Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

Synthesis of Novel Six-, Seven- and Eight-Membered Aluminum-Containing Rings by Alumole Ring Expansion

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A. Methods

A.1 Materials

1-(η^5-1,2,4-tris(*tert*-butyl)cyclopentadienyl)-2,3,4,5-tetraethylalumole (**1**),[1] was synthesised according to a literature procedure. All manipulations were performed either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves.

A.2 Physical methods

NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{11}B: 160.5 MHz). Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. High resolution mass spectrometry was performed on a Thermo Scientific Exactive Plus spectrometer using a LIFDI 700 source from Linden CMS.

B. Synthetic details and NMR data

B.1 Synthesis of 2

1-(η^5-1,2,4-tris(*tert*-butyl)cyclopentadienyl)-2,3,4,5-tetraethylalumole (**1**) (30.0 mg, 70.6 µmol, 1 equiv) was dissolved in benzene (1 mL) and diisopropylcarbodiimide (8.9 mg, 71 µmol, 1 equiv) was added dropwise. The solvent was removed under dynamic vacuum and the residue was redissolved in pentane. The solution was kept at –30 °C, and product **2** was crystallised as a colorless solid (29.0 mg, 52.6 µmol, 75%).

^{1}H NMR (500.1 MHz, 296 K, C$_6$D$_6$): δ = 6.51 (d, $^{4}J_{\mathrm{HH}}$ = 2.7 Hz, 1H, Cp-*H*), 6.34 (d, $^{4}J_{\mathrm{HH}}$ = 2.7 Hz, 1H, Cp-*H*), 3.91 (sept, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 1H, N–C*H*(CH$_3$)$_2$), 3.42 (sept, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, 6H, N–C*H*(CH$_3$)$_2$), 2.41–1.90 (m, 8H, C*H*$_2$CH$_3$), 1.87 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, N–CH(C*H*$_3$)$_2$), 1.72 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, N–CH(C*H*$_3$)$_2$), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (s, 9H, C(C*H*$_3$)$_3$), 1.32 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, N–CH(C*H*$_3$)$_2$), 1.28 (t, $^{3}J_{\mathrm{HH}}$ = 7.58 Hz, 3H, CH$_2$C*H*$_3$), 1.18 (d, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, 3H, N–CH(C*H*$_3$)$_2$), 1.07 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 6H, CH$_2$C*H*$_3$), 0.99 (t, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C$_6$D$_6$): δ = 157.3 (*C*=N–CH(CH$_3$)$_2$), 153.5 (*C*(CH$_2$CH$_3$), 152.0 (*C*(Cp)-C(CH$_3$)$_3$), 147.8 (*C*(CH$_2$CH$_3$), 137.4 (*C*(CH$_2$CH$_3$), 124.0 (*C*(CH$_2$CH$_3$), 116.6 (*C*(Cp)-H), 103.4 (*C*(Cp)-H), 51.0 (N–*C*H(CH$_3$)$_2$), 48.8 (N–*C*H(CH$_3$)$_2$), 34.9 (*C*(Cp)(CH$_3$)$_3$), 34.4 (*C*(Cp)(*C*H$_3$)$_3$), 34.0 (C(*C*H$_3$)$_3$), 33.4 (C(*C*H$_3$)$_3$), 33.4 (*C*(Cp)(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 27.0 (*C*H$_2$CH$_3$), 26.9 (N–CH(*C*H$_3$)$_2$), 25.8 (N–CH(*C*H$_3$)$_2$), 25.3 (*C*H$_2$CH$_3$), 25.2 (N–CH(*C*H$_3$)$_2$), 25.1 (*C*H$_2$CH$_3$), 22.2 (*C*H$_2$CH$_3$), 21.1 (N–CH(*C*H$_3$)$_2$), 15.5 (CH$_2$*C*H$_3$), 15.1 (CH$_2$*C*H$_3$), 13.9 (CH$_2$*C*H$_3$), 12.4 (CH$_2$*C*H$_3$) ppm.

Elemental analysis: calcd for C$_{36}$H$_{63}$AlN$_2$: C 78.49, H 11.53, N 5.09, found: C 78.20, H 11.50, N 5.10.

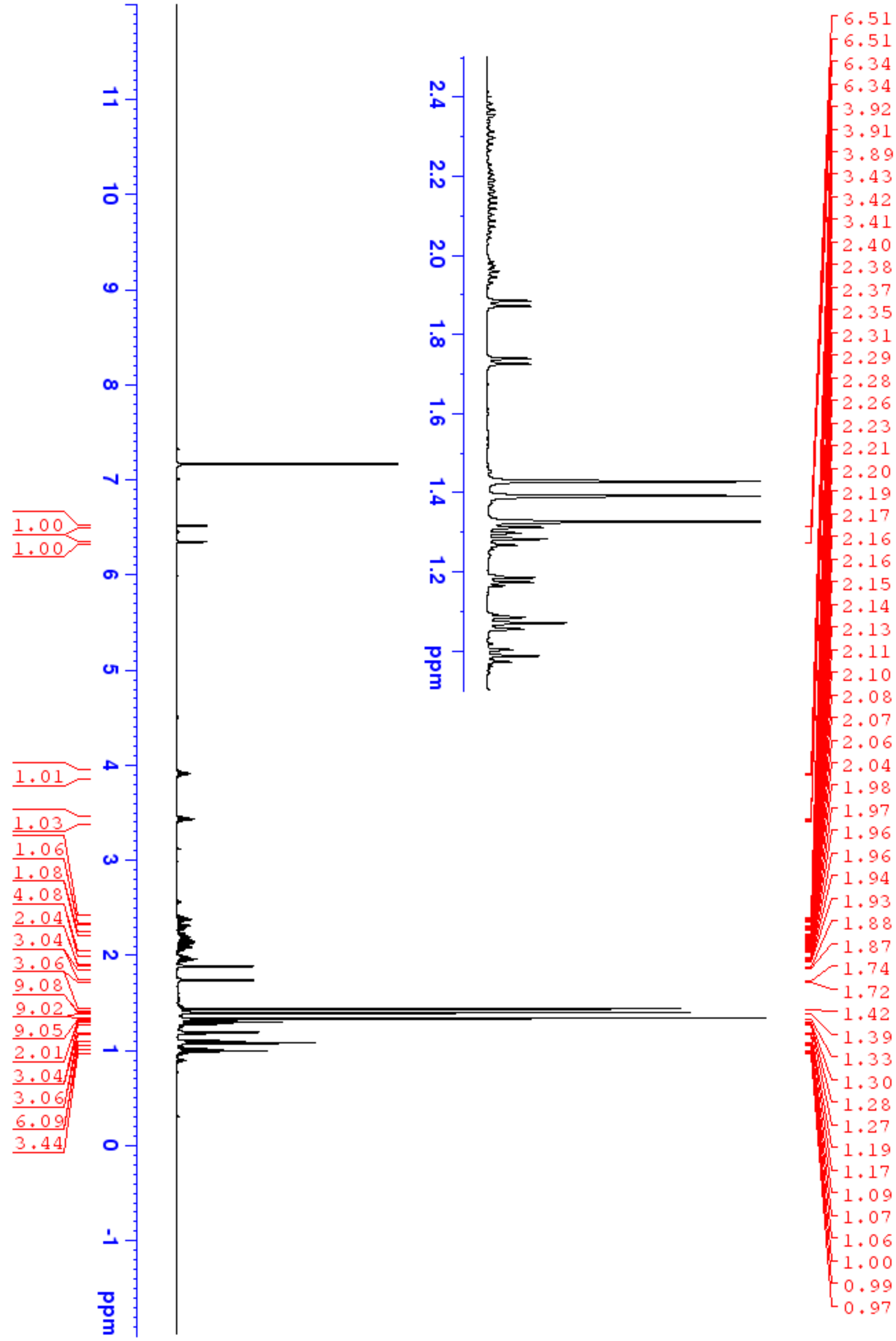

Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6.

