

SUPPLEMENTARY INFORMATION

**Comproportionation of a dialuminyne with alane or dialane dihalides as a
clean route to dialuminenes**

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Experimental Details

General Procedures

All manipulations were carried out using modified Schlenk techniques or in a Vacuum Atmospheres OMNI-Lab drybox under a N₂ or argon atmosphere. Solvents were dried over columns of activated alumina using a Grubbs type purification system¹, stored over Na (Et₂O, hexanes), K (toluene) or 3 Å molecular sieves (benzene). ¹H and ¹³C{¹H} spectra were recorded on Varian Inova 600 MHz or Bruker Avance III HD Nanobay 400 MHz spectrometers and were referenced to the residual solvent signals in C₆D₆.² UV-Visible spectra were recorded in 3.5 mL quartz cuvettes using an Olis 17 Modernized Cary 14 UV-Vis/NIR spectrophotometer. Melting points were measured in glass capillary tubes sealed under argon using a Mel-Temp II apparatus using a partial immersion thermometer.

LiAr^{iPr}₄-4-SiMe₃³ and AlH₃·NMe₃⁴ were prepared according to the literature procedures.

[LiAlH₃Ar^{iPr}₄-4-SiMe₃]. A solution of LiAr^{iPr}₄-4-SiMe₃ (7.15 g, 15.0 mmol) in Et₂O (ca. 50 mL) was added dropwise onto a solution of AlH₃·NMe₃ (1.34 g, 15.0 mmol) in Et₂O (ca. 10 mL) cooled to 0°C in an ice/water bath. The mixture was warmed to room temperature and stirred for 18 h. The volatile components removed under reduced pressure and the residue dried at 40°C for 2 h. The solid was dissolved in ca. 90 mL of hot (ca. 60°C) hexanes and filtered. Removal of the solvent afforded [LiAlH₃Ar^{iPr}₄-4-SiMe₃] as a white solid. Yield: 6.18 g (81%).

¹H NMR (600 MHz, C₆D₆, 298 K): δ 7.38 (s, 2H m-ArH), 7.27 (t, ³J = 7.6 Hz, 2H, Dipp p-ArH), 7.18 (d, ³J = 7.7 Hz, 4H, Dipp m-ArH), 3.04 (sept, ³J = 7.2 Hz, 4H, -CH(CH₃)₂), 2.25 (br, 3H, AlH), 1.29 (d, ³J = 7.0 Hz, 12H, -CH(CH₃)₂), 1.12 (d, ³J = 6.8 Hz, 12H, -CH(CH₃)₂), 0.29 (s, 9H, -Si(CH₃)₃).

¹³C{¹H} NMR (151 MHz, C₆D₆, 298 K): δ 146.57, 146.29, 143.22, 139.77, 133.50, 129.01, 123.37, 31.43, 25.04, 23.59, -1.37.

Al(Et₂O)₂Ar^{iPr}₄-4-SiMe₃ (1). A solution of [LiAlH₃Ar^{iPr}₄-4-SiMe₃] (3.67 g, 7.25 mmol) in Et₂O (ca. 40 mL) was cooled to 0°C in an ice/water bath and CH₃I (2.3 mL, 36 mmol, 5 eq) was added via syringe. The mixture was allowed to slowly come to room temperature overnight with stirring (ca. 12 h). The volatile components were removed under reduced pressure and the white residue extracted with hexanes (ca. 60 mL). The colorless solution was filtered, concentrated to ca. 15 mL, and stored at ca. -18°C overnight to give colorless blocks of **1**. Yield: 3.87 g (65%). m.p. = 185-188°C.

¹H NMR (600 MHz, C₆D₆, 298 K): δ 7.40 (s, 2H, m-ArH), 7.31 (t, ³J = 7.7 Hz, 2H, Dipp p-ArH), 7.21 (d, ³J = 7.7 Hz, 4H, Dipp m-ArH), 3.57 (q, ³J = 7.1 Hz, 4H, O(CH₂CH₃)₂), 3.15 (sept, ³J = 6.8 Hz, 4H, -CH(CH₃)₂), 1.43 (d, ³J = 6.8 Hz, 12H, -CH(CH₃)₂), 1.06 (d, ³J = 6.7 Hz, 12H -CH(CH₃)₂), 0.73 (t, ³J = 7.1 Hz, 6H, O(CH₂CH₃)₂), 0.21 (s, 9H, -Si(CH₃)₃).

¹³C{¹H} NMR (151 MHz, C₆D₆, 298 K): δ 147.68, 147.51, 143.03, 138.59, 136.15, 128.8, 123.47, 71.65, 31.09, 26.35, 23.51, 13.95, -1.45.

$\{\text{Al}(\text{I})\text{Ar}^{\text{iPr}_4\text{-4-SiMe}_3}\}_2$. **(2)** Ether (ca. 30 mL) was added to a mixture of solid **1** (1.65 g, 2.00 mmol) and KC_8 (0.350 g 2.60 mmol) at ambient temperature. The mixture was stirred for ca. 18 h during which time the color changed to yellow. The volatile components were removed under reduced pressure and the yellow residue dissolved in toluene (ca. 30 mL). The solution was filtered, concentrated to ca. 8 mL, and stored at ca. -18°C for 2 days to give pale yellow blocks of **2**. Yield: 0.536 g (43%).

m.p. = $198\text{-}201^\circ\text{C}$ (dec).

^1H NMR (600 MHz, C_6D_6 , 298 K): δ 7.37 (s, overlapping with triplet, 4H, m-ArH), 7.37 (t, overlapping with singlet, $^3J = 7.8$ Hz, 4H, Dipp, p-ArH), 7.18 (d, $^3J = 7.8$ Hz, 8H, Dipp m-ArH), 3.03 (sept, $^3J = 6.7$ Hz, 8H, $-\text{CH}(\text{CH}_3)_2$), 1.16 (d, 24H, $^3J = 6.8$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.04 (d, $^3J = 6.7$ Hz, 24H, $-\text{CH}(\text{CH}_3)_2$), 0.19 (s, 18H, $-\text{Si}(\text{CH}_3)_3$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): δ 147.83, 146.01, 140.29, 139.70, 134.83, 129.99, 124.16, 30.57, 26.44, 25.18, -1.49.

UV-Visible (hexanes): λ_{max} 386 nm ($\epsilon = 2300$ L mol $^{-1}$ cm $^{-1}$).

$\text{Na}_2(\text{AlAr}^{\text{iPr}_4\text{-4-SiMe}_3})_2$ **(3)**. *Method A:* A 100-mL Schlenk flask containing Na (0.201 g, 10.0 mmol, 5 eq) metal was heated under vacuum to mirror the interior wall of the flask with Na. The flask was then charged with a magnetic stirbar and **1** (1.65 g, 2.00 mmol). Et_2O (ca. 70 mL) was added and the mixture was vigorously stirred for 3 days, during which time the mixture turned dark green-brown to black. The volatile components were removed under reduced pressure and the residue washed with hexanes (ca. 50 mL) to remove a dark red colored fraction containing mostly 4-SiMe $_3$ -Ar $^{\text{iPr}_4\text{H}}$ (62% with respect to **1**). The residue was then extracted with toluene (ca. 40 mL) and the inky dark green solution filtered. Concentration to ca. 15 mL and storage at ca. -30°C overnight gave dark green/black blocks of **3**. Yield: 0.354 g (34%).

Method B: Et_2O (ca. 70 mL) was added to mixture of **1** (1.65 g, 2.00 mmol) and 5% w/w Na/NaCl (4.60 g, 5 eq) and stirred for 3 days. The volatile components were removed under reduced pressure and the residue washed with hexanes (ca. 50 mL) then extracted with toluene (ca. 40 mL). The dark green toluene filtrate was concentrated to ca. 20 mL and stored at ca. -30°C overnight to give dark green blocks of **3**. Yield: 0.302 g (29%)

m.p. = $204\text{-}208^\circ\text{C}$ (dec).

^1H NMR (600 MHz, C_6D_6 , 298 K): δ 7.20 (s, 4H, m-ArH), 7.16 (t, overlapping with solvent signal, 4H, Dipp, p-ArH), 6.97 (d, $^3J = 7.6$ Hz, 8H, Dipp m-ArH), 2.95 (sept, $^3J = 6.9$ Hz, 8H, $-\text{CH}(\text{CH}_3)_2$), 1.46 (d, $^3J = 6.9$ Hz, 24H, $-\text{CH}(\text{CH}_3)_2$) 1.03 (d, $^3J = 6.8$ Hz 24H, $-\text{CH}(\text{CH}_3)_2$), 0.28 (s, 18H, $-\text{Si}(\text{CH}_3)_3$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): δ 165.10, 149.70, 148.38, 133.62, 130.98, 126.08, 122.06, 31.03, 25.27, 24.59, -0.95.

UV-Visible (toluene): λ_{max} 344 nm ($\epsilon = 9400$ L mol $^{-1}$ cm $^{-1}$), 470 nm (shoulder, $\epsilon = 4800$ L mol $^{-1}$ cm $^{-1}$), 612 nm ($\epsilon = 4400$ L mol $^{-1}$ cm $^{-1}$), 660 nm (shoulder, $\epsilon = 4100$ L mol $^{-1}$ cm $^{-1}$).

[(AlAr^{iPr}₄-4-SiMe₃)₂(C₆H₆)] (4). A mixture of solid [Na₂(AlAr^{iPr}₄-4-SiMe₃)₂] (73.4 mg, 70.6 μmol) and Al(Et₂O)I₂Ar^{iPr}₄-4-SiMe₃ (58.2 mg, 70.6 μmol) was dissolved in ca. 5 mL benzene. The mixture was stirred for ca. 15 min during which time the color changed from dark green to red with formation of a white precipitate. The mixture was filtered via cannula and concentrated under reduced pressure to ca. 1 mL. Storage of the solution at ca. 8°C yielded red blocks of **4**. Yield: 0.045 g (42%)

m.p. = 110-115°C (dec).

¹H NMR (600 MHz, C₆D₆, 298 K): δ 7.27 (t, ³J = 7.7 Hz, 4H, Dipp p-Ar^H), 7.14 (d, ³J = 7.7 Hz, 8H, Dipp m-Ar^H), 7.11 (s, 4H, m-Ar^H), 3.04-2.91 (mult, br, 8H, -CH(CH₃)₂), 1.24-0.85 (mult, br, 48H, -CH(CH₃)₂), 0.13 (s, 18H, -Si(CH₃)₃). Complexed C₆H₆ signals not observed.

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ 146.15, 142.30, 138.90, 133.79, 129.19, 123.80, 30.91 (br), 25.54 (br), 23.25, -1.39.

UV-Visible (hexanes): λ_{max} 323 nm (ε = 2200 L mol⁻¹ cm⁻¹), 460 (shoulder, ε = 230 L mol⁻¹ cm⁻¹).

4-SiMe₃-Ar^{iPr}₄H NMR data:

¹H NMR (400 MHz, C₆D₆, 298K): δ 7.49 (d, ⁴J = 1.7 Hz, m-Ar^H, 2H), 7.33 (t, ³J = 7.6 Hz, 2H, Dipp p-Ar^H), 7.21 (d, ³J = 7.6 Hz, 4H, Dipp, m-Ar^H), 7.11 (t, ⁴J = 1.7 Hz, 1H, i-Ar^H), 2.94 (sept, ³J = 6.9 Hz, 4H, -CH(CH₃)₂), 1.16 (mult, 24 H, -CH(CH₃)₂), 0.21 (s, 9H, -Si(CH₃)₃).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298K) δ 146.97, 140.39, 140.18, 140.07, 133.05, 131.85, 122.97, 30.89, 24.44, 24.41, -1.10.

