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Supporting Information

Mononuclear Calcium Complex as Effective Catalyst for Alkenes Hydrogenation

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General remarks

All reactions were carried out under a dry and oxygen-free nitrogen atmosphere using Schlenk techniques and a Vigor glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored using an O_2 (GE) / H_2O (Xentaur) analyzer to ensure that both were always below 0.1 ppm. Toluene, hexane and Et_2O were purified by use of a Vigor VSPS-5 solvent purification system, and dried over fresh Na chips in the glovebox. Tetrahydrofuran (THF), Tetrahydropyran (THP), isooctane (ISO), pentane, cyclohexane-d_{12} and benzene-d_6 were distilled from Na/K alloy/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. K(*p*-$CH_2C_6H_4$-Me) was obtained as red solid from the one-pot reaction of *n*-BuLi, KO^{t}Bu and *p*-xylene, according to the previous procedure[1]. The substrates 1-hexene, 2-octene, trimethylsilylethylene, 4-phenyl-1-butene, styrene, *α*-methyl styrene, 1,1-diphenylethylene, 1,2-diphenylethylene, norbornene, 1-phenylcyclohexene, cyclohexene, cyclooctene, 4-ethenylcyclohexene, 2-ethyl-1-butene were dried over CaH_2 at 45°C for 18 h and distilled before usage. Other commercially available reagents were used without purification.

Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 or AV500 spectrometer. ^{1}H and ^{13}C NMR spectra of complexes were recorded using TMS as internal standard. Conversion was determined by integration of characteristic signals in the NMR spectra of substrate and product. The elemental analyses were performed on Elementar Vario EL cube (WO_3 was used as pro-oxidant) at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

Synthetic and analytical data for new complexes

Synthesis of [Ca(*p*-$CH_2C_6H_4$-Me)$_2$(THF)$_4$] (1)

Addition of CaI_2 (1.00 g, 3.40 mmol) to a red solution of K(*p*-$CH_2C_6H_4$-Me) (981 mg, 6.80 mmol) in 30 mL THF resulted in a gradual color change of red to orange. The reaction mixture was stirred for 6 h at room temperature then filtered. The obtained solution was concentrated to ~10 mL, and kept at -30 ^{o}C to give complex **1** (1.63 g, 3.02 mmol, 89 % yields) as yellow crystals. ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 1.42 (m, 16H, THF), 1.88 (s, 4H, Ca-C*H*$_2$), 2.22 (s, 6H, C*H*$_3$), 3.50 (m, 16H, THF), 6.72 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar-*H*$_{ortho}$), 6.82 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar-*H*$_{meta}$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ^{o}C): δ = 20.53 (s, *C*H$_3$), 25.21 (s, THF), 40.42 (s,

Ca-CH_2), 68.28 (s, THF), 119.31 (s, Ar-C_{para}), 119.54 (s, C_{ortho}), 129.85 (s, Ar-C_{meta}), 154.79 (s, Ar-C_{ipso}). Anal. calcd. for (**1**) $C_{32}H_{50}O_4Ca_1$ (538.83): C, 71.33; H, 9.35 found: C, 71.25; H, 9.42.

Synthesis of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THF)] (2)

Solid of (Tp^{Ad,iPr})H (743 mg, 1.00 mmol) was added in several portions to a stirred solution of [Ca(*p*-$CH_2C_6H_4$-Me)$_2$(THF)$_4$] (539 mg, 1.00 mmol) in Et_2O (10 mL). The mixture was stirred for 4 h at room temperature then filtered. The obtained solution was stripped off all the volatiles to give complex **2** (921 mg, 0.96 mmol, 96 % yields) as pale-yellow powder. Single crystals of complex **2** suitable for X-ray analysis, were grown from hexane at -30 °C as pale-yellow crystals. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 1.15 (d, $^3J_{HH}$ = 7 Hz, 18H, CH(CH_3)$_2$), 1.18 (m, 4H, THF), 1.76, 1.87 (dd, $^3J_{HH}$ = 12, 11.5 Hz, 18H, AdCH_2), 2.08 (br, 18H, AdCH_2), 2.14 (br, 9H, AdC*H*), 2.27 (s, 2H, Ca-CH_2), 2.36 (s, 3H, CH_3), 3.09 (m, 4H, THF), 3.57 (sept, $^3J_{HH}$ = 7 Hz, 3H, C*H*(CH$_3$)$_2$), 5.94 (s, 3H, 4-pz-*H*), 7.06 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar-H_{ortho}), 7.09 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar-H_{meta}). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ = 20.77 (s, *C*H$_3$), 23.11 (s, CH(*C*H$_3$)$_2$), 25.09 (s, THF), 26.66 (s, *C*H(CH$_3$)$_2$), 28.70 (s, Ad-γ), 34.34 (s, Ad-α), 36.65 (s, Ad-δ), 40.67 (s, Ca-*C*H$_2$), 43.42 (s, Ad-β), 68.24 (s, THF), 97.55 (s, pz-4*C*), 120.93 (s, Ar-C_{para}), 121.76 (s, C_{ortho}), 128.89 (s, Ar-C_{meta}), 156.69 (s, pz-3*C*), 156.75 (s, Ar-C_{ipso}), 163.35 (s, pz-5*C*). Anal. calcd. for (**2**) $C_{60}H_{87}B_1N_6O_1Ca_1$ (959.29): C, 75.12; H, 9.14; N, 8.76 found: C, 75.04 H, 9.31; N, 8.72.

Synthesis of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THP)] (2-THP)

[(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THF)] (800 mg, 0.83 mmol) was dissolved in THP/Hexane (10/10 mL). The resulting mixture was stirred for 1 h at room temperature then filtered. The obtained solution was stripped off all the volatiles to give complex **2-THP** (788 mg, 0.81 mmol, 97.6 % yields) as pale-yellow powder. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 1.04 (m, 6H, THP), 1.15 (d, $^3J_{HH}$ = 7 Hz, 18H, CH(CH_3)$_2$), 1.76, 1.88 (dd, $^3J_{HH}$ = 12, 11.5 Hz, 18H, AdCH_2), 2.09 (br, 18H, AdCH_2), 2.15 (br, 9H, AdC*H*), 2.24 (s, 2H, Ca-CH_2), 2.33 (s, 3H, CH_3), 2.97 (m, 4H, THP), 3.56 (sept, $^3J_{HH}$ = 6.5 Hz, 3H, C*H*(CH$_3$)$_2$), 5.93 (s, 3H, 4-pz-*H*), 7.02, 7.04 (dd, $^3J_{HH}$ = 8, 8.5 Hz, 4H, Ar). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ = 20.71 (s, *C*H$_3$), 22.51 (s, THP), (23.15 (s, CH(*C*H$_3$)$_2$), 25.97 (s, THP), 26.64 (s, *C*H(CH$_3$)$_2$), 28.71 (s, Ad-γ), 34.42 (s, Ad-α), 36.64 (s, Ad-δ), 40.36 (s, Ca-*C*H$_2$), 43.50 (s, Ad-β), 68.98 (s, THP), 97.59 (s, pz-4*C*), 120.97 (s, Ar-C_{para}), 121.61 (s, C_{ortho}), 128.96 (s, Ar-C_{meta}), 156.65 (s, Ar-C_{ipso}), 156.76 (s, pz-3*C*), 163.41 (s, pz-5*C*). Anal. calcd. for (**2-THP**) $C_{61}H_{89}B_1N_6O_1Ca_1$ (973.31): C, 75.28; H, 9.22; N, 8.63 found: C, 75.16 H, 9.29; N, 8.59.