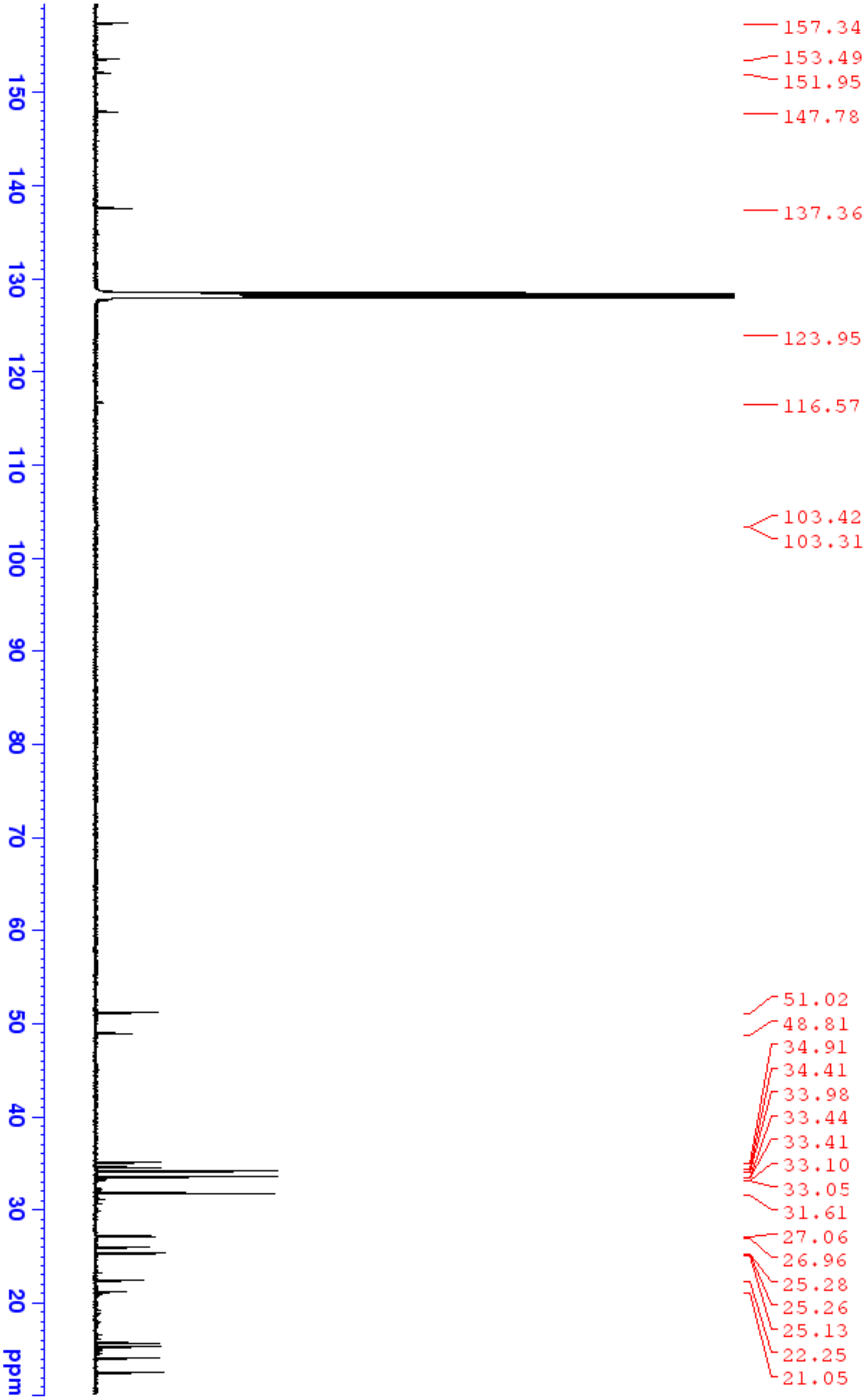

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **2** in C_6D_6.

B.2 Synthesis of 3

A solution of diphenylnitrone (7.0 mg, 35 µmol, 1.0 equiv) in C_6D_6 was added to a solution of 1-(η^5-1,2,4-tris(*tert*-butyl)cyclopentadienyl)-2,3,4,5-tetraethylalumole (**1**) (15.0 mg, 35.3 µmol, 1.00 equiv) in C_6D_6 (0.7 mL). After 10 minutes at room temperature, the solvent was removed under reduced pressure to give a red oil. Colorless crystals of the product **3** were obtained from a dichloromethane solution at –30 °C (10.3 mg, 16.6 µmol, 47%).

^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 7.32–7.27 (m, 4H, Ar*H*), 7.16 (t, $^3J_{HH}$ = 8.0 Hz, 3H, Ar*H*), 7.07 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ar*H*), 7.01–6.97 (m, 1H, Ar*H*), 6.83 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar*H*), 6.74 (d, $^5J_{HH}$ = 3.1 Hz, 1H, Cp*H*), 6.43 (d, $^5J_{HH}$ = 3.1 Hz, 1H, Cp*H*), 4.91 (s, 1H, NC*H*Ar), 4.27 (s, $CH_2^{\text{dichloromethane}}$), 2.61–2.52 (m, 1H, C*H*$_2$CH$_3$), 2.28–2.21 (m, 2H, C*H*$_2$CH$_3$), 2.15–1.94 (m, 3H, C*H*$_2$CH$_3$), 1.73–1.64 (m, 1H, C*H*$_2$CH$_3$), 1.57 (s, 9H, C(C*H*$_3$)$_3$), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.34 (s, 9H, C(C*H*$_3$)$_3$), 1.27–1.17 (m, 1H, C*H*$_2$CH$_3$), 1.11 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 1.07 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH$_2$C*H*$_3$), 1.05 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_2$C*H*$_3$), 0.97–0.87 (m, 1H, C*H*$_2$CH$_3$), 0.90 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C{^{1}H} NMR (125.8 MHz, 296 K, CH_2Cl_2): δ = 157.4 (*C*(CH$_2$CH$_3$), 155.4 (Ar*C*), 148.5 (*C*(CH$_2$CH$_3$), 143.7 (Ar*C*), 143.2 (*C*(CH$_2$CH$_3$, detected by HMBC), 138.3 (*C*(CH$_2$CH$_3$), 131.5 (*C*C(CH$_3$)$_3$-Cp), 130.1 (*C*C(CH$_3$)$_3$-Cp), 129.2 (Ar*C*-H), 128.1 (Ar*C*-H), 125.8 (Ar*C*-H), 125.1 (*C*C(CH$_3$)$_3$-Cp), 119.8 (Ar*C*-H), 116.8 (Ar*C*-H), 110.2 (*C*(Cp)-H), 109.1 (*C*(Cp)-H), 75.6 (N*C*HAr), 34.6 (*C*(CH$_3$)$_3$-Cp), 34.1 (*C*(CH$_3$)$_3$-Cp), 33.8 (C(*C*H$_3$)$_3$-Cp), 33.6 (C(*C*H$_3$)$_3$-Cp), 32.5 (*C*(CH$_3$)$_3$-Cp), 31.9 (C(*C*H$_3$)$_3$-Cp), 29.4 (*C*H$_2$CH$_3$), 27.7 (*C*H$_2$CH$_3$), 25.7 (*C*H$_2$CH$_3$), 23.7 (*C*H$_2$CH$_3$), 15.3 (CH$_2$*C*H$_3$), 15.0 (CH$_2$*C*H$_3$), 13.5 (CH$_2$*C*H$_3$), 13.4 (CH$_2$*C*H$_3$) ppm.

Elemental analysis: calcd for $C_{42}H_{60}AlNO + 0.25\ CH_2Cl_2$: C 78.90, H 9.48, N 2.18, found: C 79.61, H 9.53, N 2.13.

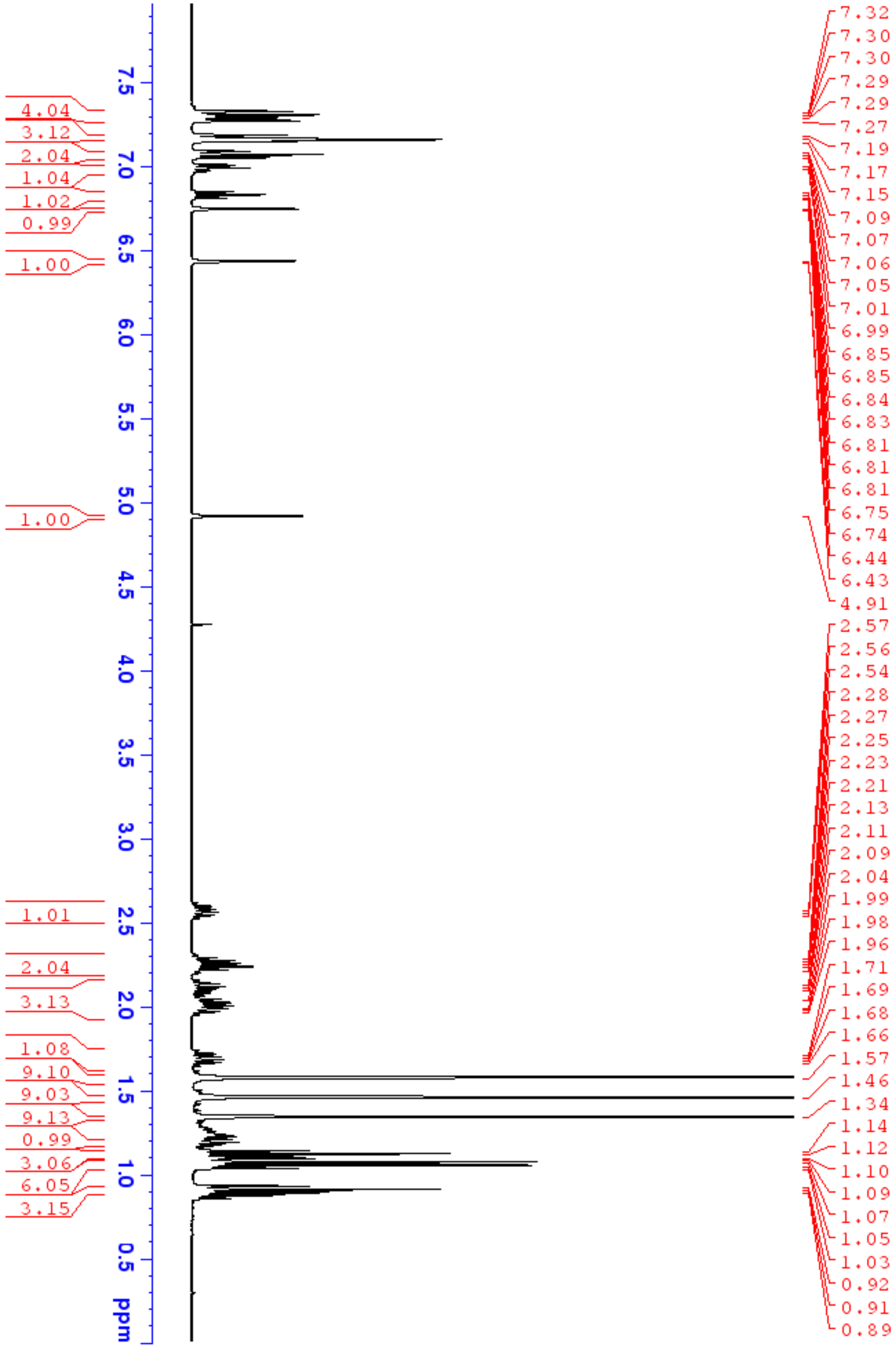

Figure S3. ^{1}H NMR spectrum of **3** in C_6D_6. The singlet at 4.27 ppm is due to residual CH_2Cl_2

