Supplementary Information

for

Amidines: A deeper look at the archetypal pro-ligand

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1. General experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere. An MBraun Labmaster glovebox with an atmosphere of N_2 was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Glassware was dried for at least 12 h at 125 °C prior to use. All chemicals were purchased from Sigma Aldrich or Fluorochem and used as received. Eutechtics are kindly thanked for their donation of *para*-bromotoluene. Trimethyl amine alane was synthesised according to literature procedures.[1] Toluene and hexane were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design, pentane was distilled over CaH_2 and all solvents were stored over activated 3Å molecular sieves and degassed via the freeze-pump-thaw method prior to use. Benzene-d_6 was purchased dry and stored over activated 3Å molecular sieves. ^{1}H (tetramethylsilane; 0 ppm) and ^{13}C (tetramethylsilane; 0 ppm) NMR spectra were obtained on a BRUKER 400 MHz or BRUKER 600 MHz instrument; all chemical shift values are quoted in ppm. Data was processed using MestReNova software.

Nomenclature

A suggested nomenclature system has been provided for amidinate ligands. "Amidine" is abbreviated to "Am". The *N,N'* substitution of the ligand is listed (separated with a comma) as the prefix and the *C*-bridgehead substitution as the suffix. For example, the general structure of the amidinate ligand in figure 1a (see main paper) would be referred to as $^{R1,R3}Am^{R2}$.

2. Synthetic Procedures

General syntheses

Route 1 general synthesis

The below is a synthesis adapted from literature procedures.[2–4]

To a Schlenk flask equipped with a reflux condenser charged with phosphorus pentoxide, P_4O_{10} (5.0 g, 0.035 mmol, 4 equiv.) under an inert atmosphere was added hexamethyldisiloxane (24.3 ml, 0.115 mmol, 13 equiv.). The resultant mixture was dissolved in dichloromethane (DCM, excess) and heated to reflux for 1.5 hours. The solution was subsequently dried *in vacuo* to afford "PPSE" as a colourless syrupy gel. To the gel was added the carboxylic acid (1 equiv.) and aniline (2.1 equivs) in quick succession. The subsequent mixture was then heated to 170 °C overnight with rapid stirring, before being cooled to 99 °C, opened to air and a 1M aqueous solution of NaOH (excess, *ca.* 100 ml) added dropwise, with vigorous stirring. The mixture was allowed to cool to room temperature with vigorous stirring over a period of at least 3 hours, before being extracted into DCM (3x 30 ml), washed with deionised water (25 ml), followed by brine (20 ml) and dried over $MgSO_4$. The resultant product was isolated *via* washing with the appropriate ice-cold solvent.

Route 2 general synthesis

To a flask under an inert atmosphere charged with a diethylether (Et_2O) solution of carbodiimide (1 equiv.) cooled to 0 °C was added dropwise a diethylether solution of $ArLi.(OEt_2)_n$ (*ca.* 1.1 equiv.) over 15 minutes. The resultant solution was allowed to warm to room temperature with stirring overnight. To the resultant pale-yellow solution was added deionised water (25 ml) and allowed to stir at room temperature in air for 45 minutes. The organic phase was extracted into DCM (3 × 30 ml), washed with deionised water and brine before being dried over $MgSO_4$ and subsequently dried *in vacuo* to afford a pale-yellow oil. The product was extracted into and precipitated out of the appropriate solvent at -78 °C and further washed with the same solvent at -78 °C to afford the product as a colourless solid. The aryl lithium salts were synthesised *via* literature procedures[5–7], and *bis*(2,6-diethylphenyl)carbodiimide was synthesised *via* the reduction of the thiourea as previously reported[8], and distilled at 185 °C *in vacuo*.

Route 3 general synthesis

Benzamide general synthesis

The appropriate aniline (1 equiv.) was mixed with the appropriate acyl chloride (1 equiv.) and triethylamine (1 equiv.) in DCM and left to stir for 16 hours. The resulting colourless solution was washed with 3 x 150 mL saturated Na_2CO_3 solution and dried over $MgSO_4$ before the solvent was removed *in vacuo* affording a colourless solid, which was then washed with hexane to afford clean product.

Amidine ligand synthesis

To a 30 mL toluene solution of the appropriate amide (1 equiv.) was added phosphorus pentachloride, PCl_5 (1.1 equiv.) and the subsequent mixture was stirred at reflux for 16 hours. The solvent was removed *in vacuo.* The resultant oil was further dried under vacuum at 50 °C for 1 hour before being redissolved in 30 mL toluene. The appropriate aniline (1 equiv.) and triethylamine (0.23 equivs) was added and the reaction heated to reflux for a further 16 hours. The resultant solution was washed with $NaHCO_3$, water and dried over $MgSO_4$. The toluene was then removed *in vacuo* to afford an oil, which was washed hexane and recrystallised from ethanol to afford the product as a crystalline solid.

Note: all ^{1}H NMR spectra are very broad due to the presence of multiple isomers and as such confident integral analysis is not possible. Integrations therefore are merely relative and should not be taken as absolute numbers of protons.

Benzamide syntheses

4-(*tert*-Butyl)-*N*-(2,6-diisopropylphenyl)benzamide

2,6-Diisopropylaniline (11.3 mL, 60 mmol), 4-*tert*-butylbenzoyl chloride (11.7 mL, 60 mmol) and triethylamine (8.4 mL, 60 mmol). Yield: 13.8 g (68%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.90 –

7.82 (m, 2H, Ar*H*), 7.53 – 7.43 (m, 3H, Ar*H*), 7.39 – 7.30 (m, 1H, Ar*H*), 7.25 – 7.18 (m, 2H, Ar*H*), 3.15 (hept, $^3J_{HH}$ = 6.9, 2H, CH_2CH$_3$),1.38 (s, 3H, C(CH_3)$_3$), 1.37 (s, 6H, C(CH_3)$_3$), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 5H, CH$_2$CH_3), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 7H, CH$_2$CH_3). (matches previously reported spectral data)[9]

***N*-(2,6-Diethylphenyl)-4-methylbenzamide**

2,6-Diethylaniline (2.96 mL, 18 mmol), *p*-toluoyl chloride (2.19 mL, 18 mmol) and triethylamine (2.5 mL, 18 mmol). Yield: 3.08 g (64%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.77 – 7.69 (m, 2H, Ar*H*), 7.24 – 7.13 (m, 3H, Ar*H*), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 2.55 (q, $^3J_{HH}$ = 7.6 Hz, 4H, CH_2CH$_3$), 2.35 (s, 3H, *p*-CH_3), 1.11 (t, $^3J_{HH}$ = 7.6 Hz, 6H, CH$_2$CH_3). (matches previously reported spectral data)[9]

***N*-(2,6-Diisopropylphenyl)-4-methylbenzamide**

2,6-Diisopropylaniline (5.65 mL, 30 mmol), *p*-toluoyl chloride (4.0 mL, 30 mmol) and triethylamine (4.18 mL, 18 mmol). Yield: 8.0 g (90%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.84 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 7.27 (m, 8H, Ar*H*), 3.13 (hept, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2CH$_3$), 2.45 (s, 3H), 1.57 (s, 2H), 1.21 (d, *J* = 6.9 Hz, 12H).

***N*-(2,6-Diisopropylphenyl)pivalamide**

2,6-Diisopropylaniline (3.40 mL, 18 mmol), pivaloyl chloride (2.20 mL, 18 mmol) and triethylamine (2.50 mL, 18 mmol). Yield: 3.22 g (69%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.17 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.04 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar*H*), 6.81 (dd, $^3J_{HH}$ = 13.5, 5.8 Hz, 1H, Ar*H*), 3.74 (s, 1H, N*H*), 2.97 (2x coincidental hept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.36 (s, 9H, C(CH_3)$_3$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$). (matches previously reported spectral data)[9]

***N*-(2,6-Diisopropylphenyl)-2-methylbenzamide**

2,6-Diisopropylaniline (6.8 mL, 40 mmol), *o*-toluoyl chloride (4.7 mL, 40 mmol) and triethylamine (5.0 mL, 40 mmol). Yield: 9.50 g (90%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.61 (dd, $^3J_{HH}$ = 7.5, 1.7 Hz, 1H, Ar*H*), 7.46 – 7.22 (m, 6H, Ar*H*), 7.03 (s, 1H, Ar*H*), 3.27 (hept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.58 (s, 3H, *p*-CH_3), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$). (matches previously reported spectral data)[9]

***N*-(2,6-Diethylphenyl)pivalamide**

2,6-Diethylaniline (2.96 mL, 18 mmol), pivaloyl chloride (2.20 mL, 18 mmol) and triethylamine (2.50 mL, 18 mmol). Yield: 3.45 g (82%). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.20 (dd, $^3J_{HH}$ = 8.3, 6.8 Hz, 1H, Ar*H*), 7.11 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 6.88 (s, 1H, N*H*), 2.55 (q, $^3J_{HH}$ = 7.6 Hz, 4H, CH_2CH$_3$), 1.36 (s, 9H, C(CH_3)$_3$), 1.18 (t, $^3J_{HH}$ = 7.6 Hz, 6H, CH$_2$CH$_3$). (matches previously reported spectral data)[9]

Ligand Syntheses

Ligand 1 ($^{dipp}Am^{pTol}H$)

Route 1: p-Toluic acid (1.2 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), hexane. Yield: 2.90 g (72%).

A modified version of route 2: To a diethyl ether solution of *para*-bromotoluene (1.71 g, 10 mmol, 1 equiv.) cooled to -78 °C was added ^{n}BuLi (4 ml 2.5M solution , 0.01 mml, 1 equiv.) dropwise over 15 minutes. This was allowed to stir at -78 °C for 1 hour. To the resultant solution warmed to 0 °C was added a diethyl ether solution of *bis*(2,6-diisopropylphenyl)carbodiimide (3.63 g, 10 mmol, 1 equiv.). From this point the standard synthesis was followed for route 2. Yield: 1.72 g (38%).

Note: We would expect the yield to be improved upon isolation of the aryl lithium intermediate.

Route 3: *N*-(2,6-diisopropylphenyl)-4-methylbenzamide (4.0 g, 13.5 mmol), phosphorus pentachloride (3.7 g, 18.0 mmol), 2,6-diisopropylaniline (2.6 mL, 13.5 mmol) and triethylamine (2.4 mL, 17.6 mmol). Yield: 4.7 g, (76%) (two step yield 68%).

^{1}H NMR (400 MHz, **Chloroform-*d***) δ 7.28 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.24 – 6.84 (m, 8H, Ar*H*), 5.68 (s, 1H), 3.47 (s, 1H, N*H*), 3.47 (s, 1H, C*H*$(CH_3)_2$) 3.21 (m, 2H, C*H*$(CH_3)_2$), 3.01 (s, 1H, C*H*$(CH_3)_2$), 2.28 (s, 3H, *p*-CH_3), 1.35 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.24 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.99 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.89 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$). Other spectroscopic data matches previous reports.[10]

Ligand 2 ($^{dipp}Am^{tBuPh}H$)

Route 1: 4-*tert*-Butylbenzoic acid (1.57 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), hexane. Yield: 2.87 g (66%).

Route 3: 4-(*tert*-Butyl)-*N*-(2,6-diisopropylphenyl)benzamide (5.1 g, 15.2 mmol), phosphorus pentachloride (4.2 g, 20.2mmol), 2,6-diisopropylaniline (2.9 mL, 15.2 mmol) and triethylamine (2.8 mL, 20.2 mmol). Yield: 5.1 g (68%) (two step yield 46%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.05 (dq, *J* = 4.4, 8.3 Hz, 5H), 6.94 (d, *J* = 7.7 Hz, 2H), 5.94 (s, 1H), 5.71 (s, 0H), 3.59 (d, *J* = 7.4 Hz, 0H), 3.53 (p, *J* = 6.9 Hz, 1H), 3.31 (p, *J* = 6.8 Hz, 2H), 1.41 (dd, *J* = 1.8, 6.9 Hz, 9H), 1.12 (d, *J* = 7.0 Hz, 2H), 1.06 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 2H), 0.92 (dd, *J* = 6.8, 10.7 Hz, 10H). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 152.7 (N*C*N), 152.6 (N*C*N), 145.1 (Ar*C*), 145.0 (Ar*C*), 139.3 (Ar*C*), 138.5 (Ar*C*), 135.1 (Ar*C*), 132.7 (Ar*C*), 129.3 (Ar*C*), 125.7 (Ar*C*), 124.9 (Ar*C*), 124.0 (Ar*C*), 124.0 (Ar*C*), 123.8 (Ar*C*), 123.5 (Ar*C*), 34.6 (Ar*C*$(CH_3)_3$), 31.1 (ArC(*C*H_3)$_3$), 31.1 (ArC(*C*H_3)$_3$), 29.2 (Ar*C*H$(CH_3)_2$), 28.8 (Ar*C*H$(CH_3)_2$), 28.5 (Ar*C*H$(CH_3)_2$), 24.9 (ArCH(*C*H_3)$_2$), 24.6

(ArCH(CH_3)$_2$), 23.0 (ArCH(CH_3)$_2$), 22.5 (ArCH(CH_3)$_2$). **HRMS** (ESI): calc. for $C_{35}H_{49}N_2$ $[M+H]^+$: 497.390 meas. 497.389. Matches previous ^{1}H NMR data.[11]

Ligand 3 ($^{dipp}Am^{DMAPh}H$)

Route 1: 4-Dimethylaminobenzoic acid (1.452 g, 8.8 mmol, 1 equiv.) 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), ethanol. Yield: 2.76 g, (65%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.24 (s, 0H), 7.21 (d, *J* = 7.7 Hz, 0H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 8.6 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 5.89 (s, 1H), 5.74 (s, 0H), 3.67 (s, 1H), 3.58 (hept, *J* = 7.1 Hz, 1H), 3.41 (h, *J* = 6.8 Hz, 2H), 2.30 (s, 6H), 1.44 (d, *J* = 6.8 Hz, 8H), 1.36 – 1.22 (m, 0H), 1.19 – 1.13 (m, 2H), 1.12 – 1.06 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 4H), 0.97 (d, *J* = 6.8 Hz, 4H). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 154.2 (N*C*N), 152.7 (Ar*C*), 151.2 (Ar*C*), 151.0 (Ar*C*), 147.0 (Ar*C*), 146.5 (Ar*C*), 145.5 (Ar*C*), 145.3 (Ar*C*), 139.5 (Ar*C*), 138.6 (Ar*C*), 135.8 (Ar*C*), 130.7 (Ar*C*), 129.5 (Ar*C*), 127.5 (Ar*C*), 124.0 (Ar*C*), 123.7 (Ar*C*), 123.4 (Ar*C*), 111.7 (Ar*C*), 111.2 (Ar*C*), 39.6 (N(*C*H$_3$)$_2$), 39.5 (N(*C*H$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$). **HRMS** (ESI): calc. for $C_{33}H_{46}N_3$ $[M+H]^+$: 484.369 meas. 484.374.

Ligand 4 ($^{dipp}Am^{pOMe}H$)

Route 1: Anisic acid (1.339 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), petroleum ether 30-60 (-78 °C). Yield: 2.66 g (56%).

^{1}H NMR (700 MHz, **Benzene-d_6**) δ 7.66 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.34 (s, 1H, Ar*H*), 7.32 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.19 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.09 – 7.05 (m, 2H, Ar*H*), 6.95 (d, *J* = 7.7 Hz, 2H, Ar*H*), 6.55 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.51 (d, *J* = 8.3 Hz, 1H, Ar*H*), 5.91 (s, 1H, N*H* major), 5.65 (s, 1H, N*H* minor), 3.59 (br. m, 1H, C*H*(CH$_3$)$_2$), 3.52 (hept, *J* = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 3.38 – 3.29 (m, *J* = 7.4, 6.2 Hz, 3H, C*H*(CH$_3$)$_2$), 3.10 (s, 3H, OC*H*$_3$), 1.41 (t, *J* = 6.2 Hz, 12H, CH(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.5 Hz, 3H CH(C*H*$_3$)$_2$), 1.07 – 0.99 (m, 3H, CH(C*H*$_3$)$_2$), 0.94 (t, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 161.0 (N*C*N), 160.8 (Ar*C*), 152.4 (Ar*C*), 147.0 (Ar*C*), 145.2 (Ar*C*), 145.0 (Ar*C*), 139.3 (Ar*C*), 138.5 (Ar*C*), 135.3 (Ar*C*), 131.0 (Ar*C*), 129.8 (Ar*C*), 129.5 (Ar*C*), 124.1 (Ar*C*), 124.0 (Ar*C*), 123.8 (Ar*C*), 123.5 (Ar*C*), 114.1 (Ar*C*), 114.1 (Ar*C*), 113.3 (Ar*C*), 54.7 (O*C*H$_3$), 29.3 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$). **HRMS** (ESI): calc. for $C_{32}H_{43}N_2O$ $[M+H]^+$: 471.338 meas. 471.337.

Ligand 5 ($^{dipp}Am^{pCN}H$)

Route 1: *Para*-cyanobenzoic acid (1.295 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), petroleum ether 30-60 (-78 °C). Yield: 2.30 g (56%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.39 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.27 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.19 (s, 1H, Ar*H*), 7.03 (t, *J* = 7.7 Hz, 2H, Ar*H*), 6.86 (d, *J* = 7.7 Hz, 2H, Ar*H*), 6.72 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.88 (s, 1H, N*H*, major), 5.45 (s, 1H, N*H*, minor), 3.42 (br. m., 1H, C*H*(CH_3)$_2$), 3.31 (hept, *J* = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 3.10 (hept, *J* = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 1.34 (dd, *J* = 8.5, 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.9 Hz, 1H, CH(C*H*$_3$)$_2$), 1.05 (br. m., 1H, CH(C*H*$_3$)$_2$), 0.86 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.78 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) *δ* = 151.6 (N*C*N), 145.0 (Ar*C*), 144.0 (Ar*C*), 138.9 (Ar*C*), 134.1 (Ar*C*), 131.5 (Ar*C*), 129.6 (Ar*C*), 124.5 (Ar*C*), 124.2 (Ar*C*), 123.9 (Ar*C*), 118.2 (Ar*C*N), 113.5 (Ar*C*N), 29.2 (*C*H(CH_3)$_2$), 28.7 (*C*H(CH_3)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$). **HRMS** (ESI): calc. for $C_{32}H_{40}N_3$ $[M+H]^+$: 466.322 meas. 466.322.

Ligand 6 (dippAm$^{p\text{CF3}}$H)

Route 1: *Para*-trifluoromethylbenzoic acid (1.673 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), ethanol. Yield: 3.04 g (68%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.58 (s, 1H, Ar*H*), 7.47 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.30 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.27 – 7.24 (m, 1H, Ar*H*), 7.19 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.08 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.04 (s, 1H, Ar*H*), 7.01 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.87 (dd, *J* = 7.8, 1.5 Hz, 2H, Ar*H*), 5.92 (s, 1H, N*H* major), 5.53 (s, 1H, N*H* minor), 3.48 (br. hept, 1H, C*H*(CH_3)$_2$), 3.40 (hept, *J* = 7.1 Hz, 2H, C*H*(CH_3)$_2$), 3.15 (hept, *J* = 6.4 Hz, 2H, C*H*(CH_3)$_2$), 3.07 (hept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 1.43 – 1.33 (m, 12H, CH(C*H*$_3$)$_2$), 1.21 (dd, *J* = 6.9, 2.6 Hz, 2H, CH(C*H*$_3$)$_2$), 1.06 (br. s, 1H, CH(C*H*$_3$)$_2$), 0.87 (d, *J* = 6.9 Hz, 7H, CH(C*H*$_3$)$_2$), 0.81 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 164.9 (N*C*N), 151.8 (Ar*C*), 147.0 (Ar*C*), 146.8 (Ar*C*), 145.0 (Ar*C*), 144.2 (Ar*C*), 139.0 (Ar*C*), 138.7 (Ar*C*), 134.3 (Ar*C*), 131.5 (Ar*C*), 131.1 (Ar*C*), 129.7 (Ar*C*), 125.8, 124.9 (q, *p*-*C*F_3), 124.4 (Ar*C*), 124.2 (Ar*C*), 123.9 (Ar*C*), 123.6 (Ar*C*), 29.3 (*C*H(CH_3)$_2$), 29.2 (*C*H(CH_3)$_2$), 28.8 (*C*H(CH_3)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$), 22.3 (CH(*C*H$_3$)$_2$). **^{19}F{^{1}H} NMR** (376 MHz, **Benzene-d_6**) δ -62.61 (major), -62.66 (minor), -62.69 (minor). **HRMS** (ESI): calc. for $C_{32}H_{40}F_3N_2$ $[M+H]^+$: 509.314 meas. 509.315.

Ligand 7 (dippAm$^{m\text{Xyl}}$H)

Route 1: 3,5-Dimethylbenzoic acid (1.32 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), petroleum ether (30-60). Yield: 2.25 g (64%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.36 – 7.29 (br. m, 3H, Ar*H*), 7.20 (br. d, *J* = 7.6 Hz, 1H, Ar*H*), 7.12 (br. s, 1H, Ar*H*), 7.05 (br. t, *J* = 7.7 Hz, 1H, Ar*H*), 6.92 (br. d, *J* = 7.7 Hz, 1H, Ar*H*), 6.65 (br. d, *J* = 9.8 Hz, 1H, Ar*H*), 5.91 (br. s, 1H, N*H* major), 5.72 (br. s, 1H, N*H*, minor), 3.63 (br. m, 1H, C*H*(CH_3)$_2$), 3.56 (br. hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.36 (br. hept., *J* = 7.0, 13.9 Hz, 2H, C*H*(CH_3)$_2$), 1.98 (s, 6H, *m*-xyl-C*H*$_3$), 1.41 (br. dd, *J* = 4.7, 6.9 Hz, 8H, CH(C*H*$_3$)$_2$), 1.29 (br. s, 8H, CH(C*H*$_3$)$_2$), 1.18 – 1.13 (br. m, 1H, CH(C*H*$_3$)$_2$), 1.05 (br. d, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 0.94 (t, *J* = 6.6 Hz, 8H,

CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 153.3 (N*C*N), 147.1 (Ar*C*), 145.3 (Ar*C*), 144.9 (Ar*C*), 139.3 (Ar*C*), 138.6 (Ar*C*), 138.1 (Ar*C*), 137.2 (Ar*C*), 135.4 (Ar*C*), 135.1 (Ar*C*), 131.2 (Ar*C*), 131.0 (Ar*C*), 127.5 (Ar*C*), 126.0 (Ar*C*), 124.0 (Ar*C*), 123.9 (Ar*C*), 123.8 (Ar*C*), 123.5 (Ar*C*), 123.2 (Ar*C*), 122.8 (Ar*C*), 29.2 (Ar*C*H(CH$_3$)$_2$), 28.8 (Ar*C*H(CH$_3$)$_2$), 28.5 (Ar*C*H(CH$_3$)$_2$), 25.1 (ArCH(*C*H$_3$)$_2$), 24.8 (ArCH(*C*H$_3$)$_2$), 24.7 (ArCH(*C*H$_3$)$_2$), 23.1 (ArCH(*C*H$_3$)$_2$), 22.6 (ArCH(*C*H$_3$)$_2$), 22.5 (ArCH(*C*H$_3$)$_2$), 21.2 (ArCH(*C*H$_3$)$_2$). **HRMS** (ESI): calc. for $C_{33}H_{45}N_2$ $[M+H]^+$: 469.358 meas. 469.360. (matches previously reported data)[2]

Ligand 8 (^{dipp}Am$^{o\text{Tol}}$H)

Route 1: *Ortho*-toluic acid (1.198 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), ethanol. Yield: 2.21 g (55%).

Route 3: *N*-(2,6-Diisopropylphenyl)-2-methylbenzamide (3.30 g, 11.2 mmol, 1 equiv.), phosphorus pentachloride (2.80 g, 13.45 mmol, 1.2 equivs), 2,6-diisopropylaniline (2.10 mL, 11.2 mmol, 1 equiv.) and triethylamine (2.04 mL, 14.6 mmol, 1.3 equivs). Yield: 3.27 g (64%) (two step yield 58%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.30 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.09 – 7.03 (m, 1H, Ar*H*), 7.02 – 6.93 (m, 2H, Ar*H*), 6.86 (t, *J* = 8.1 Hz, 3H, Ar*H*), 6.78 (s, 1H, Ar*H*), 6.70 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.05 (s, 1H, N*H* major), 5.53 (s, 1H, N*H* minor), 3.56 (hept, *J* = 7.0 Hz, 3H, C*H*(CH$_3$)$_2$), 3.30 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.26 – 3.17 (m, 1H, C*H*(CH$_3$)$_2$), 2.81 (s, 3H, *o*-C*H*$_3$), 2.41 (s, 1H, *o*-C*H*$_3$), 1.39 (d, *J* = 7.0 Hz, 7H, CH(C*H*$_3$)$_2$), 1.32 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 – 1.01 (m, 14H, CH(C*H*$_3$)$_2$), 0.95 – 0.83 (m, 12H, CH(C*H*$_3$)$_2$). **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.23 – 7.00 (m, 6H, Ar*H*), 6.93 (dd, *J* = 10.1, 5.8 Hz, 4H, Ar*H*), 5.74 (s, 1H, N*H*), 3.32 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.15 (hept, *J* = 7.1 Hz, 2H, CH(CH$_3$)$_2$), 2.59 (s, 3H, *o*-C*H*$_3$), 1.36 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 0.91 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 154.2 (N*C*N), 153.6 (N*C*N), 146.6 (Ar*C*), 144.8 (Ar*C*), 144.6 (Ar*C*), 139.3 (Ar*C*), 138.6 (Ar*C*), 137.8 (Ar*C*), 135.8 (Ar*C*), 135.6 (Ar*C*), 134.5 (Ar*C*), 132.3 (Ar*C*), 131.4 (Ar*C*), 129.1 (Ar*C*), 128.7 (Ar*C*), 127.4 (Ar*C*), 126.0 (Ar*C*), 125.0 (Ar*C*), 124.2 (Ar*C*), 123.9 (Ar*C*), 123.8 (Ar*C*), 123.4 (Ar*C*), 123.0 (Ar*C*), 119.0 (Ar*C*), 29.4 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$), 22.0 (CH(*C*H$_3$)$_2$), 20.8 (*o*-*C*H$_3$), 20.5 (*o*-*C*H$_3$). **HRMS** (ESI): calc. for $C_{32}H_{43}N_2$ $[M+H]^+$: 455.343 meas. 455.344.

Ligand 9 (^{dipp}Am$^{2,4\text{Xyl}}$H)

Route 1: 2,4-Dimethylbenzoic acid (1.32 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), hexane. Yield: 2.66 g (65%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.31 (br. d, *J* = 7.7 Hz, 1H, Ar*H*), 7.18 (br. d, *J* = 10.4 Hz, 6H, Ar*H*), 6.97 (br. t, *J* = 8.0 Hz, 1H, Ar*H*), 6.86 (br. d, *J* = 12.1 Hz, 1H, Ar*H*), 6.71 (br. s, 1H, Ar*H*), 6.57 (br. s, 1H), 6.50 (br. d, *J* = 7.9 Hz, 1H, Ar*H*), 6.02 (br. s, 1H, N*H* major), 5.53 (br. s, 1H, N*H* minor),

3.59 (br. hept, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 3.34 (br. hept, J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.29 – 3.25 (br. m, 1H, CH(CH$_3$)$_2$), 2.84 (br. s, 2H, *o*-CH_3 major), 2.44 (br. s, 1H, *o*-CH_3 minor), 1.92 (s, 3H, *p*-CH_3), 1.40 (br. d, J = 7.0 Hz, 5H, CH(CH_3)$_2$), 1.34 (br. d, J = 6.7 Hz, 4H, CH(CH_3)$_2$), 1.08 (br. s, 3H, CH(CH_3)$_2$), 0.96 (br. s, 5H, CH(CH_3)$_2$), 0.89 (br. t, J = 6.8 Hz, 4H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ = 153.6 (N*C*N), 146.5 (Ar*C*), 144.8 (Ar*C*), 139.3 (Ar*C*), 138.6 (Ar*C*), 138.3 (Ar*C*), 137.7 (Ar*C*), 134.8 (Ar*C*), 132.5 (Ar*C*), 132.1 (Ar*C*), 129.1 (Ar*C*), 127.3 (Ar*C*), 126.8 (Ar*C*), 125.7 (Ar*C*), 124.1 (Ar*C*), 123.8 (Ar*C*), 123.4 (Ar*C*), 123.1 (Ar*C*), 123.0 (Ar*C*), 29.5 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 28.7 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$), 21.0 (*p*-*C*H$_3$), 20.8 (*o*-*C*H$_3$), 20.5 (*o*-*C*H$_3$). **HRMS** (ESI): calc. for $C_{33}H_{45}N_2$ [M+H]$^+$: 469.358 meas. 469.361.

Ligand 10 (dippAm$^{o\text{Xyl}}$H)

Route 1: 2,6-Diimethylbenzoic acid (1.32 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.48 ml, 18.5 mmol, 2.1 equivs), hexane. Yield: 0.95 g (28%).

Route 2: *Ortho*-xylyl lithium (1.00 g, 8.92 mmol), *bis*(2,6-diisopropylphenyl)carbodiimide (3.23 g, 8.92 mmol), petroleum ether (30-60). Yield: 3.01 g (71%)

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**): δ = 7.26 (br. s, 1H, Ar*H*), 7.14 – 6.93 (br. m, 5H, Ar*H*), 6.93 – 6.85 (br. t, 1H, *o*-Xyl-*p*-*H*), 6.76 (br. d, 2H, J = 7.6 Hz, *o*-Xyl-*m*-*H*), 6.54 (br. s, 1H, N*H*, major), 5.58 (br. s, 1H, N*H*, minor), 3.92 – 2.91 (br. m, 4H, ArC*H*(CH$_3$)$_2$), 2.36 (br. s, 6H, *o*-Xyl-CH_3), 1.50 – 0.68 (br. m, 24H, ArCH(CH_3)$_2$) ppm. **^{1}H NMR** (400 MHz, **Chloroform-*d***): δ = 7.23 (s, 2H, Ar*H*), 7.14 – 7.01 (m, 4H, Ar*H*), 7.01 – 6.95 (m, 1H, *o*-oxyl-*p*-*H*), 6.95 – 6.86 (m, 2H, *o*-oxyl-*m*-*H*), 6.27 (s, 1H, N*H*, major), 5.67 (s, 1H, N*H*, minor), 3.48 (m, 2H, ArC*H*(CH$_3$)$_2$), 2.96 (m, 2H, ArC*H*(CH$_3$)$_2$), 2.30 (s, 6H, *o*-oxyl-CH$_3$), 1.43 – 0.51 (m, 24H, ArCH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ = 154.1 (N*C*N), 144.1 (Ar*C*), 143.6 (Ar*C*), 140.0 (Ar*C*), 136.8 (Ar*C*), 135.7 (Ar*C*), 134.3 (Ar*C*), 128.9 (Ar*C*), 127.0 (Ar*C*), 124.3 (Ar*C*), 124.1 (Ar*C*), 123.6 (Ar*C*), 123.1 (Ar*C*), 28.8 (*C*H(CH$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$), 20.8 (*o*-xyl-*C*H$_3$). **HRMS** (ESI): calc. for $C_{33}H_{45}N_2$ [M+H]$^+$: 469.358 meas. 469.361.

Ligand 11 (dippAm^{mes}H)

Route 1: 2,4,6-Trimethylbenzoic acid (1.445 g, 8.8 mmol, 1 equiv.) 2,6-diisopropylaniline (3.402 ml, 18.5 mmol, 2.1 equivs), hexane, Yield: 0.97 g (23%).

Route 2: Mesityl lithium diethyl etherate (0.83 g, 4.15 mmol), *bis*(2,6-diisopropylphenyl)carbodiimide (1.50 g, 4.15 mmol), petroleum ether (30-60). Yield: 1.5 g (73%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.27 (s, 1H, Ar*H*), 7.04 – 6.94 (m, 1H, Ar*H*), 6.89 (s, 1H, Ar*H*), 6.52 (s, 1H, N*H* major), 5.59 (s, 1H, N*H* minor), 3.73 (br. m, 1H, C*H*(CH$_3$)$_2$), 3.54 (br. m, 1H, C*H*(CH$_3$)$_2$), 3.17 (br. m, 2H, C*H*(CH$_3$)$_2$), 2.37 (s, 6H, *o*-CH_3), 2.00 (s, 3H, *p*-CH_3), 1.41 – 1.34 (m, 6H, CH(CH_3)$_2$), 1.31 (d, J = 7.3 Hz, 2H, CH(CH_3)$_2$), 0.98 (br. m, 5H, CH(CH_3)$_2$), 0.83 (br. m, 7H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ = 154.2 (N*C*N), 146.2 (Ar*C*), 144.1 (Ar*C*), 143.8

(Ar*C*), 139.9 (Ar*C*), 139.1 (Ar*C*), 137.7 (Ar*C*), 136.6 (Ar*C*), 132.9 (Ar*C*), 129.7 (Ar*C*), 124.2 (Ar*C*), 123.6 (Ar*C*), 123.0 (Ar*C*), 28.8 (*C*H(CH_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 22.9 (CH(*C*H_3)$_2$), 20.8 (*o*-*C*H_3 and *p*-*C*H_3). **HRMS** (ESI): calc. for $C_{34}H_{47}N_2$ $[M+H]^+$: 483.374 meas. 483.379.

Ligand 12 (^{dipp}Am^{dipp}H)

Route 2: Diisopropylphenyl lithium diethyl etherate (2.5 g, 10.3 mmol), *bis*(2,6-diisopropylphenyl)carbodiimide (3.4 g, 9.38 mmol), ethanol. Yield: 4.31 g (88%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.26 (br. m, 2H, Ar*H*) , 7.06 (br. m, 2H, Ar*H*), 6.93 (br. m, 1H, Ar*H*) 6.87 (br. m, 2H, Ar*H*), 6.63 (br. s, 1H, NH (major)), 5.72 (br. s, 0H, N*H* (minor)), 3.62 (br. m, 2H, ArC*H*(CH_3)$_2$), 3.21 – 3.37 (br. m, 4H, ArC*H*(CH_3)$_2$), 2.87 – 3.15 (br. m, 3H, ArC*H*(CH_3)$_2$), 1.37 (br. m, 13H, ArCH(C*H*$_3$)$_2$), 1.28 (br. m, 5H, ArCH(C*H*$_3$)$_2$), 0.85 (br. m, 19H, ArCH(C*H*$_3$)$_2$), 0.78 (br. m, 15H, ArCH(C*H*$_3$)$_2$), 0.75 (br. m, 12H, ArCH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 153.6 (N*C*(dipp)N), 147.5 (Ar*C*), 144.2 (Ar*C*), 143.7 (Ar*C*), 140.0 (Ar*C*), 134.4 (Ar*C*), 133.5 (Ar*C*), 124.6 (Ar*C*), 124.2 (Ar*C*), 124.0 (Ar*C*), 123.8 (Ar*C*), 32.1 (Ar*C*H(CH_3)$_2$), 29.2 (Ar*C*H(CH_3)$_2$), 29.0 (Ar*C*H(CH_3)$_2$), 27.1 (ArCH(*C*H_3)$_2$), 24.9 (ArCH(*C*H_3)$_2$), 22.6 (ArCH(*C*H_3)$_2$), 22.4 (ArCH(*C*H_3)$_2$), 21.3(ArCH(*C*H_3)$_2$). **HRMS** (ESI): calc. for $C_{37}H_{53}N_2$ $[M+H]^+$: 525.421 meas. 525.421.

Ligand 13 (^{dipp}Am^{tBu}H)

Route 2: *Tert*-butyl lithium (4 ml, 6.81 mmol, 1.7 M), *bis*(2,6-diisopropylphenyl)carbodiimide (2.468 g, 6.81 mmol). No further crystallisation necessary. Yield: 2.4 g (84%).

Route 3: *N*-(2,6-Diisopropylphenyl)pivalamide (2.0 g, 7.7 mmol), phosphorus pentachloride (1.9 g, 1.9 mmol), 2,6-diisopropylaniline (1.5 mL, 7.7 mmol) and triethylamine (1.4 mL, 9.9 mmol). Yield: 1.46 g (45%) (two step yield 27%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.25 (d, *J* = 7.7 Hz, 3H, Ar*H*), 7.13 – 7.06 (m, 6H, Ar*H*), 6.95 (d, *J* = 7.9 Hz, 3H, Ar*H*), 5.46 (s, 1H, N*H* major), 5.27 (s, 1H, N*H* minor), 3.47 (hept, *J* = 7.0 Hz, 4H, C*H*(CH_3)$_2$), 3.29 (hept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.22 – 3.13 (br. m, 1H, C*H*(CH_3)$_2$), 1.39 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.30 (s, 9H, C(C*H*)$_3$), 1.24 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.83 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). (data matches previous reports[12])

Ligand 14 (^{dipp}Am^{Ad}H)

Route 1: Adamantane-1-carboxylic acid (1.586 g, 8.8 mmol, 1 equiv.), 2,6-diisopropylaniline (3.49 ml, 18.5 mmol, 2.1 equivs), ethanol. Yield: 0.27 g (6%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.26 (br., d, *J* = 7.6 Hz, 2H, Ar*H*), 7.10 (br. d, *J* = 8.5 Hz, 2H, Ar*H*), 6.96 (br. d, *J* = 7.6 Hz, 2H, Ar*H*), 5.45 (s, 1H, N*H*), 3.51 (hept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.33 (br. hept, *J* = 7.6 Hz, 2H, C*H*(CH_3)$_2$), 2.19 (s, 6H, Ad*H*), 1.88 (s, 3H, Ad*H*), 1.64 – 1.52 (m, 5H, Ad*H*), 1.42 (br. d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.29 (br. d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.86 (br. d, *J* = 6.8 Hz,

6H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ = 159.4 (N*C*N), 147.8 (Ar*C*), 145.0 (Ar*C*), 138.6 (Ar*C*), 136.6 (Ar*C*), 123.3 (Ar*C*), 41.4 (Ad*C*), 37.0 (Ad*C*), 29.2 (Ad*C*), 29.0 (*C*H(CH$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 22.0 (CH(*C*H$_3$)$_2$), 21.8 (CH(*C*H$_3$)$_2$). **HRMS** (ESI): calc. for $C_{27}H_{41}N_2$ [M+H]$^+$: 393.327 meas. 393.326. (data matches previous reports[13])

Ligand 15 (^{dipp,dep}Am^{tBu}H)

Route 3: *N*-(2,6-Diisopropylphenyl)pivalamide (1.07 g, 4.09 mmol), phosphorus pentachloride (1.02 g, 4.91 mmol), 2,6-diethylaniline (0.67 mL, 4.09 mmol) and triethylamine (0.74 mL, 5.32 mmol). Yield: 0.88 g (55%) (two step yield 38%).

^{1}H NMR (400 MHz, **Chloroform-*d***) δ 7.16 – 6.89 (m, 6H, Ar*H*), 3.27 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, N*H*), 3.01 – 2.90 (m, 1H, C*H*(CH$_3$)$_2$), 2.62 (2x coincidental m, 3H, CH_2CH$_3$, CH(CH$_3$)$_2$), 2.39 (dq, $^3J_{HH}$ = 15.1, 7.6 Hz, 1H, CH_2CH$_3$), 1.26 – 1.00 (m, 27H, C(CH_3)$_3$, CH(CH_3)$_2$). **^{1}H NMR** (400 MHz, **Benzene-d_6**) δ 7.11 – 6.78 (m, 5H, Ar*H*), 5.42 (s, 1H, N*H* minor), 5.34 (s, 1H, N*H* minor), 5.23 (s, 1H, N*H* major), 3.47 (br. m, 1H, C*H*(CH$_3$)$_2$ or CH_2CH$_3$), 3.22 (hept, *J* = 7.3 Hz, 2H, C*H*(CH$_3$)$_2$), 3.00 (br. m, 1H, C*H*(CH$_3$)$_2$ or CH_2CH$_3$), 2.72 – 2.45 (m, 4H, C*H*(CH$_3$)$_2$ or *C*H$_2$CH$_3$), 1.34 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.31 (s, 15H, C(CH_3)$_3$), 1.21 (br. m, 12H, CH(CH_3)$_2$ or CH$_2$CH_3), 1.08 – 1.00 (m, 13H, CH(CH_3)$_2$ or CH$_2$CH_3), 0.82 (s, 2H, CH(CH_3)$_2$ or CH$_2$CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 160.0 (N*C*N), 147.7 (Ar*C*), 146.1 (Ar*C*), 145.2 (Ar*C*), 143.0 (Ar*C*), 137.5 (Ar*C*), 136.8 (Ar*C*), 134.6 (Ar*C*), 131.6 (Ar*C*), 126.8 (Ar*C*), 125.9 (Ar*C*), 125.0 (Ar*C*), 123.3 (Ar*C*), 121.0 (Ar*C*), 39.6 (*C*(CH$_3$)$_3$), 30.1 (*C*H(CH$_3$)$_2$), 29.9 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 25.2 (*C*H(CH$_3$)$_2$ or *C*H$_2$CH$_3$ or CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 25.1 (*C*H(CH$_3$)$_2$ or *C*H$_2$CH$_3$ or CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 24. (*C*H(CH$_3$)$_2$ or *C*H$_2$CH$_3$ or CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 22.2 (CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 21.2 (CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 14.6 (CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$), 14.3 (CH$_2$*C*H$_3$ or CH(*C*H$_3$)$_2$ or C(*C*H$_3$)$_3$). **HRMS** (ESI): calc. for $C_{35}H_{51}N_2$ [M+H]$^+$: 499.405 meas. 499.405.

Ligand 16 (^{dipp,dep}Am^{pTol}H)

Route 3: *N*-(2,6-Diisopropylphenyl)-4-methylbenzamide (3.0 g, 10 mmol), phosphorus pentachloride (2.8 g, 13 mmol), 2,6-diethylaniline (1.7 mL, 10 mmol) and triethylamine (1.8 mL, 13 mmol). Yield: 2.94 g (63%) (two step yield 57%).

^{1}H NMR (400 MHz, **Chloroform-*d***) δ 7.12 – 6.58 (m, 10H, Ar*H*), 5.53 (2 x br s, 1H, N*H*), 3.14 (hept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.02 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.71 (dq, $^3J_{HH}$ = 15.0, 7.6 Hz, 2H, CH_2CH$_3$), 2.55 – 2.38 (dq, 2H, CH_2CH$_3$), 2.12 (s, 3H, *p*-CH_3), 1.25 – 1.11 (coincidental d, t, $^3J_{HH}$ = 6.88 Hz, 6H, CH$_2$CH_3), 1.08 (d, $^3J_{HH}$ = 6.85 Hz, 3H, CH(CH_3)$_2$), 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH(CH_3)$_2$), 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.75 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$). **^{1}H NMR** (400 MHz, **Benzene-d_6**) δ 7.63 (dd, *J* = 7.9, 11.6 Hz, 3H, Ar*H*), 7.32 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.25 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.21 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.12 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.06 (q, *J* = 6.6 Hz,

1H, Ar*H*), 6.99 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.93 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.83 (d, *J* = 7.6 Hz, 2H, Ar*H*), 6.76 (p, *J* = 6.9 Hz, 6H, Ar*H*), 5.90 (s, 1H, N*H*), 5.66 (s, 1H, N*H*), 5.60 (s, 1H, N*H* minor), 5.46 (s, 1H, N*H* minor), 3.66 – 3.54 (m, 1H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 3.51 (hept, *J* = 6.5 Hz, 2H, C*H*(CH_3)$_2$), 3.35 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.27 (br. m, 1H, , C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 3.09 (br. m, 1H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 2.83 (br. m, 2H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 2.80 – 2.67 (br. m, 1H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 2.61 – 2.46 (br. m, 1H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 2.46 – 2.31 (br. m, 2H, C*H*(CH_3)$_2$ *or* C$H_2$$CH_3$), 1.92 (s, 2H, *p*-C$H_3$ minor), 1.89 (s, 6H, *p*-CH_3 major), 1.38 (dt, *J* = 7.5, 11.4 Hz, 16H, CH_2CH_3), 1.31 – 1.20 (br. m, 21H, CH_2CH_3 or CH(CH_3)$_2$), 1.11 (br. s, 4H, 21H, CH_2CH_3 or CH(CH_3)$_2$), 1.02 (br. s, 2H, 21H, CH_2CH_3 or CH(CH_3)$_2$), 0.98 – 0.88 (br. m, 13H, 21H, CH_2CH_3 or CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 153.2 (N*C*N), 152.9 (N*C*N), 146.3 (Ar*C*), 145.1 (Ar*C*), 145.0 (Ar*C*), 140.5 (Ar*C*), 139.5 (Ar*C*), 139.3 (Ar*C*), 136.9 (Ar*C*), 135.4 (Ar*C*), 134.8 (Ar*C*), 133.2 (Ar*C*), 132.8 (Ar*C*), 129.4 (Ar*C*), 129.0 (Ar*C*), 128.6 (Ar*C*), 128.6 (Ar*C*), 127.4 (Ar*C*), 127.0 (Ar*C*), 126.9 (Ar*C*), 126.3 (Ar*C*), 125.9 (Ar*C*), 124.0 (Ar*C*), 123.9 (Ar*C*), 123.8 (Ar*C*), 123.7 (Ar*C*), 123.3 (Ar*C*), 122.7 (Ar*C*), 122.3 (Ar*C*), 29.0 (*C*H(CH_3)$_2$), 29.0 (*C*H(CH_3)$_2$), 28.7 (*C*H(CH_3)$_2$), 25.1 (*C*H(CH_3)$_2$ or CH(*C*H_3)$_2$ or *C*$H_2$$CH_3$), 24.9 (*C*H($CH_3$)$_2$ or CH(*C*H_3)$_2$ or *C*$H_2$$CH_3$), 24.7 (*C*H($CH_3$)$_2$ or CH(*C*H_3)$_2$ or *C*$H_2$$CH_3$), 24.6 (*C*H($CH_3$)$_2$ or CH(*C*H_3)$_2$ or *C*$H_2$$CH_3$), 24.2 (*C*H($CH_3$)$_2$ or CH(*C*H_3)$_2$ or *C*$H_2$$CH_3$), 22.9 (CH(*C*$H_3$)$_2$ or CH_2*C*H_3), 22.6 (CH(*C*H_3)$_2$ or CH_2*C*H_3), 22.4 (CH(*C*H_3)$_2$ or CH_2*C*H_3), 21.1 (*p*-*C*H_3), 14.5 (CH(*C*H_3)$_2$ or CH_2*C*H_3), 14.3 (CH(*C*H_3)$_2$ or CH_2*C*H_3). **HRMS** (ESI): calc. for $C_{30}H_{39}N_2$ $[M+H]^+$: 427.311 meas. 427.315.

Ligand 17 (dipp,Ar*Am*p*TolH)

Route 3: has been reported previously[10], now with an improved yield of 81%.

Ligand 18 (mes,Ar*Am*p*TolH)

Route 3: has been reported previously[10], now with an improved yield of 71%.

Ligand 19 (depAm*p*TolH)

Route 3: *N*-(2,6-diethylphenyl)-4-methylbenzamide (5.6 g, 20.8 mmol, 1 equiv.), phosphorus pentachloride (5.2 g, 24.9 mmol, 1.2 equivs), 2,6-diethylaniline (3.4 mL, 20.8 mmol, 1 equiv.) and triethylamine (3.76 mL, 27.0 mmol). Yield: 5.1 g (62%) (two step yield 56%).

^{1}H NMR (400 MHz, **Chloroform-*d***) δ 7.33 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.18 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.11 – 6.93 (m, 3H, Ar*H*), 5.70 (s, 1H, N*H*), 2.86 (dq, *J* = 7.5, 15.0 Hz, 2H, C$H_2$$CH_3$), 2.69 – 2.53 (m, 3H, C$H_2$$CH_3$), 2.38 (dq, *J* = 7.6 Hz, 1H, C$H_2$$CH_3$), 2.28 (s, 3H, *p*-C$H_3$), 1.31 (t, *J* = 7.5 Hz, 6H, CH_2*C*H_3), 1.02 (t, *J* = 7.5 Hz, 6H, CH_2*C*H_3). **^{1}H NMR** (400 MHz, **Benzene-*d*$_6$**) δ 7.64 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.30 – 7.23 (m, 3H, Ar*H*), 7.14 – 7.10 (m, 1H, Ar*H*), 6.96 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.80 (dd, *J* = 7.8, 11.9 Hz, 3H), 6.73 (d, *J* = 7.7 Hz, 1H, Ar*H*), 5.70 (s, 1H, N*H* major), 5.40 (s, 1H, N*H* minor), 3.07 (dq, *J* = 7.5, 14.9 Hz, 2H, C$H_2$$CH_3$), 2.85 (br. m, 2H, C$H_2$$CH_3$), 2.71 (dq, *J* = 7.5, 14.8 Hz, 2H, C$H_2$$CH_3$), 2.56 (dq, *J* = 7.8, 11.0 Hz, 1H, C$H_2$$CH_3$), 2.44 – 2.29 (br. m, 2H, C$H_2$$CH_3$), 1.90 (s, 3H, *p*-

CH_3), 1.37 (t, J = 7.5 Hz, 6H, CH_2CH_3), 1.24 (br. m, 4H, CH_2CH_3), 1.10 (br. m, 1H, CH_2CH_3), 0.91 (t, J = 7.6 Hz, 6H, CH_2CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 152.9 (N*C*N), 146.3 (Ar*C*), 140.7 (Ar*C*), 139.5 (Ar*C*), 137.0 (Ar*C*), 134.8 (Ar*C*), 133.2 (Ar*C*), 129.2 (Ar*C*), 129.0 (Ar*C*), 128.6 (Ar*C*), 127.1 (Ar*C*), 126.9 (Ar*C*), 126.6 (Ar*C*), 126.1 (Ar*C*), 123.5 (Ar*C*), 25.2 (CH_2CH_3), 25.1 (CH_2CH_3), 21.1 (*p*-CH_3), 14.5 (CH_2CH_3), 14.3 (CH_2CH_3). **HRMS** (ESI): calc. for $C_{30}H_{39}N_2$ [M+H]$^+$: 399.280 meas. 399.279. (data matches previous reports[14])

Ligand 20 (^{dep}Am^{mes}H)

Route 1: 2,4,6-Trimethylbenzoic acid (1.445 g, 8.8 mmol, 1 equiv.), 2,6-diethylaniline (3.044 ml, 1.85 mmol, 2.1 equiv.). Recrystallised from ethanol. Yield: 1.34 g (36%).

Route 2: Mesityl lithium (1.00 g, 7.93 mmol, 1 equiv.), *bis*(2,6-diethylphenyl)carbodiimide (2.43 g, 7.93 mmol, 1 equiv.), ethanol. Yield: 0.72 g (17%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.09 – 6.70 (br. m, 1H, Ar*H*), 6.60 (s, 2H, Ar*H*), 6.41 (s, 1H, N*H* major), 5.29 (s, 1H, N*H* minor), 3.17 (br. m, 1H, CH_2CH_3), 3.06 (br. m, 1H, , CH_2CH_3), 2.77 (br. m, 4H, , CH_2CH_3), 2.51 (br. m, 1H, CH_2CH_3), 2.39 (s, 6H, *o*-CH_3), 2.00 (s, 3H, *p*-CH_3), 1.31 (br. m, 4H, CH_2CH_3), 1.20 (br. m, 1H, CH_2CH_3), 1.02 – 0.91 (br. m, 1H, CH_2CH_3), 0.79 (br. m, 4H, CH_2CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 145.5 (Ar*C*), 138.0 (Ar*C*), 136.8 (Ar*C*), 135.1 (Ar*C*), 129.4 (Ar*C*), 126.4 (Ar*C*), 25.7 (*o*-CH_3), 25.1 (CH_2CH_3), 21.1 (CH_2CH_3), 20.9 (*p*-CH_3), 14.6 (CH_2CH_3). **HRMS** (ESI): calc. for $C_{30}H_{39}N_2$ [M+H]$^+$: 427.311 meas. 427.312.

Ligand 21 (^{dep}Am$^{t\text{Bu}}$H)

Route 3: *N*-(2,6-Diethylphenyl)pivalamide (3.40 g, 14.57 mmol), phosphorus pentachloride (3.64 g, 17.48 mmol), 2,6-diethylaniline added (2.40 mL, 14.57 mmol) and triethylamine (2.64 mL, 18.94 mmol). Yield: 3.08 g (58%) (two step yield 48%).

^{1}H NMR (400 MHz, **Chloroform-*d***) δ 7.15 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 7.02 (dd, $^{3}J_{HH}$ = 15.2, 7.5 Hz, 3H, Ar*H*), 6.86 (s, 1H, Ar*H*), 5.40 (s, 1H, N*H*), 2.71 (br s, 5H, CH_2CH_3), 2.58 (br. m, $^{3}J_{HH}$ = 7.5 Hz, 1H, CH_2CH_3), 2.47 (dq, $^{3}J_{HH}$ = 14.9, 7.5 Hz, 2H, CH_2CH_3), 1.25 (s, 9H, *p*-CH_3), 1.22 – 1.19 (m, 12H, CH_2CH_3), 1.16 – 1.11 (m, 6H, CH_2CH_3). **^{1}H NMR** (400 MHz, **Benzene-*d*$_6$**) δ 7.11 – 7.00 (m, 3H, Ar*H*), 7.00 – 6.85 (m, 3H, Ar*H*), 5.27 (s, 1H, N*H*), 2.71 – 2.61 (m, 7H, CH_2CH_3), 2.54 (dq, J = 14.6, 7.5 Hz, 2H, CH_2CH_3), 1.24 (s, 9H, $C(CH_3)_3$), 1.20 (s, 6H, CH_2CH_3), 1.06 – 0.98 (m, 6H, CH_2CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ = 158.9 (N*C*N), 146.6 (Ar*C*), 143.0 (Ar*C*), 137.4 (Ar*C*), 133.4 (Ar*C*), 132.8 (Ar*C*), 126.2 (Ar*C*), 122.1 (Ar*C*), 39.6 ($C(CH_3)_3$), 29.7 (CH_2CH_3), 25.5 (CH_2CH_3), 14.8 (CH_2CH_3), 14.3 ($C(CH_3)_3$). **HRMS** (ESI): calc. for $C_{25}H_{37}N_2$ [M+H]$^+$: 365.296 meas. 365.298.

Ligand 22 (^{dep}Am^{Ad}H)

Route 1: Adamantane-1-carboxylic acid (1.59 g, 8.8 mmol, 1 equiv), 2,6-diethylaniline (2.97 ml, 18.0 mmol, 2.05 equiv.), extracted into hexane and washed with warm ethanol. Yield: 1.25 g (46%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.06 (s, 3H, Ar*H*), 7.06 – 7.00 (m, 1H, Ar*H*), 6.96 (d, *J* = 6.7 Hz, 1H, Ar*H*), 6.90 (d, *J* = 7.6 Hz, 2H, Ar*H*), 6.20 (s, 1H, N*H* minor), 5.33 (s, 1H, N*H* major), 2.80 (s, 2H, CH_2CH$_3$), 2.73 – 2.62 (m, 4H, CH_2CH$_3$), 2.54 (dq, *J* = 7.4, 10.4 Hz, 2H, CH_2CH$_3$), 2.08 (s, 6H, Ad*H*), 1.84 (t, *J* = 3.3 Hz, 3H, Ad*H*), 1.59 (d, *J* = 6.3 Hz, 1H, Ad*H*), 1.54 (d, *J* = 3.2 Hz, 6H, Ad*H*), 1.27 (v. br. t, *J* = 7.3 Hz, 6H, CH$_2$CH_3), 1.06 (v. br. t, 6H, CH$_2$CH_3). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ = 152.3 (N*C*N), 146.7 (Ar*C*), 142.9 (Ar*C*), 137.3 (Ar*C*), 134.0 (Ar*C*), 133.1 (Ar*C*), 126.5 (Ar*C*), 126.1 (Ar*C*), 121.8 (Ar*C*), 41.1 (Ad*C*), 36.9 (Ad*C*), 36.8 (Ad*C*), 29.0 (Ad*C*), 28.7 (Ad*C*), 25.6 (*C*H$_2$CH$_3$), 25.4 (*C*H$_2$CH$_3$), 14.8 (CH$_2$*C*H$_3$), 14.8 (CH$_2$*C*H$_3$), 14.4 (CH$_2$*C*H$_3$). **HRMS** (ESI): calc. for $C_{31}H_{43}N_2$ $[M+H]^+$: 443.343 meas. 443.342.

Ligand 23 (^{Ar*}Am^{pTol}H)

Route 3: has been reported previously[10], now with an improved yield of 67%.

Ligand recycling procedure

Under an inert atmosphere, the aluminium complex (*ca*. 1.2 g) was quenched with isopropanol (excess) and water (excess). To the resultant suspension was added an aqueous 1 M ammonium chloride solution (excess), which was stirred for 1 hour. The organic phase was extracted into DCM, washed with brine and dried over $MgSO_4$. Volatiles were removed *in vacuo* to afford the pro-ligand in a yield of approximately 1 g as a colourless solid (*ca.* 95% recovery).

Aluminium hydride syntheses

^{dipp}Am^{R}AlH$_2$ general synthesis

To a flask charged with a toluene solution of AlH_3•NMe_3 (1.2 equivs) cooled to -10 °C was added a toluene solution of pro-ligand (1 equiv.) dropwise over a period of 30 minutes. The resultant solution was stirred at this temperature for a further 90 minutes before being warmed to room temperature and stirred for a further hour. The reaction was then filtered if precipitate was observed and the solvent was then removed *in vacuo*.

1-Al (^{dipp}Am^{pTol}AlH$_2$)

Has been reported previously[10]

2-Al (^{dipp}Am^{tBuPh}AlH$_2$)

AlH_3•NMe_3 (0.59 g, 6.64 mmol, 1.1 equiv.), **2** (3.0 g, 6.04 mmol, 1 equiv.). Extracted solid into hexane, crystallised at -20 °C. Yield: 1.10 g (42 %).

2-Al: ^{1}H NMR (400 MHz, **Benzene-d_6**) *δ* 7.24 – 7.19 (m, 2H, Ar*H*), 7.08 – 7.04 (m, 6H, Ar*H*), 6.85 – 6.79 (m, 4H, Ar*H*), 5.05 (s, 2H, AlH_2), 3.70 (hept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.32 (d, *J* = 6.8 Hz, 12H, C*H*(CH$_3$)$_2$), 1.03 (d, *J* = 6.9 Hz, 12H, C*H*(CH$_3$)$_2$), 0.82 (s, 9H, C(CH_3)$_3$).

[2-Al.3THF]: ^{1}H NMR (700 MHz, **Benzene-d_6**) δ 7.30 (d, J = 8.6 Hz, 2H, Ar*H*), 7.11 (q, J = 5.3 Hz, 6H, Ar*H*), 6.90 – 6.87 (m, 2H, Ar*H*), 4.64 (s, 2H, AlH_2), 3.89 (hept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 3.60 – 3.54 (m, 6H, THF-CH_2), 1.39 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.25 (m, 6H, THF-CH_2), 1.09 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 0.87 (s, 9H, C(CH_3)$_2$).

[(2-Al)$_2$.Tol]: ^{1}H NMR (400 MHz, **Benzene-d_6**): δ 7.21 (d, 4H, J = 8.7 Hz, Ar*H*), 7.05 (m, 12H, *Ar*H), 6.82 (d, 4H, J = 8.7 Hz, Ar*H*), 5.02 (br. s, 4H, AlH_2), 3.71 (hept, 8H, J = 6.8 Hz, ArC*H*(CH_3)$_2$), 2.22 (s, 3H, Tol-CH_3) 1.32 (d, 24H, J = 6.8 Hz, ArCH(CH_3)$_2$), 1.03 (d, 24H, J = 6.9 Hz, J = 6.8 Hz, ArCH(CH_3)$_2$), 0.81 (s, 18H, ArC(CH_3)$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 173.7 (N*C*N), 154.6 (*C*-C(CH_3)$_3$), 144.0 (Ar*C*), 138.4 (Ar*C*), 130.2 (Ar*C*), 126.5 (Ar*C*), 126.3 (Ar*C*), 125.0 (Ar*C*), 124.0 (Ar*C*), 34.6 (*C*(CH_3)$_3$), 30.7 (C(*C*H_3)$_3$), 29.0 (*C*H(CH_3)$_2$), 25.7 (CH(*C*H_3)$_2$), 22.9 (CH(*C*H_3)$_2$).

3-Al (^{dipp}Am^{DMAPh}AlH$_2$)

AlH_3•NMe_3 (0.26 g, 2.95 mmol, 1.2 equiv.), **3** (1.2 g, 2.46 mmol, 1 equiv.). Extracted twice into toluene and washed with hexane. Yield: 0.76 g (60%)

^{1}H NMR (400 MHz, **Benzene-d_6**): δ 7.22 – 7.17 (m, 2H, Ar*H*), 7.13 – 7.11 (m, 6H, Ar*H*), 7.02 (d, 1H, J = 7.5 Hz, Ar*H*), 5.94 (d, 2H, J = 7.7 Hz, Ar*H*), 5.02 (s, 2H, AlH_2), 3.83 (hept, 4H, J = 6.4 Hz, ArC*H*(CH_3)$_2$), 1.99 (s, 6H, ArN(CH_3)$_2$), 1.36 (d, 12H, J = 6.4 Hz, ArCH(CH_3)$_2$), 1.13 (d, 12H, J = 6.6 Hz, ArCH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 174.0 (N*C*N), 151.3 (Ar*C*), 144.2 (Ar*C*), 139.4 (Ar*C*), 132.1 (Ar*C*), 129.3 (Ar*C*), 128.6 (Ar*C*), 125.9 (Ar*C*), 125.7 (Ar*C*), 124.0 (Ar*C*), 116.1 (Ar*C*), 110.4 (Ar*C*), 38.9 (ArN(*C*H_3)$_2$), 29.0 (Ar*C*H(CH_3)$_2$), 25.7 (ArCH(*C*H_3)$_2$), 23.2(ArCH(*C*H_3)$_2$), 21.4 (Tol-*C*H_3).

