**Electronic Supporting Information**

# Ring-opening of cyclic ethers by aluminum hydridotriphenylborate

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## General remarks

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Prior to use, the glassware were dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. ($Me_3$TACD)H (LH) was synthesized following a literature procedure.[S1] $AlH_3(NMe_2Et)$ (0.5 M in toluene) and pinacolborane (HBpin) were purchased from Sigma-Aldrich and used as received. $BPh_3$ (95%) was purchased from abcr and purified by sublimation. Tetrahydropyran (THP) was purchased from Sigma-Aldrich and dried, distilled, and degassed prior storing over molecular sieves inside the glove box. NMR measurements were performed on a Bruker DRX 400 at ambient temperature unless otherwise mentioned. The chemical shifts ($\delta$ ppm) in the $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane.[S2] Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), quint (quintet), sept (septet), br (broad). IR spectra were measured as KBr pellets using an AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra: w (weak), m (medium), s (strong), br. (broad). Elemental analyses were performed on an *elementar vario EL* machine.

## Synthetic procedures and spectroscopic data for 1-4

### [(L)$AlH_2$] (1) and [(L)$AlD_2$] (1-$d_2$)

A 0.5 M solution of $AlH_3(NMe_2Et)$ (2 mL) was added dropwise with a syringe to a solution of LH (0.214 g, 0.998 mmol) in 2 mL of toluene at room temperature. The solution became turbid while mixing and precipitation of a colorless solid was complete within 15 min. The solid was isolated by filtration and washed with *n*-pentane (3×5 mL). Drying the solid under

vacuum afforded analytically pure [(L)$AlH_2$] (0.184 g, 0.759 mmol, 76% yield) as a colorless powder. $^1$H NMR (400 MHz, bromobenzene-$d_5$): δ 5.00-2.90 (br, sext, $^1J_{AlH}$ = 172 Hz, 2 H, Al$H_2$), 3.13-3.06 (m, 2 H, C$H_2$), 2.88-2.83 (m, 2 H, C$H_2$), 2.77-2.72 (m, 2 H, $CH_2$), 2.65-2.59 (m, 2 H, C$H_2$), 2.57-2.52 (m, 2 H, C$H_2$), 2.50-2.47 (m, 4 H, C$H_2$), 2.38-2.28 (m, 2 H, C$H_2$), 2.31 (s, 3 H, C$H_3$), 2.11 (s, 6 H, C$H_3$). $^{13}$C{$^1$H} NMR (100 MHz, bromobenzene-$d_5$): δ 59.5, 55.5, 53.0, 44.9, 43.6, 41.6. $^{27}$Al NMR (104 MHz, bromobenzene-$d_5$): $\delta$ 100.4 (quint, $^1J_{AlH}$ = 172 Hz). IR (KBr, cm$^{-1}$): 1804 (s, $\nu_{AlH}$), 1664 (s, br, $\nu_{AlH}$). Anal. Calcd. for $C_{11}H_{27}N_4Al$: C, 52.52; H, 11.23; N, 23.12. Found: C, 52.02; H, 11.16; N, 22.80. [(L)$AlD_2$] (**1-*d*$_2$**) was synthesized in an analogous fashion using $AlD_3$($NMe_2Et$). $^{27}$Al NMR (104 MHz, bromobenzene-$d_5$): $\delta$ 100.0 (s). IR (KBr, cm$^{-1}$): 1301 (s, $\nu_{AlD}$), 1218 (s, $\nu_{AlD}$).