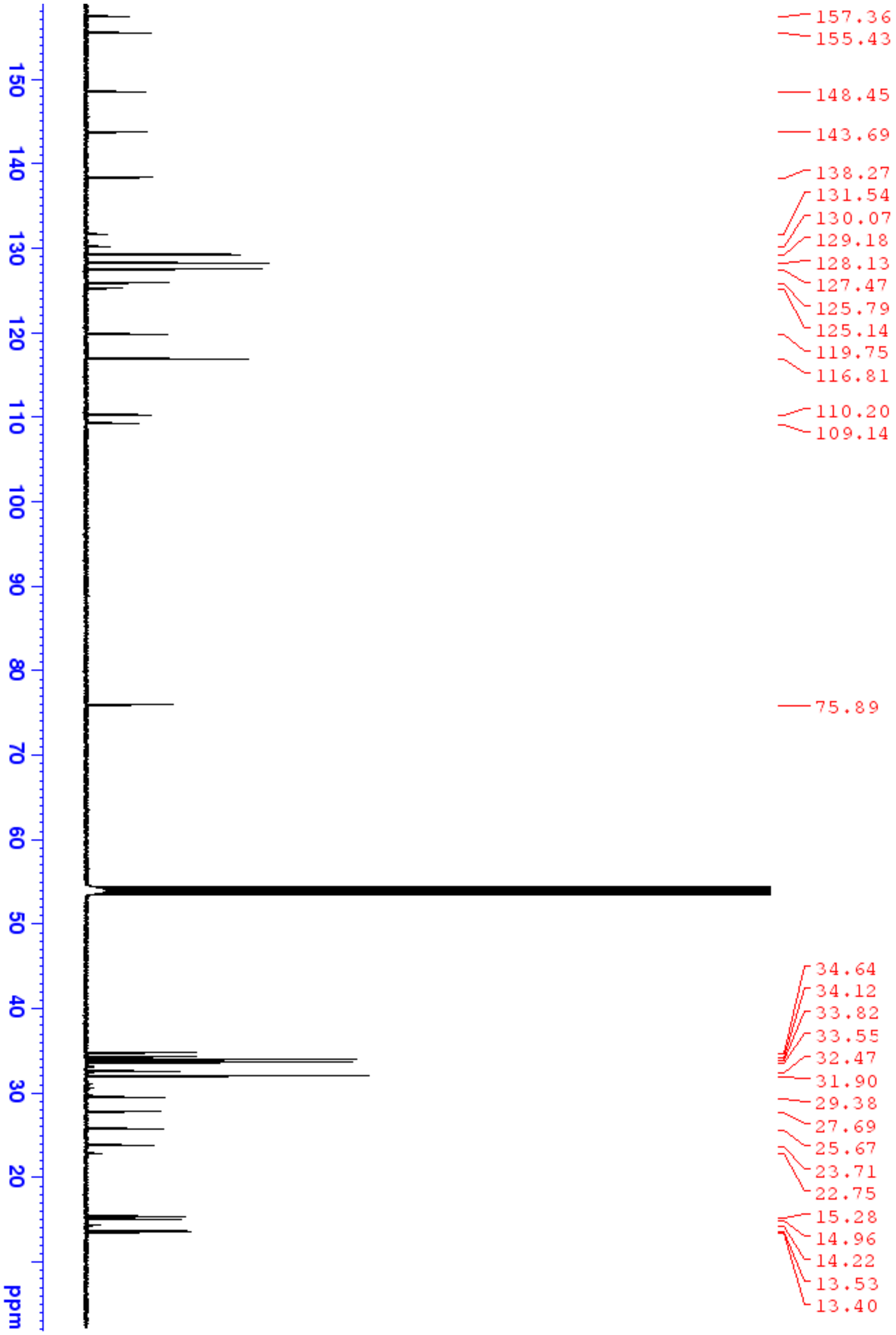

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in CD_2Cl_2.

B.3 Synthesis of 4

1-(η^5-1,2,4-tris(*tert*-butyl)cyclopentadienyl)-2,3,4,5-tetraethylalumole (**1**) (15.0 mg, 35.4 µmol, 1.00 equiv) was dissolved in toluene (2 mL) and cooled to −78 °C. (*tert*-Butylimino)mesitylborane in heptane (0.840 mol/L, 42.2 µL, 35.4 µmol, 1.00 equiv) was added dropwise. The solution was warmed to room temperature and the solvent was removed under reduced pressure. The product **4** was obtained by crystallisation at −30 °C from pentane as colorless crystals (18.7 mg, 29.9 µmol, 70%).

^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 6.85 (s, 1H, –CH^{Mes}), 6.75 (s, 1H, –CH^{Mes}), 6.66 (d, $^4J_{\mathrm{HH}}$ = 3.2 Hz, 1H, Cp*H*), 6.62 (d, $^4J_{\mathrm{HH}}$ = 3.2 Hz, 1H, Cp*H*), 2.62 (s, 3H, –CH_3^{Mes}), 2.48–2.43 (m, 1H, CH_2CH$_3$), 2.37–2.23 (m, 3H, CH_2CH$_3$), 2.19 (s, 3H, –CH_3^{Mes}), 2.17–2.12 (m, 3H, CH_2CH$_3$), 2.07 (s, 3H, –CH_3^{Mes}), 2.04–1.94 (m, 3H, CH_2CH$_3$), 1.57 (s, 9H, C(CH_3)$_3$), 1.50 (s, 9H, C(CH_3)$_3$), 1.37 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, NC(CH_3)$_3$), 1.18 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, CH$_2$CH_3), 1.09 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, CH$_2$CH_3), 1.07 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, CH$_2$CH_3), 0.58 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 3H, CH$_2$CH_3) ppm.

^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C_6D_6): δ = 40.5 ppm..

^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 171.1 (*C*(CH$_2$CH$_3$), 158.9 (*C*(CH$_2$CH$_3$), 155.9 (*C*C(CH$_3$)$_3^{\mathrm{Cp}}$), 150.9 (*C*(CH$_2$CH$_3$), 149.3 (*C*C(CH$_3$)$_3^{\mathrm{Cp}}$), 142.0 (BC^{Mes}), 140.0 (*C*CH_3^{Mes}), 137.90 (*C*CH_3^{Mes}), 136.3 (*C*CH_3^{Mes}), 133.3 (*C*H$^{\mathrm{Cp}}$), 131.6 (*C*(CH$_2$CH$_3$), 122.1 (*C*H$^{\mathrm{Cp}}$), 53.8 (N*C*CH$_3$), 35.6 (C*C*(CH$_3$)$_3^{\mathrm{Cp}}$), 34.9 (C*C*(CH$_3$)$_3^{\mathrm{Cp}}$), 34.1 (C*C*(CH$_3$)$_3^{\mathrm{Cp}}$), 34.1 (CC(*C*H$_3$)$_3^{\mathrm{Cp}}$), 33.8 (CC(*C*H$_3$)$_3^{\mathrm{Cp}}$), 33.7 (CC(*C*H$_3$)$_3^{\mathrm{Cp}}$), 30.7 (NC*C*H$_3$), 26.9 (*C*H$_2$CH$_3$), 26.8 (*C*H$_2$CH$_3$), 25.3 (C*C*H_3^{Mes}), 24.4 (*C*H$_2$CH$_3$), 23.8 (C*C*H_3^{Mes}), 23.4 (*C*H$_2$CH$_3$), 21.3 (C*C*H_3^{Mes}), 16.1 (CH$_2$*C*H$_3$), 15.3 (CH$_2$*C*H$_3$), 14.9 (CH$_2$*C*H$_3$), 14.7 (CH$_2$*C*H$_3$) ppm.

Elemental analysis: calcd for $C_{42}H_{69}AlBN$: C 80.61, H 11.11, N 2.24, found: C 80.99, H 11.47, N 2.17.

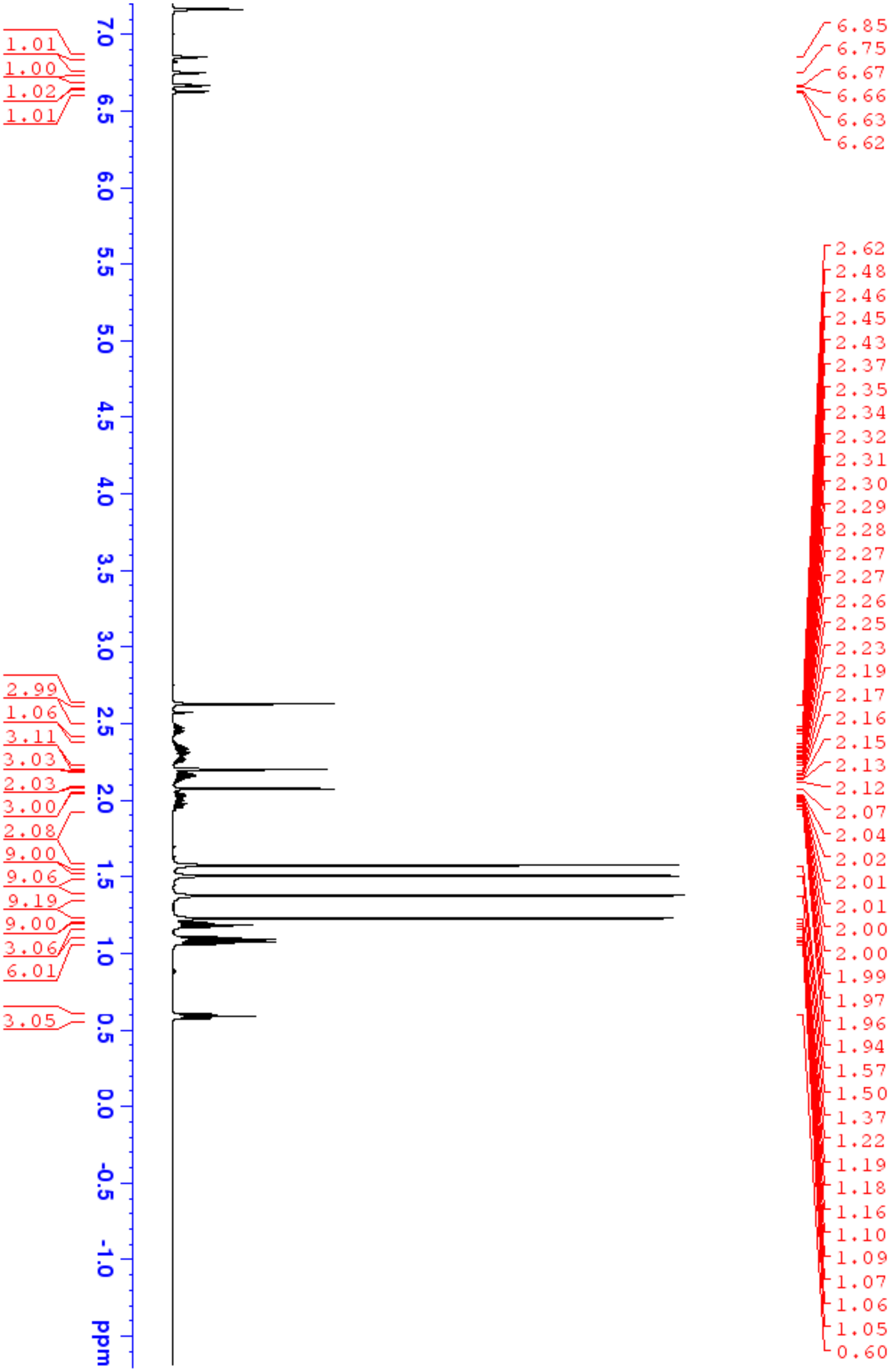

Figure S5. ^{1}H NMR spectrum of **4** in C_6D_6.

