Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 94–96

One-step synthesis of new aluminum hydrides bearing a highly sterically hindered acenaphthene-1,2-diimine ligand

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Experimental part.

General information. Compounds **1** and **2** are sensitive to air and moisture. Therefore all manipulations were carried out *in vacuo* or under argon (nitrogen) using standard Schlenk technique or under nitrogen atmosphere in a drybox. The solvents (THF and Et_2O) were dried using appropriate methods and were distilled under N_2 or condensed *in vacuo* prior to use. Tetrahydrofuran-d_8 (THF-d_8) was dried over Na/K alloy. Acenaphthenequinone, *p*-toluidine, benzhydrol, $ZnCl_2$, $LiAlH_4$, $AlCl_3$, THF-d_8 were purchased from Aldrich. The NMR spectra were obtained on Bruker DPX 200 (200 MHz) and Bruker Avance III (400 MHz) instruments. IR spectra (4000-450 cm^{-1}) were obtained on FSM-1201 instrument in mineral oil. Ligand dbhmp-bian, 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene, was synthesized as reported [L. Guo, W. Kong, Y. Xu, Y. Yang, R. Ma, L. Cong, S. Dai, Z. Liu, *J. Organomet. Chem.*, 2018, **859**, 58–67.].

[(dbhmp-bian)AlH_2]$^-$[Li(THF)$_4$]$^+$ (1). A solution of $LiAlH_4$ (0.076 g, 2 mmol) in THF (30 ml) was added to a solution of dbhmp-bian (2.34 g, 2 mmol) in THF (20 ml) in a 100 ml Schlenk flask equipped with a magnet stirrer, and the mixture was stirred for 10 hours. Hydrogen evolution was observed. The resulting green solution was filtered at Schott filter No. 4, and the

filtrate was concentrated to a volume of approximately 15 ml. Storage of the solution at room temperature for 2 days afforded emerald-green block crystals of **1** (2.79 g, 81%). M.p. = 210 °C (dec). Elemental analysis calcd (%) for $C_{114}H_{134}AlLiN_2O_9$ (1710.14): C, 80.06; H, 7.90; N, 1.64%. Found: C, 79.93; H, 7.82; N, 1.76%. ^{1}H NMR (THF-d_8, 400 MHz, 213 K) *δ*, ppm: 7.23–7.17 (ps. d, 8H, arom), 7.11–7.05 (ps. t, 8H, arom), 7.05–6.98 (m, 12H, arom), 6.78 (s, 4H), 6.70 (s, 4H), 6.67–6.60 (m, 12H, arom), 6.27 (d, 2H, arom, *J* = 8.1 Hz), 6.04 (ps. t, 2H, arom, *J* = 7.3 Hz), 4.98 (d, 2H, arom, *J* = 6.6 Hz), 4.62 (br. s, 2H, Al–*H*), 3.60-3.58 (br. s, 32H (8THF)), 2.15 (s, 6H, C*H*$_3$), 1.77-1.73 (br. s, 32H (8THF)). IR (Nujol, cm^{-1}): ν = 1951 m, 1887 m, 1757 s (Al–H), 1702 s (Al–H), 1599 s, 1507 w, 1493 w, 1455 s, 1376 s, 1356 m, 1322 m, 1295 m, 1274 m, 1247 w, 1213 m, 1195 w, 1180 s, 1156 w, 1142 w, 1124 w, 1071 s, 1035 s, 1002 m, 981 w, 918 s, 886 s, 814 s, 769 m, 754 s, 700 s, 679 w, 645 w, 634 w, 621 m, 605 s, 584 s, 556 s, 503 w, 478 s.