4-Al (^{dipp}Am$^{p\text{OMe}}$AlH$_2$)

AlH_3•NMe_3 (247 mg, 2.77 mmol, 1.2 equivs), **4** (1.09 g, 2.31 mmol, 1 equiv.). Recrystallised from toluene. Yield: 0.65 g (51%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.20 – 7.17 (m, 2H, Ar*H*), 7.07 (q, J = 5.3 Hz, 6H, Ar*H*), 6.28 – 6.18 (m, 2H, Ar*H*), 5.02 (s, 2H, AlH_2), 3.72 (hept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 2.84 (s, 3H, *p*-OCH_3), 1.32 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.05 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 173.4 (N*C*N), 161.6 (Ar*C*), 144.2 (Ar*C*), 138.6 (Ar*C*), 132.3 (Ar*C*), 129.3 (Ar*C*), 126.2 (Ar*C*), 124.0 (Ar*C*), 121.5 (Ar*C*), 113.4 (Ar*C*), 54.5 (*p*-O*C*H_3), 28.9 (Ar*C*H(CH_3)$_2$), 25.7 (ArCH(*C*H_3)$_2$), 23.1 (ArCH(*C*H_3)$_2$).

5-Al (^{dipp}Am$^{p\text{CN}}$AlH$_2$)

AlH_3•NMe_3 (0.233 g, 2.62 mmol, 1.2 equiv.), **5** (1.02 g, 2.09 mmol, 1 equiv.). Pale brown solid afforded, found to be insoluble in all hydrocarbon solvents.

6-Al ($^{dipp}Am^{pCF3}AlH_2$)

AlH_3•NMe_3 (212 mg, 2.38 mmol, 1.2 equivs), **6** (1.01 g, 1.98 mmol, 1 equiv.). Recrystallised from toluene and washed with hexane. Yield: 0.95 g (90%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.15 – 6.95 (m, 12H, Ar*H*), 6.78 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.92 (s, 2H, AlH_2), 3.53 (hept, *J* = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.25 (d, *J* = 6.7 Hz, 12H, CH(CH_3)$_2$), 0.92 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) *δ* 171.9 (N*C*N), 143.9 (Ar*C*), 137.4 (Ar*C*), 132.0 (Ar*C*), 130.5 (Ar*C*), 129.3 (Ar*C*), 126.7 (Ar*C*), 125.7 (Ar*C*), 125.0 (q, *C*F_3), 124.1 (Ar*C*), 28.9 (*C*H(CH_3)$_2$), 25.7 (CH(*C*H_3)$_2$), 22.8 (CH(*C*H_3)$_2$). **^{19}F{^{1}H} NMR** (376 MHz, **Benzene-d_6**) δ -63.0 (CF_3).

7-Al ($^{dipp}Am^{mXyl}AlH_2$)

AlH_3•NMe_3 (495 mg, 5.55 mmol, 1.2 equiv.), **7** (2.17 g, 4.62 mmol, 1 equiv.) The product was obtained as a colourless crystalline solid *via* storage of a concentrated hexane solution at -20 °C for 3 days. Yield: 1.38 g (60%).

^{1}H NMR (600 MHz, **Benzene-d_6**) δ 7.10 – 6.95 (m, 6H, Ar*H*), 6.84 (d, *J* = 1.7 Hz, 2H, Xyl-*o*-*H*), 6.41 (s, 1H, Xyl-*p*-*H*), 4.94 (s, 2H, AlH_2), 3.70 (hept, *J* = 6.8 Hz, 4H, ArCH(CH_3)$_2$), 1.76 (s, 6H, Xyl-CH_3), 1.32 (d, *J* = 6.8 Hz, 12H, ArCH(CH_3)$_2$), 1.06 (d, *J* = 6.9 Hz, 12H, ArCH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 174.5 (N*C*N), 144.3 (Ar*C*), 138.3 (Ar*C*), 137.3 (Ar*C*), 132.2 (Ar*C*), 129.2 (Ar*C*), 126.2 (Ar*C*), 123.8 (Ar*C*), 28.9 (*C*H(CH_3)$_2$), 25.9 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$), 20.8 (*m*-*C*H_3).

8-Al ($^{dipp}Am^{oTol}AlH_2$)

AlH_3•NMe_3 (0.255 g, 2.86 mmol), **8** (1.08 g, 2.38 mmol). The product was obtained as a colourless crystalline solid *via* storage of a concentrated hexane solution at -20 °C for 3 days. Yield: 0.68 g (60%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.01 (d, *J* = 6.4 Hz, 1H, *o*Tol*H*), 7.02 – 6.93 (m, 6H, Ar*H*), 6.64 (t, *J* = 7.4 Hz, 1H, *o*Tol*H*), 6.55 (t, *J* = 7.5 Hz, 1H, *o*Tol*H*), 6.47 (d, *J* = 7.6 Hz, 1H, *o*Tol*H*), 5.08 (s, 2H, AlH_2), 3.65 (hept, *J* = 6.0 Hz, 2H, C*H*(CH_3)$_2$), 3.56 (hept, *J* = 6.5 Hz, 2H, C*H*(CH_3)$_2$), 2.04 (s, 3H, *o*Tol-CH_3), 1.29 (d, *J* = 6.1 Hz, 6H, CH(CH_3)$_2$), 1.22 (d, *J* = 6.1 Hz, 6H, CH(CH_3)$_2$), 1.03 (d, *J* = 6.3 Hz, 6H, CH(CH_3)$_2$), 0.95 (d, *J* = 6.4 Hz, 6H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 176.1 (N*C*N), 144.1 (Ar*C*), 143.8 (Ar*C*), 137.5 (*o*-Tol*C*), 131.2 (Ar*C*), 130.9 (*o*-Tol*C*), 130.2 (*o*-Tol*C*), 129.5 (Ar*C*), 129.3 (Ar*C*), 128.6 (Ar*C*), 126.2 (Ar*C*), 125.7 (Ar*C*), 125.0 (*o*-Tol*C*), 123.8 (Ar*C*), 123.7 (Ar*C*), 29.2 (*C*H(CH_3)$_2$), 28.7 (*C*H(CH_3)$_2$), 26.6 (CH(*C*H_3)$_2$), 26.5 (CH(*C*H_3)$_2$), 22.6 (CH(*C*H_3)$_2$), 22.4 (CH(*C*H_3)$_2$), 20.3 (*o*-*C*H_3).

9-Al (^{dipp}Am^{2,4Xyl}AlH$_2$)

AlH_3•NMe_3 (361 mg, 4.05 mmol, 1.2 equiv.), **9** (1.58 g, 3.38 mmol, 1 equiv.). The product was obtained as a colourless crystalline solid *via* storage of a concentrated hexane solution at -20 °C for 3 days. Yield: 0.96 g (57%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**): δ 7.07 (d, 1H, *J* = 8.0 Hz, Ar*H*), 7.04 – 6.96 (m, 6H, Ar*H*), 6.36 (dd, 1H, *J* = 8.2, 1.8 Hz, Ar*H*), 6.31 (d, 1H, *J* = 1.7 Hz, Ar*H*), 5.05 (br. s, 2H, AlH_2), 3.69 (hept, 2H, *J* = 6.8 Hz, ArC*H*(CH$_3$)$_2$), 3.61 (hept, 2H, *J* = 6.8 Hz, ArC*H*(CH$_3$)$_2$), 2.06 (s, 3H, Xyl-CH_3), 1.67 (s, 3H, Xyl-CH_3), 1.33 (d, 6H, *J* = 6.7 Hz, ArCH(CH_3)$_2$), 1.21 (d, 6H, *J* = 6.7 Hz, ArCH(CH_3)$_2$), 1.07 (d, 6H, *J* = 6.9 Hz, ArCH(CH_3)$_2$), 0.99 (d, 6H, *J* = 6.9 Hz, ArCH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 176.6 (N*C*N), 144.1 (Ar*C*), 143.8 (Ar*C*), 140.4 (Ar*C*), 137.6 (Ar*C*), 137.4 (Ar*C*), 131.6 (Ar*C*), 131.2 (Ar*C*), 126.7 (Ar*C*), 126.2 (Ar*C*), 126.1 (Ar*C*), 123.8 (Ar*C*), 123.7 (Ar*C*), 29.2 (*C*H(CH$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$), 22.3 (CH(*C*H$_3$)$_2$), 20.8 (2,4-xyl-*C*H$_3$), 20.2 (2,4-xyl-*C*H$_3$).

10-Al (^{dipp}Am$^{o\text{Xyl}}$AlH$_2$)

AlH_3•NMe_3 (228 mg, 2.56 mmol, 1.2 equiv.), **10** (1.0 g, 2.13 mmol, 1 equiv.). The storage of a concentrated hexane solution at -40 °C for 16 hours afforded the product as a colourless crystalline solid. Yield: 0.7 g (55%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.03 – 6.96 (m, 6H, Ar*H*), 6.67 (t, 1H, *J* = 7.6 Hz, Ar*H*), 6.42 (d, 2H, *J* = 7.6 Hz, Ar*H*), 5.11 (br. s, 2H, AlH_2), 3.54 (br. hept, 4H, *J* = 7.0 Hz, Ar*C*H(CH$_3$)$_2$), 2.06 (s, 6H, Xyl-CH_3), 1.21 (d, 12H, *J* = 6.8 Hz, , ArCH(CH_3)$_2$), 0.90 (br. d, 12H, *J* = 6.8 Hz, ArCH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 176.2 (N*C*N), 143.3 (Ar*C*), 138.0 (Ar*C*), 137.3 (Ar*C*), 129.9 (Ar*C*), 129.8 (Ar*C*), 129.0 (Ar*C*), 126.1 (Ar*C*), 123.8 (Ar*C*), 28.8 (*C*H(CH$_3$)$_2$), 27.0 (CH(*C*H$_3$)$_2$), 21.5 (CH(*C*H$_3$)$_2$), 21.1 (CH(*C*H$_3$)$_2$).

11-Al (^{dipp}Am^{mes}AlH$_2$)

AlH_3•NMe_3 (325 mg, 3.64 mmol, 1.2 equiv.), **11** (1.46 g, 3.04 mmol, 1 equiv.) The product was obtained as a colourless crystalline solid *via* storage of a concentrated hexane solution at -20 °C for 3 days. Yield: 1.16 g (75%)

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.01 (s, 6H, dipp*H*), 6.28 (br. s, 2H, mes*H*), 5.12 (s, 2H, AlH_2), 3.58 (br. hept, 4H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 2.08 (s, 6H, *o*-CH_3), 1.75 (s, 3H, *p*-CH_3), 1.23 (br. d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 0.94 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 176.7 (N*C*N), 143.4 (dipp*C*), 139.8 (mes*C*), 137.9 (mes*C*), 137.4 (dipp*C*), 129.9 (mes*C*), 127.1 (mes*C*), 126.0 (dipp*C*), 123.8 (dipp*C*), 28.8 (*C*H(CH$_3$)$_2$), 27.0 (CH(*C*H$_3$)$_2$), 21.6 (CH(*C*H$_3$)$_2$), 21.0 (*o*-*C*H$_3$), 20.6 (*p*-*C*H$_3$).

13-Al ($^{dipp}Am^{tBu}AlH_2$)

Has been previously reported

17-Al ($^{dipp,Ar*}Am^{pTol}AlH_2$)

Has been previously reported[10]

18-Al ($^{mes,Ar*}Am^{pTol}AlH_2$)

Has been previously reported[10]

23-Al ($^{Ar*}Am^{pTol}AlH_2$)

Has been previously reported[10]

Non-standard aluminium hydride syntheses

12-Al ($^{dipp}Am^{dipp}AlH_2$)

A flask charged with a toluene suspension of **12** (1.04 g, 1.98 mmol, 1 equiv.) and $AlH_3.NMe_3$ (352 mg, 3.95 mmol, 2 equivs) fitted with a reflux condenser was heated to 100 °C for 16 hours. The resultant turbid grey suspension is allowed to cool to room temperature, settled and filtered. The toluene was removed *in vacuo* and the product washed with hexane to afford the product as a colourless solid. Yield: 612 mg (55%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.11 (dd, 2H, *J* = 7.7, 1.7 Hz, Ar*H*), 7.02 – 6.95 (m, 3H, Ar*H*), 6.92 – 6.88 (m, 4H, Ar*H*), 5.04 (s, 2H, AlH_2), 4.10 (hept, 2H, *J* = 6.7 Hz, ArC*H*$(CH_3)_2$), 3.11 (hept, 2H, *J* = 6.6 Hz, ArC*H*$(CH_3)_2$), 2.95 (hept, 2H, *J* = 6.7 Hz, ArC*H*$(CH_3)_2$), 1.32 (v t, 12H, *J* = 6.7 Hz, ArCH(C$H_3)_2$), 1.23 (d, 6H, *J* = 6.7 Hz, ArCH(C$H_3)_2$), 1.14 (d, 6H, *J* = 6.8 Hz, ArCH(C$H_3)_2$), 0.36 (d, 6H, *J* = 6.7 Hz, ArCH(C$H_3)_2$), 0.18 (d, 6H, *J* = 6.5 Hz, ArCH(C$H_3)_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, **C_6D_6**) δ 173.4 (N*C*N), 148.6 (Ar*C*), 144.0 (Ar*C*), 142.1 (Ar*C*), 137.6 (Ar*C*), 131.2 (Ar*C*), 126.0 (Ar*C*), 126.0 (Ar*C*), 124.9 (Ar*C*), 124.8 (Ar*C*), 30.9 (Ar*C*H$(CH_3)_2$), 28.9 (Ar*C*H$(CH_3)_2$), 28.9 (Ar*C*H$(CH_3)_2$), 28.4(Ar*C*H$(CH_3)_2$) (Ar*C*H$(CH_3)_2$), 25.8 (ArCH(*C*$H_3)_2$), 25.4 (ArCH(*C*$H_3)_2$), 24.4 (ArCH(*C*$H_3)_2$), 21.8 (ArCH(*C*$H_3)_2$), 21.8 (ArCH(*C*$H_3)_2$) ppm.

15-Al ($^{dipp,dep}Am^{tBu}AlH_2$)

15 (0.65 g, 1.78 mmol, 1 equiv.) in toluene solution was cooled to -78 °C and added dropwise over 20 minutes to a solution of AlH_3•NMe_3 (0.19 g, 2.14 mmol, 1.2 equiv.) in toluene at -78 °C. The reaction was allowed to warm to room temperature and stirred for 16 hours. The solvent was removed *in vacuo* to afford white powder. Colourless crystals were obtained by recrystallisation from toluene. Yield: 443 mg (64%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.09 – 6.95 (m, 6H, Ar*H*), 4.69 (br. s, 2H, AlH_2), 3.57 (hept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 3.10 (dq, $^3J_{HH}$ = 14.9, 7.5 Hz, 2H, CH_2CH_3), 2.63 (dq, $^3J_{HH}$ = 15.0, 7.5 Hz, 2H, CH_2CH_3), 1.29 (dd, $^3J_{HH}$ = 6.8, 3.3 Hz, 12H, CH(C$H_3)_2$), 1.25 (t, $^3J_{HH}$ = 7.5 Hz, 6H,

CH_2CH_3), 0.86 (s, 9H, $C(CH_3)_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, **Benzene-d_6**) δ 181.1 (N*C*N), 144.3 (Ar*C*), 140.6 (Ar*C*), 140.0 (Ar*C*), 139.2 (Ar*C*), 126.1 (Ar*C*), 125.7 (Ar*C*), 123.6 (Ar*C*), 41.2 ($C(CH_3)_3$), 28.8 ($C(CH_3)_3$), 28.8 ($CH(CH_3)_2$), 27.0 ($CH(CH_3)_2$), 25.2 (CH_2CH_3), 22.8 ($CH(CH_3)_2$), 15.0 (CH_2CH_3).

20-Al ($^{dep}Am^{mes}AlH_2$)

A solution of **20** (541 g, 1.27 mmol, 1 equiv.) in tetrahydrofuran (THF) was added dropwise over 20 minutes to a solution of AlH_3•NMe_3 (0.14 g, 1.52 mmol, 1.2 equiv.) in THF at -78 °C. The reaction was allowed to warm to room temperature and stirred for 16 hours. The solvent was removed *in vacuo* to afford a colourless solid. The solid was washed with hexane and dried *in vacuo* to afford a colourless solid. Yield: 521 mg (90%).

^1H NMR (400 MHz, **Benzene-d_6**) δ 6.96 – 6.87 (m, 6H, Ar*H*), 6.29 (s, 2H, *m-H*), 5.06 (s, 2H, AlH_2), 3.09 (dq, *J* = 7.5, 14.9 Hz, 4H, CH_2CH_3), 2.45 (dq, *J* = 7.5, 15.0 Hz, 4H, CH_2CH_3), 2.10 (s, 6H, *o*-CH_3), 1.72 (s, 3H, *p*-CH_3), 1.14 (t, *J* = 7.5 Hz, 12H, CH_2CH_3). **$^{13}C\{^1H\}$ NMR** (101 MHz, **Benzene-d_6**) δ 176.4 (N*C*N), 139.8 (Ar*C*), 139.4 (Ar*C*), 139.0 (Ar*C*), 137.6 (Ar*C*), 129.7 (Ar*C*), 126.6 (Ar*C*), 125.3 (Ar*C*), 25.7 (CH_2CH_3), 21.4 (*o*-CH_3), 20.7 (*p*-CH_3), 15.5 (CH_2CH_3).

21-Al ($^{dep}Am^{tBu}AlH_2$)

A solution of **21** (1.00 g, 2.74 mmol, 1 equiv.) in THF was added dropwise over 20 minutes to a solution of AlH_3•NMe_3 (0.29 g, 3.29 mmol, 1.2 equiv) in THF at -78 °C. The reaction was allowed to warm to room temperature and stirred for 16 hours. The solvent was removed *in vacuo* to afford an oily solid. The solid was washed with hexane and dried *in vacuo* to afford a colourless solid. Yield: 252 mg (26%).

^1H NMR (400 MHz, **Benzene-d_6**) δ 6.98 – 6.93 (m, 6H, Ar*H*), 4.57 (br. s, 2H, AlH_2), 3.09 (dq, *J* = 14.9, 7.5 Hz, 4H, CH_2CH_3), 2.61 (dq, *J* = 15.0, 7.6 Hz, 4H, CH_2CH_3), 1.24 (t, *J* = 7.5 Hz, 12H, CH_2CH_3), 0.80 (s, 9H, $C(CH_3)_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, **Benzene-d_6**) *δ* 181.2 (N*C*N), 140.6 (Ar*C*), 139.7(Ar*C*), 125.8(Ar*C*), 125.6(Ar*C*), 40.7 ($C(CH_3)_3$), 28.4 ($C(CH_3)_3$), 25.2 (CH_2CH_3), 15.1 (CH_2CH_3).

22-Al ($^{dep}Am^{Ad}AlH_2$)

A solution of **22** (1.00 g, 2.26 mmol, 1 equiv.) in THF was added dropwise over 20 minutes to a solution of AlH_3•NMe_3 (0.241 g, 2.71 mmol, 1.2 equiv.) in THF at -78 °C. The reaction was allowed to warm to room temperature and stirred for 16 hours. The solvent was removed *in vacuo* to afford colourless foam. The foam was washed with hexane and dried *in vacuo* to afford a colourless solid. Yield: 385 mg (36%).

^1H NMR (400 MHz, **Benzene-d_6**) δ 7.03 – 6.93 (m, 6H, Ar*H*), 4.61 (s, 2H, AlH_2), 3.24 – 3.06 (m, 4H, CH_2CH_3), 2.83 – 2.64 (m, 4H, CH_2CH_3), 1.82 (s, 6H, Ad*H*), 1.49 (s, 3H, Ad*H*), 1.30 (td, *J* = 1.7, 7.5 Hz, 12H, CH_2CH_3), 1.20 (s, 6H, Ad*H*). **$^{13}C\{^1H\}$ NMR** (101 MHz, **Benzene-d_6**) δ 180.6 (N*C*N), 141.0 (Ar*C*),

139.5 (Ar*C*), 125.8 (Ar*C*), 125.5 (Ar*C*), 44.6 (Ad*C*), 38.4 (Ad*C*), 36.1 (Ad*C*), 28.2 (Ad*C*), 25.3 (*C*H_2CH$_3$), 15.1 (CH$_2$*C*H$_3$).

Bis-ligated aluminium hydride syntheses

1-Al'' (^{dipp}Am$^{p\text{-}tol}$)$_2$AlH

To a flask charged with a toluene solution of **1** (1.0 g, 2.20 mmol, 2 equivs) was added a toluene solution of AlH$_3$•NMe$_3$ (0.096 g, 1.10 mmol, 1 equiv.). The resultant solution was stirred overnight at room temperature, filtered and white solid was washed with toluene. Yield: 740 mg (69%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.09 – 6.91 (m, 14H, Ar*H*), 6.40 (d, *J* = 8.1 Hz, 4H, Ar*H*), 3. 3.91 (hept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.47 (hept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.28 (hept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$) 1.65 (s, 6H, *p*-C*H*$_3$), 1.56 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.49 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.88 (overlapping d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$)), 0.65 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.62 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.55 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.39(d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR**: Could not obtained due to low solubility.

2-Al'' (^{dipp}Am$^{pt\text{BuPh}}$)$_2$AlH

To a flask charged with a toluene solution of **2** (1.2 g, 2.36 mmol, 2.1 equivs) was added a toluene solution of AlH$_3$•NMe$_3$ (0.1 g, 1.12 mmol, 1 equiv.). The resultant solution was stirred overnight at room temperature, filtered and white solid was washed with hexane. Yield: 642 mg (56%).

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) *δ* 7.18 (d, *J* = 1.6 Hz, 1H, Ar*H*), 7.15 – 7.06 (m, 8H, Ar*H*), 7.06 – 7.02 (m, 2H, Ar*H*), 6.96 (dd, *J* = 1.6, 7.8 Hz, 2H, Ar*H*), 6.81 (dq, *J* = 2.5, 9.3 Hz, 4H, Ar*H*), 5.06 (br. s, 1H, Al*H*), 3.92 (hept, *J* = 6.6 Hz, 2H, C*H*(CH$_3$)$_2$), 3.48 (hept, *J* = 6.6 Hz, 2H, C*H*(CH$_3$)$_2$), 3.47 (hept, *J* = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 3.31 (hept, *J* = 6.3 Hz, 2H, C*H*(CH$_3$)$_2$), 1.61 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.51 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.50 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.84 (s, 18H, C(C*H*$_3$)$_3$), 0.66 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.64 (d, *J* = 7.0 Hz, 6H), 0.55 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.36 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) *δ* 172.3 (N*C*N), 153.8 (Ar*C*), 144.1 (Ar*C*), 143.8 (Ar*C*), 142.8 (Ar*C*), 142.7 (Ar*C*), 142.6 (Ar*C*), 142.4 (Ar*C*), 131.7 (Ar*C*), 126.3 (Ar*C*), 125.9 (Ar*C*), 125.8 (Ar*C*), 125.2 (Ar*C*), 124.9 (Ar*C*), 124.4 (Ar*C*), 124.0 (Ar*C*), 123.4 (Ar*C*), 34.5 (*C*(CH$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 29.8 (*C*H(CH$_3$)$_2$), 29.8 (*C*H(CH$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$), 22.0 (CH(*C*H$_3$)$_2$), 21.8 (CH(*C*H$_3$)$_2$), 21.2 (CH(*C*H$_3$)$_2$).

5-Al'' (^{dipp}Am$^{p\text{-}(CN)Ph}$)$_2$AlH

To a flask charged with a toluene solution of AlH$_3$•NMe$_3$ (0.23 g, 2.57 mmol, 1.2 equivs) was added a toluene solution **5** (1.00 g, 2.14 mmol, 1 equiv.). The resultant reaction was stirred overnight at room temperature, filtered and washed with hexane to afford a greenish-yellow solid. Yield: 741 mg (72%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.15 – 6.99 (m, 12H, Ar*H*), 6.91 (dd, *J* = 2.0, 7.3 Hz, 2H, Ar*H*), 6.86 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.83 (dd, *J* = 1.9, 7.4 Hz, 2H, Ar*H*), 6.31 (d, *J* = 8.6 Hz, 4H, Ar*H*), 3.67 (hept, *J* = 6.7 Hz, 2H, Ar*H*), 3.14 (hept, *J* = 6.7 Hz, 4H, C*H*$(CH_3)_2$), 3.05 (hept, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 1.37 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 1.37 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 1.26 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.23 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 0.55 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 0.51 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.35 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.18 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 170.6 (Ar*C*), 143.8 (Ar*C*), 143.3 (Ar*C*), 142.6 (Ar*C*), 142.3 (Ar*C*), 141.1 (Ar*C*), 140.9 (Ar*C*), 137.9 (Ar*C*), 132.4 (Ar*C*), 131.6 (Ar*C*), 130.7 (Ar*C*), 129.3 (Ar*C*), 128.6 (Ar*C*), 126.5 (Ar*C*), 126.4 (Ar*C*), 125.7 (Ar*C*), 125.3 (Ar*C*), 125.0 (Ar*C*), 124.6 (Ar*C*), 117.5 (*C*N), 114.1 (Ar*C*), 29.6 (*C*H$(CH_3)_2$), 29.6 (*C*H$(CH_3)_2$), 28.3 (*C*H$(CH_3)_2$), 27.9 (*C*H$(CH_3)_2$), 26.4 (CH(*C*H$_3)_2$), 24.3 (CH(*C*H$_3)_2$), 24.1 (CH(*C*H$_3)_2$), 23.6 (CH(*C*H$_3)_2$), 22.4 (CH(*C*H$_3)_2$), 22.0 (CH(*C*H$_3)_2$), 21.6 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$).

7-Al'' (^{dipp}Am^{mXyl})$_2$AlH

To a flask charged with a toluene solution of AlH_3•NMe_3 (0.054 g, 0.61 mmol, 1 equiv.) was added a toluene solution **7** (0.53 g, 1.22 mmol, 2 equivs). The resultant reaction was stirred overnight at room temperature, filtered and washed with hexane to afford a colourless solid. Yield: 467 mg (80%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.12 – 6.89 (m, 12H, Ar*H*), 6.74 (d, *J* = 1.6 Hz, 4H, *m*Xyl-*o*-*H*), 6.44 (s, 2H, *m*Xyl-*p*-*H*), 5.14 (s, 1H, Al*H*), 3.92 (hept, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 3.53 – 3.42 (m, 4H, C*H*$(CH_3)_2$), 3.30 (hept, *J* = 6.7 Hz, 2H, C*H*$(CH_3)_2$), 1.77 (s, 12H, *m*-C*H*$_3$), 1.55 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 1.48 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 1.44 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 1.37 (d, *J* = 6.8 Hz, 6H), 0.64 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.59 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.58 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.41 (d, *J* = 7.0 Hz, 6H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-d_6**) δ 172.8 (N*C*N), 144.1 (Ar*C*), 143.8 (Ar*C*), 142.8 (Ar*C*), 142.3 (Ar*C*), 136.3 (Ar*C*), 131.4 (Ar*C*), 129.9 (Ar*C*), 125.7 (Ar*C*), 125.5 (Ar*C*), 125.0 (Ar*C*), 124.7 (Ar*C*), 124.3 (Ar*C*), 123.3 (Ar*C*), 29.6 (*C*H$(CH_3)_2$), 28.4 (*C*H$(CH_3)_2$), 28.1 (*C*H$(CH_3)_2$), 26.6 (CH(*C*H$_3)_2$), 24.7 (CH(*C*H$_3)_2$), 24.4 (CH(*C*H$_3)_2$), 24.0 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 22.1 (CH(*C*H$_3)_2$), 22.0 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$), 20.8 (*m*-*C*H$_3$).

16-Al'' (^{dipp,dep}Am^{pTol})$_2$AlH

To a flask charged with **16** (1.06 g. 2.49 mmol, 2 equiv.) and AlH_3•NMe_3 (0.111 g, 1.24 mmol, 1 equiv.) cooled to 0 °C was added toluene dropwise. The resultant solution was stirred overnight at room temperature before all volatiles were removed *in vacuo*. The resultant colourless solid was washed with hexane, to afford the product as a colourless solid. Yield: 0.647 g (59%).

^{1}H NMR (400 MHz, **Benzene-d_6**) δ 7.12 – 6.90 (m, 14H, Ar*H*), 6.41 (d, *J* = 8.3 Hz, 4H, *p*-tol*H*), 5.25 (v. br. s. 1H, Al*H*), 4.03 (hept, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 3.74 (br. m, 1H, C*H*$(CH_3)_2$), 3.39 (2x hept, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 3.22 (dq, *J* = 7.5, 15.1 Hz, 1H, C*H*$_2$CH$_3$), 2.87 (br. m, 1H, C*H*$(CH_3)_2$), 2.75

(dq, J = 7.5, 15.0 Hz, 1H, CH_2CH$_3$), 2.52 (dq, J = 7.5, 15.0 Hz, 2H, CH_2CH$_3$), 1.93 (dq, J = 7.6, 15.6 Hz, 1H, CH_2CH$_3$), 1.62 (s, 3H, *p*-CH_3), 1.61 (s, 4H, *p*-CH_3), 1.52 (d, J = 6.7 Hz, 3H, CH(CH_3)$_2$), 1.37 (d, J = 6.7 Hz, 3H, CH(CH_3)$_2$), 1.21 (br. t, 2H, CH$_2$CH_3), 1.13 (t, J = 7.5 Hz, 2H, CH$_2$CH_3), 1.09 (t, J = 7.5 Hz, 3H, CH$_2$CH_3), 1.08 (t, J = 7.5 Hz, 2H, CH$_2$CH_3), 0.77 (d, J = 6.7 Hz, 3H, CH(CH_3)$_2$), 0.56 (d, J = 6.8 Hz, 3H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR (**101 MHz, **Benzene-*d*$_6$**) δ 172.8 (N*C*N), 172.2 (N*C*N), 143.9 (Ar*C*), 143.6 (Ar*C*), 143.3 (Ar*C*), 143.1 (Ar*C*), 142.6 (Ar*C*), 141.6 (Ar*C*), 140.9 (Ar*C*), 140.4 (Ar*C*), 140.4 (Ar*C*), 139.9 (Ar*C*), 139.2 (Ar*C*), 139.1 (Ar*C*), 130.4 (Ar*C*), 130.3 (Ar*C*), 127.5 (Ar*C*), 127.4 (Ar*C*), 126.4 (Ar*C*), 126.1 (Ar*C*), 125.7 (Ar*C*), 125.7 (Ar*C*), 125.1 (Ar*C*), 125.0 (Ar*C*), 124.6 (Ar*C*), 124.4 (Ar*C*), 124.3 (Ar*C*), 124.0 (Ar*C*), 29.3 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.4, 23.6(CH(*C*H$_3$)$_2$), 23.0(CH(*C*H$_3$)$_2$), 22.5(CH(*C*H$_3$)$_2$), 20.9 (*p*-*C*H$_3$), 14.9 (CH$_2$*C*H$_3$), 14.3 (CH$_2$*C*H$_3$), 13.6 (CH$_2$*C*H$_3$), 12.9 (CH$_2$*C*H$_3$).

19-Al" (^{dep}Am^{pTol})$_2$AlH

To a flask charged with a toluene solution of **19** (1.0 g, 2.5 mmol, 2 equivs) was added a toluene solution of AlH$_3$•NMe$_3$ (0.11 g, 1.25 mmol, 1 equiv.). The resultant solution was stirred for 1 hour at room temperature, solvent was removed *in vacuo* and white solid was washed with hexane. Yield: 0.88 g (86%). *Note:* No Al*H* resonance observed due to expected broadness.

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.11 – 6.92 (m, 12H, Ar*H*), 6.43 – 6.37 (m, 4H, *p*-tol*H*), 3.09 (v. br. s, 1H, Al*H*), 2.83 (dq, J = 7.5, 15.1 Hz, 4H, CH_2CH$_3$), 2.56 (dq, J = 7.5, 15.2 Hz, 4H, CH_2CH$_3$), 2.45 (dq, J = 7.6, 15.4 Hz, 4H, CH_2CH$_3$), 1.60 (s, 6H, *p*-CH_3), 1.17 (t, J = 7.5 Hz, 12H, CH$_2$CH_3), 1.12 (t, J = 7.5 Hz, 12H, CH$_2$CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 172.4 (N*C*N), 142.2 (Ar*C*), 140.5 (Ar*C*), 139.3 (Ar*C*), 129.4 (Ar*C*), 128.5 (Ar*C*), 126.1 (Ar*C*), 125.2 (Ar*C*), 125.0 (Ar*C*), 24.9 (*C*H$_2$CH$_3$), 24.5 (*C*H$_2$CH$_3$), 21.0 (*p*-*C*H$_3$), 14.3 (CH$_2$*C*H$_3$), 13.6 (CH$_2$*C*H$_3$).

20-Al" (^{dep}Am^{mes})$_2$AlH

To a flask charged with a toluene solution of AlH$_3$•NMe$_3$ (0.25 g, 2.81 mmol, 1.2 equivs) was added a toluene solution of **20** (1.0 g, 2.34 mmol, 1 equiv.). The resultant solution was stirred at room temperature for 1 hour, the solvent was removed *in vacuo* and the resultant yellow solid was washed with toluene. Yield: 699 mg (67%). *Note:* No Al*H* resonance observed due to expected broadness.

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) *δ* 6.93 – 6.77 (m, 12H, Ar*H*), 6.29 (d, J = 3.0 Hz, 4H, Ar*H*), 2.56 (br. m., 16H, CH_2CH$_3$), 2.23 (s, 6H, ArCH_3), 2.18 (s, 6H, ArCH_3), 1.73 (s, 6H, ArCH_3), 1.08 (t, J = 7.5 Hz, 24H, CH$_2$CH_3). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) *δ* 175.2 (N*C*N), 141.7 (Ar*C*), 139.0 (Ar*C*), 138.7 (Ar*C*), 138.3 (Ar*C*), 137.6 (Ar*C*), 129.7 (Ar*C*), 129.5 (Ar*C*), 129.4 (Ar*C*), 124.9 (Ar*C*), 124.7 (Ar*C*), 124.6 (Ar*C*), 24.8 (*C*H$_2$CH$_3$), 24.1 (*C*H$_2$CH$_3$), 22.2 (Mes-*C*H$_3$), 21.7 (Mes-*C*H$_3$), 20.6 (Mes-*C*H$_3$), 13.6 (CH$_2$*C*H$_3$).

22-Al" ($^{dep}Am^{Ad}$)$_2$AlH

Obtained as a minor by-product from the synthesis of **22-Al**.

^{1}H NMR (400 MHz, **Benzene-*d*$_6$**) δ 7.06 – 6.93 (m, 6H, Ar*H*), 4.90 (v. br. s, Al*H*), 3.05 (dq, *J* = 15.0, 7.5 Hz, 2H, C*H*$_2$CH$_2$), 2.83 (dq, *J* = 15.0, 7.4 Hz, 2H, C*H*$_2$CH$_2$), 2.75 (dq, *J* = 15.1, 7.4 Hz, 2H, C*H*$_2$CH$_2$), 2.37 (dq, *J* = 15.3, 7.5 Hz, 2H, C*H*$_2$CH$_2$), 1.79 (d, *J* = 3.2 Hz, 6H, Ad*H*), 1.52 – 1.46 (m, 4H, Ad*H*), 1.27 (t, *J* = 7.5 Hz, 6H, CH$_2$C*H*$_3$), 1.25 (t, *J* = 7.5 Hz, 6H, CH$_2$C*H*$_3$), 1.21 (t, *J* = 3.2 Hz, 6H, Ad*H*). **^{13}C{^{1}H} NMR** (101 MHz, **Benzene-*d*$_6$**) δ 177.4 (N*C*N), 143.2 (Ar*C*), 139.0 (Ar*C*), 138.9 (Ar*C*), 125.6 (Ar*C*), 124.5 (Ar*C*), 123.7 (Ar*C*), 44.8 (Ad*C*), 38.5 (Ad*C*), 36.3 (Ad*C*), 28.5 (Ad*C*), 25.2 (*C*H$_2$CH$_3$), 24.6 (*C*H$_2$CH$_3$), 14.2 (CH$_2$*C*H$_3$), 13.0 (CH$_2$*C*H$_3$).

3. Supporting Figure

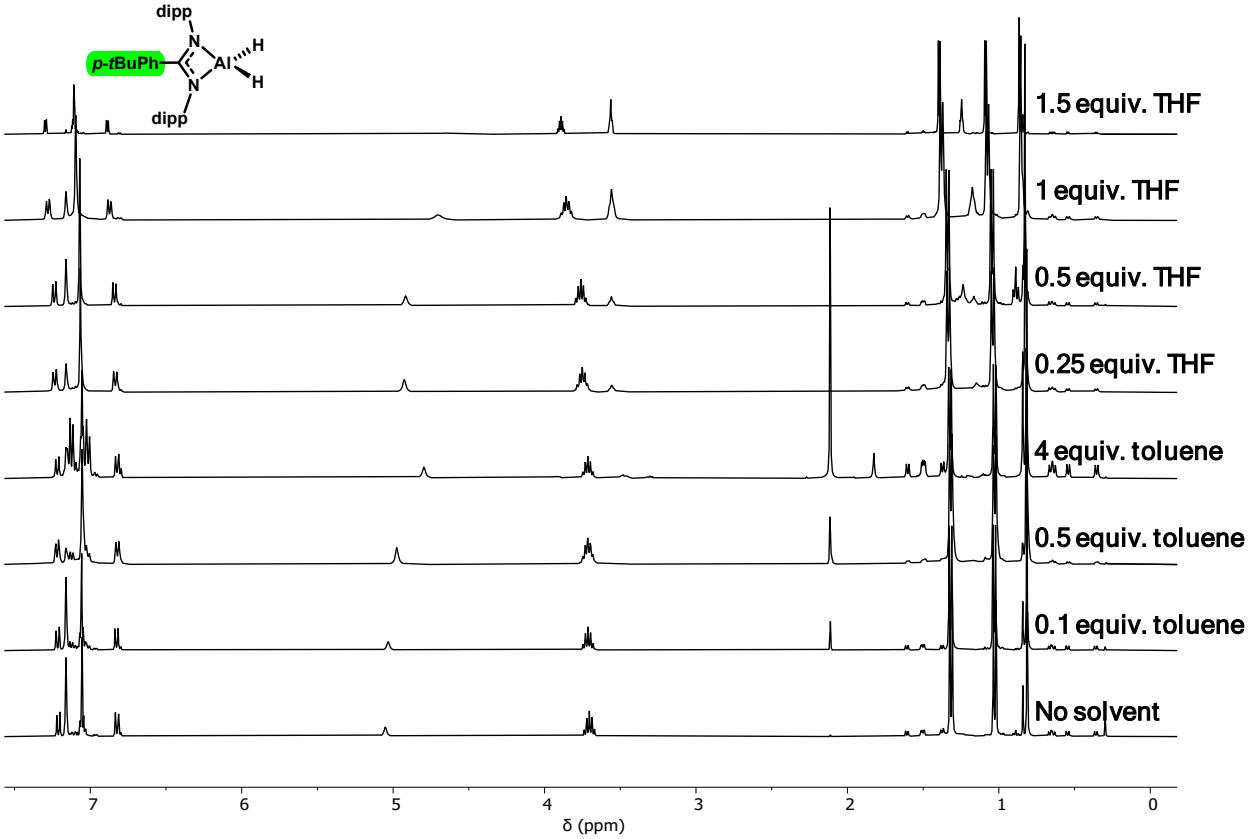


Figure S 1: ^{1}H NMR spectra (400 MHz, 298 K) of **2-Al** in C_6D_6, showing change in chemical shift with varying amounts of coordinating solvents (toluene and THF)

4. X-ray crystallographic data

General remarks

All experiments were performed at 293 K, 150 K or 100 K using a Cu Kα radiation source (λ = 1.54184 Å) or at 100 K using Mo Kα (λ = 0.7107 Å) radiation on a dual-source Agilent Oxford SuperNova diffractometer with an Atlas CCD detector, a dual-souce Synergy-S diffractometer equipped with a Dectris Eiger2 1M detector or a dual-source XtaLAB Synergy DW system diffractometer with a HyPix-Arc 100 detector. Cell refinement, data collection and data reduction for all experiments were performed using Rigaku CrysAlisPro.[15] All structures were solved with ShelXT[16] and ShelXL[17], both programs implemented within the Olex2[18] 14 suite. All atoms, except hydrogen, had atomic coordinates and anisotropic thermal parameters refined to convergence using least-square methods on F^2.

Ligands X-ray data

Table S 1: Selected bond lengths (Å) and angles (°) for crystal structures of amidine ligands **5**, **12**, **14**, **16**, **19** and **20** (table key: **compound no**.; ligand abbreviation; *ccdc no.*)

Ligand	C1-N (Å)	C1-C2 (Å)	N1-C (Å)	N2-C (Å)	N1-C1-N2 (°)
5 $^{dipp}Am^{pCN}H$ *2527302*	1.359(2) 1.284(3)	1.498(2)	1.433(3)	1.434(2)	124.41(16)
12 $^{dipp}Am^{dipp}H$ *2527303*	1.3462(14) 1.3190(14)	1.5027(14)	1.4227(14)	1.4294(15)	122.97(9)
14 $^{dipp}Am^{Ad}H$ *2527296*	1.3706(17) 1.2861(17)	1.5376(18)	1.4369(16)	1.4180(19)	121.01(12)
16 $^{dippdep}Am^{pTo}{}^{l}H$ *2527294*	1.329(2) 1.333(2)	1.486(2)	1.429(2)	1.422(2)	121.21(15)
19 $^{dep}Am^{pTol}H$ *2527288*	1.327(2) 1.327(2)	1.490(2)	1.428(2)	1.427(2)	120.97(16)
20-A $^{dep}Am^{mes}H$ *2527302*	1.373(3) 1.287(3)	1.498(4)	1.432(3)	1.429(4)	120.7(2)
20-B $^{dep}Am^{mes}H$	1.367(3) 1.291(3)	1.500(4)	1.433(4)	1.412(3)	118.7(2)

2527301					

Single crystal X-ray data for 5

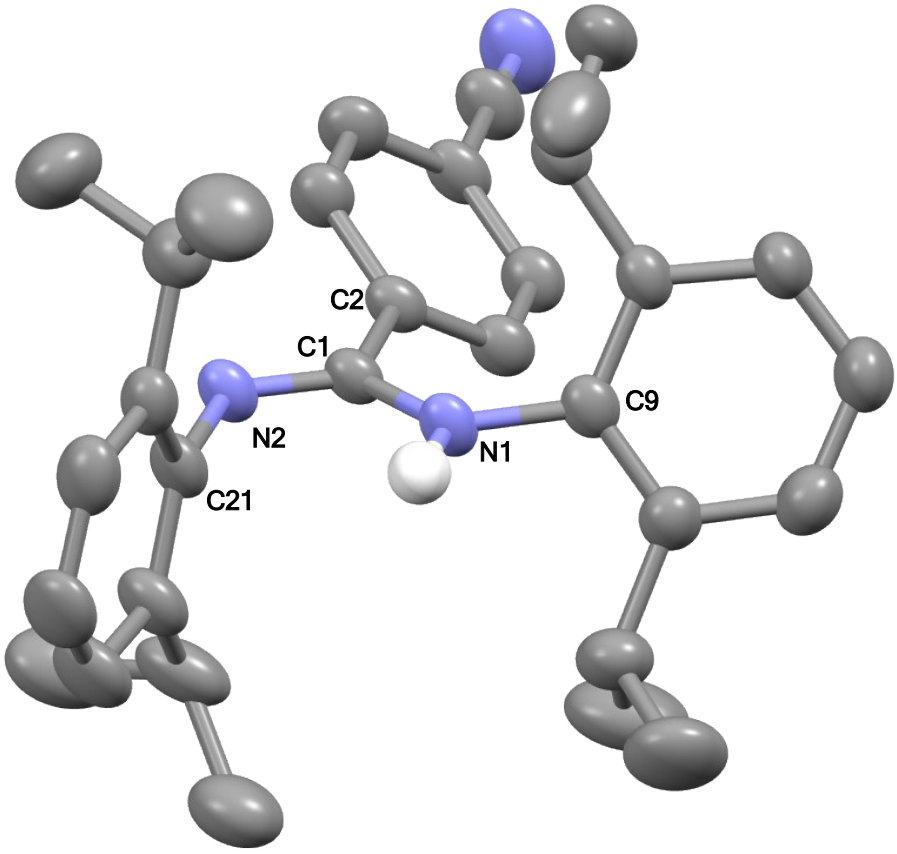


Figure S 2: The crystal structure of **5** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 30% probability)

Single crystals of **5** were obtained through the slow evaporation of an ethanol solution. **5** was found to crystallise with one molecule in the asymmetric unit in the $P2_1/c$ space group. The N*H* protons were modelled on both nitrogens in 90%:10% occupancy. The unit cell contained 1.25 molecules of ethanol per asymmetric unit, which was masked using the SQUEEZE function.

$C_{34.5}H_{46.5}N_3O_{1.25}$ (M = 523.24 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.217(2) Å, b = 10.6241(4) Å, c = 29.473(4) Å, β = 137.12(3)°, V = 3242.5(13) Å^3, Z = 4, T = 293.15(10) K, μ(Cu Kα) = 0.497 mm^{-1}, *Dcalc* = 1.072 g/cm^3, 23501 reflections measured (6.348° ≤ 2Θ ≤ 163.748°), 6127 unique (R_{int} = 0.0787, R_{sigma} = 0.0685) which were used in all calculations. The final R_1 was 0.0720 (I > 2σ(I)) and wR_2 was 0.2493 (all data). CCDC 2527302

Single crystal X-ray data for 12

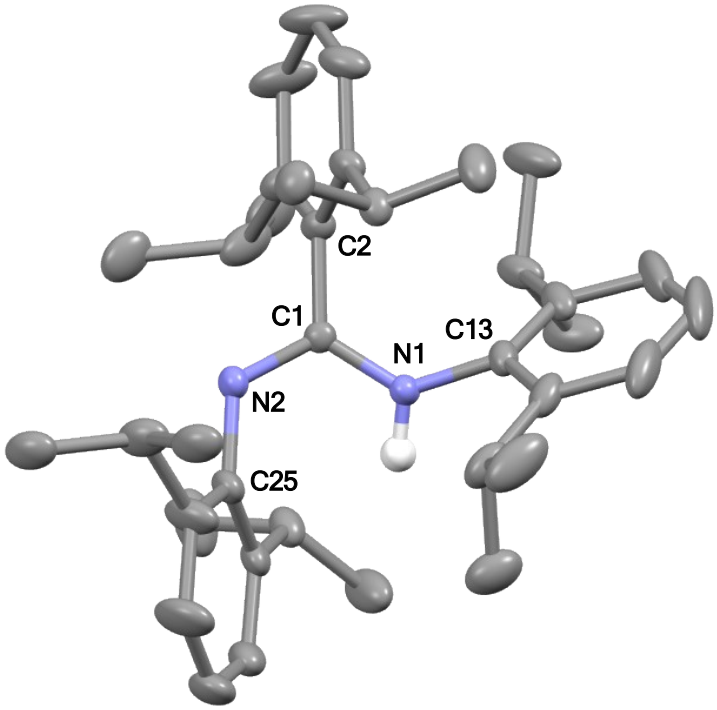


Figure S 3: The crystal structure of **12** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 50% probability)

Single crystals of **12** were obtained through the slow evaporation of a hexane solution. **12** was found to crystallise with one molecule in the asymmetric unit in the *C2/c* space group. There was disorder in two of the diisopropyl groups, which were modelled in two locations. The N*H* protons were modelled on both nitrogens in 58%:42% occupancy.

$C_{37}H_{52}N_2$ (M = 524.80 g/mol): monoclinic, space group *C2/c* (no. 15), a = 17.9252(2) Å, b = 12.26700(10) Å, c = 31.3045(3) Å, β = 107.7290(10)°, V = 6556.58(12) Å^3, Z = 8, T = 100.00(10) K, μ(Cu Kα) = 0.452 mm^{-1}, *Dcalc* = 1.063 g/cm^3, 149453 reflections measured (5.928° ≤ 2Θ ≤ 152.198°), 6834 unique (R_{int} = 0.0510, R_{sigma} = 0.0119) which were used in all calculations. The final R_1 was 0.0504 (I > 2σ(I)) and wR_2 was 0.1251 (all data). CCDC 2727303

Single crystal X-ray data for 14

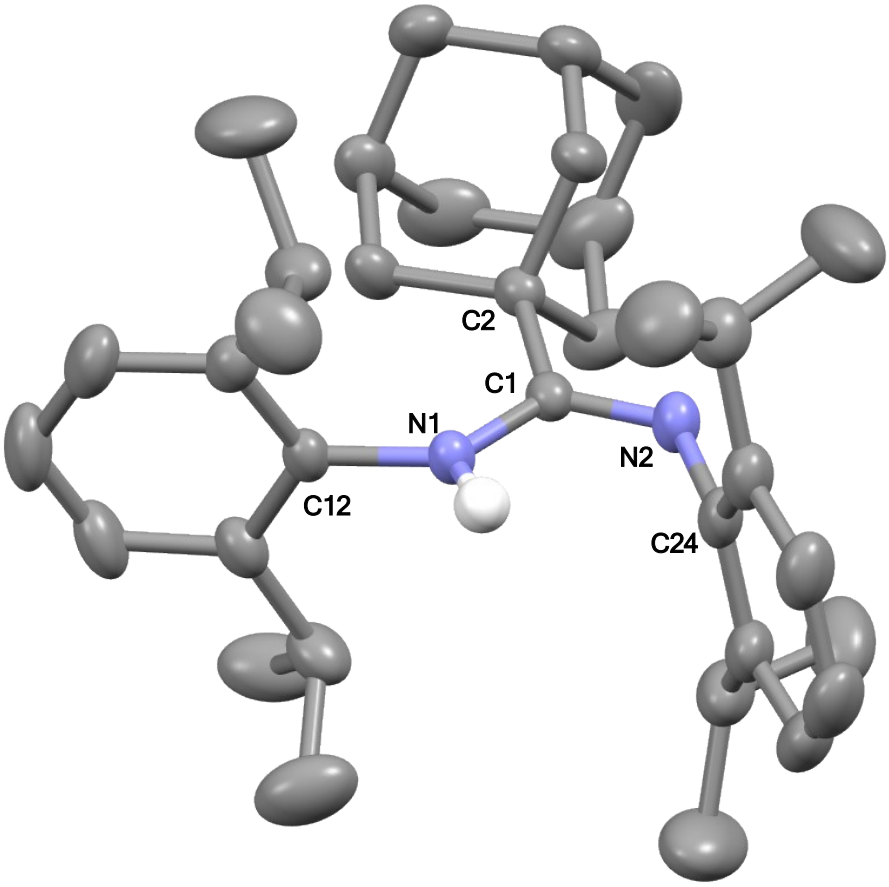


Figure S 4: The crystal structure of **14** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 30% probability)

Single crystals of **14** were obtained through the slow evaporation of an ethanol solution. **14** was found to crystallise with one molecule in the asymmetric unit in the $P2_1/n$ space group. There was disorder in the adamantyl group, which was modelled in two locations. The N*H* protons were modelled on both nitrogens in 86%:14% occupancy.

$C_{35}H_{50}N_2$ (M = 498.77 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.0630(3) Å, b = 17.1840(5) Å, c = 18.5068(5) Å, β = 102.313(3)°, V = 3126.63(16) Å^3, Z = 4, T = 293.15(10) K, μ(Cu Kα) = 0.451 mm^{-1}, *Dcalc* = 1.060 g/cm^3, 32652 reflections measured (7.096° ≤ 2Θ ≤ 152.392°), 6467 unique (R_{int} = 0.0257, R_{sigma} = 0.0167) which were used in all calculations. The final R_1 was 0.0609 (I > 2σ(I)) and wR_2 was 0.1671 (all data). CCDC 2527296

Single crystal X-ray data for 16

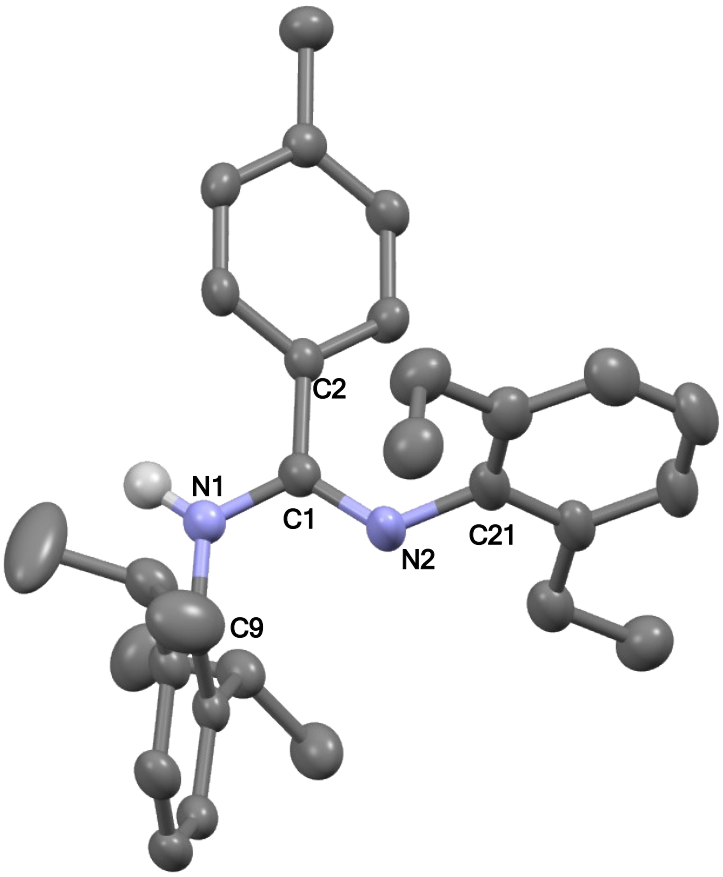


Figure S 5: The crystal structure of **16** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 50% probability)

Single crystals of **16** were obtained through the slow evaporation of a hexane solution. **16** was found to crystallise with one molecule in the asymmetric unit in the $P2_1/n$ space group. There was disorder in one diisopropyl group and one ethyl group, which were modelled over two locations. The N*H* protons were disordered over both nitrogens in 0.6:0.4 ratio.

$C_{30}H_{38}N_2$ (M = 426.62 g/mol): triclinic, space group P-1 (no. 2), a = 10.8893(9) Å, b = 10.9235(7) Å, c = 12.1064(8) Å, α = 98.176(5)°, β = 107.648(6)°, γ = 106.388(7)°, V = 1275.02(17) Å^3, Z = 2, T = 150.15 K, μ(CuKα) = 0.481 mm^{-1}, *Dcalc* = 1.111 g/cm^3, 8430 reflections measured (8.712° ≤ 2Θ ≤ 144.216°), 4895 unique (R_{int} = 0.0271, R_{sigma} = 0.0415) which were used in all calculations. The final R_1 was 0.0501 (I > 2σ(I)) and wR_2 was 0.1316 (all data). CCDC 2527294

Single crystal X-ray data for 19

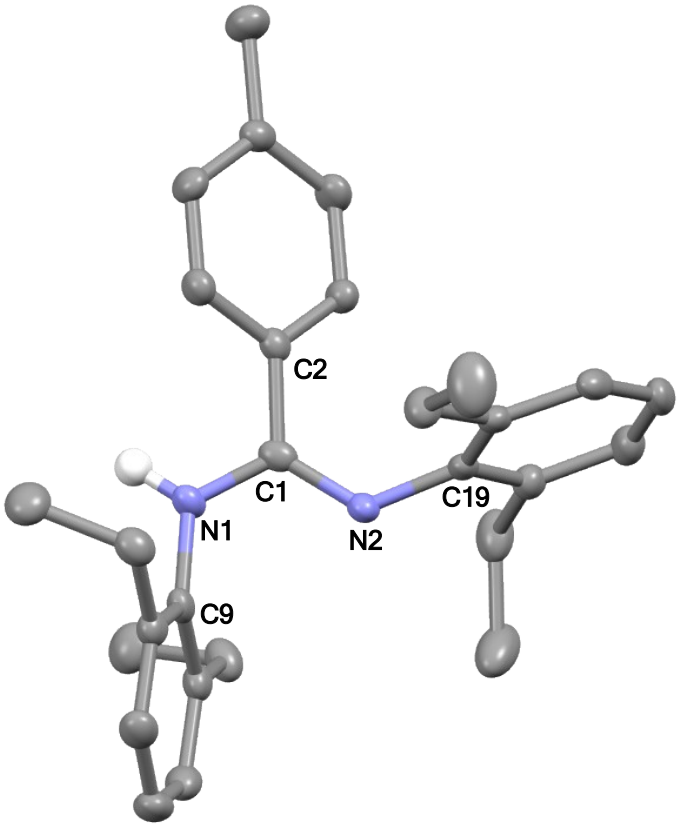


Figure S 6: The crystal structure of **19** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 50% probability)

Single crystals of **19** were obtained through the slow evaporation of an ethanol solution. **19** was found to crystallise with one molecule in the asymmetric unit in the $P2_1/n$ space group. The N*H* protons were disordered over both nitrogens in 0.56:0.44 ratio.

$C_{28}H_{34}N_2$ (M =398.57 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 15.6824(15) Å, b = 8.9748(8) Å, c = 16.5729(16) Å, β = 99.359(10)°, V = 2301.5(4) Å^3, Z = 4, T = 150.00(10) K, μ(Mo Kα) = 0.066 mm^{-1}, D_{calc} = 1.150 g/cm^3, 9251 reflections measured (6.742° ≤ 2Θ ≤ 58.724°), 5227 unique (R_{int} = 0.0473, R_{sigma} = 0.0995) which were used in all calculations. The final R_1 was 0.0670 (I > 2σ(I)) and wR_2 was 0.1226 (all data). CCDC 2527288

Single crystal X-ray data for 20

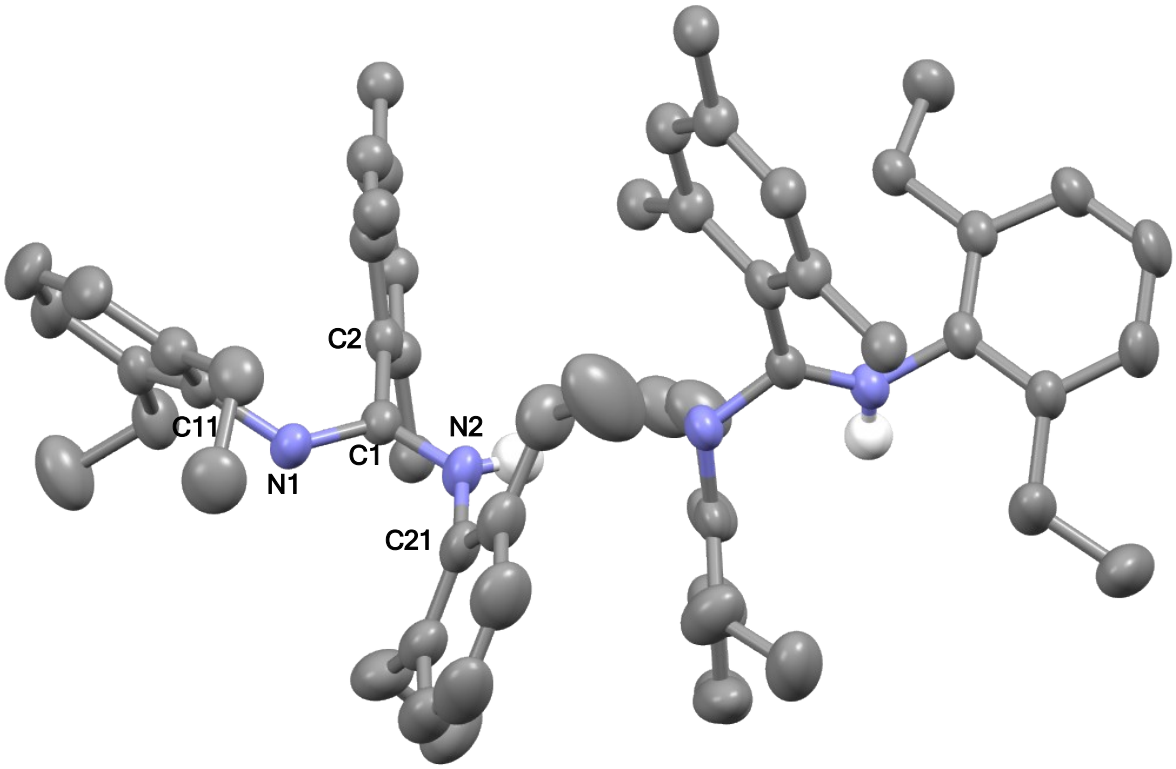


Figure S 7: The crystal structure of **20-A** and **20-B** (disorder, hydrogen atoms except N*H* atoms omitted for clarity, ellipsoids 30% probability)

Single crystals of **20** were obtained through the slow evaporation of a petroleum ether (40-60 °C) solution. **20** was found to crystallise with two full molecules in the asymmetric unit in the $P\bar{1}$ space group. There was disorder in both mesityl groups, which were both modelled in two locations, and in four ethyl groups, which were all modelled in two locations. The N*H* protons were modelled on both nitrogens of each molecule in 71%:29% occupancy for **20-A** and 68%:32% occupancy for **20-B**.

