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Electronic Supplementary Information for:

Normal and *abnormal* NHC coordination in cationic hydride iodide complexes of aluminium

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1. Experimental Section

General considerations

All reactions were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk-line and glovebox techniques. All solvents were dried and degassed prior to use. IDip,[1] IMes,[1] [(IMes)AlH_3] **1**,[2] [(IDip)AlH_3] **2**,[3] [(IDip)AlI_3] **3**,[4] [(IMes)AlI_3] **6**[4] were synthesised according to reported procedures. All other reagents were purchased and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker Advance 400 Ultrashield or on a Bruker Advance 500 Ultrashield spectrometer using the residual solvent peak (C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm). HMBC NMR spectra were recorded to aid the assignment of resonances. IR (ATR) measurements were performed on a Shimadzu IRAffinity-1S spectrometer. Mass spectrometry experiments were carried out at the EPSRC UK National Mass Spectrometry Facility (NMSF) at Swansea University. Melting points were determined in sealed glass capillaries under inert gas and are uncorrected. Elemental analyses were performed at the Science Centre, London Metropolitan University 166-220, Holloway Road, London, N7 8DB. Elemental analyses for NHCAl complexes with coordinated iodide ligands consistently showed low values for carbon. Consequently, solution state NMR spectra are included for new compounds if soluble.

1.1 General procedure for the synthesis of [(NHC)AlH_2I] 4 and 7

Toluene (≈ 5 mL) was added to a solid mixture of [(NHC)AlH_3] (2 equiv.) and [(NHC)AlI_3] (1 equiv.) and heated at 50 °C for the indicated time, then the solvent was evaporated affording the desired compound in good purity in essentially quantitative yield.

[(IDip)AlH_2I] 4: The reaction between [(IDip)AlH_3] **2** (100 mg, 0.238 mmol) and [(IDip)AlI_3] **3** (95 mg, 0.119 mmol) for 24 h afforded 194 mg of **4** (quantitative yield) as a colourless solid. ^1H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 7.23 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $C_{Ar}H$), 7.08 (d, $^3J_{HH}$ = 7.7 Hz, 4H, $C_{Ar}H$), 6.44 (s, 2H, H^4 and H^5 carbene), 3.8 (vbr, 2H, Al-H), 2.68 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ (ppm) = 169.6 (C^2 carbene), 146.2 (C_{Ar}), 134.7 (C_{Ar}), 131.8 (C_{Ar}), 125.2 (C_{Ar}), 125.0 (C^4 and C^5 carbene), 29.7 (s, $CH(CH_3)_2$), 26.2 (s, $CH(CH_3)_2$), 23.8 (s, $(CH(CH_3)_2)$. Melting point: 220-222 °C (dec.). IR: 1807 cm^{-1} (m, Al-H), with shoulder at *ca.* 1830 cm^{-1} (Al-H).

[(IMes)AlH_2I] 7: The reaction between [(IMes)AlH_3] **1** (100 mg, 0.299 mmol) and [(IMes)AlI_3] **6** (106.4 mg, 0.15 mmol) for 5 h afforded 206 mg of **7** (quantitative yield) as a colourless solid. ^1H

NMR (500 MHz, C_6D_6, 298 K): δ (ppm) = 6.71 (s, 4H, $C_{Ar}H$), 5.93 (s, 2H, H^4 and H^5 carbene), 3.87 (vbr, 2H, Al-H), 2.03 (s, br, 18H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ (ppm) = 166.3 (C^2 carbene), 139.8 (C_{Ar}), 134.6 (C_{Ar}), 133.9 (C_{Ar}), 129.3 (C_{Ar}), 122.8 (C^4 and C^5 carbene), 20.7 (CH_3), 17.8 (CH_3). Melting point: 196-198 °C (dec.). IR: 1846 cm^{-1} (m, Al-H), 1802 cm^{-1} (m, Al-H).

1.2 General procedure for the synthesis of [(NHC)AlHI$_2$] 5 and 8

[(NHC)AlH$_3$] (1 equiv.) was added into a Schlenk flask and toluene (≈ 5 mL) was added. The mixture was cooled to 0 °C and MeI (5 equiv.) was added dropwise using a syringe. The cold bath was removed and the reaction was stirred for the indicated time. The toluene was evaporated to afford the desired compound.

[(IDip)AlHI$_2$] 5: The reaction between [(IDip)AlH$_3$] **2** (250 mg, 0.597 mmol) and MeI (180 μL, 2.98 mmol) for 37 h afforded 310 mg of **5** (88%) as a colourless solid. ^1H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 7.22 (t, $^3J_{HH}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.07 (d, $^3J_{HH}$ = 7.8 Hz, 4H, $C_{Ar}H$), 6.42 (s, 2H, H^4 and H^5 carbene), 2.72 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $C\mathit{H}(CH_3)_2$), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$), 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$). Note: Al-*H* too broad. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ (ppm) = 145.4 (C_{Ar}), 133.4 (C_{Ar}), 131.3 (C_{Ar}), 125.0 (C_{Ar}), 124.4 (C^4 and C^5 carbene), 28.8 ($\mathit{C}H(CH_3)_2$), 25.7 ($CH(\mathit{C}H_3)_2$), 22.8 ($CH(\mathit{C}H_3)_2$). Note: NHC-C^2 not observed. Melting point: 246-248 °C (dec.). IR: 1884 cm^{-1} (m, Al-H), 1869 cm^{-1} (m, Al-H).

[(IMes)AlHI$_2$] 8: The reaction between [(IMes)AlH$_3$] **1** (250 mg, 0.748 mmol) and MeI (250 μL, 4.13 mmol)) for 5 h afforded 390 mg of **8** (88%) as a colourless solid. ^1H NMR (500 MHz, C_6D_6, 298 K): δ (ppm) = 6.70 (s, 4H, $C_{Ar}H$), 5.86 (s, 2H, H^4 and H^5 carbene), 2.04 (s, br, 18H, CH_3). Note: Al-*H* too broad. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ (ppm) = 140.3 (C_{Ar}), 133.3 (C_{Ar}), 133.9 (C_{Ar}), 129.5 (C_{Ar}), 123.4 (C^4 and C^5 carbene), 20.8 (CH_3), 18.1 (CH_3). Note: NHC-C^2 not observed. Melting point: 202-204 °C (dec). IR: 1869 cm^{-1} (m, Al-H).

1.3 Synthesis of *normal-abnormal* NHC complexes 9 and 10

[(IDip)AlH$_2$(*a*IDip)]I 9: Toluene (≈ 5 mL) was added to a mixture of [(IDip)AlH$_2$I] **4** (100 mg, 0.183 mmol) and IDip (78 mg, 0.201 mmol) in a J-Young Schlenk flask. The reaction mixture was heated at 85 °C for 16 h, and the formed white precipitate was filtered off at 85 °C. Toluene (2.5 mL) was added and the mixture was further stirred at 85 °C for 15 min, after which the solid was filtered off at 85 °C and dried under vacuum to afford 80 mg of **9** (47%). Melting point: 258-260 °C (dec.). IR: 1827 cm^{-1} (m, Al-H), 1811 cm^{-1} (m, Al-H). MS (TOF ASAP$^+$ on solid): found *m*/*z* =

805.5731; $C_{54}H_{74}AlN_4$ ([(IDip)AlH$_2$(*a*IDip)]$^+$) requires 805.5729. Elemental analysis: found C, 69.05; H, 8.08; N, 5.93; $C_{54}H_{74}AlIN_4$ requires: C, 69.51; H, 7.99; N, 6.00.

[(IDip)AlHI(*a*IDip)]I 10: Toluene (≈ 5 mL) was added to a mixture of [(IDip)AlHI$_2$] **5** (200 mg, 0.298 mmol) and IDip (128 mg, 0.328 mmol) in a J-Young Schlenk flask. The reaction mixture was heated at 85 °C for 16 h, and the formed white crystalline precipitate was filtered off at 85 °C. Toluene (5 mL) was added and the mixture was further stirred at 85 °C for 15 minutes, after which the solid was filtered off at 85 °C to afford 175 mg of **10** (56%). Melting point: 276-278 °C (dec.). IR: 1867 cm^{-1} (m, Al-H). MS (TOF ASAP$^+$ on solid): no characteristic heavier ion found. Elemental analysis for this compound consistently showed values too low in carbon. IR spectra are consistent with the formulation of **10** and show no noticeable quantities of compounds **5** or **9**. Small quantities of the hydride-free by-product **11** can't be ruled out though.

Crystals of **9** and **10**·C_6H_6 were obtained from similar reactions carried out in benzene. In one instance, a crystal of [(IDip)AlIX(*a*IDip)]I·2 C_6H_6 (X ≈ 75% I, 25% H), **11**$_{\mathbf{0.75}}$·**10**$_{\mathbf{0.25}}$·2 C_6H_6, was also obtained from one experiment leading to **10**.