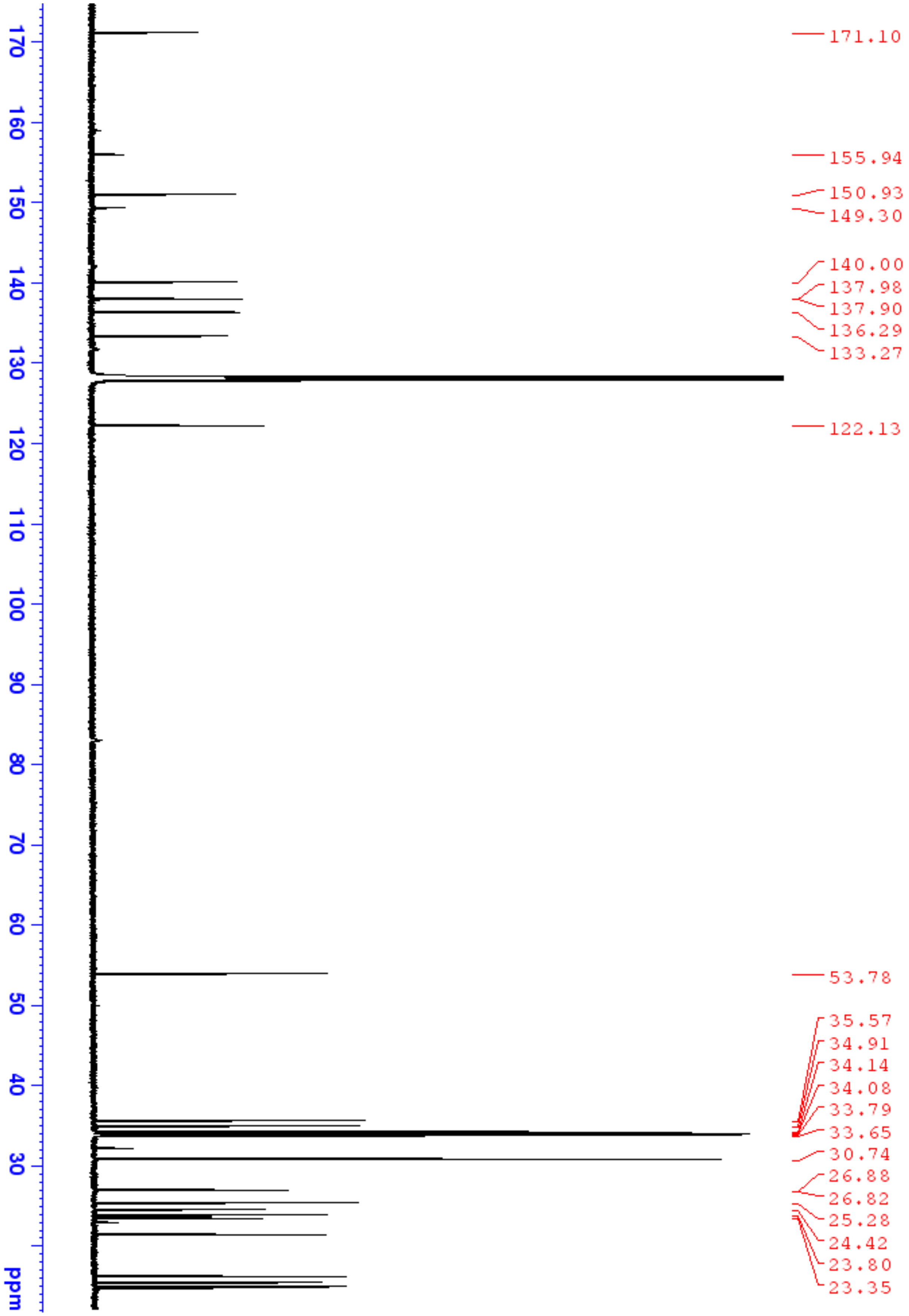

Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **4** in C_6D_6.

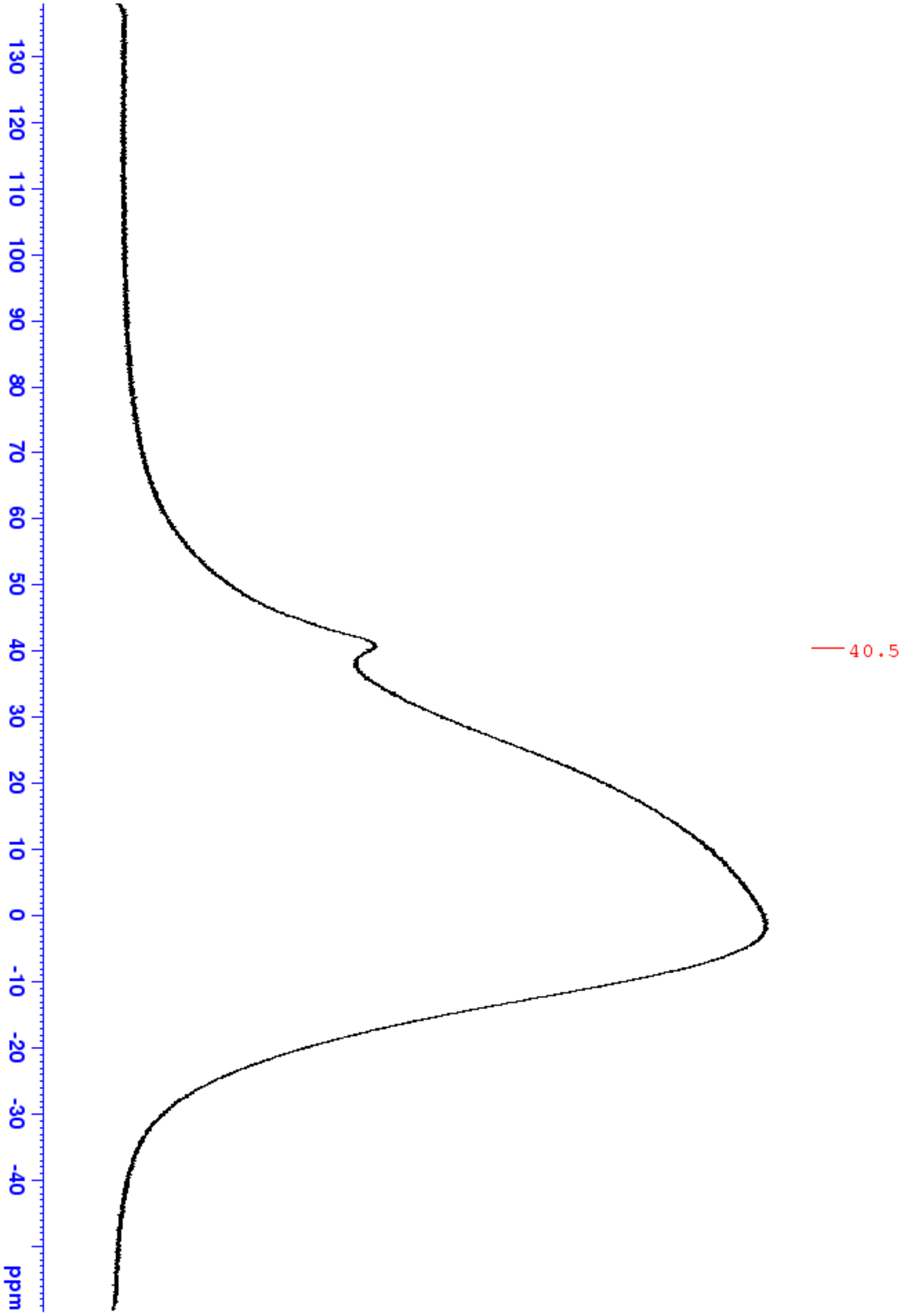

Figure S7. $^{11}B\{^1H\}$ NMR spectrum of **4** in C_6D_6.

B.4 Synthesis of 5

A suspension of *N*-methylmorpholine-*N*-oxide (8.3 mg, 71 µmol, 2.0 equiv) in C_6D_6 (0.3 mL) was added to a solution of 1-(η^5-1,2,4-tris(*tert*-butyl)cyclopentadienyl)-2,3,4,5-tetraethylalumole (**1**) (15.0 mg, 35.3 µmol, 1.00 equiv) in C_6D_6 (0.4 mL). After 10 minutes at room temperature, the solvent was removed under reduced pressure, yielding a white solid. Pentane was then added, leaving excess *N*-methylmorpholine-*N*-oxide as a solid in pentane. This was removed by filtration, and **5** was obtained as a colorless solid by cooling the filtrate to –30 °C for 48 h, followed by filtration and drying under vacuum (9.3 mg, 17 µmol, 47%).

