Supporting Information for:

Synthesis and Reactivity of a Terminal Aluminium Imide Bond

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Contents

General Synthetic Procedures

All manipulations were performed under dry nitrogen using standard Schlenk-line techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. NMR spectra were recorded using a Joel JNM-ECZ500S 500MHz spectrometer equipped with a ROYAL digital auto tune probe S, operating at 500 (^{1}H) and 125.7 (^{13}C) MHz. Spectra were recorded at 298 K (unless stated otherwise) and proton and carbon chemical shifts were referenced internally to residual solvent resonances. Coupling constants are quoted in Hz. Elemental analyses were performed by S. Boyer at London Metropolitan University. K[Al(NON^{Dipp})][S1] was prepared according to the literature procedure. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

Preparation of K[Al(NON^{Dipp})(NMes)] (1)

A colourless *n*-hexane solution mesityl azide (76.6 mg, 0.57 mmol) was added dropwise to a rapidly stirring bright yellow *n*-hexane solution of K[Al(NON^{Dipp})] (265 mg, 0.48 mmol). The solution slowly turned colourless over the course of 2 hours. The solution was concentrated *in vacuo* and stored at -30 °C overnight, yielding large colourless blocks of **1**. Yield 317 mg (96 %).

Anal. Calcd. for $C_{37}H_{57}AlKN_3OSi_2$ (*681.35*): C, 65.15; H, 8.42; N, 6.16 %. Found: C, 64.89; H, 8.60; N, 5.98 %.

^{1}H NMR (500 MHz, C_6D_6): δ 7.16 (br s, 6H, C_6H_2-Dipp), 6.75 (s, 2H, C_6H_2-Mes), 4.20 (br sept, 4H, C*H*Me$_2$), 2.31 (s, 3H, *p*-C*H*$_3$), 1.82 (s, 6H, *o*-C*H*$_3$), 1.47 (d, *J* = 6.9, 2H, CH*Me*$_2$), 1.42 (br d, 2H, CH*Me*$_2$), 0.59 (s, 12H, Si*Me*$_2$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 157.9, 143.7, 131.2, 126.6, 123.9, 123.5, 116.0 (*C*$_6$H$_3$-Dipp and *C*$_6$H$_2$-Mes), 28.1 (*C*HMe$_2$), 25.8, 24.7 (CH*Me*$_2$), 21.3 (*o*-*C*H$_3$), 20.6 (*p*-*C*H$_3$), 2.2 (Si*Me*$_2$).

Figure S1 ^{1}H NMR spectrum (500 MHz, C_6D_6) of K[Al(NON^{Dipp})(NMes)] (**1**)

