Electronic Supplementary Information for:

Monomeric $Cp^{3t}Al(I)$: Synthesis, reactivity, and the concept of valence isomerism

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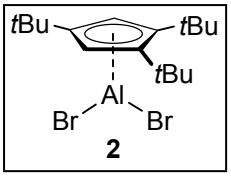
S1 Synthetic details and characterization of compounds

General remarks

All syntheses were carried out in an Argon-filled glovebox or with standard Schlenk techniques[1] unless otherwise stated. $Cp^{3t}H$, $(Cp^{3t})_2Mg$ and $(Cp^*Al)_4$ were prepared as described previously.[2-4] All solvents were dried by distillation over appropriate drying agents[5] and stored over molecular sieves. All solution NMR spectra were acquired on a Bruker Avance 400 NMR spectrometer (^1H: 400.1 MHz, ^{27}Al: 104 MHz, ^{13}C: 101 MHz). ^1H NMR and ^{13}C NMR spectra were referenced to external TMS via residual protons of the solvent (^1H) or the solvent itself (^{13}C). ^{27}Al NMR spectra were referenced to external $Al(NO_3)_3$. Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer. High-resolution mass spectrometry was obtained using a Thermo Scientific Exactive Plus spectrometer.



2

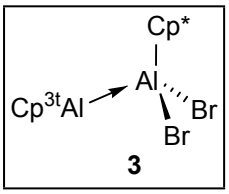
Synthesis of $Cp^{3t}AlBr_2$: $(Cp^{3t})_2Mg$ (5.00 g, 10.2 mmol) was dissolved in pentane (50 mL) and $AlBr_3$ (5.43 g, 20.3 mmol) was added. The colorless solution turned slightly yellowish and white solids precipitated immediately. After the reaction mixture was stirred for 30 minutes, the suspension was filtrered. The filtrate was concentrated and stored at −30 °C overnight to obtain colorless crystals. These were isolated by filtration, washed with pentane (3 x 2 mL) and dried under reduced pressure to give **2** (4.92 g, 11.7 mmol, 58%).

^1H NMR (C_6D_6): δ 6.64 (s, 2 H, $C_5H_2(tBu)_3$), 1.41 (s, 18 H, *t*Bu), 1.24 (s, 9 H, *t*Bu) ppm.

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.2 (Ar), 126.4 (Ar), 115.2 (Ar), 34.4 ($C(CH_3)_3$), 32.7 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$) ppm.

^{27}Al NMR (C_6D_6): δ −42 (s, br) ppm.

Anal. Found: C 47.55, H 6.93; Calcd. Data for $C_{17}H_{29}AlBr_2$: C 48.59, H 6.96.



3

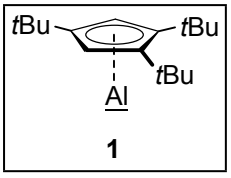
Synthesis of $Cp^{3t}Al{\rightarrow}Cp^*AlBr_2$: $Cp^{3t}AlBr_2$ (2.59 g, 6.16 mmol) was dissolved in toluene (20 mL) and $(Cp^*Al)_4$ (1.00 g, 6.16 mmol) was added. The yellow suspension was sonicated over a period of two hours until $(Cp^*Al)_4$ was consumed and the reaction mixture turned colorless. The mixture was filtered and the solvent from the filtrate was removed under reduced pressure. The residue was treated with pentane (20 mL), filtrated and the residue was dried under reduced pressure to obtain analytically pure **3**. A second fraction of **3** can be crystallized after concentrating the filtrate and storage at −30 °C overnight to give an overall yield of 2.7 g (4.64 mmol, 75%).

^{1}H NMR (C_6D_6): δ 6.25 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.90 (s, 15 H, C_5Me_5), 1.38 (s, 18 H, *t*Bu), 1.24 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 131.7 (Ar), 130.4 (Ar), 117.1 (Ar), 108.3 (Ar), 33.8($C(CH_3)_3$), 33.8($C(CH_3)_3$), 31.8($C(CH_3)_3$), 31.8($C(CH_3)_3$), 11.5 (C_5Me_5) ppm.

Note: No signal could be observed in the ^{27}Al NMR spectrum, probably due to its broadness.

LIFDI-MS (*m/z*) calculated for [$C_{27}H_{44}Al_2Br_1$ ($C_{27}H_{44}Al_2Br_2$ –Br] = 501.2252; found: 501.2236.



1

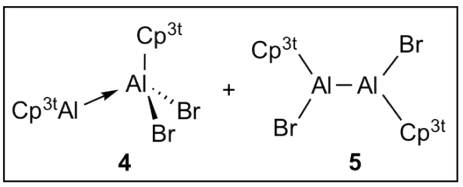
Synthesis of Cp^{3t}Al: 2 (1.00 g, 1.72 mmol) was dissolved in 20 ml pentane and cAAC^{Me} (0.490 g, 1.72 mmol) was added in portions. The reaction mixture turned yellow and slightly yellow solids precipitated immediately. After stirring for six hours, the suspension was filtered, and the solvent was removed from the filtrate under reduced pressure to give **1** as a yellow oil (0.348 g, 1.33 mmol, 78%).

^{1}H NMR (C_6D_6): δ 5.94 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.37 (s, 18 H, *t*Bu), 1.20 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 131.4 (Ar), 130.2 (Ar), 103.8 (Ar), 34.4 ($C(CH_3)_3$), 32.8 ($C(CH_3)_3$), 32.4 $C(CH_3)_3$), 30.9 ($C(CH_3)_3$) ppm.

^{27}Al NMR (C_6D_6): δ –161 (s) ppm.

LIFDI-MS (*m/z*) calculated for [$C_{17}H_{29}Al_1$] = 260.2079; found: 260.2071.



4 **5**

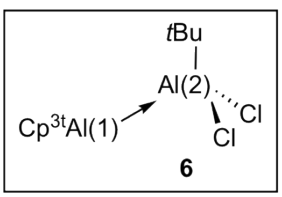
Generation of an equilibrium mixture of Cp^{3t}Al→Cp^{3t}AlBr$_2$ (4) and Cp^{3t}(Br)Al-Al(Br)Cp^{3t} (5), and their isolation: To a solution of Cp^{3t}Al (30 mg, 0.12 mmol, 0.6 mL, 0.19 M in C_6D_6) Cp^{3t}AlBr$_2$ (48 mg, 0.12 mmol) was added. The solvent was removed, and the residue was treated with 1 ml pentane, filtered and stored at room temperature overnight. Colorless crystals precipitated, which were isolated and dried under reduced pressure to give **4** (30 mg, 0.044 mmol, 36 %). Storing the mother liquor at -30 °C overnight afforded **5** (10 mg, 0.015 mmol, 12 %) as colorless crystals. Both species gave identical averaged NMR spectra for the equilibrium mixture of **4** and **5**. Recrystallization of solutions of both isolated **4** and **5** afforded again both species at the same conditions as described above. Equilibrium NMR parameters:

^{1}H NMR (C_6D_6): δ 6.39 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.43 (s, 18 H, *t*Bu), 1.29 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 130.9 (Ar), 129.1 (Ar), 111.8 (Ar), 34.1 ($C(CH_3)_3$), 33.6 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$) ppm.

^{27}Al NMR (C_6D_6): δ –64 (s, br) ppm.

Anal. Found: C 61.53, H 8.65; Calcd. Data for $C_{34}H_{58}Al_2Br_2$: C 60.00, H 8.59.



6

Synthesis of Cp^{3t}Al→*t*BuAlCl$_2$: To a solution of Cp^{3t}Al (30 mg, 0.12 mmol,

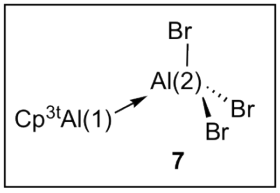
0.6 mL, 0.19 M in C_6D_6) *t*BuAlCl$_2$ (17.9 mg, 0.12 mmol) was added. The solvent was removed, and the residue was treated with 1 ml pentane, filtered and stored at –30 °C overnight. Colorless crystals precipitated, which were isolated and dried under reduced pressure to give **6** (20 mg, 0.048 mmol, 40 %).

^{1}H NMR (C_6D_6): δ 6.13 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.30 (s, 9 H, *t*Bu), 1.22 (s, 18 H, *t*Bu), 1.09 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 133.5 (Ar), 104.4. (Ar), 33.7 (C*(CH$_3$)$_3$*), 33.6 (*C*(CH$_3$)$_3$), 31.6 (*C*(CH$_3$)$_3$), 28.5 (C*(CH$_3$)$_3$*) ppm.

^{27}Al NMR (C_6D_6): δ 145.7 (Al(2), s, br) ppm. The signal for Al(1) was not observed.

Anal. Found: C 61.08, H 8.73; Calcd. Data for $C_{21}H_{38}Al_2Cl_2$: C 60.72, H 9.22.



7

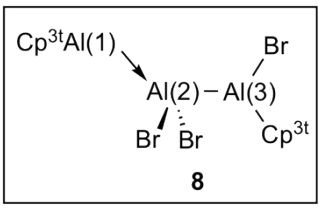
Synthesis of Cp^{3t}Al→AlBr$_3$: AlBr$_3$ (32.0 mg, 0.12 mmol) was dissolved in benzene (0.5 mL), and a solution of Cp^{3t}Al (30 mg, 0.12 mmol, 0.6 mL, 0.19 M in C_6D_6) was added. The solution was layered with pentane, which resulted in the precipitation of colorless crystals over a period of 12 h. The crystals were isolated and dried under reduced pressure to give **7** (41 mg, 0.078 mmol, 65%).

^{1}H NMR (C_6D_6): δ 6.10 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.13 (s, 18 H, *t*Bu), 0.99 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 135.0 (Ar), 134.3 (Ar), 104.5. (Ar), 33.8 (C*(CH$_3$)$_3$*), 33.6 (*C*(CH$_3$)$_3$), 31.8 (*C*(CH$_3$)$_3$), 31.5 (C*(CH$_3$)$_3$*) ppm.

^{27}Al NMR (C_6D_6): δ 95.0 (Al(2), s, br) ppm. The signal for Al(1) was not observed.

Anal. Found: C 39.59, H 5.34; Calcd. Data for $C_{17}H_{29}Al_2Br_3$: C 38.74, H 5.55.



8

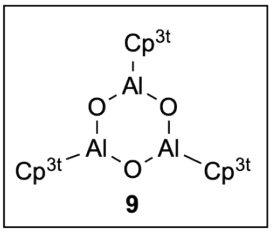
Synthesis of Cp^{3t}Al→(Br)$_2$Al-Al(Br)(Cp^{3t}): A solution of AlBr$_3$ (16.0 mg, 0.06 mmol) in benzene (0.5 mL) was added dropwise to a solution of Cp^{3t}Al (30 mg, 0.12 mmol, 0.6 mL, 0.19 M in C_6D_6). All volatiles were removed in vacuo, and the residue washed with pentane (2 x 0.5 mL) and dried in vacuo. Hereby, **8** was isolated as a colorless solid (28 mg, 0.04 mmol, 67%). Single crystals were obtained by slowly evaporating the solvent from benzene solutions of **8**.

^{1}H-NMR (C_6D_6): δ 6.37 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.42 (s, 18 H, *t*Bu), 1.27 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H}-NMR (C_6D_6): δ 130.9 (Ar), 112.4.8 (Ar), 111.4. (Ar), 34.0 (*C*(CH$_3$)$_3$), 33.6 (C*(CH$_3$)$_3$*), 32.0 (*C*(CH$_3$)$_3$), 31.8(C*(CH$_3$)$_3$*) ppm.

^{27}Al-NMR (C_6D_6): δ -71.0 (Al(3), s, br) ppm. The signals for Al(1,2) were not observed.

Anal. Found: C 51.59., H 7.40; Calcd. Data for $C_{34}H_{58}Al_2Br_2$: C 51.86, H 7.42.



9

Synthesis of (Cp^{3t}AlO)$_2$: A solution of Cp^{3t}Al (30 mg, 0.12 mmol, 0.6 mL,

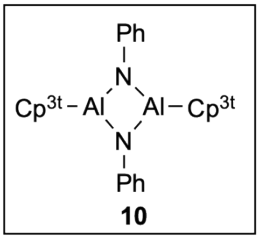
0.19 M in C_6D_6) was degassed and subjected to an atmosphere of N_2O. The solvent was removed, and the residue dissolved in small amounts of pentane (0.3 mL). Colorless crystals precipitated upon slow evaporation at −30 °C, which were isolated and dried under reduced pressure to give **9** (19 mg, 0.069 mmol, 57 %).

^{1}H NMR (C_6D_6): δ 6.49 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.61 (s, 18 H, *t*Bu), 1.39 (s, 9 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 127.9 (Ar), 125.9 (Ar), 108.4 (Ar), 34.2 ($C(CH_3)_3$), 33.4 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$) ppm.

Note: No signal could be observed in ^{27}Al NMR, probably due to its broadness.

Anal. Found: C 73.96, H 10.54; Calcd. Data for $C_{51}H_{87}Al_3O_3$: C 73.87, H 10.58.



10

Synthesis of ($Cp^{3t}AlNPh)_2$: To a solution of $Cp^{3t}Al$ (30 mg, 0.12 mmol, 0.6 mL, 0.19 M in C_6D_6) an excess of PhN_3 (40 mg, 0.34 mmol) was added, which was accompanied by the a color change of the solution to red. The solvent was removed, and the residue was washed with pentane (3 x 0.5 mL) to give colorless **10** (28 mg, 0.16 mmol, 66%). Colorless crystals precipitated out of the reaction mixture in benzene, when stored overnight at room temperature.

^{1}H NMR (C_6D_6): δ 7.35 (t, $^2J_{H,H}$ = 7.5 Hz, 2H, *o*-C_6H_5N), 7.11 (d, $^2J_{H,H}$ = 7.5 Hz, 2H, *m*-C_6H_5N), 6.97 (t, $^2J_{H,H}$ = 7.5 Hz, 1H, *p*-C_6H_5N), 6.78 (s, 2 H, $C_5H_2(t\text{Bu})_3$), 1.57 (s, 9 H, *t*Bu), 1.18 (s, 18 H, *t*Bu) ppm.

^{13}C{^{1}H} NMR (C_6D_6): δ 153.3 (Ar), 129.4 (Ar), 129.2 (Ar), 129.0 (Ar), 123.8 (Ar), 119.1 (Ar), 107.2. (Ar), 33.8 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$), 32.6 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$) ppm.

Note: Signals at δ 34.5, 22.7 and 14.3 ppm are due to remaining pentane. No signal could be observed in the ^{27}Al NMR spectrum, probably due to its broadness.

Anal. Found: C 80.21, H 9.93, N 4.32; Calcd. Data for $C_{46}H_{68}Al_2N_2$: C 78.59, H 9.75, N 3.98.

S2 NMR Spectra of all isolated species

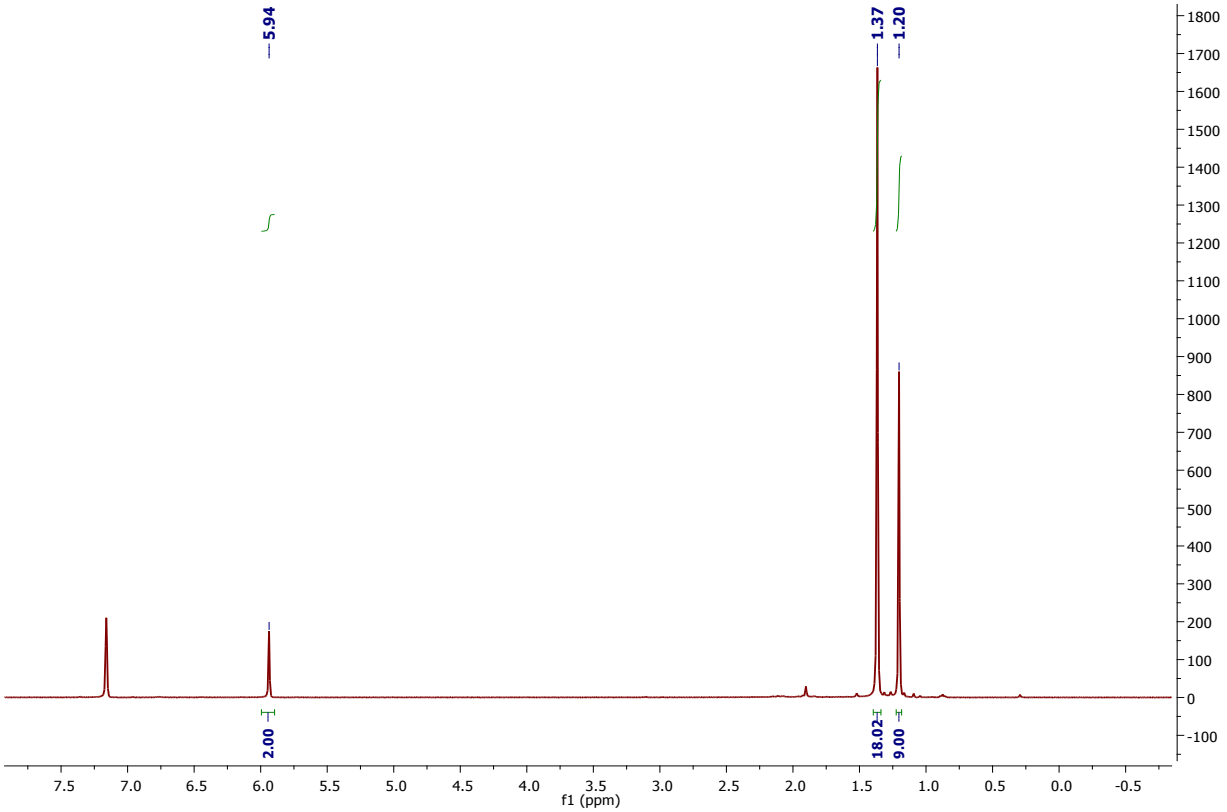


Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **1**.