1.4 Variable temperature NMR experiment: Equilibrium between [(IDip)AlH$_3$] 2 and IDip

In order to study this equilibrium, variable temperature ^{1}H NMR spectroscopic experiments were performed on a 1:1 mixture of [(IDip)AlH$_3$] **3** and IDip (Figure S1). As described in the main text, a single set of resonances for the IDip ligands was detected from room temperature down to 263 K. Further cooling of the sample resulted in splitting of these resonances into those of [(IDip)AlH$_3$] **2** (blue squares) and IDip (red circles). A value of $\Delta G^{\#} \approx 12$ kcal/mol for this equilibrium was estimated by using equation 2, after calculating the rate constant (k_{Tc}) at the coalescence temperature ($T_c \approx$ 245-250 K).

$$k_{T_c} = 2.22 \cdot \Delta\nu \qquad \text{(equation 1)}$$

$$\Delta G^{\#} = 4.574 \cdot 10^{-3} \cdot T_c \cdot [\log (T_c/k_{T_c}) + 10.318] \qquad \text{(equation 2)}$$

(for a value in kcal/mol; or similar in kJ/mol)[5]

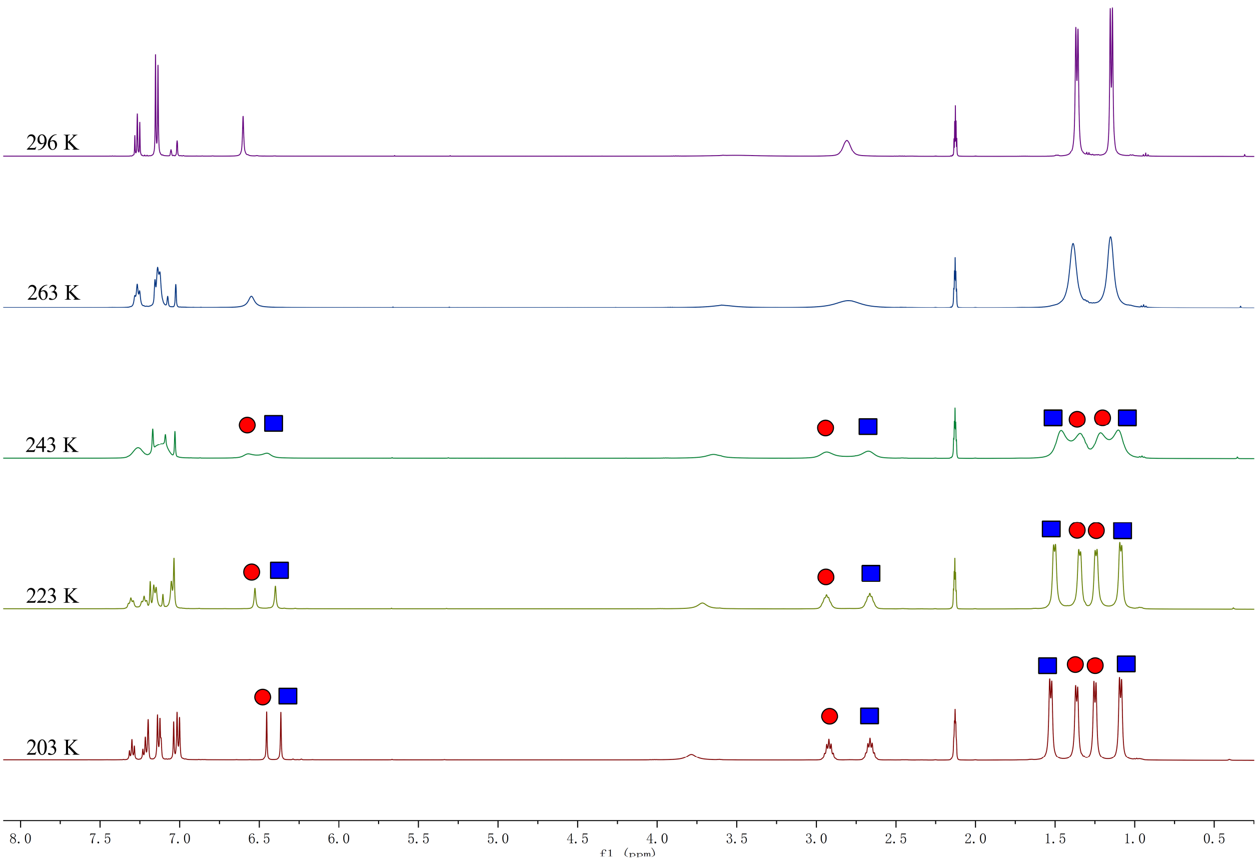


Figure S1. Variable temperature ^{1}H NMR spectra (500 MHz) of the mixture of [(IDip)AlH$_3$] **2** and IDip in toluene-*d8*. Assignment: [(IDip)AlH$_3$] **2** (blue squares); IDip (red circles).

1.5 Reaction between [(IMes)AlH$_3$] 1 and IMes

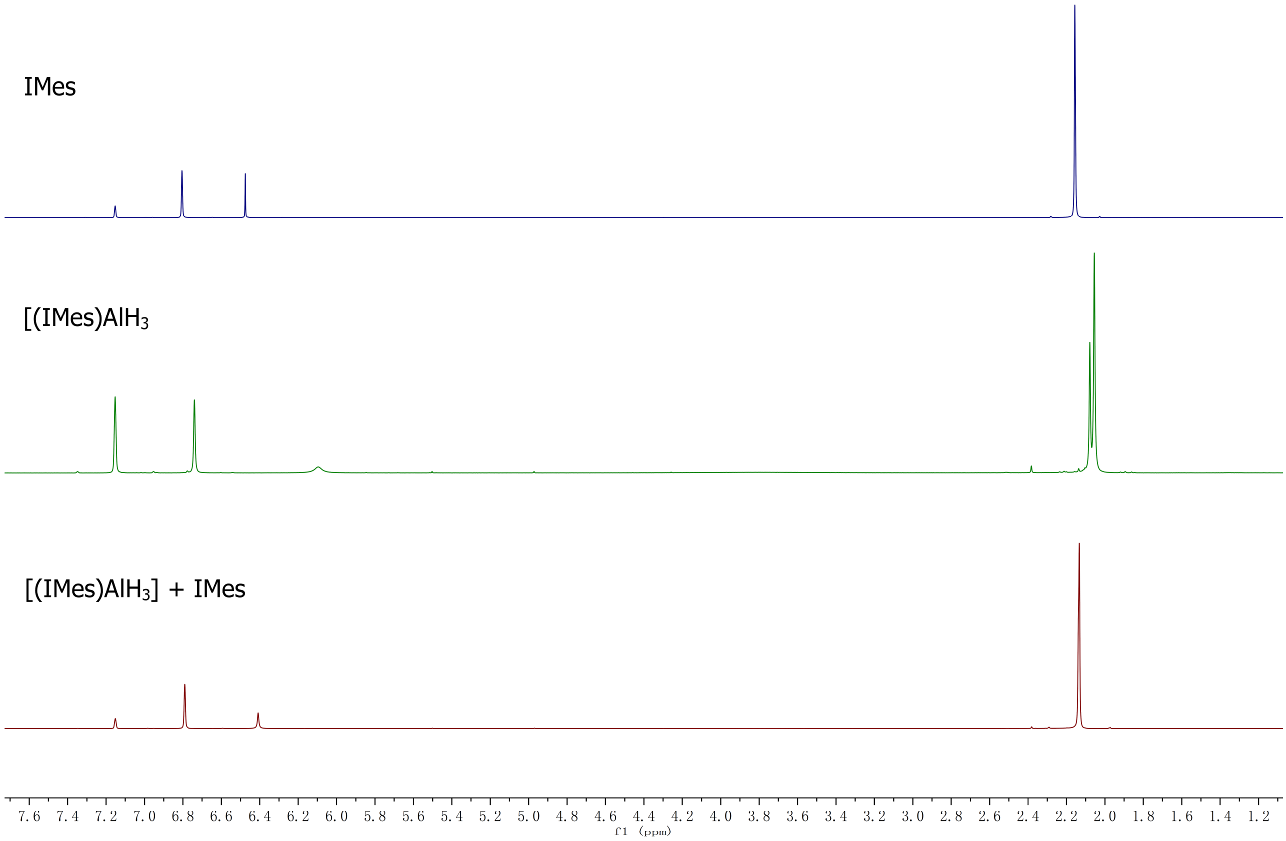


Figure S2. ^{1}H NMR spectra (400 MHz, C_6D_6 at 25 °C) of IMes (top), [(IMes)AlH$_3$] **1** (middle) and [(IMes)AlH$_3$] **1** plus IMes (bottom).

