Supplementary Information (SI) for Dalton Transactions.

Supporting Information

Divergent Reduction Chemistry of NHC-Aluminium(III) Hydrides

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Contents

1 General Methods and Instruments

All air- and moisture-sensitive synthetic work was carried out under an inert gas atmosphere (N_2 or Ar) using a glovebox and/or vacuum line using standard Schlenk techniques. 4 Å molecular sieves were dried in an oven overnight at 150°C prior to use. All glassware was heated under vacuum using a heat gun prior to use. For air- and moisture-sensitive reactions, toluene and hexane were provided by an Innovative Technology Solvent Purification System. Diethyl ether was dried by distillation over sodium benzophenone ketyl prior to use. All solvents were stored under nitrogen over molecular sieves activated at 150 °C in vacuo. C_6D_6 was purchased from Fluorochem, taken into a glovebox and stored over activated 4 Å molecular sieves under argon. All reagents were purchased from Sigma-Aldrich, Fluorochem or Alfa Aesar and used as purchased. Air- and moisture-sensitive NMR experiments were conducted in a J-Young (JY) NMR tube, which were loaded and sealed in a glovebox. Unless specified, all other air- and moisture-sensitive samples were prepared using regular NMR tubes and caps secured with parafilm in a glovebox. Air stable NMR samples were prepared open to air and moisture using regular NMR tubes and caps.

NMR spectra were recorded on a Bruker AV3-400 spectrometer operating at 400.4 MHz (^{1}H), 100.7 MHz (^{13}C), 104.3 MHz (^{27}Al), 162 MHz (^{31}P), 376.5 MHz (^{19}F), and were measured at 300K. Some ^{27}Al NMR spectra were recorded using a background suppressed experiment (^{27}Al_zgbs). All chemical shifts are expressed in parts per million (δ, ppm). ^{1}H NMR chemical shifts are referenced to residual proton resonances of the corresponding deuterated solvent. ^{13}C NMR chemical shifts are reported relative to TMS using the carbon resonances of the deuterated solvent. All ^{13}C NMR spectra were obtained with 1H broadband decoupling. Estimated molecular weights (MW) were calculated from the diffusion coefficients established from the ^{1}H DOSY NMR spectrum using *Stalke's* external calibration curve method (ECC)[1] and using the residual proton signal of solvent (C_6D_6) or tetramethylsilane (TMS) as internal standard.

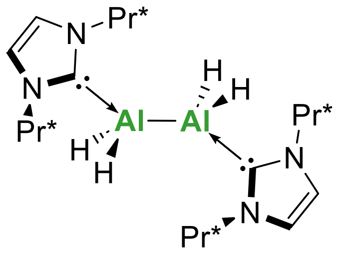
Infrared spectra were obtained on a PerkinElmer Spectrum 100 FT-IR spectrometer using nujol mull. The positions of the absorption bands are given in wavenumbers [cm^{-1}]. UV/vis spectra were recorded on a Shimadzu UV-1800 UV-vis Spectrophotometer in the range 200-1100 nm.

Free NHCs, Compound A (Mg(I)) and B (Al(I)) and NHCAlH_3 complexes were synthesised according to literature procedures.[2-8]

In all cases within this supporting information "L" refers to a β-diketiminate ligand.

2 Synthesis and Characterisation Data

2.1 Synthesis of 2-IPr*



Toluene (3 mL) was added to a mixture of **1-IPr*** (100 mg, 0.106 mmol, 2 equiv.) and Mg(I) dimer (compound A) (38 mg, 0.053 mmol, 1 equiv.). The yellow mixture was stirred at 40°C for 1 h. After cooling to room temperature, volatiles were removed from the brown mixture under reduced pressure. The crude solid was washed with hexane (2 x 2 mL) and dried under reduced pressure to produce a yellow solid. Yield: 65 mg, 65 %.

^{1}H NMR (400 MHz, C_6D_6, ppm): δ=7.66 (d, 16H; J=7.5 Hz, H_{Ar}), 7.20-6.86 (m, 72H; H_{Ar}), 5.69 (s, 8H; $CHPh_2$), 5.32 (s, 4H; NCHCHN), 4.37 (bs, Al-H), 1.69 (s, 12H; CH_3).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, ppm): δ=176.9 (NCN), 143.9 (C_{Ar}), 143.7 (C_{Ar}), 142.0 (C_{Ar}), 140.5 (C_{Ar}), 134.4 (C_{Ar}), 130.9 (C_{Ar}), 130.6 (C_{Ar}), 129.2 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 126.7 (C_{Ar}), 126.5 (C_{Ar}), 124.1 (NCHCHN), 52.0 ($CHPh_2$), 21.3 (CH_3).

^{27}Al NMR (104.3 MHz, C_6D_6, ppm): δ=Not observed.

IR (Nujol, cm^{-1}): $\tilde{\nu}$=1733 (Al-H).

m.p. 235°C.

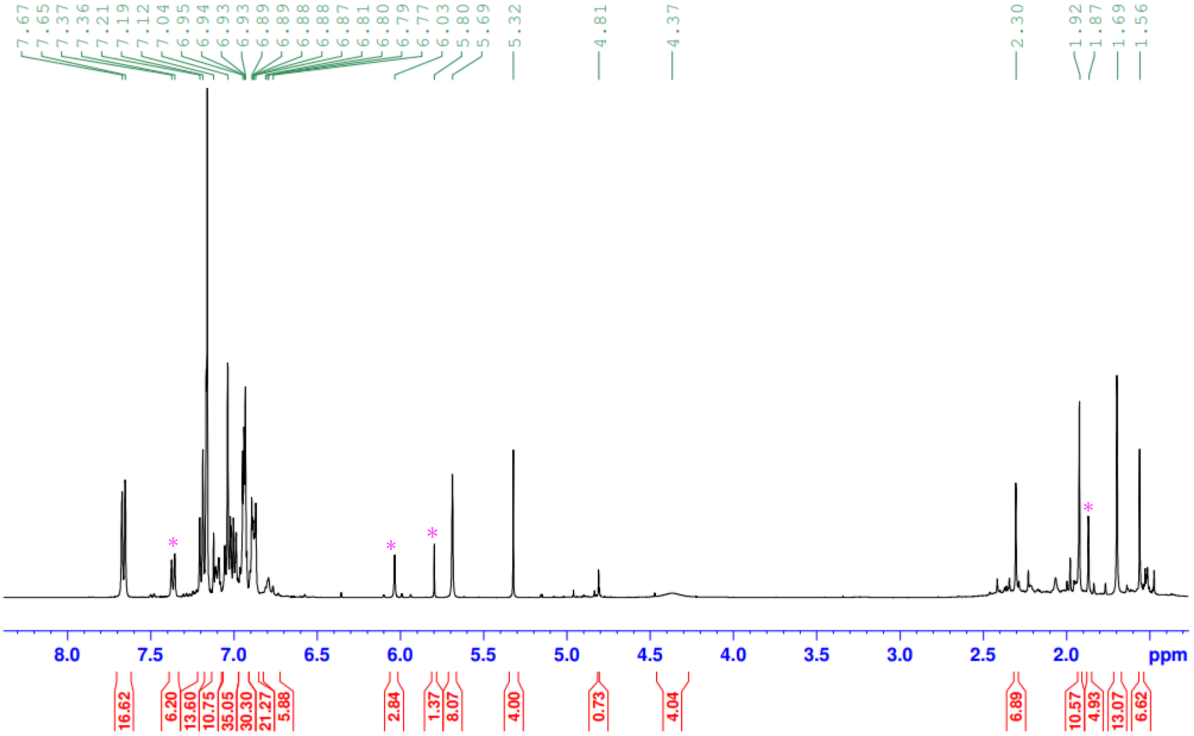


Figure S1. ^{1}H NMR spectrum of **2-IPr*** in C_6D_6. *[{(^{Mes}L)Mg(μ-H)}$_2$], *Free NHC

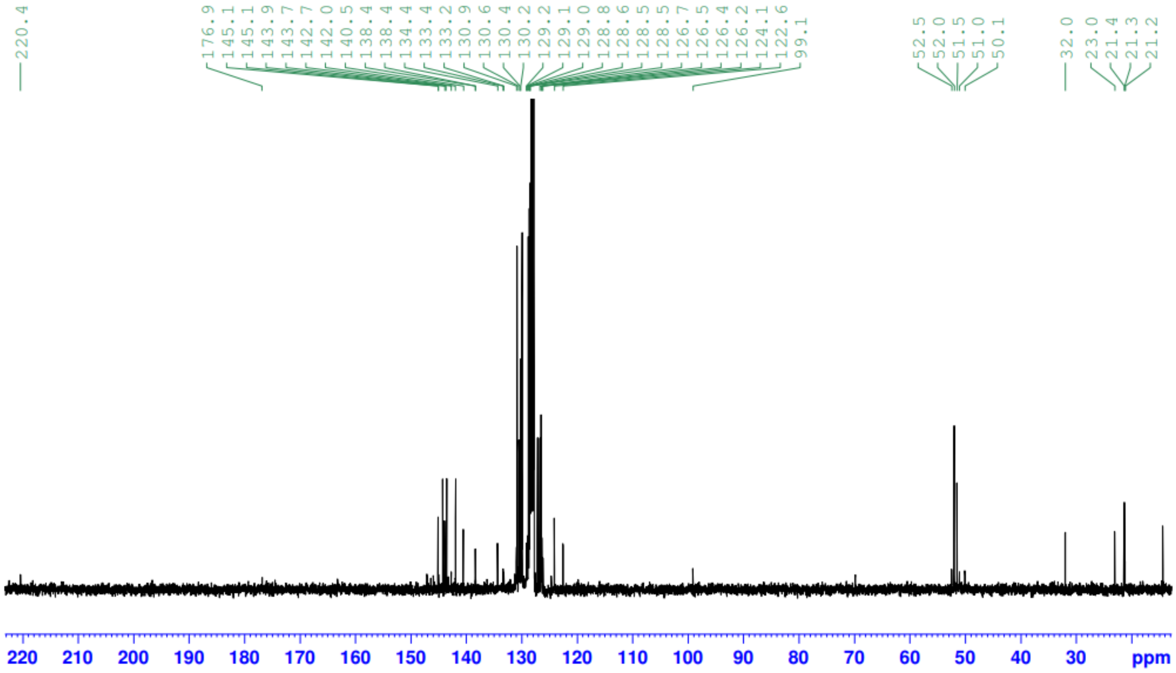


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2-IPr*** in C_6D_6.

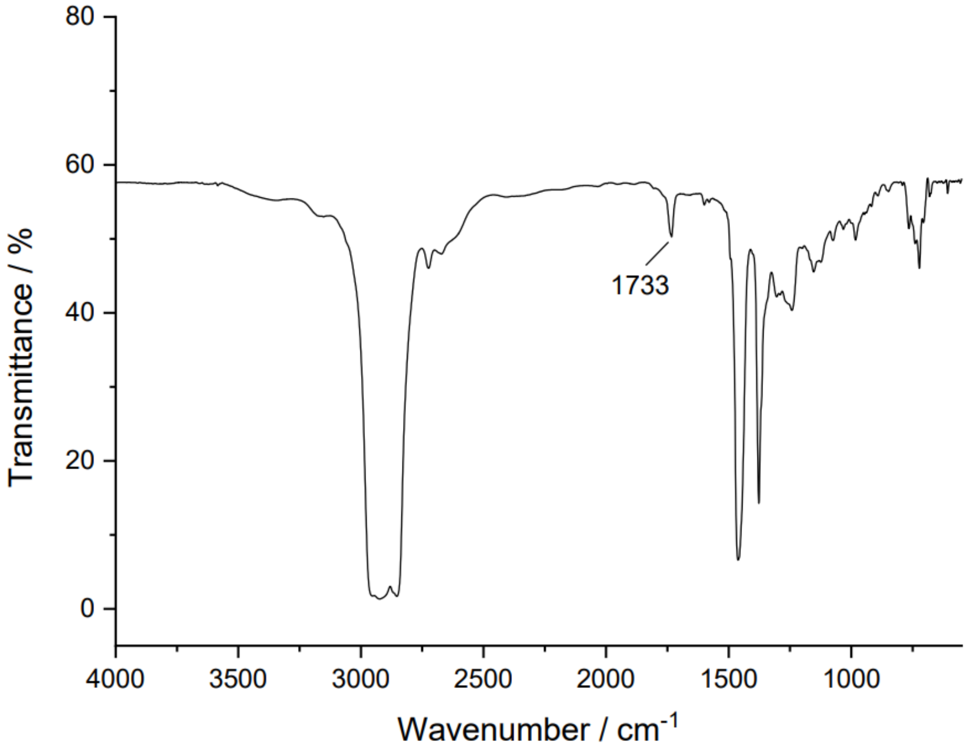


Figure S3. FT-IR spectrum of **2-IPr*** in nujol mull.

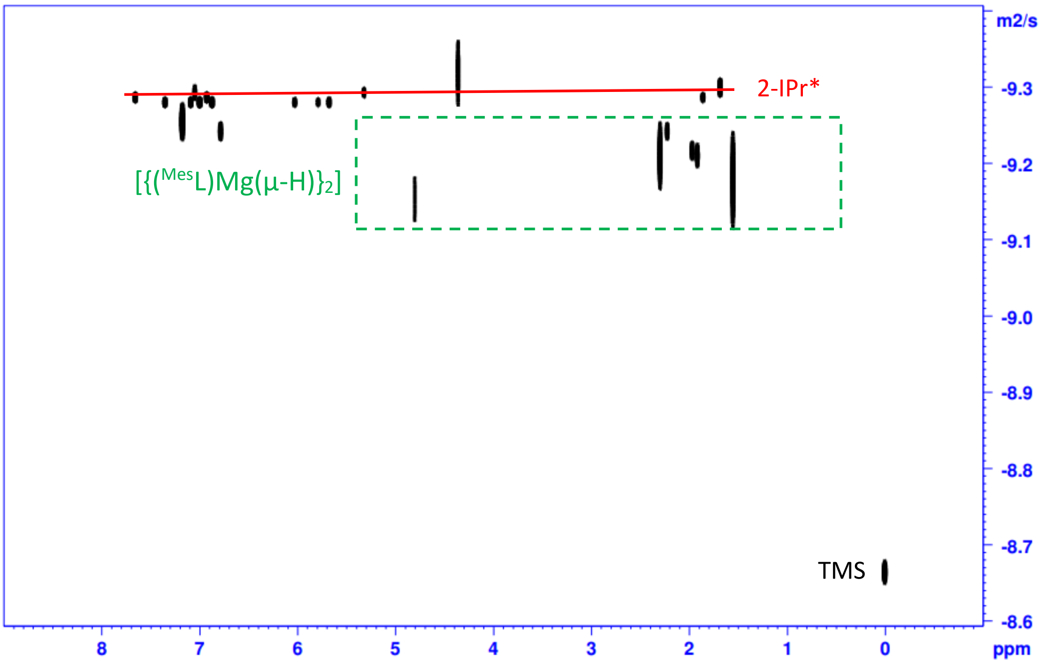


Figure S4. ^{1}H DOSY NMR spectrum of **2-IPr*** in C_6D_6 with TMS as standard in C_6D_6.

The determined diffusion coefficients for compound **2-IPr*** are summarised in Table S1 followed by the determined molecular weight in Table S2.

Table S1. Selected diffusion coefficients [m^2s^{-1}] determined by ^{1}H DOSY NMR.

Compound	D1	D2	D3	D4	D5	D6	D(TMS)
2-IPr*	4.92e-10	5.00e-10	5.09e-10	5.08e-10	5.04e-10	4.70e-10	2.13e-9

Table S2. Estimated molecular weight data determined *via* ECC-MW software.[1]

Compound	$\log D_{average}$	MW_{calc} [g mol^{-1}]	MW_{det} [g mol^{-1}]	MW_{dif} [%]
2-IPr*	-9.30	1884	1689	12

*2.1.1 Alternative Synthetic Routes to 2-IPr**

Via Al(I)

A 0.112 M stock solution of compound B was pre-made in C_6D_6. Stock of B (47.3 µL, 1 equiv.) in C_6D_6 (453 µL) was added to **1-IPr*** (10 mg, 0.0106 mmol, 2 equiv.) and the solution was transferred to a JY NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy and after 1 h, complete consumption of B was observed along with formation of **2-IPr***. Yield$_{(NMR)}$: 90 %.