Synthesis of [(Tp^{Ad,iPr})Ca(H)(THP)] (3)

A solution of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THP)] (660 mg, 0.68 mmol) in hexane (20 mL) was added into a glass tube in a medium-pressure autoclave. The autoclave was transferred outside of the glovebox and pressurized with H_2 to 20 atm. The mixture was stirred at room temperature for 24 h. Pressure was released and the autoclave was quickly returned to the glovebox. After filtration, the solution was stripped off to give complex **3** (478 mg, 0.55 mmol, 81 % yields) as colorless powder. Single crystals of complex **3** suitable for X-ray analysis, were grown from hexane at -30 ^oC as colorless crystals. ^1H NMR (500 MHz, C_6D_6, 25 ^oC): δ = 1.18 (d, $^3J_{HH}$ = 7 Hz, 18H, CH(CH_3)$_2$), 1.24 (m, 6H, THP), 1.75 (d, $^3J_{HH}$ = 12 Hz, 9H, AdCH_2), 1.88 (br, 9H, AdCH_2), 2.11 (br, 9H, AdCH), 2.19 (br, 18H, AdCH_2), 3.48 (m, 4H, THP), 3.58 (br, 3H, CH(CH$_3$)$_2$), 5.98 (s, 3+1H, 4-pz-*H* + Ca-*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 ^oC): δ = 23.05 (br, CH(*C*H$_3$)$_2$), 23.20 (s, THP), 26.09 (s, *C*H(CH$_3$)$_2$), 26.61 (s, THP), 28.83 (s, Ad-γ), 34.61 (s, Ad-α), 36.78 (s, Ad-δ), 43.36 (br, Ad-β), 68.40 (s, THP), 97.58 (s, pz-4*C*), 156.79 (s, pz-3*C*), 163.76 (s, pz-5*C*). ^1H NMR (500 MHz, d_{12}-cyclohexane, 25 ^oC): δ = 0.98 (d, $^3J_{HH}$ = 6.5 Hz, 18H, CH(CH_3)$_2$), 1.46 (m, 6H, THP), 1.64, 1.67 (dd, $^3J_{HH}$ = 11.5, 11.5Hz, 18H, AdCH_2), 1.93 (br, 27H, Ad), 3.17 (sept, $^3J_{HH}$ = 6.5 Hz, 3H, CH(CH$_3$)$_2$), 3.50 (m, 4H, THP), 5.51 (s, 1H, Ca-*H*), 5.78 (s, 3H, 4-pz-*H*). $^{13}C\{^1H\}$ NMR (125 MHz, d_{12}-cyclohexane, 25 ^oC): δ = 23.18 (s, CH(*C*H$_3$)$_2$), 24.25 (s, THP), 27.33 (s, *C*H(CH$_3$)$_2$), 27.78 (s, THP), 29.69 (s, Ad-γ), 35.28 (s, Ad-α), 37.75 (s, Ad-δ), 43.76 (br, Ad-β), 69.32 (s, THP), 98.31 (s, pz-4*C*), 157.84 (s, pz-3*C*), 164.80 (s, pz-5*C*). Anal. calcd. for (**3**) $C_{53}H_{81}B_1N_6O_1Ca_1$ (869.12): C, 73.24; H, 9.39; N, 9.67; found: C, 73.16; H, 9.45; N, 9.61.

Synthesis of [(Tp^{Ad,iPr})Ca(D)(THP)] (3-D)

The synthesis of complex **3-D** was analogous to that of complex **3** except the deuteride gas (D_2) was used (15 atm D_2, 3 days).

Reactions of [(Tp^{Ad,iPr})CaH(THP)] (3) towards alkenes

^1H NMR tracking experiments indicated that the reactions of complex **3** with one equivalent of alkenes, including 1,1-diphenylethylene, 1,2-diphenylethylene and 4-phenyl-1-butene, were very fast at room temperature, almost quantitively converted to the corresponding alkyls complexes within 30 minutes.

Synthesis of [(Tp^{Ad,iPr})Ca{CPh$_2$(Me)}] (4)

A solution of 1,1-diphenylethylene (13 mg, 0.072 mmol) and [(Tp^{Ad,iPr})CaH(THP)] (**3**) (60 mg, 0.069 mmol) in benzene (6 mL) was stirred for 2 h at room temperature and then filtered.

The resulting dark-red solution was slowly volatilized at room temperature for 2 days to give complex **4** (37 mg, 0.038 mmol, 56 % yield) as dark-red crystals. Single crystals of complex **4** suitable for X-ray analysis, were grown from benzene at room temperature. ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 1.11 (d, $^{3}J_{HH}$ = 7 Hz, 18H, CH(CH_3)$_2$), 1.68 (dd, $^{3}J_{HH}$ = 14, 14 Hz, 18H, AdCH_2), 1.91 (br, 18H, AdCH_2), 1.95 (br, 9H, AdCH), 2.07 (s, 3H, CH_3), 3.29 (sept, $^{3}J_{HH}$ = 7 Hz, 3H, CH(CH$_3$)$_2$), 5.98 (s, 3H, 4-pz-H), 6.40 (m, 2H, Ar-H_{para}), 7.05 (s, 4H, Ar-H_{ortho}), 7.06 (s, 4H, Ar-H_{meta}). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ^{o}C): δ = 22.03 (s, CH$_3$), 22.87 (s, CH(CH$_3$)$_2$), 26.46 (s, CH(CH$_3$)$_2$), 28.51 (s, Ad-γ), 34.50 (s, Ad-α), 36.57 (s, Ad-δ), 42.83 (s, Ad-β), 72.01 (s, CPh$_2$), 98.98 (s, pz-4C), 113.30 (s, Ar-C_{para}), 119.50 (s, Ar-C_{ortho}), 130.31 (s, Ar-C_{meta}),147.23 (s, Ar-C_{ipso}), 159.57 (s, pz-3C), 165.25 (s, pz-5C). Anal. calcd. for (**4**) $C_{62}H_{83}B_1N_6Ca_1$ (963.23): C, 77.31; H, 8.69; N, 8.72; found: C, 77.19; H, 8.80; N, 8.64.

