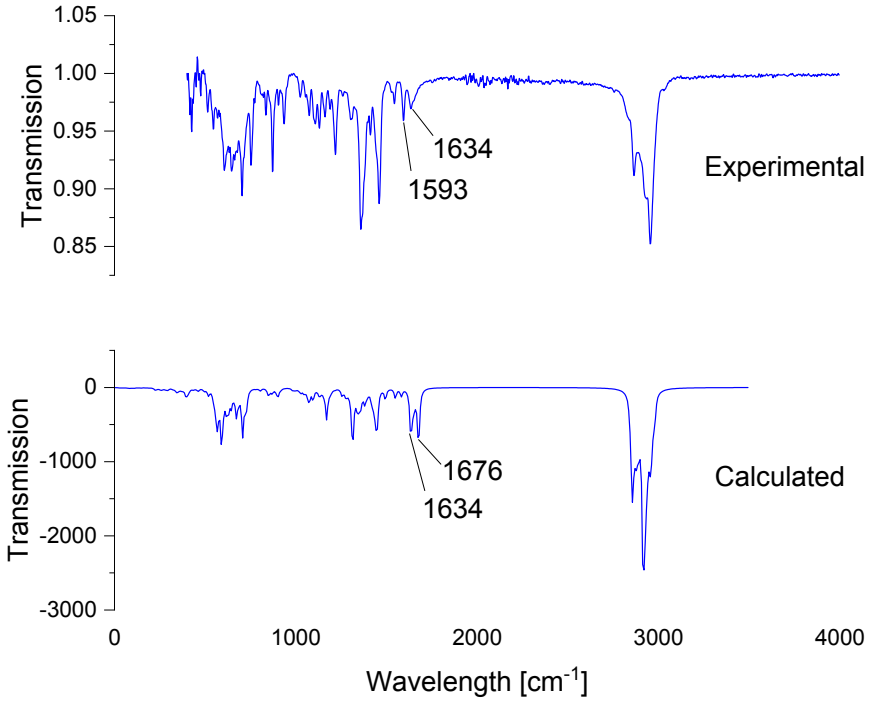



**Figure S 73.** Comparison of the experimental (top) and calculated (bottom) convoluted IR spectrum for a 1:1 mixture of **12**$^{trans}$ and **12**$^{cis}$.

### 3.3 Calculated energies at the B3LYP/6-311G(2d,2p)(SMD: benzene) level of theory

| Structure | E(SCF) [H/particle] |
|---|---|
| **3** | -2738.2007396 |
| **$3^{Si}$** | -2857.4146216 |
| **$^{IMe4}3$** | -2423.5503567 |
| **$^{IMe4}3^{Si}$** | -2542.7708198 |
| **$^{S}3$** | -1400.9566339 |
| **$^{S}3^{Si}$** | -1756.2003937 |
| **$^{M}3$** | -1369.0695033 |
| **$^{M}3^{03}$** | -1369.0349828 |
| **$^{M}3^{Si}$** | -1428.6747634 |
| **$^{M}3^{Si03}$** | -1428.6499494 |
| **7** | -3544.8086660 |
| **10** | -2888.9970507 |
| **11** | -2813.5855938 |
| **$12^{trans}$** | -2739.4575284 |
| **$12^{cis}$** | -2739.4484768 |
| **$H_2$** | -1.1796179 |
| **3-$I^iPr_2Me_2$** | -2197.2268815 |
| **$3^{Si}$-$I^iPr_2Me_2$** | -2316.4528321 |
| **$I^iPr_2Me_2$** | -540.9035241 |
| **$IMe_4$** | -383.5808291 |

## 3.4 Cartesian Coordinates (x,y,z) for the Optimized Structures

### 3

Al 0.85053 0.64423 0.41628
C 2.79757 0.19642 0.09759
Al -0.99855 -0.78368 -0.05961
C 3.58009 -0.44982 1.08412
N -0.25009 3.45278 -0.32494
C 4.90320 -0.81973 0.81590
H 5.48395 -1.33403 1.57830
N 1.46889 3.56616 0.99436
C 5.50869 -0.55049 -0.40899
N 0.36987 -3.50308 -0.45674
C 4.74634 0.10143 -1.37979
H 5.19956 0.32355 -2.34231
C 3.41638 0.46273 -1.15069
N -1.28829 -3.68725 0.92782
C 2.62936 -2.26873 2.57098
H 3.50224 -2.90861 2.40311
H 1.86302 -2.53235 1.83799
H 2.22945 -2.49735 3.56478
C 2.99732 -0.78177 2.45641
H 2.05113 -0.22941 2.54500
C 3.89715 -0.33765 3.61905
H 4.18321 0.71364 3.51851
H 4.81946 -0.92333 3.67657
H 3.37642 -0.45677 4.57438
C -2.69344 3.25821 -0.90999
H -2.95568 4.26291 -1.24889
H -2.87852 3.18627 0.16082
H -3.37047 2.55193 -1.39453
C -0.88369 3.15949 -2.70946
H 0.11818 2.78796 -2.93084
H -0.91710 4.22415 -2.95016
H -1.58822 2.64945 -3.36984
C -0.86768 5.92434 -0.58666
H -1.06445 5.85264 -1.65696
H -0.37657 6.88158 -0.40916
H -1.83514 5.95470 -0.07786
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H 1.44597 6.97739 0.73186
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H 2.99467 3.09961 4.01316
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H -6.69763 2.16799 -2.41195
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C -0.74995 -4.96553 0.77531
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H 3.05064 -4.15390 -1.53272
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H 6.38377 -2.92747 -1.49780
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C 2.69692 0.36744 -3.59756
H 3.70628 0.31948 -4.01670
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C 3.11195 2.60404 -2.48321
H 2.56882 3.07693 -3.30829
H 4.18020 2.65378 -2.71678
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H -1.15342 1.79794 -1.10175
C 1.06751 4.87918 0.74451