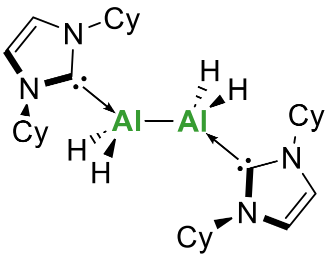
Via Cp_2Co

C_6D_6 (0.5 mL) was added to a mixture of **1-IPr*** (50 mg, 0.053 mmol, 1 equiv.) and Cp_2Co (10 mg, 0.053 mmol, 1 equiv.). The brown mixture was stirred at 70°C for 2 h. Reaction mixture was filtered, and volatiles were removed under reduced pressure to produce a brown solid. Yield: 50 mg, >99 %.

2.2 Synthesis of 2-IDipp

Synthesised according to literature procedure. [9]

2.3 Synthesis of 2-ICy



Toluene (3 mL) was added to a mixture of **1-ICy** (80 mg, 0.305 mmol, 2 equiv.) and compound A (109 mg, 0.152 mmol, 1 equiv.). The yellow mixture was stirred at 40°C for 1 h. After cooling to room temperature, volatiles were removed from the brown mixture under reduced pressure. The crude solid was washed with hexane (2 x 2 mL) and dried under reduced pressure to produce a yellow solid. Yield: 65 mg, 82 %.

^{1}H NMR (400 MHz, C_6D_6, ppm): δ=6.39 (s, 4H; NC*H*C*H*N), 4.95 (tt, $^1J_{HH}$=11.7 Hz, $^2J_{HH}$=3.8 Hz, 4H; CH), 4.55 (bs, Al-H), 1.91-0.81 (m, 40H; CH_2).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, ppm): δ=179.5 (N*C*N), 117.4 (*C*H), 59.0 (*C*H), 34.1 ($\mathit{C}H_2$), 25.4 ($\mathit{C}H_2$), 25.3 ($\mathit{C}H_2$).

^{27}Al NMR (104.3 MHz, C_6D_6, ppm): δ=Not observed.

IR (Nujol, cm^{-1}): $\tilde{v}$=1734 (Al-H).

m.p. 200°C (decomp.).

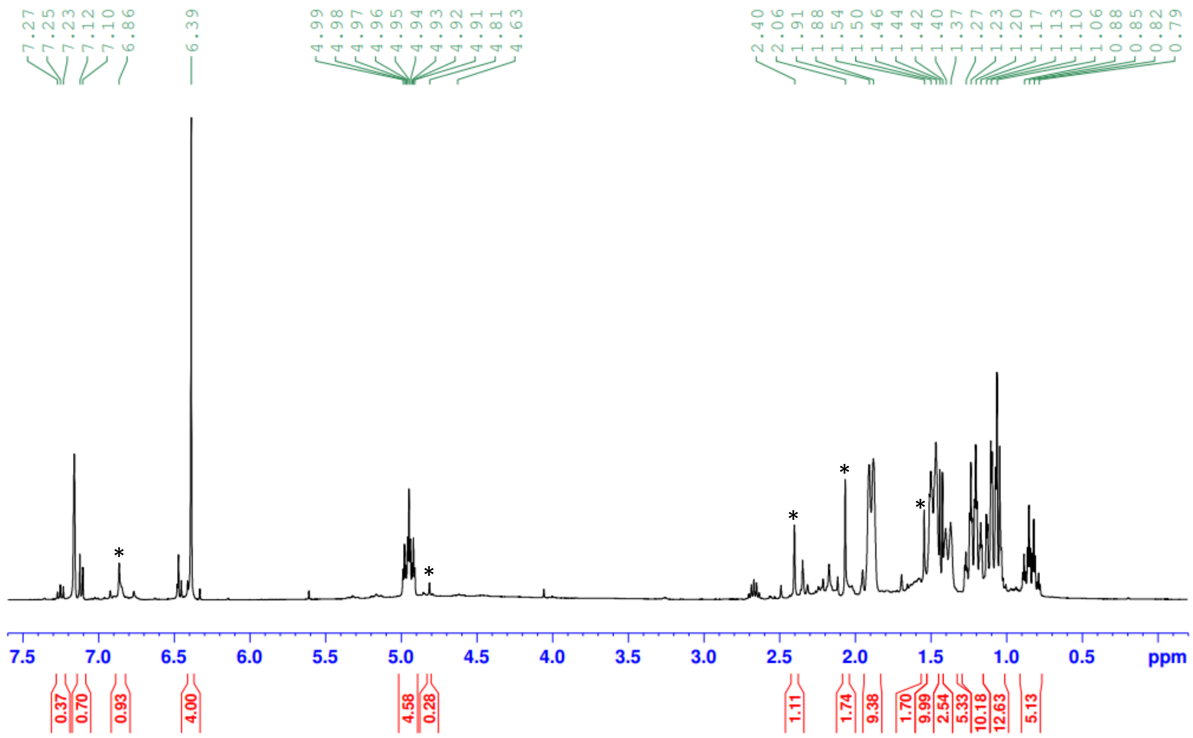


Figure S5. ^{1}H NMR spectrum of **2-ICy** in C_6D_6. *[{(^{Mes}L)Mg(μ-H)}$_2$].

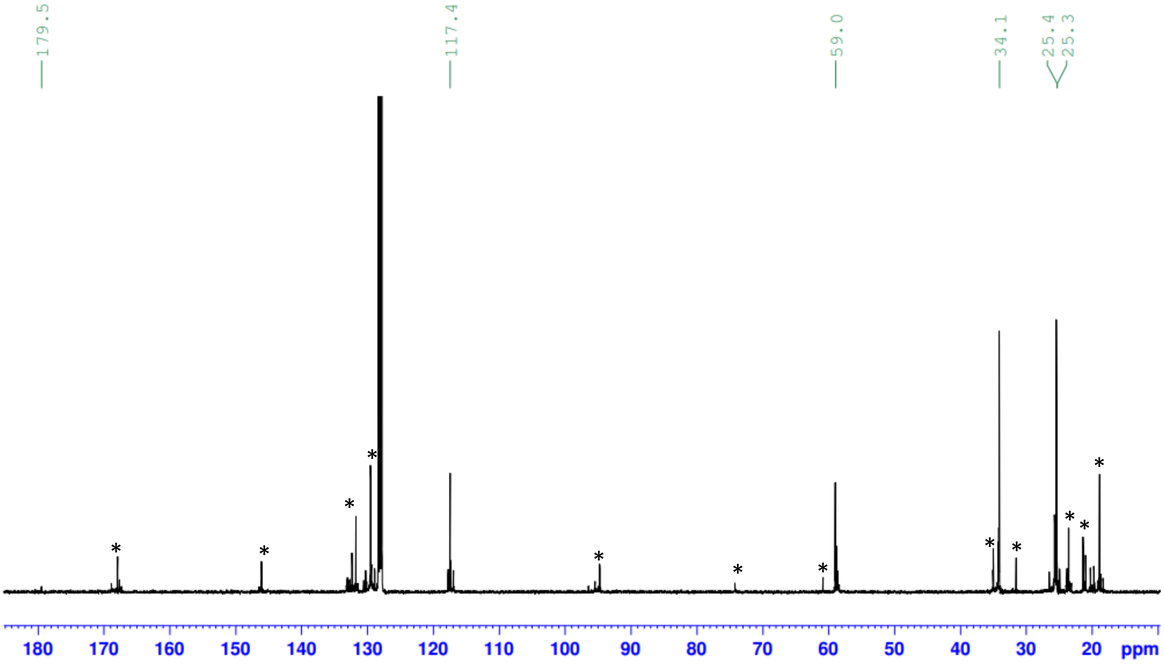


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **2-ICy** in C_6D_6. *$[\{(^{Mes}L)Mg(\mu\text{-}H)\}_2]$.

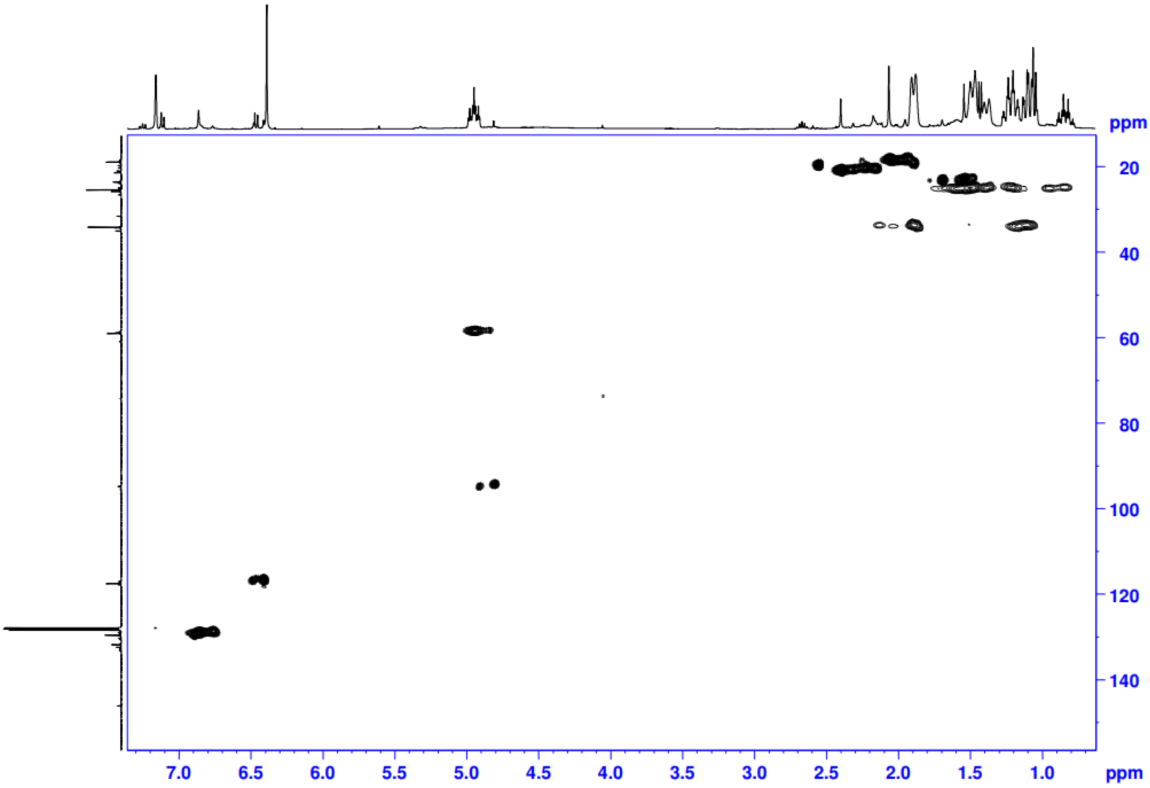


Figure S7. $[^1H, ^{13}C]$ HSQC NMR spectrum of **2-ICy** in C_6D_6.

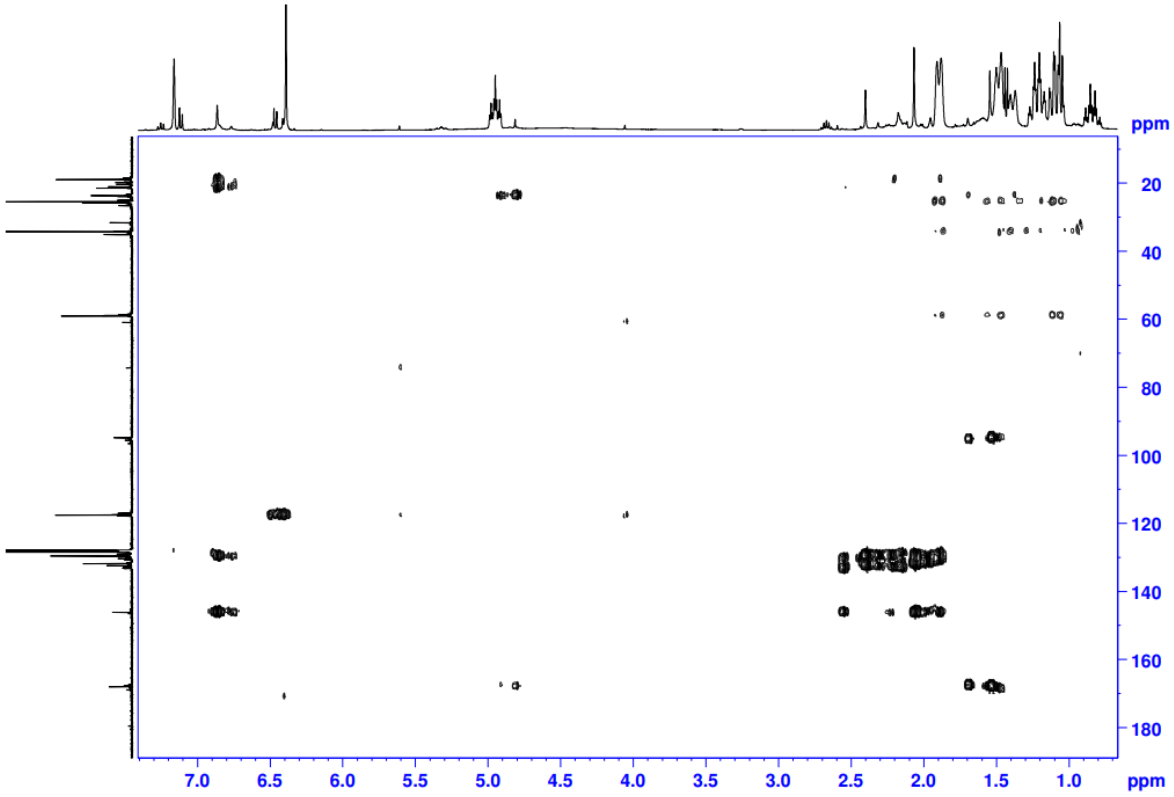


Figure S8. [^{1}H, ^{13}C] HMBC NMR spectrum of **2-ICy** in C_6D_6.

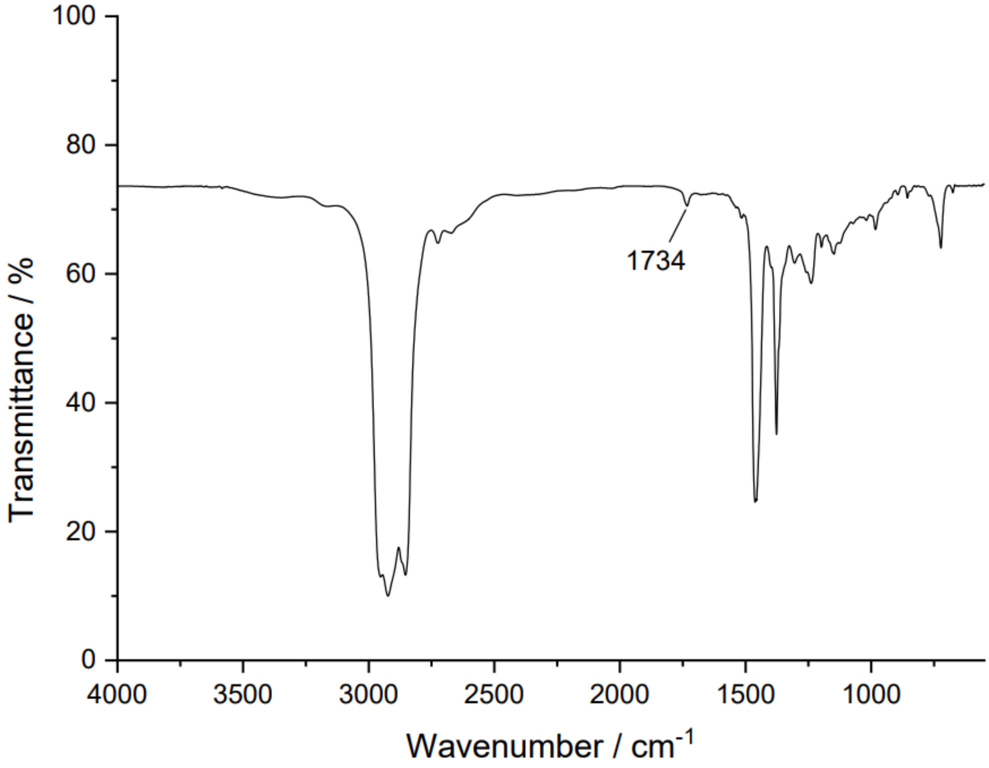


Figure S9. FT-IR spectrum of **2-ICy** in nujol mull.