NMR Scale Comproportionation Reactions:

1 + 3 to 2: Solid **1** (5.0 mg, 6.1 μmol) was added to a solution of **3** (3.0 mg, 3.0 μmol) in ca. 0.5 mL C₆D₆ resulting in a color change from dark green to yellow.

1 + 3 to 4 A mixture of solid **1** (2.1 mg, 2.5 μmol) and **3** (2.6 mg, 2.6 μmol) were dissolved in ca. 0.5 mL C₆D₆. The resulting spectrum showed **4**, excess **3**, and Et₂O.

2 + 3 to 4 A mixture of solid **2** (3.1 mg, 2.5 μmol) and **3** (2.6 mg, 2.6 μmol) were dissolved in ca. 0.5 mL C₆D₆. The resulting spectrum showed **4** and excess **3**.

NMR Spectra

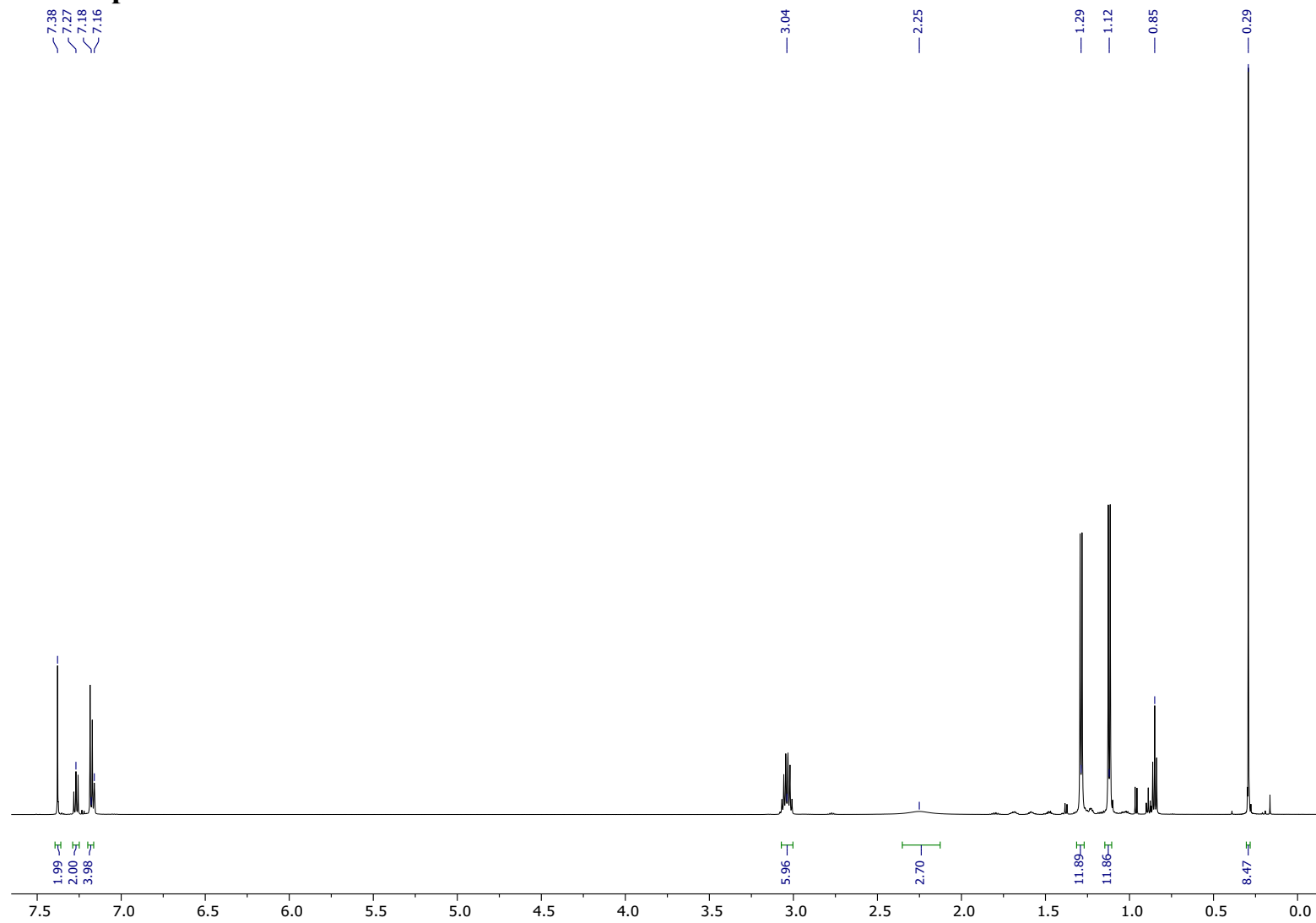


Figure S1. ^1H NMR (600 MHz, C_6D_6 , 298 K) spectrum of $[\text{LiAlH}_3\text{Ar}^{\text{iPr}_4-4}\text{-SiMe}_3]$.

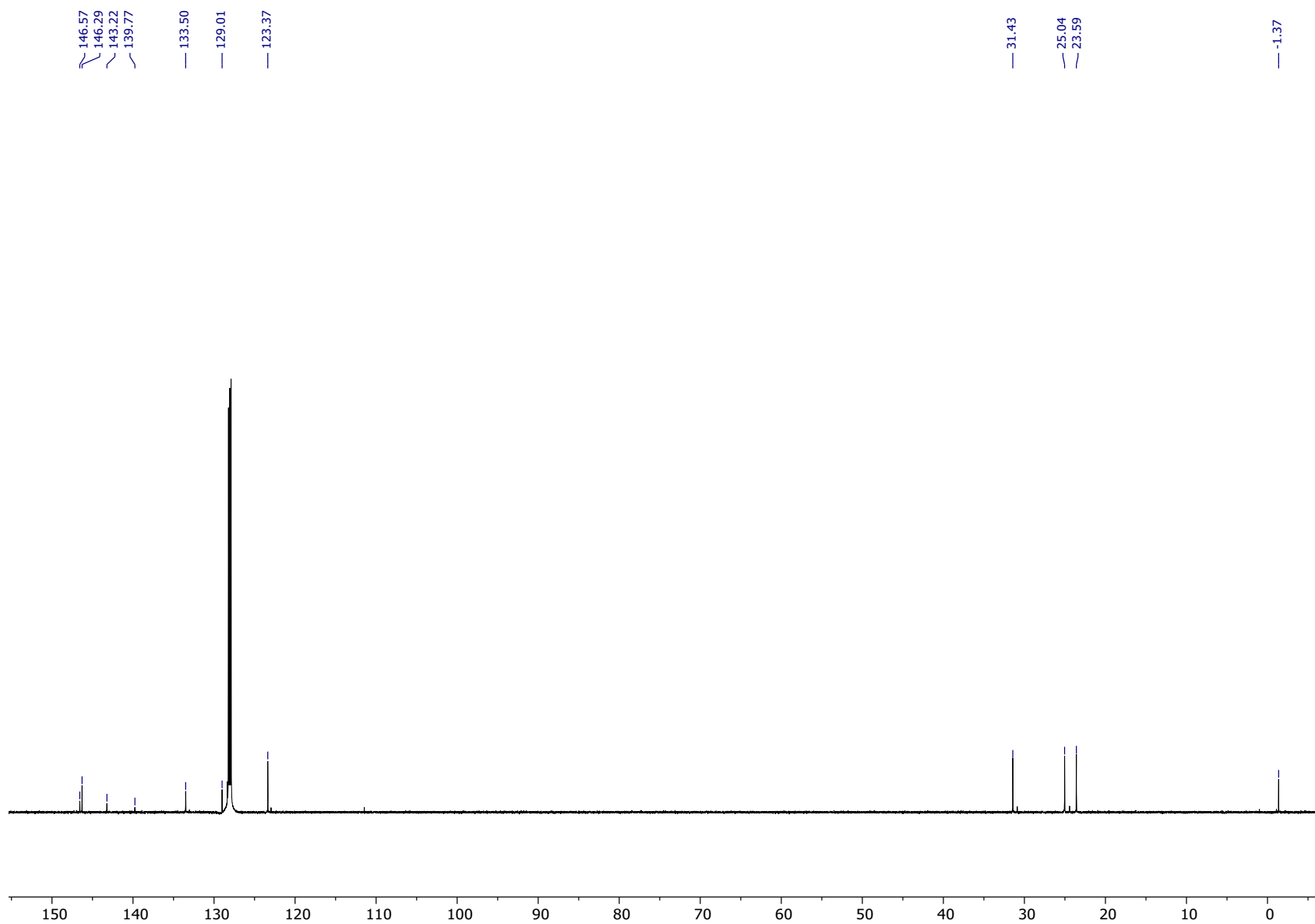


Figure S2. ^1H NMR (600 MHz, C_6D_6 , 298 K) spectrum of $[\text{LiAlH}_3\text{Ar}^{\text{iPr}_4-4}\text{-SiMe}_3]$.