### $3^{Si}$

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Al -1.17010 -0.23536 0.00345
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Si -2.51948 -2.30137 -0.13011
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N 2.72546 -2.28726 -0.91469
C 2.28068 -1.52007 0.11693
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C 3.20212 -3.51449 -0.45581
C 2.17177 -1.77293 2.59149
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C 0.91528 -2.45375 3.12494
H 1.02642 -3.53677 3.21045
H 0.07216 -2.23415 2.46951
H 0.67841 -2.06060 4.11745
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H 4.27351 -1.46986 3.08901
H 3.52957 -2.81798 3.96772
H 3.14274 -1.15912 4.40465
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H 0.47157 -2.21785 -2.40114
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H -3.52859 2.81819 3.96819
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H -4.74019 4.35560 -1.71551
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H -3.09972 4.81053 -2.17402
C -3.47279 4.54951 1.88558
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H -2.70430 4.72184 2.64003
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H -5.29314 -1.02497 0.68518
H -5.27526 -3.74460 2.25855

**IMe4$_3$**

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C -4.87840 -0.41649 -1.06373
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C -3.58189 -0.92539 -0.95681
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H -1.73686 2.19617 1.93783
H -1.83490 1.99543 3.68872
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H -1.69689 -0.17761 2.49262
C -3.40806 -0.25488 3.77095
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H -4.37317 0.23351 3.93749
H -2.81416 -0.12950 4.68203
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H -0.03678 -7.30328 0.68700
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C 7.47188 -1.43007 -0.91931
H 7.25865 -1.15975 -1.95773
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H 1.95108 1.29613 -2.35834
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H 2.84715 0.85104 -4.58660
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H -3.28813 4.77589 -0.16373
H -2.54456 5.34611 -1.65699
H -2.34773 6.27009 -0.16903
C 0.42705 6.22260 0.86464
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H -0.37830 6.95037 0.76259
H 1.29082 6.60959 0.31370
C 2.08597 3.74342 1.12620
H 2.62680 2.83860 0.86508
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H -7.90323 -0.90952 0.35307
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H -2.53916 -1.57626 -4.22868
H -2.35155 -0.07703 -3.31387
C -3.83234 -3.06528 -2.29248
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H -3.85082 -3.64353 -1.36472
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C 1.99984 -2.67247 -0.84851
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H 2.68340 4.60731 0.83264
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H -2.94828 -4.75228 0.80378
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H 2.62883 -3.30457 -1.47335

**IMe4$_3$Si**

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C 1.43267 4.41266 -1.11921
C 1.53564 4.57619 0.22843
C 1.22605 2.44599 -2.66824
H 1.03135 1.38101 -2.55203
C 1.60138 3.03006 2.20726
H 1.34057 1.98500 2.37925
Si 3.27297 -0.76784 -0.40417
C 4.07846 -0.17622 -2.04154
H 5.10068 -0.54925 -2.17237

H 4.12319 0.91553 -2.08863
H 3.49511 -0.50860 -2.90485
C 3.02962 -2.70314 -0.62760
C 2.52717 -3.35243 0.67468
H 2.27353 -4.40913 0.50643
H 1.62875 -2.85554 1.05306
H 3.28212 -3.32471 1.46473
C 4.30491 -3.42876 -1.09574
H 5.10323 -3.39971 -0.35314
H 4.70012 -3.00354 -2.02300
H 1.01132 -2.42639 -1.45901
C 4.88070 1.21555 0.81756
H 3.97183 1.82491 0.83233
H 5.40139 1.42562 -0.12052
C 3.99859 -0.49504 2.40225
H 3.77912 -1.54466 2.61170
H 3.06811 0.06146 2.54995
H 4.71474 -0.15468 3.16364
C 5.90401 -1.05772 0.88909
H 6.64580 -0.63370 1.58064
H 6.33767 -1.01617 -0.11442
H 5.78821 -2.11043 1.15739
H 4.08890 -4.48842 -1.29437
C 1.95231 -2.91575 -1.71255
H 1.75057 -3.99003 -1.83860
H 2.26727 -2.53119 -2.68692
C 4.57404 -0.28869 0.98885
H 5.52734 1.56904 1.63260
Al -1.20016 -0.30039 -0.45135
N -1.24196 -2.99644 1.14352
N -1.50428 -3.34685 -0.95433
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C -1.28439 -4.37889 0.97918
C -1.44986 -4.60202 -0.35334
C -1.09300 -2.34536 2.43896
H -0.85750 -1.29574 2.26798
C -1.65511 -3.15155 -2.38871
H -1.55074 -2.08753 -2.60395
C -4.82844 0.28751 -0.61630
C -6.15825 0.61338 0.09083
H -7.00905 0.30430 -0.53289
H -6.25128 0.08715 1.04499
H -6.27771 1.67957 0.29081
C -4.79781 0.99331 -1.98308
H -4.92984 2.07439 -1.88889
H -3.85342 0.81943 -2.50963
H -4.79335 -1.80659 0.07316
C -4.27120 3.48569 0.83660
H -4.94741 3.44637 -0.02086
H -4.81962 3.12007 1.70976
Si -3.25419 0.75550 0.45946
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H -4.51681 0.79550 2.67420
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H -5.60869 0.62599 -2.62783
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H -5.67375 -1.55380 -1.43587
H -3.90667 -1.53633 -1.42767
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C -2.02566 2.94428 1.78105
H -2.49248 2.69179 2.73726
H -1.10895 2.35550 1.69372
H -1.74210 4.00641 1.82674
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H 1.52033 6.41973 -1.83936
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### $^{S}3$

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Al 0.09047 0.39977 -1.14149
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H 2.09264 1.46111 -3.40939
H -2.47109 1.83700 1.11857
H -2.09264 -1.46111 3.40939
C -0.30993 2.21087 -1.90315
C -0.43305 2.42789 -3.29272
C -0.51100 3.34351 -1.08566
C -0.71634 3.68367 -3.83297
H -0.33333 1.58691 -3.97928
C -0.81123 4.60003 -1.61125
H -0.39833 3.24645 -0.00688
C -0.90907 4.77784 -2.99126
H -0.79987 3.80642 -4.90993
H -0.95368 5.44764 -0.94550
H -1.13395 5.75641 -3.40486
C 0.30993 -2.21087 1.90315
C 0.43305 -2.42789 3.29272
C 0.51100 -3.34351 1.08566
C 0.71634 -3.68367 3.83297
H 0.33333 -1.58691 3.97928
C 0.81123 -4.60003 1.61125
H 0.39833 -3.24645 0.00688
C 0.90907 -4.77784 2.99126
H 0.79987 -3.80642 4.90993
H 0.95368 -5.44764 0.94550
H 1.13395 -5.75641 3.40486