^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 6.17 (d, $^4J_{HH}$ = 2.1 Hz, 1H, Cp-*H*), 5.97 (d, $^4J_{HH}$ = 2.1 Hz, 1H, Cp-*H*), 4.08–4.01 (m, 2H, C*H*$_2$-morpholine), 3.09–3.05 (m, 2H, C*H*$_2$-morpholine), 2.75 (dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_2$-morpholine), 2.68 (dd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 1.5 Hz, 1H, C*H*$_2$-morpholine), 2.67–2.48 (m, 6H, C*H*$_2$CH$_3$), 2.56 (s, 3H, C*H*$_3$-morpholine), 2.42–2.32 (m, 2H, C*H*$_2$CH$_3$), 1.86–1.79 (m, 2H, C*H*$_2$-morpholine), 1.51 (s, 9H, C(C*H*$_3$)$_3$), 1.39 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 1.23 (s, 9H, C(C*H*$_3$)$_3$), 1.17 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 1.15 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$C*H*$_3$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 164.5 (*C*C(CH$_3$)$_3$-Cp), 153.2 (*C*(CH$_2$CH$_3$), 152.9 (*C*(CH$_2$CH$_3$), 149.6 (*C*C(CH$_3$)$_3$-Cp), 146.6 (*C*(CH$_2$CH$_3$), 133.6 (*C*(Cp)-H), 126.1 (*C*(Cp)-H), 95.7 (*C*C(CH$_3$)$_3$-Cp), 64.8 (*C*H$_2$-morpholine), 64.8 (*C*H$_2$-morpholine), 61.3 (*C*H$_2$-morpholine), 61.2 (*C*H$_2$-morpholine), 57.7 (*C*H$_3$-morpholine), 39.0 (*C*(CH$_3$)$_3$-Cp), 34.8 (C(*C*H$_3$)$_3$-Cp), 32.9 (*C*(CH$_3$)$_3$-Cp), 32.0 (*C*(CH$_3$)$_3$-Cp), 29.3 (C(*C*H$_3$)$_3$-Cp), 29.0 (C(*C*H$_3$)$_3$-Cp), 25.8 (*C*H$_2$CH$_3$), 25.7 (*C*H$_2$CH$_3$), 21.5 (*C*H$_2$CH$_3$), 21.4 (*C*H$_2$CH$_3$), 17.7 (CH$_2$*C*H$_3$), 17.5 (CH$_2$*C*H$_3$), 15.8 (CH$_2$*C*H$_3$), 15.6 (CH$_2$*C*H$_3$) ppm.

Elemental analysis: calcd for $C_{34}H_{60}AlBrNO_3$: C 73.21, H 10.84, N 2.51 found: C 73.05, H 10.73, N 2.48.

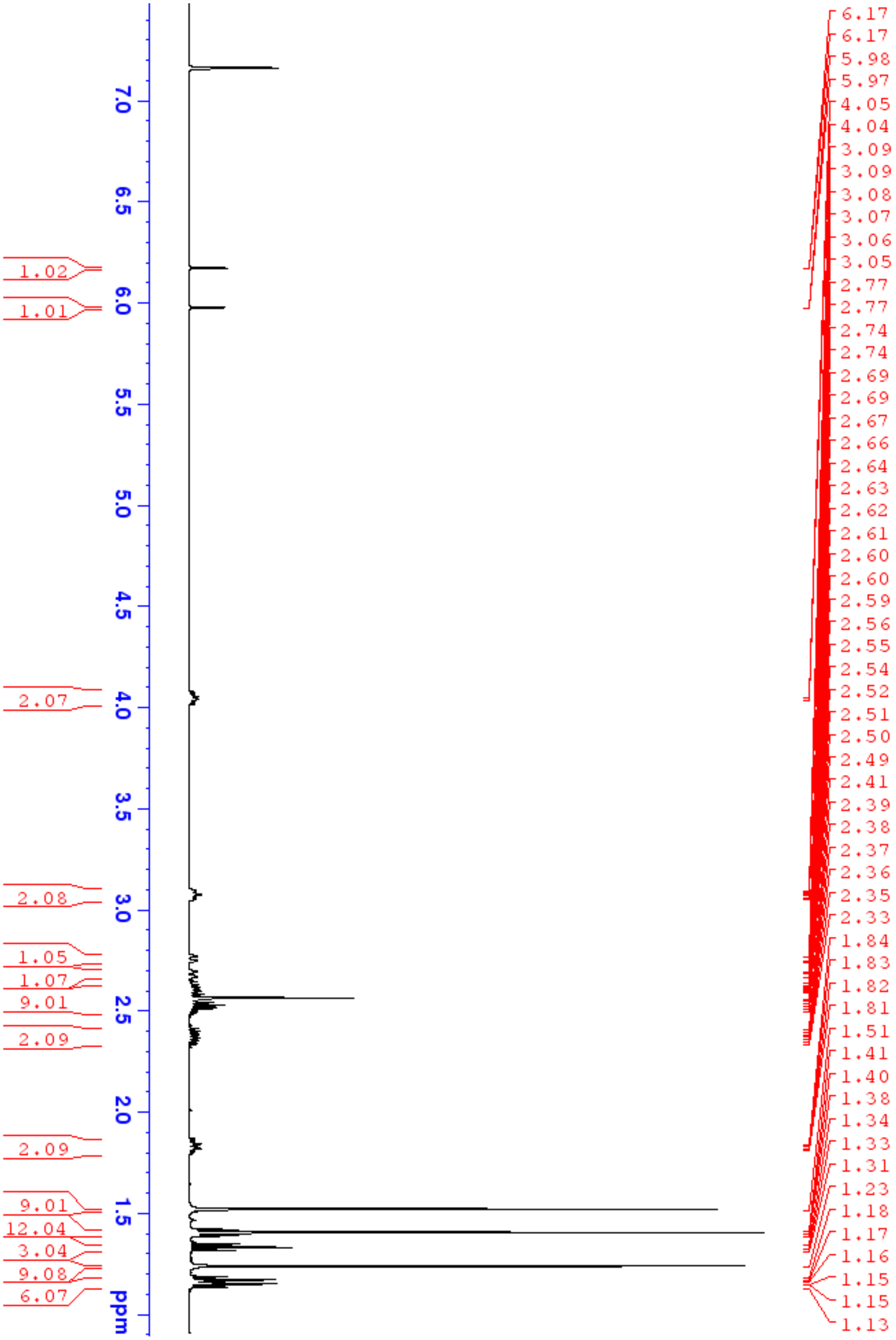

Figure S8. ^{1}H NMR spectrum of **5** in C_6D_6.

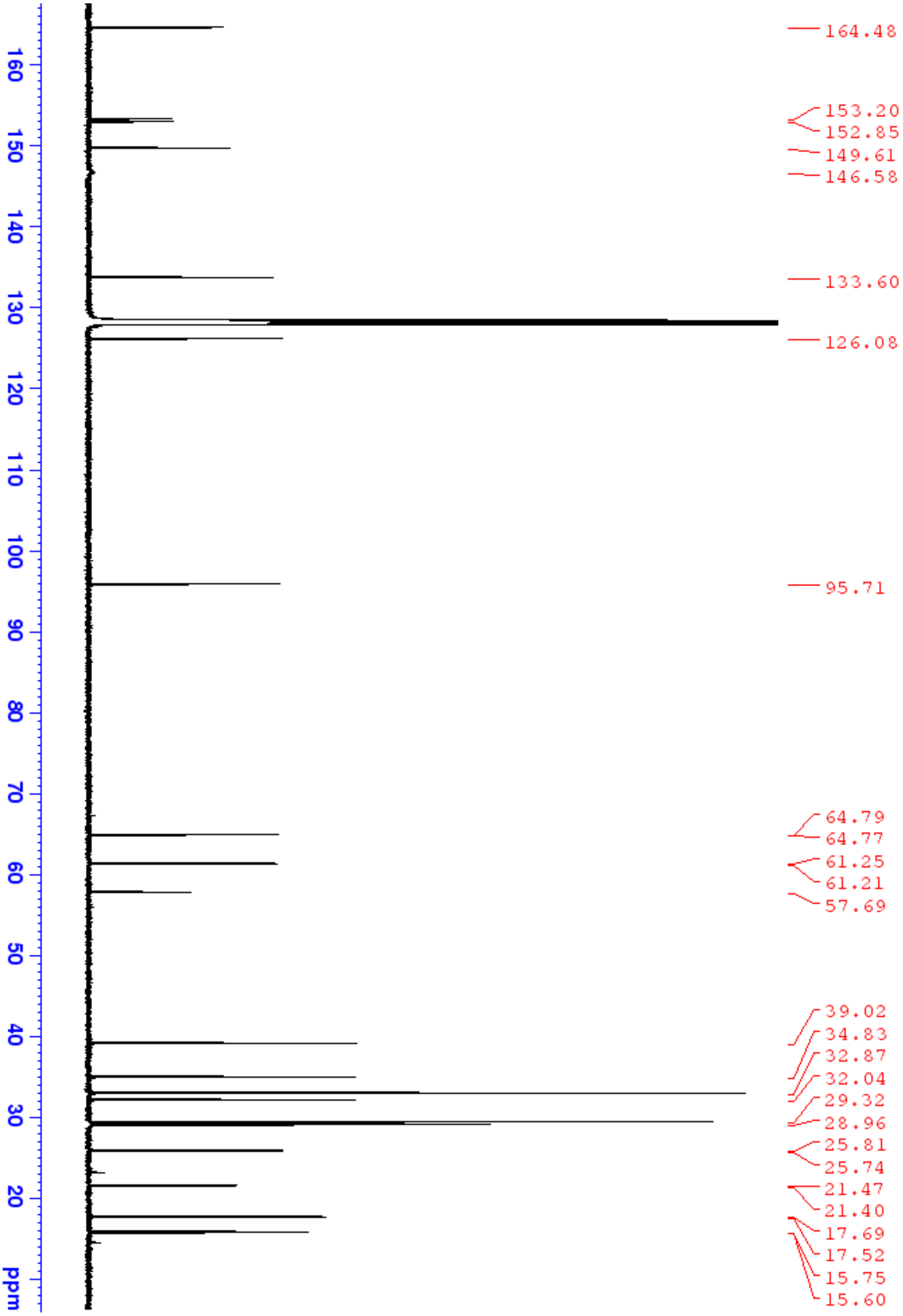

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

B.5 Synthesis of 6

A solution of **5** (15 mg, 26.9 µmol, 1.00 equiv) in C_6D_6 (0.7 mL) was heated to 80 °C. After 8 hours, the reaction was stopped and the solvent was removed under reduced pressure. The residue was extracted with pentane. Colorless crystals (19.9 mg, 21.8 µmol, 81%) were obtained from the solution by cooling it to –30 °C for 20 h, leaving the byproduct *N*-methylmorpholine-*N*-oxide in solution.