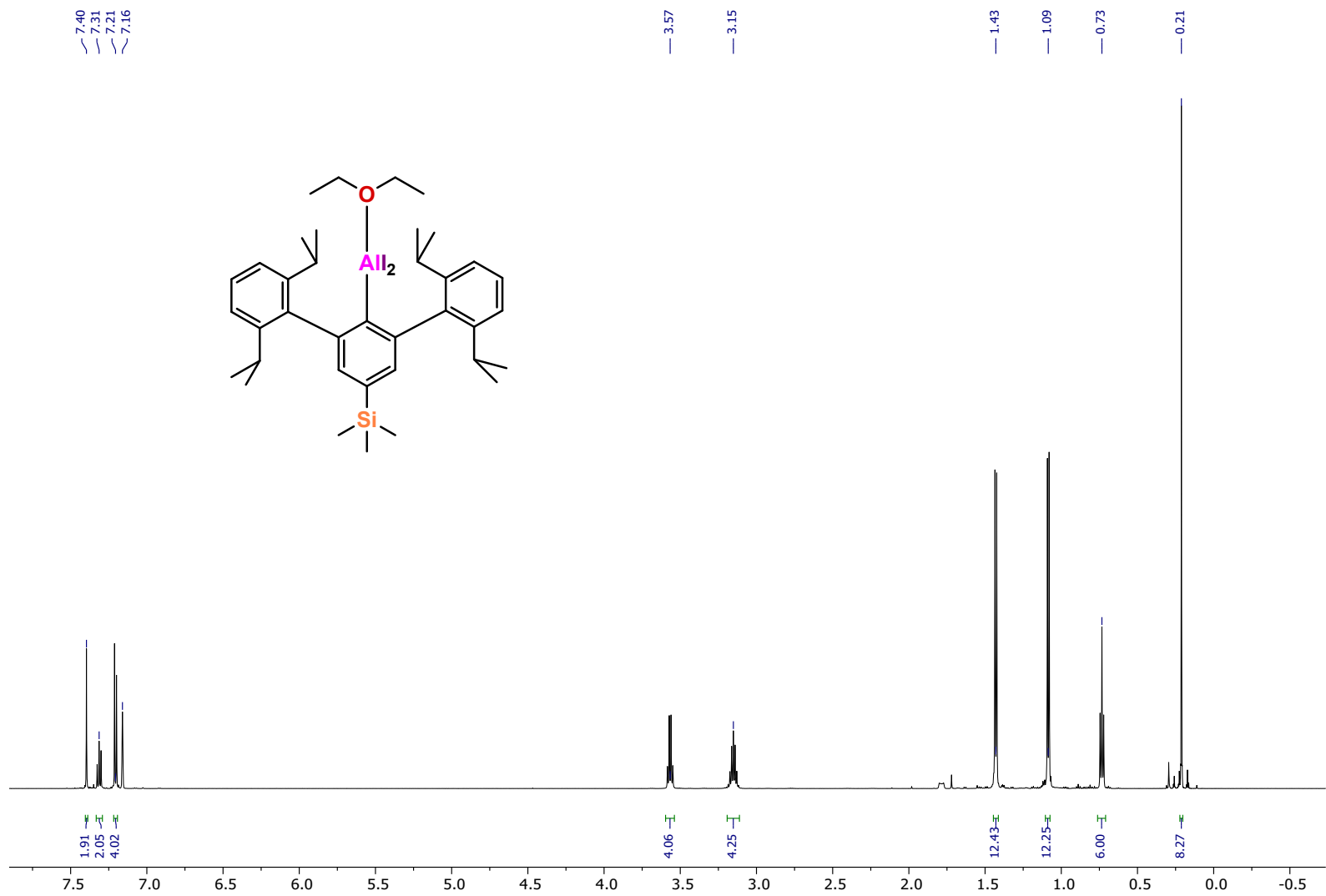


Figure S3. ^1H NMR (600 MHz, C_6D_6 , 298 K) spectrum of $\text{Al}(\text{Et}_2\text{O})_2(4\text{-SiMe}_3\text{-Ar}^{\text{iPr}_4})$ (**1**).

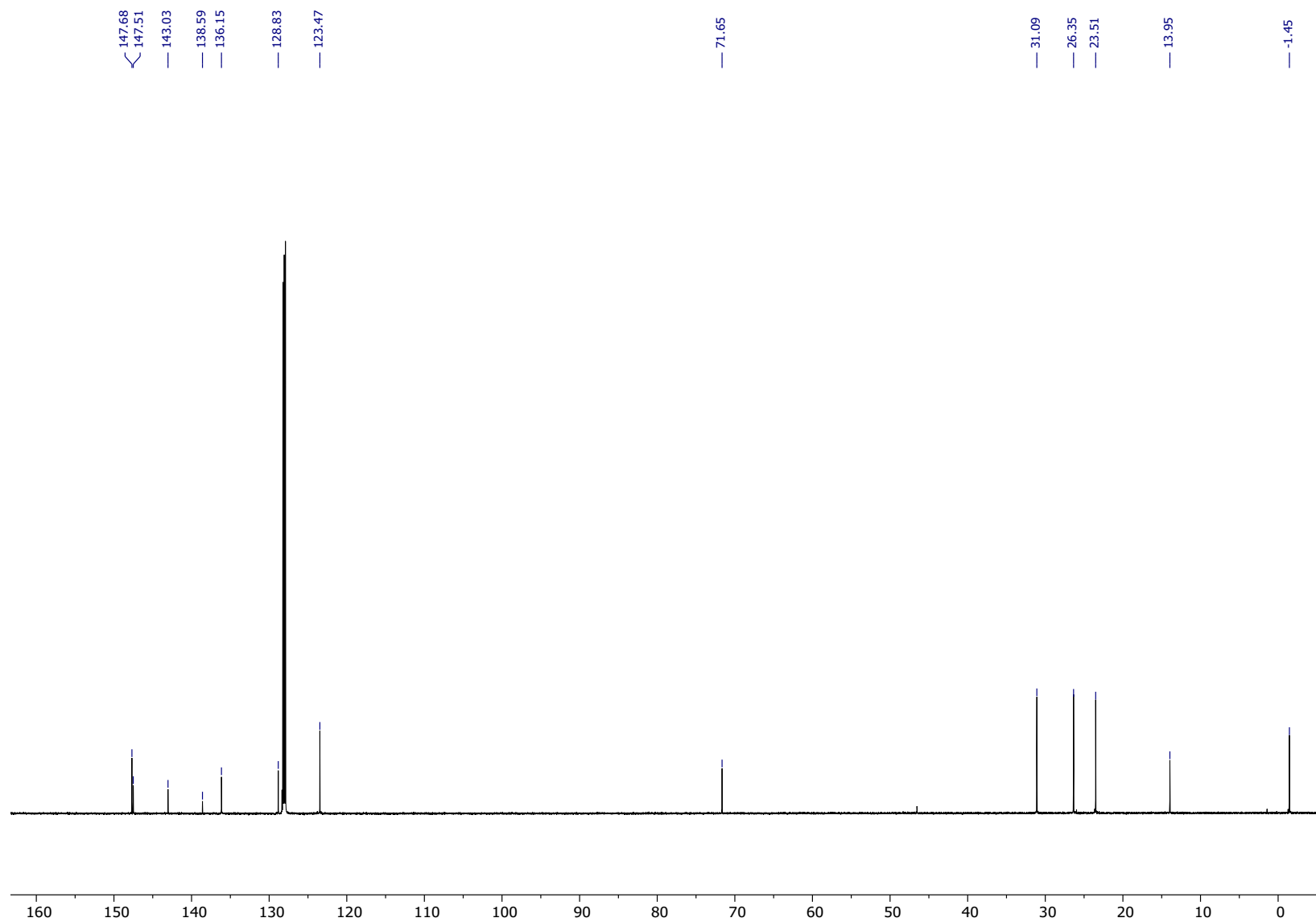


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) spectrum $\text{Al}(\text{Et}_2\text{O})_2(4\text{-SiMe}_3\text{-Ar}^{\text{iPr}_4})$ (**1**).

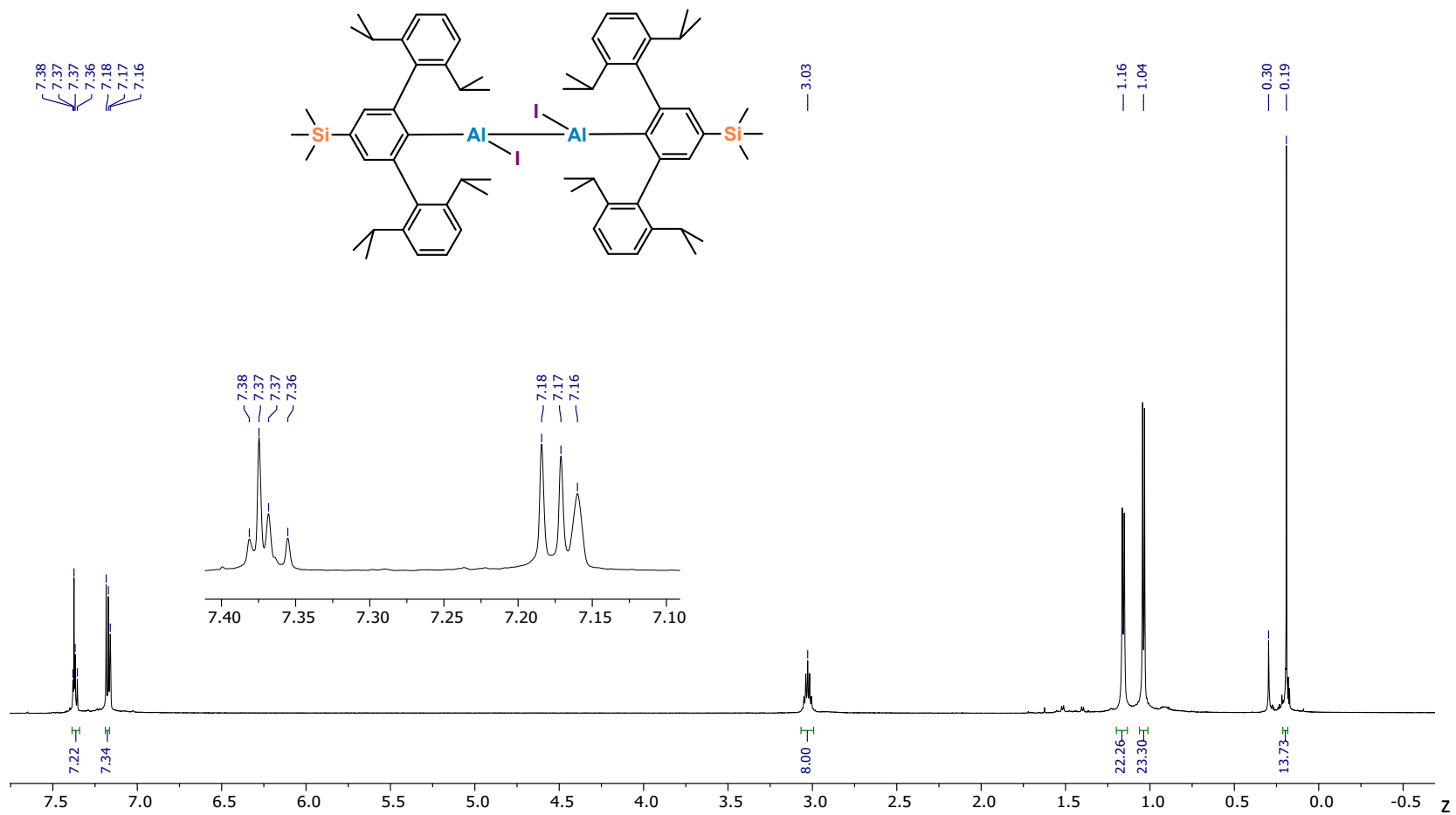


Figure S5. 1H NMR (600 MHz, C_6D_6 , 298 K) spectrum of $\{Al(I)Ar^{iPr_4-4-SiMe_3}\}_2$ (2).