### $^{S}3^{Si}$

Al 0.08769 -0.51263 1.08831
Al -0.08769 0.51263 -1.08831
C 1.74184 -1.67443 1.23622
N 2.54279 -1.92902 2.31031
C 3.59456 -2.77409 1.99292
C 3.45139 -3.07850 0.67969
N 2.32081 -2.41056 0.24588
C -1.74184 1.67443 -1.23622
N -2.54279 1.92902 -2.31031
C -3.59456 2.77409 -1.99292
C -3.45139 3.07850 -0.67969
N -2.32081 2.41056 -0.24588
H -4.04061 3.70609 -0.03274
H -4.33383 3.08264 -2.71258
H 4.04061 -3.70609 0.03274
H 4.33383 -3.08264 2.71258
Si -0.60891 0.15813 3.35623
Si 0.60891 -0.15813 -3.35623
H -2.39833 1.48517 -3.20291
H -1.94699 2.43758 0.69096
H 2.39833 -1.48517 3.20291
H 1.94699 -2.43758 -0.69096
C 0.84395 0.35596 4.59466
H 1.25540 -0.61881 4.88903
H 1.65950 0.96103 4.18707
H 0.51098 0.83535 5.52275
C -1.81923 -1.03727 4.21873
H -1.38304 -2.03477 4.33451
H -2.09725 -0.67868 5.21718
H -2.73971 -1.15745 3.63930
C -1.51432 1.84476 3.32339
H -0.89848 2.62634 2.86584
H -2.45459 1.76395 2.76445
H -1.77650 2.18197 4.33249
C -0.84395 -0.35596 -4.59466
H -1.65950 -0.96103 -4.18707
H -1.25540 0.61881 -4.88903
H -0.51098 -0.83535 -5.52275
C 1.81923 1.03727 -4.21873
H 2.09725 0.67868 -5.21718
H 1.38304 2.03477 -4.33451
H 2.73971 1.15745 -3.63930
C 1.51432 -1.84476 -3.32339
H 2.45459 -1.76395 -2.76445
H 0.89848 -2.62634 -2.86584
H 1.77650 -2.18197 -4.33249

### $^{M}3$

Al -0.60191 0.29595 2.23734
N -3.09228 -0.20009 0.30117
N -1.74627 1.14207 -0.71618
C 1.10004 -0.05101 1.09233
C 2.18376 0.85444 1.07623
C 3.34602 0.57277 0.34939
H 4.17062 1.28225 0.35160
C 3.48272 -0.60109 -0.38905
C 2.42250 -1.50926 -0.36301
H 2.50921 -2.43458 -0.92722
C 1.25808 -1.25236 0.36440
C 2.11855 2.15286 1.88053
H 1.08120 2.28045 2.22322
C 2.47456 3.40251 1.06053
H 3.52743 3.40541 0.76513
H 2.29740 4.31163 1.64339
H 1.87929 3.46634 0.14561
C 2.98819 2.05748 3.14432
H 2.67790 1.21228 3.76328
H 2.91288 2.96823 3.74734

H 4.04035 1.91141 2.88080
C 4.73858 -0.87653 -1.19935
H 5.41853 -0.02930 -1.04637
C 5.46645 -2.14308 -0.71887
H 4.84891 -3.03427 -0.86470
H 5.70611 -2.07880 0.34550
H 6.39977 -2.29279 -1.27108
C 4.43180 -0.95546 -2.70478
H 3.76785 -1.79607 -2.92793
H 5.34835 -1.09234 -3.28750
H 3.93862 -0.04406 -3.05343
C 0.14301 -2.29594 0.34285
H -0.64707 -1.94756 1.02272
C 0.60482 -3.65902 0.88087
H 1.03582 -3.55826 1.87972
H 1.36496 -4.10706 0.23474
H -0.23375 -4.36106 0.93913
C -0.48453 -2.43371 -1.05415
H -1.28285 -3.18277 -1.06320
H 0.26416 -2.74645 -1.78759
H -0.90834 -1.48614 -1.39414
C -1.89231 0.42915 0.43218
C -3.68372 0.09481 -0.92928
C -2.83228 0.94552 -1.57234
C -3.65480 -1.02476 1.39634
H -2.93535 -0.88770 2.21076
C -4.99533 -0.48015 1.89045
H -5.26213 -0.97906 2.82507
H -5.80795 -0.65329 1.18291
H -4.92575 0.59114 2.09032
C -3.69674 -2.51500 1.05801
H -3.94899 -3.08114 1.95824
H -2.72759 -2.86366 0.70259
H -4.44553 -2.75401 0.30015
C -5.00610 -0.41745 -1.39910
H -5.84335 0.11400 -0.93729
H -5.13491 -1.47956 -1.19093
H -5.09771 -0.28734 -2.47797
C -3.00831 1.58694 -2.91046
H -3.35860 2.61991 -2.82877
H -3.74934 1.03998 -3.49469
H -2.08469 1.59663 -3.48889
C -0.56495 2.00580 -0.95301
H -0.03521 1.98091 -0.00422
C 0.38140 1.42144 -2.00111
H 0.68921 0.41522 -1.71941
H 1.28293 2.03577 -2.05441
H -0.06438 1.39356 -2.99784
C -0.96063 3.45870 -1.22570
H -0.07369 4.09152 -1.14892
H -1.68893 3.81083 -0.49148
H -1.37548 3.60321 -2.22399