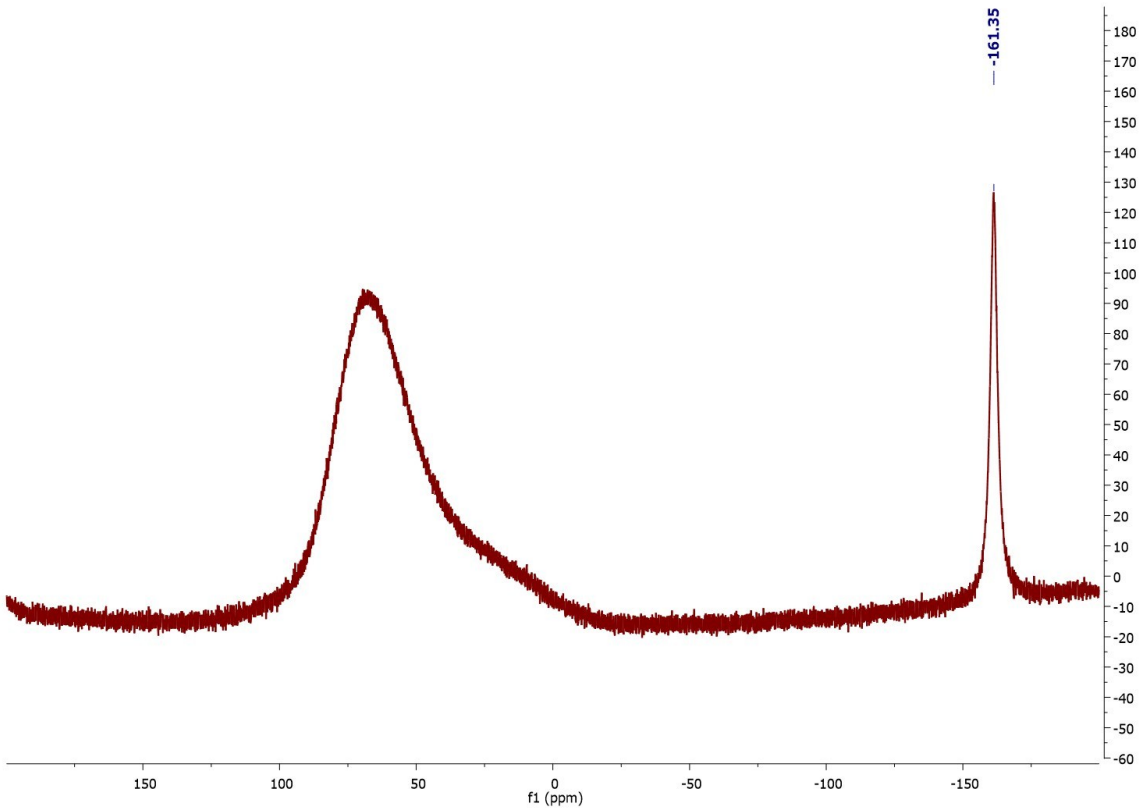


Figure S2. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **1**.

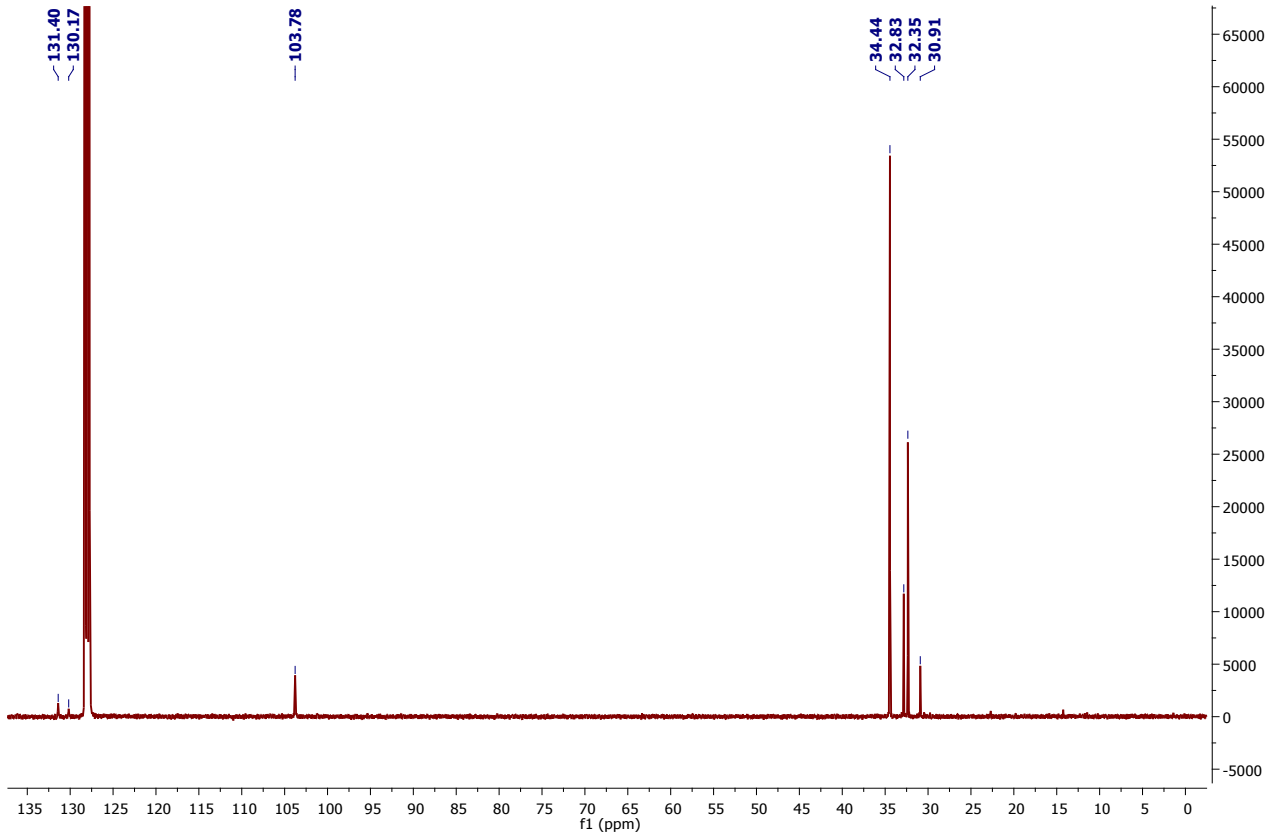


Figure S3. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **1**.

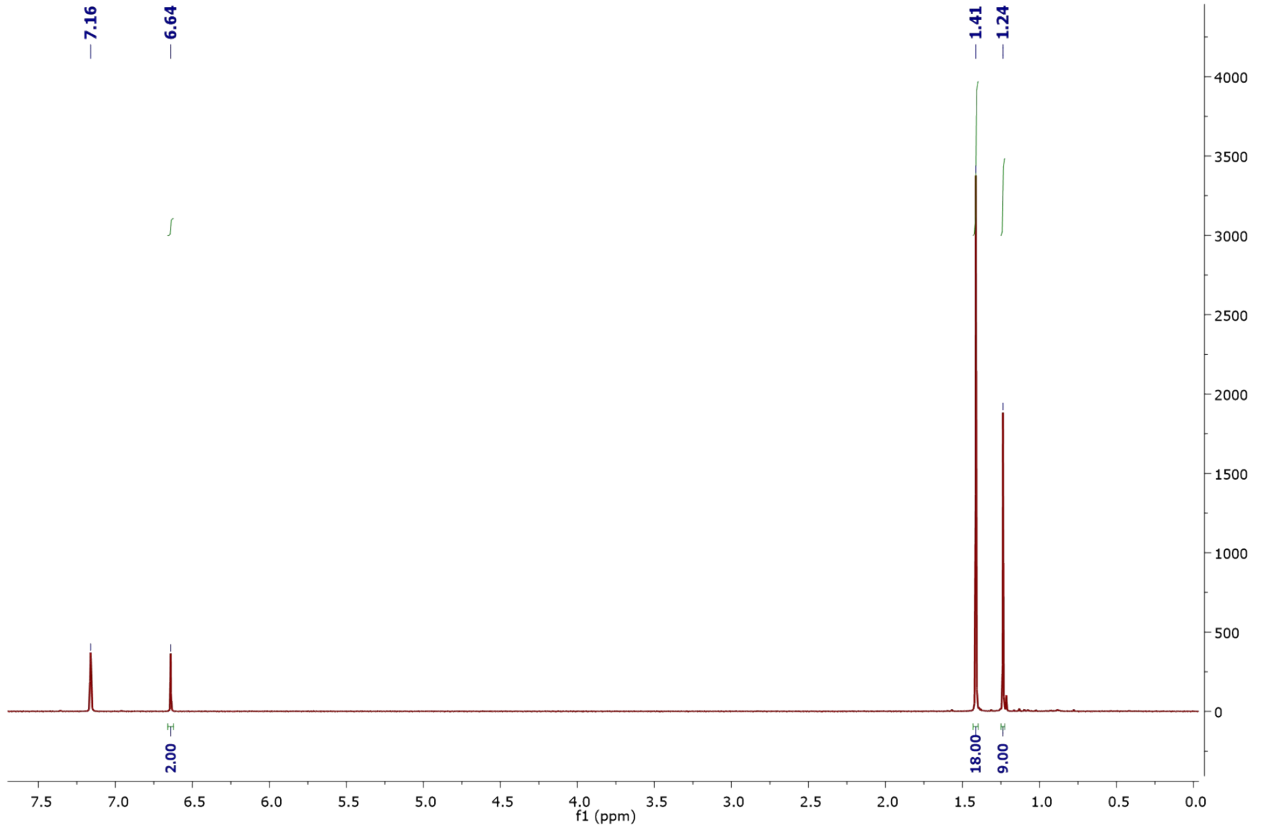


Figure S4. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **2**.

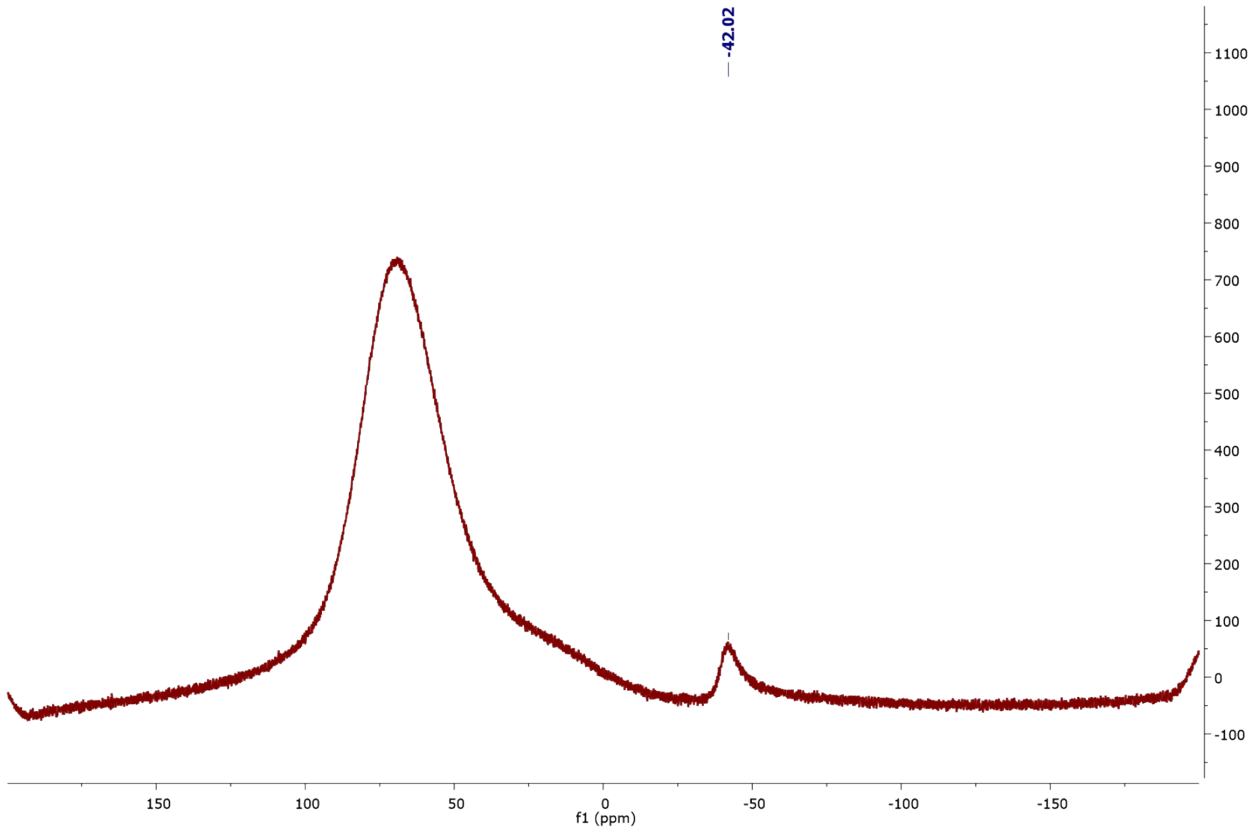


Figure S5. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **2**.

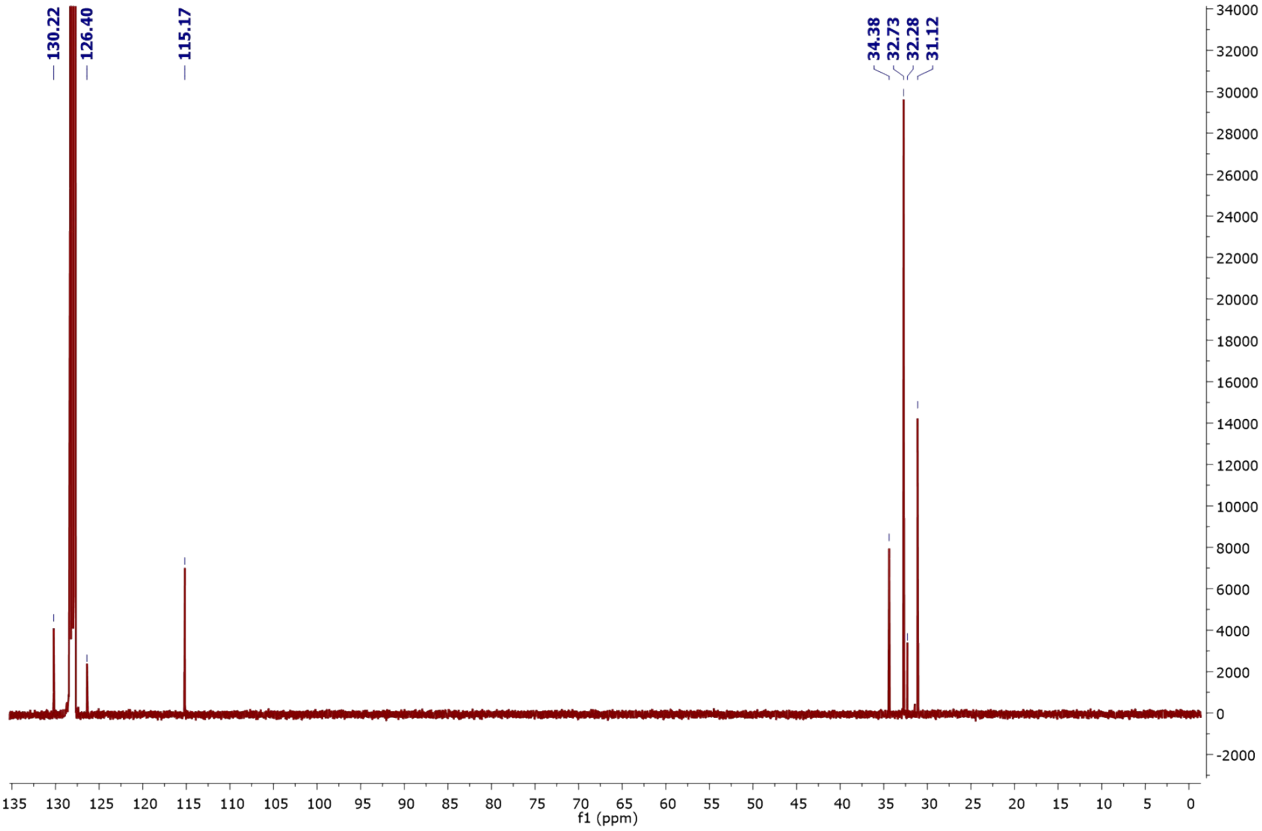


Figure S6. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) spectrum of **2**.