^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 6.14 (2 x d, $^4J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, 1H*, Cp-H), 6.12 (d, $^4J_{HH}$ = 2.0 Hz, 1H, Cp-H), 5.87 (d, $^4J_{HH}$ = 2.0 Hz, 1H, Cp-H), 5.74 (d, $^4J_{HH}$ = 2.0 Hz, 1H, Cp-H), 5.72 (d, $^4J_{HH}$ = 2.0 Hz, 1H*, Cp-H), 2.67–2.59 (m, 1H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.57–2.48 (m, 1H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.46–2.40 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.38–2.19 (m, 10H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.16–2.09 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.08–2.00 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.55 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.52 (s, 9H*, $\mathrm{C(C}H_3)_3$), 1.43 (t, $^3J_{HH}$ = 7.5 Hz, 6H, $\mathrm{CH_2C}H_3$), 1.39 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.35 (s, 9H*, $\mathrm{C(C}H_3)_3$), 1.32 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $\mathrm{CH_2C}H_3$), 1.27 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.26 (s, 9H*, $\mathrm{C(C}H_3)_3$), 1.24–1.21 (m, 6H, $\mathrm{C}H_2^{\mathrm{pentane}}$), 1.15 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.16–1.14 (m, 3H, $\mathrm{CH_2C}H_3$), 1.14 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.13 (s, 9H*, $\mathrm{C(C}H_3)_3$), 1.10 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $\mathrm{CH_2C}H_3$), 1.05–1.00 (m, 9H, $\mathrm{CH_2C}H_3$), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $\mathrm{CH_2C}H_3$), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $\mathrm{CH_2C}H_3$), 0.87 (t, $^3J_{HH}$ = 7.1 Hz, 6H, $\mathrm{C}H_3^{\mathrm{pentane}}$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 163.6 ($C\mathrm{C(CH_3)_3}$-Cp), 163.5 ($C\mathrm{C(CH_3)_3}$-Cp), 163.3 ($C\mathrm{C(CH_3)_3}$-Cp), 151.4 ($C\mathrm{C(CH_3)_3}$-Cp), 151.3 ($C\mathrm{C(CH_3)_3}$-Cp), 150.8 ($C\mathrm{C(CH_3)_3}$-Cp, 149.3 ($C\mathrm{(CH_2CH_3)}$, 149.3 ($C\mathrm{(CH_2CH_3)}$, 149.2 ($C\mathrm{(CH_2CH_3)}$, 146.0 ($C\mathrm{(CH_2CH_3)}$, 146.0 ($C\mathrm{(CH_2CH_3)}$, 145.9 ($C\mathrm{(CH_2CH_3)}$, 132.2 (C(Cp)-H), 131.9 (C(Cp)-H), 131.8 (C(Cp)-H), 127.0 (C(Cp)-H), 126.8 (C(Cp)-H), 126.7 (C(Cp)-H), 123.8 ($C\mathrm{(CH_2CH_3)}$, 123.6 ($C\mathrm{(CH_2CH_3)}$, 95.7 ($C\mathrm{C(CH_3)_3}$-Cp), 95.7 ($C\mathrm{C(CH_3)_3}$-Cp), 38.7 ($C\mathrm{(CH_3)_3}$-Cp), 38.4 ($C\mathrm{(CH_3)_3}$-Cp), 38.4 ($C\mathrm{(CH_3)_3}$-Cp), 34.8 ($C\mathrm{(CH_3)_3}$-Cp), 34.8 ($C\mathrm{(CH_3)_3}$-Cp), 34.7 ($C\mathrm{(CH_3)_3}$-Cp), 33.0 ($\mathrm{C(}C\mathrm{H_3)_3}$-Cp), 32.9 ($\mathrm{C(}C\mathrm{H_3)_3}$-Cp), 32.8 ($\mathrm{C(}C\mathrm{H_3)_3}$-Cp), 29.0 ($C\mathrm{(CH_3)_3}$-Cp), 28.9 ($C\mathrm{(CH_3)_3}$-Cp), 28.8 ($C\mathrm{(CH_3)_3}$-Cp), 28.7 ($C\mathrm{(CH_3)_3}$-Cp), 28.25 ($C\mathrm{H_2CH_3}$), 27.9 ($C\mathrm{H_2CH_3}$), 27.9 ($C\mathrm{H_2CH_3}$), 27.9 ($C\mathrm{H_2CH_3}$), 27.9 ($C\mathrm{H_2CH_3}$), 26.0 ($C\mathrm{H_2CH_3}$), 26.0 ($C\mathrm{H_2CH_3}$), 26.0 ($C\mathrm{H_2CH_3}$), 23.2 ($C\mathrm{H_2CH_3}$), 23.1 ($C\mathrm{H_2CH_3}$), 22.7 ($C\mathrm{H_2^{pentane}}$), 22.6 ($C\mathrm{H_2CH_3}$), 22.6 ($C\mathrm{H_2CH_3}$), 22.6 ($C\mathrm{H_2CH_3}$), 17.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 17.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 17.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 15.6 ($\mathrm{CH_2}C\mathrm{H_3}$), 15.5 ($\mathrm{CH_2}C\mathrm{H_3}$), 15.4 ($\mathrm{CH_2}C\mathrm{H_3}$), 15.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 14.9 ($\mathrm{CH_2}C\mathrm{H_3}$), 14.8 ($\mathrm{CH_2}C\mathrm{H_3}$), 14.3 ($C\mathrm{H_3^{pentane}}$), 14.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 14.0 ($\mathrm{CH_2}C\mathrm{H_3}$), 13.9 ($\mathrm{CH_2}C\mathrm{H_3}$) ppm.

LIFDI MS (m/z) calculated for [$C_{58}H_{98}Al_2O_4$ –H^+] = 912.7090; found: 912.6699.

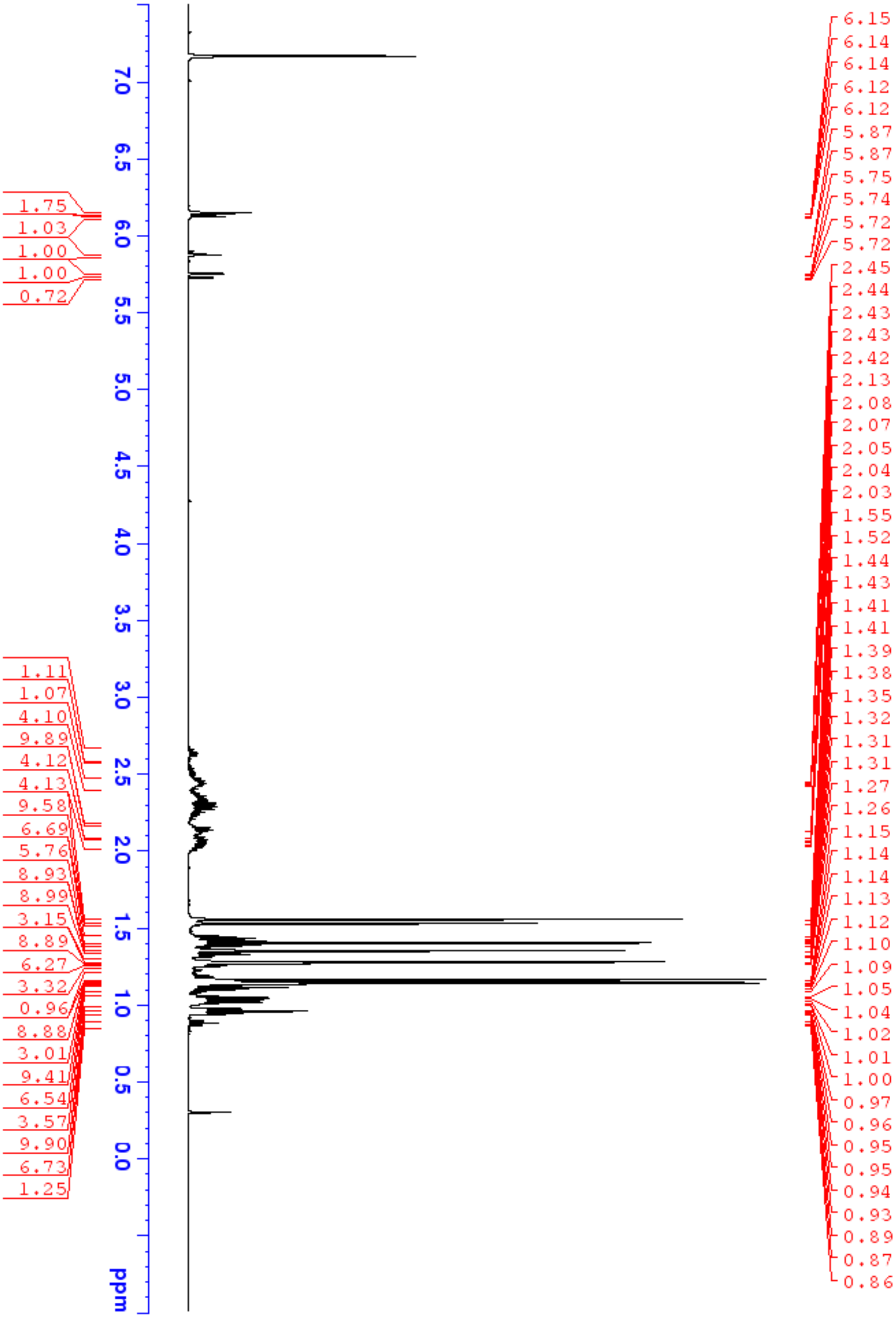

Figure S10. ^{1}H NMR spectrum of **6** in C_6D_6. The triplet at 0.87 ppm and the corresponding multiplet at 1.23 ppm are due to residual pentane.