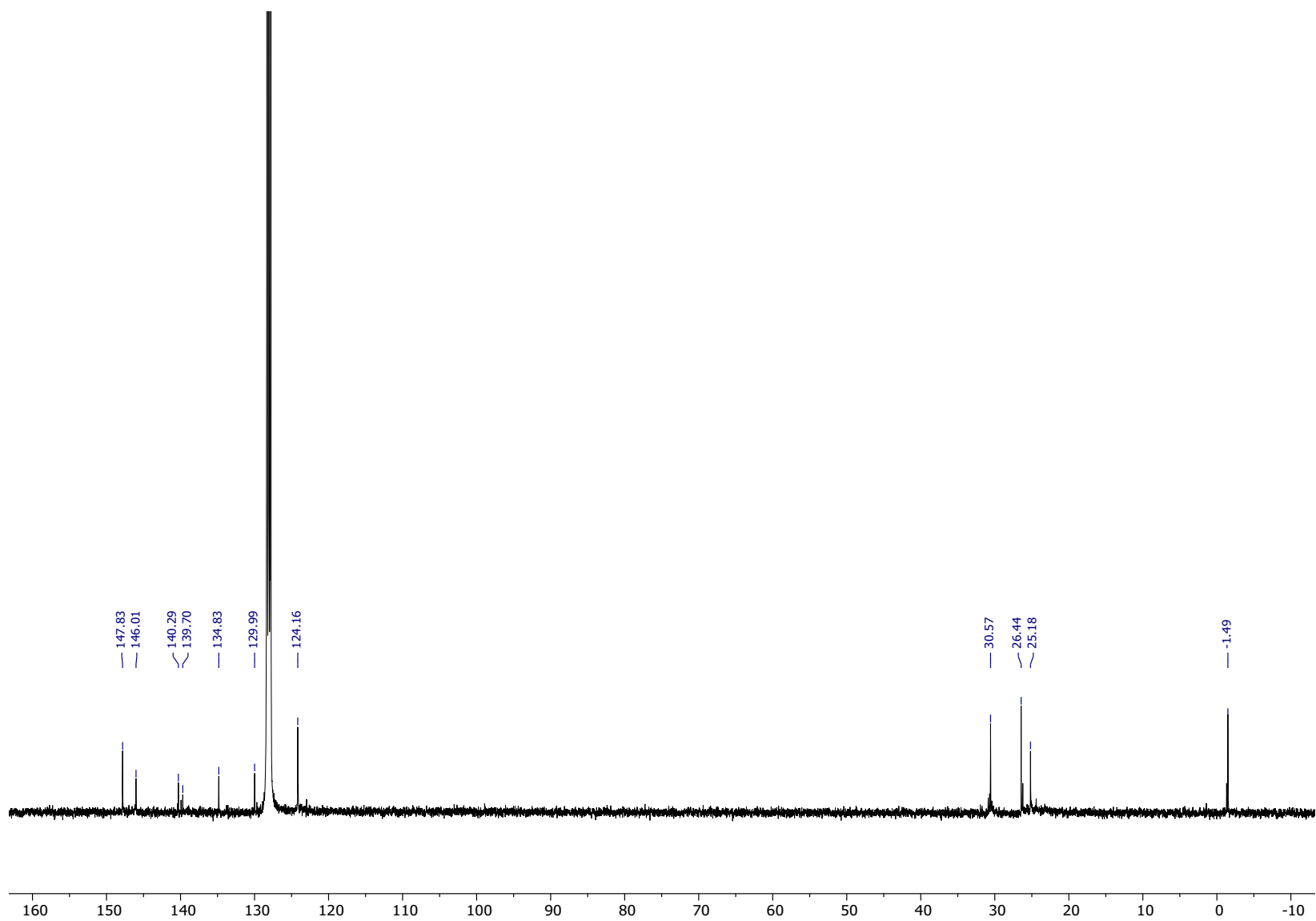


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K) spectrum of $\{\text{Al}(\text{I})\text{Ar}^{\text{iPr}^4}\text{-4-SiMe}_3\}_2$ (**2**).

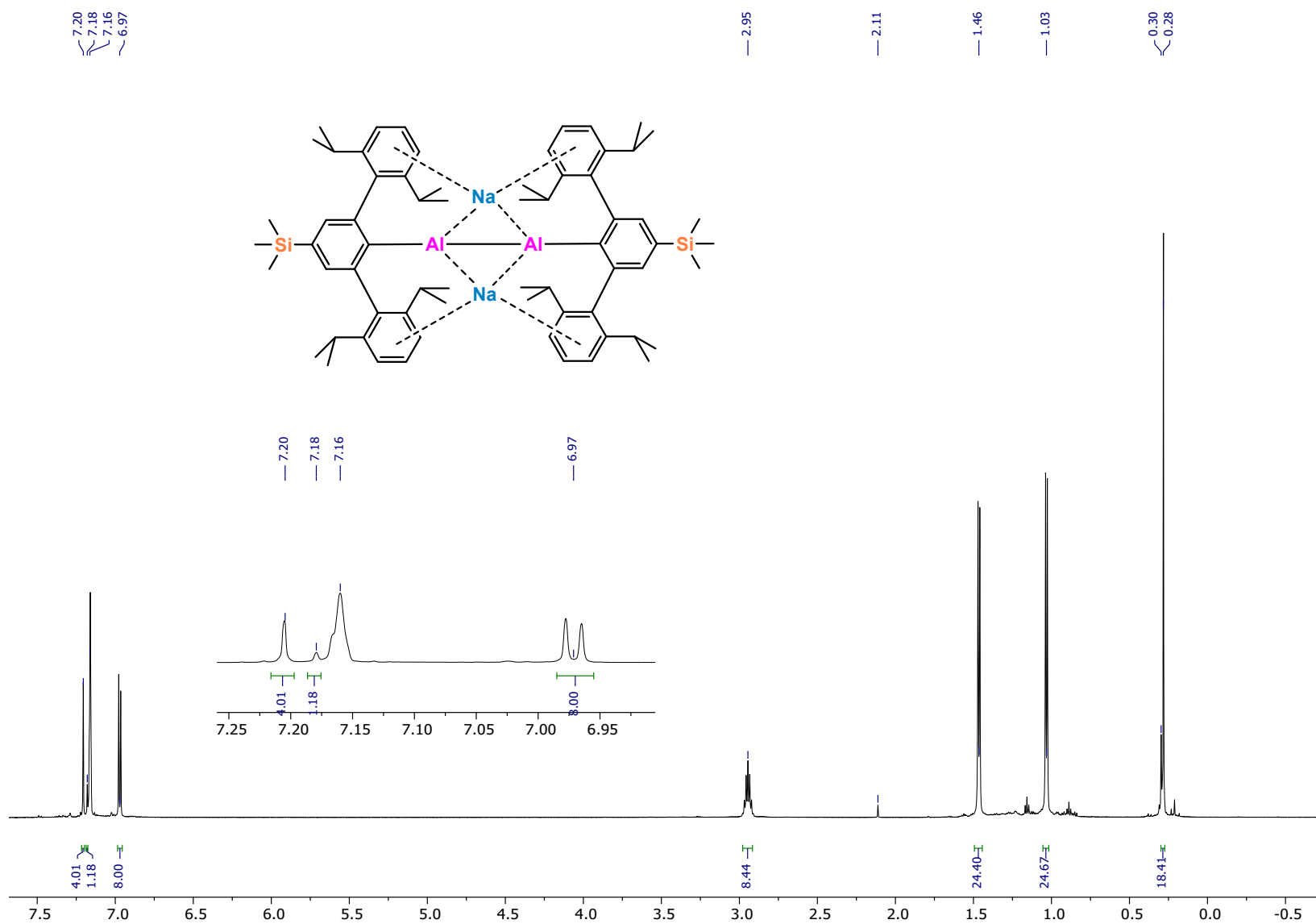


Figure S7. $^1\text{H NMR}$ (600 MHz, C_6D_6 , 298 K) spectrum of $\text{Na}_2(\text{AlAr}^{\text{iPr}_4}\text{-4-SiMe}_3)_2$ (**3**) The signal at 7.18 ppm corresponds to 25% of the 1:2:1 triplet overlapping with the benzene solvent signal.

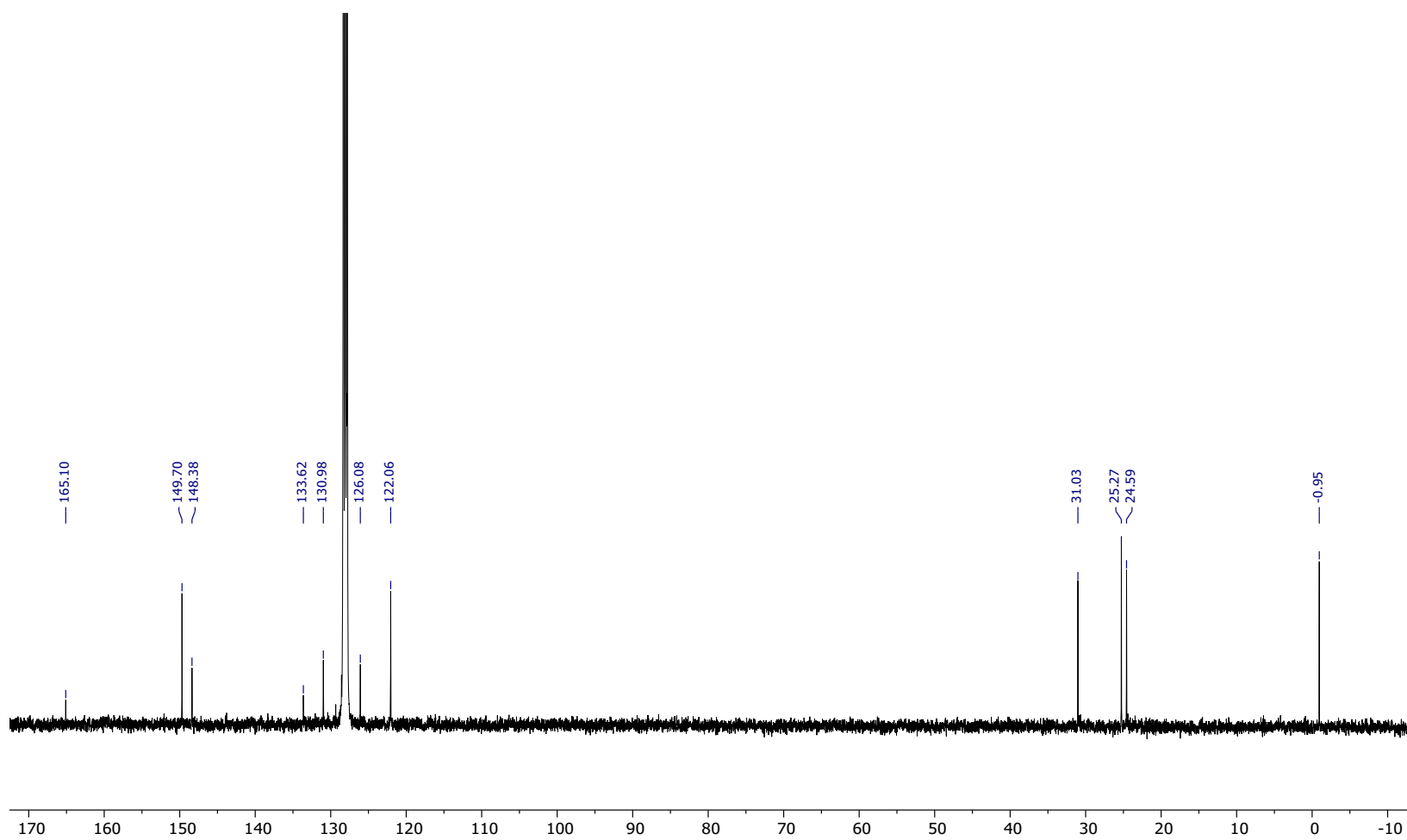


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K) spectrum of $\text{Na}_2(\text{AlAr}^{\text{iPr}4}\text{-4-SiMe}_3)_2$ (**3**).

