Supplementary Information for

An Acyclic Aluminyl Anion

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Experimental

General Methods and Considerations

All reactions dealing with air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk line and glovebox techniques. NMR experiments using air sensitive compounds were conducted in J. Young's tap NMR tubes prepared and sealed in a glovebox under argon. Toluene, hexane, and pentane were purified using an MBraun Solvent Purification System and stored over 4Å molecular sieves or sodium mirror and degassed with argon before use. Diethyl ether was dried using sodium suspended in a benzophenone solution. C_6D_6 and toluene-d_8 were dried over potassium mirrors prior to vacuum transfer into sealed ampoules and stored in a glove box under argon. All NMR data, unless otherwise stated, were acquired at 298 K on either an Agilent ProPulse instrument for ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (126 MHz) and $^{29}Si\{^{1}H\}$ (99 MHz), a Bruker Ascend 400 for ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and $^{29}Si\{^{1}H\}$ (79 MHz) or Bruker Ascend 700 for $^{13}C\{^{1}H\}$ (176 MHz) and $^{29}Si\{^{1}H\}$ (139 MHz). ^{1}H and ^{13}C NMR spectra were referenced using residual solvent resonances. IR Spectroscopy was acquired on a Brucker Alpha II or a Perkin-Elmer UATR Two FT-IR spectrometer. UV-Vis spectroscopy was acquired on a Mettler Toledo Spectrophotometer UV5. $LiAlH_4$ was recrystallised from diethyl ether before use. HN(Dipp)$SiMe_3$, HN(Si(*i*-Pr)$_3$)Dipp, [(^{Dipp}nacnac)MgI(OEt_2)], AlI_3, 5% w/w K/KI and K_2[**III^{Dipp}**] were synthesised according to their respective literature methods.[1-6] Elemental analyses of **1** were performed by Elemental Analysis Services, London Metropolitan University, London, U.K, **2**, **4** and **5** were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K.

Preparation of 1, [IAl{N(Dipp)Si(*i*-Pr)$_3$}$_2$]

To a solution of HN(Si(*i*-Pr)$_3$)Dipp (2.00 g, 6.0 mmol) in toluene (30 mL) was added *n*-butyllithium (4.20 mL of 1.6M solution in hexane, 6.7 mmol) at –78 °C dropwise. The colourless solution was warmed to r.t., becoming yellow after 2 hours, whereupon it was added to a colourless solution of aluminium iodide (1.22 g, 3.0 mmol) in toluene (20 mL). The combination immediately yielded small amounts of colourless precipitate and the reaction mixture was stirred vigorously at 70 °C overnight. The yellow solution was separated from colourless precipitate *via* cannular filtration at 70 °C. Upon cooling to r.t. the solution was concentrated under reduced pressure (ca. 2 mL). The burnt orange solution was stored overnight at room temperature to give compound **1** [IAl{N(Dipp)Si(*i*-Pr)$_3$}$_2$] as large yellow crystals which were extracted through cannular filtration. Subsequent concentration of the filtrate (ca. 1 mL) allowed for the collection of a second crop of crystalline product (1.29 g, 53%).

^{1}H NMR (400 MHz, C_6D_6): δ 6.99 – 6.93 (m, 6H, Ar-*H*), 3.71 (br., 4H, Dipp-C*H*(CH_3)$_2$), 1.69 (sept, $^{3}J_{HH}$ = 7.6 Hz, 6H, Si-C*H*(CH_3)$_2$), 1.28 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.16 (d, $^{3}J_{HH}$ = 7.6 Hz, 36H, Si-CH(C*H*$_3$)$_2$), 0.91 (br., 12H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 147.2 (*ortho*-Ar-*C*), 143.5 (*ipso*-Ar-*C*), 125.6 (*para*-Ar-*C*), 125.5 (*meta*-Ar-*C*), 28.2 (Dipp-CH(C*H*$_3$)$_2$), 24.8 (Dipp-C*H*(CH_3)$_2$), 21.0 ((Si-

CH(CH$_3$)$_2$), 17.2 (Si-CH(CH$_3$)$_2$). **^{29}Si NMR** (79 MHz, C$_6$D$_6$): δ 9.3 (N-Si-CH(CH$_3$)$_2$). **IR** (cm^{-1}) (Nujol): 3057(w), 2948(m), 2925(m), 2867(m), 2727(w), 2544(w), 2050(w), 1574(w), 1543(w), 1465(m), 1454(m), 1422(m), 1385(m), 1364(w), 1302(w), 1254(w), 1230(w), 1157(m), 1145(w), 1101(m), 1067(w), 1040(w), 1017(w), 1004(w), 965(w), 918(w), 872(s), 848(m), 820(s), 790(s), 742(w), 706(s), 661(m), 636(w), 626(w), 605(w), 597(w) 541(w), 535(m), 505(w), 490(w), 458(w), 434(w), 405(w). **anal. calc.** for C$_{42}$H$_{76}$AlIN$_2$Si$_2$: C, 61.72; H, 9.35; N, 3.43 %. Found: C, 61.37; H, 9.40; N, 3.40 %.

Preparation of 2, [IAl{N(Dipp)SiMe$_3$}$_2$]

In a glovebox, HN(Dipp)SiMe$_3$ (5.00 g, 20 mmol) and LiAlH$_4$ (0.38 g, 10 mmol) were mixed. The vessel was cooled to 0 °C and charged with diethyl ether (30 mL). This was stirred at reflux for 6 days. Upon cooling to r.t., the resulting clear solution was separated from the grey solid *via* cannular filtration. The filtrate was then cooled to 0 °C and TMSI (4.01 g, 20 mmol) was added dropwise. The mixture was allowed to warm to r.t. and stirred for 16 hours. Volatiles were removed under reduced pressure. The resulting solid washed with hexane and then dried under reduced pressure. The crude product was identified as [Et$_2$O·LiI$_2$Al{N(Dipp)SiMe$_3$}$_2$] (5.13 g, 60%). This could be sublimated and recrystalised from pentane to give a white crystalline material which ^{1}H NMR spectroscopy confirmed to be compound **2**, [IAl{N(Dipp)SiMe$_3$}$_2$]. Crystals of compound **2** that were suitable for SCXRD were obtained from a saturated solution of pentane at –30 °C.

^{1}H NMR (500 MHz, Toluene-d_8): δ 6.94 – 6.88 (m, 6H, Ar-H), 3.51 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, Dipp-CH(CH$_3$)$_2$, overlapped with HN(Dipp)SiMe$_3$ residue), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Dipp-CH(CH_3)$_2$), overlapped with HN(Dipp)SiMe$_3$ residue), 0.86 (d, $^3J_{HH}$ = 6.9 Hz, 12H, Dipp-CH(CH_3)$_2$), 0.26 (s, 18H, Si(CH_3)$_3$). **^{13}C{^{1}H} NMR** (125 MHz, Toluene-d_8): δ 145.8 (Ar-C), 142.5 (Ar-C), 125.2 (Ar-CH), 124.5 (Ar-CH), 28.5 (Dipp-CH(CH$_3$)$_2$), 25.9 (Dipp-CH(CH$_3$)$_2$), 24.2 (Dipp-CH(CH$_3$)$_2$), 4.4 (Si(CH$_3$)$_3$). **^{29}Si{^{1}H} NMR** (99 MHz, Toluene-d_8): δ 8.1 (Si(CH$_3$)$_3$). **anal. calc.** for C$_{30}$H$_{52}$AlIN$_2$Si$_2$: C, 55.37; H, 8.05; N, 4.30 %. Found: C, 55.44; H, 8.22; N, 4.30 %.

Preparation of 3, K[HAl{N(Dipp)Si(*i*-Pr)$_3$}{N(Dipp)Si(*i*-Pr)$_2$CMe$_2$}]

To a toluene (20 mL) solution of light blue precipitated 5% K/KI (1.05 g, 1.28 mmol K), a pale-yellow solution of [IAl{N(Dipp)Si(*i*-Pr)$_3$}$_2$] (205 mg, 0.25 mmol) in toluene (10 mL) was added dropwise at –20 °C over 20 minutes. Stirring at –20 °C for 18 hours yielded a dark yellow solution with grey precipitate, of which the formation of K[HAl{N(Dipp)Si(*i*-Pr)$_3$}{N(Dipp)Si(*i*-Pr)$_2$CMe$_2$}] was confirmed by ^{1}H NMR spectroscopy. Separation *via* canular filtration afforded a dark yellow solution from the grey solid. Removal of volatiles under reduced pressure yielded the burnt orange solid of compound **3** K[HAl{N(Dipp)Si(*i*-Pr)$_3$}{N(Dipp)Si(*i*-Pr)$_2$CMe$_2$}] (22 mg, 12%). Following 8 days standing at r.t. in a saturated toluene solution (ca. 1 mL) of **3** yielded crystals that were suitable for SCXRD.

^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 7.28 (dd, $^3J_{HH}$ = 7.5 Hz, 2.1 Hz, 1H, Aryl-H), 7.04-7.12 (m, 2H, Aryl-H, overlapped with toluene residue), 6.56 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Aryl-

H), 6.38 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Aryl-*H*), 4.50 (sept, $^3J_{HH}$ = 6.5 Hz, 1H, Dipp-C*H*$(CH_3)_2$), 4.29 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, Dipp-C*H*$(CH_3)_2$), 4.12 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, Dipp-C*H*$(CH_3)_2$), 3.91 (sept, $^3J_{HH}$ = 6.4 Hz, 1H, Dipp-C*H*$(CH_3)_2$), 2.96 (br., 1H, Al-*H*), 2.16 (s, 3H, Si-CH(C*H*$_3)_2$), 2.08 (s, 3H, Si-CH(C*H*$_3)_2$), 1.86 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Si-CH(C*H*$_3)_2$), 1.75-1.82 (m, 1H, Si-C*H*$(CH_3)_2$), 1.60-1.67 (m, 4H, 1H Si-C*H*$(CH)_3$, 3H Si-CH(C*H*$)_3$), 1.53 (d, $^3J_{HH}$ = 6.7 Hz, 3H, Dipp-CH(C*H*$_3)_2$), 1.40-1.53 (m, 12H, 6H Dipp-CH(C*H*$_3)_2$), 3H Si-C*H*$(CH)_3$, 3H Si-CH(C*H*$)_3$), 1.33 (d, $^3J_{HH}$ = 7.7 Hz, 18H, Si-CH(C*H*$_3)_2$), 1.32 (d, $^3J_{HH}$ = 7.4 Hz, 3H, Dipp-CH(C*H*$_3)_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Dipp-CH(C*H*$_3)_2$), 0.95 (d, $^3J_{HH}$ = 7.3 Hz, 3H, Si-CH(C*H*$_3)_2$), 0.87 (d, $^3J_{HH}$ = 6.7 Hz, 3H, Dipp-CH(C*H*$_3)_2$0.49 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Dipp-CH(C*H*$_3)_2$), 0.21 (d, $^3J_{HH}$ = 6.7 Hz, 3H, Dipp-CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6) δ 156.5 (Ar-*C*), 150.5 (Ar-*C*), 150.0 (Ar-*C*), 148.4 (Ar-*C*), 146.2 (Ar-*C*), 145.0 (Ar-*C*), 124.4 (Ar-*C*), 123.5 (Ar-*C*), 123.4 (Ar-*C*), 123.4 (Ar-*C*),121.0 (Ar-*C*),120.7 (Ar-*C*), 29.3 (Dipp-CH(*C*$H_3)_2$), 28.6 (Al-C-*C*H_3), 27.8 (Al-C-*C*H_3), 27.6 (Dipp-CH(*C*$H_3)_2$), 27.0 (Dipp-*C*H$(CH_3)_2$), 27.0 (Dipp-*C*H$(CH_3)_2$), 26.9 (Dipp-*C*H$(CH_3)_2$), 26.7 (Dipp-CH(*C*$H_3)_2$), 26.3 (Dipp-*C*H$(CH_3)_2$), 26.1 (Dipp-CH(*C*$H_3)_2$), 25.7 (Dipp-CH(*C*$H_3)_2$), 25.1 (Dipp-CH(*C*$H_3)_2$), 23.6 (Dipp-CH(*C*$H_3)_2$), 23.6 (Dipp-CH(*C*$H_3)_2$), 21.4 Si-CH(*C*$H_3)_2$), 21.4 Si-*C*H$(CH_3)_2$), 20.6 Si-CH(*C*$H_3)_2$), 20.5 Si-CH(*C*$H_3)_2$), 20.2 Si-CH(*C*$H_3)_2$), 20.0 Si-CH(*C*$H_3)_2$), 18.1 Si-*C*H$(CH_3)_2$), 15.9 Si-CH(*C*$H_3)_2$), 15.2 Si-*C*H$(CH_3)_2$). **^{29}Si{^{1}H} NMR** (139 MHz, C_6D_6) δ 2.0 (N-*Si*-CH$(CH_3)_2$), 1.0 (Al-CH_2-*Si*). **IR** (cm^{-1}) (Nujol): 2967(m), 2943(m), 2863(m), 2831(m), 1757(w), 1584(w), 1471(w), 1417(m), 1309(w), 1260(w), 1233(w), 1196(w), 1171(w), 1107(w), 1098(w), 1040(w), 1013(w), 914(w), 886(w), 914(w), 886(w), 832(w), 817(w), 794(m), 783(m), 741(w), 730(w), 689(w), 658(w), 588(w), 557(w). Despite attempts, conclusive elemental analysis was not possible.

Preparation of 4, K_2[Al{N(Dipp)SiMe$_3$}$_2$]$_2$

In a glovebox, a Schlenk flask was charged with [IAl{N(Dipp)SiMe$_3$}$_2$] (350 mg, 538 µmol) and KC_8 (363 mg, 2.69 mmol). The mixture was suspended in benzene (3.5 mL) and stirred for 1.5 hours. Subsequent cannular filtration yielded a dark yellow solution. Removal of volatiles under reduced pressure afforded compound **4** K_2[Al{N(Dipp)SiMe$_3$}$_2$]$_2$ as a vivid yellow powder (215 mg, 71%). Following 5 days standing at r.t. in a saturated benzene solution (ca. 0.3 mL) obtained crystals of **4** that were suitable for SCXRD.

^{1}H NMR (500 MHz, Toluene-d_8): δ 6.89 – 6.87 (m, 8H, Ar-H), 6.84 – 6.81 (m, 4H, Ar-H), 3.90 (sept, $^3J_{HH}$ = 7.0 Hz, 8H, Dipp-C*H*$(CH_3)_2$), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 24H, Dipp-CH(C*H*$_3)_2$), 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 24H, Dipp-CH(C*H*$_3)_2$), 0.35 (s, 36H, Si(C*H*$_3)_3$). **^{13}C{^{1}H} NMR** (125 MHz, Toluene-d_8): δ 151.6 (Ar-*C*), 149.6 (Ar-*C*), 123.2 (Ar-*C*), 122.5 (Ar-*C*), 27.9 (Dipp-*C*H$(CH_3)_2$), 25.7 (Dipp-CH(*C*$H_3)_2$), 23.9 (Dipp-CH(*C*$H_3)_2$), 5.3 (Si(*C*$H_3)_3$). **^{29}Si{^{1}H} NMR** (99 MHz, Toluene-d_8): δ −5.9 (*Si*$(CH_3)_3$). UV-vis (toluene): λ_{max} 314, 403 nm. IR (cm^{-1}): 3517, 2960, 1430, 1248. **anal. calc.** for $C_{60}H_{104}Al_2K_2N_4Si_4$: C, 64.00; H, 9.31; N, 4.98 %. Found: C, 63.79; H, 9.26; N, 4.98 %.

Thermolysis of 4

In a glovebox, a sample vial was charged with [IAl{N(Dipp)SiMe$_3$}$_2$] (22.0 mg, 33.8 µmol) and KC_8 (22.8 mg, 169 µmol). The mixture was suspended in toluene (ca. 1 mL) and allowed to rest for 1 hour. This was filtered to give a yellow solution and heated to 80 °C. After 24 hours an off-white solid had developed. The resulting solution was subjected to ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, Toluene-*d*$_8$): δ 3.63 – 3.40 (m, 2H, Dipp-C*H*(CH$_3$)$_2$ overlapped with multiple resonances), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 0.10 (s, 9H, Si(C*H*$_3$)$_3$).

Reaction of 4 with [2.2.2]-cryptand

In a glovebox, a sample vial was charged with [IAl{N(Dipp)SiMe$_3$}$_2$] (52.2 mg, 80.2 µmol) and KC_8 (54.2 mg, 401 µmol). The mixture was suspended in toluene (ca. 1 mL) and allowed to rest for 1 hour. This was filtered to give a yellow solution. The solution was then added to [2.2.2]-Kryptand (30.2 mg, 80.2 µmol). Immediately a red suspension formed which gradually became light yellow. The suspension was subjected to ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, Toluene-*d*$_8$): δ 3.39 (s, 2H, OC*H*$_2$), 3.42 (t, $^3J_{HH}$ = 5.4 Hz, 2H, OC*H*$_2$CH$_2$N), 2.45 (t, $^3J_{HH}$ = 5.4 Hz, 2H, OCH$_2$C*H*$_2$N).

Preparation of 5, [(^{Dipp}nacnac)MgAl{N(Dipp)SiMe$_3$}$_2$]

In a glovebox, a sample vial was charged with [IAl{N(Dipp)SiMe$_3$}$_2$] (49.8 mg, 76.5 µmol) and KC_8 (41.4 mg, 306 µmol). The mixture was suspended in toluene (ca. 1 mL) and allowed to rest for 1 hour. This was filtered onto a toluene solution of [(^{Dipp}nacnac)MgI(OEt$_2$)] (29.5 mg, 45.9 mmol). This was heated to 40 °C for 48 hours. The resulting suspension was filtered and recrystalised. The mother liquor was decanted away from the solid which was washed three times with cold pentane. The resulting white solid of compound **5** [(^{Dipp}nacnac)MgAl{N(Dipp)SiMe$_3$}$_2$] was then dried under reduced pressure. (15.6 mg, 21%). Crystals of compound **5** that were suitable for SCXRD were obtained from a saturated solution of toluene at –30 °C.