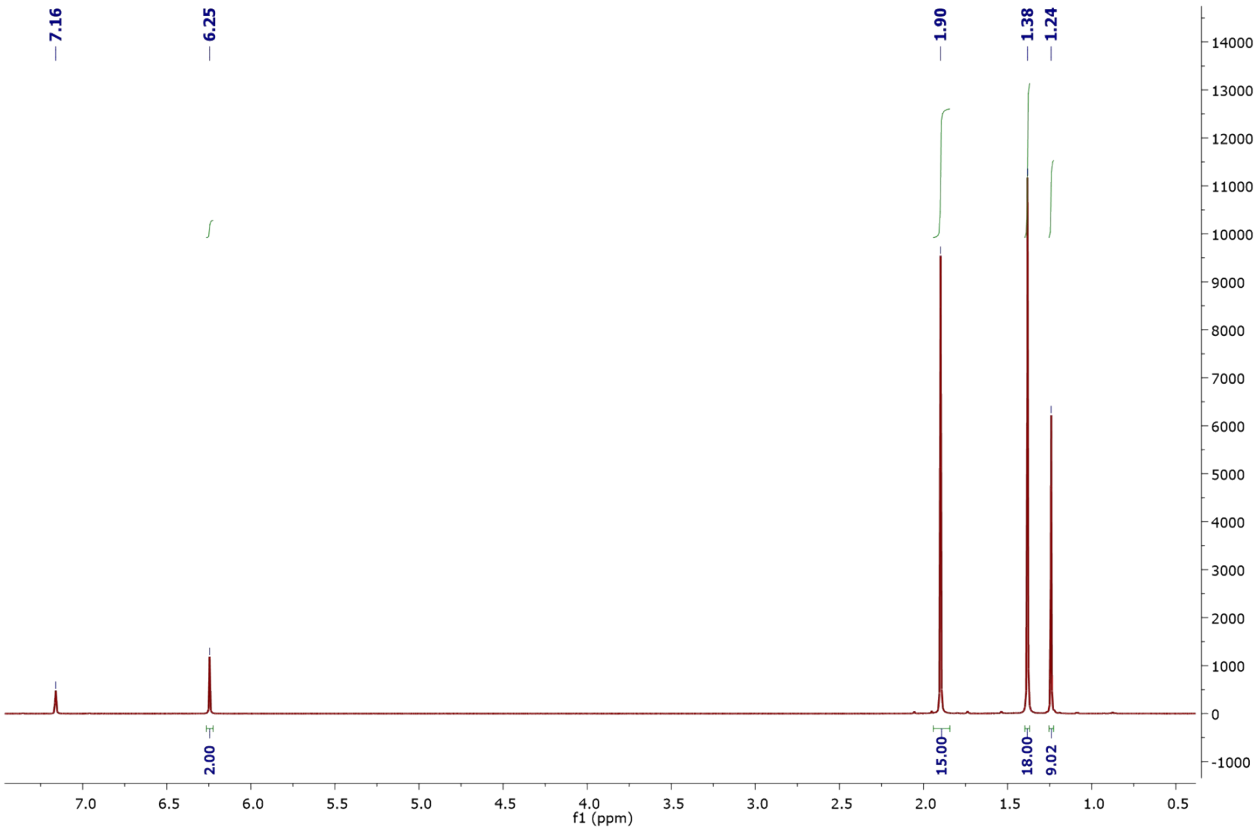


Figure S7. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **3**.

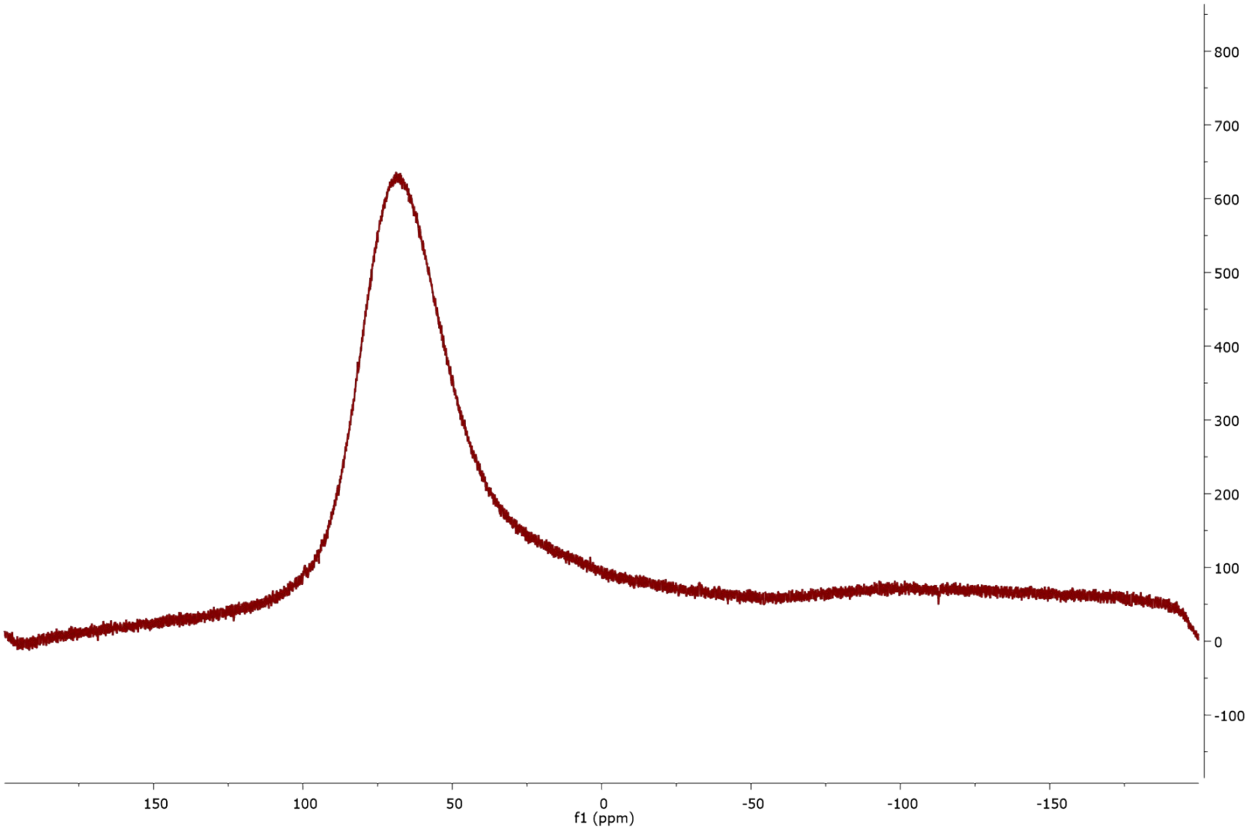


Figure S8. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **3**.

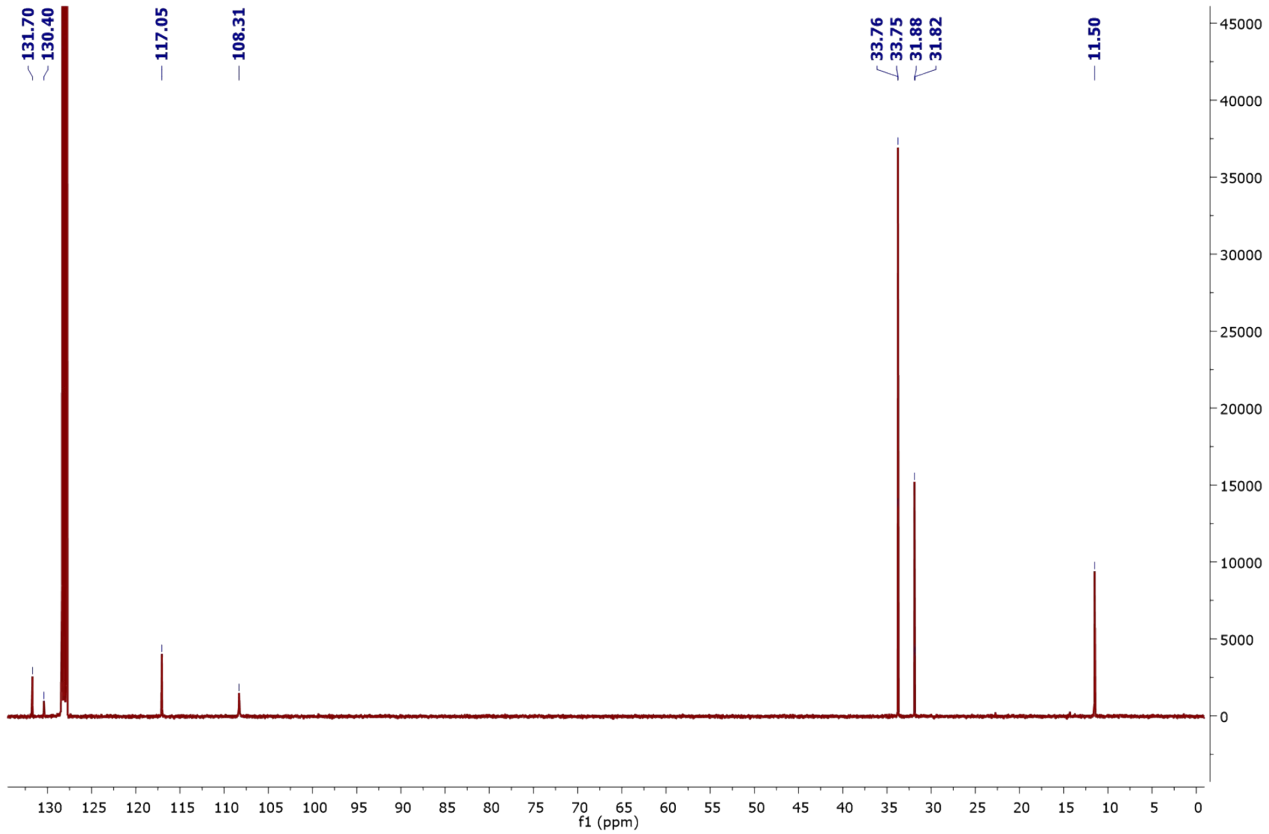


Figure S9. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **3**.

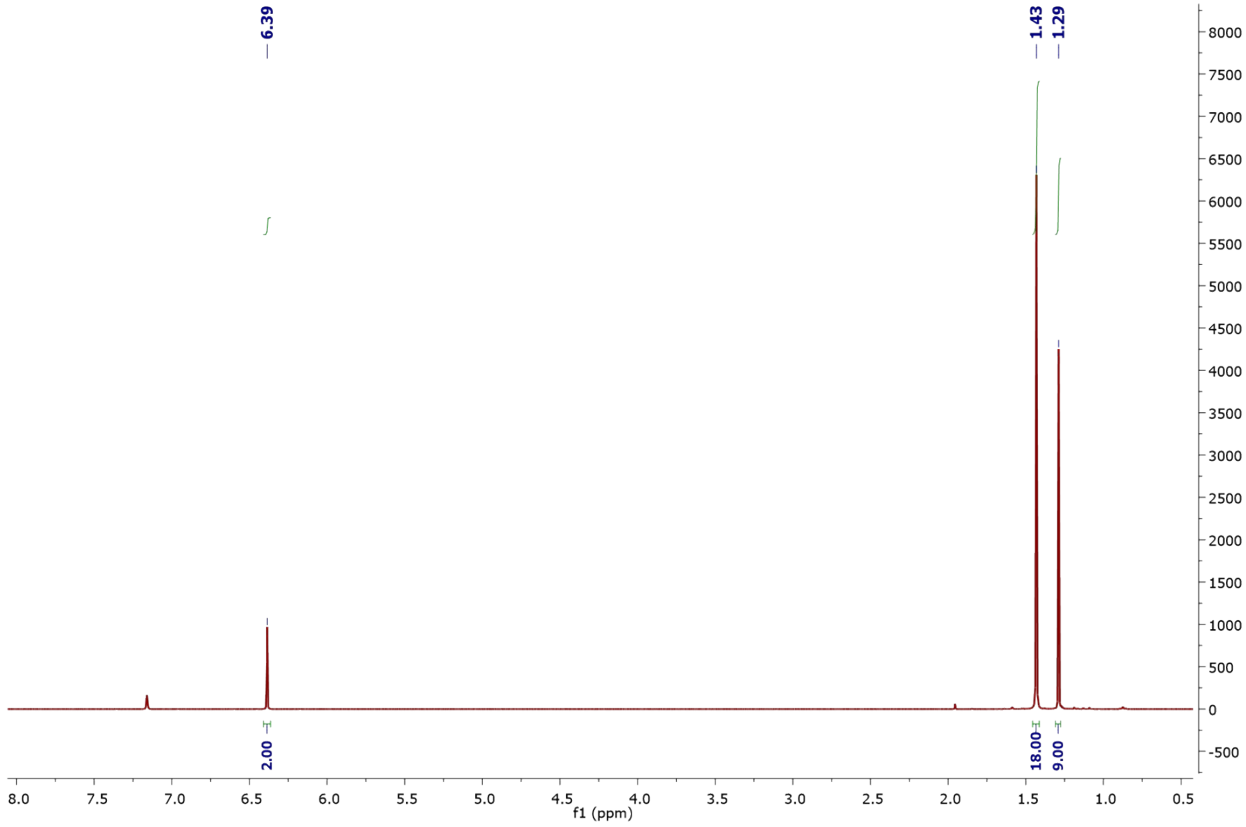


Figure S10. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **4**/**5** at rt

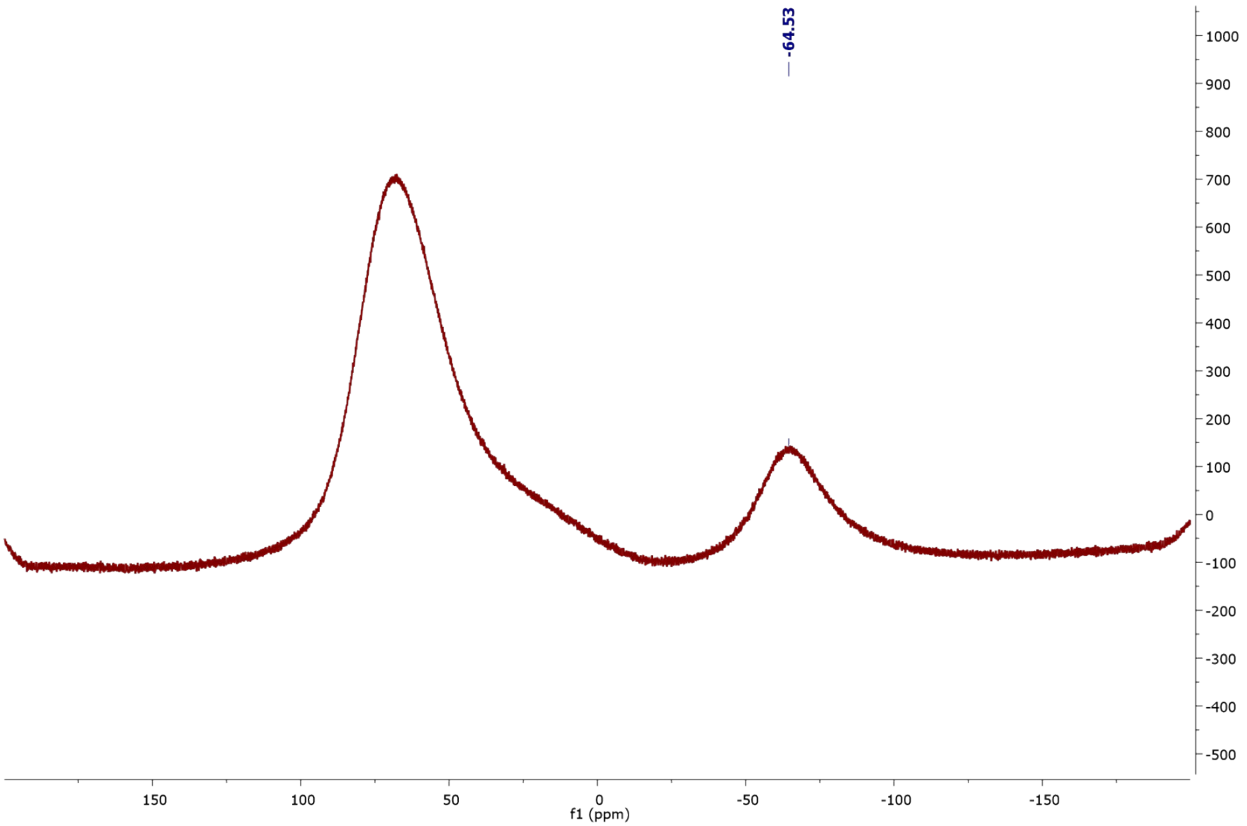


Figure S11. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **4**/**5** at rt.

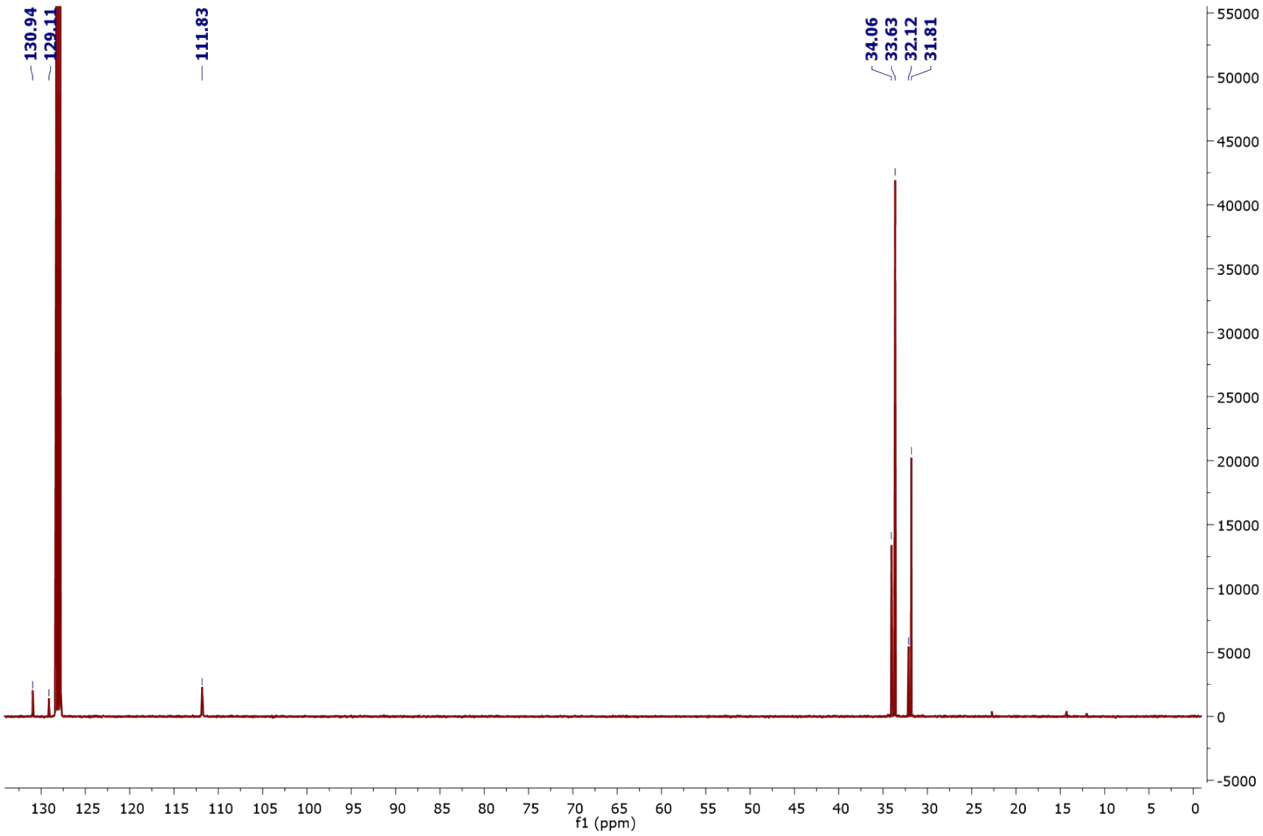


Figure S12. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) spectrum of **4**/**5** at rt.