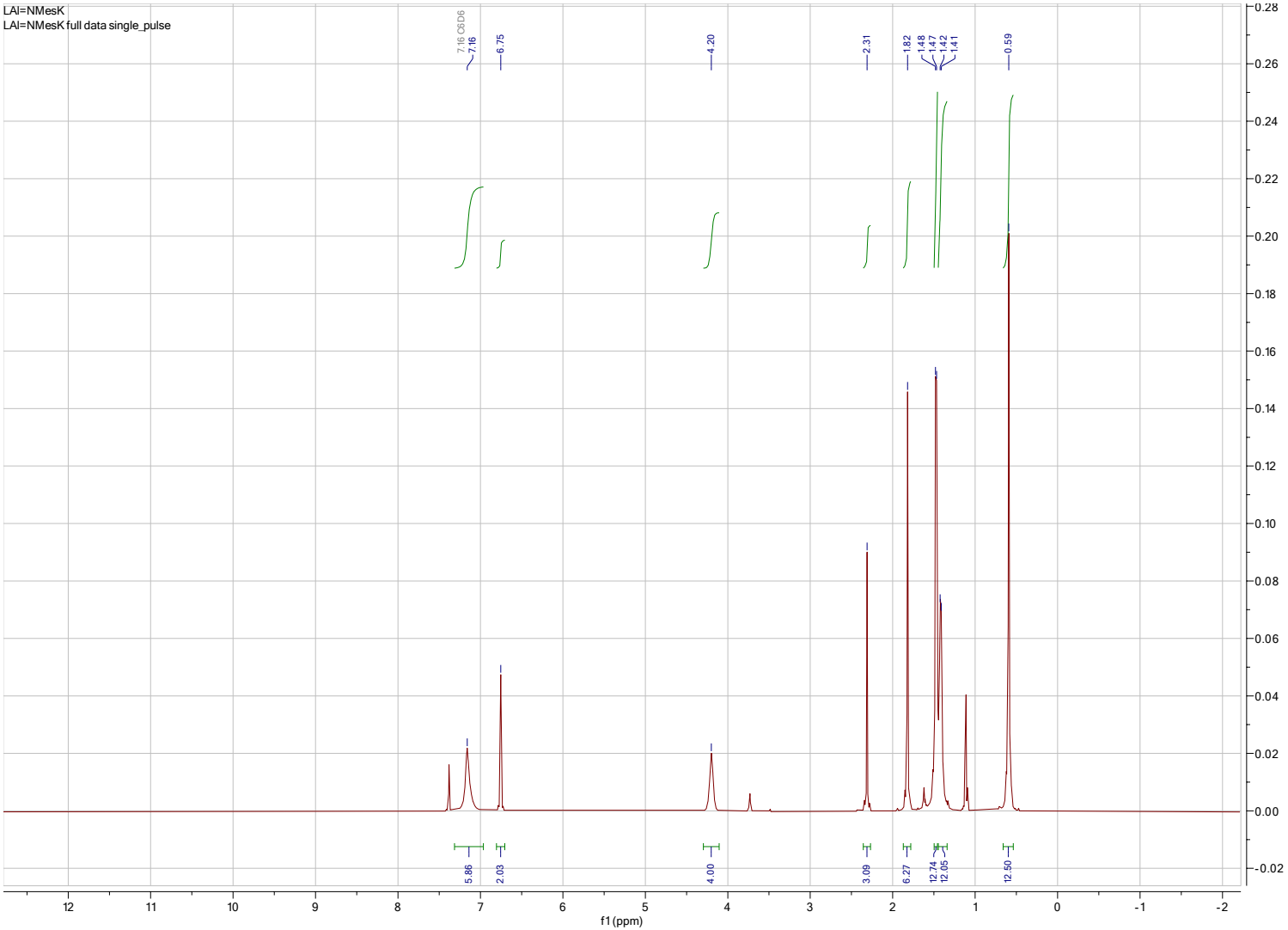


Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of K[Al(NON^{Dipp})(NMes)] (**1**)

