# Controlled hydrolysis of $AlMe_3$ to tetramethylalumoxane and a new look at incipient adducts with water

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## 1. Experimental methods.

**General remarks.** Unless otherwise stated, all reactions involving air- and moisture-sensitive organometallic compounds were conducted under an argon atmosphere using standard Schlenk techniques and glovebox techniques (MBraun UniLab Plus; < 0.1 ppm $O_2$, < 0.1 ppm $H_2O$). All glassware was stored in a 150°C oven overnight before use. All solvents were purified by passage through activated aluminium oxide (MBraun SPS) and stored over 4Å molecular sieves. Deuterated solvents were dried over Na/K, distilled under argon atmosphere prior to use and stored over molecular sieves. The spectra were referenced to residual signals of the deuterated solvents. All reagents were purchased from Sigma-Aldrich. NMR spectra were acquired on the Bruker 300 MHz, Varian 500 MHz and Varian Mercury 400 MHz (only $^{27}$Al spectra) spectrometers. Samples for variable-temperature and time-dependent NMR measurements were prepared *in situ* in NMR tubes sealed by a septum, and the reagents were added through the septum at -78°C. FT-IR spectra were acquired on a Bruker TENSOR II FTIR Spectrometer. Mass spectra were collected using Advion expression L CMS. Elemental analyses were performed using an UNICUBE (Elementar Analysensysteme GmbH).

**Synthesis of compound 3.** A starting compound $[AlMe_3(pyr)]_n$ (**1**) was prepared *in situ* by adding pyridine (5.5 mmol, 0.443 ml) to a solution of $AlMe_3$ in heptane (1 M, 5 ml) and 5 ml of THF at room temperature. Then, the vigorously stirred mixture was cooled to -78°C, and $H_2O$ (2.5 mmol, 45 µl) was carefully added by a gas-tight syringe. The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. Then, the solvent was removed in vacuo. The residue was dissolved in 3 ml of THF, layered by 7 ml of hexane and placed at -30°C for 48 hours, giving the product $[AlMe_2(pyr)(\mu_3\text{-}O)AlMe_2]_2$ (**3**) as colourless crystals (yield c.a. 75%). **Elemental analysis** (%) calc. for $C_9H_{17}NOAl_2$: C 51.67, H 8.19, N 6.70; found: C 51.81, H 8.02, N 6.83; **$^1$H NMR** (300 MHz, THF-$d_8$, 25°C), δ: -1.05 -(s, 6H, -OAl($C\underline{H}_3$)$_2$), -0.79 (s, 6H, -NAl($C\underline{H}_3$)$_2$), 7.61 (m, 2H, C<u>H</u>-*m*-py), 8.04 (tt, 1H, C<u>H</u>-*p*-py), 8.63 (dt, 2H, C<u>H</u>-*o*-py); **$^{13}$C NMR** (300 MHz, THF-$d_8$, 25°C), δ: -9.8 (OAl($\underline{C}H_3$)$_2$), -7.6 (-NAl($\underline{C}H_3$)$_2$), 126.0 (<u>C</u>H-*m*-py), 140.8 (<u>C</u>H-*p*-py), 148.7 (<u>C</u>H-*o*-py); **$^{27}$Al NMR** (400 MHz, THF-$d_8$, 25°C), δ: 148; **FTIR** (ATR) $\nu$/cm$^{-1}$: 2888(w), 1614(m), 1451(m), 1189(m), 1069(m), 1052(m), 779(s), 683(vs), 648(vs), 567(s), 433(m), **ESI-MS** (m/z): 419.2 $[M+H]^+$.

**Synthesis of compound 4.** A solution of $AlMe_3$ in heptane (1 M, 5 ml) was added to a solution of p-dimethylaminopyridine (5.5 mmol, 672 mg) in THF (5 ml) at room temperature. Then, the vigorously stirred mixture was cooled to -78°C, and $H_2O$ (2.5 mmol, 45 µl) was carefully added by a gas-tight syringe. The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. Then, the solvent was removed in vacuo. The residue was dissolved in 3 ml and colourless crystals of the product $[AlMe_2(dmap)(\mu_3\text{-}O)AlMe_2]_2$ (**4**) were obtained by slow evaporation of hexane vapours for 48 hours (yield c.a. 70%). **Elemental analysis** (%) calc. for $C_{11}H_{22}N_2OAl_2$: C 52.37, H 8.79, N 11.10; found: C 52.53, H 8.88, N 10.97; **$^1$H NMR** (500 MHz, THF-$d_8$, 25°C), δ: -1.08 -(s, 6H, -OAl($C\underline{H}_3$)$_2$), -0.85 (s, 6H, -NAl($C\underline{H}_3$)$_2$), 3.12 (s, 6H, -N($C\underline{H}_3$)$_2$, 6.77 (d, 2H, C<u>H</u>-*m*-py), 8.09 (d, 2H, C<u>H</u>-*o*-py); **$^{13}$C NMR** (300 MHz, THF-$d_8$, 25°C), δ: -9.6 (OAl($\underline{C}H_3$)$_2$), -7.6 (-NAl($\underline{C}H_3$)$_2$), 39.1 (-N($\underline{C}H_3$)$_2$), 107.3 (<u>C</u>H-*m*-pyr), 146.5 (<u>C</u>H-*o*-pyr), 156.9 (<u>C</u>H-*p*-pyr); **$^{27}$Al NMR** (400 MHz, THF-$d_8$, 25°C), δ: 151; **FTIR** (ATR) $\nu$/cm$^{-1}$: 2887(w), 1625(s), 1551(m) 1445(w), 1397(w), 1232(m), 1187(m), 1071(m), 1025(s), 815(m), 779(s), 687(vs), 648(vs), 600(s), 562(m), 525(s). **ESI-MS** (m/z): 251.4 $[M\text{-}CH_3+2Li]^{2+}$.

**$AlMe_3$ hydrolysis reaction in the presence of THF and/or pyrrolidine.** A solution of $AlMe_3$ in heptane (1 M, 2 ml) was added to: i) a solution of pyrrolidine (2.2 mmol, 0,165 ml) in THF (5 ml) or ii) pure THF

(5 ml) at room temperature. Then, the vigorously stirred mixture was cooled to -78°C, and $H_2O$ (2.5 mmol, 18 µl) was carefully added by a gas-tight syringe. The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. Then, the solvent was removed in vacuo. The residue has a colourless oil form soluble in THF and insoluble in toluene, benzene and hexane. For NMR spectra of the oiled products, see Figs S10-11.

## 2. NMR spectra.

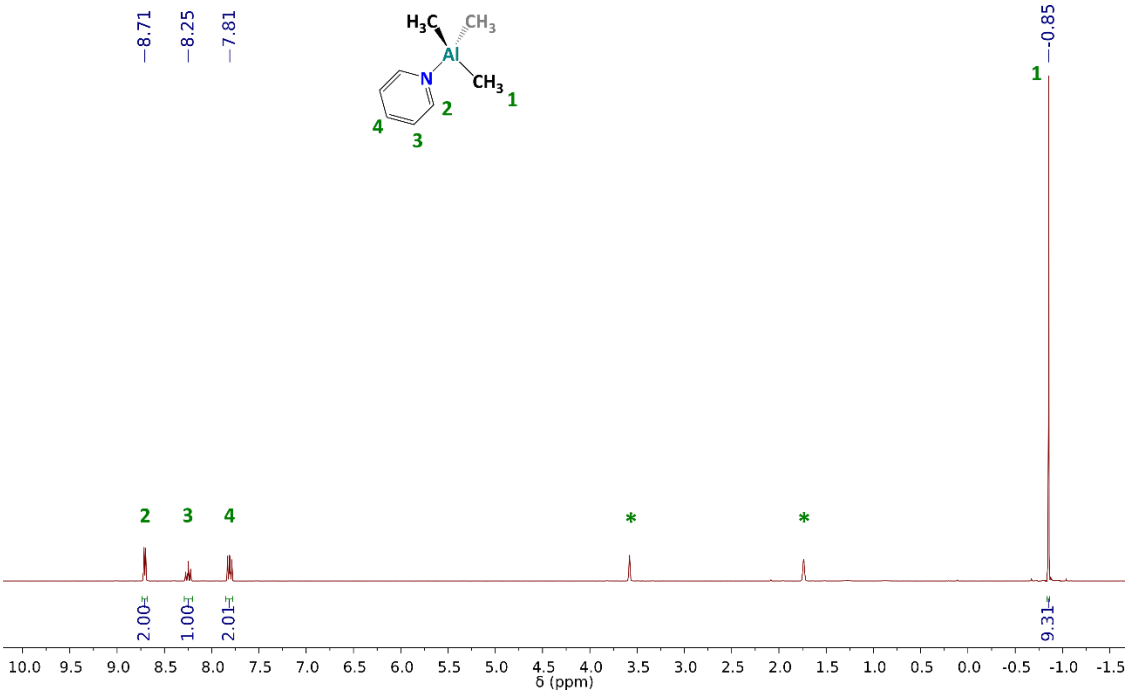



**Fig. S1.** $^1$H NMR spectrum of **1** (THF-$d_8$, 193 K). Solvent signals are marked by asterisks.

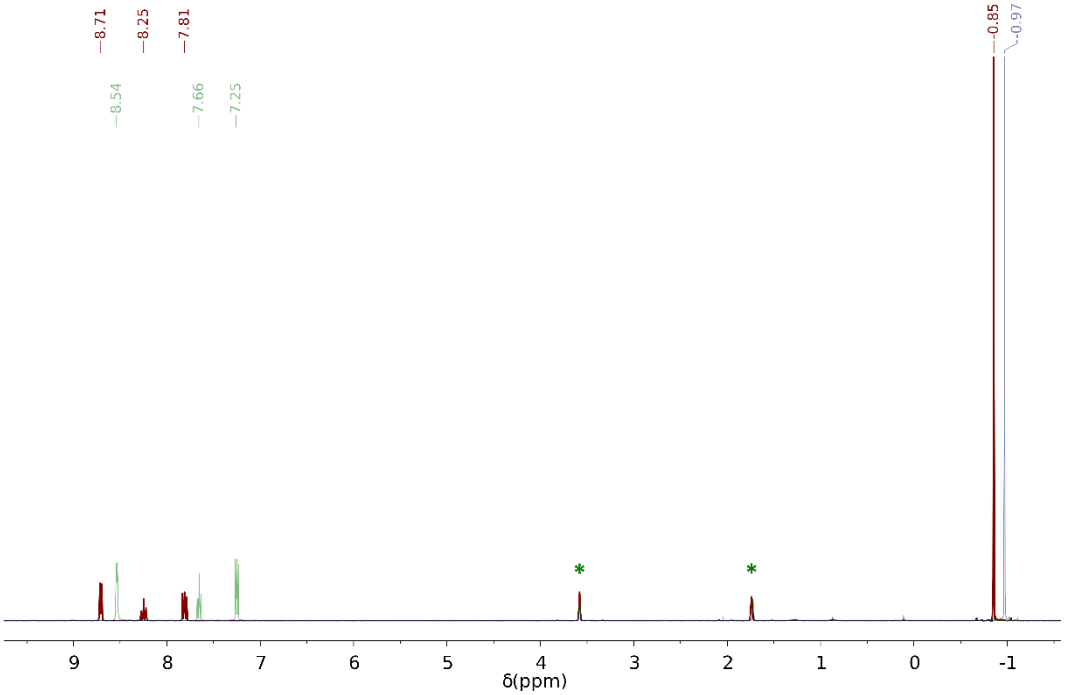



**Fig. S2.** $^1$H NMR spectrum of **1** (red line) compared to spectra of pyridine (green line) and $AlMe_3$ (blue line) in THF-$d_8$ in 298 K. Solvent signals are marked by asterisks.

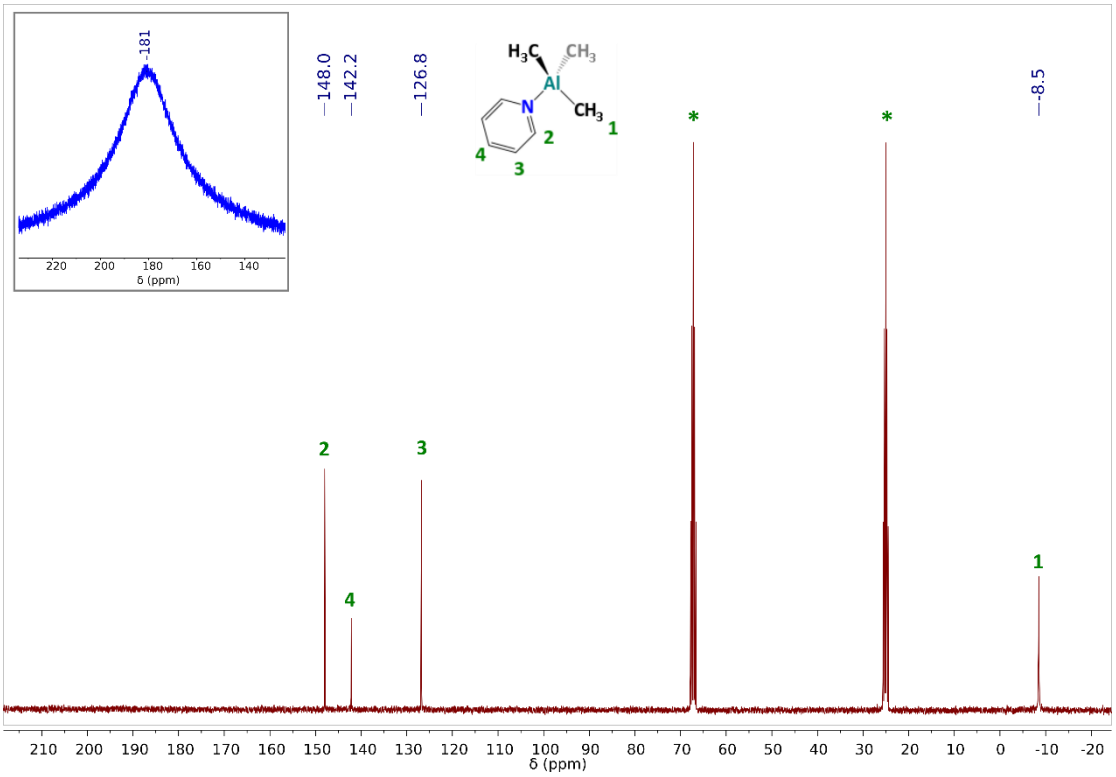



**Fig. S3.** $^{13}C$ and $^{27}Al$ (top left corner) NMR spectra of **1** (THF-$d_8$, 193 K). Solvent signals are marked by asterisks.

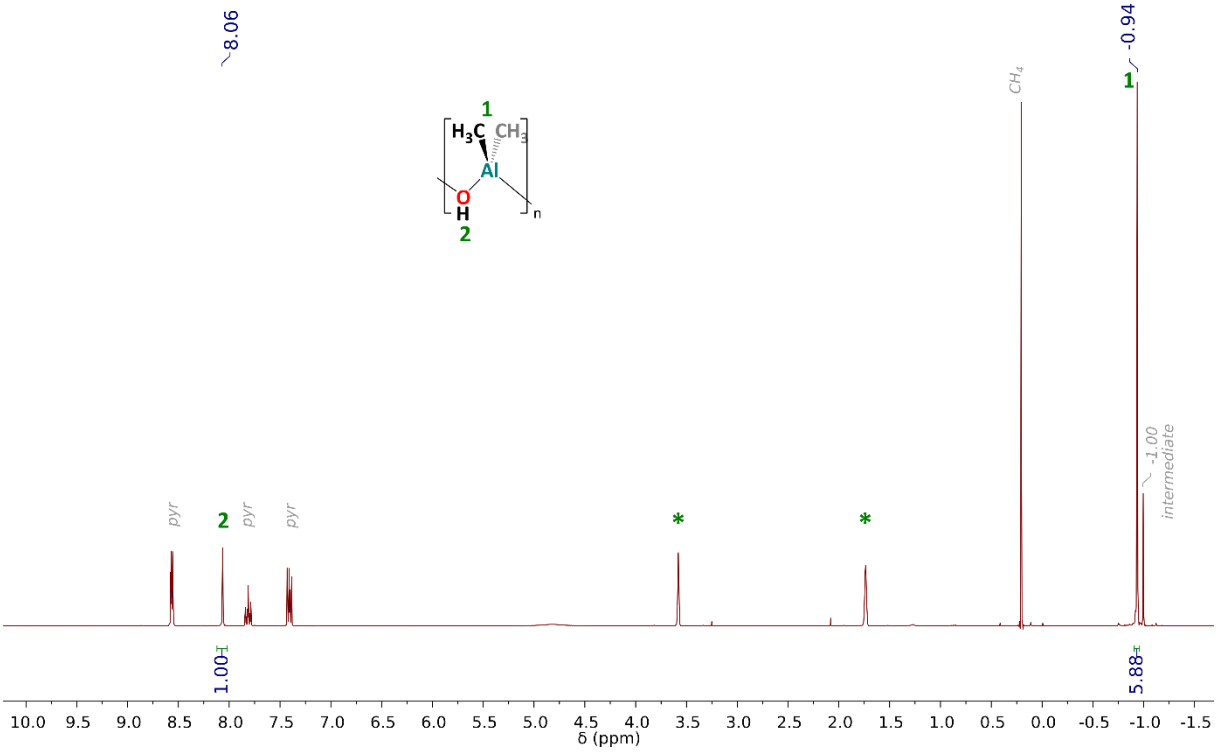



**Fig. S4.** $^{1}H$ NMR spectrum of *in-situ* generated compound **2** (THF-$d_8$, 193 K). Solvent signals are marked by asterisks. Signals from pyridine, $CH_4$ and unidentified intermediate are signed in grey italic font.