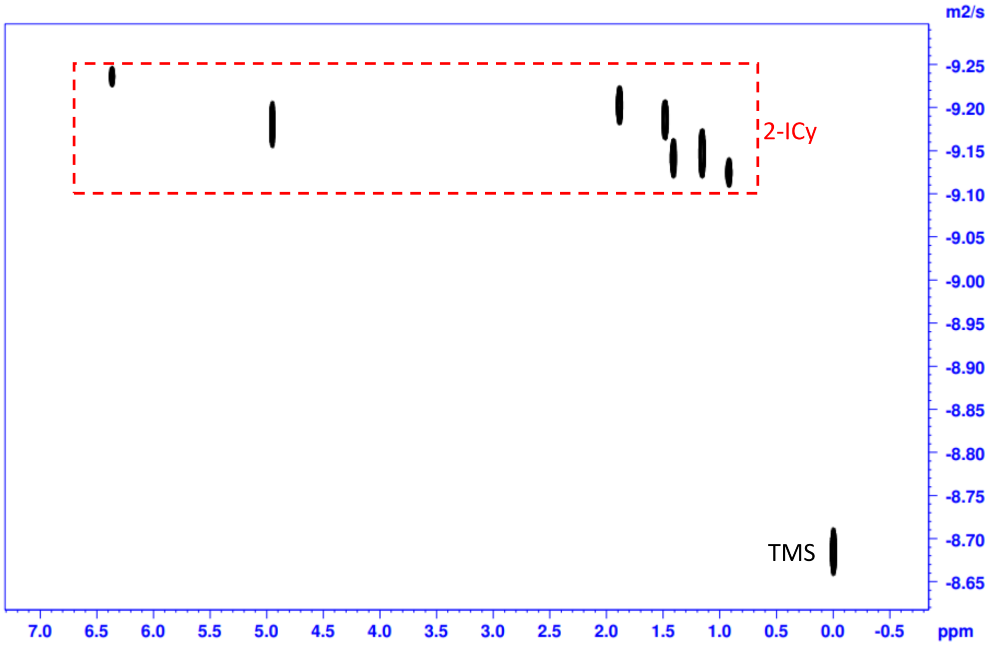


Figure S10. ^{1}H DOSY NMR spectrum of **2-ICy** with TMS as standard in C_6D_6.

The determined diffusion coefficients are summarised in Table S3 followed by the determined molecular weight in Table S4.

Table S3. Selected diffusion coefficients [m^2s^{-1}] determined by ^{1}H DOSY NMR.

Compound	D1	D2	D3	D4	D5	D(TMS)
2-ICy	7.11e-10	6.42e-10	6.61e-10	7.37e-10	7.19e-10	2.04e-9

Table S4. Estimated molecular weight data determined *via* ECC-MW software.[1]

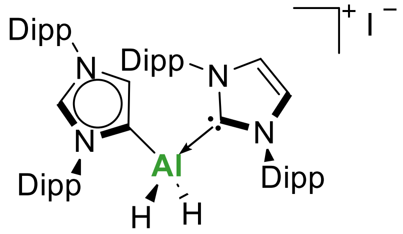
Compound	$\log D_{average}$	MW_{calc} [g mol^{-1}]	MW_{det} [g mol^{-1}]	MW_{dif} [%]
2-ICy	-9.16	522	501	4

2.3.1 Alternative Synthetic Route to 2-ICy

Via Cp_2Co

C_6D_6 (0.5 mL) was added to a mixture of **1-ICy** (20 mg, 0.076 mmol, 1 equiv.) and Cp_2Co (15 mg, 0.076 mmol, 1 equiv.). The brown mixture was stirred at 70°C for 2 h. Reaction mixture was filtered, and volatiles were removed under reduced pressure to produce a brown solid. Yield: 14 mg, 45 %.

2.4 Synthesis of Compound 4



Compound B (11 mg, 0.024 mmol, 1 equiv.) in C_6D_6 (0.5 mL) was added to **1-IDipp** (20 mg, 0.048 mmol, 2 equiv.) and the solution was transferred to a JY NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy and after 3 h, complete consumption of B was observed. Solvent was removed under reduced pressure to produce an off-white solid. A few SC-XRD quality crystals of compound 4 were produced from a concentrated toluene solution at -25°C.

Compound 4 has been reported previously *via* a different route however this compound could not be characterised by NMR.[10]

^{1}H NMR (400 MHz, C_6D_6, ppm): δ=7.29-7.21 (m, 2H; H_{Ar}), 7.20-7.08 (m, 10H; H_{Ar}), 6.49 (s, 2H; NC*H*C*H*N), 6.26 (s, 1H; NC*H*C), 4.78 (bs, Al-H), 3.35 (sept, *J*=6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 2.73 (m, 4H; C*H*(CH$_3$)$_2$), 2.56 (sept, *J*=6.9 Hz, 2H; C*H*(CH$_3$)$_2$), 1.40 (d, *J*=6.6 Hz, 12H; CH(C*H*$_3$)$_2$), 1.31 (d, *J*=6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.24 (d, *J*=6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.17 (d, *J*=6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.07 (d, *J*=6.6 Hz, 12H; CH(C*H*$_3$)$_2$), 0.97 (d, *J*=6.9 Hz, 6H; CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, ppm): δ=183.5 (NCN), 145.7 (C_{Ar}), 145.6(C_{Ar}), 145.4 (C_{Ar}), 144.9 (C_{Ar}), 144.0 (C_{Ar}), 143.4 (C_{Ar}), 136.1 (C_{Ar}), 130.4 (C_{Ar}), 130.3 (C_{Ar}), 126.0 (C_{Ar}), 124.1 (C_{Ar}), 123.9 (N*C*HC), 123.8 (N*C*H*C*HN), 29.0 (CH(CH$_3$)$_2$), 27.8 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 25.0 (CH(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 23.8 (CH(CH$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$).

^{27}Al NMR (104.3 MHz, C_6D_6, ppm): δ=Not observed.

IR (Nujol, cm^{-1}): $\tilde{v}$=1733 (Al-H).

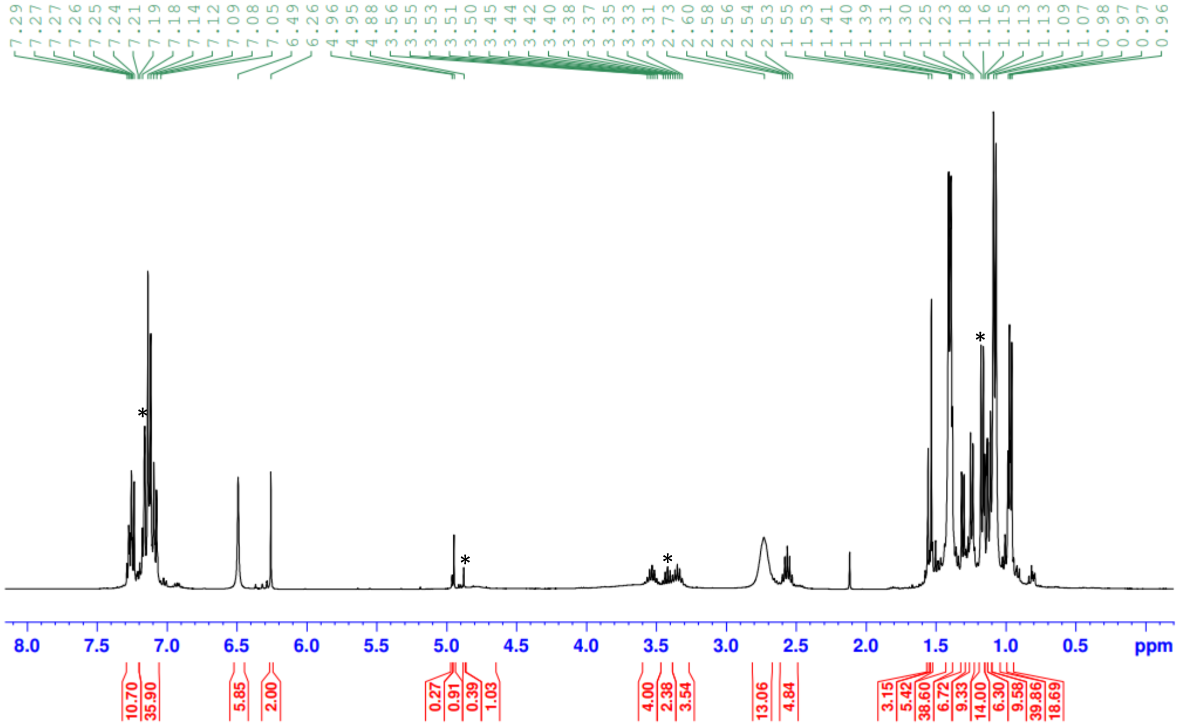


Figure S11. ^{1}H NMR spectrum of **4** in C_6D_6. *[(^{Dipp}L)AlH_2].

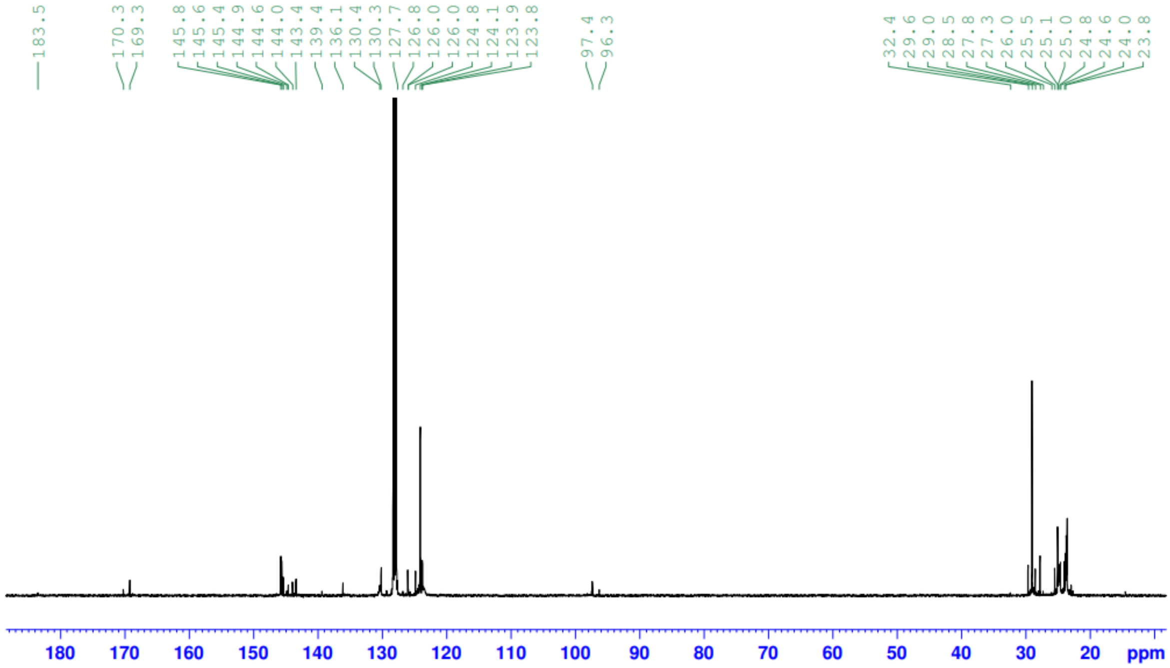


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

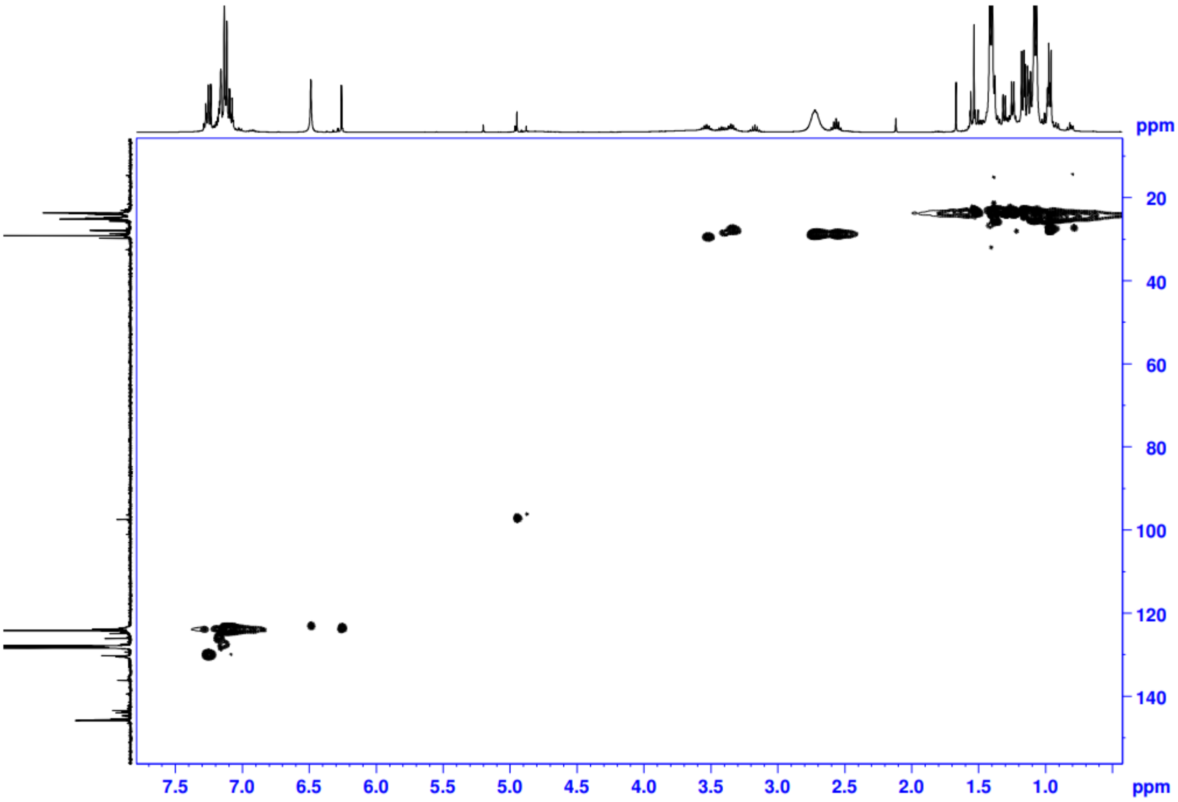


Figure S13. [^{1}H, ^{13}C] HSQC NMR spectrum of **4** in C_6D_6.

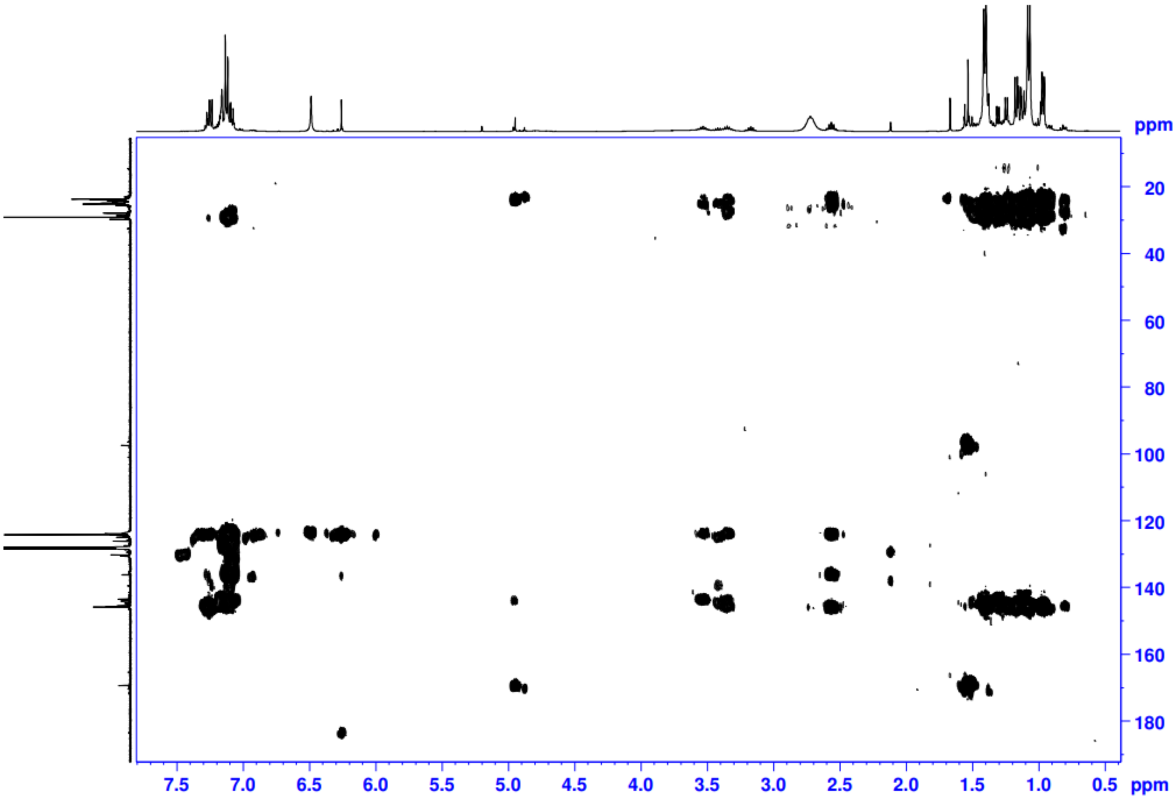


Figure S14. [^{1}H, ^{13}C] HMBC NMR spectrum of **4** in C_6D_6.