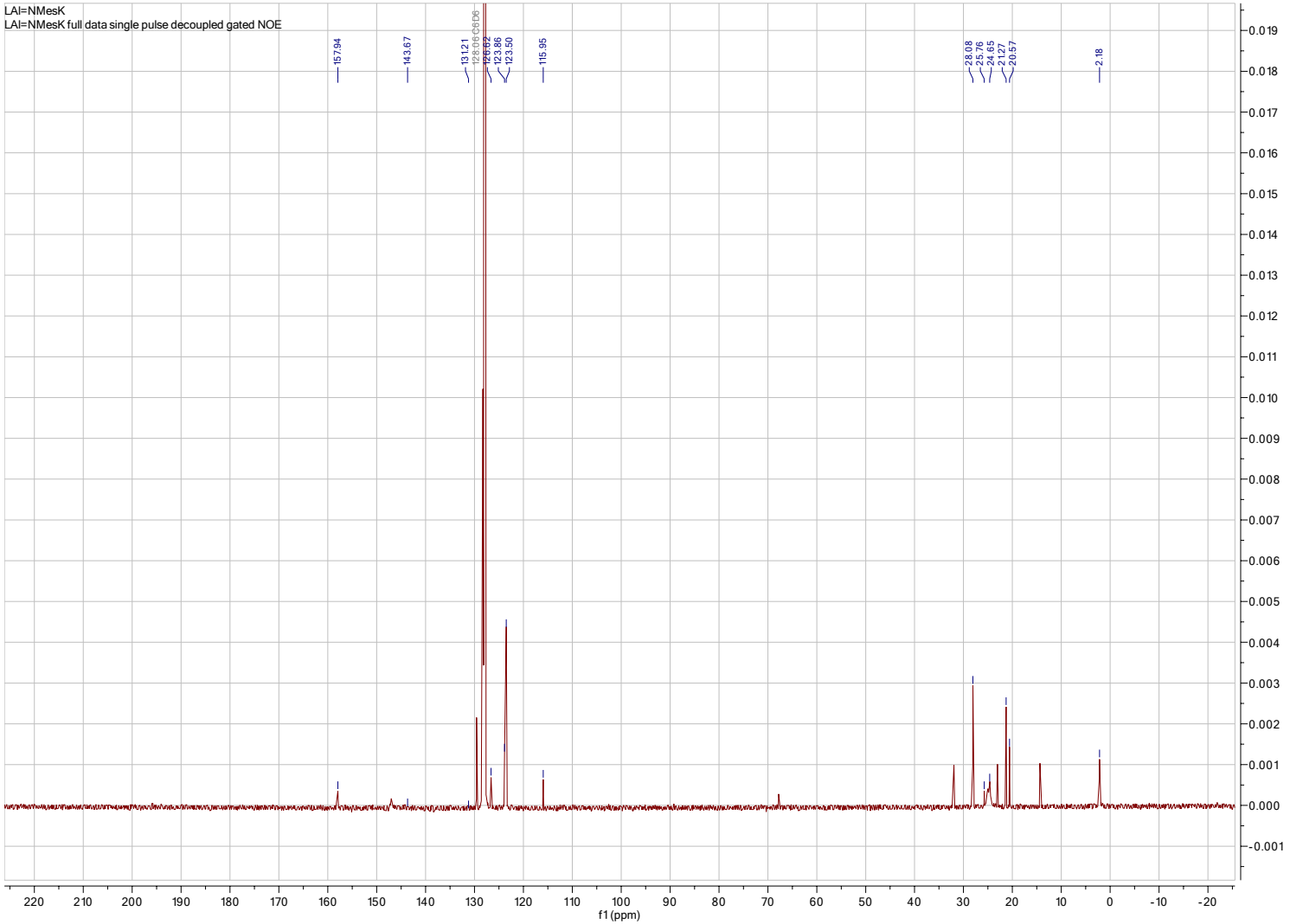