(dbhmp-bian)AlH(THF) (2). A mixture of dbhmp-bian (1.025 g, 1.0 mmol), $LiAlH_4$ (0.028 g 0.75 mmol) and $AlCl_3$ (0.033 g, 0.25 mmol) in THF (~25 ml) was sealed in a glass ampoule (50 ml) equipped with a magnetic stirrer. Stirring at 50 °C (hydrogen evolution was observed) within 3 hours resulted in a blue green solution. The obtained reaction mixture was concentrated approximately to 5 ml volume and diluted with Et_2O (~20 ml). The colorless precipitate (LiCl) was filtered on Schott filter No. 4. Crystallization of the filtrate at -10 °C affords dark green crystals of **2** (1.1 g, 86%). Mp > 245 °C (dec.). Elemental analysis calcd (%) for $C_{90}H_{85}AlN_2O_3$ (1269.66): C, 85.14; H, 6.75; N, 2.21%. Found: C, 84.73; H, 6.81; N, 2.35%. ^{1}H NMR (THF-d_8, 400 MHz, 293 K) *δ*, ppm: 7.10–7.04 (m, 20H, arom), 7.03–6.96 (m, 12H, arom), 6.94 (d, 2H, arom, *J* = 8.3) 6.85–6.80 (m, 12H, arom), 6.50 (dd, 2H, arom, *J* = 7.1, *J* = 8.2), 6.42 (s, 4H, –C*H*(Ph)$_2$), 5.43 (d, 2H, arom, *J* = 6.8), 3.66–3.61 (m, 20H (5THF)), 2.24 (s, 6H, C*H*$_3$), 1.82–1.77 (m, 20H (5THF)). ^{13}C{^{1}H} NMR (THF-d_8, 50 MHz, 293 K) *δ*, ppm: 145.59 (4C, arom), 144.52 (4C, arom), 143.36 (2C, arom), 141.34 (4C, arom), 135.24 (2C, arom), 133.12 (2C, arom), 132.34 (2C, arom), 130.02 (8C, arom), 129.96 (4C, arom), 129.74 (8C, arom), 127.60 (8C, arom), 127.27 (8C, arom), 129.99 (2C, arom), 125.84 (2C, arom), 125.39 (4C, arom), 125.25 (4C, arom), 122.30 (2C, arom), 118.39 (2C, arom), 51.25 (4C, –*C*H(Ph)$_2$), 20.53 (2C, *C*H$_3$). IR (Nujol, cm^{-1}): *ν* = 1816 s (Al–H), 1597 m, 1513 m, 1492 m, 1321 s, 1290 w, 1271 m, 1214 w, 1178 w, 1144 w, 1128 w, 1068 s, 1030 m, 1001 w, 925 s, 883 w, 852 w, 831 w, 811 w, 801 w, 782 w, 759 m, 744 s, 702 s, 635 w, 622 w, 605 m, 559 m, 479 w.

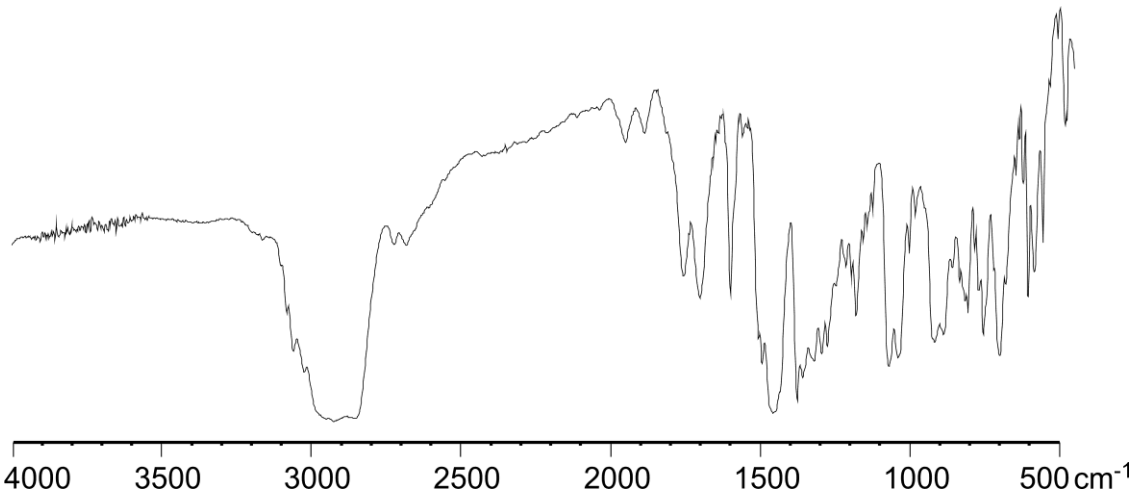

Figure S1. IR spectrum of compound **1** (mineral oil).