Synthesis of [(Tp^{Ad,iPr})Ca(PhCHCH$_2$Ph)] (5)

A solution of 1,2-diphenylethylene (13 mg, 0.072 mmol) and [(Tp^{Ad,iPr})CaH(THP)] (**3**) (60 mg, 0.069 mmol) in benzene (6 mL) was stirred for 2 h at room temperature and then filtered. The resulting yellow solution was slowly volatilized at room temperature for 2 days to give complex **5** (44.3 mg, 0.046 mmol, 67 % yield) as yellow crystals. Single crystals of complex **5** suitable for X-ray analysis, were grown from benzene at room temperature. ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 1.10 (d, $^{3}J_{HH}$ = 6.5 Hz, 9H, CH(CH_3)$_2$), 1.25 (d, $^{3}J_{HH}$ = 6.5 Hz, 9H, CH(CH_3)$_2$), 1.68, 1.74 (dd, $^{3}J_{HH}$ = 12, 11.5 Hz, 18H, AdCH_2), 1.95 (br, 18H, AdCH_2), 2.01 (br, 9H, AdCH), 2.90, (dd, $^{3}J_{HH}$ = 5, 4.5 Hz, 1H, PhCHCH$_2$Ph), 3.43 (sept, $^{3}J_{HH}$ = 7 Hz, 3H, CH(CH$_3$)$_2$), 3.68, 3.71 (dd, $^{3}J_{HH}$ = 4.5, 5 Hz, 1H, PhCHCH_2Ph), 3.87, 3.90 (dd, $^{3}J_{HH}$ = 9, 9 Hz, 1H, PhCHCH_2Ph), 5.97 (s, 3H, 4-pz-H), 6.30 (t, $^{3}J_{HH}$ = 7 Hz, 1H, PhCH, Ar-H_{para}), 6.36 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, PhCH, Ar-H_{meta}), 6.96 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, PhCH, Ar-H_{ortho}), 7.06 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, PhCH$_2$, Ar-H_{para}), 7.20 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, PhCH$_2$, Ar-H_{ortho}), 7.55 (d, $^{3}J_{HH}$ = 7 Hz, 2H, PhCH$_2$, Ar-H_{meta}). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ^{o}C): δ = 22.21 (s, CH(CH$_3$)$_2$), 23.59 (s, CH(CH$_3$)$_2$), 26.51 (s, CH(CH$_3$)$_2$), 28.66 (s, Ad-γ), 34.52 (s, Ad-α), 35.49 (s, PhCHCH$_2$Ph), 36.56 (s, Ad-δ), 43.16 (s, Ad-β), 56.85 (s, PhCHCH$_2$Ph), 98.15 (s, pz-4C), 111.19 (s, PhCH$_2$, Ar-C_{para}), 114.00 (s, PhCH$_2$, Ar-C_{meta}), 124.83 (s, PhCH, Ar-C_{para}), 128.06 (s, PhCH, Ar-H_{ortho}), 128.09 (s, PhCH, Ar-C_{meta}), 131.55 (s, PhCH$_2$, Ar-C_{ortho}), 146.25 (s, PhCH$_2$, Ar-C_{ipso}), 155.07 (s, PhCH, Ar-C_{ipso}), 158.61 (s, pz-3C), 164.18 (s, pz-5C). Anal. calcd. for (**5**) $C_{62}H_{83}B_1N_6Ca_1$ (963.23): C, 77.31; H, 8.69; N, 8.72; found: C, 77.24; H, 8.75; N, 8.66.

Synthesis of [(Tp^{Ad,iPr})Ca{(CH$_2$)$_4$Ph}(THP)] (6)

A solution of 4-Phenyl-1-butene (15 mg, 0.115 mmol) and [($Tp^{Ad,iPr}$)CaH(THP)] (**3**) (100 mg, 0.115 mmol) in hexane (10 mL) was stirred for 0.5 h at room temperature and then filtered. The resulting pale-yellow solution was concentrated to ~3 mL, and kept at -30 ^{o}C to give complex **6** (93 mg, 0.093 mmol, 81% yield) as colorless crystals. Single crystals of complex **6** suitable for X-ray analysis, were grown from hexane at -30 ^{o}C. ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 0.12 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, CaC*H*$_2$CH$_2$CH$_2$CH$_2$Ph), 1.17 (d, $^{3}J_{HH}$ = 7 Hz, 18H, CH(C*H*$_3$)$_2$), 1.17 (m, 2+6H, CaCH$_2$C*H*$_2$CH$_2$CH$_2$Ph, THP), 1.77, 1.87 (dd, $^{3}J_{HH}$ = 12.5, 11.5 Hz, 18H, AdC*H*$_2$), 2.09 (m, 2H, CaCH$_2$CH$_2$C*H*$_2$CH$_2$Ph), 2.12 (br, 27H, Ad), 2.98 (m, 2H, CaCH$_2$CH$_2$CH$_2$C*H*$_2$Ph), 3.32 (m, 4H, THP), 3.60 (sept, $^{3}J_{HH}$ = 8.5 Hz, 3H, C*H*(CH$_3$)$_2$), 5.95 (s, 3H, 4-pz-*H*), 7.08 (t, $^{3}J_{HH}$ = 7 Hz, 1H, Ar-*H*$_{para}$), 7.21 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar-*H*$_{ortho}$), 7.33 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar-*H*$_{meta}$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ^{o}C): δ = 22.75 (s, THP), 23.23 (s, CH(*C*H$_3$)$_2$), 25.84 (s, THP), 26.04 (s, Ca*C*H$_2$CH$_2$CH$_2$CH$_2$Ph), 26.63 (s, *C*H(CH$_3$)$_2$), 28.85 (s, Ad-γ), 33.08 (s, CaCH$_2$CH$_2$*C*H$_2$CH$_2$Ph), 34.35 (s, Ad-α), 36.55 (s, CaCH$_2$CH$_2$CH$_2$*C*H$_2$Ph), 36.68 (s, Ad-δ), 43.55 (s, Ad-β), 68.47 (s, THP), 97.43 (s, pz-4*C*), 124.86 (s, Ar-*C*$_{para}$), 127.98 (s, Ar-*C*$_{ortho}$), 128.72 (s, Ar-*C*$_{meta}$), 144.70 (s, Ar-*C*$_{ipso}$), 156.48 (s, pz-3*C*), 163.39 (s, pz-5*C*). Anal. calcd. for (**6**) $C_{63}H_{93}B_1N_6O_1Ca_1$ (1001.32): C, 75.57; H, 9.36; N, 8.39; found: C, 75.49; H, 9.45; N, 8.32.

Typical catalytic hydrogenation experiments:

In a stainless steel autoclave (25 mL) containing a glass tube charged with a magnetic stir bar, the catalyst (**2-THP**) (0.012 mmol, 5 mol%) and the olefinic substrate (0.24 mmol) were dissolved into dry C_6D_6 (1.0 mL). The autoclave was sealed, brought out of the nitrogen-filled glovebox, and pressurized with H_2 to 10 atm after degassed twice. The solution was stirred in a 40 ºC oil bath for the time indicated and monitored by ^1H NMR spectroscopy.