^{1}H NMR (500 MHz, Toluene-*d*$_8$): δ 7.25 – 6.82 (br., 12H. Ar-*H*), 4.79 (s, 1H, C=C*H*), 4.16 – 3.61 (br., 3H, Dipp-C*H*(CH$_3$)$_2$), 3.37 – 3.08 (br., 4H, Dipp-C*H*(CH$_3$)$_2$), 2.72 (br., 1H, Dipp-C*H*(CH$_3$)$_2$), 1.56 (s, 6H, C=C(C*H*$_3$)), 1.67 – 0.40 (br., 48H, Dipp-CH(C*H*$_3$)$_2$), 0.07 – −0.38 (br., 18H, Si(C*H*$_3$)$_3$). **^{13}C{^{1}H} NMR** (126 MHz, Toluene-*d*$_8$): 169.8 (*C*-Me), 126.0 (Ar-*C*), 96.2 (C=*C*H), 29.0, 27.5, 26.0, 24.8 (Dipp-*C*H(CH$_3$)$_2$, Dipp-CH(*C*H$_3$)$_2$), 7.8, 3.7 (Si-(*C*H$_3$)$_3$. **anal. calc.** for $C_{53}H_{82}AlMgN_4Si_2$: C, 73.37; H, 9.71; N, 5.80 %. Found: C, 74.08; H, 9.70; N, 5.90 %.

X-ray Crystallography

Data for **2** were collected an Agilent Xcalibur diffractometer, while those for **1, 3, 4** and **5** were obtained using an Agilent Supernova machine. All experiments were conducted at 150 K. The structures were solved using SHELXT[7] and refined using SHELXL[8] *via* the Olex2 interface.[9]

Some disorder was present in the structure of **1**. In particular, the methyl group containing C14 and the entire isopropyl group containing C40 were each refined as two-components, in a 70:30 ratio. The iodine was also clearly disordered (96:04 ratio) and there was evidence (albeit not as strong as for the iodine) that a similar amount of disorder also pertained to the aluminium centre. Both disorders were modelled. The largest difference peak and hole are respectively located at 1.09 Å and 0.65 Å from I1 and, as such, are chemically insignificant. They most likely manifested because of absorption ripples that accompany the crystal shape.

In **3**, the asymmetric unit comprises a monomer, which contributes to the formation of a 1-dimensional polymer along that propagates along the *b*-axis. H1 was located and refined without restraints.

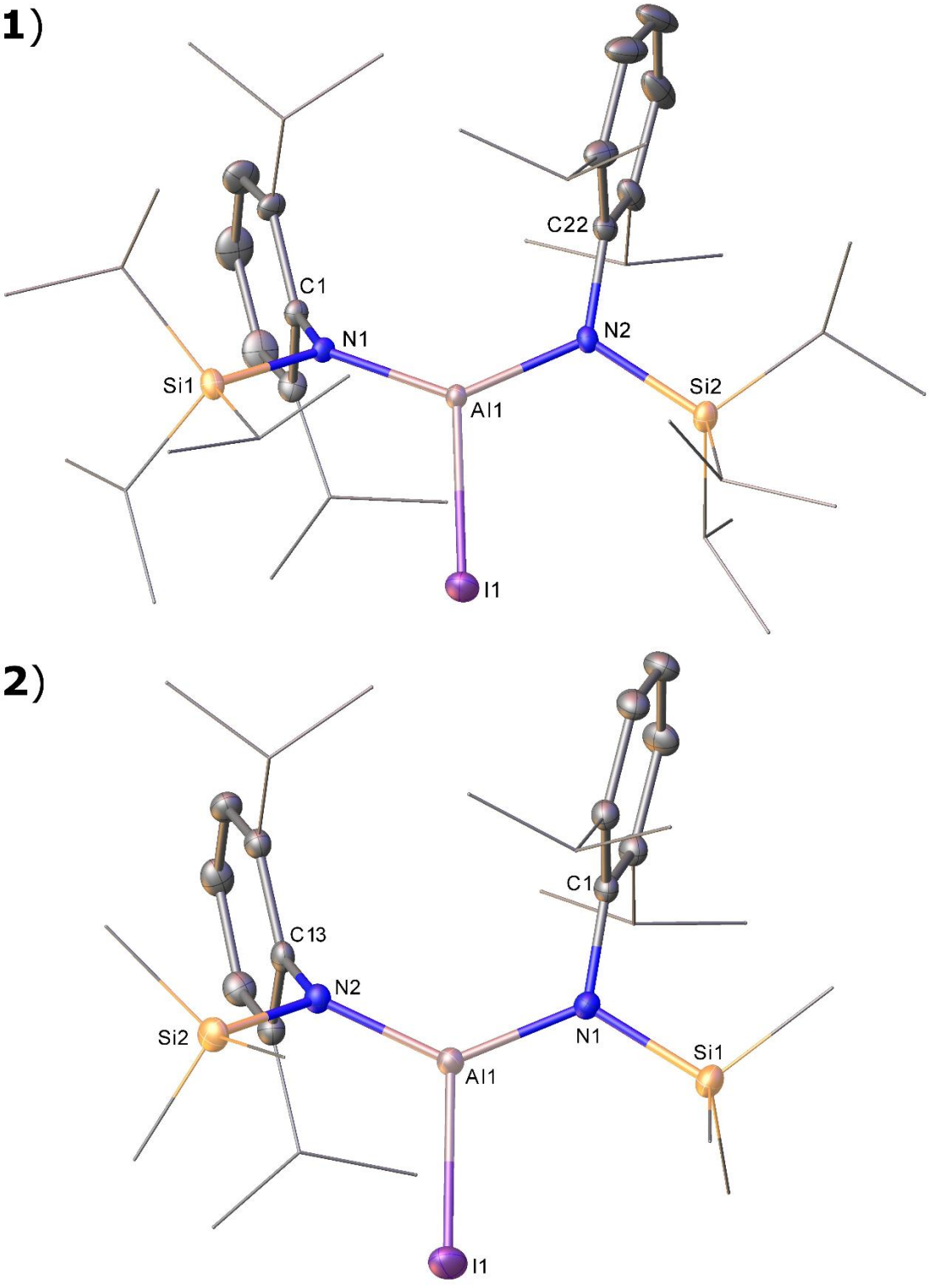
Two independent dimer halves constitute the asymmetric unit in the structure of **4**, along with some benzene solvent. The latter was disordered and while it could be modelled to take account of same, this introduced some 390 restraints. However, the sample quality was not optimal in this case and, hence, the solvent was ultimately addressed using the solvent-mask algorithm available in Olex2 with an allowance being made for eight molecules of benzene per unit cell, in the formula as presented. The aforementioned sample deficiencies are evidenced by the higher than desirable merging *R*-factor, the need to truncate the data at a resolution of 0.84 Å due to diffraction fall-off, and the suggestion of 66 systematic absence violations. These putative violations are weak and a facet of some streaking of the diffraction maxima observed. Nonetheless, to avoid unfounded assumptions, the data were integrated in a monoclinic setting and structure the was both solved and refined in the lower symmetry space-group, $P2_1$. This exercise did not provide any credible evidence for a symmetry change or for twinning beyond the racemic type implemented in the orthorhombic setting.

In conclusion, overall, this single crystal determination provides unambiguous proof of the identity of this material, but the raw data quality precludes detailed scrutiny or comparison of the metrics.

Finally, the asymmetric unit in **5** hosts one molecule of toluene in addition to one molecule of the bimetallic complex. The solvent was treated for 50:50 disorder with employment of distance and ADP restraints in this region, on merit, to assist convergence.

CCDC 2218546-2218550 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via

www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



Molecular structures (30% probability ellipsoids) of [IAl{N(Dipp)Si(*i*-Pr)$_3$}$_2$] (**1**) and [IAl{N(Dipp)SiMe$_3$}$_2$] (**2**). Hydrogen atoms have been omitted. *iso*-Propyl groups and silicon bound methyl groups have been represented in wireframe view, for clarity.

Table S1. Crystal data and structure refinement details.

Identification code	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{42}H_{76}AlIN_2Si_2$	$C_{30}H_{52}AlIN_2Si_2$	$C_{42}H_{76}AlKN_2Si_2$	$C_{36}H_{58}AlKN_2Si_2$	$C_{66}H_{101}AlMgN_4Si_2$
Formula weight	819.10	650.79	731.30	641.10	1057.97
Crystal system	150.00(10)	149.9(7)	150.00(10)	150.00(10)	150.01(10)
	monoclinic	triclinic	orthorhombic	orthorhombic	triclinic
Space group	$P2_1/c$	P-1	$P2_12_12_1$	$P2_12_12$	P-1
a/ Å	18.8006(2)	10.1072(6)	13.19442(16)	22.1102(5)	12.8772(5)
b/ Å	13.66544(13)	10.2573(6)	14.99103(15)	33.7684(8)	14.6377(6)
c/ Å	18.6649(2)	17.9608(8)	22.2823(2)	10.7300(3)	17.2412(6)
α/ °	90	89.292(4)	90	90	87.531(3)
β/ °	112.8002(15)	83.539(4)	90	90	83.372(3)
γ/ °	90	66.374(6)	90	90	84.087(3)
U/ Å^3	4420.64(10)	1694.04(18)	4407.38(8)	8011.3(3)	3209.3(2)
Z	4	2	4	8	2
ρ_{calc}/ g cm^{-3}	1.231	1.276	1.102	1.063	1.095
μ/ mm^{-1}	6.608	1.062	1.972	0.239	1.026
F(000)	1744.0	680.0	1608.0	2784.0	1156.0
Crystal size/ mm^3	0.3 × 0.18 × 0.04	0.244 × 0.165 × 0.101	0.299 × 0.219 × 0.166	0.345 × 0.275 × 0.068	0.251 × 0.176 × 0.157
	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.24 to 147.364	5.978 to 60.558	7.108 to 147.33	6.608 to 50.084	6.944 to 145.278
Index ranges	−23 ≤ h ≤ 23,	−12 ≤ h ≤ 13,	−15 ≤ h ≤ 16,	−26 ≤ h ≤ 26,	−14 ≤ h ≤ 15,
	−12 ≤ k ≤ 16,	−14 ≤ k ≤ 11,	−18 ≤ k ≤ 18,	−40 ≤ k ≤ 40,	−12 ≤ k ≤ 18,
	−22 ≤ l ≤ 23	−25 ≤ l ≤ 23	−27 ≤ l ≤ 16	−12 ≤ l ≤ 12	−20 ≤ l ≤ 21
Reflections collected	31520	16043	15603	86594	23418
Independent reflections, R_{int}	8869, 0.0379	8652, 0.0244	8594, 0.0250	14148, 0.0785	12477, 0.0176
Data/restraints/parameters	8869/97/504	8652/0/339	8594/0/457	14148/0/678	12477/217/732
Goodness–of–fit on F^2	1.034	1.035	1.038	1.073	1.008
Final R1, wR2 [I>=2σ(I)]	0.0696, 0.2034	0.0479, 0.1162	0.0409, 0.1050	0.0578, 0.1562	0.0426, 0.1183
Final R1, wR2 [all data]	0.0715, 0.2058	0.0678, 0.1280	0.0439, 0.1081	0.0616, 0.1595	0.0466, 0.1224
Largest diff. peak/hole/ e Å^{-3}	1.52/−2.42	0.79/−1.29	0.53/−0.20	0.67/−0.26	0.56/−0.31
Flack Parameter	−	−	−0.008(6)	0.41(7)	−

Diffusion Ordered Spectroscopy

DOSY was performed using the ^{1}H NMR spectroscopic resonances associated with compound **4** and K_2[**III**$^{\mathbf{Dipp}}$]$_2$[6] in toluene-d_8 respectively. The diffusion coefficient was converted to a hydrodynamic radius using.

$$D = \frac{k_B T}{6\pi\eta R_H}$$

Compound	Diffusion Coefficient /10^{-10} m^2 s^{-1}	Hydrodynamic radius / Å
4	5.87	6.74
K_2[**III**$^{\mathbf{Dipp}}$]$_2$	5.84	6.78

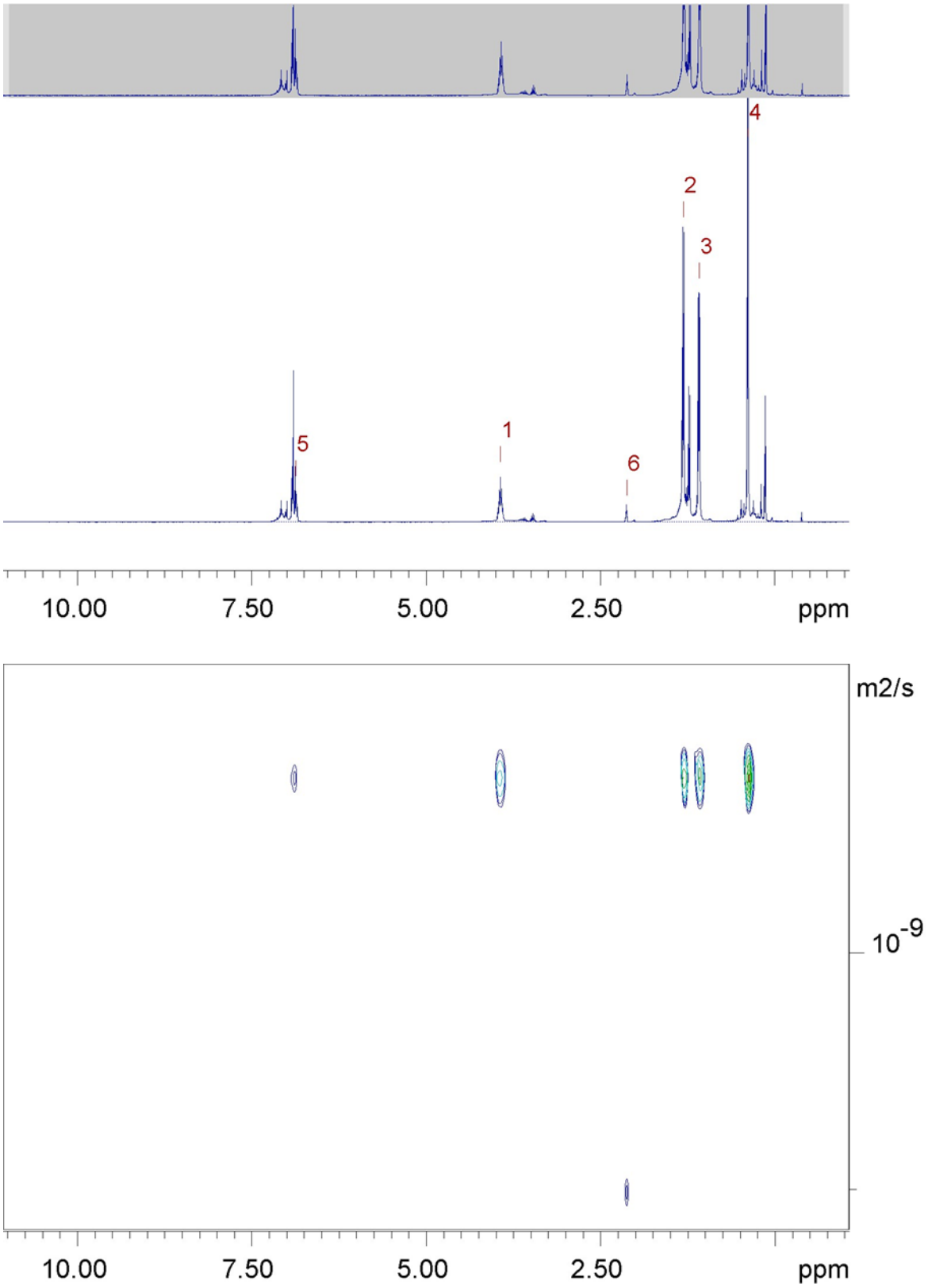
Where D = diffusion coefficient, k = Boltzmann constant, T = absolute temperature, η = viscosity and r_H = hydrodynamic radius.