1.6 Reaction between [(IDip)AlI$_3$] and IDip

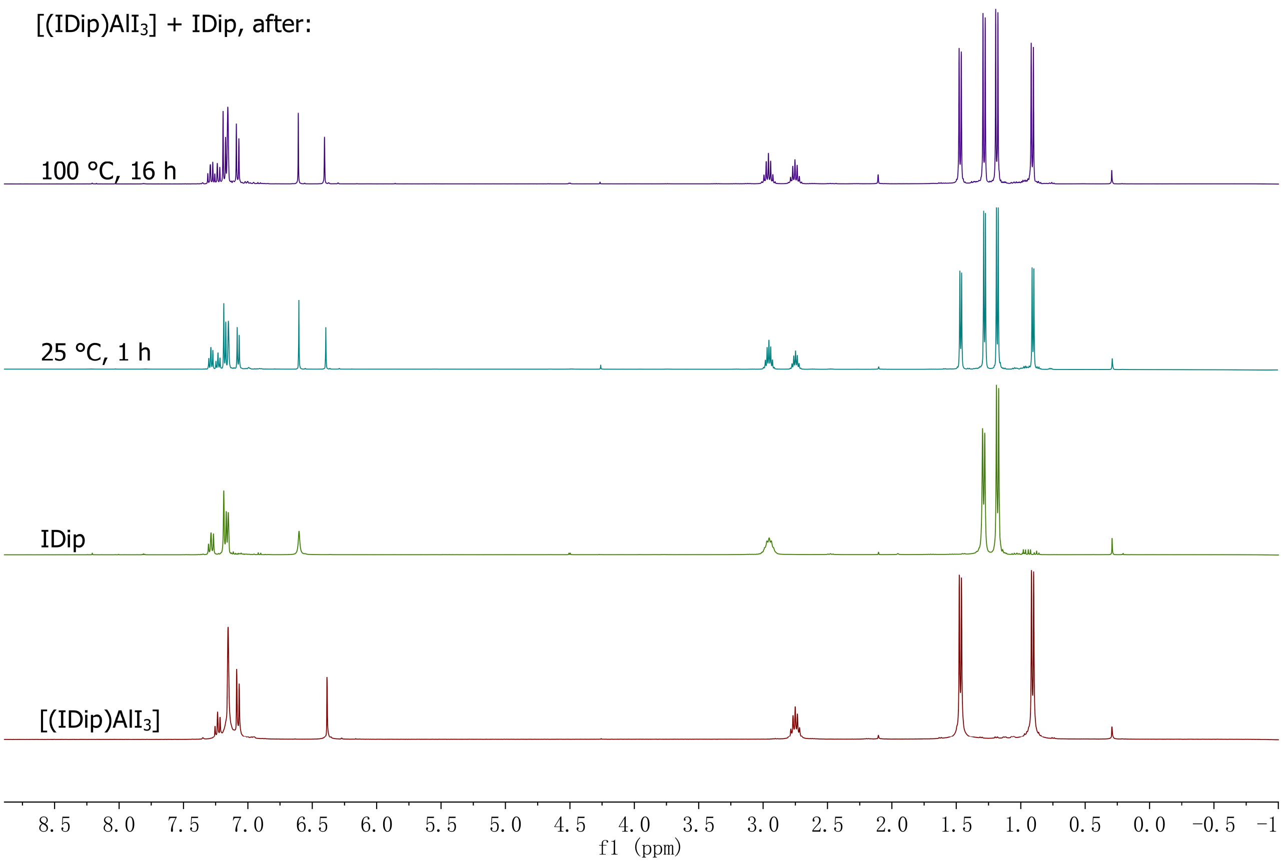
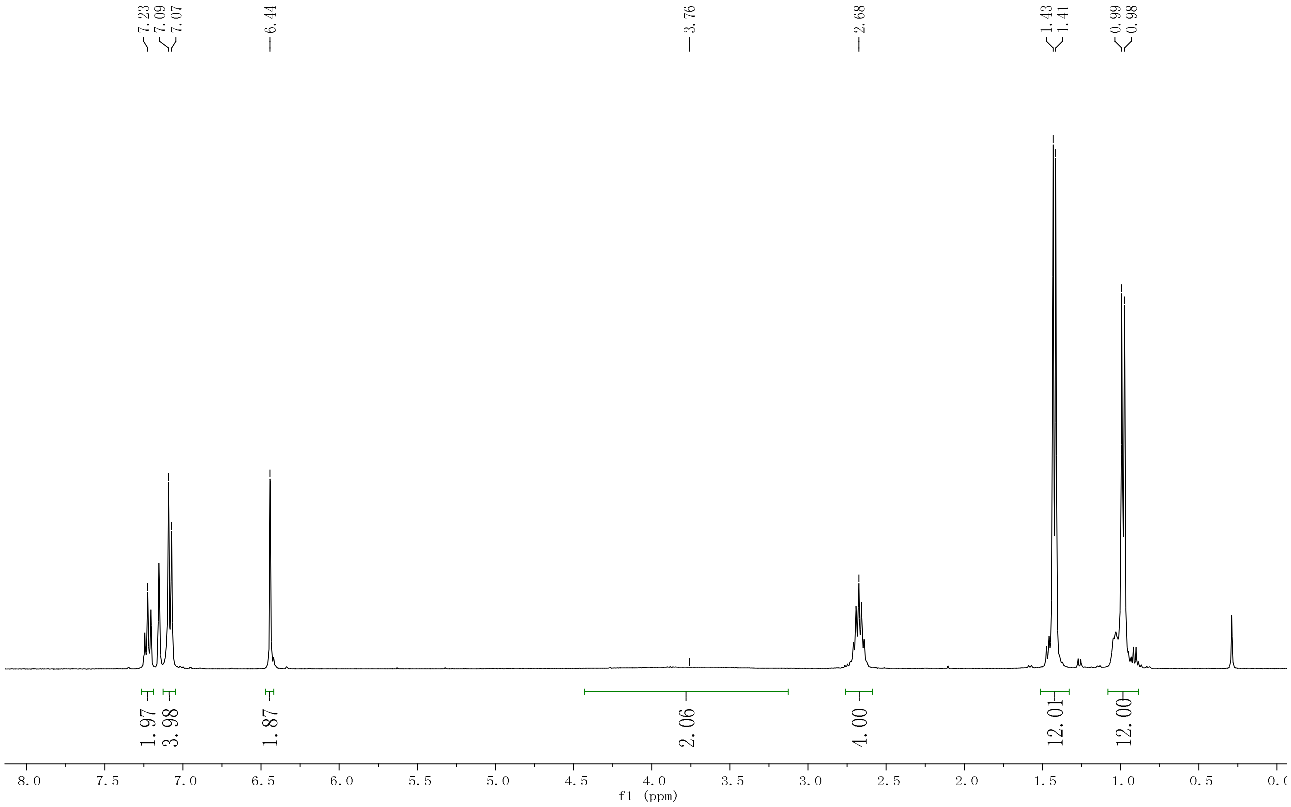


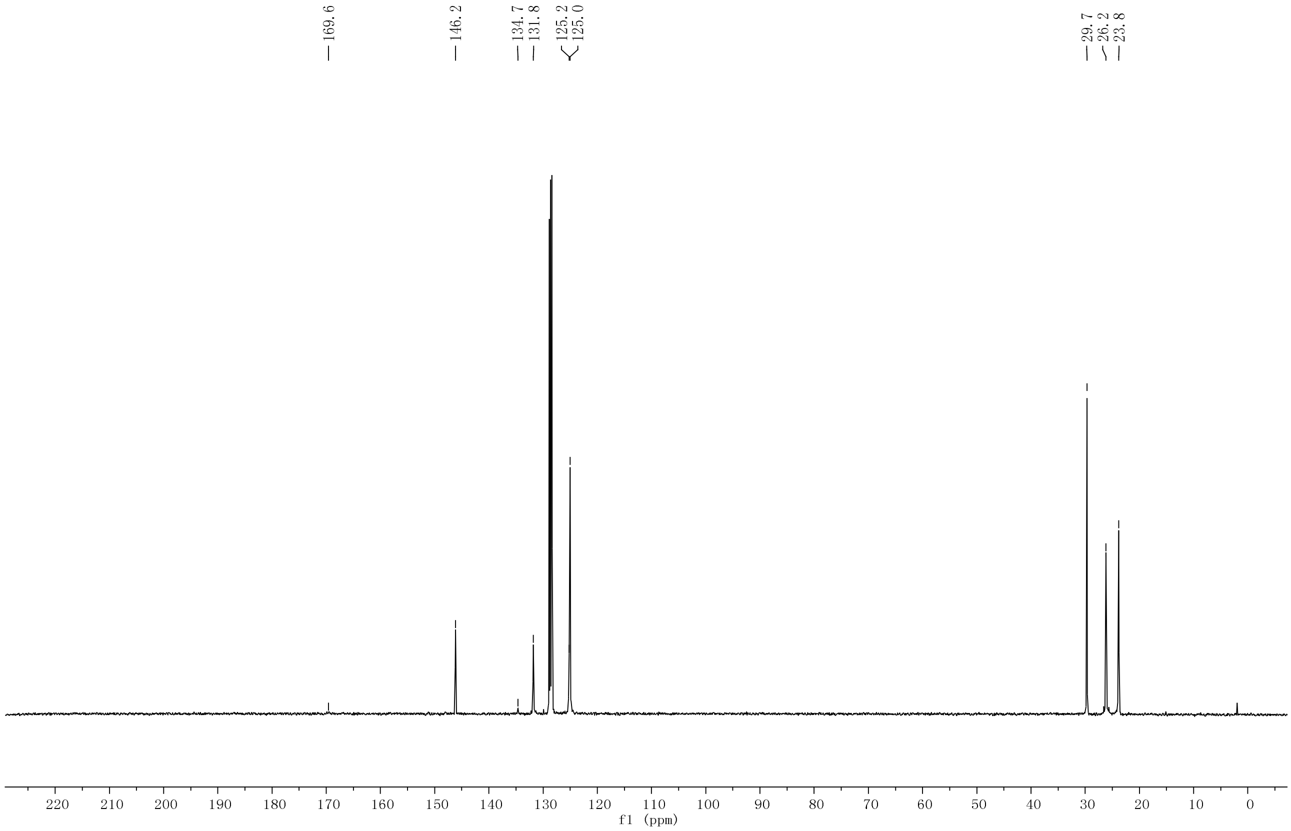
Figure S3. ^{1}H NMR spectra (400 MHz for first spectrum, 500 MHz for second spectrum) of the mixture of [(IDip)AlI$_3$] **3** and IDip in C_6D_6 after heating and after addition; plus [(IDip)AlI$_3$] **3** (400 MHz) and IDip (400 MHz) alone.

