Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Table of Contents

1. Synthetic procedures

1.1. General remarks

All experiments were carried out under an inert nitrogen atmosphere in a glove box (MBraun, Labmaster SP) or by using standard *Schlenk* techniques. Benzene, THF, diethyl ether, *n*-pentane, hexanes and toluene were degassed with nitrogen, dried over activated aluminum oxide (Innovative Technology, Pure Solv 400-4-MD, Solvent Purification System) and stored under inert atmosphere over molecular sieves (3Å). *m*-Xylene was degassed with nitrogen, refluxed on CaH_2 for 24 h, distilled under nitrogen atmosphere stored over molecular sieves (3Å). Deuterated benzene (C_6D_6; 99.6+% D), toluene-d_8 (99.6+% D), THF-d_8 (99.5+% D), $CDCl_3$ (99.8+% D) were purchased from Deutero GmbH or Sigma-Aldrich and stored over molecular sieves (3Å). Sodium tetraphenylborate (99.5%) was purchased from abcr, graphite (> 99%) was purchased from AlfaAesar, both used as is. (BDI)Al[S1] and $Li(BPh_4)$[S2] were synthesized according to a literature procedure.

The ball-mill used was a ULTRA-TURRAX® Tube Drive P control from IKA. Mechanochemical reactions were performed in a 20 mL polypropylene vessel with stainless steel balls (diameter: 5 mm, weight: 0.52 g, type: AISI 304).

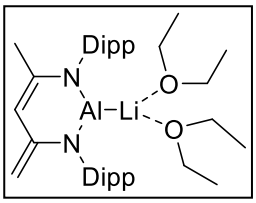
Multinuclear NMR spectra were recorded on a Bruker Avance III HD 400 MHz or 600 MHz spectrometer at ambient temperature. Chemical shifts δ are reported in *parts per million* (ppm) relative to Me_4Si as external standard and referenced internally to the carbon nuclei ($^{13}C\{^1H\}$) or residual protio solvent resonances (^1H) of the deuterated solvents. Assignments of resonance signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra were made based on two dimensional NMR correlation (HSQC, HMBC, COSY) and ATP experiments. Coupling constants *J* are given in Hertz (Hz). Signal multiplicities are abbreviated as follows: s (singlet), d (doublet), sept (septet), m (multiplet) and br (broad). Elemental analyses were obtained on a Euro Vector EA3000 Elemental Analyzer from Hekatech.

All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

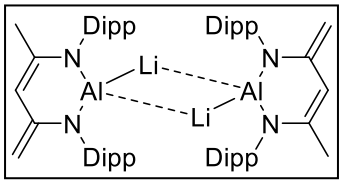
Diffusion NMR measurements (DOSY) were conducted on a Bruker AVANCE NMR spectrometer operating at 600.13 MHz for proton resonance equipped with a 5 mm PABDO BB/19F-1H/D probe with Z-GRD and actively shielded gradient coil with a maximum gradient strength of 5.3500094 G/mm (at 10 A). Parameter optimization was carried out empirically employing the pulse program ledbpgp2s1D using stimulated echo and LED (D21 = 5 ms, longitudinal eddy current delay as a Z-filter) with bipolar gradient pulses (P30) and two spoiling gradients (P19 = 600 µs) leading to values for gradient pulse length (P30 = adjusted [µs], in case of bipolar gradients *little DELTA*0.5*) and diffusion time (D_20 = 60 ms, *big DELTA*). Delay for gradient recovery was set to 200 µs. The diffusion experiment was executed with variable gradients from 2% to 98% gradient strength with 32 increment values (difframp calculated with the AU-program *DOSY*). In this case the pulse program ledbpgp2s was applied for data aquiring of this pseudo-2D Experiment. Data processing was performed with the T1/T2 software package (SimFit) of TopSpin (version 3.2, Bruker Biospin) by fitting area data (integration of all peaks of interest of the same molecule) of diffusion decays. From these Stejskal-Tanner fitting curves calculated diffusion constants were obtained and assimilated statistically

1.2 Complex Synthesis

1.2.1. Synthesis of (BDI-H)Al$^-$Li$^+$·(Et$_2$O)$_n$ and [(BDI-H)Al$^-$Li$^+$]$_2$



Dimer [(BDI-H)Al$^-$K$^+$]$_2$ (113 mg, 117 µmol) and Li(BPh$_4$) (76.4 mg, 234 µmol), were suspended in diethyl ether and stirred for 1.5 h at room temperature. During filtration of the reaction mixture crystals already started to precipitate. The mother liquor, containing crystals, was stored at – 30 °C to obtain the etherate complex as big yellow crystals suitable for XRD analysis. Full characterization of the ether complex is hindered by the very weak bonding of ether to lithium. Short term storage of crystals under nitrogen atmosphere at ambient temperature resulted in slow evaporation of diethyl ether. Elimination of ether resulted in formation of the dimer [(BDI-H)Al$^-$Li$^+$]$_2$. It was therefore considered to completely remove all ether ligands. Complete abstraction of both ether molecules could be achieved by decanting off the ether phase and adding 4 ml of toluene to the crystals. The flask was heated to 70 °C and all volatiles removed in a vacuum while maintaining heating. The dimeric complex [(BDI-H)Al$^-$Li$^+$]$_2$ was obtained as pale yellow powder containing circa 0.08 eq. of Et$_2$O as indicated by NMR (79 mg) 74% yield, based on [(BDI-H)Al$^-$K$^+$]$_2$. Elemental analysis (%) for $C_{29.32}H_{40.80}N_2Al_1Li_1O_{0.08}$. Calculated: N 5.92, C 76.72, H 9.17, found: N 5.92, C 76.92, H 9.30. Crystals suitable for XRD measurements were obtained by storing a saturated toluene solution at –30 °C.



^{1}H NMR (600.13 MHz, THF-d_8, 298 K): δ (ppm) = 7.02 (t, ^3J_H = 7.9 Hz, 4 H, aromatic *meta* CH), 6.95 (overlapping, 2 H, aromatic *para*-CH), 4.75 (s, 1H, backbone CH), 3.75 and 3.70 (each: m, 2 H, DIPP-CH), 2.98 (d, ^2J_H = 2.0 Hz, 1 H, backbone-CH$_2$), 2.17 (d, ^2J_H = 2.0 Hz, 1 H, backbone-CH$_2$), 1.39 (s, 3 H, backbone-CH$_3$), 1.26 to 1.22 (overlapping, 24 H, DIPP-CH$_3$).

^{13}C{^{1}H} NMR (150.92 MHz, THF-d_8, 298 K): δ (ppm) = 155.9 (H$_2$C=**C**-N), 148.6 and 148.5 (aromatic N-C), 147.8 and 147.5 (aromatic *ortho* C*i*Pr), 143.0 (backbone H$_3$C-**C**=CH), 124.9 and 124.6 (aromatic *para* CH), 123.6 and 123.3 (aromatic *meta* CH), 103.0 (backbone CH), 76.0 (backbone CH$_2$), 28.8 and 28.7 (DIPP-CH), 26.3 and 26.0 and 26.0 and 24.4 (DIPP-CH$_3$ and backbone CH$_3$).

^{7}Li NMR (233.23 MHz, THF-d_8, 298 K): δ (ppm) = -0.56.

^{27}Al NMR (156.44 MHz, THF-d_8, 298 K): no signal within a range of -580 to 580 ppm.

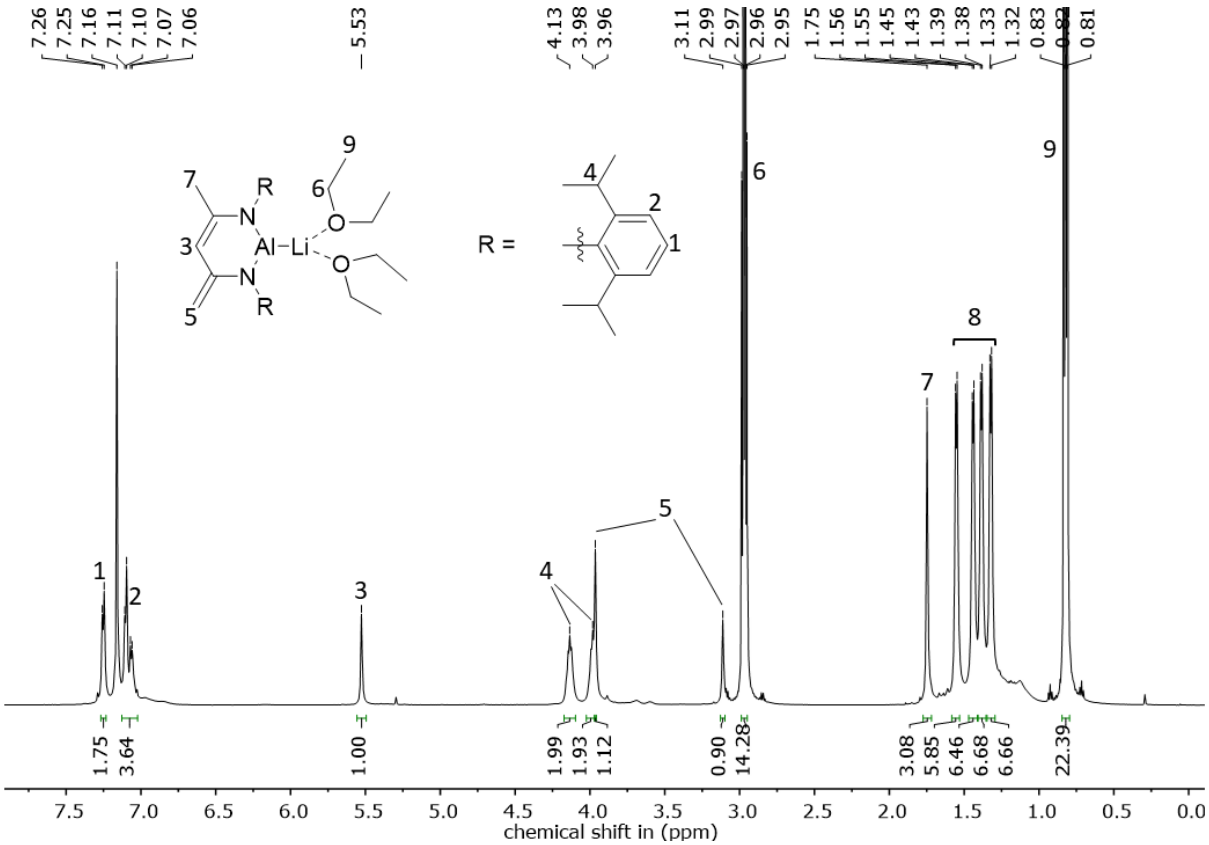


Figure S1: ^{1}H NMR spectrum of $[(BDI\text{-}H)Al^{-}Li^{+}]_2(Et_2O)_n$. 600.13 MHz, C_6D_6, 298 K. Crystals from Et_2O were not dried to prevent dimer formation and contain ca. 3 equivalents of ether.

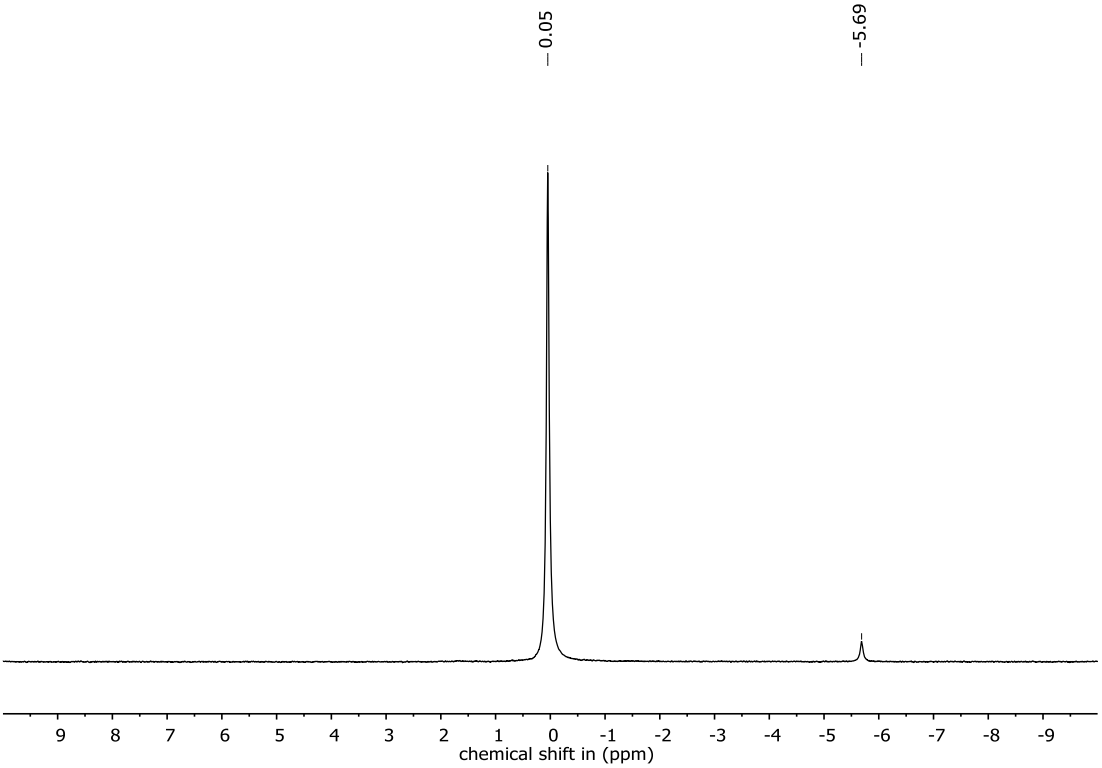


Figure S2: ^{7}Li NMR spectrum of $[(BDI\text{-}H)Al^{-}Li^{+}]_2(Et_2O)_n$. 600.13 MHz, C_6D_6, 298 K.

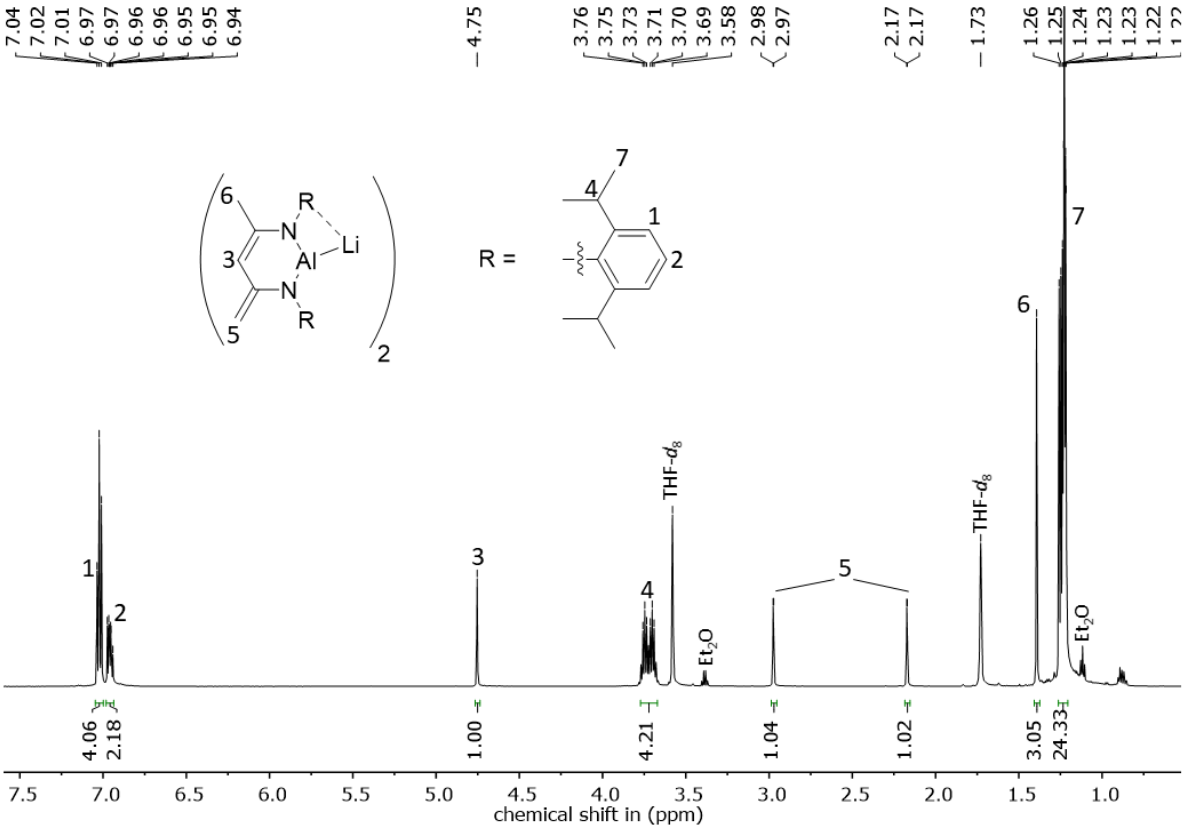


Figure S3: ^{1}H NMR spectrum of [(BDI-H)Al^{-}Li^{+}]$_2$. 600.13 MHz, THF-d_8, 298 K.

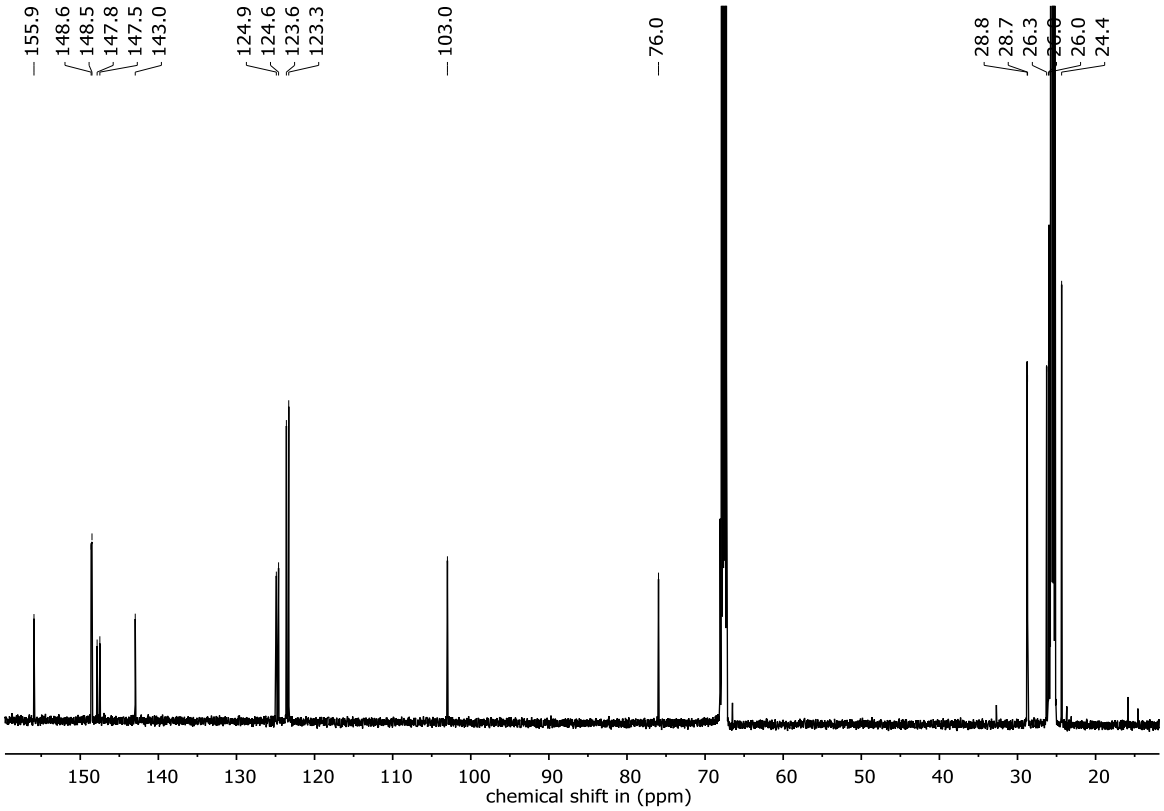


Figure S4: ^{13}C{^{1}H} NMR spectrum of [(BDI-H)Al^{-}Li^{+}]$_2$. 150.92 MHz, THF-d_8, 298 K.

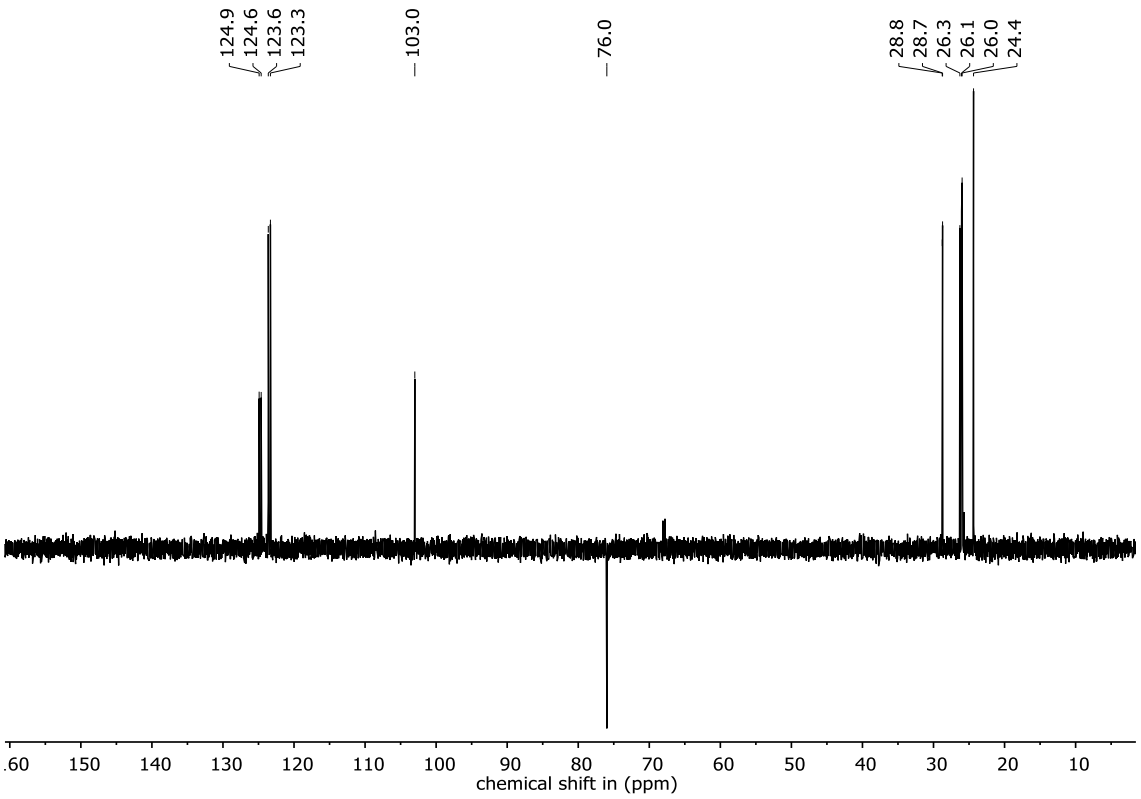


Figure S5: DEPT-135 NMR spectrum of [(BDI-H)Al^{-}Li^{+}]$_2$. 150.91 MHz, THF-d_8, 298 K.

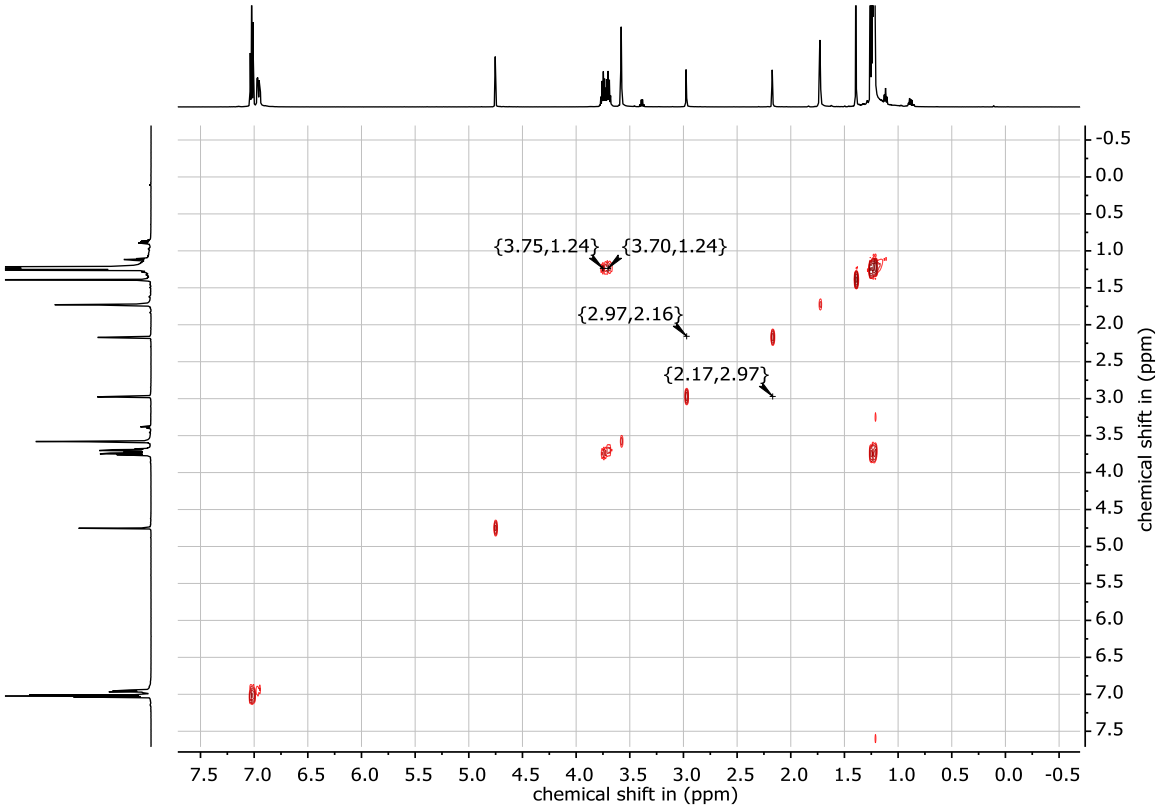


Figure S6: COSY NMR spectrum of [(BDI-H)Al^{-}Li^{+}]$_2$. 600.13 MHz, THF-d_8, 298 K.