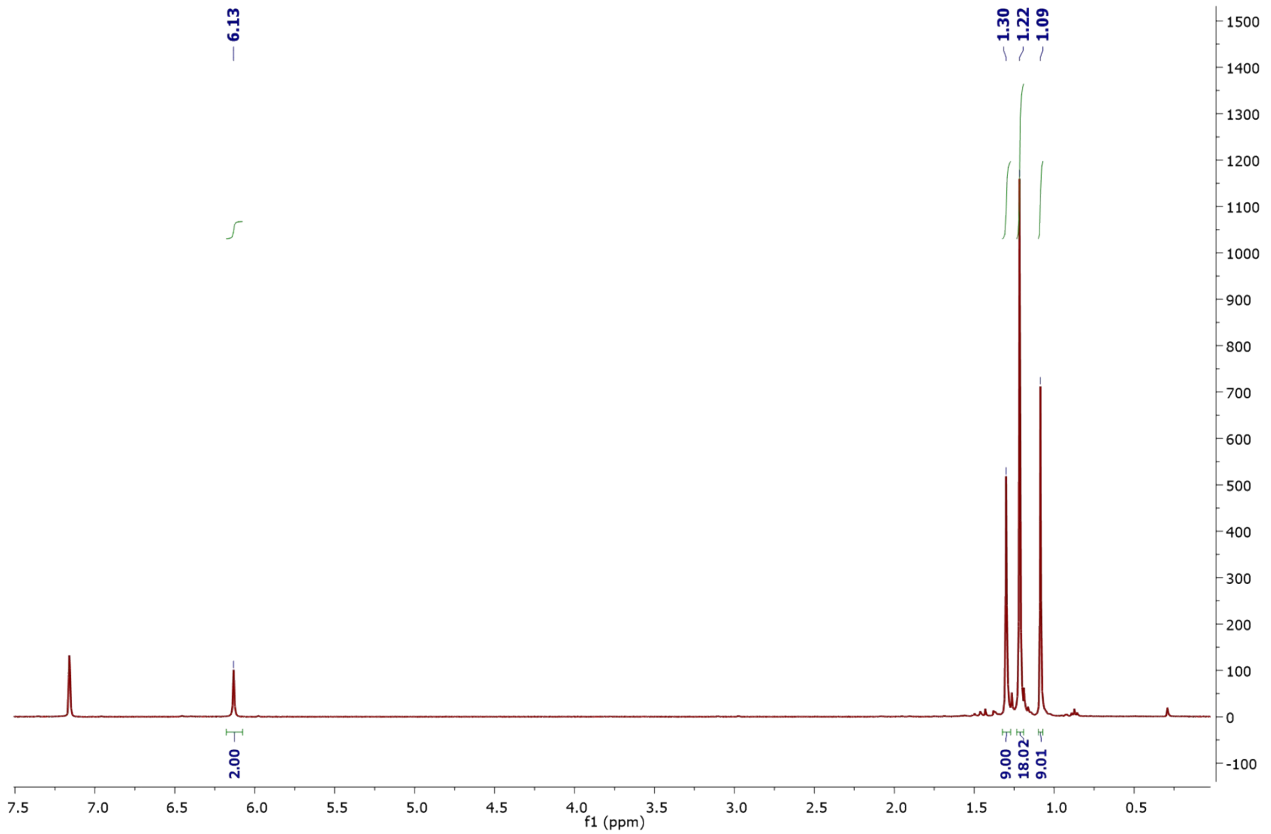


Figure 13 ^{1}H NMR (400 MHz, C_6D_6) spectrum of **6**.

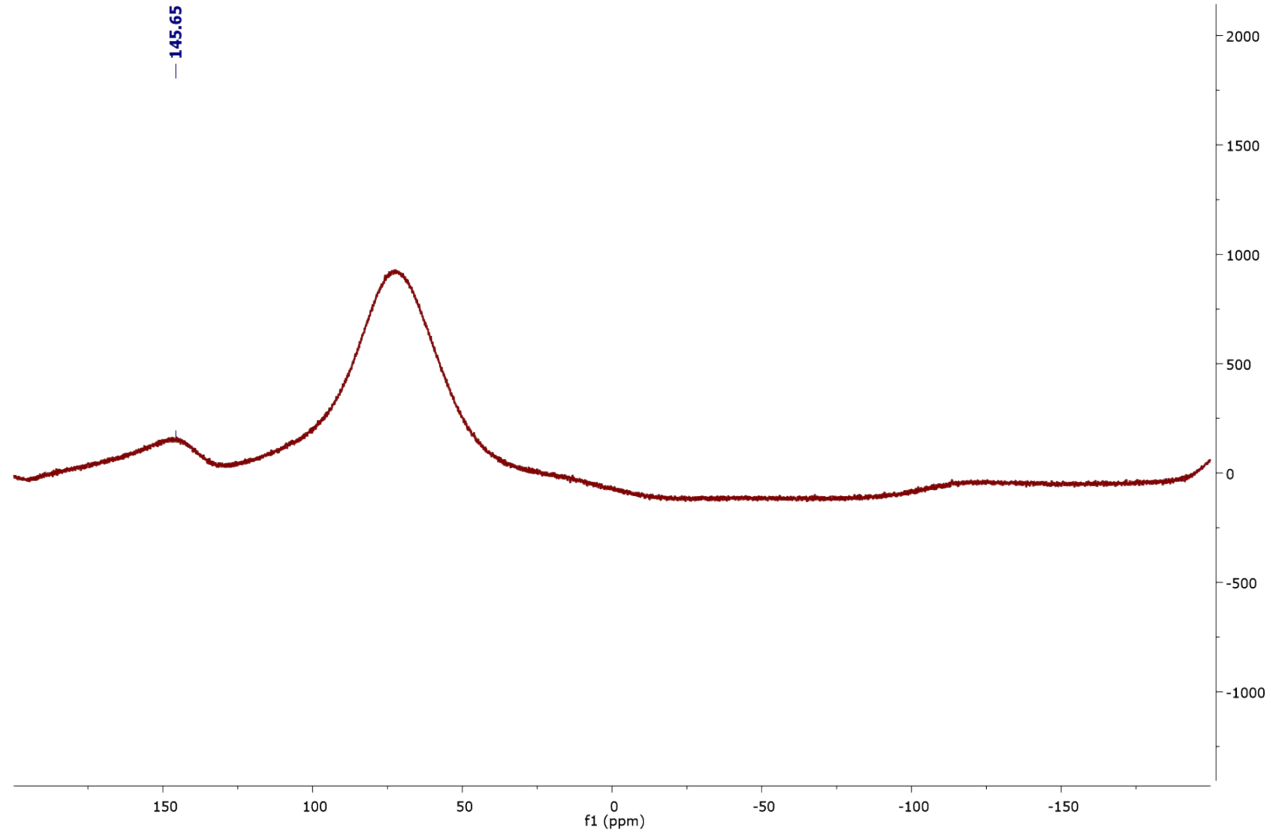


Figure S14. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **6**.

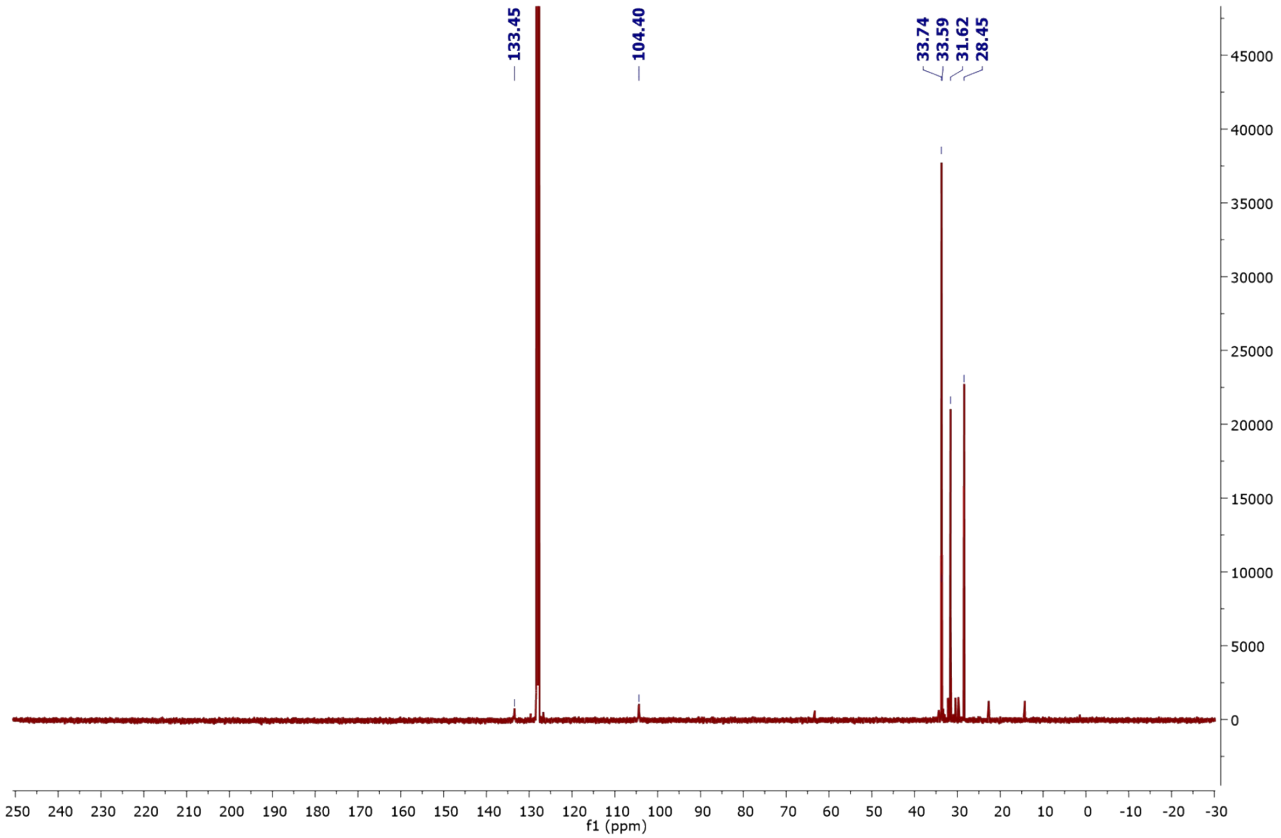


Figure S15. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **6**.

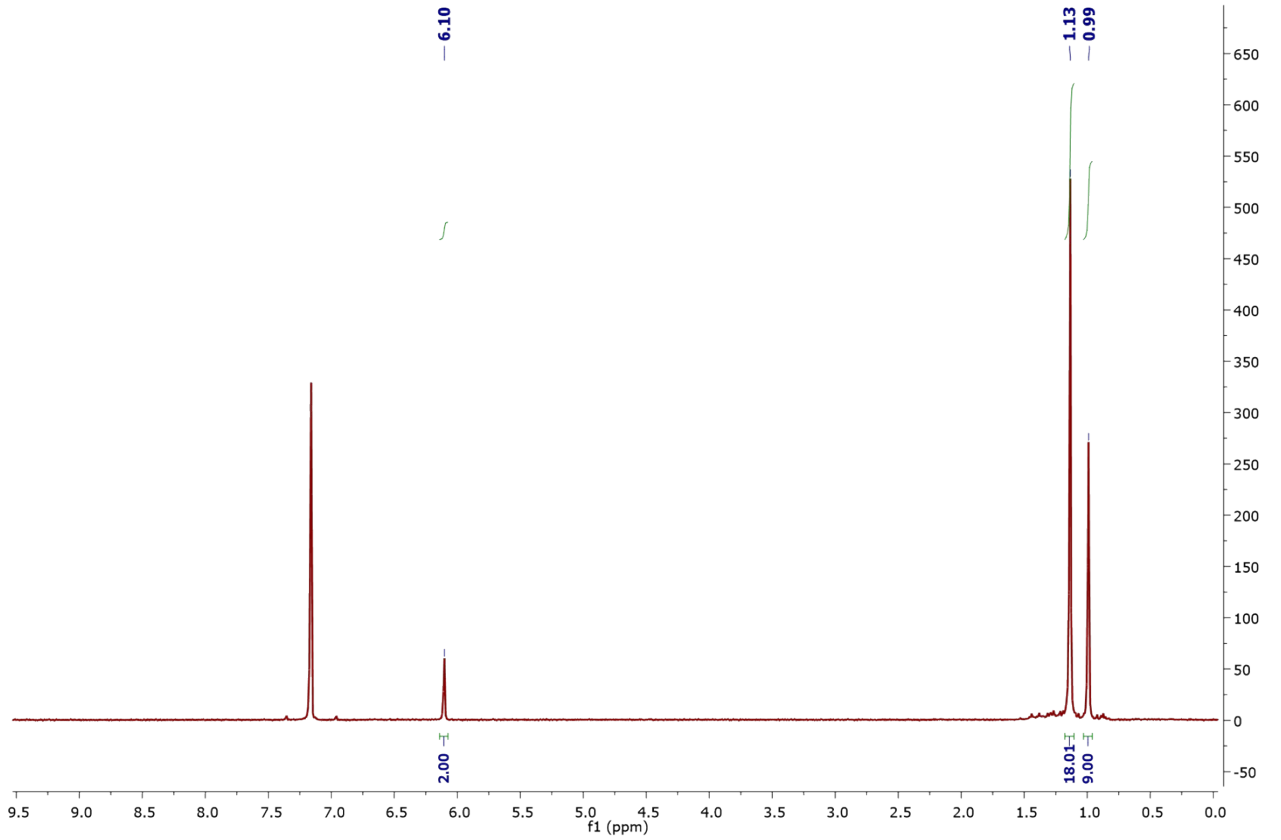


Figure S16. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **7**.

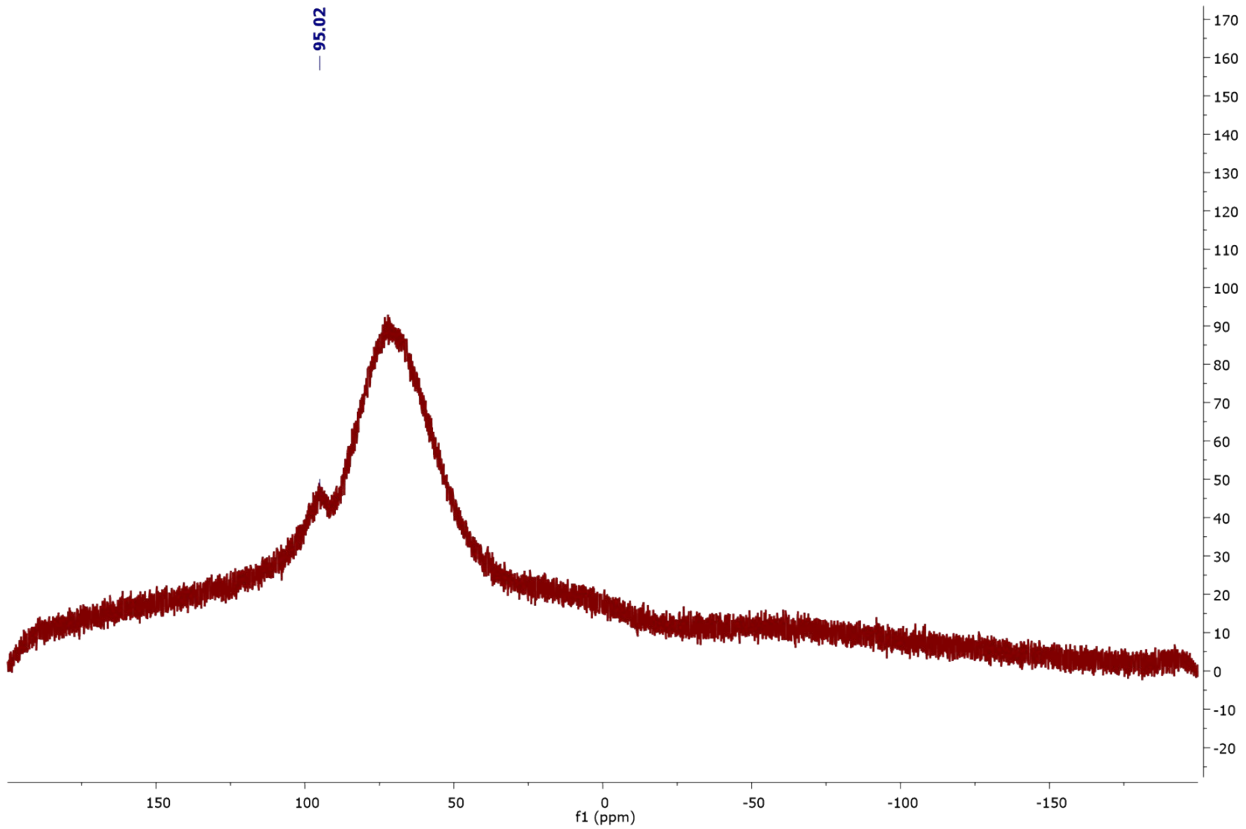


Figure S17. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **7**.