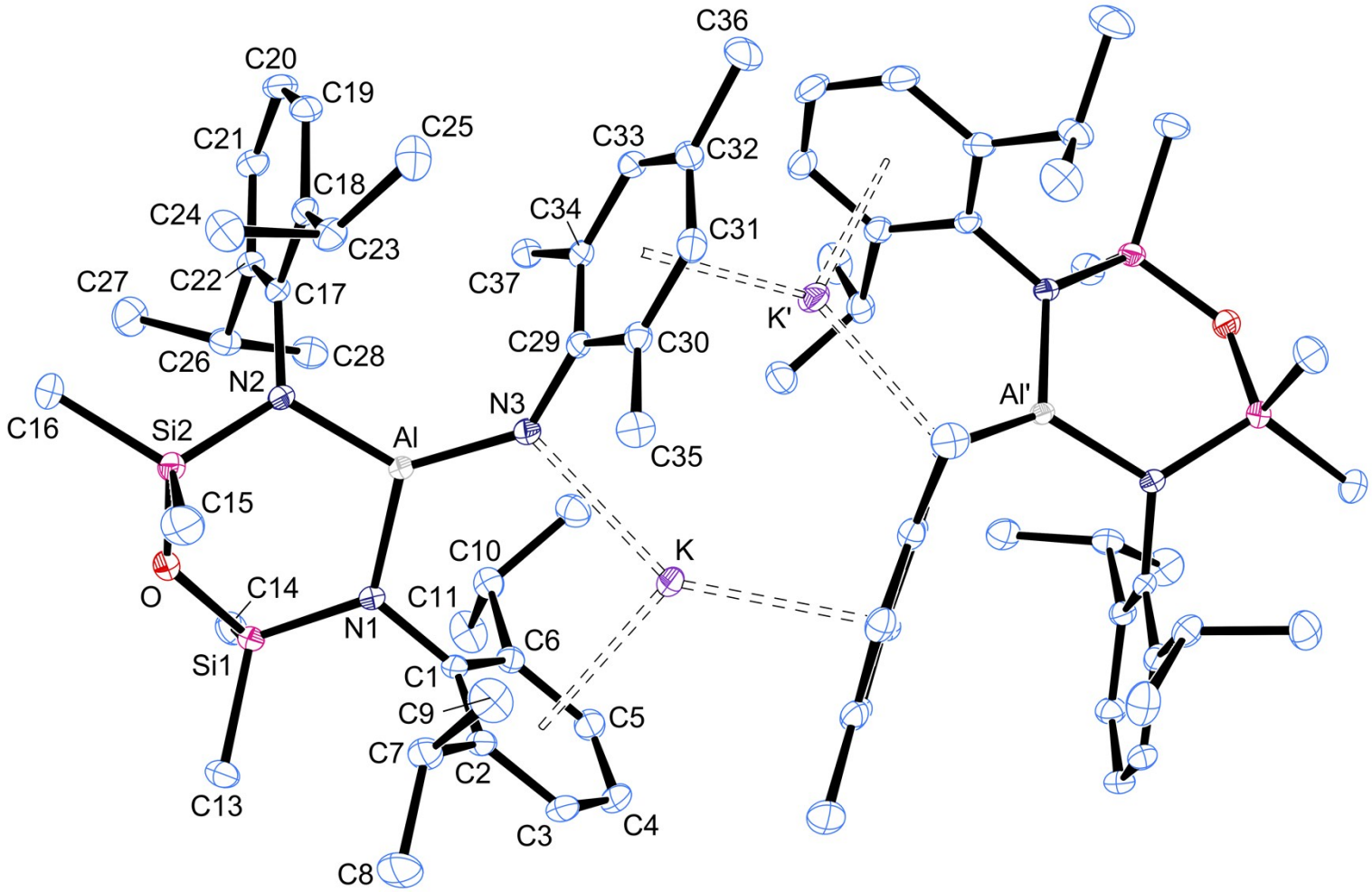