2. NMR and IR spectra

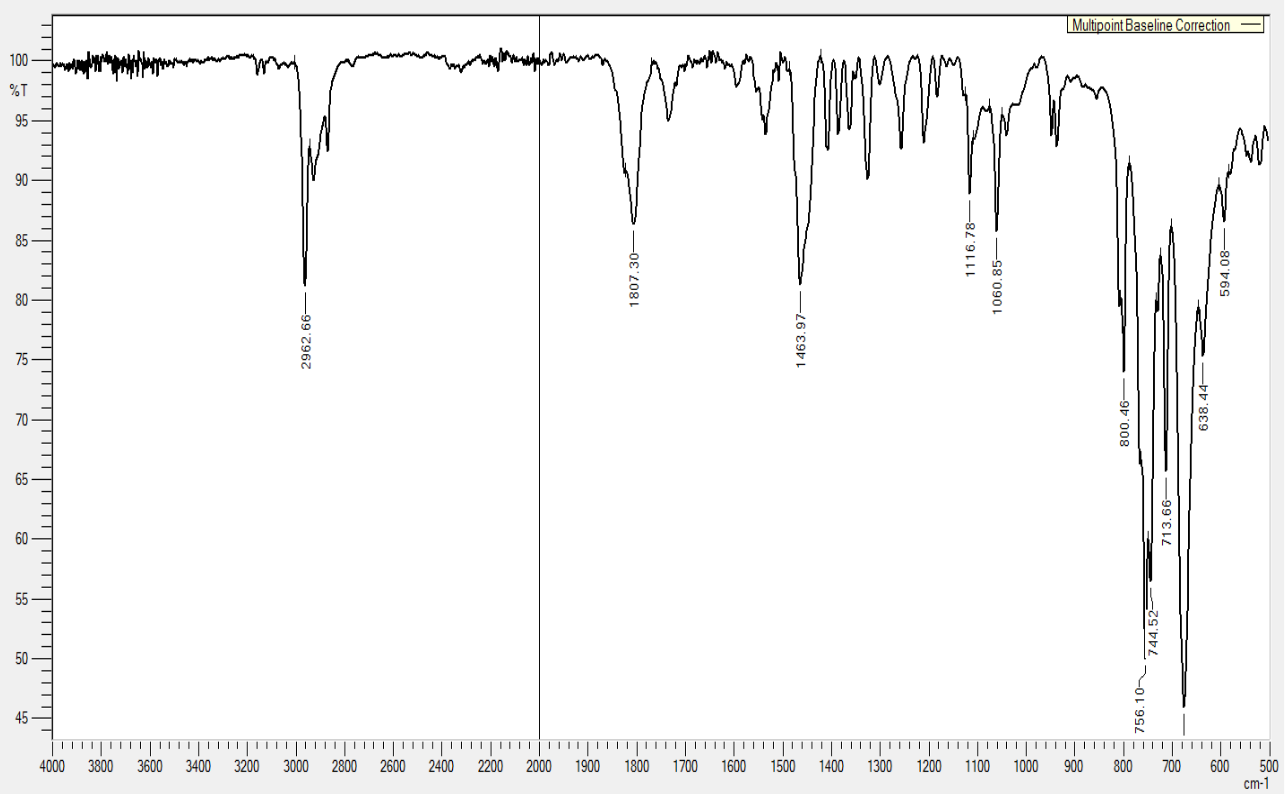
^{1}H NMR spectrum (400 MHz, C_6D_6, 298K) of [(IDip)AlH$_2$I], **4**



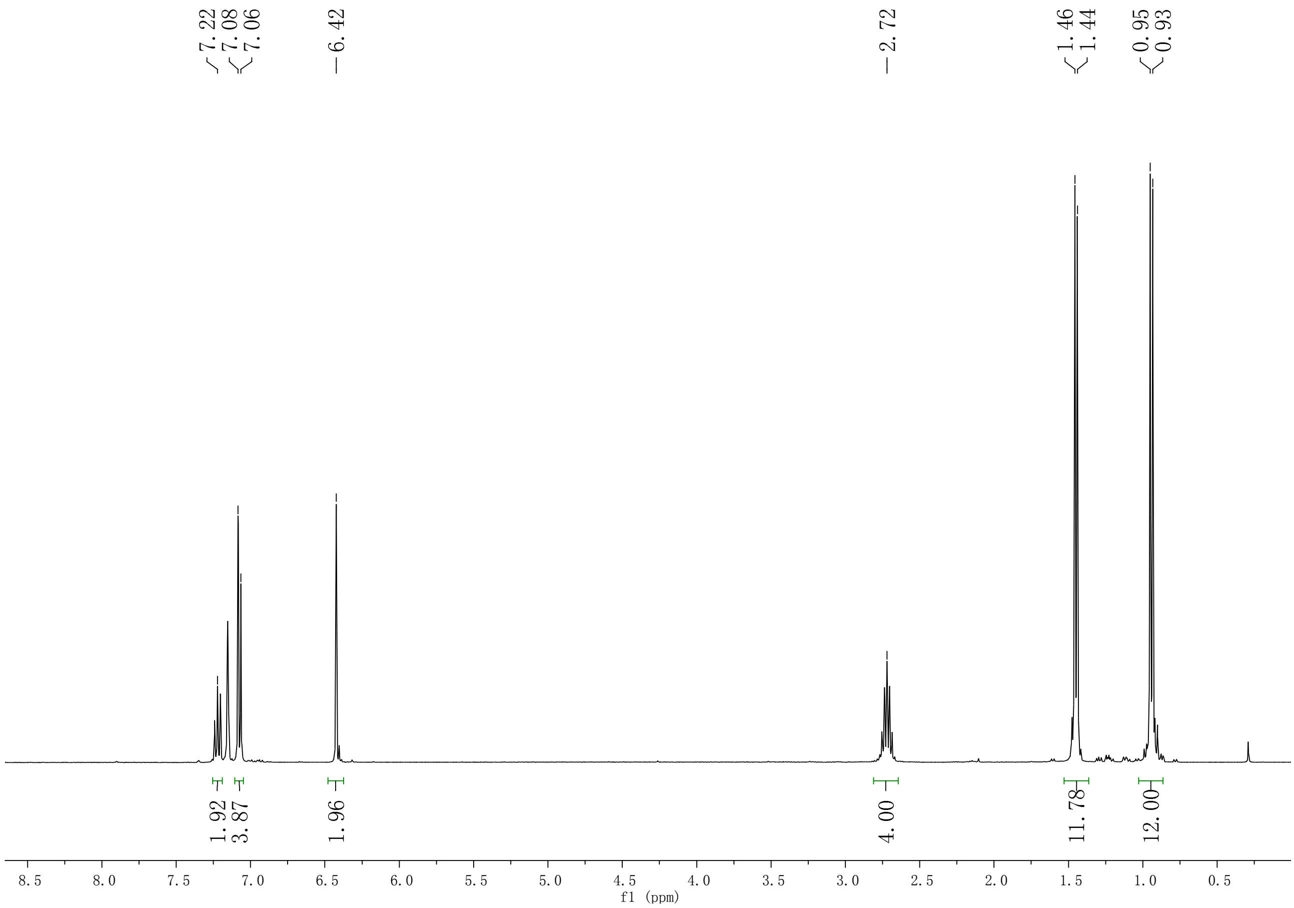
^{13}C{^{1}H} NMR spectrum (75 MHz, C_6D_6, 298K) of [(IDip)AlH$_2$I], **4**