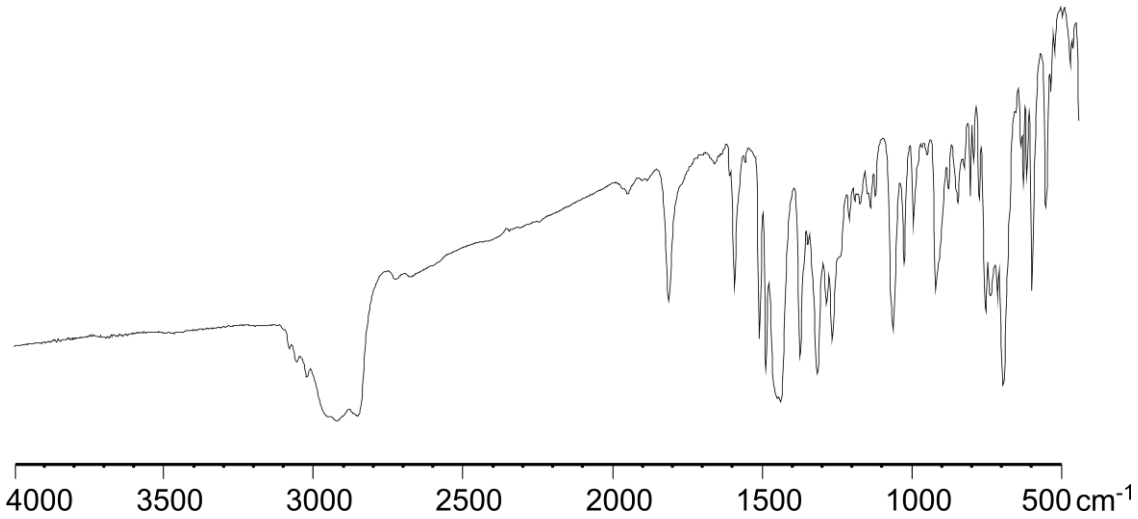

Figure S2. IR spectrum of compound **2** (mineral oil).