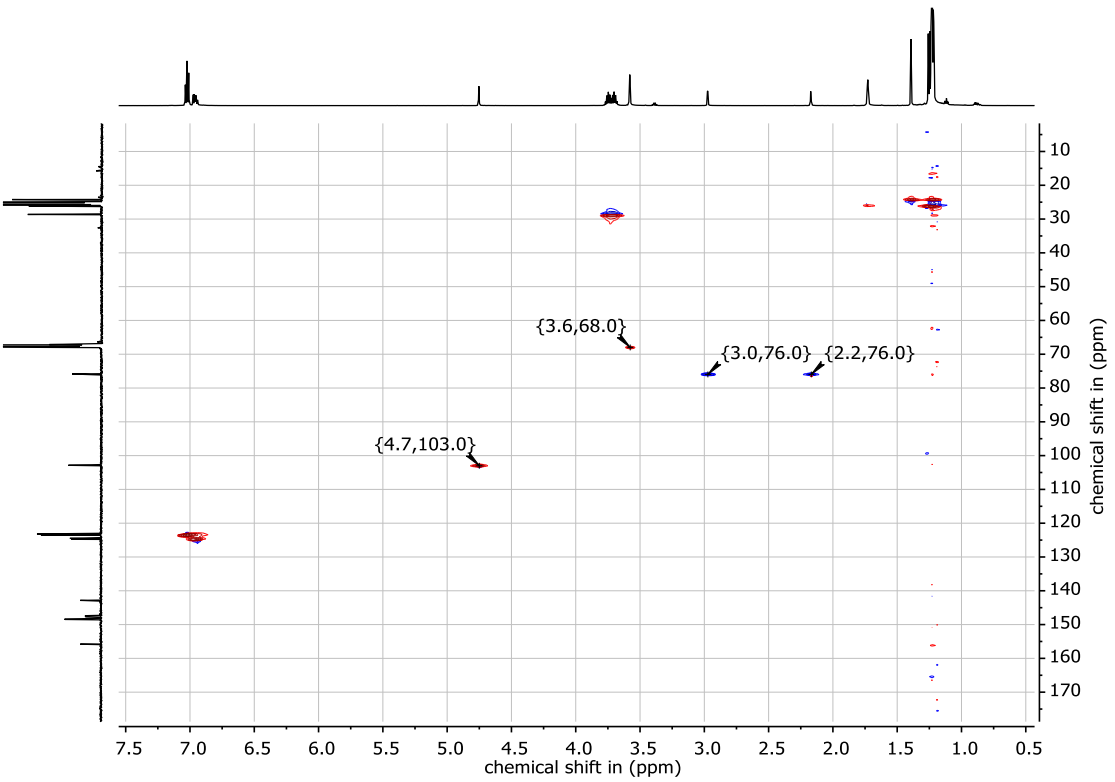


Figure S7: HSQC NMR spectrum of $[(BDI\text{-}H)Al^{-}Li^{+}]_2$. 600.13 and 150.92 MHz, THF-d_8, 298 K.

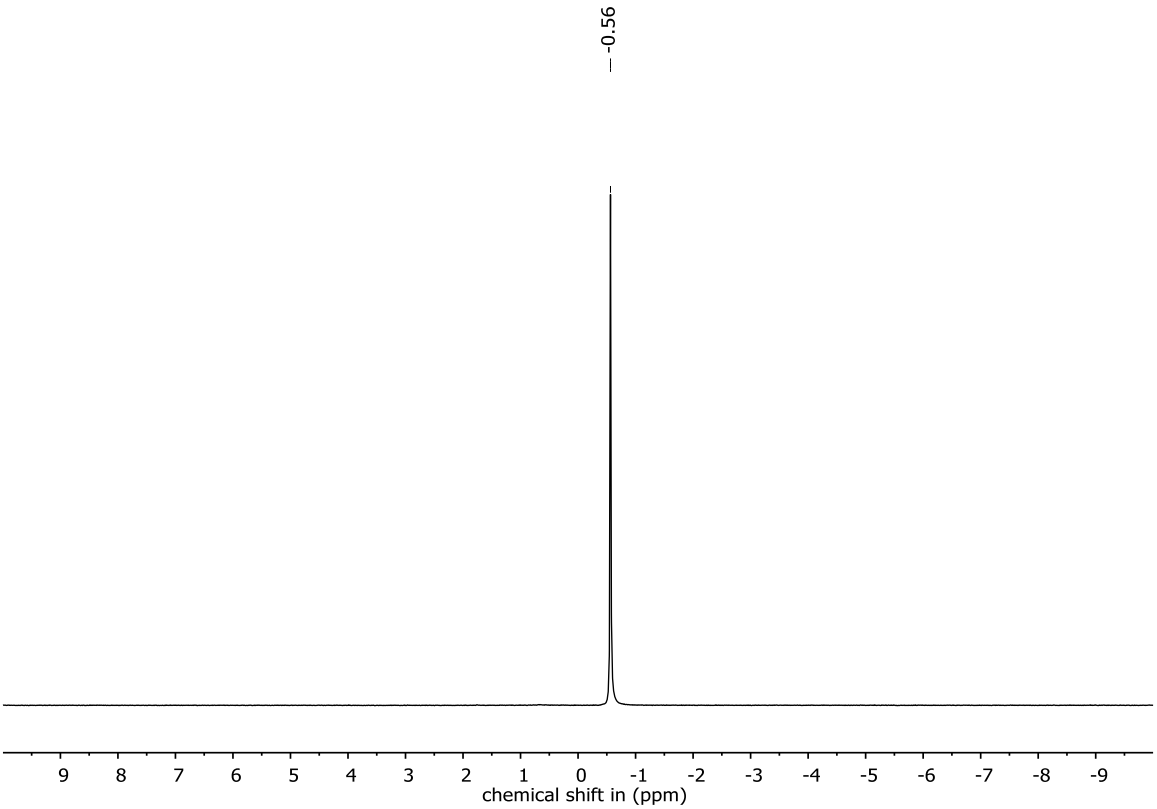
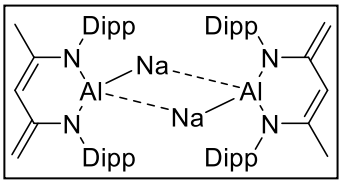


Figure S8: ^{7}Li NMR spectrum of $[(BDI\text{-}H)Al^{-}Li^{+}]_2$. 233.23 MHz, THF-$d_8$, 298 K.

1.2.2 Synthesis of $[(BDI\text{-}H)Al^{-}Na^{+}]_2$



Dimer $[(BDI\text{-}H)Al^{-}K^{+}]_2$ (158 mg, 164 µmol) and $Na(BPh_4)$ (124 mg, 362 µmol) were suspended in diethyl ether (4 ml). The reaction mixture was cooled to -78 °C for 3 days. After allowing the reaction to warm up to room temperature, all solids were filtered off and the mother liquor was reduced to dryness. The solids were charged with 4 ml of toluene, heated to 70 °C and connected to a vacuum, to remove residual coordinated diethyl ether in a stream of evaporating toluene. The product $[(BDI\text{-}H)Al^{-}Na^{+}]_2$ was obtained as pale yellow powder 133 mg, 87 %. The very low solubility of the dimeric complex hindered recrystallization of the sample. Some single crystals for X-ray diffraction were grown by heating $[(BDI\text{-}H)Al^{-}Na^{+}]_2$ in benzene in a NMR tube overnight. Elemental analysis (%) for $C_{58}H_{80}N_4Al_2Na_2$. Calculated: N 6.00, C 74.65, H 8.64, found: N 5.85, C 74.24, H 8.67.

^{1}H NMR (600.13 MHz, THF-d_8, 298 K): δ (ppm) = 7.03 (m, 4 H, aromatic *meta* CH), 6.97 (m, 2 H, aromatic *para* CH), 4.74 (s, 1 H, backbone CH), 3.90 (m, 4 H, DIPP CH), 2.99 (br, 1 H, backbone CH_2) 2.20 (br, 1 H, backbone CH_2); 1.41 (s, 3 H, backbone CH_3), 1.24 (overlapping, 24 H, DIPP CH_3).

^{13}C{^{1}H} NMR (150.92 MHz, THF-d_8, 298 K): δ (ppm) = 155.9 (backbone H_2C=**C**-N), 148.6 and 148.4 (aromatic N-C), 147.4 and 147.0 (aromatic *ortho* C*i*Pr), 142.9 (backbone H_3C-**C**=CH), 124.9 and 124.6 (aromatic *para* CH), 123.5 and 123.2 (aromatic *meta* CH), 102.8 (backbone CH), 75.9 (backbone CH_2), 28.7 and 28.6 (DIPP-CH), 26.3 and 26.1 and 25.8 and 24.3 (DIPP-CH_3), 24.3 (backbone CH_3).

^{27}Al NMR (156.38 MHz, THF-d_8, 298 K): no signal within a range of -580 to 580 ppm.

^{23}Na NMR (158.75 MHz, THF-d_8, 298 K): δ (ppm) = 11.8 (broad).

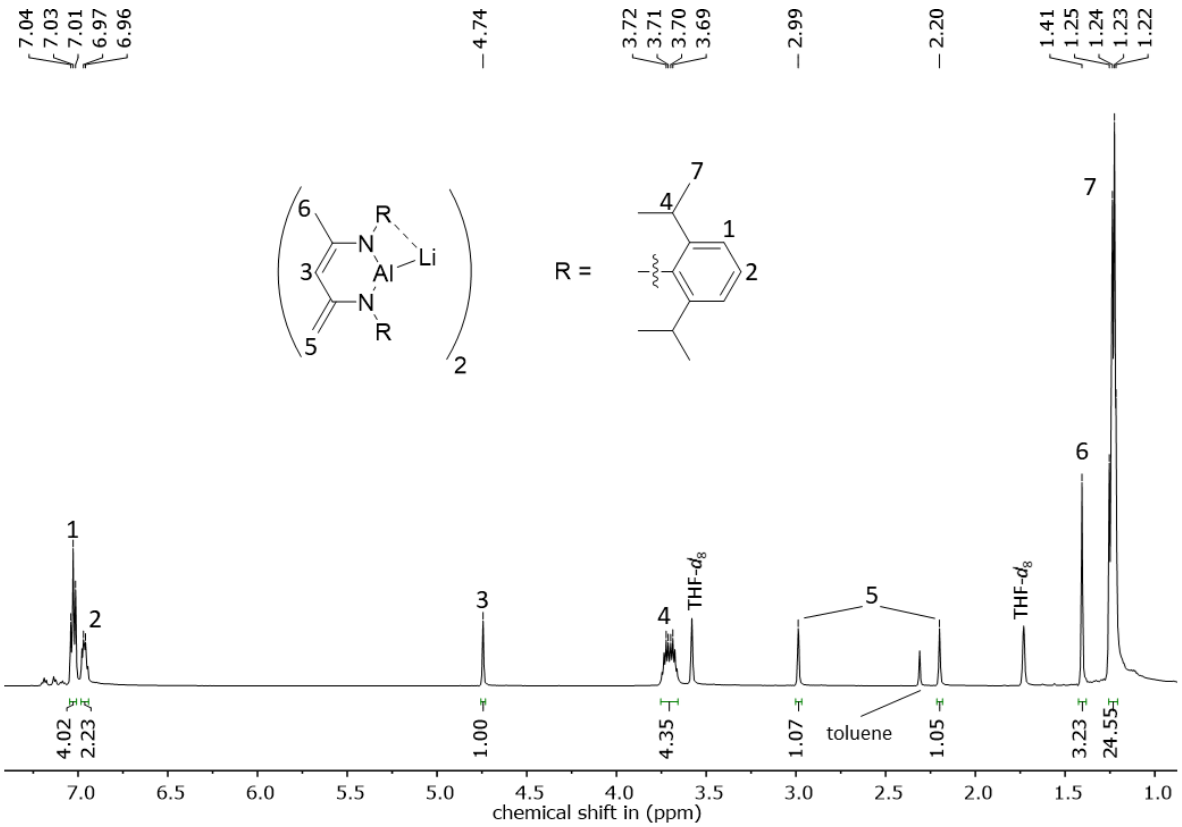


Figure S9: ^{1}H NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 600.13 MHz, THF-d_8, 298 K.

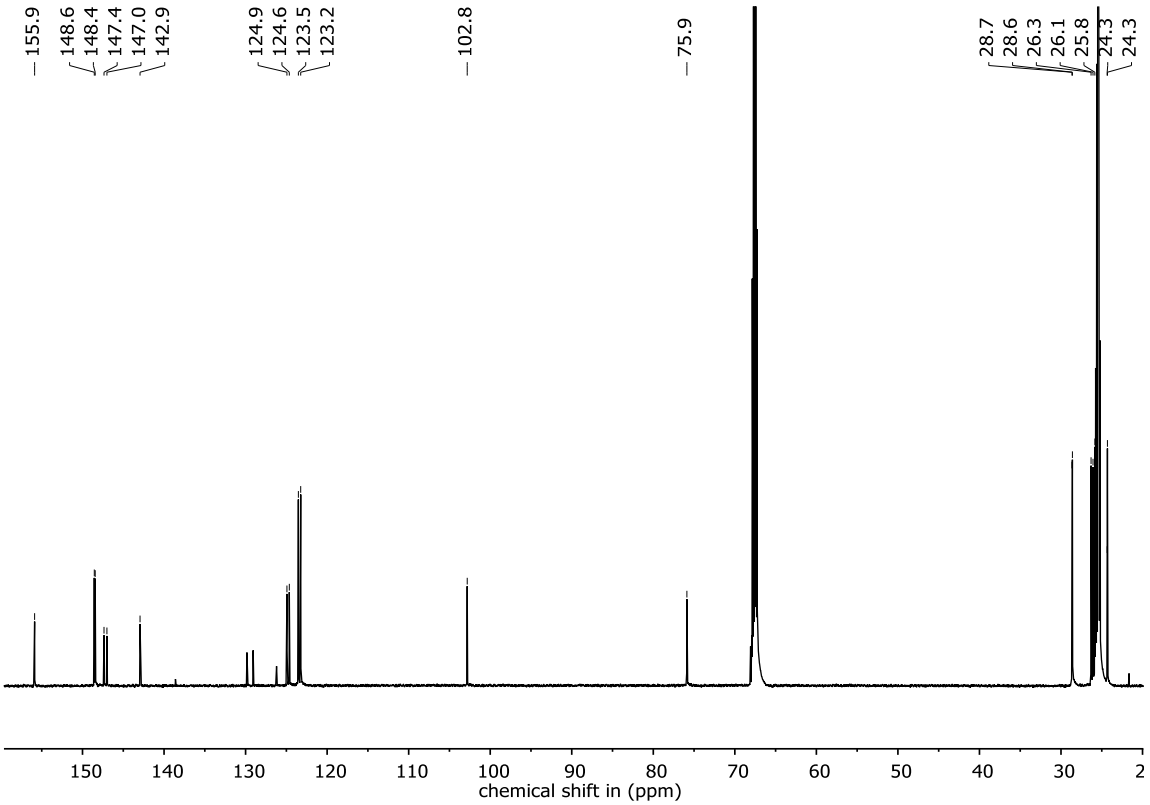


Figure S10: ^{13}C{^{1}H} NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 150.92 MHz, THF-d_8, 298 K.

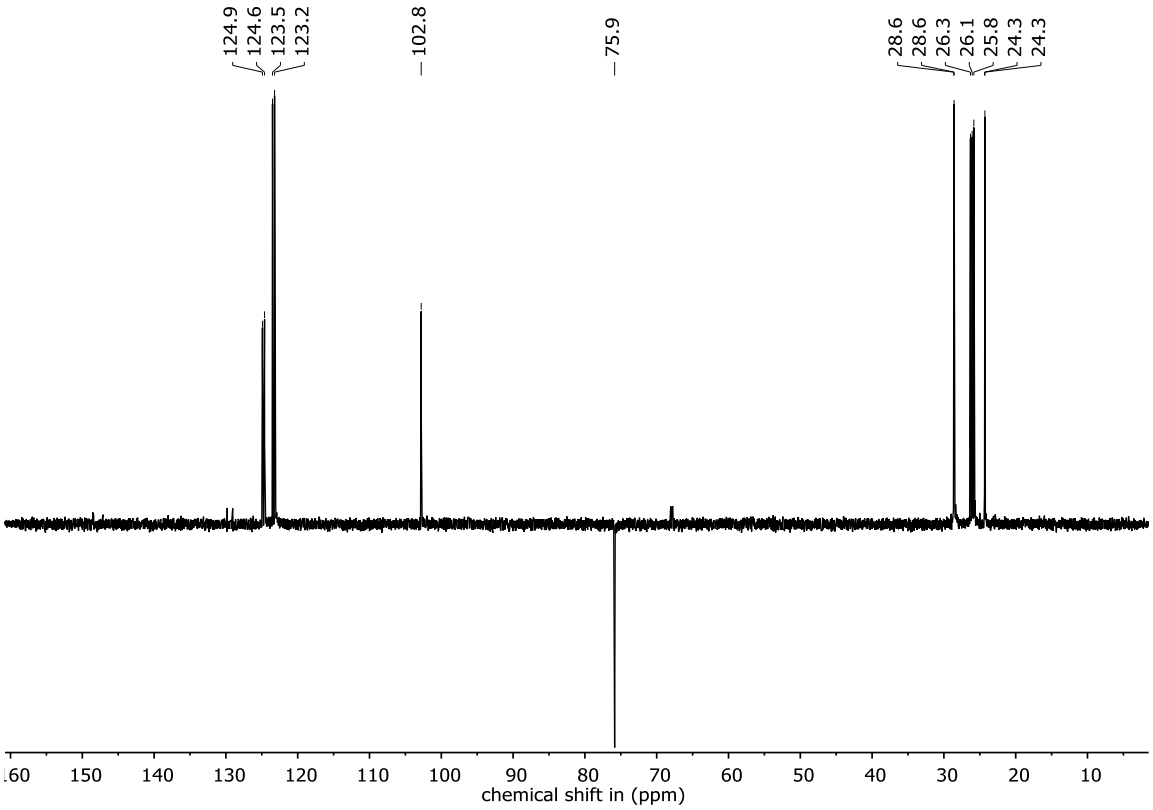


Figure S11: DEPT-135 NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 150.91 MHz, THF-d_8, 298 K.

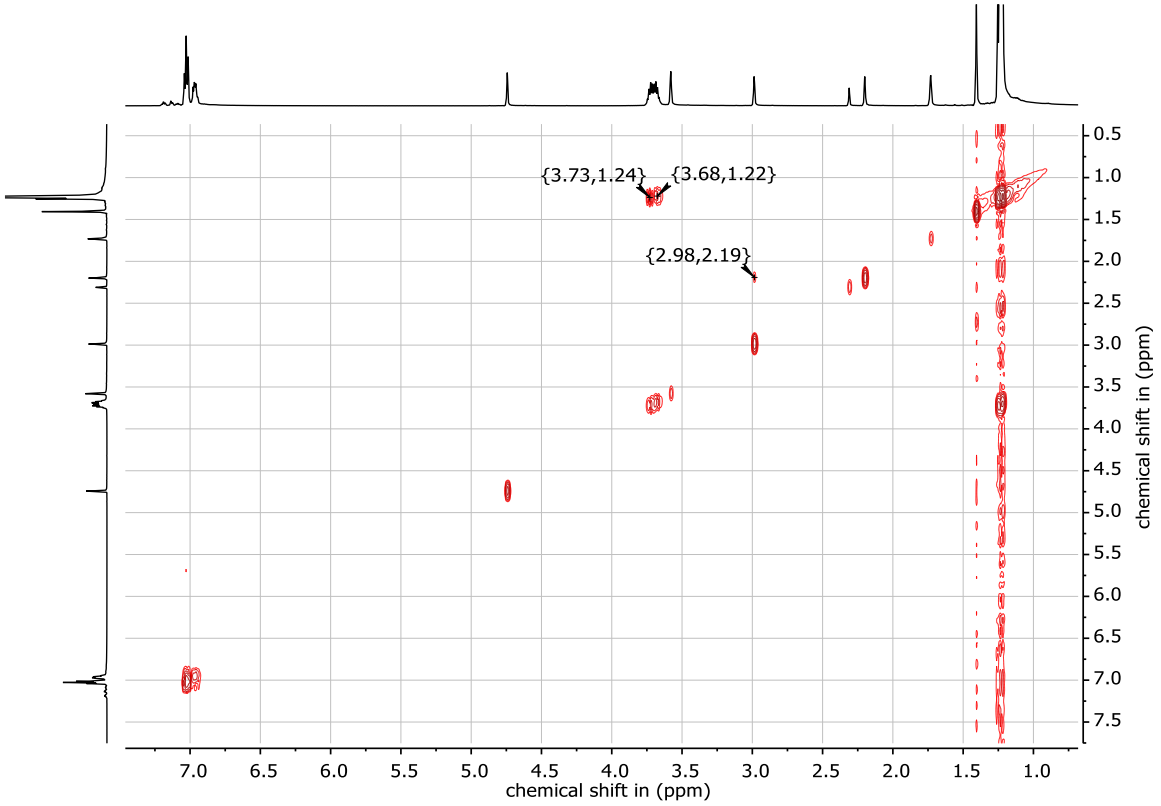


Figure 12: COSY NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 600.13 MHz, THF-d_8, 298 K.

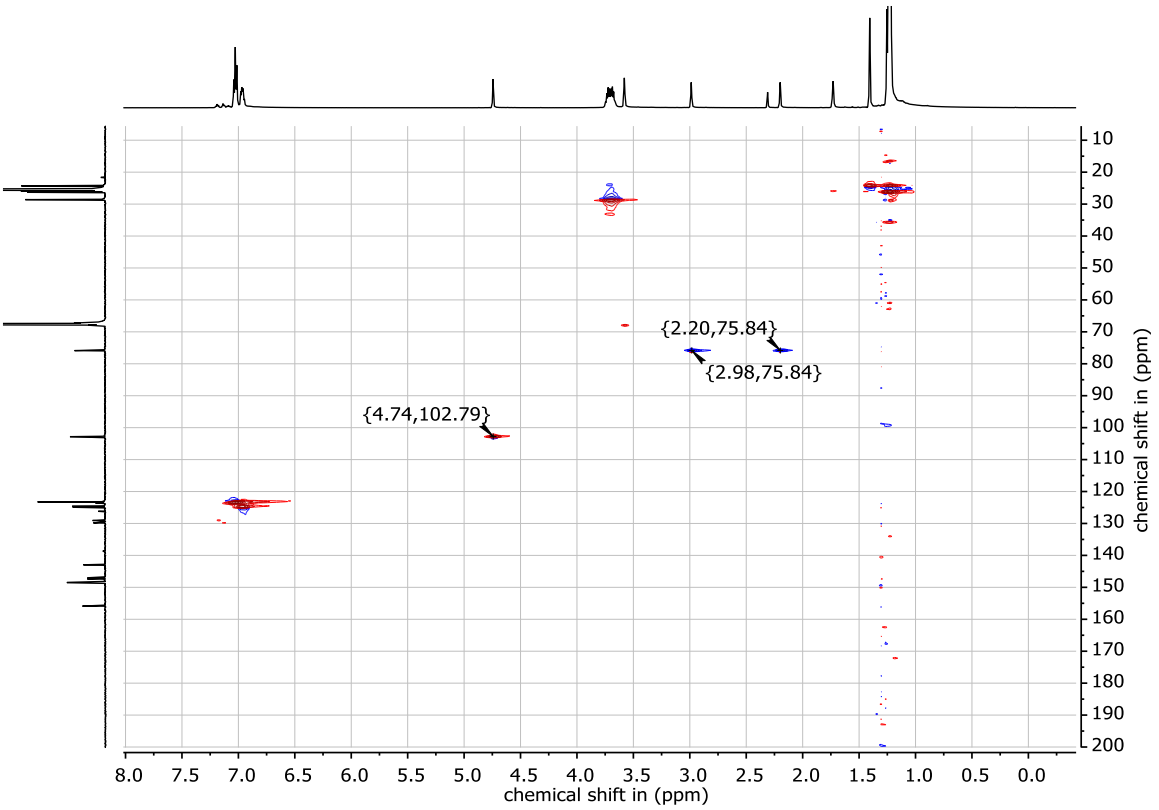


Figure S13: HSQC NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 600.13 and 150.92 MHz, THF-d_8, 298 K.

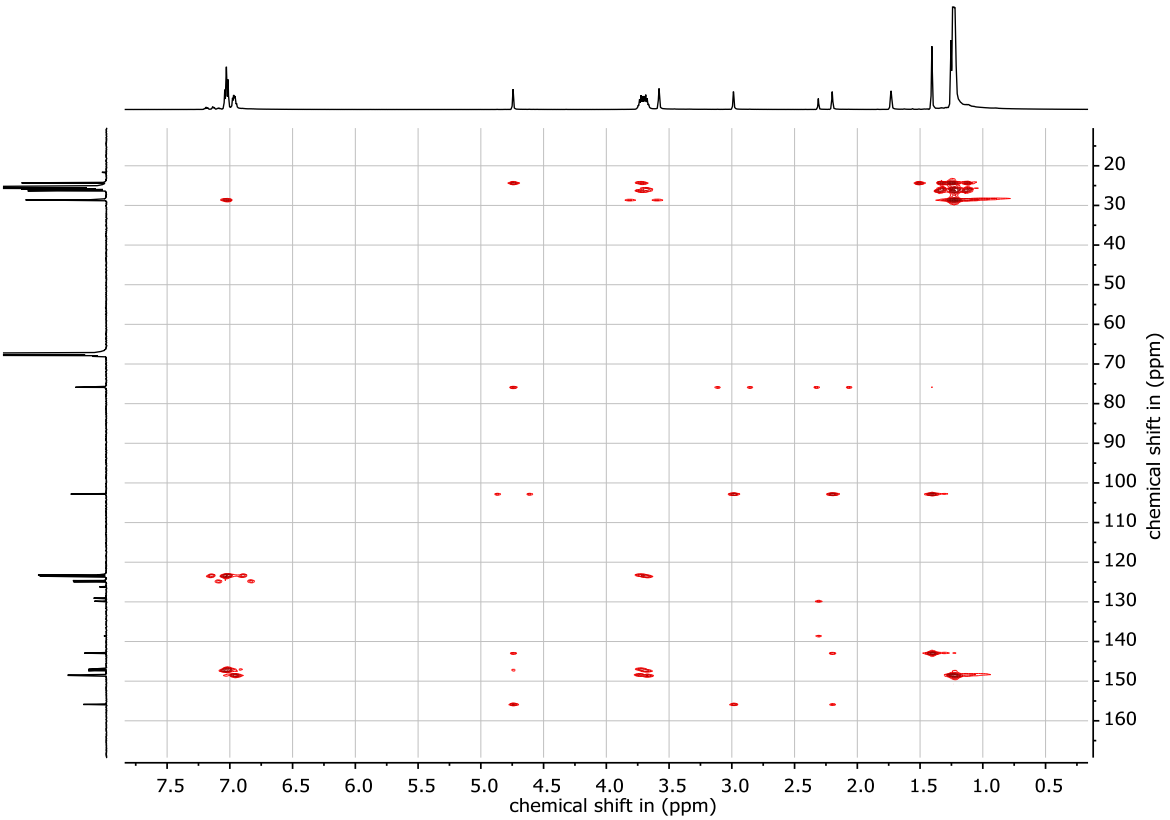


Figure S14: HMBC NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 600.13 and 150.92 MHz, THF-d_8, 298 K.

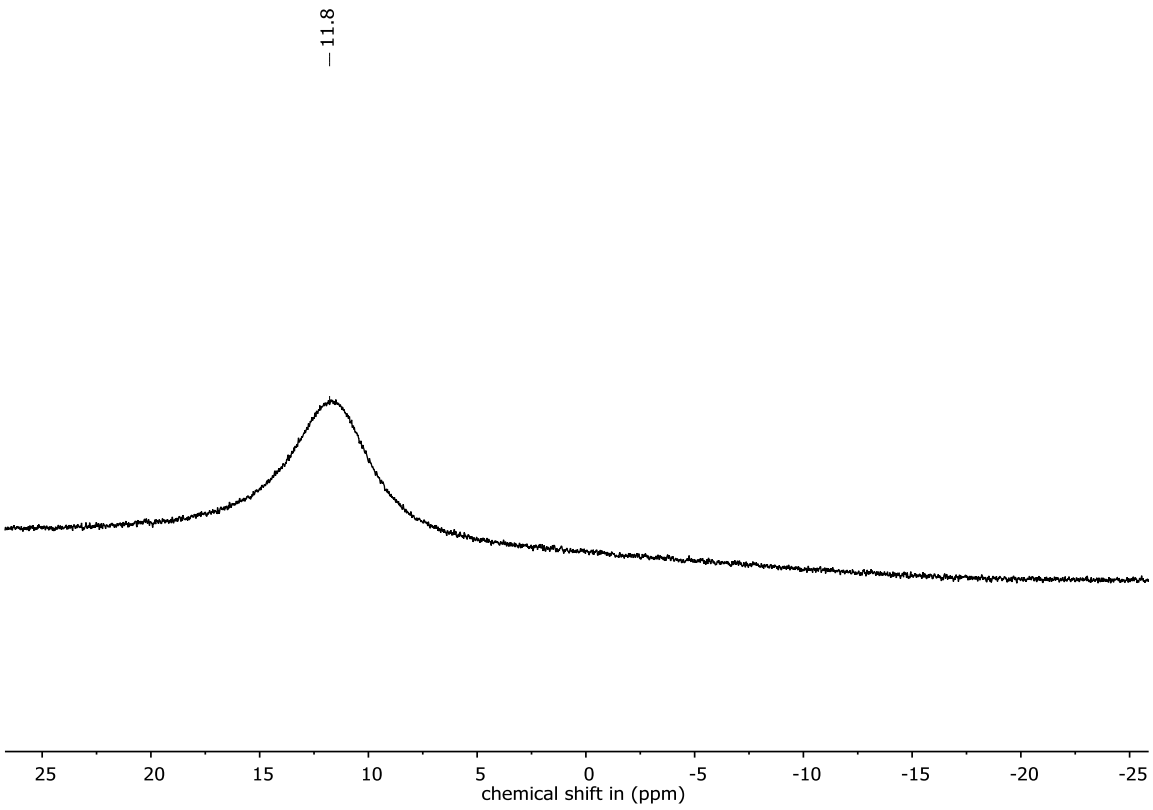
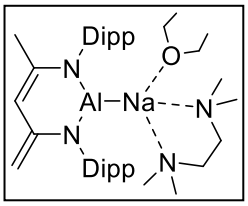


Figure S15: ^{23}Na NMR spectrum of [(BDI-H)Al^{-}Na^{+}]$_2$. 158.75 MHz, THF-d_8, 298 K.