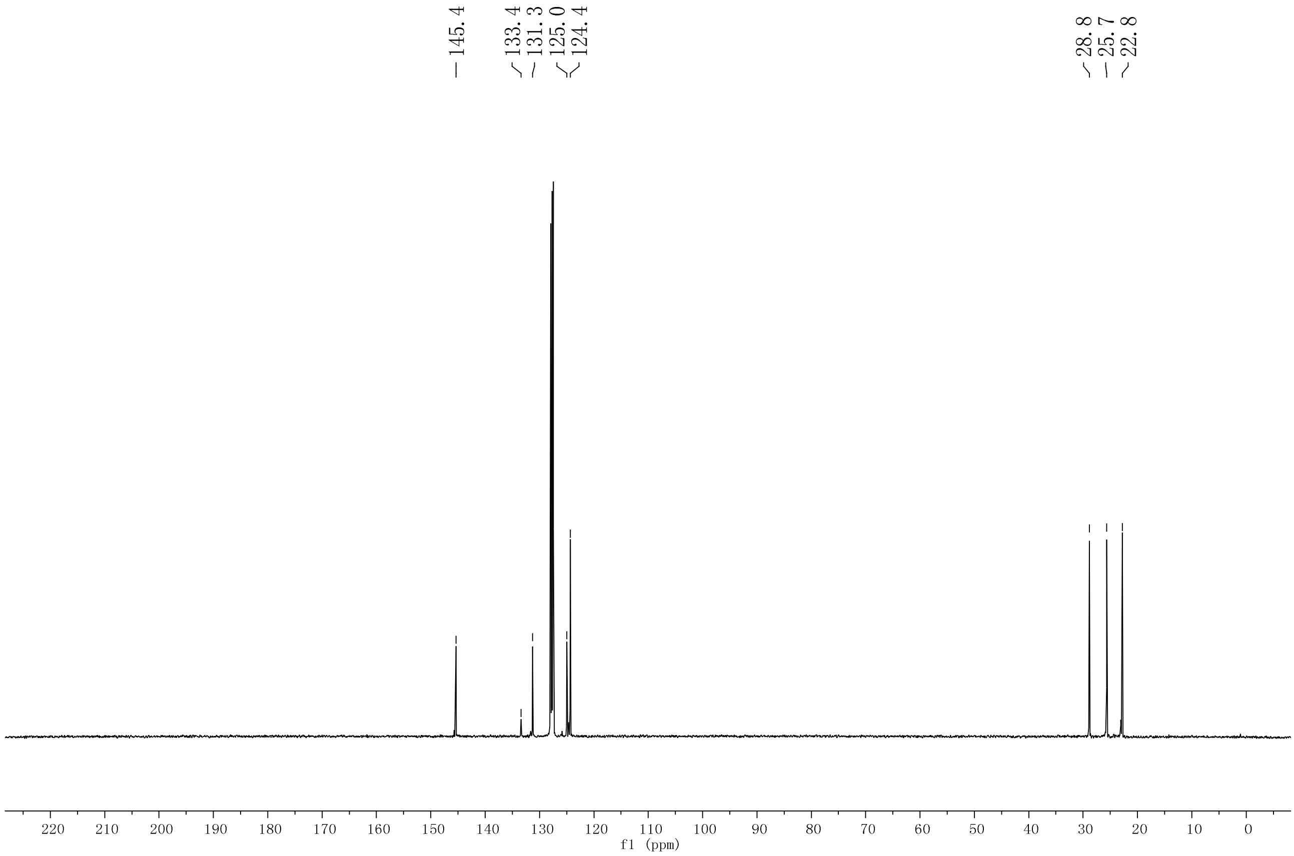
IR spectrum of [(IDip)AlH_2I], **4**



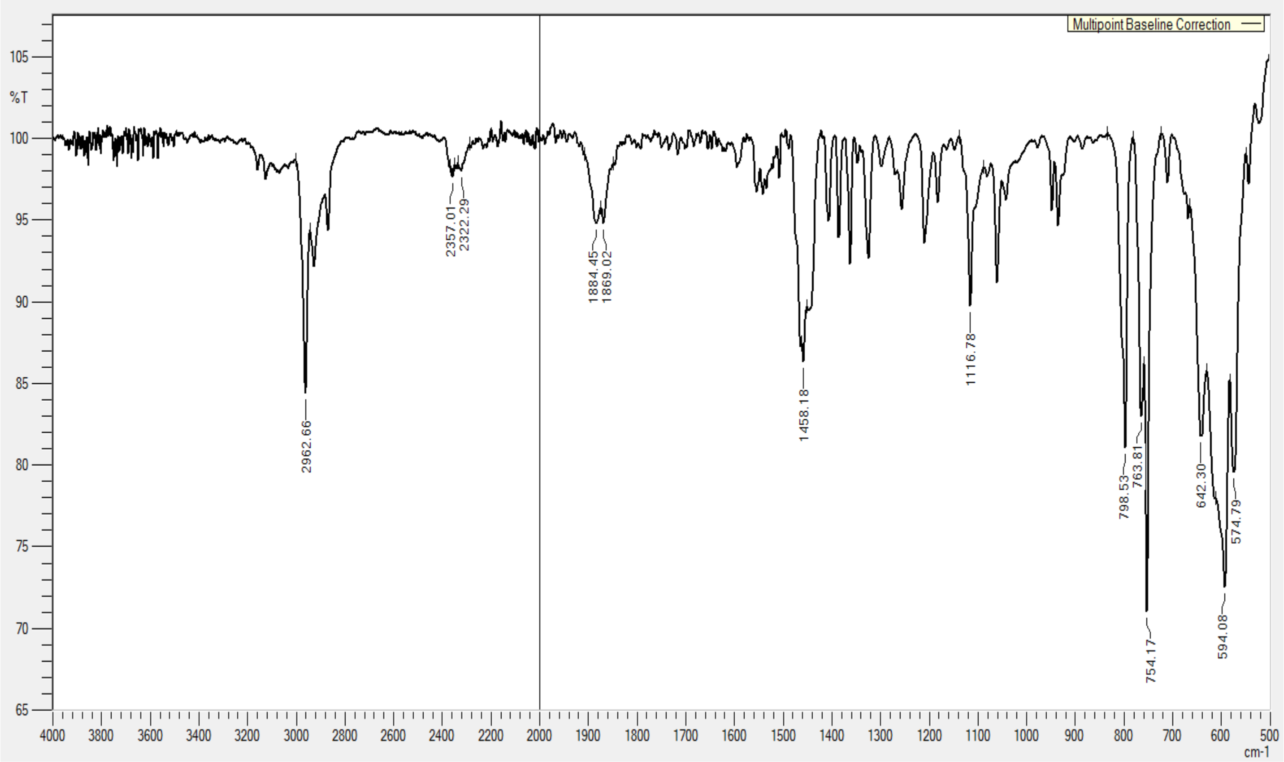
^{1}H NMR (400 MHz, C_6D_6, 298K) spectrum of [(IDip)AlHI$_2$], **5**



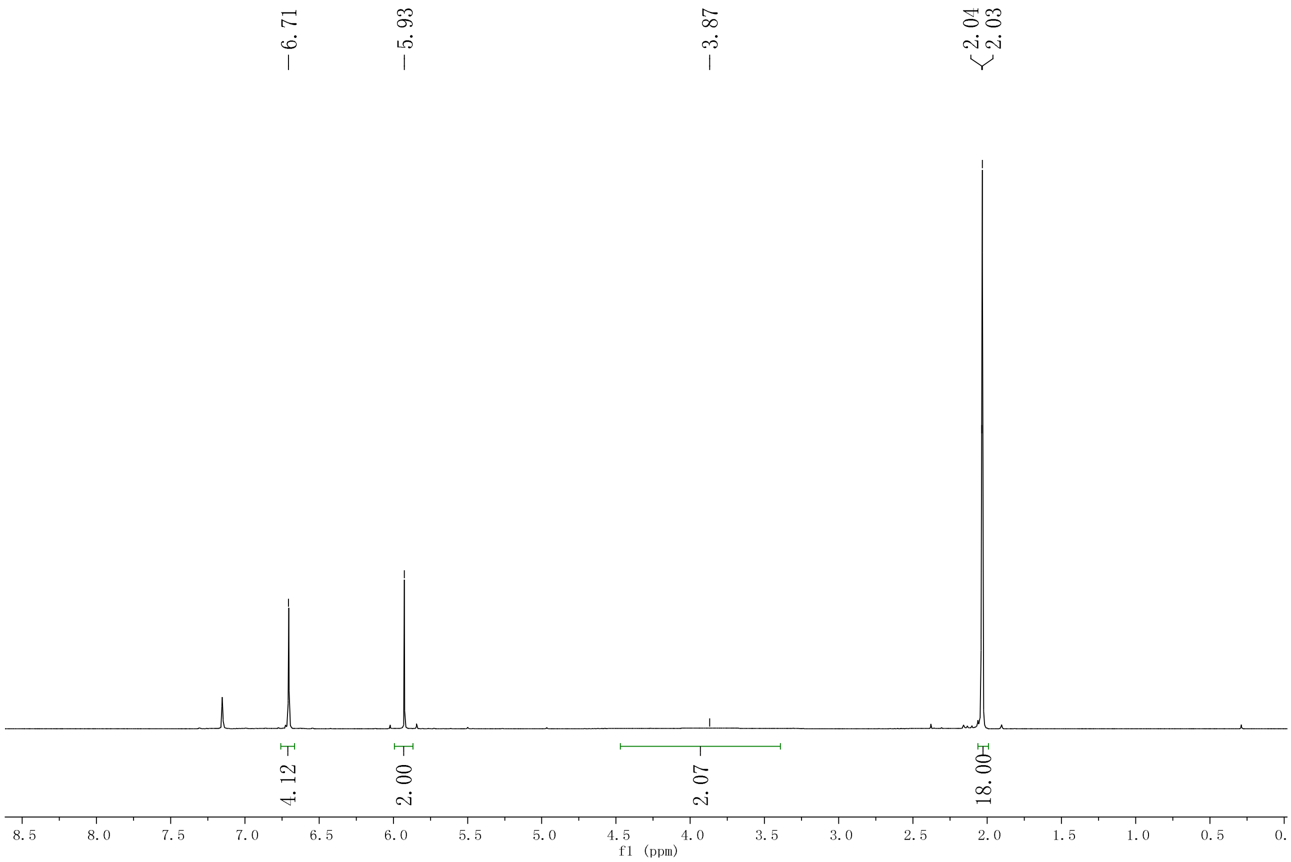
$^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, 298K) spectrum of [(IDip)AlHI$_2$], **5**