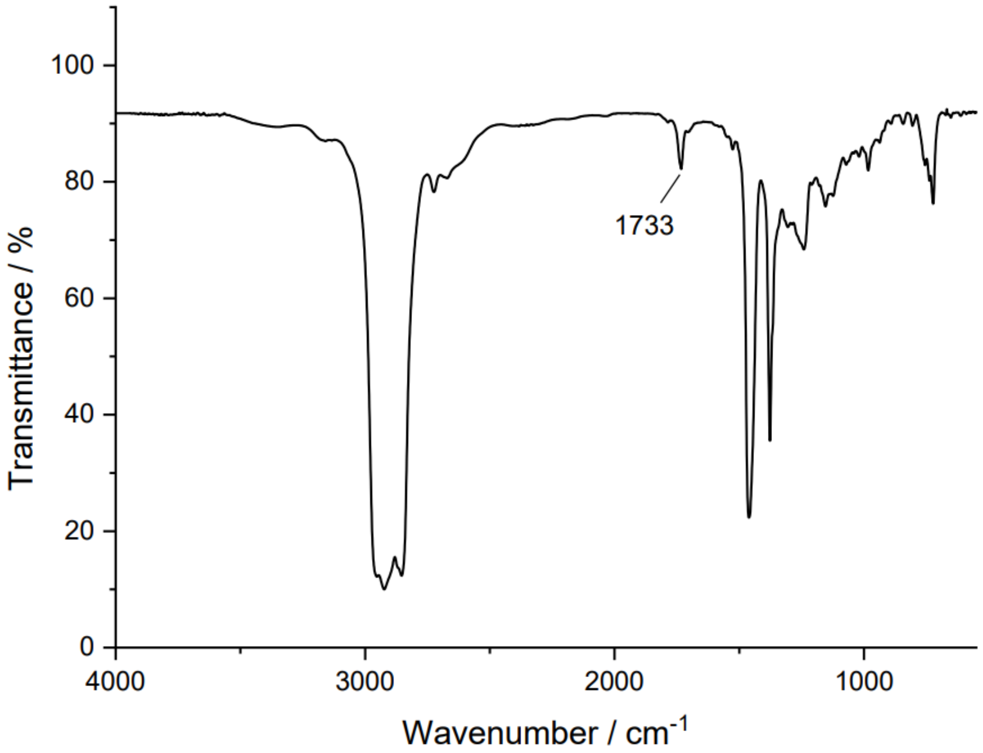
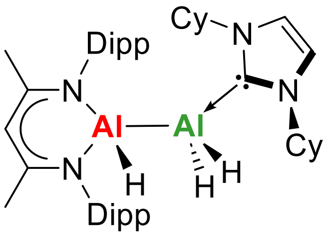


Figure S15. FT-IR spectrum of **4** in nujol mull.

2.5 Synthesis of Compound 5



Compound B (10 mg, 0.022 mmol, 1 equiv.) in C_6D_6 (0.5 mL) was added to **1-ICy** (12 mg, 0.045 mmol, 2 equiv.) and the solution was transferred to a JY NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy at room temperature and after 1 h, complete consumption of B was observed. Yield: 13 mg, 82 %. SC-XRD quality crystals were produced from slow evaporation of a benzene solution at 25°C.

^{1}H NMR (400 MHz, C_6D_6, ppm): δ=7.21-7.19 (m, 2H; H_{Ar}), 7.14-7.09 (m, 4H; H_{Ar}), 6.31 (s, 2H; NC*H*C*H*N), 5.07 (s, 1H; CH), 4.48 (tt, $^1J_{HH}$=6.0 Hz, $^2J_{HH}$=3.8 Hz, 2H; CH), 3.76 (sept, *J*=6.8 Hz, 2H; C*H*(CH_3)$_2$), 3.59 (sept, *J*=6.8 Hz, 2H; C*H*(CH_3)$_2$), 1.81 (d, *J*=11.8 Hz, 4H; CH_2), 1.72 (d, *J*= 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.60 (s, 6H; CH_3), 1.55-1.37 (m, 8H, CH_2), 1.24 (d, *J*=6.9 Hz, 12H; CH(C*H*$_3$)$_2$), 1.17 (d, *J*= 6.6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.14-0.75 (m, 8H, CH_2)

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, ppm): δ= 175.5 (NCN), 169.5 (C_{Ar}), 145.5 (C_{Ar}), 143.6 (C_{Ar}), 143.4 (C_{Ar}), 126.5 (C_{Ar}), 124.1 (C_{Ar}), 123.8 (C_{Ar}), 116.7 (NCHCHN), 97.9 (CH), 58.0 (CH), 33.9 (CH_2), 29.5 (C*H*(CH_3)$_2$), 28.0 (C*H*(CH_3)$_2$), 27.4 (CH(C*H*$_3$)$_2$), 25.6 (CH_2), 25.0 (CH_2), 24.9 (CH(C*H*$_3$)$_2$), 24.9 (CH(C*H*$_3$)$_2$), 23.6 (CH_3).

^{27}Al NMR (104.3 MHz, C_6D_6, ppm): δ=106.8, $\omega_{1/2}$=11 Hz.

IR (Nujol, cm^{-1}): $\tilde{v}$=1733, 1686, 1657 (Al-H).

UV/Vis (*n*-hexane, nm) λ_{max}: 345 (Ɛ = 959 L mol^{-1} cm^{-1}).

m.p. 158°C.

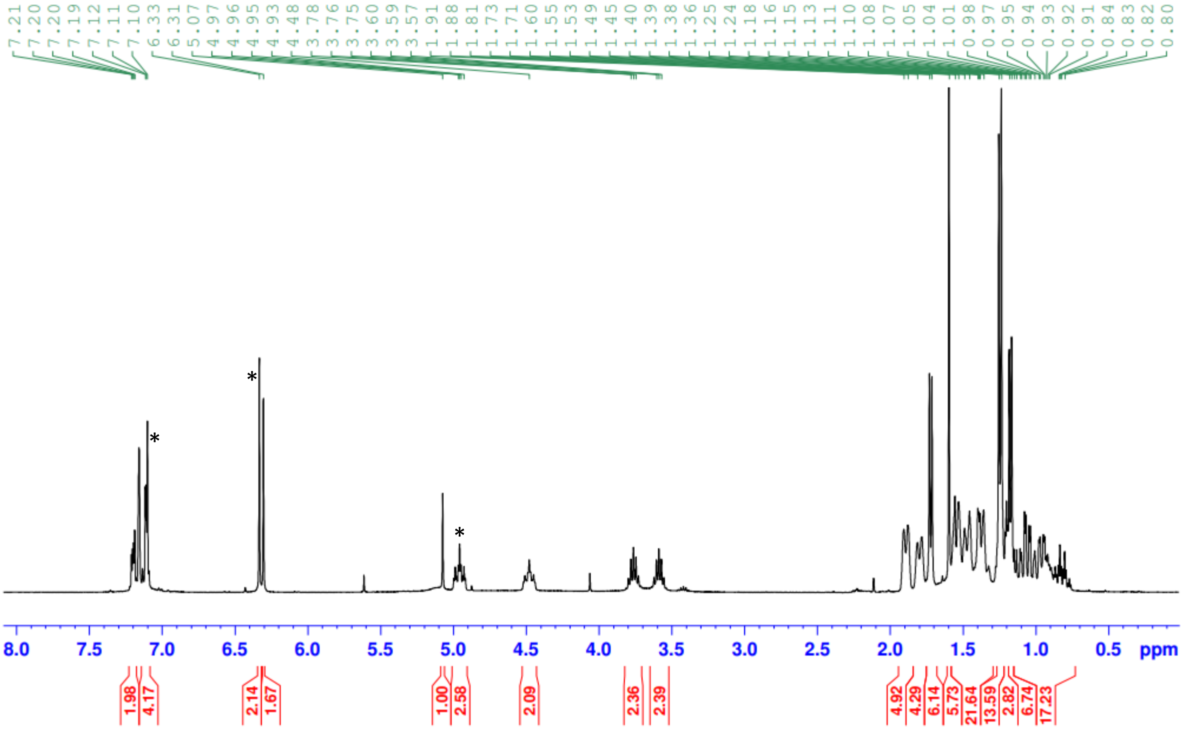


Figure S16. ^{1}H NMR spectrum of **5** in C_6D_6. ***1-ICy**

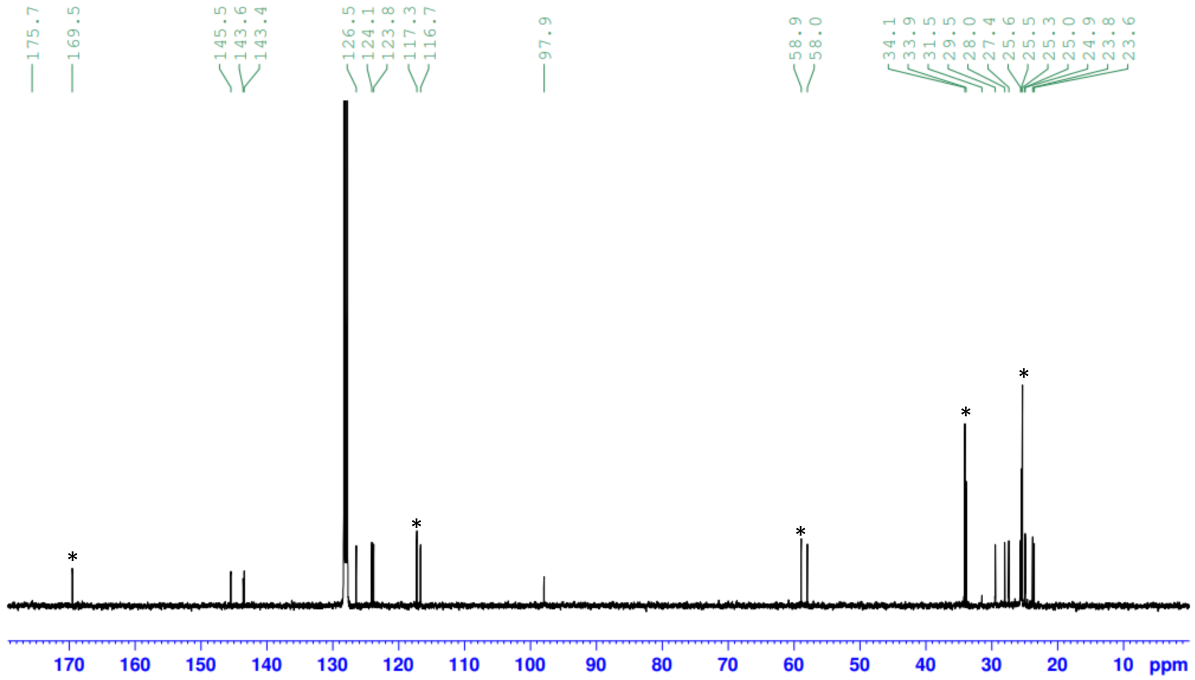


Figure S17. $^{13}C\{^1H\}$ NMR spectrum of **5** in C_6D_6. ***1-ICy**

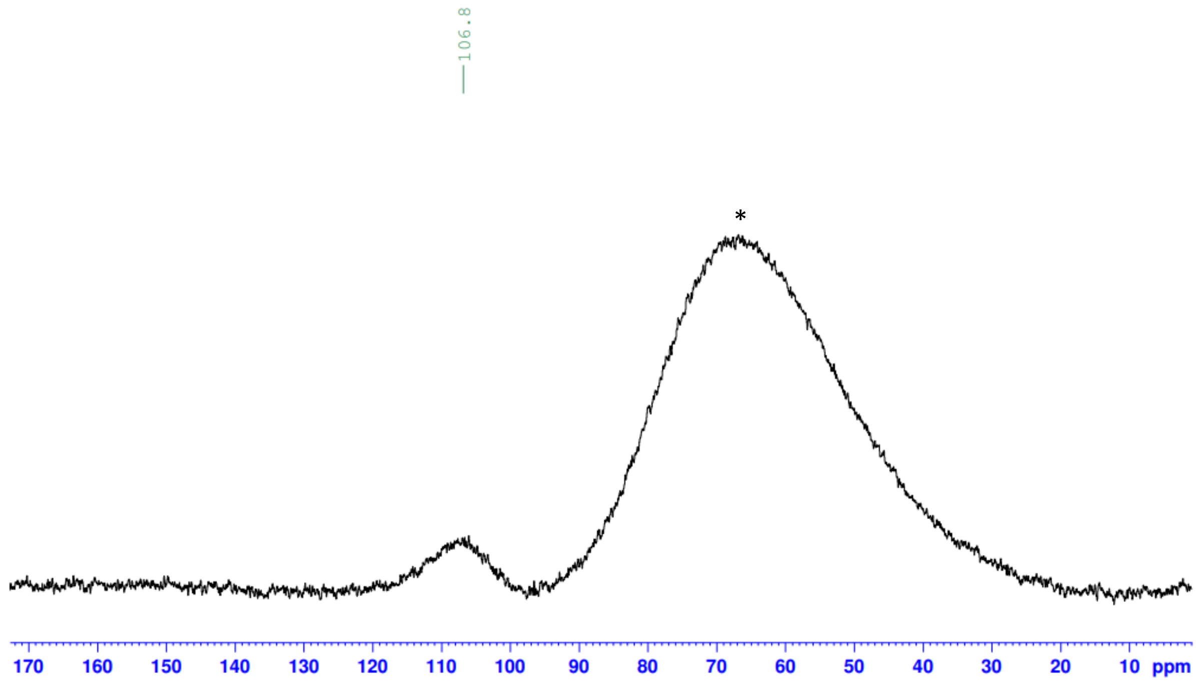


Figure S18. ^{27}Al NMR spectrum of **5** in C_6D_6. *Background peak from spectrometer

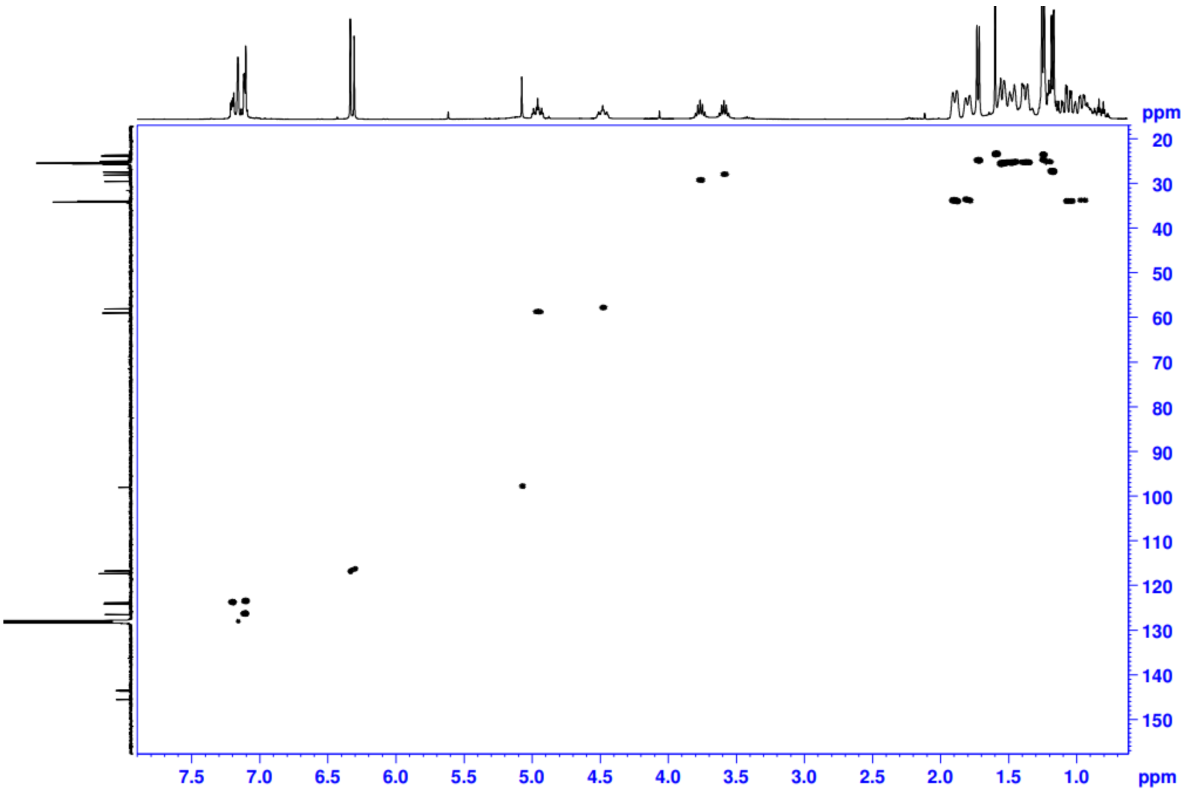


Figure S19. [^{1}H, ^{13}C] HSQC NMR spectrum of **5** in C_6D_6.