1.2.3 Preparation of (BDI-H)Al$^-$Na$^+$(TMEDA)(Et$_2$O)$_n$



[(BDI-H)Al$^-$Na$^+$]$_2$ (50 mg) was dissolved in diethyl ether (2.5 ml). To the solution one drop of TMEDA was added. In case the product already starts to crystallize at room temperature, additional ether should be added. The mother liquor was stored at -30 °C, to obtain yellow crystals within 1 hour. Crystals were suitable for XRD analysis. These are extremely sensitive towards loss of Et$_2$O and concomitant formation of the dimer [(BDI-H)Al$^-$Na$^+$]$_2$. Preparation for NMR and elemental analysis (washing with pentane and drying under reduced pressure) resulted in evaporation of some coordinated diethyl ether. Therefore, spectra relate to (BDI-H)Al$^-$Na$^+$(TMEDA)(Et$_2$O)$_n$ with n ≈ 0.11. Elemental analysis (%) for $C_{35.44}H_{57.1}N_4Al_1Na_1O_{0.11}$. Calculated: N 9.48, C 72.03, H 9.74, found: N 9.39, C 71.77, H 9.87.

^{1}H NMR (600.13 MHz, C_6D_6, 298 K): δ (ppm) = 7.28 (m, 2 H, aromatic *para* CH), 7.17 (overlapping, 4 H, aromatic *meta* CH), 5.56 (s, 1 H, backbone CH), 4.19 and 4.06 (each: m, 2 H, DIPP CH), 3.99 and 3.14 (each: br, 1 H, backbone CH$_2$), 1.79 (s, 3 H, backbone CH$_3$), 1.57 (d, ^3J_H = 7.0 Hz, 6 H, DIPP CH$_3$), 1.47 (overlapping, 12 H, DIPP CH$_3$), 1.35 (d, ^3J_H = 7.0 Hz, 6 H, DIPP CH$_3$), 1.31 (overlapping, 16 H, TMEDA CH$_3$ and CH$_2$).

^{13}C{^{1}H} NMR (150.92 MHz, C_6D_6, 298 K): δ (ppm) = 155.3 (backbone H$_2$C=**C**-N), 148.5 and 148.0 (aromatic C-N), 146.7 and 146.0 (aromatic *ortho* C*i*Pr), 143.3 (backbone H$_3$C-**C**=CH), 124.9 and 124.7(aromatic CH$^{\cdots}$Na), 123.5 (aromatic *para* CH), 123.1 (aromatic *meta* CH), 103.1 (backbone CH), 77.6 (backbone CH$_2$), 56.2 (TMEDA CH$_2$), 44.9 (TMEDA CH3), 28.3 and 28.2 (DIPP CH), 26.15 and 26.0 and 25.7 and 24.0 (DIPP CH$_3$), 24.1 (backbone CH$_3$).

^{27}Al NMR (156.26 MHz, C_6D_6, 298 K): no signal observed within a range of -580 to 580 ppm.

^{23}Na NMR (158.75 MHz, C_6D_6, 298 K): no signal observed within a range of -30 to 30 ppm.

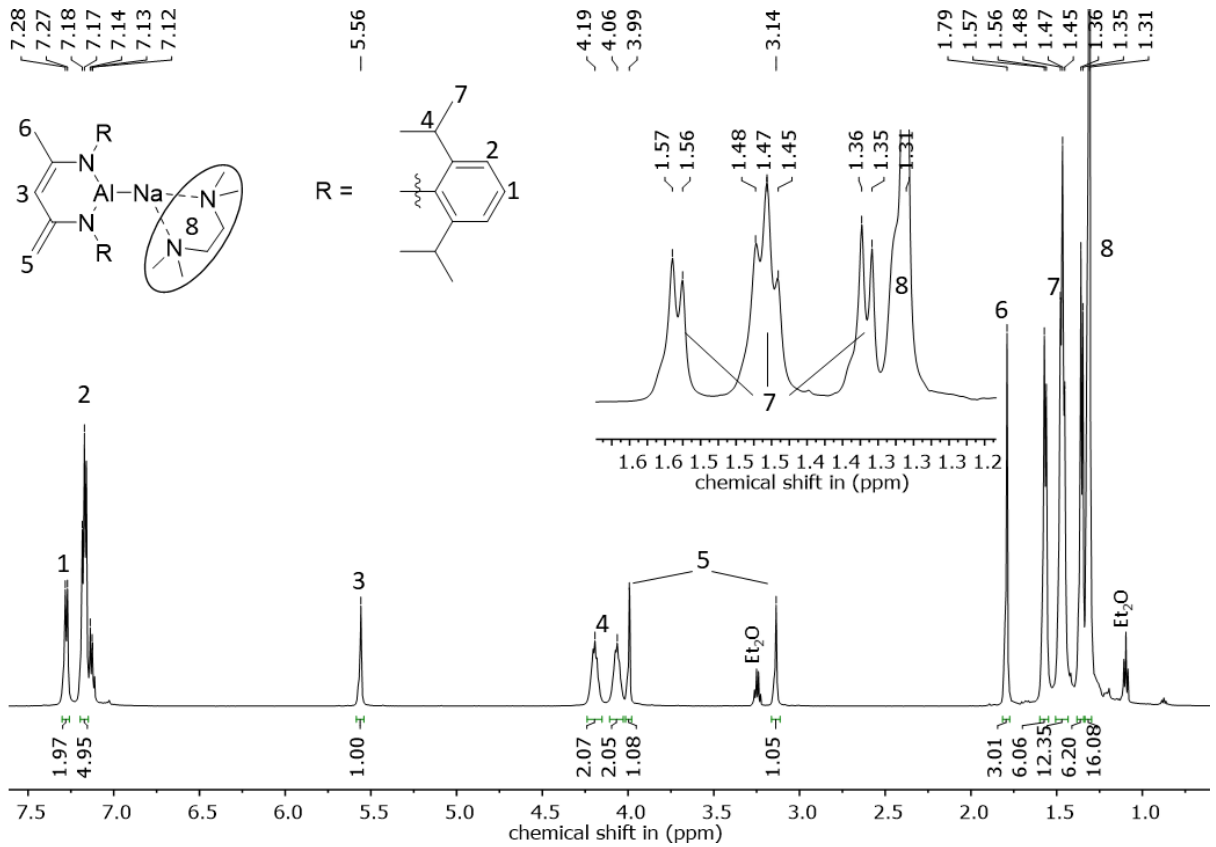


Figure S16: ^{1}H NMR spectrum of (BDI-H)$Al^{-}Li^{+}$(TMEDA)$(Et_2O)_{0.1}$. 600.13 MHz, C_6D_6, 298 K.

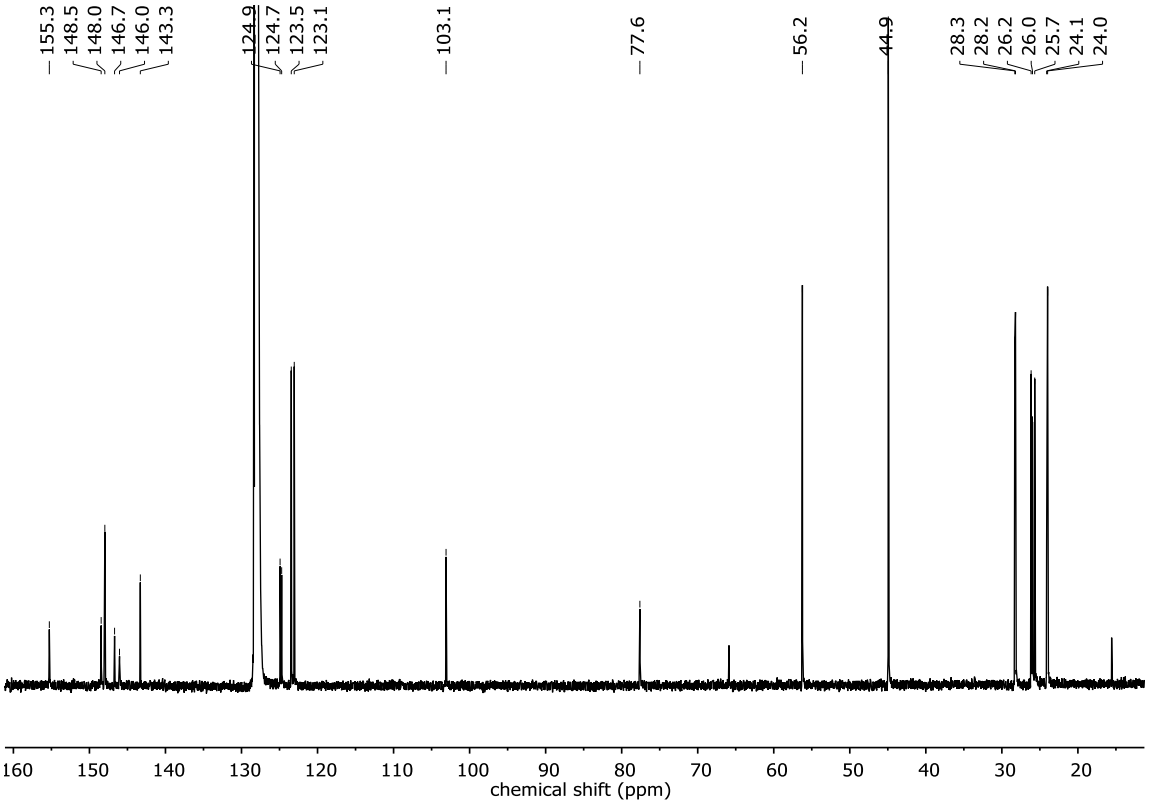


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of (BDI-H)$Al^{-}Li^{+}$(TMEDA)$(Et_2O)_{0.1}$. 150.92 MHz, C_6D_6, 298 K.

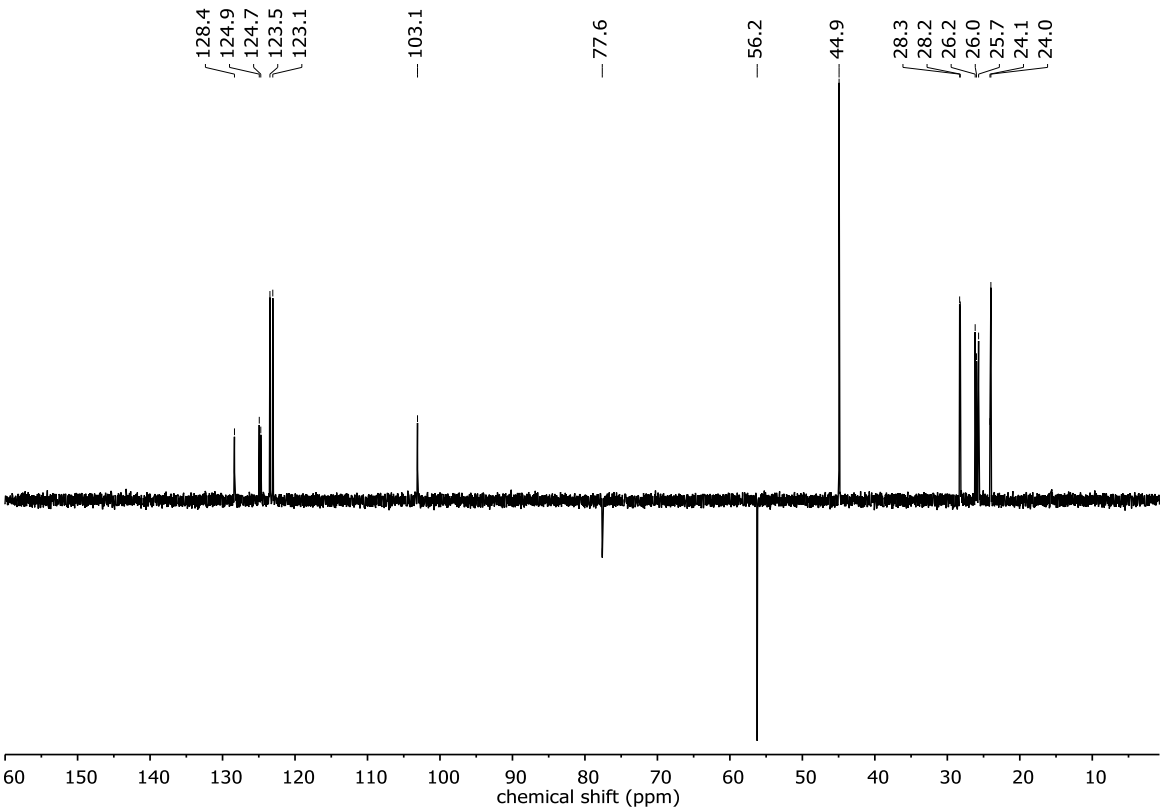


Figure S18: DEPT-135 NMR spectrum of (BDI-H)Al^{-}Li^{+}(TMEDA)$(Et_2O)_{0.1}$. 150.91 MHz, C_6D_6, 298 K.

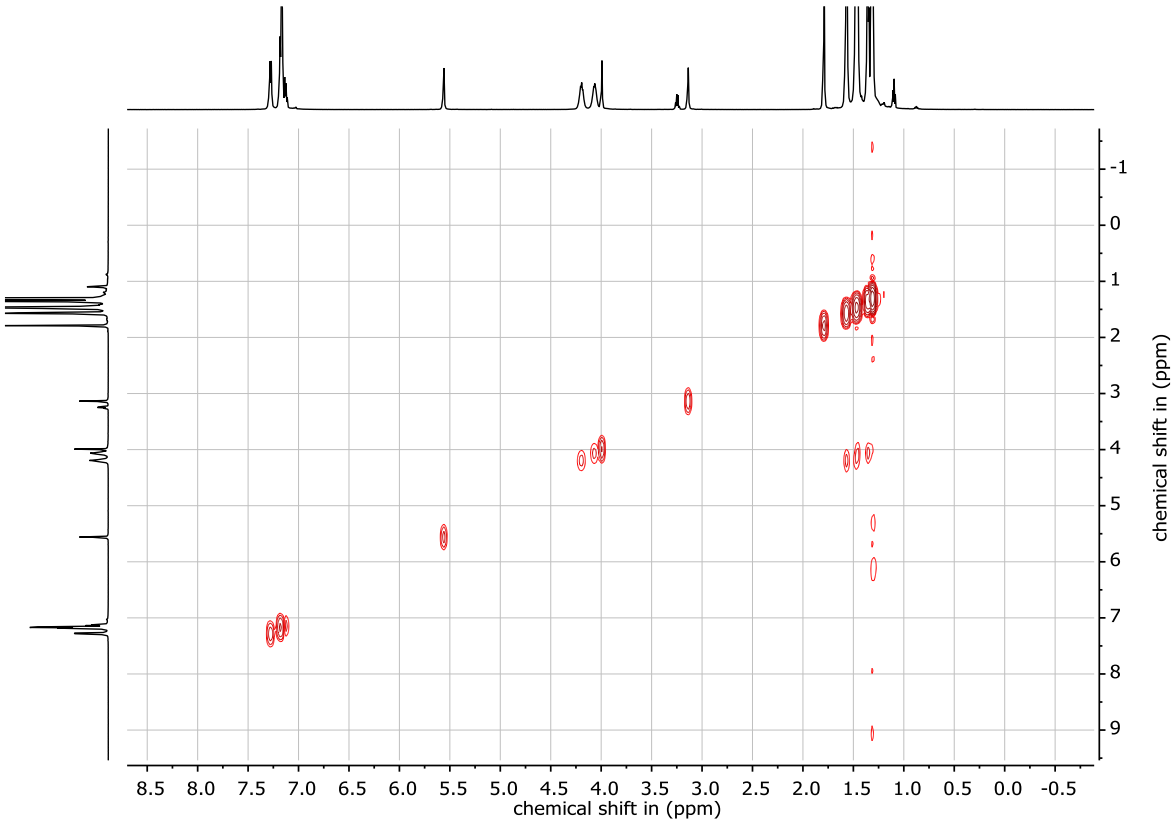


Figure S19: COSY NMR spectrum of (BDI-H)Al^{-}Li^{+}(TMEDA)$(Et_2O)_{0.1}$. 600.13 MHz, C_6D_6, 298 K.

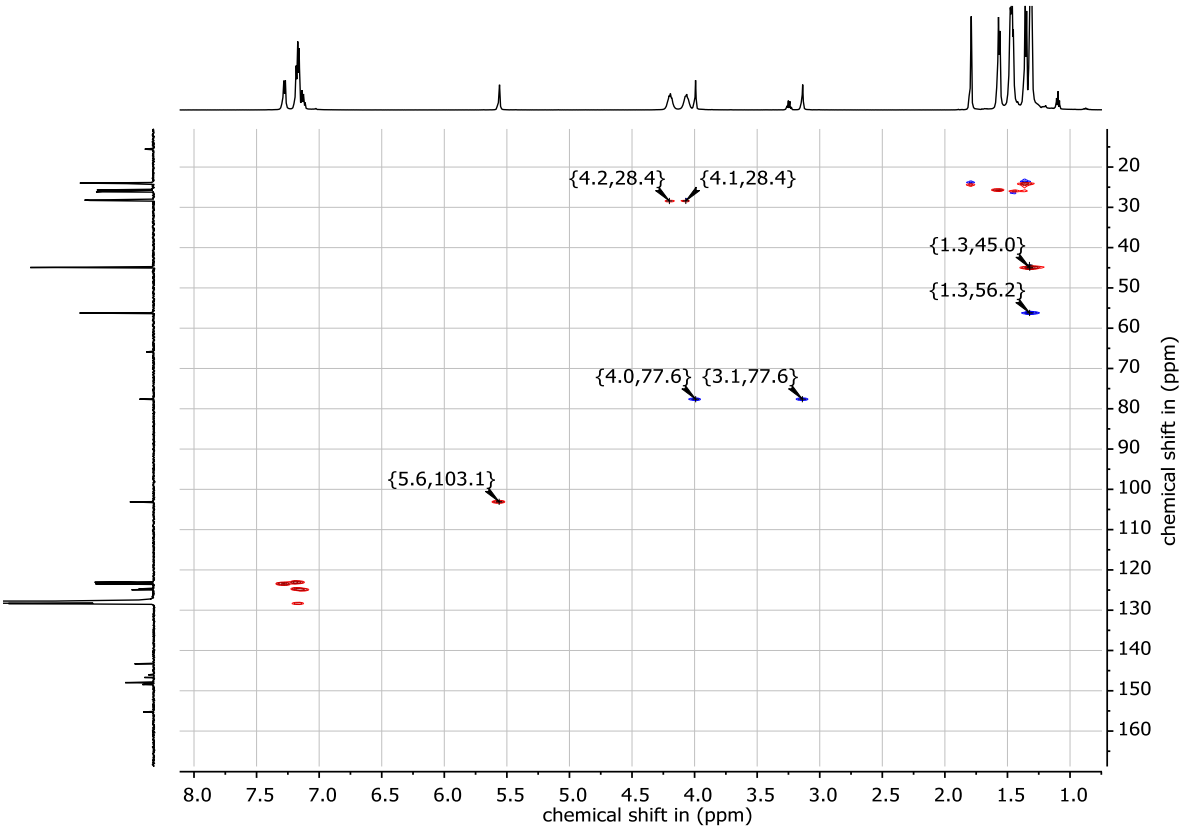


Figure S20: HSQC NMR spectrum of (BDI-H)Al^{-}Li^{+}(TMEDA)$(Et_2O)_{0.1}$. 600.13 and 150.92 MHz, C_6D_6, 298 K.

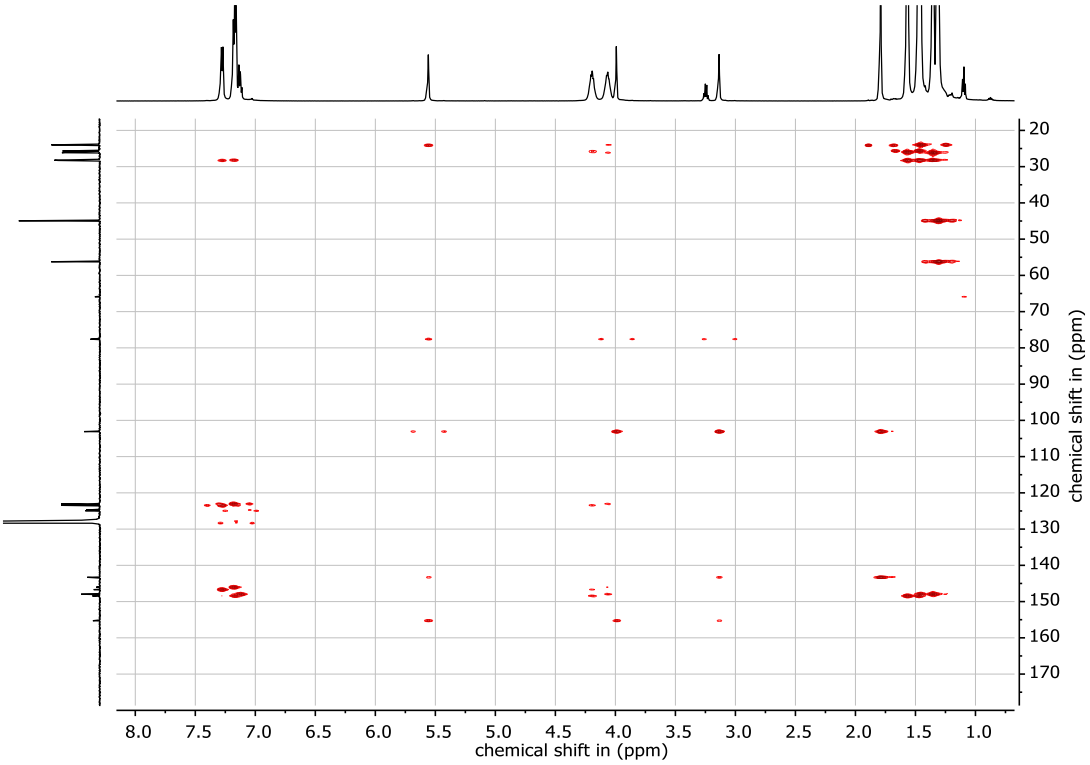
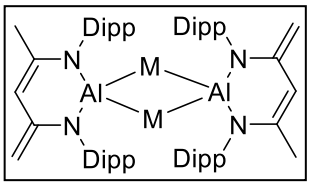


Figure S21: HMBC NMR spectrum of (BDI-H)Al^{-}Li^{+}(TMEDA)$(Et_2O)_{0.1}$. 600.13 and 150.92 MHz, C_6D_6, 298 K.

1.2.4. Synthesis of $[(BDI\text{-}H)Al^{-}M^{+}]_2$, M = Rb, Cs



(BDI)Al and two equivalents of MC_8 (M = Rb or Cs) were combined in a ball mill vessel alongside 10 stainless steel balls. Milling was set to 100 Hz for 10 minutes followed by 10 minutes at 67 Hz. The mixture was extracted with toluene. After filtering off all solids, volatiles were evaporated under reduced pressure to obtained the product as a yellow powder.

M = Rb: (BDI)Al (127 mg, 228 µmol). Isolated product $[(BDI\text{-}H)Al^{-}Rb^{+}]_2$: 97 mg, 71 % yield.
Elemental analysis for $C_{29}H_{40}N_2AlRb$. Calculated: C65.83, N5.29, H7.63; found: C65.71, N5.51, H7.63

M = Cs: (DIPP)Al (107 mg, 240 µmol). Isolated product $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$: 90 mg, 63 % yield.
Elemental analysis for $C_{29}H_{40}N_2AlCs$. Calculated: C60.42, N4.86, H6.99; found: C59.42, N4.93, H6.92

Comment on side product

Although the crystallized product gave a fitting CHN analysis, NMR investigation showed that two species are present. The second species cannot be removed by recrystallization and is found in variable amounts (in some cases nearly pure samples were obtained, see ^{1}H NMR of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ (Figure S30)). Typical ^{1}H NMR signals for the Rb & Cs aluminyl dimer $[(BDI\text{-}H)Al^{-}M^{+}]_2$ overlap with signals for the hitherto unknown complex (Figure S23). The complex has similar composition (CHN analysis) and also a very similar MW (see DOSY NMR spectrum in Figure S22 & S29). The complex shows a high degree of asymmetry demonstrated by the appearance of at least 4 heptet signals for the *i*Pr CH proton. Variable temperature NMR of $[(BDI\text{-}H)Al^{-}M^{+}]_2$ in the region of -50/+100 °C shows that the two different complexes do not interconvert into each other (Figure S28), indicating that an equilibrium between different aggregates or conformers is less likely.

NMR spectroscopy of $[(BDI\text{-}H)Al^{-}Rb^{+}]_2$

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ (ppm) = 7.0 – 6.8 (aromatic signals), 5.37 (s, 1 H, backbone CH), 4.48 (broad, DIPP-CH of unknown compound), 4.43 (overlapping sept, DIPP-CH of unknown compound), 4.38 and 4.37 (s, overlapping, backbone CH of unknown compound), 4.13 (sept, $^3J_{HH}$ = 6.9 Hz, DIPP-CH of unknown compound), 3.98 (overlapping sept, DIPP-CH of unknown compound), 3.93 (overlapping sept, DIPP-CH), 3.89 (s, backbone CH_2), 3.76 (sept, $^3J_{HH}$ = 6.8 Hz, DIPP-CH of unknown compound), 2.93 (s,

backbone CH_2), 1.69 (s, backbone CH_3 of unknown compound), 1.62 (s, backbone CH_3), 1.4 – 1.1 (DIPP-CH_3 groups of both compounds).

$^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ (ppm) = 154.2, 152.5, 151.6, 151.0, 150.3, 150.2, 149.9, 149.7, 148.5, 148.3, 142.1, 138.8, 124.8, 124.7, 124.0, 123.6, 123.5, 123.2, 123.0, 122.7, 102.5 (backbone CH_3), 77.4 (backbone CH_2), 57.8, 28.1, 28.0, 27.9, 27.9, 27.5, 26.5, 26.2, 25.7, 25.4, 25.3, 25.1, 25.1, 25.0, 25.0, 24.9, 24.1, 24.0,23.9, 23.9, 23.7, 23.7, 23.5.