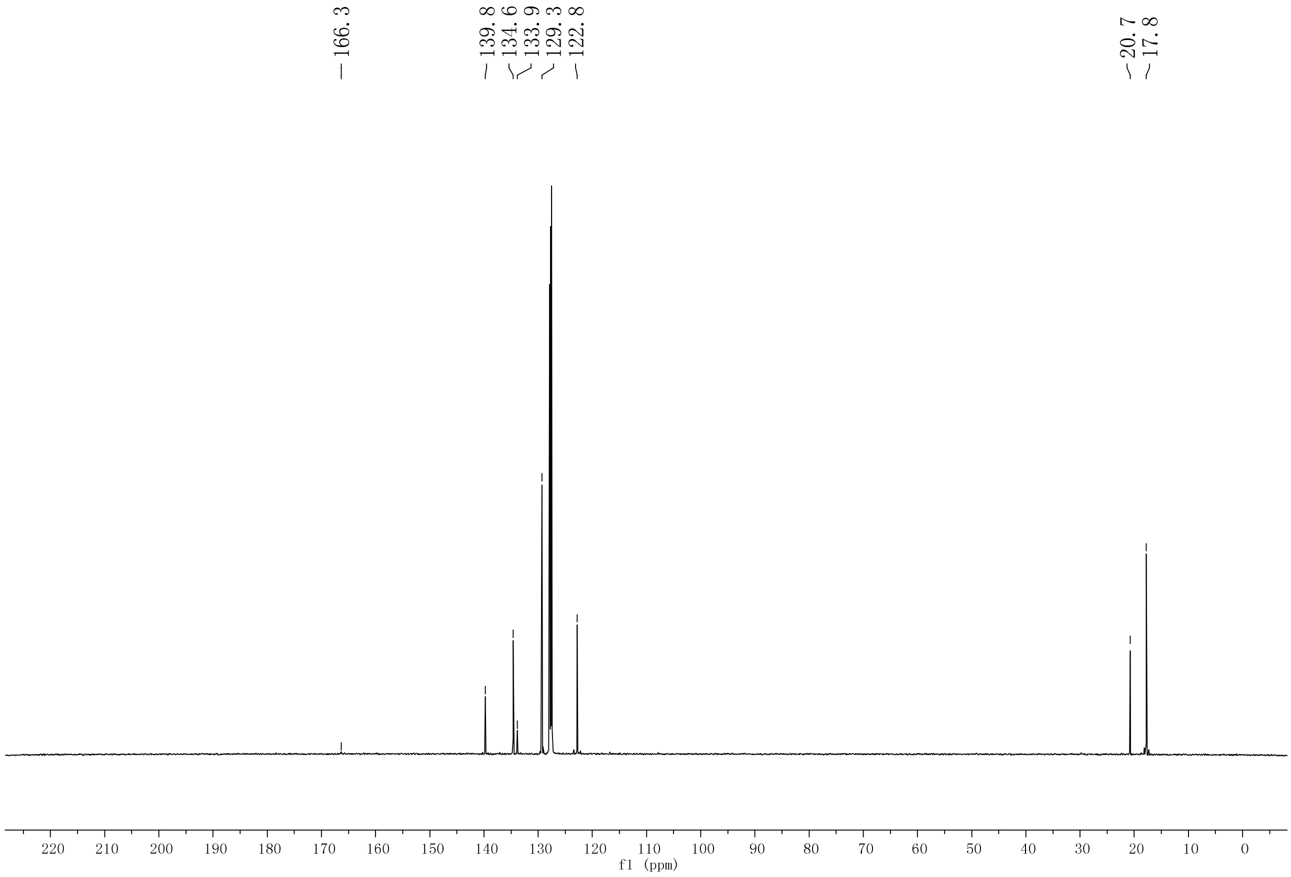
IR spectrum of [(IDip)AlHI$_2$], **5**



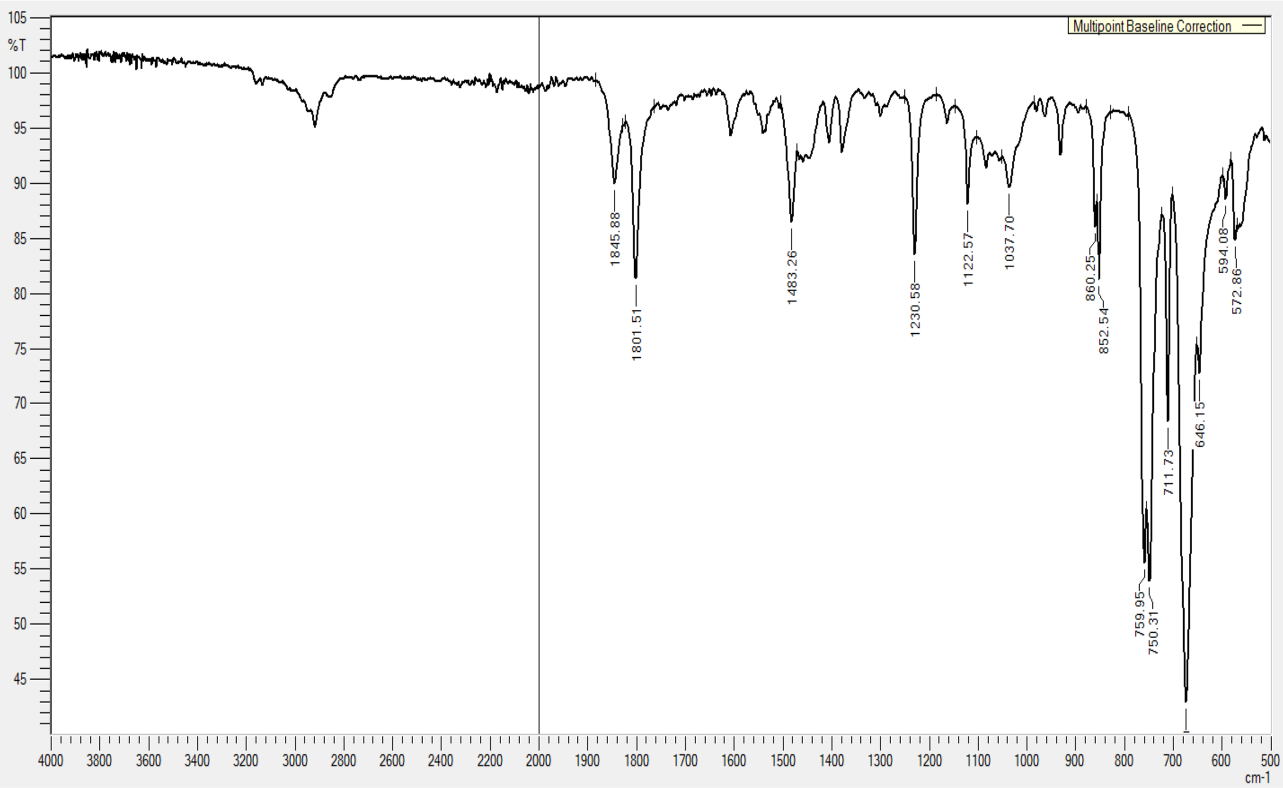
^{1}H NMR spectrum (500 MHz, C_6D_6, 298K) of [(IMes)AlH_2I], **7**



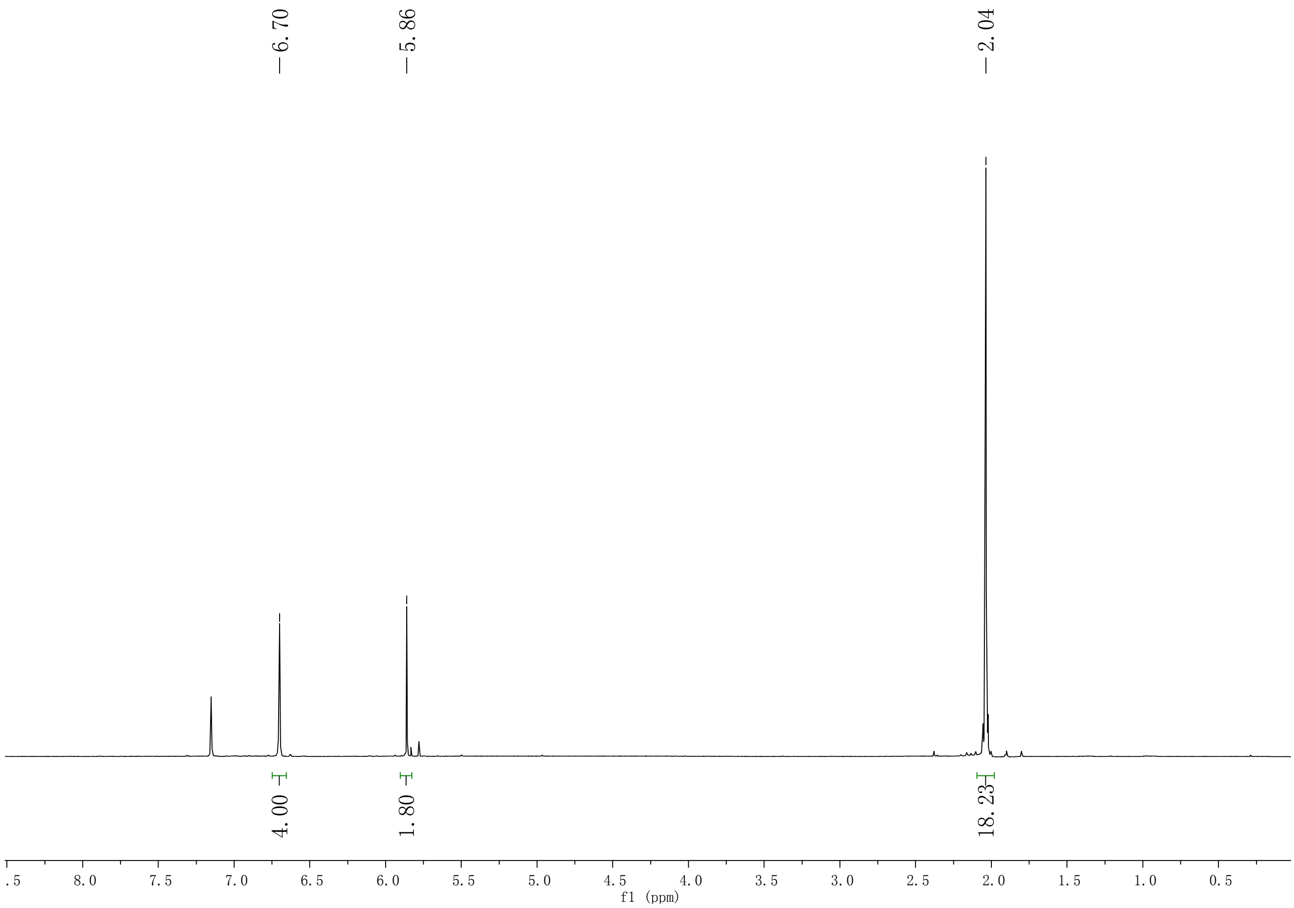
^{13}C{^{1}H} NMR spectrum (126 MHz, C_6D_6, 298K) of [(IMes)AlH_2I], **7**