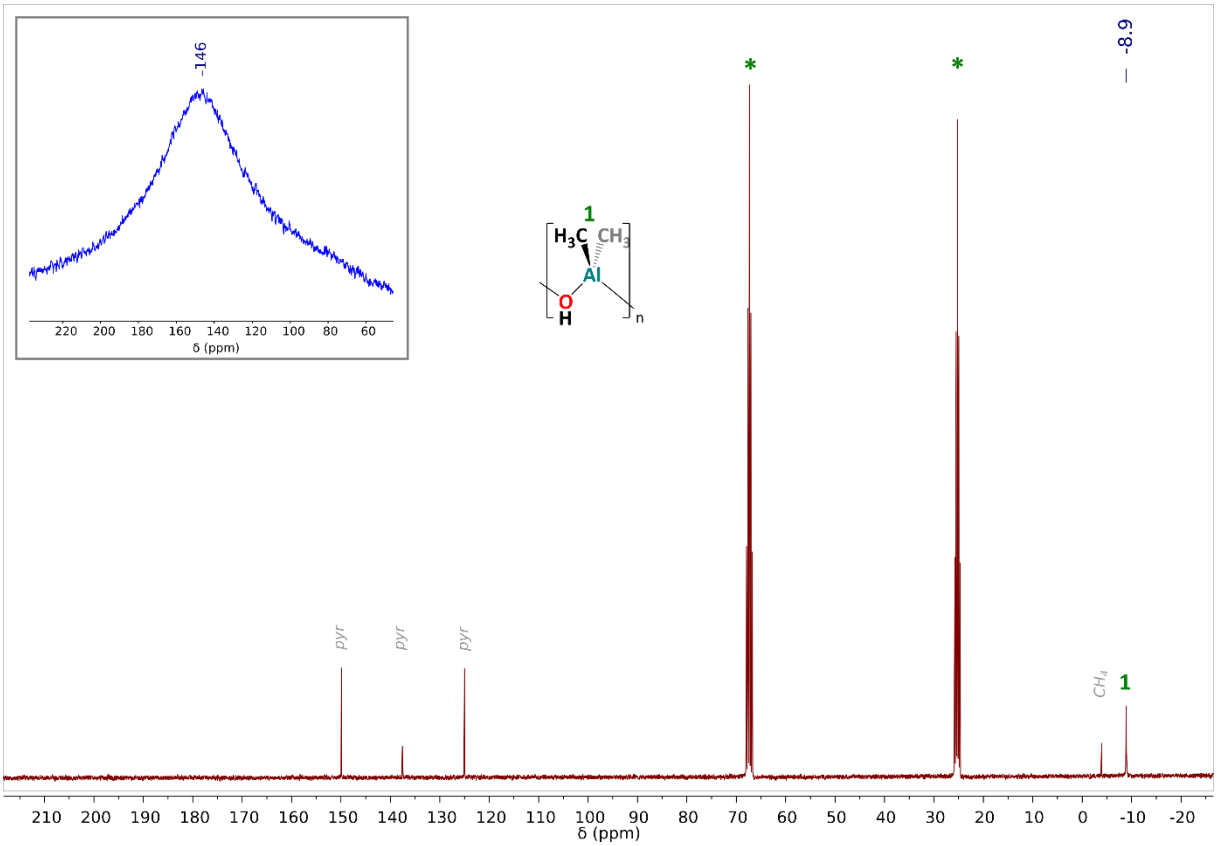



**Fig. S5.** $^{13}C$ and $^{27}Al$ (top left corner) NMR spectra of *in-situ* generated compound **2** (THF-$d_8$, 193 K). Solvent signals are marked by asterisks. Signals from pyridine and $CH_4$ are signed in grey italic font.

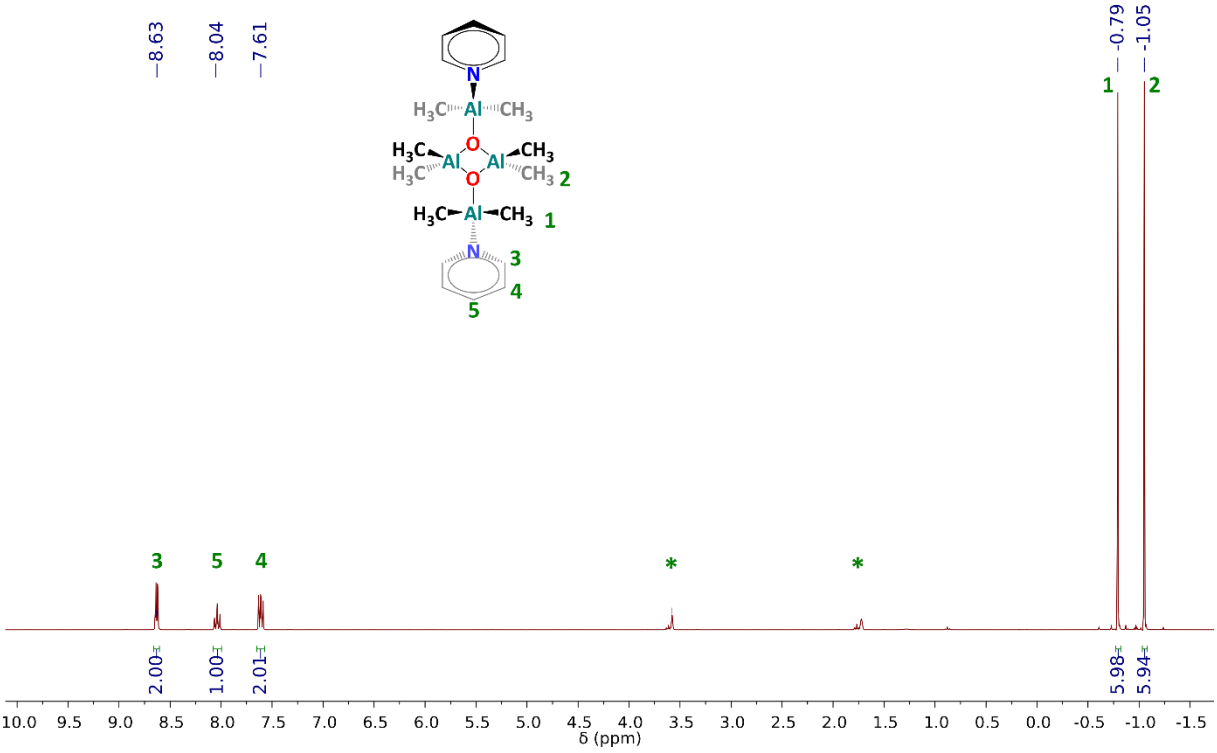



**Fig. S6.** $^{1}H$ NMR spectrum of **3** (THF-$d_8$, 298 K). Solvent signals are marked by asterisks.

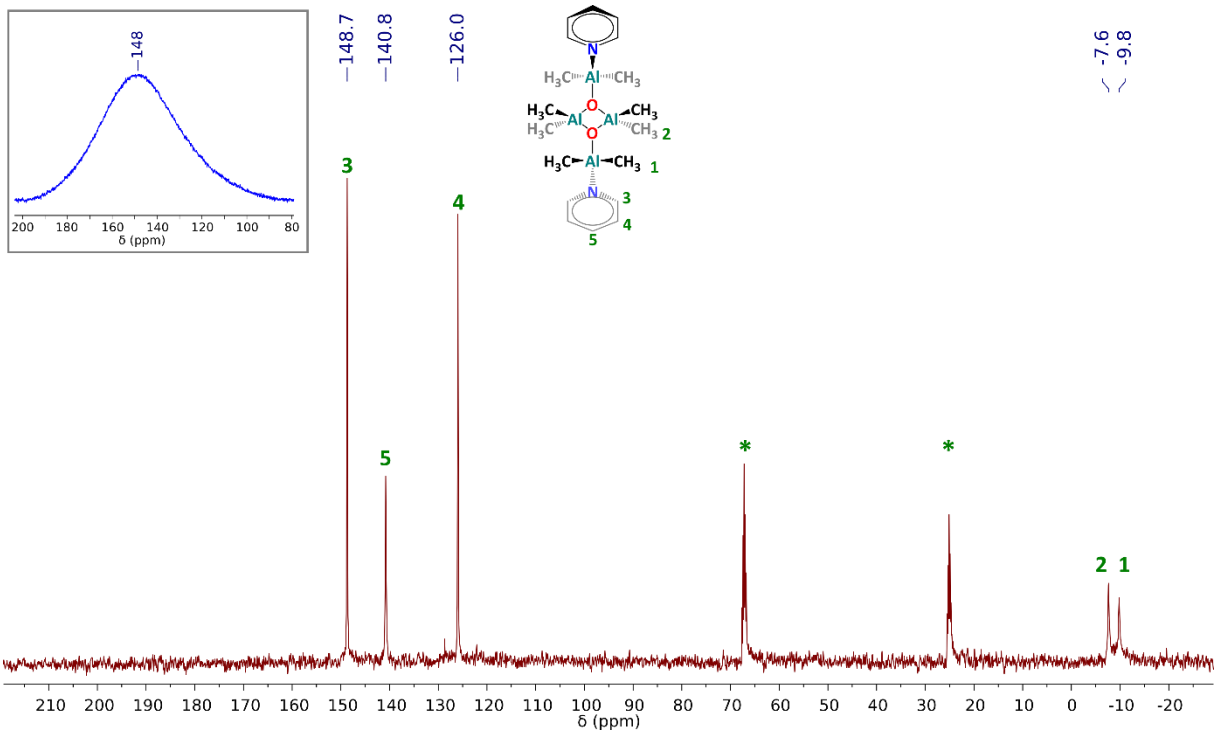



**Fig. S7.** $^{13}C$ and $^{27}Al$ (top left corner) NMR spectra of **3** (THF-$d_8$, 298 K). Solvent signals are marked by asterisks.

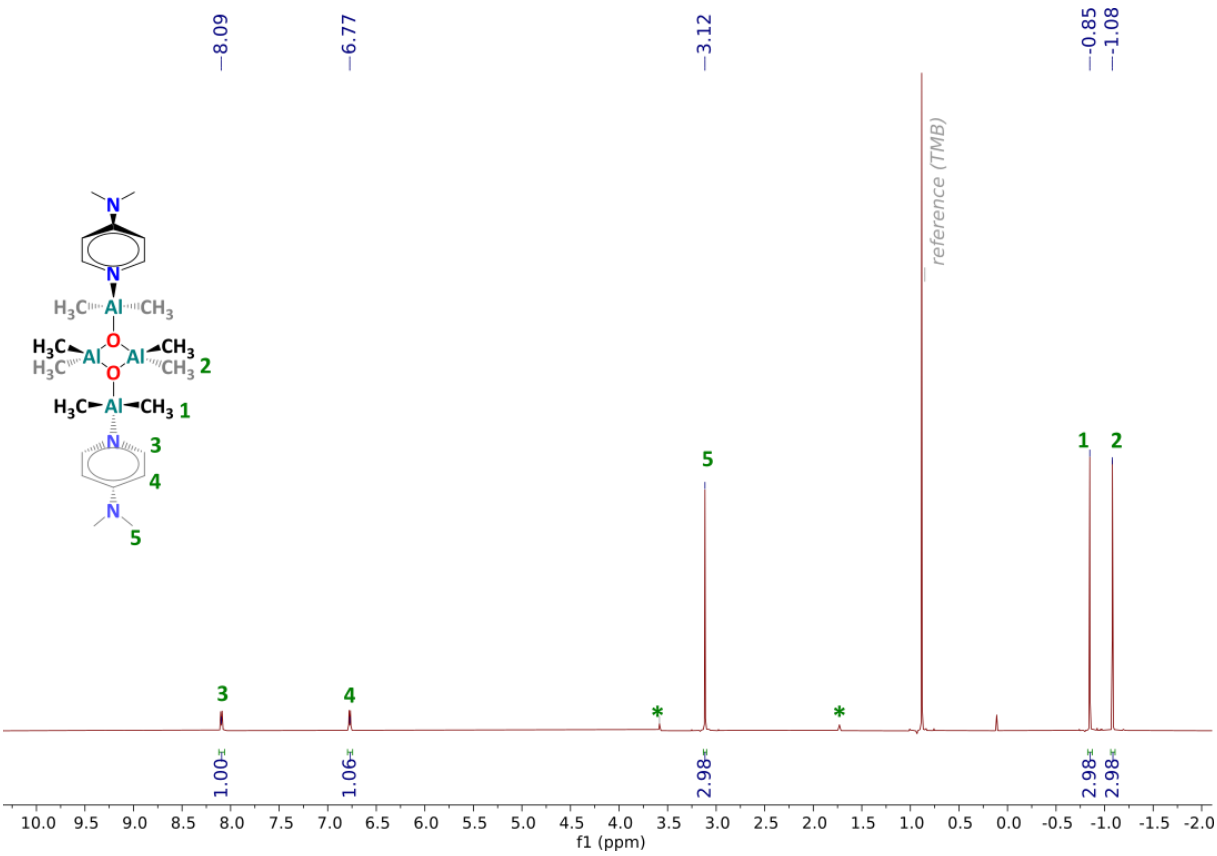



**Fig. S8.** $^{1}H$ NMR spectrum of **4** (THF-$d_8$, 298 K). Solvent signals are marked by asterisks.

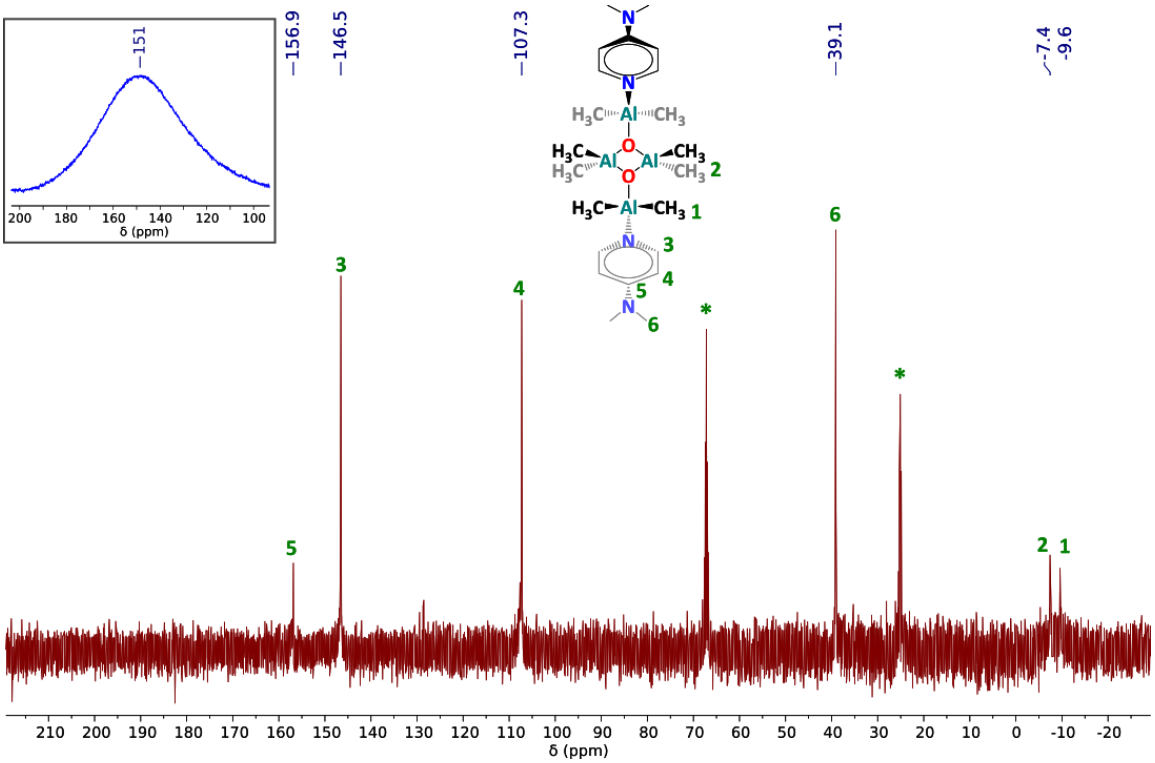



**Fig. S9.** $^{13}C$ and $^{27}Al$ (top left corner) NMR spectra of **4** (THF-$d_8$, 193 K). Solvent signals are marked by asterisks.