^{27}Al NMR (156.26 MHz, C_6D_6, 298 K): δ = no signals observed within a range of -1100 to 1100 ppm.

DOSY NMR:

Table S1: DOSY NMR results for the compound $[(BDI\text{-}H)Al^-Rb^+]_2$ in C_6D_6 at 298 K.

Compound	Log D	MW found	MW calc (monomer)
Complex 2	- 9.3065	756 (ECC) 730 (DMW)	529
benzene	- 9.0025	245	86

The ^1H NMR spectrum obviously indicates the presence of two independent species. DOSY shows that these two species have a similar molecular weight: all DOSY signals lie on a single horizontal line. Molecular weight determination applying the method of Stalke led to a value of 756 (ECC[S3,S4]). This MW could be confirmed by our own regression method based on a number of measurements collected over time within the group (MW = 730, DMW by Christian Färber). The experimental MW is considerably lower than the MW of dimeric $[(BDI\text{-}H)Al^-Rb^+]_2$ (MW = 1058) but higher than that of a monomeric species (MW = 529). We therefore assume a monomer-dimer equilibrium. Note that also the MW value for benzene is significantly too high (found: 245, calculated: 86). This indicates the presence of an attractive interaction between complex and benzene (as a ligand) and an equilibrium between bound and free benzene.

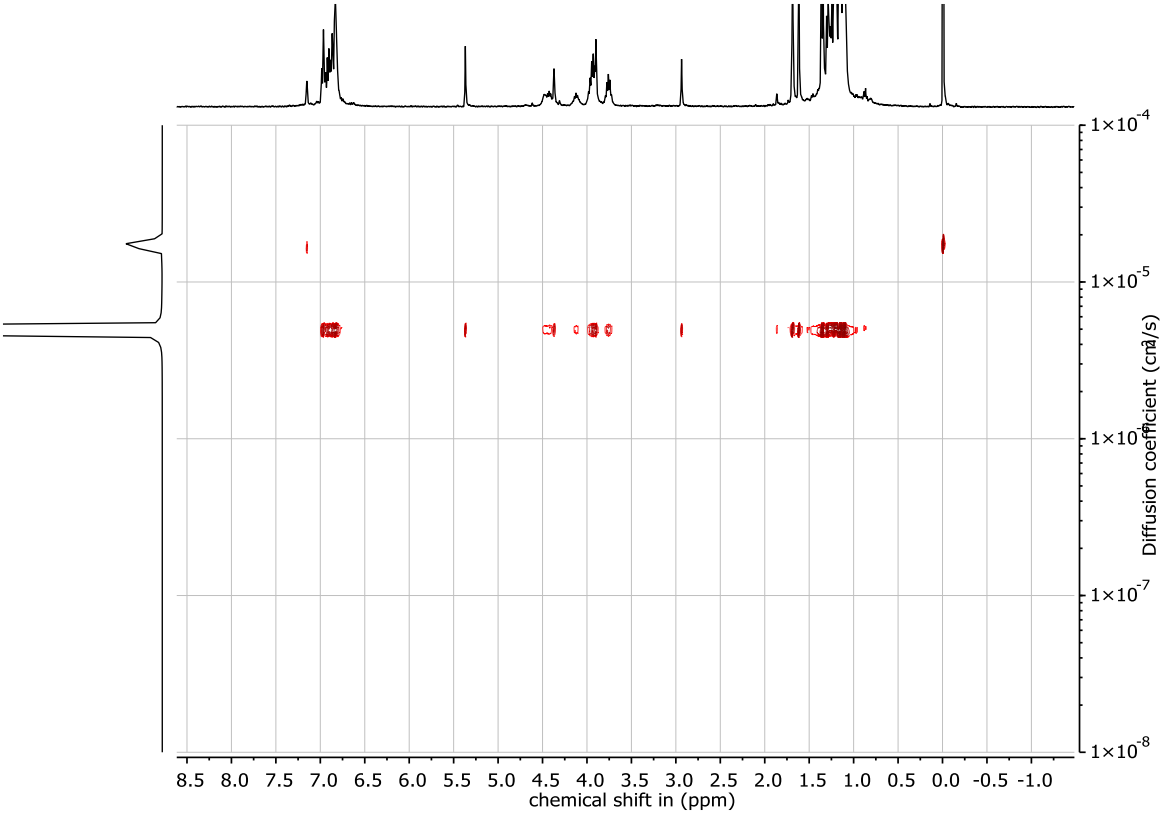


Figure S22: ^{1}H DOSY NMR of [(BDI-H)Al^{-}Rb^{+}]$_2$. 400.13 MHz, C_6D_6, 298 K.

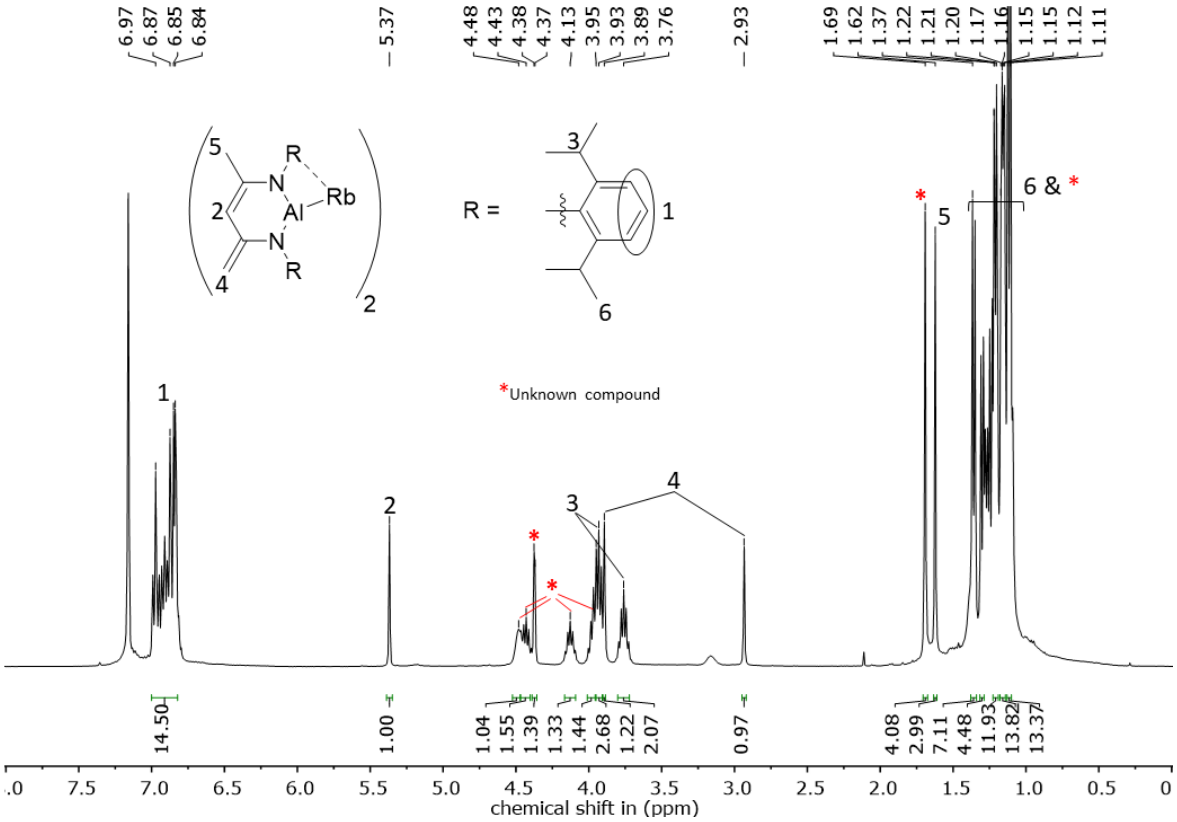


Figure S23: ^{1}H NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$. 400.13 MHz, C_6D_6, 298 K.

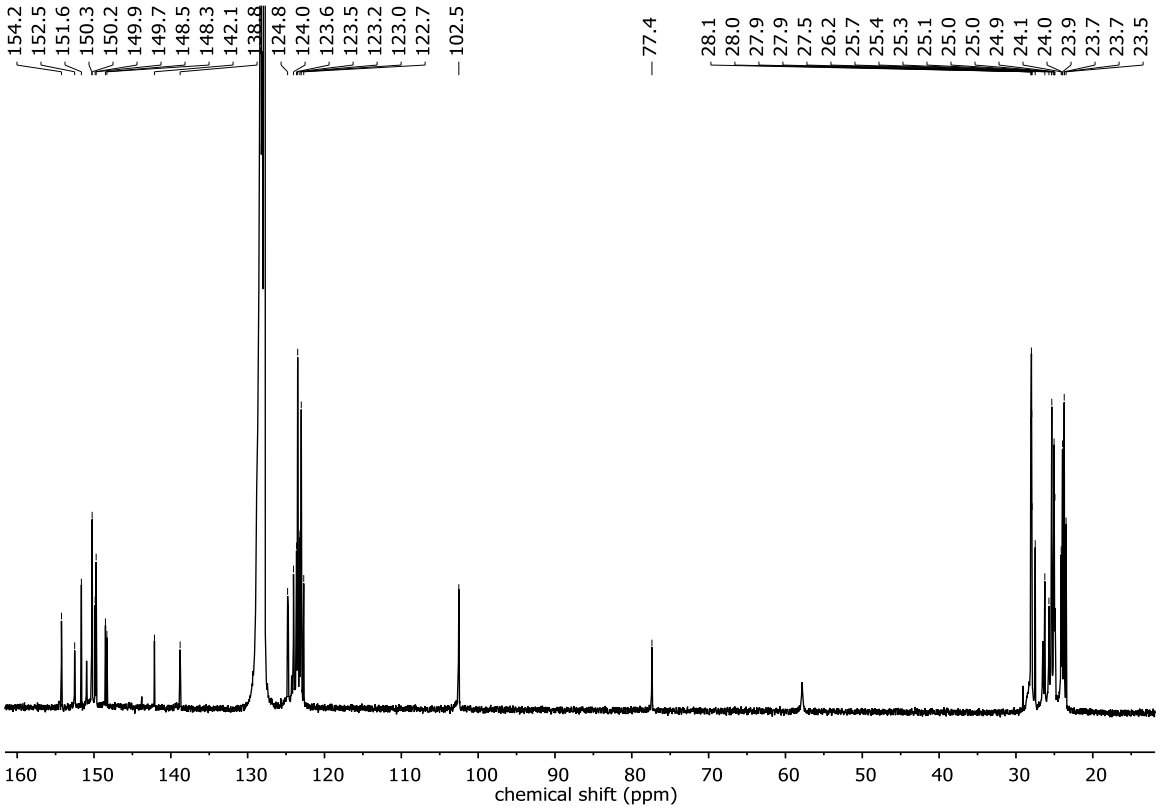


Figure S24: ^{13}C{^{1}H} NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$. 100.62 MHz, C_6D_6, 298 K.

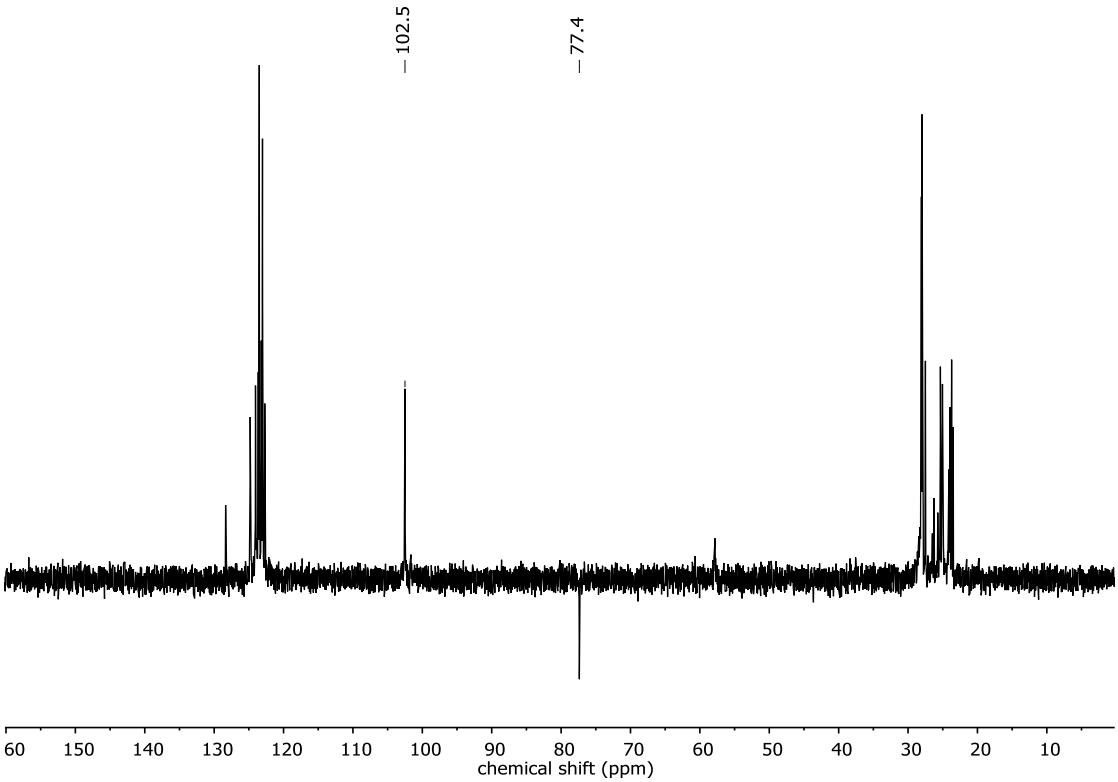


Figure S25: DEPT-135 NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$.100.62 MHz, C_6D_6, 298K.

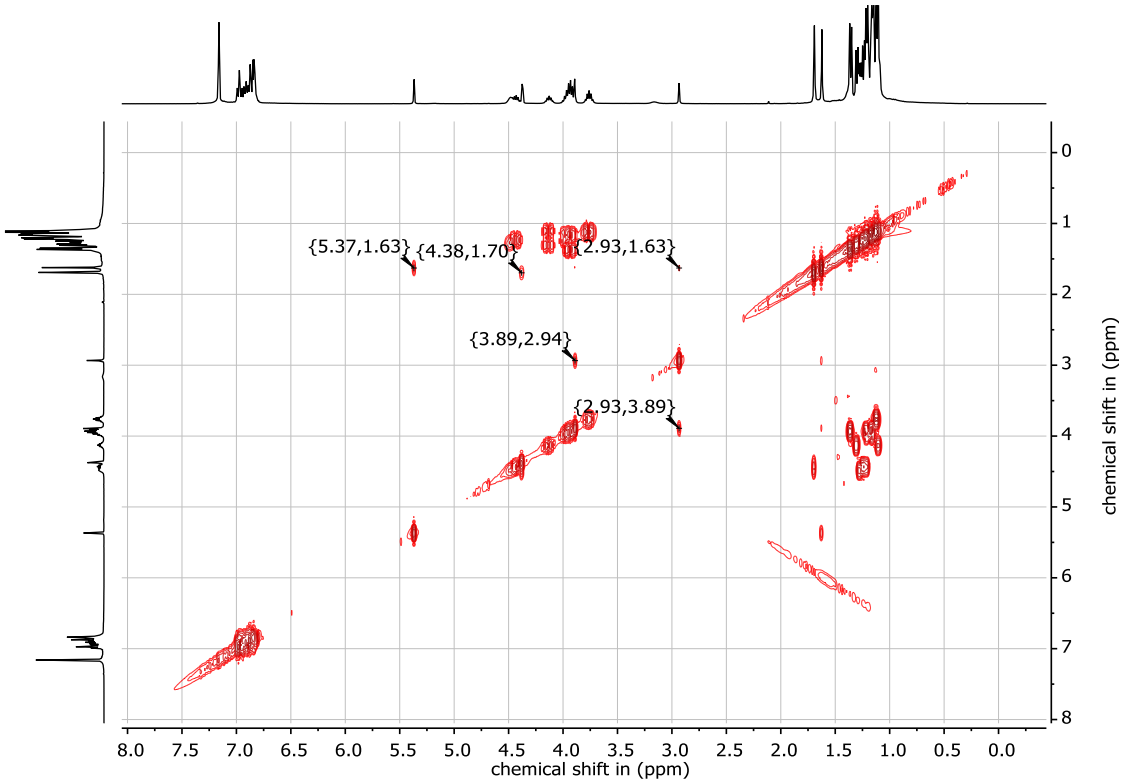


Figure S26: COSY NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$. 400.13 MHz, C_6D_6, 298K.

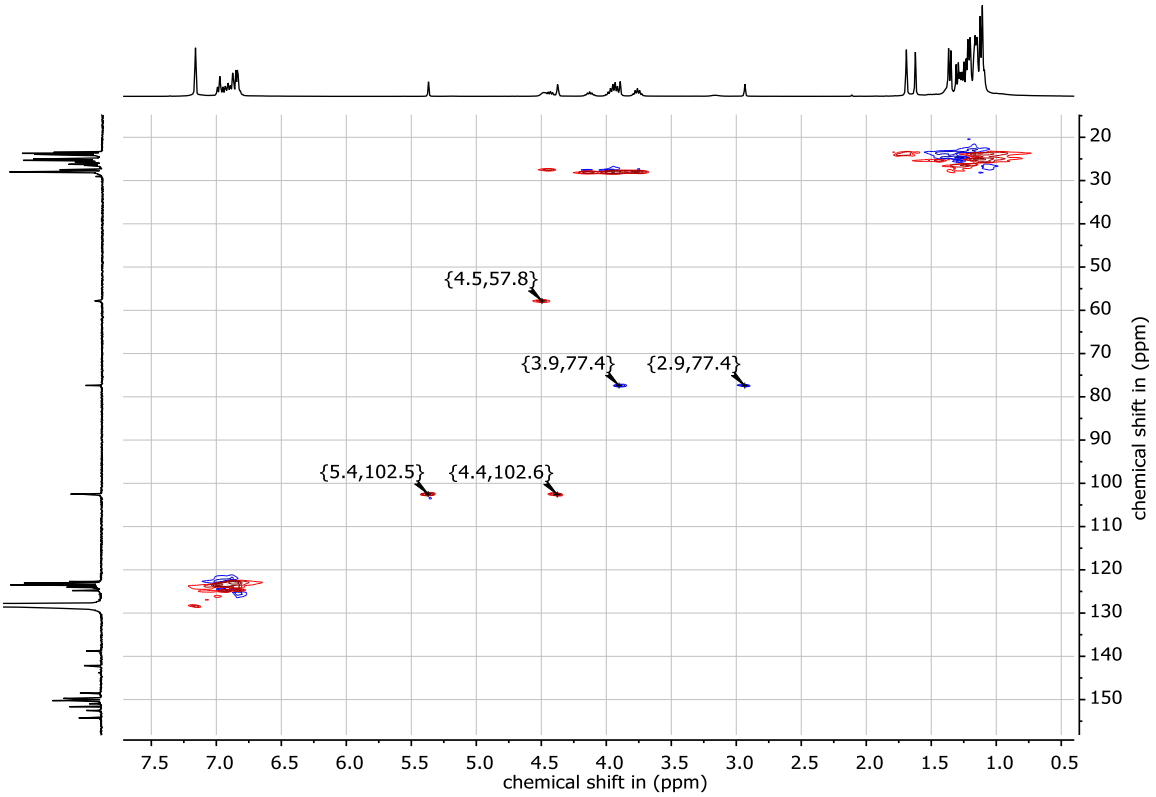


Figure S27: HSQC NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$. 400.13 and 100.62 MHz, C_6D_6, 298K.

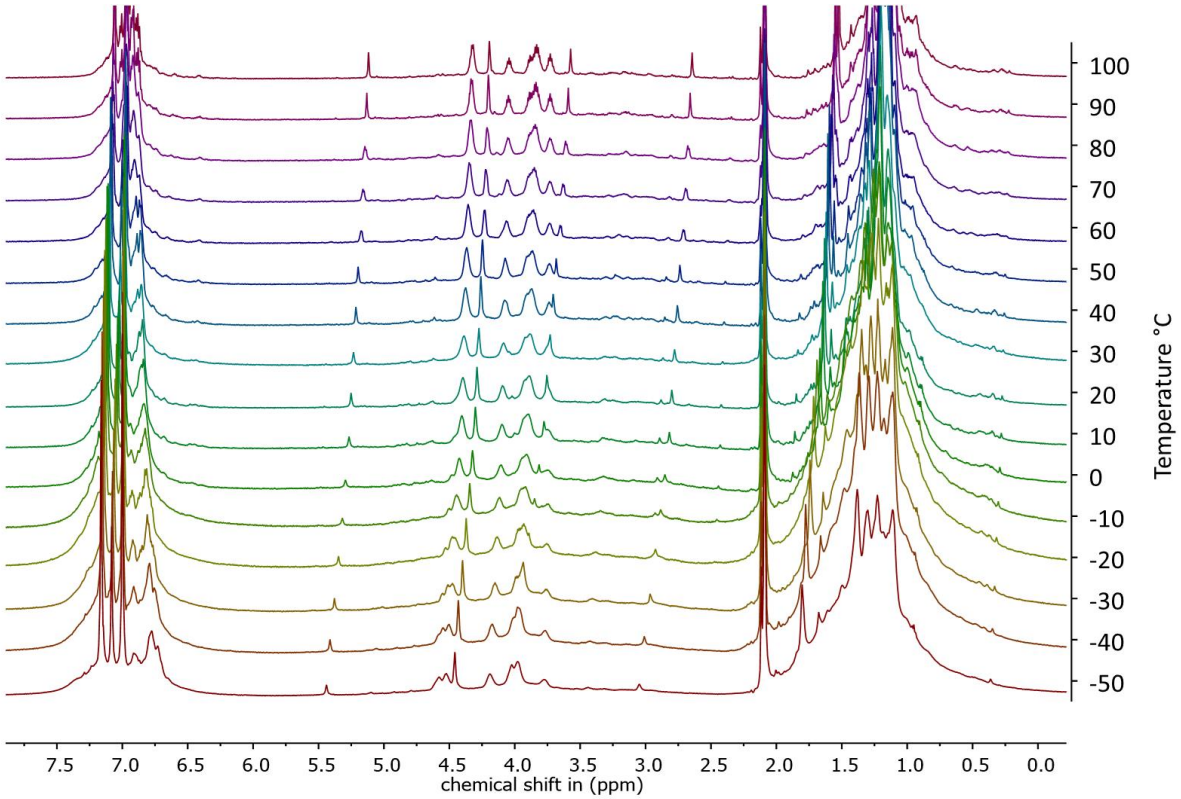


Figure S28: VT ^{1}H NMR spectrum of [(BDI-H)Al^{-}Rb^{+}]$_2$. 600.13 MHz, C_6D_6, 298K, from -50 to 100 °C.

NMR spectroscopy of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$

^{1}H NMR (600.13 MHz, C_6D_6, 298 K): δ (ppm) = 6.99 (d, $^{3}J_H$ = 7.5 Hz, 2 H, PhCH), 6.91 (t, $^{3}J_H$ = 7.5 Hz, 1 H, PhCH), 6.84 (t overlapped, 2 H, PhCH), 5.42 (s, 1 H, backbone CH), 3.90 (d, $^{2}J_H$ = 1.5 Hz, backbone CH_2), 3.83 (sept, $^{3}J_H$ = 6.6 Hz, 2 H, *i*Pr-CH), 2.90 (d, $^{2}J_H$, 1.5 Hz, 1 H, backbone CH_2), 3.08 (s, 3 H, backbone CH_3), 1.38 (d, $^{3}J_H$ = 6.9 Hz, 6 H, *i*Pr-CH_3), 1.21 (d, $^{3}J_H$ = 7.0 Hz, 6 H, *i*Pr-CH_3), 1.18 (d, $^{3}J_H$ = 6.8 Hz, 6 H, *i*Pr-CH_3), 1.15 (d, $^{3}J_H$ = 6.9 Hz, 6 H, *i*Pr-CH_3).

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, C_6D_6, 298 K): δ = 154.4 (**C**=CH_2), 150.2 and 149.1 (Ph**C**-*i*Pr), 149.5 and 149.1 (Ph**C**-N), 142.1 (CH=(N)**C**–CH_3), 23.5, 23.7, 25.2, 25.3, 25.3, 28.0, 28.1, 77.3 (backbone CH_2), 102.8 (backbone CH), 132.4, 123.9, 124.7, 124.7, 125.7, 128.6, 129.3, 142.1, 149.1, 150.2

^{27}Al NMR (156.26 MHz, C_6D_6, 298 K): δ = no signals observed within a range of -508 ppm – 580 ppm.

DOSY NMR:

Table S2: DOSY NMR results for the $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ in C_6D_6 at 298 K.

Compound	log D	MW (found, ECC)	MW calc. for
Al Complex	- 9,3558	893 (ECC) 871 (DMW)	577
Benzene	- 9.2214	540	84

The ^{1}H NMR spectrum obviously indicates the presence of two independent species. DOSY shows that these two species have a similar molecular weight: all DOSY signals lie on a single horizontal line. Molecular weight determination applying the method of Stalke led to a value of 893 (ECC[S3,S4]). This MW could be confirmed by our own regression method based on a number of measurements collected over time within the group (MW = 871, DMW by Christian Färber). The experimental MW is considerably lower than the MW of dimeric $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ (MW = 1154) but higher than that of a monomeric species (MW = 577). We therefore assume a monomer-dimer equilibrium. Note that also the MW value for benzene is significantly too high (found: 540, calculated: 86). This indicates the presence of an attractive interaction between complex and benzene (as a ligand) and an equilibrium between bound and free benzene.

The MW estimation was executed following the method described by Stalke[S4]. The ^{1}H NMR spectrum obviously indicates the presence of two independent species. DOSY shows that these two species have a similar molecular weight: all DOSY signals lie on a single horizontal line. Molecular weight determination applying the method of Stalke led to a value of 893 which is considerably lower than the MW of dimeric $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ (MW = 1154) but higher than a monomeric species (MW = 577). This determined MW of 893 (Stalke method) could be confirmed by our own regression method based on a number of measurements collected over time within the group (= DMW by Christian Färber). Here the found MW is ca. 871 und thus close to the above mentioned value. An explanation for these findings could be the existence of an equilibrium between a monomeric and a dimeric species. A molecular mass calculation for benzene (C_6D_6, solvent) is dependent on the exact spectral region which is applied for calculation of the diffusion constant. In any case the mass is higher than 250 which is strong indication of benzene interaction with the complex.