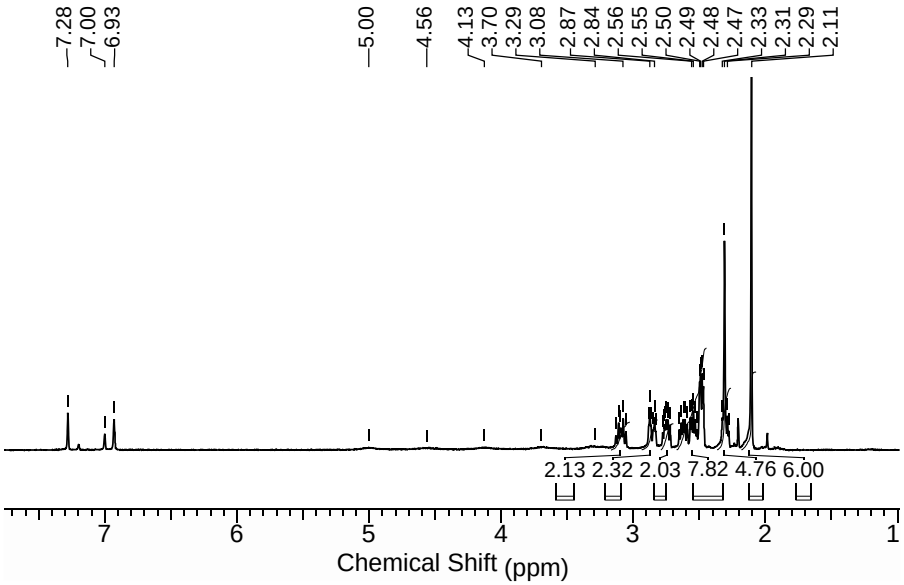


**Figure S1**. $^1$H NMR spectrum of [(L)$AlH_2$] (**1**) in bromobenzene-$d_5$.

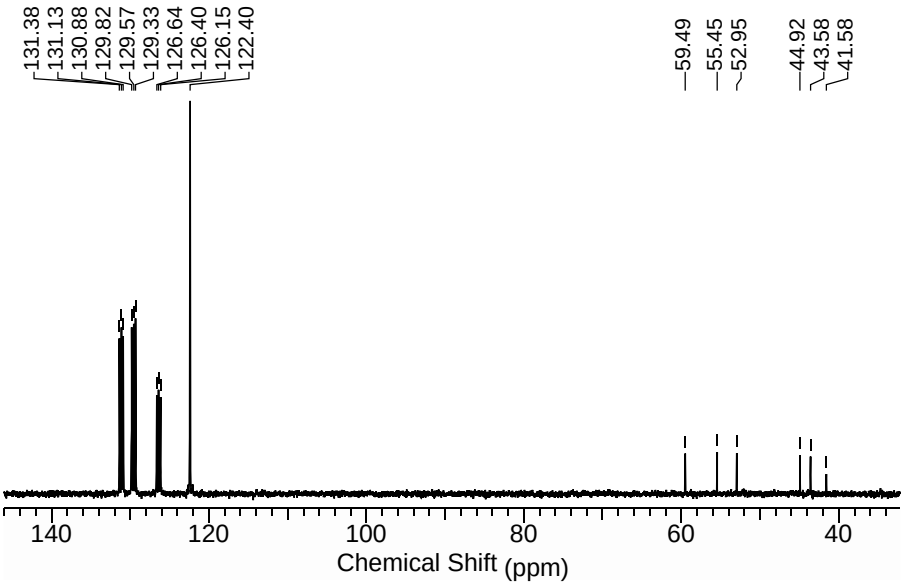


**Figure S2**. $^{13}$C{$^1$H} NMR spectrum of [(L)$AlH_2$] (**1**) in bromobenzene-$d_5$.

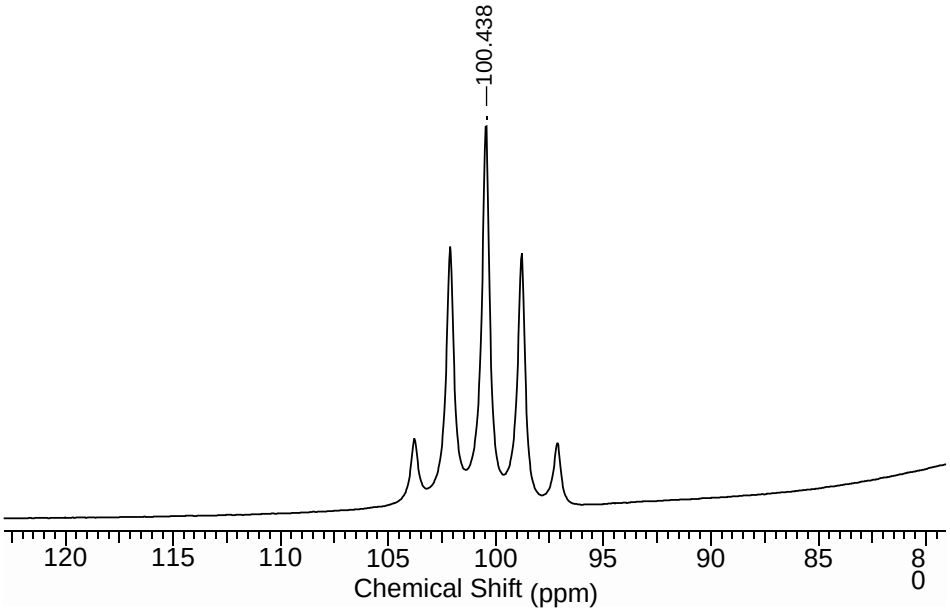


**Figure S3**. $^{27}$Al NMR spectrum of [(L)AlH$_2$] (**1**) in bromobenzene-$d_5$.

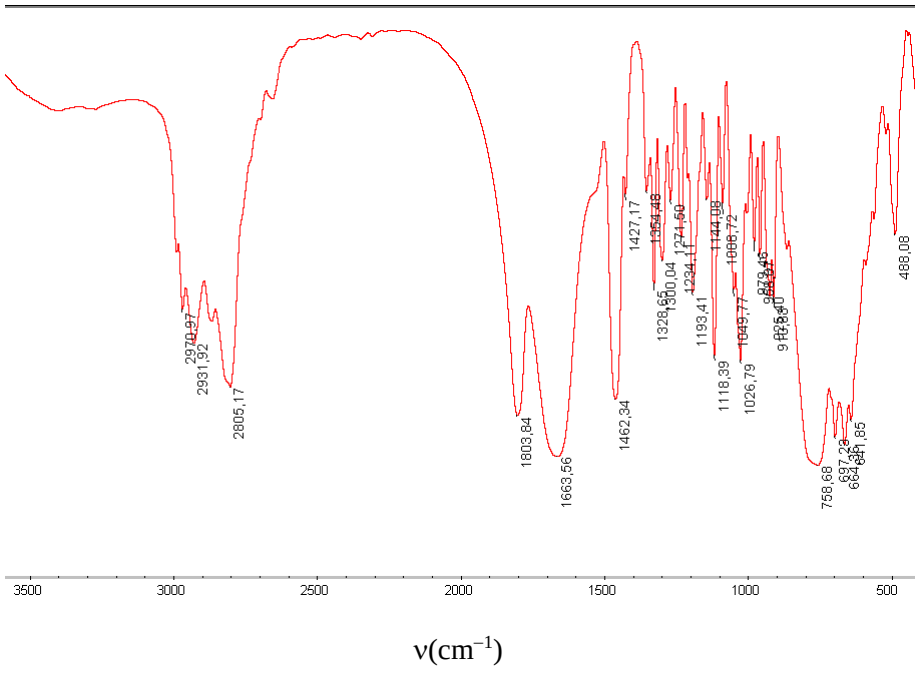


**Figure S4**. Solid-state IR (KBr pellet) spectrum of [(L)AlH$_2$] (**1**).

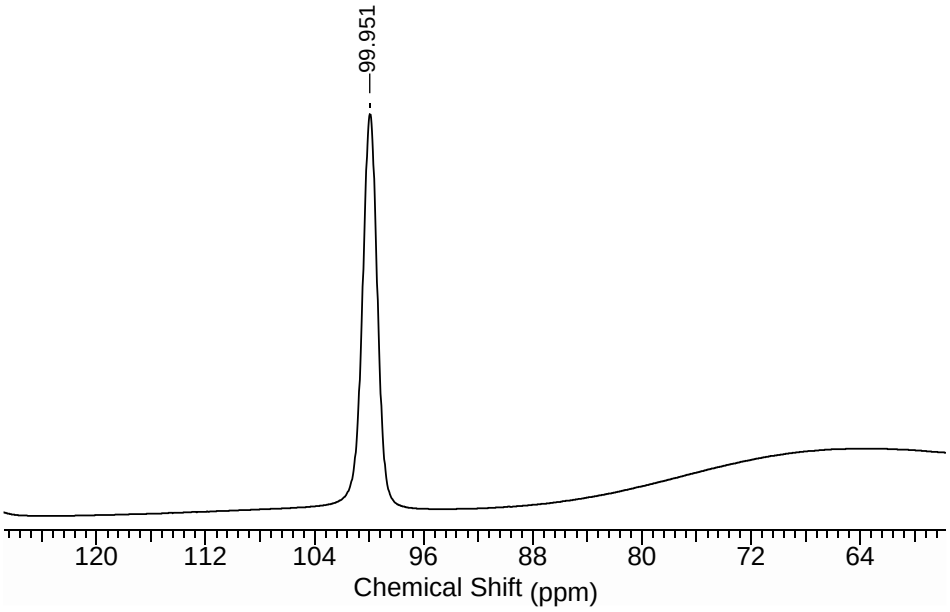


**Figure S5**. $^{27}$Al NMR spectrum of [(L)AlD$_2$] (**1-*d*$_2$**) in bromobenzene-$d_5$.

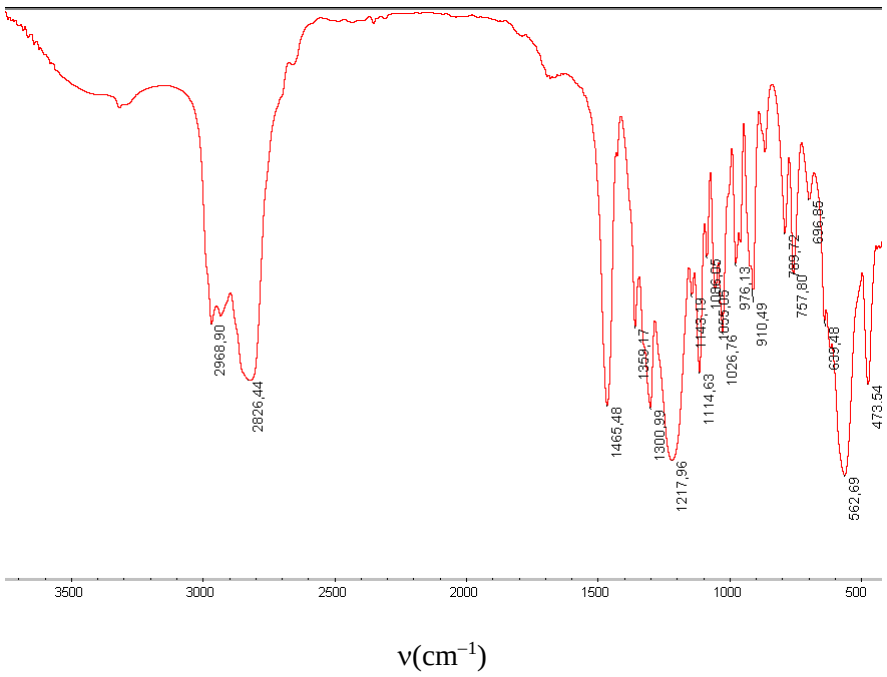


**Figure S6**. Solid-state IR (KBr pellet) spectrum of [(L)AlD$_2$] (**1-*d*$_2$**).

## [(L)Al(O*n*Bu)][HBPh$_3$] (2)

A solution of **1** (0.050 g, 0.206 mmol) and BPh$_3$ (0.100 g, 0.413 mmol) in 3 mL of THF was stirred for 30 min at room temperature. Removing all the volatiles under reduced pressure gave a colorless solid, which was recrystallized by slow diffusion of *n*-pentane into a concentrated THF solution at −30°C. Repeating the purification procedure three times followed by drying the solid under vacuum gave analytically pure [(L)Al(O*n*Bu)][HBPh$_3$] (**2**, 0.033 g, 0.117 mmol, 28% yield) as a colorless powder. Single crystals for X-ray diffraction were grown from THF/*n*-pentane. $^1$H NMR (400 MHz, THF-$d_8$): δ 7.38 (m, 6 H, *o*-aryl), 7.01 (m, 6 H, *m*-aryl), 6.90 (m, 3 H, *p*-aryl), 3.74 (t, 2 H, $^3J_{HH}$ = 6.5 Hz, C*H*$_2$), 3.48 (br, s, 1 H,

*H*B), 2.96-2.90 (m, 2 H, C$H_2$), 2.81-2.44 (m, 12 H, C$H_2$), 2.43 (s, 6 H, C$H_3$), 2.32 (s, 3H, C$H_3$), 1.49-1.42 (m, 2 H, C$H_2$), 1.39-1.26 (m., 2 H, C$H_2$), 0.90 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, C$H_3$). $^{13}C\{^1H\}$ NMR (THF-$d_8$, 100 MHz): δ 137.2, 126.9, 124.5, 64.0, 60.8, 55.5, 52.5, 45.7, 45.4, 43.3, 38.4, 20.2, 14.6. $^{11}B$ NMR (128 MHz, THF-$d_8$): $\delta$ −7.9 (d, $^1J_{BH}$ = 78 Hz). $^{27}Al$ NMR (104 MHz, THF-$d_8$): no resonance was observed. IR (KBr, cm$^{-1}$): 2019-2008 (multiple bands, $\nu_{BH}$). Anal. Calcd. for $C_{33}H_{50}BN_4OAl$: C, 71.21; H, 9.06; N, 10.07. Found: C, 70.88; H, 9.66; N, 10.40.