Figure S3 ORTEP (ellipsoid 30% probability, H atoms and hexane solvate omitted. Symmetry : ' = ½–*x*, *y*, ½–*z*) of K[Al(NON^{Dipp})(NMes)] (**1**).



Preparation of K[Al(NON^{Ar})(κ*O*,*N*-OC{O}NMes)] (2)

A colourless toluene solution of K[Al(NON^{Dipp})(NMes)] (200 mg, 0.29 mmol) in a ampoule was degassed and exposed to one atmosphere of $^{13}CO_2$ at room temperature. The solution was stirred for 5 minuets before being concentrated *in vacuo* to ca. 2 mL. Storage at –30 °C overnight gave large colourless blocks of **2**. Yield 182 mg (88 %).

Anal. Calcd. for $C_{38}H_{57}AlKN_3O_3Si_2$ (*726.14*): C, 62.86; H, 7.91; N, 5.79 % (corresponds to **2**)

Anal. Calcd. for $C_{29}H_{46}AlKN_2O_4Si_2$ (*608.89*): C, 57.20; H, 7.61; N, 4.60 % (corresponds to carbonate structure, K[Al(NON^{Ar})(CO_3)] generated from loss of 'NMes' groups and introduction of 'O').

Found: C, 57.65; H, 7.64; N, 5.07 %. Closest match to carbonate, which may represent decomposition during sample preparation / analysis due to sensitivity to air/moisture.

^{1}H NMR (500 MHz, C_6D_6): δ 7.09 – 7.01 (m, 3H, C_6H_3-Dipp), 6.94 (br m, 3H, C_6H_3-Dipp), 6.57 (s, 2H, C_6H_2-Mes), 4.11 (sept, *J* = 6.8, 2H), 3.96 – 3.81 (br sept, 2H), 2.14 (s, 3H, *p*-CH_3), 1.81 (br s, 6H, *o*-CH_3), 1.42 (d, *J* = 6.8, 6H, CHMe_2), 1.35 (d, *J* = 6.8, 6H, CHMe_2), 1.24 (d, *J* = 6.8, 6H, CHMe_2), 0.74 (d, *J* = 6.8, 6H, CHMe_2), 0.48 (s, 3H, SiMe_2), 0.30 (s, 3H, SiMe_2).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 164.2 (AlO*C*(O)N), 158.4, 147.1, 146.8, 145.1, 139.2, 134.3, 129.0, 123.8, 123.5, 122.7 (C_6H_3-Dipp and C_6H_2-Mes), 27.7, 27.5 (*C*HMe_2), 25.8, 25.1, 25.0, 24.7, 23.6 (CHMe_2), 22.7 (*p*-*C*H_3), 20.4 (*o*-*C*H_3), 3.4, 1.8 (SiMe_2).

Figure S4 ^{1}H NMR spectrum (500 MHz, C_6D_6) of K[Al(NON^{Ar})(κ*O*,*N*-OC{O}NMes)] (**2**).