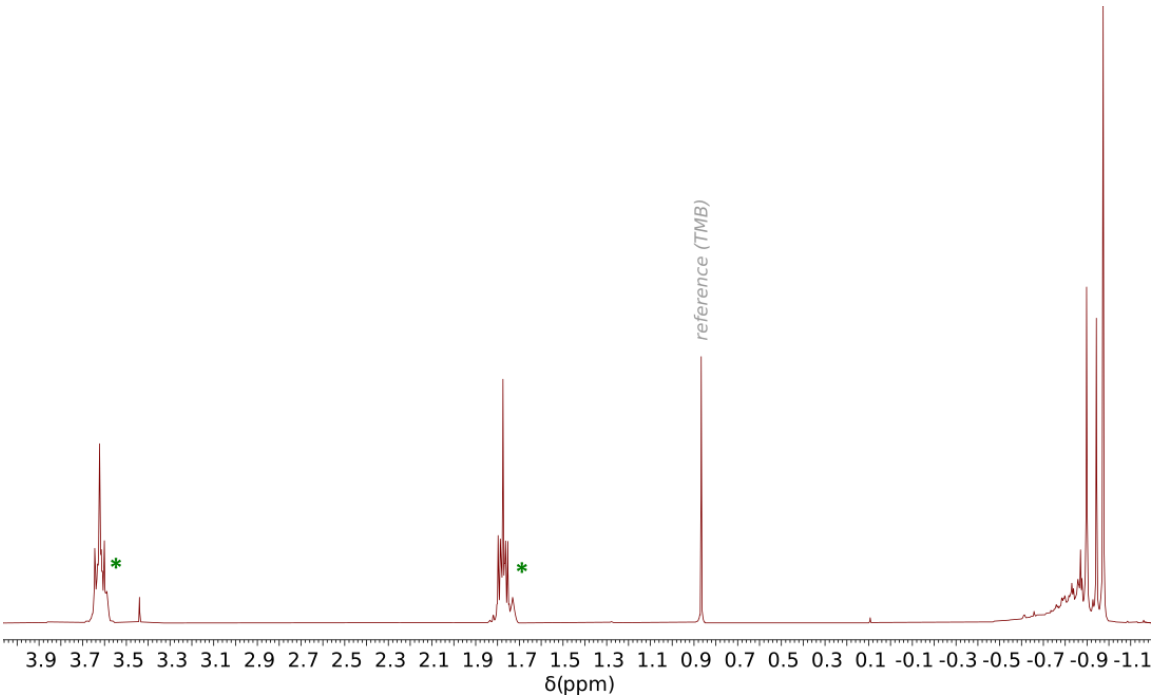



**Fig. S10.** $^{1}H$ NMR spectrum (THF-$d_8$, 193 K) of the post-reaction mixture from the $AlMe_3$ reaction with 0.5 equiv. of $H_2O$ in THF without additional Lewis bases. Solvent signals are marked by asterisks.

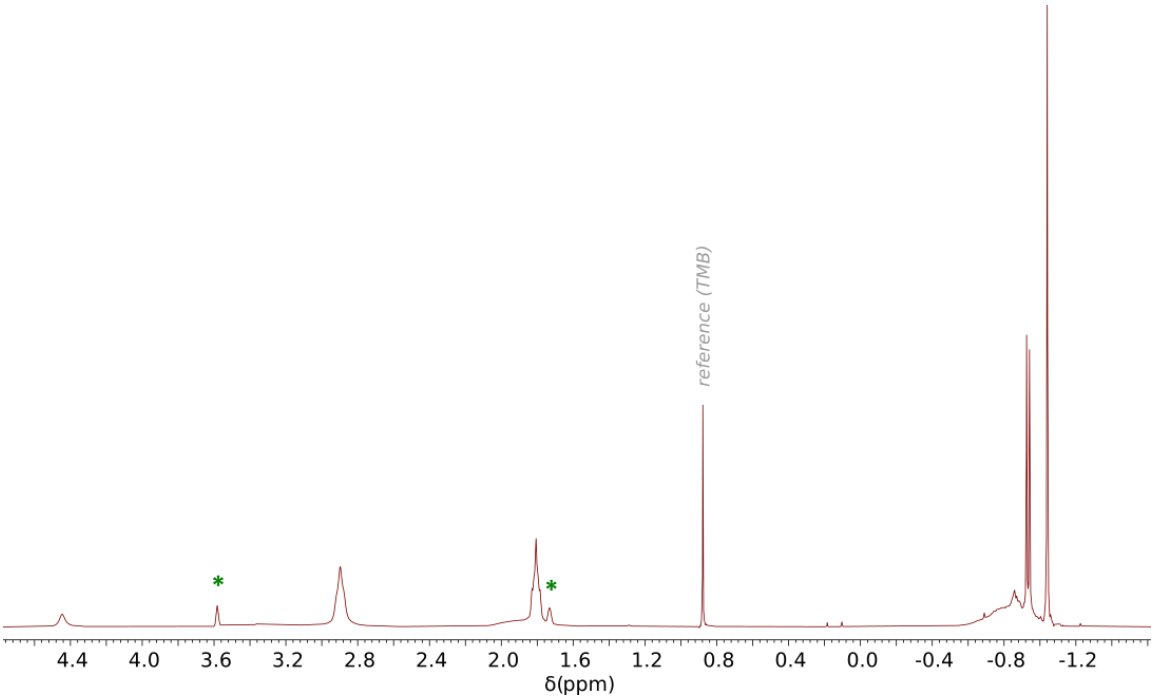



**Fig. S11.** $^{1}$H NMR spectrum (THF-$d_8$, 193 K) of the post-reaction mixture from the $AlMe_3$ reaction with 0.5 equiv. of $H_2O$ in THF in the presence of pyrrolidine. Solvent signals are marked by asterisks.

## 3. Time-dependent NMR spectra of the formation of compound 3.

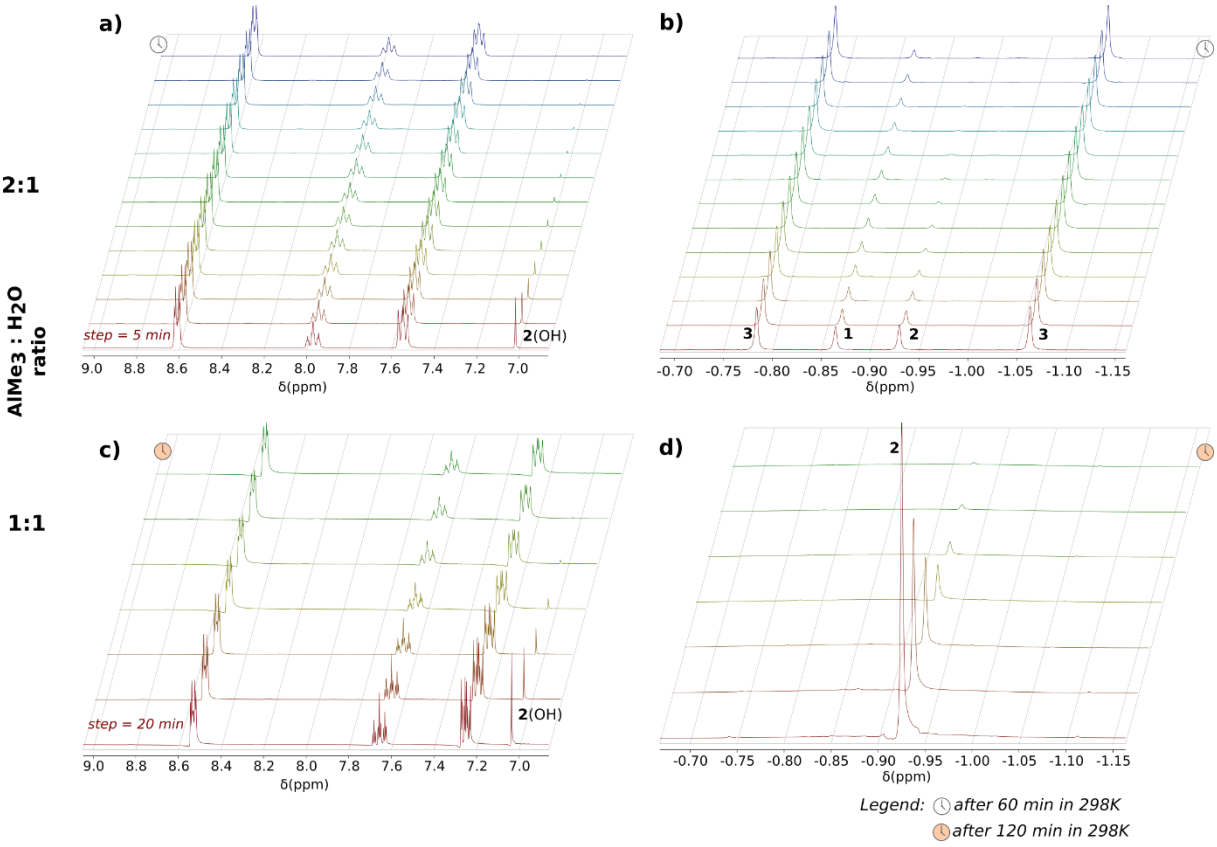



**Fig. S12.** $^{1}$H NMR spectra upon time of further steps of [$AlMe_3$(pyr)] hydrolysis reactions (THF-$d_8$, 298 K) for $AlMe_3$ : $H_2O$ ratios of 2:1 (a, b) and 1:1 (c, d).

## 4. Diffusion-Ordered NMR spectroscopy.

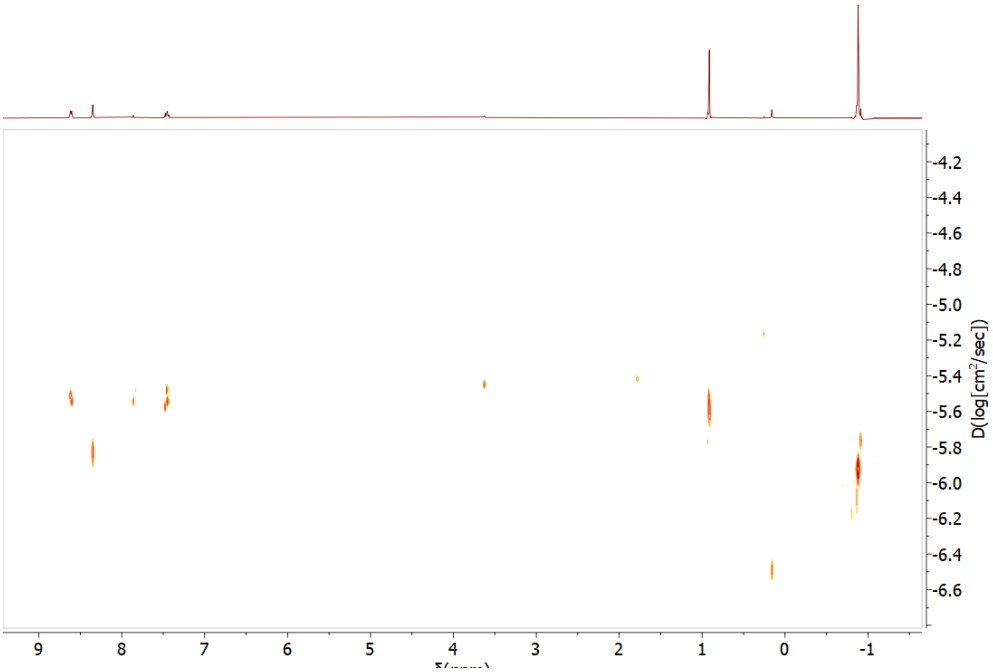



**Fig. S13.** DOSY-NMR (THF-$d_8$, 193 K, 300 MHz) spectrum of the initial steps of [$AlMe_3$(pyr)] hydrolysis in the $AlMe_3$:$H_2O$ ratio of 1:1.

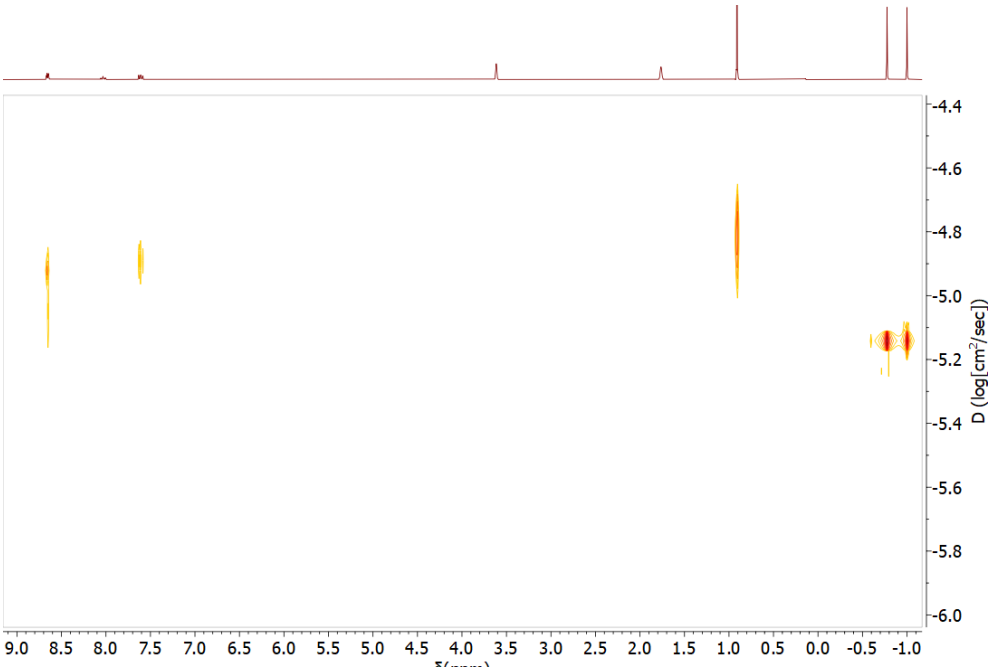



**Fig. S14.** DOSY-NMR (THF-$d_8$, 298 K, 300 MHz) spectrum of compound **3**.

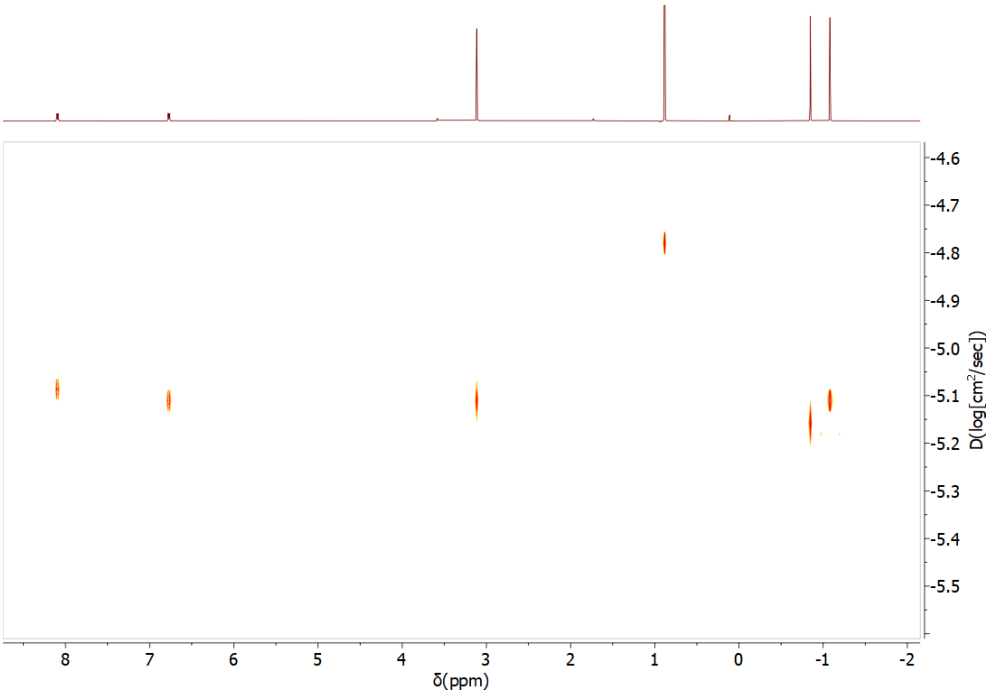



**Fig. S15.** DOSY-NMR (THF-$d_8$, 298 K, 300 MHz) spectrum of compound **4**.

**Table S1.** Averaged diffusion coefficients and determined molecular weights (**$MW_{det}$**), compared to the calculated molecular weights for compounds **2**, **3** and **4**. 2,2,3,3-tetramethylbutane (TMB) was used as an internal reference, and the molecular weights was determined using external calibration curves.[1] The **$MW_{calc}$ ≈ 460 g/mol** was assumed for the predicted form of dimethylaluminium hydroxide $[AlMe_2(OH)]_3$•3L (L = THF-$d_8$, py). The merged dissipated sphere diffusion model was assumed for compound **2**. The dissipated spheres model was assumed for alumoxanes **3** and **4**.