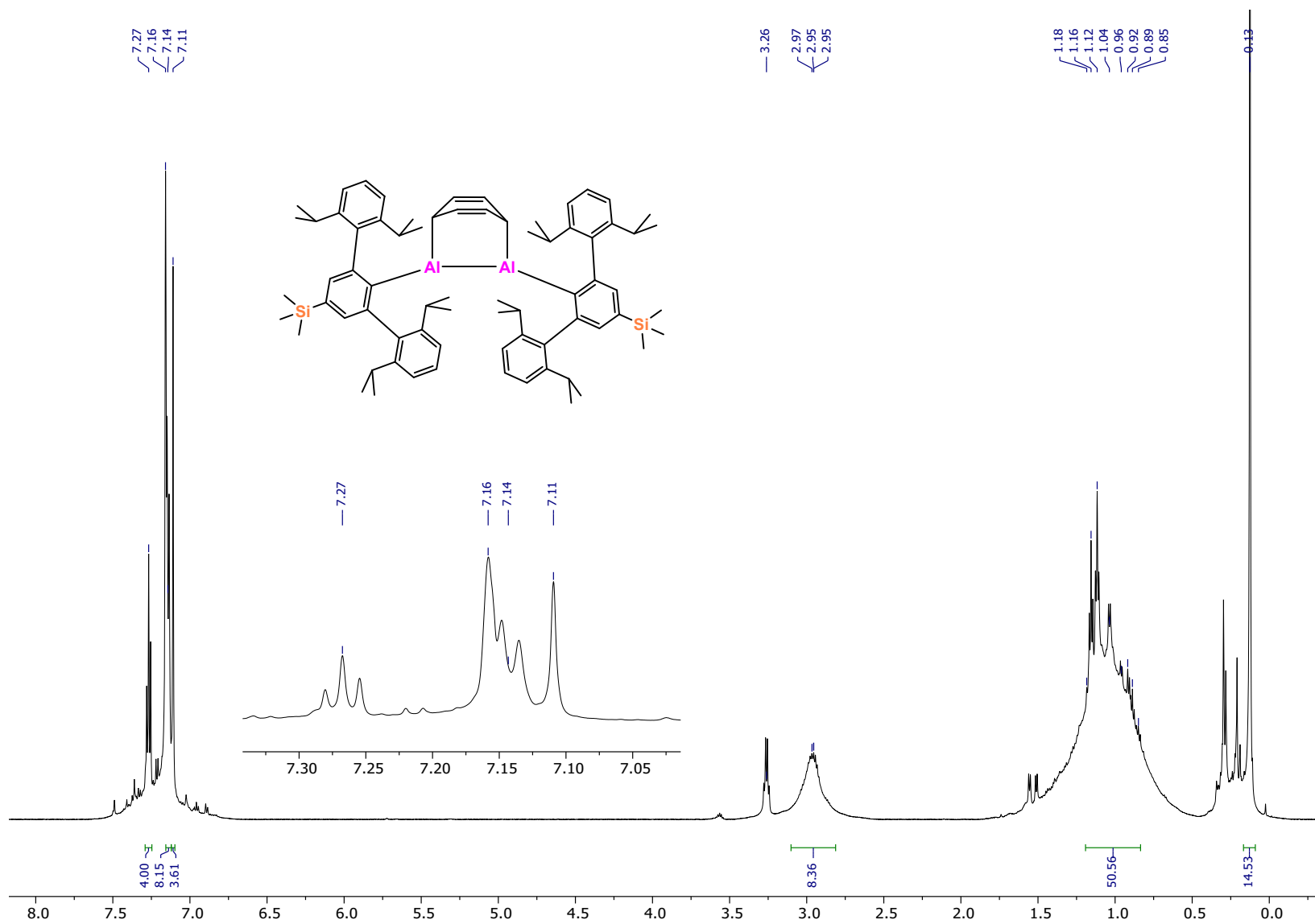


Figure S9. ¹H NMR (600 MHz, C₆D₆, 298 K) spectrum of the dialuminene-benzene cycloaddition product 4.

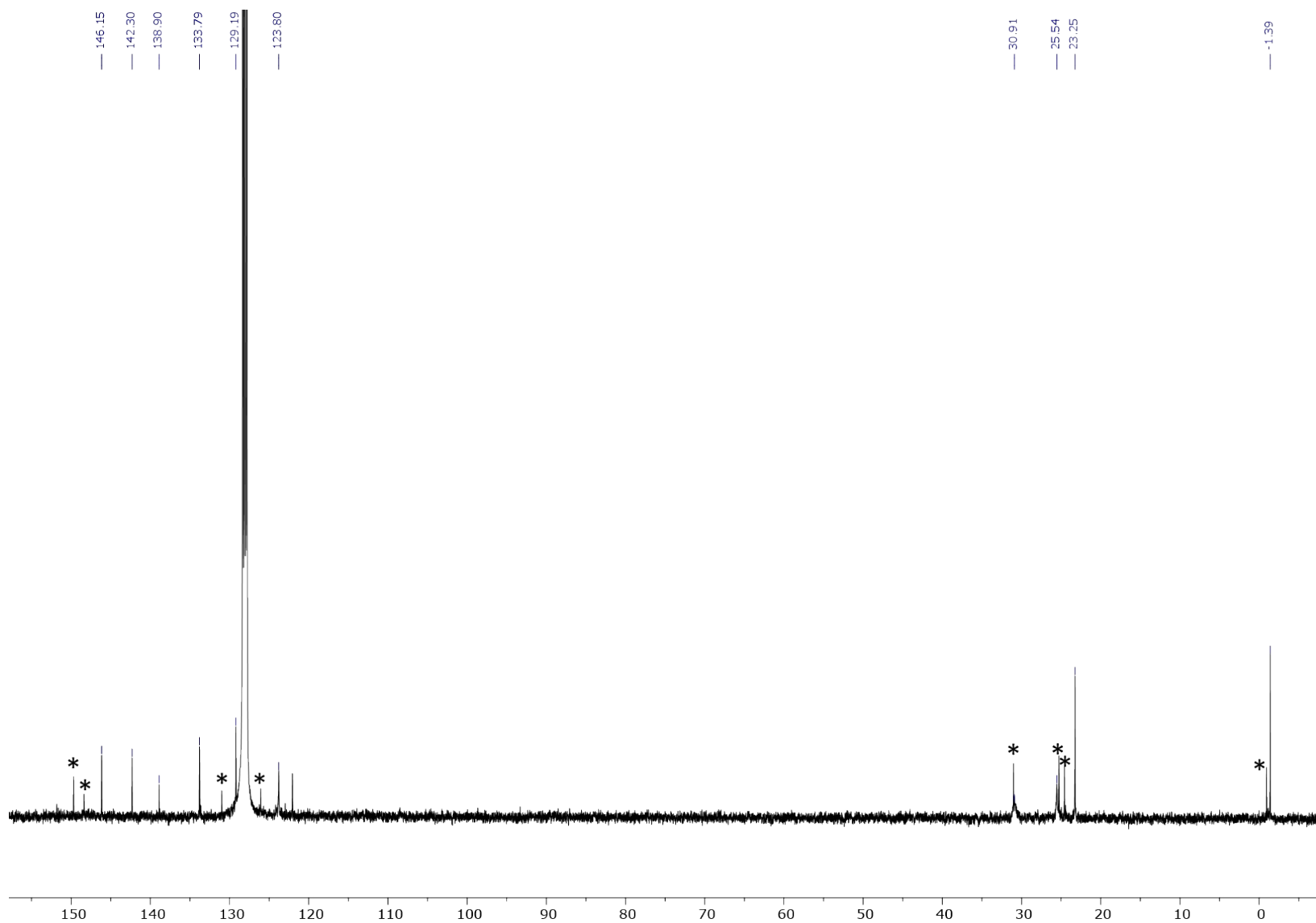


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K) of **4** generated by the reaction between **2** and **3**. Signals marked with * correspond to excess **3**.

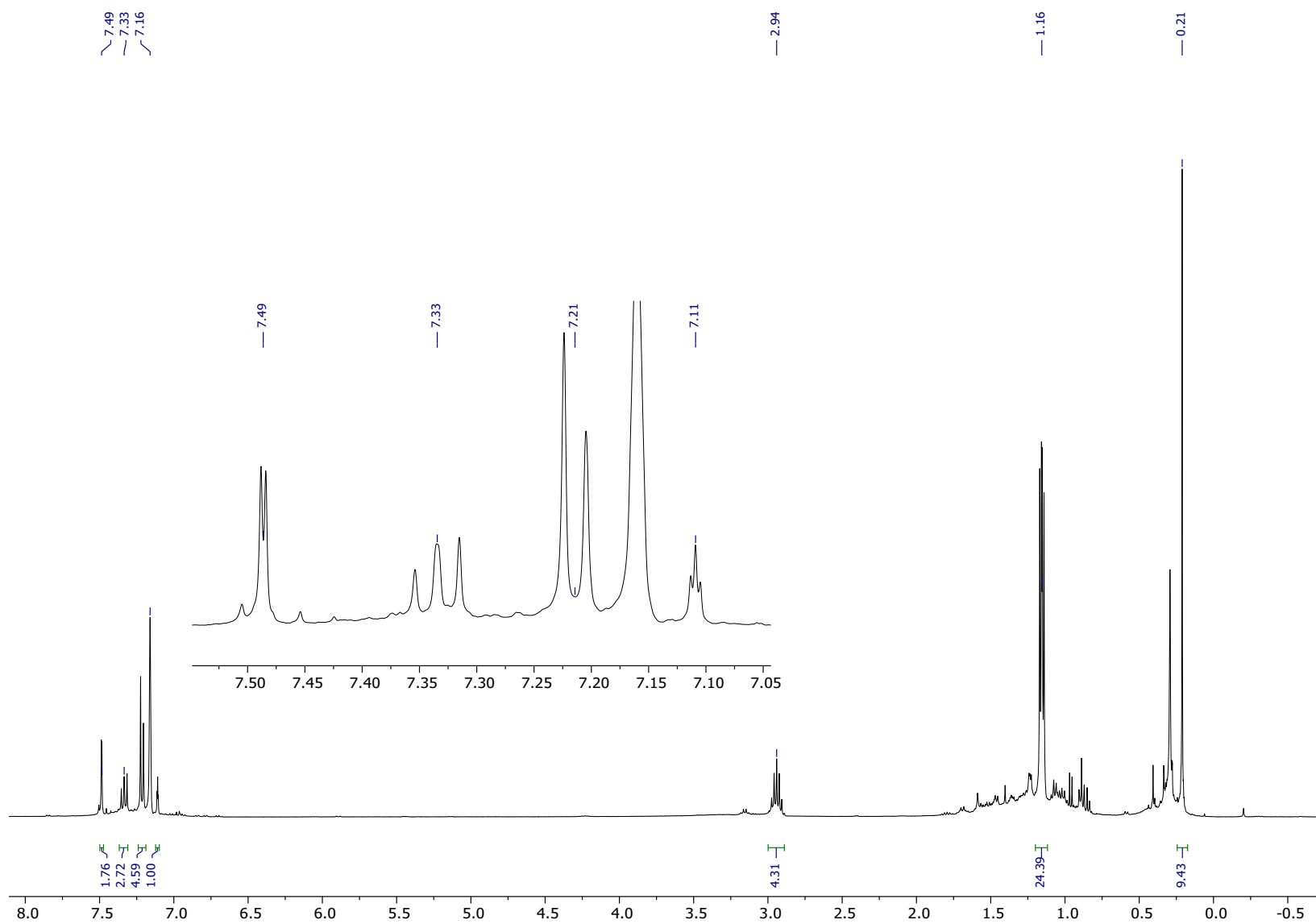


Figure S11 ^1H NMR (400 MHz, C_6D_6 , 298 K) spectrum of $4\text{-SiMe}_3\text{Ar}^{\text{iPr}_4\text{H}}$.