**$M_3^{03}$**

Al -0.68470 -0.99428 1.18521
N -3.48549 -0.25945 0.36839
N -2.05506 0.79279 -0.90727
C 1.22460 -0.48338 0.75238
C 1.81492 0.66996 1.32002
C 3.12632 1.02973 0.98650
H 3.56528 1.92217 1.42632
C 3.89481 0.27598 0.10524
C 3.31990 -0.87489 -0.43966
H 3.90967 -1.48205 -1.11922
C 2.01596 -1.26326 -0.13149
C 1.05838 1.55188 2.30883
H 0.03864 1.14926 2.39224
C 0.92682 3.00408 1.82614
H 1.89953 3.50071 1.76461
H 0.30325 3.58553 2.51259
H 0.47029 3.04906 0.83473
C 1.68184 1.48454 3.71168
H 1.71932 0.45330 4.07200
H 1.09969 2.07446 4.42690
H 2.70440 1.87396 3.71129
C 5.31258 0.69183 -0.25062
H 5.53382 1.60903 0.30906
C 6.34343 -0.36712 0.17508
H 6.19899 -1.30416 -0.37069
H 6.26115 -0.59003 1.24183
H 7.36286 -0.02201 -0.02414
C 5.44710 1.02138 -1.74697
H 5.25460 0.13948 -2.36504
H 6.45560 1.37680 -1.98072
H 4.73545 1.79592 -2.04502
C 1.47573 -2.56672 -0.71245
H 0.37793 -2.49868 -0.68727
C 1.87246 -3.75278 0.18326
H 1.51946 -3.60504 1.20702
H 2.96115 -3.86162 0.21740
H 1.44770 -4.68994 -0.19132
C 1.87799 -2.82820 -2.17034
H 1.32251 -3.68228 -2.56913
H 2.94140 -3.06642 -2.26690
H 1.67216 -1.96306 -2.80497
C -2.12902 -0.06869 0.17283
C -4.22378 0.41836 -0.60317
C -3.33262 1.07185 -1.40011
C -3.98173 -1.19370 1.39226
H -3.10821 -1.37008 2.03040
C -5.06299 -0.59017 2.29214
H -5.18607 -1.22167 3.17550
H -6.03544 -0.52597 1.80260
H -4.77512 0.40808 2.62914
C -4.38070 -2.53671 0.77660
H -4.62095 -3.25641 1.56370
H -3.55431 -2.93999 0.18763
H -5.25629 -2.44428 0.12934
C -5.71562 0.43330 -0.67772
H -6.16345 1.03329 0.12013
H -6.14340 -0.56906 -0.61341
H -6.04146 0.86129 -1.62590
C -3.61544 1.96322 -2.56430
H -3.41377 3.01458 -2.33993
H -4.66498 1.88801 -2.84911
H -3.02284 1.69618 -3.44211
C -0.76087 1.14997 -1.51790
H -0.02853 0.92136 -0.74588
C -0.45095 0.25130 -2.71708
H -0.52888 -0.79897 -2.43065
H 0.56880 0.43153 -3.06618
H -1.13378 0.43343 -3.55121
C -0.61830 2.64175 -1.83348
H 0.44287 2.87799 -1.94204
H -1.01687 3.25566 -1.02321
H -1.11203 2.93165 -2.76182

**$M_3^{Si}$**

Al 0.21958 -0.08535 2.04631
N -1.76675 1.30264 0.03506
N -2.28364 -0.77754 0.28386
C -1.31770 0.13709 0.57726
C -3.01924 1.12970 -0.56573
C -3.34309 -0.18544 -0.41445
C -0.98927 2.54818 0.18989
H -0.00086 2.19690 0.49620
C -1.55587 3.41984 1.31269
H -2.54754 3.80455 1.06204
H -1.62879 2.84827 2.24002
H -0.89970 4.27563 1.48981
C -0.79942 3.30589 -1.12557
H -0.53717 2.62479 -1.93728
H -1.68768 3.86812 -1.41449
H 0.01728 4.02184 -1.01153
C -2.17972 -2.16812 0.77109
H -1.16536 -2.22792 1.17560
C -3.14562 -2.42879 1.92854
H -2.96169 -3.42036 2.34931
H -2.99807 -1.69081 2.71922
H -4.18836 -2.39273 1.60675
C -2.27957 -3.19988 -0.35347
H -1.64131 -2.92576 -1.19472
H -1.94656 -4.17204 0.01737
H -3.30226 -3.32066 -0.71288
C -3.79157 2.20475 -1.25691
H -3.35892 2.46828 -2.22619
H -4.81506 1.87515 -1.43683
H -3.84814 3.11797 -0.66145
C -4.53815 -0.91449 -0.93504
H -4.29120 -1.53703 -1.79982
H -4.99336 -1.56104 -0.18326
H -5.30210 -0.20536 -1.25487
C 3.25998 1.12558 0.08045
C 4.76157 0.83467 -0.11093
H 5.30702 1.76528 -0.32331
H 5.21007 0.39669 0.78410
H 4.95266 0.15183 -0.94149
C 2.73874 1.85219 -1.16964
H 2.94671 1.29391 -2.08494
H 1.65970 2.01878 -1.12871
H 3.41993 1.60139 2.22781
C 3.20216 -1.78214 -2.00023
H 3.53593 -0.84894 -2.46025
H 4.03631 -2.18131 -1.41617
Si 2.23152 -0.50749 0.46195
C 3.41362 -1.56219 1.54262
H 4.28789 -1.92875 0.99446
H 3.78175 -0.97625 2.39068
H 2.90207 -2.43129 1.96662
H 3.21837 2.83523 -1.27698
C 3.11803 2.07490 1.28886
H 3.74680 2.96624 1.15594
H 2.08952 2.42732 1.42400
C 1.93290 -1.59144 -1.14953
C 1.47151 -2.98392 -0.67181
H 2.25618 -3.51091 -0.12353
H 0.59714 -2.92440 -0.01605
H 1.19129 -3.61448 -1.52693
C 0.82544 -0.99996 -2.04067
H 0.62321 -1.66191 -2.89500
H -0.10866 -0.87116 -1.49039
H 1.09779 -0.02420 -2.44935
H 3.01372 -2.49075 -2.81981