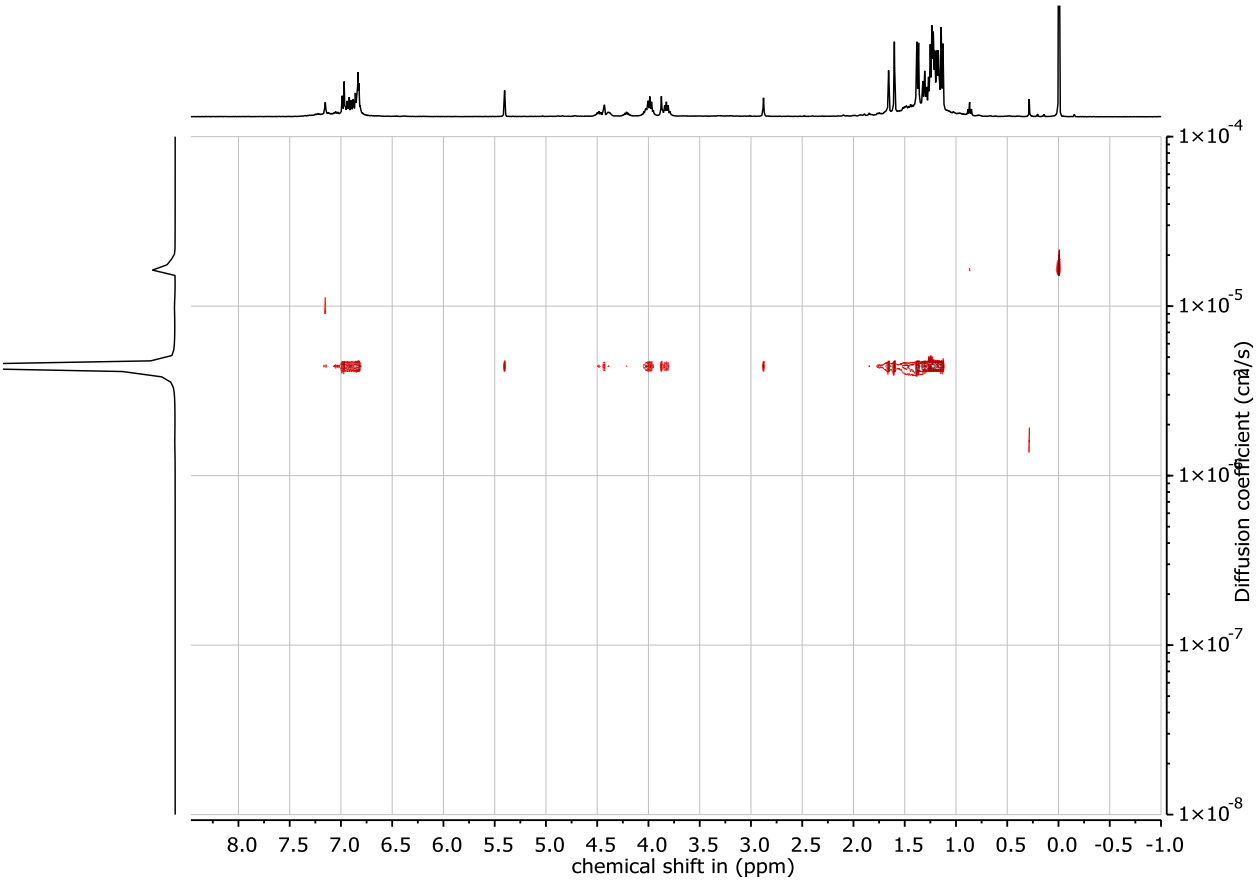


Figure S29: ^{1}H DOSY NMR of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$. 400.13 MHz, C_6D_6, 298 K.

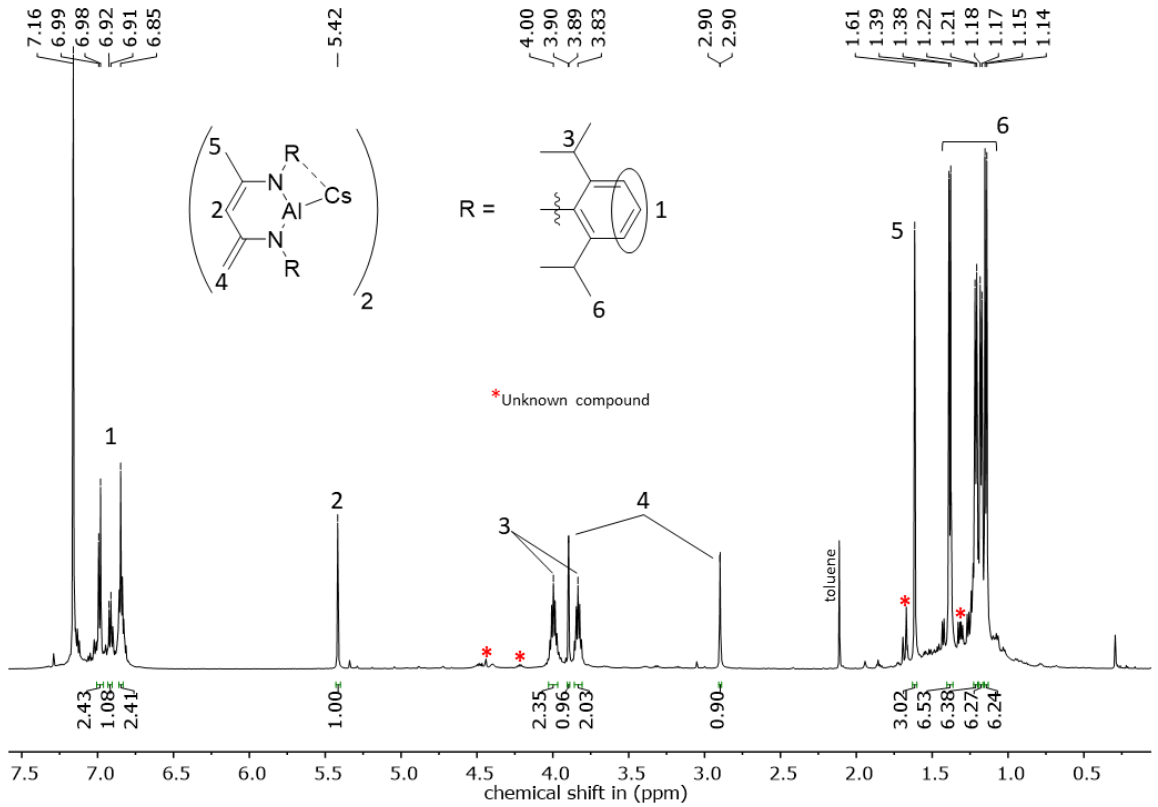


Figure S30: ^{1}H NMR spectrum of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$. 600.13 MHz, C_6D_6, 298 K.

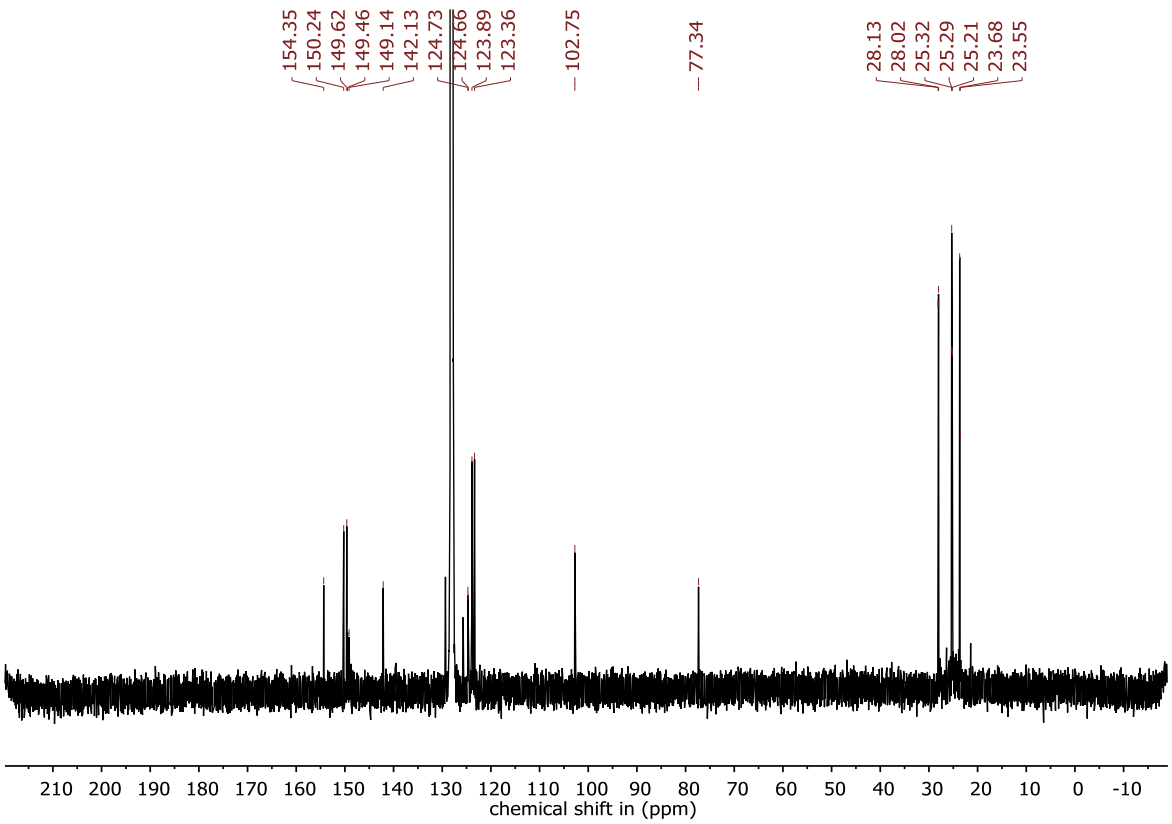


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$. 150.92 MHz, C_6D_6, 298 K.

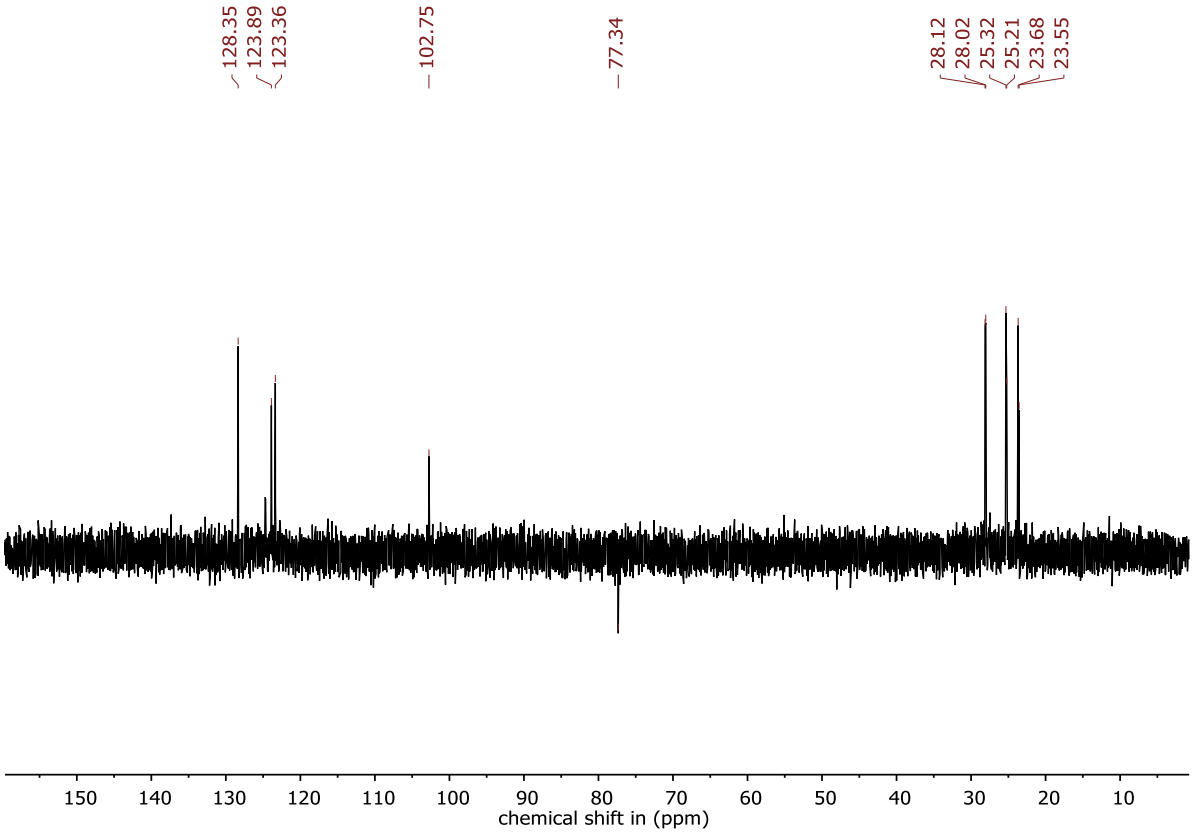


Figure S32: DEPT-135 NMR spectrum of [(BDI-H)Al^{-}Cs^{+}]$_2$. 150.92 MHz, C_6D_6, 298K.

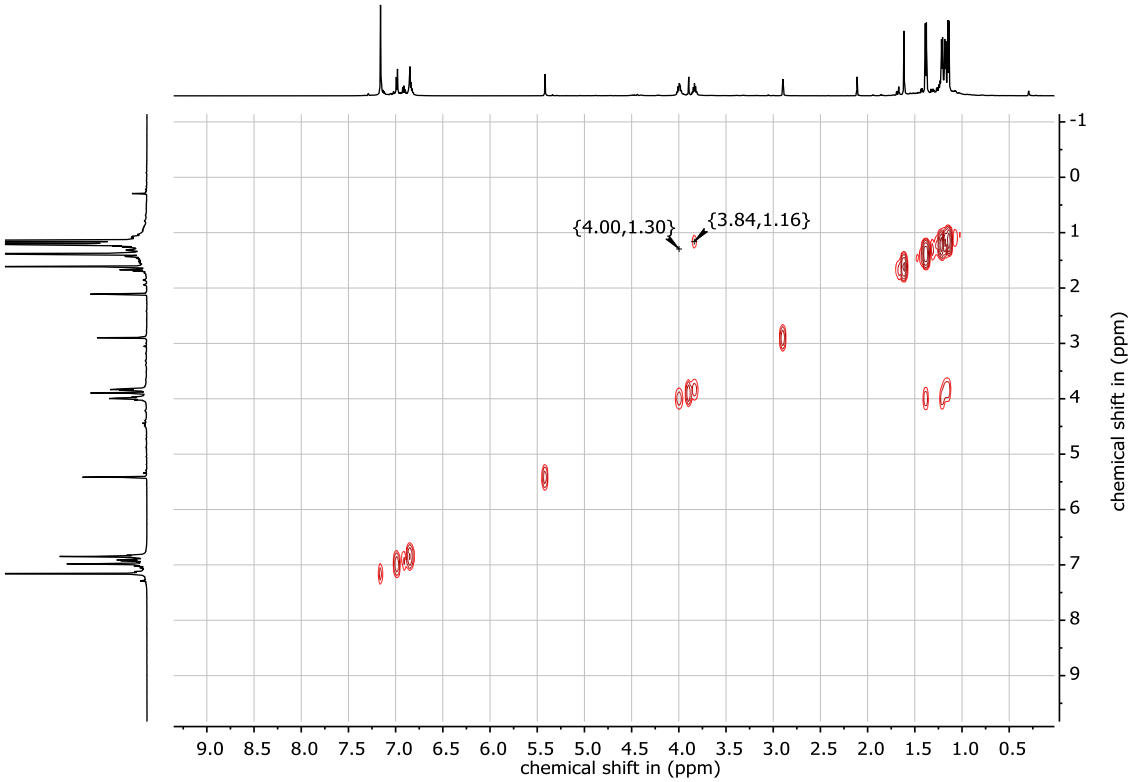


Figure S33: COSY NMR spectrum of [(BDI-H)Al^{-}Cs^{+}]$_2$. 600.13 MHz, C_6D_6, 298K.

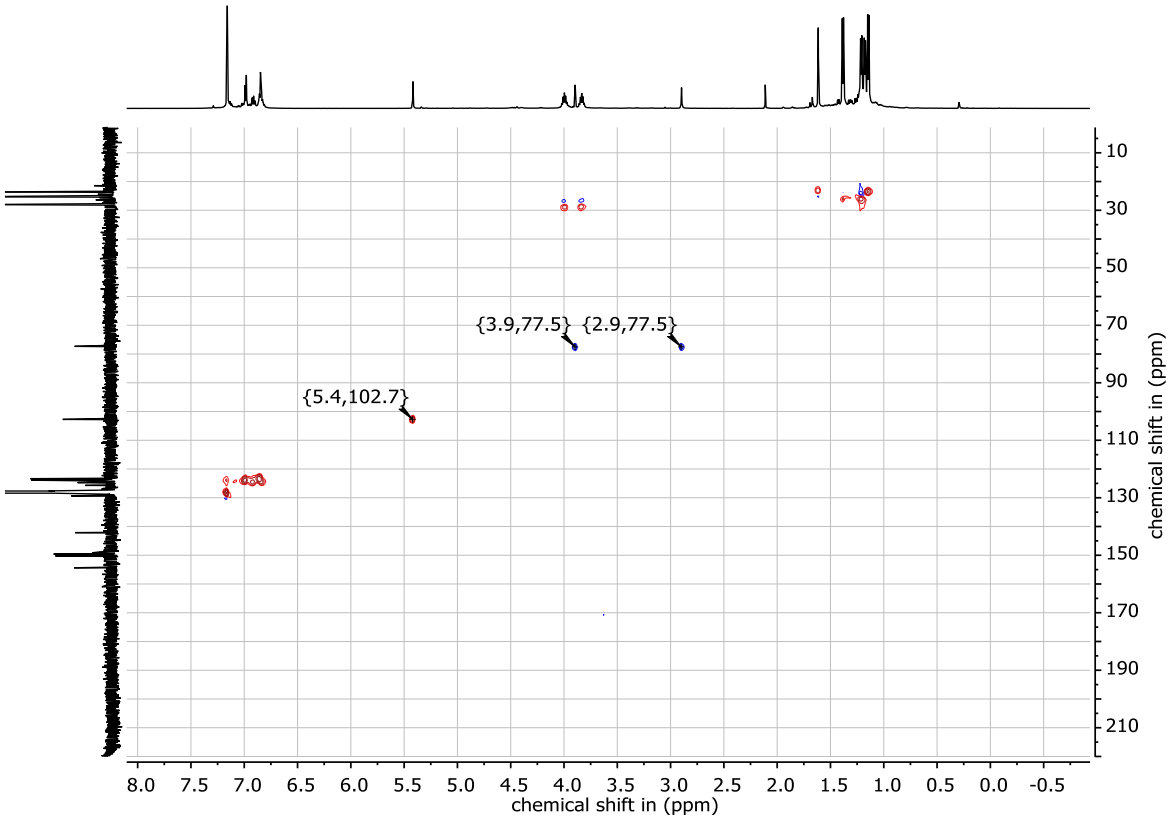


Figure S34: HSQC NMR spectrum of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$. 600.13 and 150.92 MHz, C_6D_6, 298K.

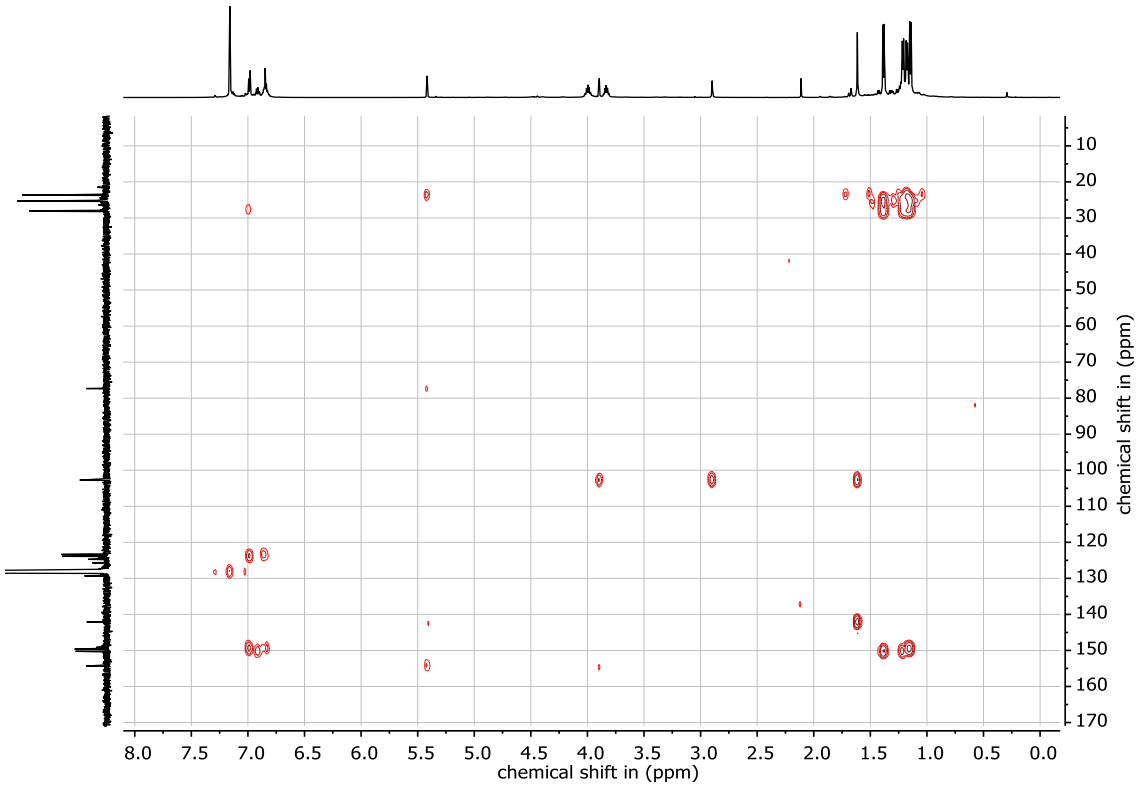


Figure S35: HMBC NMR spectrum of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$. 600.13 and 150.92 MHz, C_6D_6, 298 K.

2. Computational Details

2.1. General methods

All geometry optimizations were carried out using Gaussian 16 Rev. A.0.3. [S5] All structures were fully optimized at the B3PW91/def2TZVP level of theory.[S6] In order to determine zero-point energies and to characterize the structures as minima, frequency analysis has been applied. Implicit solvent effects were computed using the polarizable continuum model (PCM, benzene).[S7] Dispersion correction was computed using Grimme`s third dispersion correction with Becke-Johnson damping (GD3BJ).[S8] Charges were calculated via NBO Analyses.[S9] Molecules were drawn and evaluated using Molecules V2.311.[S10] Topological analyses were carried out using AIMAll V17 with the wavefunctions obtained from the B3LYP/def2TZVP calculations.[S11]

2.2 XYZ-files

73
(BDI-H)Al$^-$Li$^+$

Al	-0.060948	-0.000008	-0.694791
N	-1.408216	0.000014	0.626424
N	1.395829	0.000002	0.470464
C	-2.347576	0.000061	2.849397
H	-3.365420	0.000064	2.482001
H	-2.199677	0.000079	3.920474
C	-1.280508	0.000038	2.010029
C	0.077175	0.000035	2.523079
H	0.143681	0.000047	3.603341
C	1.261056	0.000019	1.852923
C	2.526343	0.000020	2.666437
H	3.142811	-0.874753	2.445207
H	2.294894	0.000023	3.730329
H	3.142813	0.874789	2.445203
C	-2.674062	0.000005	0.009761
C	-3.243248	1.225247	-0.417704
C	-4.247662	1.200669	-1.390452
H	-4.651319	2.135632	-1.762420
C	-4.728842	-0.000024	-1.901215
H	-5.491696	-0.000035	-2.671285
C	-4.247658	-1.200702	-1.390420
H	-4.651312	-2.135676	-1.762363
C	-3.243244	-1.225250	-0.417672
C	-2.762181	2.550904	0.134984
H	-1.947205	2.325558	0.824069
C	-2.224272	3.483825	-0.950640
H	-3.003158	3.770077	-1.663368
H	-1.407982	3.016875	-1.507902
H	-1.840553	4.402633	-0.501379
C	-3.877972	3.227418	0.937184
H	-4.234872	2.578736	1.738530
H	-4.729185	3.490644	0.302607
H	-3.505373	4.148635	1.391165
C	-2.762175	-2.550891	0.135054
H	-1.947184	-2.325525	0.824116
C	-3.877956	-3.227367	0.937301
H	-4.729184	-3.490607	0.302749
H	-4.234833	-2.578654	1.738631
H	-3.505355	-4.148572	1.391307
C	-2.224293	-3.483856	-0.950545
H	-1.408013	-3.016933	-1.507842
H	-3.003196	-3.770134	-1.663245
H	-1.840569	-4.402649	-0.501255
C	2.704693	-0.000007	-0.106113
C	3.335304	-1.220755	-0.421294
C	4.576343	-1.195072	-1.052091
H	5.065207	-2.130135	-1.302957
C	5.197704	-0.000024	-1.368718
H	6.163661	-0.000030	-1.861379
C	4.576368	1.195033	-1.052072
H	5.065252	2.130090	-1.302925
C	3.335329	1.220732	-0.421276
C	2.688406	2.558948	-0.116358
H	1.809677	2.362298	0.501171
C	2.209503	3.239325	-1.402045
H	3.050021	3.458116	-2.066425
H	1.705601	4.183252	-1.176136
H	1.512199	2.601012	-1.950700
C	3.608212	3.490984	0.675170
H	3.075590	4.405701	0.948359
H	4.485775	3.785121	0.093887
H	3.962444	3.020901	1.594936
C	2.688358	-2.558964	-0.116392
H	1.809617	-2.362304	0.501117
C	2.209480	-3.239340	-1.402088
H	1.512194	-2.601022	-1.950761
H	1.705565	-4.183262	-1.176187
H	3.050011	-3.458140	-2.066448
C	3.608138	-3.491005	0.675161
H	3.962343	-3.020926	1.594940
H	4.485717	-3.785141	0.093903
H	3.075506	-4.405722	0.948331
Li	-2.270021	-0.000034	-2.281210

73
(BDI-H)Al$^-$Na$^+$

Al	-0.026049	0.000005	0.626912
Na	2.110181	0.000011	2.627204
N	1.319334	-0.000004	-0.679747
N	-1.501106	-0.000001	-0.508644
C	2.214332	-0.000021	-2.925509
H	3.240334	-0.000021	-2.583482
H	2.040298	-0.000028	-3.992754
C	1.164839	-0.000013	-2.064415
C	-0.198220	-0.000015	-2.566524
H	-0.270125	-0.000022	-3.646497
C	-1.378434	-0.000011	-1.892717
C	-2.649470	-0.000019	-2.696622
H	-3.264412	-0.874906	-2.471197
H	-2.425507	-0.000013	-3.762149
H	-3.264428	0.874856	-2.471190
C	2.620535	-0.000003	-0.126076
C	3.235882	-1.223232	0.228334
C	4.373999	-1.198691	1.037725
H	4.836741	-2.134178	1.333594
C	4.931437	0.000001	1.462371
H	5.814873	0.000002	2.091460
C	4.374003	1.198690	1.037713
H	4.836749	2.134178	1.333572
C	3.235886	1.223227	0.228321
C	2.684543	-2.553295	-0.246267
H	1.806212	-2.332112	-0.854014
C	2.244099	-3.448818	0.913228
H	3.082515	-3.704160	1.568288
H	1.827932	-4.385575	0.534813
H	1.471247	-2.964890	1.517576
C	3.696931	-3.275231	-1.139730
H	3.984962	-2.650886	-1.986705
H	3.260388	-4.196443	-1.533384
H	4.602242	-3.546472	-0.589093
C	2.684551	2.553287	-0.246293
H	1.806216	2.332101	-0.854032
C	2.244119	3.448827	0.913194
H	3.082541	3.704176	1.568243
H	1.471271	2.964910	1.517555
H	1.827951	4.385580	0.534769
C	3.696939	3.275206	-1.139770
H	3.260398	4.196416	-1.533433
H	3.984962	2.650850	-1.986739
H	4.602254	3.546449	-0.589141
C	-2.802713	0.000005	0.081971
C	-3.430198	-1.220672	0.403611
C	-4.662921	-1.195094	1.050553
H	-5.149140	-2.130172	1.306569
C	-5.279738	0.000016	1.375978
H	-6.239284	0.000020	1.881065
C	-4.662908	1.195119	1.050557
H	-5.149117	2.130202	1.306577