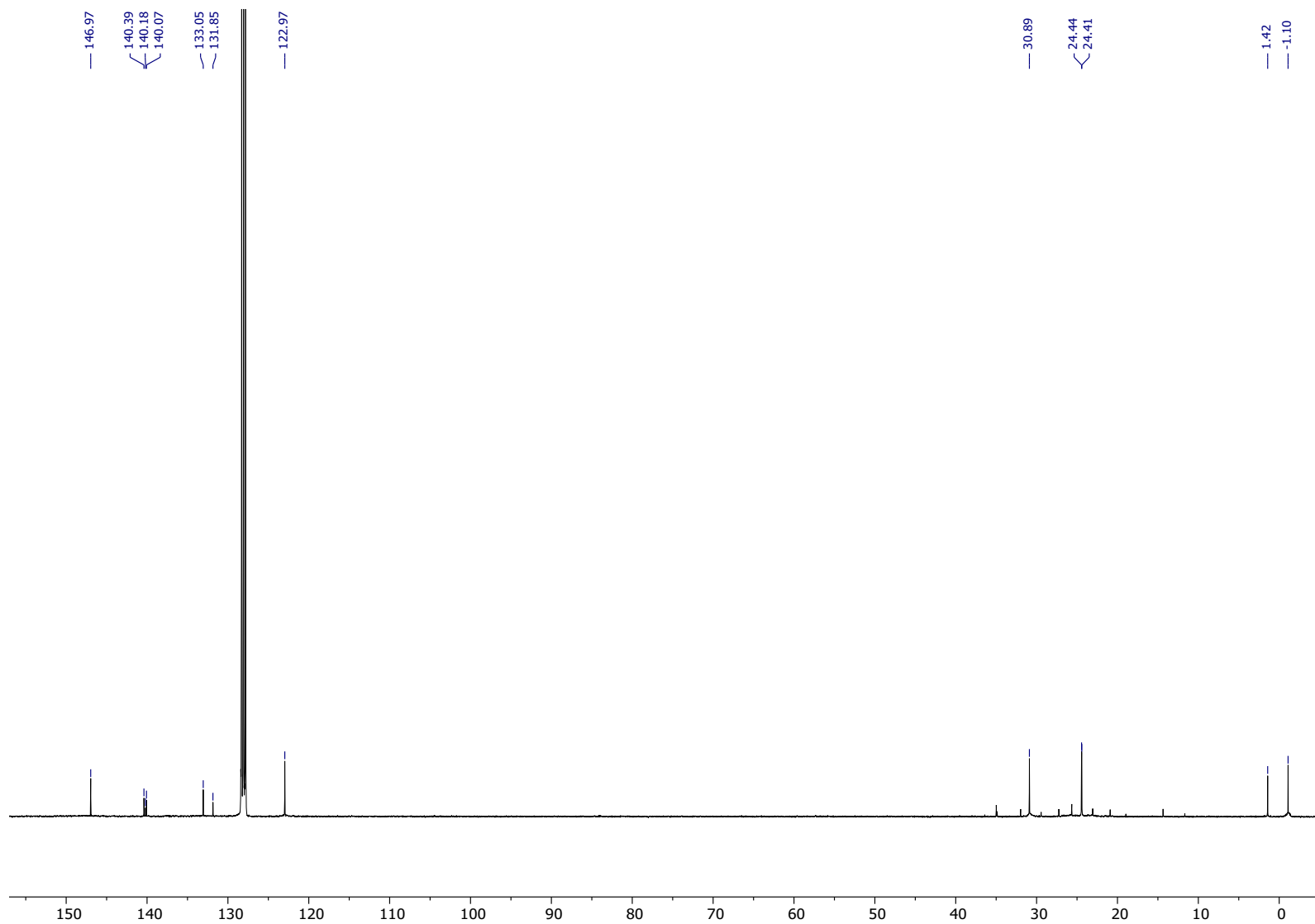


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K) spectrum of 4-SiMe₃Ar^{iPr}₄H.

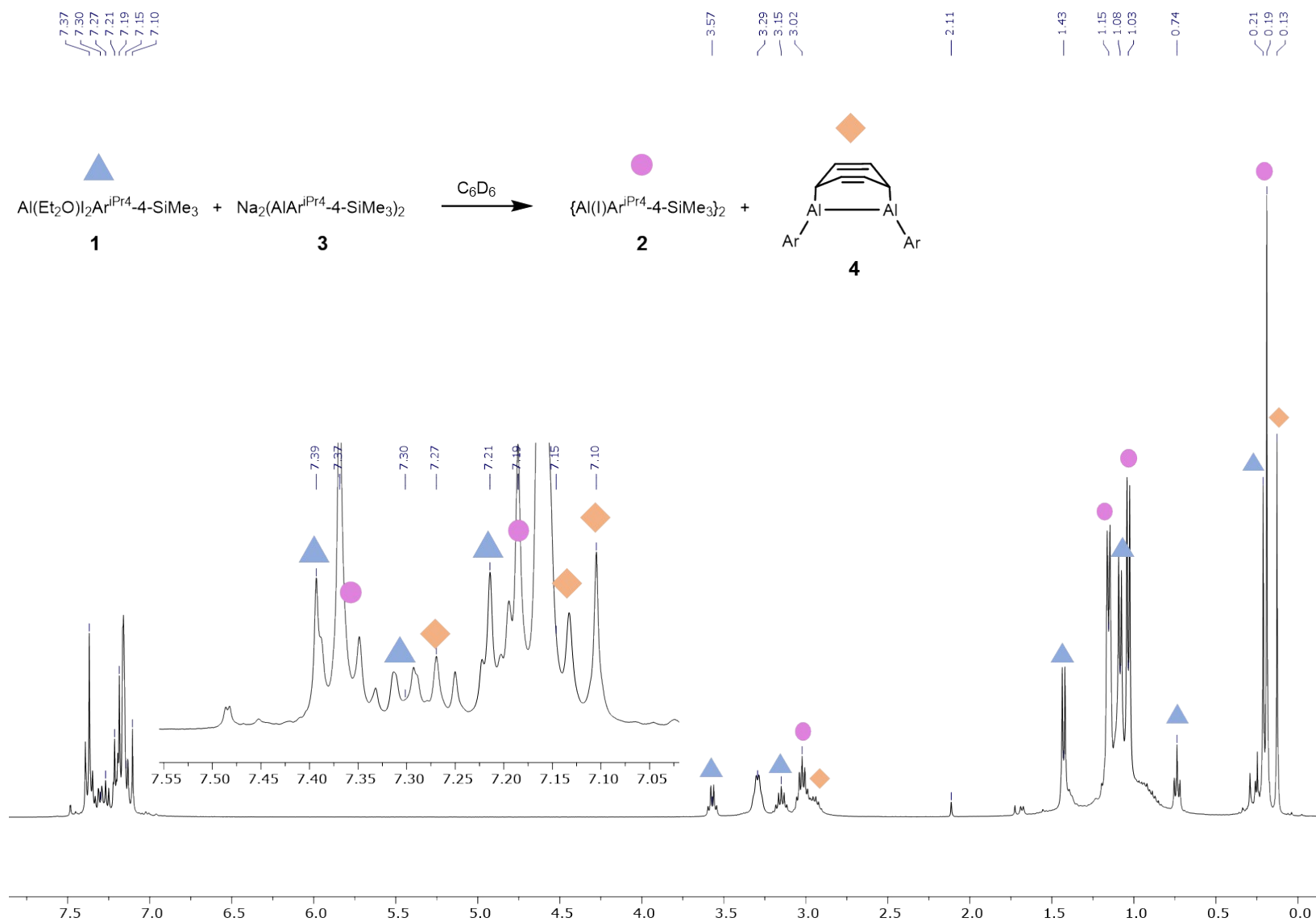


Figure S13. $^1\text{H NMR}$ spectrum of the comproportionation reaction between excess **1** (blue ▲) and **3** in C_6D_6 to give **2** (magenta ●) and **4** (orange ◆).

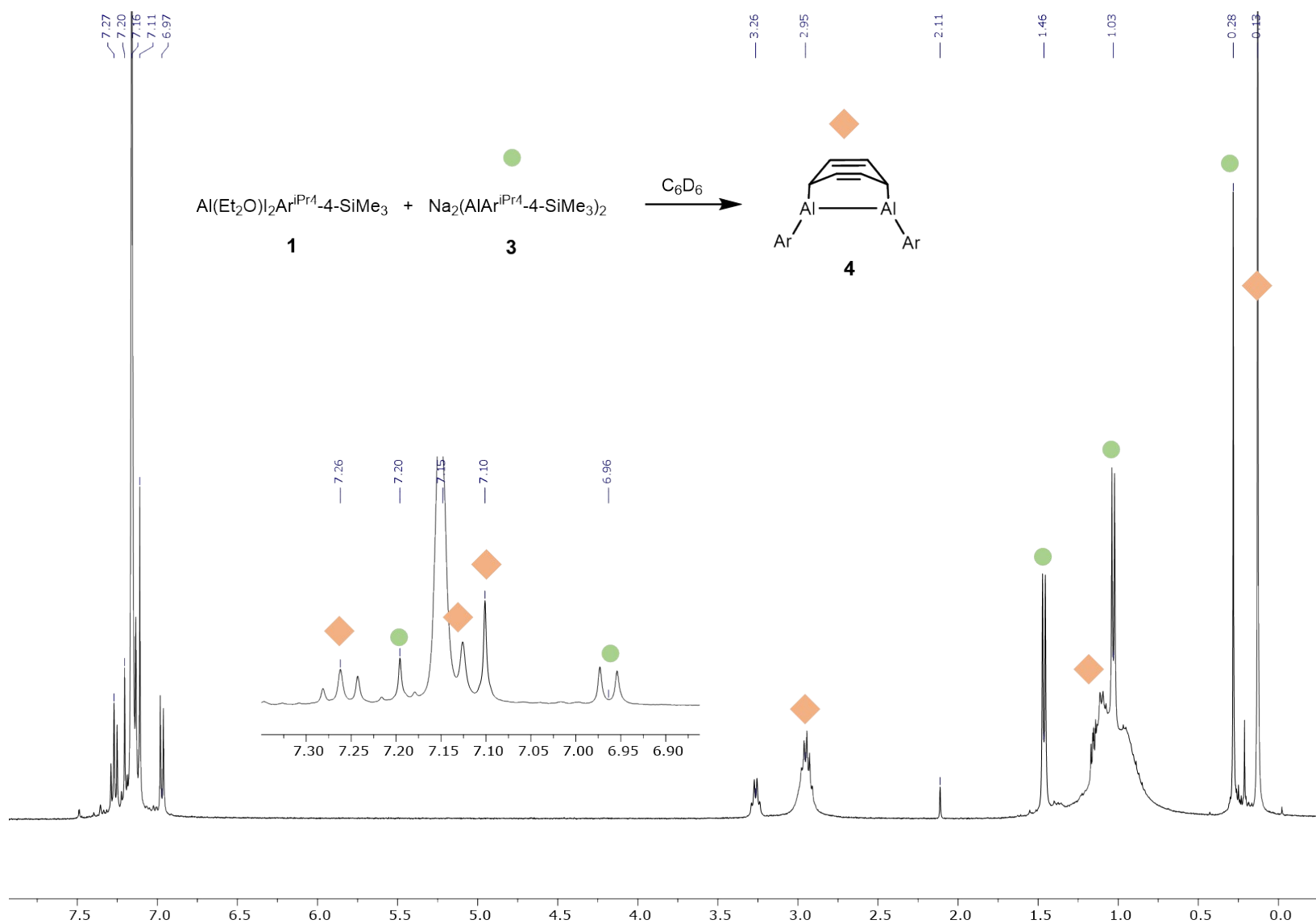


Figure S14. ^1H NMR spectrum of the comproportionation reaction **1** and excess **3** (green ●) in C_6D_6 to give **4** (orange ◆).