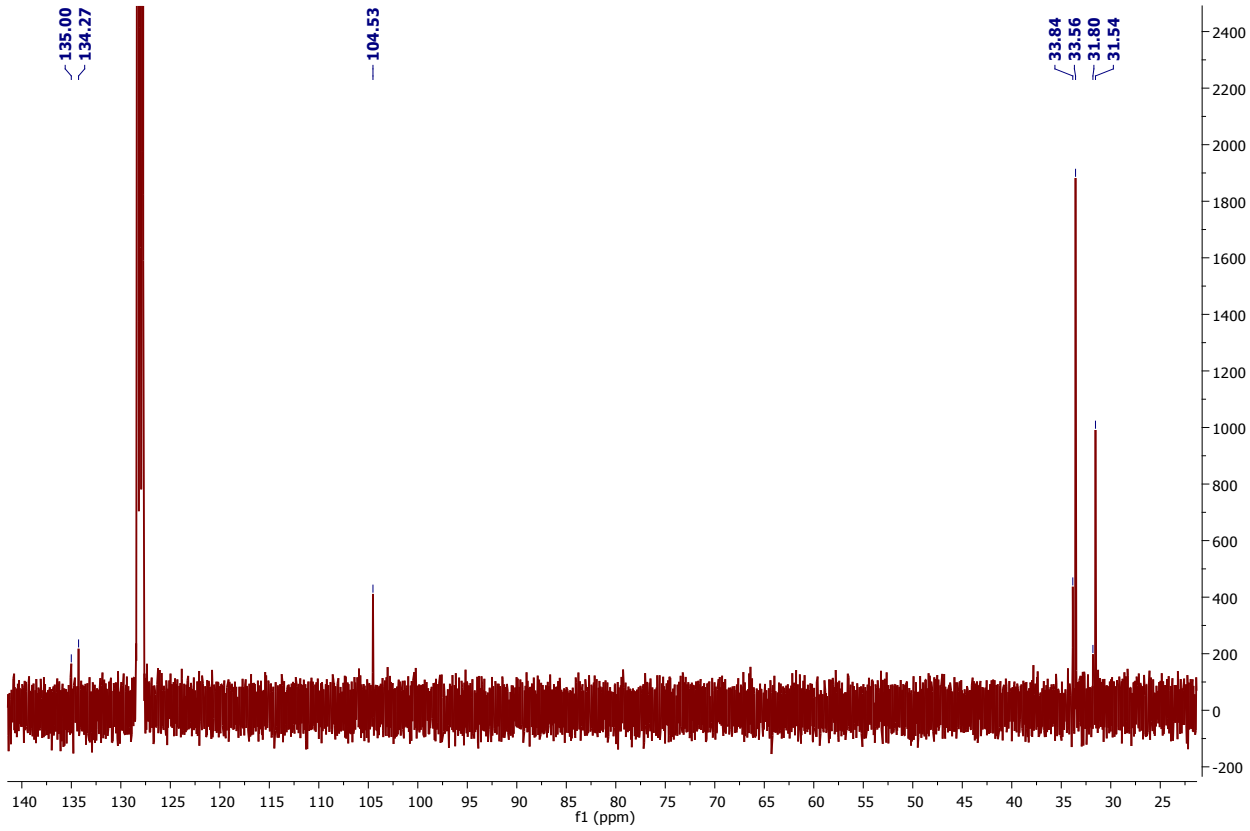


Figure S18. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) spectrum of **7**.

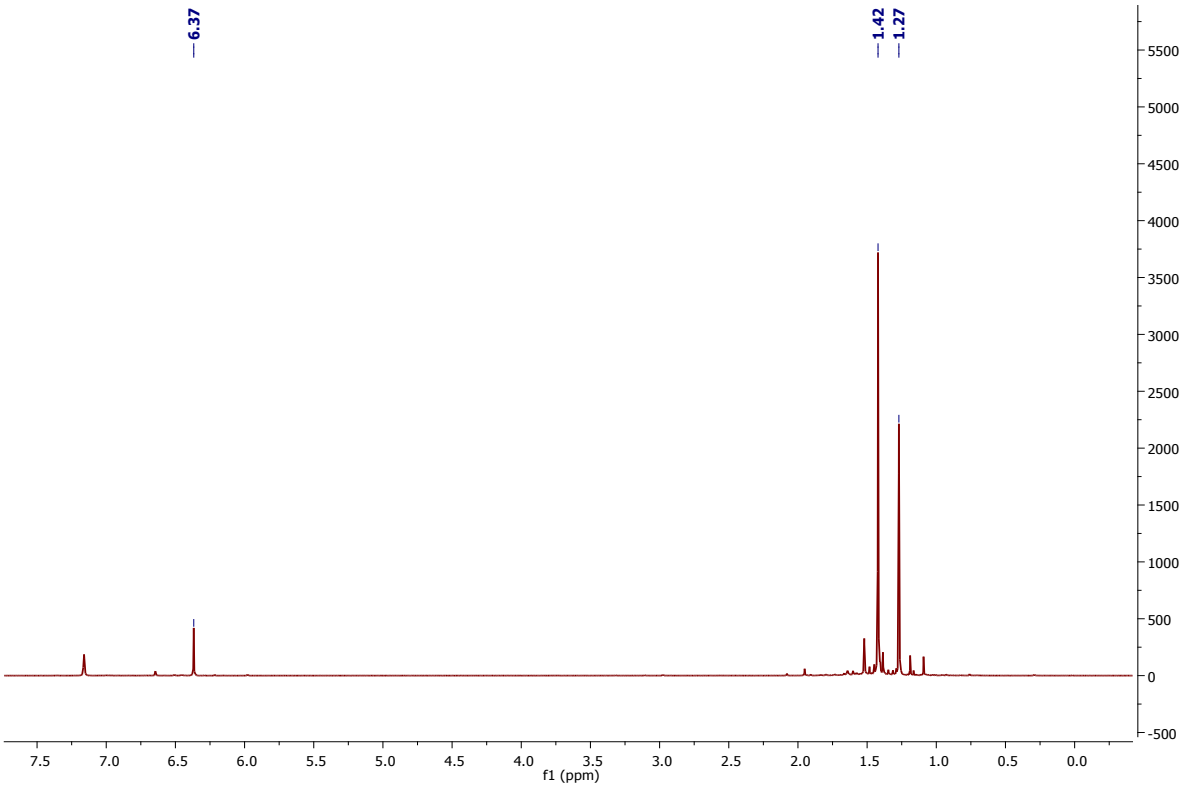


Figure S19. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **8**.

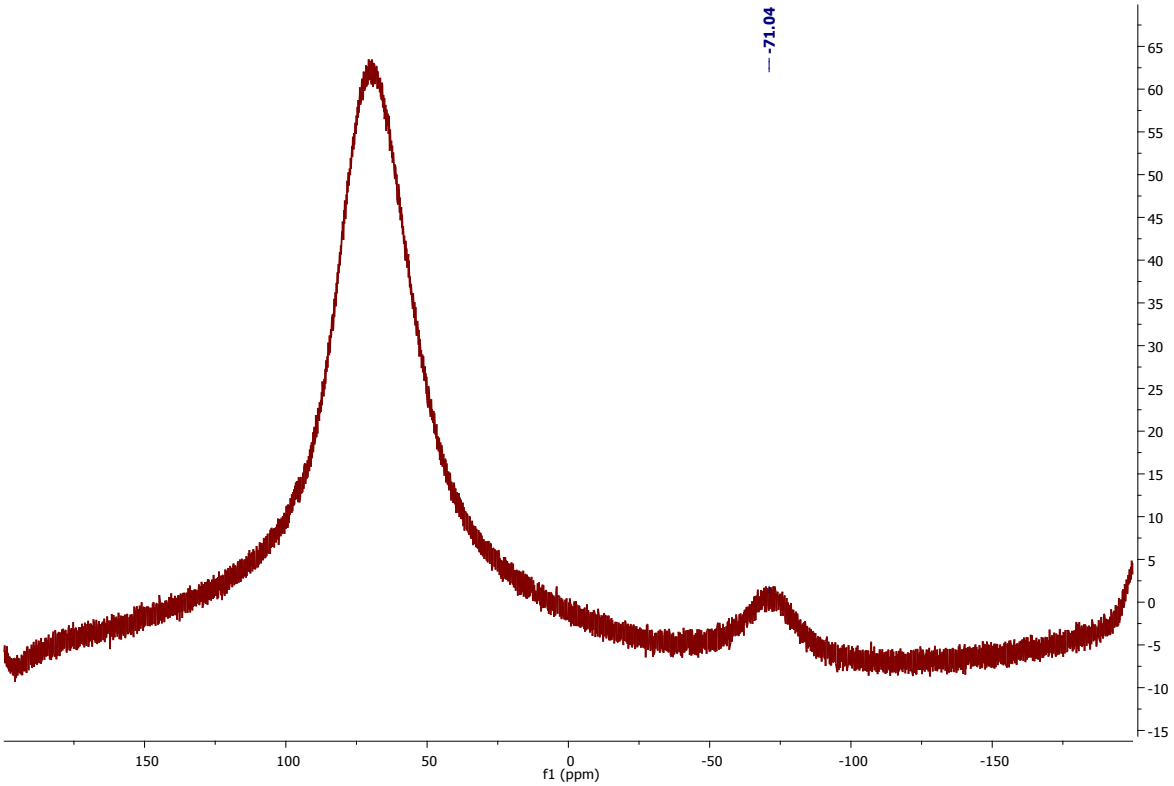


Figure S20. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **8**.

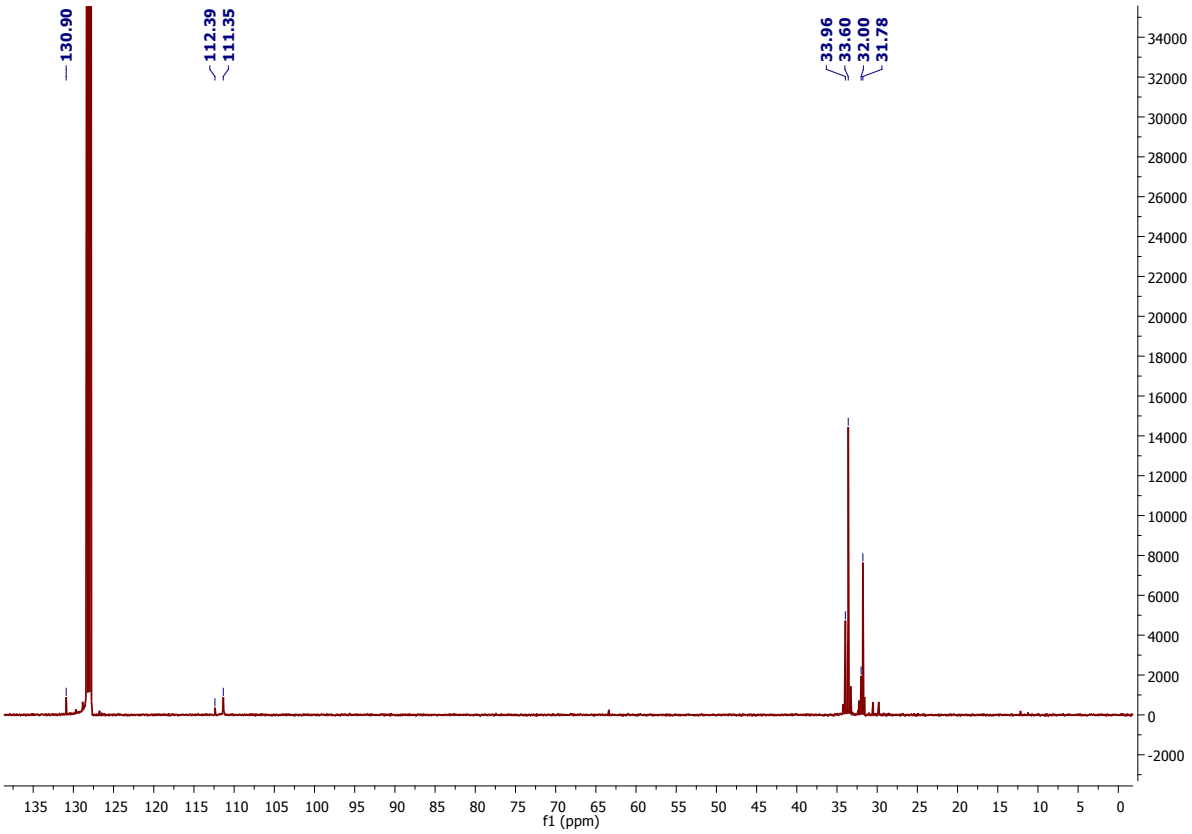


Figure S21. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **8**.

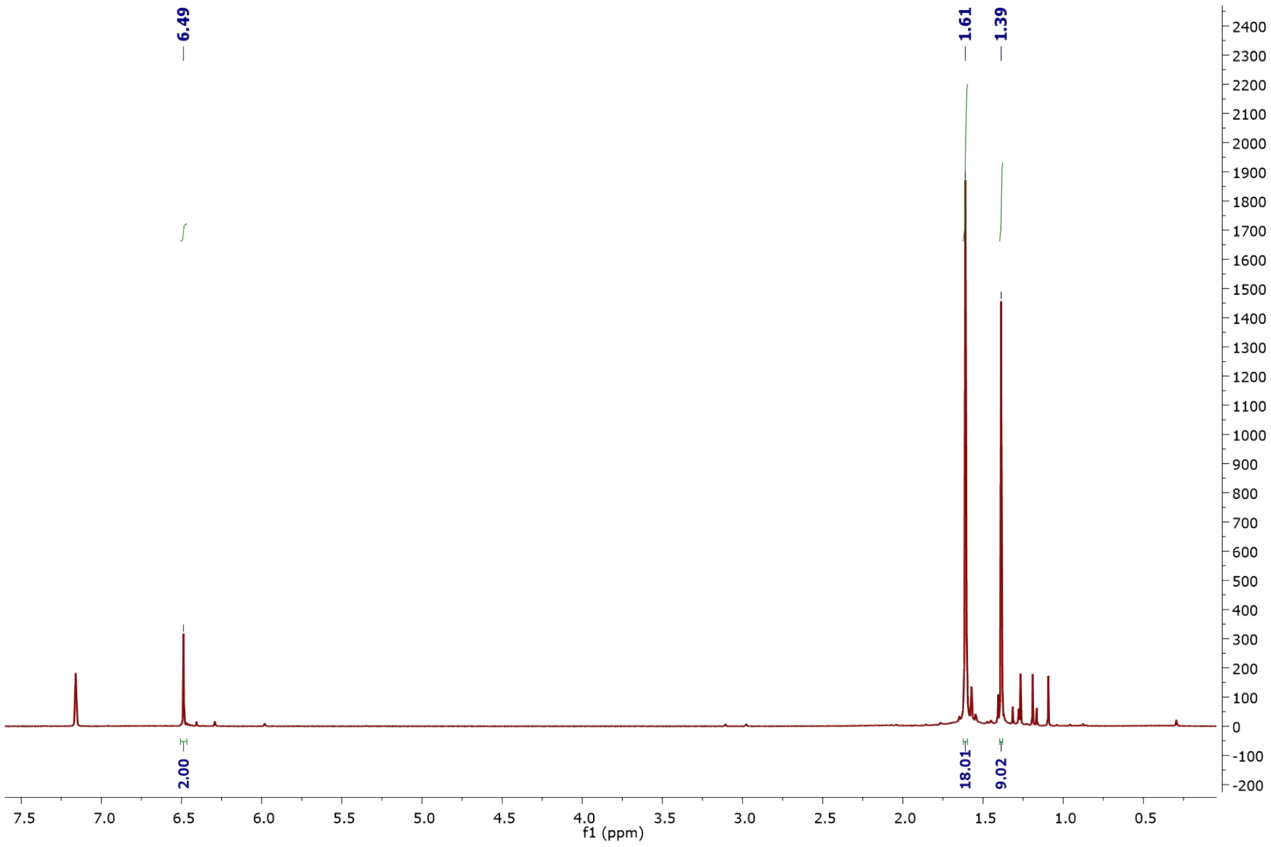


Figure S22. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **9**.

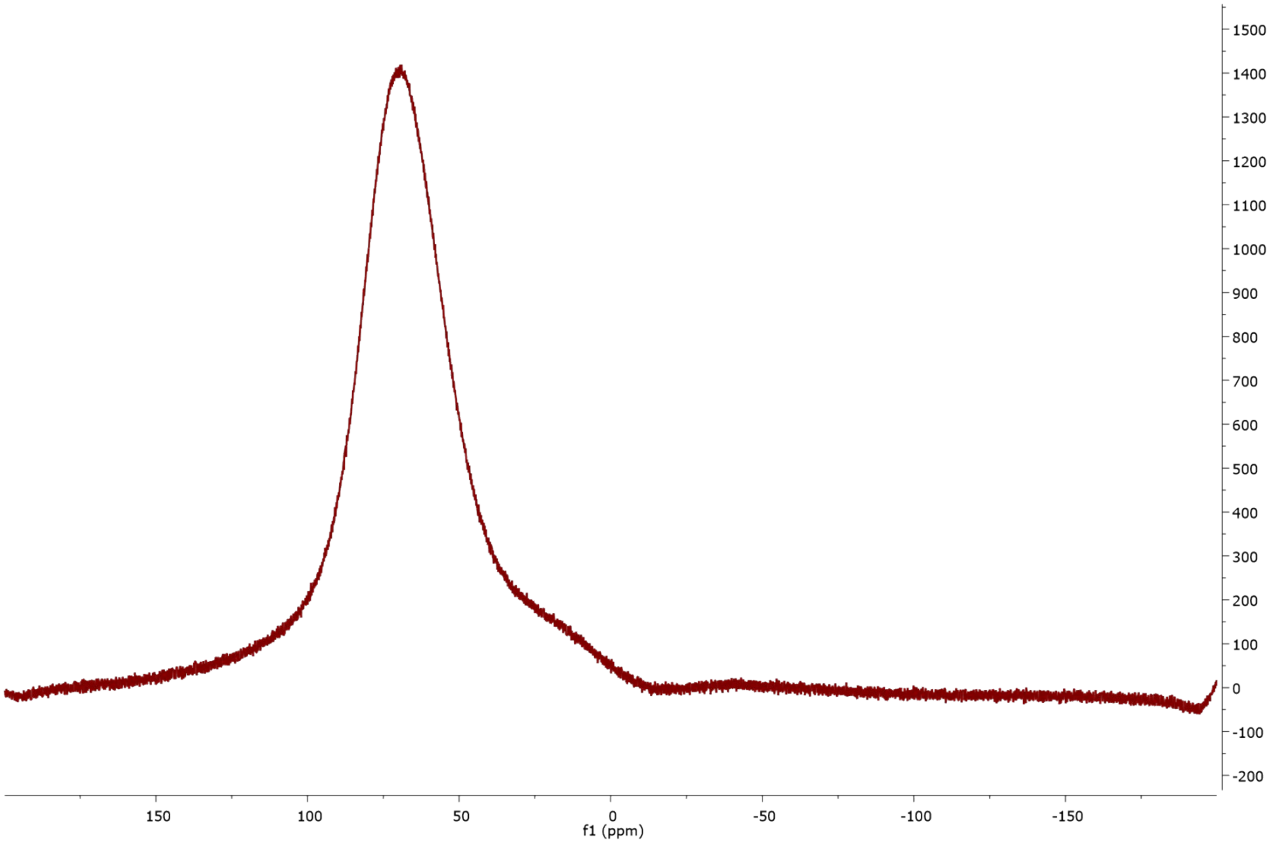


Figure S23. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **9**.