| Compound | $MW_{calc}$ [g/mol] | $MW_{det}$ [g/mol] | Error [%] |
|---|---|---|---|
| **2** | 460 | 494 | +7.3 |
| **3** | 418 | 399 | -4.6 |
| **4** | 505 | 503 | -0.5 |

## 5. Nuclear Overhauser Effect NMR spectroscopy.

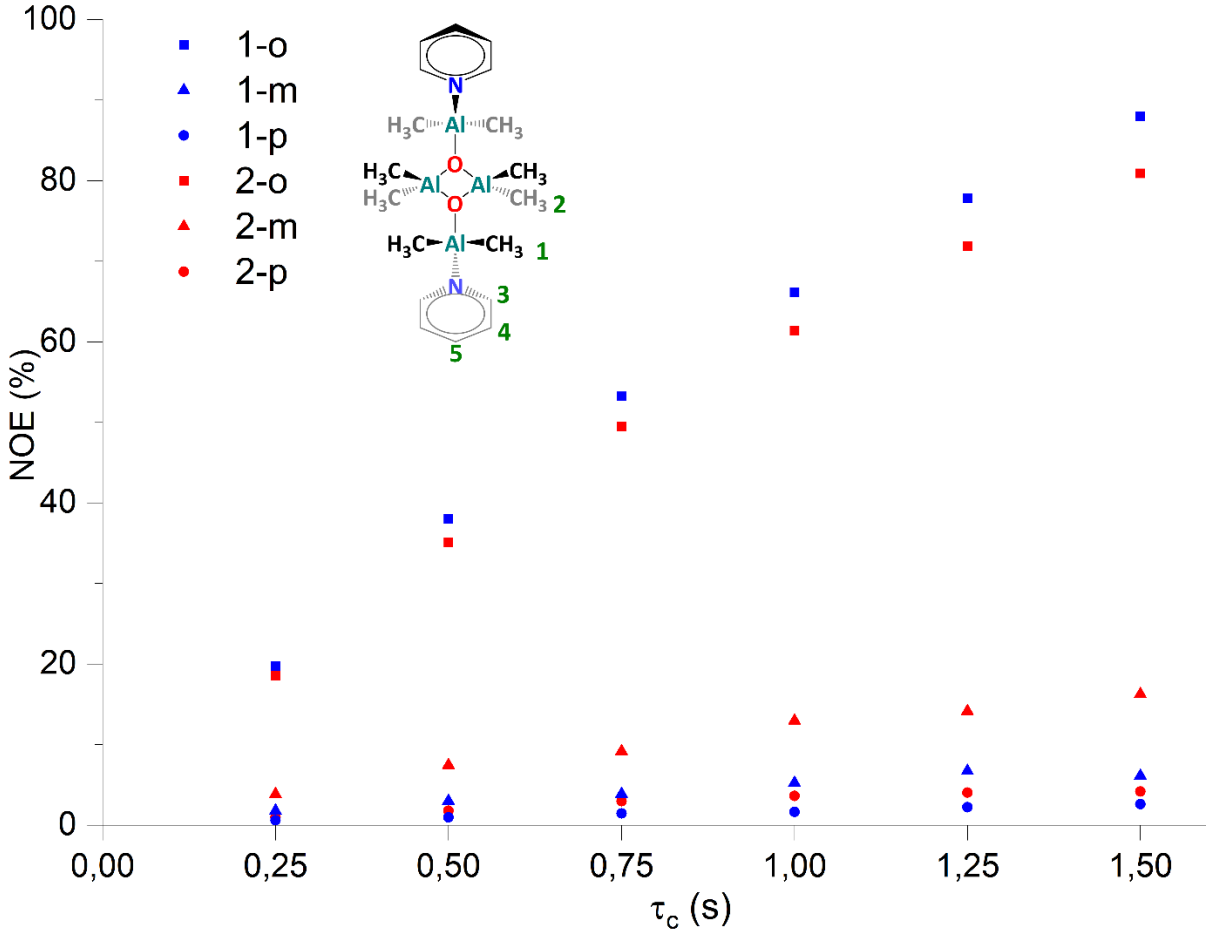



**Fig. S16.** Transient NOE enhancement (THF-$d_8$, 298 K, 300 MHz) *vs* mixing time ($\tau_c$) for *orto* (square), *meta* (triangle) and *para* (circle) pyridine protons of compound **3**, irradiating methyl protons at -1.05 (red) and -0.79 ppm (blue).

**Table S2.** Average dipole-dipole coupling constants between methyl and pyridine protons in **3** based on calculated distances from the crystal structure. It was assumed that: i) compound **3** exists in the solution in a similar conformation to that in the solid state; ii) methyl groups rotate faster than the entire molecule.

| $J_{H-H}$ (Hz) | *orto* | *meta* | *para* |
|---|---|---|---|
| **1** (-1.05) | 4595 | 840 | 399 |
| **2** (-0.79) | 3885 | 1533 | 755 |

## 6. $^{1}H$-$^{13}C$ HSQC NMR spectroscopy.

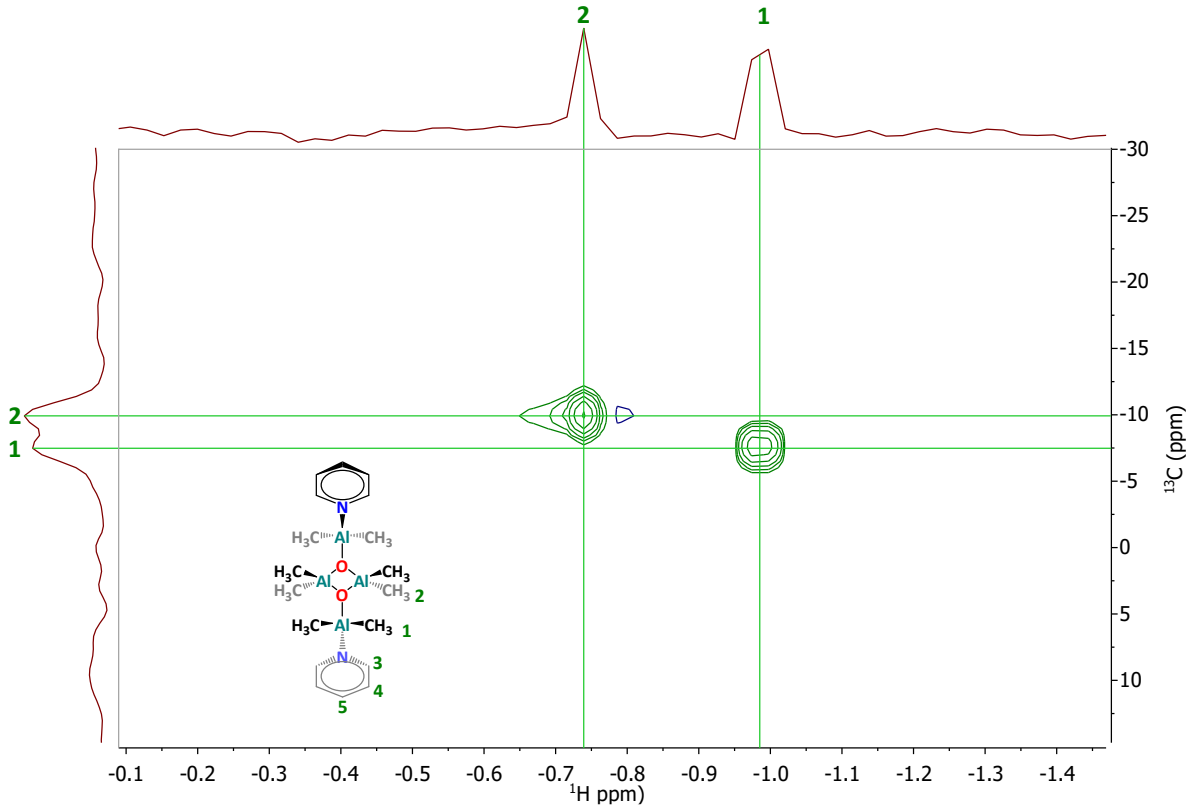



**Fig. S17.** $^{1}H$-$^{13}C$ HSQC spectrum of **3** (THF-$d_8$, 298 K, 300 MHz).

## 7. ESI-MS spectra.

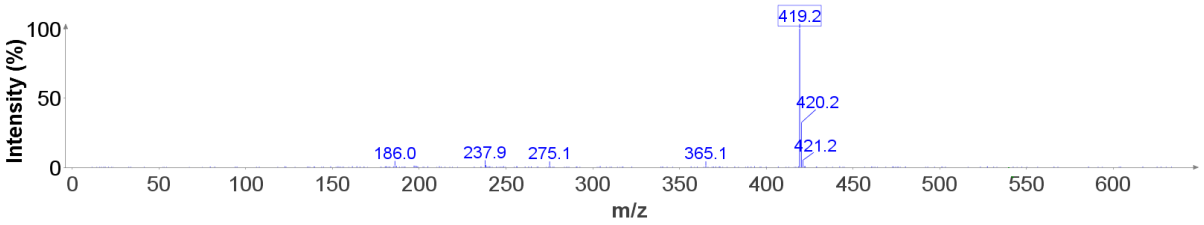



**Fig. S18.** ESI-MS spectrum of **3** (THF, 120V/250°C).

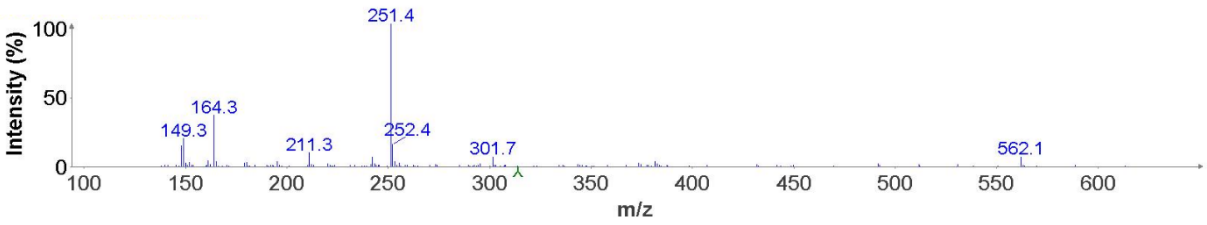



**Fig. S19.** ESI-MS spectrum of **4** (MeCN/LiI, 120V/250°C).

## 8. FTIR-ATR spectra.

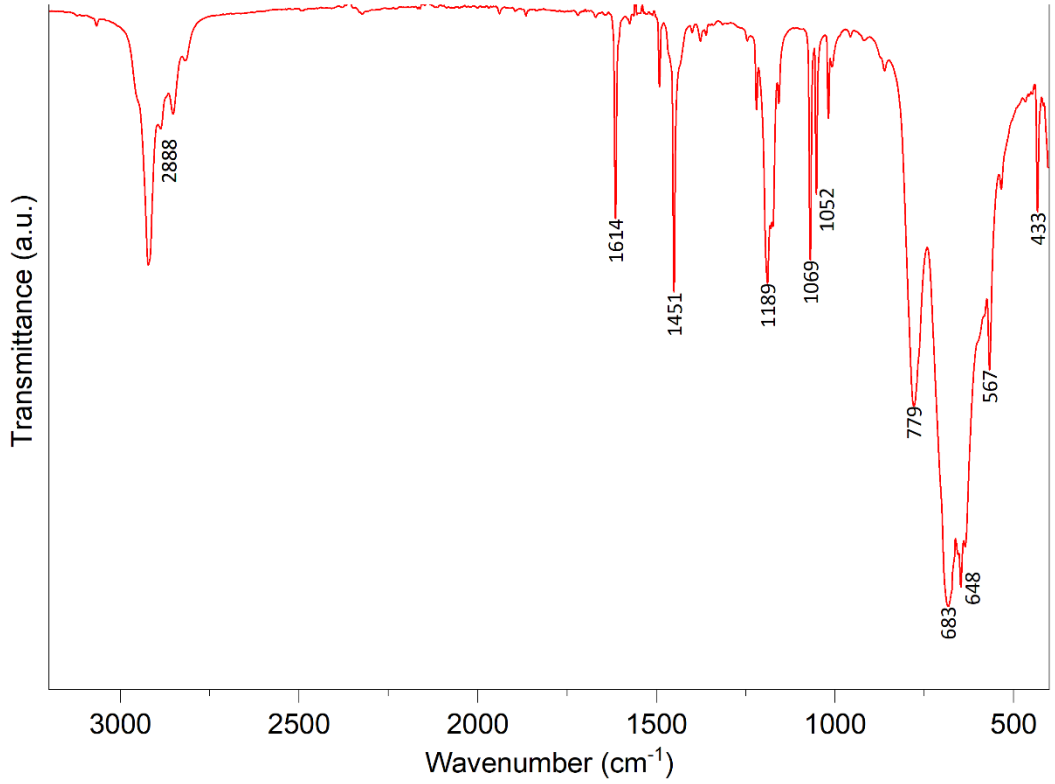



**Fig. S20**. FTIR-ATR spectrum of **3** in nujol.

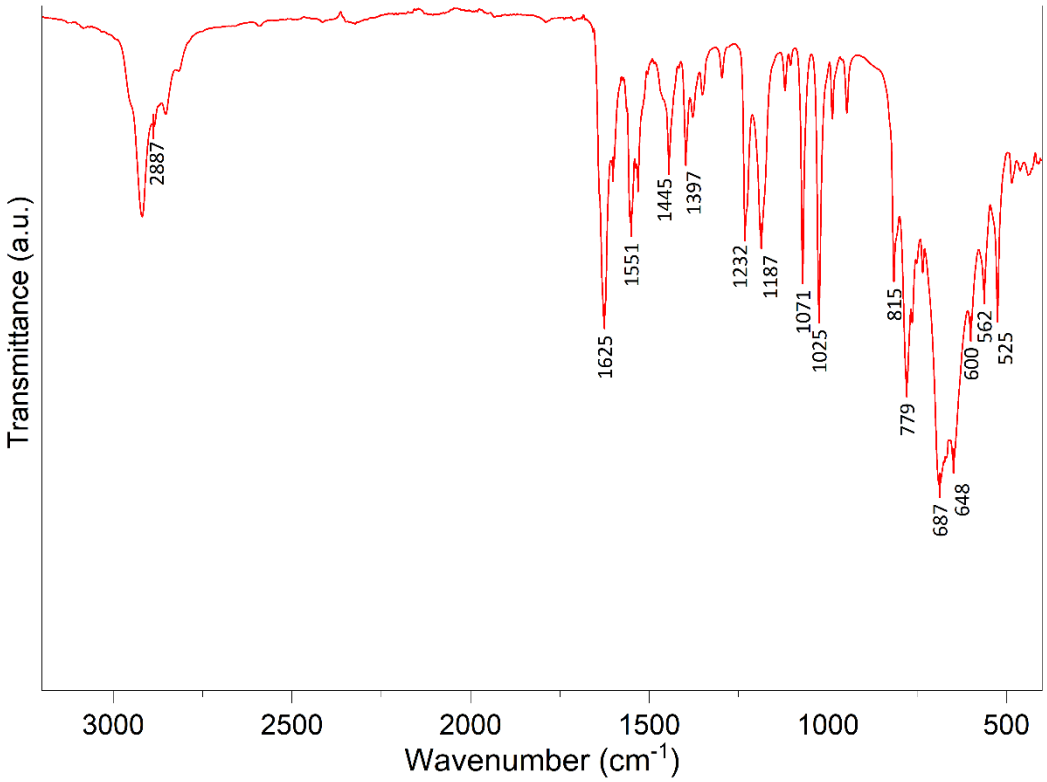



**Fig. S21**. FTIR-ATR spectrum of **4** in nujol.

## 9. X-Ray crystallographic data.

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data were collected at 100(2)K on a SuperNova Agilent diffractometer using graphite monochromated CuKα radiation (λ=1.54184 Å). The data were processed with CrysAlisPro.[2] The crystal structures were solved by direct methods using the SHELXS-97 program and were refined by full-matrix least-squares on $F^2$ using the program SHELXL[3] implemented in the Olex2[4] suite. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealised coordinates and refined as riding atoms.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk ). CCDC-2352082 (**3**), CCDC- 2369858 (**4**).