Selected NMR Spectra

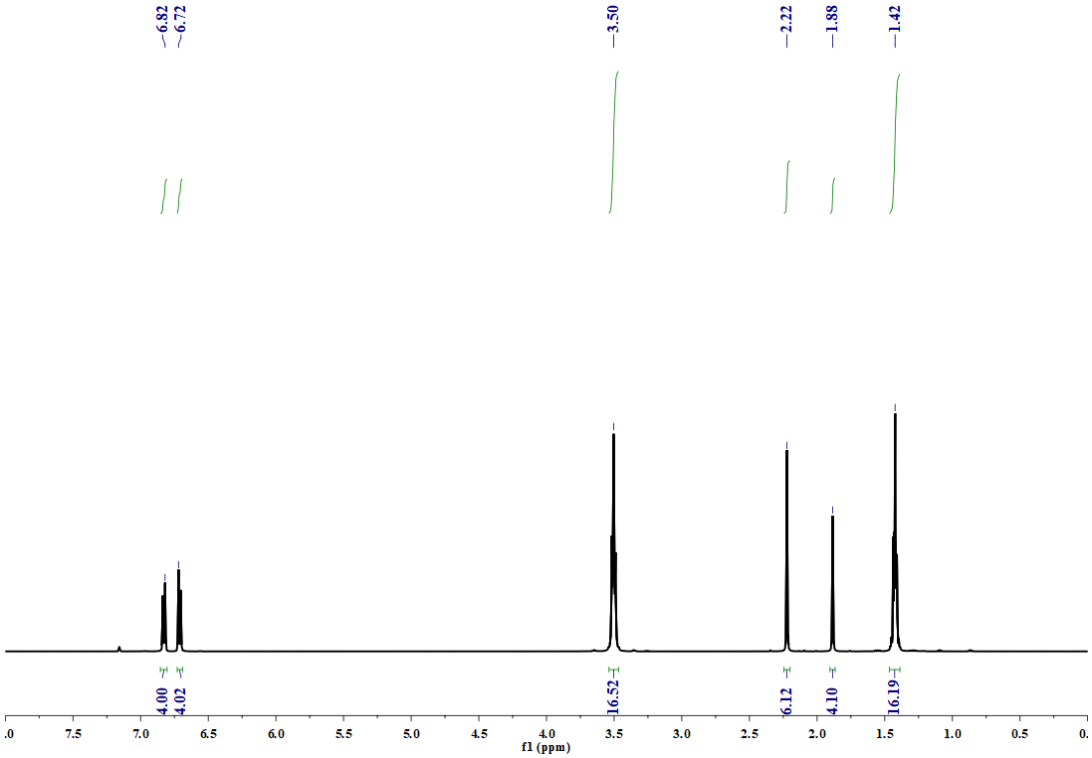

Figure S1. ^{1}H NMR spectrum (500 MHz) of [Ca(*p*-$CH_2C_6H_4$-Me)$_2$(THF)$_4$] (**1**) in C_6D_6 at 25 ^{o}C.

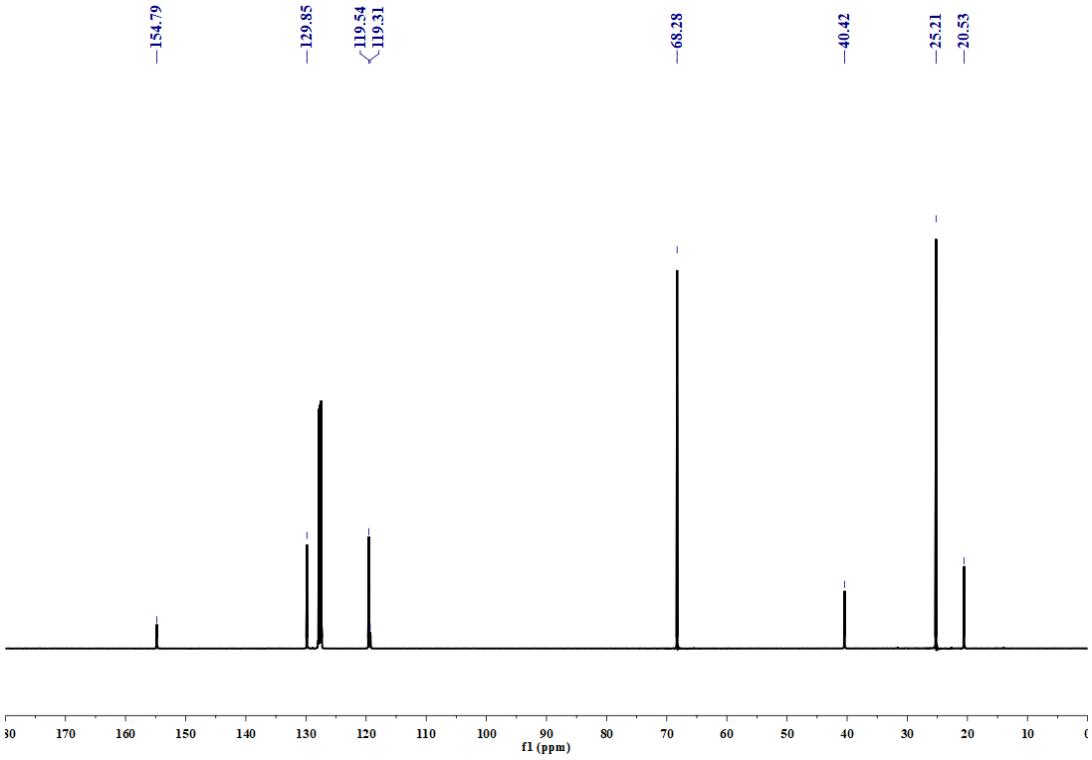

Figure S2. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [Ca(*p*-$CH_2C_6H_4$-Me)$_2$(THF)$_4$] (**1**) in C_6D_6 at 25 ^{o}C.

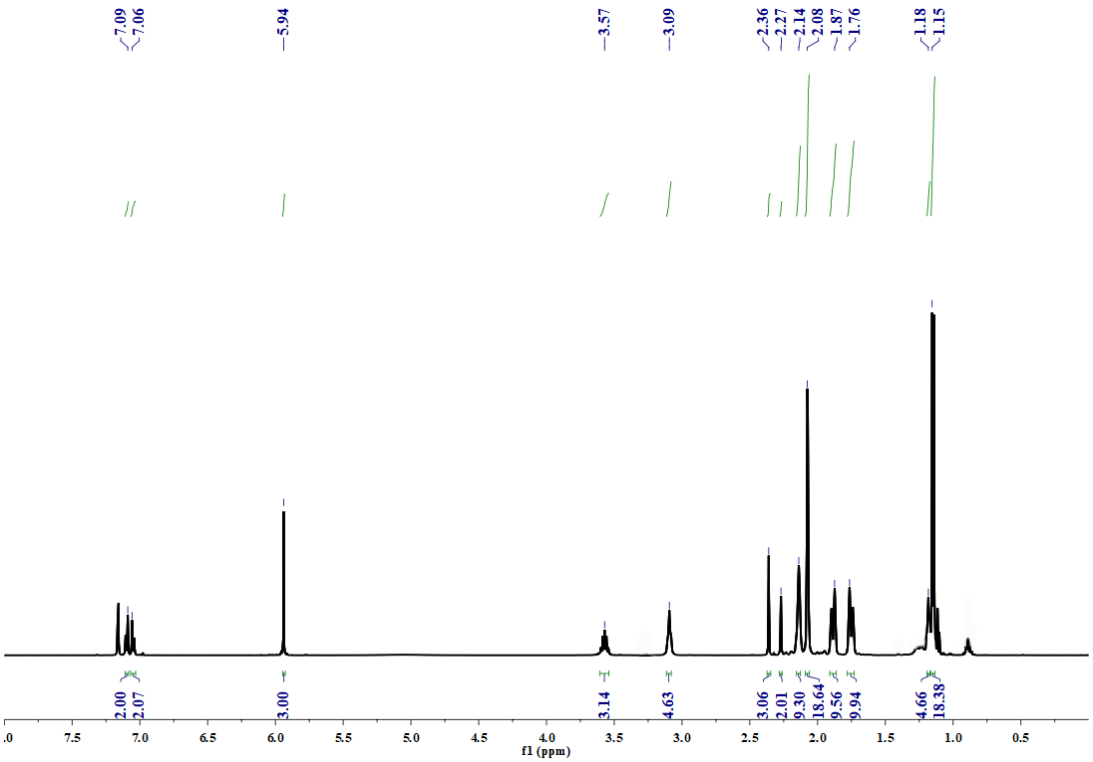

Figure S3. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THF)] (**2**) in C_6D_6 at 25 ^{o}C.