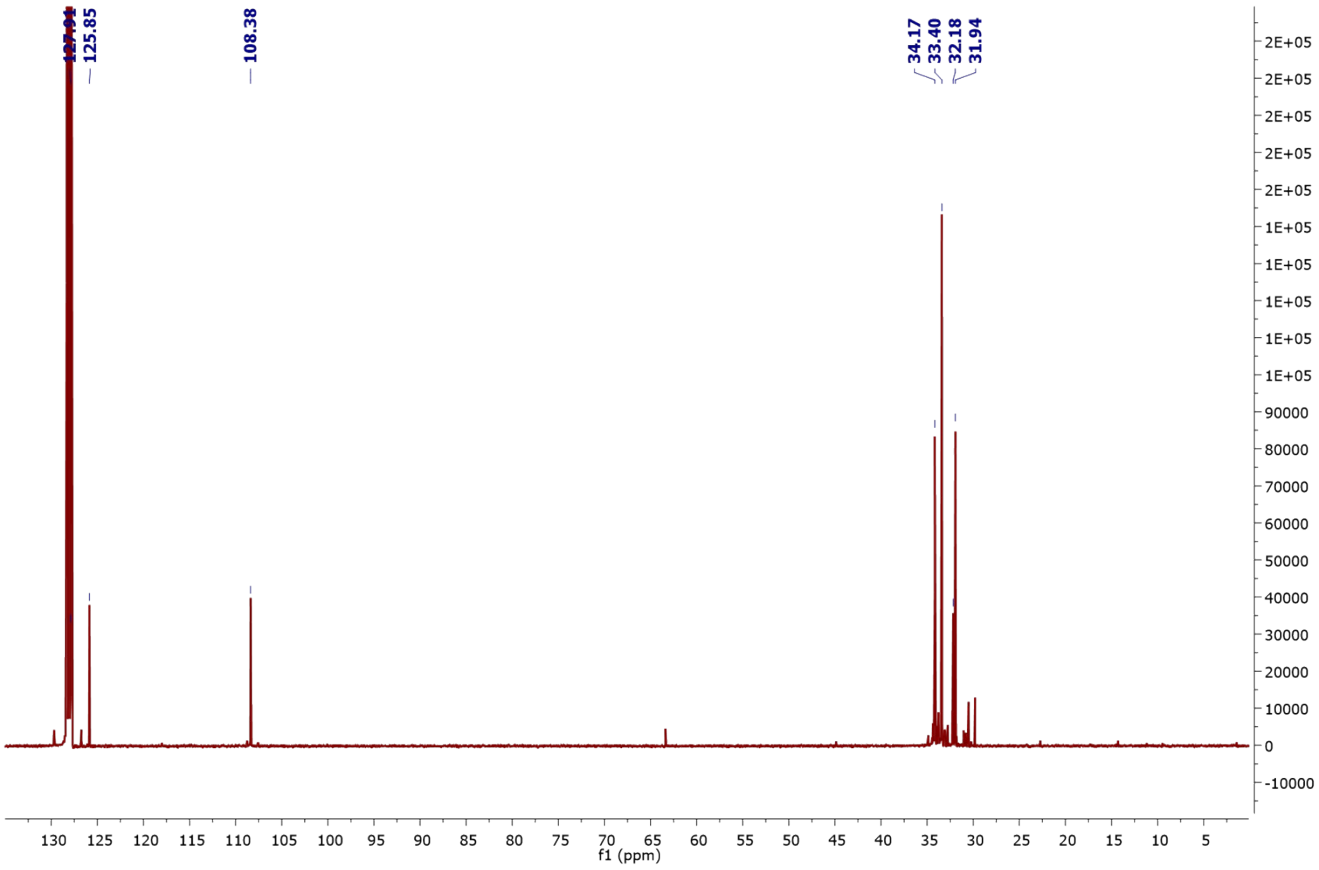


Figure S24. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) spectrum of **9**.

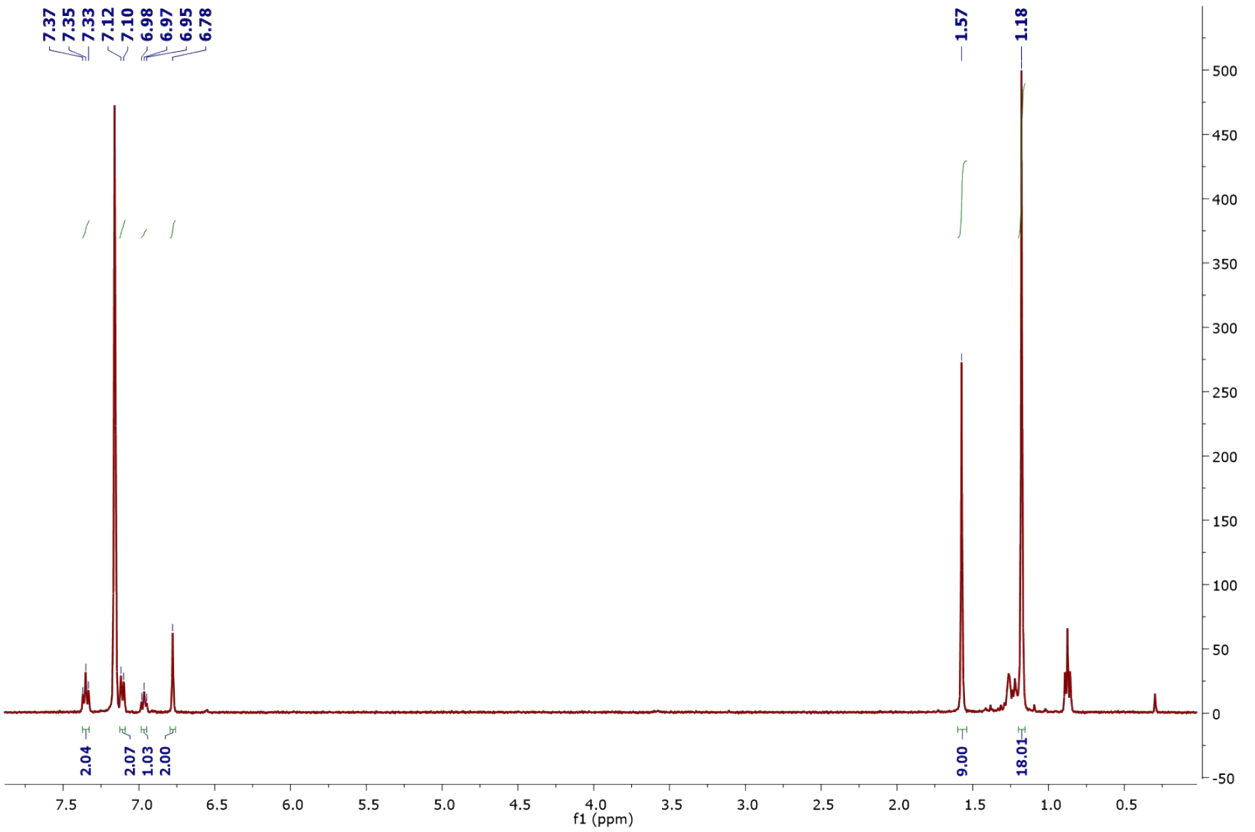


Figure S25. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **10**.

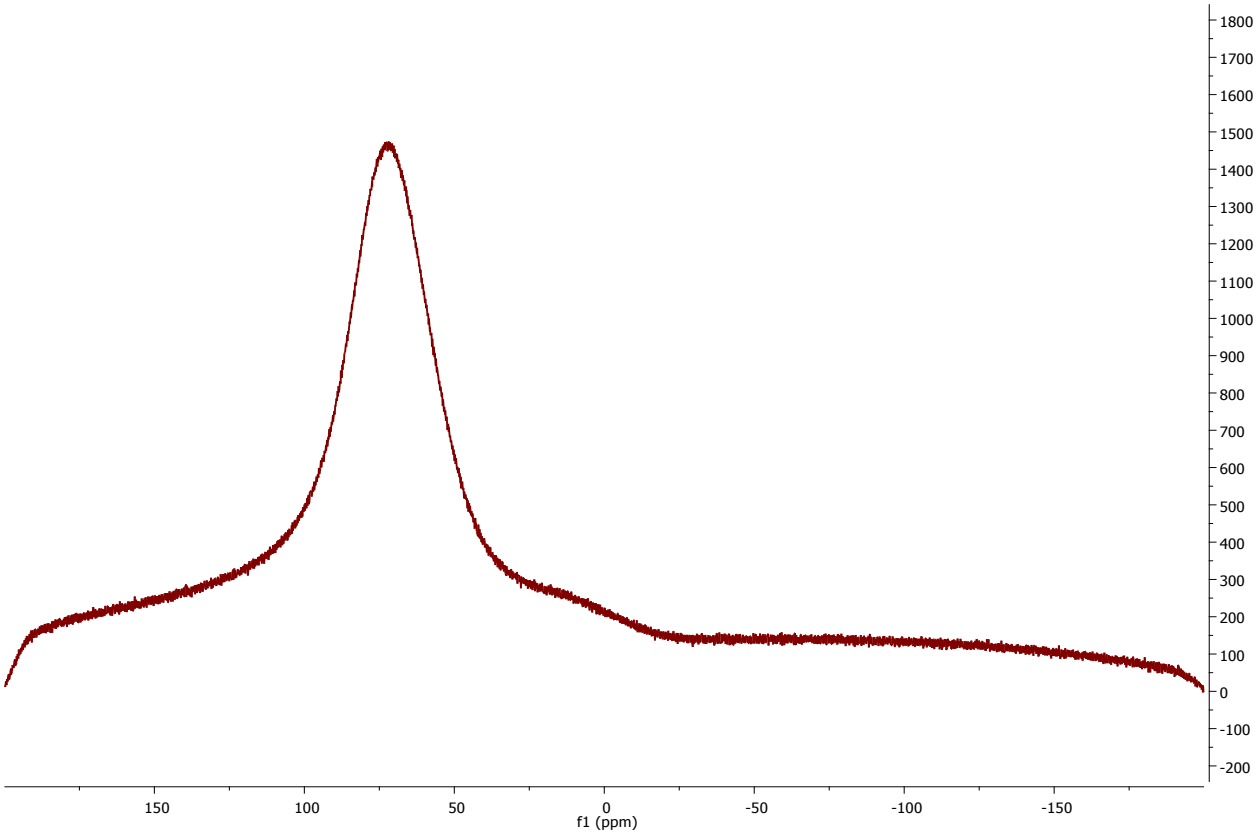


Figure S26. ^{27}Al NMR (104 MHz, C_6D_6) spectrum of **10**.

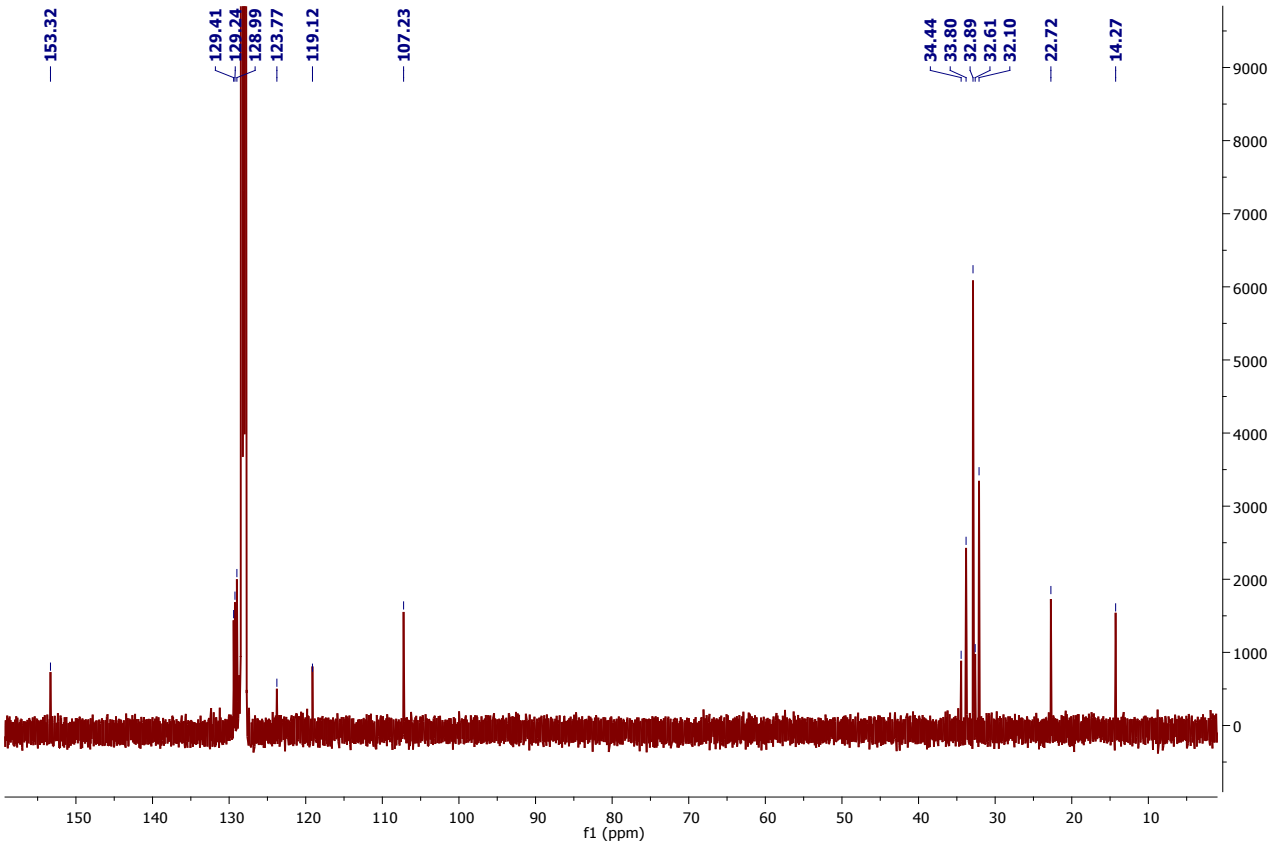


Figure S27. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **10**.

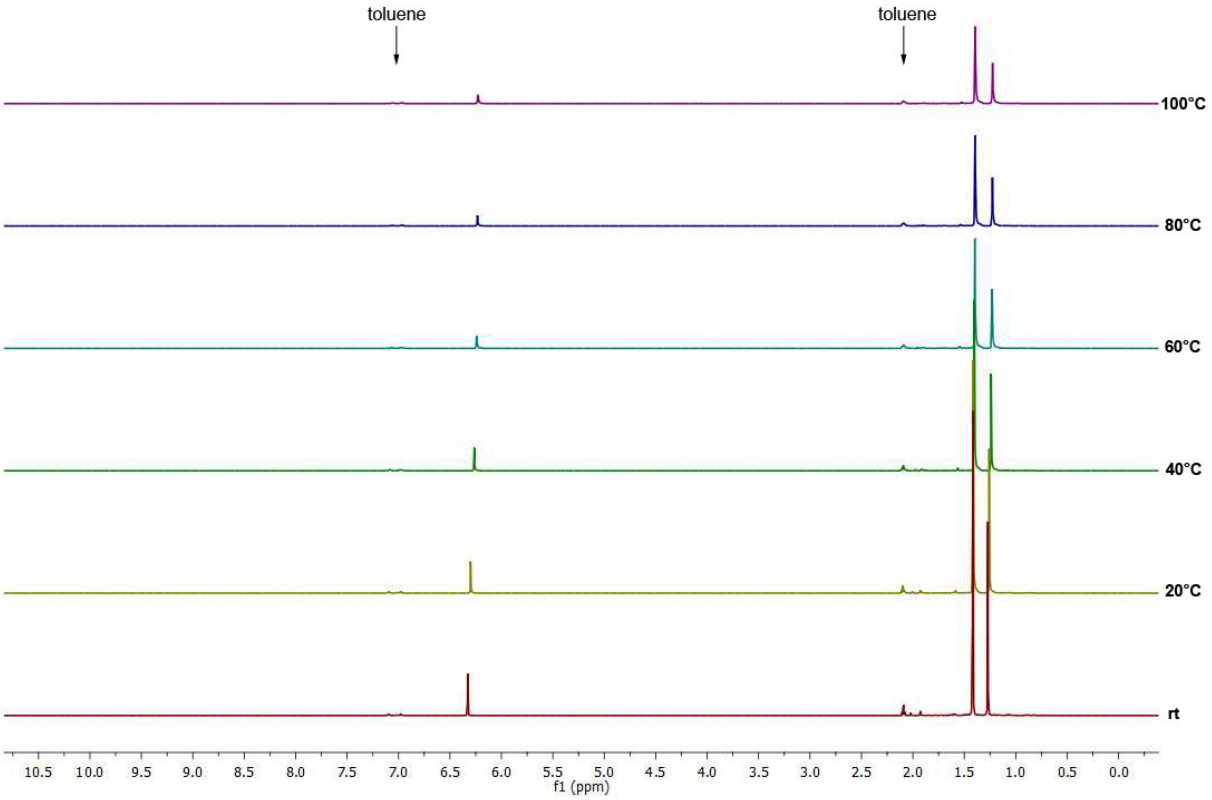


Figure S28. VT ^{1}H NMR (104 MHz, toluene-d_8) spectrum of **4**/**5** (rt to 100 °C).