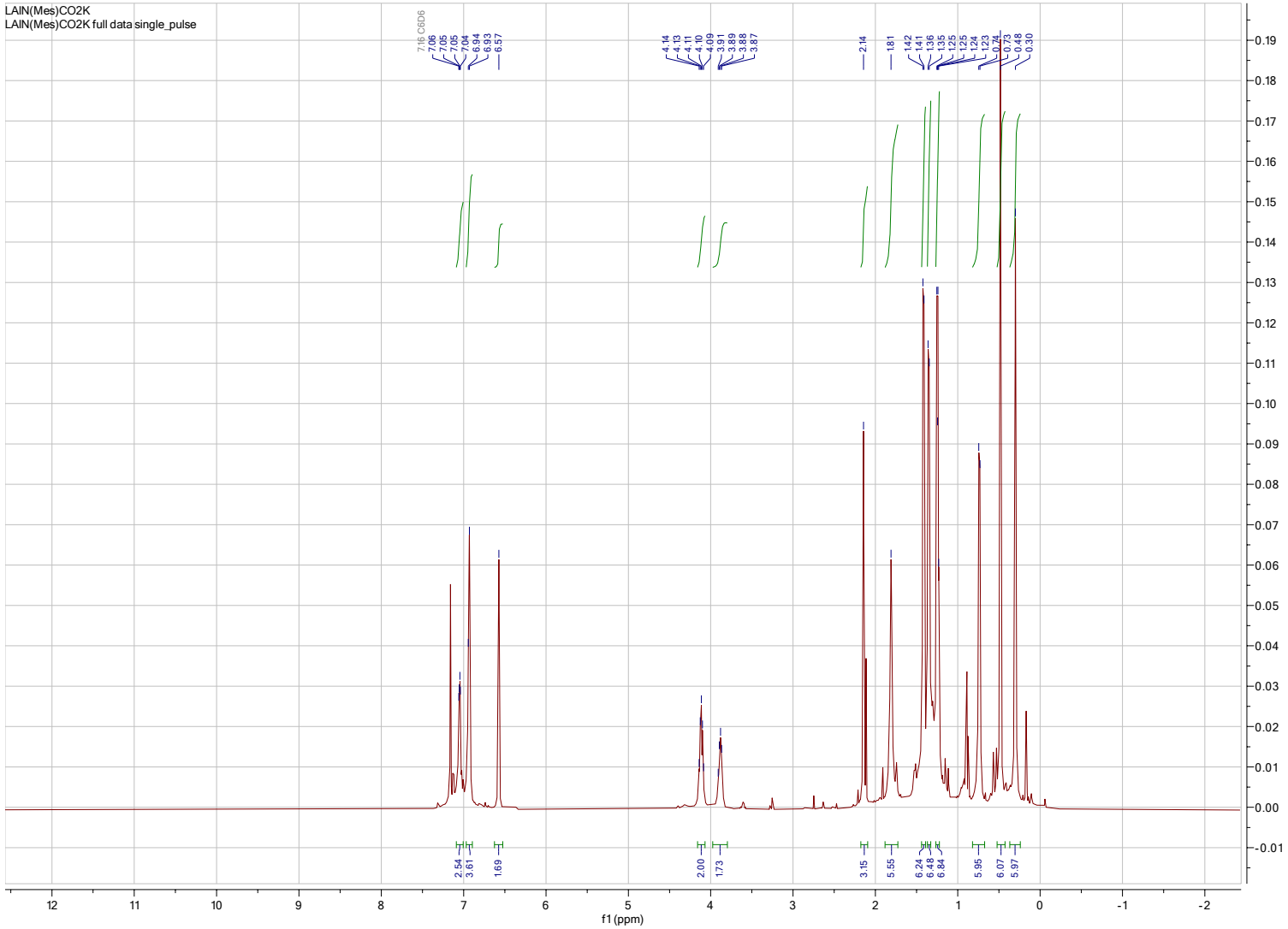


Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of K[Al(NON^{Ar})(κ*O*,*N*-OC{O}NMes)] (**2**)