**$M_3^{Si03}$**

Al 0.01606 -1.29156 0.71984
N -1.75514 1.11397 -0.13098
N -2.88520 -0.72999 0.11708
C -1.60678 -0.21982 0.17459
C -3.10000 1.42916 -0.33722
C -3.80660 0.27377 -0.18324
C -0.62964 2.05526 0.00951
H 0.24408 1.40353 0.03316
C -0.70290 2.79332 1.34878
H -1.56877 3.45773 1.39803
H -0.76900 2.07767 2.17096
H 0.19301 3.40060 1.49713
C -0.45630 2.99220 -1.18672
H -0.52764 2.44516 -2.12810
H -1.18317 3.80475 -1.19549

H 0.53629 3.44604 -1.13942
C -3.16463 -2.14367 0.43222
H -2.16926 -2.60539 0.44266
C -3.75607 -2.29632 1.83421
H -3.82966 -3.35539 2.09488
H -3.11295 -1.80973 2.57035
H -4.75685 -1.86397 1.90892
C -3.96904 -2.85588 -0.65651
H -3.55181 -2.64877 -1.64452
H -3.91614 -3.93444 -0.48921
H -5.02414 -2.57961 -0.65763
C -3.60965 2.78241 -0.71014
H -3.32090 3.06464 -1.72668
H -4.69870 2.79879 -0.66680
H -3.24879 3.56342 -0.03789
C -5.27701 0.06203 -0.34116
H -5.52395 -0.44198 -1.28009
H -5.69780 -0.53237 0.47141
H -5.79760 1.01983 -0.34086
C 3.30761 0.57270 1.24280
C 4.81952 0.28442 1.35987
H 5.30709 1.06816 1.95575
H 5.01871 -0.66729 1.85774
H 5.31926 0.26030 0.38921
C 3.13246 1.98038 0.64600
H 3.59685 2.07850 -0.33760
H 2.08179 2.25926 0.54524
H 2.79736 -0.40366 3.14895
C 4.14937 -0.35060 -2.08908
H 4.47206 0.63115 -1.73556
H 4.84064 -1.09516 -1.68298
Si 2.40877 -0.82961 0.20398
C 3.27192 -2.45388 0.71823
H 4.30052 -2.50639 0.34753
H 3.30843 -2.55368 1.80696
H 2.73378 -3.32381 0.33483
H 3.59985 2.73050 1.29812
C 2.71451 0.57494 2.66630
H 3.24531 1.29767 3.30127
H 1.65463 0.84505 2.66885
C 2.68423 -0.65628 -1.72492
C 2.29903 -1.99732 -2.38364
H 2.96355 -2.81033 -2.07951
H 1.27510 -2.29543 -2.13729
H 2.36519 -1.91470 -3.47702
C 1.78019 0.44006 -2.31638
H 1.91853 0.50944 -3.40393
H 0.72251 0.22378 -2.13730
H 1.99468 1.42738 -1.90125
H 4.27748 -0.35563 -3.18024