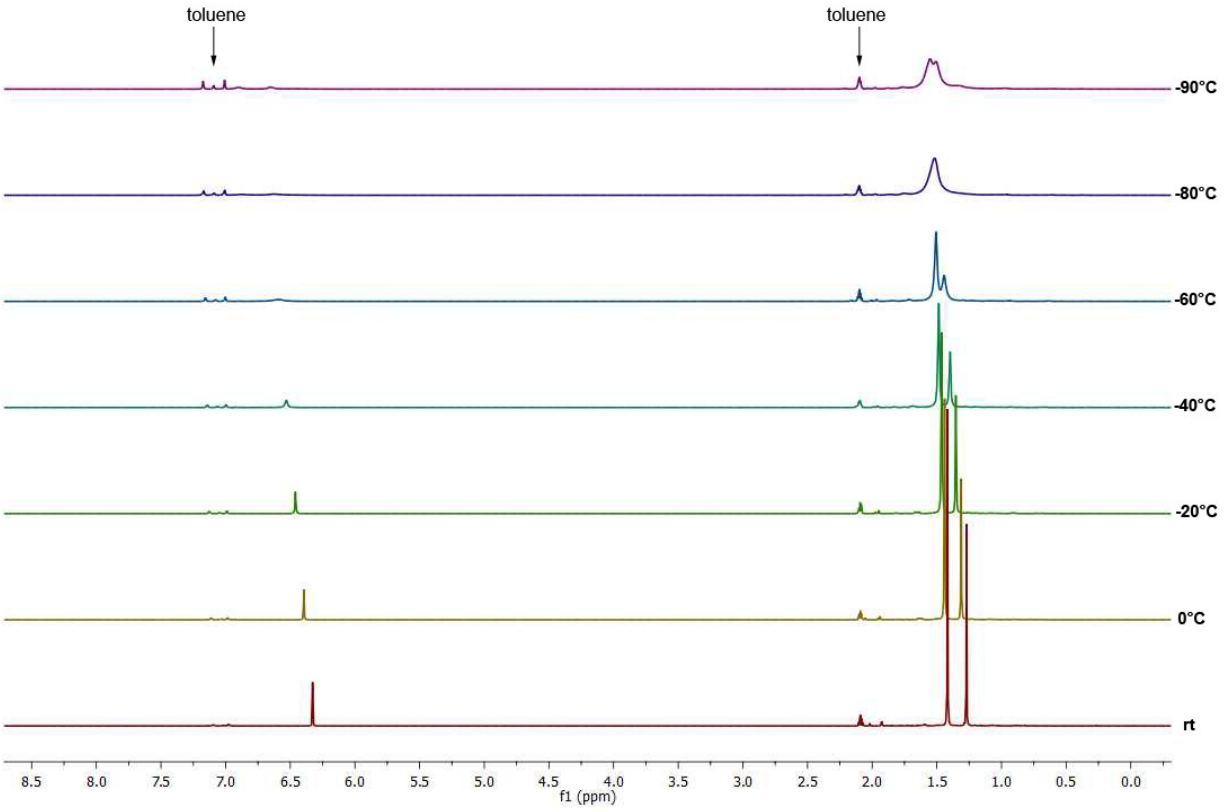


Figure S29. VT ^{1}H NMR (104 MHz, toluene-d_8) spectrum of **4**/**5** (rt to -90 °C).

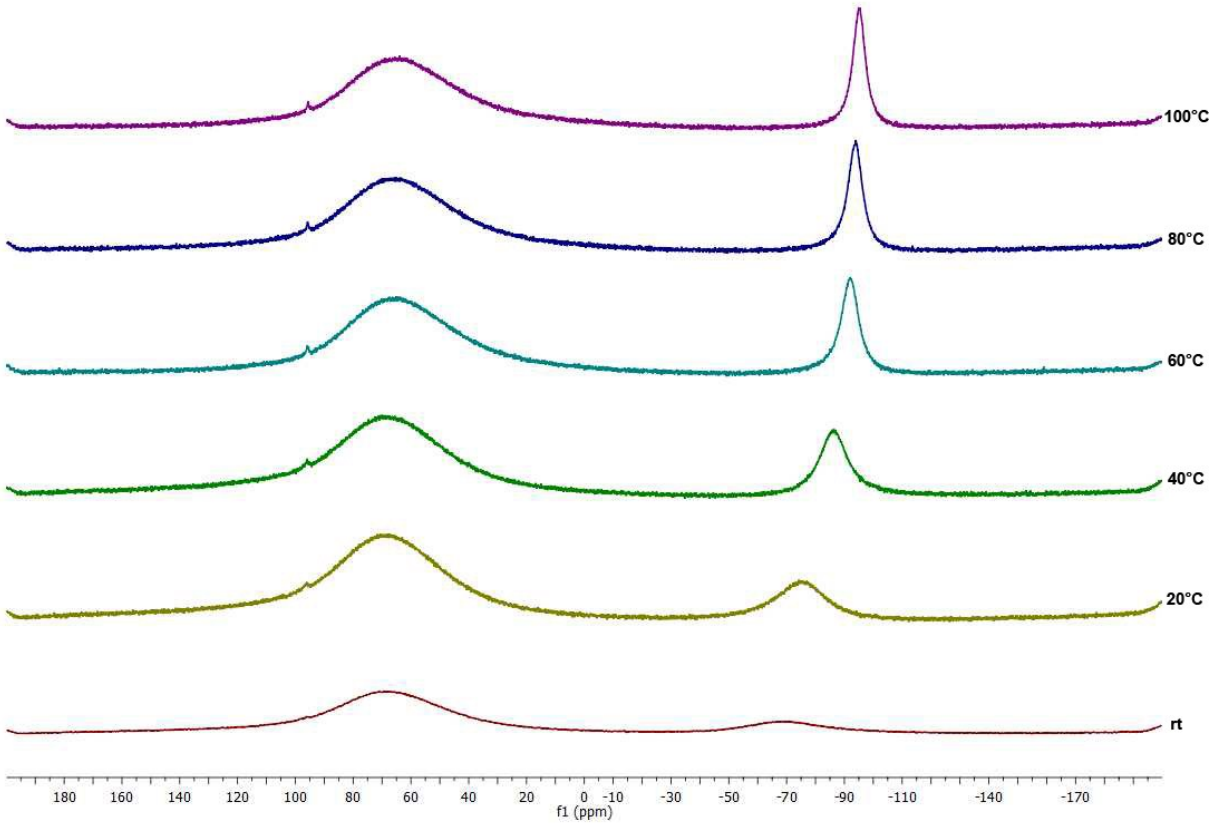


Figure S30. VT ^{27}Al NMR (104 MHz, toluene-d_8) spectrum of **4**/**5** (rt to 100 °C).

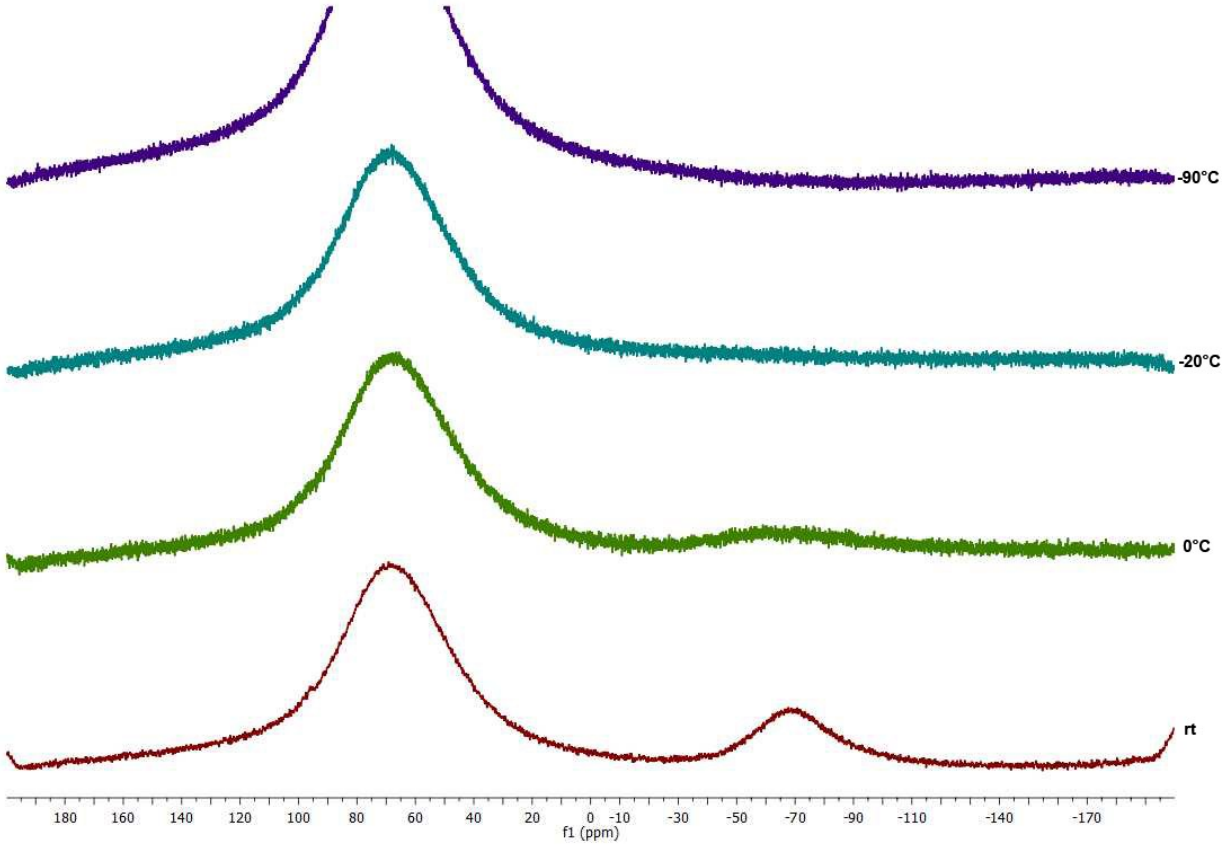


Figure S31. VT ^{27}Al NMR (104 MHz, toluene-d_8) spectrum of **4**/**5** (rt to -90 °C).

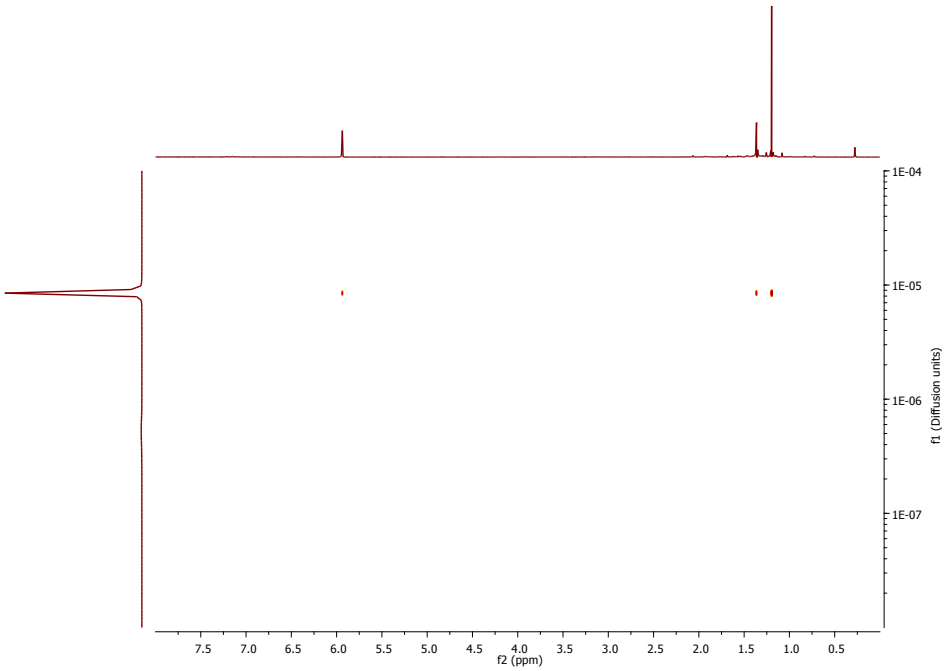


Figure S32. ^{1}H DOSY NMR (C_6D_6, 298 K) spectrum of **1**.

$D = K \cdot M_w^{\alpha}$

$D_{(1)}$ =8.703 x e^{-10} m^2/s

$$Mw = \sqrt[\alpha]{\frac{D}{K}}$$

Depending on α and K, an average M_w of 253 g/mol is calculated.[6]

S3 Crystal structure determinations

The crystal data of **2**, **3**, **4** and **6**, were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **5**, and **7**-**10** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using intrinsic phasing method (ShelXT, G. Sheldrick, *Acta Cryst.*, **2015**, *A71*, 3–8),[7] refined with the ShelXL program (G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122)[8] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. The structure of **4** was refined using TWIN keyword (matrix: Twin -1 0 0 0 1 0 0 0 -1). The BASF parameter was refined to 48%. The crystal of **5** was a pseudo-merohedral twin with domains rotated by 179.9 ° around real axis. The structure was refined using TWIN keyword (matrix: Twin 0.95 0.10 -0.05 0.975 -0.95 -0.03 0 0 -1 2). The BASF parameter was refined to 32%. The structure **6** was refined using TWIN keyword (matrix: twin -1 0 -0.014 0 -1 0 0 0 1). The BASF parameter was refined to 7%.

Crystal data for **2**: $C_{17}H_{29}AlBr_2$, M_r = 420.20, colourless block, 0.675×0.447×0.289 mm^3, Monoclinic space group $P2_1/c$, a = 9.400(5) Å, b = 14.876(9) Å, c = 13.886(9) Å, β = 105.24(4)°, V = 1873(2) Å^3, Z = 4, ρ_{calcd} = 1.490 g·cm^{-3}, μ = 4.365 mm^{-1}, $F(000)$ = 856, T = 100(2) K, R_1 = 0.0725, wR^2 = 0.0841, 3680 independent reflections [$2\theta \leq 52.042°$] and 190 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878105. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **3**: $C_{27}H_{44}Al_2Br_2$, M_r = 582.40, colourless needle, 0.537×0.133×0.085 mm^3, Monoclinic space group $P2_1/c$, a = 8.824(3) Å, b = 29.234(6) Å, c = 12.125(3) Å, β = 108.80(2)°, V = 2961.1(14) Å^3, Z = 4, ρ_{calcd} = 1.306 g·cm^{-3}, μ = 2.809 mm^{-1}, $F(000)$ = 1208, T = 100(2) K, R_1 = 0.0711, wR^2 = 0.0700, 5818 independent reflections [$2\theta \leq 52.044°$] and 294 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878107. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **4**: $C_{34}H_{58}Al_2Br_2$, M_r = 680.58, colourless block, 0.216×0.21×0.143 mm^3, Monoclinic space group *Cc*, *a* = 19.582(6) Å, *b* = 8.479(2) Å, *c* = 21.301(8) Å, β = 93.33(2)°, *V* = 3531(2) Å^3, *Z* = 4, ρ_{calcd} = 1.280 g·cm^{-3}, μ = 2.366 mm^{-1}, *F*(000) = 1432, *T* = 100(2) K, R_1 = 0.0428, wR^2 = 0.1182, 6954 independent reflections [2θ≤52.042°] and 362 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878106. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **5**: : $C_{34}H_{58}Al_2Br_2$, M_r = 680.58, colourless block, 0.623×0.544×0.534 mm^3, Triclinic space group $P\bar{1}$, *a* = 10.367(2) Å, *b* = 12.452(3) Å, *c* = 15.704(3) Å, α = 69.094(5)°, β = 88.918(6)°, γ = 67.783(5)°, *V* = 1737.3(6) Å^3, *Z* = 2, ρ_{calcd} = 1.301 g·cm^{-3}, μ = 2.404 mm^{-1}, *F*(000) = 716, *T* = 100(2) K, R_1 = 0.0987, wR^2 = 0.2664, 6846 independent reflections [2θ≤52.042°] and 362 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878104. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **6**: $C_{21}H_{38}Al_2Cl_2$, M_r = 415.37, colourless block, 0.303×0.225×0.166 mm^3, Monoclinic space group $P2_1$, *a* = 9.8915(4) Å, *b* = 21.5331(9) Å, *c* = 11.5146(5) Å, β = 90.4570(10)°, *V* = 2452.47(18) Å^3, *Z* = 4, ρ_{calcd} = 1.125 g·cm^{-3}, μ = 0.339 mm^{-1}, *F*(000) = 896, *T* = 100(2) K, R_1 = 0.0437, wR^2 = 0.0778, 9603 independent reflections [2θ≤52.042°] and 476 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878109. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **7**: $C_{17}H_{29}Al_2Br_3$, M_r = 527.09, colourless block, 0.297×0.276×0.232 mm^3, Triclinic space group $P\bar{1}$, *a* = 10.6448(18) Å, *b* = 10.6844(20) Å, *c* = 11.1041(12) Å, α = 63.541(5)°, β = 81.455(7)°, γ = 73.465(6)°, *V* = 1083.5(3) Å^3, *Z* = 2, ρ_{calcd} = 1.616 g·cm^{-3}, μ = 5.662 mm^{-1}, *F*(000) = 524, *T* = 100(2) K, R_1 = 0.0154, wR^2 = 0.0350, 4275 independent reflections [2θ≤52.04°] and 208 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878108. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **8**: $C_{34}H_{58}Al_3Br_3$, M_r = 787.47, colourless plate, 0.256×0.234×0.213 mm^3, Monoclinic space group $P2_1/c$, a = 10.1424(16) Å, b = 38.371(7) Å, c = 10.1825(19) Å, β = 105.719(13)°, V = 3814.6(12) Å^3, Z = 4, ρ_{calcd} = 1.371 g·cm^{-3}, μ = 3.263 mm^{-1}, F(000) = 1624, T = 100(2) K, R_1 = 0.0331, wR^2 = 0.0517, 7525 independent reflections [2θ≤52.04°] and 379 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1879323. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **9**: $C_{51}H_{87}Al_3O_3$, M_r = 829.14, colourless plate, 0.36×0.167×0.084 mm^3, Monoclinic space group $P2_1/c$, a = 14.173(9) Å, b = 19.091(14) Å, c = 19.858(14) Å, β = 109.37(2)°, V = 5069(6) Å^3, Z = 4, ρ_{calcd} = 1.086 g·cm^{-3}, μ = 0.112 mm^{-1}, F(000) = 1824, T = 100(2) K, R_1 = 0.1473, wR^2 = 0.1370, 9985 independent reflections [2θ≤52.044°] and 541 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878111. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **10**: $C_{46}H_{68}Al_2N_2$, M_r = 702.98, colourless plate, 0.16×0.138×0.099 mm^3, Orthorhombic space group *Pbca*, a = 17.2467(17) Å, b = 13.0572(9) Å, c = 18.6141(16) Å, V = 4191.8(6) Å^3, Z = 4, ρ_{calcd} = 1.114 g·cm^{-3}, μ = 0.102 mm^{-1}, F(000) = 1536, T = 100(2) K, R_1 = 0.1067, wR^2 = 0.1138, 4122 independent reflections [2θ≤52.038°] and 235 parameters.