$C_{30}H_{38}N_2$ (M = 426.62 g/mol): triclinic, space group P-1 (no. 2), a = 11.9554(4) Å, b = 12.4312(5) Å, c = 20.2934(6) Å, α = 72.226(3)°, β = 89.976(2)°, γ = 67.510(3)°, V = 2630.31(17) Å^3, Z = 4, T = 293.15(10) K, μ(Cu Kα) = 0.467 mm^{-1}, *Dcalc* = 1.077 g/cm^3, 54476 reflections measured (4.614° ≤ 2Θ ≤ 152.184°), 10832 unique (R_{int} = 0.0275, R_{sigma} = 0.0173) which were used in all calculations. The final R_1 was 0.0938 (I > 2σ(I)) and wR_2 was 0.2450 (all data). CCDC 2527301

Aluminium dihydride X-ray data

Table S 2: Selected bond lengths (Å) and angles (°) for crystallographically characterised aluminium hydrides **4-Al**, **6-Al**, **7-Al**, **9-Al**, **10-Al**, **11-Al**, **15-Al** and **20-Al**. (table key: **compound no**.; ligand abbreviation; *ccdc no.*)

Complex	Al-N (Å)	Al-H (terminal) (Å)	Al-H (bridging) (Å)	N-Al-N (°)	Backbone Ar-NCNAl plane angle (°)
4-Al-A $^{dipp}Am^{pOMe}AlH_2$ *2527295*	1.9899(13) 1.9120(13)	1.51(2)	1.61(2)	68.11(5)	40.11
4-Al-B $^{dipp}Am^{pOMe}AlH_2$ *2527295*	1.9943(13) 1.9231(13)	1.53(2)	1.64(2)	67.82(5)	48.42
6-Al $^{dipp}Am^{pCF3}AlH_2$ *2527289*	1.983(5) 1.924(5)	1.55(7)	1.79(5)	68.12(17)	45.09
7-Al $^{dipp}Am^{mXyl}AlH_2$ *2527290*	1.9297(19) 1.973(2)	1.49(3)	1.60(3)	67.83(9)	38.35
9-Al-A* $^{dipp}Am^{2,4Xyl}AlH_2$ *2527298*	1.9155(14) 1.9809(15)	1.49(2)	1.58(4)	68.17(6)	52.15
9-Al-B* $^{dipp}Am^{2,4Xyl}AlH_2$ *2527298*	1.9205(14) 1.9923(14)	1.40(3)	1.576(19)	67.89(6)	55.87
10-Al $^{dipp}Am^{oXyl}AlH_2$ *2527300*	1.9262(7) 1.9309(7)	1.482(13) 1.497(14)	-	69.14(3)	56.30
11-Al-A $^{dipp}Am^{mes}AlH_2$ *2527292*	1.9238(12) 1.9768(13)	1.489(18)	1.622(16)	67.86(5)	59.98
11-Al-B $^{dipp}Am^{mes}AlH_2$ *2527292*	1.9227(13) 1.9228(13)	1.46(2) 1.460(19)	-	69.64(7)	57.51
15-Al $^{dipp,dep}Am^{tBu}AlH_2$	1.9562(11) 1.9250(11)	1.490(16)	1.634(14)	67.68(4)	*n/a*

2527297					
20-Al $^{dep}Am^{mes}AlH_2$ *2527299*	2.006(3) 1.912(2)	1.52(4)	1.56(3)	67.70(10)	58.13

Single crystal X-ray data for 4-Al

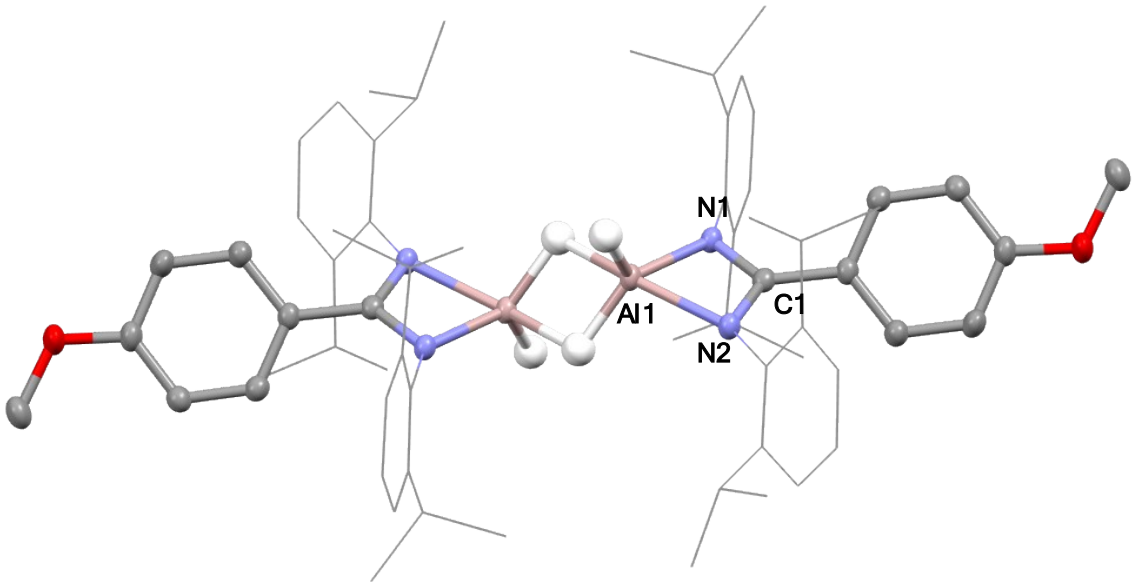


Figure S 8: The crystal structure of **4-Al-A** (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

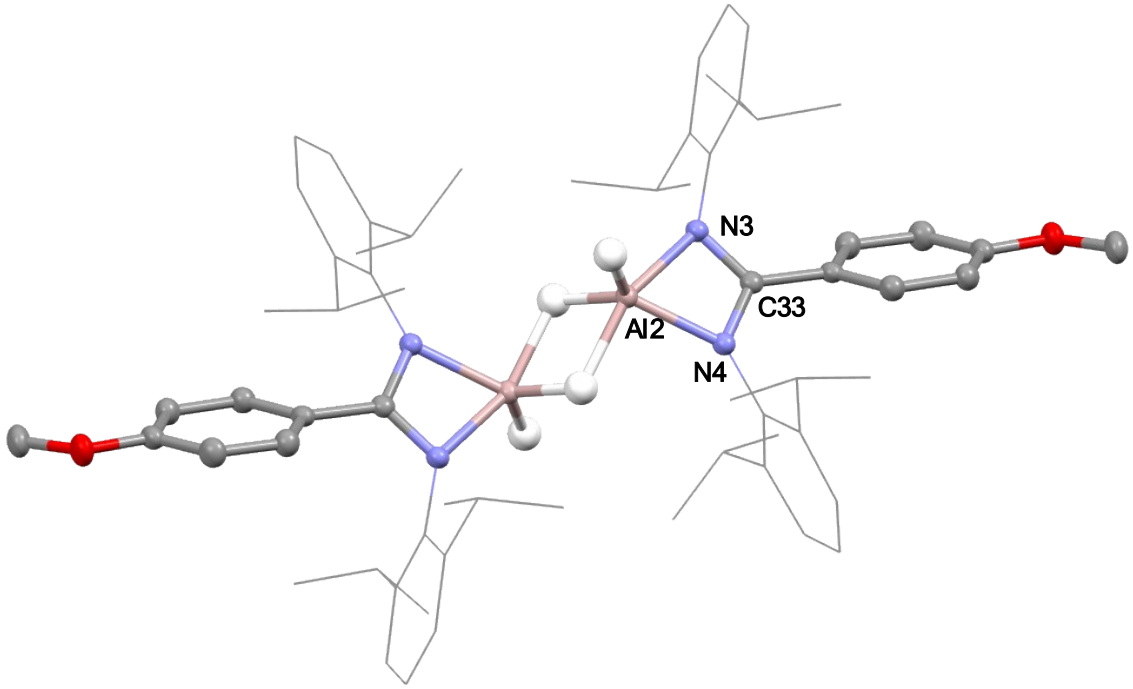


Figure S 9: The crystal structure of **4-Al-B**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single-crystals of **4-Al** were grown from the cooling of a saturated toluene solution. **4-Al** was found to crystallise with two half dimers, **4-Al-A** and **4-Al-B** in the asymmetric unit in the $P2_1/c$ space group. The unit cell contained two molecules of toluene per asymmetric unit.

$C_{149}H_{196}Al_4N_8O_4$ (M = 2271.05 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 19.0940(2) Å, b = 21.9118(2) Å, c = 18.2392(2) Å, β = 117.8520(10)°, V = 6746.99(13) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 0.741 mm^{-1}, D_{calc} = 1.118 g/cm^3, 291494 reflections measured (5.234° ≤ 2Θ ≤ 140.142°), 12802 unique (R_{int} = 0.0788, R_{sigma} = 0.0193) which were used in all calculations. The final R_1 was 0.0515 (I > 2σ(I)) and wR_2 was 0.1450 (all data). CCDC 2527295

Single crystal X-ray data for 6-Al

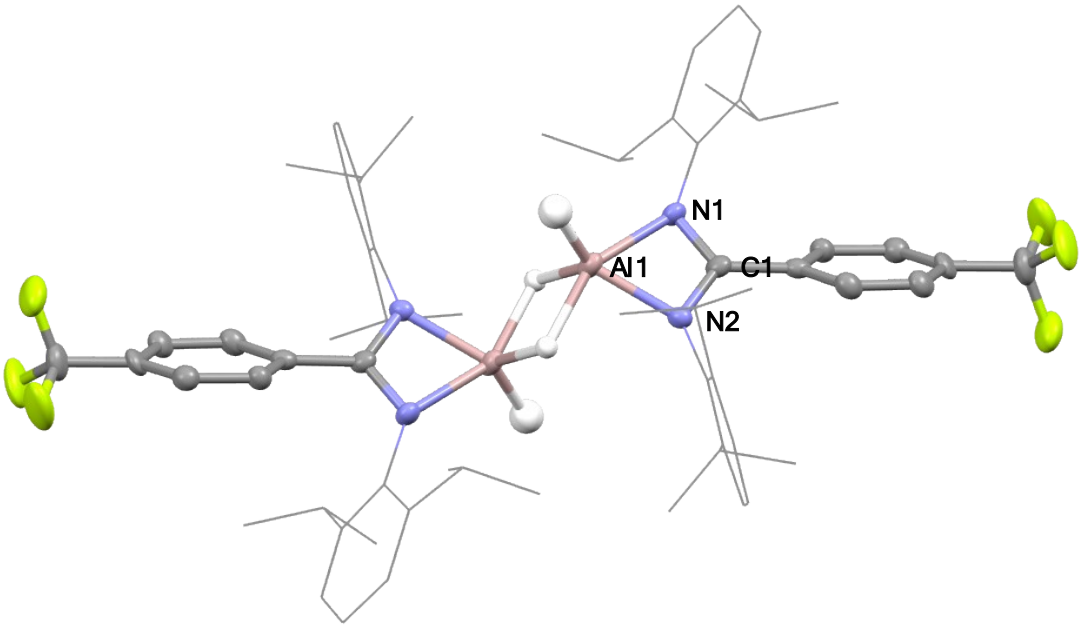


Figure S 10: The crystal structure of **6-Al**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **6-Al** were grown from the cooling of a saturated toluene solution. **6-Al** crystallised with half a dimer in the asymmetric unit in the *P2/c* space group. The unit cell contained two half molecules of toluene per asymmetric unit.

$C_{78}H_{96}Al_2F_6N_4$ (M = 1257.54 g/mol): monoclinic, space group P2/c (no. 13), a = 11.1717(2) Å, b = 15.5948(2) Å, c = 20.5002(4) Å, β = 92.516(2)°, V = 3568.11(11) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 0.852 mm^{-1}, D_{calc} = 1.170 g/cm^3, 40309 reflections measured (5.668° ≤ 2Θ ≤ 152.148°), 7315 unique (R_{int} = 0.0575, R_{sigma} = 0.0350) which were used in all calculations. The final R_1 was 0.1288 (I > 2σ(I)) and wR_2 was 0.2807 (all data). CCDC 2527289

Single crystal X-ray data for 7-Al

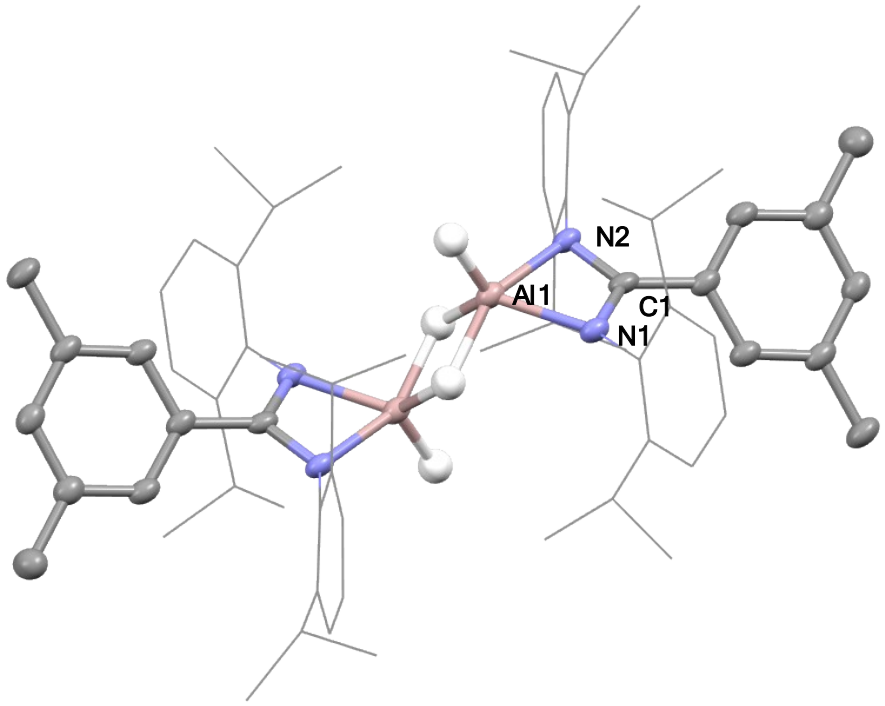


Figure S 11: The crystal structure of **7-Al**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **7-Al** were grown from the cooling of a saturated toluene solution. **7-Al** crystallised with half a dimer in the asymmetric unit in the $P\bar{1}$ space group. The unit cell contained 1.5 molecules of toluene per asymmetric unit.

$C_{87}H_{114}Al_2N_4$ (M = 1269.78 g/mol): triclinic, space group P-1 (no. 2), a = 12.2254(3) Å, b = 13.2838(3) Å, c = 13.9435(4) Å, α = 72.394(2)°, β = 64.263(3)°, γ = 75.267(2)°, V = 1924.19(10) Å^3, Z = 1, T = 100.00(10) K, μ(Cu Kα) = 0.677 mm^{-1}, D_{calc} = 1.096 g/cm^3, 88262 reflections measured (7.054° ≤ 2Θ ≤ 148.994°), 7810 unique (R_{int} = 0.1402, R_{sigma} = 0.0511) which were used in all calculations. The final R_1 was 0.0739 (I > 2σ(I)) and wR_2 was 0.1719 (all data). CCDC 2527290

Single crystal X-ray data for 9-Al

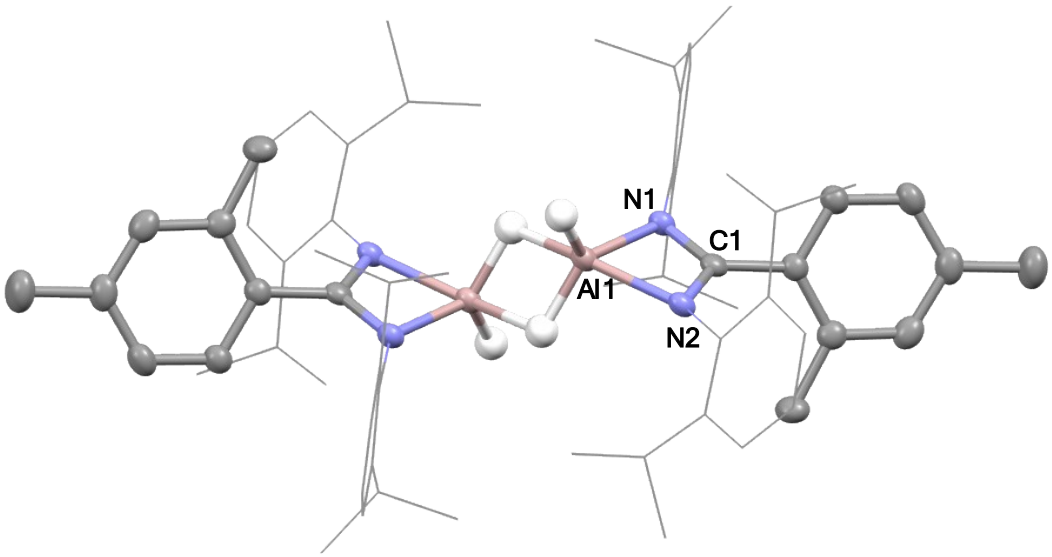


Figure S 12: The crystal structure of **9-Al-A** (major component). (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

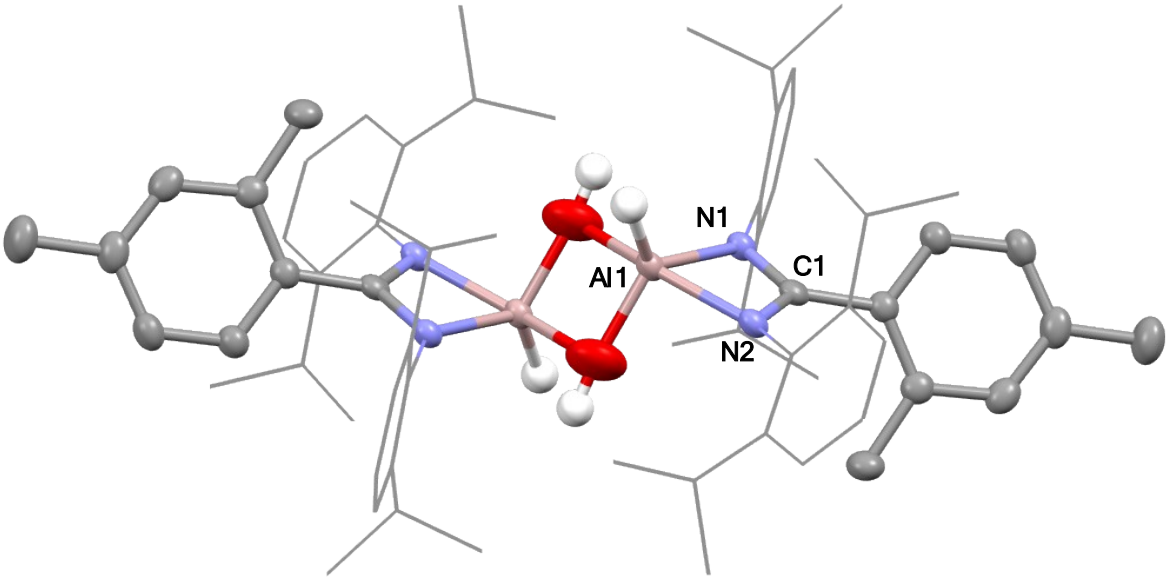


Figure S 13: The crystal structure of hydride-hydroxide impurity **9-Al-A-OH** (minor component). (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

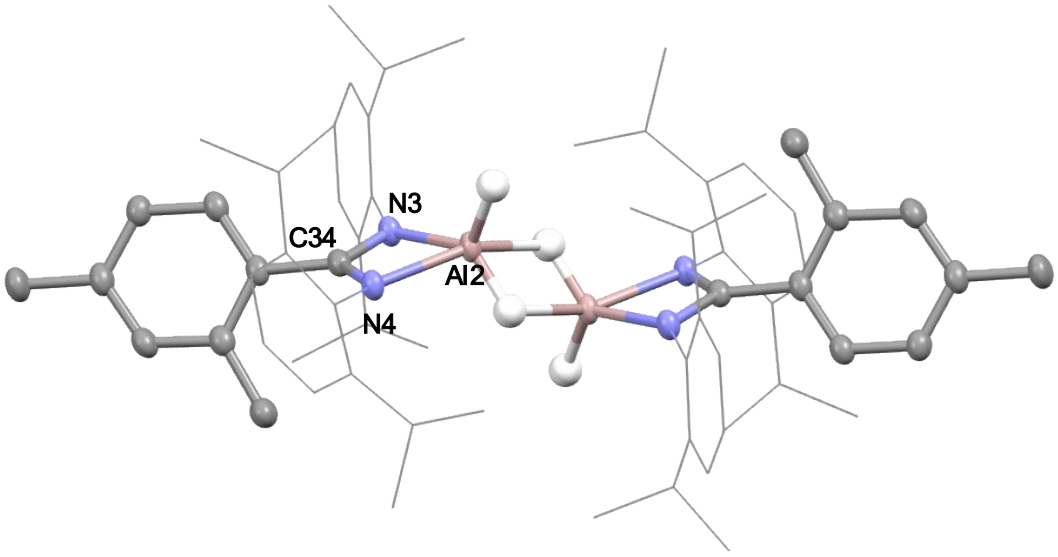


Figure S 14: The crystal structure of **9-Al-B** (major component). (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

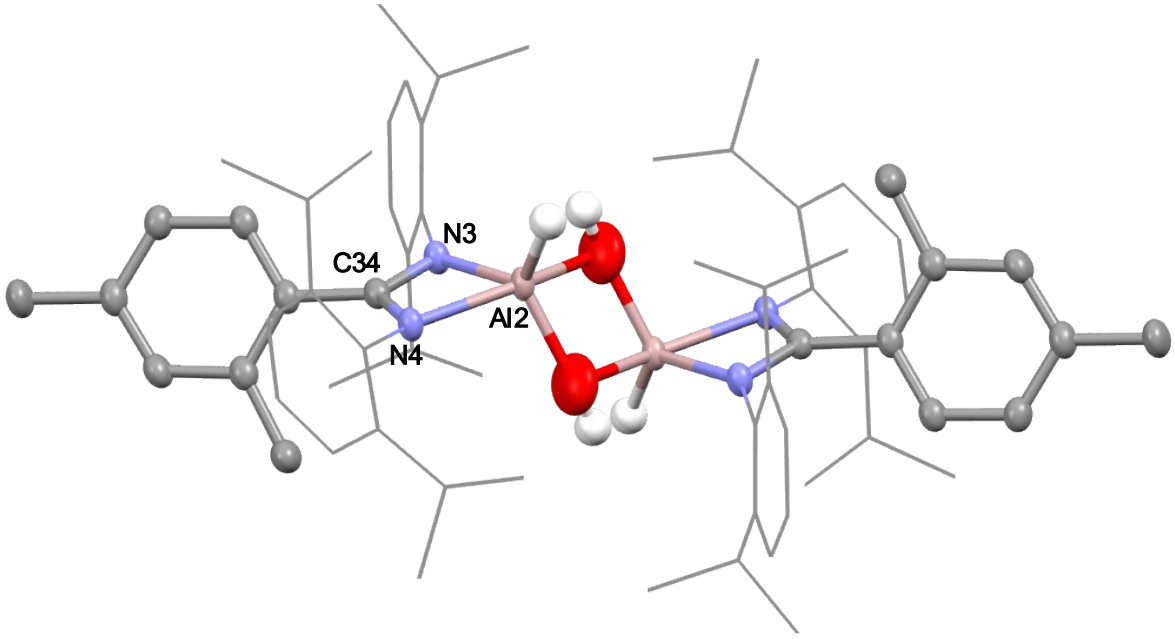


Figure S 15: The crystal structure of hydride-hydroxide impurity **9-Al-B-OH** (minor component). (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **9-Al** were grown from the cooling of a saturated toluene solution. **9-Al** was found to crystallise with two half dimers, **9-Al-A** and **9-Al-B** in the asymmetric unit in the *I*2/a space group. **9-Al** and **9-Al-OH** co-crystallised, in a 0.88:0.12 and 0.85:0.15 ratio for **9-Al-A** and **9-Al-B**, respectively. The unit cell contained 1 molecule of toluene per asymmetric unit, containing disorder which was modelled over two locations.

$C_{73}H_{98}Al_2N_4O_{0.27}$ (M =1089.83 g/mol): monoclinic, space group I2/a (no. 15), a = 31.6819(3) Å, b = 12.94370(10) Å, c = 32.8715(4) Å, β = 90.3080(10)°, V = 13479.8(2) Å^3, Z = 8, T = 100.00(10) K, μ(Cu Kα) = 0.703 mm^{-1}, *Dcalc* = 1.074 g/cm^3, 160551 reflections measured (5.376° ≤ 2Θ ≤ 152.19°), 13972 unique (R_{int} = 0.0933, R_{sigma} = 0.0352) which were used in all calculations. The final R_1 was 0.0528 (I > 2σ(I)) and wR_2 was 0.1450 (all data). CCDC 2527298

Single crystal X-ray data for 10-Al

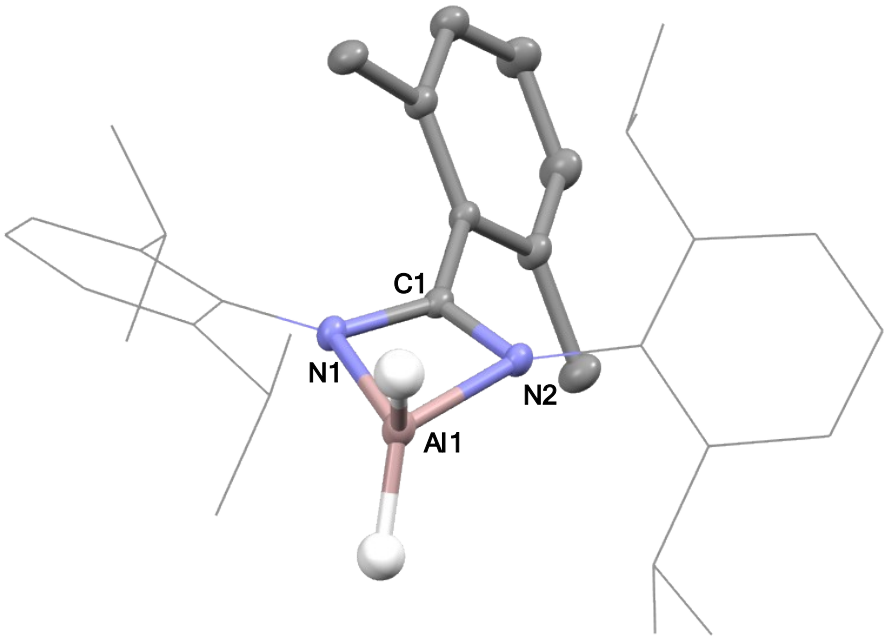


Figure S 16: The crystal structure of **10-Al**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **10-Al** were grown from the cooling of a saturated hexane solution. **10-Al** was found to crystallise with one monomer in the asymmetric unit in the $P\bar{1}$ space group.

$C_{33}H_{45}AlN_2$ (M =496.69 g/mol): triclinic, space group P-1 (no. 2), a = 9.5994(2) Å, b = 11.5430(3) Å, c = 14.6201(4) Å, α = 83.387(2)°, β = 72.037(2)°, γ = 79.219(2)°, V = 1510.96(7) Å^3, Z = 2, T = 100.01(10) K, μ(Mo Kα) = 0.089 mm^{-1}, D_{calc} = 1.092 g/cm^3, 64695 reflections measured (5.262° ≤ 2Θ ≤ 74.498°), 14592 unique (R_{int} = 0.0700, R_{sigma} = 0.0596) which were used in all calculations. The final R_1 was 0.0514 (I > 2σ(I)) and wR_2 was 0.1385 (all data). CCDC 2527300

Single crystal X-ray data for 11-Al

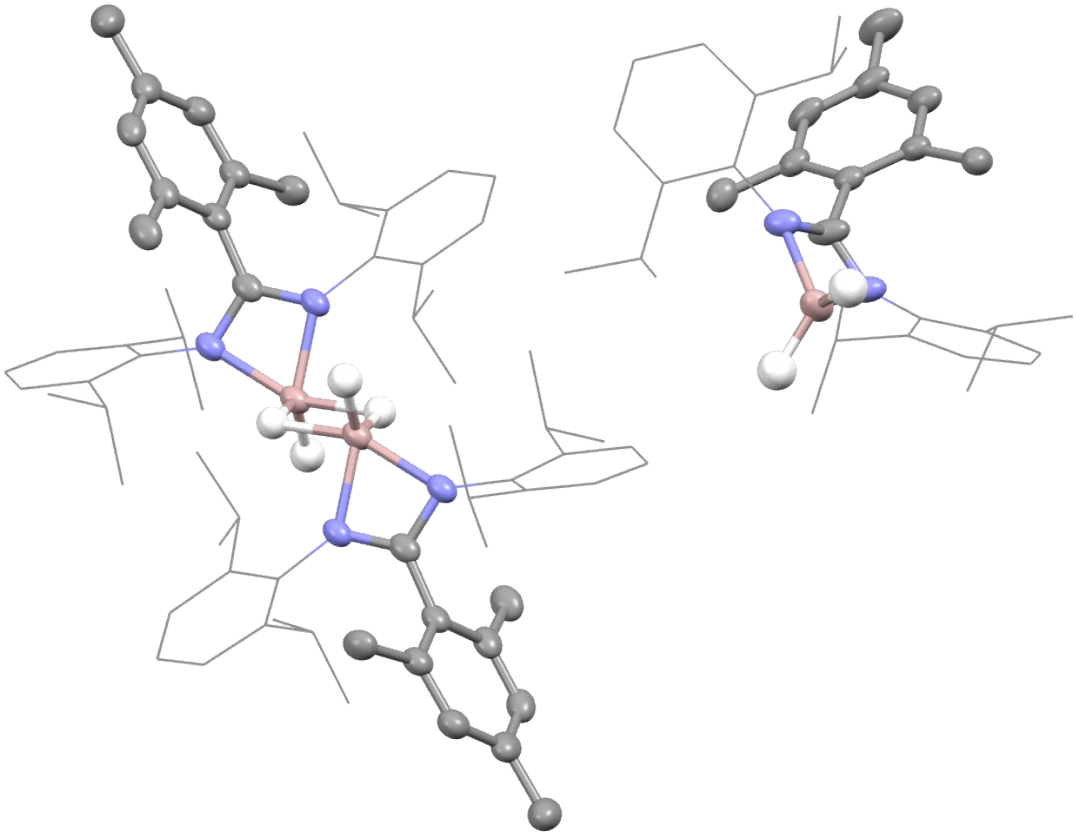


Figure S 17: Asymmetric unit of **11-Al**

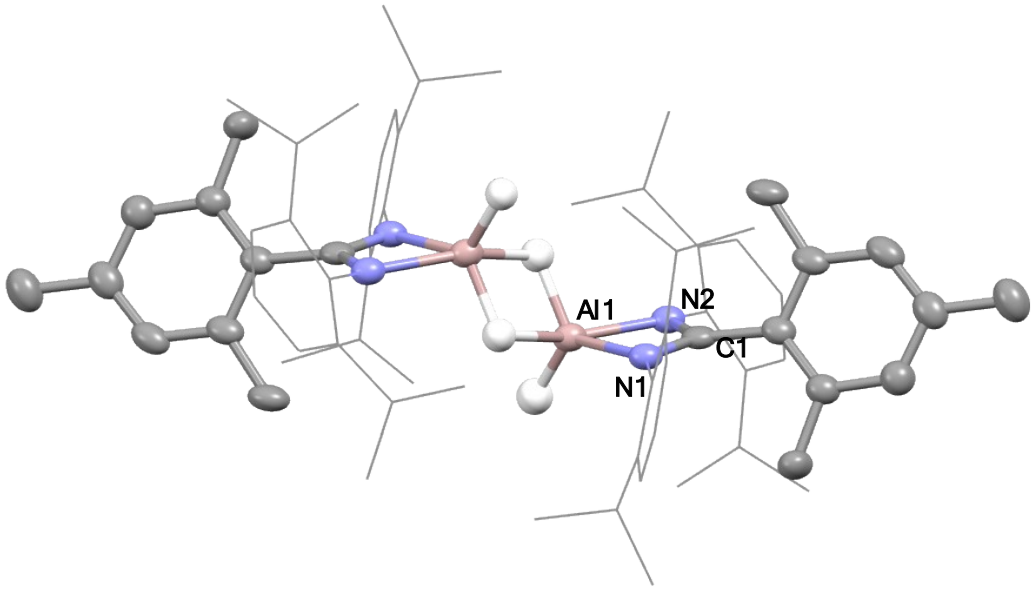


Figure S 18: The crystal structure of **11-Al-A**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

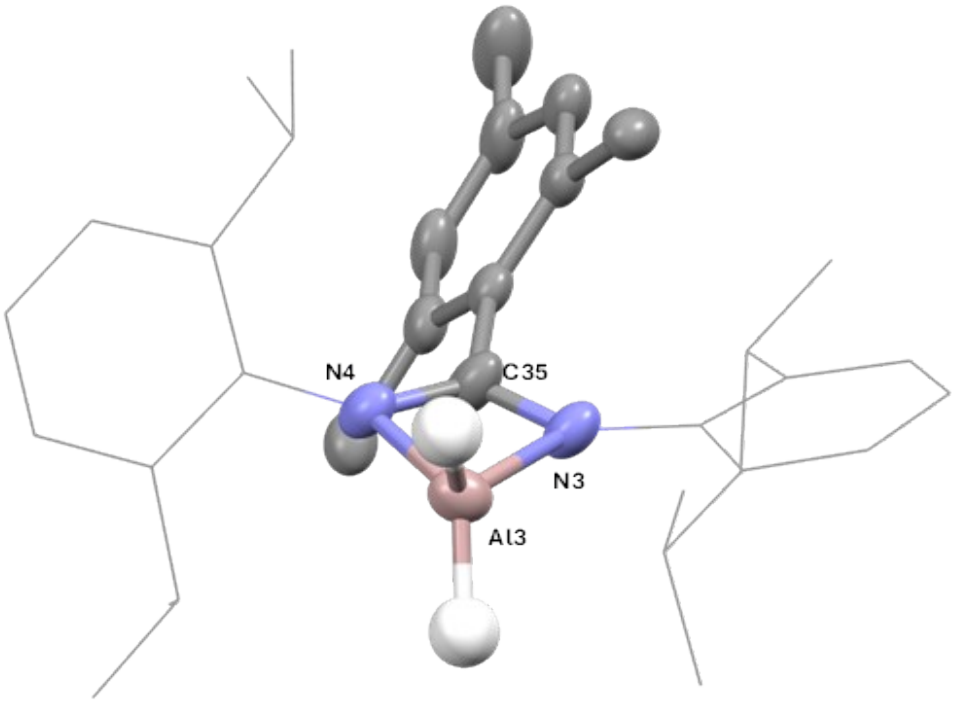


Figure S 19: The crystal structure of **11-Al-B**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **11-Al** were grown from the cooling of a saturated hexane solution. **11-Al** was found to crystallise with one half molecule of dimer **11-Al-A** and one half molecule of monomer **11-Al-B** in the asymmetric unit in the *I2/a* space group. There was disorder over one isopropyl group, which was modelled over two positions and one mesityl group which was modelled over two positions. Due to the disorder of the molecule the structure could not be solved adequately in the *I*a space group, so the structure was solved in the higher symmetry *I*2/a space group.

$C_{102}H_{141}Al_3N_6$ (M = 1532.14 g/mol): monoclinic, space group *I*2/a (no. 15), a = 15.5008(2) Å, b = 23.4406(3) Å, c = 25.4848(3) Å, β = 93.0560(10)°, V = 9246.7(2) Å^3, Z = 4, T = 100.00(10) K, μ(Mo Kα) = 0.089 mm^{-1}, *Dcalc* = 1.101 g/cm^3, 102333 reflections measured (5.454° ≤ 2Θ ≤ 61.908°), 12839 unique (R_{int} = 0.0470, R_{sigma} = 0.0341) which were used in all calculations. The final R_1 was 0.0527 (I > 2σ(I)) and wR_2 was 0.1411 (all data). CCDC 2527292

Single crystal X-ray data for 15-Al

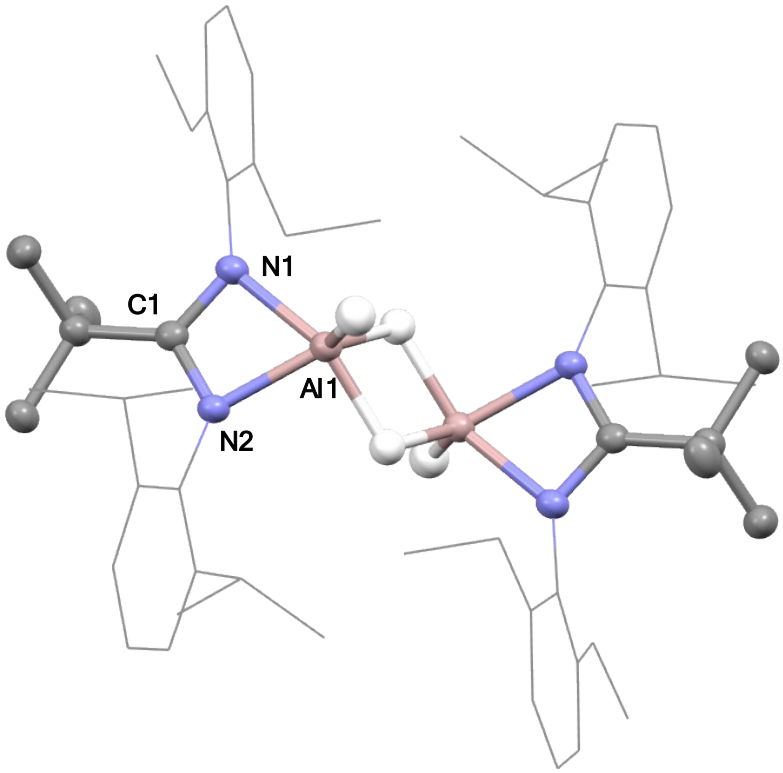


Figure S 20: The crystal structure of **15-Al**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **15-Al** were grown from the cooling of a saturated hexane solution. **15-Al** was found to crystallise with half a molecule of dimer in the asymmetric unit in the *I2/a* space group. The unit cell contained one half molecule of hexane per asymmetric unit, which was masked using the SQUEEZE function.

$C_{60}H_{96}Al_2N_4$ (M =927.36 g/mol): monoclinic, space group I2/a (no. 15), a = 23.8685(2) Å, b = 9.27690(10) Å, c = 25.8714(3) Å, β = 98.5120(10)°, V = 5665.49(10) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.748 mm^{-1}, D_{calc} = 1.087 g/cm^3, 130611 reflections measured (6.91° ≤ 2Θ ≤ 152.45°), 5889 unique (R_{int} = 0.0461, R_{sigma} = 0.0154) which were used in all calculations. The final R_1 was 0.0399 (I > 2σ(I)) and wR_2 was 0.1119 (all data). CCDC 2527297

Single crystal X-ray data for 20-Al

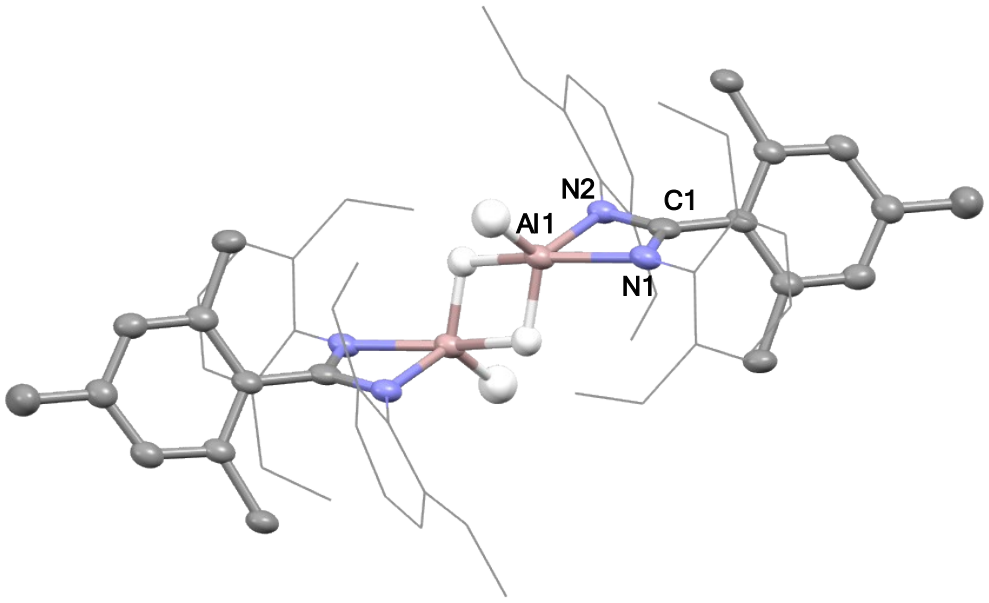


Figure S 21: The crystal structure of **20-Al**. (Solvent molecules and all hydrogens bar aluminium hydride atoms omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Crystals of **20-Al** were grown from the slow evaporation of a saturated hexane solution. Data was measured on a twinned crystal with three components. The model was solved from the data of the major component and refined against the HKL4 reflection file. Attempts to solve the crystal structure from the data from the minor twin components resulted in unsatisfactory models. **20-Al** was found to crystallise with one half molecule of dimer in the asymmetric unit in the $P\bar{1}$ space group.

$C_{60}H_{78}Al_2N_4$ (M =909.22 g/mol): triclinic, space group P-1 (no. 2), a = 9.0212(2) Å, b = 12.7128(5) Å, c = 13.2559(4) Å, α = 117.251(4)°, β = 91.690(2)°, γ = 97.297(2)°, V = 1333.93(8) Å^3, Z = 1, T = 100.00(10) K, μ(Cu Kα) = 0.793 mm^{-1}, *Dcalc* = 1.132 g/cm^3, 25371 reflections measured (7.54° ≤ 2Θ ≤ 136.488°), 4815 unique (R_{int} = 0.1196, R_{sigma} = 0.0649) which were used in all calculations. The final R_1 was 0.0775 (I > 2σ(I)) and wR_2 was 0.2251 (all data). CCDC 2527299

Aluminium monohydride X-ray data

Table S 3: Selected bond lengths (Å) and angles (°) for crystallographically characterised aluminium hydrides **2-Al''** and **16-Al''** [minor component] (table key: **compound no**.; ligand abbreviation; *ccdc no.*)

Complex	Al-N (Å)	Al-H (terminal) (Å)	N-Al-N (°)	Backbone Ar-NCNAl plane angle (°)	τ_5 value
2-Al'' ($^{dipp}Am^{p\text{-}t\text{BuPh}}$)$_2$AlH *2527291*	2.070(6) 1.927(5) 1.978(5) 1.997(5) [1.935(6)] [2.045(5)] [1.977(5)] [1.985(5)]	1.54(2) [1.65(5)]	66.02(15) 66.62(12) [66.37(15)] [66.88(12)]	26.71 [24.61]	0.18 [0.13]
16-Al'' ($^{dep}Am^{p\text{-}Tol}$)$_2$AlH *2527293*	1.961(2) 2.111(2) [1.9770(16)] [2.0026(16)]	1.52(5) [1.52(4)]	64.84(8) [66.67(7)]	42.81	0.13 [0.22]

Single crystal X-ray data for 2-Al''

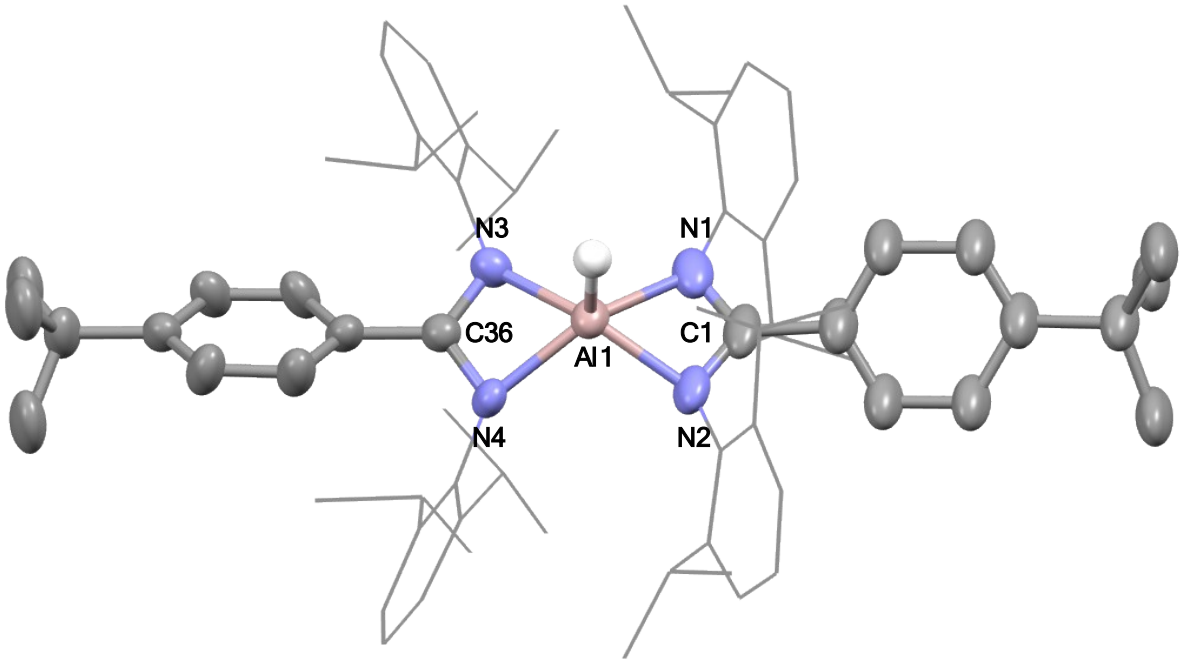


Figure S 22: The crystal structure of **2-Al''**. (All hydrogens bar aluminium hydride atoms, solvent molecules and disorder omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **2-Al''** were grown from the storage of a concentrated hexane solution at -40 °C. **2-Al''** was found to crystallise with one full molecule in the asymmetric unit, in the $^{P}{}_{n}$ space group. There was disorder over two isopropyl groups, the Al-H unit, and on *para-tert*-butyl phenyl group, which were all modelled over two positions. Due to the disorder of the molecule the structure could not be solved adequately in the *P*2/n space group, so the structure was solved in the lower symmetry *P*n space group. Twin law for merohedral inversion twins (-1, 0, 0, 0, -1, 0, 0, 0, -1) has been applied, with composition of 64(12)% of the major twin. The unit cell contained one molecule of hexane per asymmetric unit, which was masked using the SQUEEZE function.

$C_{76}H_{109}AlN_4$ (M = 1105.65 g/mol): monoclinic, space group Pn (no. 7), a = 12.0013(3) Å, b = 21.8264(6) Å, c = 13.1336(3) Å, β = 96.842(2)°, V = 3415.78(15) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 0.575 mm^{-1}, *Dcalc* = 1.075 g/cm^3, 42481 reflections measured (7.898° ≤ 2Θ ≤ 151.358°), 10787 unique (R_{int} = 0.0391, R_{sigma} = 0.0374) which were used in all calculations. The final R_1 was 0.0666 (I > 2σ(I)) and wR_2 was 0.2122 (all data). CCDC 2527291

Single crystal X-ray data for 16-Al''

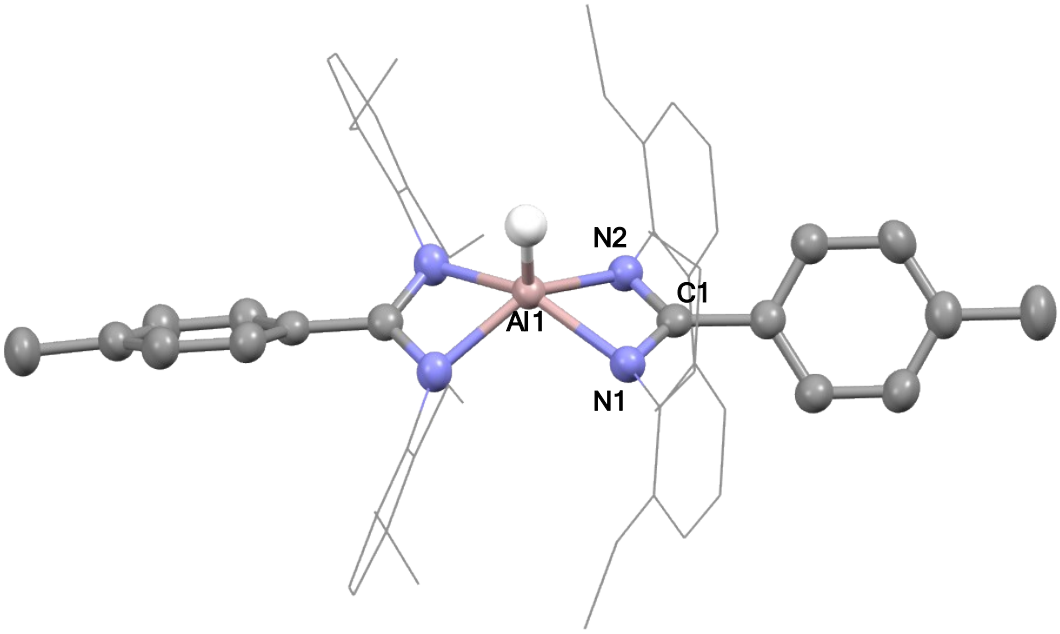


Figure S 23: The crystal structure of **16-Al''**. (All hydrogens bar aluminium hydride atoms, solvent molecules and disorder omitted, *N*-aryl groups wireframe for clarity, thermal ellipsoids 50% probability)

Single crystals of **16-Al''** were grown from benzene at room temperature. **16-Al''** crystallised with half a molecule in the asymmetric unit in the *C2/c* space group. There was disorder over the Al-H unit, which was modelled in two positions, in a 0.775:0.225 ratio. The unit cell contained 0.5 molecules of benzene per asymmetric unit.

$C_{62}H_{73}AlN_4$ (M =901.22 g/mol): monoclinic, space group C2/c (no. 15), a = 22.1834(5) Å, b = 9.6461(2) Å, c = 25.8423(6) Å, β = 102.843(2)°, V = 5391.5(2) Å^3, Z = 4, T = 150.00(10) K, μ(Cu Kα) = 0.633 mm^{-1}, D_{calc} = 1.110 g/cm^3, 64599 reflections measured (7.016° ≤ 2Θ ≤ 157.79°), 5699 unique (R_{int} = 0.0894, R_{sigma} = 0.0349) which were used in all calculations. The final R_1 was 0.0699 (I > 2σ(I)) and wR_2 was 0.2130 (all data). CCDC 2527293

5. Computational details

General remarks

All DFT calculations were performed using the Gaussian 16 software (Revision C.01) as compiled on King's College London's CREATE High Performance Computing (HPC) cluster.[19,20] Initial coordinates were obtained from the relevant SC-XRD structures where possible. All geometries were optimised at the M06-2X-D3 level of theory, including Grimme's atom-pairwise correction to account for dispersion effects, using either 6-31G** for ligands or a split 6-31G**(C, H, N, O, F)/SDDAll (Al) basis set for the aluminium hydride species. Solvent corrections were carried out using the 6-311G basis set utilising the PCM solvent model. HOMO-LUMO gaps were calculated as single point calculations using def2-SVP. For all calculations, an ultrafine integration grid corresponding to a pruned grid of 99 radial shells and 590 angular points per shell was employed to ensure highly accurate numerical integration of the electron density. The same procedure was used for literature compounds. In all cases, ground state geometries were confirmed by way of frequency calculation at the same level of theory to indicate the absence of negative eigenvalues in the Hessian matrix. Buried volume calculations were carried out on the SambVCA website.[21]

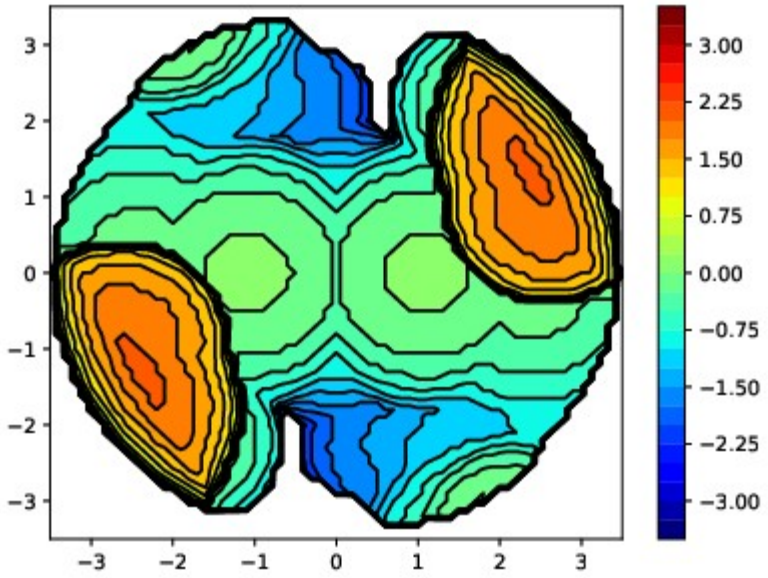
Calculated energies of ligand conformations

Table S 4: Calculated energies of the E_{syn}, E_{anti}, Z_{syn} and Z_{anti} conformations of ligands **7**, **8**, **12** and **22**, calculated at M062x (6-31G**), with solvent corrections carried out at M062x (6-311G) with the solvent PCM model, with GD3 dispersion model

Ligand	**E_{syn} (benzene) [chloroform]**	**E_{anti} (benzene) [chloroform]**	**Z_{anti} (benzene) [chloroform]**	**Z_{syn} (benzene) [chloroform]**
7	0 (0) [0]	1.46 (1.04) [1.17]	0.08 (0.17) [0.35]	8.17 (7.99) [8.10]
10	1.52 (1.71) [1.79]	5.04 (4.29) [4.34]	0 (0) [0]	3.68 (3.22) [3.03]
12	3.62 (2.91) [2.88]	12.18 (11.34) [11.52]	0 (0) [0]	9.16 (6.92) [7.11]
22	11.46 (9.47) [9.84]	8.04 (7.54) [8.25]	1.50 (0.60) [1.29]	0 (0) [0]

Steric quantification

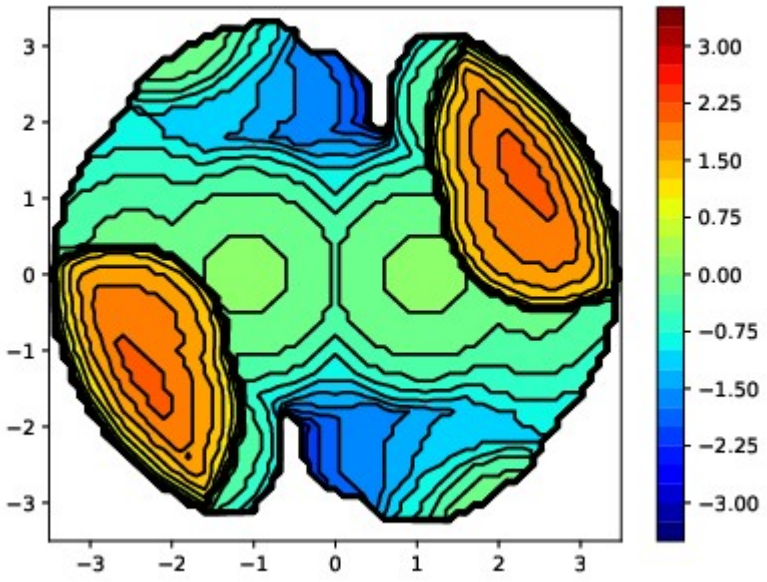
Buried volume maps



%V Free	**%V Buried**	% V Tot/V Ex
51.2	**48.8**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	18.7	26.1	44.9	**41.7**	58.3
NW	27.2	17.7	44.9	**60.6**	39.4
NE	18.7	26.1	44.9	**41.8**	58.2
SE	27.2	17.7	44.9	**60.6**	39.4

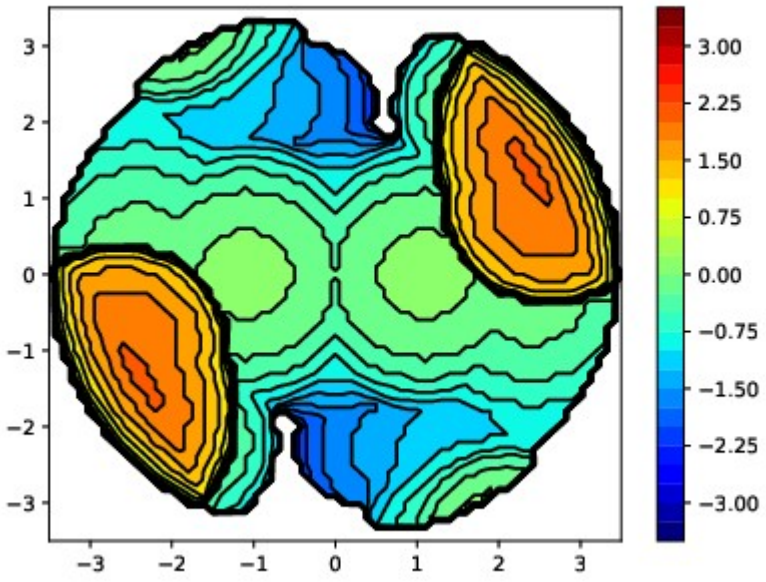
Figure S 24: Buried volume map of **1-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.1	**48.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	18.6	26.3	44.9	**41.4**	58.6
NW	27.3	17.5	44.9	**60.9**	39.1
NE	18.4	26.5	44.9	**40.9**	59.1
SE	27.4	17.5	44.9	**61.0**	39.0

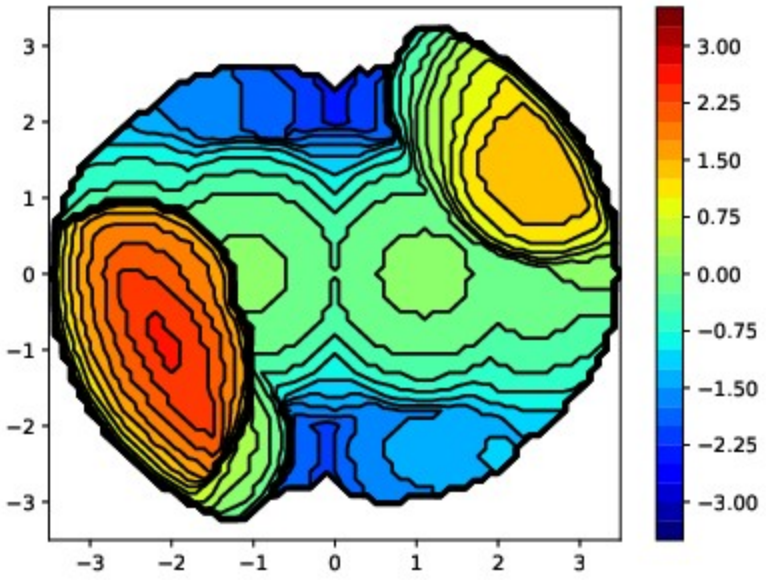
Figure S 25: Buried volume map of **2-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.2	**48.8**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	19.0	25.9	44.9	**42.3**	57.7
NW	27.0	17.9	44.9	**60.1**	39.9
NE	19.0	25.9	44.9	**42.3**	57.7
SE	27.0	17.9	44.9	**60.1**	39.9

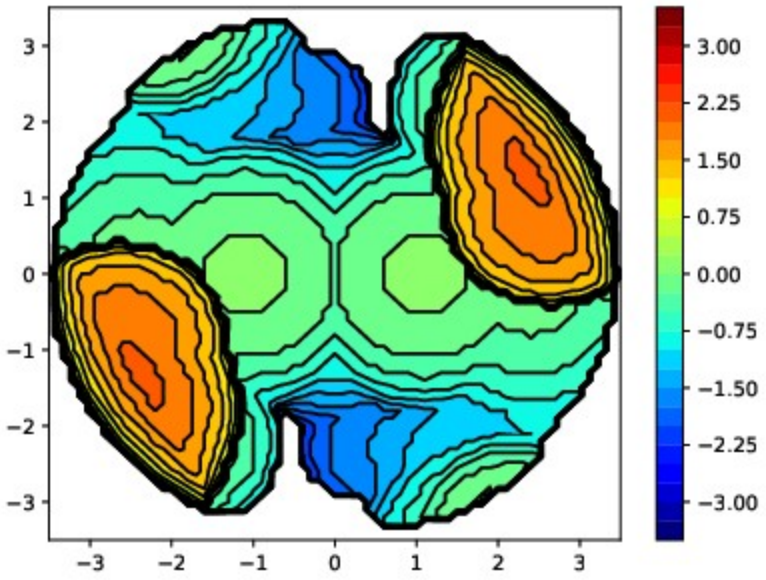
Figure S 26: Buried volume map of **3-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.4	**48.6**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	15.1	29.7	44.9	**33.7**	66.3
NW	27.4	17.4	44.9	**61.2**	38.8
NE	20.7	24.2	44.9	**46.2**	53.8
SE	29.0	15.9	44.9	**64.6**	35.4