Calculated volumes were obtained from X-ray structures using the molinfo command in Olex2. These were then converted into radii using the following equation:

$$r = \sqrt[3]{\frac{3V}{4\pi}}$$

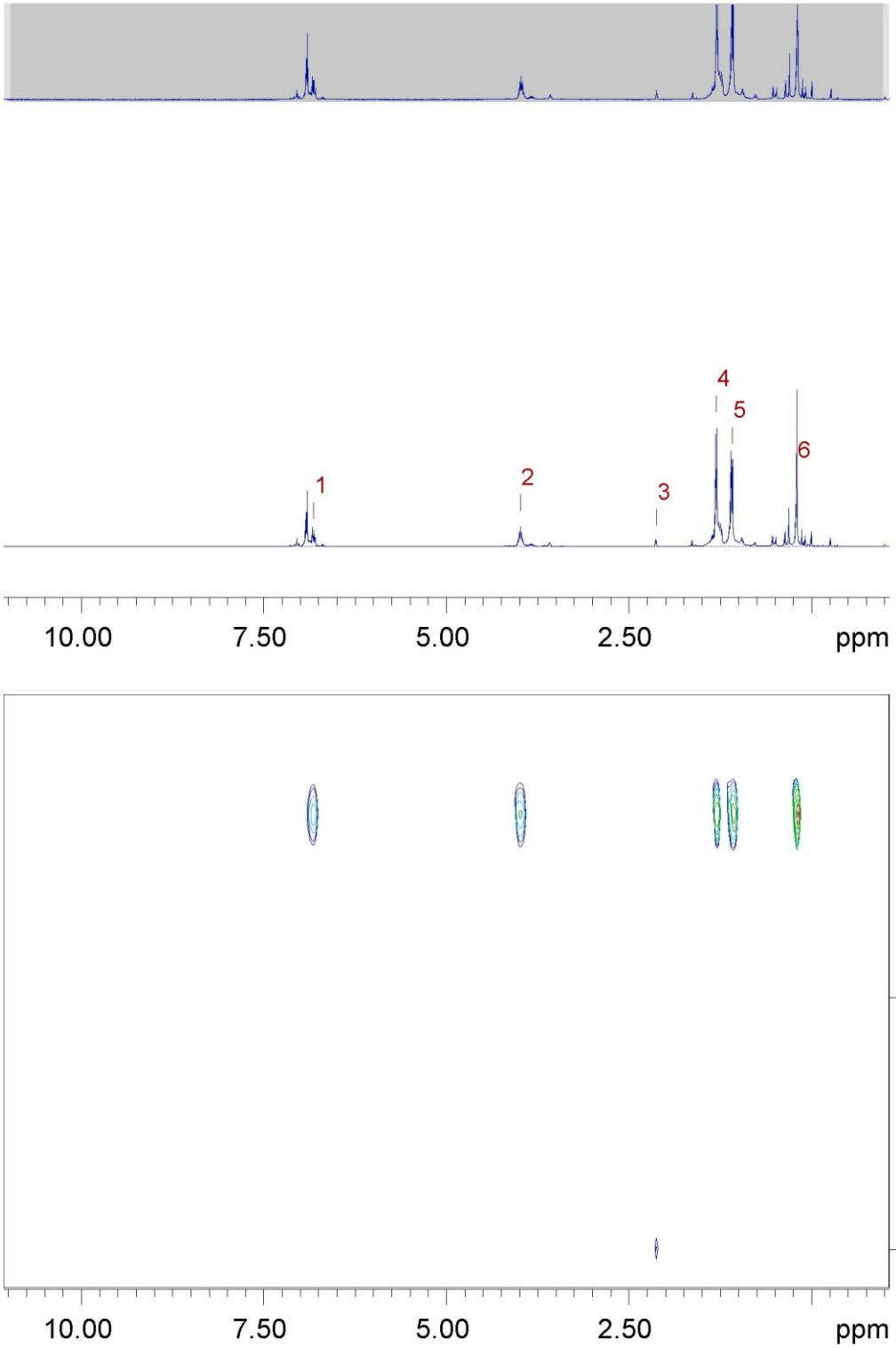
Compound	Volume$_{x\text{-}ray}$ / Å^3	Radius$_{x\text{-}ray}$ / Å^3
4	1107.22	6.42
K_2[**III**$^{\mathbf{Dipp}}$]$_2$	1079.00	6.36

^{1}H NMR DOSY Data for Compound 4



Peak	Chemical shift	Diffusion Coefficient	Error
	/ppm	/10^{-10} m^2 s^{-1}	/10^{-10} m^2 s^{-1}
1	3.934	5.87	0.02436
2	1.312	5.96	0.03849
3	1.085	6.03	0.1612
4	0.382	5.75	0.3027
5	6.876	5.86	0.3972
6 (solvent)	2.126	20.9	0.1365

^{1}H NMR DOSY Data for Compound $K_2[III^{Dipp}]_2$



Peak	Chemical shift /ppm	Diffusion Coefficient /10^{-10} m^2 s^{-1}	Error /10^{-10} m^2 s^{-1}
1	6.815	5.86	0.06501
2	3.982	5.84	0.03075
3 (Solvent)	2.125	20.6	0.3617
4	1.300	5.96	0.08137
5	1.082	5.83	0.1383
6	0.194	5.86	0.1332

NMR Spectra

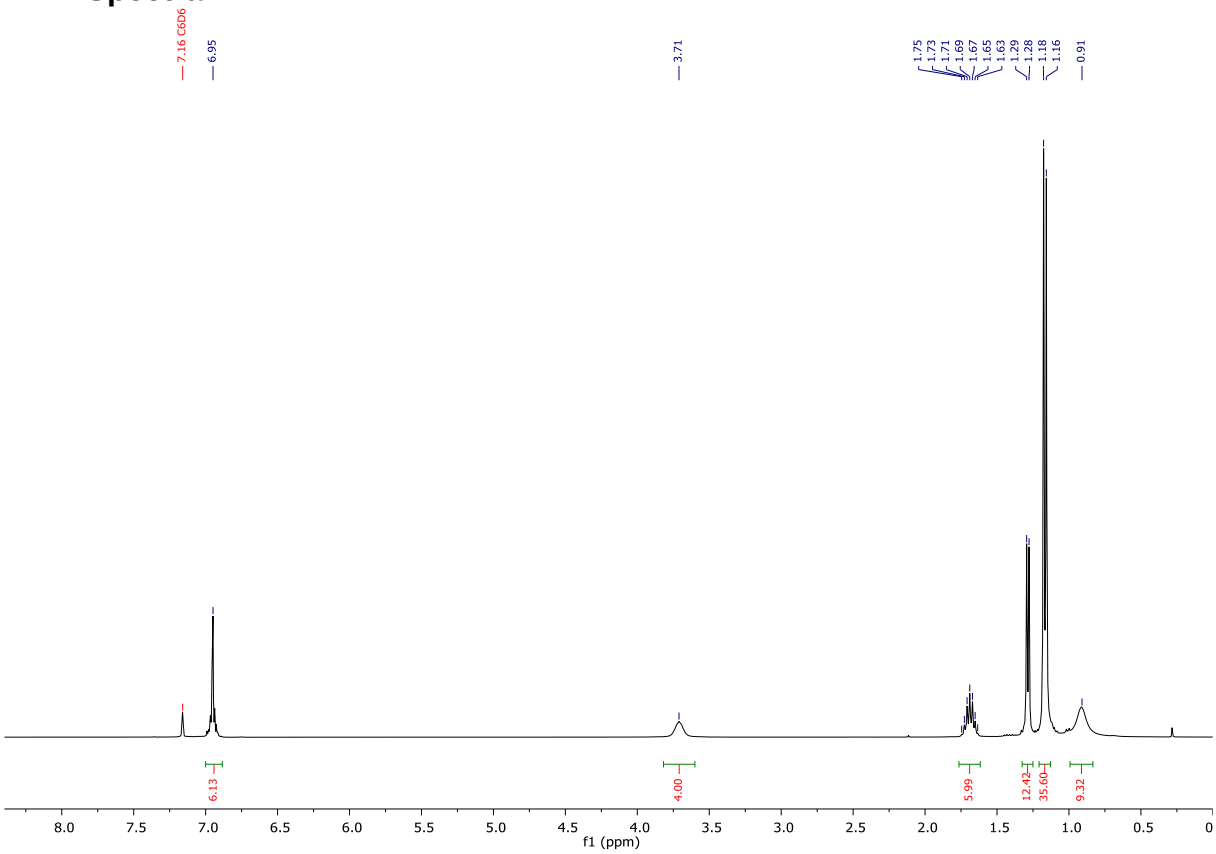


Figure S1: The ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **1**.

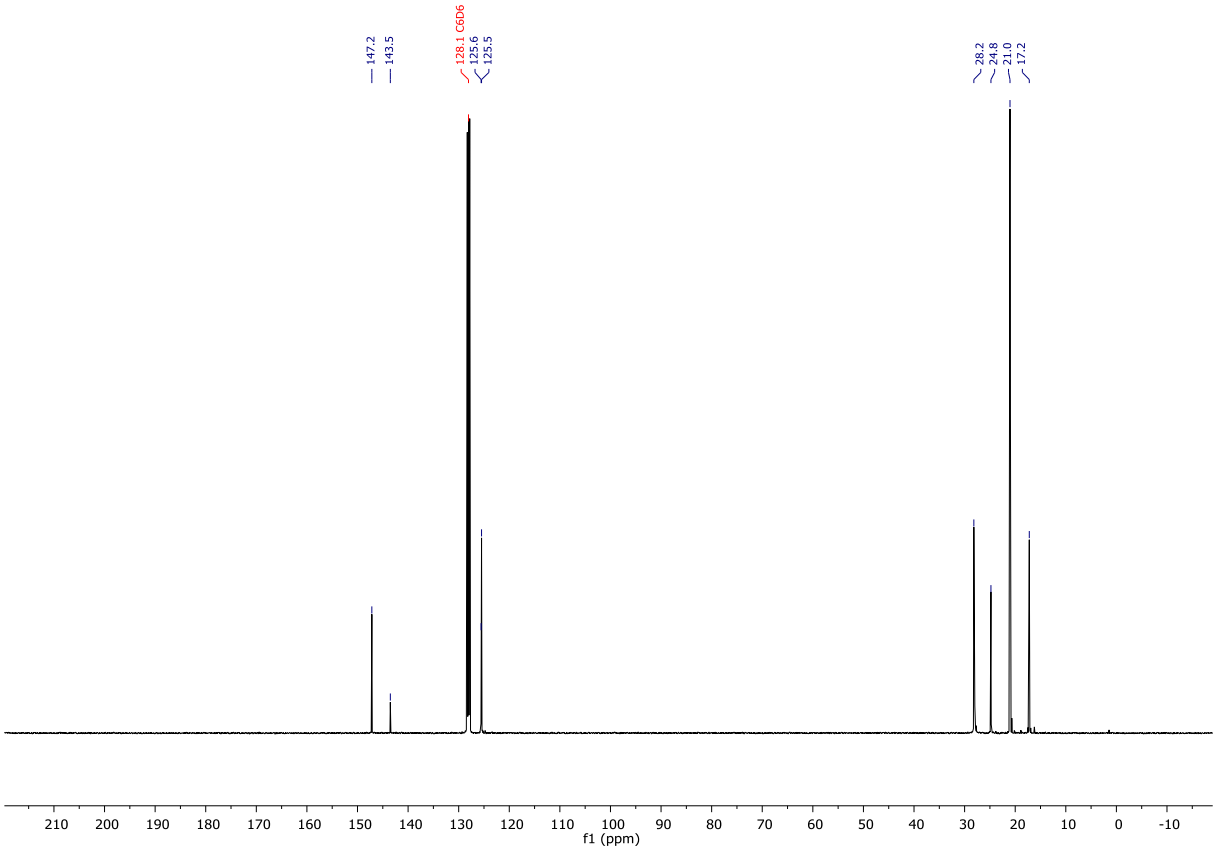


Figure S2: The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of compound **1**.

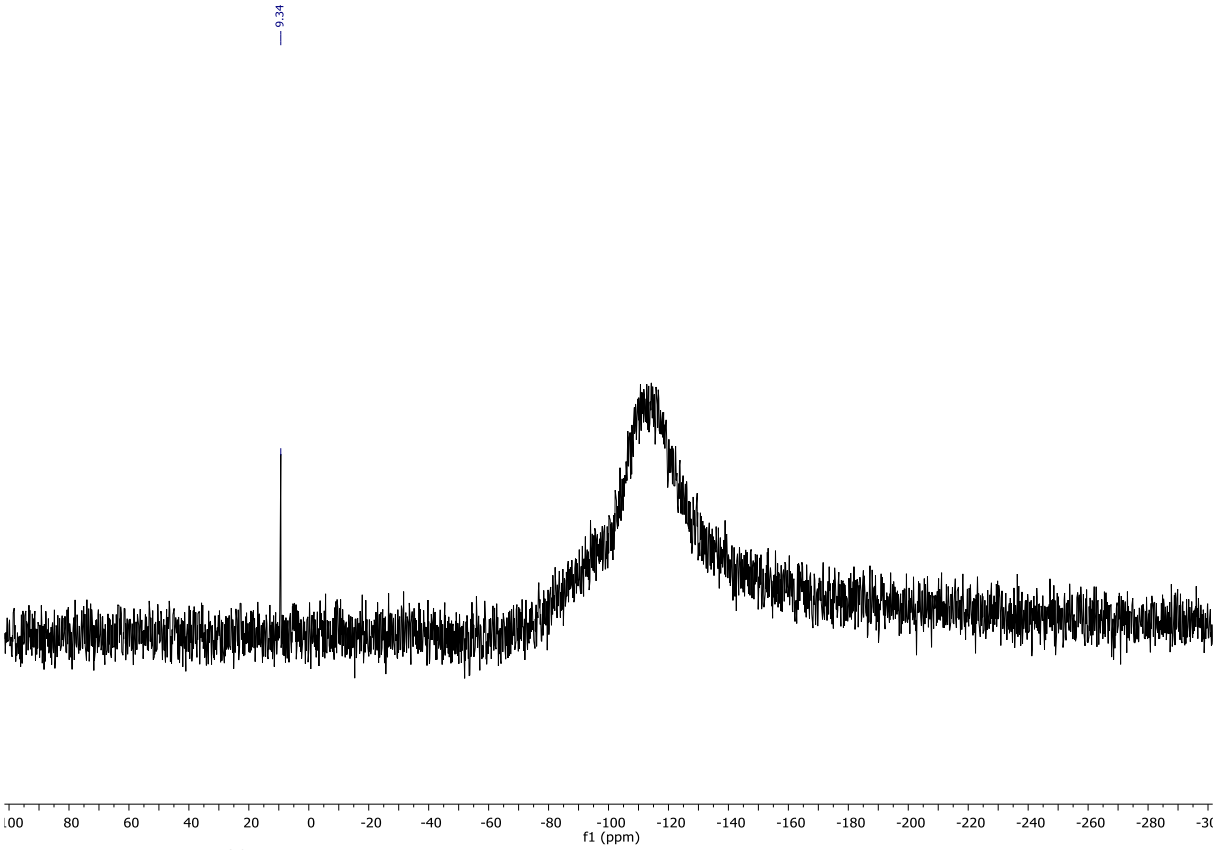


Figure S3: The $^{29}Si\{^{1}H\}$ NMR spectrum (79 MHz, C_6D_6) of compound **1**.

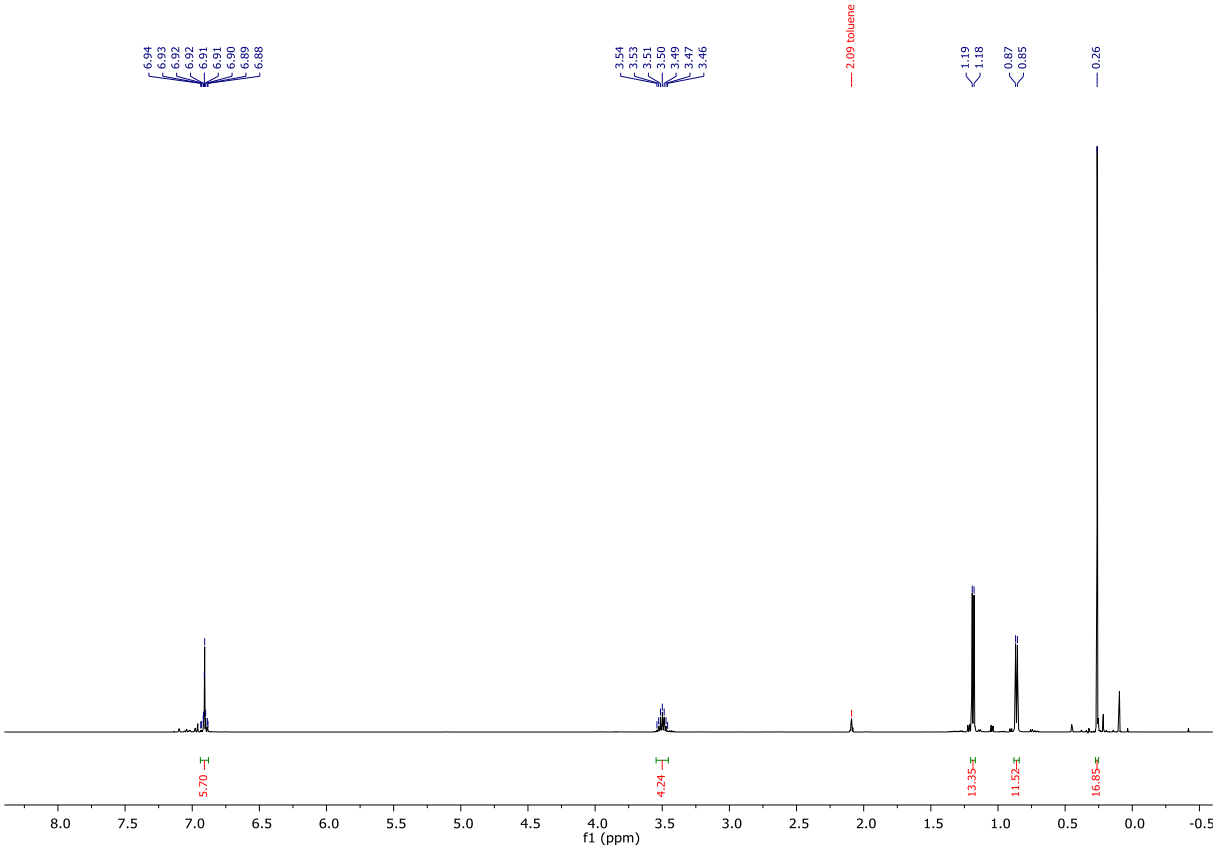


Figure S4: The ^{1}H NMR spectrum (500 MHz, Toluene-d_8) of compound **2**.