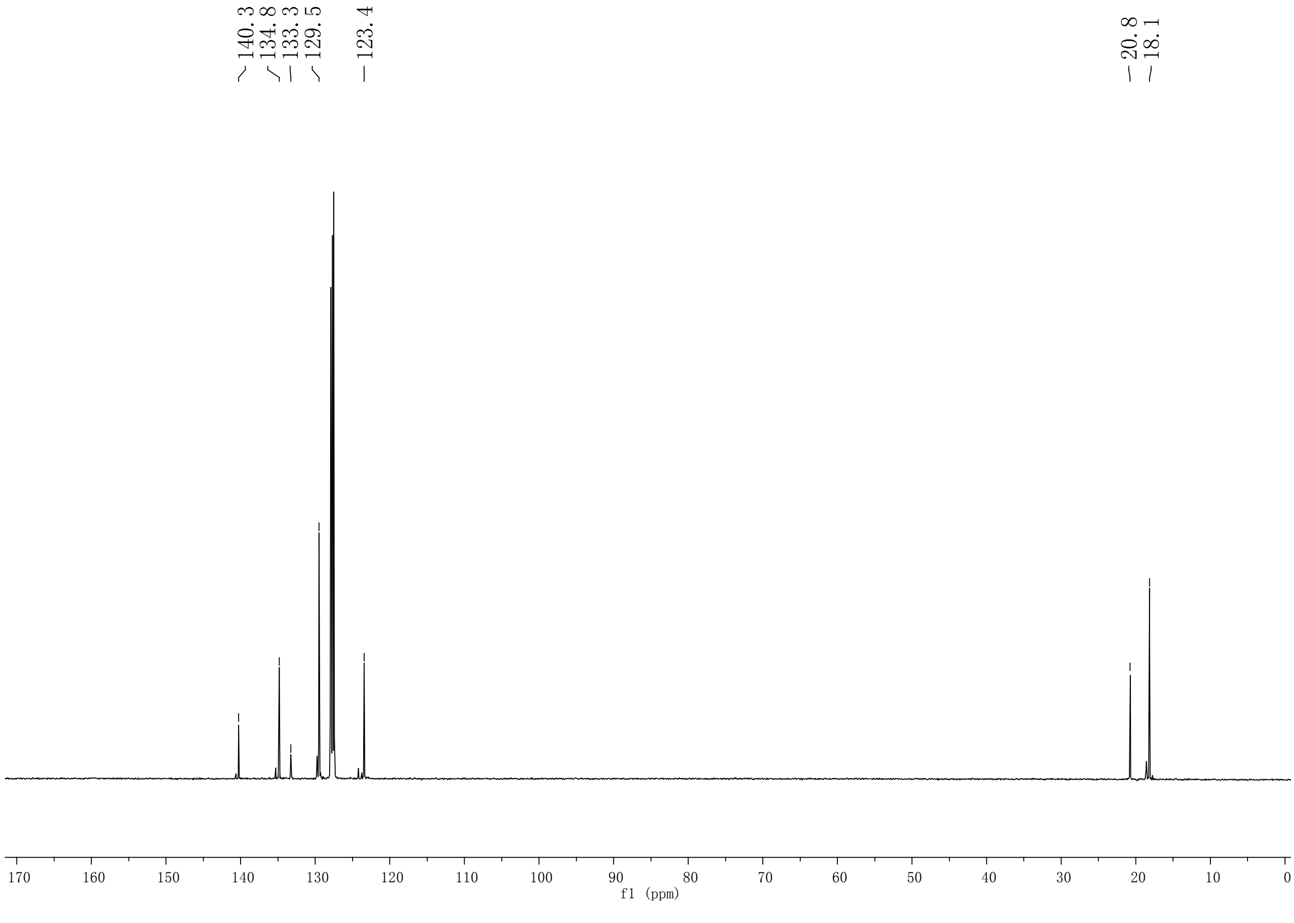
IR spectrum of [(IMes)AlH$_2$I], **7**



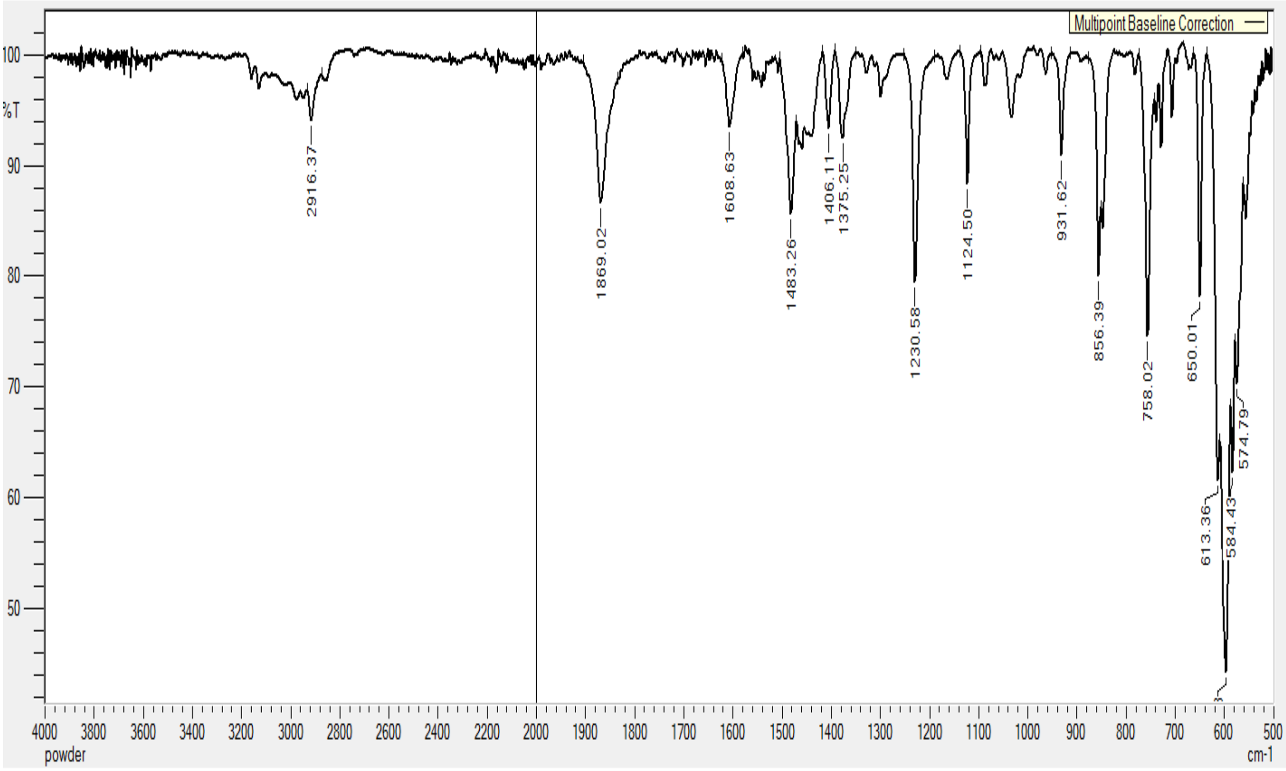
^{1}H NMR spectrum (500 MHz, C_6D_6, 298K of [(IMes)$AlHI_2$], **8**



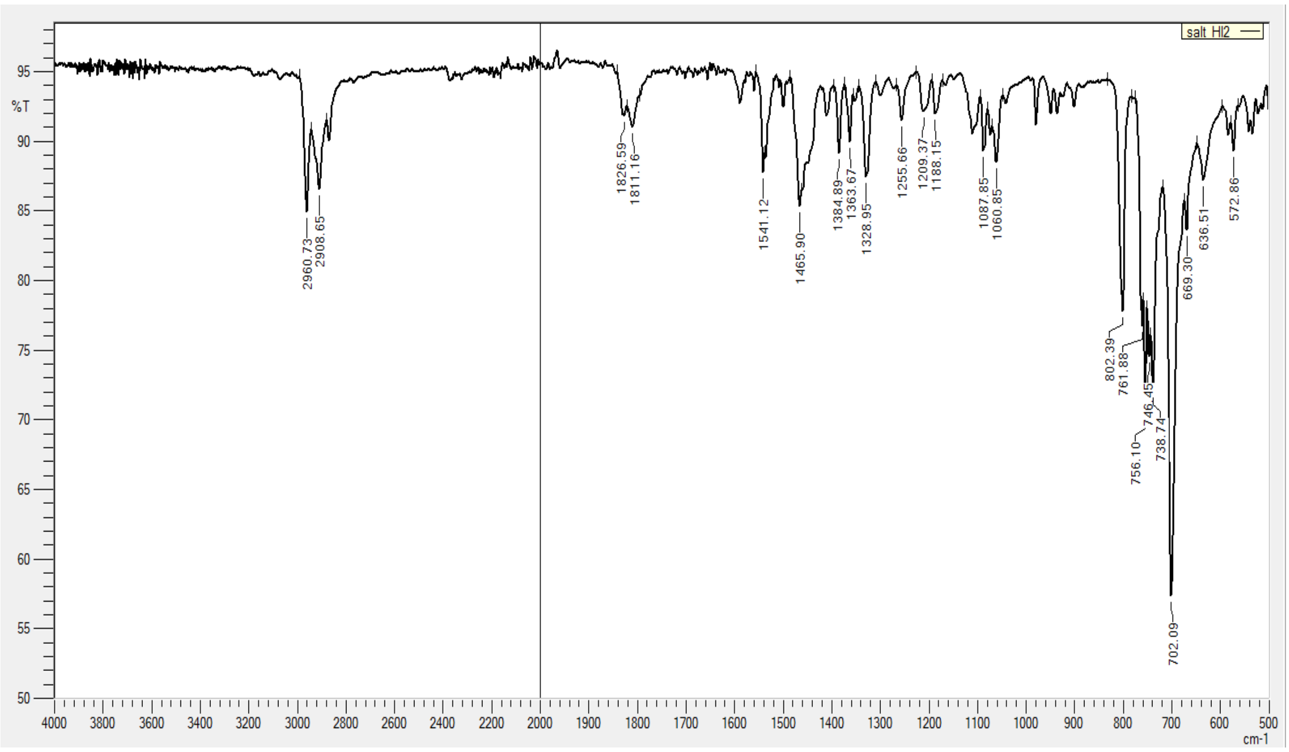
^{13}C{^{1}H} NMR spectrum (126 MHz, C_6D_6, 298K) of [(IMes)$AlHI_2$], **8**