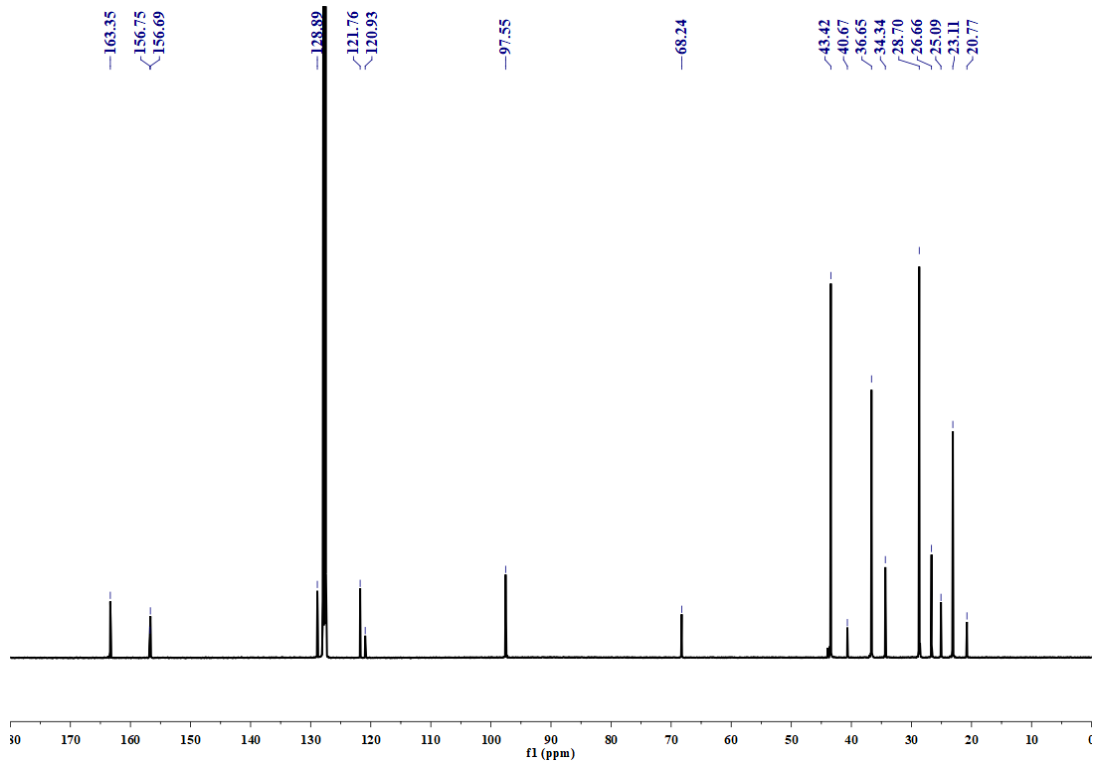

Figure S4. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THF)] (**2**) in C_6D_6 at 25 ^{o}C.

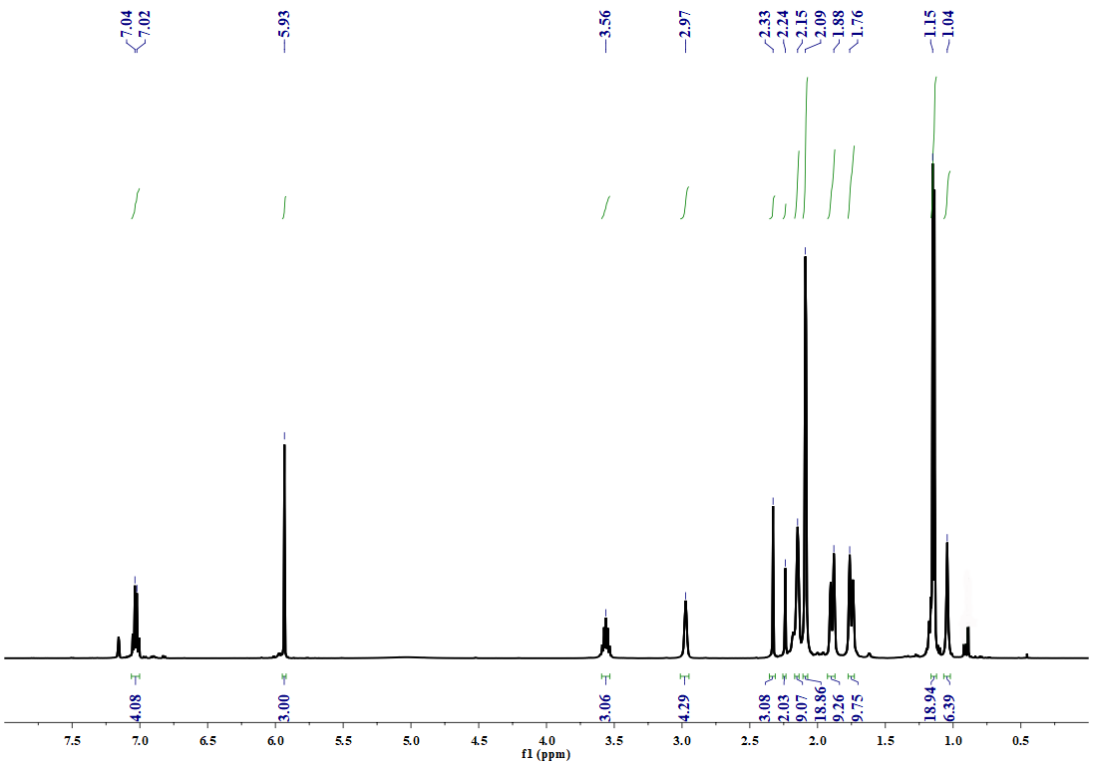

Figure S5. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(*p*-CH$_2$C$_6$H$_4$-Me)(THP)] (**2-THP**) in C$_6$D$_6$ at 25 ^{o}C.

