Stoichiometric reactions and catalytic dehydrogenations of amine-boranes with calcium aryloxide

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Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried with Na and distilled under a dry nitrogen atmosphere prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. Fourier transform infrared spectroscopy was measured with a Bruker VERTEX70. $NaBD_4$, $BF_3{\cdot}Et_2O$ (1 mol/L in Et_2O), 2,6-diisopropylphenol, anhydrous CaI_2, $KN(SiMe_3)_2$ (1 mol/L in THF) and $H_3B{\cdot}THF$ (1 mol/L in THF) were purchased from Strem. All the dialkylamine and tetraglyme used in experiments were purchased from Adamas and distilled under a dry nitrogen atmosphere prior to use. D_2O was purchased from Cambridge Isotope Laboratories and was degassed (3×freeze-pump-thaw cycles) prior to use. Complex **1**[1], dialkylamine-boranes[2], $BD_3{\cdot}THF$[3] and deuterated dialkylamine-borane[4] were synthesized using modified literature procedures.

References

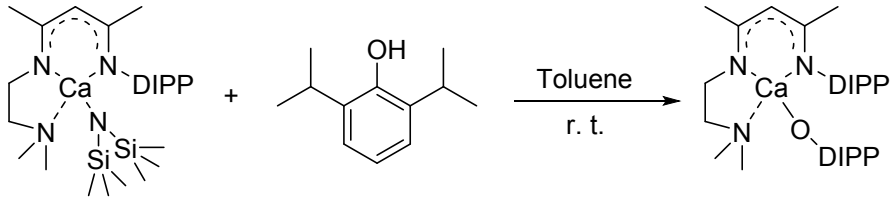
1 X. Xu, Y. Chen, G. Zou, Z. Ma and G. Li, *J. Organomet. Chem*., 2010, **695**, 1155-1162.

2 C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc*., 2003, **125**, 9424-9434.

3 R. C. Todd, M. Mahmun Hossain, K. V. Josyula, P. Gao, J. Kuo and C. T. Tan, *Tetrahedron Lett.* 2007, **48**, 2335-2337.

4 M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones and I Manners, *J. Am. Chem. Soc*., 2010, **132**, 3831-3841.

Preparation of complex 2:



1 DIPP = 2,6-$^{i}Pr_2$-C_6H_3 **2**

Scheme S1

A solution of 2,6-di-*iso*-propylphenol (178 mg, 1.0 mmol) in toluene (2 mL) was slowly added to a solution of complex **1** (529 mg, 1.0 mmol) in 3 mL of toluene at -30°C. The reaction mixture was then warmed to room temperature and stirred for 1h. The volatiles were removed under vacuum and the residue was washed with hexane (3*0.5 mL) to eventually give **2** as a pale yellow solid (442 mg, 81%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{33}H_{51}CaN_3O$: C, 72.61; H, 9.42; N, 7.70. Found: C, 72.89; H, 9.42; N, 7.58.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.27 (m, 2H, *m*-O*Ar)*, 7.10 (m, 3H, *m*, *p*-N*Ar*), 6.92 (m, 1H, *p*-O*Ar*), 4.79 (s, 1H, MeC(N)C*H*), 3.40 (m, 2H, OArC*H*Me$_2$), 3.25 (m, 2H, NArC*H*Me$_2$), 2.94 (t, $^{3}J_{HH}$ = 5.4 Hz, 2H, NCH_2), 2.14 (t, $^{3}J_{HH}$ = 5.4 Hz, 2H, NCH_2), 1.79 (s, 3H, *Me*C), 1.70 (s, 3H, *Me*C), 1.62 (s, 6H, N*Me$_2$*), 1.36 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, OArCH*Me$_2$*), 1.16 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me$_2$*), 1.14 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me$_2$*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.1 (Me*C*), 164.0 (Me*C*), 161.1 (*i*-O*Ar*), 146.3 (*i*-N*Ar*), 142.4 (*o*-N*Ar*), 135.6 (*o*-O*Ar*), 124.9 (*p*-N*Ar*), 124.5 (*m*-N*Ar*), 122.8 (*m*-O*Ar*), 114.0 (*p*-O*Ar*), 95.2 (MeC(N)*C*H), 59.5 (N*C*H$_2$), 46.7 (N*C*H$_2$), 44.0 (N*Me$_2$*), 28.3 (NAr*C*HMe$_2$), 27.4 (OAr*C*HMe$_2$), 24.9 (NArCH*Me$_2$*), 24.3 (OArCH*Me$_2$*), 24.0 (*Me*C), 22.8 (*Me*C).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.27 / 6.92 (*m*-O*Ar* / *p*-O*Ar*), 3.40 / 1.36 (OArC*H*Me$_2$ / OArCH*Me$_2$*), 3.25 / 1.16, 1.14 (NArC*H*Me$_2$ / NArCH*Me$_2$*), 2.94 / 2.14 (NCH_2 / NCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.27 / 122.8 (*m*-O*Ar*), 7.10 / 124.5, 124.9 (*m*, *p*-N*Ar*), 6.92 / 114.0 (*p*-O*Ar*), 4.79 / 95.2 (MeC(N)*CH*), 3.40 / 27.4 (OAr*CH*Me_2), 3.25 / 28.3 (NAr*CH*Me_2), 2.94 / 46.7 (N*C*H_2), 2.14 / 59.5 (N*C*H_2), 1.79 / 22.8 (*Me*C), 1.70 / 24.0 (*Me*C), 1.62 / 44.0 (N*Me*$_2$), 1.36 / 24.3 (OArCH*Me*$_2$), 1.16, 1.14 / 24.9 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.27 / 161.1 (m-O*Ar* / *i*-O*Ar*), 7.10 / 146.3 (*m*-N*Ar* / *i*-N*Ar*), 7.10 / 142.4 (*p*-N*Ar* / *o*-N*Ar*), 6.92 / 135.6 (*p*-O*Ar* / *o*-O*Ar*), 3.40 / 161.1, 135.6, 124.5 (OArC*H*Me_2 / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 3.25 / 146.3, 142.4, 124.9 (NArC*H*Me_2 / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 2.94 / 167.1, 59.5 (NC*H*$_2$ / MeC, NCH_2), 2.94 / 59.5 (NC*H*$_2$ / NCH_2), 1.79 / 167.1 (*Me*C / MeC), 1.62 / 59.5 (N*Me*$_2$ / NCH_2), 1.36 / 135.6 (OArCH*Me*$_2$ / *o*-O*Ar*), 1.16, 1.14 / 142.4 (NArCH*Me*$_2$ / *o*-N*Ar*).

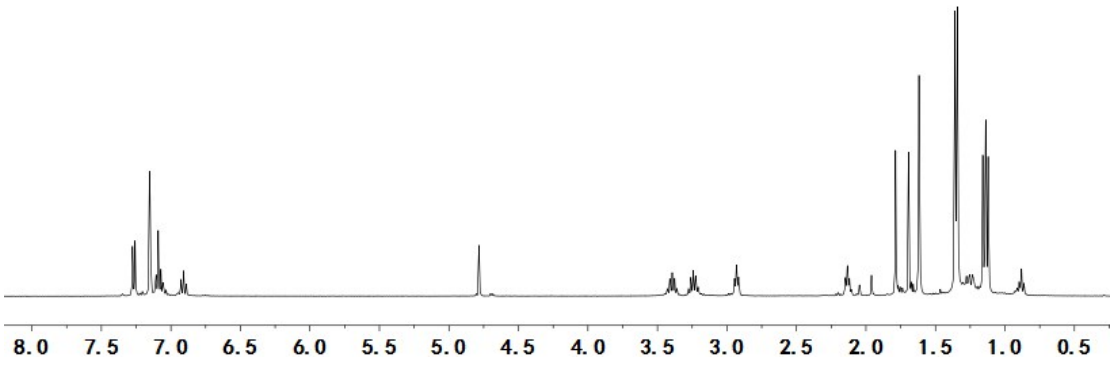


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

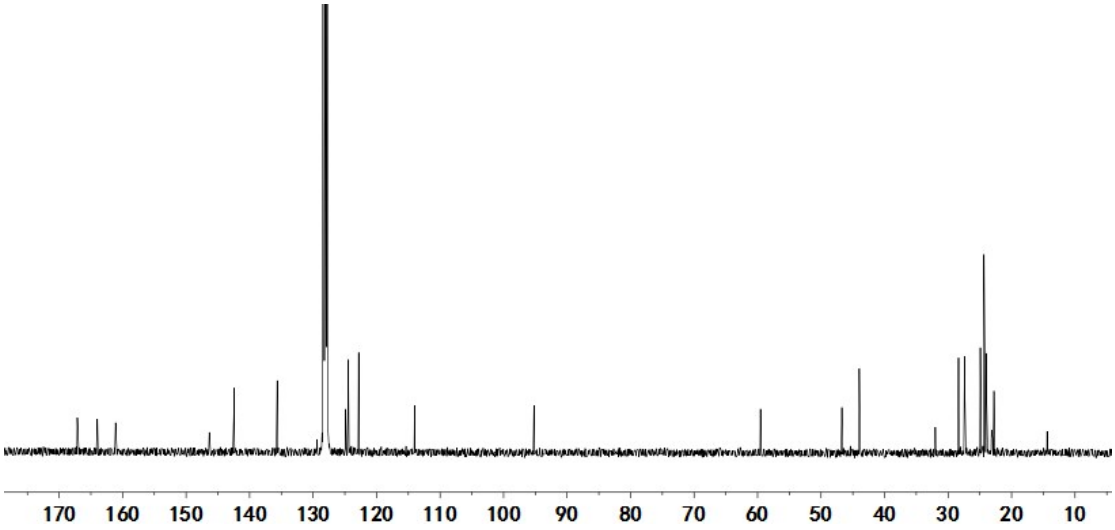


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 2: formula $C_{66}H_{102}Ca_2N_6O_2$, M = 1091.7 $gmol^{-1}$, colorless, 0.25 x 0.20 x 0.15 mm, Triclinic, space group *P -1*, a = 11.6129(5), b = 12.0953(5), c = 13.3673(5) Å, V = 1603.75(11) $Å^3$, ρcalc = 1.130 gcm^{-3}, μ = 0.224 mm^{-1}, empirical absorption correction ($0.6605 \leq T \leq 0.7456$), Z = 1, λ = 0.71073 Å, T = 120(2) K, 25631 reflections collected ($-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$), 7366 independent (Rint = 0.0802) and 4999 observed reflections [$I>2\sigma(I)$], 359 refined parameters, the final R_1 was 0.0507 ($I > 2\sigma(I)$) and wR_2 was 0.1338 (all data). max. (min.) residual electron density 0.524 (-0.720) $e.Å^{-3}$, hydrogen atoms were placed in calculated positions and refined using a riding model.

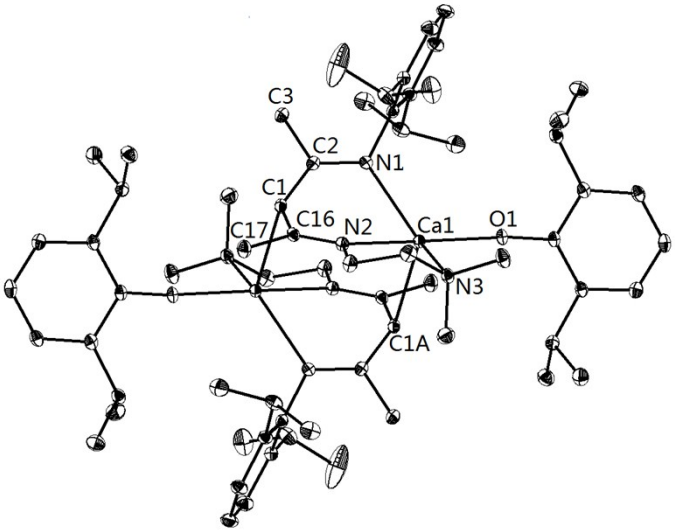
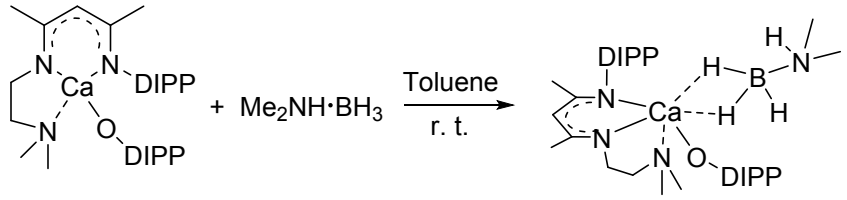


Fig. S3. Molecular structure of complex **2**.

Preparation of complex 3:



2 DIPP=2,6-^{i}Pr$_2$-C$_6$H$_3$ **3**

Scheme S2

A solution of $H_3B{\cdot}NMe_2H$ (18 mg, 0.30 mmol) in toluene (1 mL) was added to a solution of **2** (164 mg, 0.30 mmol) in 1 mL of toluene. The reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum, and then the residue was washed with hexane (3*0.5 mL) to eventually give **3** as a white solid (156 mg, 86%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30 ^{o}C.

Elemental Analysis: calcd. for $C_{35}H_{61}BCaN_4O$: C, 69.51; H, 10.17; N, 9.26. Found: C, 69.98; H, 10.02; N, 9.28.