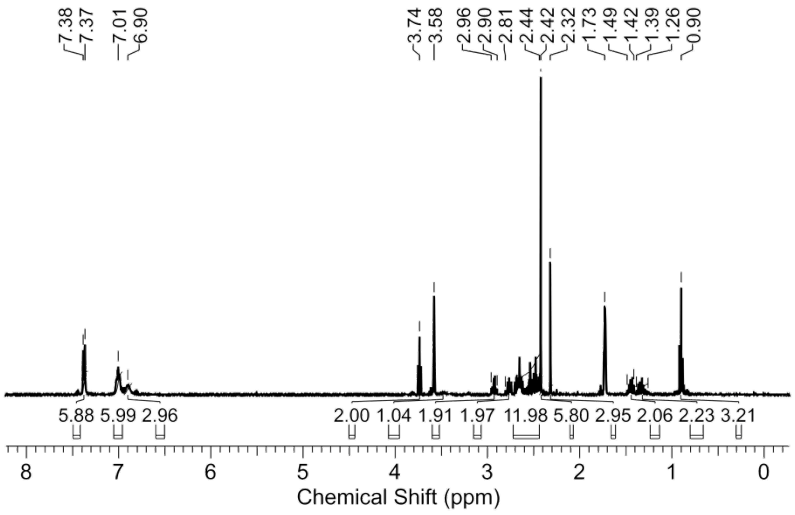


**Figure S7**. $^1H$ NMR spectrum of [(L)Al(O*n*Bu)][HBPh$_3$] (**2**) in THF-$d_8$.

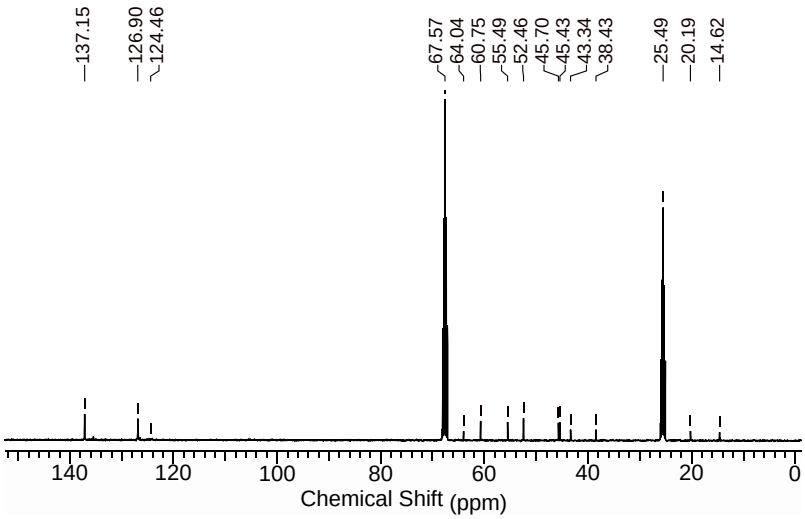


**Figure S8**. $^{13}C\{^1H\}$ NMR spectrum of [(L)Al(O*n*Bu)][HBPh$_3$] (**2**) in THF-$d_8$.

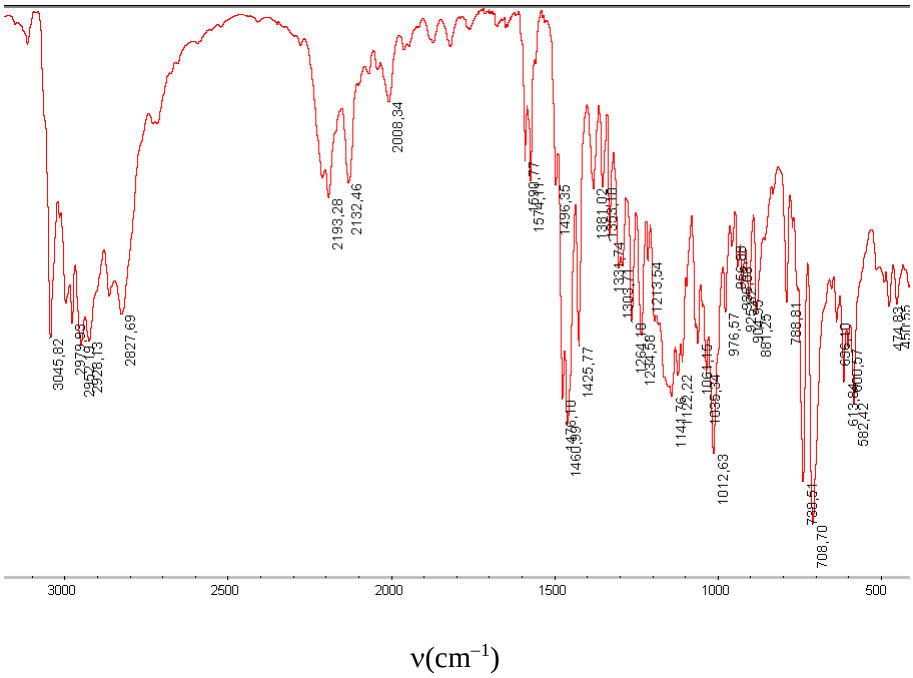


**Figure S9**. Solid-state IR spectrum (KBr pellet) of [(L)Al(O*n*Bu)][HBPh$_3$] (**2**).

## [(L)Al(O*n*Pent)][HBPh$_3$] (3)

A solution of **1** (0.050 g, 0.206 mmol) and BPh$_3$ (0.100 g, 0.413 mmol) in 3 mL of THP was stirred for 12 h at room temperature. Removing all the volatiles under reduced pressure gave a white sticky residue, which was purified by slow precipitation by diffusion of *n*-pentane into a concentrated THF solution at −30 °C. Repeating the purification procedure three times followed by drying under vacuum gave [(L)Al(O*n*Pent)][HBPh$_3$] (**3**, 0.047 g, 0.082 mmol, 40% yield) as a sticky colorless solid. $^1$H NMR (400 MHz, THF-$d_8$): δ 7.38 (m, 6 H, *o*-aryl), 6.97 (m, 6 H, *m*-aryl), 6.80 (m, 3 H, *p*-aryl), 3.69 (m, 2 H, C$H_2$), 3.48 (br s, 1 H, *H*B), 2.89-2.83 (m, 2 H, C$H_2$), 2.64-2.42 (m, 10 H, C$H_2$), 2.38-2.32 (m, 2 H, C$H_2$), 2.29 (s, 6 H, C$H_3$), 2.29-2.23 (m, 2 H, C$H_2$), 2.16 (s, 3 H, C$H_3$), 1.48-1.26 (m, 6 H, C$H_2$), 0.91 (m, 3 H, C$H_3$). $^{13}$C{$^1$H} NMR (THF-$d_8$, 100 MHz): δ 164.5, 136.8, 126.7, 122.9, 64.3, 60.6, 55.4, 52.2, 45.6, 45.4, 43.3, 38.4, 29,3, 20.2, 14.7. $^{11}$B NMR (128 MHz, THF-$d_8$): $\delta$ –7.9 (d, $^1J_{BH}$ = 78 Hz). $^{27}$Al NMR (104 MHz, THF-$d_8$): no resonance was observed. IR (KBr, cm$^{-1}$): 2203 (br, $\nu_{BH}$). Anal. Calcd. for $C_{34}H_{52}BN_4OAl$: C, 71.57; H, 9.19; N, 9.82. Found: C, 70.90; H, 9.47; N, 9.39.