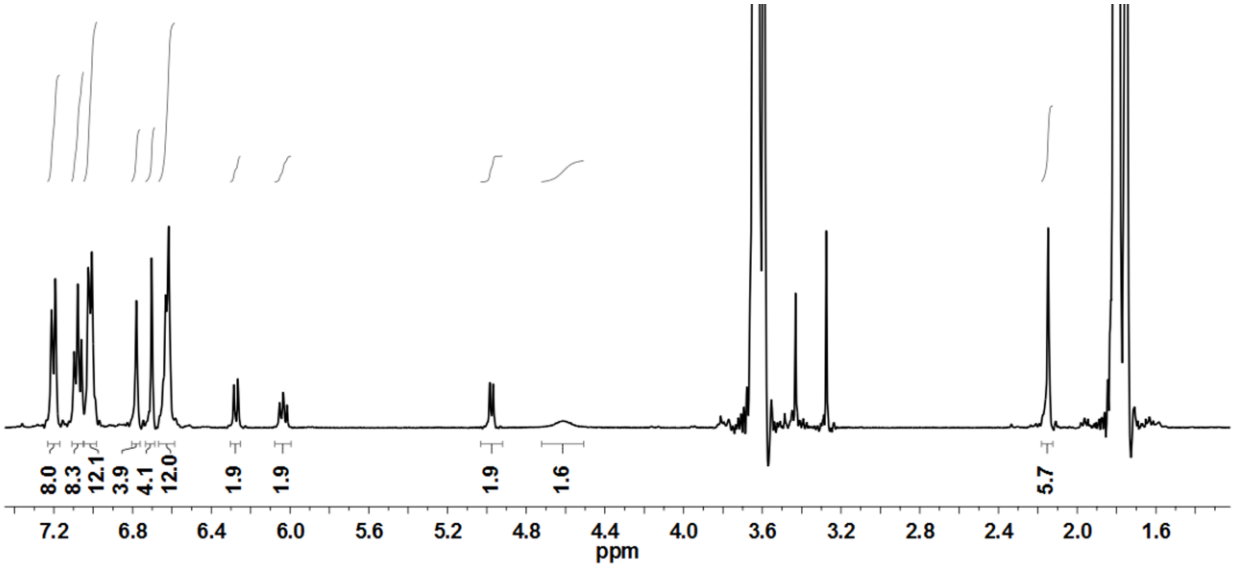

Figure S3. ^{1}H NMR spectrum of compound **1** (THF-d_8, 400 MHz, 213 K).

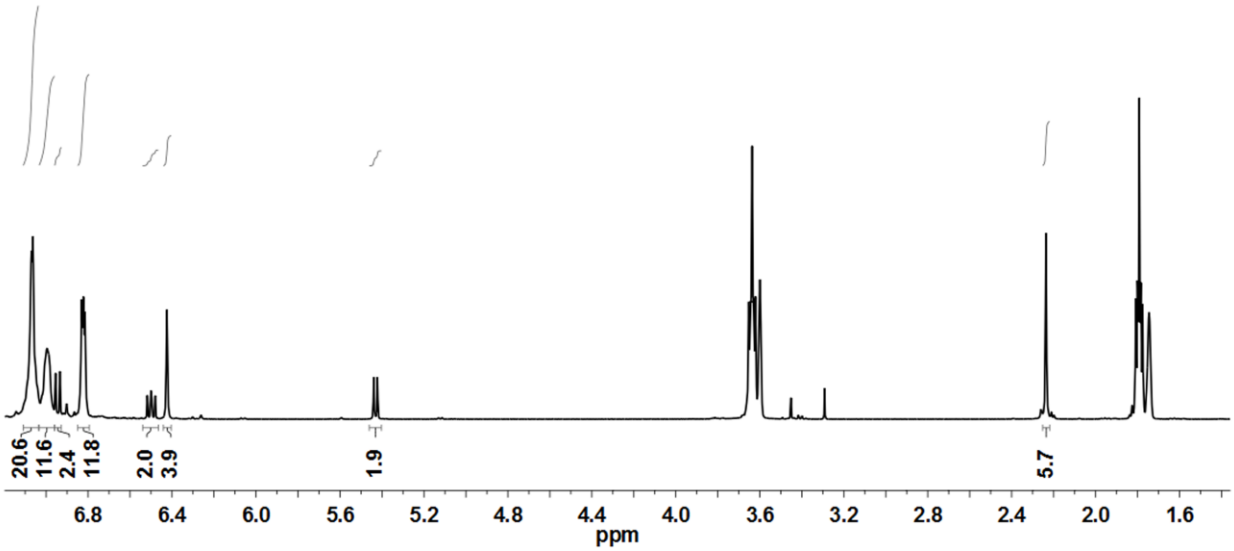

Figure S4. ^{1}H NMR spectrum of compound **2** (THF-d_8, 400 MHz, 293 K).