IR (KBr cell, cm^{-1}): ν = 3233 (N-H), 2365-2221(B-H).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.33 (m, 2H, *m*-O*Ar*), 6.90 (m, 1H, *p*-O*Ar*), 6.86 (m, 2H, *m*-N*Ar*), 6.68 (m, 1H, *p*-N*Ar*), 4.86 (s, 1H, MeC(N)C*H*), 3.81 (m, 2H, OArC*H*Me$_2$), 3.41 (m, 2H, NArC*H*Me$_2$), 3.14 (m, 2H, NC*H*$_2$), 2.37 (br, 2H, NC*H*$_2$), 2.13 (s, 6H, N*Me*$_2$), 1.91 (s, 3H, *Me*C), 1.72 (s, 3H, *Me*C), 1.54 (s, 6H, HN*Me*$_2$), 1.50 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, OArCH*Me*$_2$), 1.36 (br, 3H, B*H*$_3$),[1] 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 1.09 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), [[1] from the ^{1}H{^{11}B} experiment]. (The signal of N*H* was not observed)

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.1 (Me*C*), 162.7 (Me*C*), 162.4 (*i*-O*Ar*), 149.6 (*i*-N*Ar*), 143.8 (*o*-N*Ar*), 136.0 (*o*-O*Ar*), 123.5 (*m*-N*Ar*), 122.5 (*m*-O*Ar*), 122.3 (*p*-N*Ar*), 112.8 (*p*-O*Ar*), 94.8 (MeC(N)*C*H), 59.5 (N*C*H$_2$) 47.4 (N*C*H$_2$), 44.2 (N*Me*$_2$, HN*Me*$_2$), 27.9 (NAr*C*HMe$_2$), 27.3 (OAr*C*HMe$_2$), 24.40 (NArCH*Me*$_2$), 24.38 (OArCH*Me*$_2$), 24.3 (*Me*C), 22.9 (*Me*C).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -14.1.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.33 / 6.90 (*m*-O*Ar* / *p*-O*Ar*), 6.86 / 6.68 (*m*-N*Ar* / *p*-N*Ar*), 3.81 / 1.50 (OArC*H*Me$_2$ / OArCH*Me*$_2$), 3.41 / 1.11, 1.09 (NArC*H*Me$_2$ / NArCH*Me*$_2$), 3.14 / 2.37 (NC*H*$_2$ / NC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.33 / 122.5 (*m*-O*Ar*), 6.90 / 112.8 (*p*-O*Ar*), 6.86 / 123.5 (*m*-N*Ar*), 6.68 / 122.3 (*p*-N*Ar*), 4.86 / 94.8 (MeC(N)*CH*), 3.81 / 27.3 (OAr*CH*Me$_2$), 3.41 / 27.9 (NAr*CH*Me$_2$), 3.14 / 47.4 (NC*H*$_2$), 2.37 / 59.5 (NC*H*$_2$), 2.13 / 44.2 (N*Me*$_2$), 1.91 / 22.9 (*Me*C), 1.72 / 24.3 (*Me*C), 1.55 / 44.2 (HN*Me*$_2$), 1.50 / 24.38 (OArCH*Me*$_2$), 1.11, 1.09 / 24.40 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.33 / 162.4 (m-O*Ar* / *i*-O*Ar*), 6.90 / 136.0 (*p*-O*Ar* / *o*-O*Ar*), 6.86 / 149.6 (*m*-N*Ar* / *i*-N*Ar*), 6.68 / 143.8 (*p*-N*Ar* / *o*-N*Ar*), 3.81 / 162.4, 136.0, 122.5 (OArC*H*Me$_2$ / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 3.41 / 149.6, 143.8, 123.5 (NArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.14 / 167.1, 59.5 (NC*H*$_2$ / Me*C,* N*C*H$_2$), 2.37 / 47.4 (NC*H*$_2$ / N*C*H$_2$), 2.13 / 59.5 (N*Me*$_2$ / N*C*H$_2$), 1.91 / 167.1 (*Me*C / Me*C*), 1.50 / 136.0 (OArCH*Me*$_2$ / *o*-O*Ar*), 1.11, 1.09 / 143.8 (NArCH*Me*$_2$ / *o*-N*Ar*).

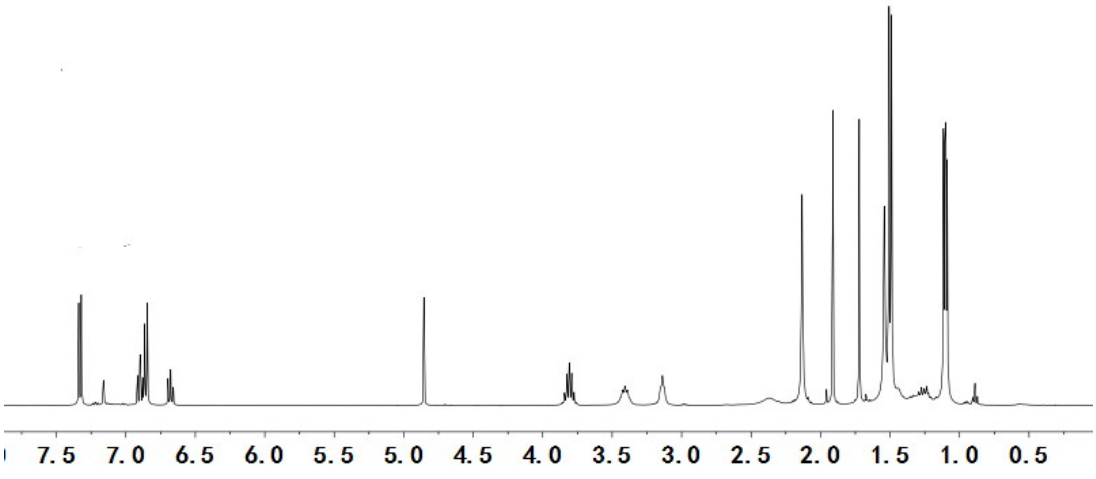


Fig. S4. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

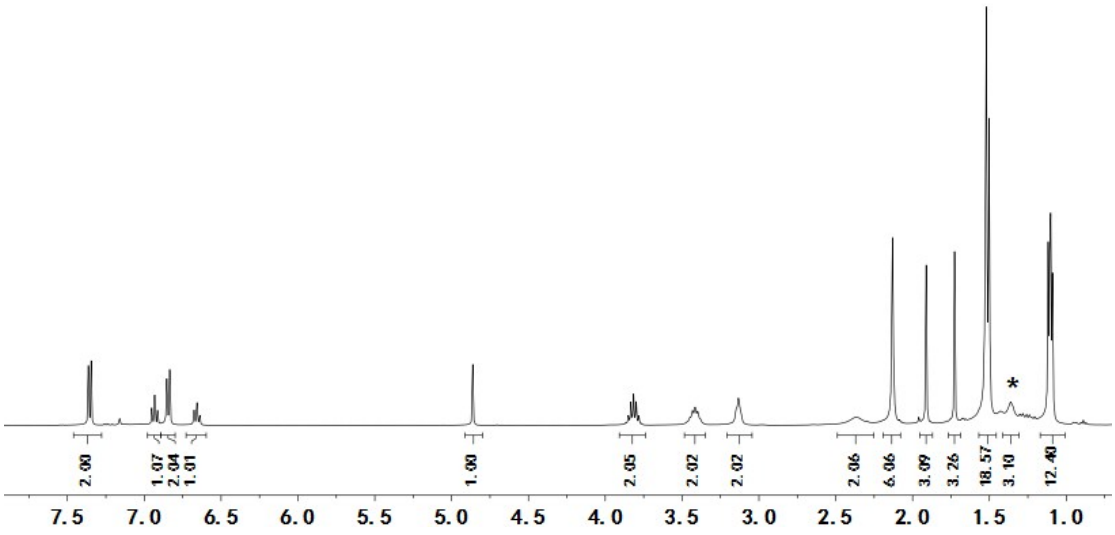


Fig. S5. $^{1}H\{^{11}B\}$ NMR (400 MHz, C_6D_6, 298 K) [*: BH_3]

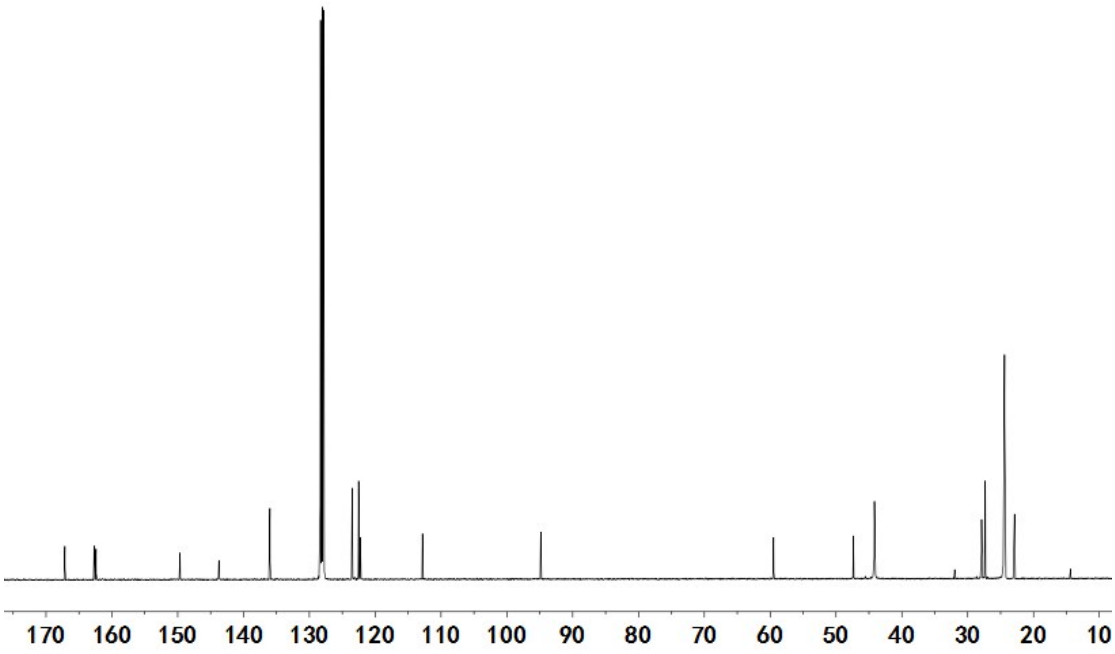


Fig. S6. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

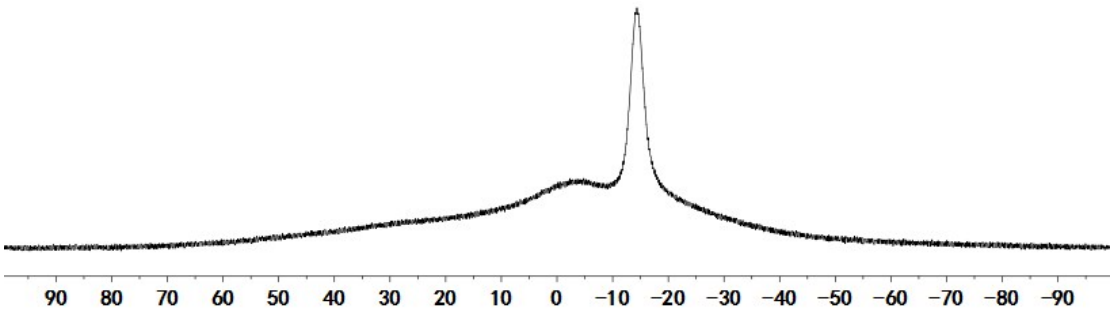


Fig. S7. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 3: formula $C_{35}H_{61}BCaN_4O$, M = 604.77 gmol^{-1}, colorless, 0.3 x 0.2 x 0.2 mm, Triclinic, space group *P -1*, a = 10.7981(8), b = 11.0571(7), c = 18.4471(8) Å, V = 1876.8(2) Å^3, ρ_{calc} = 1.070 gcm^{-3}, μ = 0.197 mm^{-1}, empirical absorption correction (0.98618 ≤ T ≤ 1.00000), Z = 2, λ = 0.71073 Å, T = 153(2) K, 18922 reflections collected (-14 ≤ h ≤ 14, -14 ≤ k ≤ 15, -24 ≤ l ≤ 26), 11390 independent (R_{int} = 0.0410) and 6164 observed reflections [I>2σ(I)], 409 refined parameters, the final R_1 was 0.0654 (I > 2σ(I)) and wR_2 was 0.1742 (all data). max. (min.) residual electron density 0.508 (-0.306) e.Å^{-3}, hydrogen atoms (expect B-H and N-H) were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

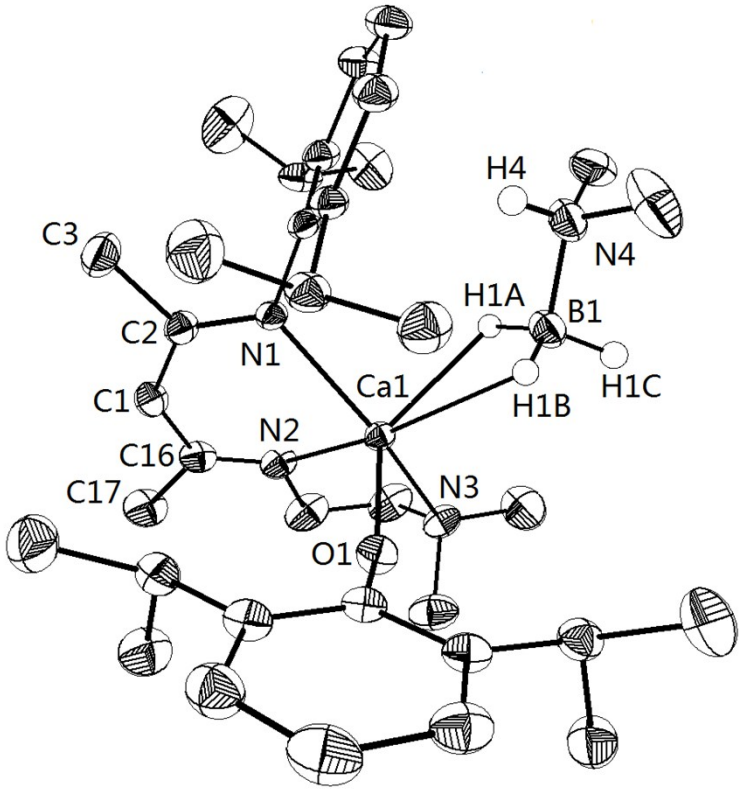
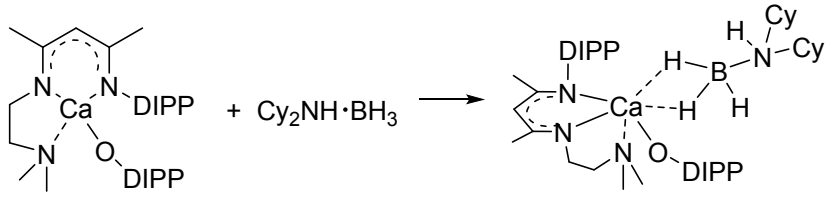


Fig. S8. Molecular structure of complex **3**.