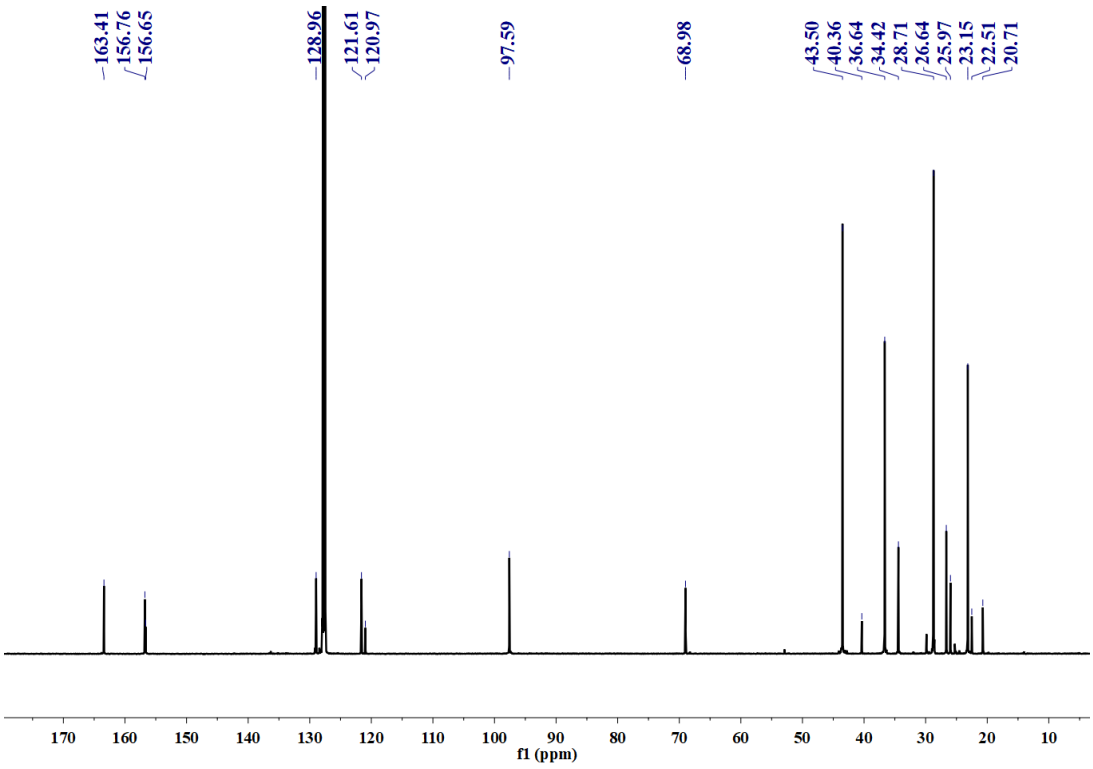

Figure S6. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca(*p*-CH$_2$C$_6$H$_4$-Me)(THP)] (**2-THP**) in C$_6$D$_6$ at 25 ^{o}C.

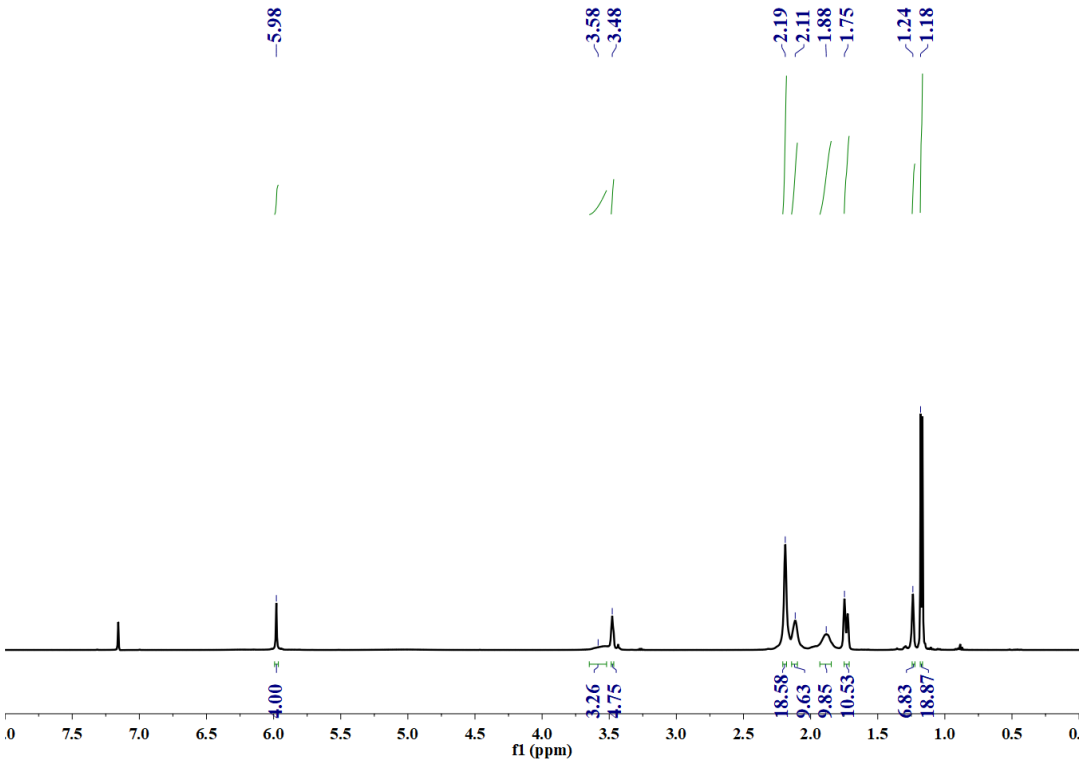

Figure S7. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) in C_6D_6 at 25 ^{o}C.

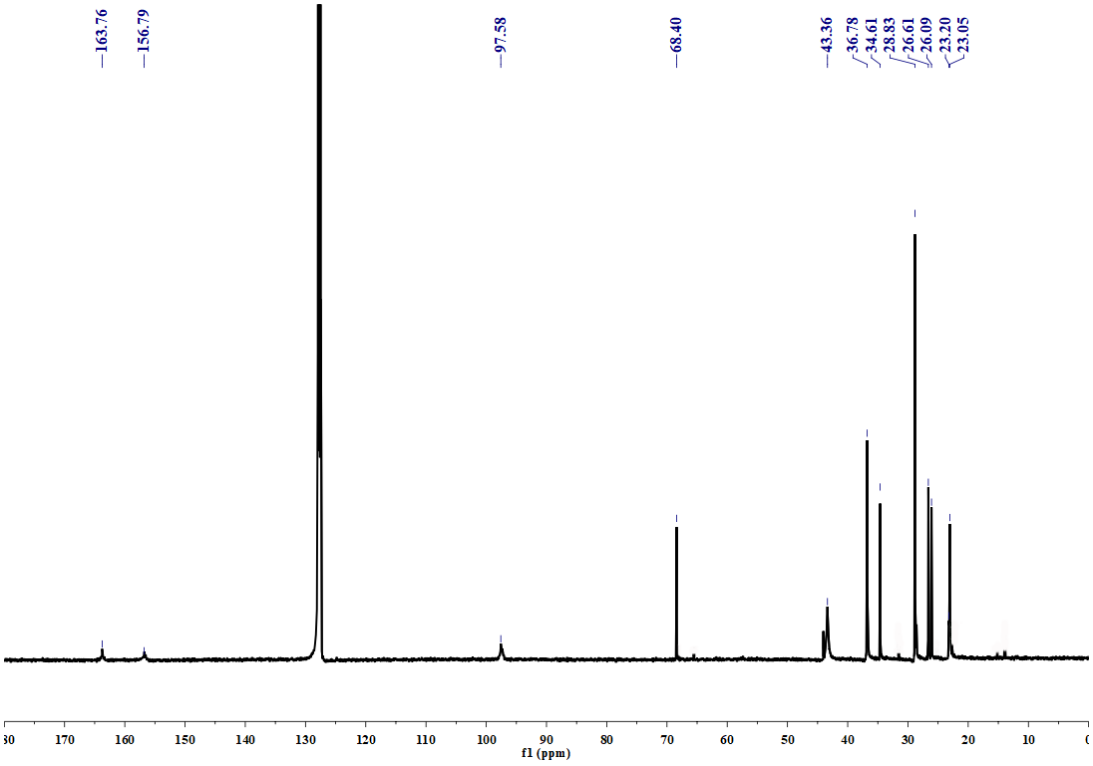

Figure S8. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) in C_6D_6 at 25 ^{o}C.