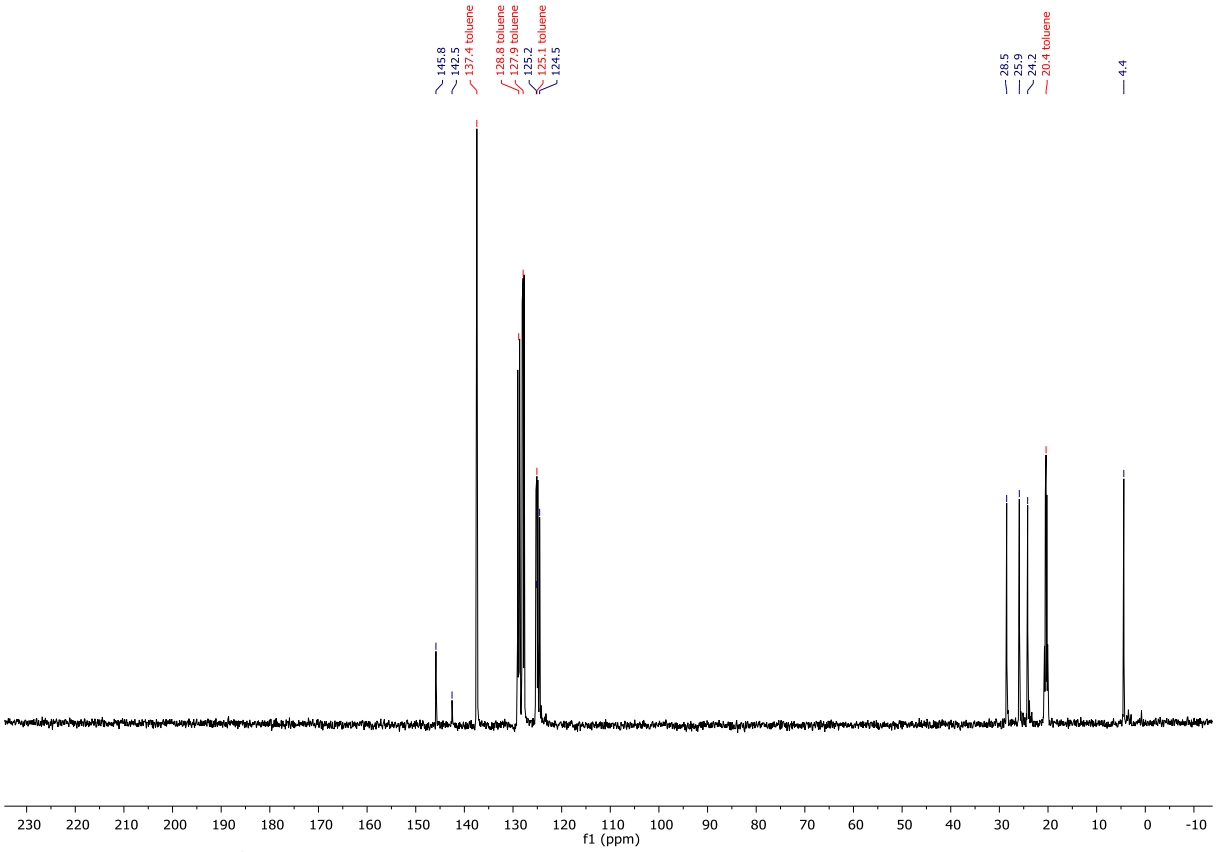


Figure S5: The $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, Toluene-d_8) of compound **2**.

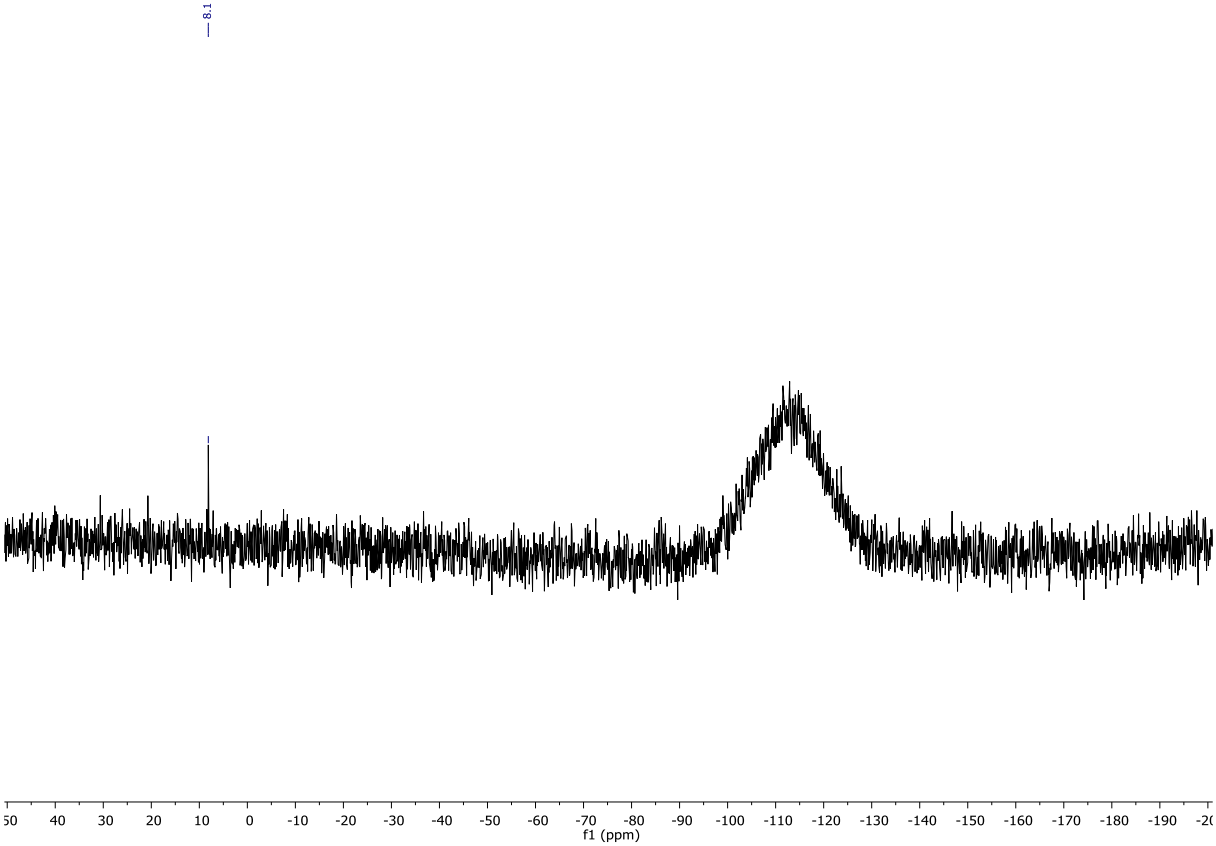


Figure S6: The $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, Toluene-d_8) of compound **2**.

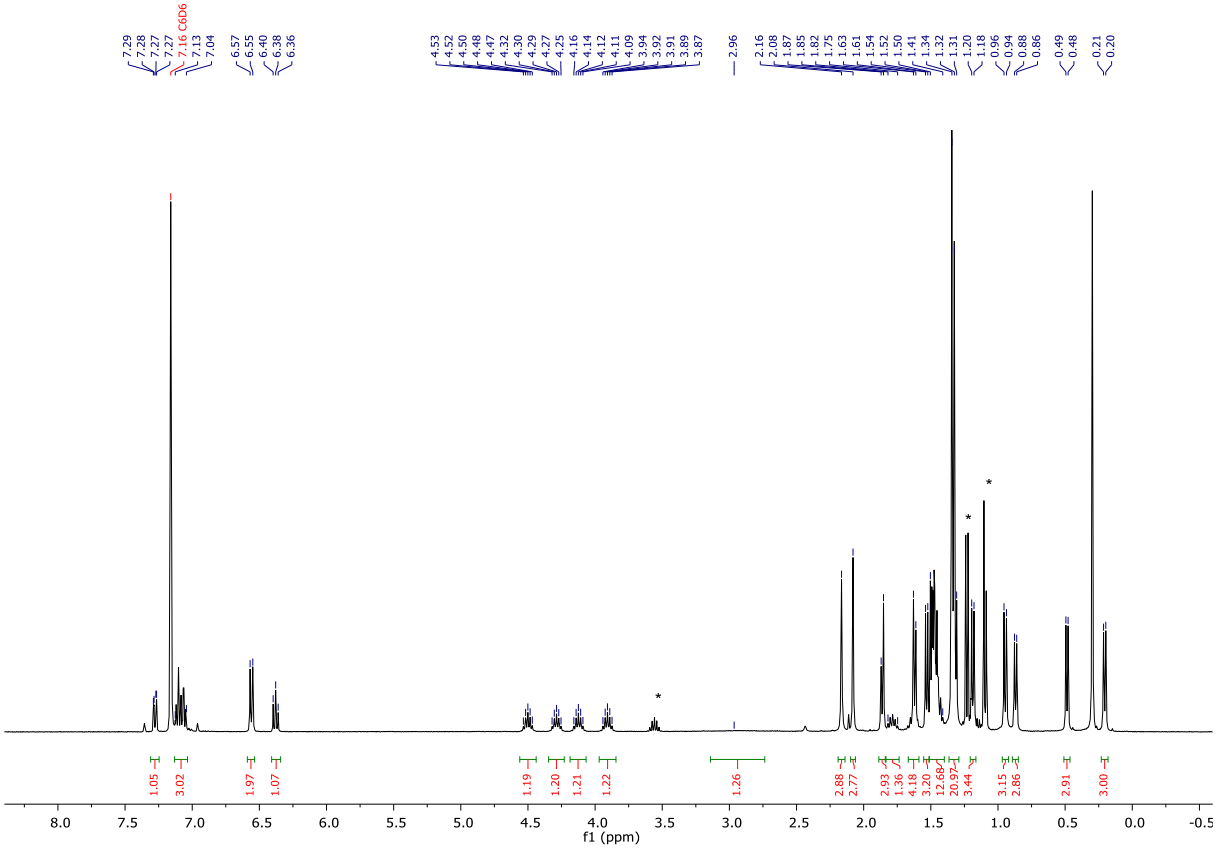


Figure S7: The ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **3**. * = HN(Si(*i*-Pr)$_3$)Dipp residue.

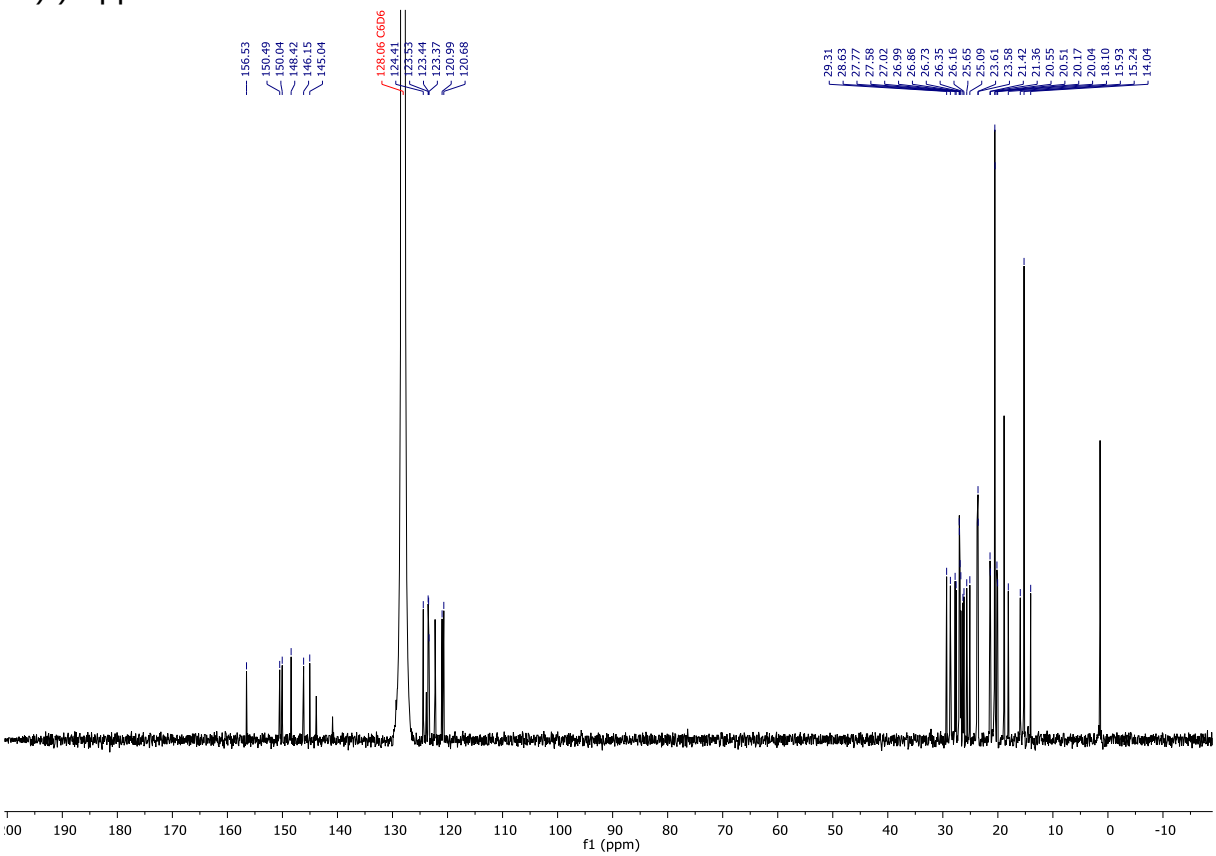


Figure S8: The $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, C_6D_6) of compound **3**.

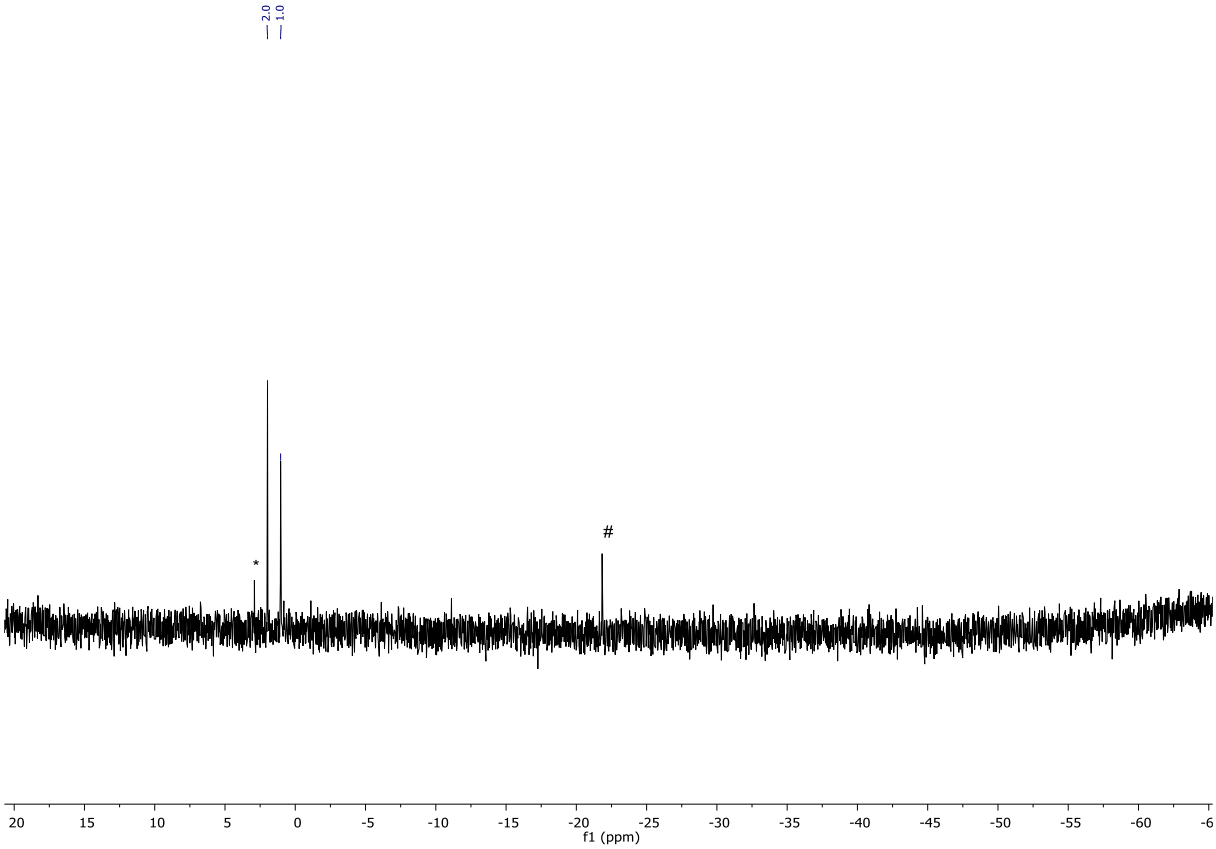


Figure S9: The $^{29}Si\{^{1}H\}$ NMR spectrum (139 MHz, C_6D_6) of compound **3**. * = HN(Si(*i*-Pr)$_3$)Dipp residue. # = Silicon grease.

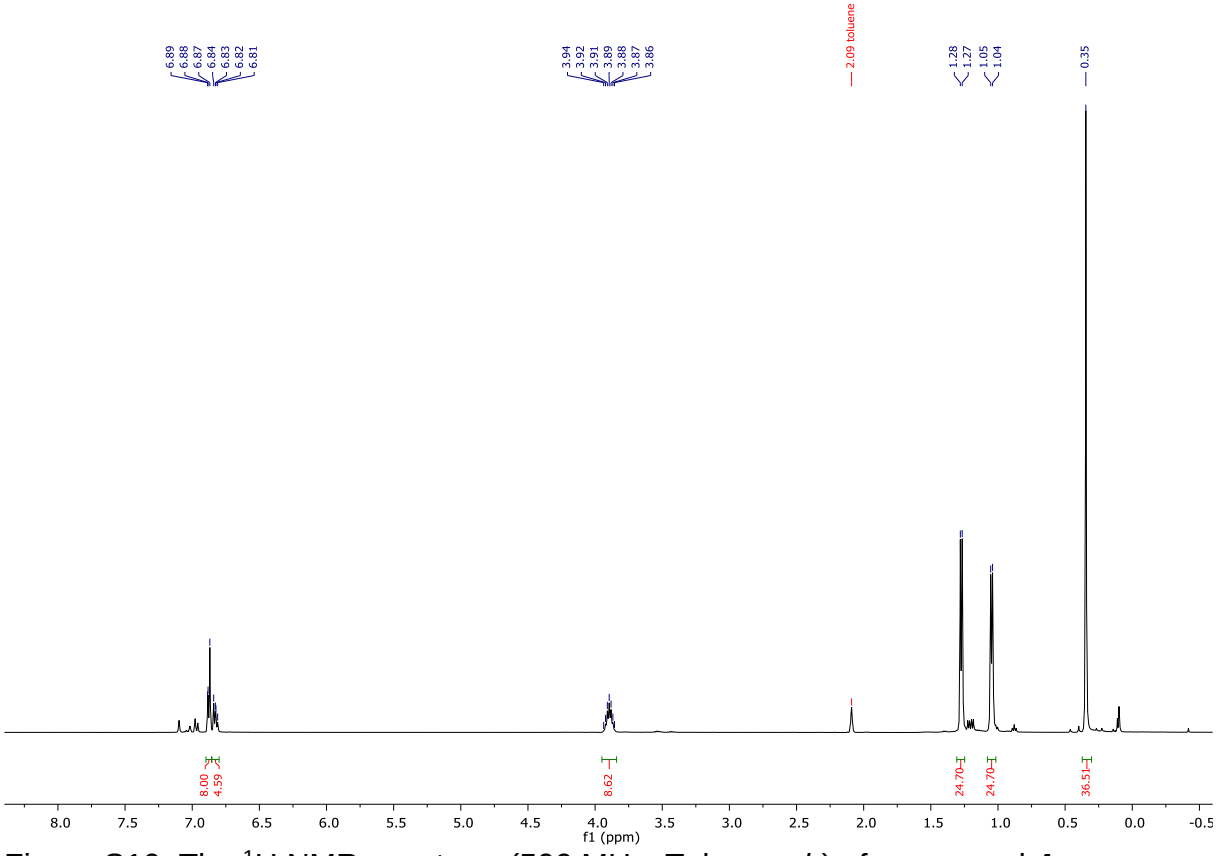


Figure S10: The ^{1}H NMR spectrum (500 MHz, Toluene-d_8) of compound **4**.