Preparation of complex 4:



2 DIPP=2,6-^{i}Pr$_2$-C$_6$H$_3$ **4**

Scheme S3

Following the procedure described for **3**, reaction of $H_3B{\cdot}NCy_2H$ (59 mg, 0.30 mmol) with **2** (164 mg, 0.30 mmol) gave **4** as a colorless crystalline solid (182 mg, 82%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^{o}C.

Elemental Analysis: calcd. for $C_{45}H_{77}BCaN_4O$: C, 72.94; H, 10.47; N, 7.56. Found: C, 73.18; H, 10.13; N, 7.58.

IR (KBr cell, cm^{-1}): ν= 3189 (N-H), 2392-2279 (B-H).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.32 (m, 2H, *m*-O*Ar*), 6.98 (m, , 2H, *m*-N*Ar*), 6.88 (m, 1H, *p*-O*Ar*), 6.85 (m, 1H, *p*-N*Ar*), 4.84 (s, 1H, MeC(N)C*H*), 3.82 (m, 2H, OArC*H*Me$_2$), 3.45 (m, 2H, NArC*H*Me$_2$), 3.20 (m, 2H, NCH_2), 2.41 (m, 2H, NCH_2), 2.35 (m, 2H, overlapped with NCH_2, HN*Cy*$_2$), 2.20 (s, 6H, N*Me*$_2$), 1.95 (s, 3H, *Me*C), 1.76 (s, 3H, *Me*C), 1.57 (m, 8H, HN*Cy*$_2$), 1.49 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, OArCH*Me*$_2$), 1.32 (br, 3H, BH_3)[1], 1.29 (m, 4H, HN*Cy*$_2$), 1.20 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 1.18 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 0.98 (m, 8H, HN*Cy*$_2$), [[1] from the ^{1}H{^{11}B} experiment]. (The signal of N*H* was not observed).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.6 (Me*C*), 163.2 (Me*C*), 162.4 (*i*-O*Ar*), 149.5 (*i*-N*Ar*), 142.9 (*o*-N*Ar*), 136.0 (*o*-O*Ar*), 123.3 (*m*-N*Ar*), 123.1 (*p*-N*Ar*), 122.5 (*m*-O*Ar*), 112.7 (*p*-O*Ar*), 94.7 (MeC(N)*C*H), 61.0 (HN*Cy*$_2$), 59.9 (NCH_2), 47.6 (NCH_2), 44.7 (N*Me*$_2$), 30.4 (HN*Cy*$_2$), 28.0 (NAr*C*HMe$_2$), 27.2 (OAr*C*HMe$_2$), 25.9, 25.4 (HN*Cy*$_2$), 24.7 (OArCH*Me*$_2$), 24.6 (overlapped with OArCH*Me*$_2$, NArCH*Me*$_2$), 24.5 (*Me*C), 23.2 (*Me*C).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -20.1.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.32 / 6.88 (*m*-O*Ar* / *p*-O*Ar*), 6.98 / 6.85 (*m*-N*Ar* / *p*-N*Ar*), 3.82 / 1.49 (OArC*H*Me$_2$ / OArCH*Me*$_2$), 3.45 / 1.20, 1.18 (NArC*H*Me$_2$ / NArCH*Me*$_2$), 3.20 / 2.41 (NC*H*$_2$ / NC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.32 / 122.5 (*m*-O*Ar*), 6.98 / 123.3 (*m*-N*Ar*), 6.88 / 112.7 (*p*-O*Ar*), 6.85 / 123.1 (*p*-N*Ar*), 4.84 / 94.7 (MeC(N)*CH*), 3.82 / 27.2 (OAr*CH*Me$_2$), 3.45 / 28.0 (OAr*CH*Me$_2$), 3.20 / 47.6 (NC*H*$_2$), 2.41 / 59.9 (NC*H*$_2$), 2.35 / 61.0, 1.57 / 25.9, 1.29 / 30.4, 0.98 / 25.4 (HN*Cy*$_2$), 2.20 / 44.7 (N*Me*$_2$), 1.95 / 23.2 (*Me*C), 1.76 / 24.5 (*Me*C), 1.49 / 24.7 (OArCH*Me*$_2$), 1.20, 1.18 / 24.6 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.32 / 162.4 (m-O*Ar* / *i*-O*Ar*), 6.98 / 149.5 (*m*-N*Ar* / *i*-N*Ar*), 6.88 / 136.0 (*p*-O*Ar* / *o*-O*Ar*), 6.85 / 142.9 (*p*-N*Ar* / *o*-N*Ar*), 3.82 / 162.4, 136.0, 122.5 (OArC*H*Me$_2$ / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 3.45 / 149.5, 142.9, 123.3 (NArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.20 / 166.6, 59.9 (NC*H*$_2$ / Me*C*, NCH$_2$), 2.41 / 47.6 (NC*H*$_2$ / NCH$_2$), 2.20 / 59.9 (N*Me*$_2$ / NCH$_2$), 1.95 / 166.6 (*Me*C / Me*C*), 1.49 / 136.0 (OArCH*Me*$_2$ / *o*-O*Ar*), 1.20, 1.18 / 142.9 (NArCH*Me*$_2$ / *o*-N*Ar*).

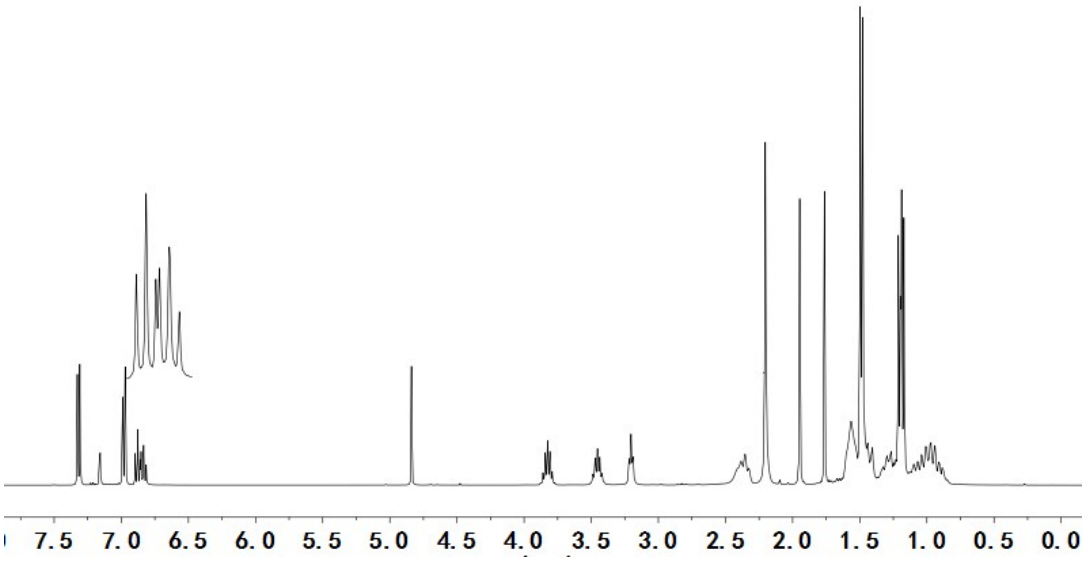


Fig. S9. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

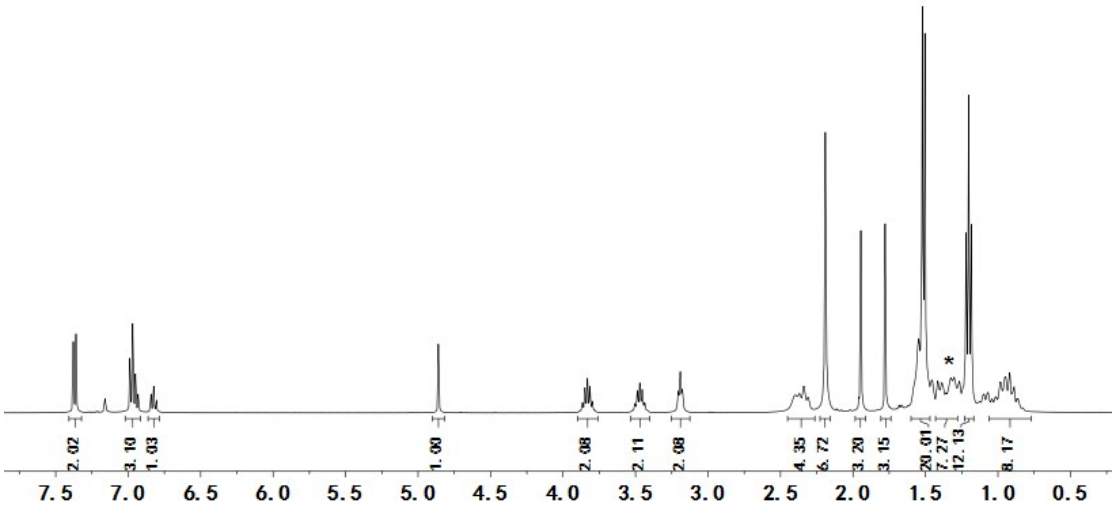


Fig. S10. $^{1}H\{^{11}B\}$ NMR (400 MHz, C_6D_6, 298 K) [*: BH_3]

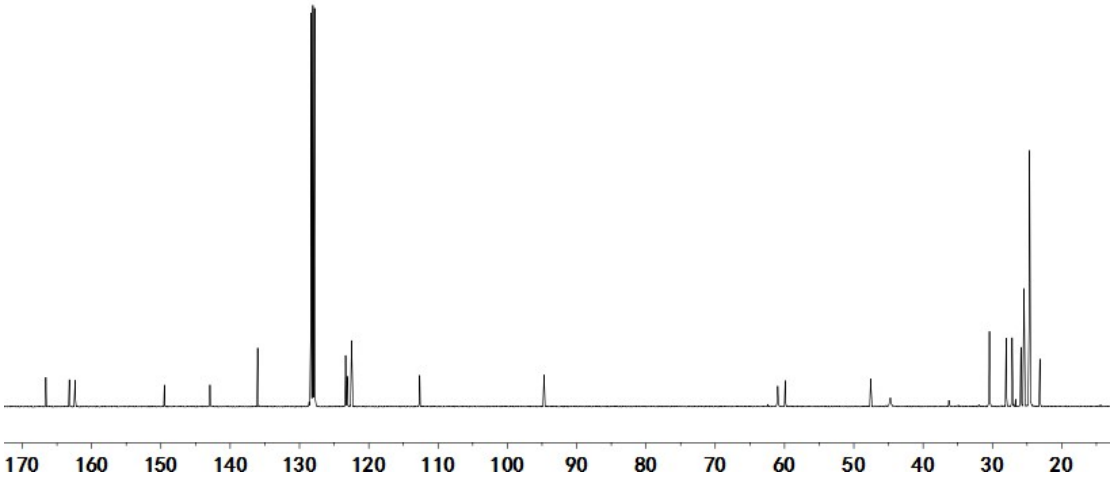


Fig. S11. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

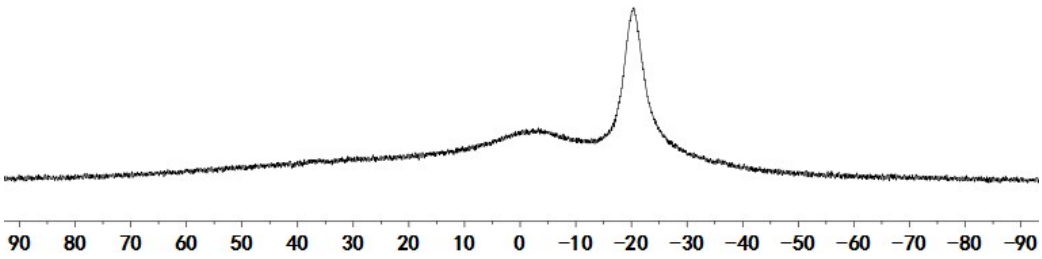


Fig. S12. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 4: formula $C_{45}H_{77}BCaN_4O$, M = 741.00

gmol^{-1}, colorless, 0.18 x 0.15 x 0.10 mm, Monoclinic, space group *P 21*, *a* = 10.5271(7), *b* = 18.2281(10), *c* = 12.1212(7) Å, *V* = 2259.5(2) Å^3, ρ_{calc} = 1.089 gcm^{-3}, μ = 0.175 mm^{-1}, empirical absorption correction (0.6495 ≤ T ≤ 0.7456), *Z* = 2, λ = 0.71073 Å, T = 120(2) K, 37048 reflections collected (-13 ≤ h ≤ 13, -23 ≤ k ≤ 23, -15 ≤ l ≤ 15), 10388 independent (R_{int} = 0.0737) and 8614 observed reflections [I>2σ(I)], 497 refined parameters, the final R_1 was 0.0439 (I > 2σ(I)) and wR_2 was 0.1061 (all data). max. (min.) residual electron density 0.254 (-0.2616) e.Å^{-3}, hydrogen atoms (expect B-H and N-H) were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

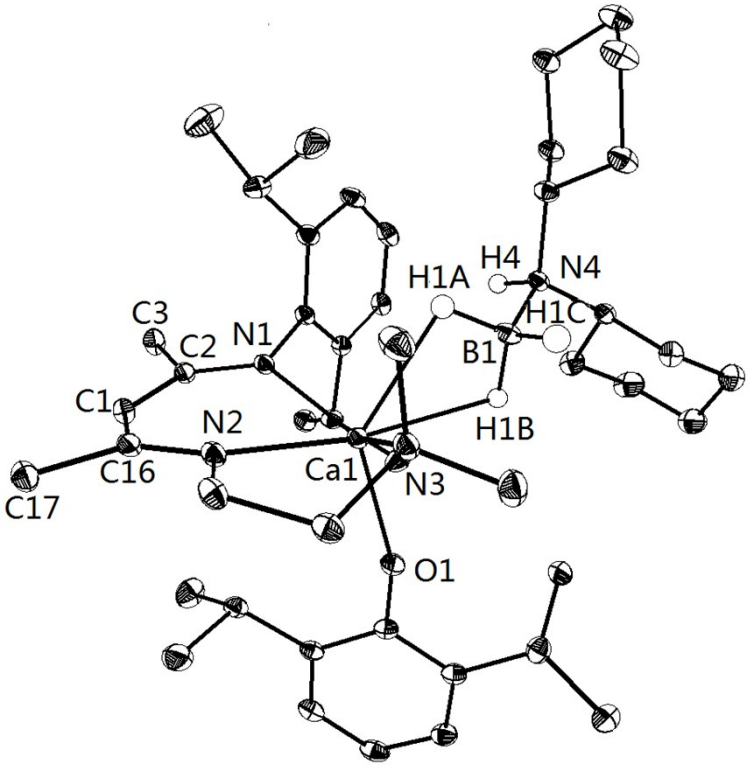
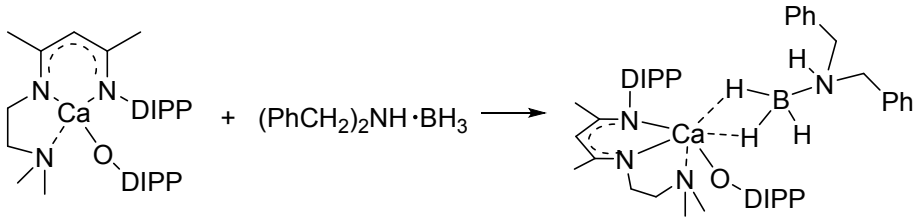


Fig. S13. Molecular structure of complex **4**.