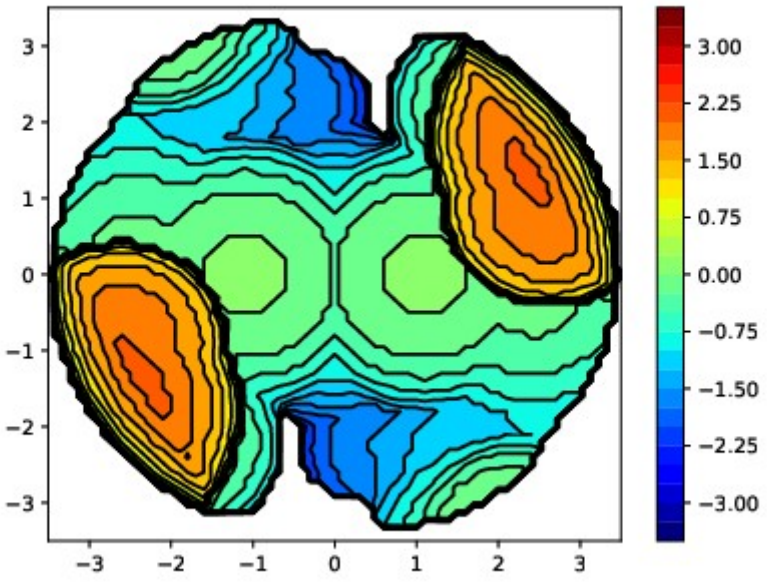
Figure S 27: Buried volume map of **4-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N, O: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.1	**48.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	18.7	26.2	44.9	**41.7**	58.3
NW	27.2	17.7	44.9	**60.6**	39.4
NE	18.7	26.2	44.9	**41.7**	58.3
SE	27.2	17.7	44.9	**60.6**	39.4

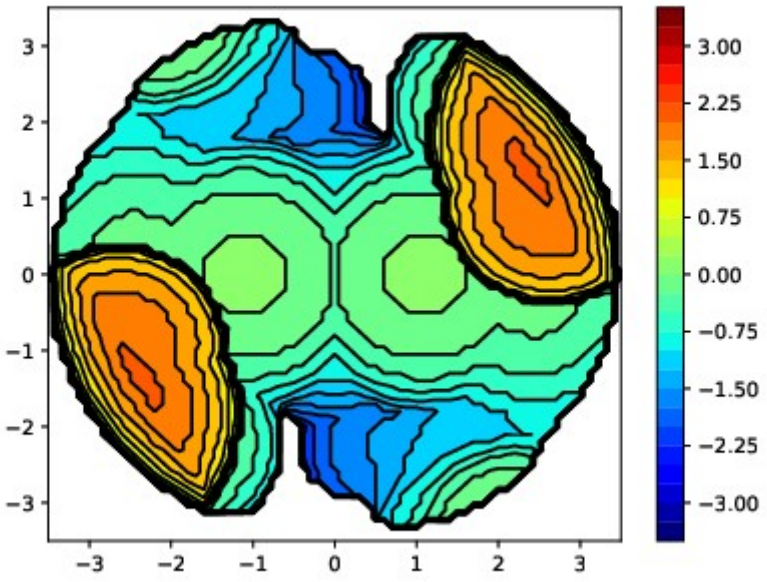
Figure S 28: Buried volume map of **5-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.2	**48.8**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	18.5	26.3	44.9	**41.3**	58.7
NW	27.3	17.5	44.9	**60.9**	39.1
NE	18.7	26.2	44.9	**41.6**	58.4
SE	27.3	17.6	44.9	**60.8**	39.2

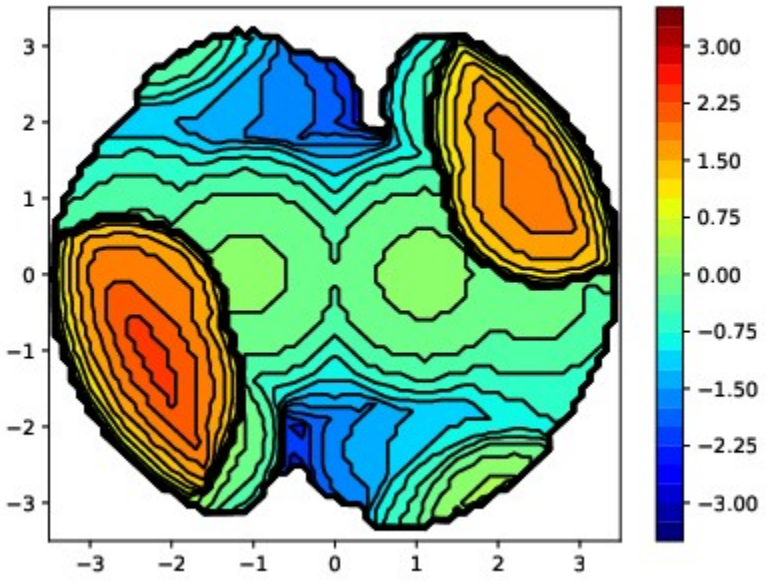
Figure S 29: Buried volume map of **6-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N, F: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.4	**48.6**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	18.7	26.1	44.9	**41.7**	58.3
NW	27.4	17.4	44.9	**61.1**	38.9
NE	18.7	26.1	44.9	**41.7**	58.3
SE	27.4	17.4	44.9	**61.1**	38.9

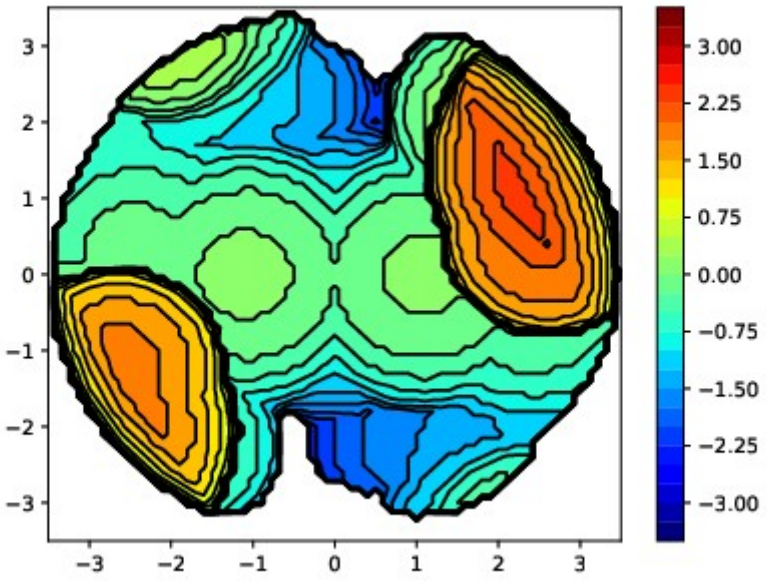
Figure S 30: Buried volume map of **7-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
50.3	**49.7**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	17.2	27.7	44.9	**38.3**	61.7
NW	27.0	17.8	44.9	**60.2**	39.8
NE	19.3	25.5	44.9	**43.1**	56.9
SE	26.8	18.1	44.9	**59.7**	40.3

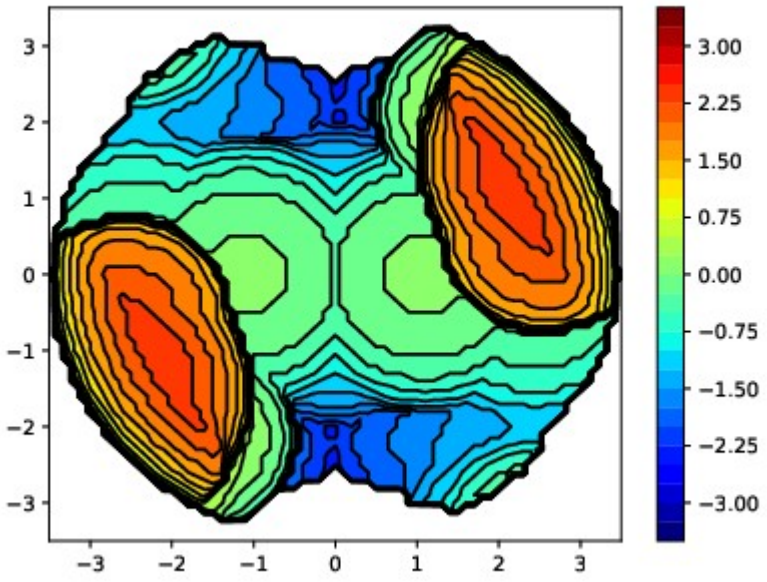
Figure S 31: Buried volume map of **8-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
50.3	**49.7**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	19.9	24.9	44.9	**44.5**	55.5
NW	26.3	18.5	44.9	**58.7**	41.3
NE	17.0	27.9	44.9	**37.9**	62.1
SE	27.0	17.8	44.9	**60.3**	39.7

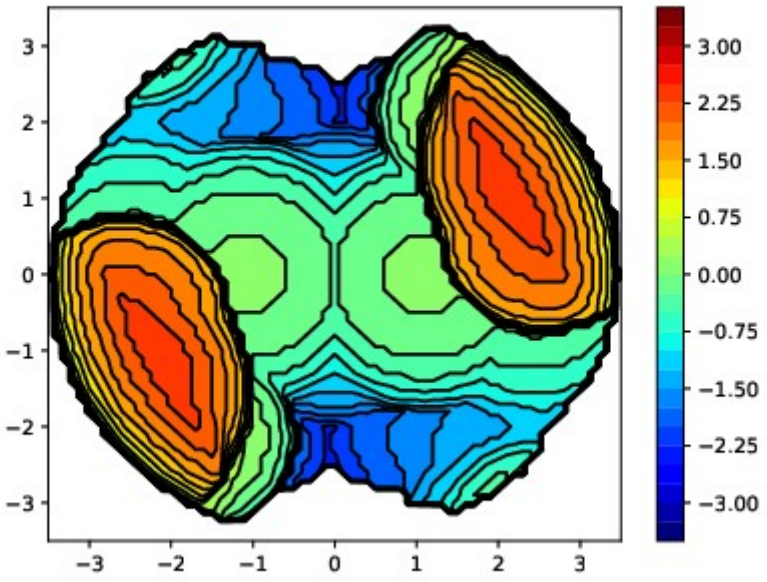
Figure S 32: Buried volume map of **9-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
48.1	**51.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	15.7	29.2	44.9	**35.0**	65.0
NW	27.5	17.4	44.9	**61.3**	38.7
NE	15.7	29.2	44.9	**35.0**	65.0
SE	27.5	17.4	44.9	**61.3**	38.7

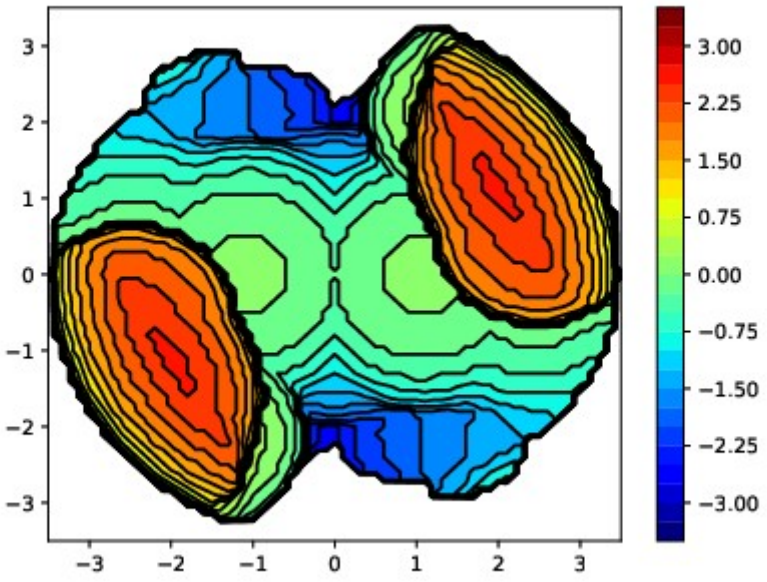
Figure S 33: Buried volume map of **10-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
48.2	51.8	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	15.7	29.1	44.9	35.1	64.9
NW	27.5	17.4	44.9	61.3	38.7
NE	15.7	29.1	44.9	35.1	64.9
SE	27.5	17.4	44.9	61.3	38.7

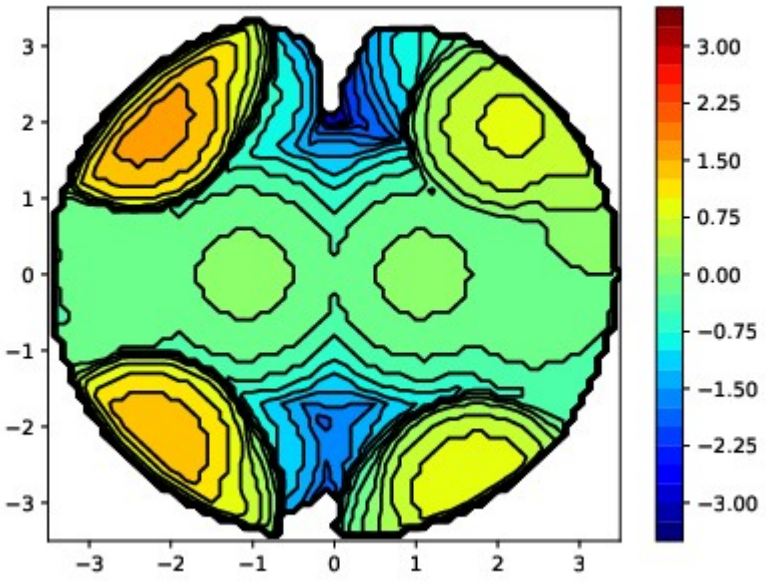
Figure S 34: Buried volume map of **11-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
47.3	**52.7**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	14.3	30.5	44.9	**31.9**	68.1
NW	28.1	16.7	44.9	**62.7**	37.3
NE	14.3	30.5	44.9	**31.9**	68.1
SE	28.1	16.7	44.9	**62.7**	37.3

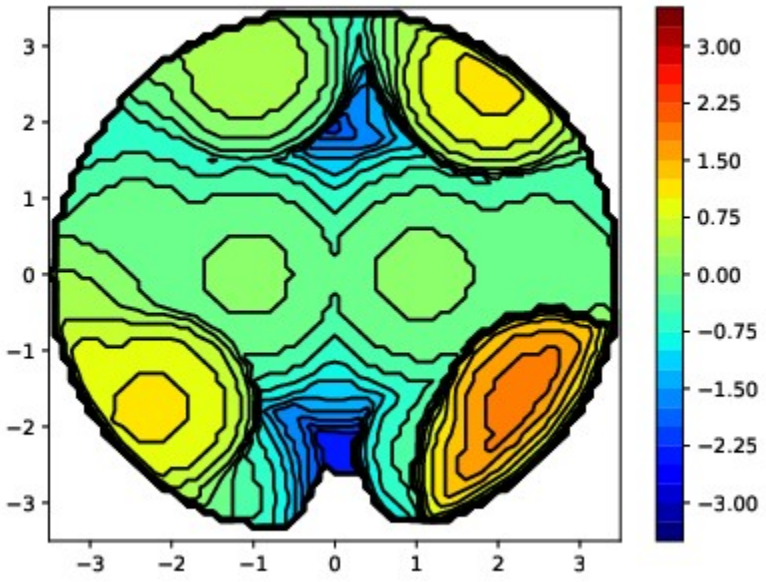
Figure S 35: Buried volume map of **12-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
49.3	**50.7**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	21.6	23.3	44.9	**48.1**	51.9
NW	20.9	24.0	44.9	**46.5**	53.5
NE	23.3	21.5	44.9	**52.0**	48.0
SE	22.7	22.1	44.9	**50.7**	49.3

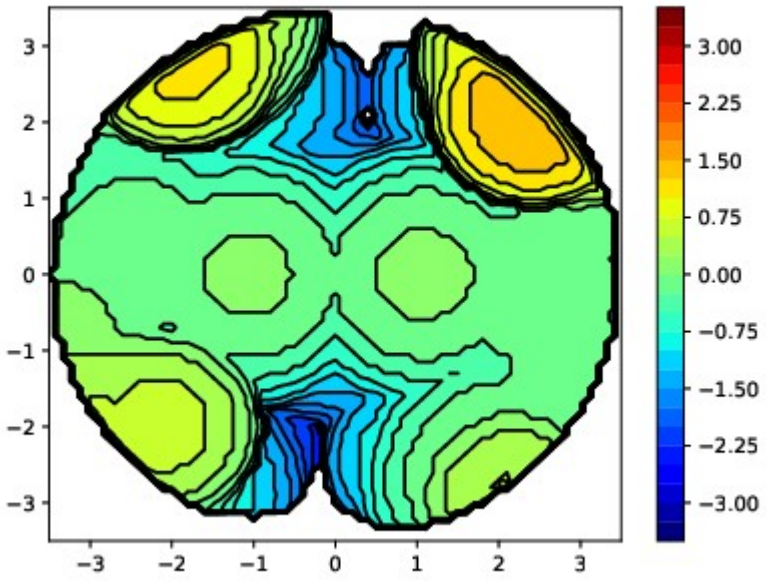
Figure S 36: Buried volume map of **13-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
48.3	51.7	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	21.7	23.1	44.9	48.4	51.6
NW	23.1	21.8	44.9	51.4	48.6
NE	22.2	22.7	44.9	49.4	50.6
SE	19.6	25.2	44.9	43.7	56.3

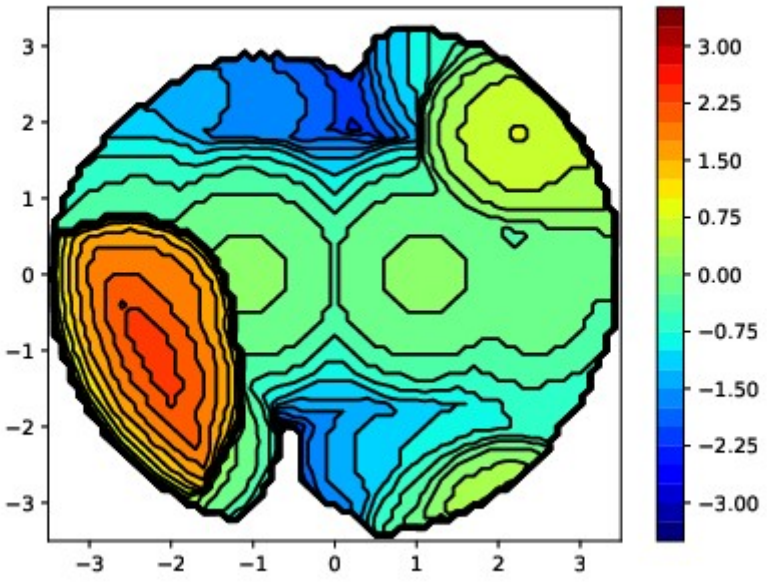
Figure S 37: Buried volume map of **14-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
51.9	**48.1**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	24.1	20.7	44.9	**53.8**	46.2
NW	22.6	22.3	44.9	**50.3**	49.7
NE	22.3	22.6	44.9	**49.7**	50.3
SE	24.1	20.8	44.9	**53.7**	46.3

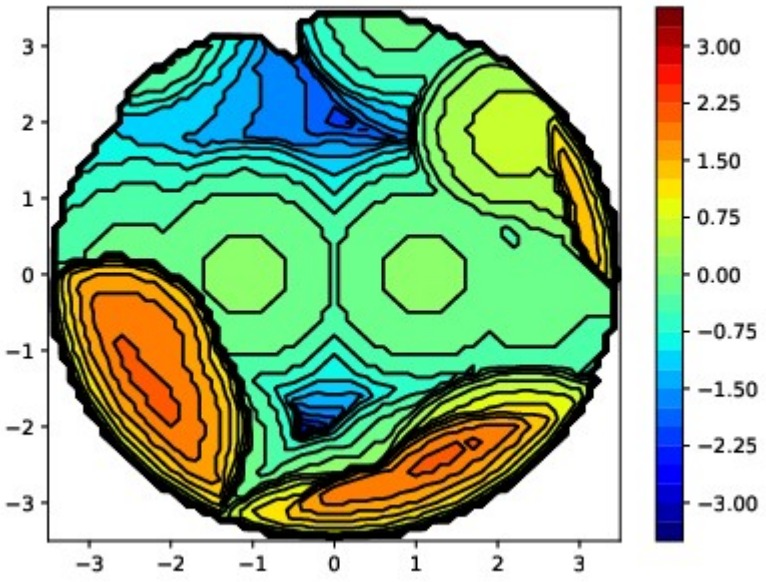
Figure S 38: Buried volume map of **15-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
53.1	**46.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	17.3	27.6	44.9	**38.5**	61.5
NW	27.7	17.2	44.9	**61.7**	38.3
NE	24.2	20.7	44.9	**53.9**	46.1
SE	26.2	18.6	44.9	**58.5**	41.5

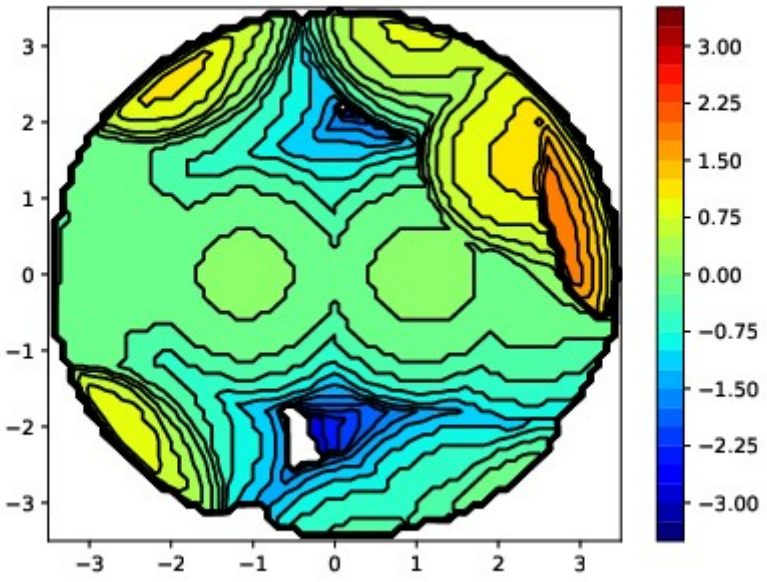
Figure S 39: Buried volume map of **16-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
47.2	52.8	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	15.4	29.5	44.9	34.2	65.8
NW	28.4	16.5	44.9	63.3	36.7
NE	22.3	22.6	44.9	49.6	50.4
SE	18.7	26.2	44.9	41.6	58.4

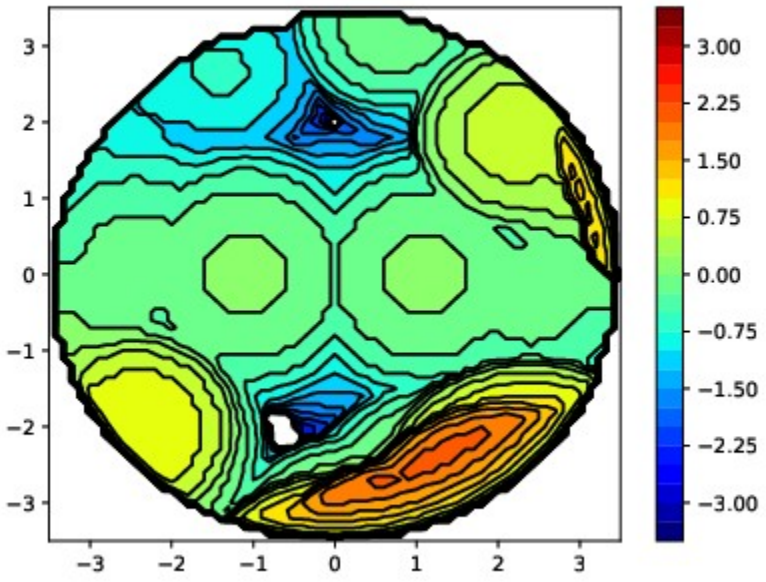
Figure S 40: Buried volume map of **17-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
52.3	47.7	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	25.7	19.1	44.9	57.4	42.6
NW	23.2	21.7	44.9	51.7	48.3
NE	18.3	26.5	44.9	40.8	59.2
SE	26.5	18.3	44.9	59.2	40.8

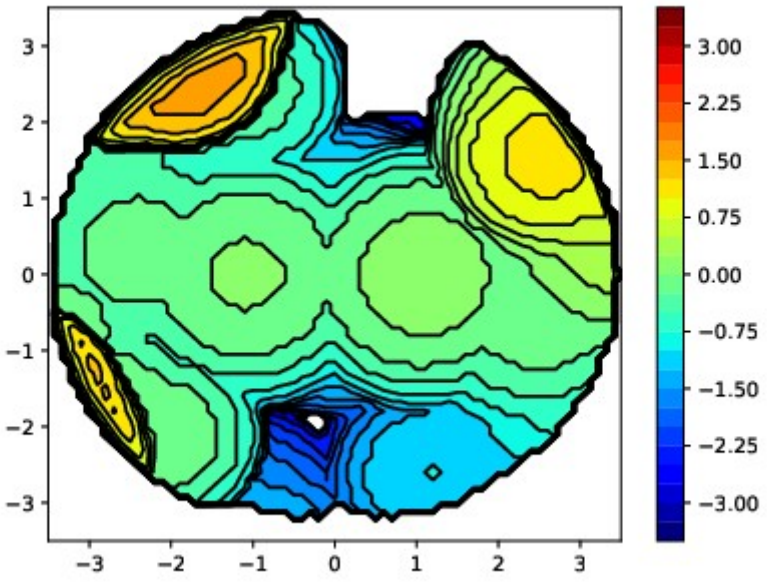
Figure S 41: Buried volume map of **17-Al**, from crystal structure



%V Free	%V Buried	% V Tot/V Ex
49.7	50.3	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	21.5	23.4	44.9	47.8	52.2
NW	27.6	17.3	44.9	61.4	38.6
NE	22.0	22.9	44.9	48.9	51.1
SE	18.2	26.7	44.9	40.5	59.5

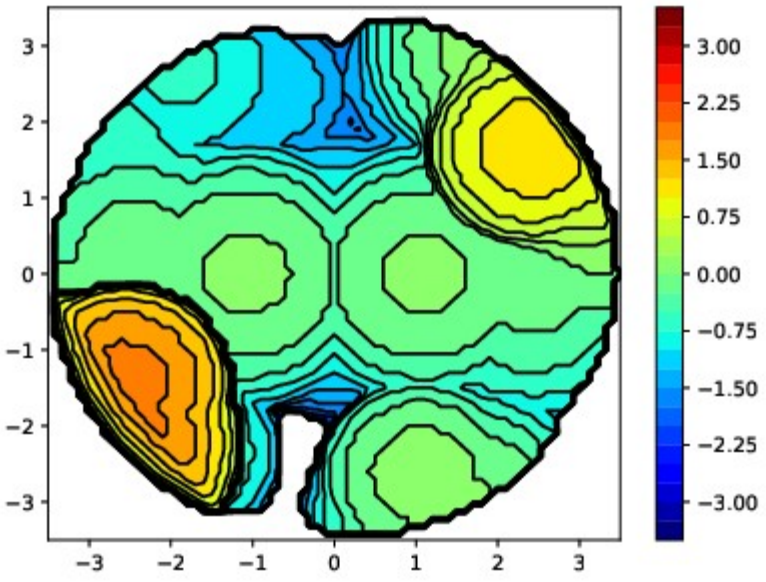
Figure S 42: Buried volume map of **18-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
55.2	44.8	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	26.2	18.7	44.9	58.4	41.6
NW	21.8	23.1	44.9	48.6	51.4
NE	23.8	21.0	44.9	53.1	46.9
SE	27.3	17.6	44.9	60.8	39.2

Figure S 43: Buried volume map of **18-Al**, from crystal structure



%V Free	%V Buried	% V Tot/V Ex
51.9	**48.1**	99.9

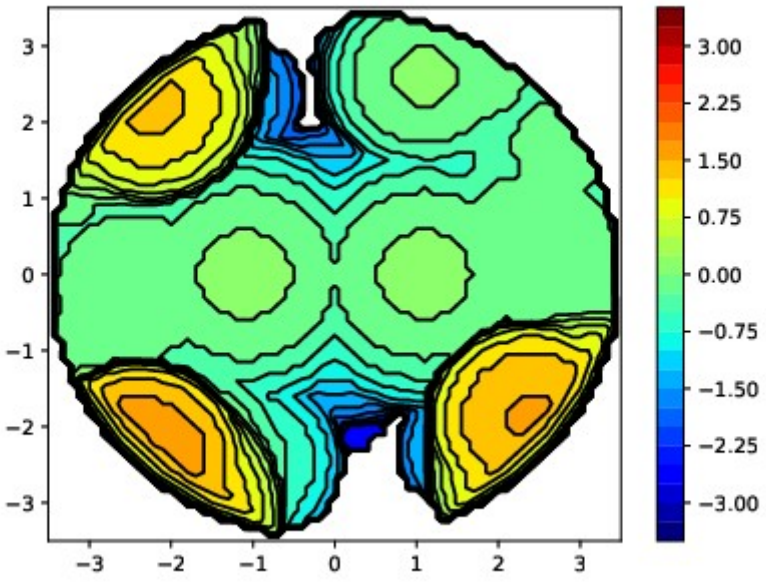
Quadrant	V f	V b	V t	%V f	%V b
SW	20.0	24.9	44.9	**44.6**	55.4
NW	27.4	17.4	44.9	**61.1**	38.9
NE	21.3	23.6	44.9	**47.5**	52.5
SE	24.4	20.5	44.9	**54.3**	45.7

Figure S 44: Buried volume map of **19-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)

%V Free	**%V Buried**	% V Tot/V Ex
51.4	**48.6**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	15.1	29.7	44.9	**33.7**	66.3
NW	27.4	17.4	44.9	**61.2**	38.8
NE	20.7	24.2	44.9	**46.2**	53.8
SE	29.0	15.9	44.9	**64.6**	35.4

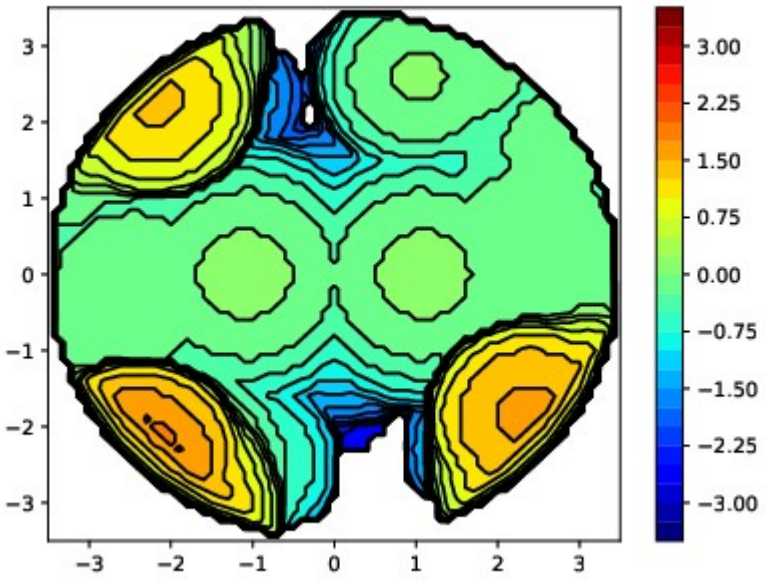
Figure S 45: Buried volume map of **20-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
49.9	50.1	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	20.5	24.3	44.9	45.8	54.2
NW	22.7	22.2	44.9	50.5	49.5
NE	23.8	21.0	44.9	53.1	46.9
SE	22.5	22.4	44.9	50.1	49.9

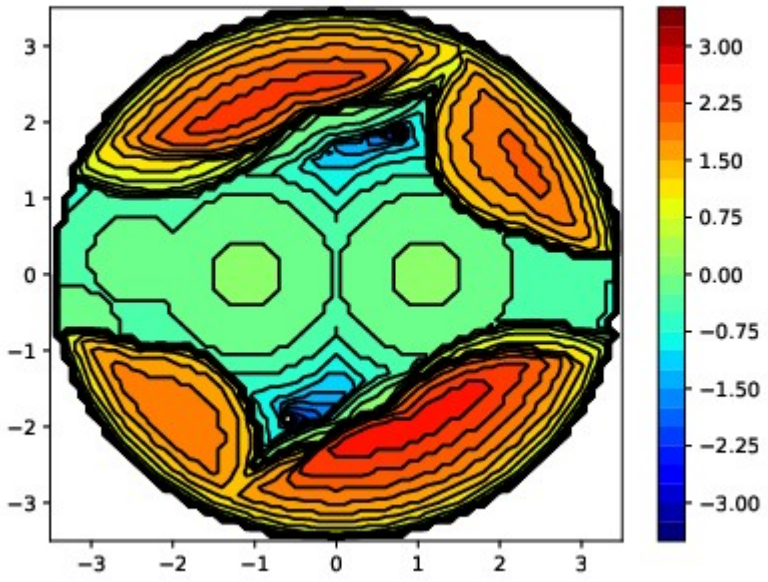
Figure S 46: Buried volume map of **21-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	**%V Buried**	% V Tot/V Ex
49.6	**50.4**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	20.3	24.5	44.9	**45.3**	54.7
NW	22.5	22.4	44.9	**50.1**	49.9
NE	23.7	21.1	44.9	**52.9**	47.1
SE	22.5	22.4	44.9	**50.1**	49.9

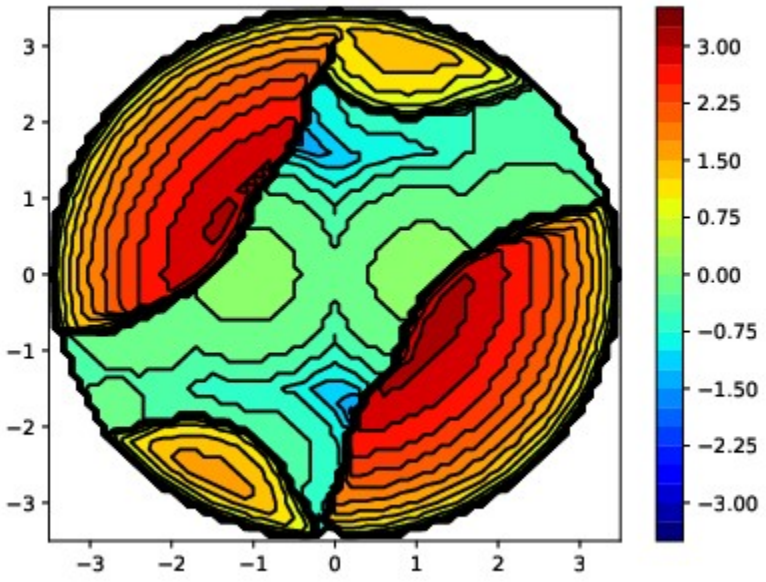
Figure S 47: Buried volume map of **22-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
35.1	64.9	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	17.5	27.4	44.9	39.0	61.0
NW	16.0	28.9	44.9	35.7	64.3
NE	16.5	28.4	44.9	36.8	63.2
SE	12.9	31.9	44.9	28.8	71.2

Figure S 48: Buried volume map of **23-Al**, calculated monomeric structure (M062x-D3 Al: SDDAll, C, H, N: 6-31G**)



%V Free	%V Buried	% V Tot/V Ex
33.3	66.7	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	19.7	25.1	44.9	44.0	56.0
NW	10.5	34.4	44.9	23.4	76.6
NE	19.4	25.5	44.9	43.2	56.8
SE	10.1	34.8	44.9	22.5	77.5

Figure S 49: Buried volume map of **23-Al**, from crystal structure

HOMO-LUMO gaps of aluminium hydride complexes

Table S 5: Calculated HOMO-LUMO gaps(eV) for aluminium hydrides **1-Al** – **23-Al** calculated at M062x (def2-SVP) level of theory, with the GD3 dispersion model

Aluminium complex	***ΔE (eV)***
1-Al	6.547122
2-Al	6.538158
3-Al	6.587811
4-Al	6.681393
5-Al	5.921262
6-Al	6.21405
7-Al	6.581466
8-Al	6.649074
9-Al	6.695136
10-Al	6.655176
11-Al	6.684471
12-Al	6.620319
13-Al	7.663275
14-Al	7.391007
15-Al	7.765362
16-Al	6.464934
17-Al	6.600474
18-Al	6.561216
19-Al	6.556329
20-Al	6.621615
21-Al	7.950663
22-Al	7.877061
23-Al	6.937542

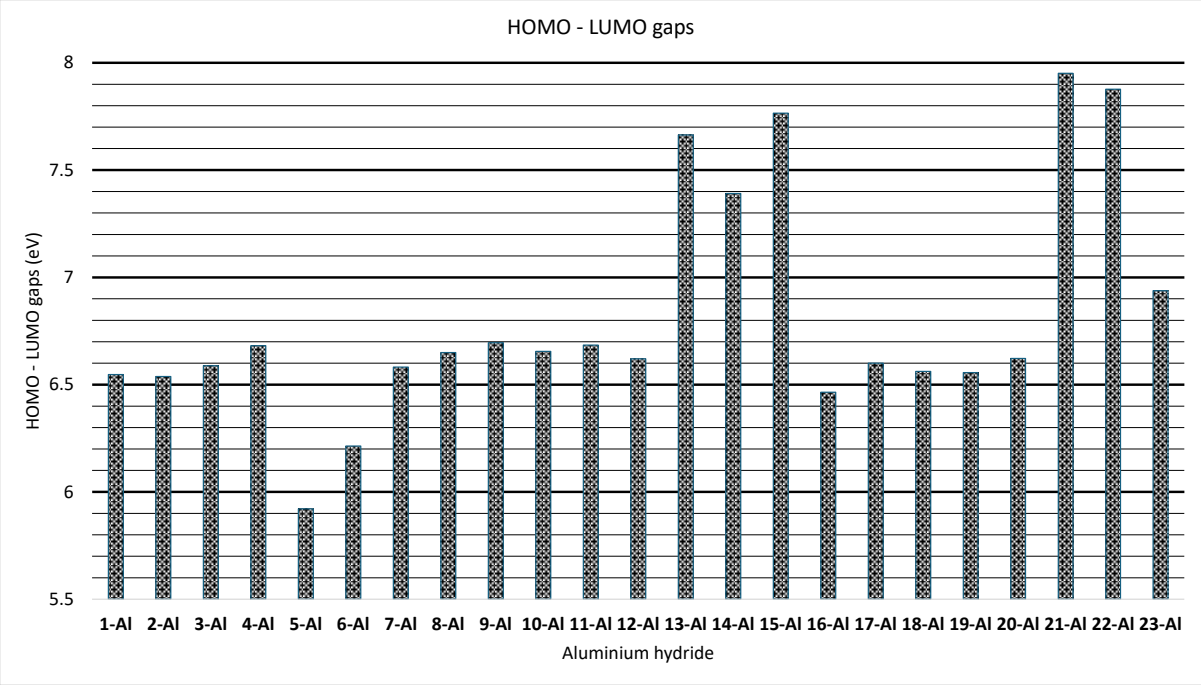


Figure S 50: Graph showing the calculated HOMO-LUMO gaps (eV) for aluminium hydrides **1-Al** – **23-Al** calculated at M062x (def2-SVP) level of theory, with the GD3 dispersion model

6. Multinuclear NMR data

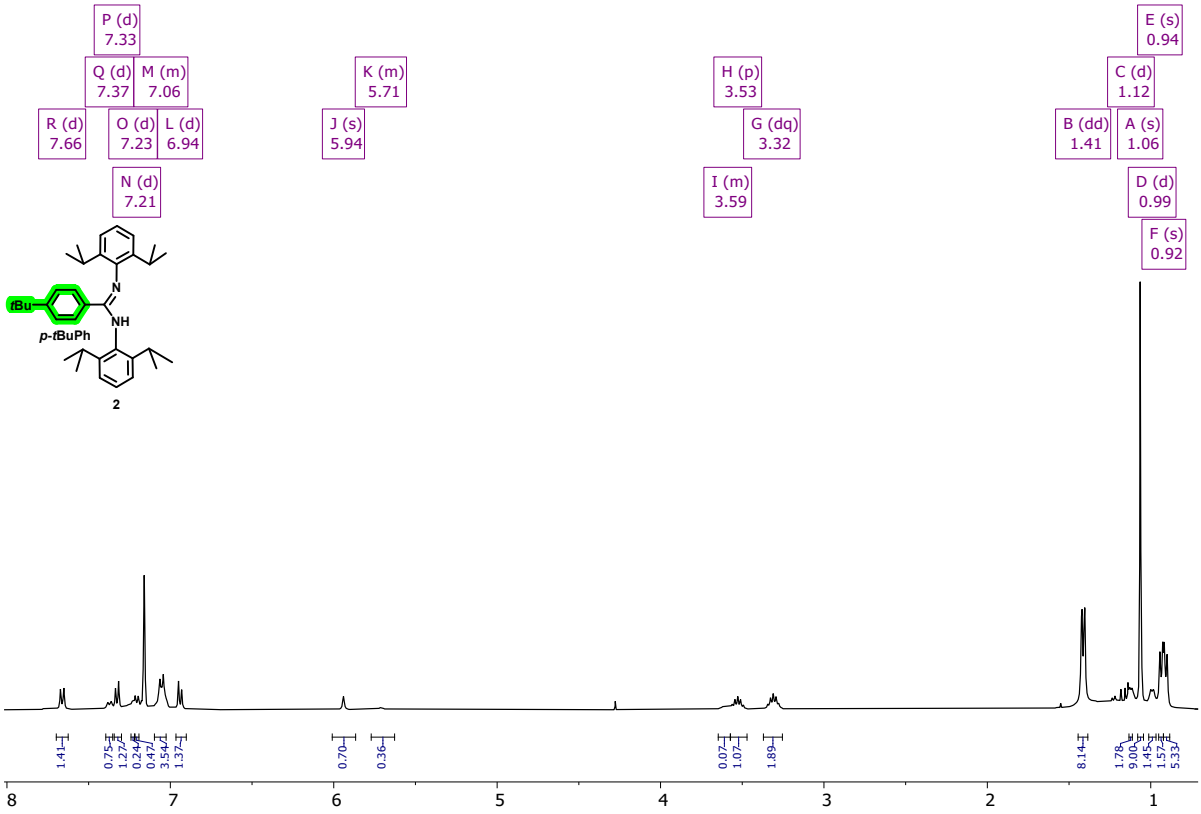


Figure S 51: ^{1}H NMR spectrum (400 MHz, 298 K) of **2** in benzene-d_6

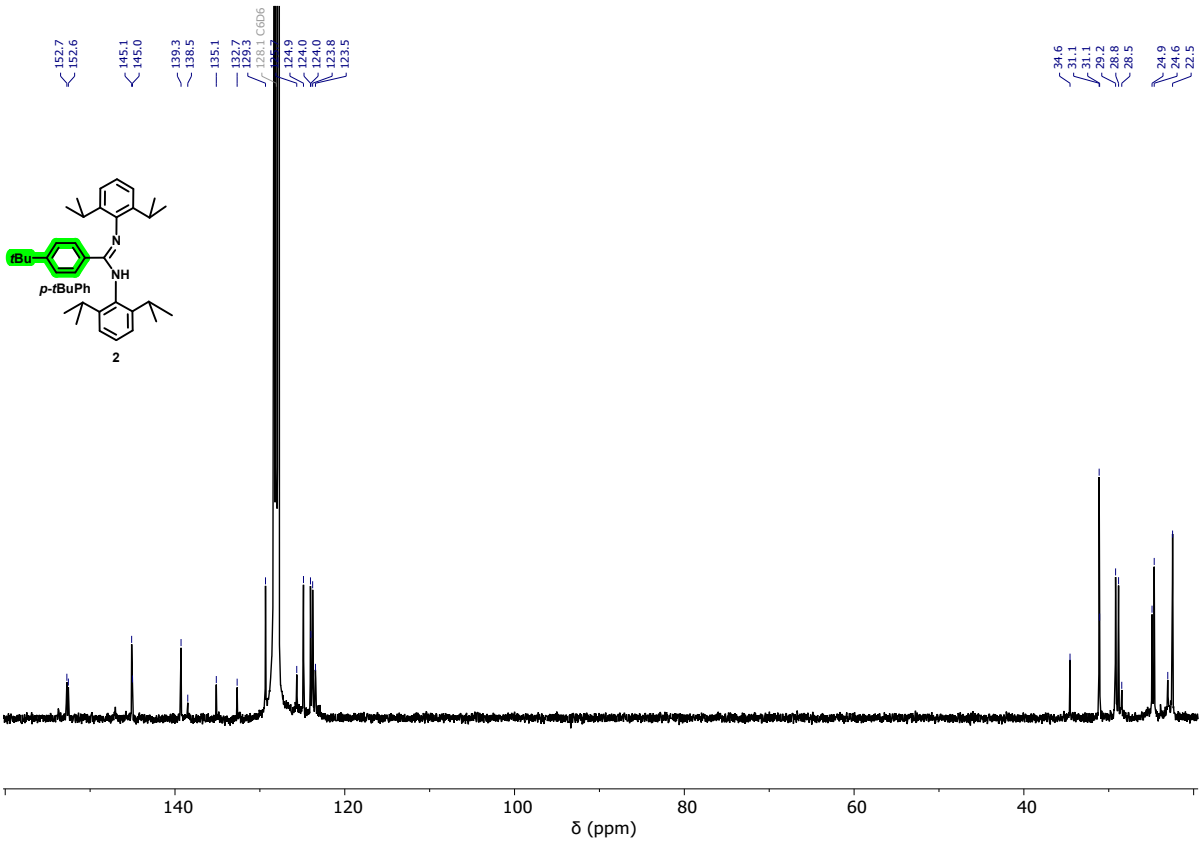


Figure S 52: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **2** in benzene-d_6

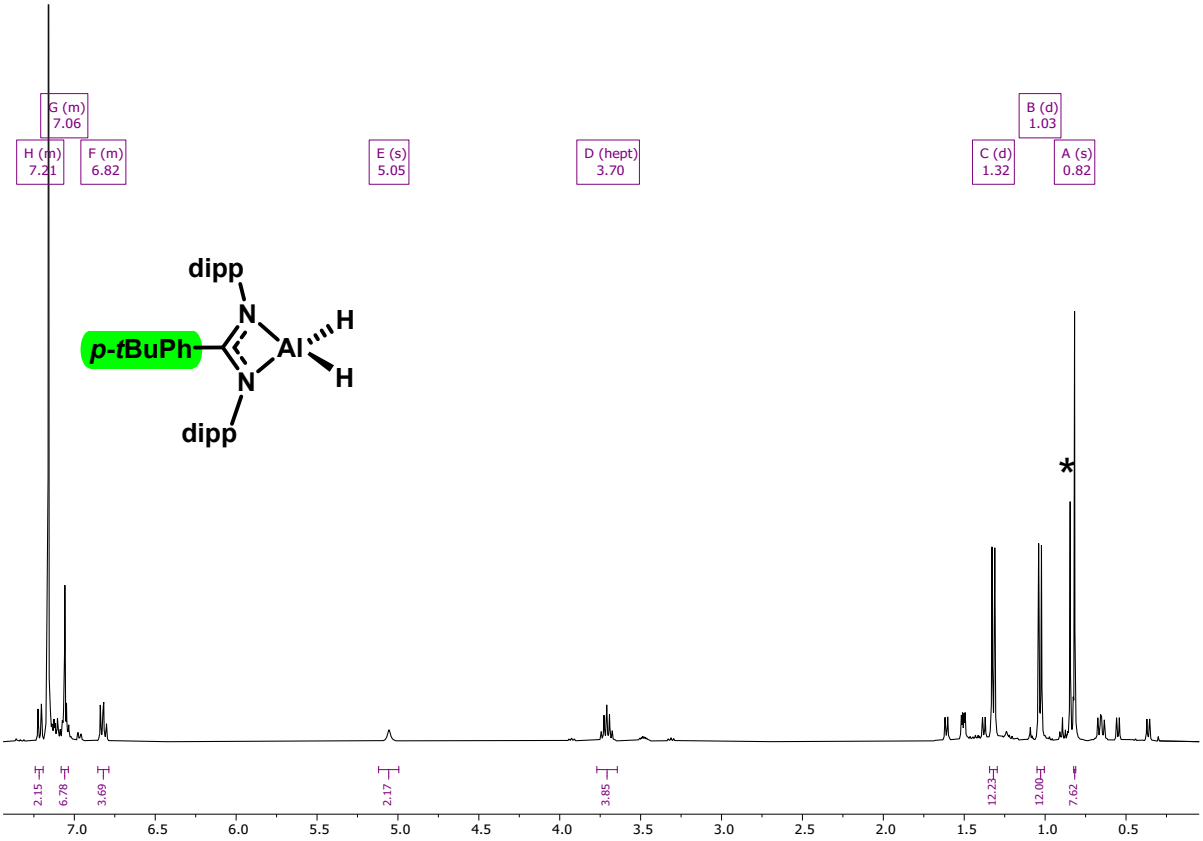


Figure S 53: ^{1}H NMR spectrum (400 MHz, 298 K) of **2-Al** in benzene-d_6 with **2-Al''** impurity, *t*Bu CH_3 signal marked with a *

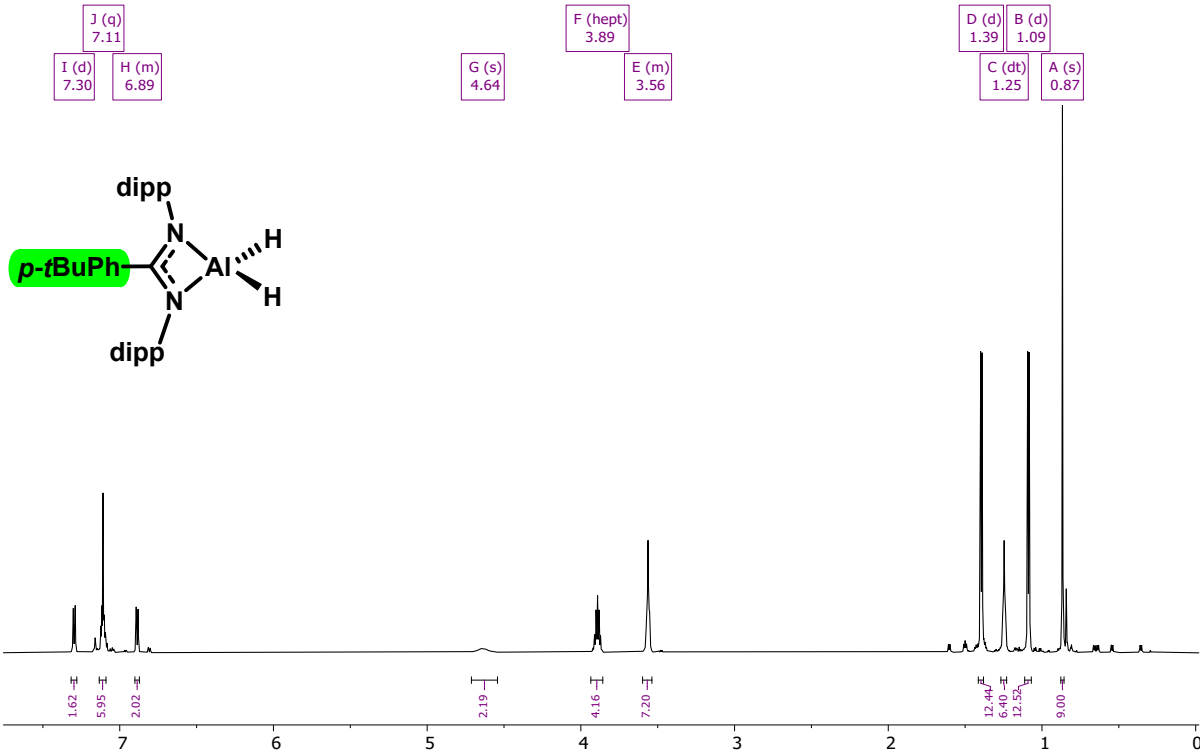


Figure S 54: ^{1}H NMR spectrum (400 MHz, 298 K) of **[(2-Al).3THF]** in benzene-d_6 with slight **2-Al''** impurity

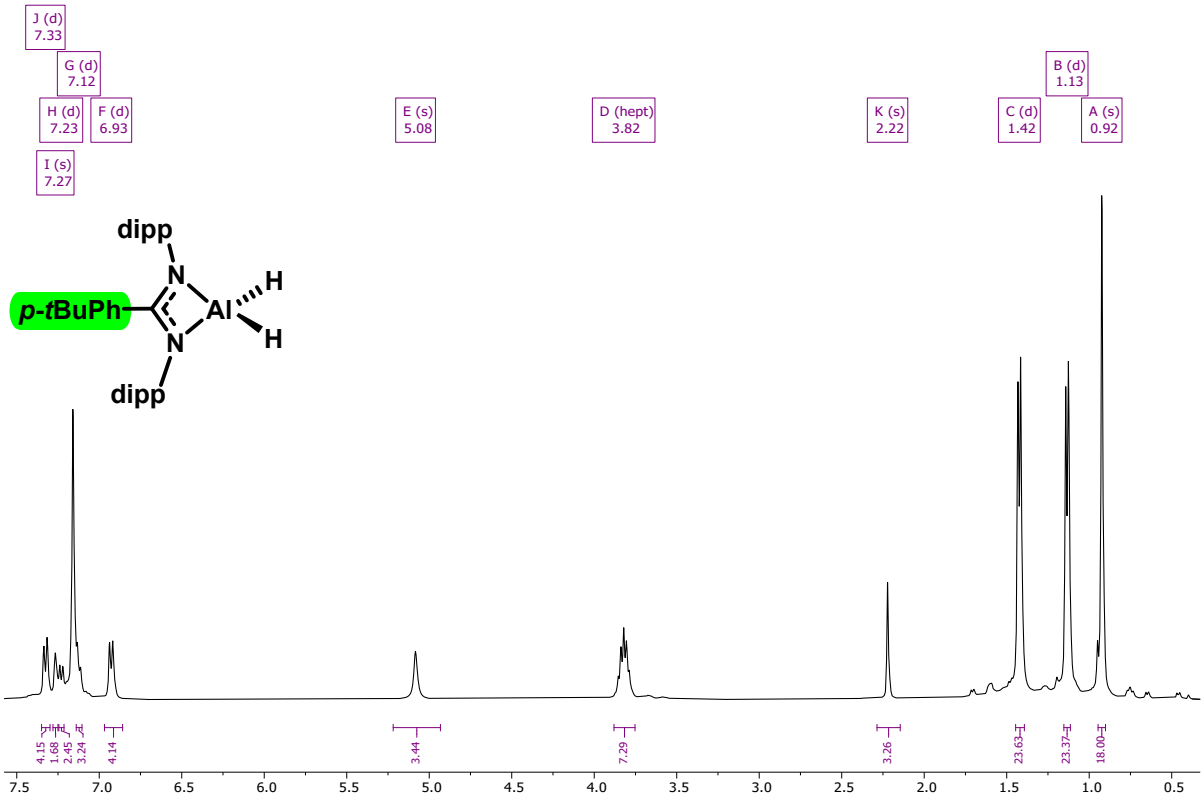


Figure S 55: ^{1}H NMR spectrum (400 MHz, 298 K) of **[(2-Al)$_2$.Tol]** in benzene-d_6

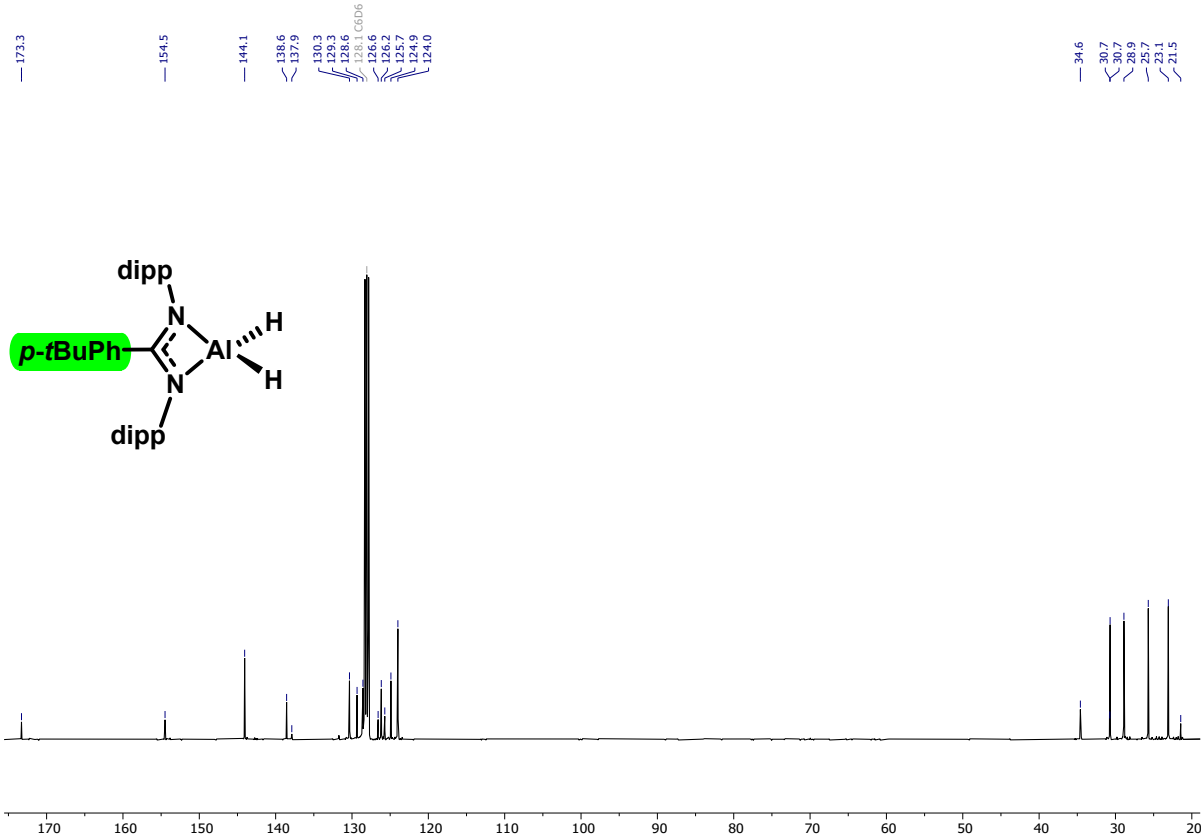


Figure S 56: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of [(**2-Al)$_2$.Tol]** in benzene-d_6

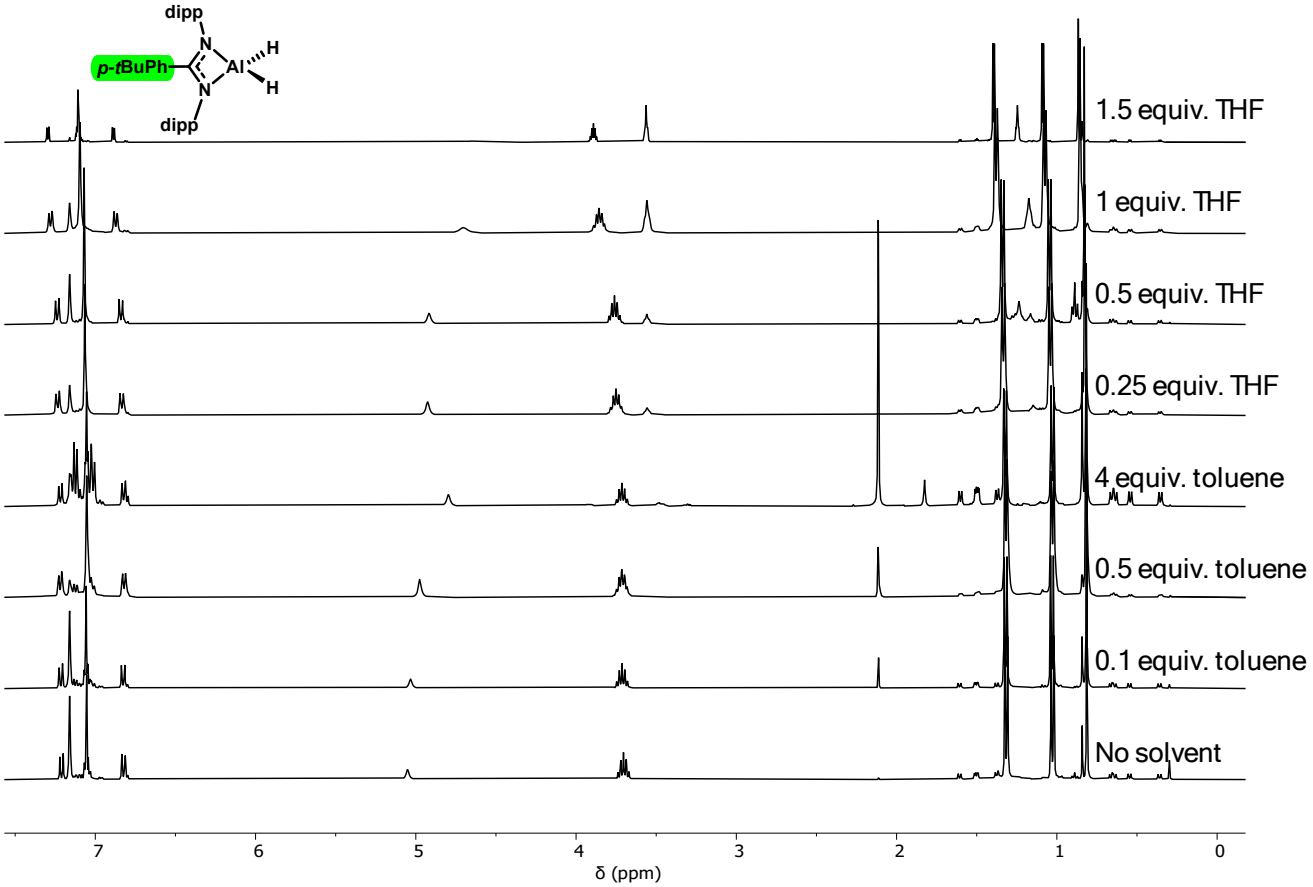


Figure S 57: ^{1}H NMR spectrum (400 MHz, 298 K) of **2-Al** in benzene-d_6 with varying levels of solvent impurities (THF and toluene)