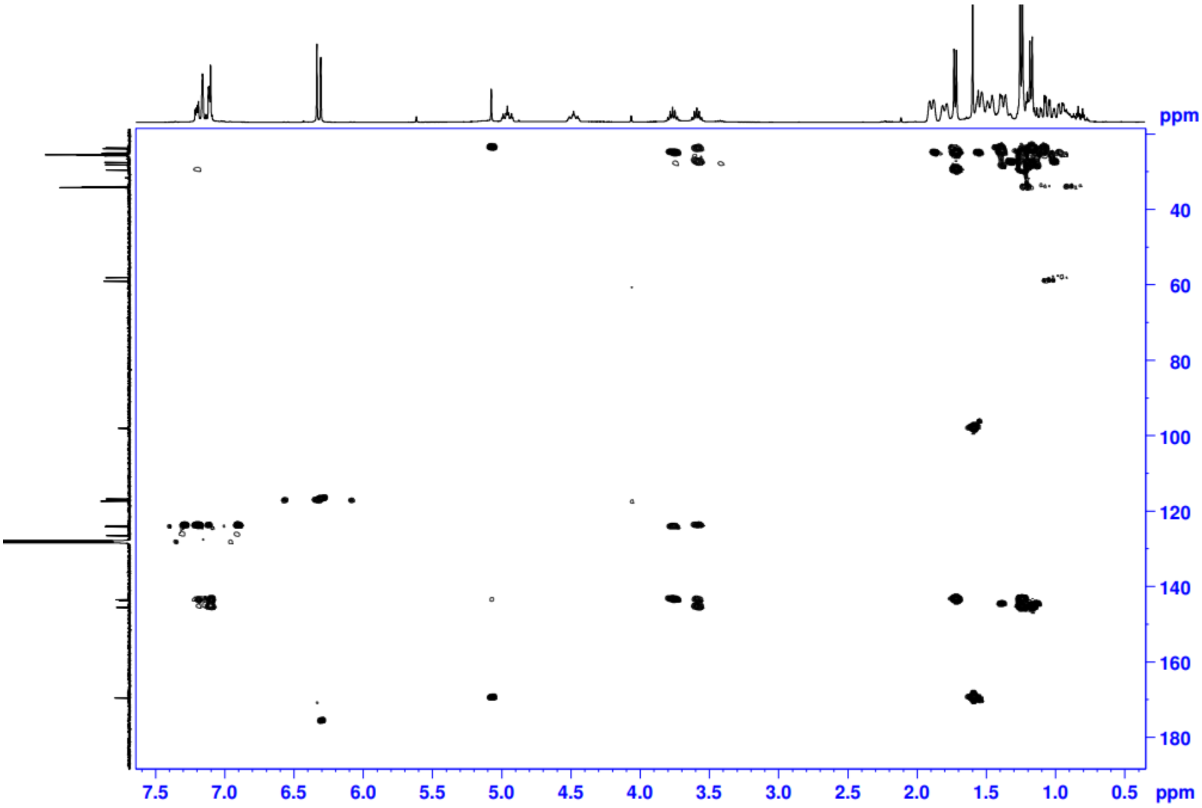


Figure S20. [^{1}H, ^{13}C] HMBC NMR spectrum of **5** in C_6D_6.

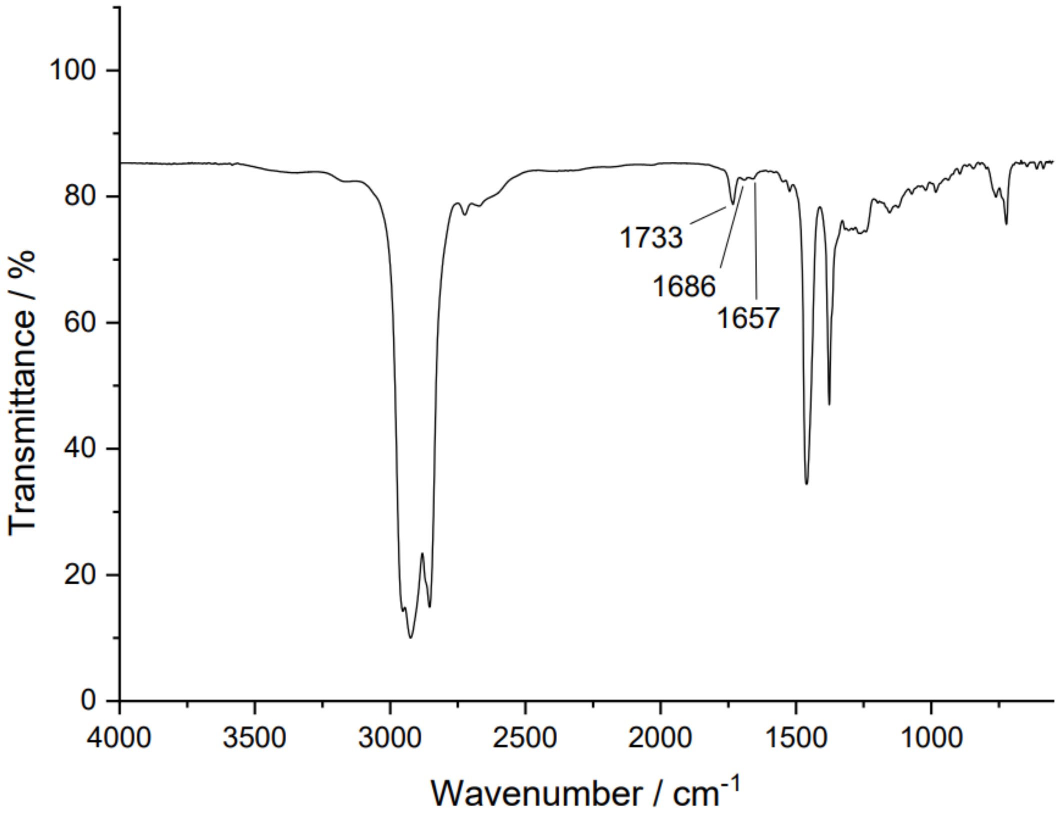


Figure S21. FT-IR spectrum of **5** in nujol mull.

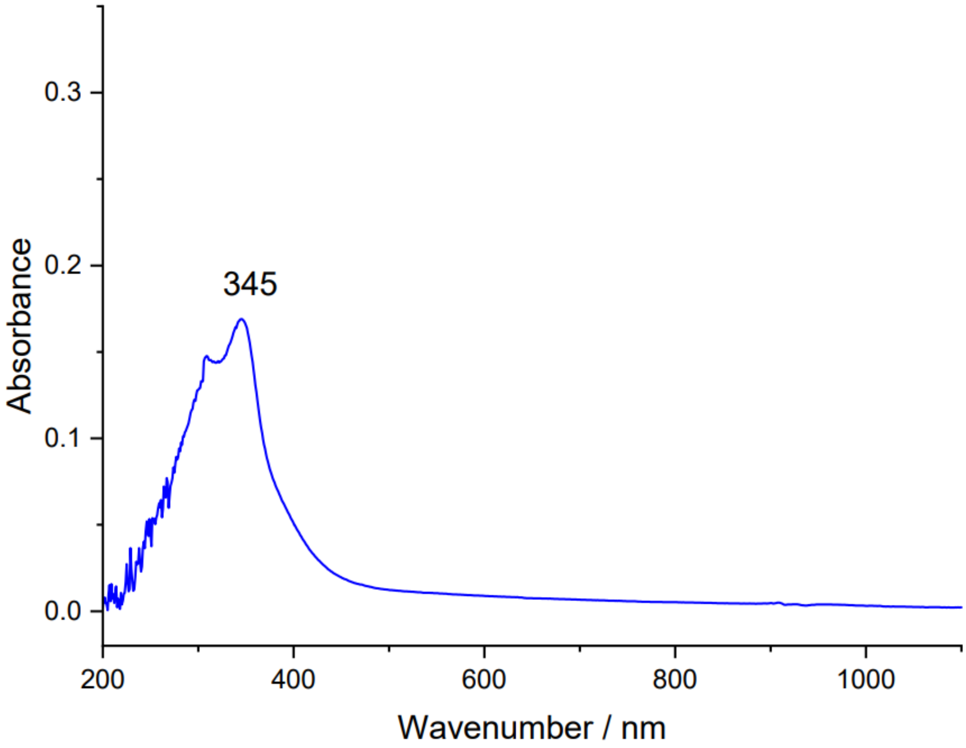


Figure S22. UV/vis of **5** in *n*-Hexane.

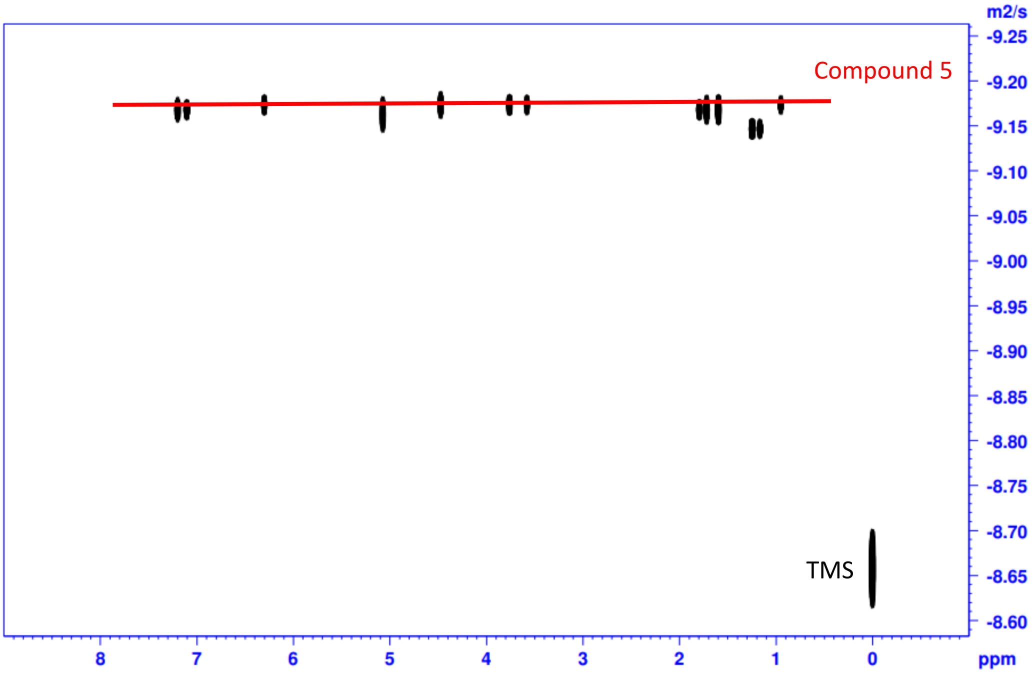


Figure S23. ^{1}H DOSY NMR spectrum of **5** in C_6D_6 with TMS as standard in C_6D_6.

The determined diffusion coefficients are summarised in Table S5 followed by the determined molecular weight in Table S6.

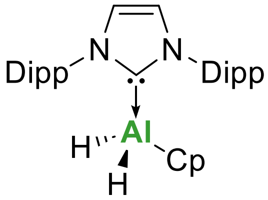
Table S5. Selected diffusion coefficients [m^2s^{-1}] determined by ^{1}H DOSY NMR.

Compound	D1	D2	D3	D4	D5	D6	D(TMS)
5	6.65e-10	6.67e-10	6.55e-10	6.72e-10	6.60e-10	6.59e-10	2.18e-9

Table S6. Estimated molecular weight data determined *via* ECC-MW software.[1]

Compound	log$D_{average}$	MW_{calc} [g mol^{-1}]	MW_{det} [g mol^{-1}]	MW_{dif} [%]
5	-9.18	706	687	3

2.6 Synthesis of Compound 6



Toluene (10 mL) was added to a mixture of 1-IDipp (100 mg, 0.24 mmol, 1 equiv.) and Cp_2Co (46 mg, 0.24 mmol, 1 equiv.). The brown/orange mixture was stirred at 70°C for 2 h. Upon cooling to room temperature, the reaction mixture was filtered, and volatiles were removed under reduced pressure. Yield: 115 mg, >99 %.

SC-XRD quality crystals were produced from a concentrated C_6D_6 solution at 25°C.

Compound 6 has been reported previously *via* a different route. NMR data below matches literature.[11]

^{1}H NMR (400 MHz, C_6D_6, ppm): δ=7.25 (m, 2H; H_{Ar}), 7.12 (m, 4H; H_{Ar}), 6.46 (s, 2H; NC*H*C*H*N), 6.15 (s, 5H, Cp), 3.69 (bs, Al-H), 2.73 (m, 4H; C*H*(CH_3)$_2$), 1.41 (d, *J*=6.8 Hz, 12H; CH(CH_3)$_2$), 1.07 (d, *J*=6.8 Hz, 12H; CH(CH_3)$_2$).

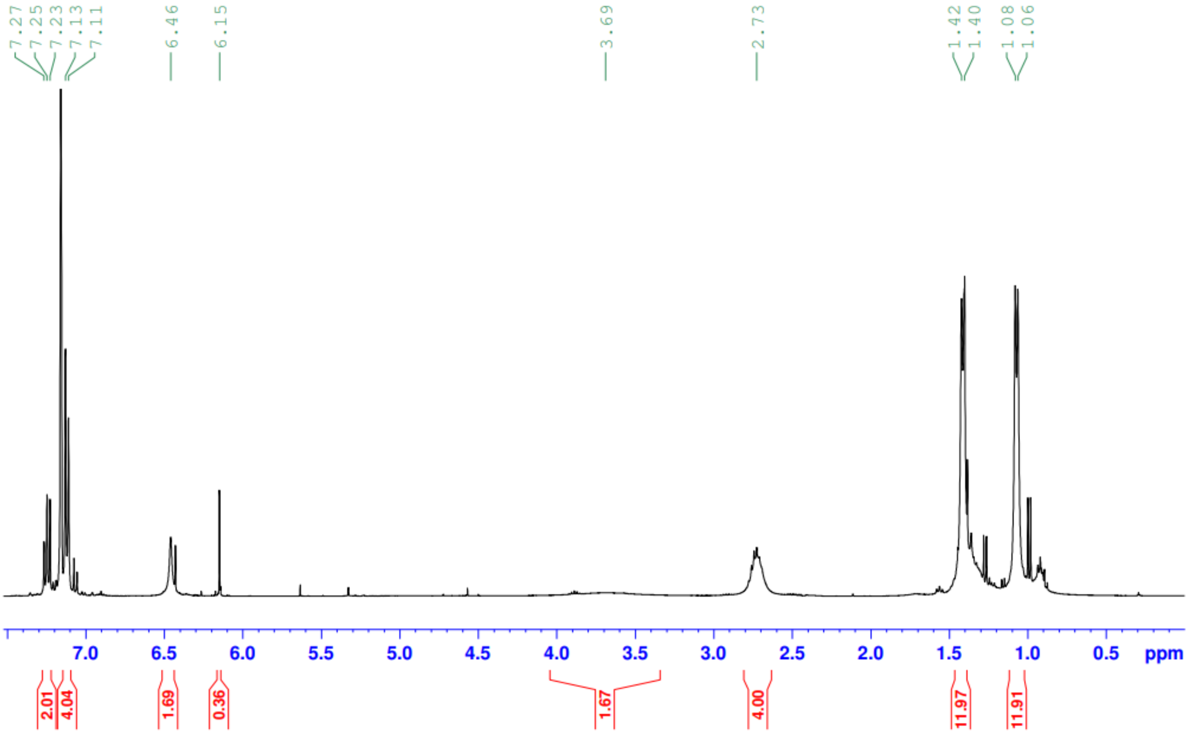


Figure S24. ^{1}H NMR spectrum of **6** in C_6D_6.