Preparation of complex 5:



2 DIPP=2,6-^{i}Pr$_2$-C$_6$H$_3$ **5**

Scheme S4

Following the procedure described for **3**, reaction of $H_3B{\cdot}N(PhCH_2)_2H$ (63 mg, 0.30 mmol) with **2** (164 mg, 0.30 mmol) gave **5** as a colorless crystalline solid (170 mg, 75%) Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^{o}C.

Elemental Analysis: calcd. for $C_{47}H_{69}BCaN_4O$: C, 74.57; H, 9.19; N, 7.40. Found: C, 74.34; H, 8.66; N, 7.22.

IR (KBr cell, cm^{-1}): ν = 3203(N-H), 2371-2275 (B-H).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.35 (m, 2H, *m*-O*Ar*), 7.05 (m, 6H, *Ph*CH$_2$), 7.00 (m, 2H, *m*-N*Ar*), 6.94 (m, 1H, *p*-O*Ar*), 6.92 (m, 4H, *Ph*CH$_2$), 6.86 (m, 1H, *p*-N*Ar*), 4.85 (s, 1H, MeC(N)C*H*), 3.83 (m, 2H, OArC*H*Me$_2$), 3.44 (m, 2H, NArC*H*Me$_2$), 3.36 (br, 4H, PhC*H*$_2$,), 3.15 (m, 2H, NC*H*$_2$), 2.37 (br, 2H, NC*H*$_2$), 2.15 (s, 6H, N*Me*$_2$), 1.92 (s, 3H, *Me*C), 1.77 (s, 3H, *Me*C), 1.62 (br, 3H, B*H*$_3$)[1], 1.50 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, OArCH*Me*$_2$), 1.17 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, NArCH*Me*$_2$) [[1] from the ^{1}H{^{11}B} experiment]. (The signal of N*H* was not observed)

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.8 (Me*C*), 163.4 (Me*C*), 162.2 (*i*-O*Ar*), 149.2 (*i*-N*Ar*), 143.2 (*o*-N*Ar*), 136.0 (*o*-O*Ar*), 130.2, 129.0 (*o*, *m*-*Ph*CH$_2$), n.o. (*i*, *p*-*Ph*CH$_2$), 123.7 (*m*-N*Ar*), 123.2 (*p*-N*Ar*), 122.6 (*m*-O*Ar*), 113.1 (*p*-O*Ar*), 94.6 (MeC(N)*C*H), 59.8 (N*C*H$_2$), 57.7 (Ph*C*H$_2$), 47.4 (N*C*H$_2$), 44.6 (N*Me*$_2$), 28.1 (NAr*C*HMe$_2$), 27.2 (OAr*C*HMe$_2$), 24.6 (OArCH*Me*$_2$), 24.5 (*Me*C), 24.4 (NArCH*Me*$_2$), 23.1 (*Me*C). [n.o.: not observed]

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -15.4.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.35 / 6.94 (*m*-O*Ar* / *p*-O*Ar*), 7.00 / 6.86 (*m*-N*Ar* / *p*-N*Ar*), 3.83 / 1.50 (OArC*H*Me$_2$ / OArCH*Me*$_2$), 3.44 / 1.17 (NArC*H*Me$_2$ / NArCH*Me*$_2$), 3.14 / 2.37 (NC*H*$_2$ / NC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.35 / 122.6 (*m*-O*Ar*), 7.05 / 129.0 (*Ph*CH$_2$), 7.00 / 123.7 (*m*-N*Ar*), 6.94 / 113.1 (*p*-O*Ar*), 6.92 / 130.2 (*Ph*CH$_2$), 6.86 / 123.2 (*p*-N*Ar*), 4.85 / 94.6 (MeC(N)*CH*), 3.83 / 27.2 (OAr*CH*Me$_2$), 3.44 / 28.1 (NAr*CH*Me$_2$), 3.36 / 57.6 (Ph*CH*$_2$), 3.14 / 47.4 (N*CH*$_2$), 2.37 / 59.8 (N*CH*$_2$), 2.15 / 44.6 (N*Me*$_2$), 1.92 / 23.1 (*Me*C), 1.77 / 24.5 (*Me*C), 1.50 / 24.6 (OArCH*Me*$_2$), 1.17 / 24.4 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.35 / 162.2 (*m*-O*Ar* / *i*-O*Ar*), 7.00 / 149.2 (*m*-N*Ar* / *i*-N*Ar*), 7.05 / 130.2 (*Ph*CH$_2$ / *Ph*CH$_2$), 6.94 / 136.0 (*p*-O*Ar* / *o*-O*Ar*), 6.86 / 143.2 (*p*-N*Ar* / *o*-N*Ar*), 3.83 / 162.2, 136.0, 122.6 (OArC*H*Me$_2$ / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 3.44 / 149.2, 143.2, 123.7 (NArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.14 / 166.8, 59.8 (NC*H*$_2$ / Me*C*, N*C*H$_2$), 2.37 / 47.4 (NC*H*$_2$ / N*C*H$_2$), 2.15 / 59.8 (N*Me*$_2$ / N*C*H$_2$), 1.92 / 166.8 (*Me*C / Me*C*), 1.50 / 136.0 (OArCH*Me*$_2$ / *o*-O*Ar*), 1.17 / 143.2 (NArCH*Me*$_2$ / *o*-N*Ar*).

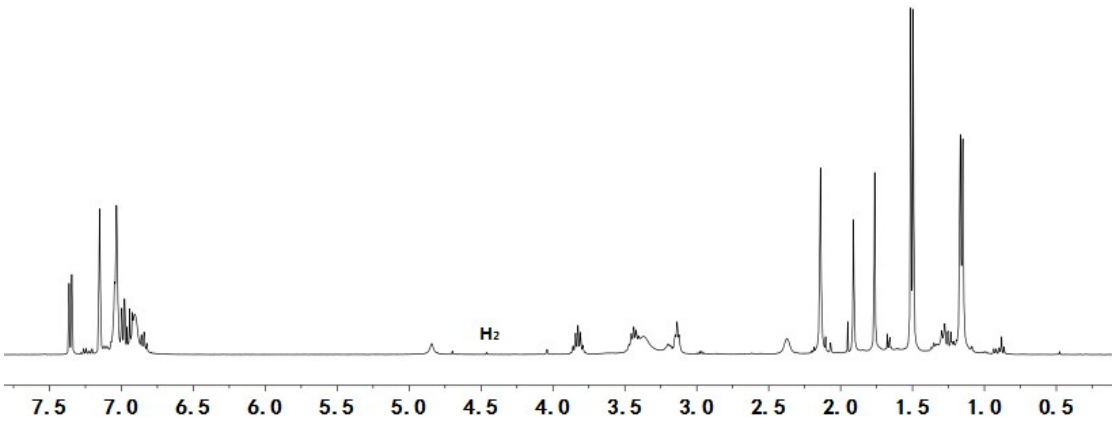


Fig. S14. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

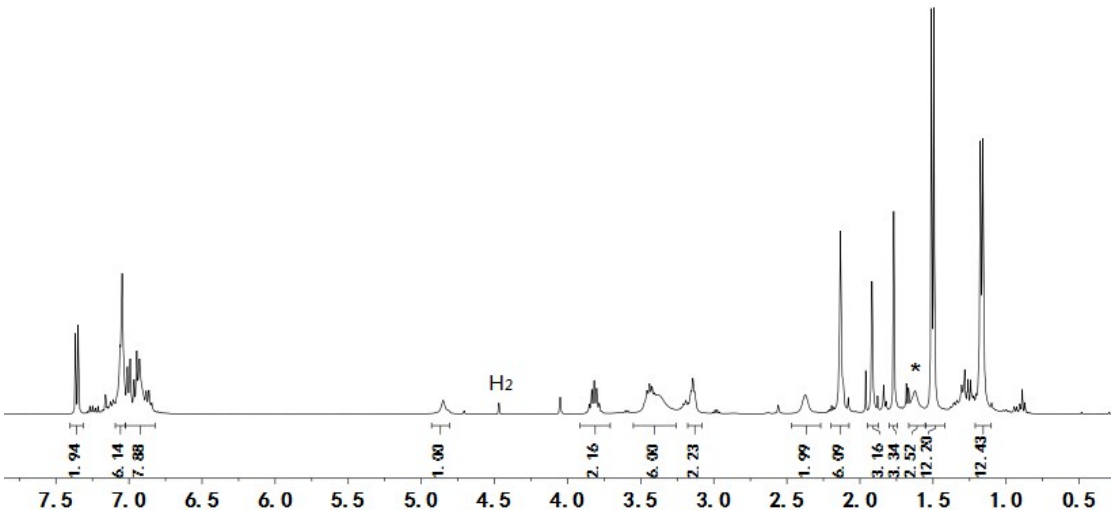


Fig. S15. $^{1}H\{^{11}B\}$ NMR (400 MHz, C_6D_6, 298 K) [*: BH_3]

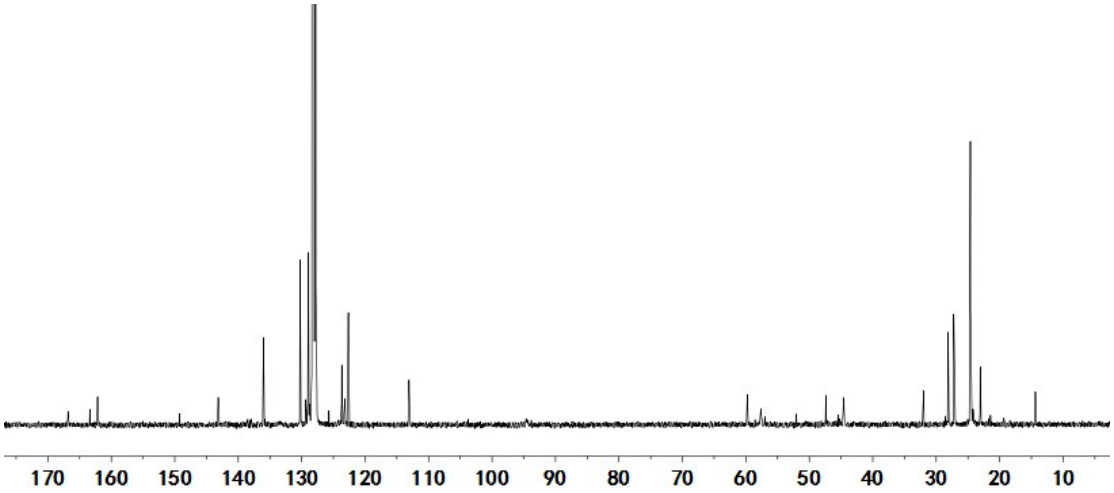


Fig. S16. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

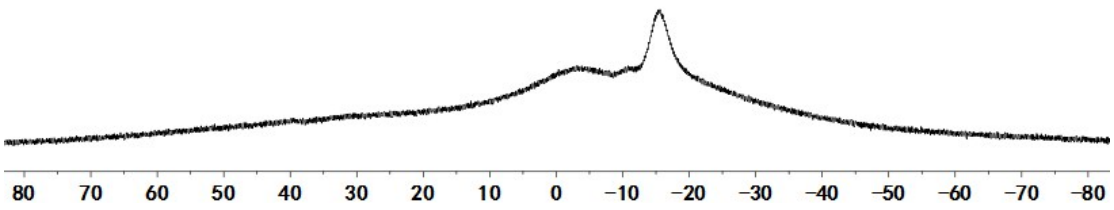


Fig. S17. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 5: formula $C_{47}H_{69}BCaN_4O$, M = 756.95 gmol^{-1}, colorless, 0.2 x 0.2 x 0.15 mm, Triclinic, space group *P -1*, a = 11.3589(4), b = 12.5204(4), c = 16.7864(6) Å, V = 2278.19(14) Å^3, ρ_{calc} = 1.104 gcm^{-3}, μ = 0.175

mm^{-1}, empirical absorption correction ($0.6778 \leq T \leq 0.7456$), $Z = 2$, $\lambda = 0.71073$ Å, T = 120(2) K, 87383 reflections collected ($-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$), 10491 independent (R_{int} = 0.0707) and 7559 observed reflections [$I>2\sigma(I)$], 511 refined parameters, the final R_1 was 0.0531 ($I > 2\sigma(I)$) and wR_2 was 0.1549 (all data). max. (min.) residual electron density 1.260 (-0.468) e.$Å^{-3}$, hydrogen atoms (expect B-H and N-H) were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

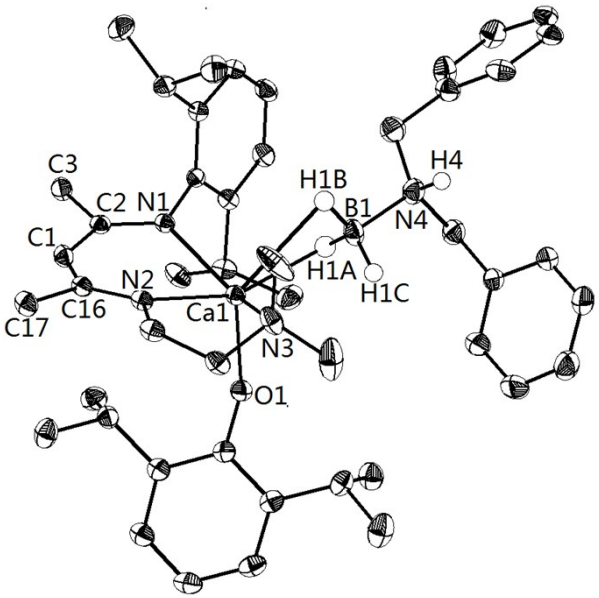
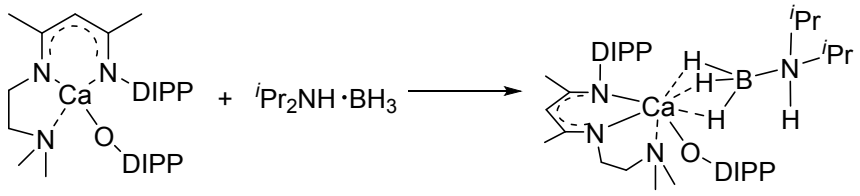


Fig. S18. Molecular structure of complex **5**.