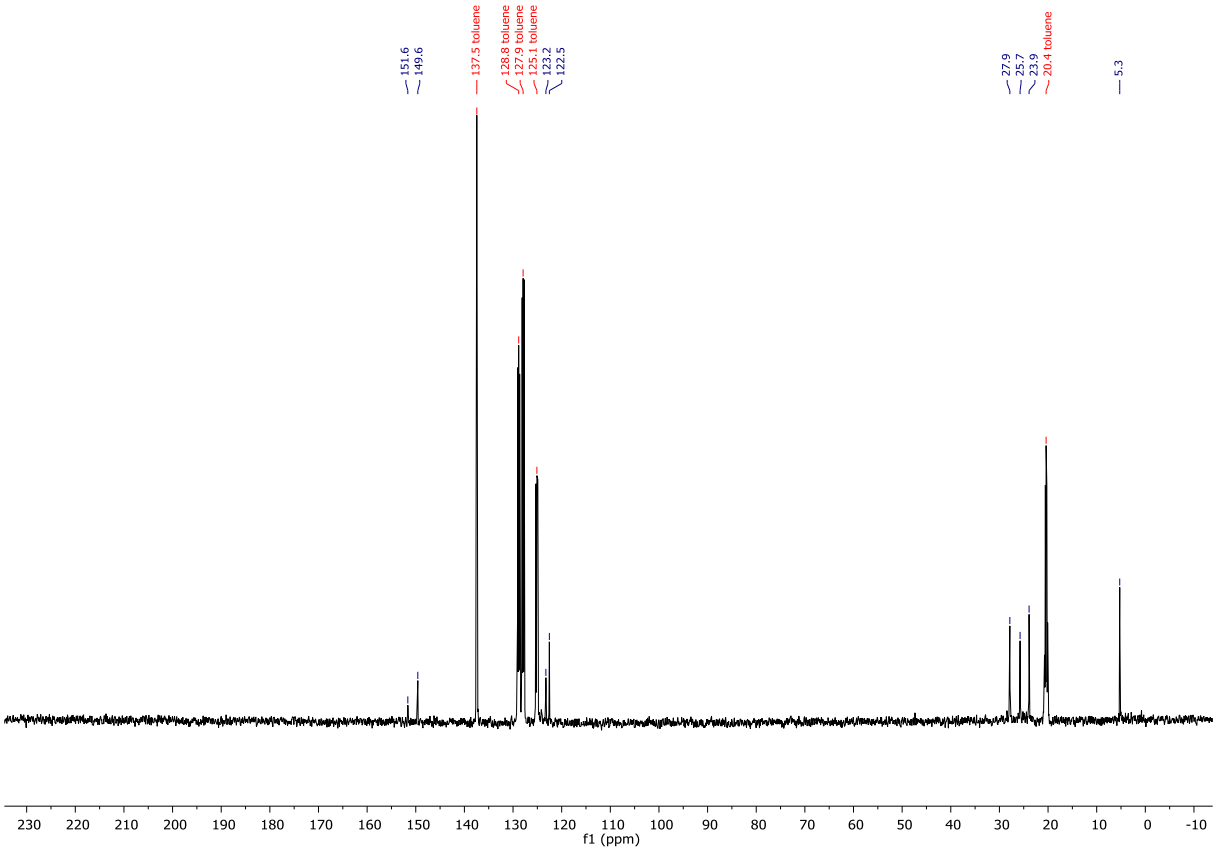


Figure S11: The $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, Toluene-d_8) of compound **4**.

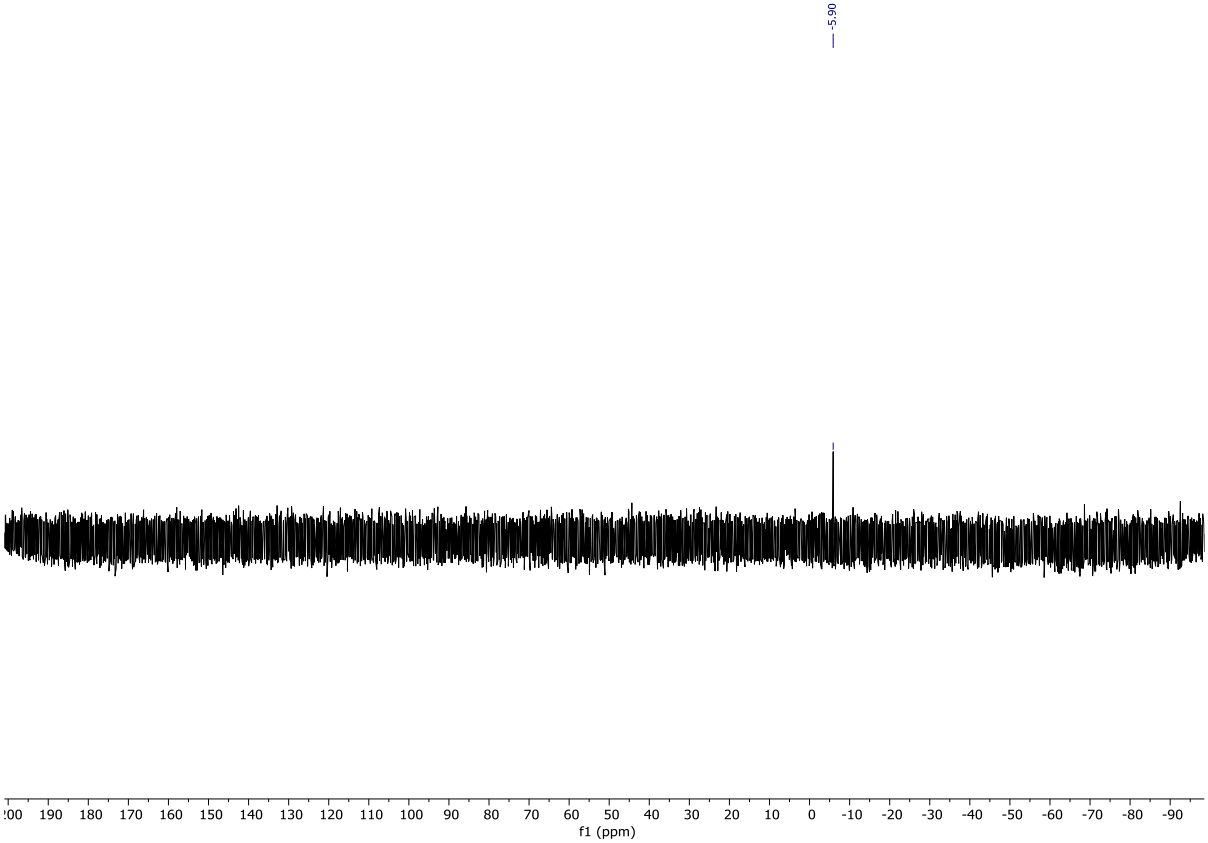


Figure S12: The $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, Toluene-d_8) of compound **4**.

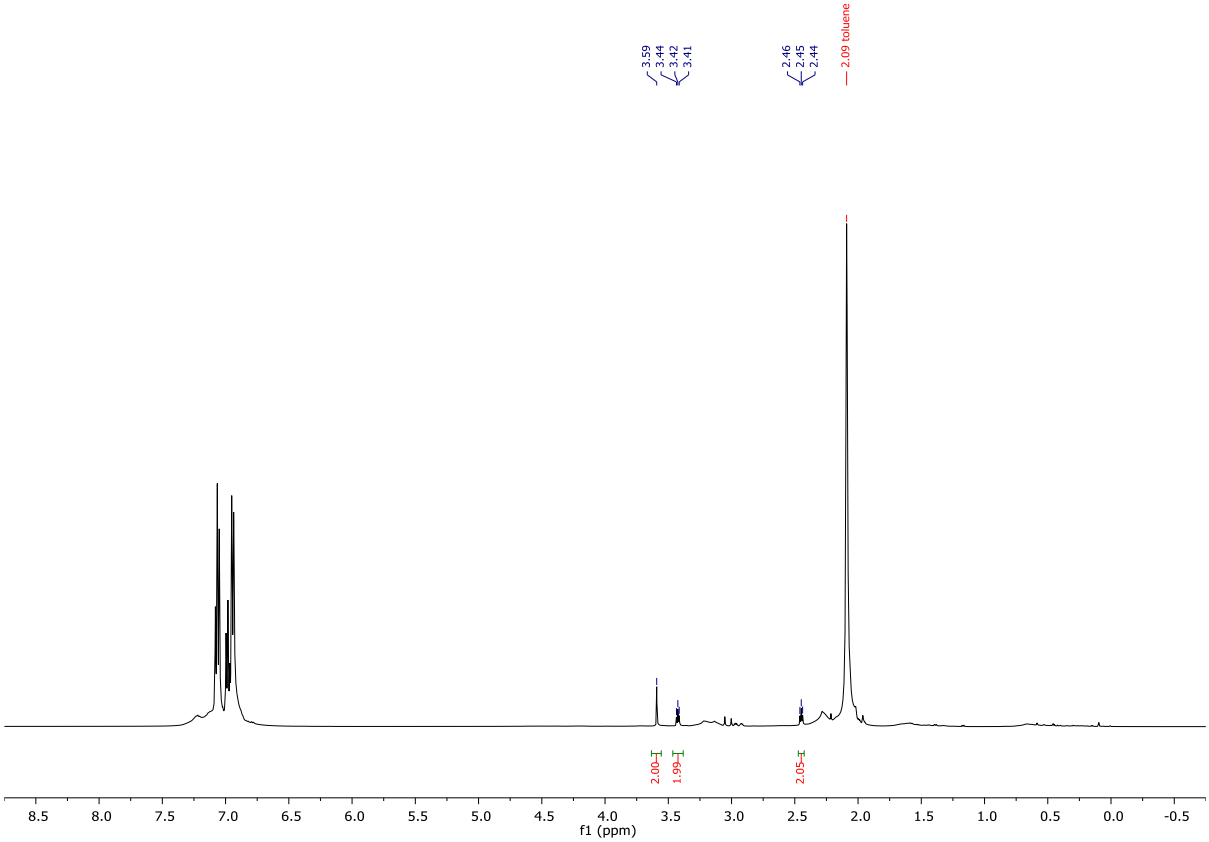


Figure S13. The ^{1}H NMR spectrum (400 MHz, Toluene-d_8) of the reaction mixture obtained after 1 equiv. of 2.2.2-cryptand to compound **4**.

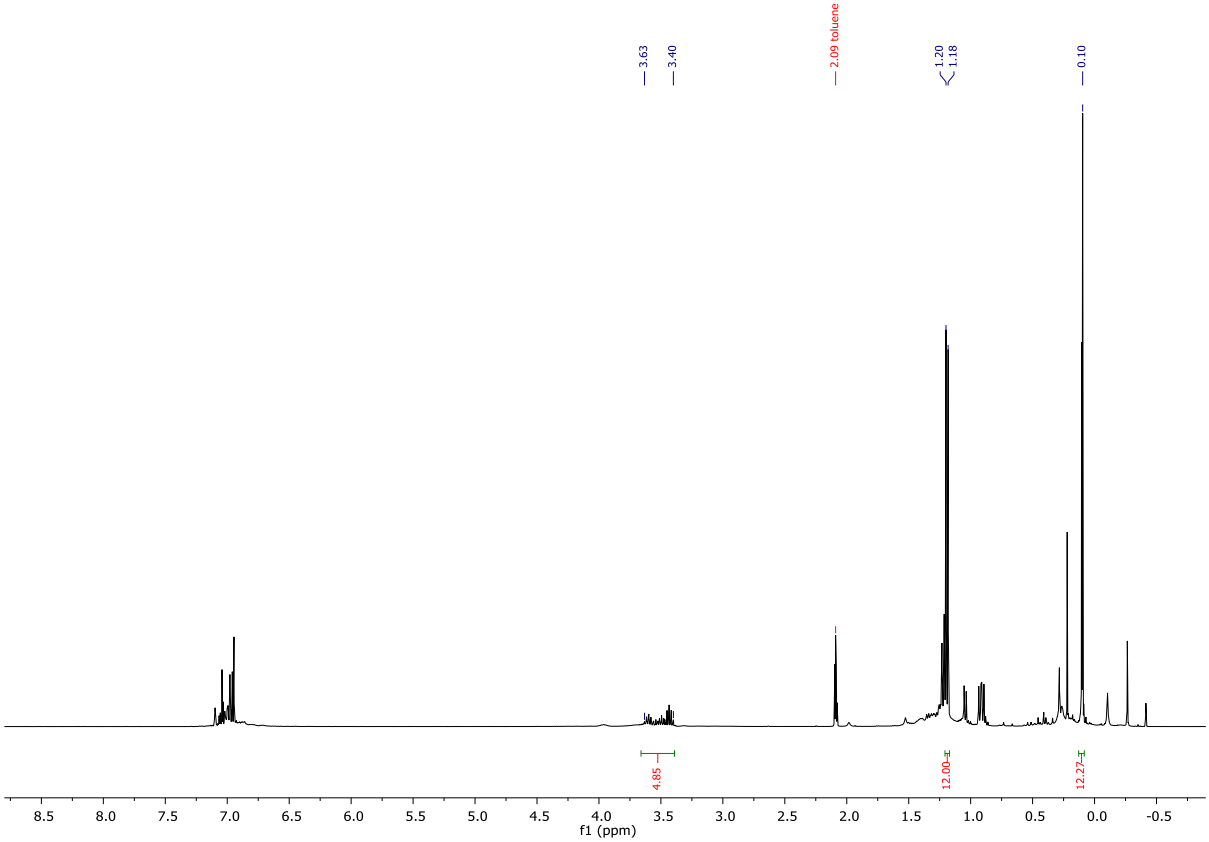


Figure S14. The ^{1}H NMR spectrum (400 MHz, Toluene-d_8) of compound **4** after heating at 80 °C for 24 hours.

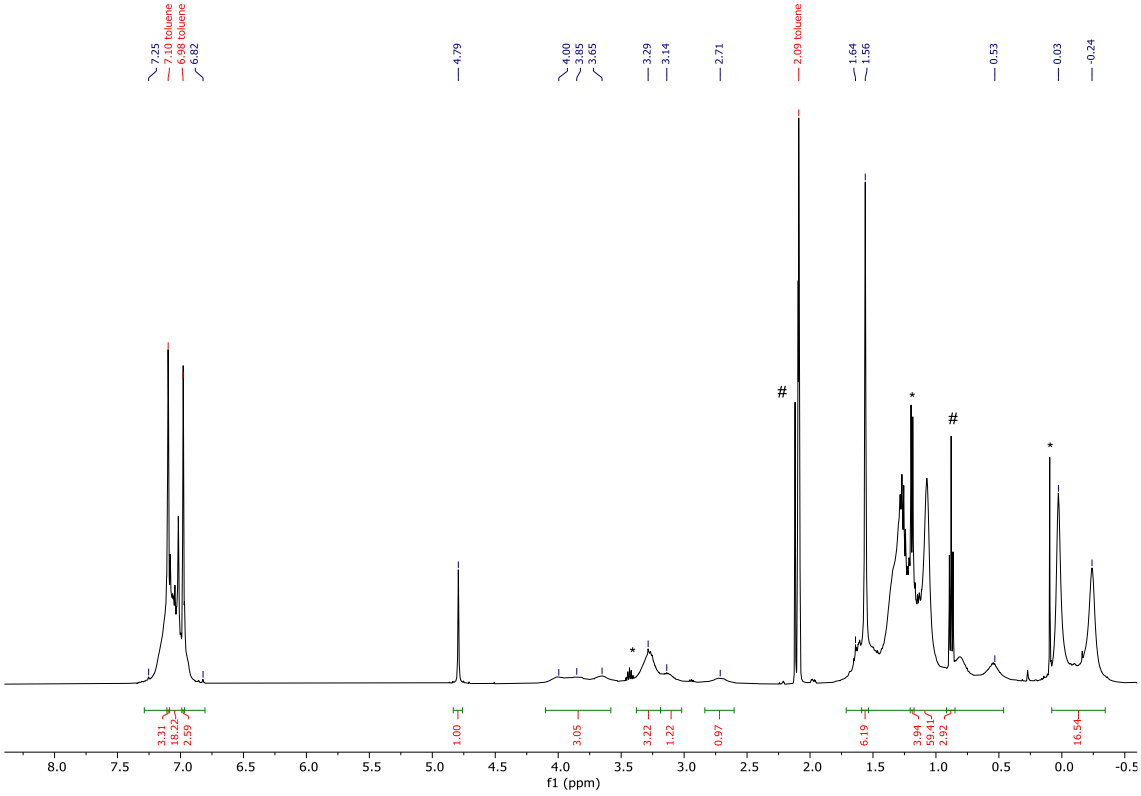


Figure S15: The ^{1}H NMR spectrum (500 MHz, Toluene-d_8) of compound **5**. * = HN(Dipp)SiMe$_3$ residue. # = Solvent residue.