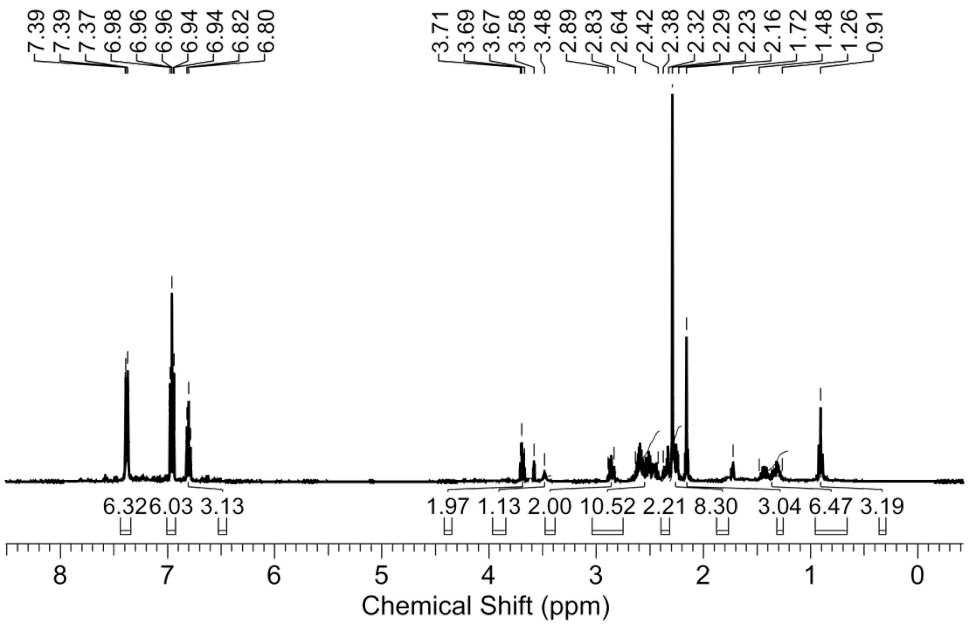


**Figure S10**. $^{1}$H NMR spectrum of [(L)Al(O*n*Pent)][HBPh$_3$**]** (**3**) in THF-$d_8$.

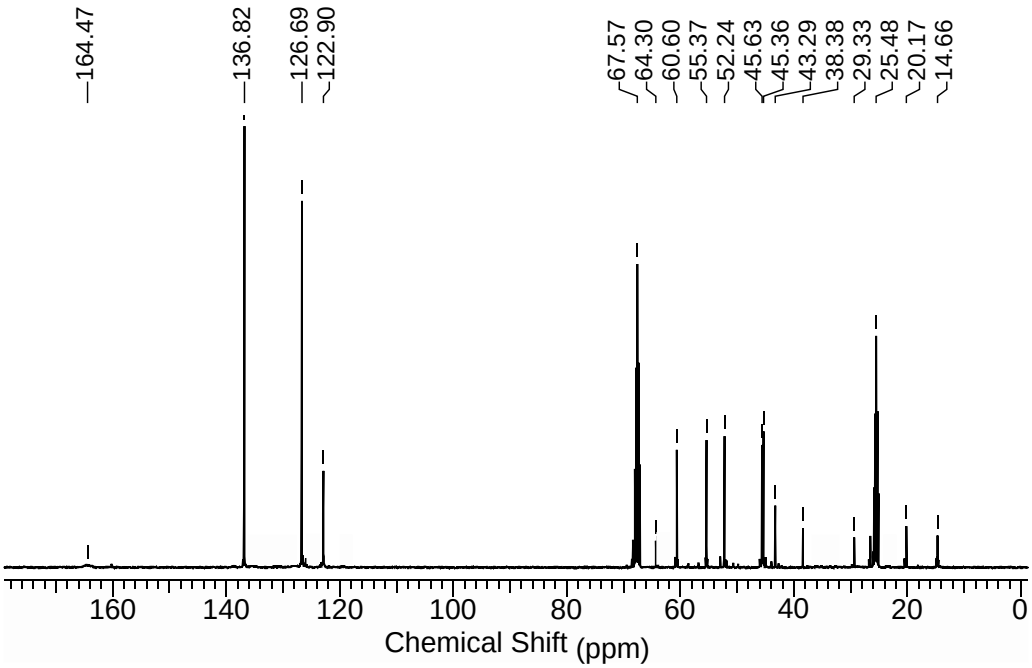


**Figure S11**. $^{13}$C{$^{1}$H} NMR spectrum of [(L)Al(O*n*Pent)][HBPh$_3$**]** (**3**) in THF-$d_8$.

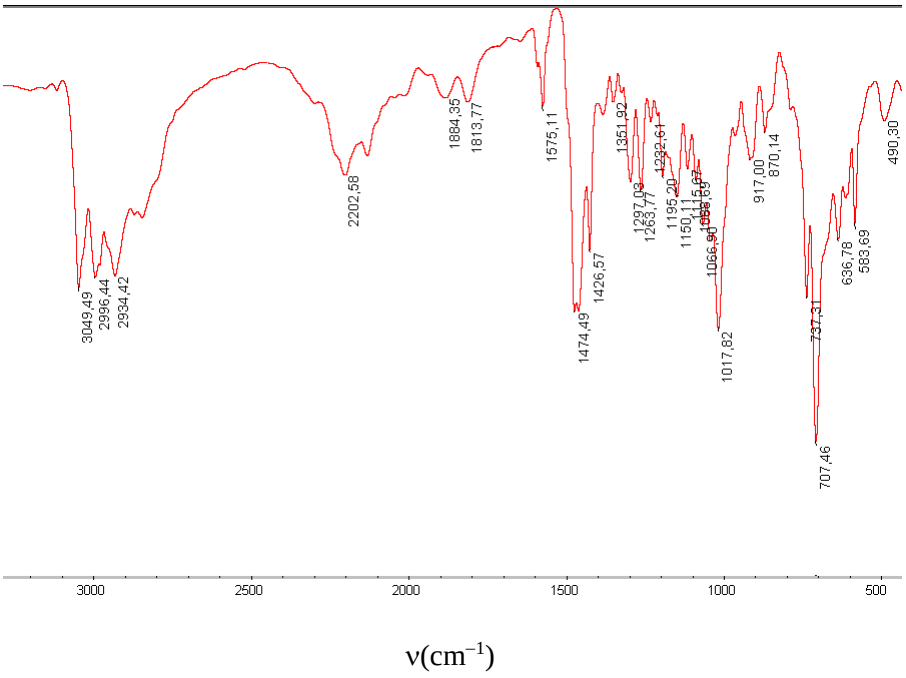


**Figure S12**. Solid-state IR spectrum (KBr pellet) of [(L)Al(O*n*Pent)][HBPH$_3$] (**3**).

## [(L)AlH][HBPh$_3$] (4)

A suspension of [(L)Al(H)$_2$]$_2$ (**1**, 0.050 g, 0.206 mmol) and BPh$_3$ (0.050 g, 0.206 mmol) in 5 mL of benzene was stirred at room temperature for 30 min. A colorless solid was isolated by filtration and washed with *n*-pentane (3×5mL). Drying the solid under vacuum afforded analytical pure [(L)AlH][HBPh$_3$] (**4**, 0.065 g, 0.117 mmol, 57% yield) as a colorless powder. $^1$H NMR (400 MHz, THF-$d_8$): δ 7.31 (m, 6 H, *o*-aryl), 6.89 (m, 6 H, *m*-aryl), 6.72 (m, 3 H, *p*-aryl), 3.78-3.18 (br, q, 1 H, *H*B),* 3.00-2.94 (m, 2 H, C*H*$_2$), 2.81-2.72 (m, 4 H, C*H*$_2$), 2.70-2.48 (m, 10 H, C*H*$_2$), 2.34 (s, 6 H, C*H*$_3$), 2.26 (s, 3H, C*H*$_3$). $^{13}$C{$^1$H} NMR (100 MHz, THF-$d_8$): δ 165.9, 136.7, 129.2, 122.1, 60.3, 56.2, 53.7, 46.0, 44.1, 41.5, 25.5. $^{11}$B NMR (128 MHz, THF-$d_8$): $\delta$ −7.9 (d, $^1J_{BH}$ = 78 Hz). $^{27}$Al NMR (104 MHz, THF-$d_8$): $\delta$ 101.9 (br). IR (KBr, cm$^{-1}$): 2196-2134 ($\nu_{BH}$), 1803 ($\nu_{AlH}$). Anal. Calcd. for $C_{29}H_{42}BN_4Al$: C, 71.90; H, 8.74; N, 11.56. Found: C, 71.45; H, 8.49; N, 11.77. *The Al*H* resonance is broad and likely overlapping with the B*H* resonance and could not be assigned unambiguously.