Preparation of complex 6:



2 DIPP=2,6-$^{i}Pr_2$-C_6H_3 **6**

Scheme S5

Following the procedure described for **3**, reaction of $H_3B{\cdot}N^{i}Pr_2H$ (35 mg, 0.30 mmol) with **2** (164 mg, 0.30 mmol) gave **6** as a colorless crystalline solid (165 mg, 83%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30°C.

Elemental Analysis: calcd. for $C_{39}H_{69}BCaN_4O{\cdot}C_7H_8$: C, 73.37; H, 10.31; N, 7.44. Found: C, 73.17; H, 10.00; N, 7.49.

IR (KBr cell, cm^{-1}): ν = 3213 (N-H), 2389-2287 (B-H).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.34 (m, 2H, *m*-O*Ar*), 6.96 (m, 2H, *m*-N*Ar*) 6.92 (m, 1H, *p*-N*Ar*), 6.81 (m, 1H, *p*-O*Ar*), 4.84 (s, 1H, MeC(N)C*H*), 3.82 (m, 2H, OArC*H*Me_2), 3.43 (m, 2H, NArC*H*Me_2), 3.19 (m, 2H, NCH_2), 2.49 (m, 2H, HNC*H*Me_2), 2.39 (br, 2H, NCH_2), 2.17 (s, 6H, NMe_2), 1.94 (s, 3H, *Me*C), 1.77 (s, 3H, *Me*C), 1.49 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, OArCHMe_2), 1.18 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCHMe_2), 1.18 (br, 3H, BH_3, overlapped with NArCHMe_2)[1],1.17 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCHMe_2), 0.74 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, HNCHMe_2), 0.71 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, HNCHMe_2). [1 from the ^{1}H{^{11}B} experiment]. (The signal of N*H* was not observed).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.6 (Me*C*), 163.2 (Me*C*), 162.2 (*i*-O*Ar*), 149.3 (*i*-N*Ar*), 143.0 (*o*-N*Ar*), 136.0 (*o*-O*Ar*), 123.5 (*m*-N*Ar*), 122.9 (*p*-N*Ar*), 122.5 (*m*-O*Ar*), 112.9 (*p*-O*Ar*), 94.6 (MeC(N)*C*H), 59.9 (N*C*H_2) 51.8 (HN*C*HMe_2), 47.5 (N*C*H_2), 44.6 (NMe_2), 28.0 (NAr*C*HMe_2), 27.1 (OAr*C*HMe_2), 24.6 (NArCHMe_2, OArCHMe_2), 24.5 (*Me*C), 23.1 (*Me*C), 20.0 (HNCHMe_2), 19.5 (HNCHMe_2).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -20.8

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.34 / 6.81 (*m*-O*Ar* / *p*-O*Ar*), 6.96 / 6.92 (*m*-N*Ar* / *p*-N*Ar*), 3.82 / 1.49 (OArC*H*Me_2 /

OArCH*Me*$_2$), 3.43 / 1.18, 1.17 (NArC*H*Me$_2$ / NArCH*Me*$_2$), 3.19 / 2.39 (NC*H*$_2$ / NC*H*$_2$), 2.49 / 0.74, 0.71 (HNC*H*Me$_2$ / HNCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.34 / 122.5 (*m*-O*Ar*), 6.96 / 123.5 (*m*-N*Ar*), 6.92 / 122.9 (*p*-N*Ar*), 6.81 / 112.9 (*p*-O*Ar*), 4.84 / 94.6 (MeC(N)*CH*), 3.82 / 27.1 (OAr*CH*Me$_2$), 3.43 / 28.0 (NAr*CH*Me$_2$), 3.19 / 47.5 (NC*H*$_2$), 2.49 / 51.8 (HNC*H*Me$_2$), 2.39 / 59.9 (NC*H*$_2$), 2.17 / 44.6 (N*Me*$_2$), 1.94 / 23.1 (*Me*C), 1.77 / 24.5 (*Me*C), 1.49 / 24.6 (OArCH*Me*$_2$), 1.18, 1.17 / 24.6 (NArCH*Me*$_2$), 0.74 / 19.5 (HNCH*Me*$_2$), 0.71 / 20.0 (HNCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.34 / 162.2 (m-O*Ar* / *i*-O*Ar*), 6.96 / 149.3 (*m*-N*Ar* / *i*-N*Ar*), 6.92 / 143.0 (*p*-N*Ar* / *o*-N*Ar*), 6.81 / 136.0 (*p*-O*Ar* / *o*-O*Ar*), 3.82 / 162.2, 136.0, 122.5 (OArC*H*Me$_2$ / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 3.43 / 149.3, 143.0, 123.5 (NArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.19 / 166.6, 59.9 (NC*H*$_2$ / Me*C*, NC*H*$_2$), 2.39 / 47.5 (NC*H*$_2$ / NC*H*$_2$), 2.17 / 59.9 (N*Me*$_2$ / NC*H*$_2$), 1.94 / 166.6 (*Me*C / Me*C*), 1.49 / 136.0 (OArCH*Me*$_2$ / *o*-O*Ar*), 1.18, 1.17 / 143.0 (NArCH*Me*$_2$ / *o*-N*Ar*), 0.74, 0.71 / 51.8 (HNCH*Me*$_2$ / HN*C*HMe$_2$).

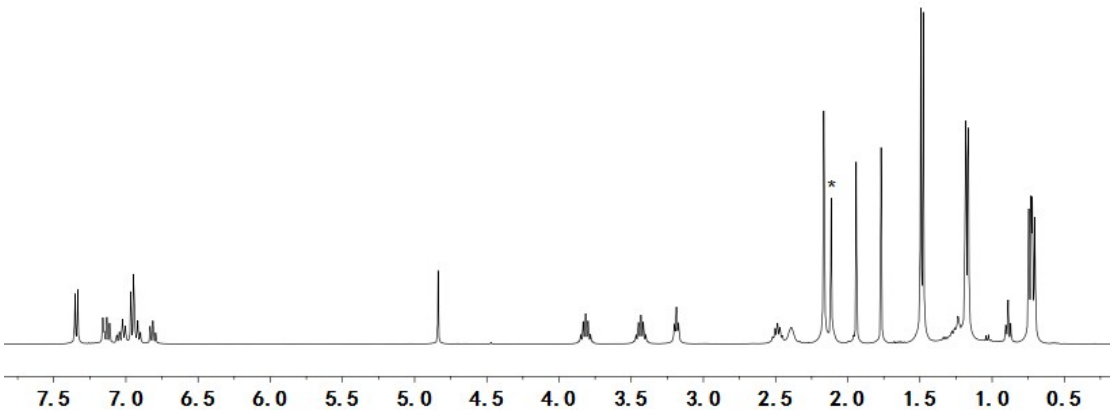


Fig. S19. ^{1}H NMR (400 MHz, C_6D_6, 298 K) [*: Toluene].

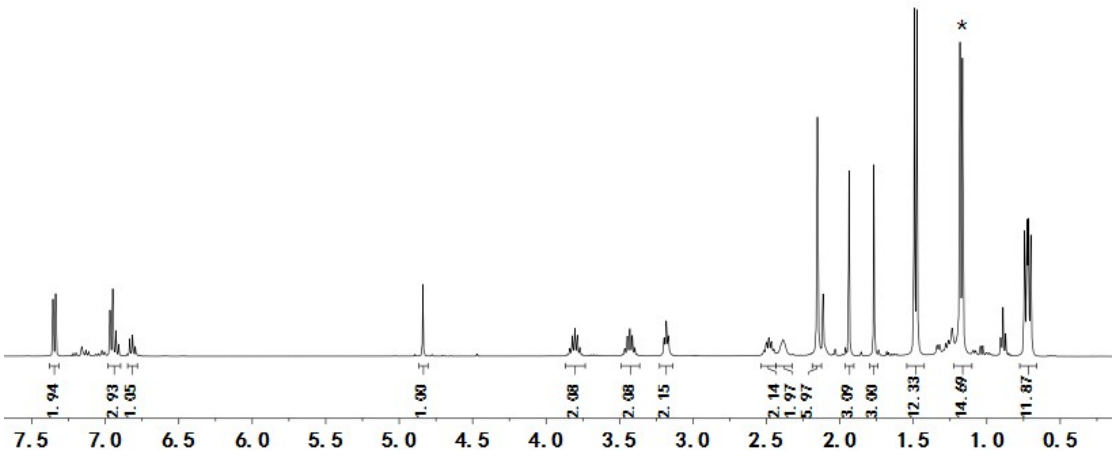


Fig. S20. $^{1}H\{^{11}B\}$ NMR (400 MHz, C_6D_6, 298 K) [*: BH_3]

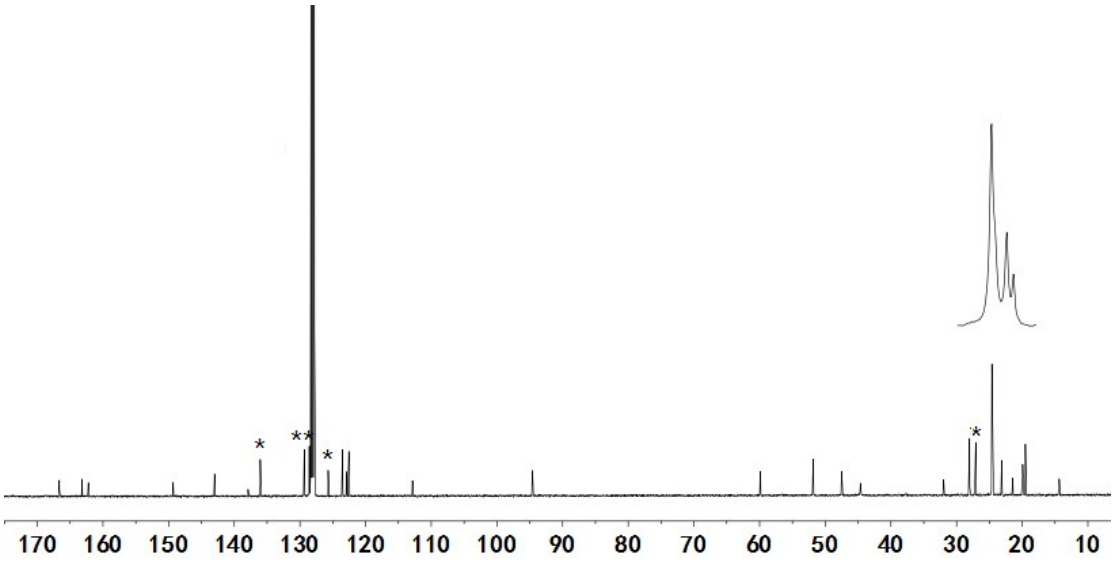


Fig. S21. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) [*: Toluene].

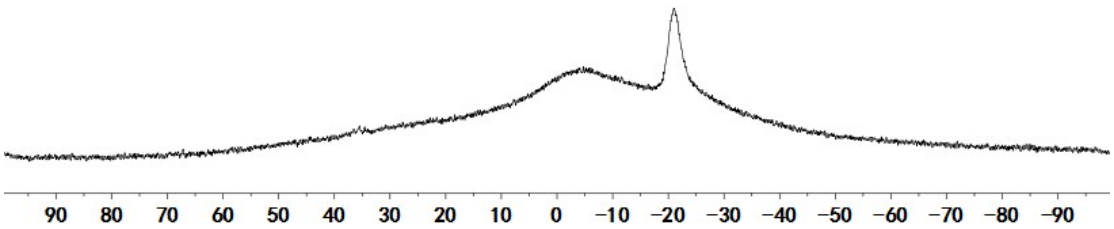


Fig. S22. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 6: formula $C_{39}H_{69}BCaN_4O{\cdot}C_7H_8$, M =

660.87 gmol^{-1}, colorless, 0.22 x 0.15 x 0.12 mm, Monoclinic, space group *P 21/c*, *a* = 12.6088(4), *b* = 15.1912(7), *c* = 21.9255(8) Å, *V* = 4034.1(3) Å^3, ρ_{calc} = 1.088 gcm^{-3}, μ = 0.188 mm^{-1}, empirical absorption correction (0.965 ≤ T ≤ 0.978), *Z* = 4, λ = 0.71073 Å, T = 120(2) K, 63556 reflections collected (-15 ≤ h ≤ 16, -19 ≤ k ≤ 19, -26 ≤ l ≤ 28), 9279 independent (R_{int} = 0.0834) and 5957 observed reflections [I>2σ(I)], 447 refined parameters, the final R_1 was 0.0604 (I > 2σ(I)) and wR_2 was 0.1948 (all data). max. (min.) residual electron density 1.370 (-0.509) e.Å^{-3}, hydrogen atoms (expect B-H and N-H) were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

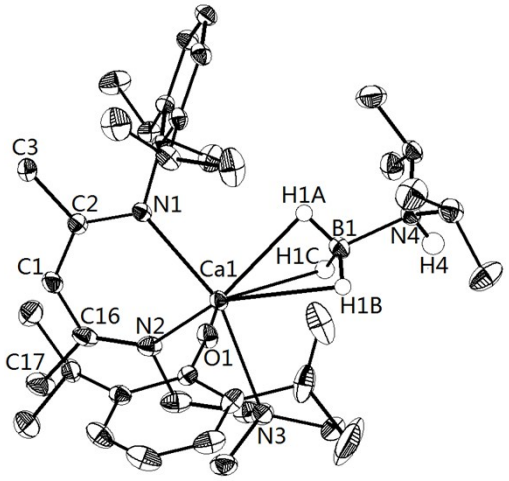


Fig. S23. Molecular structure of complex **6**.