C	-3.430184	1.220687	0.403615
C	-2.788437	-2.558486	0.086233
H	-1.920114	-2.360657	-0.545400
C	-2.287588	-3.241352	1.362126
H	-1.579514	-2.603940	1.897953
H	-1.788622	-4.185386	1.125800
H	-3.116390	-3.460058	2.041203
C	-3.721312	-3.489141	-0.691479
H	-4.588503	-3.785495	-0.095890
H	-3.192851	-4.402696	-0.976359
H	-4.091719	-3.016764	-1.603656
C	-2.788413	2.558496	0.086239
H	-1.920082	2.360660	-0.545381
C	-3.721274	3.489150	-0.691492
H	-4.091662	3.016772	-1.603675
H	-3.192809	4.402706	-0.976362
H	-4.588477	3.785502	-0.095919
C	-2.287579	3.241368	1.362135
H	-3.116389	3.460083	2.041199
H	-1.788605	4.185399	1.125809
H	-1.579515	2.603957	1.897976

73

(BDI-H)Al^{-}K^{+}

Al	-0.106346	0.000006	0.571684
N	1.206572	-0.000038	-0.783832
N	-1.607611	-0.000012	-0.551410
C	2.039346	-0.000124	-3.057174
H	3.075877	-0.000135	-2.749631
H	1.831501	-0.000154	-4.118500
C	1.013836	-0.000077	-2.165244
C	-0.358886	-0.000067	-2.637086
H	-0.454884	-0.000087	-3.715223
C	-1.522593	-0.000036	-1.935136
C	-2.811995	-0.000031	-2.710106
H	-3.421790	-0.874813	-2.470593
H	-2.612625	-0.000051	-3.780644
H	-3.421764	0.874777	-2.470621
C	2.536627	-0.000014	-0.303754
C	3.187429	1.222239	-0.016335
C	4.416218	1.198103	0.646222
H	4.913818	2.134070	0.878290
C	5.025623	0.000033	0.992999
H	5.986764	0.000051	1.496132
C	4.416240	-1.198061	0.646266
H	4.913857	-2.134011	0.878368
C	3.187454	-1.222244	-0.016293
C	2.582089	2.553550	-0.416542
H	1.662796	2.330281	-0.959259
C	2.214262	3.406660	0.799348
H	3.093649	3.643869	1.406721
H	1.480570	2.896446	1.431233
H	1.769939	4.353776	0.483634
C	3.505975	3.321351	-1.364829
H	3.744600	2.721779	-2.244433
H	4.443263	3.607425	-0.878847
H	3.017462	4.238091	-1.704361
C	2.582135	-2.553580	-0.416449
H	1.662895	-2.330343	-0.959270
C	3.506095	-3.321474	-1.364586
H	4.443332	-3.607531	-0.878498
H	3.744814	-2.721979	-2.244217
H	3.017595	-4.238231	-1.704091
C	2.214181	-3.406574	0.799483
H	1.480425	-2.896294	1.431241
H	3.093508	-3.643724	1.406968
H	1.769888	-4.353721	0.483815
C	-2.893400	0.000004	0.070024
C	-3.514089	-1.220191	0.407745
C	-4.730650	-1.194852	1.084631
H	-5.210443	-2.130202	1.352075
C	-5.339751	0.000032	1.425230
H	-6.286911	0.000042	1.953324
C	-4.730625	1.194902	1.084627
H	-5.210399	2.130262	1.352067
C	-3.514064	1.220213	0.407740
C	-2.881645	2.558416	0.073551
H	-2.023878	2.359146	-0.571822
C	-2.359858	3.248629	1.336927
H	-3.176691	3.468115	2.030316
H	-1.868246	4.193224	1.086988
H	-1.639820	2.614151	1.860105
C	-3.831004	3.482804	-0.691682
H	-3.311094	4.397397	-0.989067
H	-4.689216	3.777864	-0.082413
H	-4.215147	3.005621	-1.595643
C	-2.881693	-2.558407	0.073564
H	-2.023937	-2.359158	-0.571830
C	-2.359889	-3.248606	1.336940
H	-1.639831	-2.614129	1.860094
H	-1.868294	-4.193211	1.087008
H	-3.176710	-3.468069	2.030351
C	-3.831076	-3.482798	-0.691637
H	-4.215233	-3.005623	-1.595597
H	-4.689279	-3.777842	-0.082347
H	-3.311180	-4.397399	-0.989019
K	2.332255	0.000095	2.861649

73

(BDI-H)Al^{-}Rb^{+}

Al	0.236308	0.000045	0.381682
N	-0.982935	-0.000059	-1.058026
N	1.811257	0.000031	-0.638970
C	-1.657677	0.000025	-3.383918
H	-2.712909	0.000040	-3.148966
H	-1.376636	0.000058	-4.428281
C	-0.695896	-0.000028	-2.423393
C	0.705351	-0.000026	-2.802640
H	0.872784	-0.000023	-3.872029
C	1.819701	-0.000001	-2.025000
C	3.157962	0.000031	-2.712310
H	3.750467	0.874913	-2.432893
H	3.030280	-0.000001	-3.793777
H	3.750541	-0.874785	-2.432851
C	-2.345449	-0.000081	-0.676565
C	-3.018040	-1.221947	-0.445323
C	-4.300670	-1.197835	0.104927
H	-4.817258	-2.133859	0.291236
C	-4.939185	-0.000061	0.394158
H	-5.942283	-0.000054	0.807663
C	-4.300761	1.197700	0.104662
H	-4.817417	2.133728	0.290767
C	-3.018141	1.221782	-0.445604
C	-2.380215	-2.553443	-0.791703
H	-1.421454	-2.330006	-1.261210
C	-2.106667	-3.400294	0.453103
H	-3.030178	-3.630762	0.994184
H	-1.420331	-2.887631	1.134223
H	-1.642972	-4.350753	0.177558
C	-3.223771	-3.328904	-1.806175
H	-3.396845	-2.732694	-2.703241
H	-4.194406	-3.619110	-1.393559
H	-2.705655	-4.243853	-2.104356
C	-2.380408	2.553244	-0.792280

H	-1.421800	2.329770	-1.262076
C	-3.224265	3.328657	-1.806532
H	-4.194759	3.618940	-1.393638
H	-3.397651	2.732385	-2.703498
H	-2.706211	4.243562	-2.104956
C	-2.106451	3.400148	0.452404
H	-1.419894	2.887501	1.133312
H	-3.029791	3.630629	0.993773
H	-1.642844	4.350597	0.176676
C	3.051873	0.000045	0.067620
C	3.648473	1.220132	0.446762
C	4.816148	1.194932	1.204912
H	5.276817	2.130282	1.504209
C	5.400798	0.000062	1.586150
H	6.309971	0.000068	2.177286
C	4.816274	-1.194819	1.204742
H	5.277042	-2.130161	1.503913
C	3.648606	-1.220034	0.446586
C	3.040473	-2.557993	0.069298
H	2.228663	-2.357969	-0.632747
C	2.433272	-3.248645	1.293634
H	3.200648	-3.468654	2.041256
H	1.959415	-4.192893	1.010212
H	1.679314	-2.613447	1.765803
C	4.039630	-3.482019	-0.630073
H	3.541019	-4.396185	-0.963154
H	4.854273	-3.777891	0.036026
H	4.484648	-3.004084	-1.505278
C	3.040216	2.558091	0.069671
H	2.228317	2.358088	-0.632277
C	2.433167	3.248628	1.294147
H	1.679329	2.613351	1.766400
H	1.959196	4.192859	1.010857
H	3.200644	3.468649	2.041660
C	4.039244	3.482209	-0.629766
H	4.484114	3.004382	-1.505105
H	4.853999	3.777996	0.036234
H	3.540573	4.396414	-0.962649
Rb	-2.381151	0.000078	2.711660

73

(BDI-H)Al^{-}Cs^{+}

Al	0.377587	-0.000027	0.226969
N	-0.730981	0.000149	-1.300465
N	2.023263	0.000051	-0.682406
C	-1.237639	0.000352	-3.669414
H	-2.307161	0.000330	-3.512099
H	-0.881526	0.000438	-4.690665
C	-0.347292	0.000268	-2.641974
C	1.077271	0.000296	-2.919982
H	1.321244	0.000406	-3.974559
C	2.132465	0.000203	-2.063581
C	3.516713	0.000271	-2.653102
H	4.087722	0.875092	-2.331880
H	3.467007	0.000336	-3.740978
H	4.087772	-0.874553	-2.331982
C	-2.118746	0.000137	-1.023875
C	-2.809448	-1.221615	-0.854429
C	-4.137556	-1.197601	-0.425776
H	-4.669337	-2.133648	-0.288535
C	-4.800578	0.000072	-0.198697
H	-5.838155	0.000048	0.118523
C	-4.137523	1.197784	-0.425481
H	-4.669279	2.133810	-0.288010
C	-2.809412	1.221869	-0.854124
C	-2.140816	-2.552101	-1.141136
H	-1.155182	-2.325748	-1.549616
C	-1.941346	-3.377283	0.131930
H	-2.896056	-3.602654	0.618707
H	-1.298910	-2.849469	0.843897
H	-1.458049	-4.330136	-0.098023
C	-2.907885	-3.350329	-2.197304
H	-3.030045	-2.767185	-3.111244
H	-3.899485	-3.649250	-1.845277
H	-2.360171	-4.261756	-2.449867
C	-2.140747	2.552405	-1.140516
H	-1.155071	2.326119	-1.548934
C	-2.907705	3.350825	-2.196621
H	-3.899339	3.649682	-1.844638
H	-3.029773	2.767846	-3.110679
H	-2.359962	4.262297	-2.448962
C	-1.941409	3.377366	0.132712
H	-1.299095	2.849409	0.844684
H	-2.896171	3.602709	0.619398
H	-1.458036	4.330234	-0.097022
C	3.209802	-0.000048	0.111292
C	3.778336	1.219849	0.532334
C	4.890424	1.194585	1.369901
H	5.328819	2.129955	1.700983
C	5.447524	-0.000244	1.790485
H	6.313585	-0.000321	2.443182
C	4.890291	-1.194975	1.369800
H	5.328582	-2.130422	1.700799
C	3.778199	-1.220044	0.532229
C	3.196454	-2.558172	0.116028
H	2.432767	-2.358413	-0.638130
C	2.509422	-3.247450	1.298214
H	3.225710	-3.467779	2.094879
H	2.054042	-4.191394	0.984947
H	1.726937	-2.610516	1.718834
C	4.239361	-3.482932	-0.515080
H	3.763874	-4.397857	-0.878592
H	5.008997	-3.777389	0.203188
H	4.740331	-3.006194	-1.360186
C	3.196710	2.558070	0.116265
H	2.433110	2.358465	-0.638022
C	2.509550	3.247176	1.298479
H	1.726985	2.610203	1.718893
H	2.054249	4.191192	0.985314
H	3.225748	3.467338	2.095272
C	4.239727	3.482899	-0.514557
H	4.740829	3.006264	-1.359644
H	5.009250	3.777268	0.203866
H	3.764302	4.397871	-0.878032
Cs	-2.484373	-0.000245	2.488465

146

[(BDI-H)Al^{-}Li^{+}]$_2$

Al	2.550278	0.767077	-0.000012
N	2.320455	2.617241	-0.000024
N	4.417310	0.725040	0.000000
C	3.050763	4.924621	-0.000059
H	2.042578	5.314363	-0.000073
H	3.862496	5.638879	-0.000067
C	3.321284	3.594789	-0.000034
C	4.698390	3.136443	-0.000020
H	5.427863	3.935845	-0.000023
C	5.196803	1.873976	-0.000004
C	6.690203	1.701103	0.000010
H	7.185110	2.670902	0.000005
H	7.027782	1.140419	-0.875200
H	7.027767	1.140437	0.875238
C	0.980261	3.064721	-0.000020
C	0.296329	3.252343	1.225072

C	-1.078164	3.506175	1.198996
H	-1.616862	3.614866	2.132832
C	-1.770860	3.616834	-0.000015
H	-2.841371	3.782624	-0.000013
C	-1.078168	3.506176	-1.199028
H	-1.616869	3.614868	-2.132863
C	0.296325	3.252347	-1.225108
C	1.024165	3.197150	2.553044
H	2.082774	3.066112	2.326059
C	0.572387	2.013207	3.408197
H	-0.487030	2.084927	3.668663
H	1.140430	1.978969	4.340993
H	0.728287	1.065995	2.885647
C	0.875168	4.515818	3.315913
H	1.220877	5.357922	2.714485
H	1.473368	4.486794	4.229749
H	-0.162057	4.702899	3.607144
C	1.024157	3.197150	-2.553083
H	2.082778	3.066208	-2.326100
C	0.572466	2.013126	-3.408171
H	0.728470	1.065953	-2.885580
H	1.140487	1.978897	-4.340981
H	-0.486966	2.084735	-3.668608
C	0.875051	4.515766	-3.316019
H	-0.162188	4.702747	-3.607265
H	1.473256	4.486746	-4.229852
H	1.220686	5.357931	-2.714635
C	5.051757	-0.554432	0.000020
C	5.335603	-1.200252	1.221002
C	5.847696	-2.495235	1.195729
H	6.062723	-3.001431	2.130608
C	6.095867	-3.147449	0.000059
H	6.495434	-4.155581	0.000074
C	5.847716	-2.495263	-1.195631
H	6.062759	-3.001481	-2.130494
C	5.335623	-1.200281	-1.220942
C	5.100156	-0.520708	2.557500
H	4.853150	0.522488	2.351167
C	3.911032	-1.137529	3.297016
H	2.999954	-1.073785	2.696601
H	3.731569	-0.619312	4.242812
H	4.092924	-2.192295	3.522149
C	6.347086	-0.533696	3.444904
H	6.614686	-1.547040	3.754809
H	6.171070	0.049920	4.352120
H	7.210779	-0.105761	2.932020
Li	-0.831482	1.402065	-0.000003
C	5.100200	-0.520768	-2.557461
C	3.911106	-1.137624	-3.296997
H	4.093024	-2.192391	-3.522107
H	3.731660	-0.619428	-4.242807
H	3.000013	-1.073887	-2.696607
C	6.347155	-0.533754	-3.444830
H	7.210826	-0.105791	-2.931933
H	6.171154	0.049836	-4.352065
H	6.614782	-1.547102	-3.754703
H	4.853171	0.522428	-2.351155
Al	-2.550279	-0.767077	-0.000008
N	-2.320455	-2.617241	-0.000021
N	-4.417311	-0.725040	0.000002
C	-3.050763	-4.924620	-0.000047
H	-2.042578	-5.314363	-0.000057
H	-3.862496	-5.638879	-0.000053
C	-3.321284	-3.594789	-0.000029
C	-4.698390	-3.136442	-0.000018
H	-5.427864	-3.935845	-0.000023
C	-5.196803	-1.873976	-0.000004
C	-6.690203	-1.701103	0.000005
H	-7.185110	-2.670902	0.000002
H	-7.027780	-1.140422	-0.875208
H	-7.027770	-1.140434	0.875230
C	-0.980261	-3.064721	-0.000020
C	-0.296328	-3.252345	1.225070
C	1.078165	-3.506176	1.198992
H	1.616865	-3.614869	2.132827
C	1.770860	-3.616834	-0.000020
H	2.841371	-3.782623	-0.000020
C	1.078166	-3.506173	-1.199032
H	1.616865	-3.614864	-2.132868
C	-0.296327	-3.252344	-1.225110
C	-1.024161	-3.197154	2.553044
H	-2.082772	-3.066126	2.326061
C	-0.572391	-2.013204	3.408192
H	0.487028	-2.084911	3.668652
H	-1.140430	-1.978968	4.340990
H	-0.728304	-1.065995	2.885639
C	-0.875150	-4.515817	3.315918
H	-1.220852	-5.357927	2.714494
H	-1.473349	-4.486795	4.229755
H	0.162076	-4.702888	3.607148
C	-1.024161	-3.197145	-2.553084
H	-2.082780	-3.066187	-2.326098
C	-0.572457	-2.013134	-3.408181
H	-0.728443	-1.065955	-2.885596
H	-1.140482	-1.978902	-4.340988
H	0.486972	-2.084761	-3.668624
C	-0.875074	-4.515769	-3.316010
H	0.162162	-4.702766	-3.607256
H	-1.473280	-4.486747	-4.229843
H	-1.220721	-5.357925	-2.714620
C	-5.051758	0.554433	0.000021
C	-5.335601	1.200253	1.221003
C	-5.847695	2.495236	1.195729
H	-6.062720	3.001433	2.130608
C	-6.095866	3.147449	0.000059
H	-6.495433	4.155582	0.000074
C	-5.847717	2.495262	-1.195630
H	-6.062761	3.001480	-2.130494
C	-5.335624	1.200280	-1.220942
C	-5.100155	0.520710	2.557501
H	-4.853144	-0.522485	2.351168
C	-3.911035	1.137536	3.297020
H	-2.999956	1.073797	2.696607
H	-3.731572	0.619320	4.242816
H	-4.092933	2.192301	3.522154
C	-6.347087	0.533692	3.444902
H	-6.614693	1.547036	3.754804
H	-6.171071	-0.049921	4.352120
H	-7.210777	0.105752	2.932017
Li	0.831480	-1.402064	-0.000004
C	-5.100201	0.520766	-2.557460
H	-4.853180	-0.522431	-2.351153
C	-3.911101	1.137615	-3.296992
H	-4.093011	2.192383	-3.522101
H	-3.731655	0.619418	-4.242801
H	-3.000010	1.073870	-2.696599
C	-6.347153	0.533760	-3.444833
H	-7.210829	0.105805	-2.931938
H	-6.171153	-0.049833	-4.352067
H	-6.614771	1.547109	-3.754709

146

$[(BDI\text{-}H)Al^{-}Na^{+}]_2$

Al	2.724862	-0.759854	0.000001

Na	-0.705407	-1.568151	-0.000001
N	2.816886	-2.617966	0.000002
N	4.550919	-0.382163	-0.000003
C	3.952764	-4.756375	0.000005
H	3.031973	-5.322148	0.000008
H	4.880926	-5.311107	0.000005
C	3.978175	-3.399715	0.000002
C	5.253334	-2.704190	-0.000002
H	6.112195	-3.362731	-0.000003
C	5.522749	-1.374401	-0.000005
C	6.961203	-0.938281	-0.000012
H	7.621321	-1.804165	0.000000
H	7.193354	-0.326273	0.875230
H	7.193352	-0.326298	-0.875271
C	1.578695	-3.307563	0.000004
C	0.945999	-3.624853	1.223940
C	-0.342262	-4.163809	1.198476
H	-0.842223	-4.392544	2.133091
C	-0.992971	-4.422314	0.000008
H	-1.996320	-4.831872	0.000009
C	-0.342262	-4.163817	-1.198462
H	-0.842223	-4.392558	-2.133076
C	0.946000	-3.624860	-1.223930
C	1.634813	-3.398872	2.555420
H	2.646025	-3.055314	2.334126
C	1.754603	-4.700637	3.351067
H	0.776040	-5.092543	3.641808
H	2.325086	-4.528351	4.267052
H	2.272255	-5.466075	2.771030
C	0.936943	-2.315001	3.379560
H	0.907154	-1.363676	2.839867
H	1.468592	-2.145507	4.319110
H	-0.090063	-2.597070	3.628055
C	1.634813	-3.398887	-2.555411
H	2.646027	-3.055332	-2.334119
C	1.754598	-4.700655	-3.351054
H	2.272248	-5.466093	-2.771015
H	2.325079	-4.528373	-4.267040
H	0.776032	-5.092559	-3.641792
C	0.936947	-2.315016	-3.379553
H	-0.090061	-2.597081	-3.628045
H	1.468595	-2.145527	-4.319105
H	0.907163	-1.363689	-2.839863
C	4.941521	0.990580	-0.000003
C	5.100779	1.678454	-1.221128
C	5.373800	3.044039	-1.195531
H	5.493044	3.580865	-2.130465
C	5.504121	3.729382	-0.000003
H	5.719708	4.792197	-0.000003
C	5.373804	3.044038	1.195525
H	5.493051	3.580863	2.130458
C	5.100783	1.678453	1.221121
C	4.983726	0.970689	2.558751
H	4.921002	-0.099918	2.354633
C	3.704587	1.375027	3.295210
H	3.694430	2.447637	3.507941
H	3.620056	0.843387	4.246745
H	2.818236	1.141541	2.699216
C	6.207970	1.201115	3.447983
H	7.133266	0.926422	2.937634
H	6.133423	0.598909	4.357041
H	6.296571	2.246488	3.754352
C	4.983716	0.970691	-2.558758
H	4.920996	-0.099916	-2.354641
C	6.207954	1.201122	-3.447997
H	6.133404	0.598915	-4.357054
H	7.133254	0.926433	-2.937653
H	6.296548	2.246494	-3.754368
C	3.704571	1.375027	-3.295208
H	2.818224	1.141538	-2.699209
H	3.620036	0.843388	-4.246744
H	3.694410	2.447637	-3.507937
Al	-2.724862	0.759854	0.000001
Na	0.705407	1.568151	0.000009
N	-2.816886	2.617966	0.000001
N	-4.550919	0.382162	-0.000001
C	-3.952764	4.756375	-0.000003
H	-3.031973	5.322148	-0.000002
H	-4.880926	5.311106	-0.000004
C	-3.978175	3.399715	-0.000001
C	-5.253334	2.704190	-0.000001
H	-6.112195	3.362731	-0.000001
C	-5.522749	1.374401	0.000000
C	-6.961203	0.938281	0.000002
H	-7.621321	1.804165	-0.000010
H	-7.193351	0.326274	-0.875241
H	-7.193354	0.326297	0.875261
C	-1.578695	3.307563	0.000002
C	-0.945997	3.624855	-1.223932
C	0.342264	4.163811	-1.198465
H	0.842227	4.392548	-2.133079
C	0.992971	4.422314	0.000005
H	1.996320	4.831872	0.000006
C	0.342260	4.163815	1.198473
H	0.842219	4.392555	2.133088
C	-0.946002	3.624859	1.223937
C	-1.634808	3.398876	-2.555414
H	-2.646021	3.055317	-2.334122
C	-1.754598	4.700642	-3.351058
H	-0.776034	5.092550	-3.641797
H	-2.325079	4.528358	-4.267044
H	-2.272252	5.466079	-2.771021
C	-0.936937	2.315007	-3.379554
H	-0.907148	1.363681	-2.839864
H	-1.468585	2.145515	-4.319106
H	0.090069	2.597077	-3.628047
C	-1.634818	3.398883	2.555417
H	-2.646032	3.055329	2.334123
C	-1.754603	4.700649	3.351062
H	-2.272251	5.466089	2.771025
H	-2.325086	4.528366	4.267047
H	-0.776037	5.092552	3.641803
C	-0.936953	2.315010	3.379558
H	0.090054	2.597074	3.628052
H	-1.468603	2.145520	4.319109
H	-0.907170	1.363684	2.839867
C	-4.941521	-0.990581	-0.000003
C	-5.100783	-1.678456	1.221120
C	-5.373803	-3.044041	1.195521
H	-5.493050	-3.580868	2.130453
C	-5.504121	-3.729382	-0.000009
H	-5.719708	-4.792197	-0.000011
C	-5.373800	-3.044037	-1.195535
H	-5.493045	-3.580860	-2.130470
C	-5.100780	-1.678452	-1.221129
C	-4.983719	-0.970686	-2.558758
H	-4.920995	0.099921	-2.354638
C	-3.704577	-1.375022	-3.295213
H	-3.694420	-2.447632	-3.507946
H	-3.620043	-0.843381	-4.246747
H	-2.818227	-1.141538	-2.699216
C	-6.207960	-1.201111	-3.447993
H	-7.133258	-0.926418	-2.937648
H	-6.133409	-0.598904	-4.357051

H	-6.296559	-2.246483	-3.754364
C	-4.983724	-0.970695	2.558751
H	-4.921003	0.099913	2.354636
C	-6.207964	-1.201126	3.447986
H	-6.133417	-0.598920	4.357044
H	-7.133263	-0.926437	2.937640
H	-6.296560	-2.246499	3.754355
C	-3.704581	-1.375031	3.295205
H	-2.818232	-1.141541	2.699209
H	-3.620049	-0.843394	4.246741
H	-3.694421	-2.447642	3.507933

146

$[(BDI\text{-}H)Al^{-}K^{+}]_2$

K	-0.094507	2.301328	0.003217
K	0.094507	-2.301329	0.003216
Al	-2.822990	-0.109317	0.000900
Al	2.822990	0.109317	0.000901
N	-4.152227	1.228084	-0.029265
N	-3.971984	-1.581952	0.028828
N	4.152227	-1.228084	-0.029266
N	3.971984	1.581952	0.028825
C	-6.452193	2.135465	-0.056028
C	-6.037049	-0.289321	-0.000835
C	-3.665075	2.560677	-0.052773
C	-3.348715	3.177593	-1.284778
C	-2.705468	4.414820	-1.279322
C	-2.389134	5.057474	-0.092997
C	-2.735227	4.468445	1.112903
C	-3.378582	3.232225	1.157856
C	-3.695584	2.529055	-2.612105
C	-4.555372	3.443634	-3.488235
C	-2.442094	2.084035	-3.368441
C	-3.753786	2.640368	2.503912
C	-4.615356	3.597017	3.331839
C	-2.516296	2.210889	3.294885
C	-3.312906	-2.838230	0.052045
C	-2.958064	-3.472579	-1.158920
C	-2.168907	-4.622178	-1.114328
C	-1.756983	-5.166407	0.092901
C	-2.155085	-4.570944	1.280243
C	-2.944415	-3.420491	1.284789
C	-3.427178	-2.941140	-2.499447
C	-2.262178	-2.434088	-3.351467
C	-4.247204	-3.985413	-3.260484
C	-3.400273	-2.833919	2.606718
C	-2.226748	-2.295845	3.427402
C	-4.215819	-3.844692	3.416328
C	6.452193	-2.135465	-0.056033
C	5.513335	-0.961772	-0.026865
C	6.037049	0.289322	-0.000840
C	5.368152	1.581182	0.028927
C	6.110501	2.717424	0.054542
C	3.665075	-2.560677	-0.052774
C	3.378583	-3.232225	1.157855
C	2.735229	-4.468445	1.112903
C	2.389134	-5.057474	-0.092997
C	2.705467	-4.414820	-1.279323
C	3.348713	-3.177593	-1.284779
C	3.753789	-2.640369	2.503911
C	4.615360	-3.597017	3.331836
C	2.516300	-2.210890	3.294886
C	3.695581	-2.529054	-2.612106
C	4.555368	-3.443634	-3.488238
C	2.442090	-2.084034	-3.368440
C	3.312906	2.838230	0.052043
C	2.944419	3.420492	1.284788
C	2.155088	4.570945	1.280243
C	1.756983	5.166407	0.092902
C	2.168904	4.622177	-1.114328
C	2.958061	3.472578	-1.158922
C	3.400279	2.833921	2.606716
C	2.226757	2.295845	3.427402
C	4.215826	3.844696	3.416324
C	3.427172	2.941138	-2.499449
C	2.262169	2.434087	-3.351467
C	4.247198	3.985410	-3.260488
C	-6.110501	-2.717424	0.054549
C	-5.368152	-1.581182	0.028932
C	-5.513335	0.961772	-0.026861
H	-7.487497	1.797867	-0.053966
H	-7.117697	-0.352603	-0.002410
H	-2.457104	4.889714	-2.222515
H	-1.895481	6.022516	-0.108608
H	-2.509574	4.985135	2.039666
H	-4.279450	1.634445	-2.388540
H	-5.452815	3.776401	-2.963017
H	-4.870484	2.913977	-4.390626
H	-4.007154	4.334591	-3.805469
H	-1.796647	2.935073	-3.604731
H	-2.710814	1.601199	-4.311375
H	-1.863258	1.365555	-2.780787
H	-4.344192	1.743879	2.306896
H	-4.061076	4.492141	3.625910
H	-4.951602	3.104521	4.247528
H	-5.499976	3.921485	2.780283
H	-1.938561	1.462786	2.744183
H	-2.803340	1.768757	4.252264
H	-1.863955	3.063338	3.506144
H	-1.885730	-5.109761	-2.041265
H	-1.151643	-6.065746	0.108806
H	-1.861204	-5.018589	2.223852
H	-4.083811	-2.095242	-2.291895
H	-1.551157	-3.234539	-3.576648
H	-1.723499	-1.628523	-2.843727
H	-2.624664	-2.039599	-4.304207
H	-5.092109	-4.328689	-2.661669
H	-3.644836	-4.856183	-3.534368
H	-4.641445	-3.554232	-4.184269
H	-4.056876	-1.995392	2.370694
H	-1.516152	-3.088487	3.679711
H	-2.580245	-1.861064	4.365881
H	-1.689952	-1.514304	2.881729
H	-4.600574	-3.375877	4.325672
H	-3.612757	-4.705266	3.719290
H	-5.066922	-4.209665	2.839504
H	6.293573	-2.752481	-0.944756
H	7.487497	-1.797867	-0.053973
H	7.117697	0.352603	-0.002418
H	7.190212	2.656298	0.052934
H	5.663803	3.701469	0.077251
H	2.509577	-4.985135	2.039666
H	1.895481	-6.022516	-0.108608
H	2.457102	-4.889713	-2.222515
H	4.344195	-1.743879	2.306894
H	5.499980	-3.921485	2.780279
H	4.951607	-3.104522	4.247525
H	4.061081	-4.492142	3.625908
H	1.863959	-3.063340	3.506145
H	2.803345	-1.768758	4.252264
H	1.938564	-1.462787	2.744185
H	4.279448	-1.634444	-2.388542
H	4.007148	-4.334590	-3.805472
H	4.870478	-2.913976	-4.390629