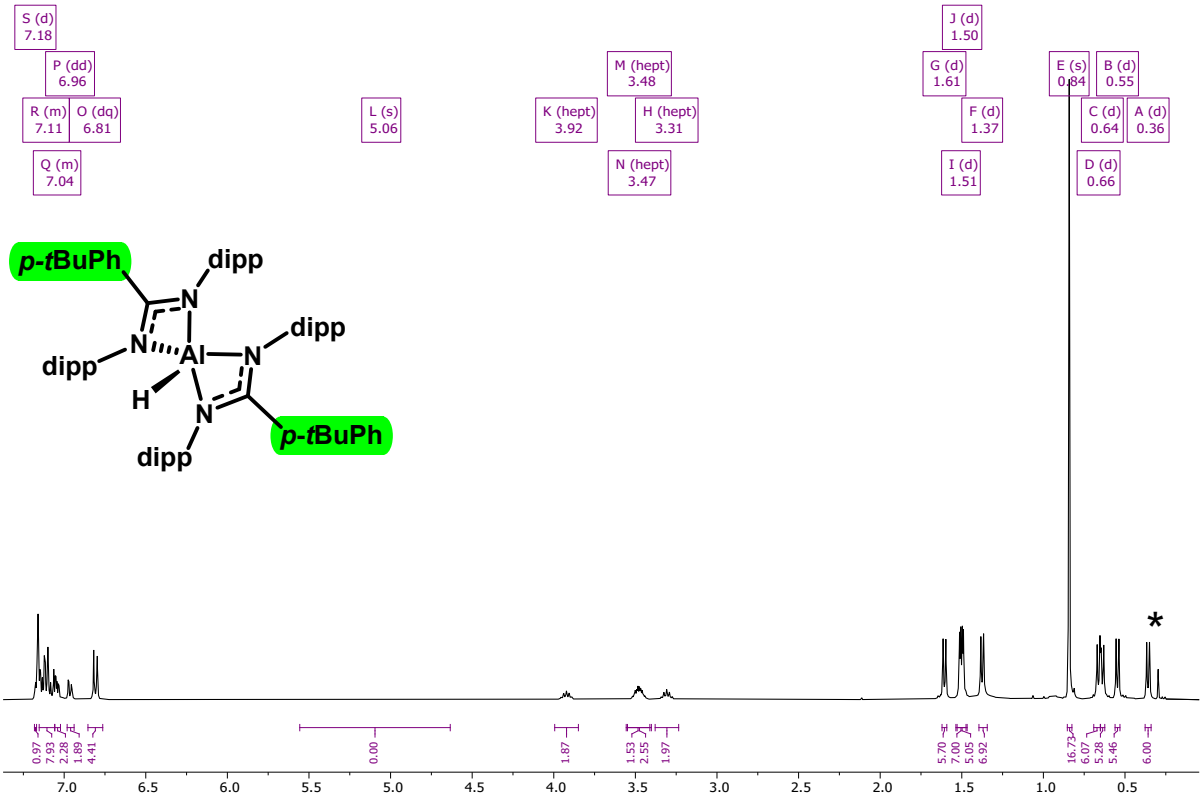


Figure S 58: ^{1}H NMR (400 MHz, 298 K) spectrum of **2-Al''** in benzene-d_6 with silicone grease impurity (*)

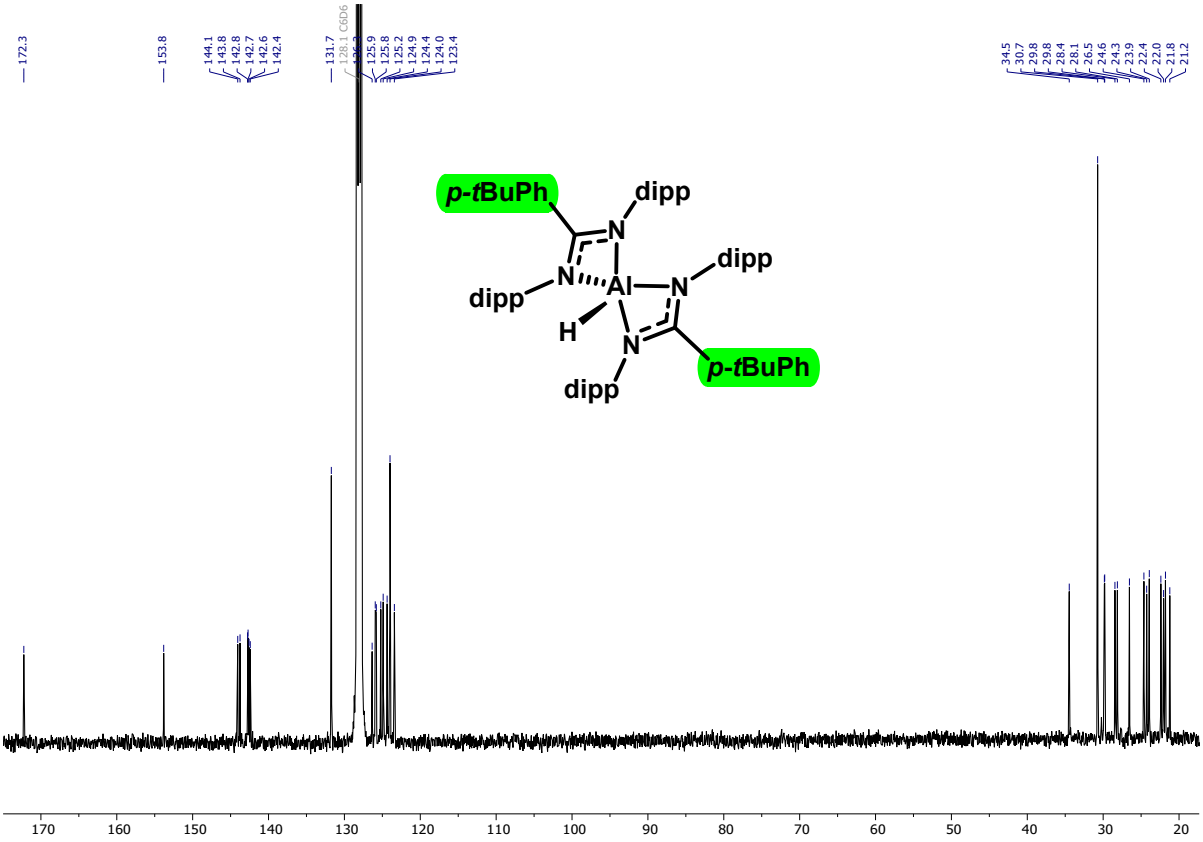


Figure S 59: ^{13}C{^{1}H} NMR (101 MHz, 298 K) spectrum of **2-Al''** in benzene-d_6

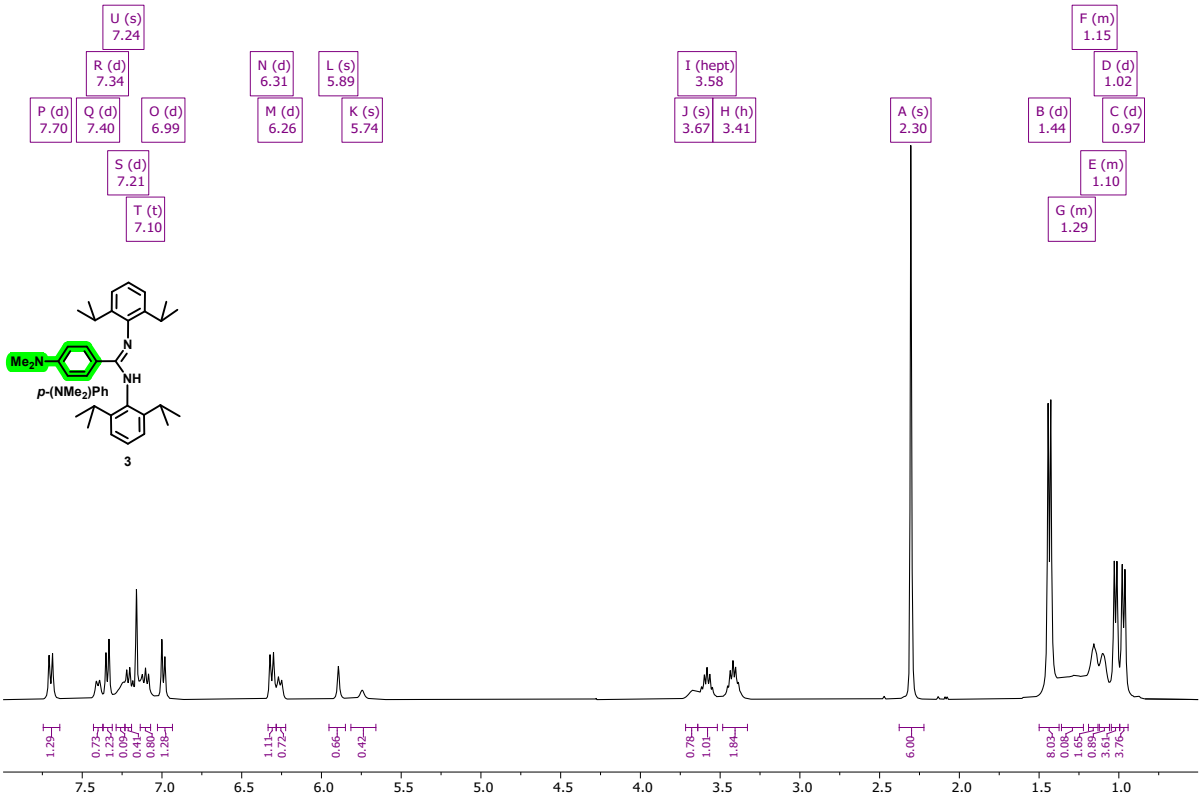


Figure S 60: ^{1}H NMR (400 MHz, 298 K) spectrum of **3** in benzene-d_6

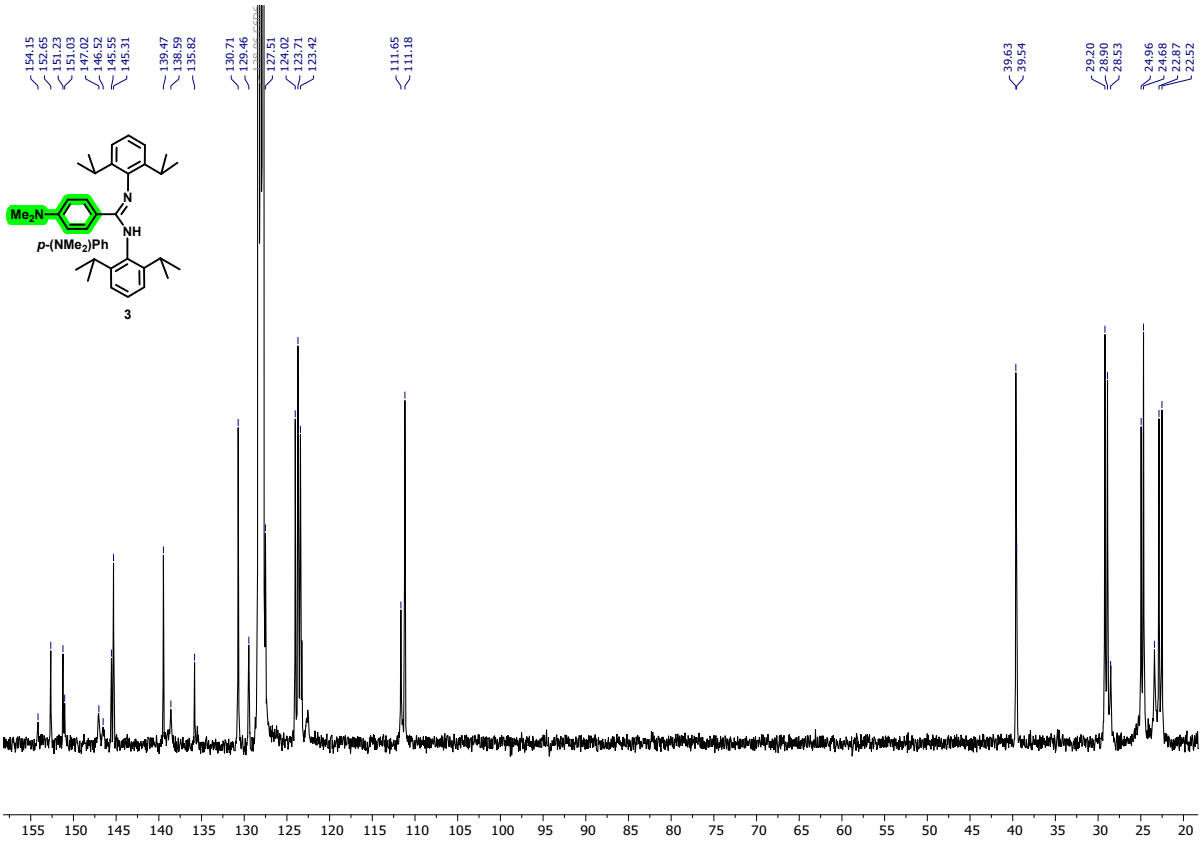


Figure S 61: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **3** in benzene-d_6

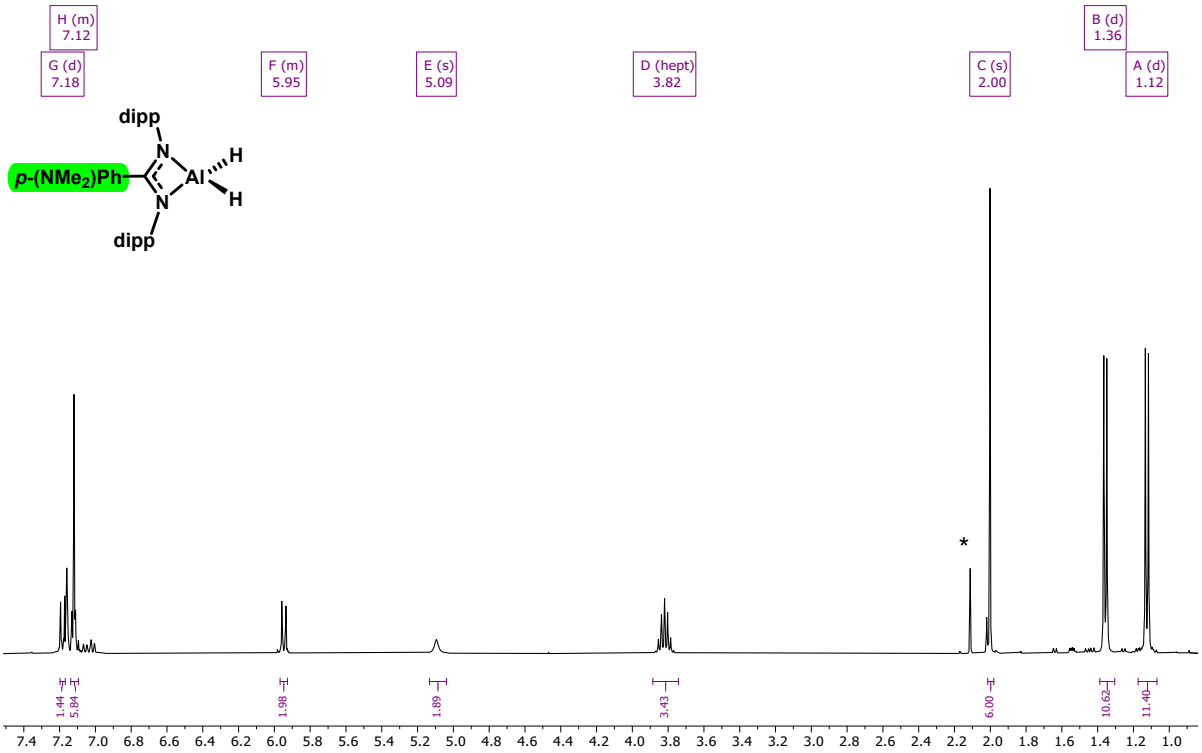


Figure S 62: ^{1}H NMR (400 MHz, 298 K) spectrum of **3-Al** in benzene-d_6 (toluene impurity labelled with a *)

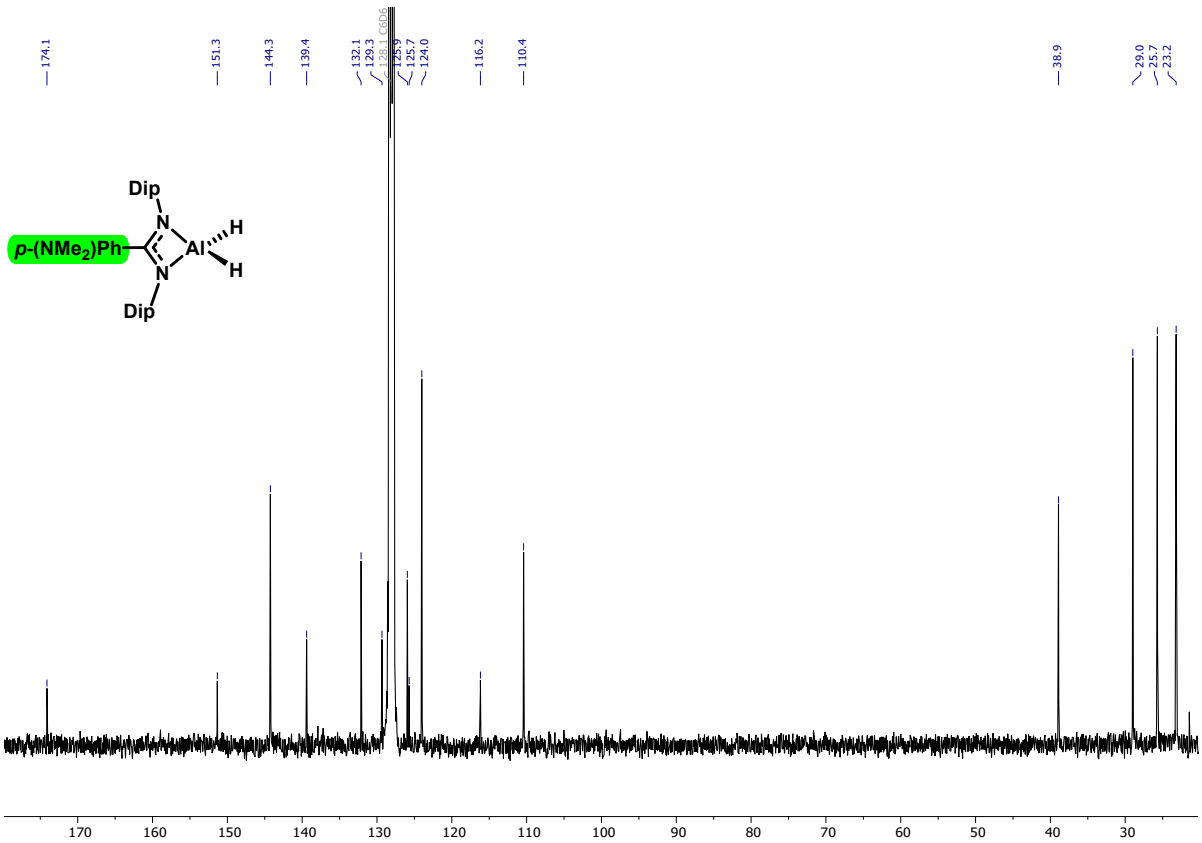


Figure S 63: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **3-Al** in benzene-d_6

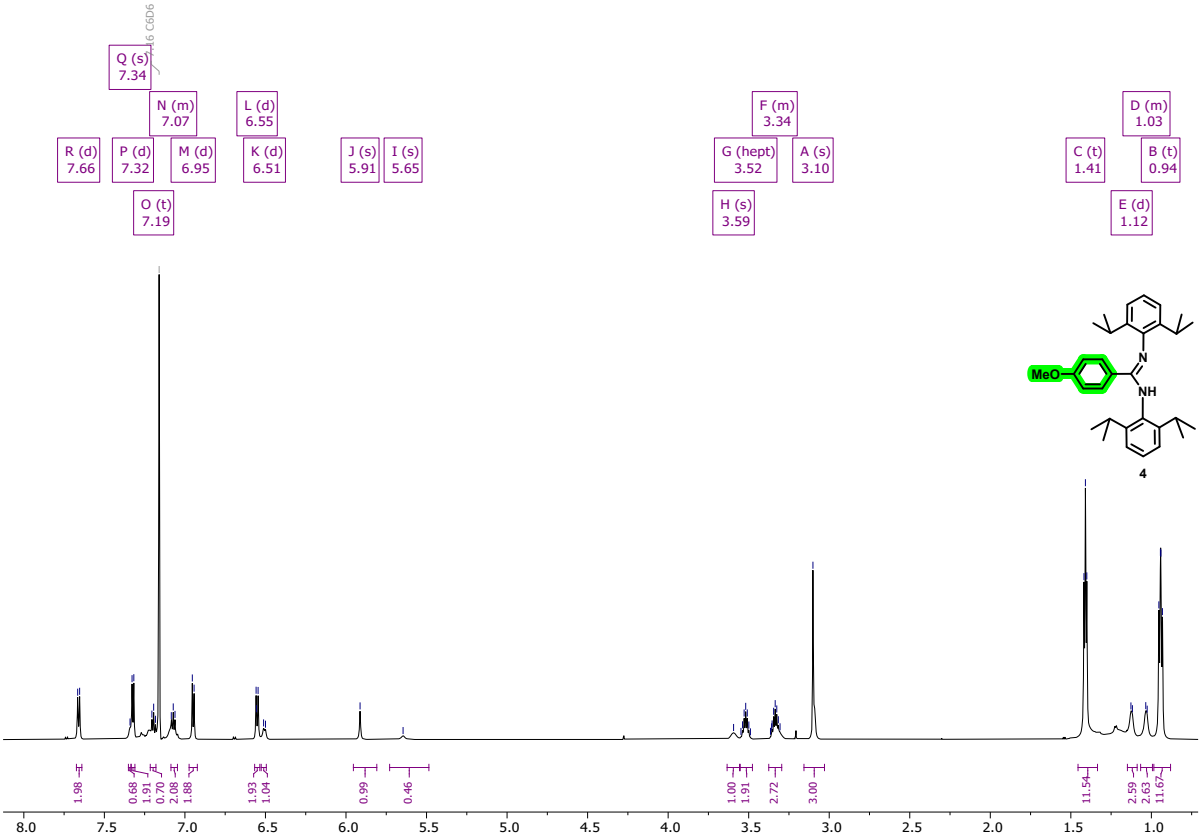


Figure S 64: ^{1}H NMR spectrum (400 MHz, 298 K) of **4** in benzene-d_6

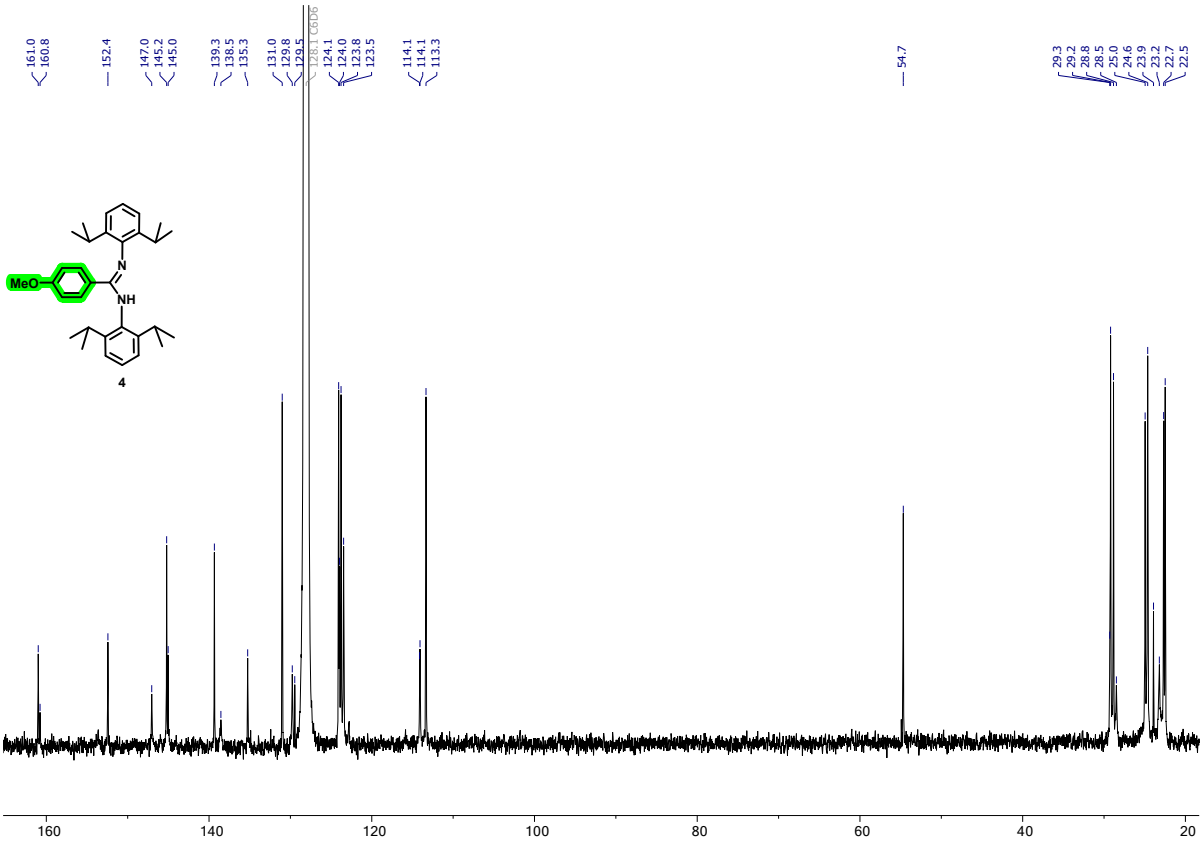


Figure S 65: ^{13}C{^{1}H} NMR spectrum (125.7 MHz, 298 K) of **4** in benzene-d_6

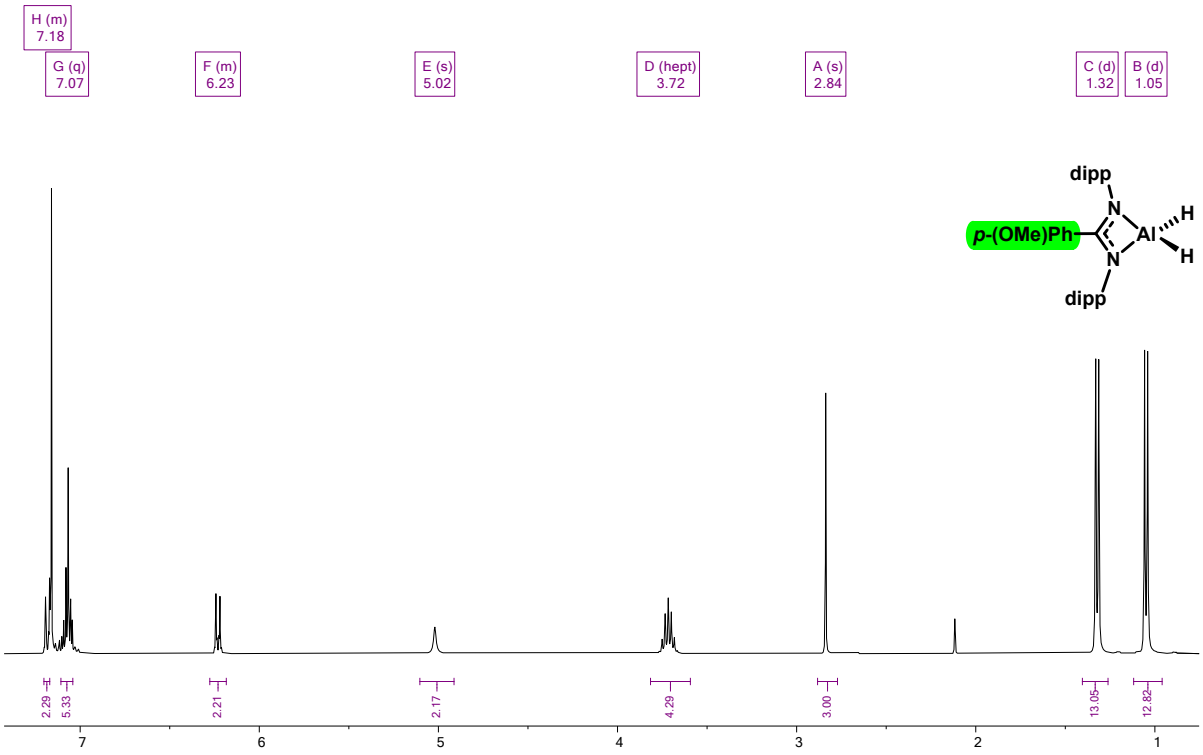


Figure S 66: ^{1}H NMR spectrum (400 MHz, 298 K) of **4-Al** in benzene-d_6

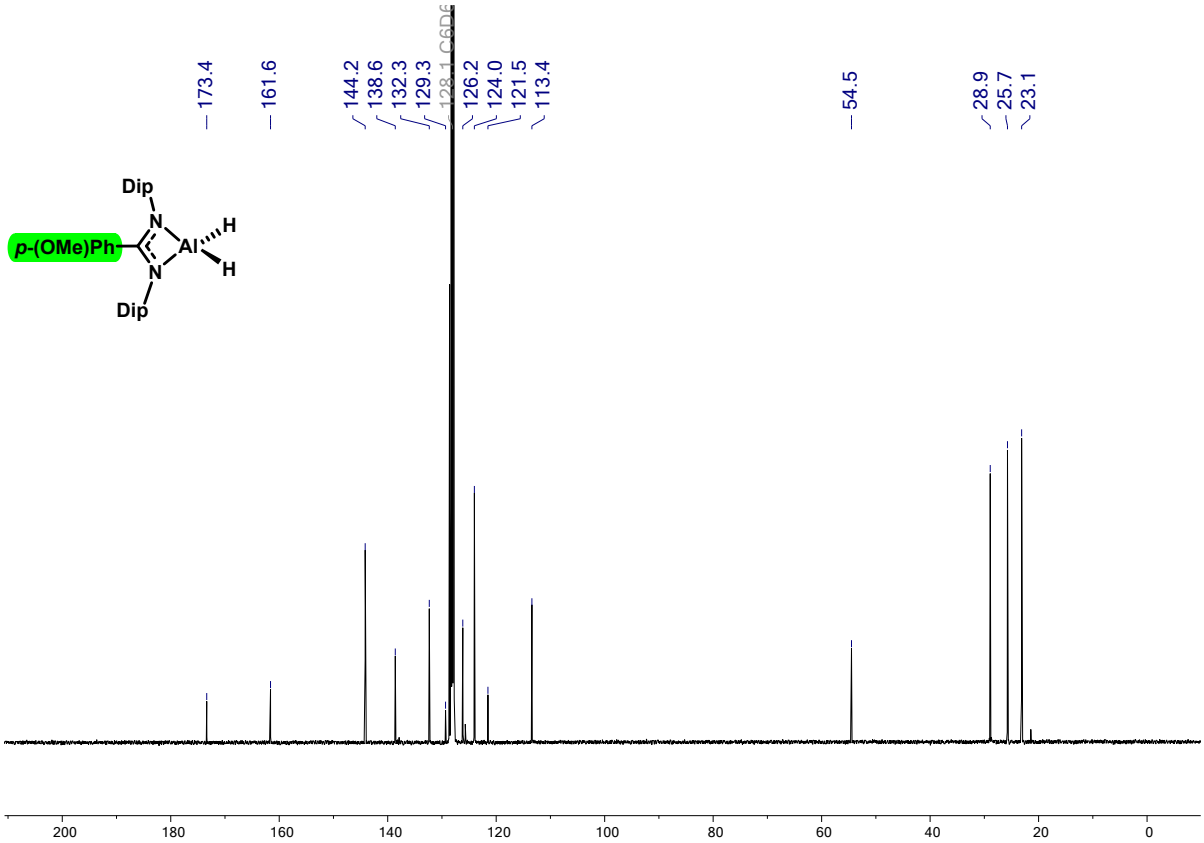


Figure S 67: ^{13}C{^{1}H} NMR spectrum of **4-Al** in benzene-d_6

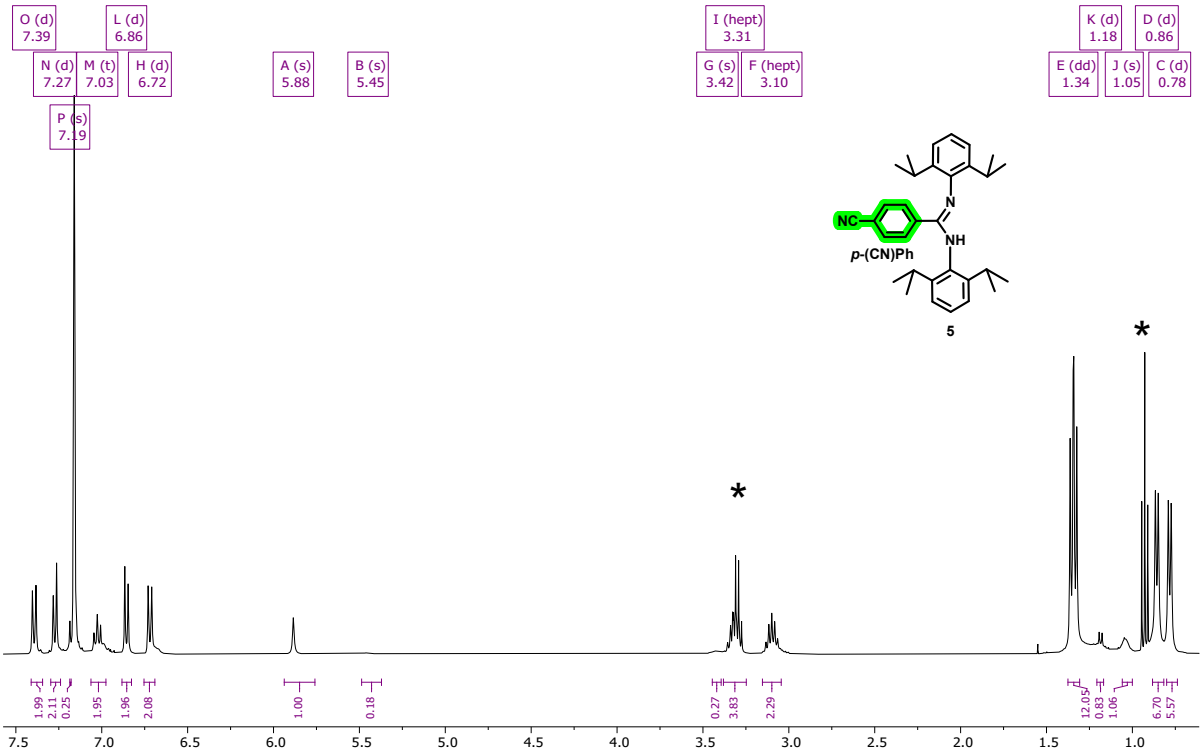


Figure S 68: ^{1}H NMR spectrum (400 MHz, 298 K) of **5** in benzene-d_6 with pet ether impurity marked with a *

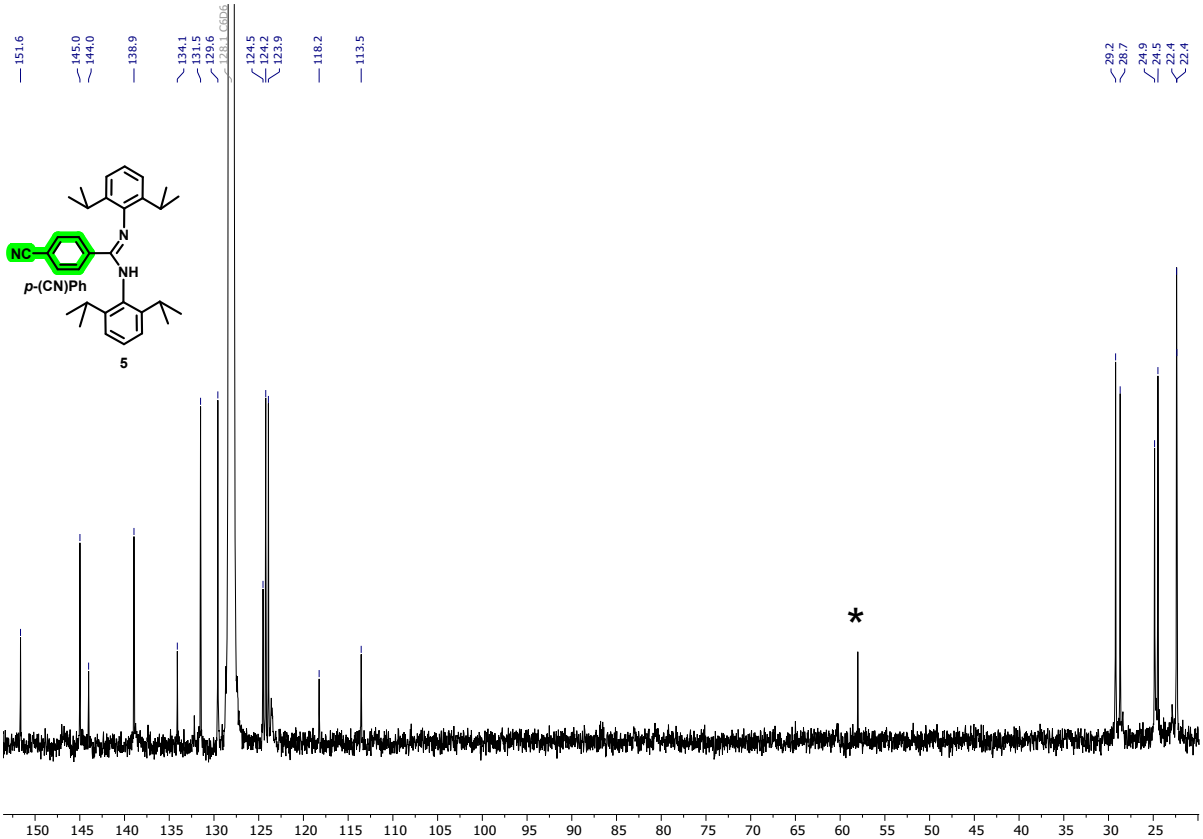


Figure S 69: ^{13}C{^{1}H} NMR (101 MHz, 298 K) spectrum of **5** in benzene-d_6 with pet ether impurity (*)

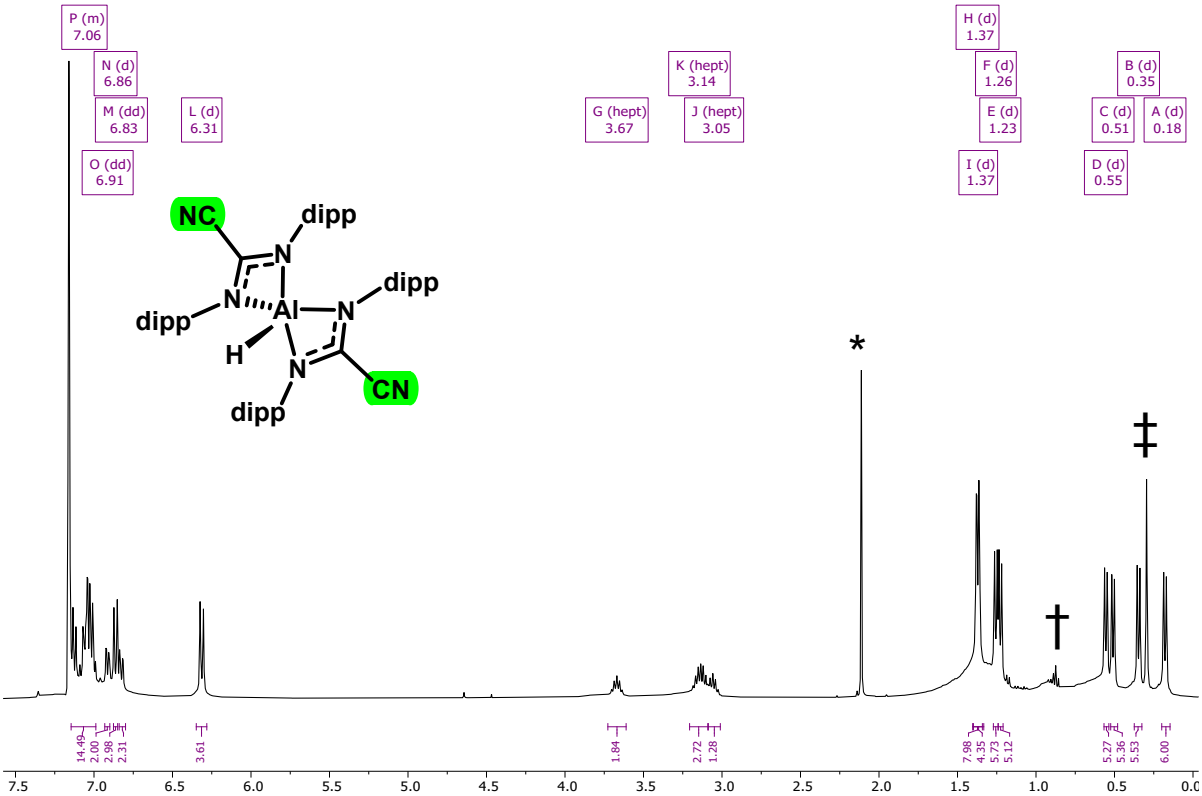


Figure S 70: ^{1}H NMR spectrum (400 MHz, 298 K) of **5-Al''** in benzene-d_6, with toluene (*), hexane (†) and silicone grease (‡) impurities

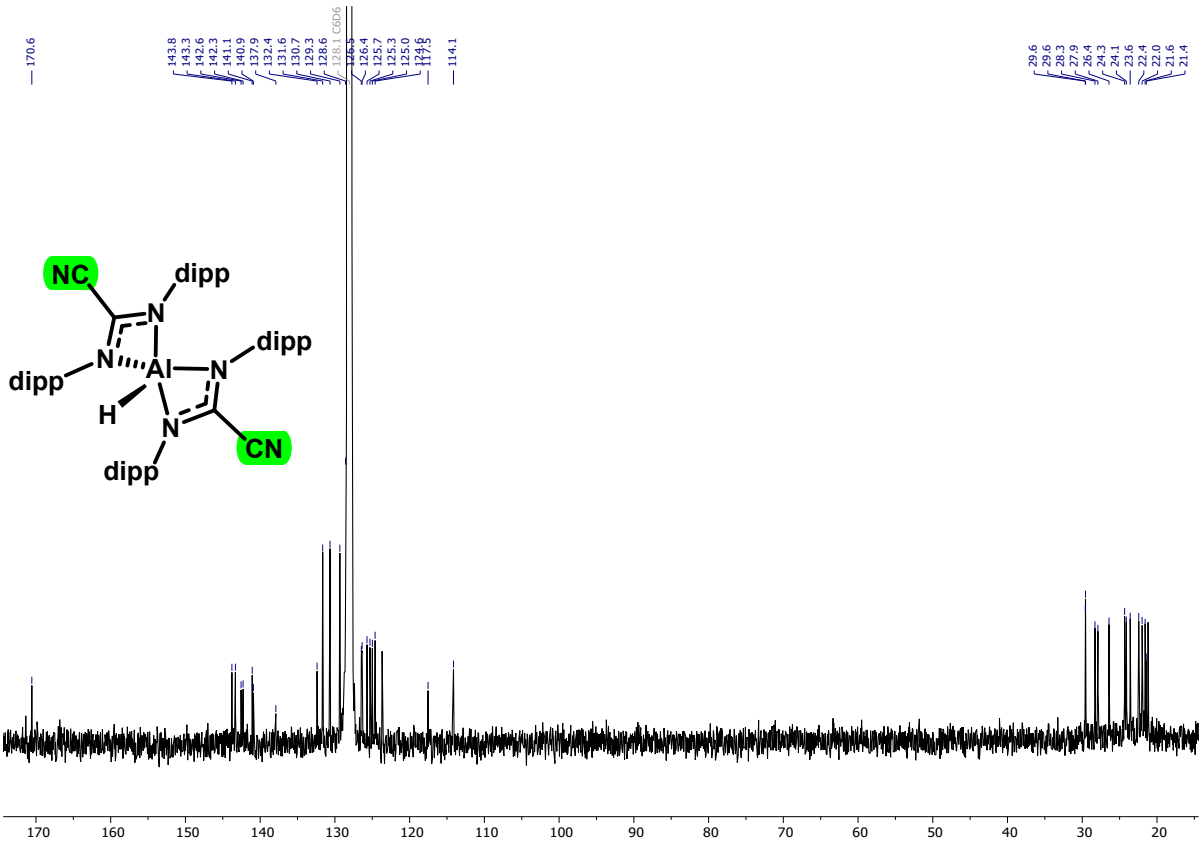


Figure S 71: ^{13}C{^{1}H} NMR (101 MHz, 298 K) spectrum of **5-Al''** in benzene-d_6

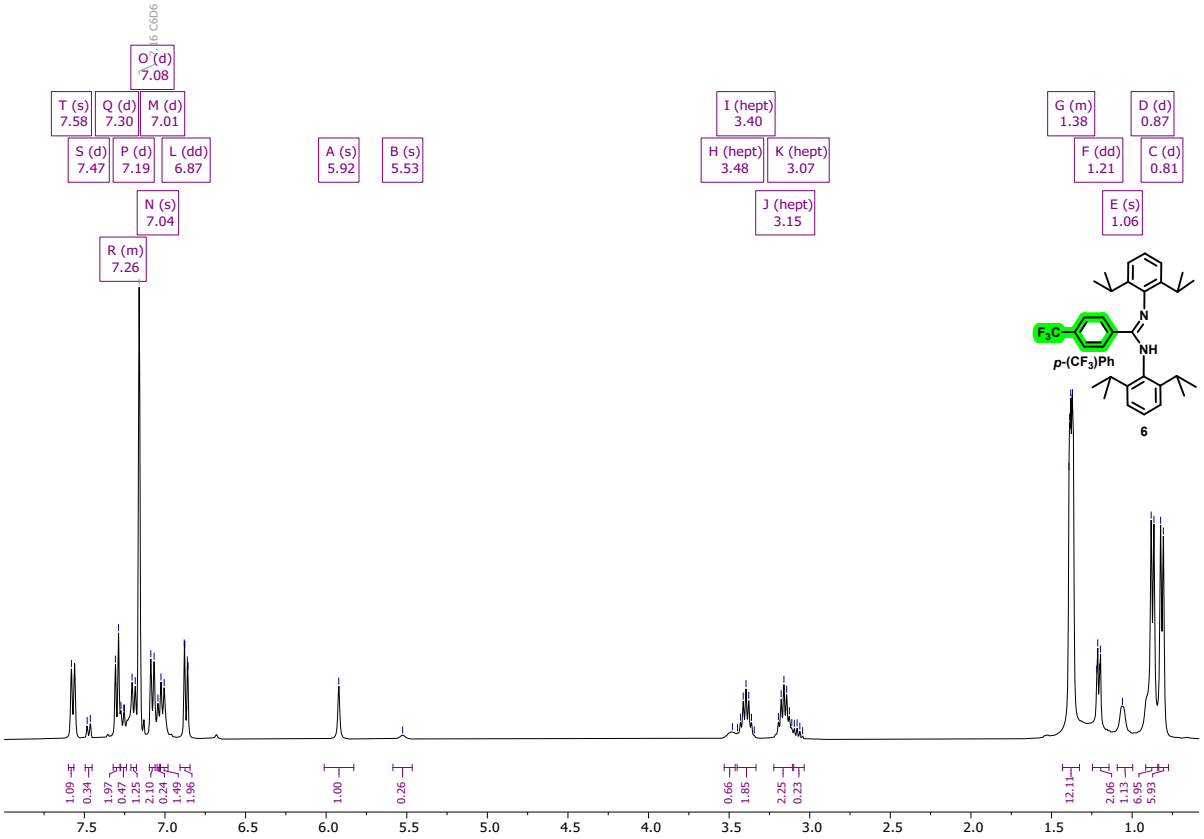


Figure S 72: ^{1}H NMR spectrum (400 MHz, 298 K) of **6** in benzene-d_6

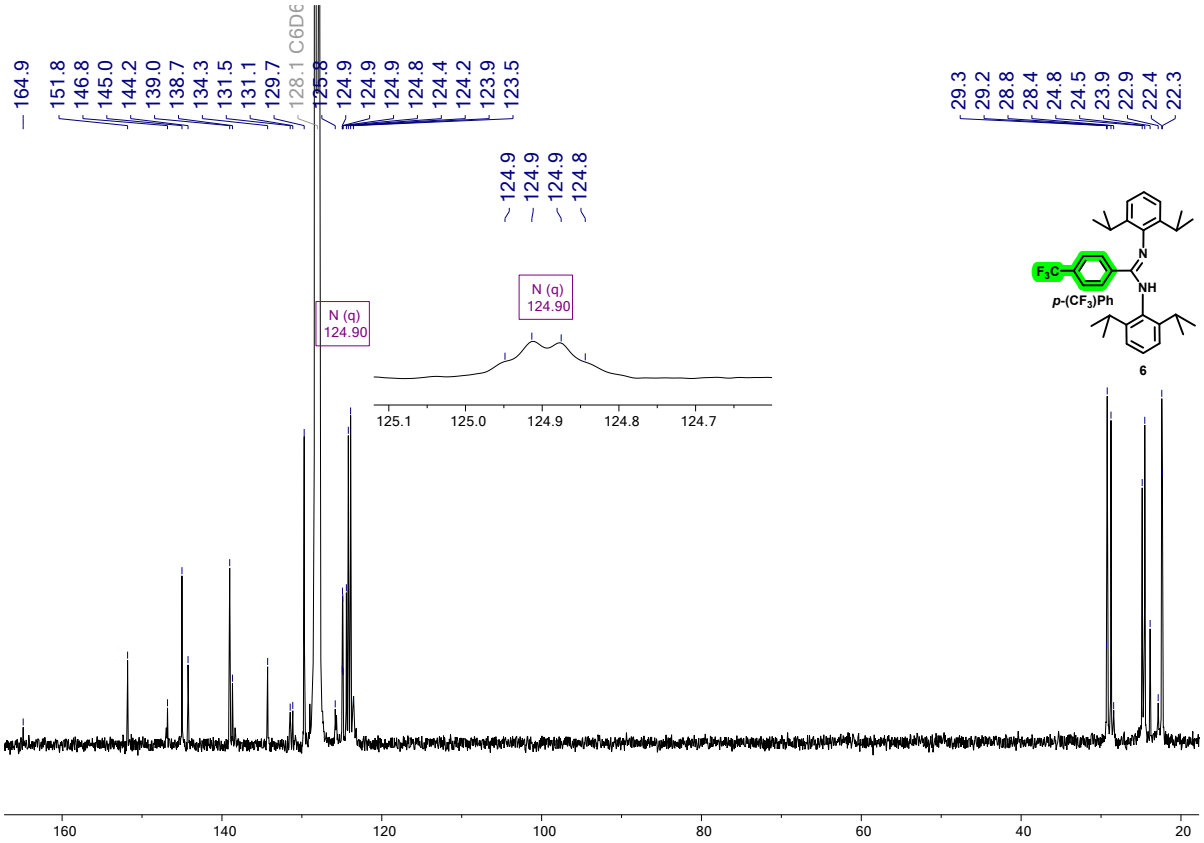


Figure S 73: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **6** in benzene-d_6 with inset region 124.6-125.1 ppm, showing quartet arising from CF_3 group

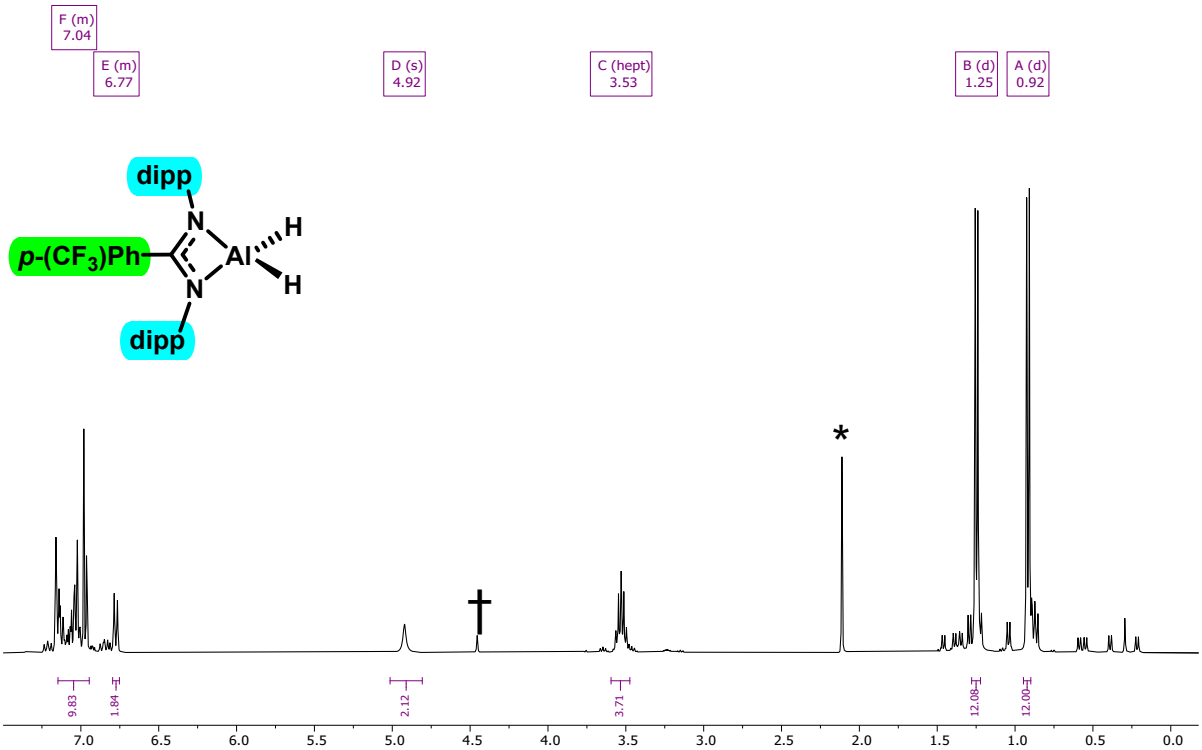


Figure S 74: ^{1}H NMR spectrum (400 MHz, 298 K) of **6-Al** in benzene-d_6 with toluene (*), hydrogen (†), **6-Al''** and an additional unidentified impurity)

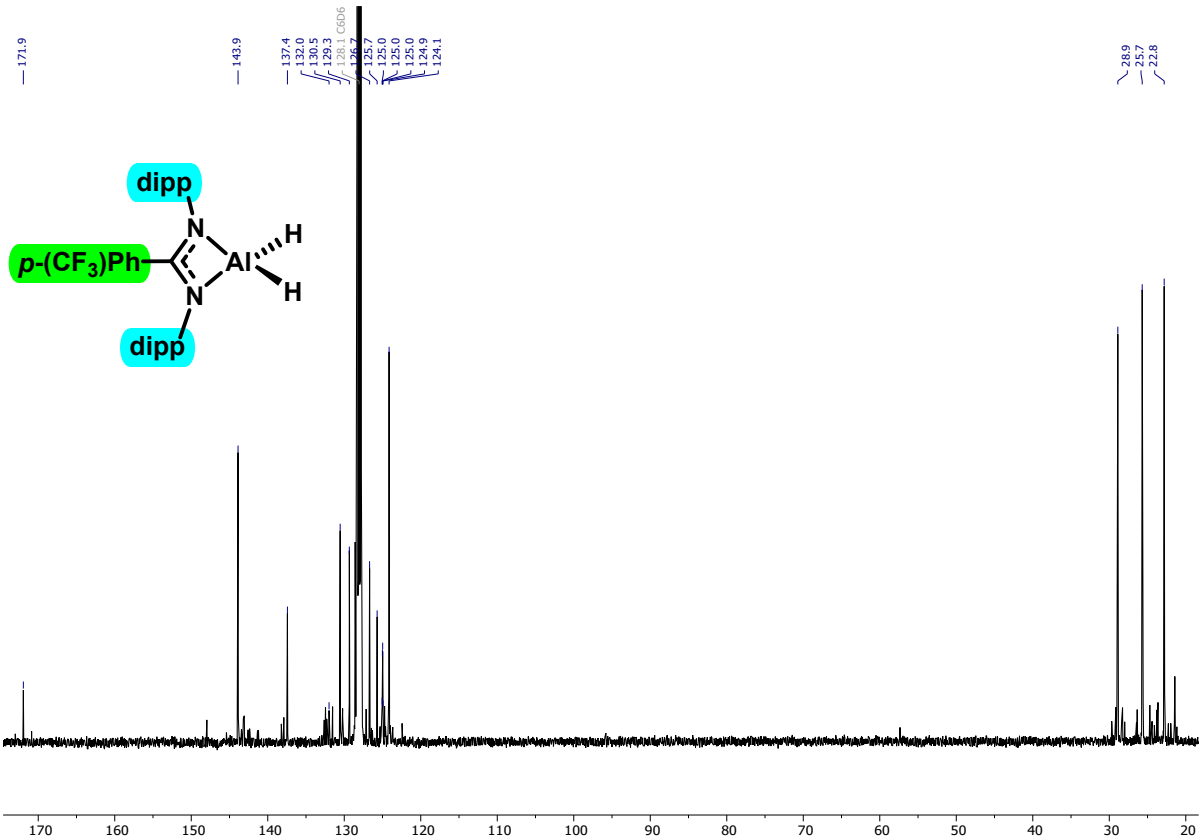


Figure S 75: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **6-Al** in benzene-d_6 with multiple minor impurities

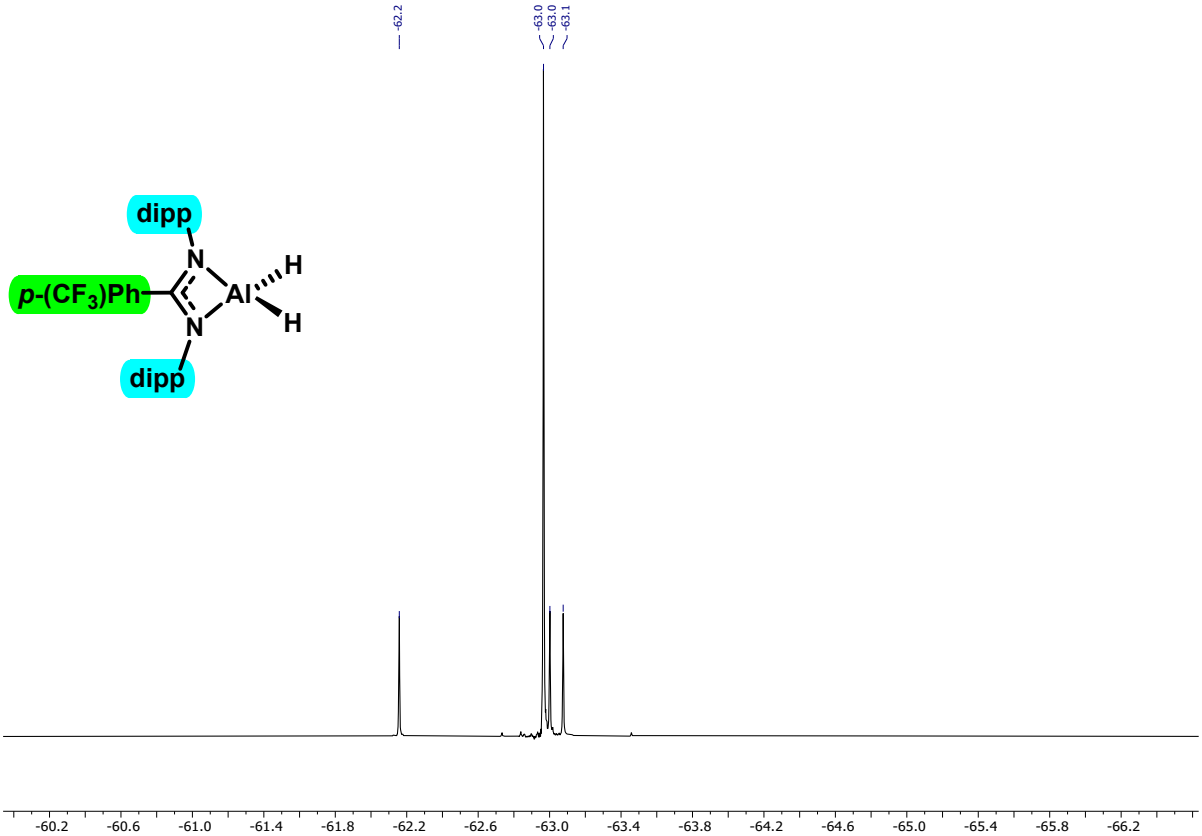


Figure S 76: $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, 298 K) of **6-Al** in benzene-d_6 with multiple minor impurities, likely **6-Al''** and an additional unidentified impurity