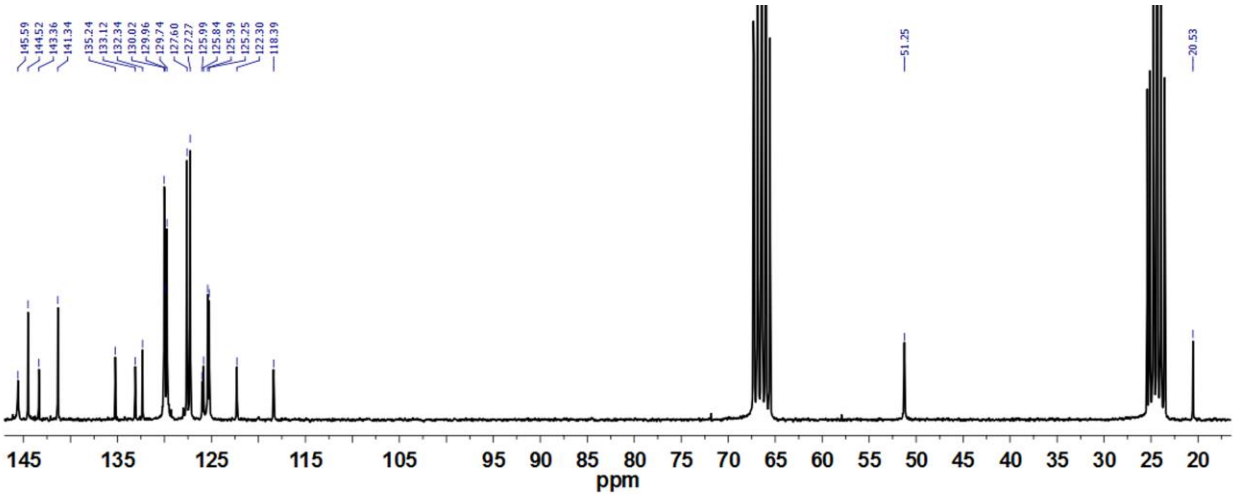

Figure S5. ^{13}C{^{1}H} NMR spectrum of compound **2** (THF-d_8, 50 MHz, 293 K).