**Table S3.** Crystal data and structure refinement for **3** (CCDC-2352082).

| | |
|---|---|
| Empirical formula | $C_{18}H_{34}Al_4N_2O_2$ |
| Formula weight | 418.39 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 Å |
| Crystal system | triclinic |
| Space group | *P*-1 |
| a | 8.3590(3) Å |
| b | 8.9229(3) Å |
| c | 9.2090(3) Å |
| α | 99.654(3)° |
| β | 111.823(3)° |
| γ | 91.082(3)° |
| Volume | 626.13(4) $Å^3$ |
| Z | 1 |
| $\rho_{calc}$ | 1.028 $g/cm^3$ |
| μ | 1.833 $mm^{-1}$ |
| F(000) | 224 |
| Crystal size | 0.17 x 0.11 x 0.06 $mm^3$ |
| θ range for data collection | 5.048 to 69.952° |
| Index ranges | -9≤h≤10, -10≤k≤9, -11≤/≤11 |
| Reflections collected | 4688 |
| Independent reflections | 2348 [R(int) = 0.0196] |
| Completeness to θ=67.684° | 99.8 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2348 / 0 / 122 |
| Goodness-of-fit on $F^2$ | 1.070 |
| Final R indexes [I≥2σ (I)] | $R_1$ = 0.0334, $wR_2$ = 0.0925 |
| Final R indexes [all data] | $R_1$ = 0.0343, $wR_2$ = 0.0929 |
| Largest diff. peak/hole | 0.316 / -0.278 e.$Å^{-3}$ |

$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$;  $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

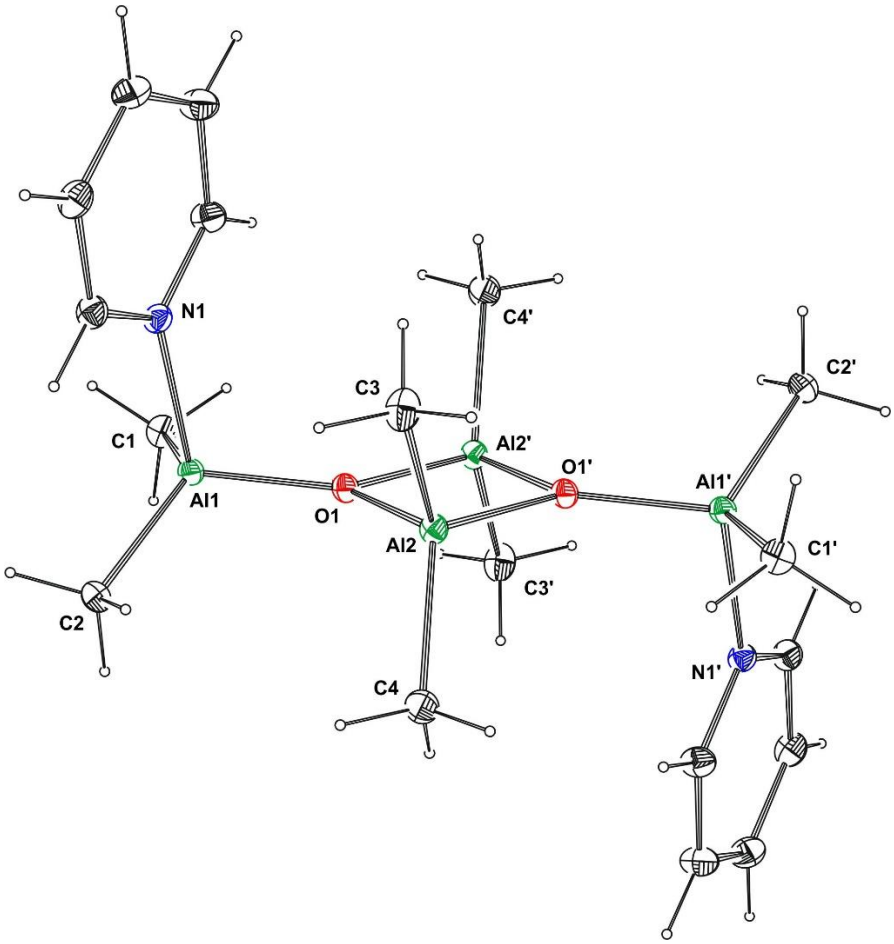



**Fig. S22**. The molecular structure of **3** with thermal ellipsoids set at 30% probability. Operators for generated equivalent atoms: (*-x+1, -y, -z+1*).

**Table S4.** Selected intermolecular bond lengths [Å] and angles [deg] for **3**.

| **Bond Lengths (Å)** | | | | | |
|---|---|---|---|---|---|
| Al1-O1 | 1.7650(9) | Al2 O1 | 1.8263(9) | | |
| Al1-N1 | 2.0096(11) | Al2-C3 | 1.9727(14) | | |
| Al1-C1 | 1.9576(13) | Al2-C4 | 1.9642(14) | | |
| Al1-C2 | 1.9679(14) | | | | |
| **Bond Angles (°)** | | | | | |
| Al1-O1-Al2 | 130.42(5) | O1-Al1-C1 | 111.72(5) | O1-Al2-C4 | 110.82(5) |
| Al1-O1-Al2’ | 135.04(5) | O1-Al1-C2 | 110.72(5) | Al2-O1-Al2’ | 94.02(4) |
| N1-Al1-O1 | 100.28(4) | N1-Al1-C2 | 104.86(5) | | |
| N1-Al1-C1 | 104.69(5) | O1-Al2-C3 | 113.58(6) | | |

**Table S5.** Crystal data and structure refinement for **4** (CCDC-2369858).

| | |
|---|---|
| Empirical formula | $(C_{11}H_{22}Al_2N_2O)x2$ |
| Formula weight | 504.53 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 Å |
| Crystal system | triclinic |
| Space group | P-1 |
| a | 8.1180(4) Å |
| b | 13.7490(6) Å |
| c | 14.0249(4) Å |
| α | 86.298(3)° |
| β | 77.725(3)° |
| γ | 73.794(4)° |
| Volume | 1468.79(11) $Å^3$ |
| Z | 2 |
| $\rho_{calc}$ | 1.141 $g/cm^3$ |
| μ | 1.659 $mm^{-1}$ |
| F(000) | 544 |
| Crystal size | 0.14 x 0.09 x 0.06 $mm^3$ |
| θ range for data collection | 3.225 to 70.072° |
| Index ranges | -9<=h<=9, -12<=k<=16, -10<=l<=17 |
| Reflections collected | 7000 |
| Independent reflections | 4558 [R(int) = 0.0252] |
| Completeness to θ=67.684° | 83.3 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4558 / 0 / 301 |
| Goodness-of-fit on $F^2$ | 1.087 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0390, $wR_2$ = 0.1025 |
| Final R indexes [all data] | $R_1$ = 0.0461, $wR_2$ = 0.1044 |
| Largest diff. peak/hole | 0.342 / -0.278 e.$Å^{-3}$ |

$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

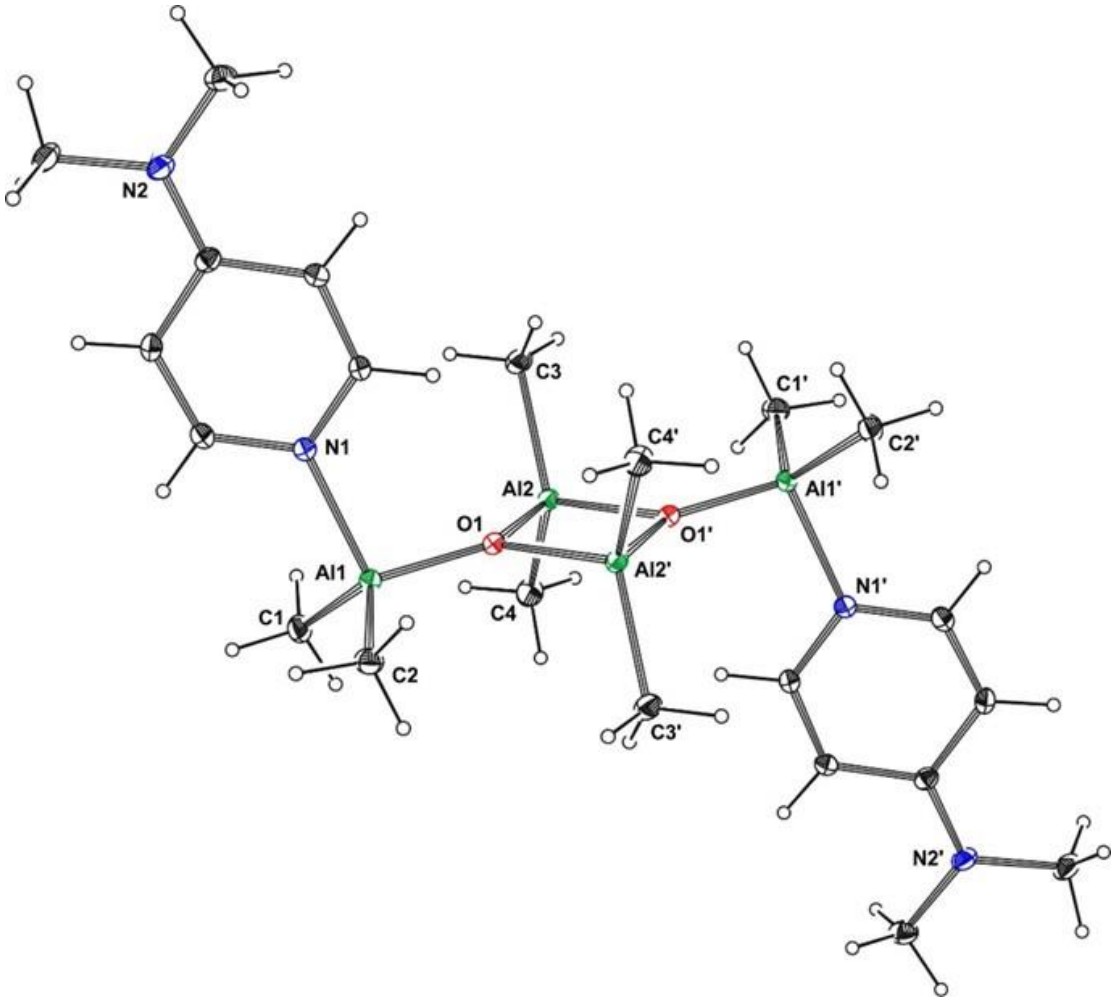



**Fig. S23**. The molecular structure of **4** with thermal ellipsoids set at 30% probability. Operators for generated equivalent atoms: (*-x+1, -y, -z+1*).

**Table S6.** Selected intermolecular bond lengths [Å] and angles [deg] for **4**.

| **Bond Lengths (Å)** | | | | | |
|---|---|---|---|---|---|
| Al1-O1 | 1.7575(16) | Al2 O1 | 1.8261(17) | | |
| Al1-N1 | 1.975(2) | Al2-C3 | 1.967(3) | | |
| Al1-C1 | 1.977(3) | Al2-C4 | 1.966(2) | | |
| Al1-C2 | 1.971(2) | | | | |
| **Bond Angles (°)** | | | | | |
| Al1-O1-Al2 | 133.48(10) | O1-Al1-C1 | 110.39(10) | O1-Al2-C4 | 111.92(10) |
| Al1-O1-Al2’ | 132.00(10) | O1-Al1-C2 | 111.21(10) | Al2-O1-Al2’ | 93.56(8) |
| N1-Al1-O1 | 102.60(8) | N1-Al1-C2 | 105.84(10) | | |
| N1-Al1-C1 | 104.25(10) | O1-Al2-C3 | 110.33(10) | | |

## 10. Quantum-chemical calculations.

All calculations have been performed with the ORCA 5.0 package.[5] Geometries have been obtained at the density functional theory level with BP86 functional[6] augmented with D3BJ dispersion correction[7,8] and def2-TZVP basis set[9]. This setup is denoted later as BP86+D3. Optimisations have been carried out in vacuum and in the THF solvent, using the CPCM method. All structures have been subjected to cartesian second derivative calculations: all minima possessed only positive Hessian eigenvalues, while transition states had exactly one imaginary frequency. 3D structures are provided in Fig. S24, and the XYZ coordinates of all species are reported below.

To provide energies with chemical accuracy, single point calculations in vacuum and in THF as the solvent (CPCM method) have been performed using the domain-based local pair natural orbital coupled cluster method with singles, doubles, and iterative triples (DLPNO-CCSD(T1))[10–12] and def2-TZVPP basis set[9] on the respective BP86+D3 structures. The error caused by the incomplete PNO space has been corrected with the recently developed cDLPNO method.[13] The coupled-cluster complete basis set limit has been estimated with the MP2-based approach of Šponer and Hobza[14] using def2-TZVPP and def2-QZVPP basis sets. All reported energies include zero-point energy correction (ZPE) obtained at the BP86+D3 level. These reference calculations are denoted later as cDLPNO-CCSD(T1).

**Table S7.** Binding energies (kcal/mol) of ligands such as water, THF and pyridine to $Al(CH_3)_3$ in vacuum and THF calculated at the cDLPNO-CCSD(T1) and BP86+D3 levels as defined in the methods section.

| Ligand | cDLPNO-CCSD(T1)/CBS | | BP86+D3/def2-TZVP | |
|---|---|---|---|---|
| | vacuum | THF | vacuum | THF |
| $H_2O$ | -14.9 | -16.8 | -14.7 | -16.0 |
| THF | -23.0 | -23.3 | -21.2 | -21.8 |
| Pyridine | -26.4 | -26.5 | -25.8 | -26.2 |

**Table S8.** Energies (kcal/mol) of species A, B, and C as well as transition states TS(A→B) and TS(B→C) that connect them relative to A presented in Figure 4 of the main text calculated in vacuum and THF at the cDLPNO-CCSD(T1)/CBS and BP86+D3/def2-TZVP levels as defined in the methods section.