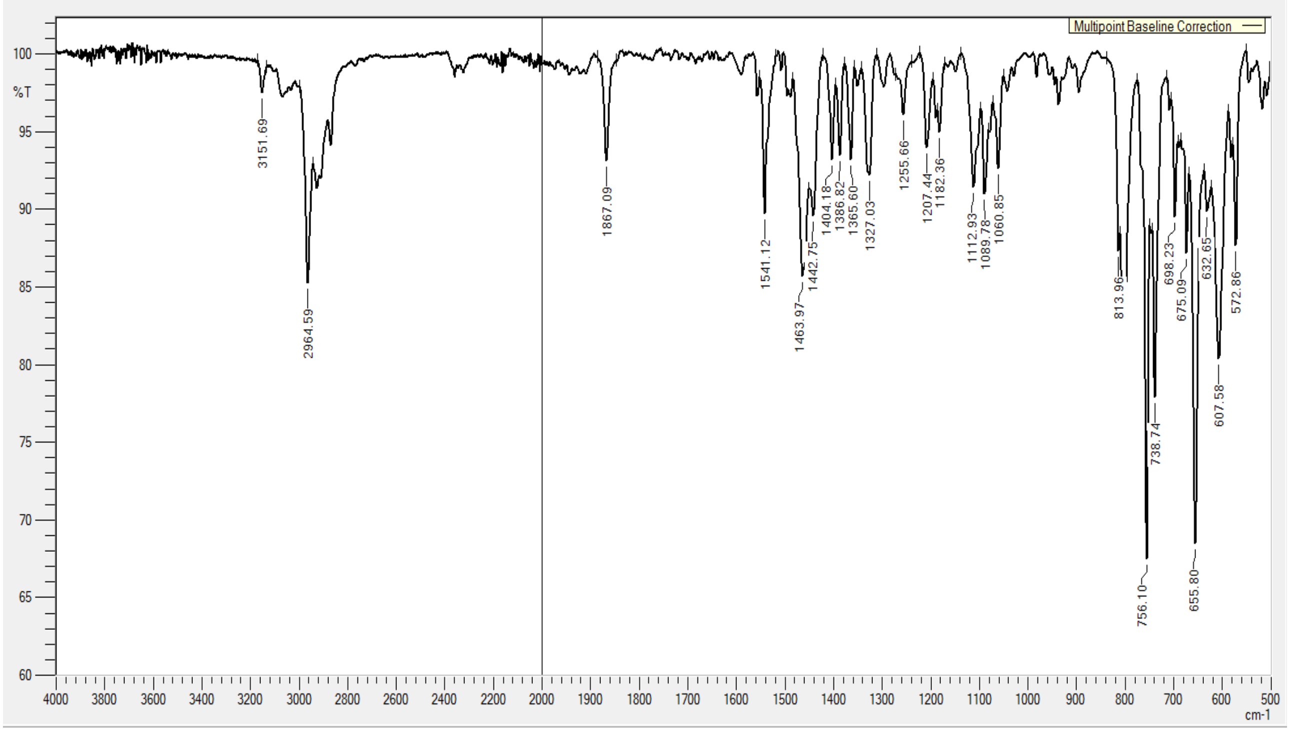
IR spectrum of [(IMes)AlHI$_2$], **8**



IR spectrum of [(IDip)AlH$_2$(*a*IDip)]I, **9**



IR spectrum of [(IDip)AlHI(*a*IDip)]I, **10**



3. X-ray Crystallography

Suitable crystals were mounted in silicone oil and were measured using a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P100 or P200 diffractometer using the CrystalClear (Rigaku) program suite.[6] Structures were solved by Patterson (PATTY)[7] or dual-space (SHELXT)[8] methods and refined by full-matrix least-squares against F^2 using SHELXL.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (riding model), except for the Al-H atoms which were freely refined (geometry restraints were used on the Al-H distance of **10**). Crystallographic data is summarized in Table S1. Details on selected individual crystal structure determinations and refinements are given below. Further experimental and refinement details are given in the crystallographic information files. CCDC 1840598–1840601 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Molecular structure of [(IDip)AlIX(*a*IDip)]I·2 C_6H_6 (X ≈ 75% I, 25% H), $\mathbf{11_{0.75}\cdot 10_{0.25}}\cdot 2\ C_6H_6$: The crystal was obtained from a reaction that gave **10** and it is likely that **10** was further iodinated towards **11** before crystallizing, rather than from a direct reaction of IDipAlI_3 with IDip which does not yield **11**. In $\mathbf{11_{0.75}\cdot 10_{0.25}}\cdot 2\ C_6H_6$, one Al-coordinated iodide position was modelled as disordered I^-/H^-, with about 75% iodide occupancy. This was estimated from the relative values of U_{eq} for that iodide and the other Al-coordinated one, thus giving 75% **11** and 25% **10**. An Al-H hydrogen atom (25%) was included in the model with geometry restraints. The Dip group on N2 is poorly ordered and geometry restraints were applied during refinement and one isopropyl group (C22-C24) was modelled with two positions for each atom using geometry restraints. Geometry restraints were further applied to the refinement of one lattice benzene molecule.

Molecular structure of [(IDip)Al(Ph)I_2]: A crystal of this complex was obtained as a low yield by-product from the small scale reaction of [(IDip)AlHI_2] **5** with Na[BPh_4]. Attempts to model the poorly ordered Al-bound phenyl group with two positions for each atom using geometry restraints did not improve the overall model and thus these atoms were freely refined and show a relatively large libration mode or "waving" of the group.

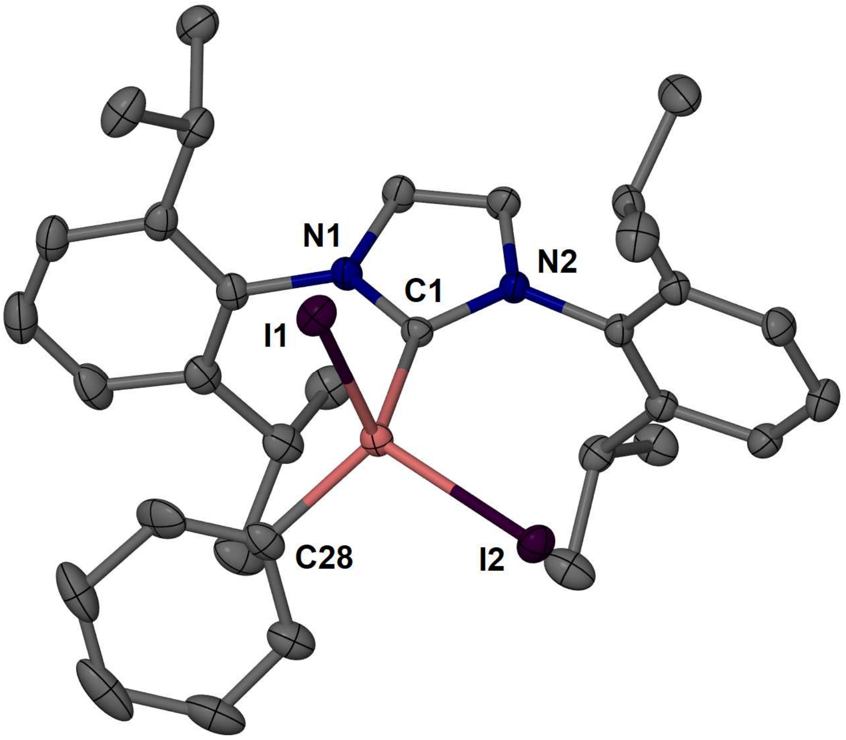


Figure S4. Molecular structure of [(IDip)Al(Ph)I_2] (25% thermal ellipsoids). Selected bond lengths (Å) and angles (°): I(1)-Al(1) 2.5597(15), I(2)-Al(1) 2.5469(14), Al(1)-C(28) 1.968(6), Al(1)-C(1) 2.047(4); I(2)-Al(1)-I(1) 105.77(5), C(28)-Al(1)-C(1) 114.3(2).

Table S1 Crystallographic data.

Compound reference	**9**	**10**$\cdot C_6H_6$	**11**$_{0.75}\cdot$**10**$_{0.25}\cdot 2\ C_6H_6$	$[(IDip)Al(Ph)I_2]$
Chemical formula	$C_{54}H_{74}AlIN_4$	$C_{60}H_{79}AlI_2N_4$	$C_{66}H_{84.25}AlI_{2.75}N_4$	$C_{33}H_{41}AlI_2N_2$
Formula Mass	933.05	1137.05	1309.57	746.46
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$
a/Å	10.9058(8)	10.563(3)	10.6622(2)	12.5143(14)
b/Å	22.4121(13)	14.900(4)	25.1991(5)	19.343(2)
c/Å	21.6328(14)	19.515(5)	24.3924(6)	13.9711(16)
α/°	90	110.305(17)	90	90
β/°	92.055(2)	93.09(2)	93.201(2)	99.898(2)
γ/°	90	92.671(18)	90	90
Unit cell volume/Å^3	5284.1(6)	2869.4(14)	6543.5(2)	3331.6(6)
Temperature/K	173(2)	173(2)	173(2)	173(2)
No. of formula units per unit cell, Z	4	2	4	4
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα
Wavelength/Å	0.71075	0.71075	0.71075	1.54187
Density (calc)/ Mg/m^3	1.173	1.316	1.329	1.488
Absorption coefficient, μ/mm^{-1}	0.659	1.151	1.368	15.243
F(000)	1968	1172	2668	1488
Reflections collected	107445	33057	84485	34064
Independent reflections	9698	10341	15084	6018
Theta range/°	1.817 to 25.413	2.127 to 25.422	1.672 to 29.062	3.942 to 68.165
Completeness (to theta)/%	99.7 (at 25.242°)	98.2 (at 25.242°)	99.8 (at 25.242°)	99.5 % (at 67.687°)
R_{int}	0.0197	0.1116	0.0321	0.1546
Data / restraints / parameter	9698 / 0 / 565	10341 / 1 / 623	15084 / 15 / 707	6018 / 0 / 352
Final R_1 values ($I > 2\sigma(I)$)	0.0359	0.1093	0.0557	0.0726
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0854	0.2715	0.1658	0.1905
Final R_1 values (all data)	0.0393	0.1871	0.0734	0.0742
Final $wR(F^2)$ values (all data)	0.0880	0.3086	0.1750	0.1940
Goodness of fit on F^2	1.021	1.114	1.052	1.050
Largest diff. peak and hole/e·Å^{-3}	1.228 and -1.308	2.450, -0.788	2.118, -2.390	1.702, -1.398
CCDC number	1840601	1840598	1840599	1840600

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