**7**

Al -1.44717 -0.26209 0.10936
Al 1.47003 -0.26129 -0.15594
N 0.07827 -1.28425 2.47946
N -0.04377 -1.62666 -2.35987
N -3.54788 -2.35073 1.28979
N -4.31516 -1.22435 -0.38862
N 4.33873 -1.12168 0.49482
N 3.59156 -2.48074 -1.01156
C -5.48152 5.55338 0.79398
H -5.70850 5.06636 1.74704
H -5.98167 4.98549 0.00491
H -5.91978 6.55600 0.82305
C -3.96514 5.62302 0.55030
H -3.80843 6.14153 -0.40368
C -3.34569 4.24241 0.42158
C -3.40659 3.31707 1.46046
H -3.92070 3.59079 2.37717
C -2.13576 1.65122 0.17747
C 2.15145 1.62241 -0.49734
C 2.85173 1.84612 -1.71130
C 3.43621 3.08451 -1.99487
H 3.96585 3.22730 -2.93357
C 3.36290 4.15086 -1.10693
C 3.99605 5.49330 -1.43029
H 4.48761 5.39684 -2.40633
C 5.07642 5.87539 -0.40468
H 5.56470 6.81527 -0.68101
H 5.84389 5.09990 -0.33409
H 4.64637 6.00668 0.59262
C 2.93500 6.60007 -1.55375
H 3.39279 7.55229 -1.84034
H 2.41301 6.75339 -0.60479
H 2.18336 6.34164 -2.30392
C 2.05627 2.72560 0.39199
C 1.29251 2.67809 1.71651
H 0.77036 1.71914 1.77460
C 2.24435 2.78219 2.92250
H 2.87602 3.67199 2.84868
H 2.90196 1.91450 2.99966
H 1.68626 2.85526 3.85967
C 0.22481 3.78365 1.79853
H 0.67843 4.77810 1.84664
H -0.38627 3.66357 2.69554
H -0.44372 3.75803 0.94001
C 2.66600 3.94523 0.08058
H 2.58480 4.76929 0.78264
C 0.13867 -0.66614 1.35268
C 1.14866 -1.78443 3.23458
C 1.47875 -1.14621 4.45077
C 0.74062 0.10331 4.84586
H 1.17409 0.56527 5.73597
H -0.30979 -0.12530 5.05286
H 0.73557 0.83903 4.04371
C 2.42948 -1.72654 5.28833
H 2.68617 -1.22798 6.21939
C 3.04356 -2.93257 4.95657
H 3.77939 -3.37528 5.62032
C 2.69373 -3.56909 3.76865
H 3.15518 -4.51917 3.51056
C 1.75159 -3.01671 2.89726
C 1.32141 -3.76454 1.66162
H 1.52793 -3.20890 0.74833
H 0.24498 -3.95207 1.66404
H 1.82804 -4.72992 1.59523
C -0.10810 -0.85728 -1.33046
C -1.11589 -2.24357 -3.02095
C -1.70917 -3.41243 -2.49403
C -2.65804 -4.09298 -3.26127
H -3.11357 -4.99355 -2.85698
C -3.02179 -3.64616 -4.52870
H -3.76256 -4.18647 -5.10950
C -2.41520 -2.50381 -5.04725
H -2.68189 -2.15445 -6.04133
C -1.45900 -1.80020 -4.31732
C -0.73043 -0.62186 -4.90361
H -1.14901 -0.32694 -5.86861
H 0.32830 -0.86160 -5.04392
H -0.75715 0.24012 -4.23881
C -1.26104 -3.96532 -1.16589
H -1.77111 -4.90536 -0.94415
H -1.44892 -3.27566 -0.34485
H -0.18574 -4.15983 -1.15770
C -3.19834 -1.41463 0.36317
C -4.87936 -2.73091 1.12514
C -5.36225 -2.02272 0.06291
C -6.71954 -2.10273 -0.55569
H -7.41613 -2.58410 0.13122
H -6.71064 -2.69075 -1.47727
H -7.12643 -1.12051 -0.79405
C -4.35891 -0.27033 -1.52720
H -3.32232 0.04643 -1.63598
C -5.19317 0.96867 -1.20445
H -6.25412 0.73320 -1.09800
H -5.09316 1.68784 -2.01960
H -4.84377 1.45340 -0.29493
C -4.76140 -0.95208 -2.83322
H -4.22761 -1.89070 -2.96884
H -4.49703 -0.30164 -3.66901
H -5.83452 -1.13839 -2.89419
C -5.60130 -3.74305 1.95391
H -5.38922 -3.63401 3.01717
H -5.34726 -4.76738 1.66812
H -6.67810 -3.62834 1.82690
C -2.60274 -2.88748 2.30497
H -1.63476 -2.47629 2.02929
C -2.88172 -2.37245 3.71666
H -2.78084 -1.29241 3.76417
H -2.13470 -2.79440 4.39226
H -3.87093 -2.65336 4.08495
C -2.50984 -4.41591 2.26866
H -3.35093 -4.90179 2.76440
H -1.60687 -4.72099 2.80163
H -2.44205 -4.79400 1.24909
C -2.66769 3.86190 -0.72966
H -2.60127 4.57902 -1.54310
C -2.05838 2.60732 -0.86679
C -1.31719 2.36404 -2.18271
H -0.80046 1.40309 -2.10908
C -0.24975 3.44215 -2.44270
H -0.70414 4.42119 -2.62095
H 0.34102 3.19406 -3.32742
H 0.43724 3.53667 -1.60349
C -2.28928 2.29675 -3.37582
H -2.91738 3.19075 -3.42131
H -2.95013 1.42983 -3.31808
H -1.74642 2.23154 -4.32260
C -3.26646 6.44800 1.64468
H -3.67115 7.46418 1.68933
H -2.19143 6.51426 1.45959
H -3.40342 5.99120 2.62935
C -2.99135 1.12315 2.55622
H -2.40970 0.21720 2.36578
C -4.46553 0.72024 2.74195
H -5.08924 1.60081 2.91909
H -4.59295 0.05067 3.59702
H -4.85711 0.21266 1.85885
C -2.42792 1.72071 3.85431
H -1.37155 1.96599 3.74531
H -2.52140 1.00833 4.67976
H -2.95780 2.63124 4.14652
C 3.22875 -1.42540 -0.22913
C 5.39528 -1.96546 0.16505
C 4.92540 -2.82103 -0.78893
C 5.66082 -3.93406 -1.46159
H 6.73598 -3.79000 -1.35145
H 5.44970 -3.98277 -2.52944
H 5.41726 -4.90879 -1.03014
C 2.65498 -3.16882 -1.93982
H 1.68237 -2.73195 -1.72817
C 2.93498 -2.86452 -3.41138
H 2.82065 -1.80503 -3.61947
H 2.19734 -3.39234 -4.01941
H 3.92979 -3.18346 -3.73062
C 2.57648 -4.67659 -1.68050
H 3.42218 -5.22118 -2.10184
H 1.67631 -5.06453 -2.16204
H 2.51285 -4.90363 -0.61664

C 6.74989 -1.94323 0.79402
H 7.45937 -2.49363 0.17544
H 6.74531 -2.41189 1.78175
H 7.13706 -0.93156 0.90962
C 4.36333 -0.02053 1.49224
H 3.32183 0.29389 1.55059
C 5.18720 1.17333 1.01040
H 6.25352 0.94249 0.95997
H 5.05997 2.00040 1.71138
H 4.85170 1.51885 0.03422
C 4.76184 -0.51358 2.88166
H 4.24089 -1.43433 3.13758
H 4.47715 0.23827 3.62002
H 5.83717 -0.67130 2.97761
C 3.03047 0.75064 -2.76034
H 2.46062 -0.12328 -2.43459
C 4.50878 0.34177 -2.89123
H 5.11860 1.18922 -3.21610
H 4.63997 -0.45689 -3.62641
H 4.91425 -0.00932 -1.94056
C 2.45133 1.14075 -4.12855
H 2.96047 2.00966 -4.55443
H 1.39055 1.37765 -4.04753
H 2.55495 0.31737 -4.84214
C -2.82335 2.05330 1.35540