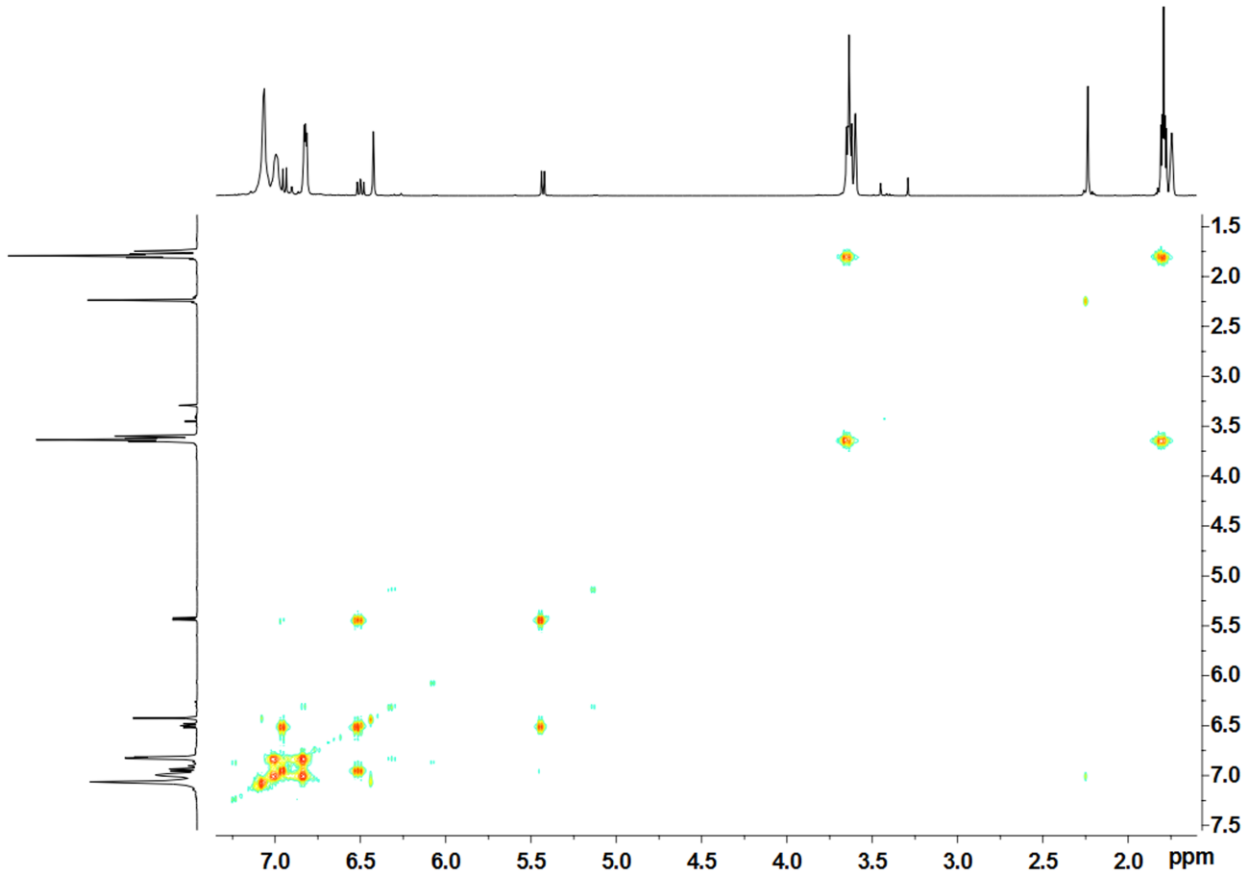

Figure S6. COSY ^{1}H-^{1}H NMR spectrum of compound **2** (THF-d$_8$, 293 K).