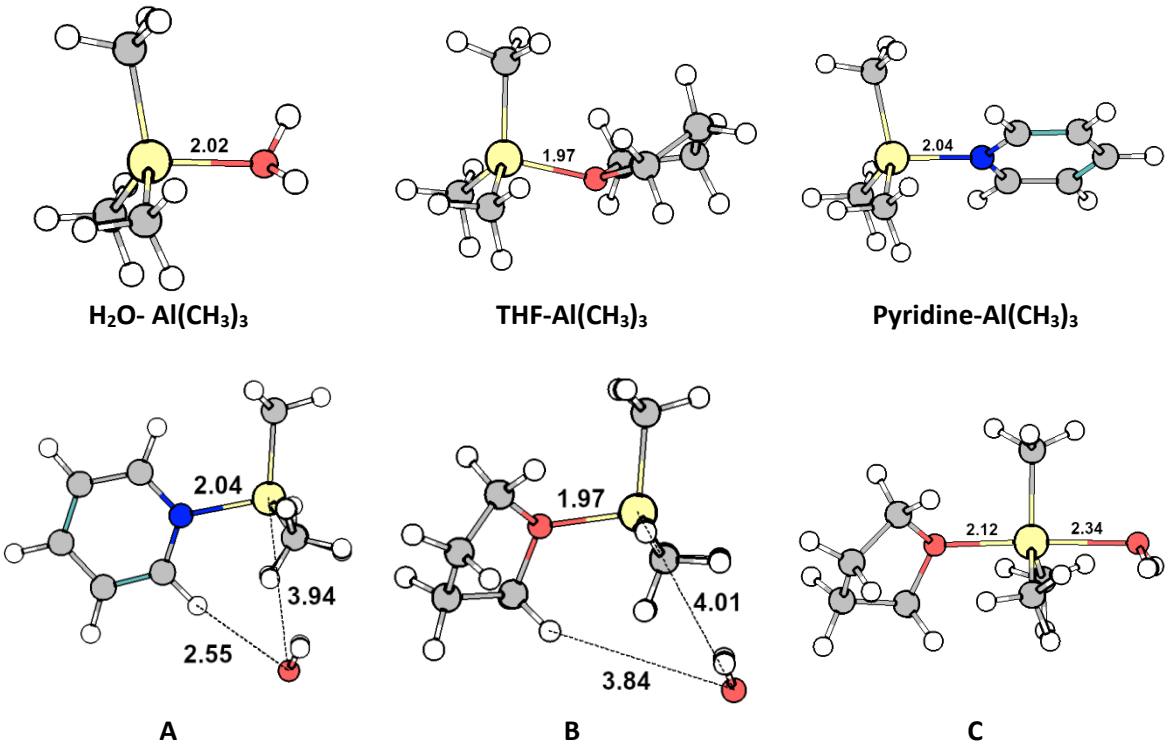
| Species | cDLPNO-CCSD(T1)/CBS | | BP86+D3/def2-TZVP | |
|---|---|---|---|---|
| | vacuum | THF | vacuum | THF |
| A | 0.0 | 0.0 | 0.0 | 0.0 |
| TS(A→B) | 3.9 | 3.3 | 0.8 | 0.3 |
| B | 4.2 | 2.7 | -1.4 | 4.2 |
| TS(B→C) | 6.7 | 9.0 | 8.7 | 9.5 |
| C | 4.6 | 3.6 | 6.8 | 5.8 |

**Table S9.** Energies (kcal/mol) of species A, B, and C relative to A presented in Figure 4 of the main text calculated in vacuum and THF at the cDLPNO-CCSD(T1)/CBS and BP86+D3/def2-TZVP levels as defined in the methods section.

| Species | cDLPNO-CCSD(T1)/CBS | | BP86+D3/def2-TZVP | |
|---|---|---|---|---|
| | vacuum | THF | vacuum | THF |
| A | 0.0 | 0.0 | 0.0 | 0.0 |
| B | 4.2 | 2.7 | -1.4 | 4.2 |
| C | 4.6 | 3.6 | 6.8 | 5.8 |

**Table S10.** Equilibrium constants at 195.15 K of two reactions presented in Fig. 4 of the main text (A ↔ B and B ↔ C) calculated in vacuum and THF at the cDLPNO-CCSD(T1)/CBS and BP86+D3/def2-TZVP levels as defined in the methods section.

| Species | cDLPNO-CCSD(T1)/CBS | | BP86+D3/def2-TZVP | |
|---|---|---|---|---|
| | vacuum | THF | vacuum | THF |
| $K_{AB}$ | $2.1 \cdot 10^{-5}$ | $8.5 \cdot 10^{-4}$ | 40 | $1.8 \cdot 10^{-5}$ |
| $K_{BC}$ | $3.6 \cdot 10^{-1}$ | $1.1 \cdot 10^{-1}$ | $5.4 \cdot 10^{-10}$ | $2.0 \cdot 10^{-2}$ |




**$H_2O$- $Al(CH_3)_3$** **THF-$Al(CH_3)_3$** **Pyridine-$Al(CH_3)_3$**

**A** **B** **C**

**Fig. S24.** 3D structures of key species discussed in the main text (optimised using THF as the solvent), with key interatomic distances highlighted (Å).

**XYZ coordinates (Å) obtained at BP86+D3 level of all species discussed in the manuscript. Structures optimised in vacuum are listed first, then CPCM(THF) structures are presented.**

alme3.xyz

| | | | |
|---|---|---|---|
| Al | -0.24820195888167 | 0.00124324761115 | 0.02206715106143 |
| C | -0.83164293431322 | -1.81741459182182 | -0.45560697725727 |
| H | -0.18400192413724 | -2.24050606850776 | -1.24219147246211 |
| H | -0.82510865636032 | -2.51799259962344 | 0.39213428202325 |
| H | -1.85099769972154 | -1.80898056989724 | -0.87639919902244 |
| C | 0.33322242710987 | 0.39729764218099 | 1.86085127045322 |
| H | -0.48771689797772 | 0.22004747600113 | 2.57623809932532 |
| H | 1.15267555805821 | -0.27286488827078 | 2.17008529180387 |
| H | 0.67673849856619 | 1.43274542598120 | 1.99990417532583 |
| C | -0.23591889581012 | 1.42118747271802 | -1.34160292678767 |
| H | 0.79099404788443 | 1.78654393160364 | -1.51286348364770 |
| H | -0.63961737232023 | 1.10115945069896 | -2.31326031557981 |
| H | -0.81618223409663 | 2.29753707032595 | -1.00800626623592 |

al-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 1.29366983119581 | -0.14905562723661 | -0.72881636276224 |
| C | 0.85032144778074 | -2.01779321168972 | -1.24702978550261 |

| | | | |
|---|---|---|---|
| H | 1.68508196435289 | -2.47138740753687 | -1.80761096908437 |
| H | 0.66875750617799 | -2.68255692242574 | -0.38511928837195 |
| H | -0.02739670590411 | -2.08815636925743 | -1.91269717731202 |
| C | 2.42552279805706 | 0.11622806327592 | 0.88584568770254 |
| H | 2.34897830384293 | 1.13360509664745 | 1.30721656194698 |
| H | 2.21325809029770 | -0.59791243085391 | 1.69988333665334 |
| H | 3.49090479936969 | -0.02108065386017 | 0.63463250770216 |
| C | 1.36767588788023 | 1.22514767683789 | -2.14650120123027 |
| H | 2.30299754430587 | 1.14585739039130 | -2.72582062846259 |
| H | 0.54158508625261 | 1.13623886166941 | -2.87023805577230 |
| H | 1.33754832116232 | 2.24834479807092 | -1.73825906078624 |
| O | -0.53173009956905 | 0.26084199435746 | 0.20631363385654 |
| H | -0.35235956907757 | 0.42241082439804 | 1.15139395263877 |
| H | -1.07760290812510 | -0.54629755378795 | 0.16175231678426 |

al-thf.xyz

| | | | |
|---|---|---|---|
| Al | 1.761781 | -0.460930 | -0.947904 |
| C | 0.892829 | -2.218651 | -1.313505 |
| H | 0.822575 | -2.460499 | -2.387792 |
| H | 1.394115 | -3.069494 | -0.821685 |
| H | -0.143609 | -2.217916 | -0.935326 |
| C | 2.249083 | -0.087884 | 0.940790 |
| H | 1.357166 | 0.229026 | 1.507470 |
| H | 2.655741 | -0.962048 | 1.475600 |
| H | 2.982995 | 0.729357 | 1.036969 |
| C | 1.177190 | 1.070607 | -2.067901 |
| H | 1.902109 | 1.901191 | -2.054255 |
| H | 0.994697 | 0.811522 | -3.123880 |
| H | 0.227183 | 1.481167 | -1.685637 |
| H | 3.832285 | -2.475106 | -0.492550 |
| O | 3.583401 | -0.807402 | -1.723997 |
| C | 3.675702 | -1.055898 | -3.169459 |
| C | 4.392015 | -2.392396 | -3.292798 |
| C | 5.335563 | -2.369995 | -2.080673 |
| C | 4.466911 | -1.735733 | -1.002470 |
| H | 2.656123 | -1.050108 | -3.571921 |
| H | 4.247557 | -0.224952 | -3.607471 |
| H | 4.920147 | -2.492765 | -4.249372 |
| H | 3.670118 | -3.217006 | -3.204227 |
| H | 6.215730 | -1.743796 | -2.288228 |
| H | 5.685737 | -3.367845 | -1.788178 |
| H | 5.014292 | -1.147261 | -0.257472 |

al-pyr.xyz

| | | | |
|---|---|---|---|
| Al | 0.52656604672953 | -0.23935443691924 | -0.29944255469086 |
| C | -0.58199504592931 | -1.88428955990063 | -0.48860681675158 |
| H | -0.69777415223268 | -2.22117639460713 | -1.53302510904737 |
| H | -0.21379078890567 | -2.74234429233066 | 0.09922577617711 |
| H | -1.60303670576092 | -1.68395539988209 | -0.12183765106827 |
| C | 1.08776085736304 | 0.25759142878050 | 1.54726604587351 |
| H | 0.23288834583730 | 0.63980968551001 | 2.12976415959730 |
| H | 1.49469190570654 | -0.59987929506101 | 2.10821869251909 |
| H | 1.85387851732437 | 1.05121622091697 | 1.56586668524208 |
| C | 0.08561252358947 | 1.27239749174908 | -1.52108803458454 |
| H | 0.80737045312051 | 2.10510638996474 | -1.47162753501316 |
| H | 0.02428305006393 | 0.95671417888391 | -2.57570662073239 |
| H | -0.89697277516425 | 1.70232333870712 | -1.26377362532855 |

| | | | |
|---|---|---|---|
| C | 4.83073482488029 | -1.58820526747500 | -2.08215626289133 |
| C | 4.59831226508046 | -0.27615538245626 | -1.66368417879465 |
| C | 3.34310183836031 | 0.05736235344834 | -1.16878666712442 |
| N | 2.34169390892985 | -0.84107413896800 | -1.07789575633845 |
| C | 2.56519291608602 | -2.10661694533786 | -1.48217904076504 |
| C | 3.79497803159475 | -2.51760834607026 | -1.98923571401871 |
| H | 5.37771950528773 | 0.48283925621440 | -1.71843398445993 |
| H | 3.10617898192879 | 1.06626366937618 | -0.82966213875562 |
| H | 1.71934163279438 | -2.78744749054736 | -1.38618826392130 |
| H | 3.93104514475196 | -3.55149243619747 | -2.30424796360025 |
| H | 5.80515404256358 | -1.88026976179829 | -2.47502945552267 |

al-pyr-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 0.27929847308456 | -1.00623921155227 | -0.44709088869471 |
| C | -0.62990608345197 | -2.76608144750598 | -0.63972276178267 |
| H | -0.69660824622899 | -3.12349337201234 | -1.68140679530165 |
| H | -0.17302814233134 | -3.57120639755353 | -0.03941098402050 |
| H | -1.67113937386816 | -2.67989201682107 | -0.28448438184884 |
| C | 0.66169145969195 | -0.44551321891435 | 1.43758524011760 |
| H | -0.01958910629139 | 0.34966640719539 | 1.78786811723611 |
| H | 0.52088311735905 | -1.29022174147360 | 2.13187788268265 |
| H | 1.69490412126778 | -0.09392667495694 | 1.60415934052741 |
| C | -0.34784111213397 | 0.41667392277869 | -1.71180874910448 |
| H | 0.46616761847581 | 0.97451358324026 | -2.20735257742801 |
| H | -0.94308924121389 | -0.02399556858257 | -2.52839118693561 |
| H | -1.00602507560499 | 1.15587129278040 | -1.22257043224156 |
| C | 4.74201020853900 | -1.86188054965482 | -2.11558418456456 |
| C | 4.38186858138661 | -0.59985039425267 | -1.63983900135768 |
| C | 3.08909558303559 | -0.39736738696255 | -1.16840014841543 |
| N | 2.16992098531653 | -1.38800643837331 | -1.15799660327210 |
| C | 2.51637400239830 | -2.60709901764831 | -1.61724041366213 |
| C | 3.79100410852082 | -2.88251925372482 | -2.10317314410671 |
| H | 5.09093518726256 | 0.22706050938080 | -1.63067047968100 |
| H | 2.75985718920009 | 0.57452608260370 | -0.78549852101717 |
| H | 1.73283265199720 | -3.36401412781210 | -1.58310854977043 |
| H | 4.02687626710985 | -3.88276035581028 | -2.46441295020255 |
| O | 1.67865599262095 | 2.35806884208844 | 0.01561799588470 |
| H | 1.40535257737937 | 1.85550560512966 | 0.80531188883928 |
| H | 0.94869258309872 | 2.18811069118960 | -0.60895373514119 |
| H | 5.74927062937984 | -2.04733130477532 | -2.49037635873870 |

al-thf-h2o_vdw.xyz

| | | | |
|---|---|---|---|
| Al | 1.44086568960784 | -0.39096142094909 | -0.82079758244998 |
| C | 0.19032437461874 | -1.88554655124652 | -0.45115738538504 |
| H | -0.19088999220636 | -2.35169745181530 | -1.37465596838266 |
| H | 0.62219355450089 | -2.68960265684313 | 0.16722422756653 |
| H | -0.69241587956188 | -1.51706929519551 | 0.09876901794759 |
| C | 2.58844912649601 | 0.17453806663713 | 0.72083099190403 |
| H | 2.24387553356089 | 1.12650392680547 | 1.16120764389666 |
| H | 2.56910161703177 | -0.55948294756296 | 1.54301858354157 |
| H | 3.65192157672693 | 0.30738331514330 | 0.45412087093414 |
| C | 0.76535111026618 | 1.03510754714703 | -2.04153710017292 |
| H | 1.49330128802956 | 1.42503350946955 | -2.77353319096182 |
| H | -0.08317576939008 | 0.66265555294072 | -2.63870035068610 |
| H | 0.38014799184058 | 1.90181292311541 | -1.47650845916822 |
| H | 3.17649229939225 | -3.33927958421673 | -1.96078820589165 |
| O | 2.79124887962192 | -1.29351816441320 | -1.97044413481506 |

| | | | |
|---|---|---|---|
| C | 3.73297452939760 | -0.48914215510251 | -2.77694084779103 |
| C | 4.98718675338093 | -1.34637400090692 | -2.88525989520486 |
| C | 4.97047715834994 | -2.13803076081017 | -1.56895891102107 |
| C | 3.49193448454165 | -2.45010451852048 | -1.39573826337448 |
| H | 3.23996128517325 | -0.28864699933392 | -3.73523594771489 |
| H | 3.91146629764450 | 0.45858105442902 | -2.24711577332902 |
| H | 5.88695851944324 | -0.72982756169476 | -3.00313380782372 |
| H | 4.92240223317933 | -2.02953501424991 | -3.74480166488045 |
| H | 5.32836064487259 | -1.51401779731766 | -0.73749671273089 |
| H | 5.58202683337132 | -3.04843357303296 | -1.60611881032297 |
| H | 3.16945678375667 | -2.54761255017969 | -0.35223826058617 |
| O | 3.61779181703050 | 2.63681357591380 | -1.25511777997653 |
| H | 3.59102333386355 | 2.26027038871115 | -0.35699570814409 |
| H | 2.69943273345915 | 2.52380002407894 | -1.56315464997664 |