Preparation of $^{i}Pr_2NH{\cdot}BD_3$

A solution of $BD_3{\cdot}THF$ (11 mmol, in 11 mL of THF) was slowly added to a solution of $^{i}Pr_2NH$ (1.0 g, 10 mmol) in THF at -30°C. The reaction mixture was warmed to 25°C and stirred overnight. The solvent was removed and resulting liquid was distilled under vacuum to give $^{i}Pr_2NH{\cdot}BD_3$ (863 mg, 73% yield).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.66 (m, 2H, C*H*Me$_2$), 2.50 (br, s, N*H*), 0.96 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 0.82 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$).

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 1.94 (B*D*$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 51.7 (*C*HMe$_2$), 20.7, 18.9 (CH*Me*$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -20.5.

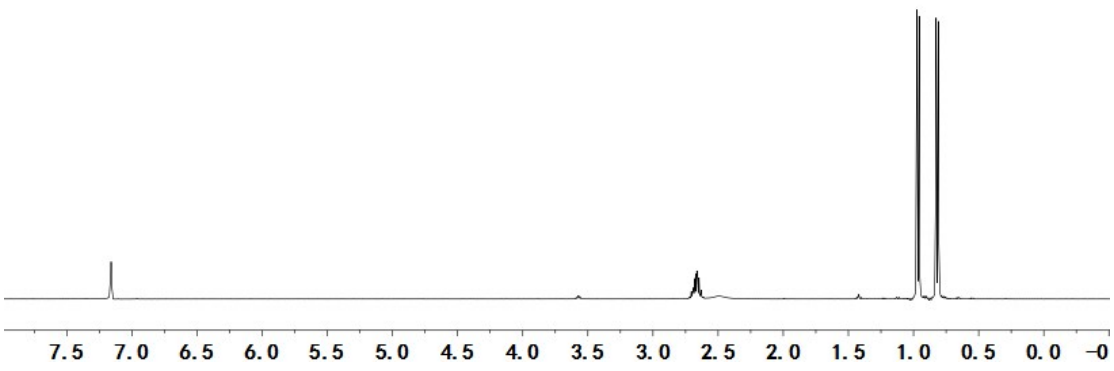


Fig. S24. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

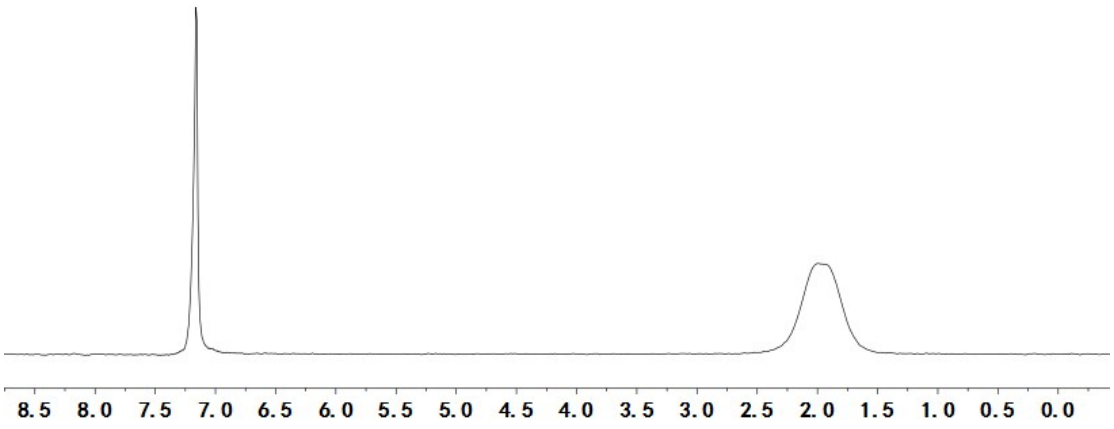


Fig. S25. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

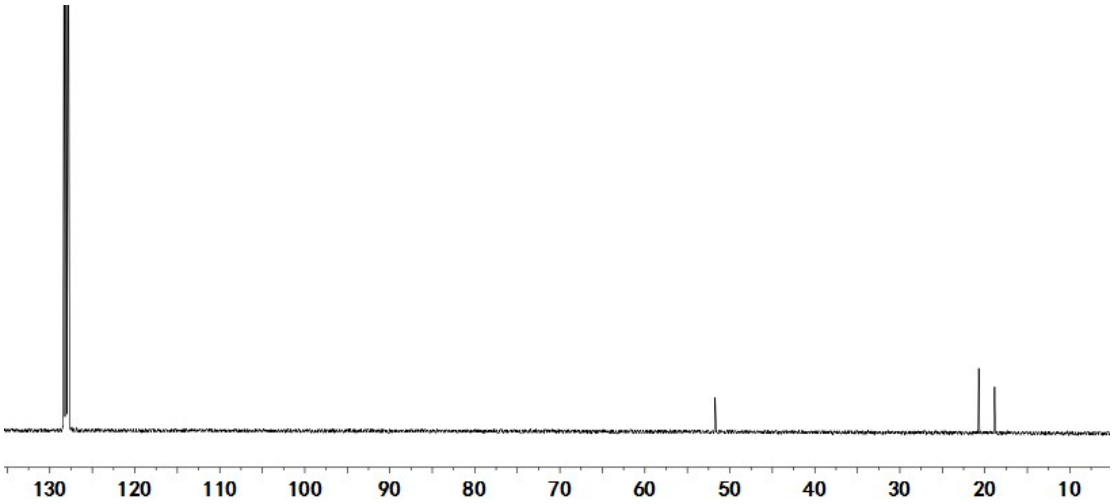


Fig. S26. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

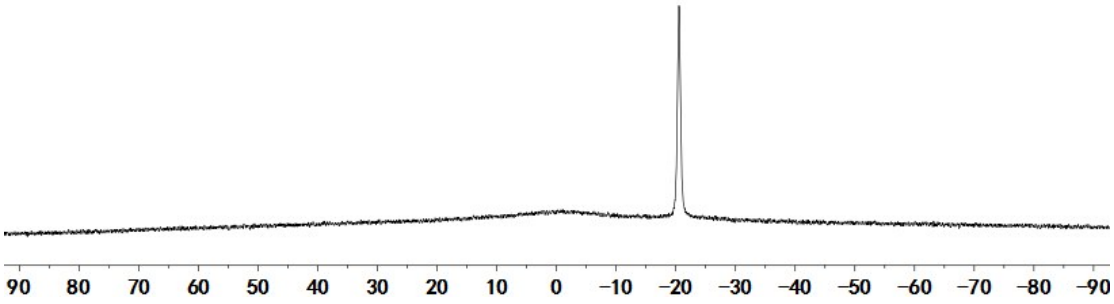


Fig. S27. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

Preparation of $^{i}Pr_2ND{\cdot}BH_3$

$^{i}Pr_2NH{\cdot}BH_3$ (402 mg, 3.5 mmol) was dissolved in degassed D_2O (700 µL, 38 mmol) and the reaction mixture was stirred at 40°C for 24h. The solution was extracted with CH_2Cl_2 (3*2 mL) and dried with $MgSO_4$. The resulting liquid was distilled under vacuum to give $^{i}Pr_2ND{\cdot}BH_3$ (264 mg, 65% yield).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.69 (m, 2H, C*H*Me$_2$), 2.06 (q, $^{1}J_{BH}$ = 94 Hz, B*H*$_3$), 0.97 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 0.84 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$).

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 2.75 (N*D*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 51.7 (*C*HMe$_2$), 20.6, 18.9 (CH*Me*$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -20.2 (q, $^{1}J_{BH}$ =94 Hz, *B*H$_3$).

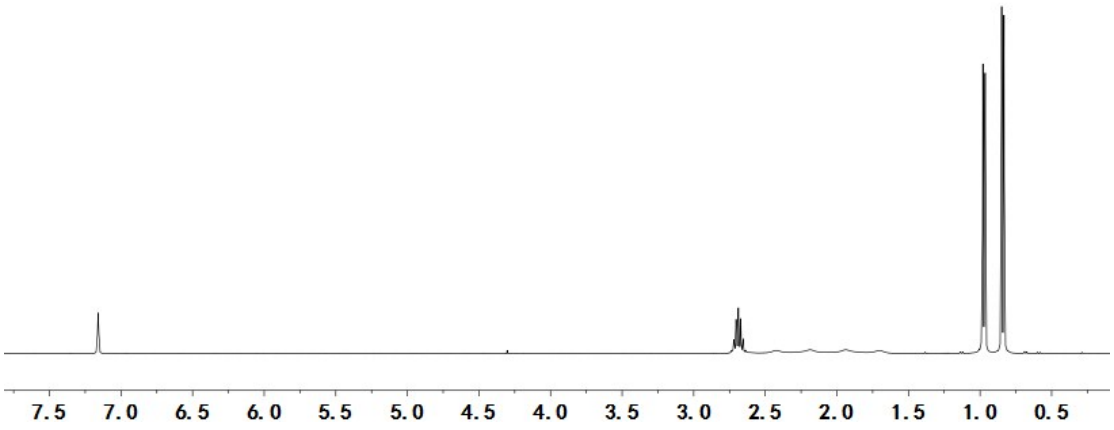


Fig. S28. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

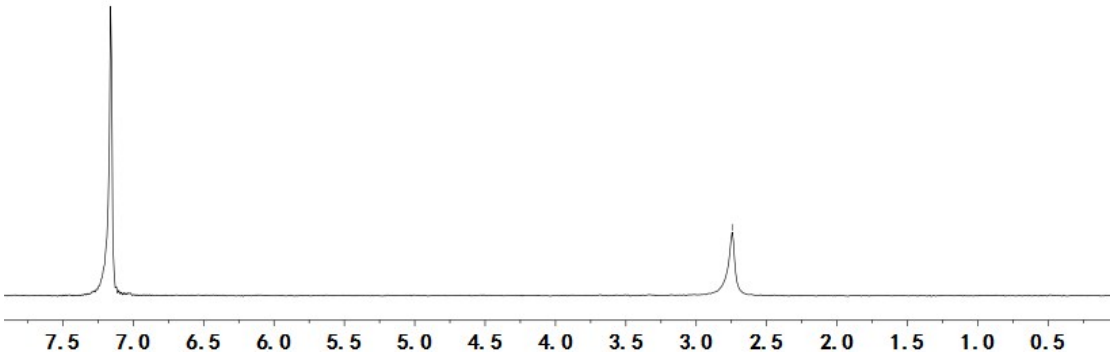


Fig. S29. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

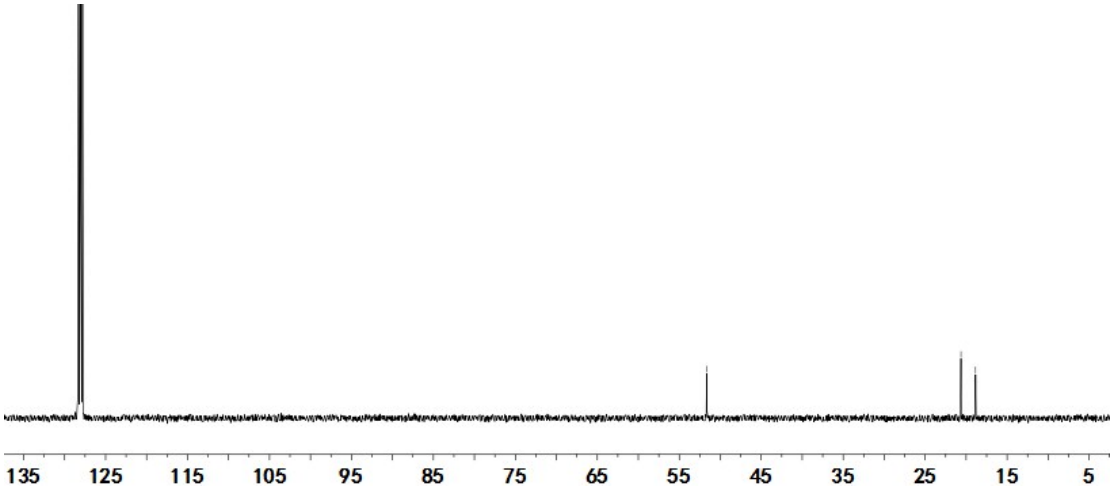


Fig. S30. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

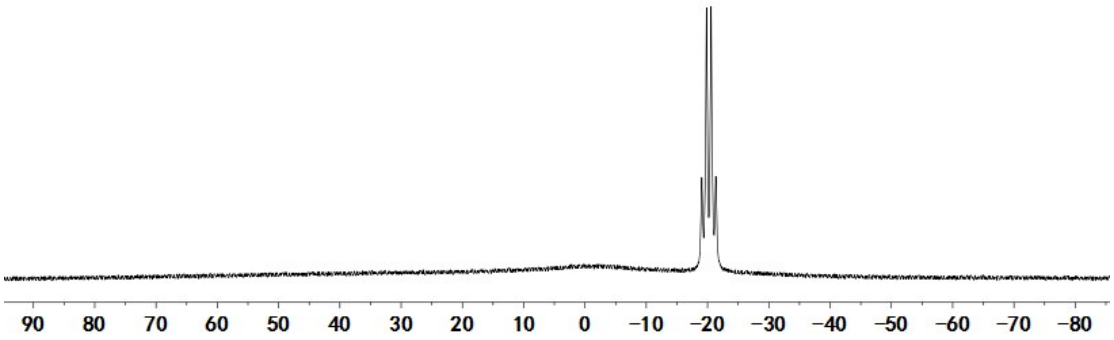


Fig. S31. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

Preparation of $^{i}Pr_2ND{\cdot}BD_3$

Following the procedure described for $^{i}Pr_2ND{\cdot}BH_3$, reaction of $^{i}Pr_2NH{\cdot}BD_3$ (400 mg, 3.4 mmol) with D_2O (700 µL, 38 mmol) gave $^{i}Pr_2ND{\cdot}BD_3$ as a colorless oil (240 mg, 60%).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.70 (m, 2H, C*H*Me$_2$), 0.98 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 0.86 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$).