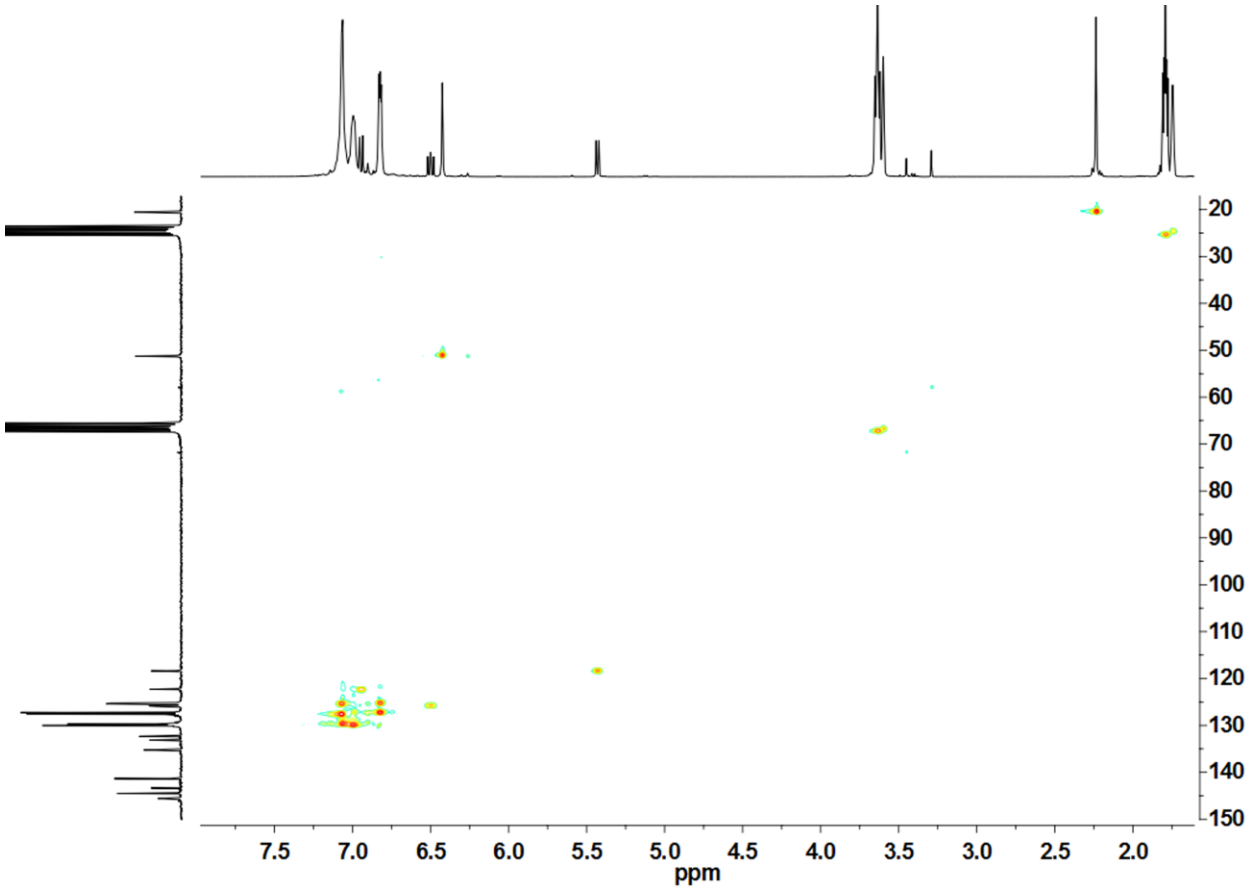

Figure S7. COSY ^{1}H-^{13}C HSQC NMR spectrum of compound **2** (THF-d$_8$, 293 K).

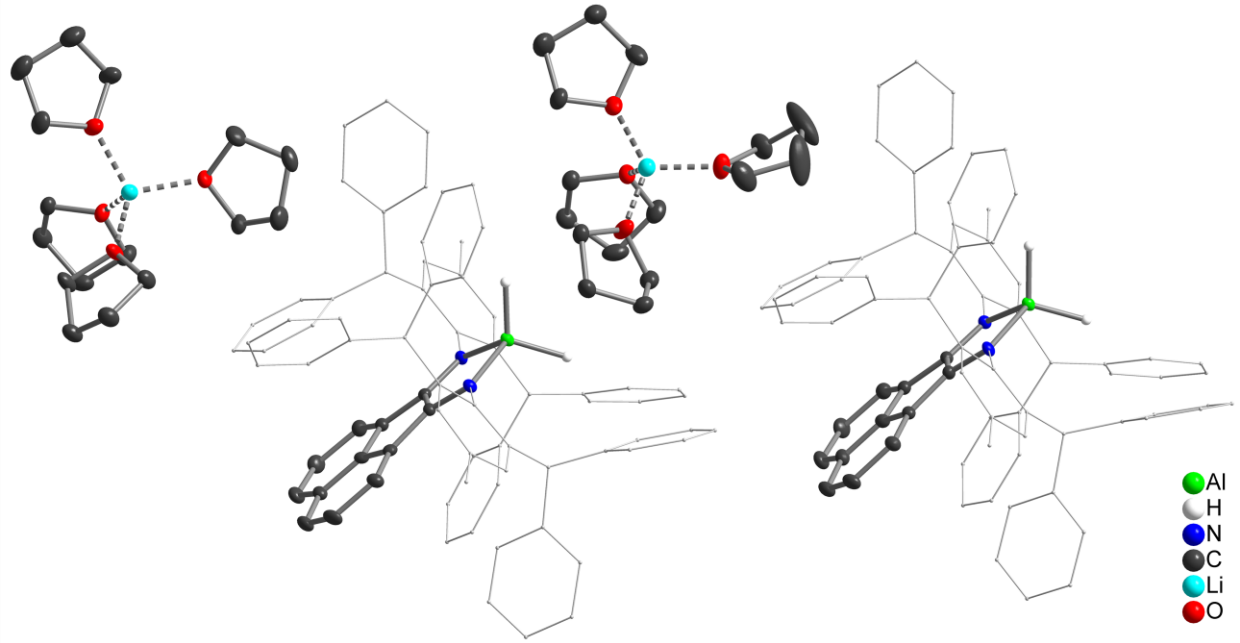

Figure S8. Molecular structure of **1**. Both molecules are represented. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms with the exception of Al–*H* hydrogen atoms and co-crystallized THF molecules are omitted. Aryl substituents at *N*-diimine atoms are represented schematically for clarity.