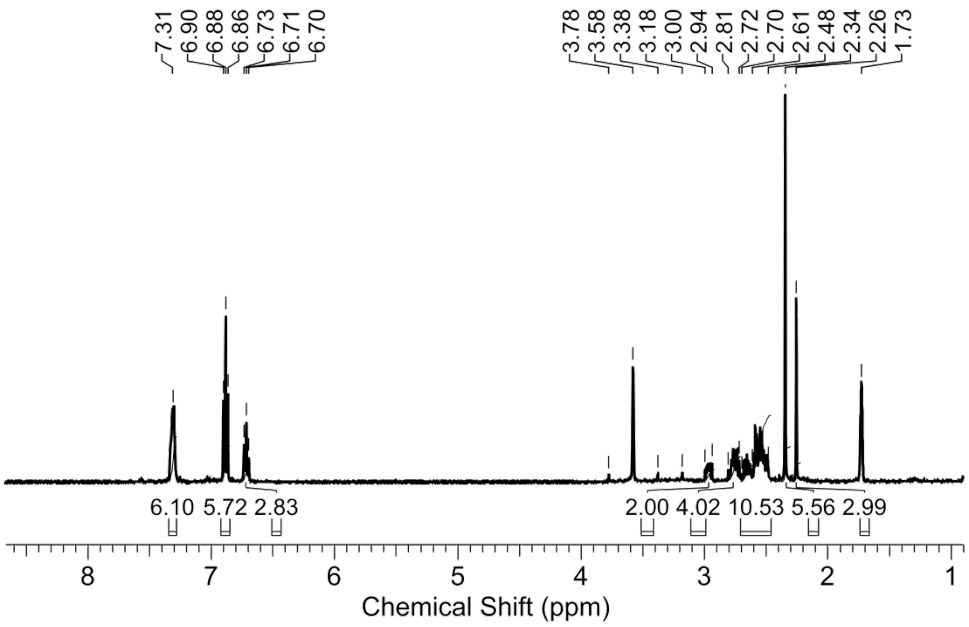


**Figure S13.** $^{1}$H NMR spectrum of [(L)AlH][HBPh$_3$] (**4**) in THF-$d_8$.

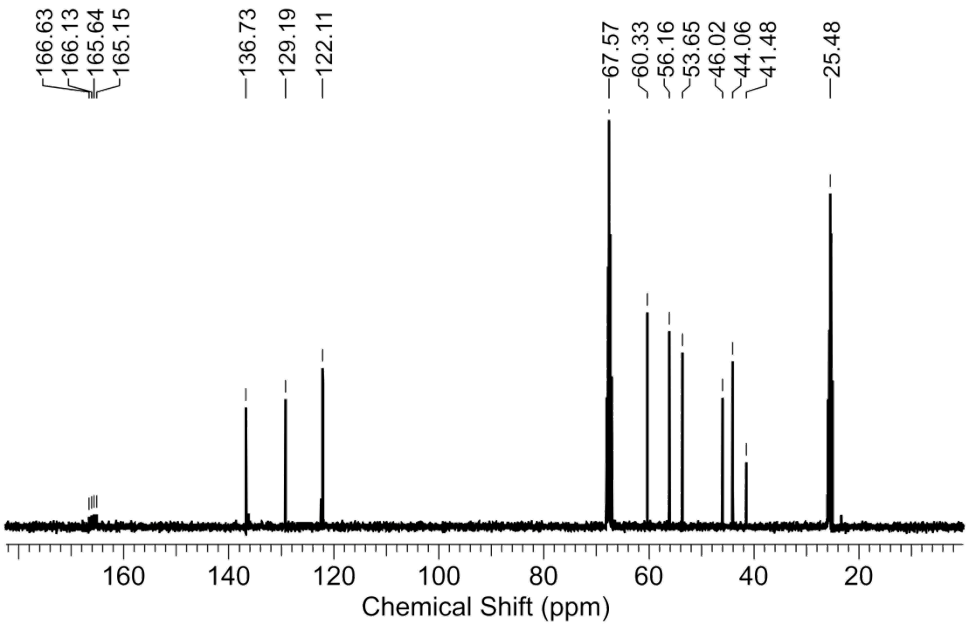


**Figure S14.** $^{13}$C{$^{1}$H} NMR spectrum of [(L)AlH][HBPh$_3$] (**4**) in THF-$d_8$.

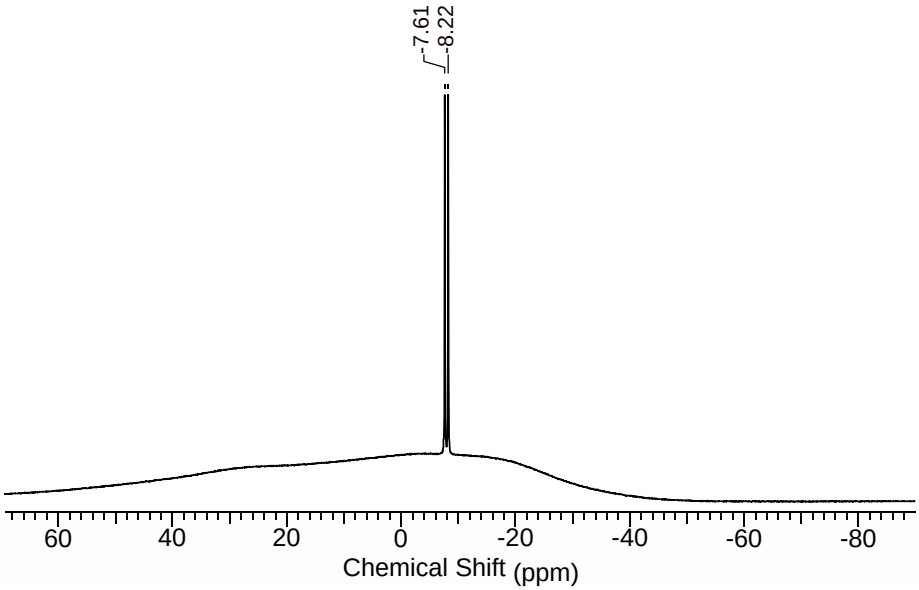


**Figure S15.** $^{11}$B NMR spectrum of [(L)AlH][HBPh$_3$] (**4**) in THF-$d_8$.

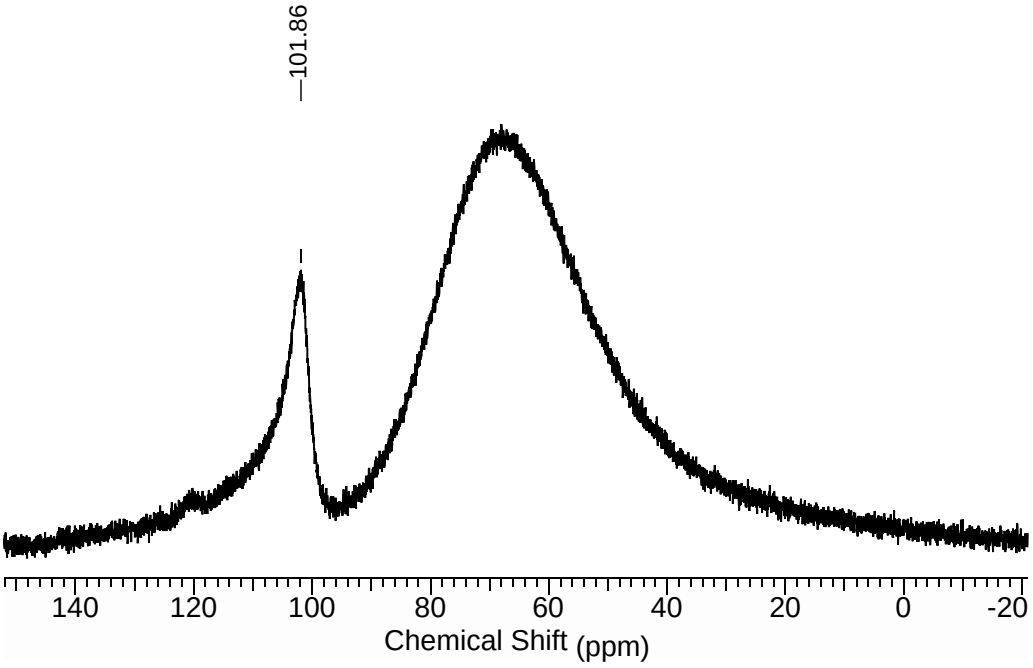


**Figure S16.** $^{27}$Al NMR spectrum of [(L)AlH][HBPh$_3$] (**4**) in THF-$d_8$.

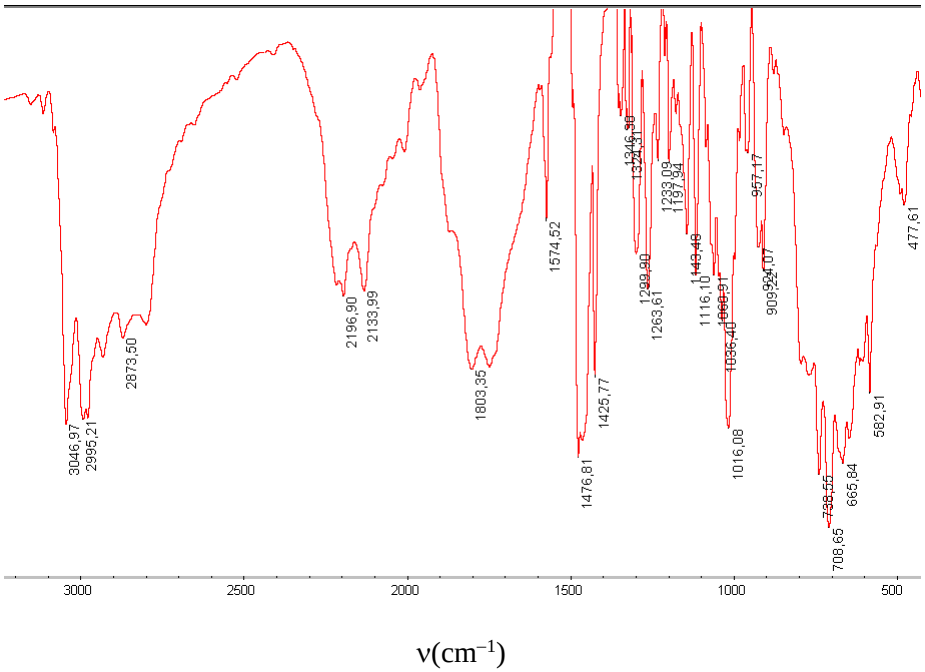


**Figure S17**. Solid-state IR spectrum (KBr pellet) of [(L)AlH][$HBPH_3$] (**4**).

## Deuterium labeling study

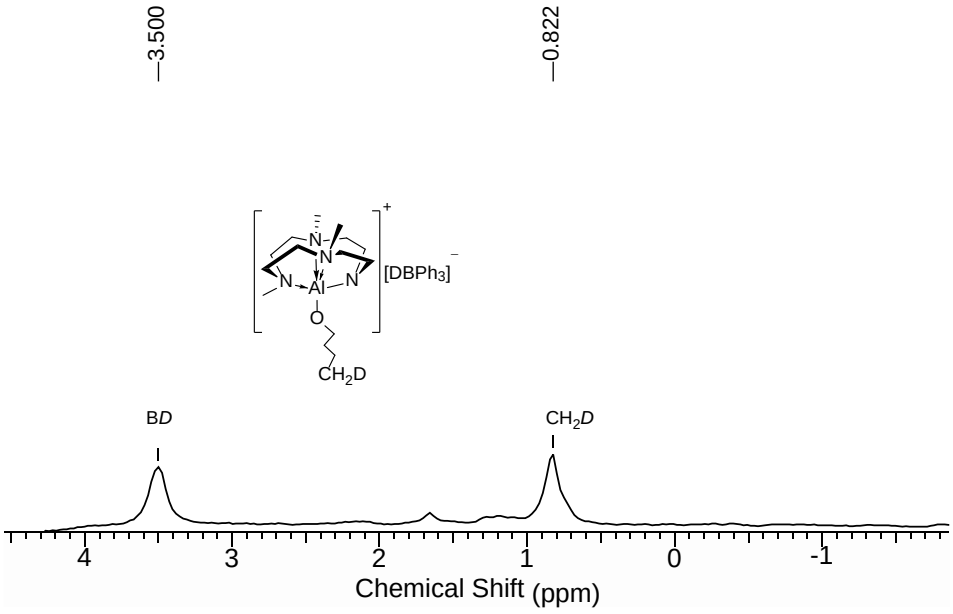


**Figure S18.** $^{2}D\{^{1}H\}$ NMR of **2-*d*₂** in THF.

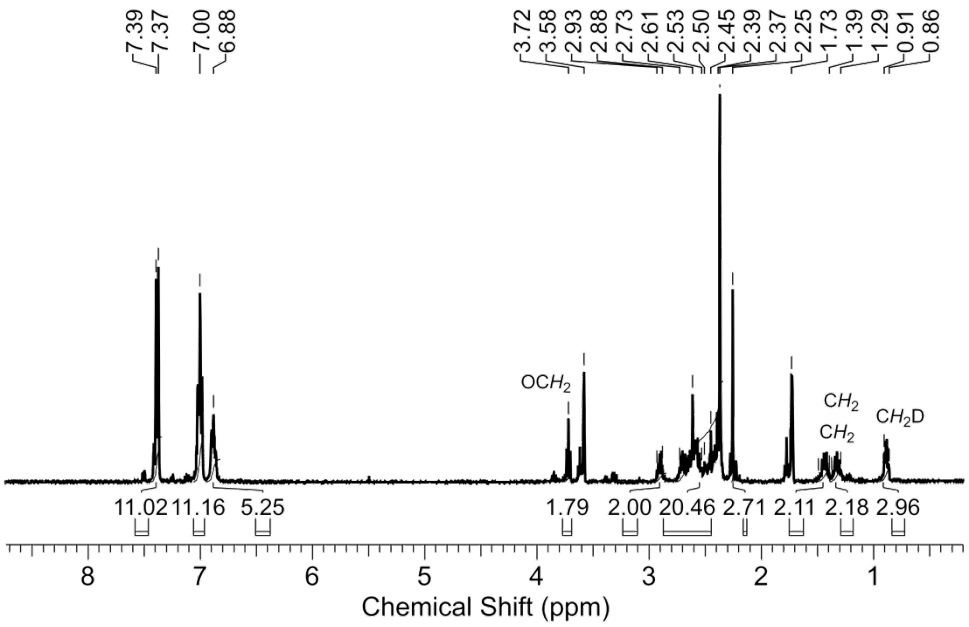


**Figure S19.** $^{1}$H NMR of **2-*d*$_2$** in THF-$d_8$.

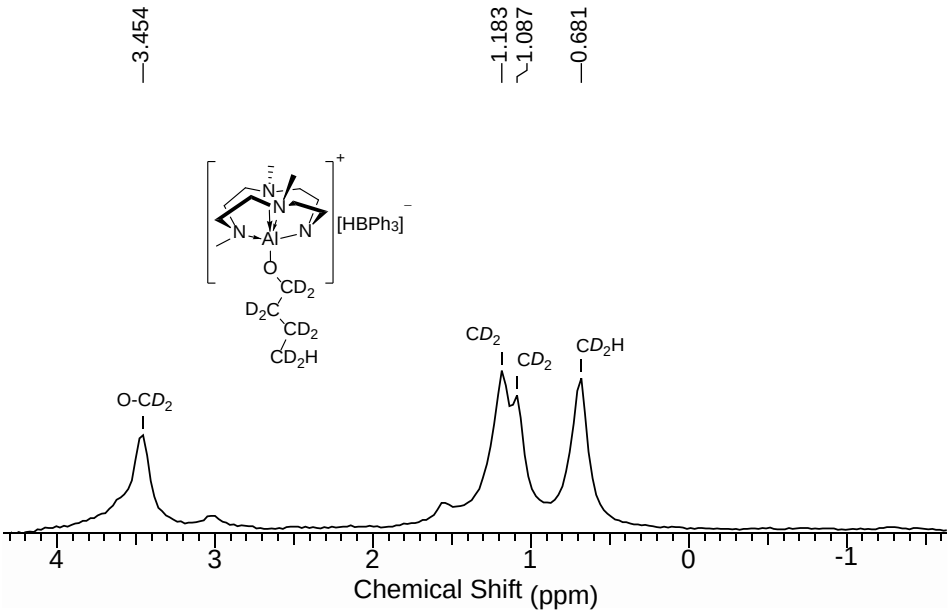


**Figure S20.** $^{2}$D{$^{1}$H} NMR of **2-*d*$_8$** in THF.

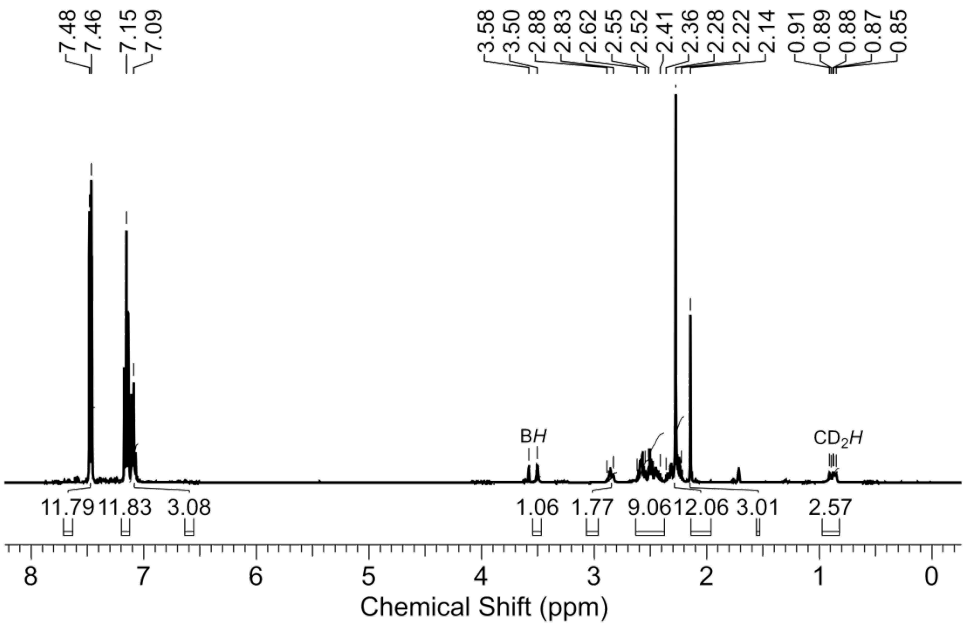


**Figure S20.** $^{1}$H NMR of **2-*d*$_8$** in THF-$d_8$.

## Hydroboration catalysis

In a typical run, a 2.5 mL solution of **1** (0.019 mg, 0.078 mmol), $BPh_3$ (0.038 mg, 0.157 mmol) and HBpin (0.100 mg, 0.781 mmol) in THF or THP was transferred to a 25 mL Schlenk tube. The mixture was stirred at