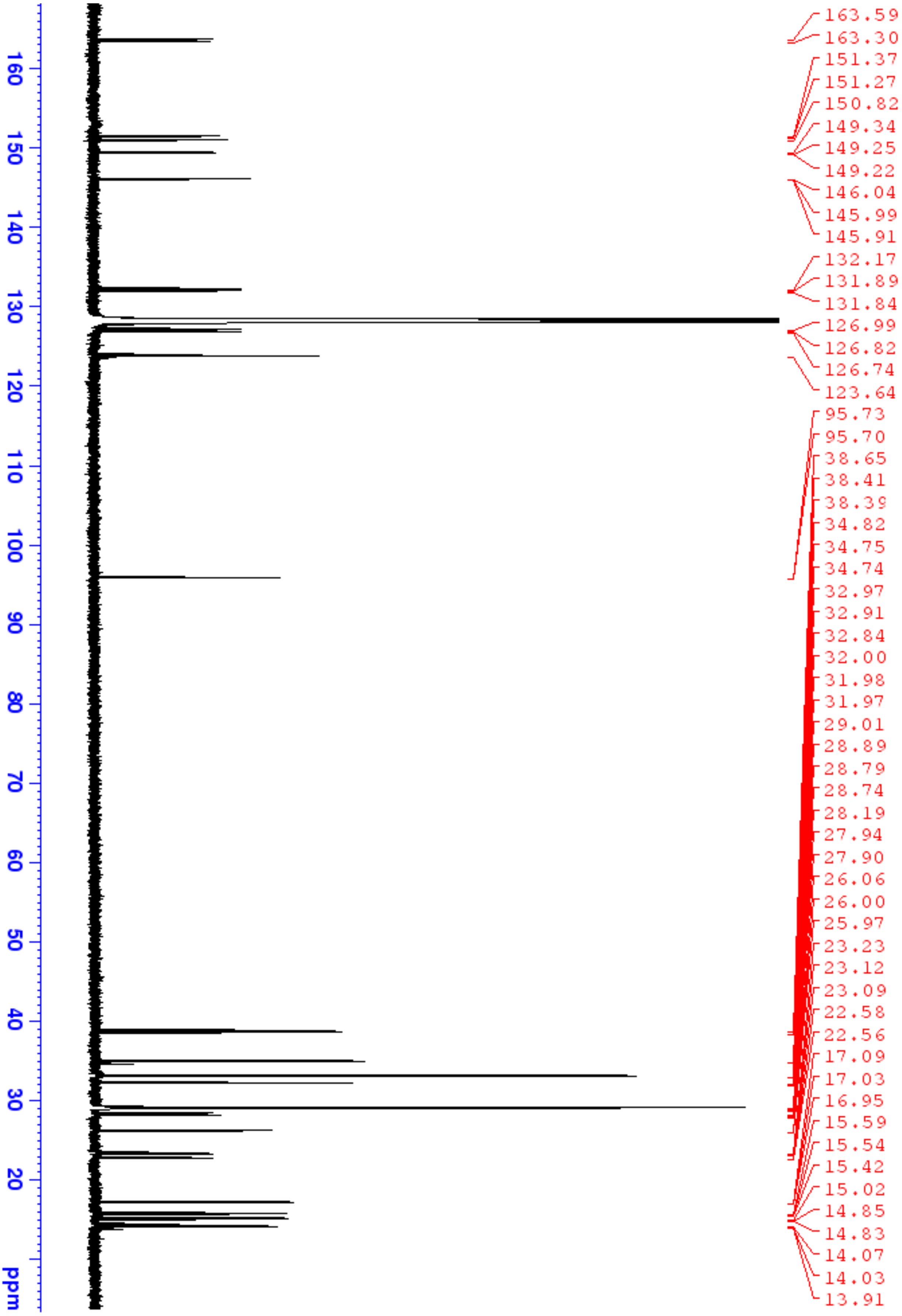

Figure S11. $^{13}C\{^1H\}$ NMR spectrum of **6** in C_6D_6.

C. Computational details

Starting coordinates were obtained from the crystal structure analysis. All calculations were done with the Gaussian 09 software package[2] using density functional theory (DFT) with the B3LYP functional in the gas phase. Geometry optimisations on the real systems were performed with Def2SVP basis set. The energetic minimum of the structure optimisation was confirmed via harmonic vibrational frequency analyses on the same level of theory as used for the energy optimisations (no imaginary frequencies).The Wiberg bond indices were obtained by natural bond order (NBO) analyses with the energy-optimised structures using the NBO 6.0 program.[3] Table 1 gives the energies and the Cartesian coordinates of the calculated compound. Figure 12 shows the structure of the compound.

Table 1: Calculated energies [in kJ/mol] and coordinates of the optimised structure **4** [B3Lyp/Def2SVP].

Compound RD163	SCF energy	corrected electronic and zero-point energies	corrected electronic and thermal energies	corrected electronic and thermal enthalpies	corrected electronic and thermal free energies
	-5153387.45	-5148054.98	-5147766.11	-5147761.15	-5148502.69

Element	X	Y	Z
Al	0.335683000000	-0.282594000000	-0.031081000000
C	0.602561000000	1.270.780.000.000	-1.215.065.000.000
N	-1.290.835.000.000	-1.121.686.000.000	-0.489372000000
B	-2.191.253.000.000	-0.183869000000	0.052582000000
C	0.760146000000	0.573994000000	-3.687.187.000.000
H	1.378.666.000.000	0.675725000000	-4.594.060.000.000
H	-0.250943000000	0.940977000000	-3.926.526.000.000
H	0.675889000000	-0.500721000000	-3.465.829.000.000
C	1.378.169.000.000	1.351.920.000.000	-2.515.259.000.000
H	2.392.856.000.000	0.960614000000	-2.339.906.000.000
H	1.516.483.000.000	2.397.504.000.000	-2.833.889.000.000
C	-0.192397000000	2.289.050.000.000	-0.781037000000
C	-0.399653000000	3.593.459.000.000	-1.558.673.000.000
H	-1.370.984.000.000	4.033.681.000.000	-1.277.193.000.000
H	-0.499687000000	3.339.937.000.000	-2.626.287.000.000
C	-0.880012000000	2.158.851.000.000	0.544241000000
C	0.691782000000	4.668.326.000.000	-1.417.577.000.000
H	1.682.413.000.000	4.277.465.000.000	-1.695.315.000.000
H	0.770148000000	5.049.996.000.000	-0.388723000000
H	0.474896000000	5.528.242.000.000	-2.072.684.000.000
C	0.699885000000	3.454.806.000.000	2.103.730.000.000
H	0.875541000000	2.612.308.000.000	2.790.751.000.000
H	0.802204000000	4.386.296.000.000	2.683.630.000.000
H	1.496.834.000.000	3.436.112.000.000	1.346.384.000.000
C	-0.692080000000	3.365.875.000.000	1.461.726.000.000
H	-1.449.288.000.000	3.386.868.000.000	2.252.613.000.000
H	-0.865168000000	4.278.304.000.000	0.869997000000

C	-1.584.226.000.000	1.043.004.000.000	0.951199000000
C	-2.138.302.000.000	1.021.114.000.000	2.389.632.000.000
H	-1.380.907.000.000	1.416.203.000.000	3.085.120.000.000
H	-2.288.451.000.000	-0.022939000000	2.701.657.000.000
C	-3.462.599.000.000	1.772.736.000.000	2.620.270.000.000
H	-4.281.078.000.000	1.345.258.000.000	2.026.772.000.000
H	-3.387.143.000.000	2.837.410.000.000	2.351.257.000.000
H	-3.749.930.000.000	1.719.376.000.000	3.683.685.000.000
C	-3.792.728.000.000	-0.205898000000	-0.062459000000
C	-4.426.388.000.000	0.647047000000	-1.007.502.000.000
C	-5.819.289.000.000	0.643795000000	-1.141.952.000.000
H	-6.280.257.000.000	1.299.086.000.000	-1.888.642.000.000
C	-6.639.679.000.000	-0.169130000000	-0.347664000000
C	-6.015.596.000.000	-0.978607000000	0.603580000000
H	-6.632.115.000.000	-1.613.505.000.000	1.248.814.000.000
C	-4.619.344.000.000	-1.006.738.000.000	0.762239000000
C	-3.622.257.000.000	1.603.274.000.000	-1.859.913.000.000
H	-2.664.947.000.000	1.172.184.000.000	-2.187.310.000.000
H	-3.377.941.000.000	2.518.235.000.000	-1.294.008.000.000
H	-4.182.146.000.000	1.910.621.000.000	-2.756.186.000.000
C	-8.137.999.000.000	-0.173601000000	-0.531347000000
H	-8.646.967.000.000	-0.686867000000	0.298347000000
H	-8.424.442.000.000	-0.688626000000	-1.465.024.000.000
H	-8.540.082.000.000	0.850658000000	-0.595435000000
C	-4.070.777.000.000	-1.880.546.000.000	1.872.129.000.000
H	-4.528.853.000.000	-2.882.561.000.000	1.856.863.000.000
H	-4.297.932.000.000	-1.442.446.000.000	2.859.376.000.000
H	-2.983.477.000.000	-2.012.246.000.000	1.809.168.000.000
C	-1.602.321.000.000	-2.267.488.000.000	-1.400.029.000.000
C	-2.275.910.000.000	-1.764.059.000.000	-2.693.022.000.000
H	-2.445.831.000.000	-2.603.743.000.000	-3.386.486.000.000
H	-1.643.934.000.000	-1.024.129.000.000	-3.204.334.000.000
H	-3.249.592.000.000	-1.302.814.000.000	-2.481.704.000.000
C	-2.519.044.000.000	-3.316.442.000.000	-0.741705000000
H	-2.626.989.000.000	-4.186.261.000.000	-1.409.729.000.000
H	-3.522.603.000.000	-2.916.772.000.000	-0.554467000000
H	-2.097.090.000.000	-3.674.959.000.000	0.208751000000
C	-0.295045000000	-2.979.831.000.000	-1.785.185.000.000
H	0.173444000000	-3.450.955.000.000	-0.909507000000
H	0.430169000000	-2.284.652.000.000	-2.234.528.000.000
H	-0.491749000000	-3.772.543.000.000	-2.523.149.000.000
C	1.765.549.000.000	-1.068.741.000.000	1.250.251.000.000
C	2.428.924.000.000	-1.721.055.000.000	0.107485000000
H	2.129.454.000.000	-2.689.848.000.000	-0.279990000000
C	3.555.368.000.000	-1.024.287.000.000	-0.309460000000
C	3.688.139.000.000	0.150293000000	0.587558000000
C	2.631.353.000.000	0.090087000000	1.478.656.000.000
H	2.454.090.000.000	0.806107000000	2.275.612.000.000
C	1.363.149.000.000	-1.941.306.000.000	2.486.674.000.000
C	0.386357000000	-3.066.862.000.000	2.103.924.000.000
H	0.819038000000	-3.745.279.000.000	1.352.383.000.000