H	5.452811	-3.776401	-2.963021
H	1.863255	-1.365554	-2.780785
H	2.710808	-1.601198	-4.311375
H	1.796642	-2.935072	-3.604729
H	1.861210	5.018590	2.223853
H	1.151643	6.065746	0.108808
H	1.885724	5.109760	-2.041265
H	4.056884	1.995395	2.370691
H	1.516160	3.088486	3.679712
H	1.689962	1.514303	2.881731
H	2.580257	1.861066	4.365882
H	5.066927	4.209669	2.839498
H	3.612763	4.705269	3.719288
H	4.600583	3.375881	4.325668
H	4.083803	2.095239	-2.291898
H	1.551149	3.234540	-3.576648
H	2.624652	2.039598	-4.304207
H	1.723489	1.628524	-2.843725
H	4.641436	3.554228	-4.184274
H	3.644830	4.856180	-3.534371
H	5.092104	4.328685	-2.661675
H	-5.663803	-3.701469	0.077257
H	-7.190212	-2.656298	0.052942
H	-6.302411	2.789457	0.807379
H	-6.293574	2.752480	-0.944751
H	6.302412	-2.789457	0.807374

146

$[(BDI\text{-}H)Al^{-}Rb^{+}]_2$

Al	-2.955835	-0.059888	0.000037
N	-4.154700	-1.496569	-0.000096
N	-4.243884	1.323541	0.000059
C	-3.550273	-2.780956	-0.000123
C	-3.729079	2.646145	0.000125
C	-3.421819	3.288135	1.221692
C	-5.550434	-1.447978	-0.000147
C	-3.222680	-3.408731	1.221626
C	-3.421887	3.288288	-1.221383
C	-5.613182	1.098794	-0.000005
C	-3.222559	-3.408621	-1.221897
C	-6.176360	-0.134938	-0.000095
H	-7.258479	-0.163299	-0.000130
C	-2.437795	5.136492	0.000241
H	-1.939973	6.099803	0.000286
C	-2.771611	4.521564	-1.196209
H	-2.532513	5.016422	-2.131576
C	-2.771542	4.521415	1.196634
H	-2.532394	5.016159	2.132049
C	-6.517161	2.300294	0.000039
H	-6.345108	2.931429	0.876205
H	-7.561733	1.992568	0.000013
H	-6.345090	2.931508	-0.876067
C	-2.503436	-4.603815	1.197160
H	-2.243551	-5.087723	2.132922
C	-3.648412	-2.822511	2.553805
H	-4.262539	-1.948571	2.332562
C	-3.785173	2.669262	2.558936
H	-4.388136	1.784180	2.348680
C	-3.785292	2.669562	-2.558680
H	-4.388300	1.784492	-2.348504
C	-2.503318	-4.603710	-1.197469
H	-2.243343	-5.087535	-2.133249
C	-6.332655	-2.557773	-0.000237
H	-5.922495	-3.557712	-0.000275
H	-7.409457	-2.457297	-0.000272
C	-2.134076	-5.197867	-0.000165
H	-1.585033	-6.133208	-0.000181
C	-2.542041	2.207940	-3.322415
H	-2.821274	1.750078	-4.274733
H	-1.982725	1.463487	-2.748243
H	-1.875924	3.047773	-3.542118
C	-4.512322	-3.803243	3.349816
H	-3.953004	-4.697266	3.639615
H	-5.380723	-4.116640	2.768472
H	-4.872885	-3.329300	4.266432
C	-3.648157	-2.822269	-2.554061
H	-4.262345	-1.948380	-2.332787
C	-2.541894	2.207639	3.322625
H	-1.875814	3.047483	3.542394
H	-1.982547	1.463258	2.748389
H	-2.821101	1.749686	4.274907
C	-2.448127	-2.355854	3.379873
H	-2.777307	-1.922737	4.327978
H	-1.877866	-1.589457	2.846554
H	-1.774827	-3.185999	3.614250
C	-4.624760	3.614821	3.421392
H	-4.954792	3.103531	4.329009
H	-5.512727	3.962488	2.889762
H	-4.056639	4.496197	3.730300
C	-2.447791	-2.355468	-3.379931
H	-1.774441	-3.185565	-3.614336
H	-1.877613	-1.589121	-2.846451
H	-2.776874	-1.922244	-4.328021
C	-4.624831	3.615242	-3.421050
H	-4.056659	4.496602	-3.729906
H	-5.512766	3.962928	-2.889379
H	-4.954913	3.104041	-4.328699
C	-4.511929	-3.802940	-3.350296
H	-5.380371	-4.116470	-2.769085
H	-3.952531	-4.696890	-3.640166
H	-4.872426	-3.328888	-4.266881
Rb	-0.043245	2.399453	0.000047
Al	2.955835	0.059888	0.000047
N	4.154709	1.496561	-0.000093
N	4.243877	-1.323547	0.000076
C	3.550288	2.780951	-0.000131
C	3.729067	-2.646148	0.000143
C	3.421787	-3.288131	1.221711
C	5.550443	1.447964	-0.000147
C	3.222700	3.408737	1.221615
C	3.421888	-3.288297	-1.221364
C	5.613177	-1.098808	0.000014
C	3.222576	3.408610	-1.221909
C	6.176362	0.134921	-0.000083
H	7.258481	0.163276	-0.000116
C	2.437769	-5.136489	0.000257
H	1.939940	-6.099798	0.000300
C	2.771605	-4.521569	-1.196192
H	2.532518	-5.016431	-2.131560
C	2.771502	-4.521408	1.196651
H	2.532338	-5.016146	2.132065
C	6.517149	-2.300313	0.000067
H	6.345086	-2.931445	0.876233
H	7.561723	-1.992593	0.000047
H	6.345081	-2.931528	-0.876039
C	2.503465	4.603826	1.197141
H	2.243585	5.087742	2.132900
C	3.648428	2.822522	2.553797
H	4.262538	1.948570	2.332559
C	3.785128	-2.669255	2.558956
H	4.388096	-1.784176	2.348704
C	3.785314	-2.669578	-2.558659
H	4.388329	-1.784515	-2.348478
C	2.503341	4.603704	-1.197488

H	2.243367	5.087523	-2.133272
C	6.332668	2.557755	-0.000251
H	5.922513	3.557696	-0.000299
H	7.409470	2.457274	-0.000288
C	2.134106	5.197872	-0.000186
H	1.585070	6.133217	-0.000207
C	2.542076	-2.207944	-3.322407
H	2.821323	-1.750088	-4.274724
H	1.982763	-1.463481	-2.748243
H	1.875950	-3.047769	-3.542113
C	4.512359	3.803247	3.349794
H	3.953058	4.697283	3.639586
H	5.380763	4.116621	2.768442
H	4.872918	3.329306	4.266413
C	3.648168	2.822247	-2.554070
H	4.262355	1.948358	-2.332792
C	2.541844	-2.207628	3.322633
H	1.875760	-3.047470	3.542398
H	1.982504	-1.463247	2.748391
H	2.821044	-1.749674	4.274917
C	2.448140	2.355893	3.379876
H	2.777318	1.922778	4.327983
H	1.877860	1.589503	2.846568
H	1.774858	3.186054	3.614252
C	4.624706	-3.614815	3.421422
H	4.954729	-3.103525	4.329042
H	5.512678	-3.962483	2.889801
H	4.056580	-4.496190	3.730325
C	2.447797	2.355442	-3.379931
H	1.774447	3.185539	-3.614337
H	1.877621	1.589100	-2.846441
H	2.776875	1.922210	-4.328019
C	4.624851	-3.615269	-3.421019
H	4.056671	-4.496622	-3.729881
H	5.512775	-3.962967	-2.889337
H	4.954950	-3.104072	-4.328664
C	4.511939	3.802910	-3.350314
H	5.380385	4.116441	-2.769110
H	3.952543	4.696860	-3.640188
H	4.872430	3.328852	-4.266899
Rb	0.043236	-2.399423	-0.000012

146

$[(BDI\text{-}H)Al^{-}Cs^{+}]_2$

H	-7.558173	-2.398223	0.000034
Cs	-0.020459	2.502661	-0.000037
Al	-3.077648	-0.044839	-0.000020
N	-4.292513	-1.472395	-0.000026
N	-4.357762	1.350793	0.000084
C	-6.482638	-2.511804	-0.000002
H	-6.085290	-3.516746	-0.000051
C	-5.688148	-1.410367	0.000014
C	-6.302545	-0.092536	0.000083
H	-7.384847	-0.111818	0.000116
C	-5.729135	1.136157	0.000118
C	-6.625837	2.343496	0.000203
H	-6.450553	2.973930	0.876206
H	-7.672040	2.041382	0.000207
H	-6.450590	2.974035	-0.875732
C	-3.712921	-2.768593	-0.000088
C	-3.406786	-3.407542	1.221442
C	-2.735572	-4.630131	1.196918
H	-2.495019	-5.123869	2.132748
C	-2.392177	-5.239621	-0.000188
H	-1.882307	-6.197073	-0.000227
C	-2.735549	-4.630020	-1.197243
H	-2.494979	-5.123673	-2.133114
C	-3.406762	-3.407427	-1.221670
C	-3.806623	-2.804220	2.554034
H	-4.396806	-1.913927	2.332925
C	-2.586721	-2.367563	3.367930
H	-1.933894	-3.215126	3.598493
H	-2.895232	-1.923188	4.317812
H	-2.001861	-1.617567	2.826973
C	-4.692156	-3.754984	3.362229
H	-5.572499	-4.047781	2.788160
H	-5.033670	-3.264782	4.277611
H	-4.156540	-4.662327	3.655393
C	-3.806600	-2.804002	-2.554216
H	-4.396644	-1.913634	-2.333037
C	-2.586704	-2.367492	-3.368195
H	-1.934025	-3.215140	-3.598861
H	-2.001680	-1.617613	-2.827254
H	-2.895222	-1.923021	-4.318028
C	-4.692328	-3.754625	-3.362368
H	-5.033819	-3.264363	-4.277727
H	-5.572681	-4.047288	-2.788248
H	-4.156865	-4.662047	-3.655566
C	-3.846233	2.675011	0.000096
C	-3.549653	3.322258	1.221498
C	-2.925302	4.568776	1.196421
H	-2.697064	5.068750	2.131809
C	-2.605996	5.191473	0.000103
H	-2.129857	6.165906	0.000106
C	-2.925400	4.568832	-1.196217
H	-2.697239	5.068848	-2.131601
C	-3.549758	3.322316	-1.221301
C	-3.899569	2.694954	-2.558278
H	-4.500226	1.808360	-2.347757
C	-2.647073	2.233407	-3.306921
H	-2.914814	1.769717	-4.259762
H	-2.092298	1.493351	-2.722592
H	-1.981924	3.074874	-3.524107
C	-4.735422	3.630074	-3.435295
H	-4.168398	4.510693	-3.748357
H	-5.628761	3.979109	-2.913658
H	-5.056708	3.109473	-4.340754
H	-4.499957	1.808202	2.347950
C	-3.899364	2.694838	2.558474
C	-4.735264	3.629877	3.435534
H	-4.168301	4.510538	3.748590
H	-5.056480	3.109235	4.340996
H	-5.628647	3.978847	2.913932
C	-2.646808	2.233379	3.307072
H	-2.091980	1.493389	2.722711
H	-2.914486	1.769637	4.259904
H	-1.981727	3.074896	3.524271
H	7.558170	2.398229	-0.000079
Cs	0.020462	-2.502661	-0.000040
Al	3.077649	0.044838	0.000039
N	4.292511	1.472396	-0.000038
N	4.357765	-1.350792	0.000081
C	6.482634	2.511809	-0.000082
H	6.085284	3.516750	-0.000118
C	5.688146	1.410370	-0.000040
C	6.302545	0.092540	0.000013
H	7.384847	0.111824	0.000015
C	5.729138	-1.136154	0.000068
C	6.625842	-2.343492	0.000131
H	6.450568	-2.973935	0.876129
H	7.672044	-2.041376	0.000126
H	6.450585	-2.974022	-0.875808
C	3.712917	2.768593	-0.000087
C	3.406787	3.407535	1.221448

C	2.735569	4.630123	1.196933
H	2.495019	5.123855	2.132766
C	2.392167	5.239618	-0.000168
H	1.882294	6.197069	-0.000200
C	2.735535	4.630025	-1.197229
H	2.494959	5.123682	-2.133095
C	3.406751	3.407434	-1.221665
C	3.806637	2.804214	2.554036
H	4.396791	1.913903	2.332923
C	2.586743	2.367598	3.367967
H	1.933941	3.215180	3.598535
H	2.895266	1.923229	4.317847
H	2.001851	1.617610	2.827034
C	4.692215	3.754965	3.362198
H	5.572555	4.047724	2.788108
H	5.033731	3.264768	4.277582
H	4.156631	4.662329	3.655356
C	3.806580	2.804012	-2.554215
H	4.396675	1.913676	-2.333042
C	2.586678	2.367431	-3.368147
H	1.933948	3.215046	-3.598794
H	2.001713	1.617526	-2.827181
H	2.895186	1.922973	-4.317990
C	4.692236	3.754665	-3.362409
H	5.033734	3.264400	-4.277764
H	5.572587	4.047391	-2.788317
H	4.156718	4.662051	-3.655618
C	3.846238	-2.675011	0.000109
C	3.549652	-3.322241	1.221519
C	2.925300	-4.568760	1.196455
H	2.697058	-5.068721	2.131849
C	2.606003	-5.191474	0.000145
H	2.129865	-6.165908	0.000159
C	2.925415	-4.568850	-1.196183
H	2.697258	-5.068880	-2.131560
C	3.549769	-3.322334	-1.221281
C	3.899578	-2.694983	-2.558263
H	4.500252	-1.808398	-2.347751
C	2.647081	-2.233415	-3.306892
H	2.914817	-1.769727	-4.259734
H	2.092323	-1.493353	-2.722554
H	1.981917	-3.074872	-3.524071
C	4.735403	-3.630118	-3.435289
H	4.168358	-4.510723	-3.748352
H	5.628738	-3.979175	-2.913660
H	5.056695	-3.109520	-4.340749
H	4.499934	-1.808160	2.347956
C	3.899363	-2.694809	2.558489
C	4.735297	-3.629829	3.435537
H	4.168361	-4.510508	3.748591
H	5.056505	-3.109183	4.341000
H	5.628686	-3.978770	2.913925
C	2.646807	-2.233379	3.307104
H	2.091956	-1.493399	2.722752
H	2.914488	-1.769634	4.259934
H	1.981746	-3.074911	3.524310

3. Single crystal X-ray diffraction

In each case, an appropriate crystal was selected under the microscope, embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The selected crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structures were measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a MoKα microfocus source for $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$ or a CuKα microfocus source for all other compounds. The measured data were processed with the CrysAlisPro software package.[S12] Using Olex2,[S13] the structures were solved with the ShelXT[S14] structure solution program using Intrinsic Phasing and refined with the ShelXL[S15] refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The positions of the hydrides at aluminum in compound $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$, and of H1a and H1b in $[(BDI\text{-}H)Al^-Cs^+]_2$ were observed from difference Fourier maps and refined isotropically.

The backbone of the ligand coordinated to Al is deprotonated in all compounds and therefore becomes unsymmetrical. Consequently, disorder of this ligand backbone was noticed in almost all compounds under investigation. However, since the alternative positions of the C atoms of the two orientations only differ slightly and strong restraints or even constraints would be necessary to model their disorder without gaining any meaningful information about the true situation, a disorder model for these C atoms was not implemented. Instead, only the disorder of the hydrogen atoms of the superimposed CH_2 and CH_3 groups is taken into account.

Additionally, in compound $[(BDI\text{-}H)Al^-Li^+]_2$ a disorder of one *i*Pr group was observed and treated using similarity restraints (SADI, SIMU). The relative occupancies of the two alternative orientations were refined to 0.843(10) and 0.157(10).

The crystal of $(BDI\text{-}H)Al^-Li^+(Et_2O)_2$ was a racemic twin. The fractional contributions of the two twin domains were refined to 0.51(6) and 0.49(6) later on.

In complex $[(BDI\text{-}H)Al^-Na^+]_2$ a disorder of one *i*Pr group was observed and treated using similarity restraints (SADI, SIMU). The relative occupancies of the two alternative orientations were refined to 0.759(16) and 0.241(16).

Derivative $(BDI\text{-}H)Al^-Na^+(TMEDA)(Et_2O)$ showed a disorder of the diethyl ether moieties. The disorder was treated using similarity restraints (SADI, SIMU). The relative occupancies of the two alternative orientations were refined to 0.898(3)/0.102(3) (Et_2O coordinated) and 0.593(4)/0.407(4) (Et_2O co-crystallized), respectively.

In complex $[(BDI\text{-}H)Al^-Rb^+]_2$ a disorder of the Rb and Al atoms was observed and treated using similarity restraints (SIMU). The relative occupancies of the two alternative positions were refined to 0.860(11) and 0.140(11). Additionally, the four co-crystallized toluene molecules are severely disordered about inversion centers, while occupying two alternative positions each. In order to facilitate the refinement, the aromatic rings of these molecules were treated as rigid hexagons (AFIX 66) and a substantial number of similarity restraints (SADI, SIMU) were applied. Furthermore, one ISOR restraint was used.

For compound $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$ a disorder of two *i*Pr groups was observed and treated using similarity restraints (SADI, SIMU) and rigid bond restraints (RIGU).[S16] The relative occupancies of the two alternative positions were refined to 0.68(6)/0.32(6) (*i*Pr 1) and 0.59(6)/0.41(6) (*i*Pr 2), respectively. Additionally, the co-crystallized toluene molecule was severely disordered about an inversion center. In the asymmetric unit, it adopts three orientations (two of which only differ in the orientation of the methyl group). This disorder was modeled with the help of similarity restraints (SADI, SIMU) and rigid bond restraints (RIGU).[S16] Furthermore, the aromatic ring of toluene in its least occupied orientation was treated as regular hexagon (AFIX 66). Hydrogen placement was done using additional DFIX restraints and geometric restraints (FLAT).

The data for $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+]_2$ also showed additional disorder. In this case, an *i*Pr group and four THF moieties are affected. The disorder was treated using similarity restraints (SADI, SIMU). The relative occupancies of the two alternative orientations were refined to 0.55(5)/0.45(5) (*i*Pr), 0.59(2)/0.41(2) (THF coordinated), 0.755(10)/0.245(10) (THF coordinated), 0.633(11)/0.367(11) (THF co-crystallized) and 0.833(5)/0.167(5) (THF co-crystallized), respectively.

Crystallographic and refinement data of all compounds are summarized in Tables S3 – S6.

The crystal structure data of the compounds have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2182254 $(BDI\text{-}H)Al^-Li^+(Et_2O)_2$, CCDC 2182255 $(BDI\text{-}H)Al^-Na^+(TMEDA)(Et_2O)$, CCDC 2182256 $[(BDI\text{-}H)Al^-Li^+]_2$, CCDC 2182257 $[(BDI\text{-}H)Al^-Na^+]_2$, CCDC 2182258 $[(BDI\text{-}H)Al^-Rb^+]_2$, CCDC 2182259 $[(BDI\text{-}H)Al^-Cs^+]_2$ and CCDC 2182260 $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$ contain the supplementary crystallographic data for the compounds. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3: Crystal data and structure refinement for Li aluminyl complexes.

Compound	$[(BDI\text{-}H)Al^{-}Li^{+}]_2$	$(BDI\text{-}H)Al^{-}Li^{+}(Et_2O)_2$
Identification code	hasj211026d	hasj210908b
Empirical formula	$C_{58}H_{80}Al_2Li_2N_4$	$C_{37}H_{60}AlLiN_2O_2$
Formula weight	901.10	598.79
Temperature/K	100.0(6)	100.0(6)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	12.6973(3)	10.73160(10)
b/Å	17.1843(6)	17.1793(2)
c/Å	12.9109(4)	20.4541(3)
α/°	90	90
β/°	100.304(3)	90
γ/°	90	90
Volume/Å^3	2771.66(14)	3770.95(8)
Z	2	4
ρ_{calc}g/cm^3	1.080	1.055
μ/mm^{-1}	0.751	0.694
F(000)	976.0	1312.0
Crystal size/mm^3	0.161 × 0.102 × 0.087	0.35 × 0.202 × 0.127
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.656 to 144.53	6.72 to 145.246
Index ranges	-15 ≤ h ≤ 12, -12 ≤ k ≤ 20, -10 ≤ l ≤ 15	-12 ≤ h ≤ 11, -20 ≤ k ≤ 20, -25 ≤ l ≤ 15
Reflections collected	9860	13066
Independent reflections	5296 [Rint = 0.0338, Rsigma = 0.0473]	7208 [Rint = 0.0302, Rsigma = 0.0421]
Data/restraints/parameters	5296/97/337	7208/674/520
Goodness-of-fit on F^2	1.057	1.078
Final R indexes [I>=2σ (I)]	R1 = 0.0436, wR2 = 0.1043	R1 = 0.0463, wR2 = 0.1223
Final R indexes [all data]	R1 = 0.0579, wR2 = 0.1139	R1 = 0.0552, wR2 = 0.1286
Largest diff. peak/hole / e Å^{-3}	0.23/-0.30	0.47/-0.21

Table S4: Crystal data and structure refinement for for Na aluminyl complexes.

Compound	$[(BDI\text{-}H)Al^{-}Na^{+}]_2$	$(BDI\text{-}H)Al^{-}Na^{+}$ (Et_2O, TMEDA)
Identification code	hasj220502a	hasj220328b
Empirical formula	$C_{58}H_{80}Al_2N_4Na_2$	$C_{41}H_{71}AlN_4NaO_{1.5}$
Formula weight	933.20	693.98
Temperature/K	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.98403(11)	21.4823(3)
b/Å	16.98245(14)	20.6133(3)
c/Å	13.13426(12)	21.7946(3)
α/°	90	90
β/°	98.5389(8)	114.3945(17)
γ/°	90	90
Volume/Å^3	2864.01(4)	8789.5(2)
Z	2	8
ρ_{calc}g/cm^3	1.082	1.049
μ/mm^{-1}	0.885	0.750
F(000)	1008.0	3048.0
Crystal size/mm^3	0.478 × 0.402 × 0.361	0.401 × 0.268 × 0.203
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.57 to 145.22	6.182 to 149.142
Index ranges	-16 ≤ h ≤ 15, -20 ≤ k ≤ 20, -15 ≤ l ≤ 16	-26 ≤ h ≤ 26, -23 ≤ k ≤ 25, -25 ≤ l ≤ 27
Reflections collected	21077	81308
Independent reflections	5602 [R_{int} = 0.0168, R_{sigma} = 0.0127]	17734 [R_{int} = 0.0256, R_{sigma} = 0.0183]
Data/restraints/parameters	5602/97/340	17734/523/1004
Goodness-of-fit on F^2	1.031	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0875	R_1 = 0.0389, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0340, wR_2 = 0.0885	R_1 = 0.0443, wR_2 = 0.1089
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21	0.36/-0.23

Table S5: Crystal data and structure refinement for Rb and Cs aluminyl complexes.

Compound	$[(BDI\text{-}H)Al^{-}Rb^{+}]_2$	$[(BDI\text{-}H)Al^{-}Cs^{+}]_2$
Identification code	hasj210324a	hasj210202a
Empirical formula	$C_{86}H_{112}Al_2N_4Rb_2$	$C_{61.5}H_{84}Al_2Cs_2N_4$
Formula weight	1426.69	1199.10
Temperature/K	100.0(2)	100.0(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.6926(4)	12.1714(2)
b/Å	12.8395(4)	15.2939(2)
c/Å	14.2842(5)	17.2744(2)
α/°	71.822(3)	96.6030(10)
β/°	72.863(3)	96.2390(10)
γ/°	69.306(3)	96.2070(10)
Volume/Å^3	2023.95(13)	3151.57(8)
Z	1	2
ρ_{calc}g/cm^3	1.171	1.264
μ/mm^{-1}	2.102	9.564
F(000)	756.0	1234.0
Crystal size/mm^3	0.225 × 0.118 × 0.096	0.18 × 0.118 × 0.074
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.658 to 144.732	5.862 to 145.444
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	29152	48647
Independent reflections	7859 [R_{int} = 0.0292, R_{sigma} = 0.0251]	12306 [R_{int} = 0.0294, R_{sigma} = 0.0254]
Data/restraints/parameters	7859/1835/746	12306/893/834
Goodness-of-fit on F^2	1.174	1.138
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1424	R_1 = 0.0354, wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0621, wR_2 = 0.1457	R_1 = 0.0366, wR_2 = 0.0841
Largest diff. peak/hole / e Å^{-3}	0.57/-0.51	1.39/-1.63

Table S6: Crystal data and structure refinement for compound $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$.