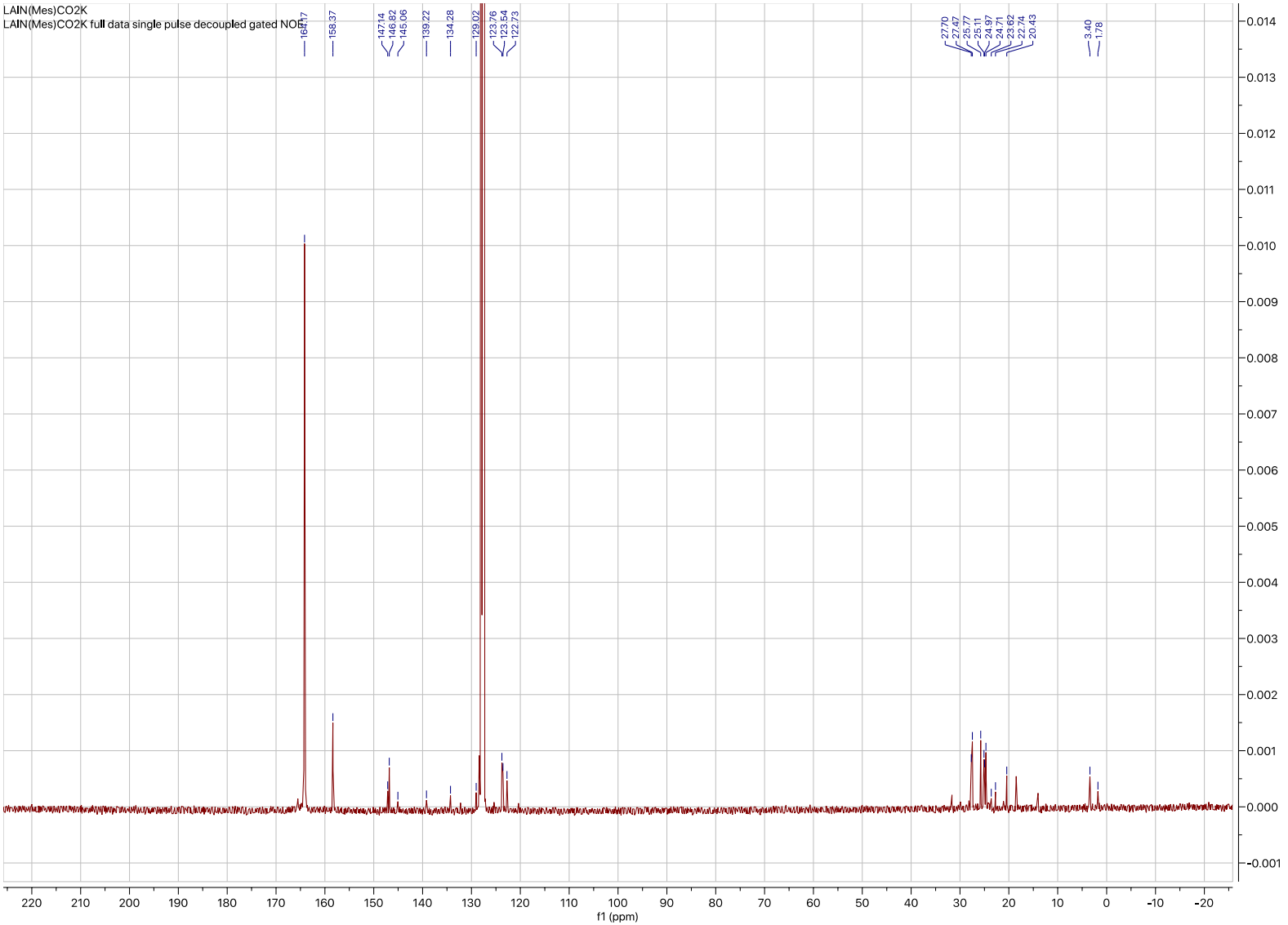
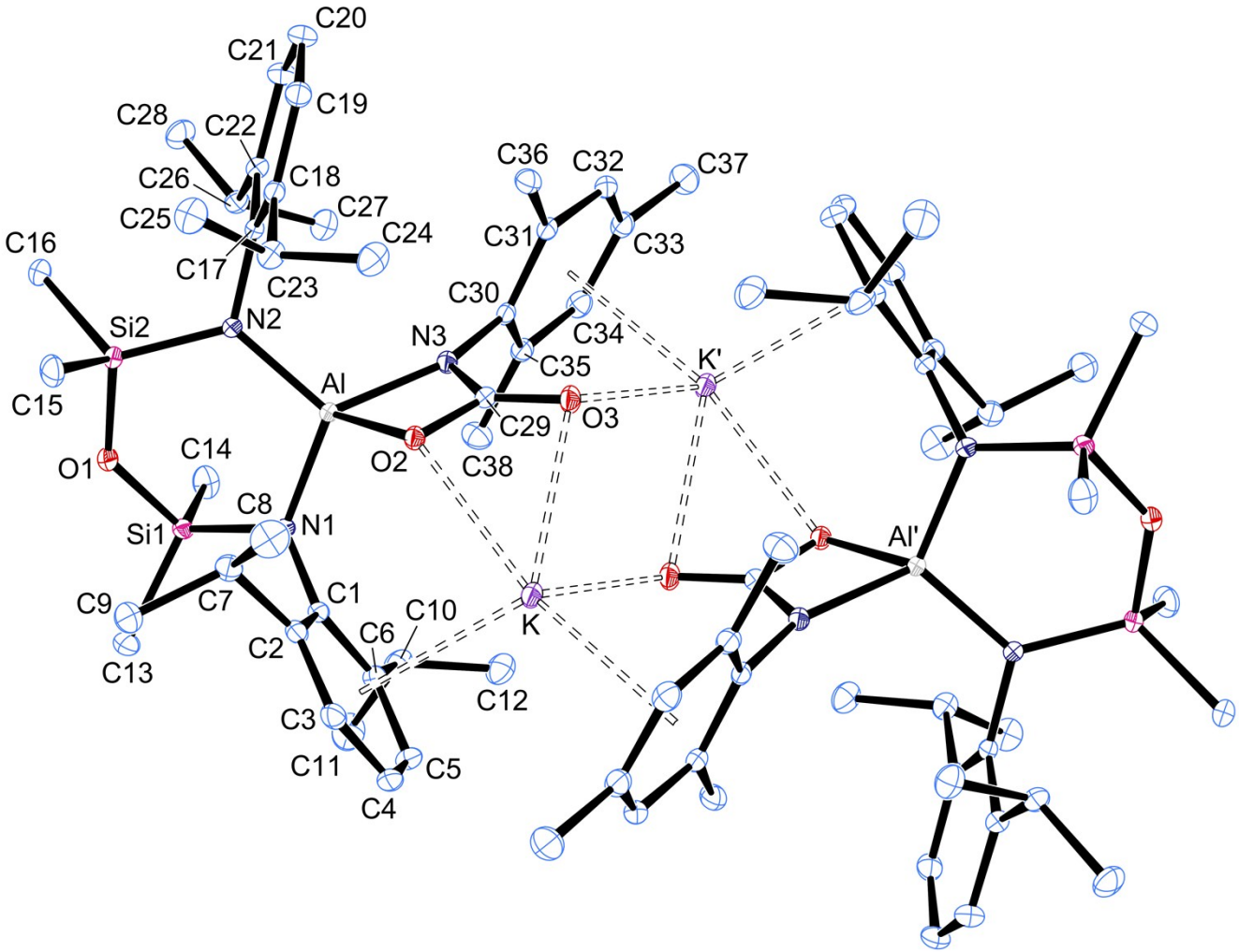