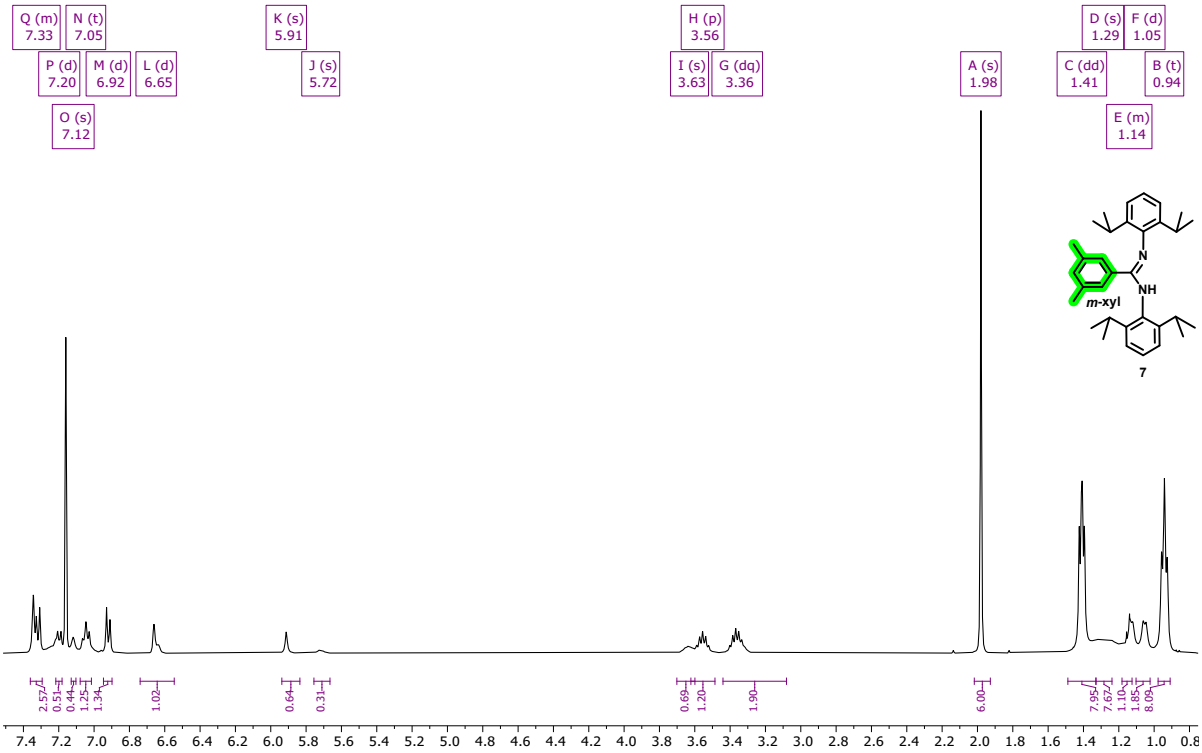


Figure S 77: ^{1}H NMR (400 MHz, 298 K) spectrum of **7** in benzene-d_6

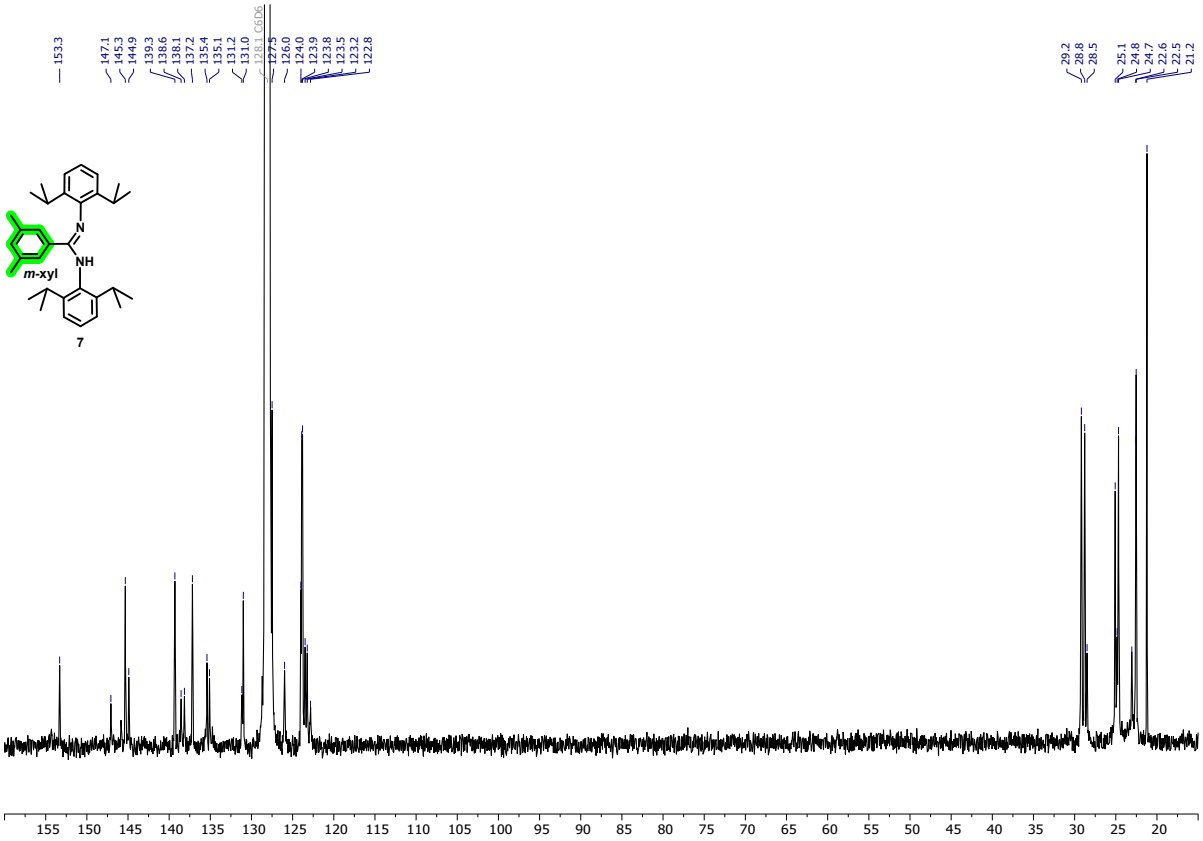


Figure S 78: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **7** in benzene-d_6

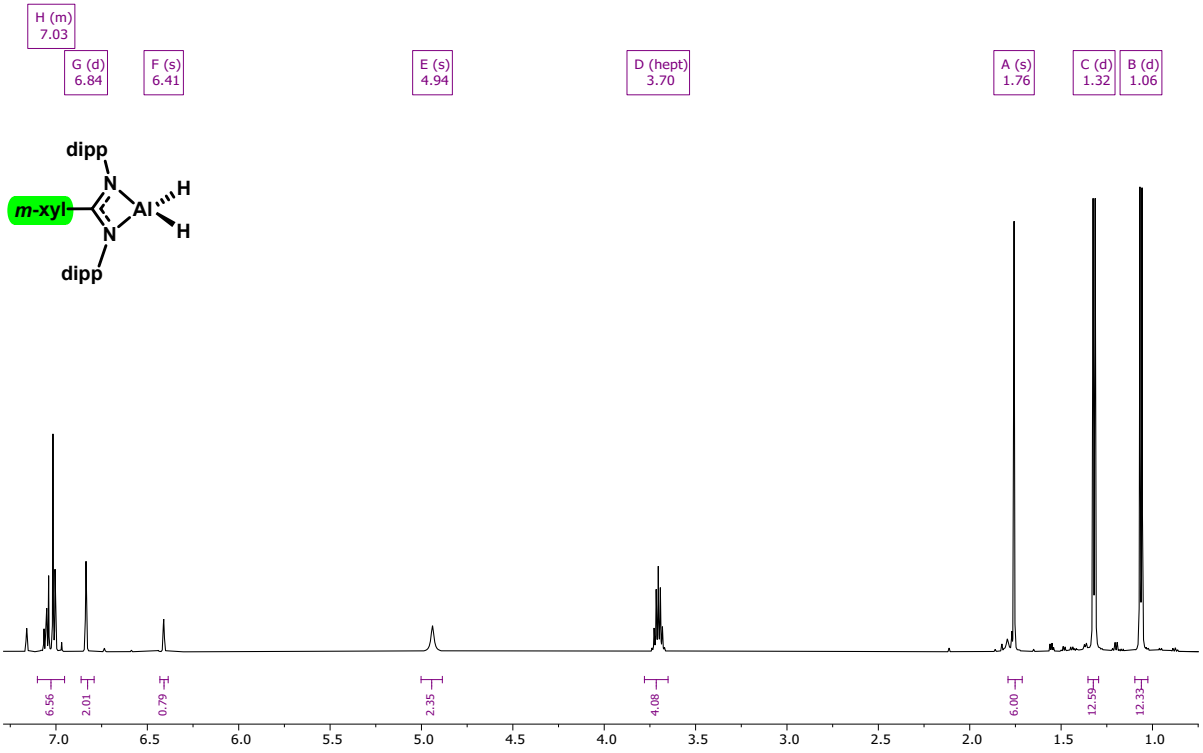


Figure S 79: ^{1}H NMR (600 MHz, 298 K) spectrum of **7-Al** in benzene-d_6

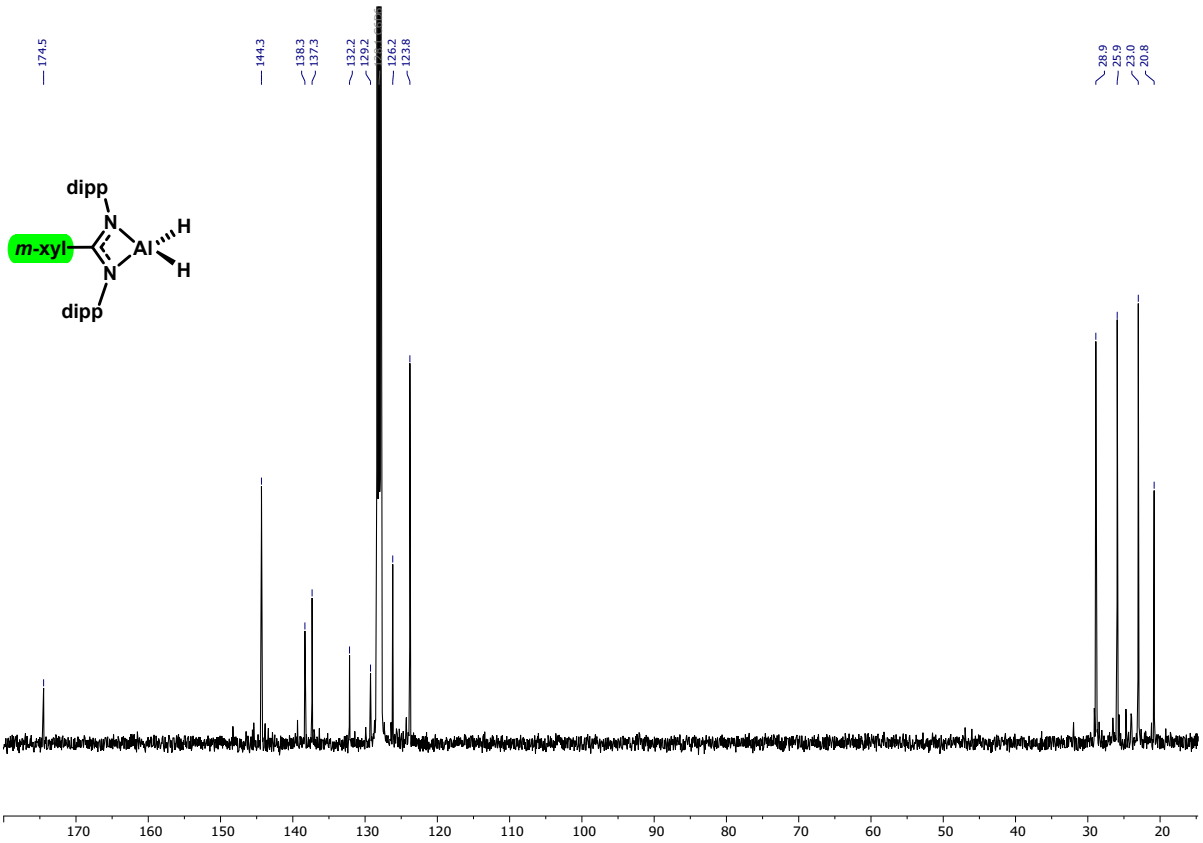


Figure S 80: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **7-Al** in benzene-d_6

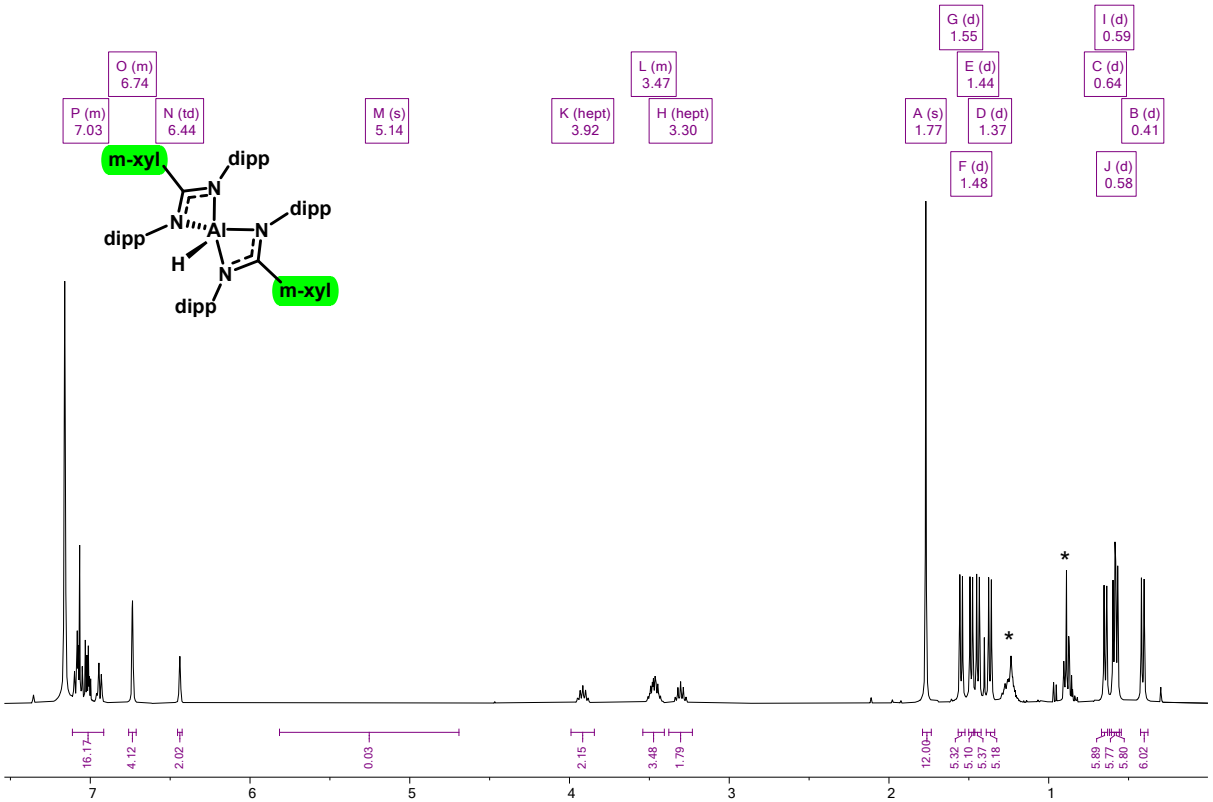


Figure S 81: ^{1}H NMR spectrum (400 MHz, 298 K) of **7-Al''** in benzene-d_6 with hexane impurity (*)

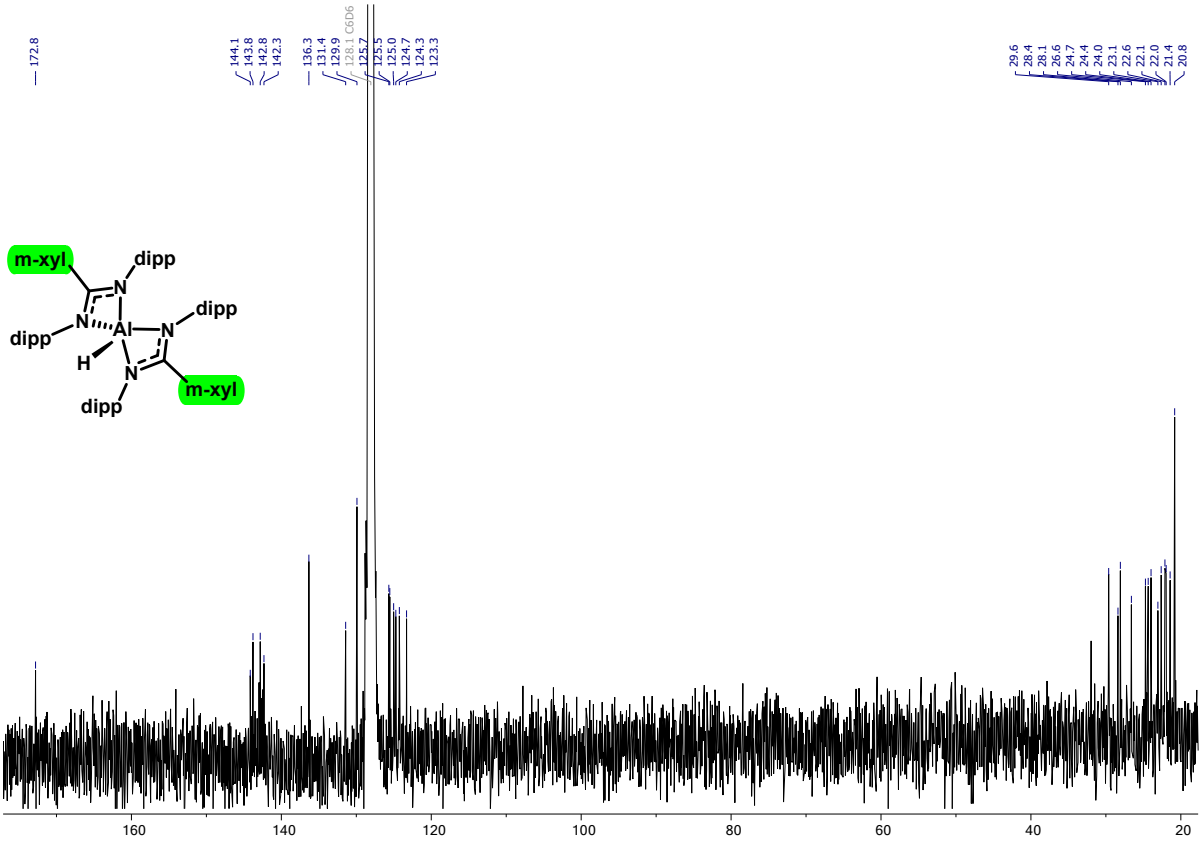


Figure S 82: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **7-Al''** in benzene-d_6

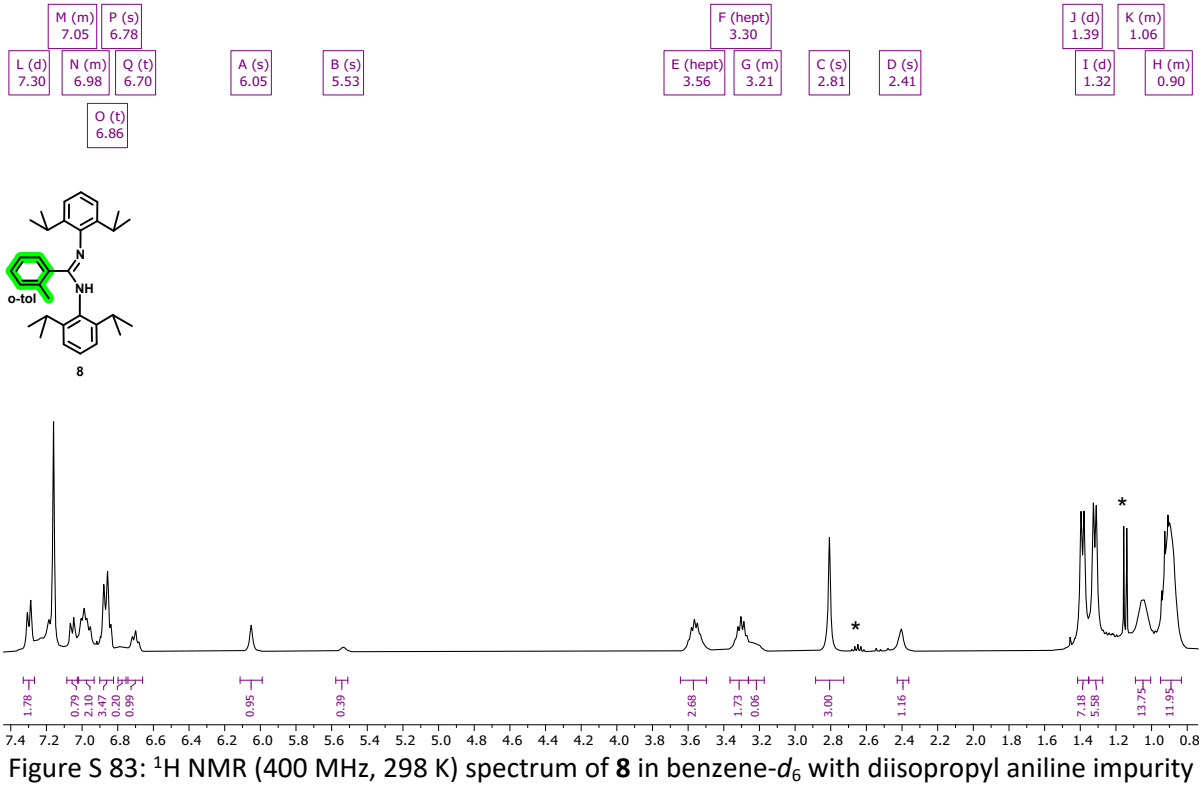


Figure S 83: ^{1}H NMR (400 MHz, 298 K) spectrum of **8** in benzene-d_6 with diisopropyl aniline impurity (*)

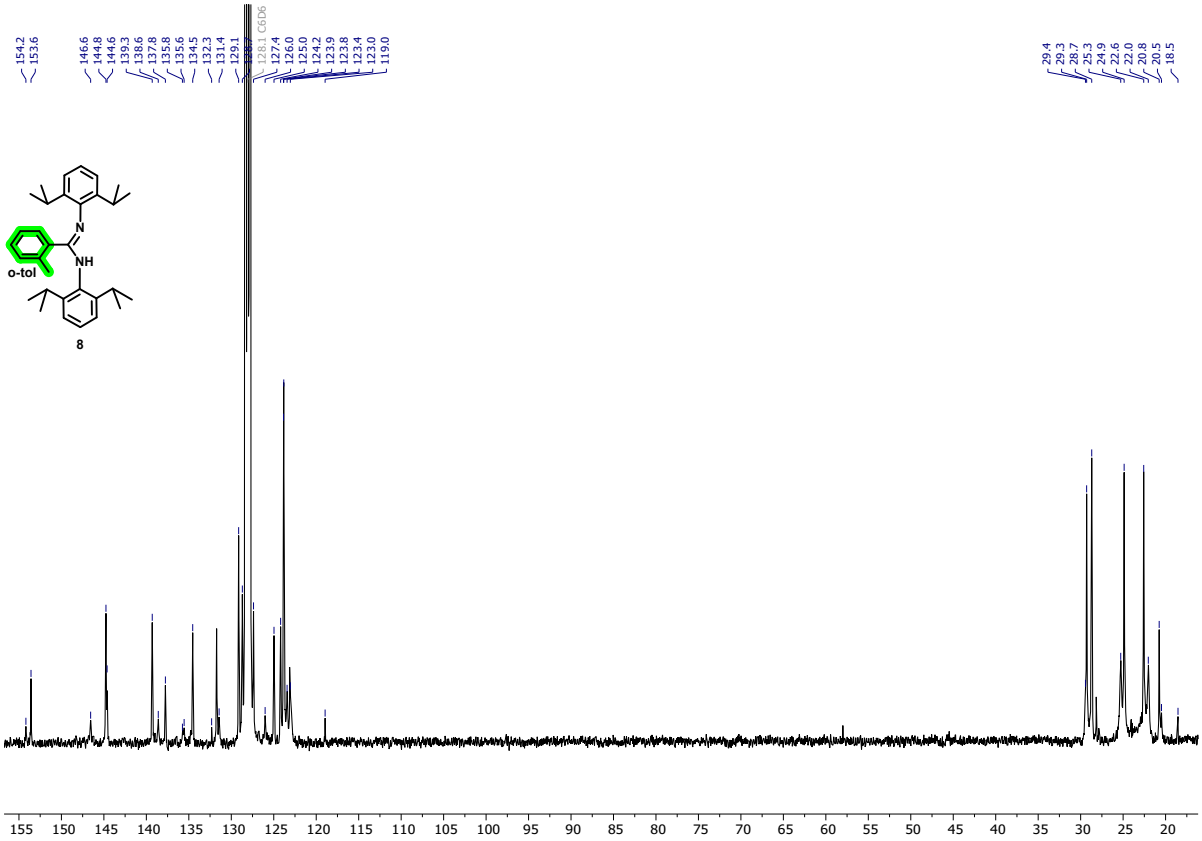


Figure S 84: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **8** in benzene-d_6

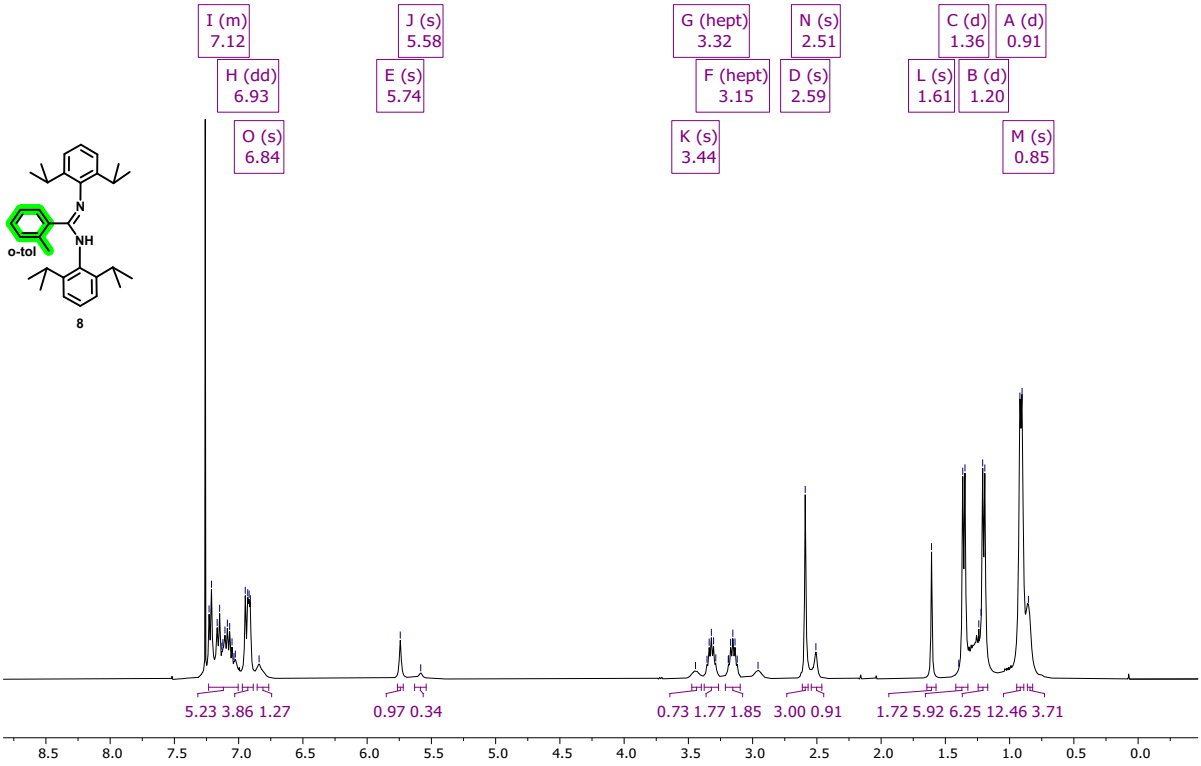


Figure S 85: ^{1}H NMR (400 MHz, 298 K) spectrum of **8** in chloroform-*d*

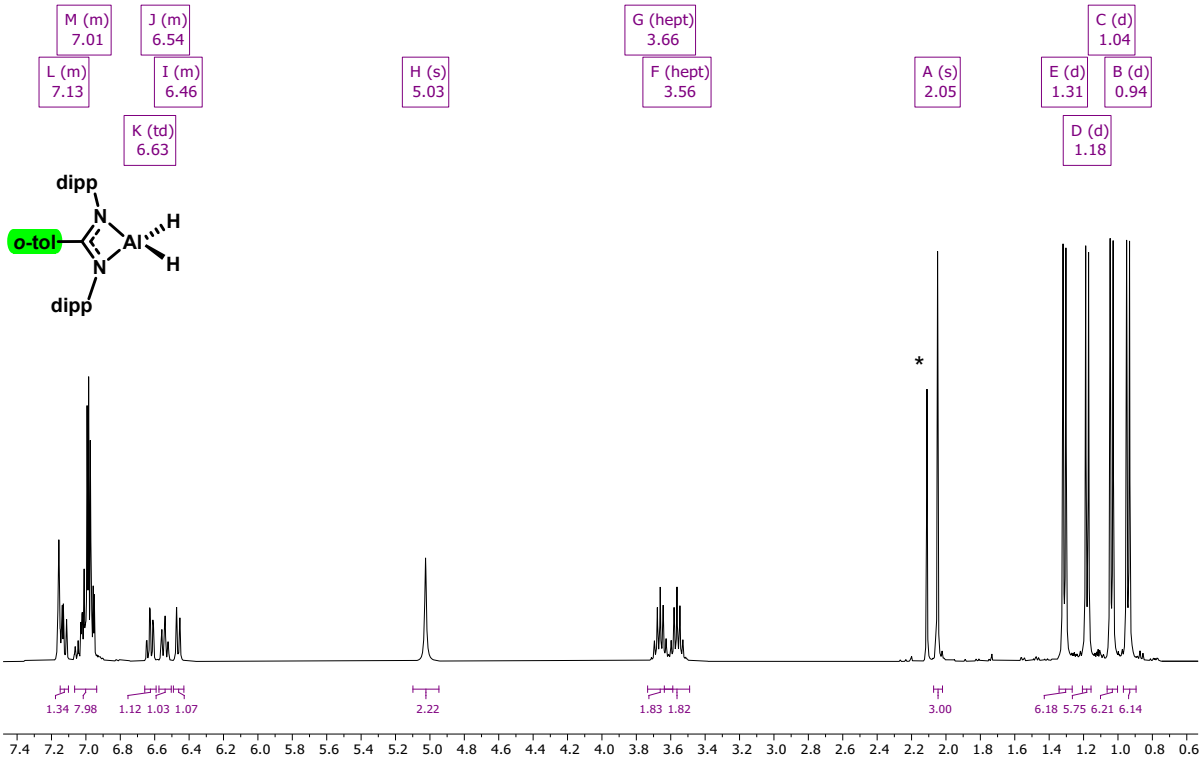


Figure S 86: ^{1}H NMR spectrum (400 MHz, 298 K) of **8-Al** in benzene-d_6 with toluene impurity (*)

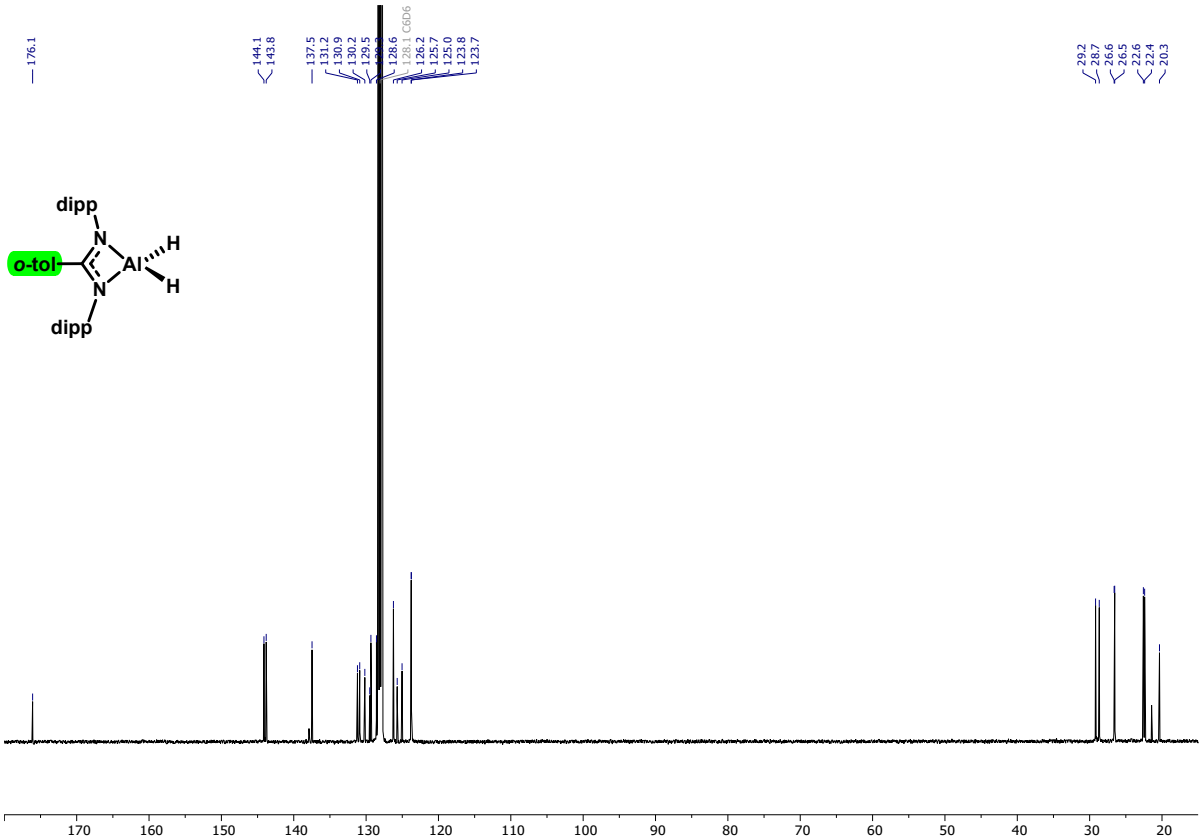


Figure S 87: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **8-Al** in benzene-d_6

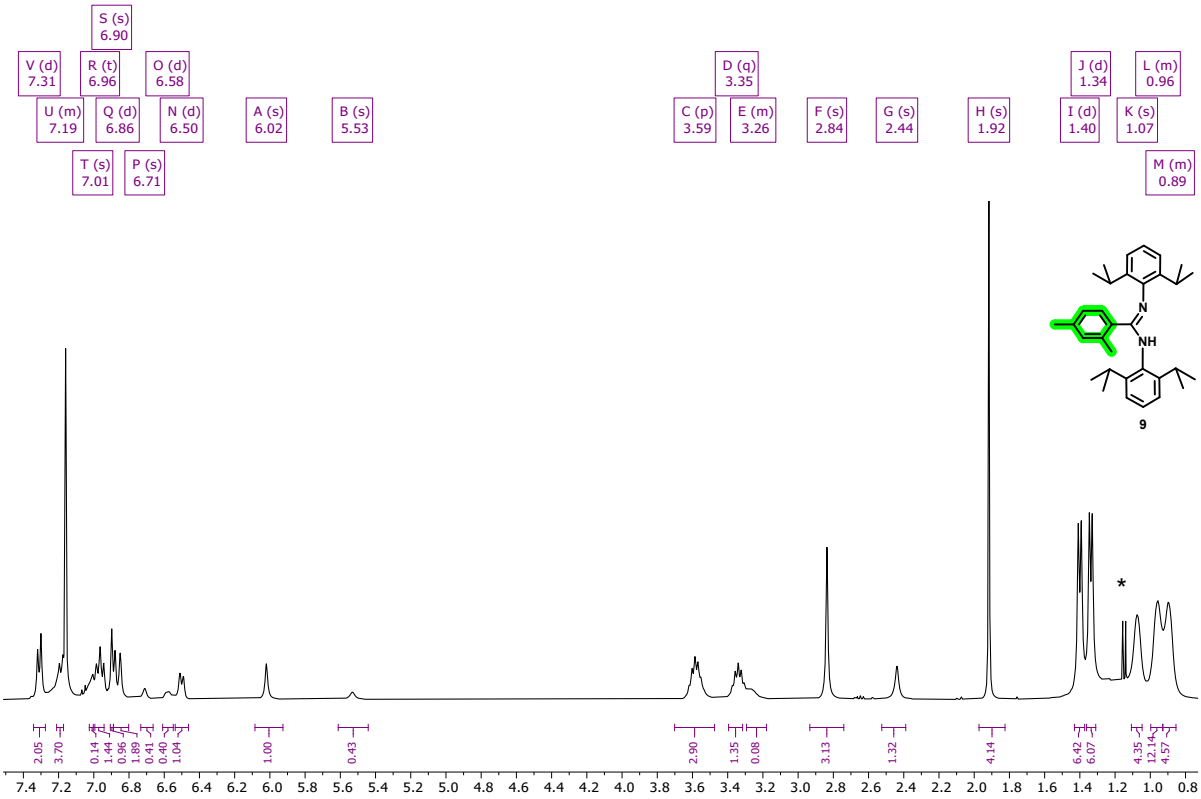


Figure S 88: ^{1}H NMR (400 MHz, 298 K) spectrum of **9** in benzene-d_6 with diisopropyl aniline impurity (*)

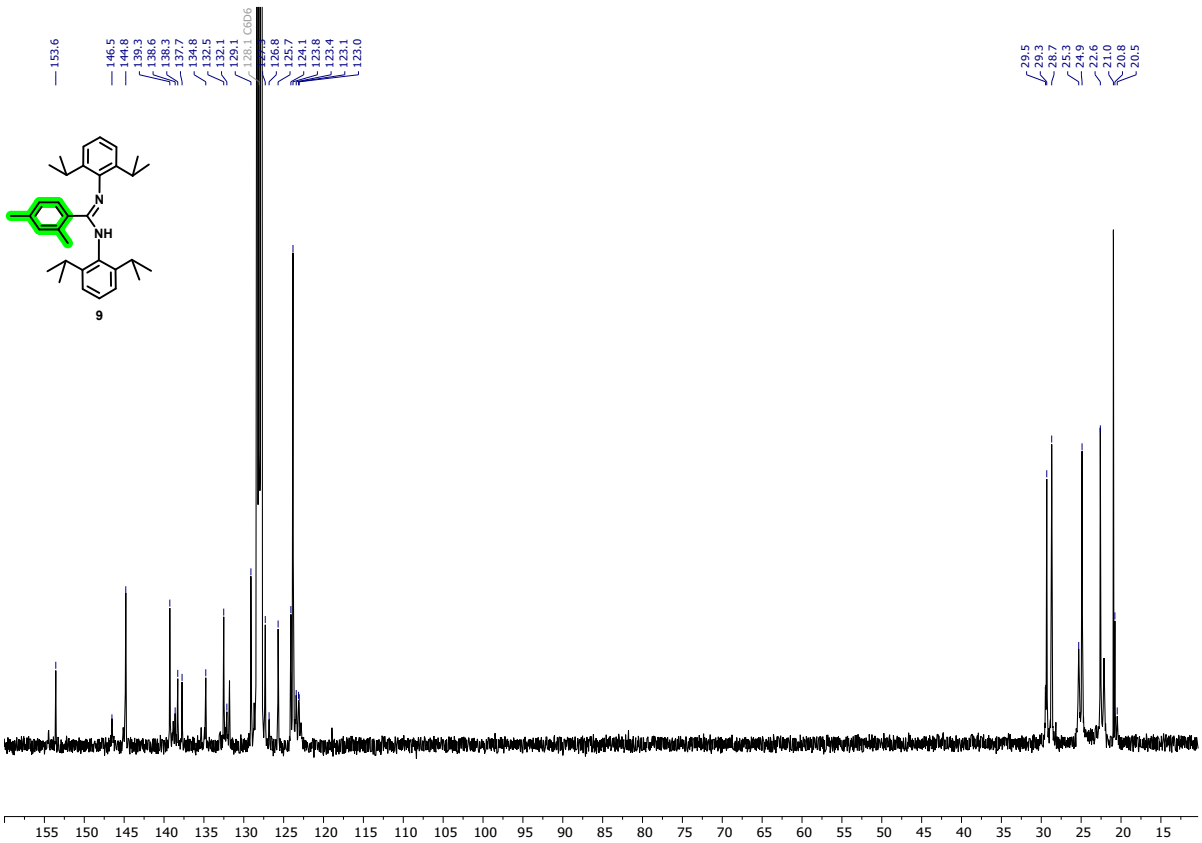


Figure S 89: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **9** in benzene-d_6

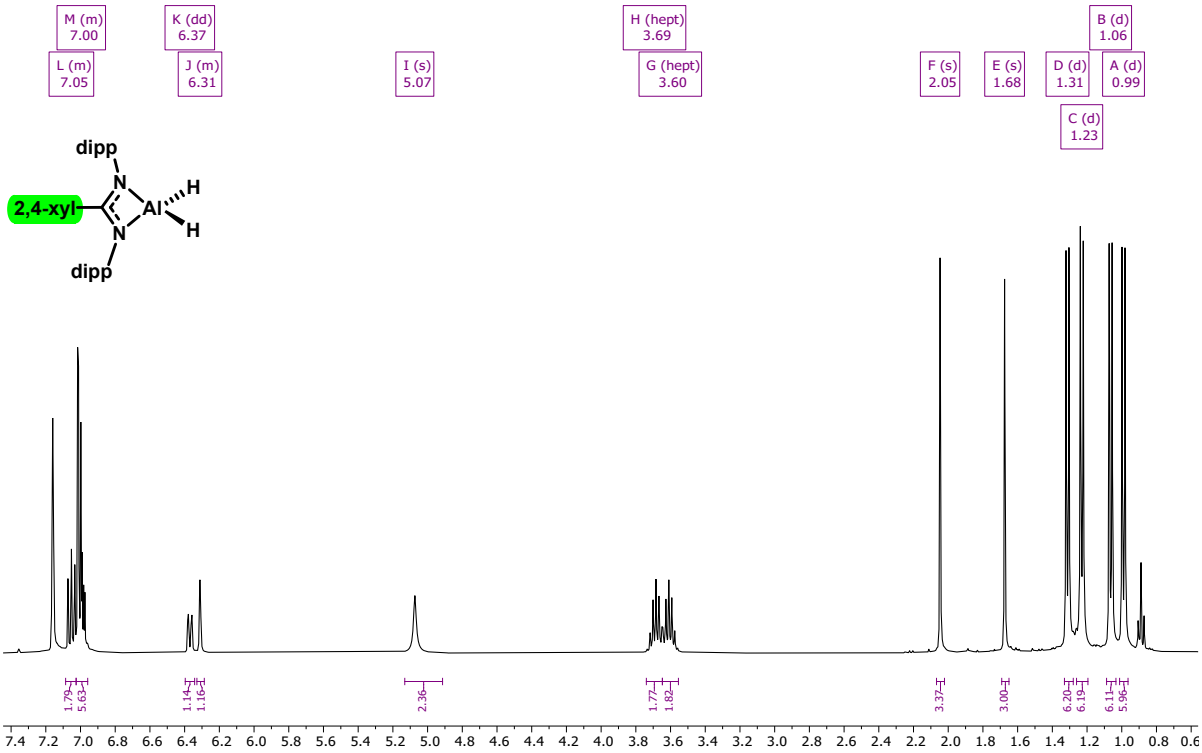


Figure S 90: ^{1}H NMR (400 MHz, 298 K) spectrum of **9-Al** in benzene-d_6

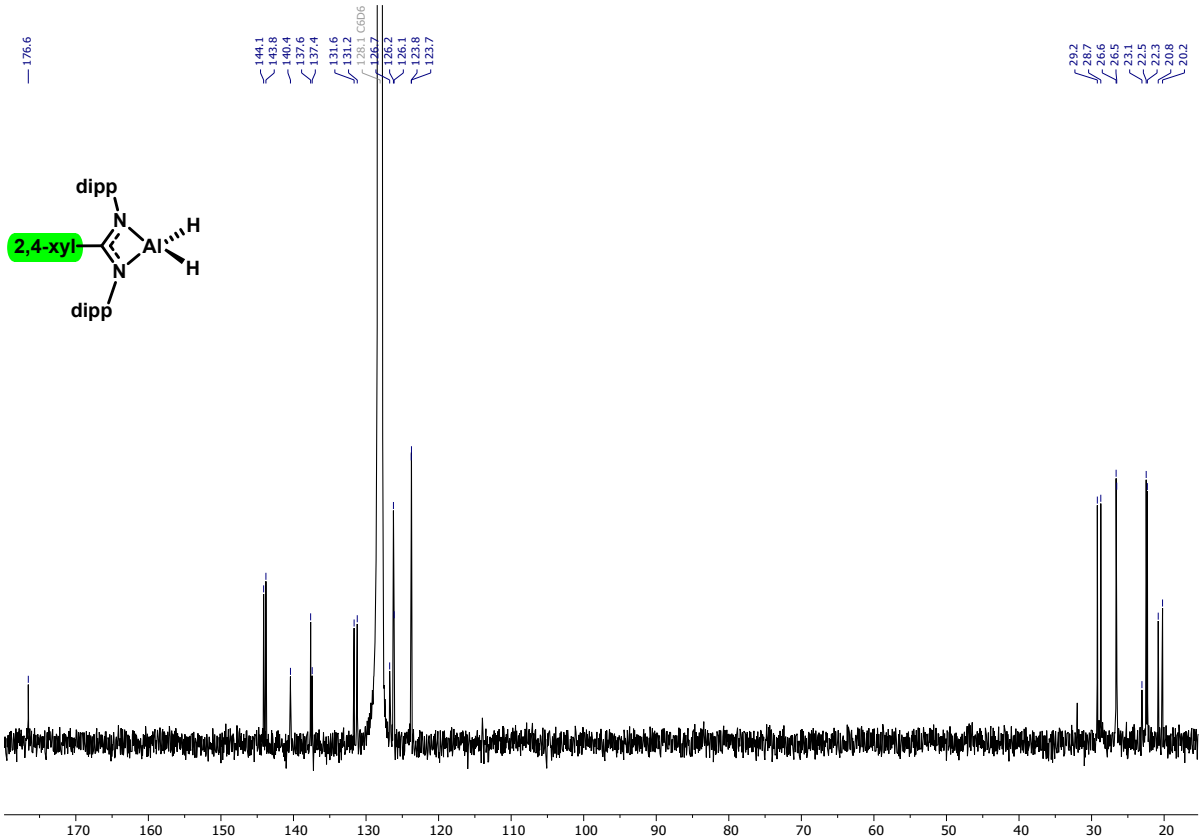


Figure S 91: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **9-Al** in benzene-d_6

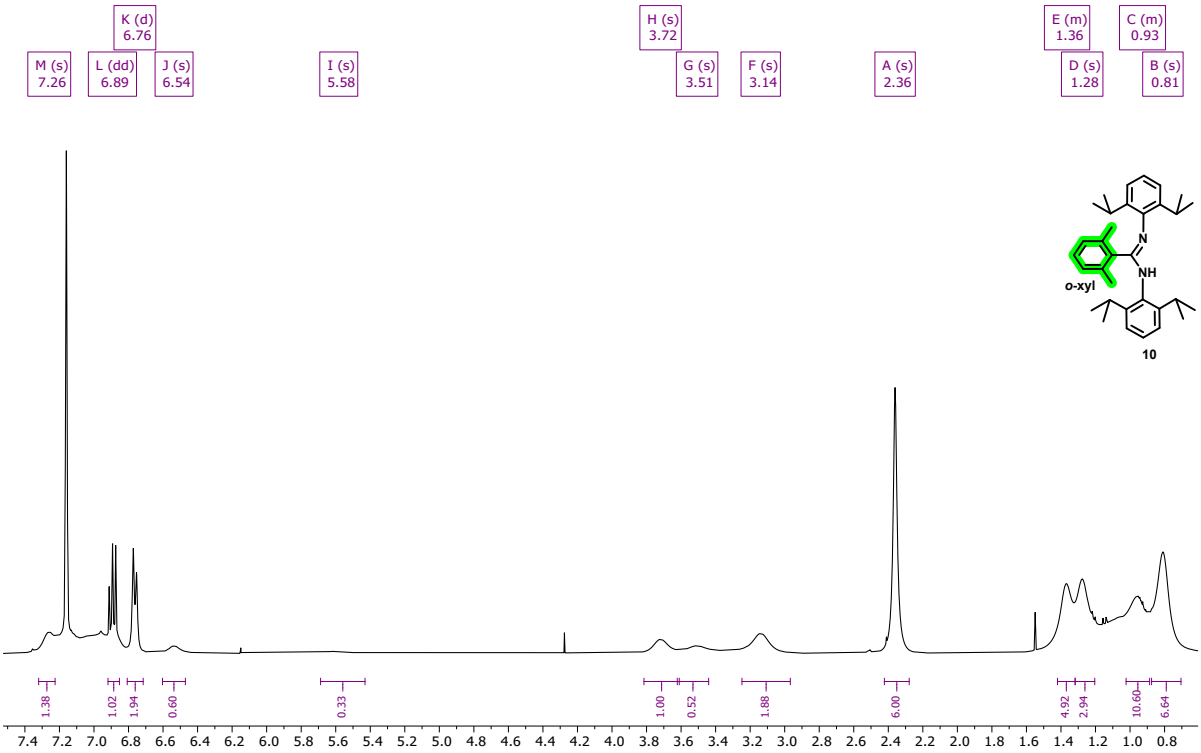


Figure S 92: ^{1}H NMR (400 MHz, 298 K) spectrum of **10** in benzene-d_6

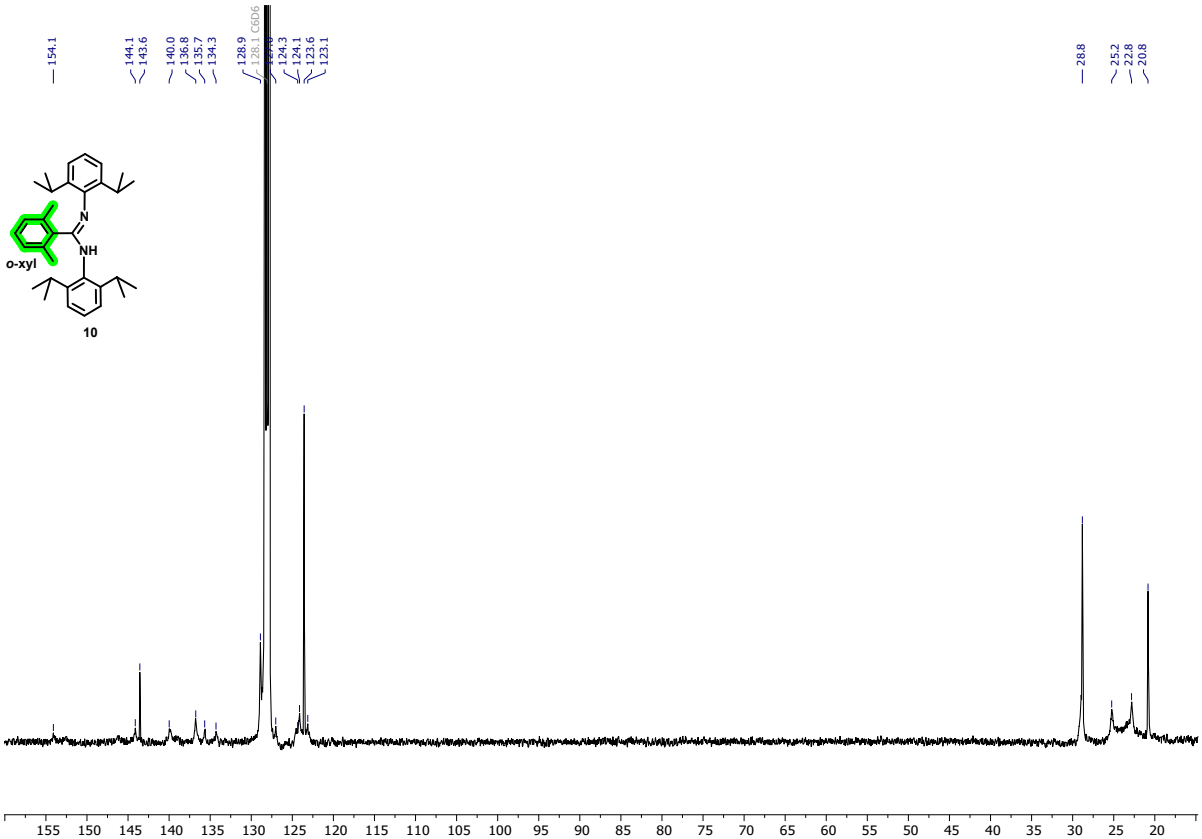


Figure S 93: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **10** in benzene-d_6

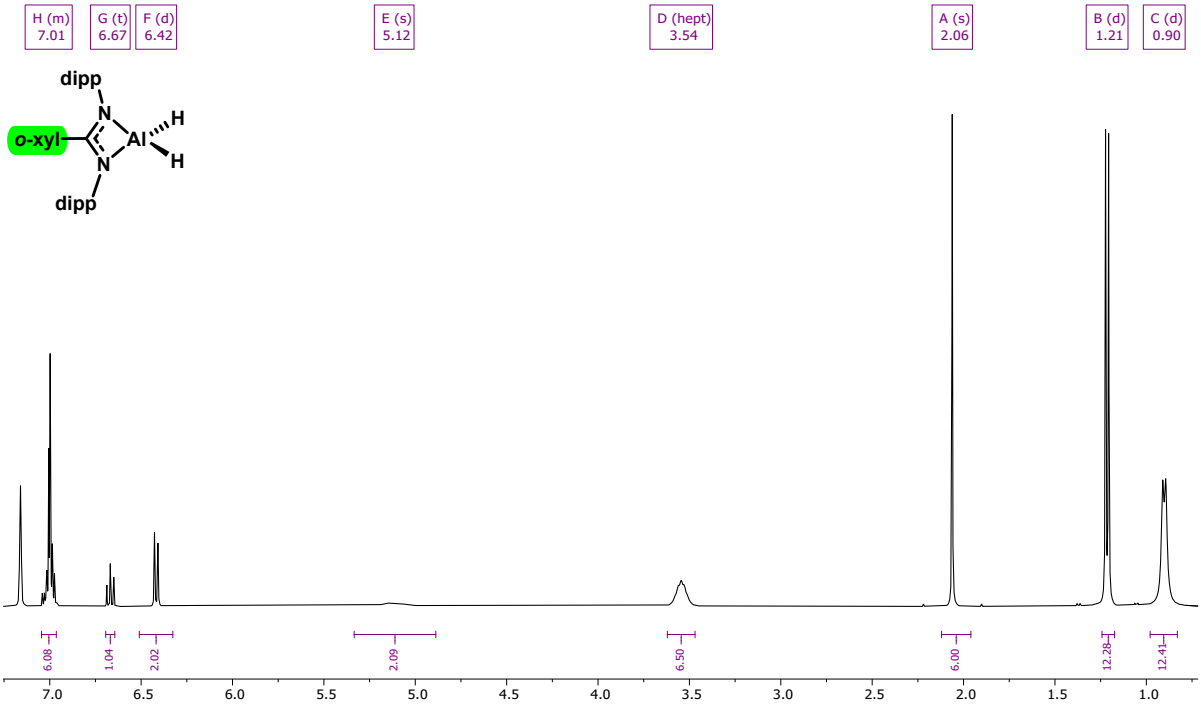


Figure S 94: ^{1}H NMR spectrum (400 MHz, 298 K) of **10-Al** in benzene-d_6

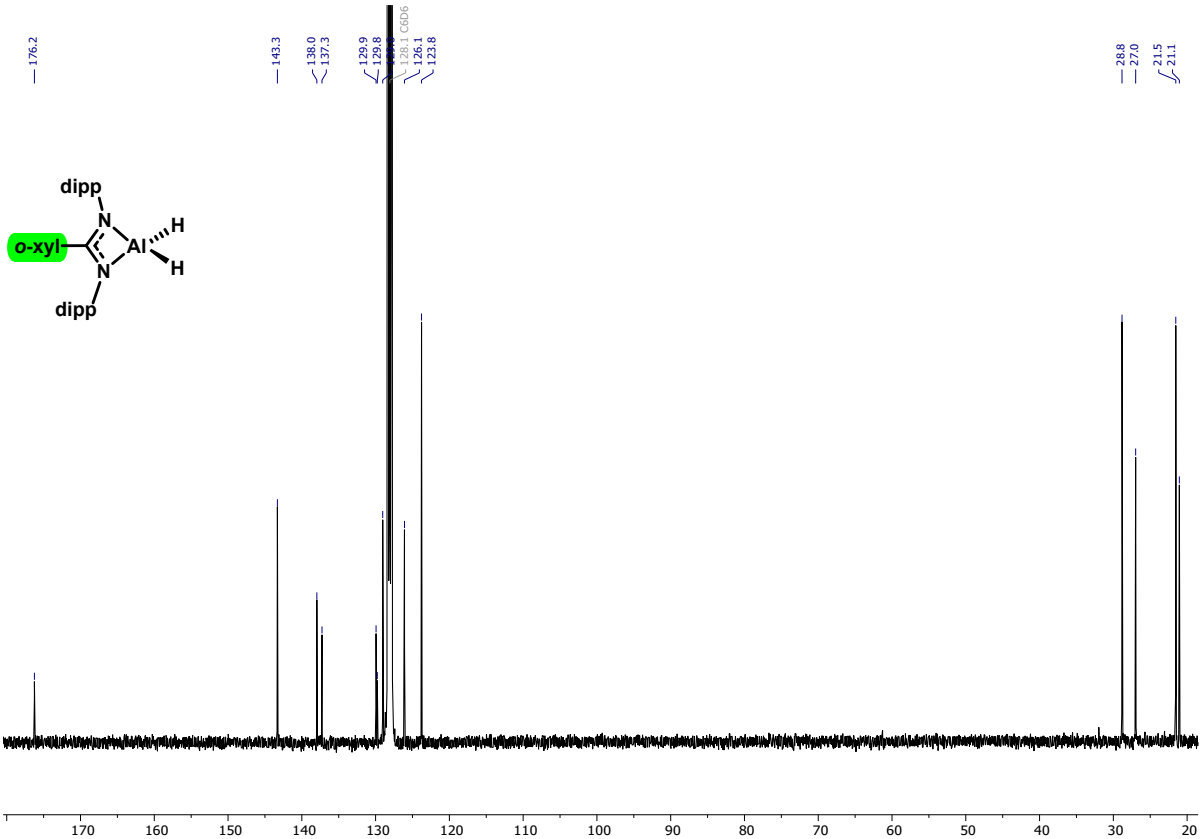


Figure S 95: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **9-Al** in benzene-d_6

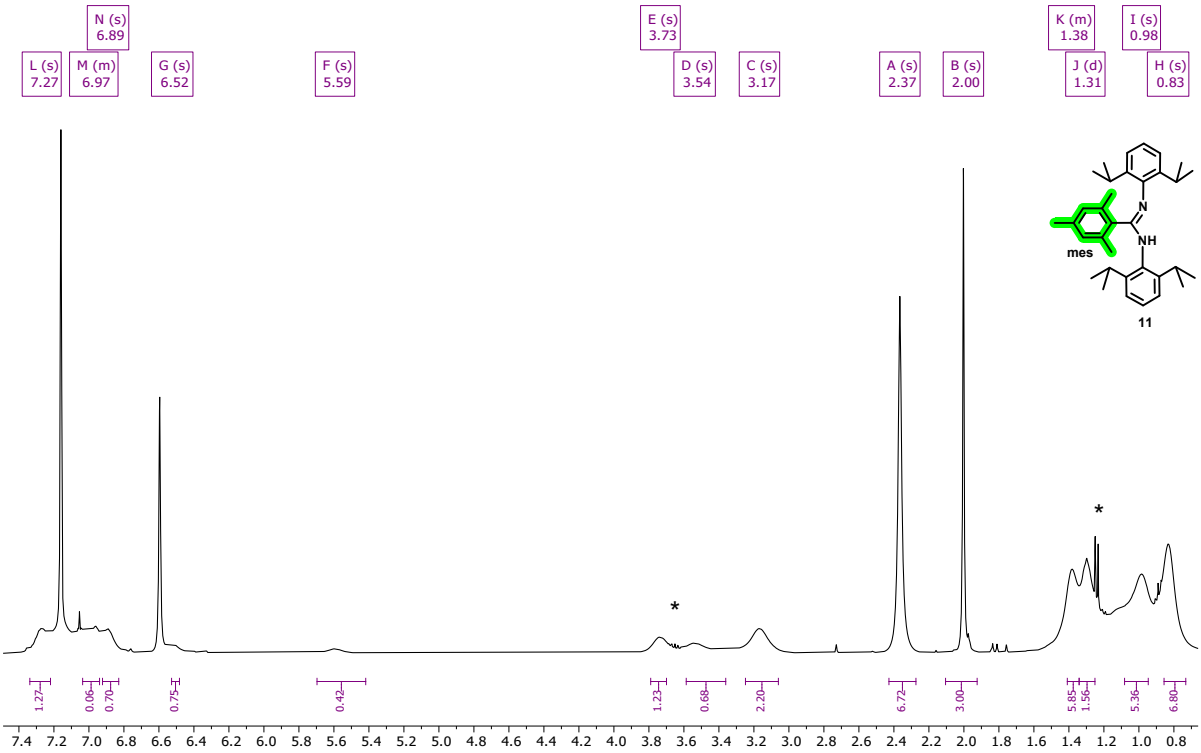


Figure S 96: ^{1}H NMR (400 MHz, 298 K) spectrum of **11** in benzene-d_6 with diisopropylphenyl carbodiimide (*)