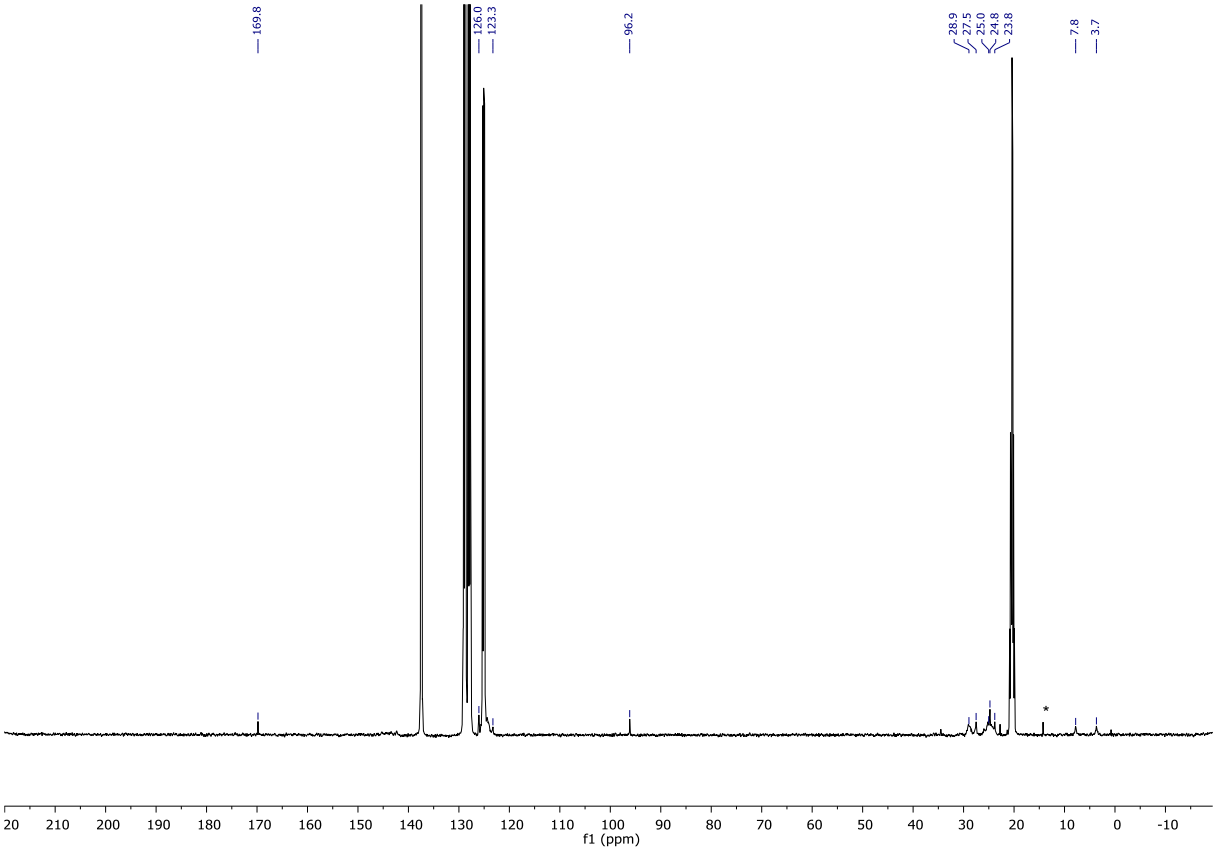


Figure S16. The $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, Toluene-d_8) of compound **5**. * = Solvent residue.

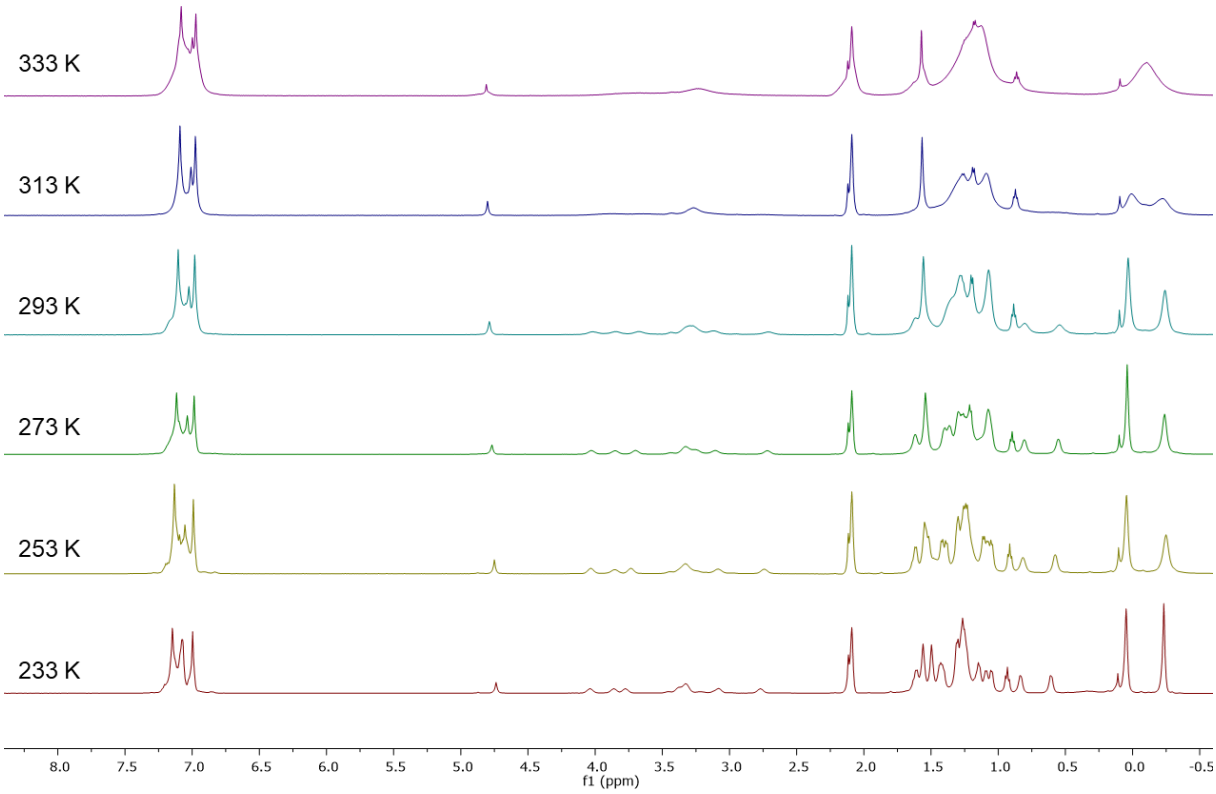


Figure S17: The variable temperature ^{1}H NMR spectra of compound **5** in Toluene-d_8 (500 MHz).

IR Spectrum

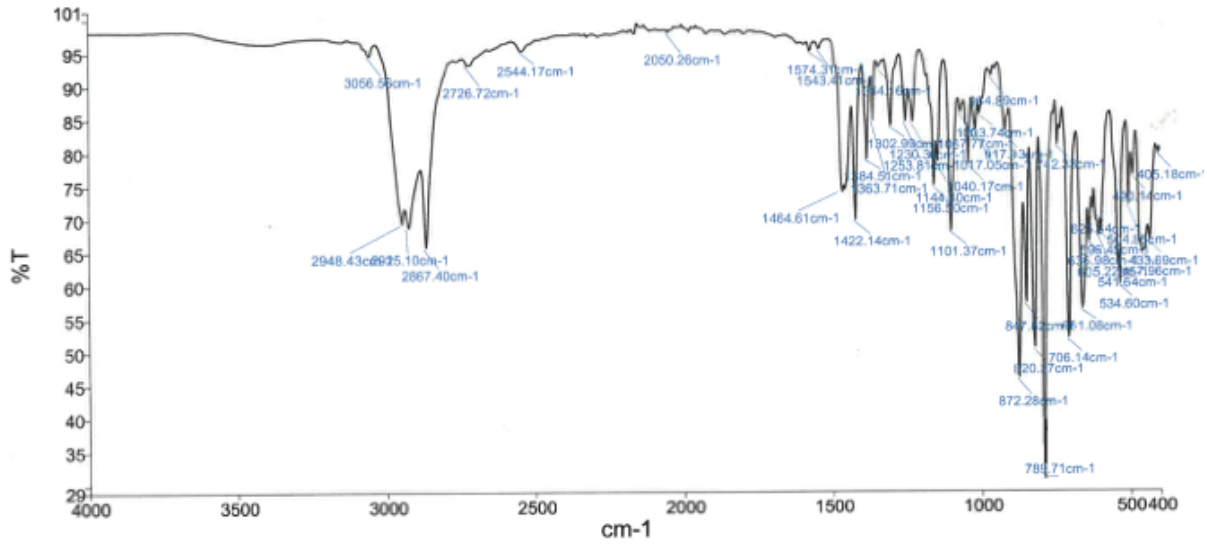


Figure S18: The IR spectrum of compound **1**.

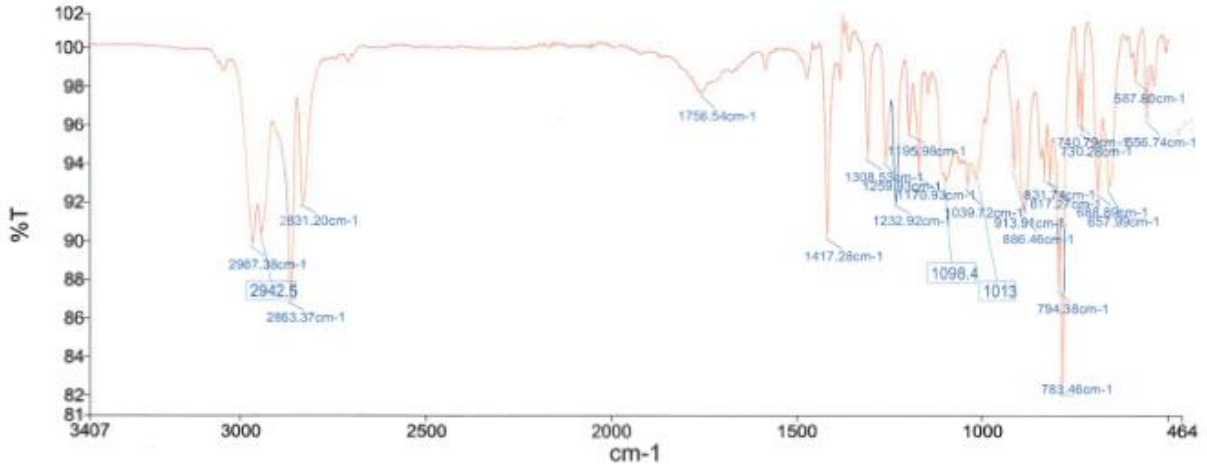


Figure S19: The IR spectrum of compound **3**.

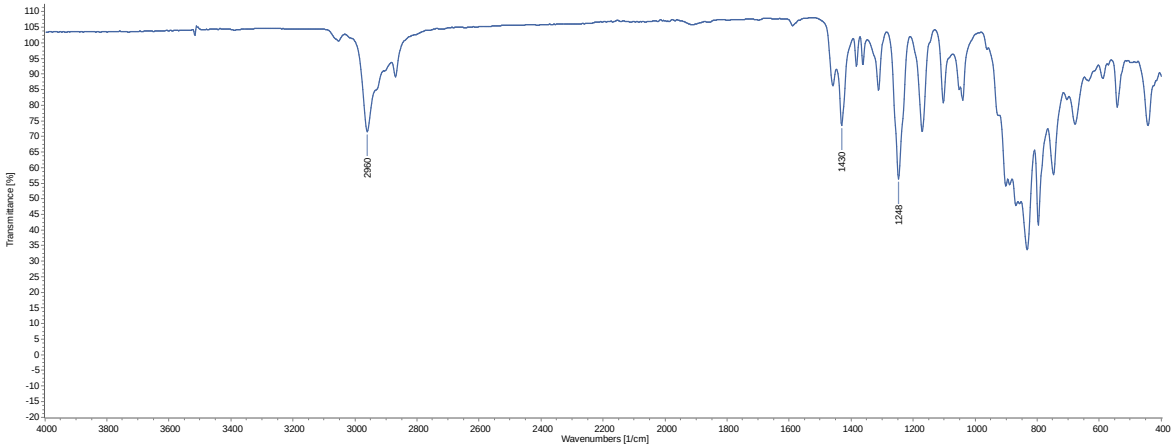


Figure S20: The IR spectrum of compound **4**. Peaks (cm^{-1}) 2960, 1430, 1248.

UV-Vis Spectrum

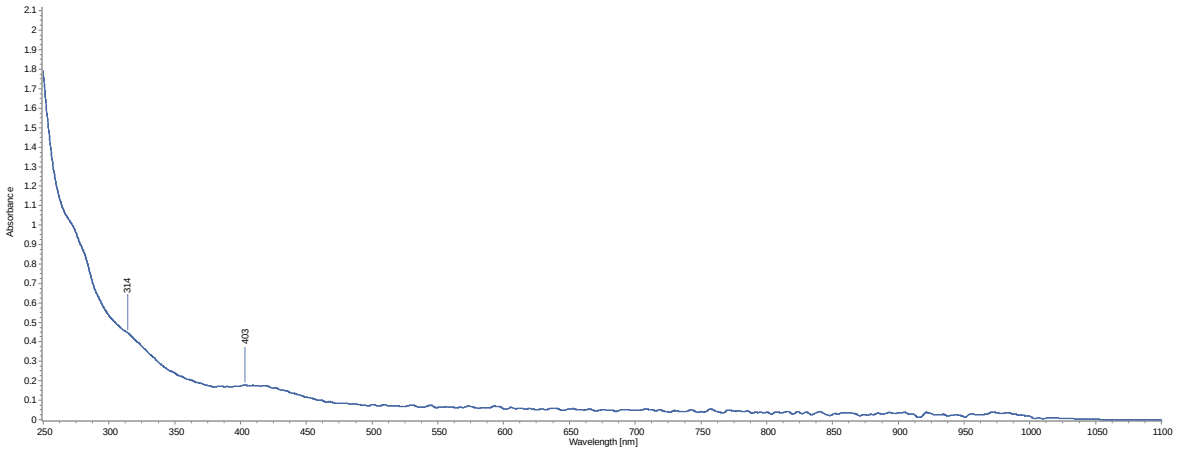


Figure S21: The UV-Vis spectrum of compound **4** in toluene.

Computational details

All DFT work presented here was done using Gaussian16 (Revision C.01)[10]. Geometry optimizations and frequency calculations were done by using the PBE1PBE functional,[11–13] Def2-TZVP basis set[14] for all atoms (for I, an effective core potential was used to treat the core electrons), Grimme's empirical dispersion correction with Becke-Johnson damping (GD3BJ)[15] and an ultrafine integration grid. The stationary points found were confirmed to be minima on the potential energy surface (no imaginary frequencies). Bond analyses using NBO3.1 as implemented in Gaussian16 or AIMAll (QTAIM) programmes were performed for the optimized geometry of **5**.[16]

FMOs for compounds 1 and 2

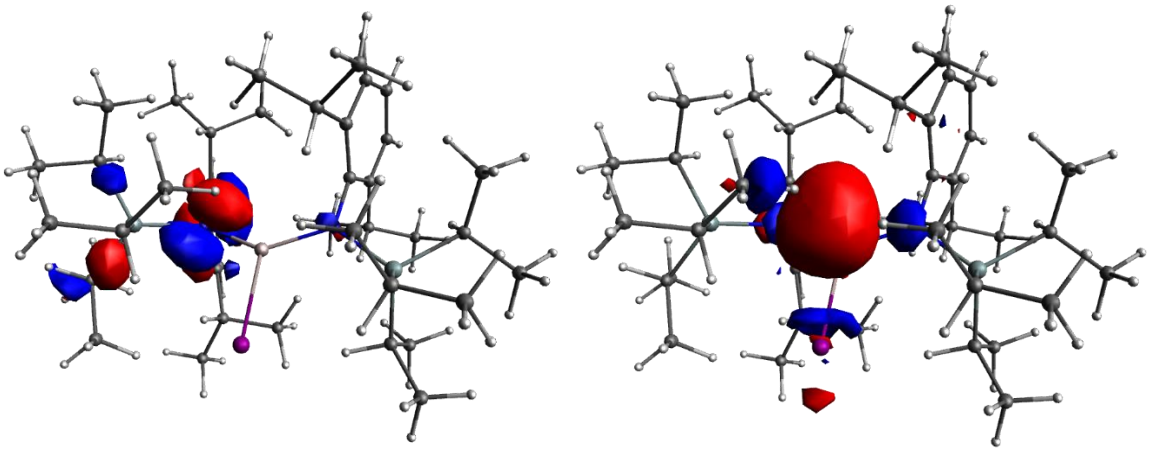


Figure S19. HOMO (left, -6.458 eV) and LUMO (right, -0.685 eV) of **1**.

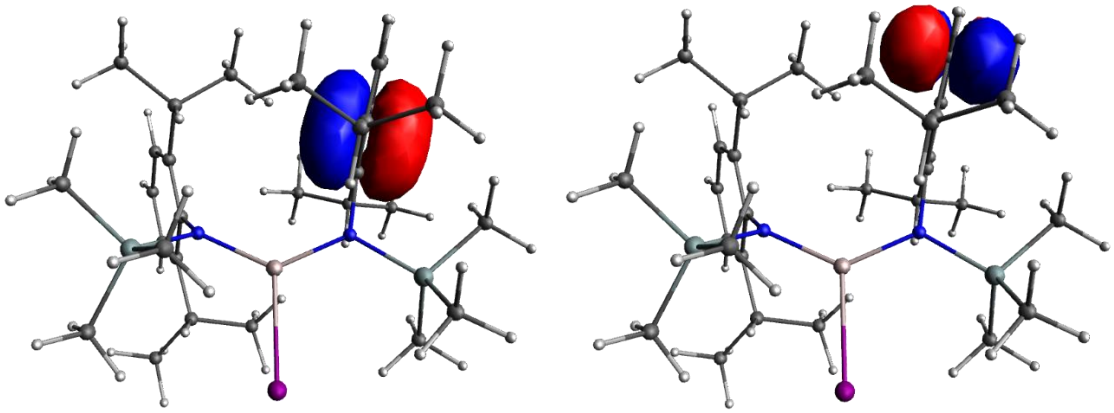


Figure S20. HOMO (left, -6.825 eV) and LUMO (right, 1.130 eV) of **2**.