Figure S6 ORTEP (ellipsoid 30% probability, H atoms omitted. Symmetry : ' 1–*x*, –*y*, 2–*z*) of K[Al(NON^{Ar})(κ*O*,N-OC{O}NMes)] (**2**)



Crystallography

Crystals were covered in inert oil and suitable single crystals were selected under a microscope and mounted on an Agilent SuperNova diffractometer fitted with an EOS S2 detector. Data were collected at the temperature indicated using focused microsource Cu Kα radiation at 1.54184 Å. Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods.[S2] Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS,[S3] refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97,[S4] within the WinGX[S5] program. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate, unless otherwise stated. The functions minimized were Σ*w*(*F2*o-*F2c),* with *w* = [σ2(F2o) + *a*P2 + *bP*]-1, where *P* = [max(Fo)2 + 2F2c]/3. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Computational Methods

All structural optimisations were carried out with the Gaussian 09 suite of programs (Revision D.01),[S6] using the density functional method (DFT) with the the PBE0 hybrid functional,[S7] and the split valence, polarised def2-SVP basis-set,[S8] of double-ζ quality. Grimme's empirical dispersion correction[S9] along with Becke-Johnson damping[S10] (D3BJ) was applied. We refer to the resulting computational model as PBE0-D3BJ/def2-SVP. Frequency calculations at the same level of theory were employed to ensure that the obtained structures are minima on the potential energy surface.

The bonding was analysed using the Natural Bond Orbital (NBO) approach[S11-S17] using the NBO 6.0 program.[S18-S19] and Wiberg Bond Indices (WBI) were computed.[S20]

References

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Cartesian (x, y, z) coordinates: *K[Al(NON^{Dipp})(NMes)]* (***1***)

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