H	-0.554169000000	-2.667.870.000.000	1.697.593.000.000
H	0.142120000000	-3.676.787.000.000	2.988.907.000.000
C	0.712669000000	-1.079.168.000.000	3.582.429.000.000
H	0.441630000000	-1.703.735.000.000	4.449.387.000.000
H	-0.204302000000	-0.592610000000	3.223.921.000.000
H	1.393.710.000.000	-0.294622000000	3.945.983.000.000
C	2.641.574.000.000	-2.585.694.000.000	3.070.605.000.000
H	2.397.556.000.000	-3.193.351.000.000	3.958.236.000.000
H	3.371.644.000.000	-1.819.624.000.000	3.373.320.000.000
H	3.130.334.000.000	-3.243.511.000.000	2.335.614.000.000
C	4.467.346.000.000	-1.616.054.000.000	-1.414.131.000.000
C	3.692.375.000.000	-2.648.642.000.000	-2.267.076.000.000
H	4.348.291.000.000	-3.033.297.000.000	-3.063.828.000.000
H	2.810.370.000.000	-2.198.256.000.000	-2.747.071.000.000
H	3.358.153.000.000	-3.516.884.000.000	-1.681.440.000.000
C	5.028.321.000.000	-0.587557000000	-2.419.013.000.000
H	5.695.886.000.000	0.149289000000	-1.960.145.000.000
H	4.217.729.000.000	-0.042382000000	-2.926.409.000.000
H	5.610.375.000.000	-1.110.245.000.000	-3.195.209.000.000
C	5.636.380.000.000	-2.381.777.000.000	-0.742203000000
H	5.248.539.000.000	-3.192.109.000.000	-0.105507000000
H	6.255.345.000.000	-1.733.069.000.000	-0.110350000000
H	6.290.429.000.000	-2.833.312.000.000	-1.507.405.000.000
C	4.713.249.000.000	1.308.709.000.000	0.649326000000
C	4.506.075.000.000	2.305.789.000.000	-0.515735000000
H	4.642.101.000.000	1.842.720.000.000	-1.499.984.000.000
H	5.221.774.000.000	3.141.614.000.000	-0.437044000000
H	3.488.925.000.000	2.725.022.000.000	-0.483999000000
C	6.176.458.000.000	0.811888000000	0.674724000000
H	6.337.735.000.000	0.108755000000	1.507.332.000.000
H	6.857.300.000.000	1.666.226.000.000	0.821883000000
H	6.483.261.000.000	0.313589000000	-0.251301000000
C	4.532.306.000.000	2.117.251.000.000	1.956.073.000.000
H	4.653.725.000.000	1.483.363.000.000	2.848.059.000.000
H	3.549.778.000.000	2.605.298.000.000	2.012.699.000.000
H	5.293.453.000.000	2.911.935.000.000	2.003.686.000.000

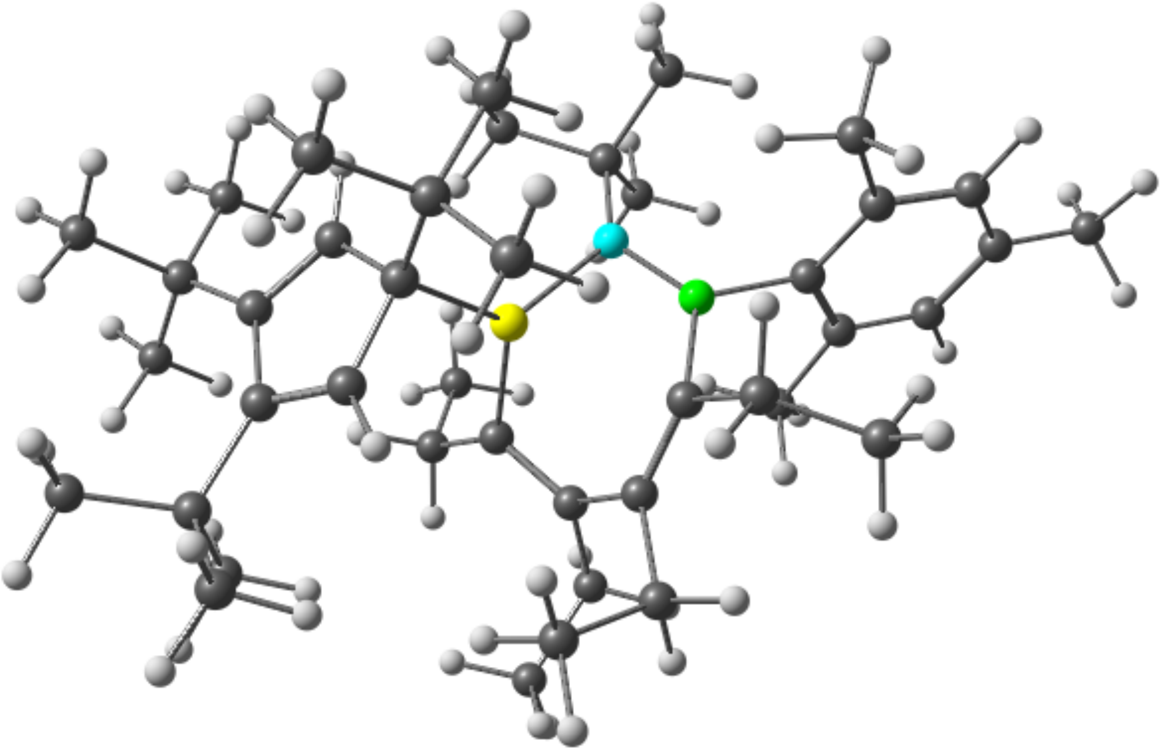

Figure 12. Optimised structure of **4** [B3LYP/Def2SVP].

D. Crystallographic details

The crystal data of **2**, **3**, **4**, **5** and **6** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[4] refined with the *SHELXL* program[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-2084214 (**2**), CCDC-2084216 (**3**), CCDC-2084215 (**4**), CCDC-2084218 (**5**) and CCDC-2084217 (**6**). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **2**: $C_{36}H_{63}AlN_2$, $M_r = 550.86$, colorless block, $0.638\times0.229\times0.184$ mm^3, monoclinic space group $P2_1/n$, $a = 9.941(5)$ Å, $b = 34.115(13)$ Å, $c = 10.622(4)$ Å, $\beta = 106.275(14)°$, $V = 3458(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.058$ g·cm^{-3}, $\mu = 0.083$ mm^{-1}, $F(000) = 1224$, $T = 100(2)$ K, $R_1 = 0.0728$, $wR^2 = 0.1457$, 6797 independent reflections [$2\theta\leq52.04°$] and 369 parameters.

Crystal data for **3**: $C_{42}H_{60}AlNO$, $M_r = 621.89$, colorless block, $0.12\times0.103\times0.088$ mm^3, monoclinic space group $P2_1/c$, $a = 10.154(4)$ Å, $b = 35.675(14)$ Å, $c = 10.784(4)$ Å, $\beta = 111.840(9)°$, $V = 3626(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.139$ g·cm^{-3}, $\mu = 0.088$ mm^{-1}, $F(000) = 1360$, $T = 100(2)$ K, $R_1 = 0.0814$, $wR^2 = 0.1204$, 7422 independent reflections [$2\theta\leq52.742°$] and 419 parameters.

Crystal data for **4**: $C_{42}H_{69}AlBN$, $M_r = 625.77$, colorless block, $0.473\times0.32\times0.192$ mm^3, triclinic space group $P\bar{1}$, $a = 9.255(3)$ Å, $b = 13.353(3)$ Å, $c = 17.129(5)$ Å, $\alpha = 83.886(6)°$, $\beta = 83.022(11)°$, $\gamma = 71.208(7)°$, $V = 1984.1(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.047$ g·cm^{-3}, $\mu = 0.079$ mm^{-1}, $F(000) = 692$, $T = 100(2)$ K, $R_1 = 0.0579$, $wR^2 = 0.1185$, 7759 independent reflections [$2\theta\leq52.044°$] and 425 parameters.

Crystal data for **5**: The whole molecule is disordered, thus the displacement parameters of atoms C1_3 > C5_13, C1_5 > C4_15, C1_6 > C4_16, C1_7 > C2_17 and C1_8 > C2_18 were restrained to the same value with similarity restraint SIMU. The distances between atoms C5_13 C1_16 and C5_3 and C1_6 were restrained during refinement to the same value. The atomic displacement parameters of atoms C1_3 > C5_13, C1_5 > C4_15, C1_6 > C4_16, C1_7 > C2_17 and C1_8 > C2_18 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). $C_{34}H_{60}AlNO_3$, $M_r = 557.81$, colorless block, 0.498×0.316×0.17 mm^3, monoclinic space group $P2_1/c$, $a = 20.5142(11)$ Å, $b = 11.6374(5)$ Å, $c = 14.3998(7)$ Å, $\beta = 93.907(2)°$, $V = 3429.7(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.080$ g·cm^{-3}, $\mu = 0.090$ mm^{-1}, $F(000) = 1232$, $T = 100(2)$ K, $R_1 = 0.0769$, $wR^2 = 0.1539$, 6040 independent reflections [$2\theta \leq 50.054°$] and 496 parameters.

Crystal data for **6**: $C_{58}H_{98}Al_2O_4$, $M_r = 913.32$, colorless block, 0.15×0.095×0.087 mm^3, triclinic space group $P\,\overline{1}$, $a = 10.3237(16)$ Å, $b = 10.969(2)$ Å, $c = 13.631(2)$ Å, $\alpha = 69.689(8)°$, $\beta = 83.282(7)°$, $\gamma = 74.821(6)°$, $V = 1396.6(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.086$ g·cm^{-3}, $\mu = 0.094$ mm^{-1}, $F(000) = 504$, $T = 100(2)$ K, $R_1 = 0.1034$, $wR^2 = 0.1631$, 5068 independent reflections [$2\theta \leq 50.7°$] and 302 parameters.

E. References

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