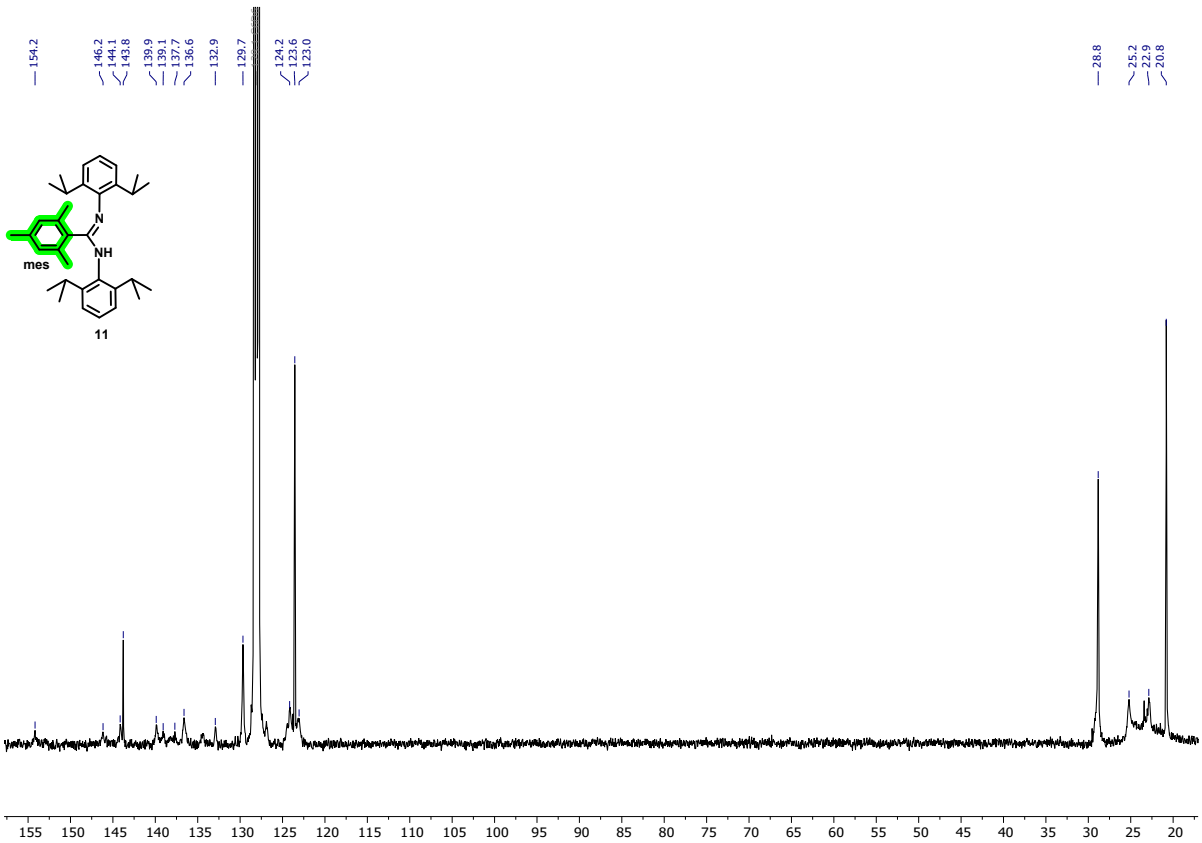


Figure S 97: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **11** in benzene-d_6

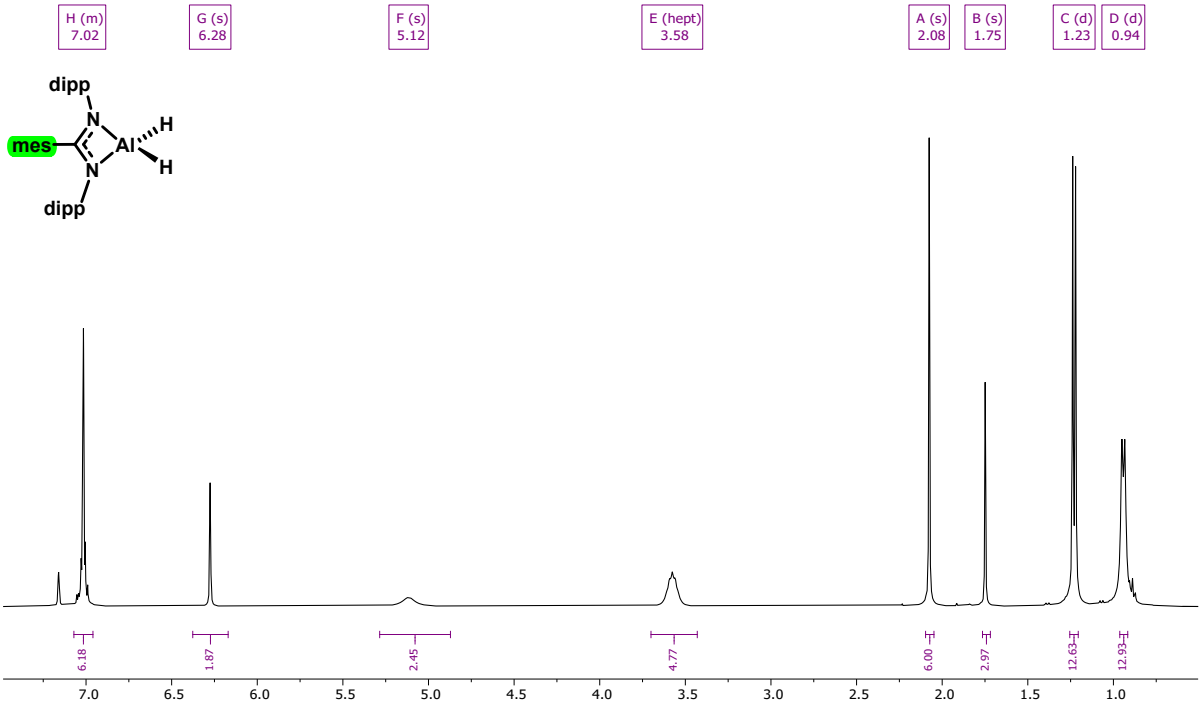


Figure S 98: ^{1}H NMR (400 MHz, 298 K) spectrum of **11-Al** in benzene-d_6

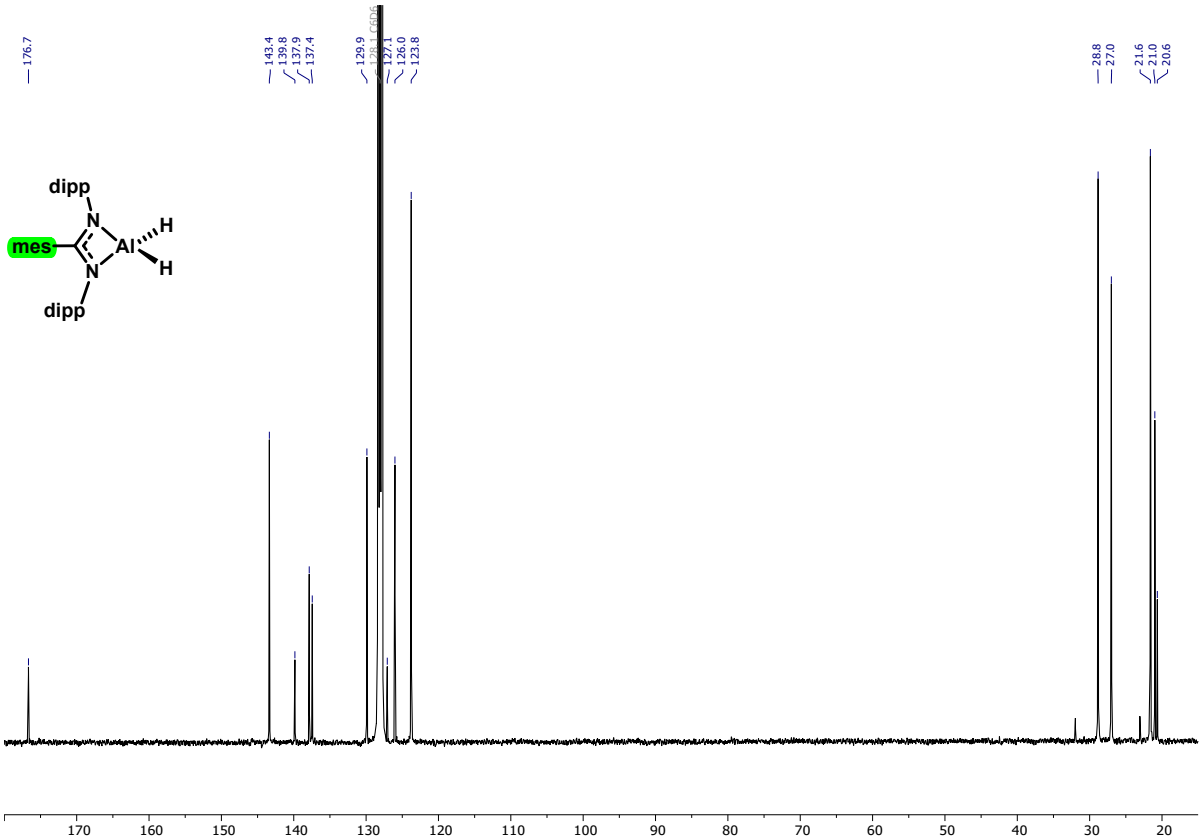


Figure S 99: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **11-Al** in benzene-d_6

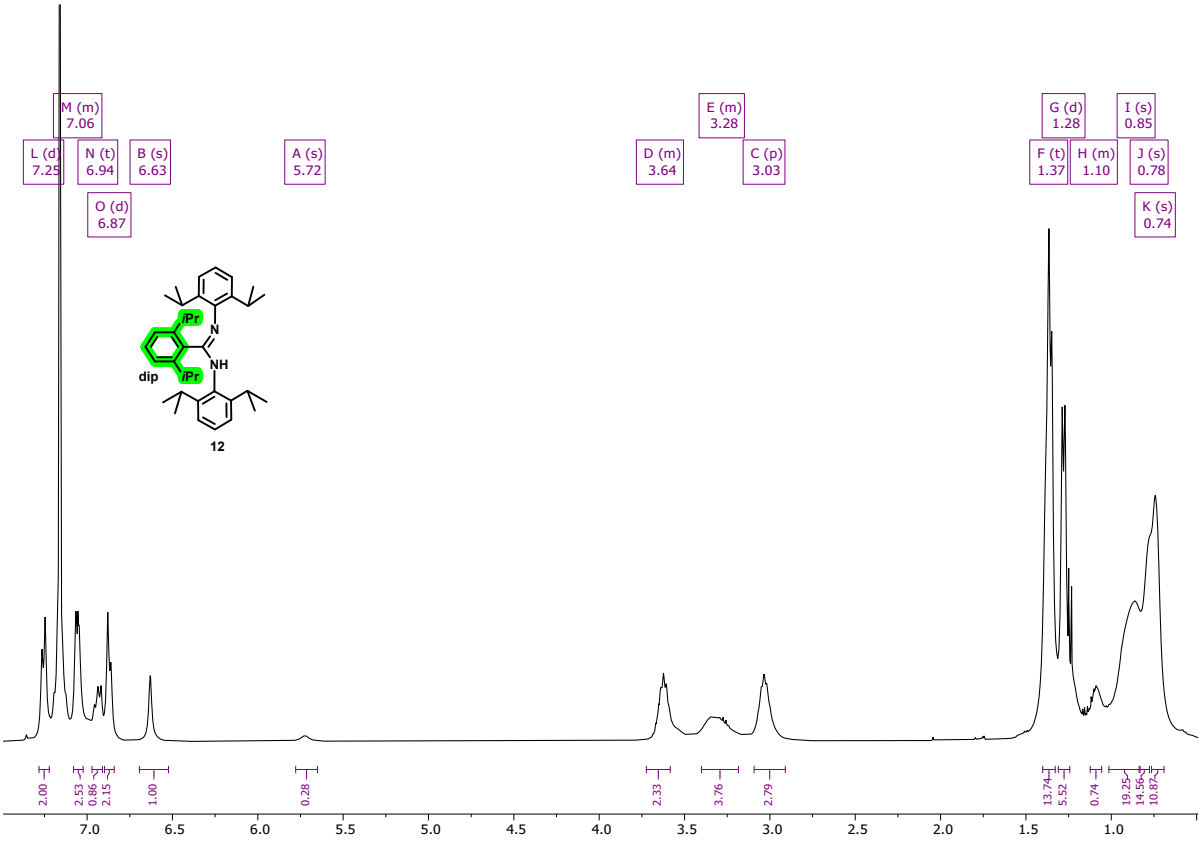


Figure S 100: ^{1}H NMR (400 MHz, 298 K) spectrum of **12** in benzene-d_6

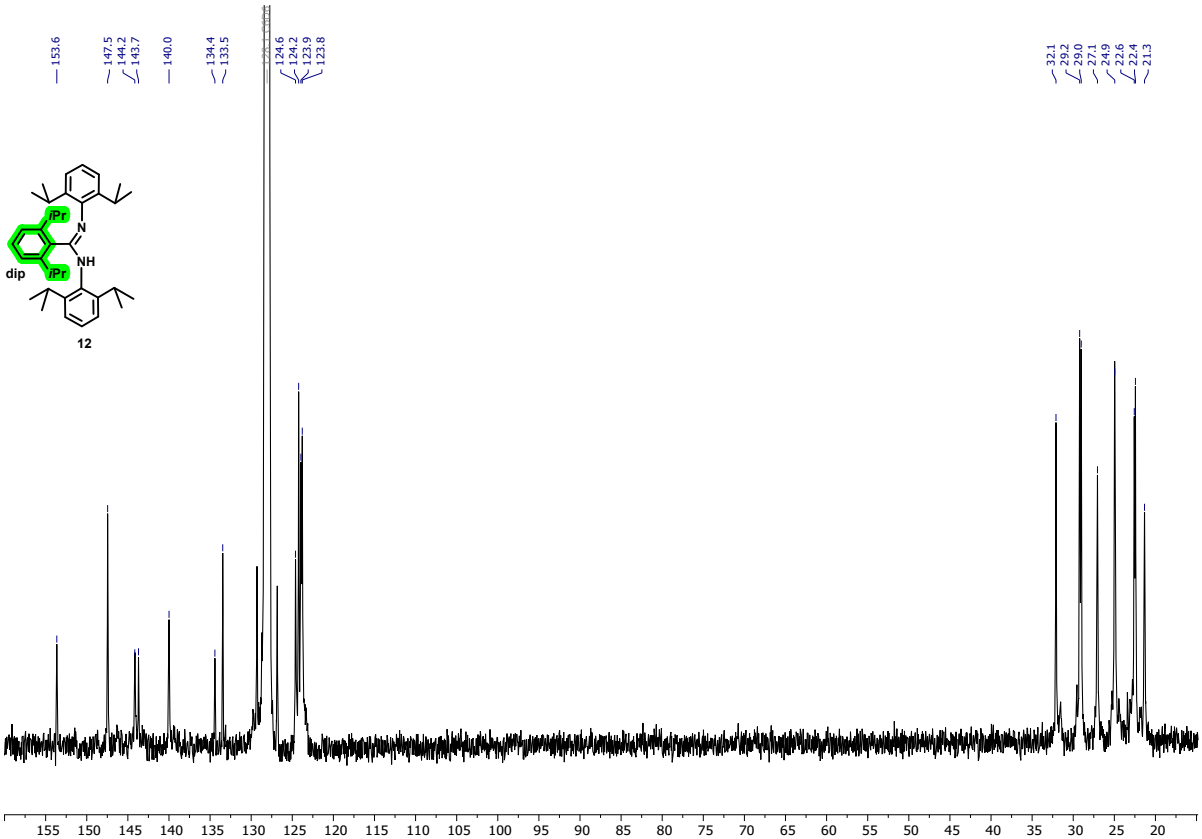


Figure S 101: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **12** in benzene-d_6

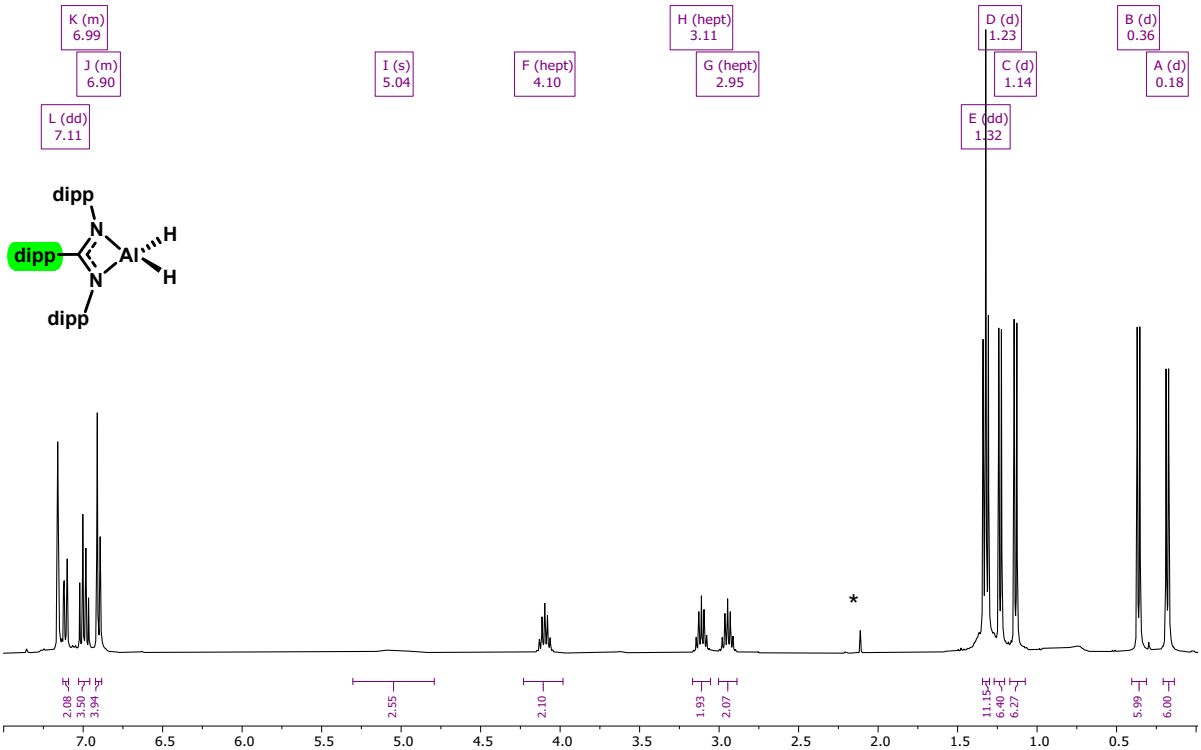


Figure S 102: ^{1}H NMR (400 MHz, 298 K) spectrum of **12-Al** in benzene-d_6 (with toluene impurity labelled with a *)

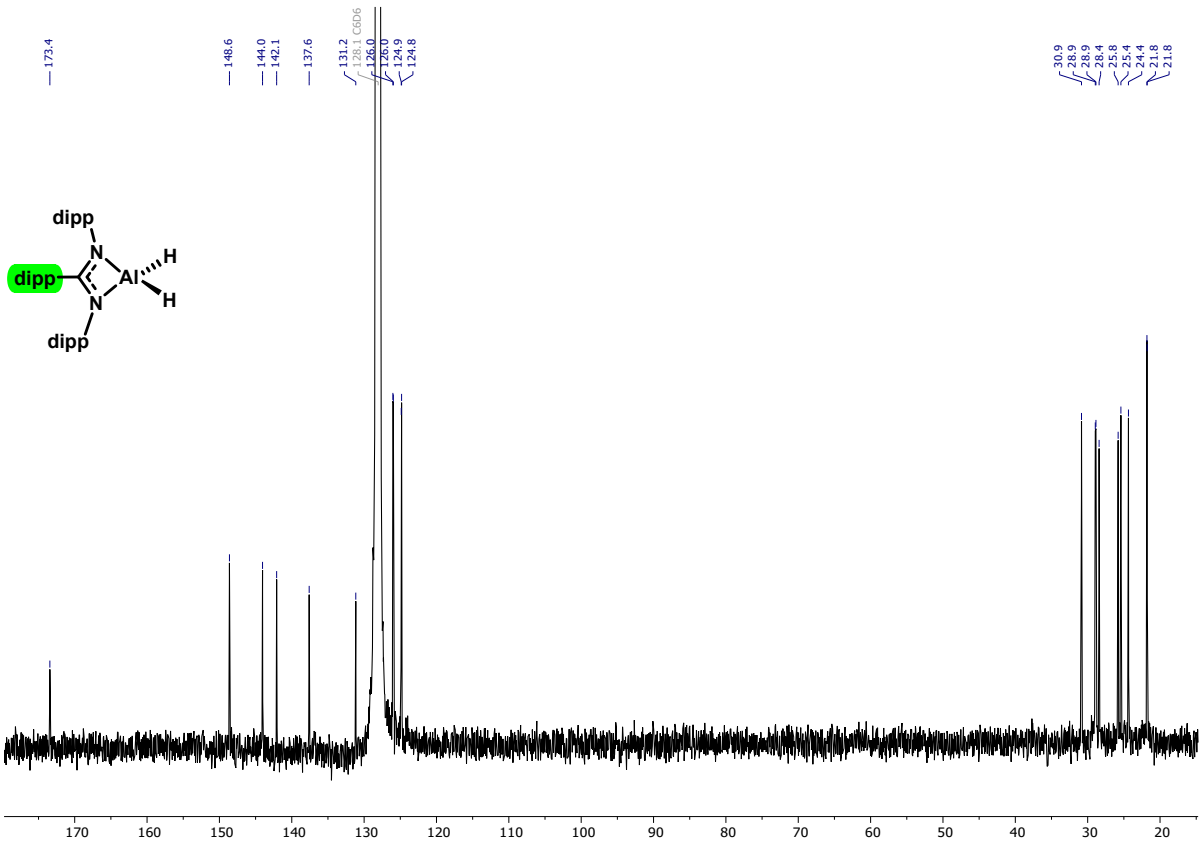


Figure S 103: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **12-Al** in benzene-d_6

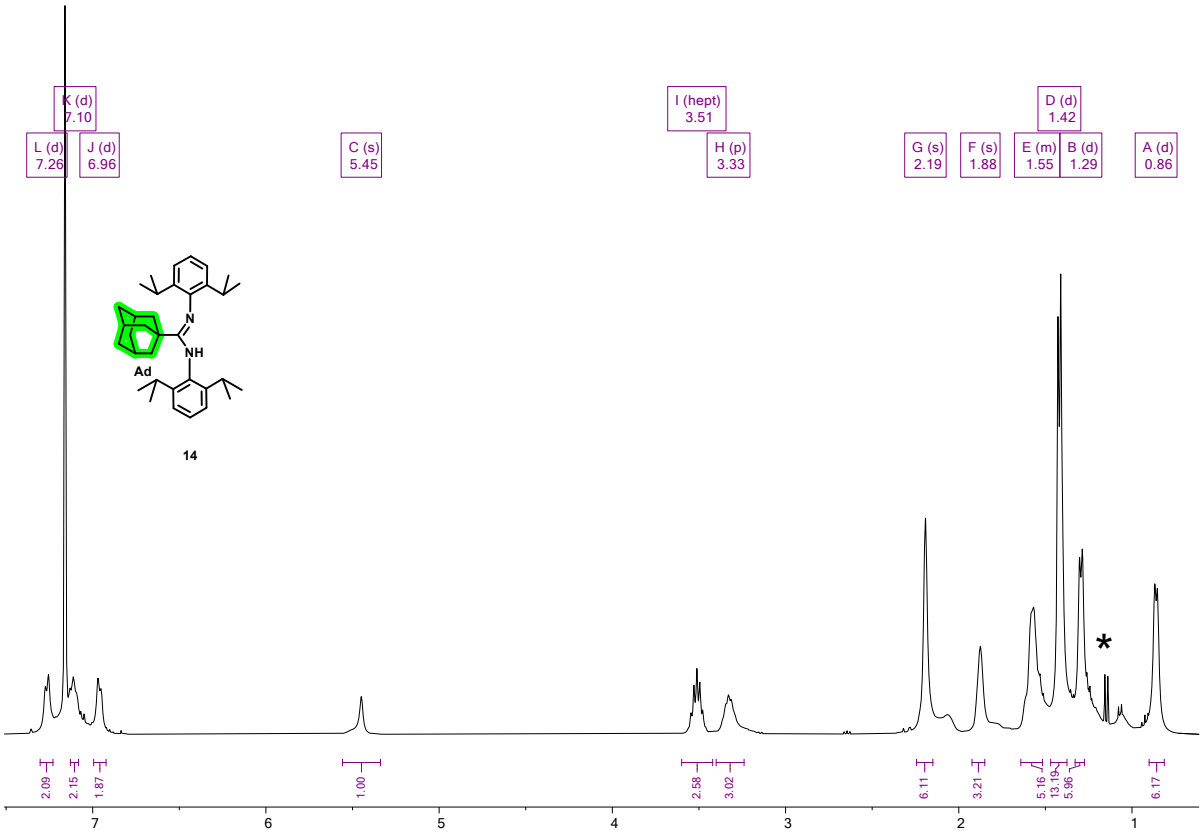


Figure S 104: ^{1}H NMR spectrum (400 MHz, 298 K) of **14** in benzene-d_6 (with diisopropyl aniline impurity, marked with a *)

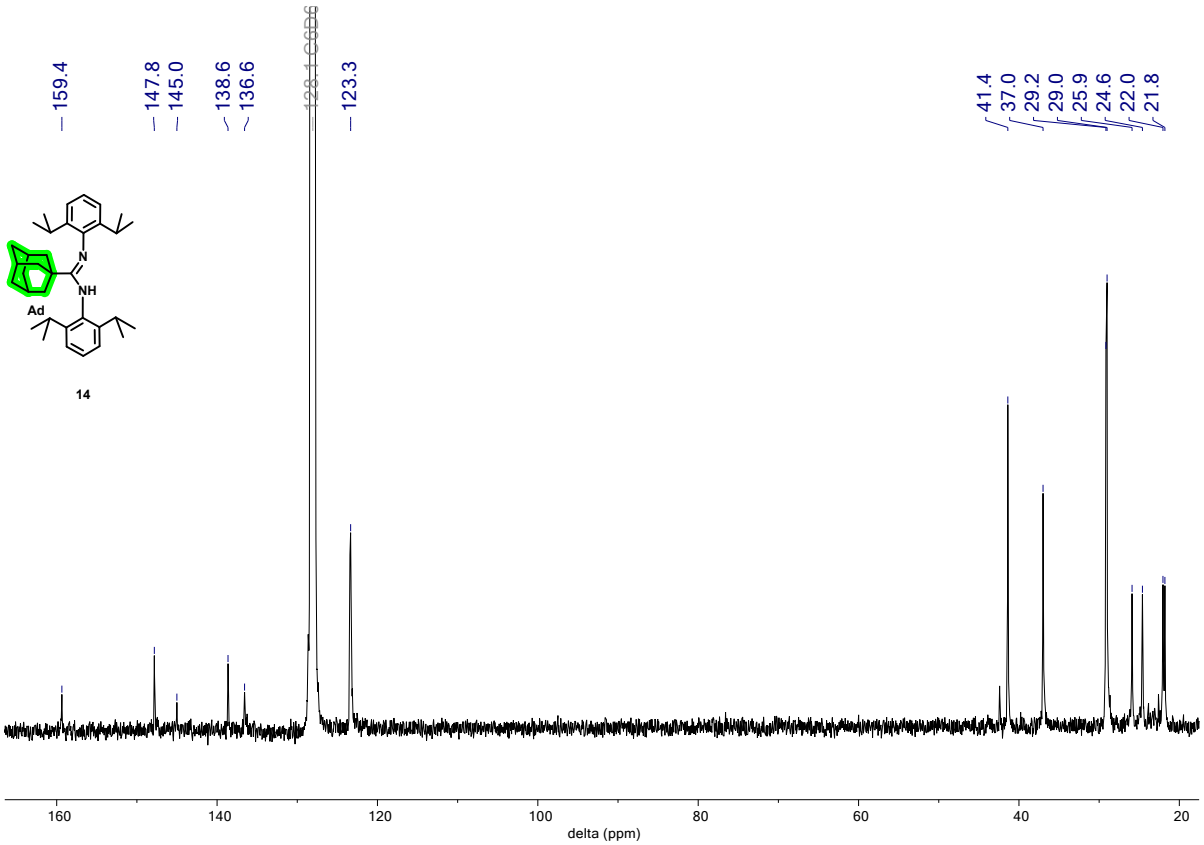


Figure S 105: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **14** in benzene-d_6

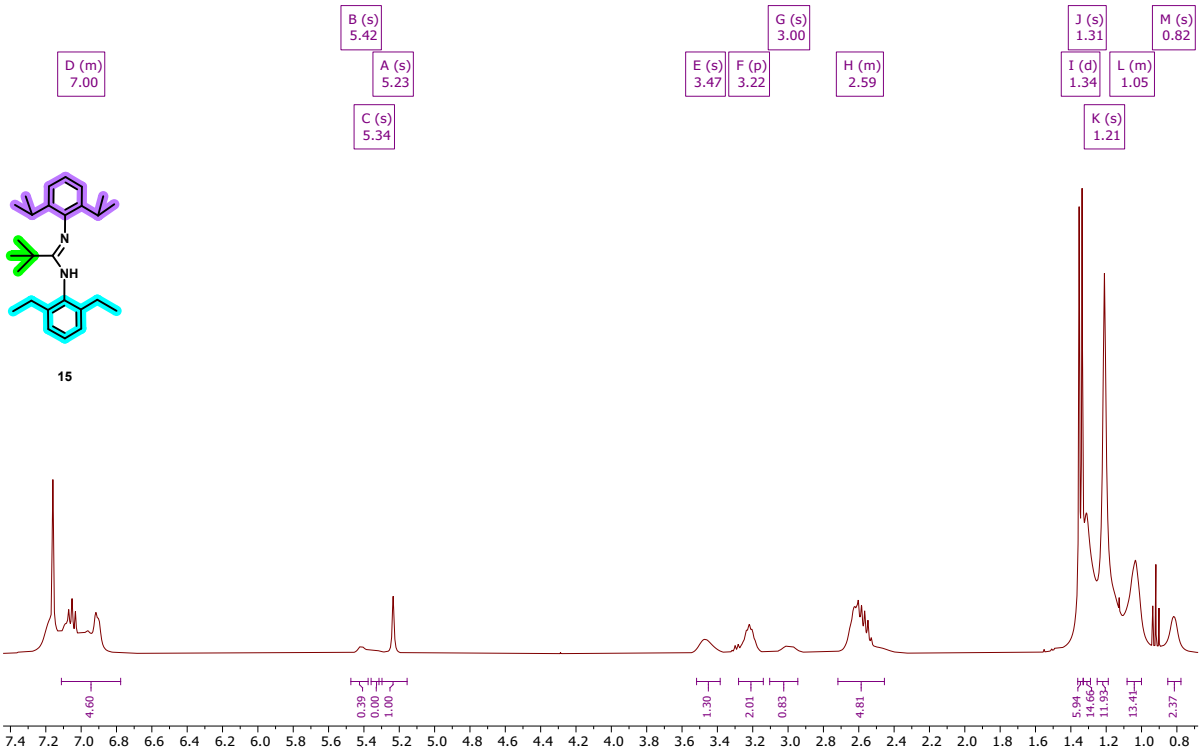


Figure S 106: ^{1}H NMR spectrum (400 MHz, 298 K) of ***15*** in benzene-d_6

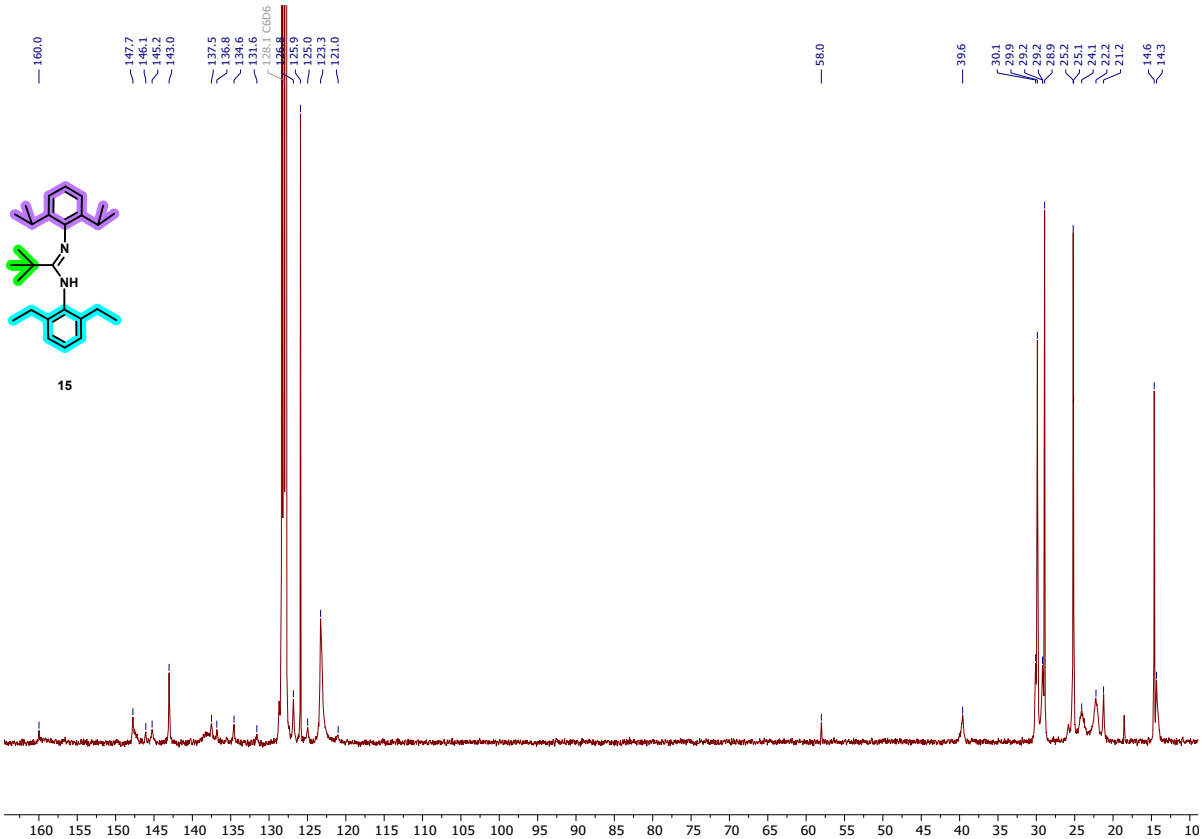


Figure S 107: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **15** in benzene-d_6

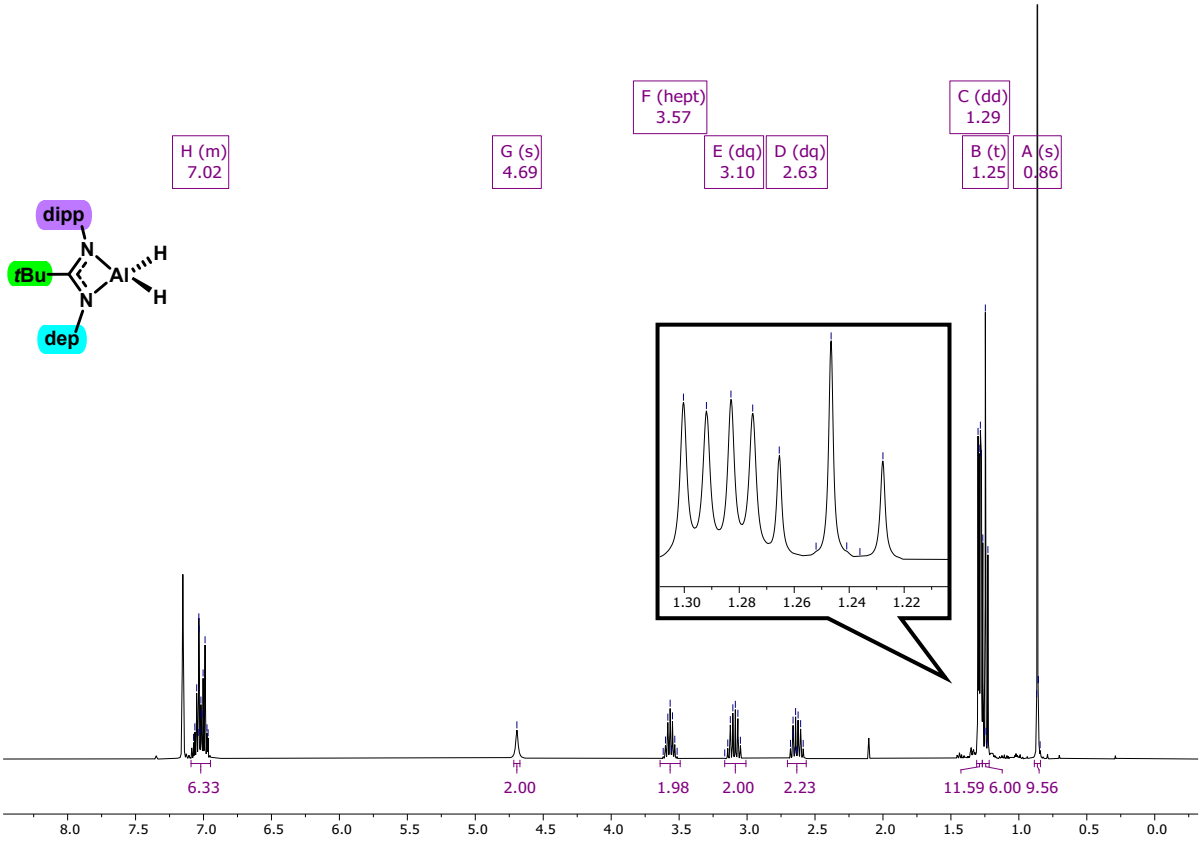


Figure S 108: ^{1}H NMR spectrum (400 MHz, 298 K) of **15-Al** in benzene-d_6 with callout showing the region 1.21-1.31 ppm

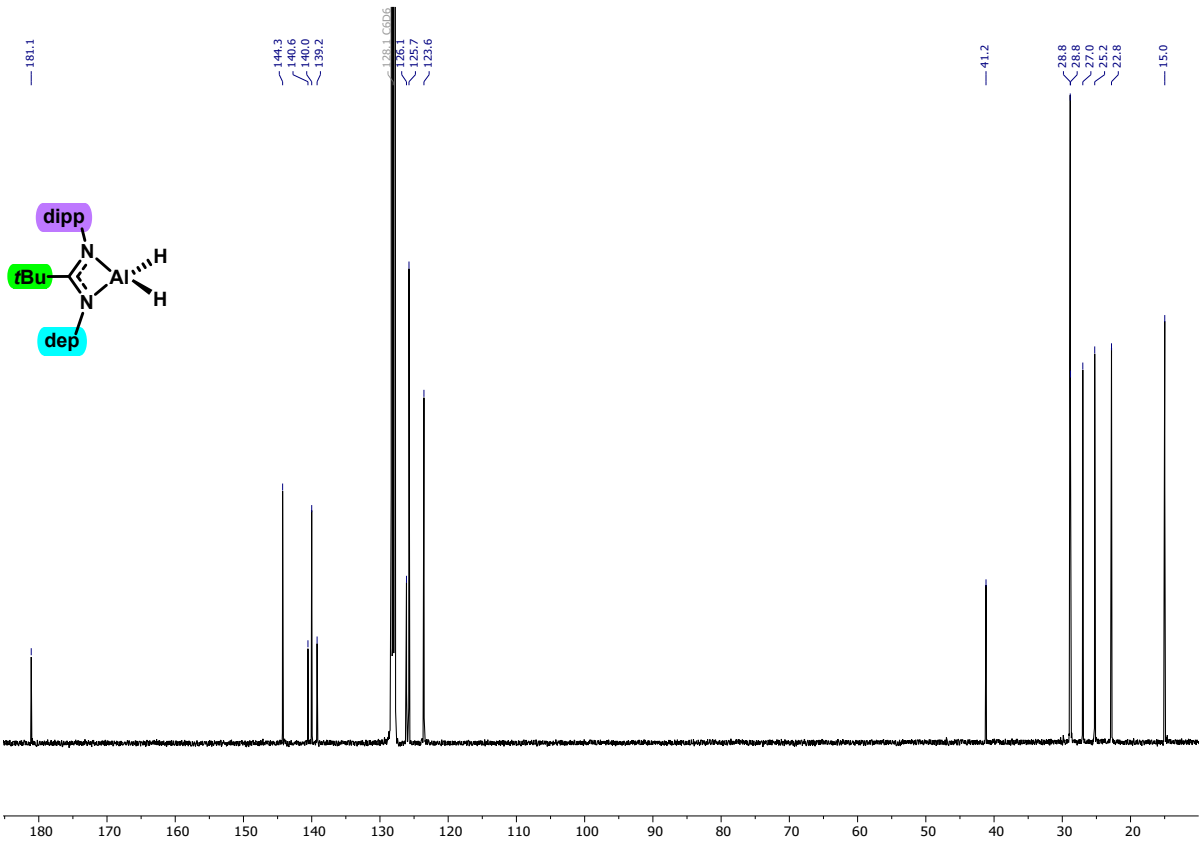
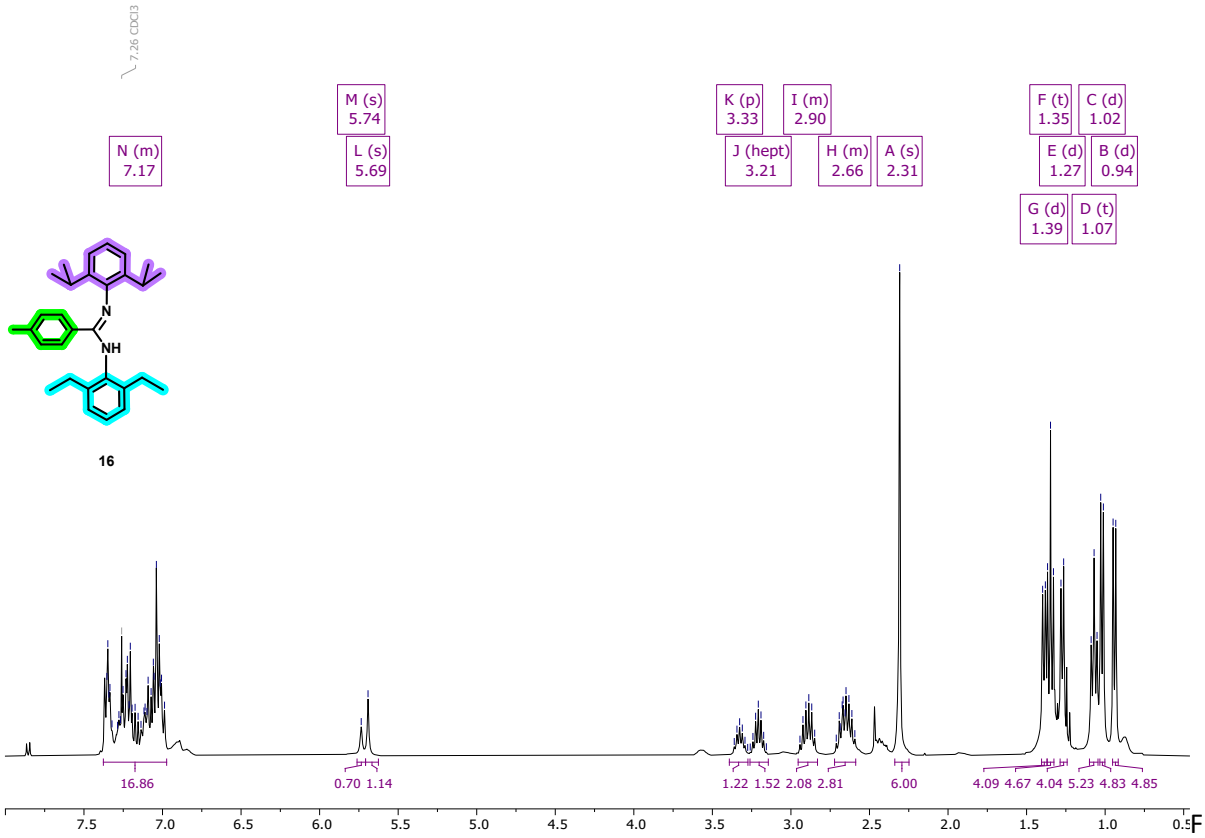


Figure S 109: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **15-Al** in benzene-d_6



igure S 110: ^{1}H NMR spectrum (400 MHz, 298 K) of **16** in chloroform-*d*

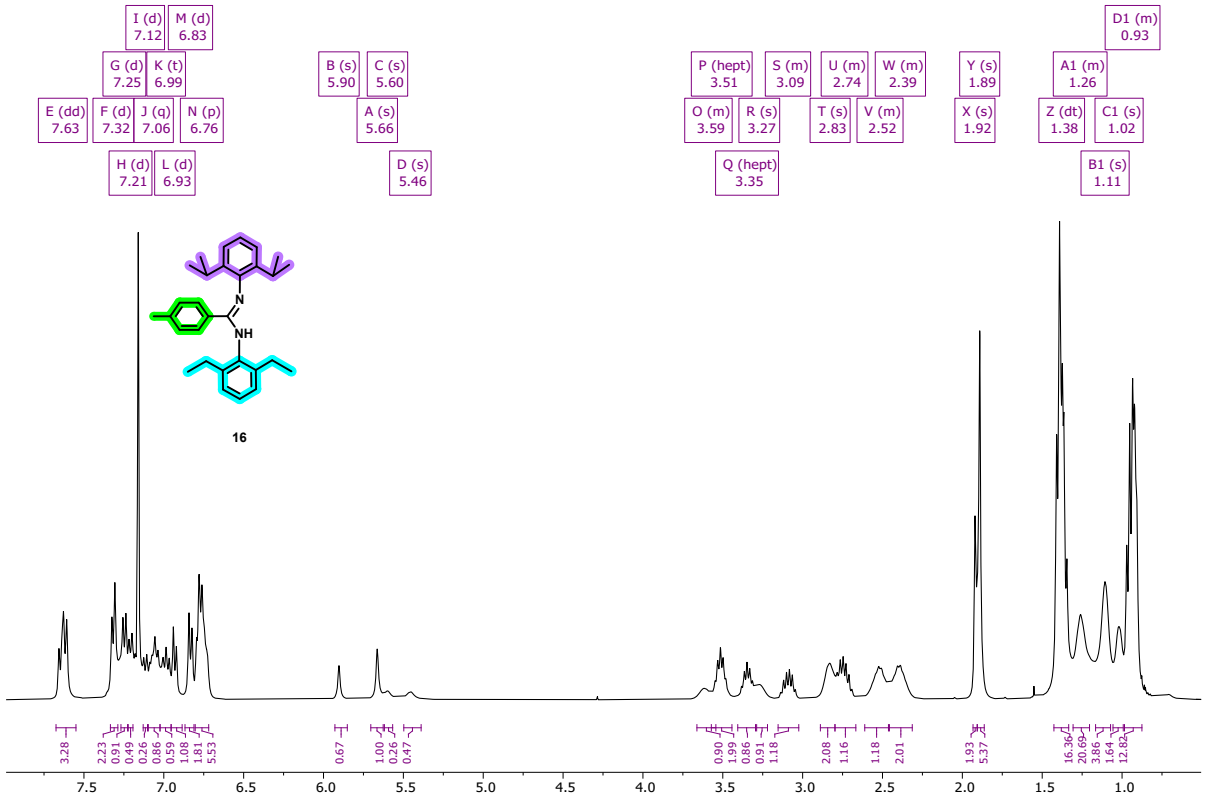


Figure S 111: ^{1}H NMR spectrum (400 MHz, 298 K) of **16** in benzene-d_6

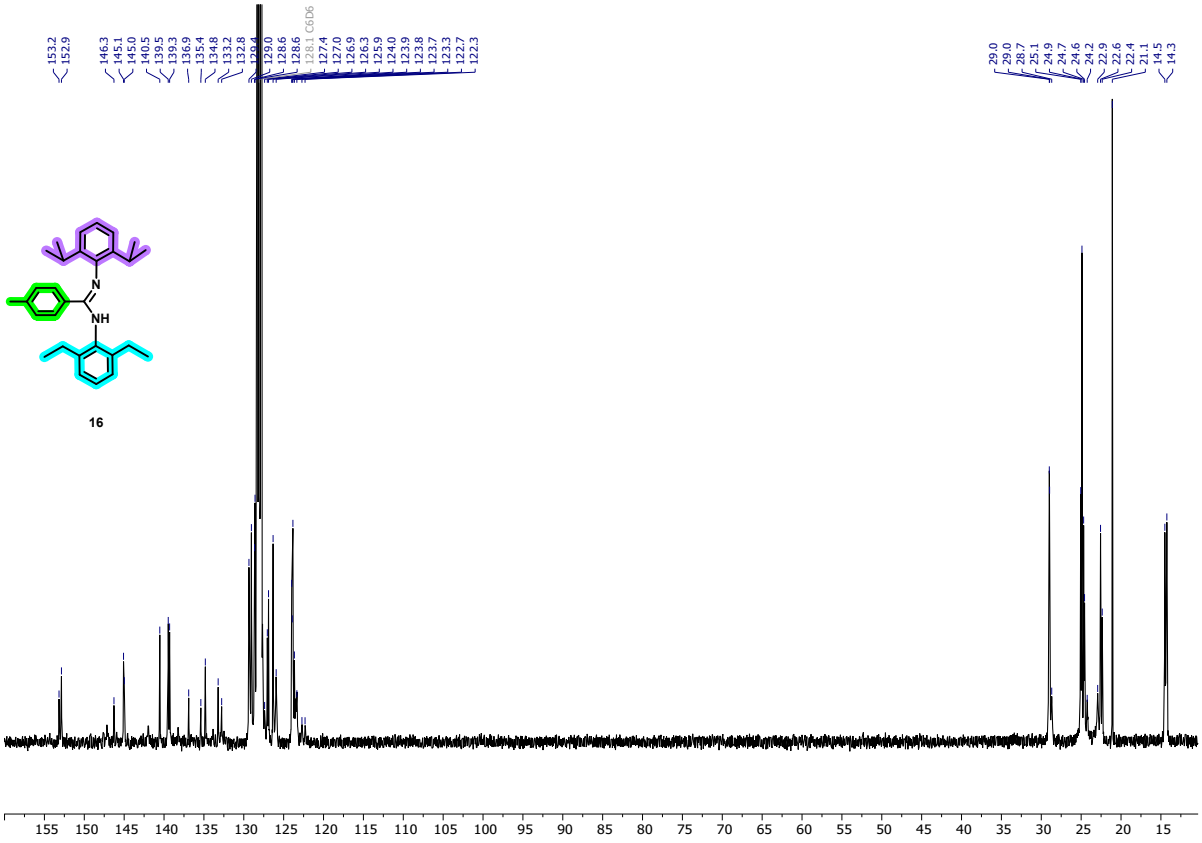


Figure S 112: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **16** in benzene-d_6

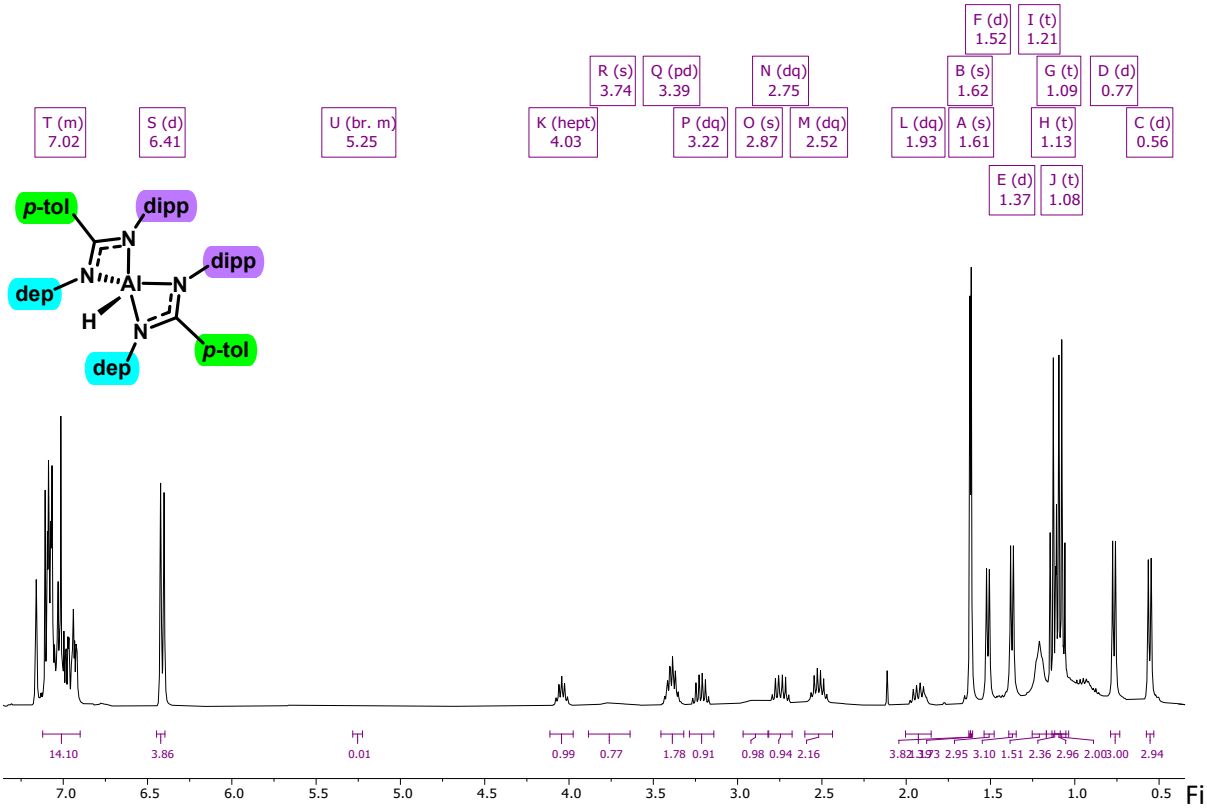


Figure S 113: ^{1}H NMR spectrum (400 MHz, 298 K) of **16-Al''** in benzene-d_6

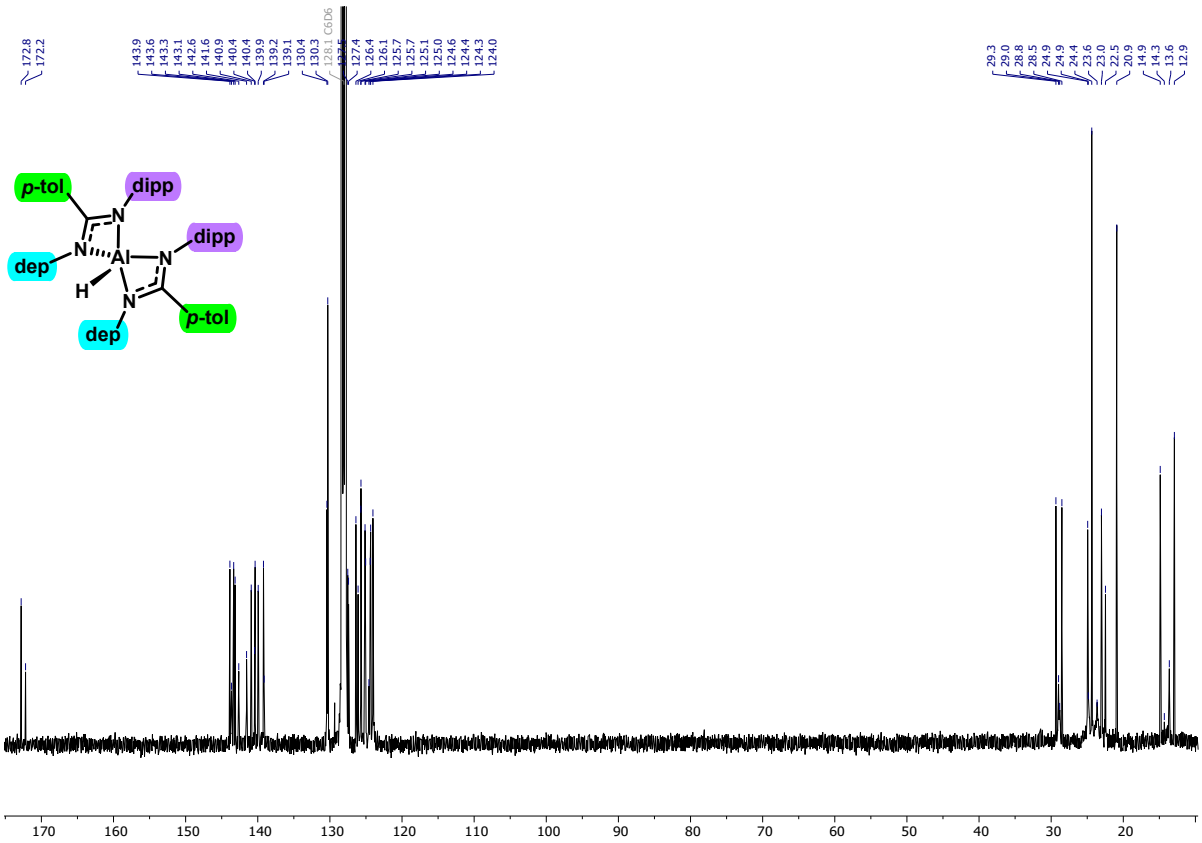


Figure S 114: $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, 298 K) of **16-Al''** in benzene-d_6

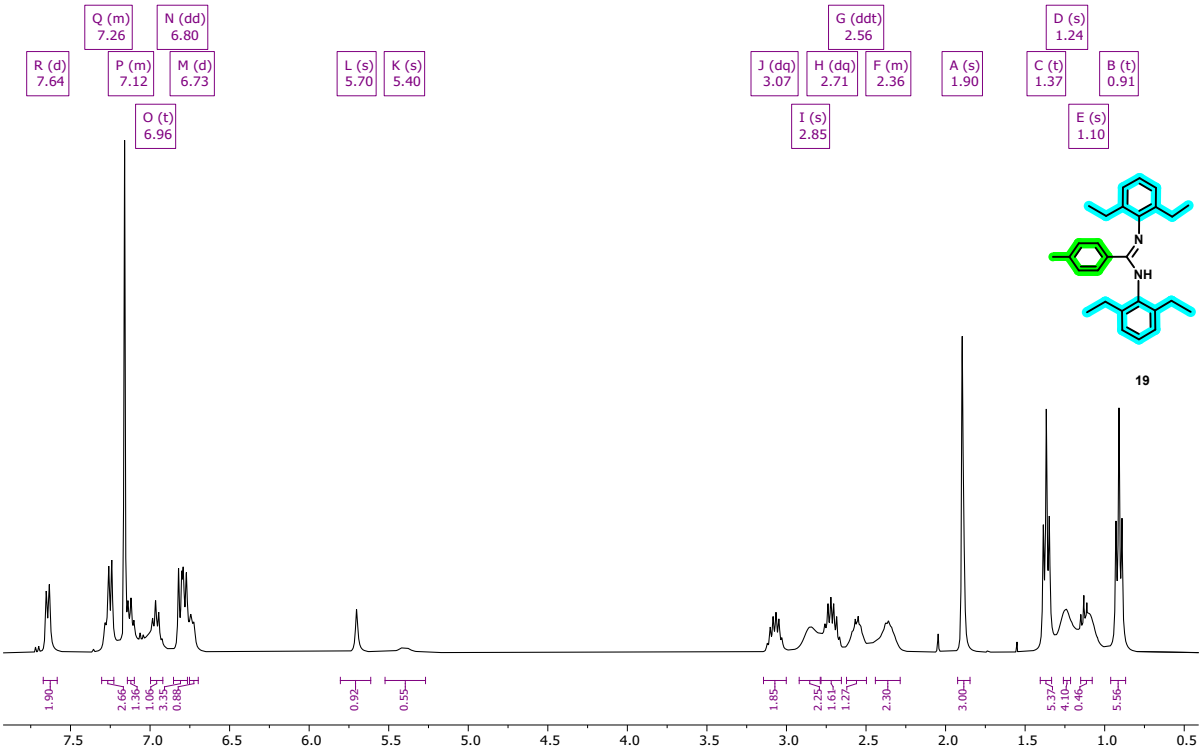


Figure S 115: ^{1}H NMR spectrum (400 MHz, 298 K) of **19** in benzene-d_6

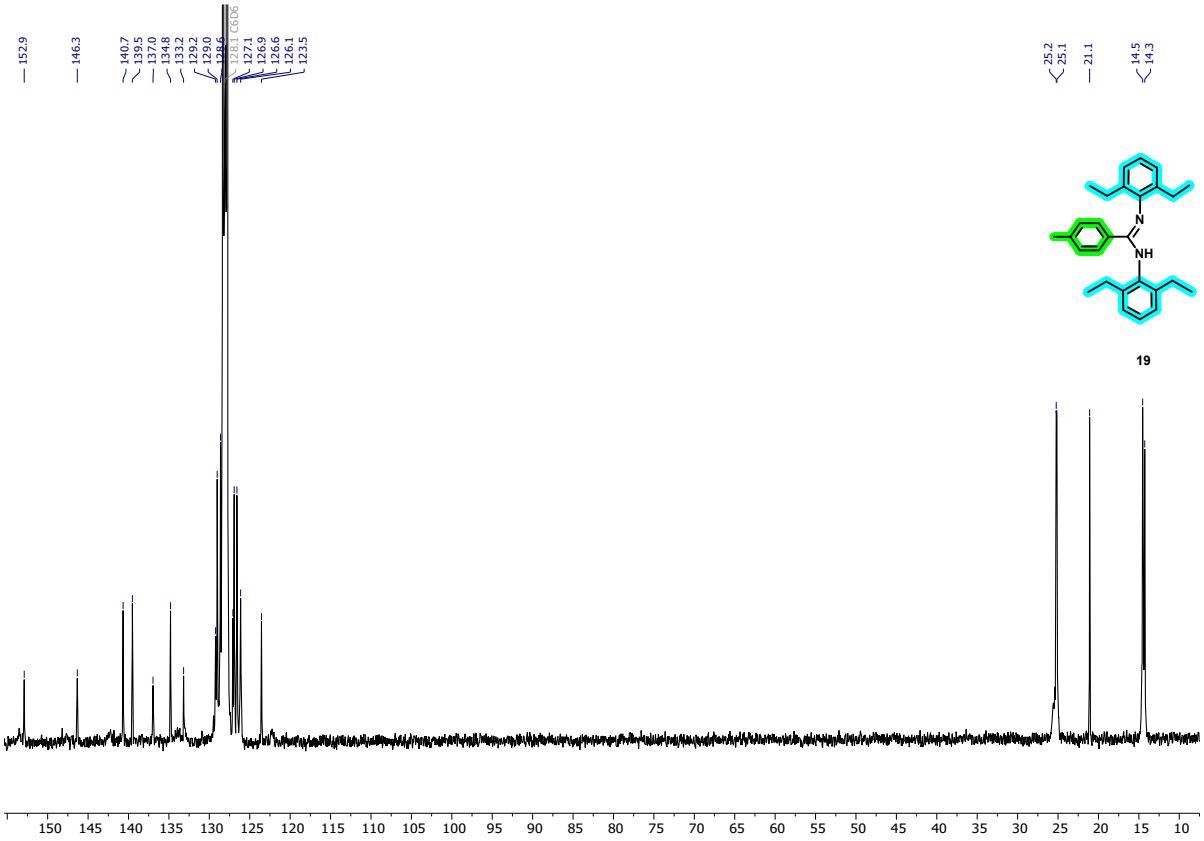


Figure S 116: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K) of **19** in benzene-d_6