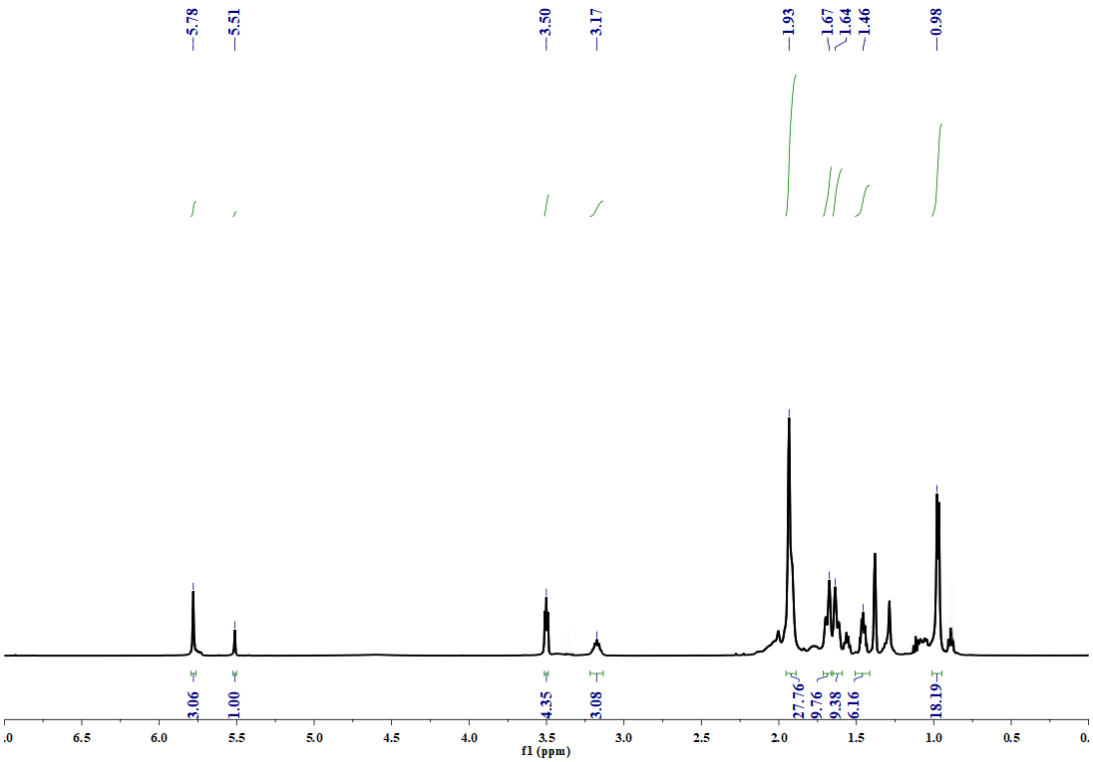

Figure S9. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) in d_{12}-cyclohexane at 25 ^{o}C

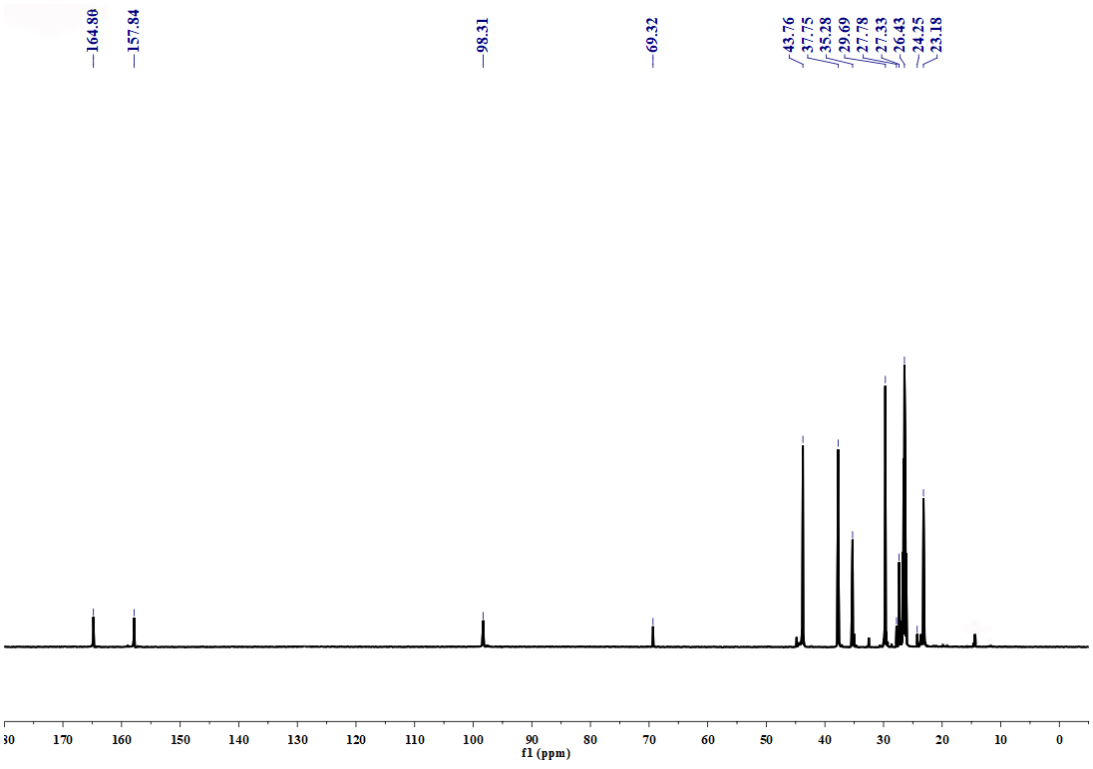

Figure S10. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) in d_{12}-cyclohexane at 25 ^{o}C.

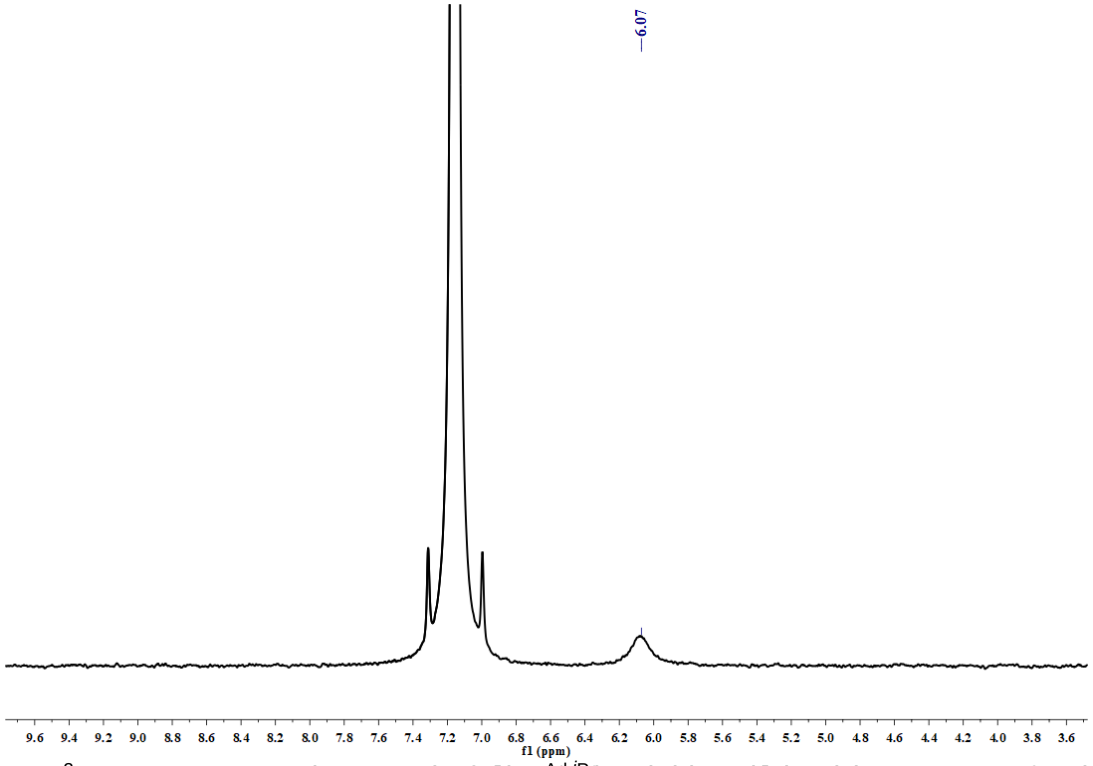

Figure S11. ^{2}D NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(D)(THP)] (**3-D**) in C_6H_6 at 25 ^{o}C. (Drops of C_6D_6 were added as internal standard)