2.7 Alkali-Metal reduction attempts

All reactions, except for those performed in C_6D_6, were performed as small-scale reactions with stirring inside the glove box. Those performed in C_6D_6 were performed in a J-Youngs NMR tube with regular monitoring by ^1H NMR spectroscopy.

Table S7. Details of attempted reduction reactions of NHC-alanes with Alkali Metal (AM) species.

AM Reductant (equivalents)	**Alane**	**Conditions**	**Main Outcome**	**^1H NMR Data**
Li Metal (5)	1-IPr*	0.053 mmol, Toluene (2 mL), 25°C, 48 h	1-IPr* + Free NHC	Figure S25
$LiAlH_4$ (1)	1-IPr*	0.032 mmol, C_6D_6 (0.5 mL), 25°C, 24 h	No Reaction	Figure S26
NaH (1)	1-IPr*	0.021 mmol, C_6D_6 (0.5 mL), 25°C, 48 h	No Reaction	Figure S27
5% Na/NaCl (10)	1-IPr*	0.053 mmol, Et_2O (2 mL), 25°C, 96 h	No Reaction	Figure S28
RbC_8 (1)	1-IPr*	0.053 mmol, Toluene (2 mL), 25°C, 48 h	Free NHC	Figure S29
CsC_8 (1)	1-IPr*	0.053 mmol, Toluene (2 mL), 25°C, 48 h	Free NHC	Figure S30
KC_8 (1)	1-IPr*	0.053 mmol, C_6D_6 (2 mL), 25°C, 72 h	Free NHC + Unidentified products	Figure S33
KC_8 (10)	1-IPr*	0.110 mmol, Et_2O (2 mL), 25°C, 96 h	Free NHC + Unidentified products	Figure S34
KC_8 (10)	1-IPr*	0.053 mmol, n-Hexane (2 mL), 25°C, 72 h	Unidentified products	Figure S35
KC_8 (1)	1-IDipp	0.239 mmol, Et_2O (3 mL), 25°C, 120 h	Free NHC	Figure S32
KC_8 (3)	1-ICy	0.191 mmol, Et_2O (2 mL), 25°C, 72 h	Free NHC	Figure S31

^{1}H NMR spectra of AM reduction attempts

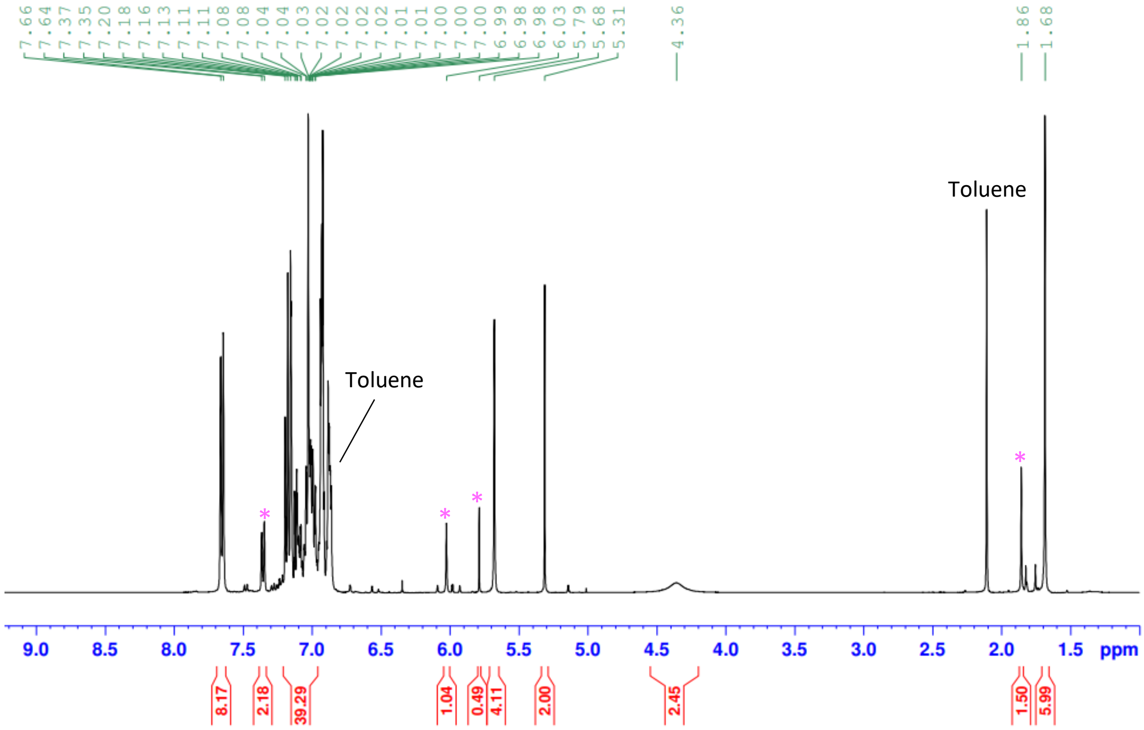


Figure S25. ^{1}H NMR spectrum of **1-IPr*** + Li (5 equiv.) in C_6D_6. *Free NHC

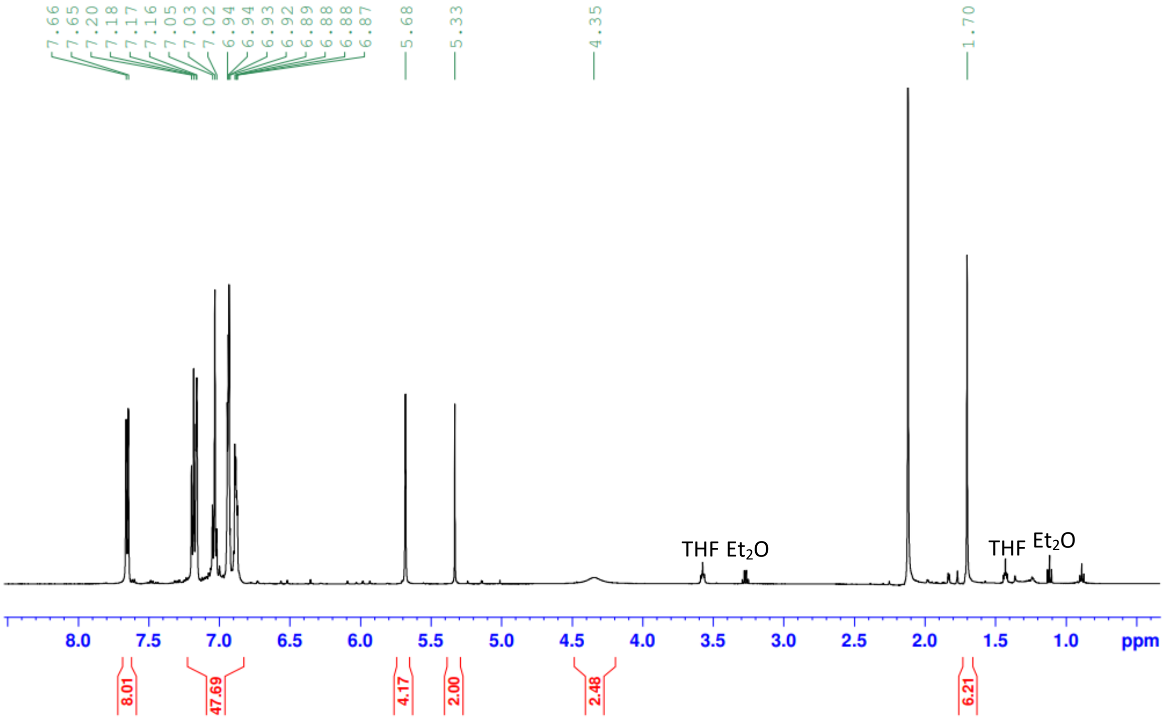


Figure S26. ^{1}H NMR spectrum of **1-IPr*** + $LiAlH_4$ (1 equiv.) in C_6D_6.

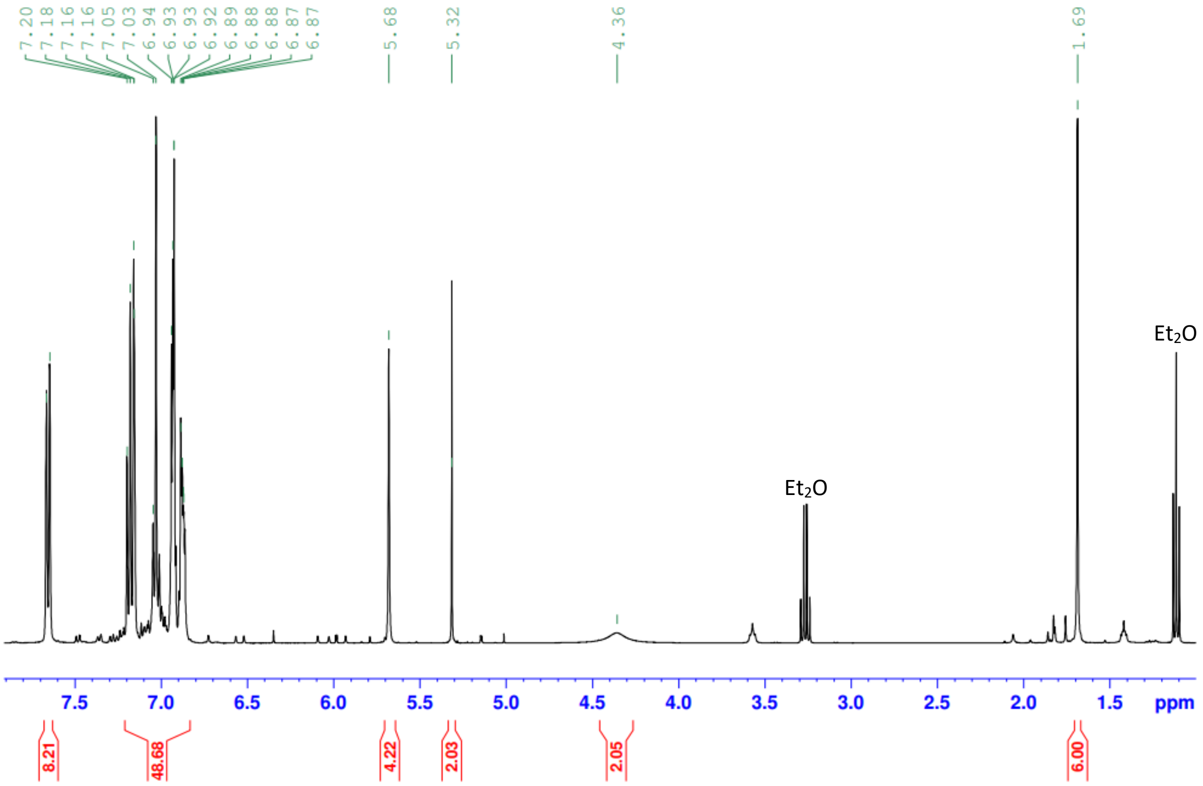


Figure S27. ^{1}H NMR spectrum of **1-IPr*** + NaH (1 equiv.) in C_6D_6.

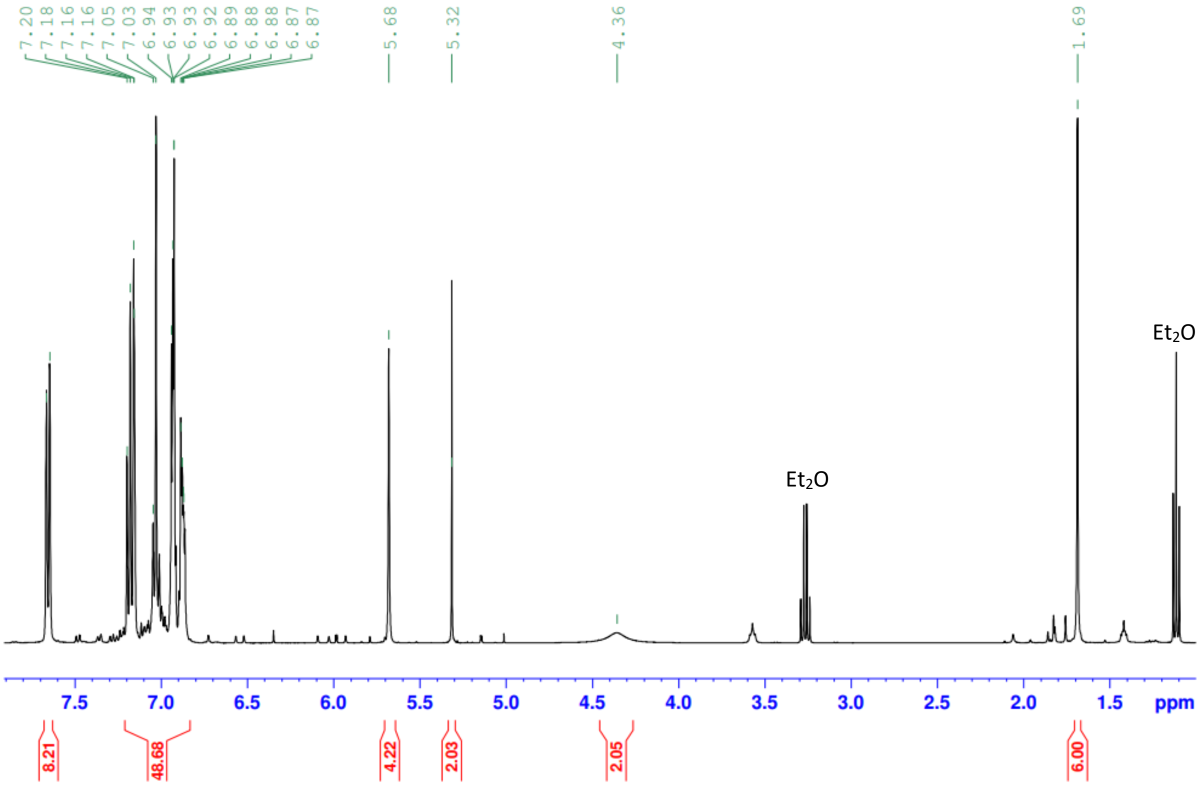


Figure S28. ^{1}H NMR spectrum of **1-IPr*** + 5% Na/NaCl (10 equiv.) in C_6D_6.