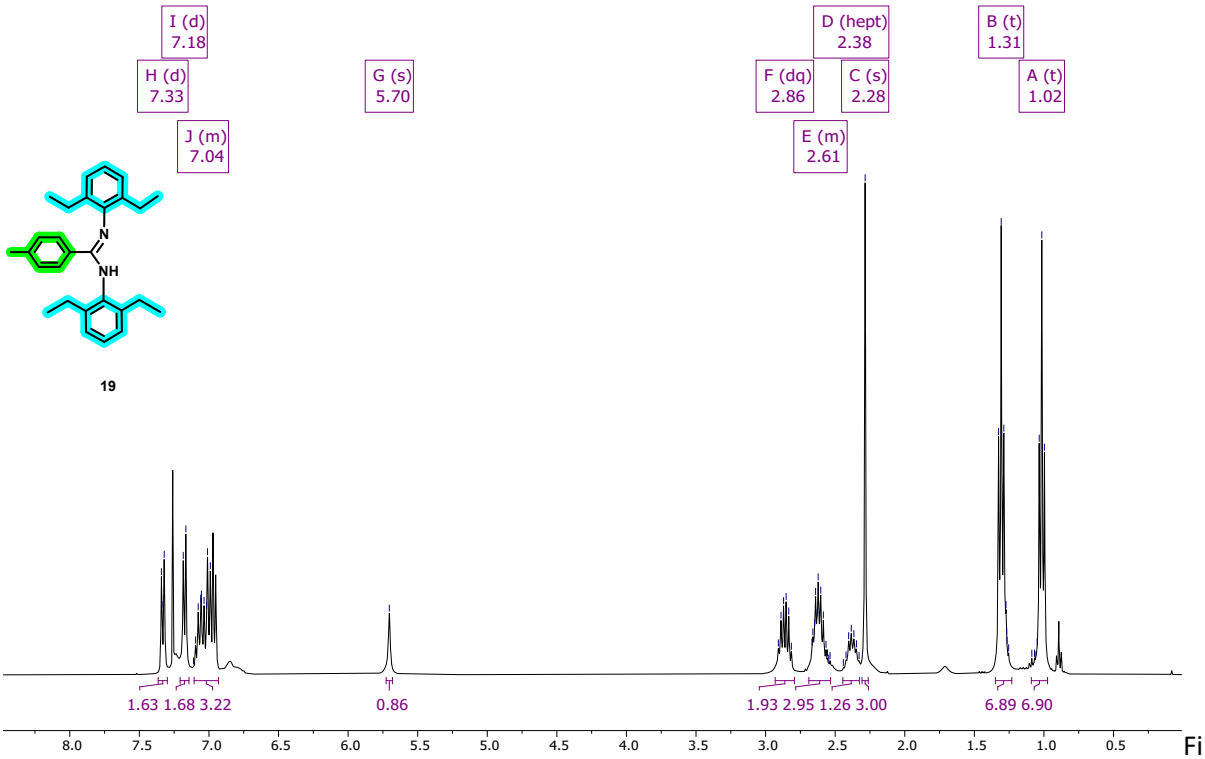


Figure S 117: ^{1}H NMR spectrum (400 MHz, 298 K) of **19** in chloroform-*d*

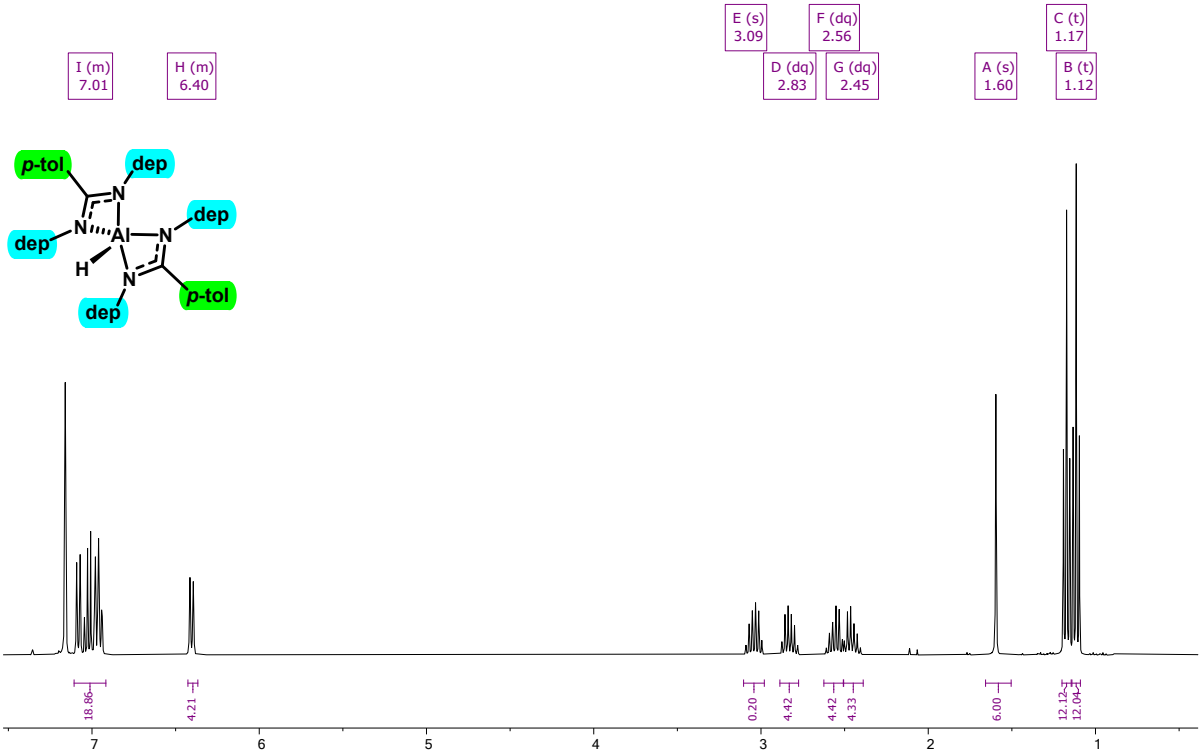


Figure S 118: ^{1}H NMR spectrum (400 MHz, 298 K) of **19-Al''** in benzene-d_6

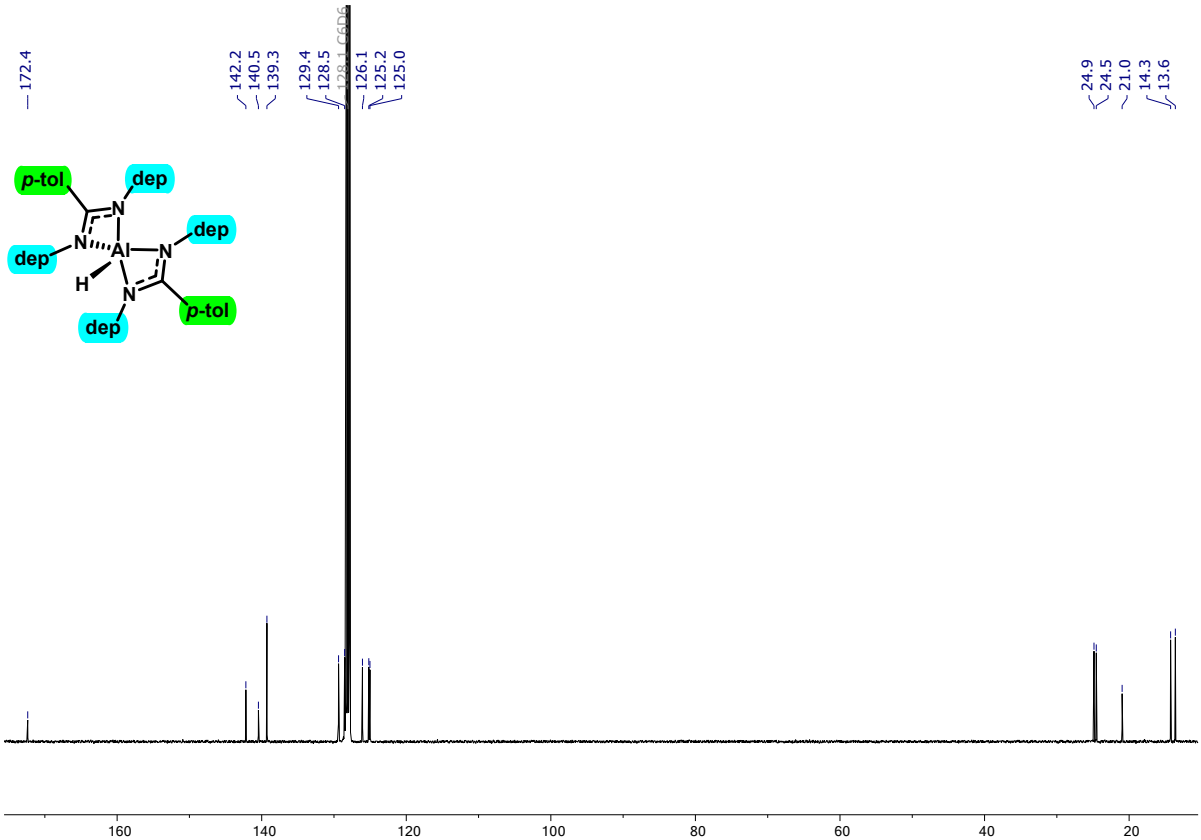


Figure S 119: ^{13}C{^{1}H} NMR spectrum (400 MHz, 298 K) of **19-Al''** in benzene-d_6

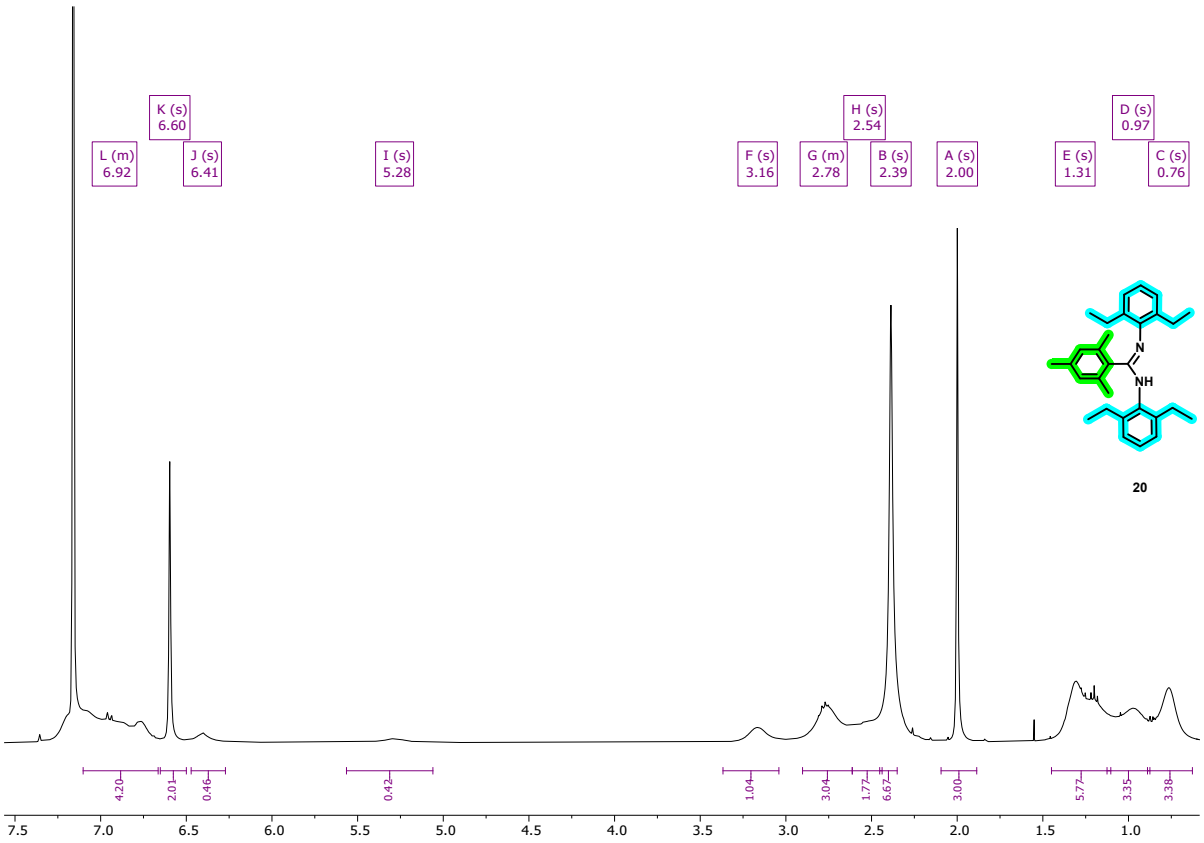


Figure S 120: ^{1}H NMR spectrum (400 MHz, 298 K) of **20** in benzene-d_6

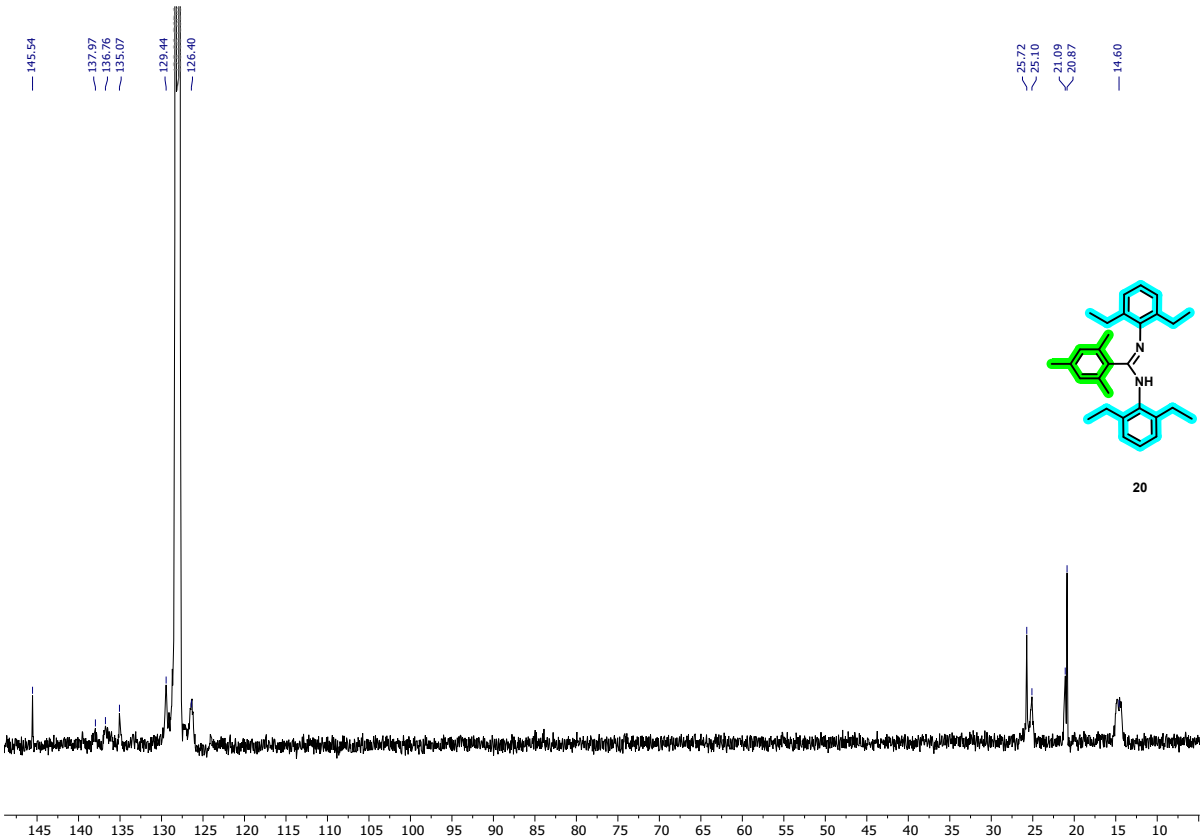


Figure S 121: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **20** in benzene-d_6

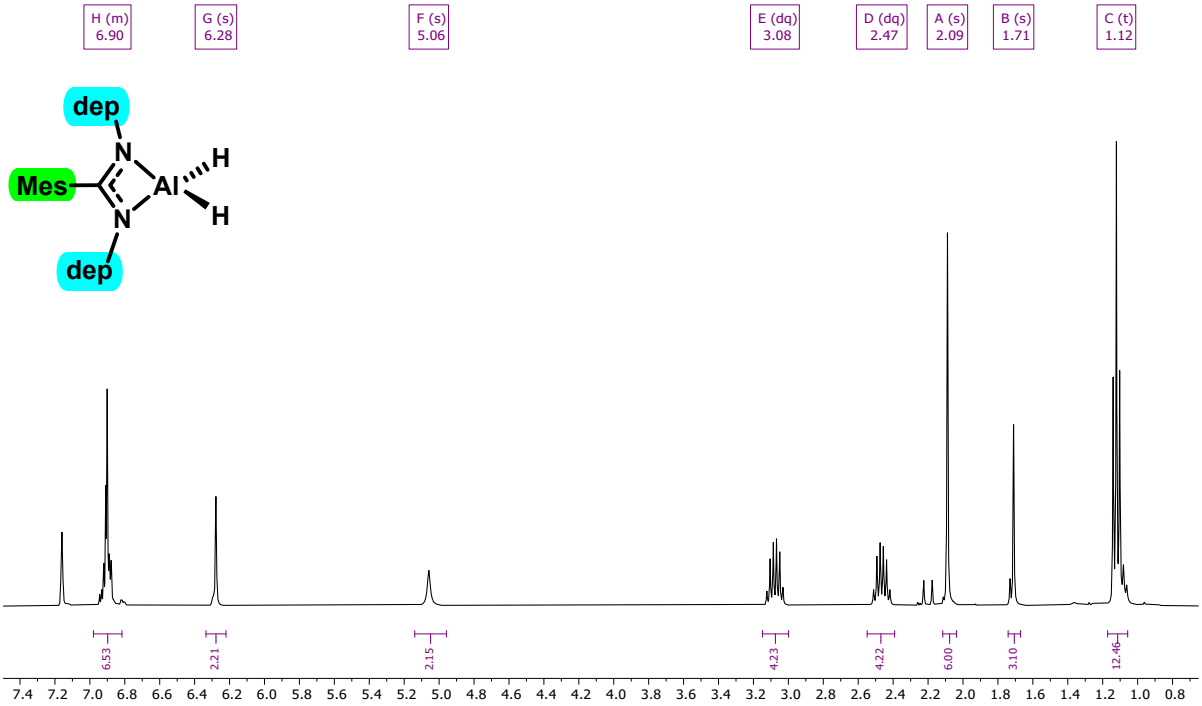


Figure S 122: ^{1}H NMR spectrum (400 MHz, 298 K) of **20-Al** in benzene-d_6 with minor unidentified impurity

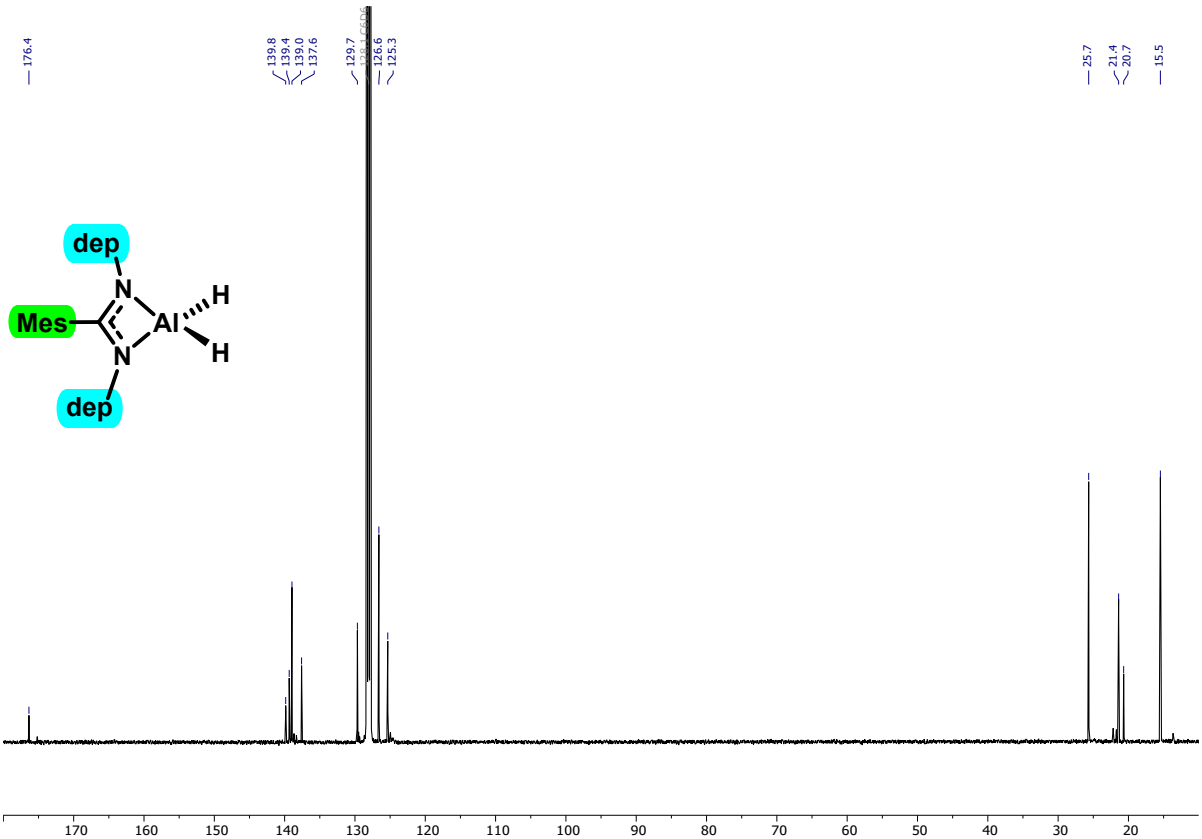


Figure S 123: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **20-Al** in benzene-d_6

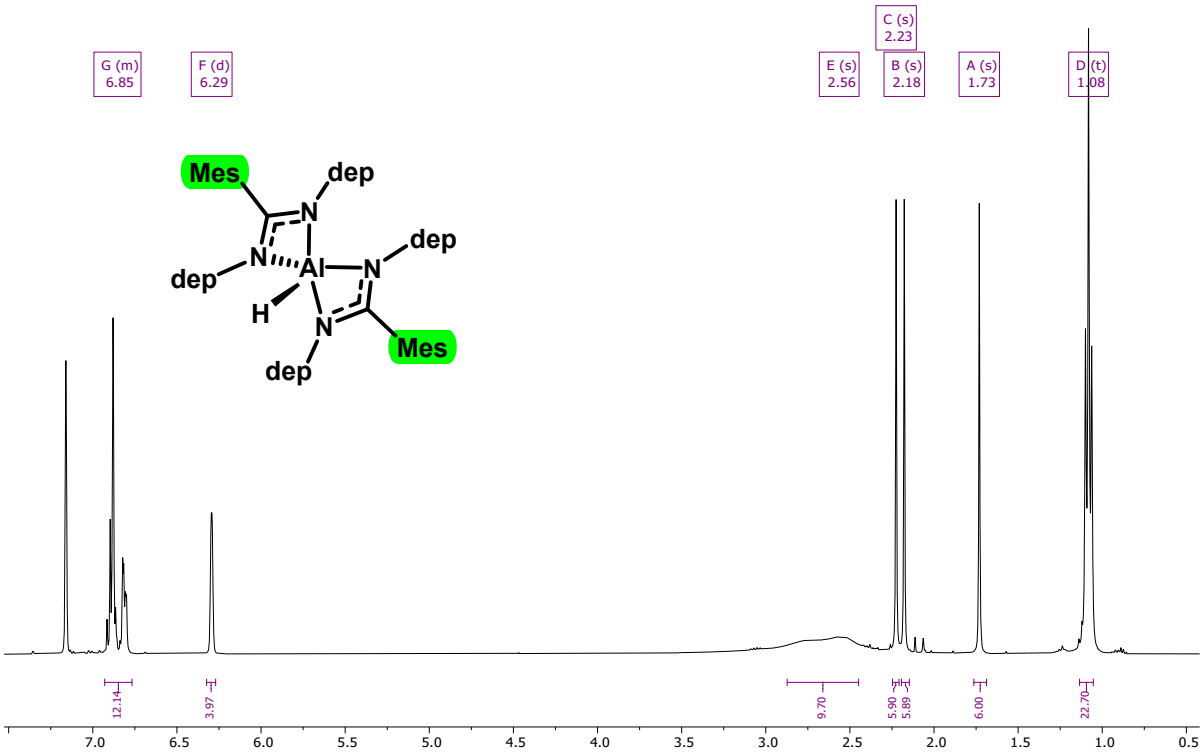


Figure S 124: ^{1}H NMR (400 MHz, 298 K) spectrum of **20-Al''** in benzene-d_6

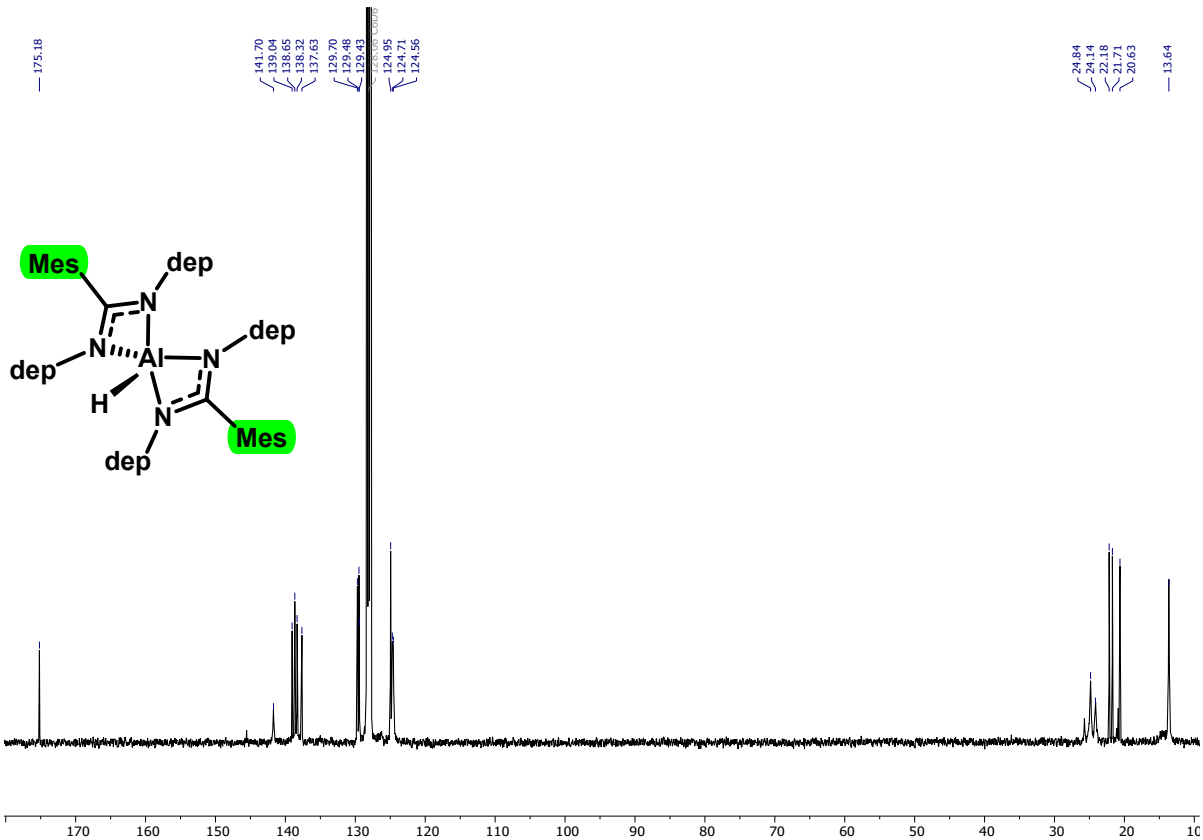


Figure S 125: : ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **20-Al''** in benzene-d_6 with minor **20** impurity

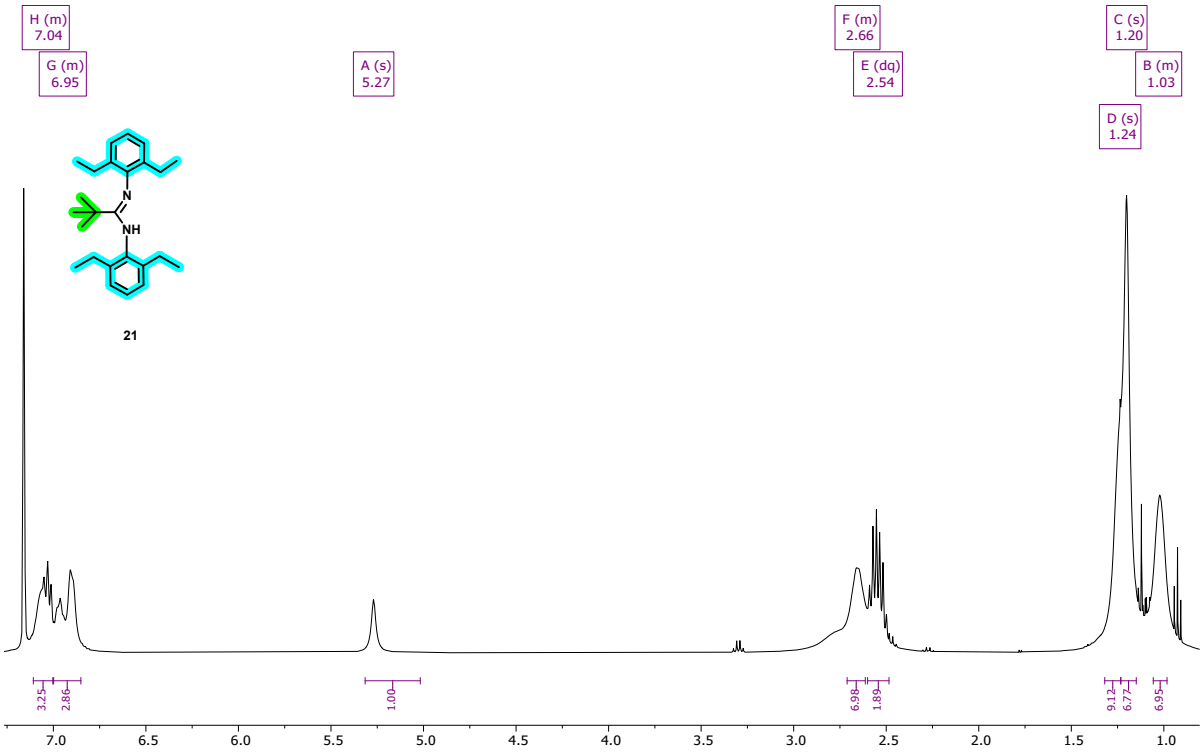


Figure S 126: ^{1}H NMR spectrum (400 MHz, 298 K) of **21** in benzene-d_6

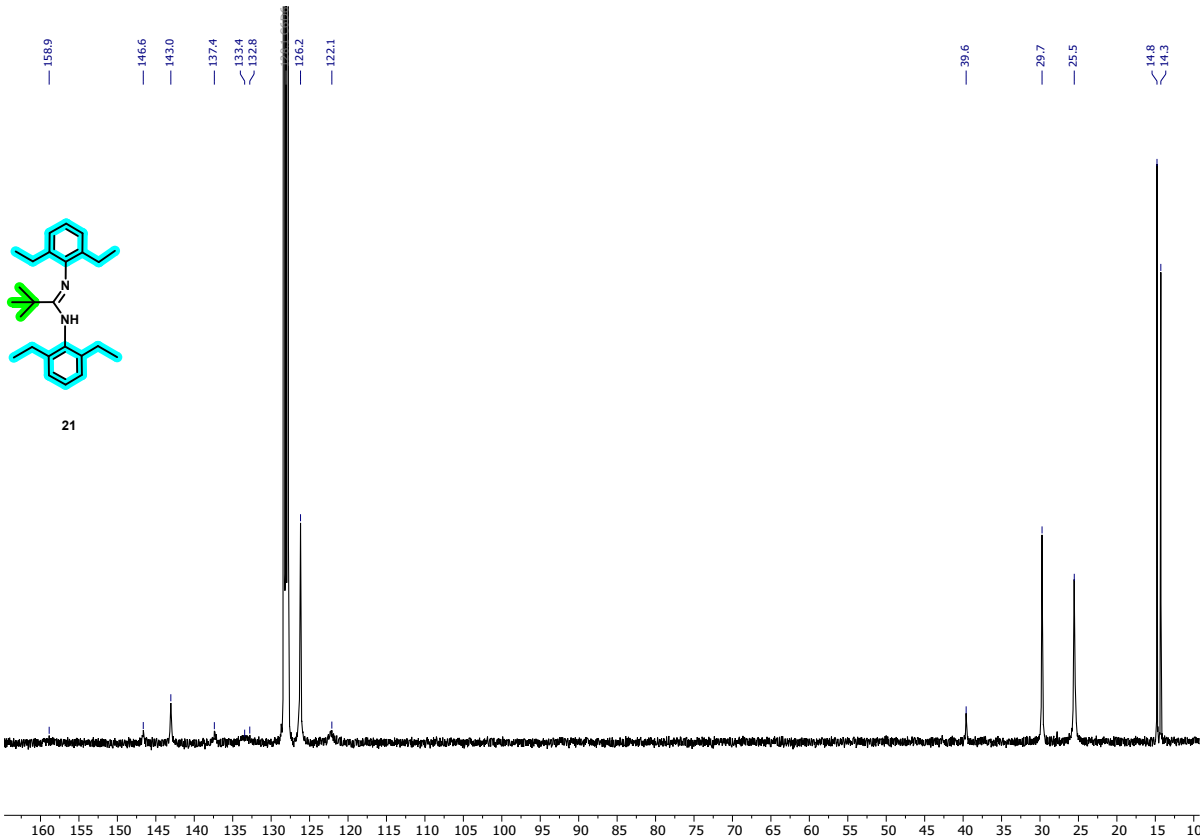


Figure S 127: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **21** in benzene-d_6

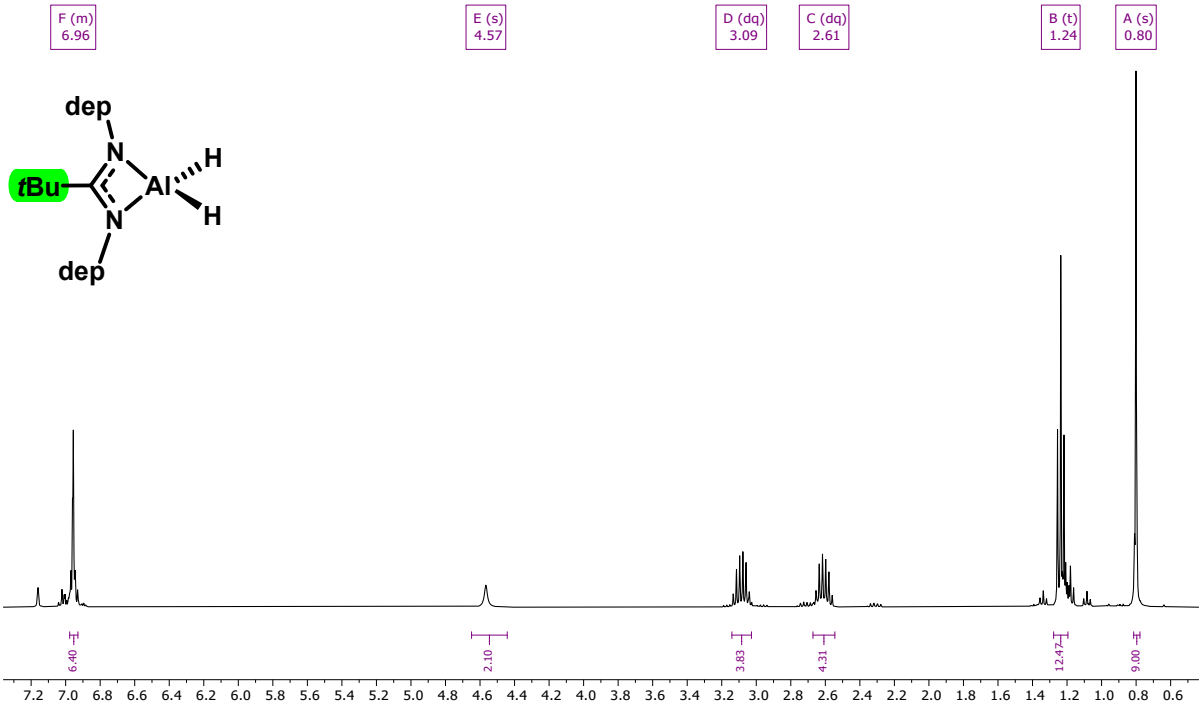


Figure S 128: ^{1}H NMR spectrum (400 MHz, 298 K) of **21-Al** in benzene-d_6 with slight **21-Al''** impurity

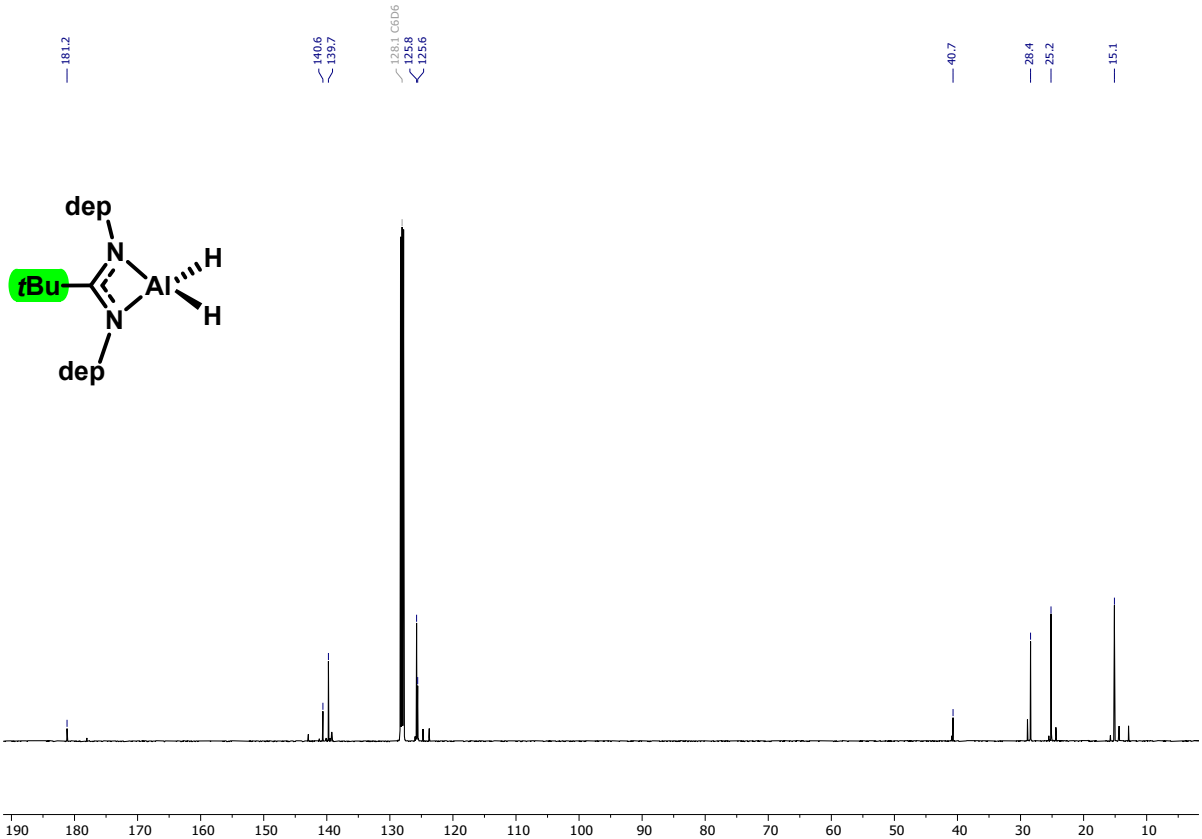


Figure S 129: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **21-Al** in benzene-d_6 with slight **21-Al''** impurity

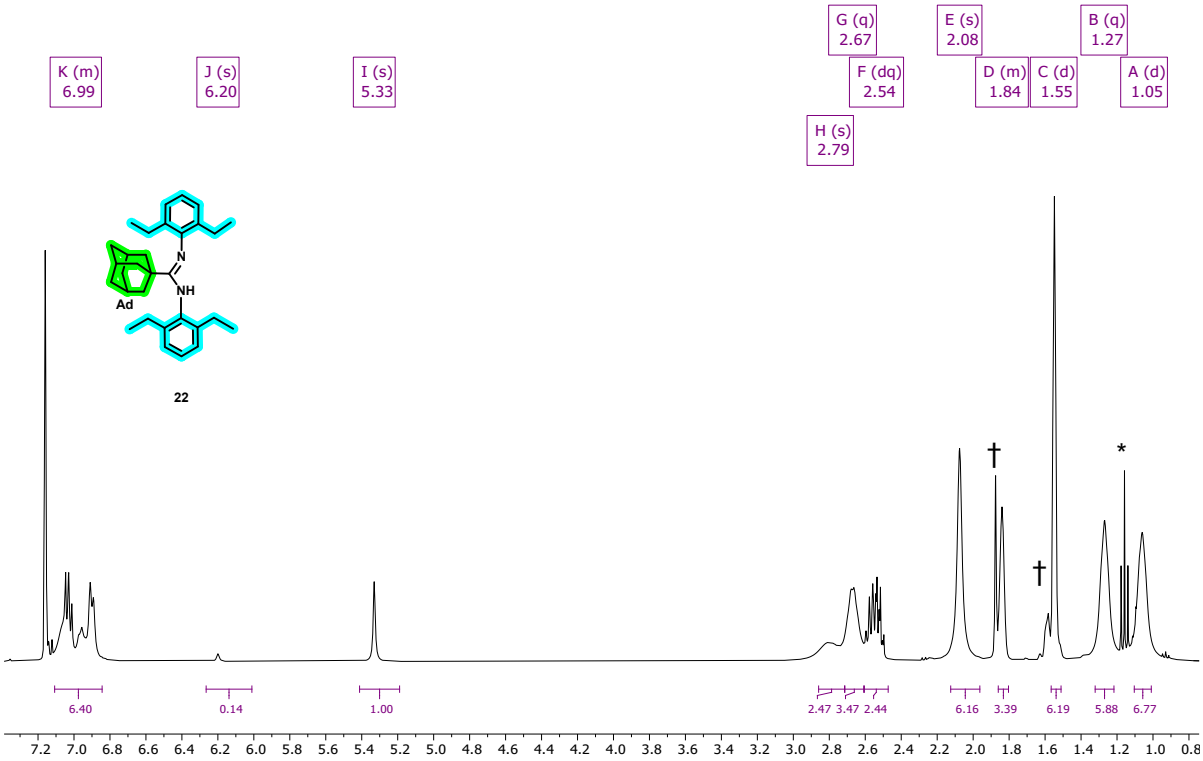


Figure S 130: ^{1}H NMR spectrum (400 MHz, 298 K) of **21** in benzene-d_6 (with ethanol* and adamantane-1-carboxylic acid† impurity labelled)

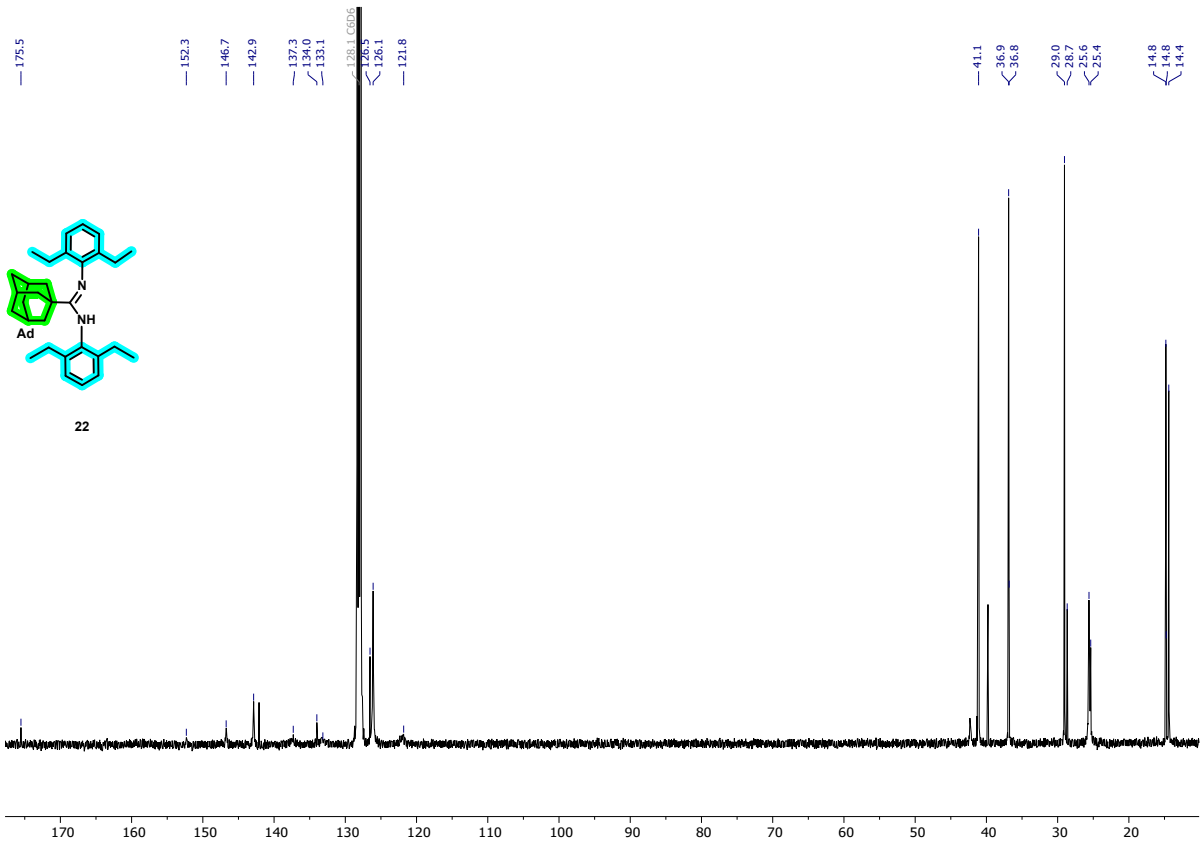


Figure S 131: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of ***22*** in benzene-d_6

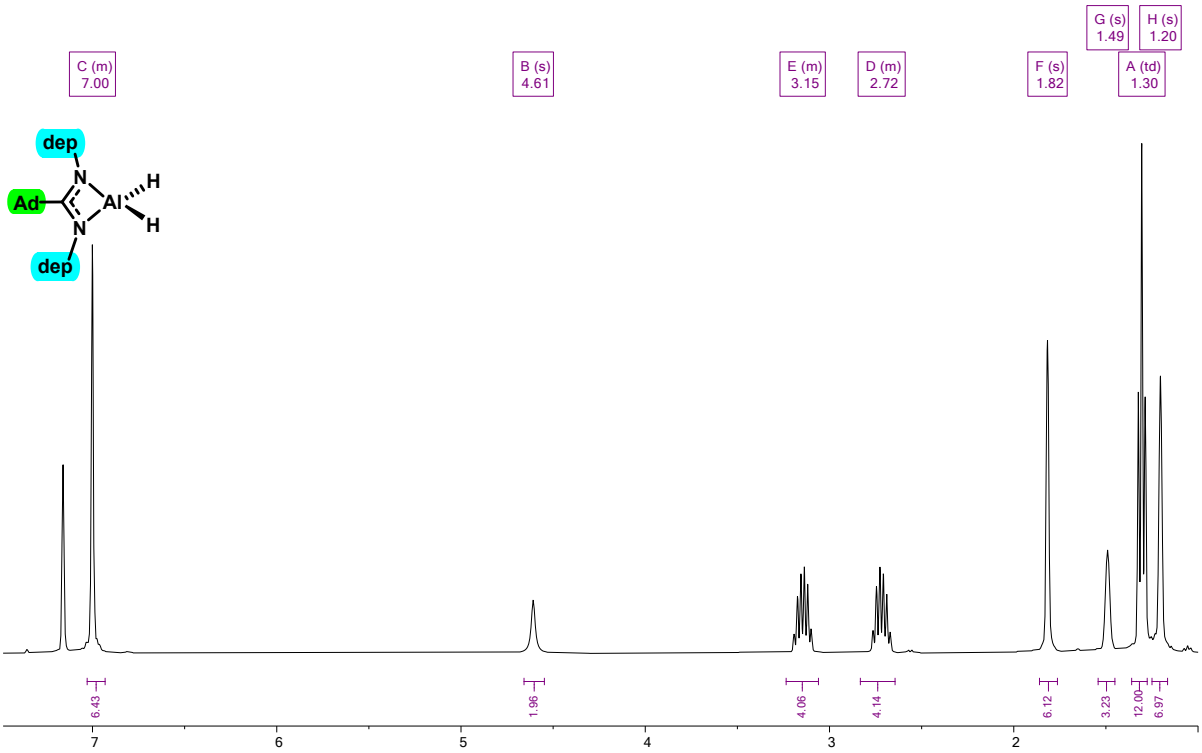


Figure S 132: ^{1}H NMR spectrum (400 MHz, 298 K) of **22-Al** in benzene-d_6

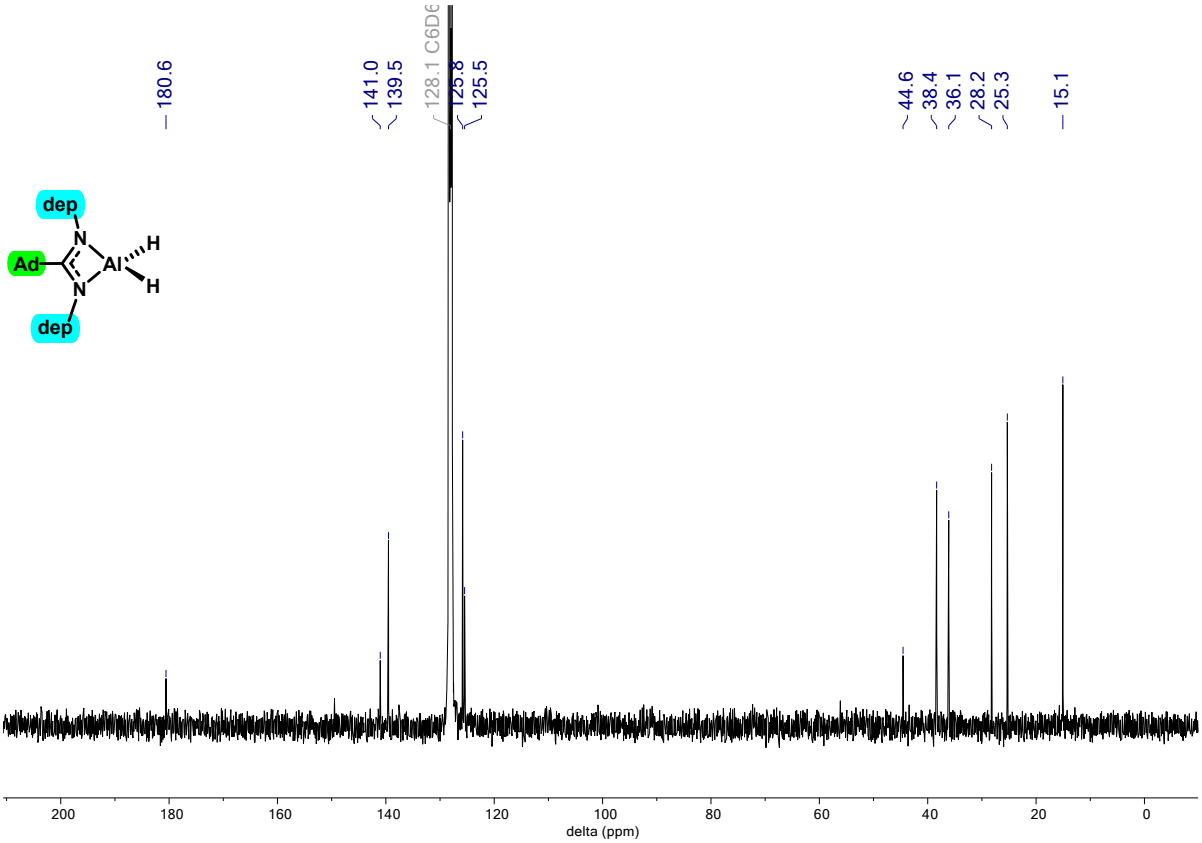


Figure S 133: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K) of **22-Al** in benzene-d_6

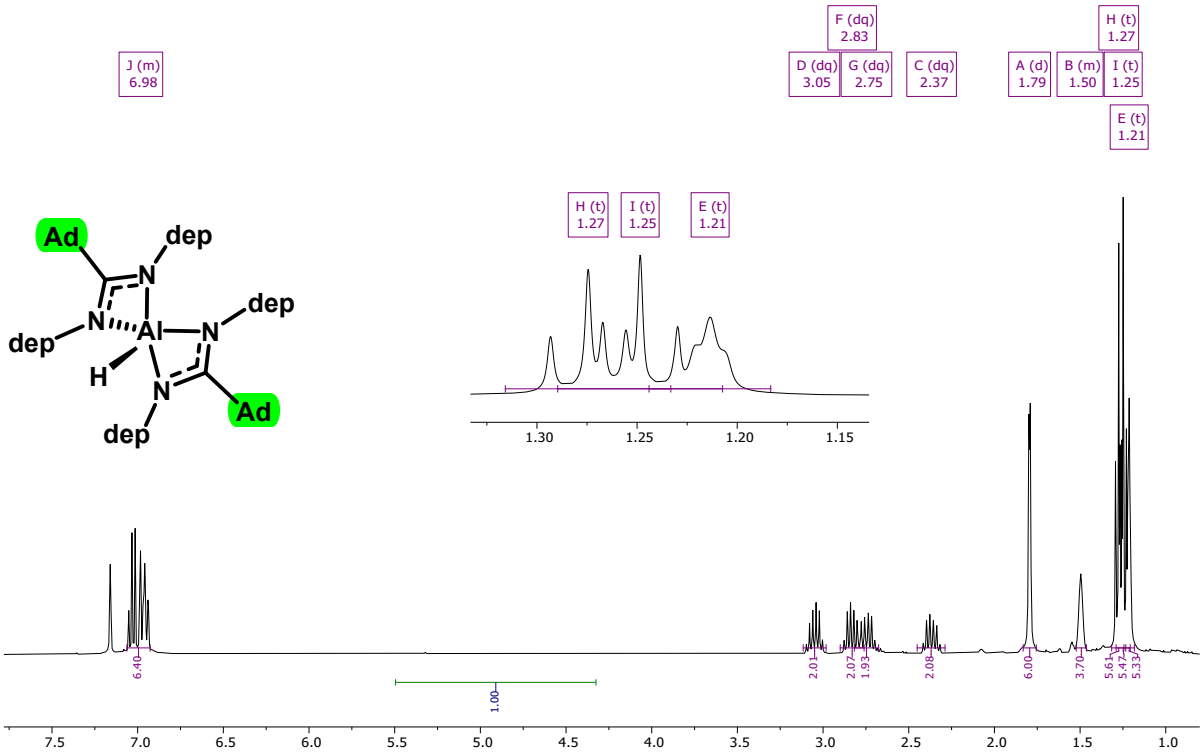


Figure S 134: ^{1}H NMR spectrum (400 MHz, 298 K) of **22-Al''** in benzene-d_6 with callout showing region 1.14-1.35 ppm

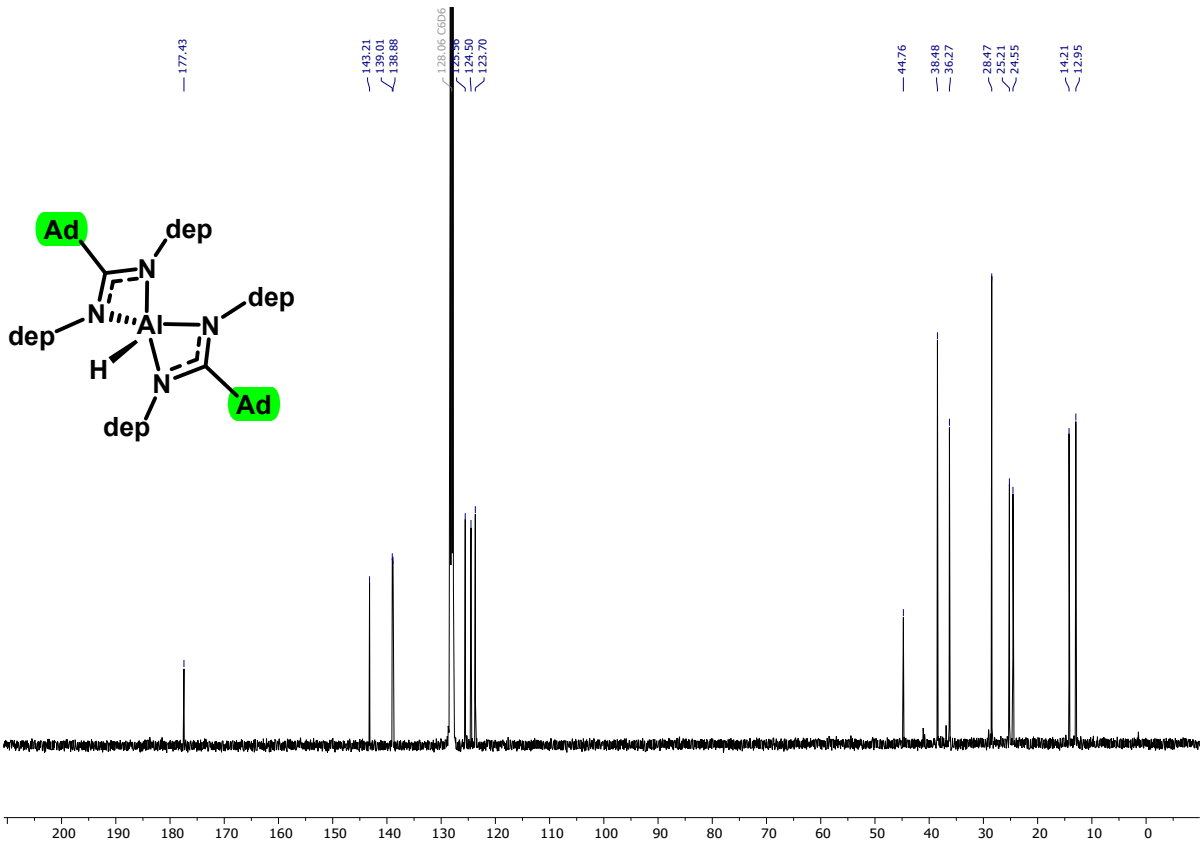


Figure S 135: ^{13}C{^{1}H} NMR (101 MHz, 298 K) spectrum of **22-Al''** in benzene-d_6

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