FMOs for [Al{N(Dipp)Si(*i*-Pr)$_3$}$_2$]$^-$ and [Al{N(Dipp)SiMe$_3$}$_2$]$^-$

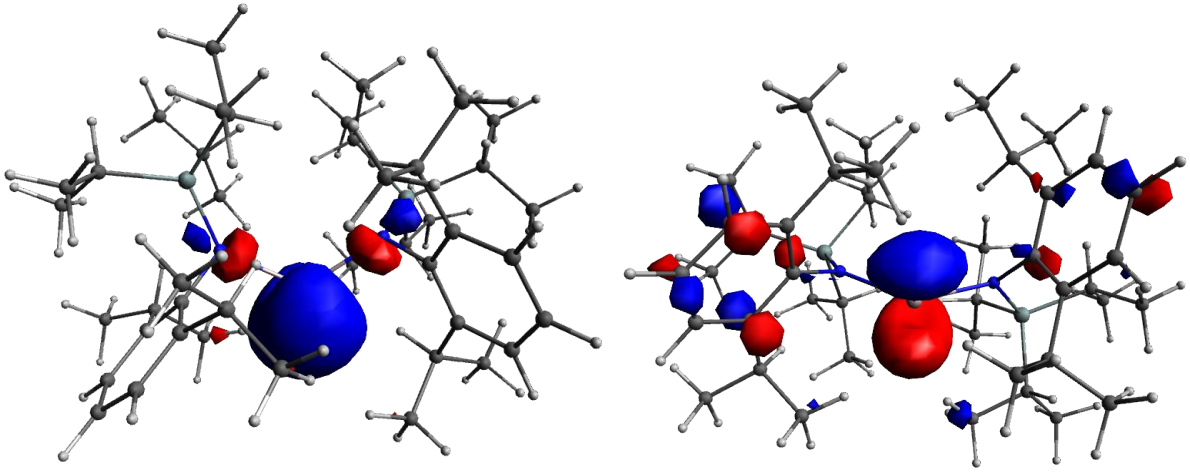


Figure S21. HOMO (left, -1.019 eV) and LUMO (right, 2.345 eV) of [Al{N(Dipp)Si(*i*-Pr)$_3$}$_2$]$^-$.

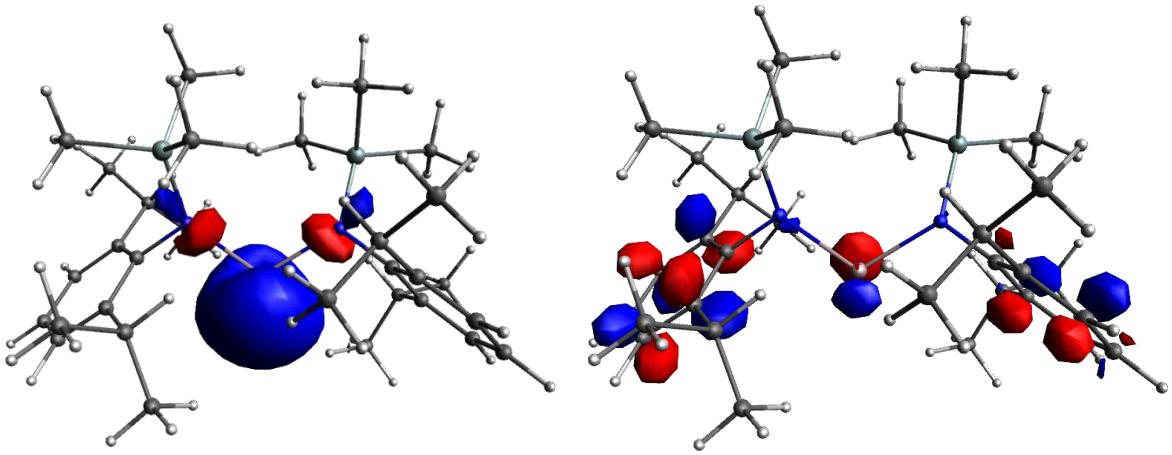


Figure S22. HOMO (left, -0.845 eV) and LUMO (right, 2.620 eV) of [Al{N(Dipp)SiMe$_3$}$_2$]$^-$.

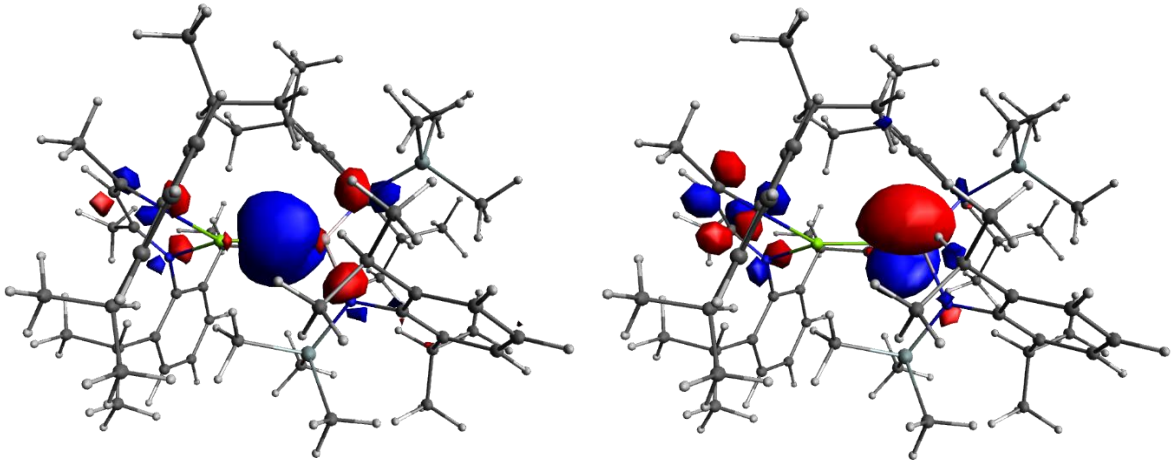


Figure S23. HOMO (left, -5.388 eV) and LUMO+1 (right, -0.716 eV) of **5**.

Key NBO results for compound 5

Natural charges: Al 0.876, Mg 1.575

Wiberg bond index: Al-Mg 0.4516

Key QTAIM results for compound 5

Bader charges: Al 1.034, Mg 1.600

Type = (3,-1) BCP Al3 Mg88

$\rho(r) = 0.0333$ e Å^{-3}

$\nabla^2\rho(r) = 0.0381$ e Å^{-5}

$\varepsilon = 0.0205$

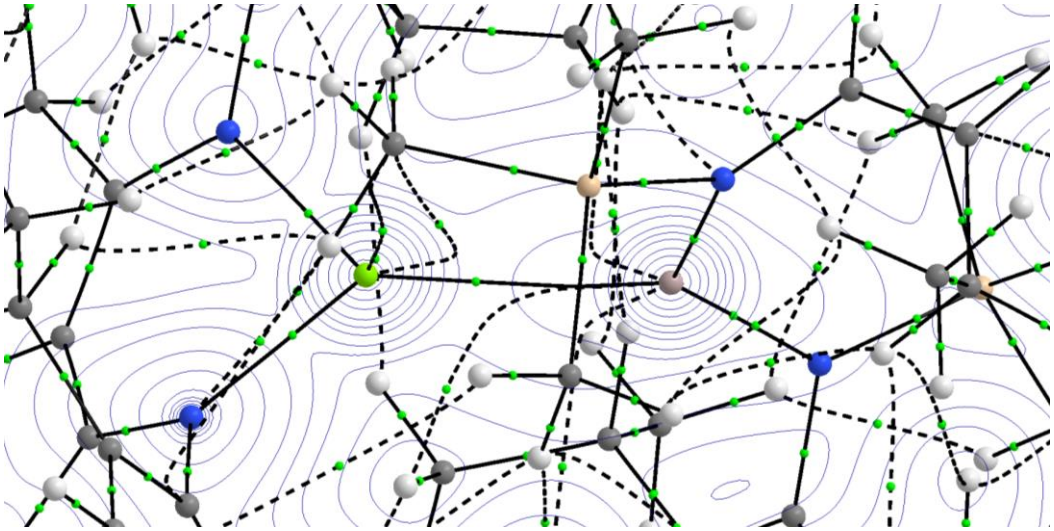


Figure S24. QTAIM molecular graph of **5**. The electron density contour is computed (N-Mg-Al plane, N blue, Mg green and Al pink) and BCPs are given as green spheres.

xyz-coordinates of the optimized structures

Compound **1**
124
E = -2873.432728

C	3.242047	-2.559229	2.900730
H	3.300611	-3.646082	2.994319
H	3.186430	-2.150928	3.912750
H	4.173902	-2.212433	2.451927
C	2.014558	-2.136197	2.100825
H	1.953152	-1.051152	2.118188
C	0.757401	-2.691740	2.764217
H	0.774256	-3.784889	2.760734
H	0.691380	-2.360460	3.803719
H	-0.150139	-2.375404	2.251502
C	2.060245	-2.543954	0.649356
C	2.339473	-3.877684	0.375277
H	2.569363	-4.542296	1.199901
C	2.310887	-4.377160	-0.910408
H	2.532912	-5.419869	-1.104902
C	1.964347	-3.526621	-1.937827
H	1.906319	-3.911128	-2.949676
C	1.770463	-1.651844	-0.409482
N	1.614325	-0.235166	-0.163214
C	1.693513	-2.179902	-1.717410
C	3.180189	1.674631	1.664838
H	2.145680	2.017964	1.759896
C	3.504298	0.911156	2.948949
H	2.738022	0.188129	3.217913
H	3.578126	1.616105	3.784117
H	4.453008	0.374050	2.901737
C	4.027961	2.949133	1.626873
H	3.875791	3.516233	2.551119
H	5.097008	2.732867	1.560180
H	3.767606	3.608191	0.798502
Si	3.163182	0.705575	0.000804
C	4.621960	-0.520803	-0.024601
H	4.316050	-1.302882	0.677668
C	4.915575	-1.211715	-1.353828
H	4.093763	-1.842394	-1.683666
H	5.131987	-0.490618	-2.146168
H	5.799205	-1.851552	-1.254712
C	5.924837	0.078488	0.512951
H	5.801732	0.627228	1.445739
H	6.648165	-0.723016	0.696740
H	6.380416	0.757010	-0.209469
H	3.307323	-1.202841	-3.746791
C	3.344376	2.047763	-1.358989
H	2.325180	-2.457411	-4.499392

H	2.858474	2.920292	-0.911383
H	2.789814	2.677184	-3.344104
H	3.040214	0.940254	-3.211550
H	2.012147	-0.763889	-4.868921
C	2.645490	1.811781	-2.687860
H	1.569473	1.681951	-2.568233
C	4.798973	2.438270	-1.624609
H	5.344570	1.639815	-2.131960
H	5.347632	2.689853	-0.717423
H	4.832082	3.315425	-2.279868
C	1.292893	-1.368065	-2.924071
H	1.232779	-0.326319	-2.615220
C	2.296484	-1.453054	-4.069811
C	-0.083616	-1.811418	-3.403017
H	-0.072532	-2.863719	-3.697621
H	-0.818623	-1.700705	-2.605999
Al	-0.021782	0.553016	-0.057905
H	-2.241385	-2.233300	-1.166303
N	-1.733321	-0.078379	0.036756
C	-2.095555	-0.948733	1.136315
C	-2.480873	-2.291651	0.927414
C	-3.588927	-3.847827	-0.757109
H	-3.631842	-4.749549	-0.141385
H	-3.520957	-4.174828	-1.797222
H	-4.533796	-3.317561	-0.628818
C	-1.558335	0.925751	2.788174
C	-1.132500	-3.886087	-0.417670
H	-1.210688	-4.662319	0.348467
H	-0.226239	-3.317645	-0.224522
H	-1.023232	-4.377127	-1.387543
H	0.501986	0.362548	2.264855
C	-0.064957	0.836258	3.077149
H	0.113927	0.213992	3.957829
C	-2.089967	-0.449264	2.461714
C	-2.240599	1.628820	3.954525
H	-2.002254	1.154584	4.909741
H	-1.887939	2.661425	4.012331
H	-3.325568	1.651021	3.849298
C	-2.512025	-1.255553	3.509671
H	-2.510237	-0.856059	4.516445
H	-3.203392	-4.082920	1.838416
H	-3.273566	-3.166535	4.120964
C	-2.904824	-3.055841	2.011983
H	-1.693526	1.549512	1.903250
Si	-3.122194	0.705560	-0.787493
C	-4.292357	-0.579077	-1.578956
C	-4.273180	1.736852	0.321414
H	-5.051429	1.967189	-0.420362
H	-4.289887	0.759914	2.267227
C	-4.965149	0.958114	1.437839

H	-5.334923	-0.014679	1.106499
H	-5.817441	1.522694	1.831778
C	-5.740503	-0.113781	-1.753373
H	-6.219994	0.157213	-0.813408
H	-6.333022	-0.919968	-2.199993
H	-5.815644	0.745106	-2.424748
H	-4.315688	-1.396917	-0.854039
H	-4.580056	3.649572	1.282600
C	-3.764523	3.086690	0.814846
H	-2.974200	2.992257	1.559707
H	-4.418973	-2.011311	-3.202375
C	-3.816861	-1.142623	-2.916702
H	-3.367645	3.699631	0.003035
H	-3.931361	-0.402214	-3.712324
H	-2.774102	-1.454663	-2.917488
C	-2.463423	1.901383	-2.105283
H	-2.034663	2.726489	-1.531357
C	-3.583305	2.502147	-2.954504
H	-4.065818	1.754466	-3.587364
H	-4.358401	2.970886	-2.344542
H	-3.180086	3.274530	-3.617944
C	-1.363326	1.359604	-3.003226
H	-1.740899	0.605473	-3.694436
H	-0.900585	2.159213	-3.590226
H	-0.545281	0.877043	-2.451742
H	-0.410232	-1.222306	-4.262787
C	-2.370771	-2.997511	-0.403505
H	0.369473	1.823445	3.244029
I	0.140943	3.077382	0.084216
C	-2.937298	-2.551568	3.294361

Compound **2**

88

E = -2402.126720

C	3.278405	2.805110	2.171964
C	3.223011	1.452852	2.450443
C	2.641779	0.558142	1.560920
C	2.092953	1.034669	0.350665
C	2.148767	2.413950	0.064653
C	2.741741	3.269789	0.987785
N	1.509337	0.111768	-0.581073
Si	2.571928	-0.480342	-1.862068
C	1.488460	-1.212963	-3.203338
C	1.536051	3.023484	-1.174656
C	0.231084	3.726690	-0.821847
C	2.541506	-0.899896	1.941680
C	3.751549	-1.434580	2.693945
Al	0.064253	-0.880142	-0.160525
I	0.402735	-3.374963	-0.181091
N	-1.624177	-0.389630	0.170686

Si	-2.941007	-1.519469	0.568781
C	-3.272212	-2.741186	-0.811664
C	-2.075974	0.964019	0.032731
C	-2.193083	1.789831	1.167960
C	-2.763295	3.049782	1.029467
C	-3.211235	3.508601	-0.194989
C	-3.060737	2.708178	-1.310750
C	-2.492912	1.442086	-1.223549
C	-1.690910	1.365699	2.529858
C	-0.452107	2.171251	2.912987
C	-2.343961	0.630727	-2.490510
C	-1.395006	1.317497	-3.468381
C	-2.750504	1.473141	3.621351
C	-2.571253	-2.416393	2.169525
C	-4.530286	-0.556822	0.787235
C	-3.689128	0.351429	-3.153798
C	1.269772	-1.140395	2.750479
C	3.601681	0.873636	-2.633331
C	3.814030	-1.736910	-1.237706
C	2.464817	4.003104	-1.886462
H	-3.069920	2.507423	3.770533
H	-2.346028	1.115961	4.571959
H	-3.637485	0.880844	3.390482
H	-1.403123	0.316256	2.456063
H	-0.696248	3.232905	3.006210
H	-0.053509	1.833494	3.873114
H	0.339013	2.080562	2.167809
H	-2.855928	3.685585	1.902978
H	-3.660626	4.491009	-0.281359
H	-3.391199	3.073665	-2.277018
H	-4.378666	-0.145572	-2.468988
H	-4.164271	1.277869	-3.486276
H	-3.559043	-0.288625	-4.030286
H	-1.908093	-0.333647	-2.217800
H	-1.793403	2.283182	-3.789796
H	-0.421264	1.498956	-3.009733
H	1.301521	2.205407	-1.857120
H	2.593881	4.918894	-1.304236
H	2.032247	4.294171	-2.847332
H	3.453168	3.582834	-2.071046
H	0.417934	4.555462	-0.133162
H	-0.472397	3.048714	-0.344258
H	-0.244354	4.132845	-1.717997
H	0.362942	-0.791867	2.234241
H	1.300131	-0.580079	3.688692
H	3.835156	-1.008508	3.696754
H	3.667570	-2.517876	2.807586
H	4.677784	-1.219652	2.157505
H	3.639499	1.082707	3.379616
H	2.775324	4.331128	0.770297

H	3.734344	3.492342	2.875179
H	2.465545	-1.478137	1.019431
H	-1.249248	0.703238	-4.360917
H	1.128469	-2.200318	2.970390
H	2.132245	-1.597759	-4.000038
H	0.865121	-2.045478	-2.871268
H	0.844299	-0.447323	-3.641488
H	4.321829	0.395555	-3.304327
H	3.018095	1.582671	-3.220408
H	4.169339	1.427158	-1.882784
H	4.457930	-2.049933	-2.065070
H	4.457490	-1.292410	-0.473379
H	3.346313	-2.628777	-0.818833
H	-5.326007	-1.268086	1.029267
H	-4.481176	0.181400	1.587140
H	-4.816272	-0.029339	-0.124754
H	-4.143027	-3.347270	-0.542808
H	-3.509862	-2.219086	-1.741533
H	-2.439458	-3.416863	-1.002677
H	-3.372579	-3.128895	2.386216
H	-1.634090	-2.973639	2.128227
H	-2.517208	-1.712933	3.004373