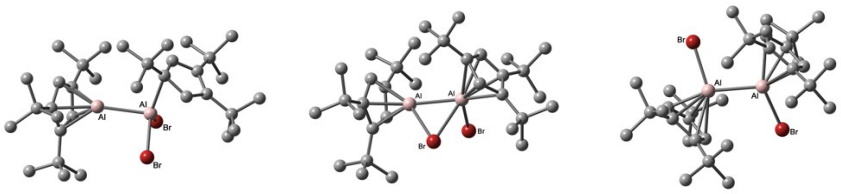
Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1878110. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

S4 Density functional theory (DFT) calculations

General remarks

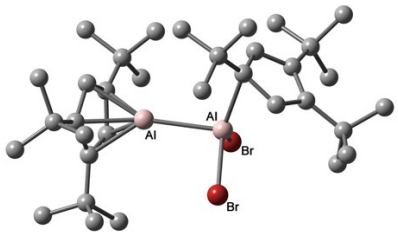
Geometry optimizations of $\mathbf{4}_{calc}$ and $\mathbf{5}_{calc}$ were performed using the *GAUSSIAN 16* program.[9] The M06L hybrid functional and def2-SVP basis sets were used for all these computations.[10,11] We ensured that the calculated geometries are minima on the potential energy surface by carrying out harmonic frequency calculations (zero negative eigenvalues of the Hessian). The transition state **TS** for the transformation of $\mathbf{4}_{calc}$ into $\mathbf{5}_{calc}$ was localized by optimization (opt=TS) of an initial structural guess, and its nature as transition state was also verified by harmonic frequency calculations (one negative eigenvalues of the Hessian).

Optimized structures



Free energy G in a.u.	-6961.056518	-6961.047599	-6961.062887
ΔG in kcal/mol	0	+5.6	-4.0

Cartesian coordinates for optimized structures



$\mathbf{4}_{calc}$

Al	-1.63183200	0.18755100	0.13059300
Al	0.75687200	-0.80561800	-0.04552000
Br	0.14302600	-2.98688300	-0.67853300
Br	1.01761600	0.49143300	-1.98813500
C	-2.57590900	2.15107300	-0.24411600
C	-3.16466500	1.53880500	0.89500300
H	-3.13929900	1.95672000	1.90016700
C	-3.79921900	0.30267700	0.53793000
C	-3.55144800	0.11012500	-0.88237600
C	-2.81991300	1.27019800	-1.32306700
H	-2.44544900	1.41759600	-2.33361900
C	-1.82248600	3.46866900	-0.26090500
C	-0.62930000	3.38881900	0.69636300
H	-0.07444100	4.33896500	0.71570900
H	0.07931300	2.60362900	0.38096900

H	-0.94317900	3.16837800	1.72869400
C	-1.31639900	3.77479700	-1.66753900
H	-0.77780300	4.73294100	-1.67953400
H	-2.14269100	3.85260300	-2.38953200
H	-0.61988500	3.00137800	-2.02417300
C	-2.77627500	4.57771500	0.19514900
H	-2.26637000	5.55223800	0.18791900
H	-3.14534200	4.40577400	1.21682300
H	-3.65132300	4.65322900	-0.46650600
C	-4.51998300	-0.54278500	1.59938300
C	-4.71638800	0.28749500	2.87498700
H	-5.28439000	-0.29843800	3.61108200
H	-5.27739600	1.21392700	2.68506200
H	-3.76324400	0.55509100	3.35317800
C	-5.91953600	-0.94754300	1.12830400
H	-6.45698600	-1.45531200	1.94229700
H	-5.91302000	-1.63257600	0.27444100
H	-6.51114600	-0.06519100	0.84276400
C	-3.68728800	-1.76829400	2.00018400
H	-4.23625100	-2.39185800	2.72170100
H	-2.75490900	-1.45163600	2.49476800
H	-3.40537300	-2.40778800	1.15505700
C	-3.95396200	-0.96922700	-1.89886700
C	-5.37484800	-0.66708300	-2.39324000
H	-5.67241500	-1.39122800	-3.16627300
H	-5.43178900	0.33655600	-2.83924100
H	-6.12224100	-0.71193400	-1.59085200
C	-3.86289000	-2.39895600	-1.36435500
H	-4.09654400	-3.10646000	-2.17279100
H	-4.56221300	-2.61491900	-0.55001600
H	-2.84364100	-2.63517100	-1.01956300
C	-3.01119200	-0.91250800	-3.11023500
H	-3.24934600	-1.73424300	-3.79940900
H	-1.95451700	-1.02711500	-2.81931100
H	-3.10975500	0.01778200	-3.68564000
C	1.73504700	-0.27709400	1.76750300
C	2.28681600	0.97499800	1.37606300
H	1.88926200	1.93367600	1.70752800
C	3.37001200	0.81495300	0.49648400
C	3.55511600	-0.60255100	0.30775100
C	2.55757600	-1.25544200	1.07387700
H	2.52631000	-2.32390000	1.28111100
C	1.02308900	-0.55889900	3.09112600
C	2.09907500	-0.64840400	4.18156900
H	1.65128800	-0.85413600	5.16656600
H	2.66670000	0.29018900	4.25614400
H	2.81728300	-1.45214000	3.96464300
C	0.26328100	-1.88420000	3.04008500
H	-0.22751200	-2.09326500	4.00276900
H	0.92657800	-2.73353700	2.82157600
H	-0.51992400	-1.88514400	2.26453400
C	0.05657100	0.56772500	3.45096000
H	-0.43832000	0.36488900	4.41337700
H	-0.73657800	0.68612200	2.69312600
H	0.56945500	1.53625400	3.54437100
C	4.11503400	2.04811500	-0.03693800
C	3.21531100	3.28876600	0.06236700
H	3.73135800	4.16029200	-0.36747800
H	2.96270600	3.55231200	1.09921400
H	2.27617900	3.14686800	-0.49493900
C	5.34671400	2.30422500	0.84465000
H	5.88584300	3.20575000	0.51198600
H	6.05673900	1.46757400	0.82888400
H	5.05107000	2.45887400	1.89282600
C	4.53833700	1.96719800	-1.50566400
H	4.99036600	2.92322100	-1.81127400
H	3.67491900	1.78599000	-2.16135000

H	5.28371300	1.19184700	-1.70873900
C	4.53047700	-1.43450800	-0.53406000
C	5.98374600	-1.00998600	-0.29741700
H	6.66630600	-1.69001300	-0.82920000
H	6.23916700	-1.05664200	0.77190000
H	6.21037600	0.00292600	-0.64553000
C	4.17651300	-1.38730000	-2.02675500
H	4.90723600	-1.96768600	-2.61207500
H	4.14464800	-0.37264900	-2.43743700
H	3.18627700	-1.83500100	-2.20126600
C	4.45055300	-2.91251400	-0.12530500
H	5.17910700	-3.49671400	-0.70622300
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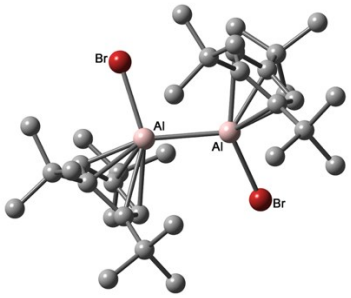
H	4.68327000	-3.06070200	0.93977900



5$_{calc}$

Al	1.18799400	0.21237800	-0.50611600
Al	-1.18852300	0.30519900	0.44178600
Br	0.93228000	0.64957200	-2.84961900
Br	-0.90395700	1.26510500	2.62911400
C	2.84923600	1.36552800	0.41267700
C	3.30663200	0.44575300	-0.56964300
H	3.71925600	0.72036700	-1.53820800
C	3.07564900	-0.90588100	-0.13253400
C	2.54786400	-0.80414100	1.22933100
C	2.41837600	0.57233600	1.51141600
H	1.96907700	0.97919800	2.41275600
C	3.01262200	2.87572000	0.38147300
C	4.49859600	3.18724700	0.59986500
H	4.67017400	4.27395100	0.62732600
H	5.12034400	2.77121500	-0.20636000
H	4.86004500	2.76649800	1.54930700
C	2.56918500	3.44552300	-0.96550600
H	2.76554000	4.52707100	-1.01113500
H	1.49110400	3.29698400	-1.13320900
H	3.09447400	2.97870200	-1.81188000
C	2.19155000	3.52206500	1.49438000
H	2.27701600	4.61756300	1.44949000
H	2.53091100	3.20919600	2.49258800
H	1.12444200	3.26277200	1.41769500
C	3.65044400	-2.07936100	-0.94341800
C	3.87358600	-1.66972700	-2.40543300
H	4.24101700	-2.53593400	-2.97406500
H	4.63133200	-0.88209900	-2.51158100
H	2.95181900	-1.31990700	-2.89032700
C	5.03280400	-2.43368100	-0.37455600
H	5.49133000	-3.24347700	-0.96264500
H	5.00401400	-2.75705300	0.67125000
H	5.70521400	-1.56473000	-0.42912700
C	2.74293800	-3.30938300	-0.97970400

H	3.20240600	-4.09754900	-1.59429100
H	1.77145500	-3.06948300	-1.43713100
H	2.54652700	-3.74860200	0.00367000
C	2.14172200	-1.86242900	2.26717500
C	3.23214100	-2.91486100	2.49640600
H	2.94923100	-3.55827800	3.34264500
H	4.19127600	-2.44198200	2.75428100
H	3.40281100	-3.57755800	1.64204500
C	1.92100900	-1.19327200	3.63062600
H	1.67684300	-1.95985200	4.38004800
H	1.08869600	-0.47781700	3.61865700
H	2.82305400	-0.66820500	3.97687100
C	0.82069900	-2.53719500	1.88410300
H	0.57137600	-3.34476400	2.59041400
H	0.82653500	-2.96378600	0.87168800
H	-0.00116700	-1.80365500	1.93289300
C	-2.84908500	1.35770500	-0.56593400
C	-2.44003400	0.42245300	-1.55980900
H	-2.00124600	0.70118000	-2.51533400
C	-2.60735800	-0.90351700	-1.10652200
C	-3.09207500	-0.82044300	0.27210700
C	-3.30698100	0.58245300	0.52795400
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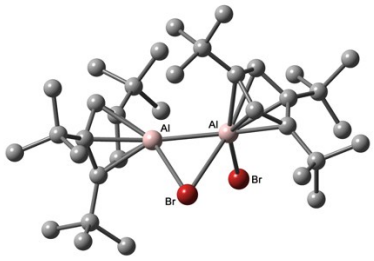
C	-2.87244300	2.87000400	-0.71354800
C	-3.45388400	3.51666200	0.54109400
H	-3.44097700	4.61295900	0.45003700
H	-2.87506800	3.25216600	1.43903000
H	-4.49824300	3.21150900	0.70829700
C	-1.44964800	3.39138800	-0.94131100
H	-1.44663200	4.47702500	-1.12224400
H	-0.96939600	2.90658800	-1.80607400
H	-0.81744800	3.20817900	-0.05525600
C	-3.74246300	3.22649700	-1.92330800
H	-3.80616000	4.31781800	-2.04796400
H	-4.76621000	2.84176000	-1.80730600
H	-3.33380600	2.81004900	-2.85517600
C	-2.30309500	-2.09878900	-2.01873900
C	-2.06966000	-1.61213200	-3.45490300
H	-1.89868800	-2.47717100	-4.11147700
H	-1.19091200	-0.96123300	-3.54160400
H	-2.94233000	-1.06905300	-3.84576400
C	-3.48962500	-3.06672200	-2.10437200
H	-3.28409100	-3.83662200	-2.86263900
H	-4.40368300	-2.53915300	-2.41576500
H	-3.71199700	-3.59379000	-1.17184900
C	-1.02953500	-2.82498500	-1.57673400
H	-0.83299400	-3.70094500	-2.21451600
H	-1.06356200	-3.16827100	-0.53487600
H	-0.16376600	-2.15095300	-1.67859700
C	-3.66408900	-1.85986100	1.25262800
C	-3.68993100	-1.29049100	2.67775100
H	-2.69007300	-0.99459800	3.02632000
H	-4.07105600	-2.05440100	3.37031900
H	-4.34991300	-0.41916400	2.78071400
C	-2.86613900	-3.16144000	1.34191700
H	-1.82753000	-2.97487800	1.64932200
H	-2.83854300	-3.73659600	0.41150700
H	-3.31364000	-3.81666800	2.10361300
C	-5.11808600	-2.15033800	0.85301400
H	-5.20858200	-2.57481100	-0.15394100
H	-5.71759300	-1.22846800	0.87405800
H	-5.57675300	-2.86048200	1.55814600



TS

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Al	1.19054600	-0.09109100	-0.08139400
Br	-0.30782800	-2.37174700	-0.62686800
Br	1.05154600	0.63341600	-2.37062500
C	-2.43823000	2.07407400	-0.05067200
C	-2.88797900	1.31035500	1.04479900
H	-2.82259900	1.62322200	2.08567900
C	-3.38201500	0.02904800	0.61168700
C	-3.22780400	0.00226700	-0.83969400
C	-2.62035200	1.26046900	-1.19189800
H	-2.33210400	1.53777600	-2.20357400
C	-1.84441900	3.46975400	-0.00467600
C	-0.76941100	3.56370000	1.08033000
H	-0.33403200	4.57409300	1.10807100
H	0.05005600	2.84963700	0.89692400
H	-1.17648600	3.35637600	2.08129600
C	-1.22872200	3.83360700	-1.35349400
H	-0.78448300	4.83866600	-1.31347700
H	-1.98092600	3.84370400	-2.15586900
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C	-2.97573200	4.45232900	0.32195900
H	-2.59591300	5.48457800	0.35915200
H	-3.43579900	4.23056500	1.29621400
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C	-4.03824400	-0.94291400	1.60200600
C	-3.91561400	-0.39292200	3.02814900
H	-4.35852300	-1.10656500	3.73719200
H	-4.44101100	0.56385400	3.15816000
H	-2.86492700	-0.25144600	3.32530700
C	-5.53507300	-1.04921900	1.28747300
H	-6.04270700	-1.66459700	2.04522200
H	-5.73536200	-1.50535000	0.31057900
H	-6.01031200	-0.05689700	1.29100600
C	-3.37750900	-2.32393300	1.61798700
H	-3.92081400	-2.99515800	2.29989200
H	-2.34197100	-2.25934000	1.98292200
H	-3.33318900	-2.80755100	0.63929000
C	-3.76055600	-0.88519900	-1.97863600
C	-5.12200300	-0.29282900	-2.37758100
H	-5.54523500	-0.84520300	-3.23017400
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H	-4.67633400	-2.56670100	-0.88327900
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C	-2.81969800	-0.80136400	-3.19001200
H	-3.17490300	-1.47867400	-3.97927500
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C	2.44176800	0.95526200	1.49492100
H	2.26724000	1.98484100	1.80295900
C	3.25714100	0.57483200	0.37832400
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C	2.33541000	-1.29217700	1.38776800
H	2.04097300	-2.32175100	1.57332100
C	1.06523100	-0.22071900	3.40082000
C	2.02454200	-0.31282600	4.59480200
H	1.46670600	-0.35697300	5.54302900
H	2.69352400	0.55899300	4.63889200
H	2.65508500	-1.21150300	4.53294400
C	0.15126300	-1.44465400	3.39370900
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H	-0.37769700	1.01256400	4.46297400
H	-0.47415000	1.15272100	2.68987600
H	0.83592600	1.95292600	3.58027700
C	4.11665000	1.65704500	-0.29590700
C	3.34576300	2.98577200	-0.34590900
H	3.94530000	3.74293900	-0.87124800
H	3.12944300	3.39621400	0.64987000
H	2.39530800	2.88105800	-0.89155600
C	5.34927000	1.85059000	0.60297400
H	5.99111100	2.65376600	0.20953700
H	5.95867500	0.93807900	0.66611100
H	5.05911200	2.12352000	1.62813300
C	4.59158600	1.37867700	-1.72089900
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C	3.93760600	-1.92172400	-0.54386900
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C	3.54508600	-3.33448200	-0.09256300
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H	2.46876500	-3.52396900	-0.21639900
H	3.81337700	-3.52817500	0.95604300

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