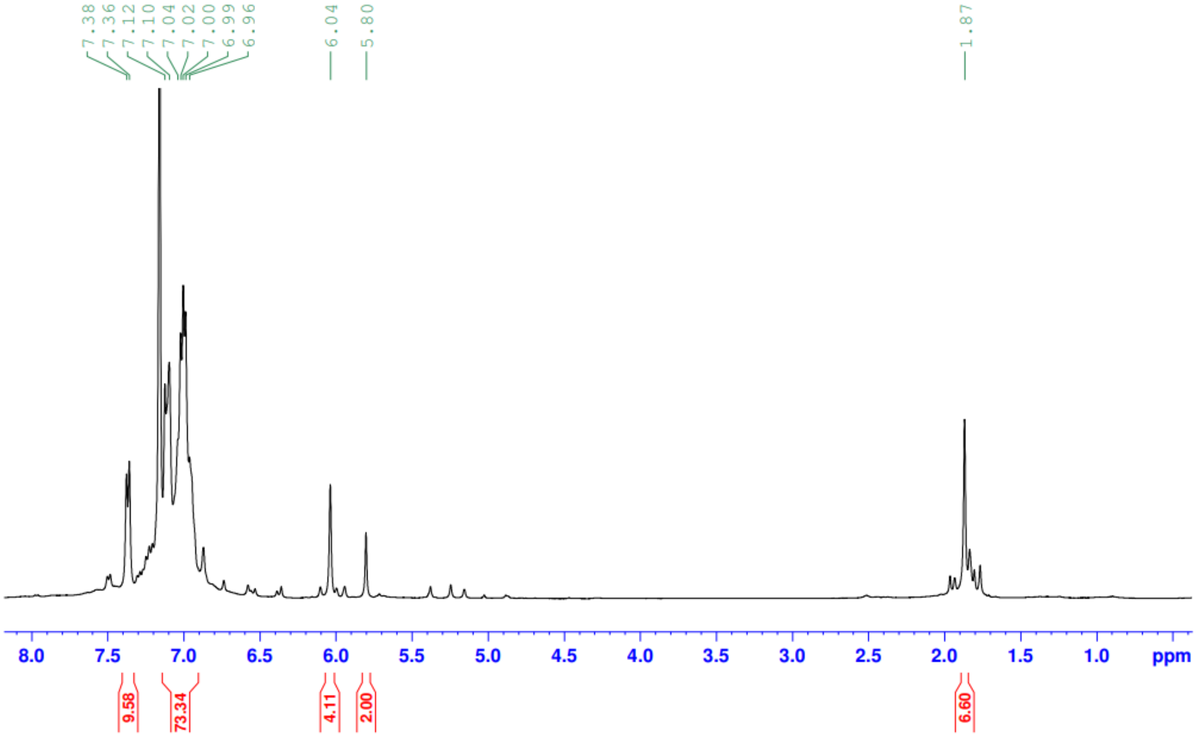


Figure S29. ^{1}H NMR spectrum of **1-IPr*** + RbC_8 (1 equiv.) in C_6D_6.

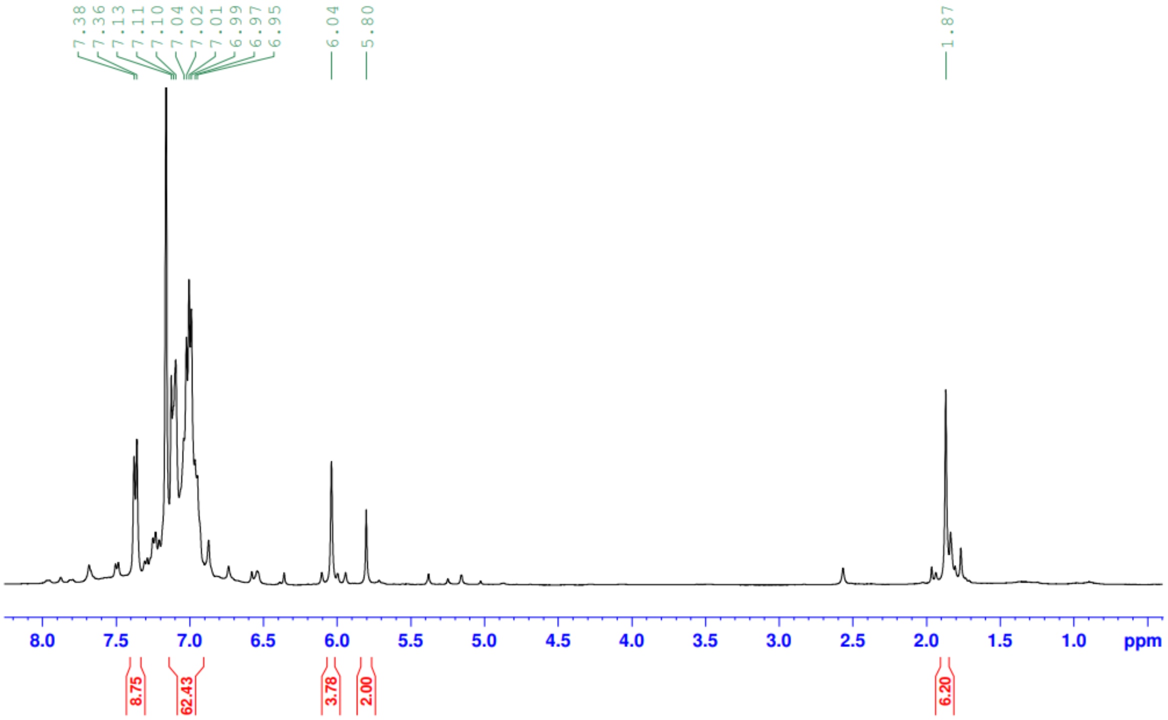


Figure S30. ^{1}H NMR spectrum of **1-IPr*** + CsC_8 (1 equiv.) in C_6D_6.

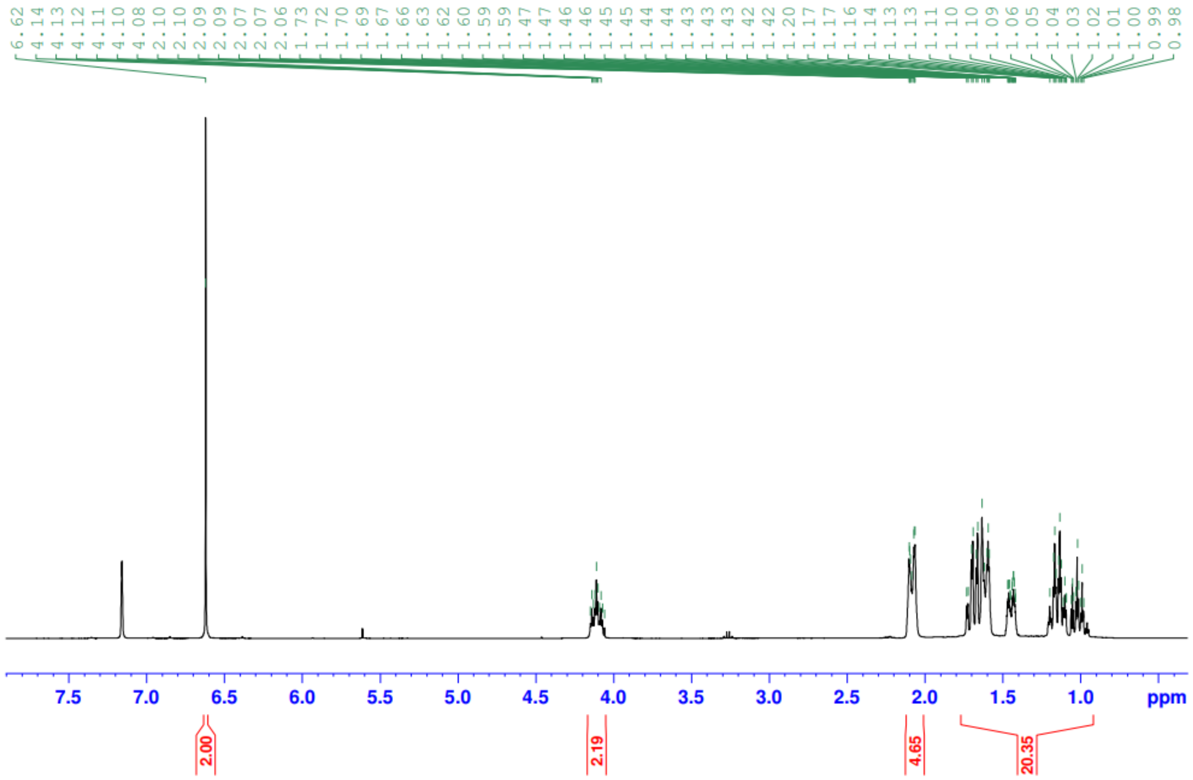


Figure S31. ^{1}H NMR spectrum of **1-ICy** + KC_8 (3 equiv.) in C_6D_6.

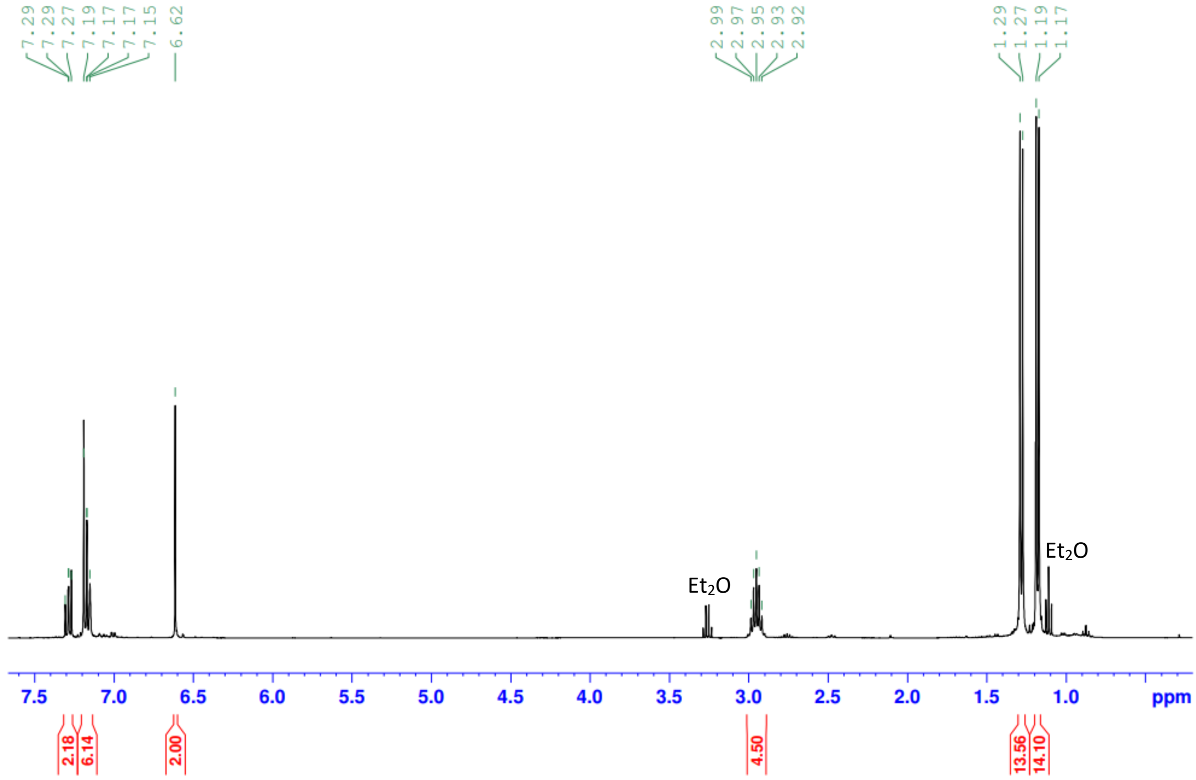


Figure S32. ^{1}H NMR spectrum of **1-IDipp** + KC_8 (1 equiv.) in C_6D_6.

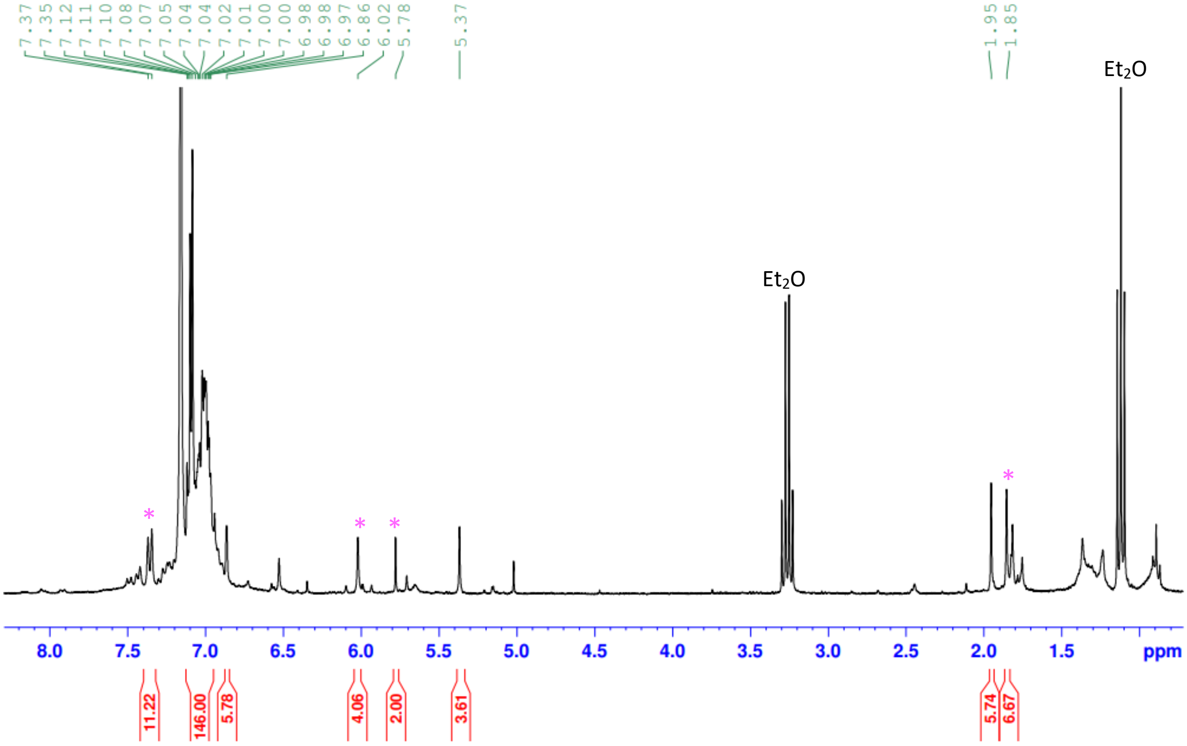


Figure S33. ^{1}H NMR spectrum of **1-IPr*** + KC_8 (1 equiv.) in C_6D_6. *Free NHC

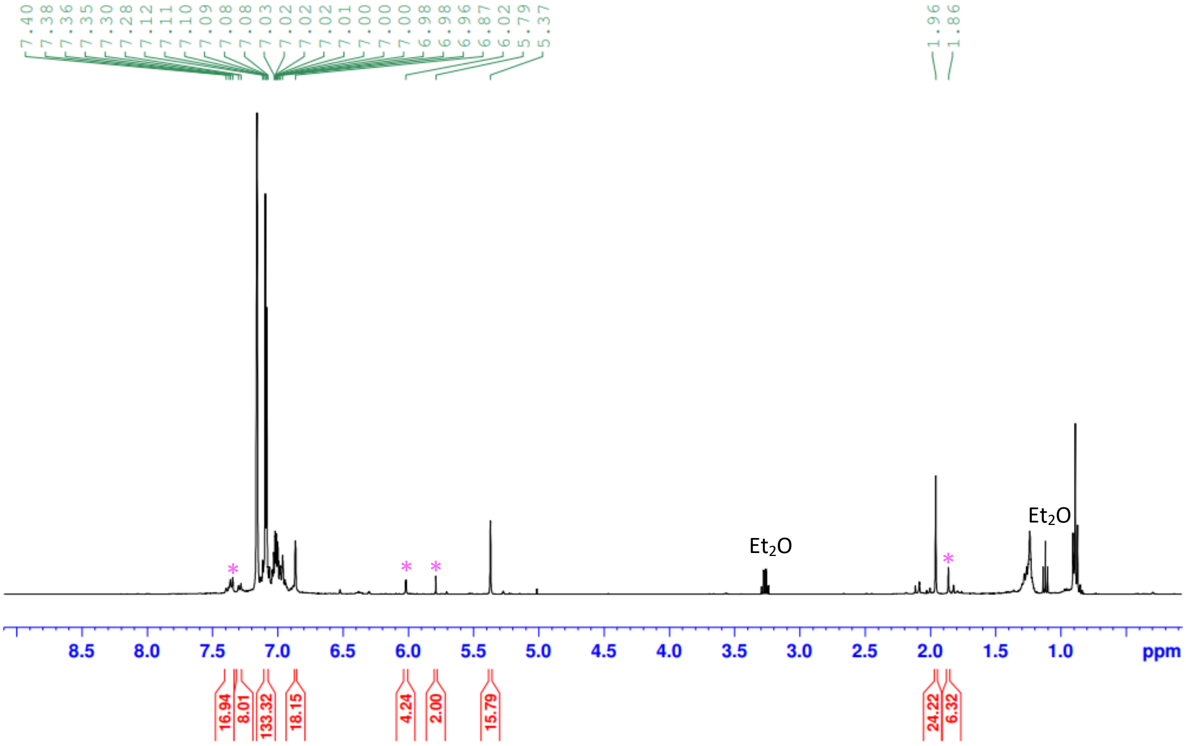


Figure S34. ^{1}H NMR spectrum of **1-IPr*** + KC_8 (10 equiv.) in C_6D_6. *Free NHC