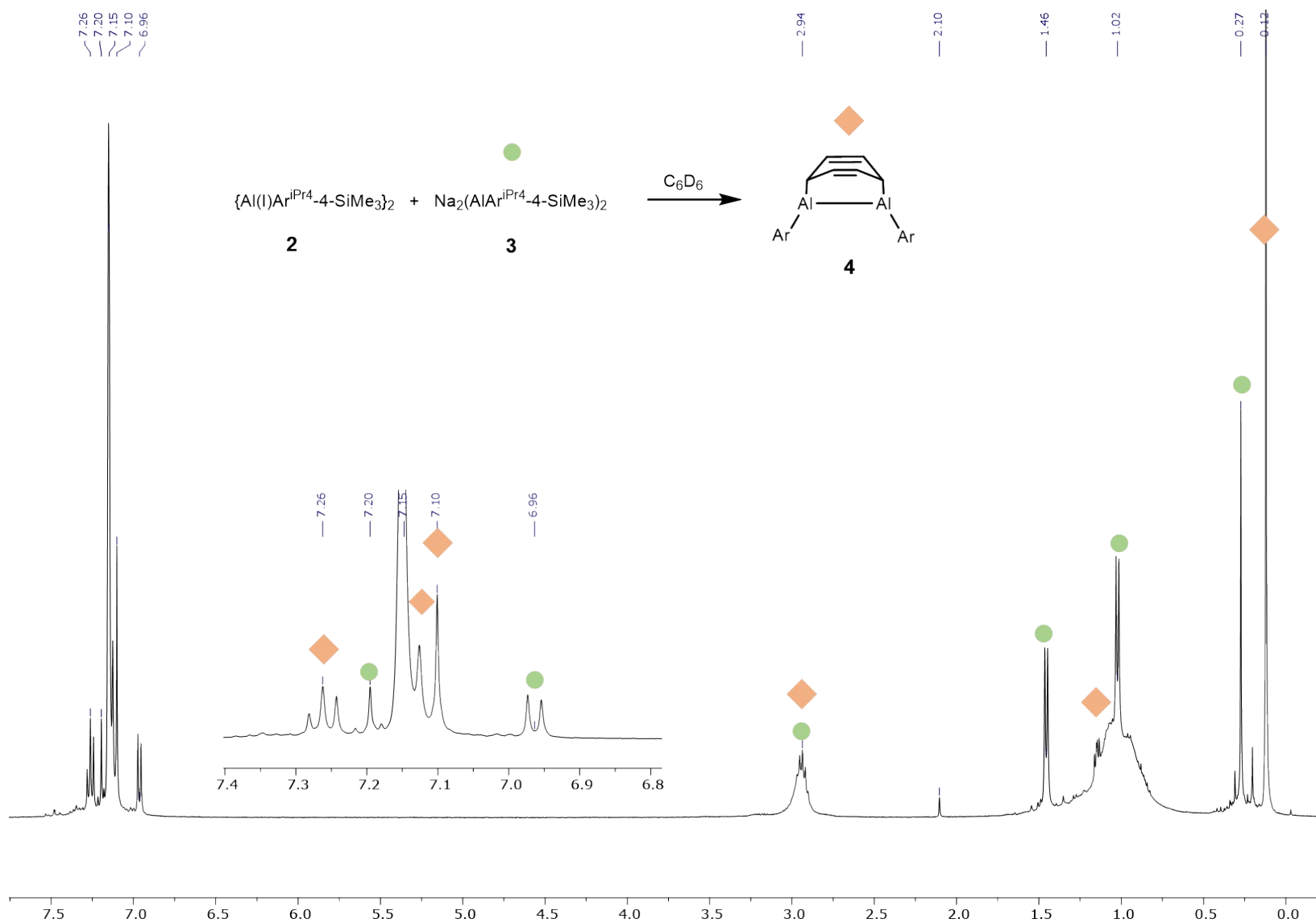


Figure S15. 1H NMR spectrum of the comproportionation reaction **2** and excess **3** (green ●) in C_6D_6 to give **4** (orange ◆).

UV-Visible Spectra

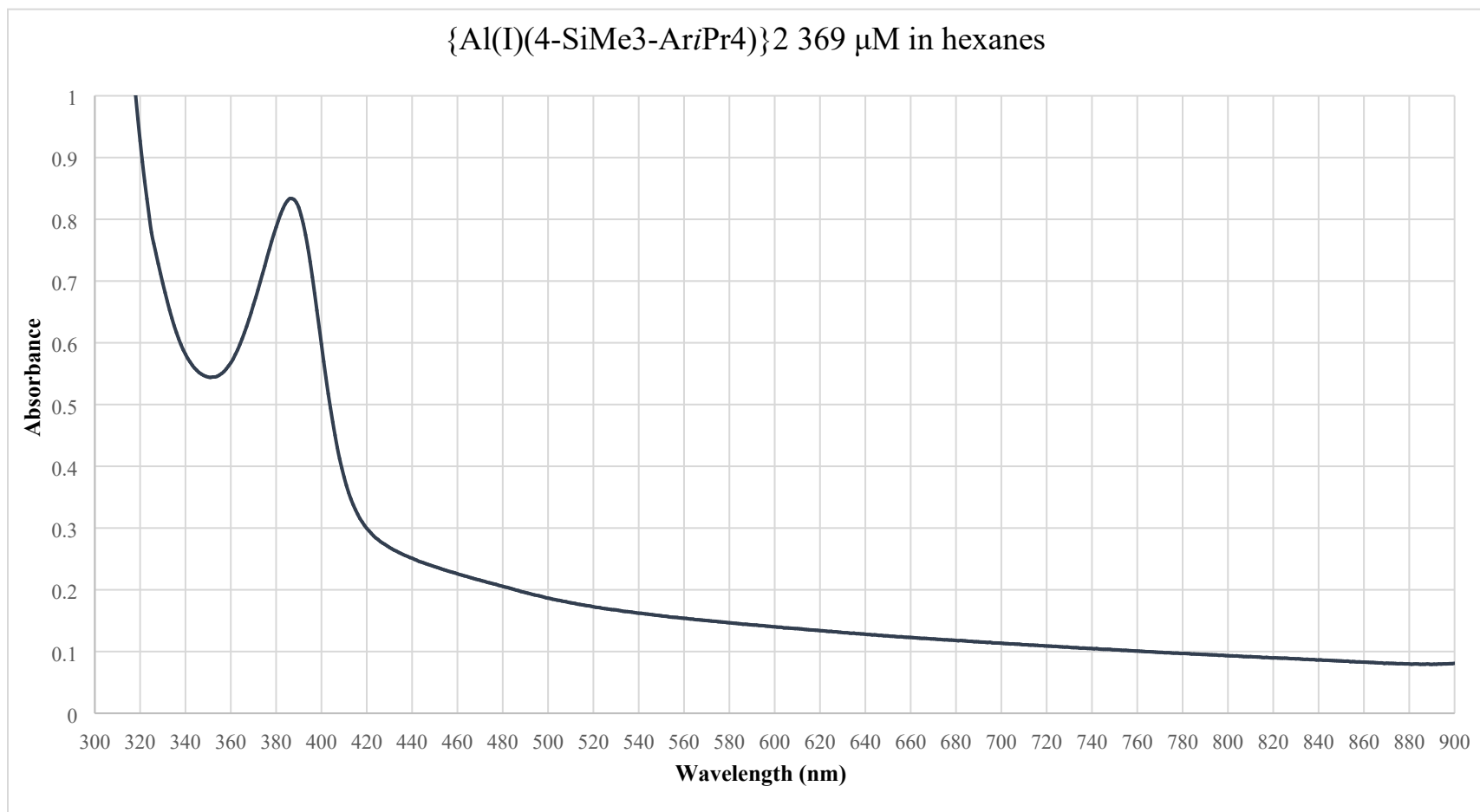


Figure S16. UV-Visible spectrum of **2** in hexanes.