al-thf-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 1.45953083895069 | -0.14237328430111 | -0.79715543594926 |
| C | 0.70347686717827 | -1.97316494122196 | -1.18486019396453 |
| H | 1.32425421138807 | -2.59329470963846 | -1.85351118149789 |
| H | 0.56456301738881 | -2.57586937393026 | -0.26905828816424 |
| H | -0.28222824911527 | -1.91332030252406 | -1.68041674475427 |
| C | 2.21839021880648 | 0.23173888357507 | 1.02374274174676 |
| H | 1.69644114317064 | 1.06012275151629 | 1.53662478433819 |
| H | 2.18276342439094 | -0.63514554560997 | 1.70694808188833 |
| H | 3.27349215866187 | 0.54822900451374 | 0.97736247254308 |
| C | 1.15563179267218 | 1.35091062804332 | -2.07473139229553 |
| H | 2.08487106791088 | 1.88574398274974 | -2.33178764738986 |
| H | 0.69775811685074 | 1.02531485251304 | -3.02411799314060 |
| H | 0.46853753603429 | 2.09488088114102 | -1.64146342544543 |
| H | 3.48806820836766 | -2.36243960334175 | -0.44629351421061 |
| O | 3.36421945381791 | -0.62573874569246 | -1.59865203588733 |
| C | 3.44169135752519 | -0.85344692180464 | -3.04194601284580 |
| C | 4.14764271318369 | -2.19519130996956 | -3.20716078213442 |
| C | 5.05592133871680 | -2.24391168507517 | -1.96960234918841 |
| C | 4.16825492551402 | -1.62309908416140 | -0.89816528534530 |
| H | 2.42078988091143 | -0.83582488339541 | -3.44247407146663 |
| H | 4.01311503758822 | -0.02015626360699 | -3.47717006187077 |
| H | 4.69928074119865 | -2.26047040989360 | -4.15365288708380 |
| H | 3.41637184138891 | -3.01598567997427 | -3.17583853063583 |
| H | 5.95627845839249 | -1.63172551196799 | -2.12699117649430 |
| H | 5.37310819136809 | -3.26075544270562 | -1.70516719105512 |
| H | 4.71447639252771 | -1.10419182103865 | -0.10161010092136 |
| O | -0.66435837767411 | 0.23003267048565 | 0.22796777458286 |
| H | -0.35866853133541 | 0.29601449028317 | 1.15079912805642 |
| H | -1.04416493977999 | -0.66341091096768 | 0.14712538258572 |

h2o.xyz

| | | | |
|---|---|---|---|
| O | -0.227769 | 0.904287 | 0.140909 |
| H | -0.435407 | 1.001352 | 1.084896 |
| H | -0.610091 | 0.045272 | -0.103153 |

pyr.xyz

| | | | |
|---|---|---|---|
| C | -1.62297215784914 | -1.66990029248705 | -2.55113003112494 |
| C | -1.62297215311471 | -0.47055523033601 | -1.83791220415124 |
| C | -1.62297215661014 | -0.52525608944279 | -0.44137154086042 |
| N | -1.62297215750516 | -1.66990028629110 | 0.25912707492482 |
| C | -1.62297215260413 | -2.81454448240815 | -0.44137154524664 |
| C | -1.62297215594778 | -2.86924534957697 | -1.83791220819506 |

| | | | |
|---|---|---|---|
| H | -1.62297214695728 | 0.49218024446653 | -2.35043356019766 |
| H | -1.62297215175362 | 0.39725912067585 | 0.14672786090133 |
| H | -1.62297214615343 | -3.73705969483110 | 0.14672785308480 |
| H | -1.62297215286321 | -3.83198082320320 | -2.35043356508983 |
| H | -1.62297215164141 | -1.66990029556600 | -3.64220438904515 |

thf.xyz

| | | | |
|---|---|---|---|
| H | 3.78732282506446 | -2.83574194548107 | -0.70905186973931 |
| O | 3.22074635657353 | -1.13527162094943 | -1.77562420444043 |
| C | 3.52489722717771 | -1.15106083168167 | -3.18439478992847 |
| C | 4.61235331969951 | -2.21050899431104 | -3.38004510882572 |
| C | 5.36765934955646 | -2.12802306825697 | -2.04550139414438 |
| C | 4.22378258595056 | -1.88168194171786 | -1.05855156931426 |
| H | 2.59978871936030 | -1.37123801508940 | -3.73846100409702 |
| H | 3.88354549822507 | -0.15089758125708 | -3.49091100499984 |
| H | 5.24696446730858 | -2.01117691419282 | -4.25374935968820 |
| H | 4.16140716539077 | -3.20689730125945 | -3.50284753123238 |
| H | 6.06263951843143 | -1.27454089886364 | -2.05143549491147 |
| H | 5.94171949298823 | -3.03469952530370 | -1.81242091632509 |
| H | 4.52953599227337 | -1.29799466563586 | -0.17701815535341 |

CPCM_alme3.xyz

| | | | |
|---|---|---|---|
| Al | -0.24496241511147 | 0.00030799965768 | 0.02097499982486 |
| C | -0.83285419438780 | -1.81871935386619 | -0.45703111419157 |
| H | -0.18829823998484 | -2.23594365248080 | -1.24922955655571 |
| H | -0.81657732956765 | -2.51838568613125 | 0.39214325114695 |
| H | -1.85834101589338 | -1.80296707507199 | -0.86269784982588 |
| C | 0.33320862454156 | 0.39654984502782 | 1.86263412215975 |
| H | -0.49377192927478 | 0.21961354392133 | 2.57110097851995 |
| H | 1.15527764920996 | -0.27284472628651 | 2.16670390018276 |
| H | 0.67466043271718 | 1.43384690025954 | 1.99785726258429 |
| C | -0.23299457450512 | 1.42263781418890 | -1.34252726553743 |
| H | 0.79509873301559 | 1.78808709635153 | -1.50616257363001 |
| H | -0.63151557054741 | 1.09698632096536 | -2.31513109965506 |
| H | -0.82468821221182 | 2.29083397246458 | -1.00728542602291 |

CPCM_al-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 1.24714308308158 | -0.16606887953911 | -0.66681905552849 |
| C | 0.90961421460551 | -2.03940568739062 | -1.25088514340436 |
| H | 1.76653131819981 | -2.43314668639010 | -1.82251170557758 |
| H | 0.74619186571652 | -2.72096777548840 | -0.39911143778531 |
| H | 0.02552720563955 | -2.11696229016020 | -1.90689590660981 |
| C | 2.47457719240906 | 0.10170852298012 | 0.87767490408584 |
| H | 2.39376526990716 | 1.11721317847695 | 1.30193456855805 |
| H | 2.28205970912077 | -0.61196089595399 | 1.69667345489721 |
| H | 3.52480060218466 | -0.03368529366151 | 0.57038635060353 |
| C | 1.33545294402325 | 1.19630780875584 | -2.11188728124390 |
| H | 2.26035837222389 | 1.07334963099866 | -2.70127786440891 |
| H | 0.49244400259571 | 1.11715918841513 | -2.81881480640853 |
| H | 1.33734022054257 | 2.22736929570492 | -1.72065994851169 |
| O | -0.50707670158963 | 0.29700416099091 | 0.22321023897522 |
| H | -0.47613877401631 | 0.37567833784290 | 1.19579800465380 |
| H | -1.27537822664413 | -0.26915808658153 | 0.01813109570495 |

CPCM_al-thf.xyz

| | | | |
|---|---|---|---|
| Al | 1.77841372599292 | -0.48024466850961 | -0.95487412205332 |
| C | 0.80503214379495 | -2.19362674326479 | -1.26990733189163 |
| H | 0.76845181671578 | -2.46884003137493 | -2.33787651321513 |

| | | | |
|---|---|---|---|
| H | 1.25846266165445 | -3.04292964832444 | -0.73118459336856 |
| H | -0.24171284036086 | -2.12364054738361 | -0.92624045955310 |
| C | 2.25140339770295 | -0.08179693522600 | 0.93836616052922 |
| H | 1.35132795553258 | 0.22435132946162 | 1.49976349794662 |
| H | 2.67597984606460 | -0.94812888073550 | 1.47232733597245 |
| H | 2.97610816468480 | 0.74534275737424 | 1.02608059570989 |
| C | 1.19480789329848 | 1.07065643563983 | -2.06059822643918 |
| H | 1.91895721495350 | 1.90228617879683 | -2.02793200362011 |
| H | 1.03897597110208 | 0.81388927725672 | -3.12165062125150 |
| H | 0.23518323873592 | 1.46979559346814 | -1.68831397219698 |
| H | 3.86087981535076 | -2.55812874390306 | -0.53194928445376 |
| O | 3.54741092000293 | -0.86811381611888 | -1.72797988044186 |
| C | 3.66564944177109 | -1.09042307906553 | -3.18433666046715 |
| C | 4.44850416674421 | -2.38607800458322 | -3.31656065941040 |
| C | 5.37654775351881 | -2.33760355948410 | -2.09378735728264 |
| C | 4.46754799563384 | -1.77663472355078 | -1.01140965017841 |
| H | 2.65143167967764 | -1.13048715962783 | -3.59818716632597 |
| H | 4.20303679964210 | -0.22644999898856 | -3.59856580050100 |
| H | 4.99290242793049 | -2.43798355184603 | -4.26749574784757 |
| H | 3.77052610438182 | -3.24924913053795 | -3.25126757995349 |
| H | 6.22206230580824 | -1.65903116485715 | -2.27703079332872 |
| H | 5.77308474051187 | -3.32225151114253 | -1.81696091704313 |
| H | 4.97846065915401 | -1.17949467347285 | -0.24830024933454 |

CPCM_al-pyr.xyz

| | | | |
|---|---|---|---|
| Al | 0.55845298267857 | -0.25116727516361 | -0.31440810362767 |
| C | -0.58675589953181 | -1.87895765433338 | -0.46820349874527 |
| H | -0.71528276759068 | -2.22020206711425 | -1.50967794302952 |
| H | -0.20668133024589 | -2.73581664112672 | 0.11379435027140 |
| H | -1.59769918619204 | -1.66104083896401 | -0.08213843991559 |
| C | 1.07015296212993 | 0.27469732741867 | 1.54354352134509 |
| H | 0.20137306642589 | 0.65877207056535 | 2.10518476403262 |
| H | 1.47461830511511 | -0.57547148299226 | 2.11861026969864 |
| H | 1.83504275368940 | 1.06986619433474 | 1.55695704638065 |
| C | 0.06676088960190 | 1.26033762815884 | -1.52441556568334 |
| H | 0.80110753103455 | 2.08327955876337 | -1.49744431040210 |
| H | -0.02093925030528 | 0.93654248436612 | -2.57543748405744 |
| H | -0.90737678098629 | 1.69356065784416 | -1.23938021683923 |
| C | 4.84244660232686 | -1.59082786922185 | -2.08772291044284 |
| C | 4.61887644325510 | -0.28553683081762 | -1.64278047071210 |
| C | 3.36450316065117 | 0.04900511505986 | -1.14717366178871 |
| N | 2.35351454789325 | -0.84488056184213 | -1.08063680578488 |
| C | 2.56963257434939 | -2.10552002140373 | -1.51125612384227 |
| C | 3.79858447977017 | -2.51441357983629 | -2.02015408138448 |
| H | 5.40441414908529 | 0.46825119561138 | -1.67713526725166 |
| H | 3.14101987490867 | 1.05415534578743 | -0.78829791980480 |
| H | 1.72314178762461 | -2.78754945756320 | -1.43702869414160 |
| H | 3.92740527275411 | -3.54261506744581 | -2.35590700734790 |
| H | 5.81662315555797 | -1.88271336408507 | -2.48115746092699 |

CPCM_al-pyr-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 0.29646444292999 | -1.04230336578137 | -0.46409096455192 |
| C | -0.67500136622216 | -2.77473789076089 | -0.64494830556668 |
| H | -0.73369089177984 | -3.13189366635663 | -1.68728501117660 |
| H | -0.23415940811287 | -3.58772716109690 | -0.04330929785541 |
| H | -1.71544714358867 | -2.65462887618492 | -0.29566306855180 |
| C | 0.69021589258668 | -0.48799641791137 | 1.41879009333348 |

| | | | |
|---|---|---|---|
| H | -0.12296356017973 | 0.12240760053596 | 1.84749427850211 |
| H | 0.81118332466897 | -1.36498448924292 | 2.07708833282658 |
| H | 1.62248556984161 | 0.09591720024927 | 1.51156075761658 |
| C | -0.32464677529822 | 0.40443910225364 | -1.70339912763321 |
| H | 0.50175546549975 | 1.03136117849658 | -2.08162658220551 |
| H | -0.82082666670465 | -0.01602033096774 | -2.59431781102938 |
| H | -1.05562152954108 | 1.07656992809837 | -1.22184042967809 |
| C | 4.74592577976975 | -1.89677236542934 | -2.11058453016361 |
| C | 4.37374487799327 | -0.63226698869186 | -1.64786034876373 |
| C | 3.07675465832462 | -0.43931845971922 | -1.18762478598742 |
| N | 2.16381078348977 | -1.43643084249382 | -1.17393774848661 |
| C | 2.52267191500851 | -2.65803934080181 | -1.62109753429718 |
| C | 3.80302625650709 | -2.92546626598502 | -2.09606364751464 |
| H | 5.07697433374879 | 0.19957077404229 | -1.64096108565361 |
| H | 2.73809945093981 | 0.53042514654218 | -0.81513076637792 |
| H | 1.74949029814344 | -3.42521429082970 | -1.58828065237843 |
| H | 4.04933281196048 | -3.92680771930933 | -2.44702718700967 |
| O | 1.60623671625919 | 2.63215592203282 | 0.07674001725163 |
| H | 1.39478177430448 | 2.06248471897639 | 0.83917809915358 |
| H | 0.92081856425551 | 2.39087013570878 | -0.57390249673470 |
| H | 5.75704938119532 | -2.07699477737328 | -2.47697257906772 |

CPCM_al-thf-h2o_vdw.xyz

| | | | |
|---|---|---|---|
| Al | 1.58164431099869 | -0.36778294961240 | -0.88640526632550 |
| C | 0.24396259198242 | -1.74900213730672 | -0.37624295276825 |
| H | -0.20789683969274 | -2.23685361363765 | -1.25627931881166 |
| H | 0.66268254090967 | -2.54561954643125 | 0.26083212226979 |
| H | -0.58298554811249 | -1.28998108137157 | 0.19288070476207 |
| C | 2.78630227701242 | 0.25450915945922 | 0.58099259230765 |
| H | 2.27294995195179 | 0.96728000637509 | 1.25037875674783 |
| H | 3.12735163401712 | -0.57847691093491 | 1.21863566210693 |
| H | 3.69645840443028 | 0.75165117154815 | 0.20190824693167 |
| C | 0.94315254430746 | 1.01602518620122 | -2.17314009111663 |
| H | 1.75708794436004 | 1.57890506298043 | -2.66164239944410 |
| H | 0.34064536358824 | 0.57133272086094 | -2.98307974266885 |
| H | 0.28992447331195 | 1.75066043179484 | -1.66927758876846 |
| H | 3.07173276447152 | -3.46191860677064 | -2.02136523567644 |
| O | 2.82974870546864 | -1.39153253641733 | -2.00792870640606 |
| C | 3.82911269143024 | -0.65763263214964 | -2.81600094321899 |
| C | 5.00960726266967 | -1.61004629373973 | -2.93637086451453 |
| C | 4.94380730479965 | -2.39671685389343 | -1.61886641531591 |
| C | 3.45032635467142 | -2.60850750895116 | -1.44226433622156 |
| H | 3.34844540584209 | -0.40247878076605 | -3.76677636728492 |
| H | 4.08888785517422 | 0.26067832306655 | -2.27049982352820 |
| H | 5.95324357838928 | -1.06542679611511 | -3.06380947127260 |
| H | 4.87661374971857 | -2.28437998066838 | -3.79442907714661 |
| H | 5.34431689897756 | -1.79633954905260 | -0.78927751343692 |
| H | 5.48834886762912 | -3.34814515477765 | -1.65958428728025 |
| H | 3.12370288665900 | -2.69248651494429 | -0.39946809373527 |
| O | 2.76233261865919 | 3.45009143142323 | -0.60101827962606 |
| H | 2.96240545955200 | 2.75887474854524 | 0.05692253373551 |
| H | 2.08433275482208 | 3.02693608628575 | -1.16008191929326 |