**10**

O 0.00008 -0.00012 -1.23486
O -0.00003 -0.00014 1.34190
Al -0.83112 0.91653 0.05277
Al 0.83118 -0.91679 0.05285
N 0.07686 -3.57694 1.30122
N -1.10410 -3.27989 -0.48299
N -0.07699 3.57673 1.30128
N 1.10422 3.27970 -0.48277
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C 3.64833 -0.33222 0.90110
C 5.00206 -0.10616 0.62057
H 5.63046 0.38429 1.36098
C 5.57283 -0.47786 -0.59420
C 4.75929 -1.12469 -1.52787
H 5.18752 -1.42737 -2.47950
C 3.41096 -1.37410 -1.27066
C 3.09758 0.12523 2.25094
H 2.04066 -0.14291 2.29196
C 3.80715 -0.56812 3.42508
H 3.33961 -0.29433 4.37674
H 4.86459 -0.29319 3.48557
H 3.76005 -1.65707 3.32683
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C 7.14720 0.86515 -2.03559
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H 6.74058 0.46804 -2.97043
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C 3.21680 -3.36586 -2.85709
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C 2.21676 -1.11965 -3.49598
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C -0.06033 -2.77637 0.21733
C -1.63780 -4.39237 0.16860
C -0.89932 -4.57223 1.30458
C 1.07574 -3.25922 2.35375
H 1.77300 -2.58529 1.85254
C 1.89124 -4.47641 2.79049
H 2.77244 -4.12872 3.33442
H 2.23613 -5.05108 1.92770
H 1.33930 -5.13969 3.45708
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H 1.19615 -2.20344 4.22767
H -0.30957 -3.11101 4.03567
H -0.05430 -1.59526 3.12848
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H -2.88797 -6.11802 0.23959
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H -3.75528 -4.62846 -0.13342
C -1.52689 -2.69030 -1.78412
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H -3.28619 -1.74015 -0.92245
H -3.67018 -3.17426 -1.90112
C -2.81614 0.95415 -0.05610
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H -5.63050 -0.38442 1.36069
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H -4.17474 -2.03394 2.35186
C -7.02906 0.16758 -0.90053
H -7.46362 -0.28321 0.00030
C -7.84055 1.43370 -1.21999
H -8.89733 1.19264 -1.37291
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H -1.62519 2.36767 -1.87499
C -3.21655 3.36598 -2.85707
H -2.53152 3.89666 -3.52644
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H -4.13173 3.16989 -3.42286
C -2.21661 1.11973 -3.49600
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H -1.62409 0.28362 -3.12261
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C 0.89919 4.57202 1.30479
C 1.63783 4.39218 0.16892
C -1.07596 3.25897 2.35373
H -1.77316 2.58503 1.85246
C -1.89150 4.47615 2.79040
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H -2.23650 5.05069 1.92757
H -1.33957 5.13955 3.45687
C -0.42677 2.49747 3.50942
H 0.30925 3.11084 4.03574
H 0.05407 1.59505 3.12856
H -1.19646 2.20322 4.22766
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H 2.02647 6.11214 2.24952
H 1.08294 5.14719 3.37074
H 0.28457 6.35359 2.36115
C 2.82200 5.17271 -0.29930
H 2.88800 6.11782 0.24010
H 2.76509 5.41133 -1.36185
H 3.75536 4.62826 -0.13277
C 1.52718 2.69013 -1.78385
H 0.96130 1.75819 -1.84197
C 1.10659 3.58481 -2.95066
H 1.29902 3.06240 -3.89104
H 1.65580 4.52940 -2.97884
H 0.03885 3.81025 -2.90485
C 3.00789 2.31176 -1.80779
H 3.18775 1.66599 -2.66886
H 3.28650 1.74030 -0.92190
H 3.67044 3.17423 -1.90084

**11**

Al 0.78456 -0.84008 0.12769
Al -0.84872 0.91499 0.08977
O -0.03652 0.00819 -1.22678
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N 0.31020 -3.61653 1.29264
N -0.29764 3.68786 1.21933
N 0.99481 3.32174 -0.47804
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C 6.97619 0.08100 -0.83736
C 5.53172 -0.27685 -0.52717
C 4.73343 -0.94224 -1.45980
C 3.39262 -1.23237 -1.20094
C 2.78796 -0.83280 0.01591
C -2.85111 0.88798 0.00659
C -3.64557 0.26930 0.99695
C -4.98873 -0.03431 0.74309
C -5.58702 0.25400 -0.48140
C -7.02635 -0.14674 -0.76141
C -7.09450 -1.23452 -1.84774
C -7.90606 1.05793 -1.13282
C 4.95270 0.07581 0.68959
C 3.60628 -0.18789 0.97001
C 3.04625 0.26289 2.31772
C 3.78086 -0.38829 3.49968
C 3.02692 1.79432 2.44521
C 7.82415 -1.15409 -1.18154
C 0.02447 -2.74739 0.28650
C -1.57100 -2.68313 -1.62023
C -1.12163 -3.44489 -2.86825
C -3.08280 -2.46950 -1.54893
C -1.38436 -4.51855 0.19576
C -2.52040 -5.37394 -0.25891
C -0.54755 -4.71613 1.25673
C -0.53380 -5.84521 2.23403
C 1.41848 -3.34875 2.23429

C 0.97598 -3.38679 3.69724
C 2.63411 -4.22228 1.92642
C -0.06680 2.81290 0.20249
C 0.63780 4.72284 1.20240
C 0.70013 5.83731 2.19465
C 1.44466 4.49804 0.12389
C 2.61254 5.30336 -0.34272
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C 2.99636 2.41867 -1.70610
C 1.03608 3.48513 -2.95522
C -3.47531 1.22266 -1.22012
C -2.68576 1.91453 -2.33029
C -2.33763 0.94478 -3.47091
C -3.38623 3.17665 -2.85728
C -4.81259 0.89532 -1.45058
C -3.05778 -0.11008 2.35463
C -2.98238 -1.63407 2.53917
C -3.80362 0.55900 3.51925
H 8.08972 1.43864 -2.14107
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H 6.65291 0.73589 -2.89540
H 7.40297 0.53147 0.06741
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H -5.58463 -0.52419 1.51042
H -7.43150 -0.57797 0.16246
H -6.71251 -0.85943 -2.80185
H -8.12472 -1.56845 -2.00827
H -6.49157 -2.10362 -1.57143
H -7.57268 1.52052 -2.06613
H -7.87316 1.82421 -0.35411
H -8.94882 0.75386 -1.26883
H 5.56781 0.58402 1.42937
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H 4.82290 -0.06089 3.56231
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H 7.47006 -1.63674 -2.09687
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H -1.10389 -1.69683 -1.64619
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H -0.97782 -5.56414 3.19337
H 0.47648 -6.20705 2.43226
H 1.70540 -2.31982 2.01682
H 0.82371 -4.40102 4.06868
H 0.05348 -2.81854 3.83474
H 1.75077 -2.92490 4.31357
H 2.43360 -5.28396 2.08875
H 3.46831 -3.93554 2.57146
H 2.94743 -4.07807 0.89090
H 0.66841 5.47246 3.22309
H -0.12020 6.55003 2.07127
H 1.63387 6.38768 2.08022
H 3.56137 4.80882 -0.11796
H 2.62065 6.27662 0.14865
H 2.58394 5.48485 -1.41797
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H 3.29825 1.94003 -0.77431
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H 3.23722 1.71930 -2.50816
H 1.29946 2.93379 -3.86144
H 1.50494 4.47093 -3.01729
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H -1.73691 2.24756 -1.89714
H -1.71205 0.13543 -3.09314
H -1.77780 1.45722 -4.26074
H -3.24420 0.52592 -3.92057
H -2.73954 3.70884 -3.56271
H -3.63547 3.86061 -2.04115
H -4.31446 2.93971 -3.38516
H -5.26168 1.13193 -2.41144
H -2.02209 0.24831 2.37296
H -2.36299 -2.08578 1.76110
H -3.97440 -2.09456 2.49402
H -2.53889 -1.88883 3.50811
H -4.83305 0.19887 3.60521
H -3.84965 1.64405 3.38617
H -3.30280 0.35425 4.47141
C 2.57997 -1.96015 -2.27072
C 2.23761 -1.04089 -3.45399
C 3.25203 -3.25907 -2.74221
C -1.32791 3.39963 2.24292
C -0.69282 2.80207 3.49945
C -2.24852 4.58741 2.52363
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H 1.62464 -0.20697 -3.11056
H 1.66562 -1.58315 -4.21469
H 3.49424 -3.90976 -1.89689
H 4.18070 -3.06526 -3.28658
H 2.59025 -3.81135 -3.41753
H -1.94931 2.63293 1.77737
H -0.09673 1.92649 3.23428
H -1.47334 2.48769 4.19626
H -0.04973 3.52119 4.01265
H -2.59428 5.04245 1.59285
H -1.77646 5.35624 3.13654
H -3.12631 4.23038 3.06756