Identification code	hasj210113b
Empirical formula	$C_{88}H_{134}Al_2Cs_2N_4O_6$
Formula weight	1663.76
Temperature/K	190.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	15.07005(19)
b/Å	15.6249(3)
c/Å	20.9706(4)
α/°	90.9024(16)
β/°	94.7632(13)
γ/°	113.7230(15)
Volume/Å^3	4498.49(15)
Z	2
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.880
F(000)	1748.0
Crystal size/mm^3	0.411 × 0.26 × 0.192
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.542 to 58.918
Index ranges	-20 ≤ h ≤ 20, -19 ≤ k ≤ 20, -28 ≤ l ≤ 27
Reflections collected	80107
Independent reflections	22043 [R_{int} = 0.0268, R_{sigma} = 0.0296]
Data/restraints/parameters	22043/1077/1143
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.0941
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1033
Largest diff. peak/hole / e Å^{-3}	1.08/-0.78

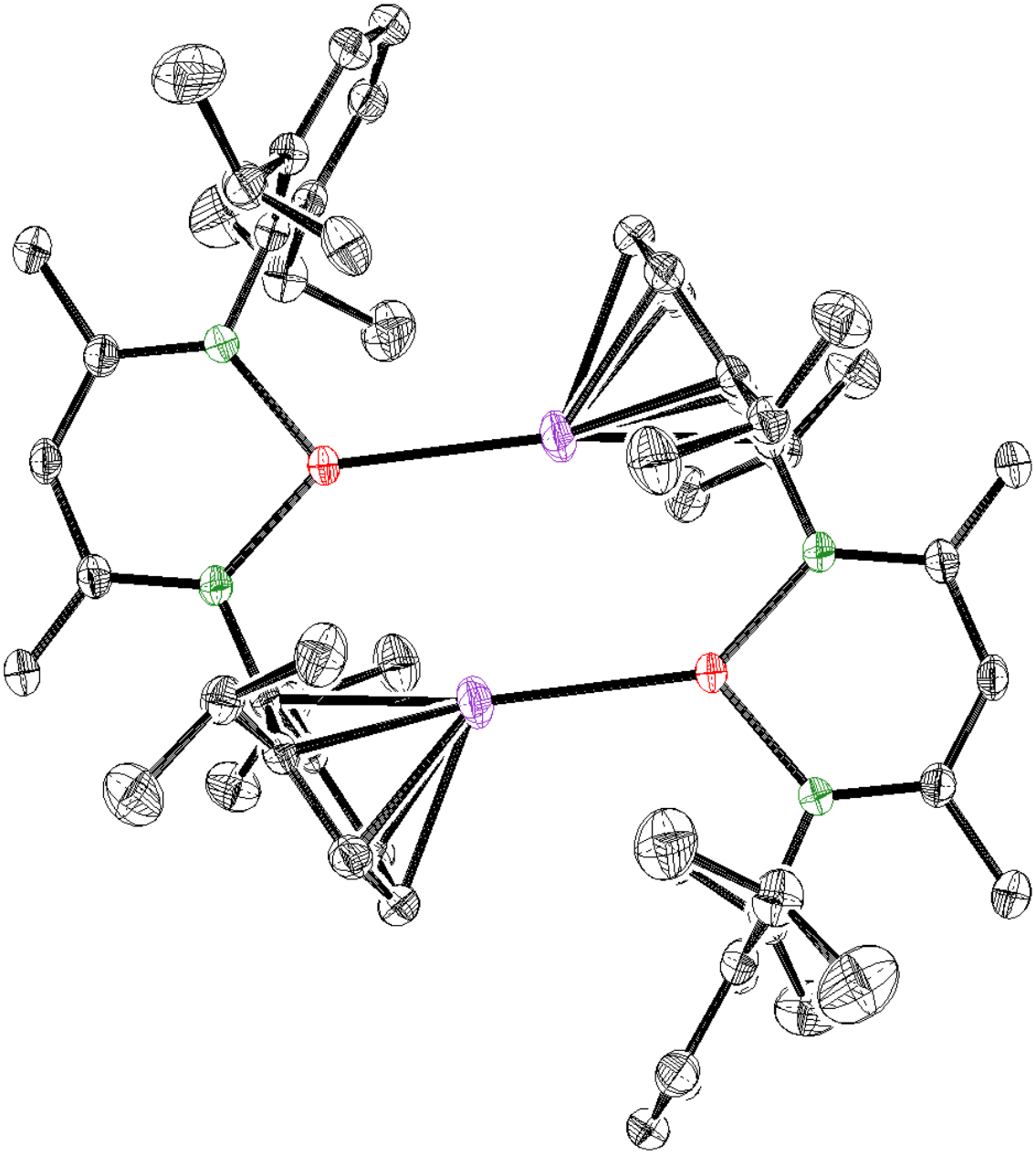


Figure S36: Ellipsoid plot of $[(BDI\text{-}H)Al^{-}Li^{+}]_2$ (50 % probability).

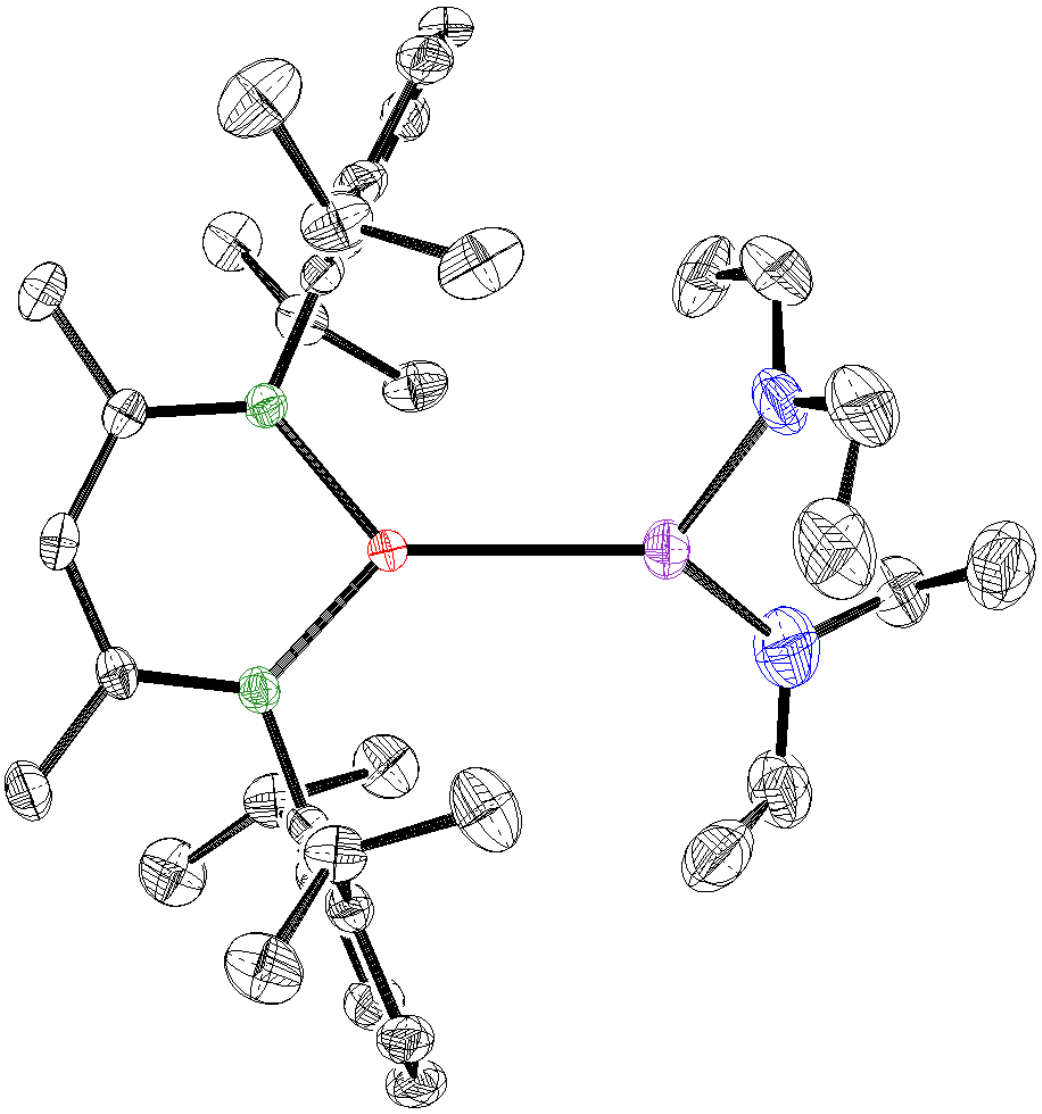


Figure S37: Ellipsoid plot of (BDI-H)$Al^{-}Li^{+}(Et_2O)_2$ (50 % probability).

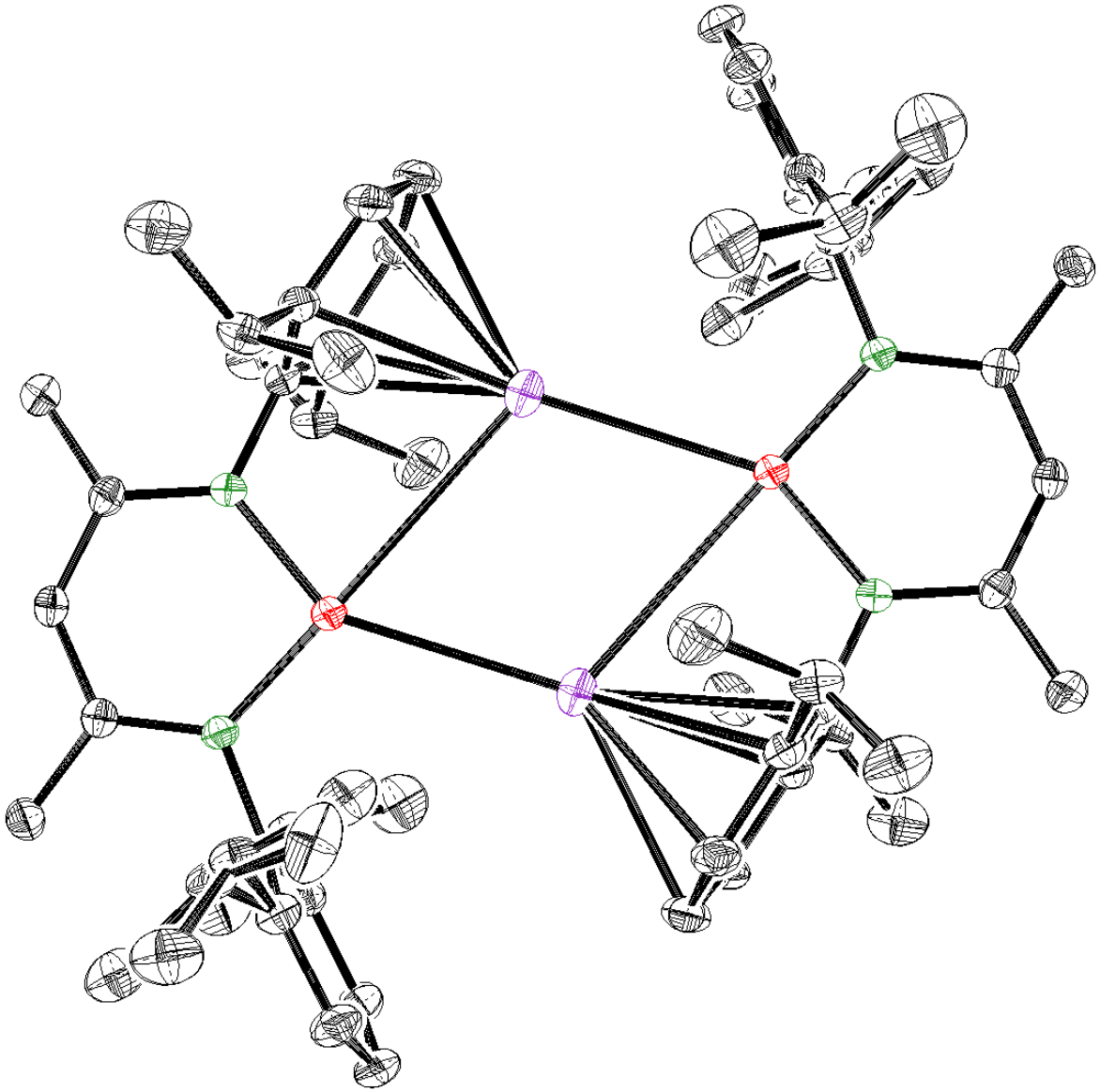


Figure S38: Ellipsoid plot of $[(BDI\text{-}H)Al^{-}Na^{+}]_2$ (50 % probability).

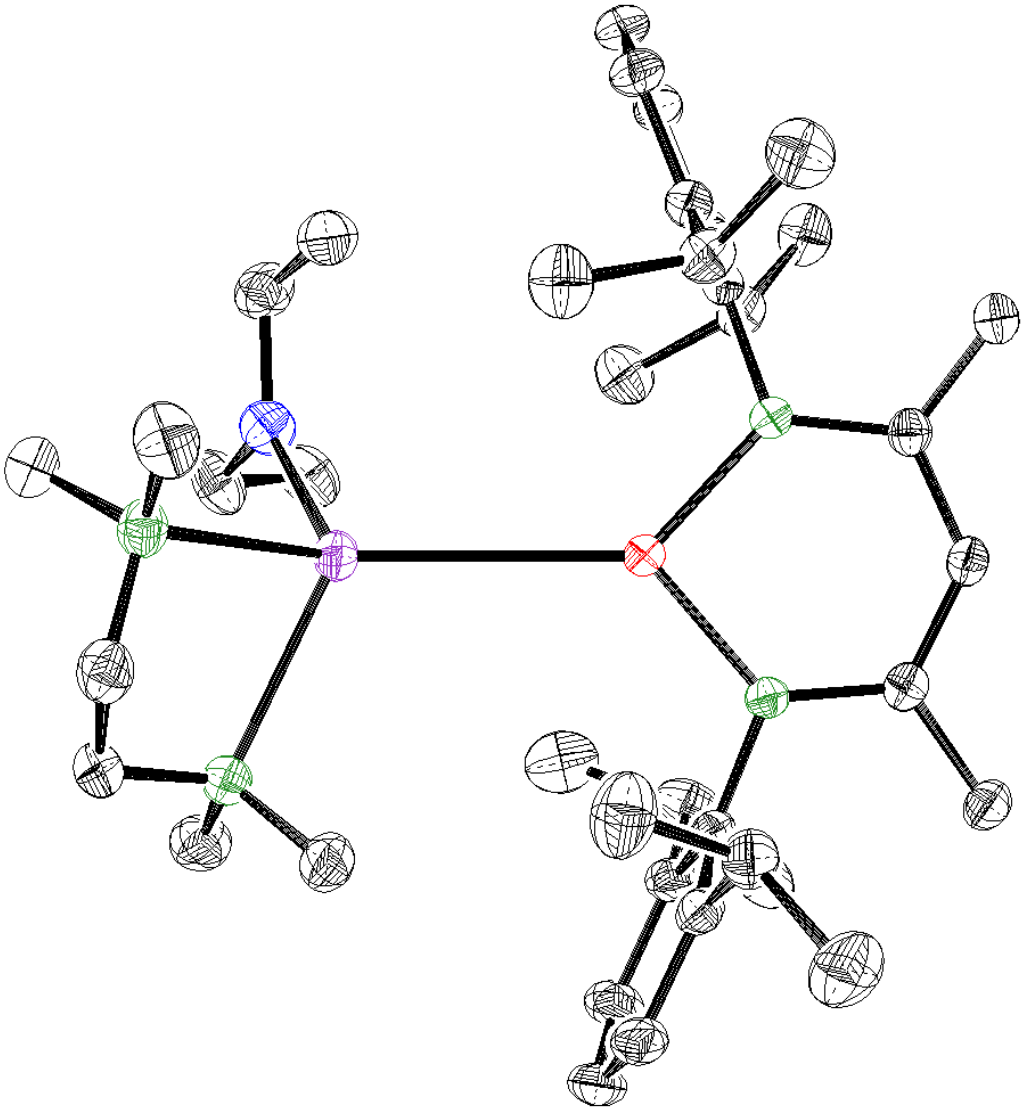


Figure S39: Ellipsoid plot of (BDI-H)$Al^{-}Na^{+}(Et_2O$, TMEDA) (50 % probability).

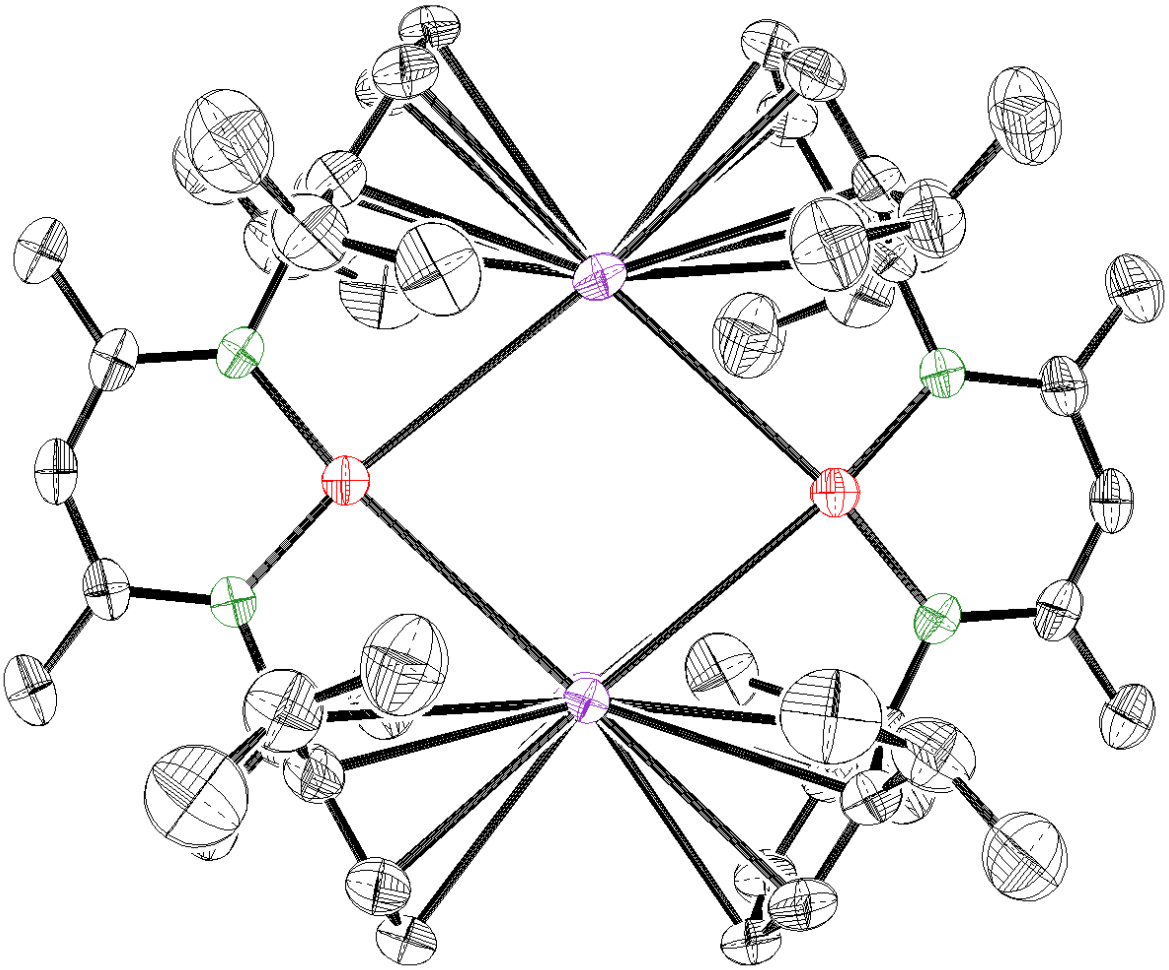


Figure S40: Ellipsoid plot of $[(BDI\text{-}H)Al^{-}Rb^{+}]_2$ (50 % probability).

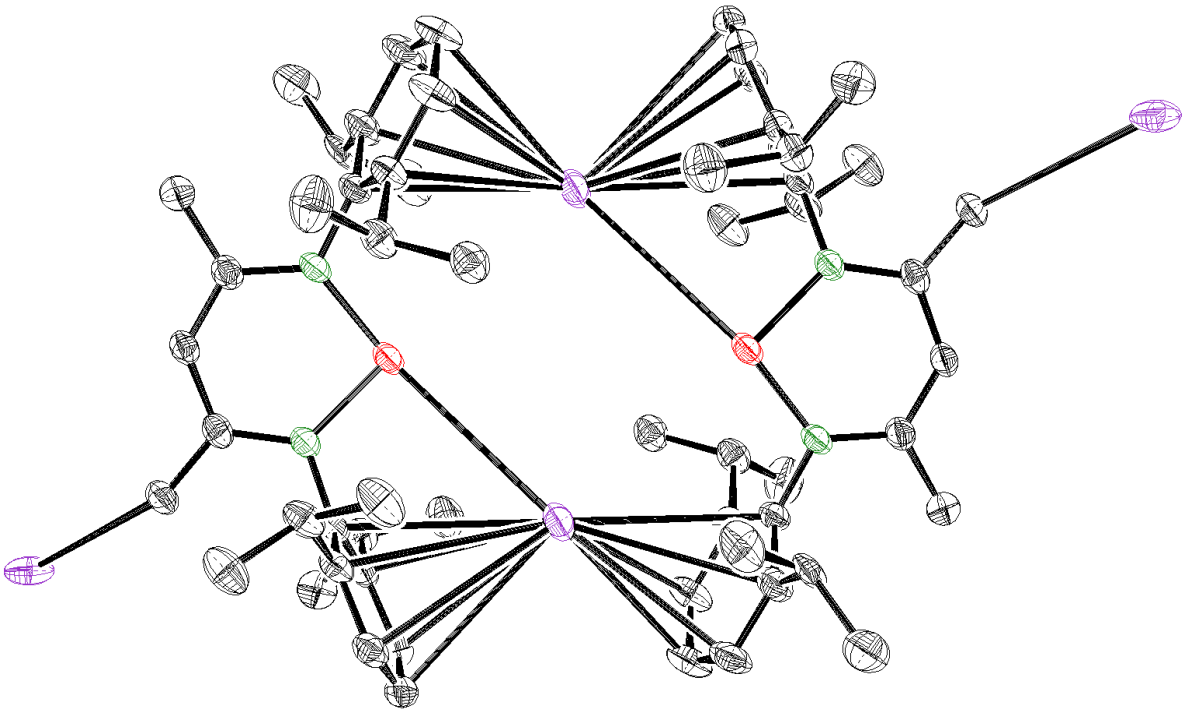


Figure S41: Ellipsoid plot of $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ (50 % probability).

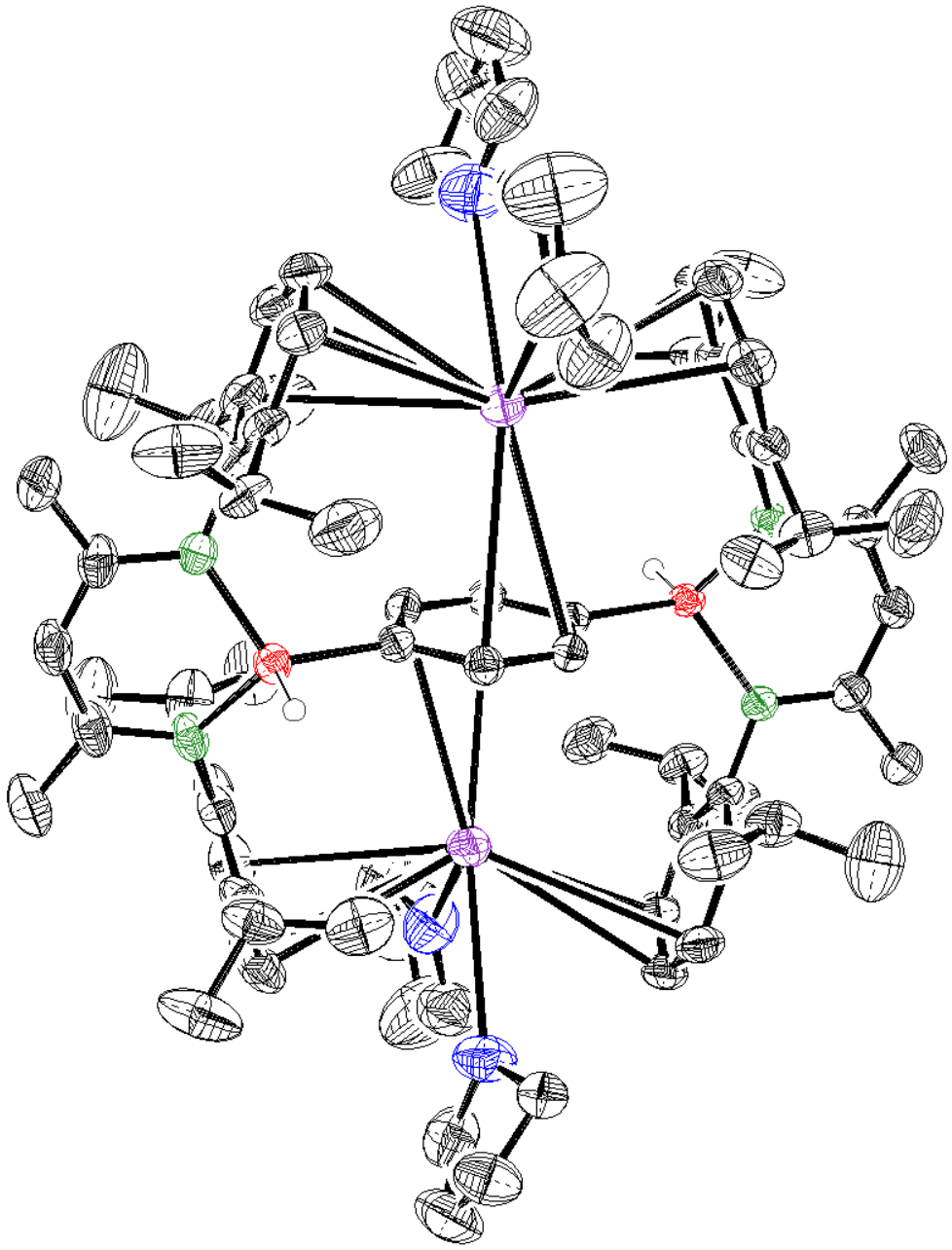


Figure S42: Ellipsoid plot of $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^+\cdot(THF)_2]_2$ (50 % probability).

4. References

S1 C. Cui, H. W. Roesky, H-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.*, 2000, **39**, 4274; *Angew. Chem.*, 2000, **112**, 4444.

S2 G. Wittig, P. Raff, *Justus Liebigs Ann. Chem.*, 1951, **573**, 195.

S3 Sebastian Bachmann, Roman Neufeld, Martin Dzemski, and Dietmar Stalke, *Chem. Eur. J.,* 2016, **22**, 8462-8465

S4 Roman Neufeld and Dietmar Stalke, *Chem. Sci.,* 2015, **6**, 3354-3364

S5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Rev. A.03, Wallingford CT, 2016.

S6 a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; b) J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B, 1992, **46**, 6671 - 6687; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297-305; d) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.

S7 A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B, 2009, **113**, 6378-6396.

S8 S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.,* 2011, **32**, 1456 – 1465.

S9 A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys*., 1985, **83**, 735–746.

S10 N. van Eikema Hommes, Molecule, Erlangen, 2018.

S11 a) R. F. W. Bader, *Chem. Rev*., 1991, **91**, 893-928; b) T. A. Keith, *AIMAll (Version 17.01.25)*, TK Gristmill Software, Overland Park KS USA, 2017.

S12 a) Rigaku Oxford Diffraction, 2019, CrysAlisPro Software system, version 1.171.40.67a, Rigaku Corporation, Oxford, UK (compounds $[(BDI\text{-}H)Al^{-}Cs^{+}]_2$ and $\{[(BDI\text{-}H)AlH]_2(C_6H_4)\}^{2-}[Cs^{+}\cdot(THF)_2]_2$); b) Rigaku Oxford Diffraction, 2020, CrysAlisPro Software system, version 1.171.40.84a, Rigaku Corporation, Oxford, UK (compounds $[(BDI\text{-}H)Al^{-}Li^{+}]_2$ and $(BDI\text{-}H)Al^{-}Li^{+}(Et_2O)_2$); c) Rigaku Oxford

Diffraction, 2021, CrysAlisPro Software system, version 1.171.41.113a, Rigaku Corporation, Oxford, UK (compounds $[(BDI\text{-}H)Al^{-}Na^{+}]_2$, $(BDI\text{-}H)Al^{-}Na^{+}(Et_2O$, TMEDA) and $[(BDI\text{-}H)Al^{-}Rb^{+}]_2$).

S13 O. V. Dolomanov, L. J. Bourhis, R.J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

S14 G. M. Sheldrick, *Acta Cryst. A,* 2015, **71**, 3–8.

S15 G. M. Sheldrick, *Acta Cryst. C,* 2015, **71**, 3–8.

S16 A. Thorn, B. Dittrich and G. M. Sheldrick, *Acta Cryst. A,* 2012, **68**, 448–451.