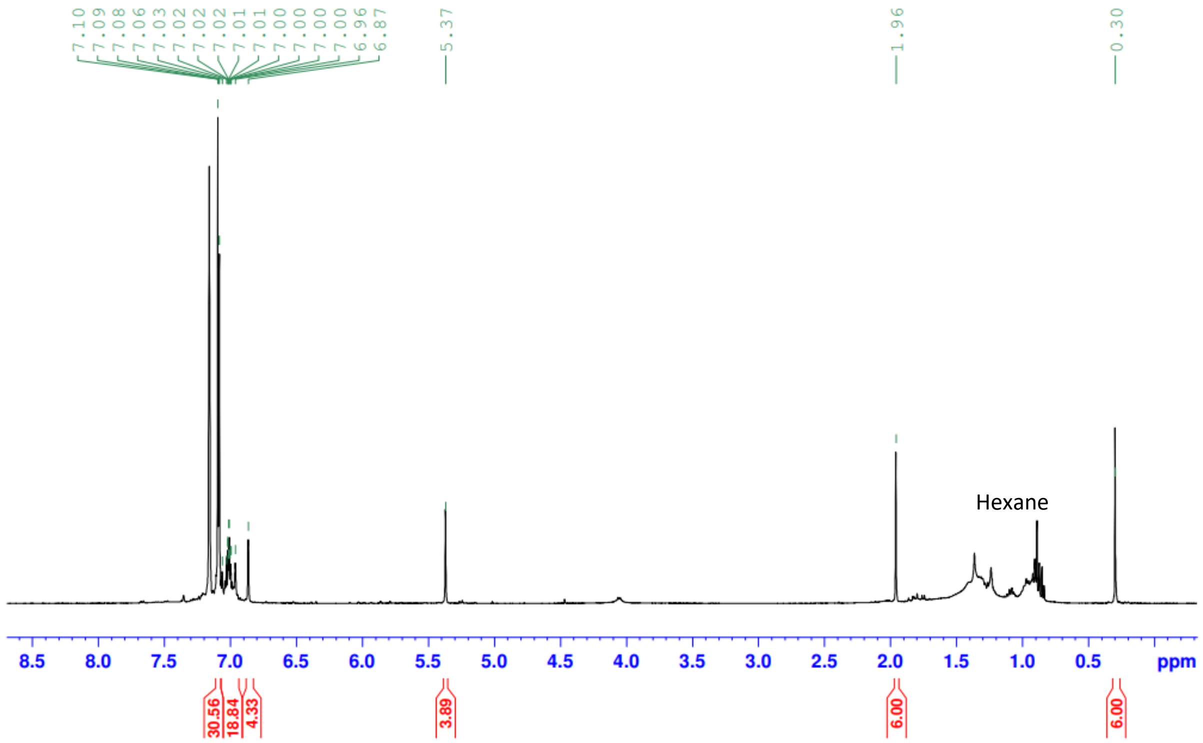


Figure S35. ^{1}H NMR spectrum of **1-IPr*** + KC_8 (10 equiv.) in C_6D_6.

3 Crystallography

Crystallographic data was measured with a Rigaku Synergy-i instrument with monochromated Cu−Kα (λ 1.54184 Å) radiation. The measured data was processed with the CrysAlisPro[12] software package. The structures were solved with the ShelXT[13] structure solution program and refined with ShelXL-2018[14] to convergence against F^2. Final refinement was within OLEX or WinGX.[14] All non-hydrogen atoms were refined using anisotropic thermal parameters and the hydride H atom positions were refined freely. Selected crystallographic and refinement data is given in Table S8.

Single crystal diffraction data for **3** and **5** are reported in crystallographic information files (CIF) accompanying this document and deposited with the CCDC as deposition numbers **2403858** and **2403860.** Full details on data collection, reduction and refinement can be found in the individual CIFs. For **3**, the solvent mask function in OLEX was used to remove a total of 91 electron equivalents from 365 A^3 of cell volume, approximating to one benzene per target molecule. The reported molecular weights include this solvent assumption. A phenyl ring was modelled as disordered and appropriate constraints and restraints were applied to ensure that the displacement and geometric parameters of this group approximated to normal behaviour. Modelling in this way left a small residual Q peak approximately 1.4 Å from atom C1. Although small, this was significantly larger than any other residual feature (0.9 vs 0.3 e $Å^{-3}$). The final model adopted thus modelled this feature as a hydroxy unit which refined to 14.1(8) % occupancy. The source of this impurity is presumably a hydrolysis reaction. This model fits well w.r.t structural position and electron density. Note that the structure here is used as proof that **3** has been formed, and note also that a message of this paper is that this system is difficult, unreliable, and messy to work with. The given structural model supports both these statements.

Table S8. Selected Crystallographic and Refinement Parameters for compounds **3** and **5**.

Compound	**3**	**5**
CCDC no.	**2403858**	**2403860**
Formula	$C_{69}H_{58}N_2$	$Al_2N_4C_{51}H_{76}$
Form. Wt.	915.17	799.11
Space Group	P-1	Cc
Crystal system	Triclinic	Monoclinic
Temp. (K)	99.9(6)	100(1)
Wavelength (λ)	1.54184	1.54184
a (Å)	10.6507(3)	13.14920(10)
b (Å)	13.2966(3)	29.02130(10)
c (Å)	20.0613(4)	13.06140(10)
α (°)	76.589(2)	90
β (°)	80.628(2)	100.5480(10)
γ (°)	85.538(2)	90
Volume ($Å^3$)	2724.31(12)	4900.09(6)
Z	2	4
Measured Reflections	55429	48351
Unique Reflections	10332	8750
R_{int}	0.1121	0.0369
2Θ range for data collection/°	4.58 to 140.246	6.09 to 143.044
No. Parameters	664	538
Goodness-of-fit on F^2	1.025	1.042
R [on *F*, obs refs only]	R_1 = 0.0759 wR_2 = 0.1923	R_1 = 0.0268 wR_2 = 0.0733
ωR [on F^2, all data]	R_1 = 0.1348 wR_2 = 0.2475	R_1 = 0.0272 wR_2 = 0.0735
Largest diff. peak /hole ($eÅ^{-3}$)	0.94/-0.43	0.15/-0.16

3.1 Solid state structure of compound 4 (JIGZAD)

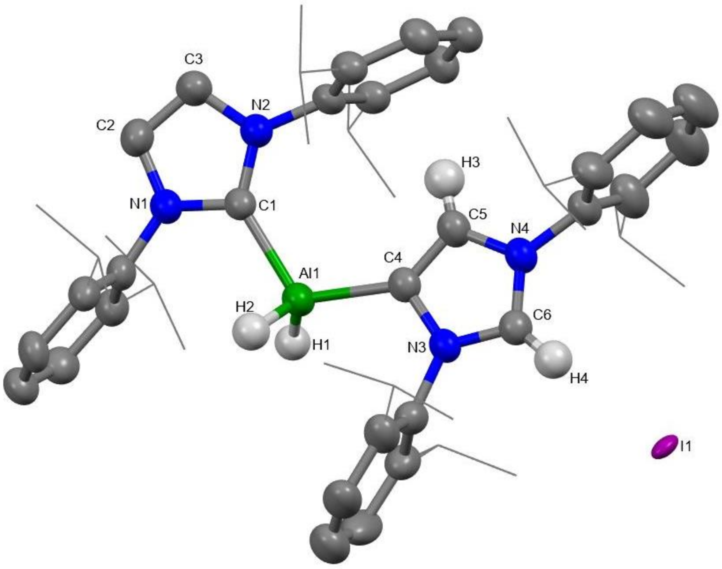


Figure S36. Solid state structure of compound **4**. Ellipsoids are drawn at 50 % probability; isopropyl groups have been depicted in wireframe for clarity. Solvent and hydrogen atoms other than those on Al(1), C(5) and C(6) have been omitted for clarity.

3.2 Solid state structure of compound 6 (DITJAV)

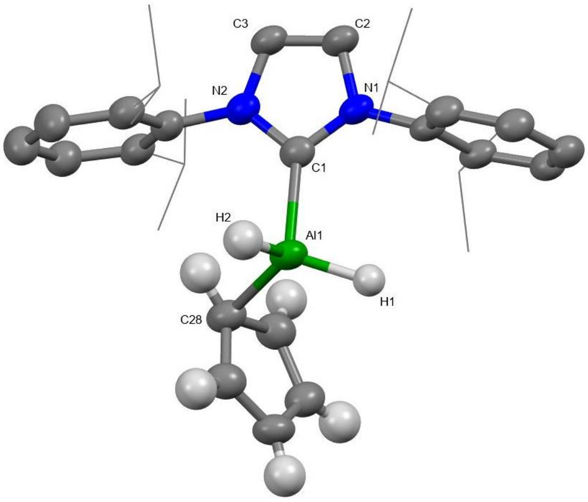


Figure S37. Solid state structure of compound **6**. Ellipsoids are drawn at 50 % probability; isopropyl groups have been depicted in wireframe for clarity. Solvent and hydrogen atoms other than those on Al(1) and Cp ring have been omitted for clarity.

3.3 Solid state structure (connectivity) of 2-IPr*

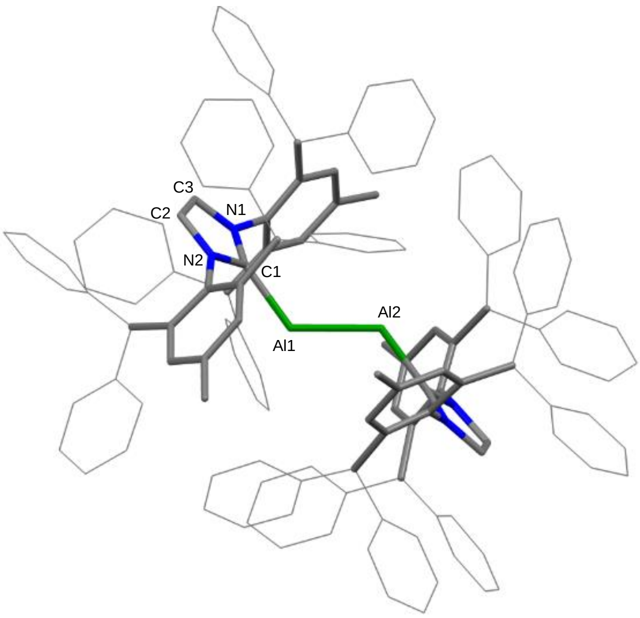
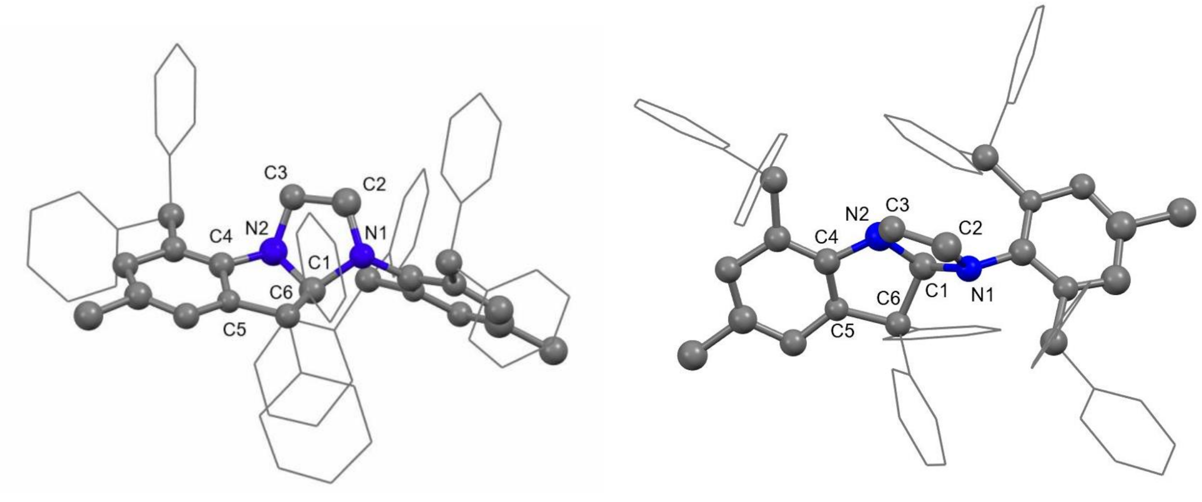


Figure S38. Solid state structure to show connectivity only of **2-IPr***. Isopropyl phenyl groups have been depicted in wireframe. Solvent atoms have been omitted for clarity.

3.4 Solid state structure (connectivity) of IPr* C-C coupled product



Side view

Top view

Figure S39. Solid state structure to show connectivity only of **IPr* C-C coupled product**. Isopropyl phenyl groups have been depicted in wireframe. Solvent and hydrogen atoms have been omitted for clarity.

3.5 Solid state structure of 3-OH

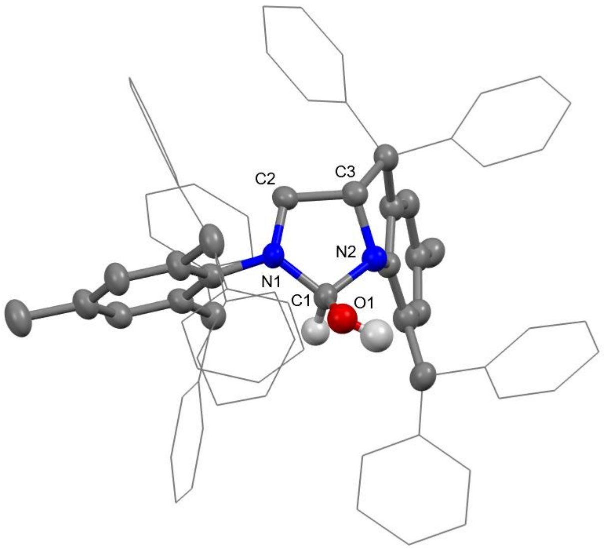


Figure S40. Solid state structure of compound **3-OH**. Ellipsoids are drawn at 50 % probability; isopropyl phenyl groups have been depicted in wireframe for clarity. Solvent and hydrogen atoms other than those on C(1) and O(1) have been omitted for clarity.

References

[1] S. Bachmann, B. Gernert, D. Stalke, *Chem. Comm.* **2016**, *52*, 12861-12864.

[2] L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49-54.

[3] A. Gómez-Suárez, R. S. Ramón, O. Songis, A. M. Z. Slawin, C. S. J. Cazin, S. P. Nolan, *Organometallics* **2011**, *30*, 5463-5470.

[4] N. Ortega, C. Richter, F. Glorius, *Org. Lett.* **2013**, *15*, 1776-1779.

[5] S. P. Green, C. Jones, A. Stasch, *Science,* **2007**, 318, 1754-1757.

[6] C. M. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. J. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.* **2000**, *39*, 4274-4276.

[7] R. J. Baker, A. J. Davies, C. Jones, M. Kloth, *J. Organomet. Chem.* **2002**, *656*, 203-210.

[8] F. Murphy, A. R. Kennedy and C. E. Weetman, *Inorganics*, **2023**, *11*, 13.

[9] S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* **2010**, *2*, 865-869.

[10] M. Trose, S. Burnett, S. J. Bonyhady, C. Jones, D. B. Cordes, A. M. Z. Slawin and A. Stasch, *Dalton Trans.* **2018**, *47*, 10281-10287.

[11] L. Werner, S. Mann and U. Radius, *Eur. J. Inorg. Chem.* **2023**, *26*, e202300398.

[12] 2018, CrysAlisPro Software system, version 1.171.39.46, Rigaku Corporation, Oxford, UK Rigaku Oxford Diffraction Rigaku Oxford Diffraction, **2018**.

[13] G. M. Sheldrick, *Acta Crystallographica Section C Structural Chemistry* **2015**, *71*, 3–8.

[14] O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, **2009**, *42*, 339-341.