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 2.78 (N*D*), 1.94 (B*D*$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 51.6 (*C*HMe$_2$), 20.7, 18.8 (CH*Me*$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -20.6

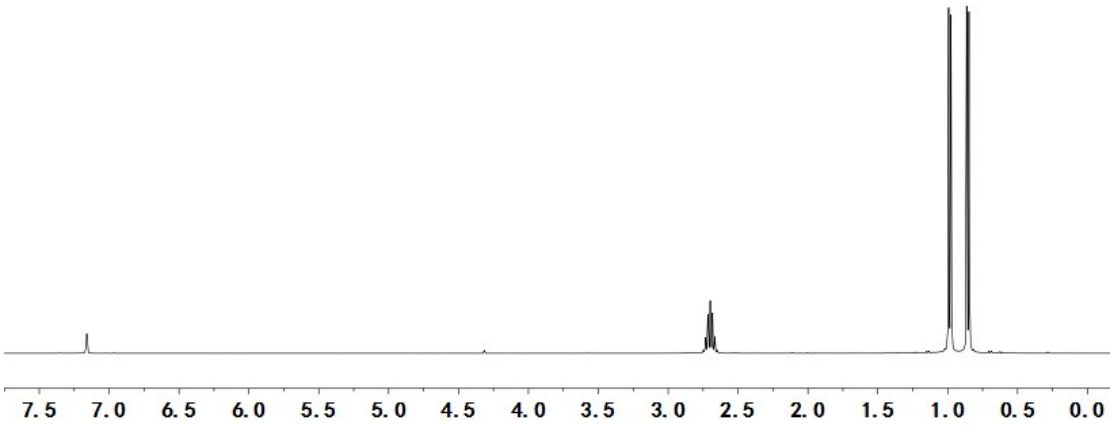


Fig. S32. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

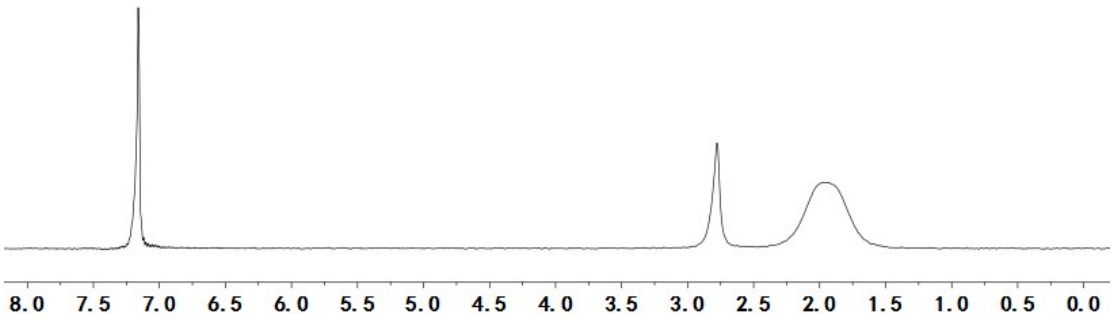


Fig. S33. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

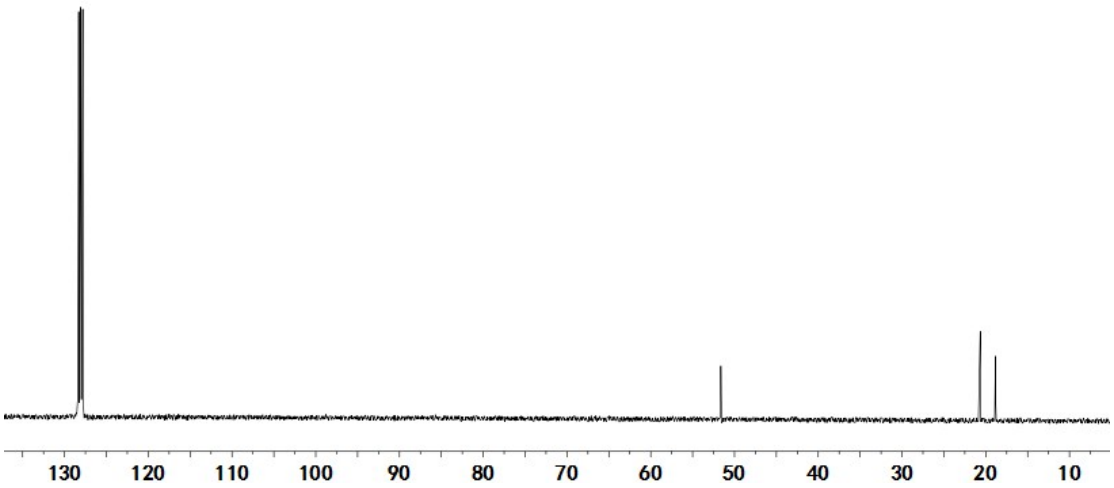


Fig. S34. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

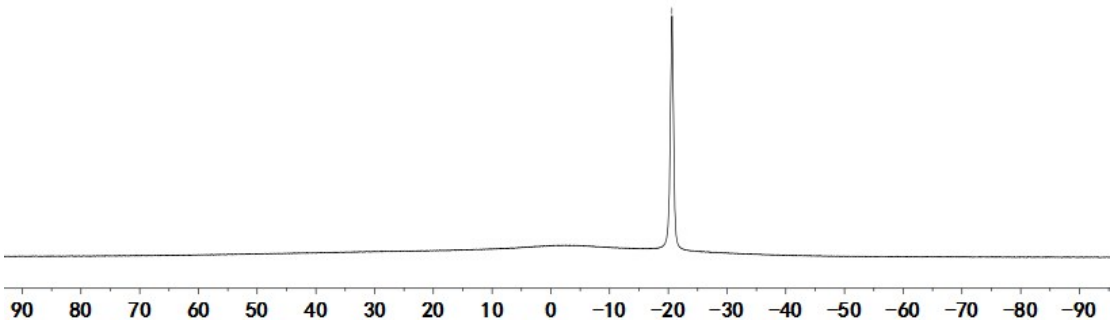
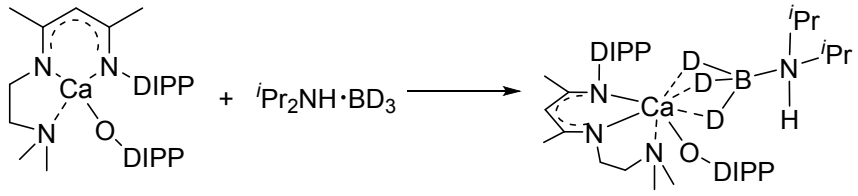


Fig. S35. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

Preparation of complex 6-*D*:



2 DIPP=2,6-$^{i}Pr_2$-C_6H_3 **6-*D***

Scheme S6

Following the procedure described for **3**, reaction of $D_3B\cdot N^{i}Pr_2H$ (36 mg, 0.30 mmol) with **2** (164 mg, 0.30 mmol) gave **6-*D*** as a colorless crystalline solid (165 mg, 83%).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.36 (m, 2H, *m*-O*Ar*), 6.96 (m, 2H, *m*-N*Ar*) 6.94 (m, 1H, *p*-N*Ar*), 6.81 (m, 1H, *p*-O*Ar*), 4.84 (s, 1H, MeC(N)C*H*), 3.82 (m, 2H, OArC*H*Me$_2$), 3.44 (m, 2H, NArC*H*Me$_2$), 3.18 (m, 2H, NCH_2), 2.48 (m, 2H, HNC*H*Me$_2$), 2.39 (br, s, 2H, NCH_2), 2.16 (s, 6H, N*Me*$_2$), 1.94 (s, 3H, *Me*C), 1.77 (s, 3H, *Me*C), 1.49 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, OArCH*Me*$_2$), 1.17 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 1.17 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 0.74 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, HNCH*Me*$_2$), 0.71 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, HNCH*Me*$_2$). (The signals of N*H* were not observed).

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 1.18 (s, BD_3).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = -21.3.

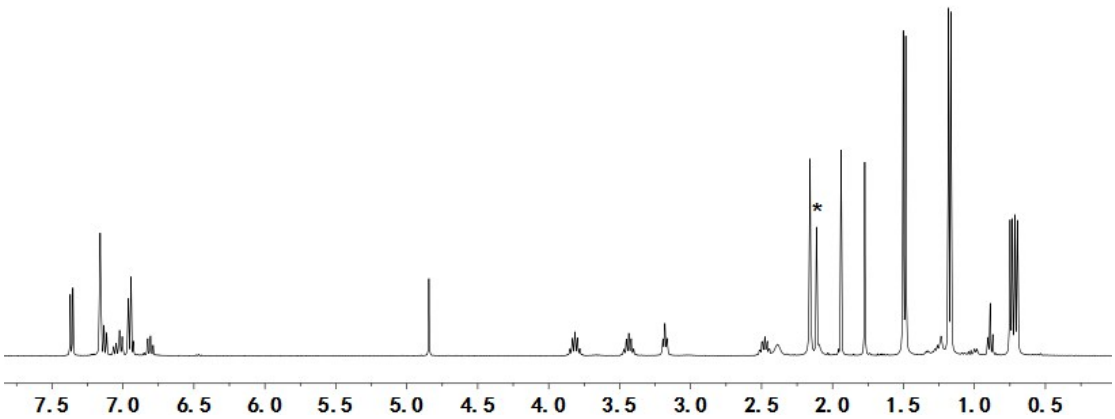


Fig. S36. ^{1}H NMR (400 MHz, C_6D_6, 298 K) [*: Toluene].

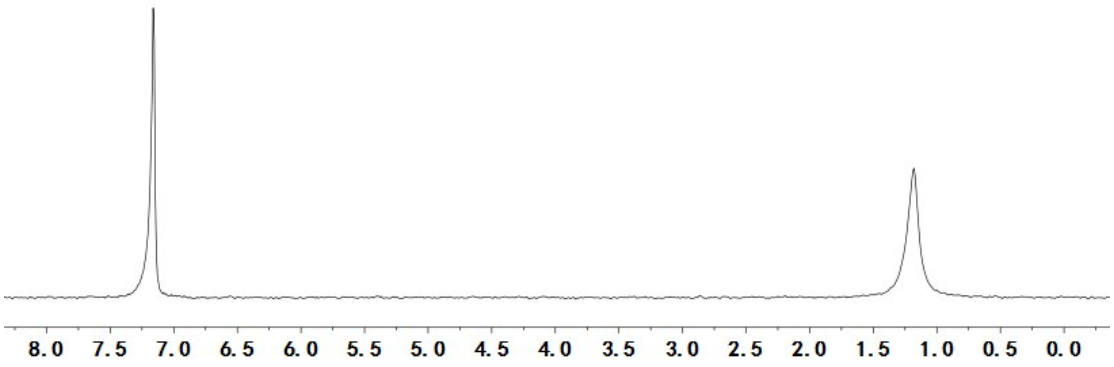


Fig. S37. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

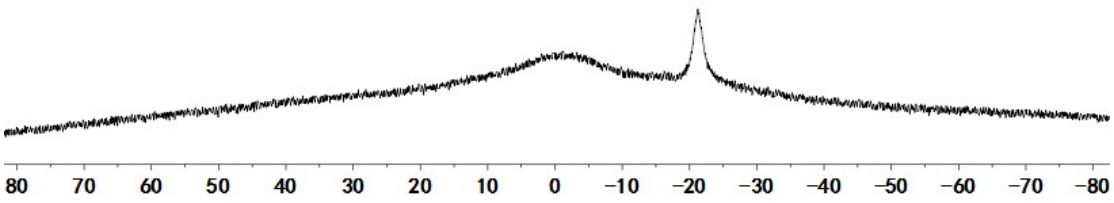


Fig. S38. ^{11}B NMR (128 MHz, C_6D_6, 298 K)

General catalytic dehydrogenation procedure

A solution of predetermined amount of calcium catalyst in C_6D_6 (0.25 mL) was added to a solution of amine-borane substrate in 0.25 mL of C_6D_6 in a J-Young NMR tube. The reaction mixture was heated at 60°C and monitored by NMR spectroscopy.

Investigation of the thermal stability of complex 4

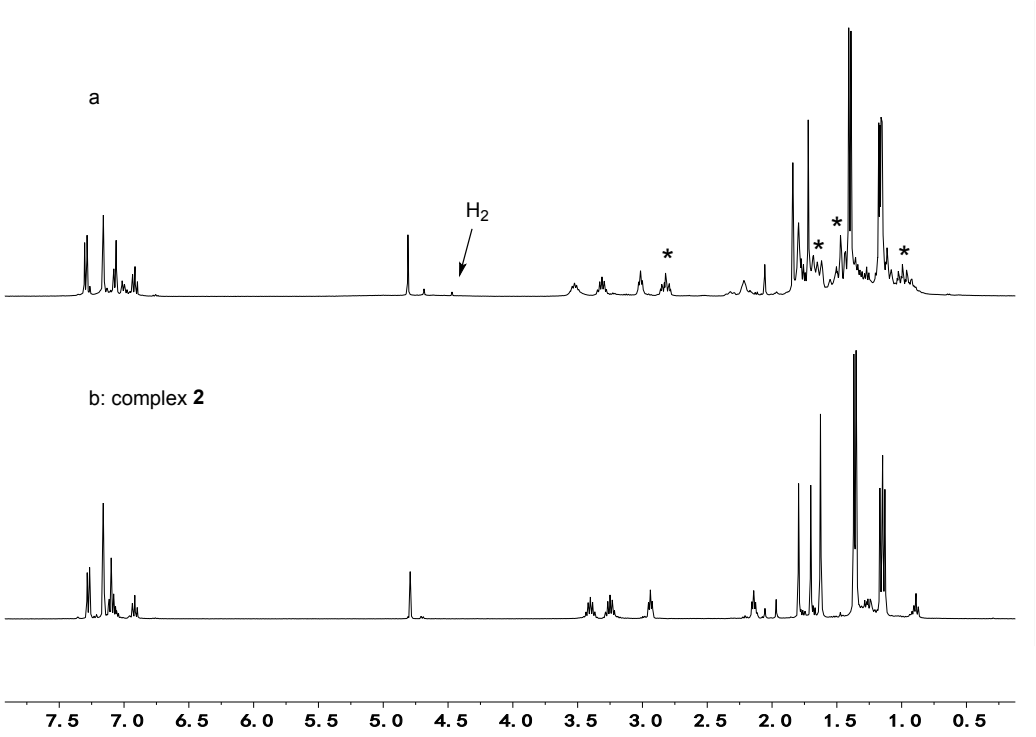


Fig. S39. (a) ^{1}H NMR spectroscopy of the reaction of heating complex **4** at 60°C for 3h [*: $H_2B{=}NCy_2$]; (b) complex **2**.