CPCM_al-thf-h2o.xyz

| | | | |
|---|---|---|---|
| Al | 1.45412797672260 | -0.16999429299457 | -0.77226037941452 |
| C | 0.69855728872504 | -1.99169434941613 | -1.18695617323875 |
| H | 1.33065114857515 | -2.59432996704011 | -1.86009761545721 |

| | | | |
|---|---|---|---|
| H | 0.55770944803541 | -2.59284659182737 | -0.27111316654817 |
| H | -0.29151350149504 | -1.92361221321511 | -1.67232987047791 |
| C | 2.25119058538816 | 0.22034967662235 | 1.02983900345917 |
| H | 1.68484407779136 | 0.98826101719998 | 1.58526267364851 |
| H | 2.29031094540143 | -0.67317559690796 | 1.67725816963371 |
| H | 3.28470113175861 | 0.59730208028740 | 0.95066116333124 |
| C | 1.16562517681772 | 1.34677450369469 | -2.04769679579371 |
| H | 2.11287228816779 | 1.81571678436549 | -2.36309498306369 |
| H | 0.64459537562898 | 1.03159158172100 | -2.96845257250461 |
| H | 0.54859978029886 | 2.13885129235823 | -1.59223860403778 |
| H | 3.51938709590808 | -2.37664233989952 | -0.44534936468188 |
| O | 3.34768901026734 | -0.63726480324472 | -1.59461885449928 |
| C | 3.42364746626453 | -0.87228020972321 | -3.04248662534573 |
| C | 4.15396242910781 | -2.19961125865988 | -3.20369618314519 |
| C | 5.07356077495375 | -2.22098507380543 | -1.97439872847034 |
| C | 4.18096707877992 | -1.62115664834018 | -0.89729665620009 |
| H | 2.40053513748096 | -0.87807275714031 | -3.43800450808241 |
| H | 3.98002472560497 | -0.03214235468765 | -3.48285662967615 |
| H | 4.69972400978645 | -2.25566534176551 | -4.15396228207292 |
| H | 3.44018723695497 | -3.03521846148007 | -3.16061156052303 |
| H | 5.95599053263912 | -1.58581403339170 | -2.14070009116823 |
| H | 5.41527398548024 | -3.22933675945696 | -1.70858561741579 |
| H | 4.72196728227108 | -1.09038486270843 | -0.10536436653895 |
| O | -0.63792625765226 | 0.25075105161145 | 0.18115446454196 |
| H | -0.50420743885326 | 0.34906480698347 | 1.14199036047207 |
| H | -1.16354595480996 | -0.56496316513920 | 0.08474985726982 |

TS-AB.xyz

| | | | |
|---|---|---|---|
| Al | 1.63858442665185 | -0.37569748243734 | -0.89125991381017 |
| C | 1.14277133420207 | -2.23096111401324 | -1.51739708834030 |
| H | 1.42728928422988 | -2.40900251650357 | -2.56795273505464 |
| H | 1.63472990376937 | -3.02120832706593 | -0.92443476941269 |
| H | 0.06118659838185 | -2.43185188670172 | -1.45676384660793 |
| C | 2.50834902153411 | -0.09083151418576 | 0.89669666769648 |
| H | 1.95222005896469 | 0.62846695982593 | 1.52103401855702 |
| H | 2.62704001597651 | -1.00871826298316 | 1.49886683263876 |
| H | 3.51910991407884 | 0.33002764198656 | 0.77349863934436 |
| C | 1.51732418418290 | 1.17859967951132 | -2.15247806719383 |
| H | 2.51872066439877 | 1.51051041069027 | -2.46906904023780 |
| H | 0.95051900233306 | 0.97407014746613 | -3.07775992579904 |
| H | 1.04460140129802 | 2.05536836665859 | -1.67706995883590 |
| H | 3.85951344648284 | -2.48835342491821 | -0.51083380761397 |
| O | 3.75855222425520 | -0.80013826350096 | -1.72080803426375 |
| C | 3.88491096659797 | -0.99832522620913 | -3.15408101093071 |
| C | 4.47698074704925 | -2.39263781318905 | -3.32565211130831 |
| C | 5.37968161618944 | -2.50514815565933 | -2.08841663450366 |
| C | 4.55055529195762 | -1.79778928409426 | -1.01784572093028 |
| H | 2.88926468232709 | -0.87667808720166 | -3.59784160374062 |
| H | 4.55190442548629 | -0.21703698272227 | -3.55539908963098 |
| H | 5.02155996238809 | -2.50444819737219 | -4.27242231842567 |
| H | 3.68004705411870 | -3.14930188905635 | -3.28948434462225 |
| H | 6.32870707173083 | -1.97455407427170 | -2.25754950355231 |
| H | 5.61224293961714 | -3.54227807407935 | -1.81402272980899 |
| H | 5.15225957768904 | -1.27918766974757 | -0.26025784356044 |
| C | -2.98956278959952 | -0.04317101126076 | 0.89149867890837 |
| C | -2.67692202032810 | 0.53866039924670 | -0.33724376651496 |
| C | -1.35963043580251 | 0.48793197115058 | -0.78915499418943 |
| N | -0.37517469342227 | -0.09988386952022 | -0.08695761716672 |
| C | -0.67992149358910 | -0.66049593042786 | 1.09751883404651 |
| C | -1.96943277372974 | -0.65505706179329 | 1.62182015012233 |
| H | -4.01072720725206 | -0.02062846333927 | 1.27394409083947 |
| H | -3.43964741556068 | 1.02750144191682 | -0.94288769726955 |

| | | | |
|---|---|---|---|
| H | -1.06177772973164 | 0.92587074553437 | -1.74214050925853 |
| H | 0.15347656805603 | -1.12392416911136 | 1.62684523307573 |
| H | -2.16548161793184 | -1.12299355962176 | 2.58622867635445 |

CPCM-TS-AB.xyz

| | | | |
|---|---|---|---|
| Al | 1.60965603496073 | -0.38818603201236 | -0.87940645533166 |
| C | 1.14555815169072 | -2.24745451473505 | -1.51525385874636 |
| H | 1.35130541834208 | -2.37484906730665 | -2.59174644667359 |
| H | 1.73671828687497 | -3.01923317518636 | -0.99265429977409 |
| H | 0.08441654465894 | -2.50263154986532 | -1.36185147017150 |
| C | 2.49913553354454 | -0.08801162004088 | 0.90082064082069 |
| H | 1.94736390300838 | 0.64547096237349 | 1.51313403725677 |
| H | 2.59296022296168 | -1.00392578415509 | 1.51004589762103 |
| H | 3.52002278991344 | 0.30727832868238 | 0.77253356067502 |
| C | 1.52030385718832 | 1.17748104315649 | -2.13694854121798 |
| H | 2.52692231179615 | 1.48495370513516 | -2.46282677027904 |
| H | 0.93822163728778 | 0.98096531680032 | -3.05430522793612 |
| H | 1.06086735923081 | 2.05713631146098 | -1.65323169538644 |
| H | 3.89185380475013 | -2.50690550179685 | -0.51693484598769 |
| O | 3.75263910302520 | -0.81401729088479 | -1.72405015582453 |
| C | 3.87633645145757 | -1.01673054686513 | -3.16171298487236 |
| C | 4.49479996323743 | -2.39888309534180 | -3.33129807673045 |
| C | 5.40567275522780 | -2.49030875881417 | -2.09843017405482 |
| C | 4.56768279206664 | -1.80105842157860 | -1.02433911260380 |
| H | 2.87628145945895 | -0.91912520235288 | -3.60221448310592 |
| H | 4.52705227175915 | -0.22534827279565 | -3.56864614643858 |
| H | 5.03825434715624 | -2.49865579086147 | -4.27976376360626 |
| H | 3.71399895180002 | -3.17254017520129 | -3.29168638514966 |
| H | 6.34064165081443 | -1.93742538634378 | -2.27291457777701 |
| H | 5.66021329270676 | -3.52185191882716 | -1.82305373787852 |
| H | 5.16452333775917 | -1.27321270785813 | -0.26901471237809 |
| C | -3.00269625963879 | -0.01622323211815 | 0.89154333607122 |
| C | -2.68109542828737 | 0.56449794983845 | -0.33609895506705 |
| C | -1.36463924540888 | 0.49740282139924 | -0.78763319774607 |
| N | -0.38614168978679 | -0.10568765494054 | -0.08573521368240 |
| C | -0.70159203009448 | -0.66731743169661 | 1.09832604918952 |
| C | -1.99136434508842 | -0.64509785735861 | 1.62102918536674 |
| H | -4.02364821701536 | 0.01936646612173 | 1.27336224363327 |
| H | -3.43607475754598 | 1.06504262044378 | -0.94180287310603 |
| H | -1.06758653088906 | 0.93454585857319 | -1.74090171795518 |
| H | 0.11940534777220 | -1.14867526557799 | 1.63091909824633 |
| H | -2.19414486969512 | -1.11407967646989 | 2.58350896960060 |

TS-BC.xyz

| | | | |
|---|---|---|---|
| Al | 1.60896330869997 | -0.38578898914689 | -0.95347742515357 |
| C | 0.79929556312858 | -2.16885243175222 | -1.33496797380658 |
| H | 1.00069875630275 | -2.52895491840161 | -2.35879839432479 |
| H | 1.12770083916549 | -2.96198885646093 | -0.64294652118441 |
| H | -0.29963203174317 | -2.12151274894362 | -1.24771465366317 |
| C | 2.00924087939103 | 0.02747094269308 | 0.95278397174109 |
| H | 1.23955020833259 | 0.71516165947070 | 1.34538764811338 |
| H | 2.01559217903796 | -0.85229363310279 | 1.61528744381702 |
| H | 2.96964902333590 | 0.55229515532143 | 1.08634304288887 |
| C | 1.00261676139934 | 1.12983713790584 | -2.08045823510821 |
| H | 1.79503599349411 | 1.88196711154832 | -2.23095998293607 |
| H | 0.63498145005131 | 0.83558509273427 | -3.07697705723535 |
| H | 0.17420020385709 | 1.66464743844733 | -1.58830220464773 |
| H | 3.65497537961265 | -2.36716815310811 | -0.45173596016252 |
| O | 3.45957931846444 | -0.67690222963949 | -1.66126541542033 |
| C | 3.60755957623615 | -0.88483345781886 | -3.10894659893212 |
| C | 4.30175362284458 | -2.23171330495068 | -3.24107210857282 |
| C | 5.20368015647184 | -2.25630675114862 | -1.99753466131517 |
| C | 4.31324765158146 | -1.62886505856464 | -0.93253711643580 |
| H | 2.60563993466420 | -0.84277083747596 | -3.55211973766985 |
| H | 4.21426087297545 | -0.05419732321679 | -3.49787639369147 |

| | | | |
|---|---|---|---|
| H | 4.86047337612868 | -2.31967171409170 | -4.18126651359949 |
| H | 3.56210040431695 | -3.04377880329074 | -3.19567822125225 |
| H | 6.10273534610140 | -1.64432334778753 | -2.16105501392805 |
| H | 5.52320482639864 | -3.26781547534023 | -1.71737474966492 |
| H | 4.84927069291863 | -1.06057092965507 | -0.16393185086692 |
| O | -1.20193431317555 | 2.10175780951980 | 1.23134282335381 |
| H | -0.53262828081918 | 1.91325730581571 | 1.90977319314486 |
| H | -1.18480331417341 | 1.30251288744003 | 0.67842208851265 |

CPCM-TS-BC.xyz

| | | | |
|---|---|---|---|
| Al | 1.55011581655656 | -0.54355687248802 | -0.98542673354651 |
| C | 0.80377512410014 | -2.34027878136422 | -1.42545217508791 |
| H | 0.90626775399782 | -2.58493085252774 | -2.49721255507912 |
| H | 1.28472924399018 | -3.15494185598875 | -0.85763926532316 |
| H | -0.27418067454907 | -2.38512216631416 | -1.19241011983886 |
| C | 1.85596183703957 | -0.14391659569269 | 0.94514857881994 |
| H | 1.15414004830086 | 0.63521459288295 | 1.28604986635215 |
| H | 1.72033295186124 | -1.01583177523525 | 1.59944027827101 |
| H | 2.86611745552270 | 0.24835671201037 | 1.13381123506520 |
| C | 0.87669258572950 | 0.97653539555760 | -2.08616651830963 |
| H | 1.64134960120307 | 1.75896167283825 | -2.22980672169186 |
| H | 0.52934784282008 | 0.67214856319248 | -3.08735825299613 |
| H | 0.02176688283306 | 1.46292549575478 | -1.58546279658173 |
| H | 3.70269697725661 | -2.41490128964913 | -0.46377226521528 |
| O | 3.40440768992867 | -0.71197235630919 | -1.64166390620956 |
| C | 3.62167661730031 | -0.85542628998476 | -3.09756364596601 |
| C | 4.38496633093942 | -2.15964945484724 | -3.24676985095881 |
| C | 5.26018526853015 | -2.16722041293228 | -1.98492006159510 |
| C | 4.31741155030226 | -1.62456651846267 | -0.91812257318353 |
| H | 2.63741356787436 | -0.84473349043386 | -3.57985941114978 |
| H | 4.20677551120458 | 0.01629557923802 | -3.42528105406041 |
| H | 4.96958037988208 | -2.18900097713423 | -4.17567947665293 |
| H | 3.68820746938037 | -3.01062387050874 | -3.23894815385963 |
| H | 6.12411278354931 | -1.49885202267636 | -2.11290829457384 |
| H | 5.62801413209461 | -3.16729932354459 | -1.72506846968828 |
| H | 4.80648413400907 | -1.03532092764010 | -0.13481588643343 |
| O | -0.91819804695207 | 2.66070879087670 | 1.31788584006786 |
| H | -0.28669337413592 | 2.41916577077455 | 2.01206448114197 |
| H | -1.06644907556972 | 1.82401683760833 | 0.84025133028344 |

CPCM_h2o.xyz

| | | | |
|---|---|---|---|
| O | -0.22610687197980 | 0.90643649382326 | 0.13894242598982 |
| H | -0.43642460568280 | 0.99925155482347 | 1.08460157873080 |
| H | -0.61073552233740 | 0.04522295135328 | -0.10089200472061 |

CPCM_pyr.xyz

| | | | |
|---|---|---|---|
| C | -1.62297215312730 | -1.66990029275099 | -2.55072978277013 |
| C | -1.62297215504394 | -0.46957653282707 | -1.83754927163958 |
| C | -1.62297215511364 | -0.52202162312484 | -0.44129240471601 |
| N | -1.62297215540864 | -1.66990028436861 | 0.26070154156017 |
| C | -1.62297215149138 | -2.81777894437676 | -0.44129241097907 |
| C | -1.62297215470919 | -2.87022405312174 | -1.83754927914435 |
| H | -1.62297215259180 | 0.49296131827272 | -2.35007247029399 |
| H | -1.62297215243166 | 0.40139823429264 | 0.14472100062427 |
| H | -1.62297214635151 | -3.74119880280011 | 0.14472098767270 |
| H | -1.62297216049446 | -3.83276190393626 | -2.35007247787766 |
| H | -1.62297214623649 | -1.66990029425898 | -3.64177168743633 |

CPCM_thf.xyz

| | | | |
|---|---|---|---|
| H | 3.79051458983044 | -2.83936815027173 | -0.71151140857235 |
| O | 3.21669859420692 | -1.13424831384407 | -1.77397415024713 |
| C | 3.52580654170814 | -1.15072302457176 | -3.18968467952277 |
| C | 4.61008984888078 | -2.21169834401545 | -3.37878987835408 |

| | | | |
|---|---|---|---|
| C | 5.36709748785925 | -2.12525904824772 | -2.04542237215915 |
| C | 4.22722101288532 | -1.88456611033359 | -1.05551788594756 |
| H | 2.60131280314164 | -1.36903774481871 | -3.74485189600713 |
| H | 3.88918418085180 | -0.15183658746931 | -3.49132041540296 |
| H | 5.24436804780124 | -2.01249597087019 | -4.25247907139902 |
| H | 4.15752947989933 | -3.20772650599998 | -3.49785634525199 |
| H | 6.05914964568999 | -1.26950880089267 | -2.05263824752010 |
| H | 5.94105626508958 | -3.03170582109975 | -1.81225197258890 |
| H | 4.53233402015554 | -1.30155888156506 | -0.17371408002683 |

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