Anion $[Al\{N(Dipp)Si(i\text{-}Pr)_3\}_2]^-$
123
E = -2575.64327224

C	-4.51251	-1.70947	-2.21617
C	-3.60854	-0.76471	-1.75064
C	-2.75687	-1.06493	-0.65229
C	-2.78384	-2.39318	-0.15678
C	-3.70170	-3.31013	-0.66220
C	-4.58355	-2.97849	-1.66852
N	-1.84526	-0.10999	-0.12528
Si	-2.44361	1.15484	0.89920
C	-4.30436	1.07970	1.34735
C	-3.49783	0.55420	-2.47701
C	-2.37866	0.49268	-3.51271
C	-1.84487	-2.88890	0.92062
C	-0.93806	-4.00100	0.39973
Al	-0.02765	-0.65473	-0.92787
N	1.78155	-0.10788	-0.10290
C	2.52454	-1.29558	0.11242
C	3.06951	-2.06471	-0.95376
C	3.86438	-3.17204	-0.67372
C	4.13860	-3.57000	0.61944
C	3.54269	-2.88084	1.65834
C	2.71641	-1.78737	1.42982
C	2.85496	-1.73721	-2.41687
C	2.08823	-2.84696	-3.12957
C	1.99302	-1.19917	2.62158

C	1.13638	-2.26823	3.29680
Si	2.65476	1.38176	-0.28522
C	4.37252	1.32608	0.56038
C	2.90965	1.81824	-2.13220
C	1.58455	2.70473	0.56285
C	4.16680	-1.46281	-3.15039
C	2.92705	-0.57730	3.65478
C	-1.46381	1.15797	2.54433
C	-2.04511	2.94377	0.26592
C	-4.77541	1.02891	-3.15862
C	-2.59024	-3.35641	2.16785
H	3.39537	0.91863	-2.52449
C	1.59622	1.97073	-2.89009
C	3.84625	2.98278	-2.44471
H	0.57988	2.34539	0.30732
C	1.68492	4.14513	0.07718
C	1.70411	2.66003	2.08347
H	3.70811	-3.21104	2.67934
H	4.78171	-4.42147	0.81409
H	4.28801	-3.73177	-1.50162
H	2.23000	-0.84299	-2.46107
H	4.76879	-0.70528	-2.64684
H	4.77550	-2.36926	-3.22184
H	3.96599	-1.11996	-4.16987
H	2.63228	-3.79595	-3.09012
H	1.10702	-2.97753	-2.66922
H	1.93607	-2.58601	-4.18178
H	1.33182	-0.42249	2.23178
C	5.40535	0.43670	-0.12442
H	2.35222	-0.16222	4.48840
H	3.53155	0.22617	3.23317
H	3.61105	-1.32774	4.06271
H	0.57278	-1.84543	4.13105
H	1.75699	-3.07870	3.68889
H	0.42827	-2.70550	2.59318
H	4.15389	0.86783	1.53136
C	4.99274	2.69589	0.83626
C	-1.59816	-0.06701	3.43632
H	-0.43092	1.16965	2.17186
C	-1.65993	2.40052	3.40875
H	-1.11538	3.14116	0.81353
C	-3.02637	4.02978	0.70595
C	-1.70313	3.13076	-1.20649
H	-4.36790	1.87305	2.10810
C	-5.28873	1.43096	0.23724
C	-4.77385	-0.21862	1.99872
H	-3.21698	1.29727	-1.73229
H	-4.64029	2.05568	-3.51133
H	-5.64028	1.01106	-2.49409
H	-5.01030	0.42054	-4.03693

H	-2.22084	1.47253	-3.97491
H	-2.63621	-0.22378	-4.29886
H	-3.20106	-4.23748	1.95021
H	-1.43676	0.15715	-3.06663
H	-3.25202	-2.58152	2.55603
H	-1.88321	-3.63054	2.95663
H	-1.21076	-2.04250	1.19566
H	-1.52359	-4.86835	0.08036
H	-0.35383	-3.64648	-0.45292
H	-0.24259	-4.33215	1.17669
H	-3.71681	-4.31447	-0.25078
H	-5.29842	-3.70369	-2.04221
H	-5.17025	-1.44994	-3.03791
H	-5.81766	-0.12677	2.32517
H	-4.72576	-1.04644	1.28767
H	-4.18109	-0.49476	2.86976
H	-6.27598	1.66523	0.65446
H	-4.97630	2.27947	-0.37251
H	-5.41306	0.57537	-0.42765
H	-0.81725	-0.06599	4.20557
H	-2.55525	-0.06924	3.96475
H	-1.51756	-1.00067	2.88453
H	-0.99940	2.36709	4.28390
H	-1.44961	3.33189	2.88187
H	-2.68667	2.45836	3.78684
H	-2.59775	5.02563	0.53738
H	-3.95675	3.98370	0.13542
H	-3.29130	3.96269	1.76283
H	-1.14215	4.06056	-1.35715
H	-1.10278	2.30880	-1.60107
H	-2.60326	3.20047	-1.82333
H	1.77188	2.05381	-3.96980
H	0.93304	1.10956	-2.73811
H	1.04641	2.86422	-2.58333
H	3.90581	3.14247	-3.52875
H	3.50943	3.92239	-2.00031
H	4.86185	2.79733	-2.09036
H	0.91106	3.24727	2.55859
H	1.64107	1.64371	2.47263
H	2.65545	3.07771	2.42201
H	0.94679	4.77530	0.58961
H	2.67018	4.57416	0.28185
H	1.50283	4.23693	-0.99415
H	5.89140	2.58791	1.45640
H	5.30158	3.19305	-0.08574
H	4.31649	3.37465	1.35647
H	6.34291	0.42869	0.44555
H	5.06580	-0.59471	-0.21860
H	5.64596	0.80531	-1.12685

Compound $[Al\{N(Dipp)SiMe_3\}_2]^-$
87
E = -2104.33392674

Al	-0.03370	-0.16015	-0.85369
N	-1.65479	-0.37107	0.24667
Si	-1.91233	-1.30323	1.67085
C	-0.64301	-2.68660	1.70700
H	-0.92060	-3.43749	0.96143
H	0.35286	-2.32325	1.45182
H	-0.58875	-3.17748	2.68289
C	-1.86918	-0.28628	3.26312
H	-1.00098	0.36805	3.34165
H	-1.88149	-0.93964	4.14202
H	-2.76342	0.34287	3.30762
C	-2.79804	0.19269	-0.36855
C	-3.56682	-0.53554	-1.30883
C	-4.67357	0.06203	-1.90175
C	-5.04766	1.36006	-1.60612
C	-4.28675	2.08451	-0.70728
C	-3.17216	1.52747	-0.09264
H	-4.55811	3.11139	-0.48260
H	-5.91547	1.80551	-2.08096
H	-5.25352	-0.50480	-2.62310
C	-3.19820	-1.94106	-1.72938
H	-2.45136	-2.30128	-1.01818
C	-4.38749	-2.89748	-1.71342
H	-4.92744	-2.86125	-0.76553
H	-5.09930	-2.66281	-2.51038
H	-4.04737	-3.92437	-1.87780
C	-2.54709	-1.93956	-3.11079
H	-3.24006	-1.54368	-3.86078
H	-1.64594	-1.32094	-3.10741
H	-2.26798	-2.95676	-3.40572
C	-2.33047	2.38045	0.82391
H	-1.66497	1.69175	1.34420
H	-3.69463	-2.94527	1.02706
C	-3.14192	3.13395	1.86893
H	-2.47478	3.64630	2.56845
H	-3.77893	2.45497	2.44099
H	-3.78634	3.89298	1.41546
C	-1.46252	3.33415	0.00813
H	-0.80142	3.91705	0.65635
H	-2.08475	4.02820	-0.56567
H	-0.84652	2.77731	-0.70457
C	-3.60919	-2.12135	1.73710
H	-4.40888	-1.40699	1.52544
H	-3.77303	-2.52575	2.74142
N	1.59095	0.02697	0.28244
Si	2.01861	0.51608	1.88911
C	1.15098	2.10578	2.40125

H	1.47684	2.93536	1.76841
H	0.06682	2.03087	2.31104
H	1.38740	2.35713	3.44002
C	1.71204	-0.75165	3.25342
H	0.67027	-1.03741	3.38079
H	2.05863	-0.32118	4.19937
H	2.29123	-1.66176	3.07435
C	3.87112	0.84063	2.03591
H	4.09503	1.22663	3.03612
H	4.43833	-0.08316	1.89483
H	4.23844	1.55618	1.29926
C	2.71359	-0.03556	-0.58909
C	3.44882	-1.23427	-0.72110
C	3.02028	-2.47415	0.02680
H	2.36093	-2.13588	0.82687
C	4.17572	-3.23271	0.66557
H	3.79410	-4.05523	1.27776
H	4.77317	-2.57937	1.30670
H	4.84467	-3.66803	-0.08264
C	2.19692	-3.38106	-0.88242
H	1.82040	-4.24993	-0.33341
H	2.80207	-3.73653	-1.72243
H	4.08928	3.72001	-1.41952
H	1.34355	-2.83498	-1.29746
C	3.23292	3.53443	-0.76389
H	3.62021	3.31310	0.23260
H	2.65331	4.46077	-0.70311
C	2.36291	2.39943	-1.29680
H	1.53201	2.25752	-0.60285
C	1.76826	2.76962	-2.65152
H	2.55062	2.91642	-3.40299
H	1.09814	1.97768	-2.99388
H	1.19494	3.69913	-2.57597
C	3.10746	1.08356	-1.35783
H	4.50670	1.85306	-2.78138
C	4.21179	0.98610	-2.19765
C	4.93698	-0.18501	-2.30990
H	5.79547	-0.24087	-2.97087
C	4.54387	-1.28879	-1.57315
H	5.10023	-2.21620	-1.66518

Compound **5**
160
E = -3541.333390

Si	0.41558	-0.29910	-2.81663
Si	3.89323	-0.85250	1.84635
Al	1.19873	-0.09986	0.09650
N	1.55210	-0.79400	-1.58018
N	2.60253	0.18563	1.26425
C	2.55923	-1.72922	-1.93679

C	2.42417	-3.07660	-1.52472
C	3.37767	-4.00704	-1.91734
H	3.27644	-5.03775	-1.60093
C	4.45012	-3.64963	-2.71513
H	5.17716	-4.39268	-3.02159
C	4.59057	-2.33211	-3.09913
H	5.44167	-2.04550	-3.70653
C	3.67793	-1.35600	-2.70945
C	1.23629	-3.53712	-0.70701
H	0.96677	-2.72416	-0.01837
C	1.49865	-4.78161	0.13096
H	1.57044	-5.67239	-0.49866
H	0.66377	-4.94175	0.81649
H	2.41788	-4.70922	0.71364
C	0.01759	-3.79240	-1.58897
H	-0.23476	-2.92067	-2.18685
H	-0.85094	-4.05778	-0.98182
H	0.22328	-4.61766	-2.27645
C	3.94675	0.07622	-3.12075
H	3.26436	0.70881	-2.54805
C	5.37525	0.49936	-2.78979
H	5.61492	0.32468	-1.74224
H	5.51455	1.56122	-3.00539
H	6.10290	-0.04836	-3.39319
C	3.69907	0.31421	-4.60918
H	4.35396	-0.32251	-5.21077
H	3.91592	1.35439	-4.86864
H	2.67233	0.10257	-4.90303
C	0.55726	1.51762	-3.25520
H	0.38389	2.13442	-2.36794
H	-0.21417	1.78907	-3.98301
H	1.52804	1.78979	-3.67090
C	-1.39110	-0.48272	-2.26577
H	-1.54037	-1.28355	-1.53452
H	-2.00060	-0.75736	-3.13247
H	-1.81568	0.46825	-1.92278
C	0.57455	-1.38185	-4.34361
H	1.59292	-1.72489	-4.52443
H	0.23668	-0.82577	-5.22302
H	-0.05511	-2.26967	-4.25382
C	2.58568	1.48073	1.87323
C	3.43890	2.49513	1.38698
C	3.51569	3.70899	2.05849
H	4.18675	4.47628	1.68768
C	2.74917	3.96324	3.18068
H	2.82609	4.91320	3.69704
C	1.86782	2.99433	3.62033
H	1.24776	3.19440	4.48803
C	1.76673	1.75925	2.98766
C	4.25944	2.31342	0.12988

H	4.14463	1.27503	-0.18349
C	5.74348	2.58146	0.35366
H	5.92578	3.62141	0.63637
H	6.30744	2.38703	-0.56172
H	6.15153	1.94734	1.14299
C	3.71696	3.19809	-0.99018
H	2.68611	2.93920	-1.23778
H	4.31935	3.08995	-1.89465
H	3.73204	4.25195	-0.69944
C	0.78143	0.75574	3.54033
H	0.80431	-0.11241	2.88009
C	1.16404	0.29003	4.94180
H	2.13501	-0.20809	4.94568
H	0.42123	-0.41093	5.33279
H	1.22026	1.13306	5.63540
C	-0.63824	1.31245	3.53678
H	-0.74369	2.15718	4.22253
H	-1.36284	0.55257	3.83918
H	-0.91466	1.67816	2.54366
C	5.17420	-1.30593	0.56214
H	4.74311	-1.77575	-0.32300
H	5.87521	-2.01778	1.00927
H	5.75279	-0.43656	0.24440
C	3.19348	-2.45425	2.51407
H	2.63047	-2.28497	3.43344
H	4.00607	-3.15128	2.73777
H	2.52926	-2.94130	1.80064
C	4.79576	-0.00973	3.25718
H	5.30813	0.90010	2.94084
H	5.54747	-0.70076	3.65091
H	4.12720	0.26488	4.07483
Mg	-1.52226	0.25020	0.34779
N	-2.98891	-0.97646	1.14999
N	-2.84018	1.82981	0.15398
C	-4.78977	-1.26411	2.79093
H	-5.06018	-2.20006	2.30247
H	-5.69489	-0.73035	3.07424
H	-4.24995	-1.52604	3.70449
C	-3.91553	-0.41145	1.91161
C	-4.16028	0.96900	1.97565
H	-4.89492	1.26705	2.71074
C	-3.74491	1.98895	1.10884
C	-4.38593	3.33340	1.31887
H	-3.71989	3.95139	1.92842
H	-5.33563	3.24184	1.84307
H	-4.53889	3.86210	0.37875
C	-2.95723	-2.39652	1.04106
C	-3.56140	-3.00550	-0.07611
C	-3.51535	-4.38946	-0.19388
H	-3.97947	-4.86581	-1.04853

C	-2.87919	-5.17144	0.75356
H	-2.84744	-6.24892	0.64103
C	-2.27906	-4.56490	1.83913
H	-1.77611	-5.17531	2.58101
C	-2.31146	-3.18403	2.00688
C	-4.28274	-2.18229	-1.11803
H	-3.79549	-1.20579	-1.14078
C	-5.74066	-1.94344	-0.73145
H	-6.26772	-2.89380	-0.61012
H	-6.25202	-1.37000	-1.50913
H	-5.82425	-1.38502	0.20151
C	-4.19594	-2.78090	-2.51572
H	-3.16923	-3.04336	-2.77911
H	-4.56392	-2.06460	-3.25282
H	-4.80825	-3.68123	-2.61064
C	-1.63399	-2.58447	3.21529
H	-1.87498	-1.51984	3.23872
C	-2.10931	-3.20741	4.52488
H	-3.19694	-3.18946	4.61641
H	-1.68467	-2.66823	5.37546
H	-1.79002	-4.24912	4.60744
C	-0.12407	-2.71712	3.08933
H	0.17535	-3.76590	3.02587
H	0.38027	-2.27682	3.95057
H	0.23889	-2.21440	2.19052
C	-2.70617	2.81868	-0.86161
C	-3.43752	2.65718	-2.05581
C	-3.24869	3.57200	-3.08434
H	-3.80176	3.45574	-4.00840
C	-2.36700	4.63051	-2.95184
H	-2.22866	5.33068	-3.76757
C	-1.66916	4.78877	-1.77135
H	-0.98202	5.62063	-1.66359
C	-1.82696	3.89956	-0.71268
C	-4.44797	1.54194	-2.20730
H	-4.11677	0.72194	-1.56600
C	-4.55949	1.01737	-3.63230
H	-5.02489	1.74848	-4.29797
H	-5.18934	0.12534	-3.65176
H	-3.58423	0.75771	-4.04824
C	-5.82590	1.97323	-1.70641
H	-5.81100	2.22717	-0.64688
H	-6.55147	1.16747	-1.84453
H	-6.17884	2.84714	-2.26104
C	-1.03284	4.11873	0.55052
H	-1.36080	3.37924	1.28430
C	0.44770	3.89241	0.29065
H	0.62195	2.87896	-0.07814
H	1.03180	4.01837	1.20162
H	0.82466	4.59212	-0.45973

C	-1.26462	5.50164	1.15158
H	-0.73893	5.58754	2.10574
H	-2.32522	5.69837	1.32215
H	-0.88409	6.28828	0.49527

References

[1] Y. Wei Chao, P. A. Wexler, D. E. Wigley, *Inorg. Chem.* **1989**, *28*, 3860–3868.

[2] B. Shen, L. Ying, J. Chen, Y. Luo, *Inorganica Chim. Acta* **2008**, *361*, 1255–1260.

[3] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955.

[4] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92–95.

[5] J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics* **2018**, *37*, 4810–4813.

[6] R. J. Schwamm, M. P. Coles, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi, A. S. S. Wilson, *Angew. Chem. Int. Ed.* **2020**, *59*, 3928–3932.

[7] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8.

[8] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

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

[10] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. a. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. a. Petersson, H. Nakatsuji, X. Li, M. Caricato, a. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, a. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. a. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. a. Keith, R. Kobayashi, J. Normand, K. Raghavachari, a. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

[11] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

[12] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[13] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.

[14] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[15] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[16] Keith, T. A. AIMAll Version 19.10.12; TK Gristmill Software: Overland Park KS, USA, **2019**.