**12**[trans]

Al -1.16213 0.10554 0.75642
Al 0.88698 0.83971 -0.64003
N -0.62037 -2.99280 0.84611
N -1.85046 -2.49326 -0.85519
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C -1.68004 -3.87759 -0.88066
C 0.23120 -2.81114 2.04642
H 0.34428 -1.73169 2.11366
C -0.48214 -3.27361 3.31712
H -1.44330 -2.77032 3.42544
H 0.12982 -3.02455 4.18782
H -0.65423 -4.35241 3.32979
C 1.62363 -3.41635 1.86945
H 2.28702 -3.00889 2.63338
H 2.04793 -3.14753 0.90236
H 1.62991 -4.50199 1.97588
C -0.39577 -5.53873 0.59775
H -0.44595 -5.69764 1.67494
H 0.64229 -5.68909 0.28823
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C -2.56740 -1.66893 -1.85795
H -2.40956 -0.65239 -1.51242
C -4.07827 -1.89917 -1.85204
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H -4.55300 -1.12738 -2.46152
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H 3.17581 6.59994 1.25419
H 2.83959 5.53700 2.61792
C 4.49292 5.18308 -0.80881
H 4.27981 5.73092 -1.73097
H 5.36476 4.55518 -0.99302
H 4.77874 5.91337 -0.05165
C 3.50414 2.43991 -2.02144
H 2.78729 1.64595 -2.22418

C 3.59413 3.28911 -3.28993
H 2.64689 3.79616 -3.48619
H 3.80457 2.63386 -4.13863
H 4.39023 4.03420 -3.24934
C 4.82831 1.78549 -1.62634
H 4.69385 1.12869 -0.76782
H 5.60723 2.51658 -1.39765
H 5.18454 1.17059 -2.45645
C 2.45151 -0.43898 -0.23241
C 3.20141 -0.36301 0.97027
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H 4.87241 -1.10346 2.11226
C 4.71584 -2.14116 0.25451
C 3.95908 -2.25655 -0.91033
H 4.23921 -3.00677 -1.64494
C 2.84719 -1.44409 -1.15458
C 2.85871 0.63221 2.08090
H 1.92788 1.12761 1.80165
C 2.59195 -0.04439 3.43527
H 2.32089 0.69994 4.19078
H 3.47039 -0.58078 3.80531
H 1.76398 -0.75028 3.36723
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H 3.68424 2.44216 2.99626
H 4.11698 2.24352 1.29619
H 4.90219 1.25664 2.52726
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H 6.35710 -2.72258 1.46841
C 5.46029 -4.50988 0.70352
H 4.72025 -4.59828 1.50337
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H 1.20600 -1.03477 -2.44803
C 2.90102 -1.32822 -3.69039
H 2.31615 -1.46130 -4.60644
H 3.79840 -1.94927 -3.77258
H 3.22218 -0.28417 -3.64832
C 1.55131 -3.13868 -2.53674
H 0.93372 -3.38335 -1.66986
H 2.36585 -3.86743 -2.58192
H 0.94046 -3.27691 -3.43489
H 0.71919 1.02539 -2.24478
H -0.76698 0.08956 2.33435

**12$^{cis}$**

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**$H_2$**

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H 0.00000 0.00000 -0.37095

**3-I$^i$Pr$_2$Me$_2$**

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Al -1.21624 -2.20270 -0.17617
C 3.57334 -1.23989 1.25446
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### $3^{Si}$-I$^{i}$Pr$_2$Me$_2$

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H 7.20036 -2.01968 0.18677

### I$^{i}$Pr$_2$Me$_2$

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N 1.06768 -0.40267 0.12934
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C 0.68171 0.92754 -0.08943

C -2.42998 -0.95968 0.15760
H -2.25440 -1.99636 0.44979
C -3.06991 -0.96432 -1.23416
H -3.27367 0.04528 -1.59880
H -2.41074 -1.45919 -1.95039
H -4.02013 -1.50535 -1.21110
C -3.32068 -0.31036 1.22055
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H -4.23099 -0.90226 1.34833
C 2.42992 -0.95972 0.15762
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H 4.02032 -1.50510 -1.21090
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H 3.27374 0.04548 -1.59859
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H 2.80456 -0.26954 2.18268
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C -1.61077 2.09019 -0.22903
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H 2.42731 1.89026 -0.92615
H 1.07421 2.96218 -0.60624

**IMe$_4$**

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C -0.67999 0.63703 -0.00014
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C -2.43662 -1.16534 -0.00005
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H 2.96935 -0.81316 0.88821
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C -1.66333 1.75778 0.00017
H -2.31412 1.73065 -0.88064
H -2.31367 1.73038 0.88132
H -1.15316 2.72238 0.00017

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