^{11}B NMR spectra of catalytic dehydrogenation products

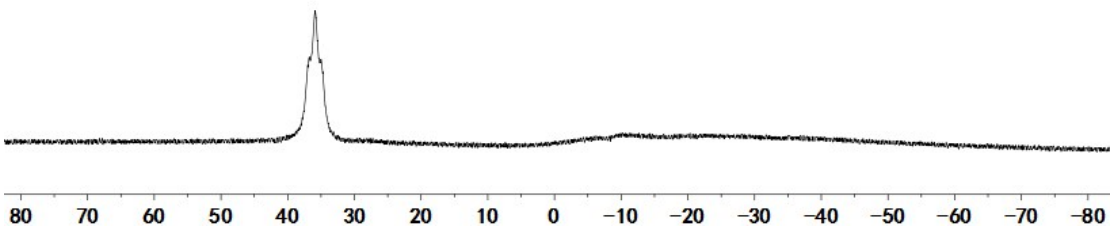


Fig. S40. ^{11}B NMR of the $H_2B{=}NCy_2$ (128 MHz, C_6D_6, 298 K).

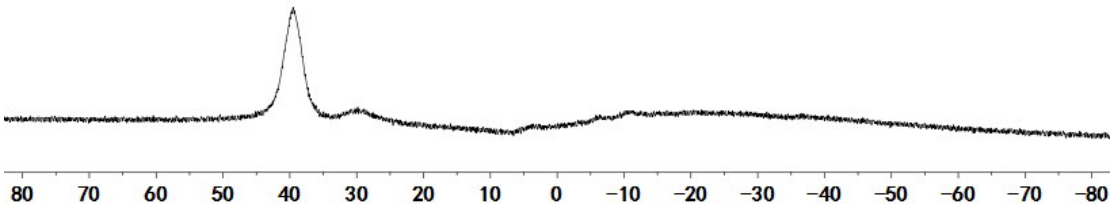


Fig. S41. ^{11}B NMR of the $H_2B{=}N(PhCH_2)_2$ (128 MHz, C_6D_6, 298 K).

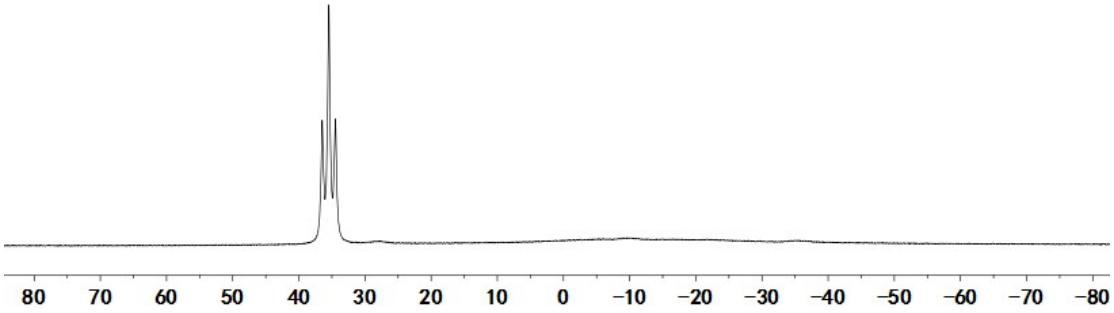


Fig. S42. ^{11}B NMR of the $H_2B{=}N^iPr_2$ (128 MHz, C_6D_6, 298 K).

General method for kinetic studies

A solution of complex **2** (0.04 mmol) in C_6D_6 (0.5 mL) was added to a solution of $^iPr_2N(H/D)\cdot B(H/D)_3$ (0.8 mmol) in C_6D_6 (2 mL), and the resulting mixture was heated at 60^{o}C and monitored by ^{1}H NMR spectroscopy at regular time intervals.

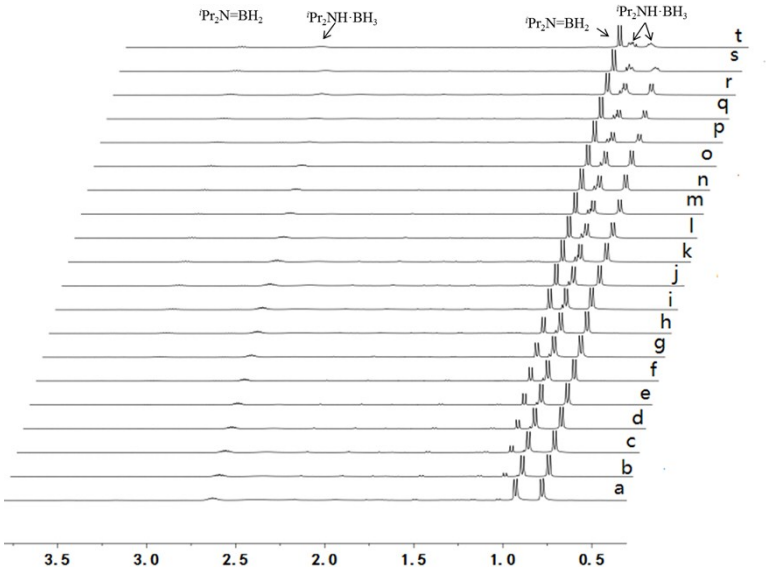


Fig. S43. ^{1}H NMR (400 MHz, C_6D_6) of spectra showing conversion of $^iPr_2NH\cdot BH_3$ to

$^{i}Pr_2N{=}BH_2$ by complex **2** as catalyst (5 mol %, C_6D_6, 60 °C). (a) t = 20 min, (b) t = 40 min, (c) t = 60 min, (d) t = 80 min, (e) t = 100 min, (f) t = 120 min, (g) t = 140 min, (h) t = 160 min, (i) t = 180 min, (j) t = 200 min, (k) t = 220 min, (l) t = 240 min, (m) t = 260 min, (n) t = 280 min, (o) t = 300 min, (p) t = 320 min, (q) t = 340 min, (r) t = 360 min, (s) t = 380 min, (t) t = 400 min.

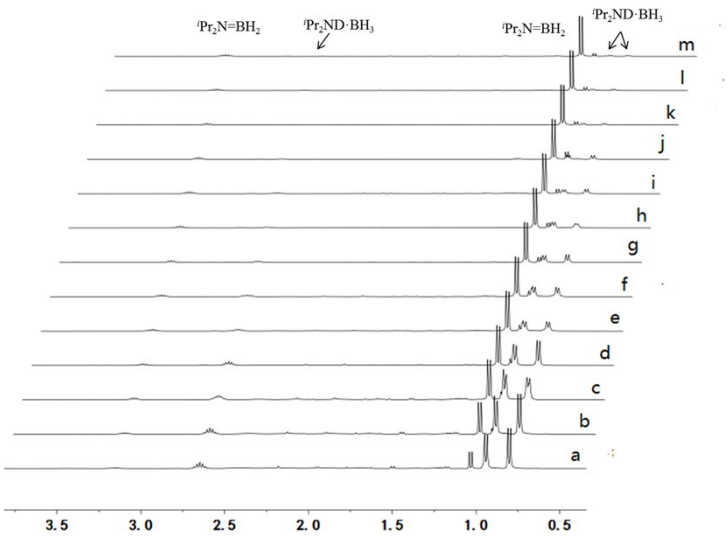


Fig. S44. ^{1}H NMR (400 MHz, C_6D_6) of spectra showing conversion of $^{i}Pr_2ND{\cdot}BH_3$ to $^{i}Pr_2N{=}BH_2$ by complex **2** as ecatalyst (5 mol %, C_6D_6, 60 °C). (a) t = 30 min, (b) t = 60 min, (c) t = 90 min, (d) t = 120 min, (e) t = 180 min, (f) t = 210 min, (g) t = 240 min, (h) t = 270 min, (i) t = 330 min, (j) t = 360 min, (k) t = 390 min, (l) t = 420 min, (m) t = 450 min.

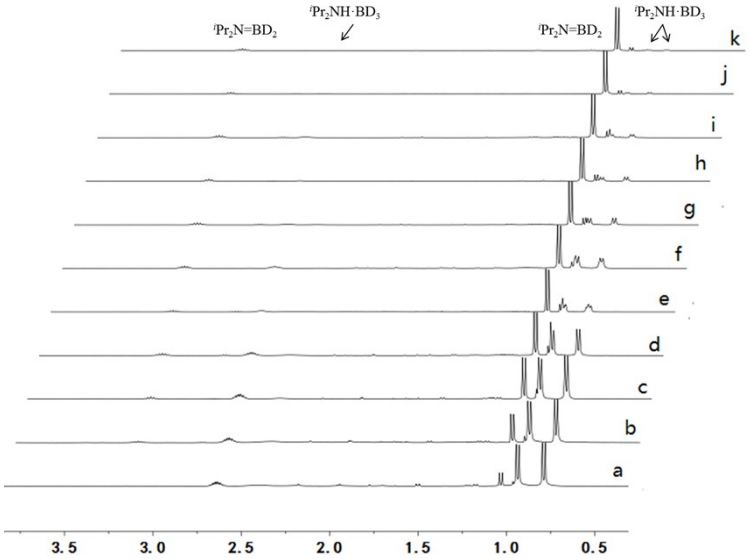


Fig. S45. ^{1}H NMR (400 MHz, C_6D_6) of spectra showing conversion of $^{i}Pr_2NH{\cdot}BD_3$ to $^{i}Pr_2N{=}BD_2$ by complex **2** as catalyst (5 mol %, C_6D_6, 60 °C). (a) t = 60 min, (b) t =

120 min, (c) t = 180 min, (d) t = 240 min, (e) t = 360 min, (f) t = 420 min, (g) t = 480 min, (h) t = 540 min, (i) t = 600 min, (j) t = 660 min, (k) t = 720 min.

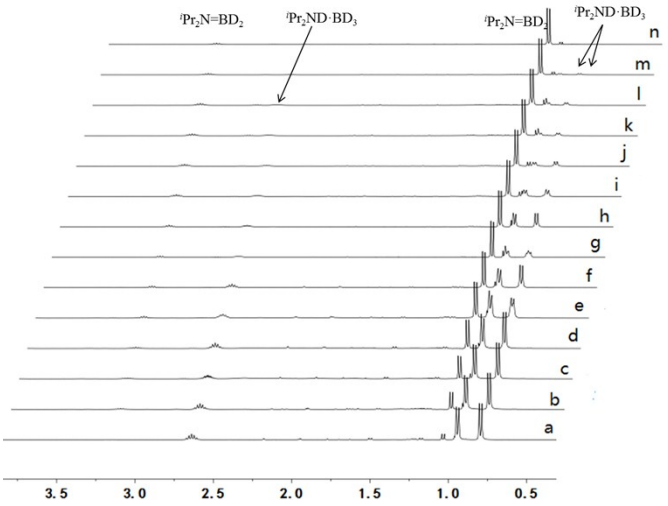


Fig. S46. ^{1}H NMR (400 MHz, C_6D_6) of spectra showing conversion of ^{i}Pr$_2$ND·BD$_3$ to ^{i}Pr$_2$N=BD$_2$ by complex **2** as catalyst (5 mol %, C_6D_6, 60 °C). (a) t = 30 min, (b) t = 60 min, (c) t = 120 min, (d) t = 180 min, (e) t = 240 min, (f) t = 300 min, (g) t = 360 min, (h) t = 420 min, (i) t = 540 min, (j) t = 600 min, (k) t = 660 min, (l) t = 720 min, (m) t = 780 min, (n) t = 840 min.

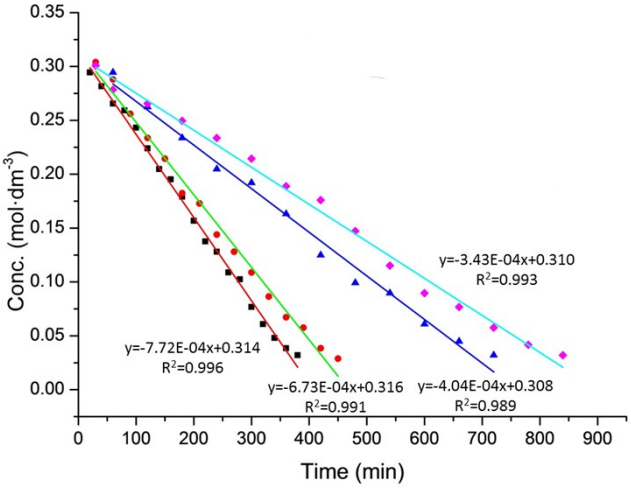


Fig. S47. Graph of substrate concentration versus time for the catalytic dehydrogenation of ^{i}Pr$_2$NH·BH$_3$ (black squares, k = -7.72·10^{-4} ± 1.10·10^{-5} mol / dm^3·min), ^{i}Pr$_2$ND·BH$_3$ (red dots, k = -6.73·10^{-4} ± 1.70·10^{-5} mol / dm^3·min), ^{i}Pr$_2$NH·BD$_3$ (blue triangles, k = -4.04·10^{-4} ± 1.28·10^{-5} mol / dm^3·min), and ^{i}Pr$_2$ND·BD$_3$ (pink diamonds, k = -3.43·10^{-4} ± 7.95·10^{-6} mol / dm^3·min).