room temperature and aliquots were drawn intermittently to monitor the reaction progress by analyzing by $^{1}$H and $^{11}$B NMR spectroscopy. The products pinB(OR) (R = *n*Bu and *n*Pent) were characterized by NMR spectroscopy and confirmed by comparison with literature data.[S3]

## X-ray crystallography

Single-crystal X-ray diffraction measurements of **2** and **4** were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoKα radiation (λ = 0.71073 Å), multilayer optics and ω-scans. Temperature control was achieved with an Oxford cryostream 700. The SMART program was used for data collection and unit cell determination; processing of the raw data frame was performed using SAINT+,[S4] multi scan absorption corrections were applied with SADABS.[S5] The structures were solved by direct methods (SHELXS-2013).[S6] Refinements were performed against $F^2$ using all reflections with the program SHELXL-2013.[S6] Hydrogen atoms were included as riding on calculated positions with $U_{iso}$(H) = 1.2$U_{eq.}$ or 1.5$U_{eq.}$(non-H), except for the hydride atoms H1 in **2** as well as H1 and H2 in **4**. These atoms were localized in difference Fourier maps and refined in their positions with isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically. The structure of **2** contains one co-crystallized solvent molecule

THF within the lattice. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.[S7] CCDC reference numbers CCDC-1530667 (**2**) and 1530668 (**4**). These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1. Crystal data and structure refinement.**

| | 2 | 4 |
|---|---|---|
| chemical formula | $C_{15}H_{34}AlN_4O$, $C_{18}H_{16}B$ | $C_{11}H_{26}AlN_4$,$C_{18}H_{16}B$ |
| fw ($g \cdot mol^{-1}$) | 628.66 | 484.45 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| crystal size (mm) | 0.12 × 0.14 × 0.19 | 0.20 × 0.25 × 0.29 |
| unit cell parameters | | |
| $a$ (Å) | 10.748(8) | 9.8159(18) |
| $b$ (Å) | 11.615(9) | 10.726(2) |
| $c$ (Å) | 15.531(12) | 13.269(2) |
| α (°) | 103.493(11) | 87.579(4) |
| β (°) | 107.633(10) | 75.801(3) |
| γ (°) | 97.170(9) | 83.365(3) |
| $V$ ($Å^3$) | 1756(2) | 1345.2(4) |
| Z | 2 | 2 |
| $T$ (K) | 100(2) | 100(2) |
| μ(Mo $K_\alpha$) ($mm^{-1}$) | 0.096 | 0.100 |
| reflns | 11357 | 16590 |
| independent reflns ($R_{int.}$) | 6333 (0.1492) | 5563 (0.0886) |
| observed reflns | 3782 | 4247 |
| parameters | 414 | 325 |
| goodness of fit on $F^2$ | 1.025 | 1.035 |
| final R indices | | |
| $R1$, $wR2$ [$I \geq 2\sigma(I)$] | 0.0778, 0.1795 | 0.0592, 0.1361 |
| $R1$, $wR2$ (all data) | 0.1335, 0.2089 | 0.0793, 0.1454 |

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