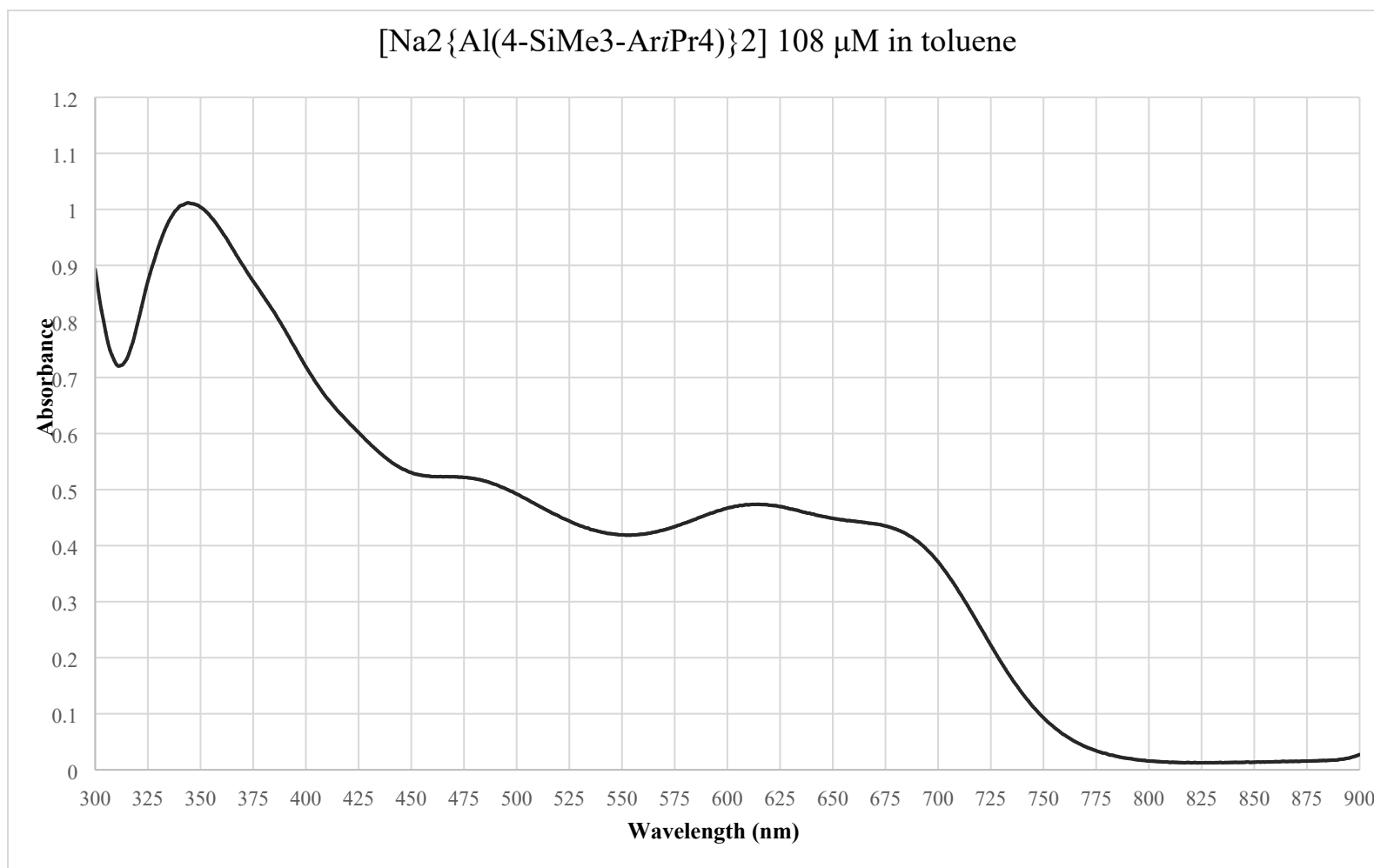


Figure S17. UV-Visible spectrum of **3** in toluene

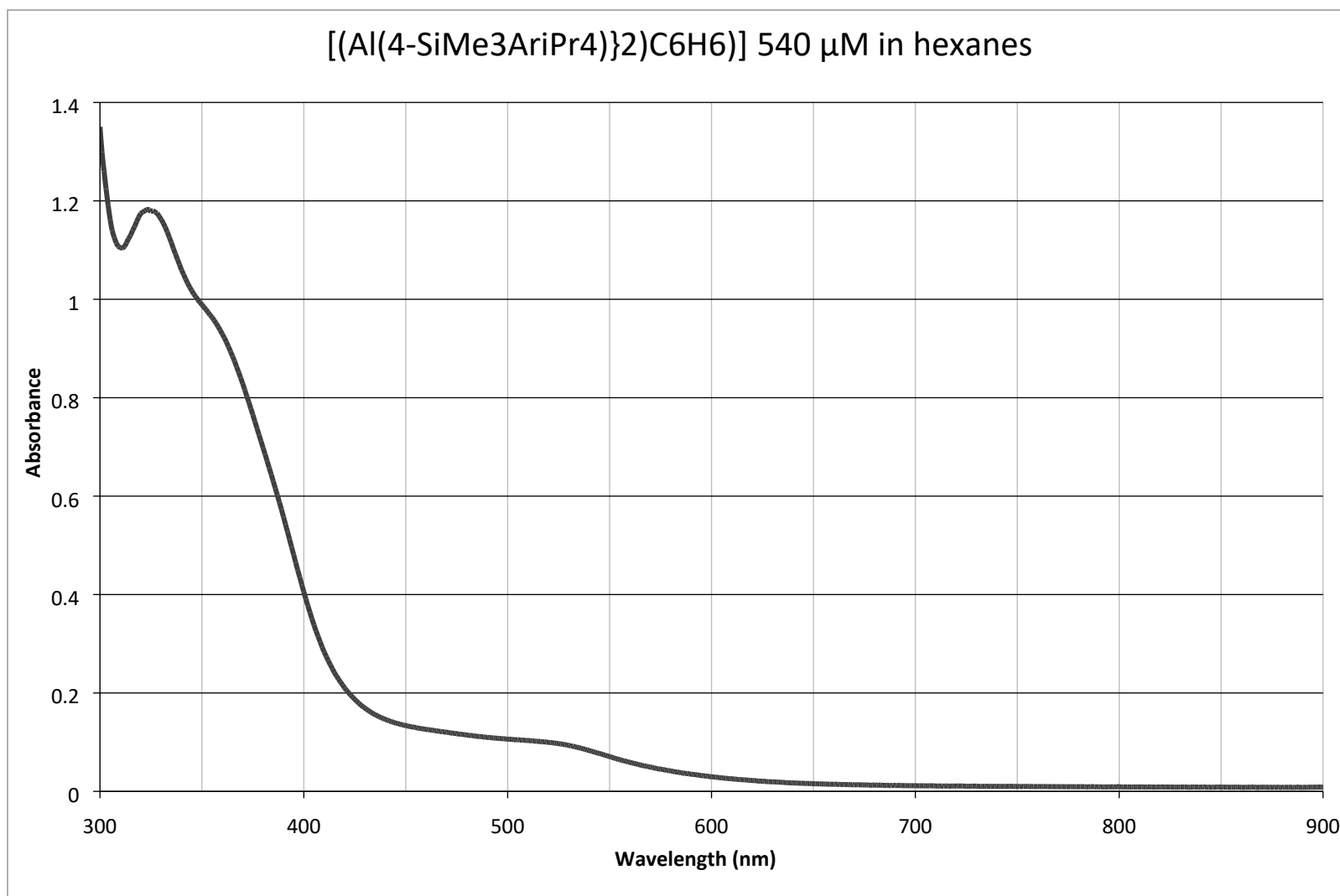


Figure S18. UV-Visible spectrum of **4** in hexanes.

X-Ray Crystallography

Crystals of **1-4** were removed from a Schlenk flask under a stream of argon and immediately covered with hydrocarbon oil. A suitable crystal was selected, attached to a MiTeGen microloop, and mounted on the goniometer of the diffractometer under a cold stream of N₂. Data were collected at 90 K on a Bruker Duo APEXII CCD diffractometer (**1, 2, 3**) or 100 K on a Bruker D8 VENTURE diffractometer (**4**) with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) (**1, 3, 4**) or Cu K α radiation $\lambda = 1.54178$ (**2**). Data were integrated with SAINT⁵ and an absorption correction (multi-scan) was applied using SADABS⁶. The structures were solved using SHELXTL program package⁷ by intrinsic phasing methods using SHELXT⁸ and were refined by full matrix least-squares procedures using SHELXL.⁹ All non-H atoms were refined anisotropically.

Table S1. X-ray crystallographic data for **1**.

| | |
|--------------------------------------|---|
| Empirical formula | C ₃₇ H ₅₅ OAlSi ₂ |
| Formula weight | 824.68 |
| Temperature/K | 90.15 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /c |
| a/Å | 10.998(2) |
| b/Å | 13.500(3) |
| c/Å | 26.336(5) |
| α/° | 90 |
| β/° | 97.410(3) |
| γ/° | 90 |
| Volume/Å ³ | 3877.6(13) |
| Z | 4 |
| ρ _{calc} /g/cm ³ | 1.413 |
| μ/mm ⁻¹ | 1.701 |
| F(000) | 1672.0 |
| Crystal size/mm ³ | 0.163 × 0.111 × 0.076 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 3.118 to 54.932 |
| Index ranges | -14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -34 ≤ l ≤ 34 |
| Reflections collected | 34107 |
| Independent reflections | 8898 [R _{int} = 0.0287, R _{sigma} = 0.0221] |
| Data/restraints/parameters | 8898/0/392 |
| Goodness-of-fit on F ² | 1.058 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0238, wR ₂ = 0.0566 |
| Final R indexes [all data] | R ₁ = 0.0289, wR ₂ = 0.0596 |

Table S2. X-ray crystallographic data for **2**.

| | |
|------------------------------------|---|
| Empirical formula | C ₄₀ H ₅₃ AlISi |
| Formula weight | 715.79 |
| Temperature/K | 90.15 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /n |
| a/Å | 17.4939(8) |
| b/Å | 12.7921(7) |
| c/Å | 18.3769(9) |
| α/° | 90 |
| β/° | 109.048(2) |
| γ/° | 90 |
| Volume/Å ³ | 3887.3(3) |
| Z | 4 |
| ρ _{calc} /cm ³ | 1.223 |
| μ/mm ⁻¹ | 7.154 |
| F(000) | 1492.0 |
| Crystal size/mm ³ | 0.209 × 0.155 × 0.121 |
| Radiation | CuKα (λ = 1.54178) |
| 2θ range for data collection/° | 6.058 to 144.582 |
| Index ranges | -17 ≤ h ≤ 21, -15 ≤ k ≤ 15, -22 ≤ l ≤ 20 |
| Reflections collected | 15859 |
| Independent reflections | 7423 [R _{int} = 0.0265, R _{sigma} = 0.0341] |
| Data/restraints/parameters | 7423/20/464 |
| Goodness-of-fit on F ² | 1.012 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0554, wR ₂ = 0.1441 |
| Final R indexes [all data] | R ₁ = 0.0583, wR ₂ = 0.1464 |

Table S3. X-ray crystallographic data for **3**.

| | |
|------------------------------------|--|
| Empirical formula | C _{43.5} H ₅₇ AlNaSi |
| Formula weight | 657.95 |
| Temperature/K | 90.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.4744(10) |
| b/Å | 17.7494(15) |
| c/Å | 21.1607(18) |
| α/° | 98.4810(10) |
| β/° | 90.4220(10) |
| γ/° | 106.9270(10) |
| Volume/Å ³ | 4072.1(6) |
| Z | 4 |
| ρ _{calc} /cm ³ | 1.073 |
| μ/mm ⁻¹ | 0.117 |
| F(000) | 1424.0 |
| Crystal size/mm ³ | 0.629 × 0.326 × 0.282 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 3.342 to 54.982 |
| Index ranges | -14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -27 ≤ l ≤ 27 |
| Reflections collected | 37051 |
| Independent reflections | 18661 [R _{int} = 0.0203, R _{sigma} = 0.0303] |
| Data/restraints/parameters | 18661/34/982 |
| Goodness-of-fit on F ² | 1.020 |
| Final R indexes [I >= 2σ (I)] | R ₁ = 0.0496, wR ₂ = 0.1363 |
| Final R indexes [all data] | R ₁ = 0.0632, wR ₂ = 0.1480 |

Table S4. X-ray crystallographic data for **4**.

| | |
|------------------------------------|--|
| Empirical formula | C ₈₁ H ₁₀₅ Al ₂ Si ₂ |
| Formula weight | 1188.78 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /n |
| a/Å | 11.3894(11) |
| b/Å | 19.669(2) |
| c/Å | 32.660(6) |
| α/° | 90 |
| β/° | 91.426(6) |
| γ/° | 90 |
| Volume/Å ³ | 7314.1(16) |
| Z | 4 |
| ρ _{calc} /cm ³ | 1.080 |
| μ/mm ⁻¹ | 0.113 |
| F(000) | 2580.0 |
| Crystal size/mm ³ | 0.244 × 0.196 × 0.18 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 2.418 to 52.844 |
| Index ranges | -12 ≤ h ≤ 14, -24 ≤ k ≤ 24, -40 ≤ l ≤ 39 |
| Reflections collected | 43076 |
| Independent reflections | 14960 [R _{int} = 0.0330, R _{sigma} = 0.0307] |
| Data/restraints/parameters | 14960/0/789 |
| Goodness-of-fit on F ² | 1.044 |
| Final R indexes [I >= 2σ (I)] | R ₁ = 0.0443, wR ₂ = 0.1137 |
| Final R indexes [all data] | R ₁ = 0.0471, wR ₂ = 0.1157 |

Photos of Compounds



Figure S19. An ice-cold solution of **1** and **3** in Et₂O turns dark purple before rapidly fading to colorless.



Figure S20. A pale yellow crystal of **2** mounted on a goniometer.

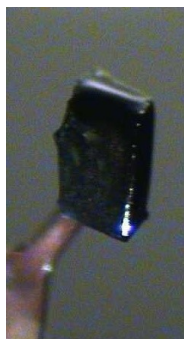


Figure S21. A dark green crystal of **3** mounted on a goniometer.

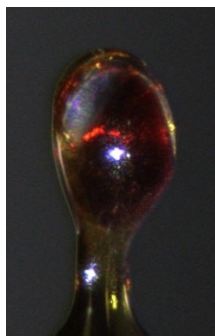


Figure S22. A red crystal of **4** mounted on a goniometer.

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