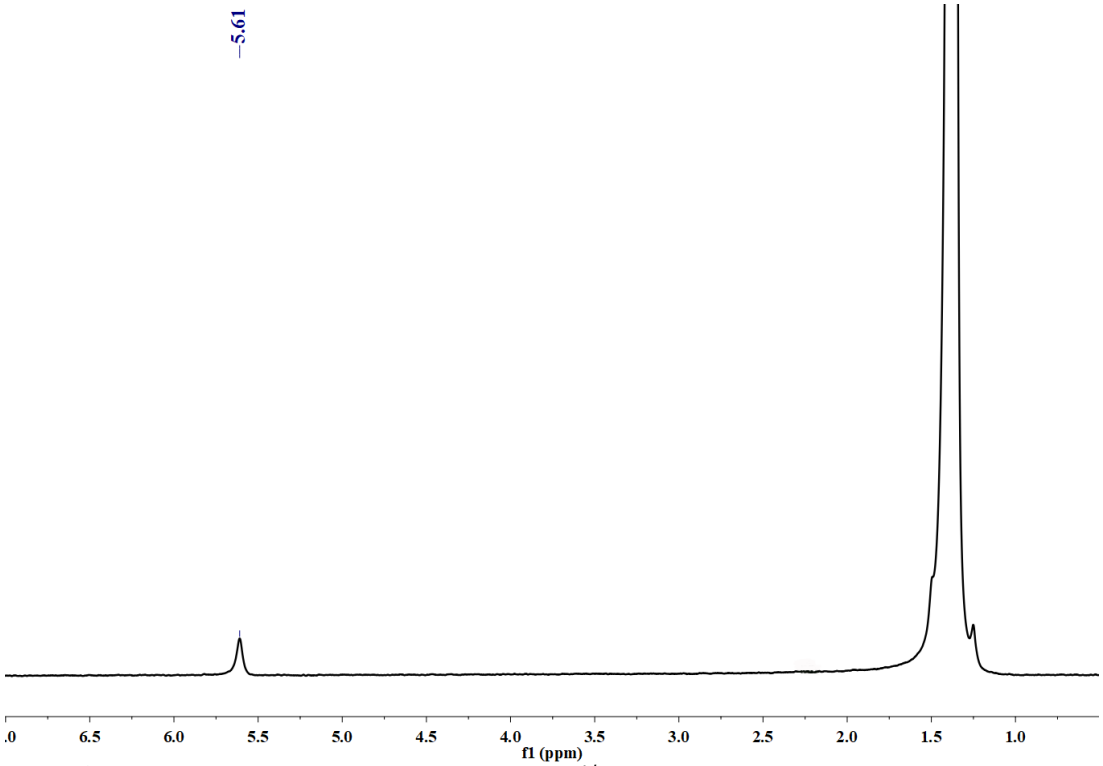

Figure S12. ^{2}D NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(D)(THP)] (**3-D**) in cyclohexane at 25 ^{o}C. (Drops of d_{12}-cyclohexane were added as internal standard)

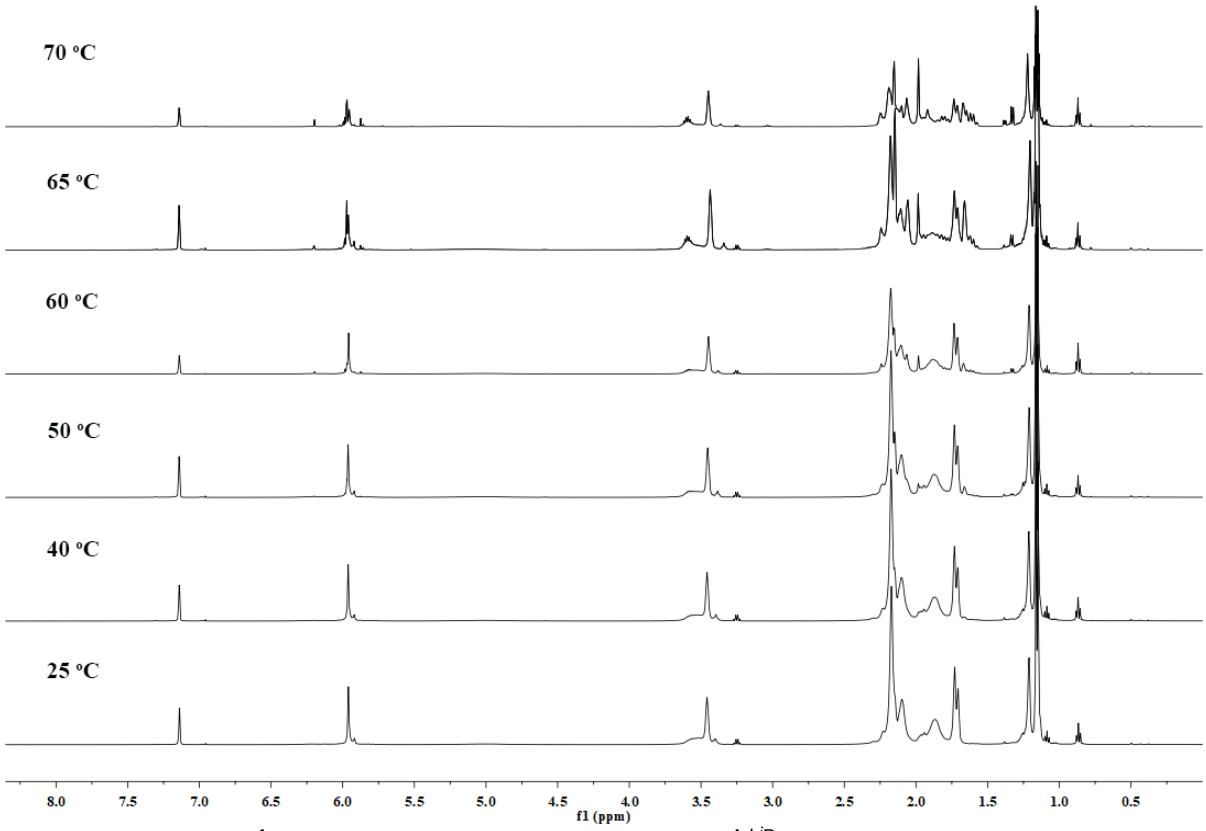

Figure S13. Stacked ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) in C_6D_6 at varied temperatures. Complex **3** decomposed quickly above 60 °C.

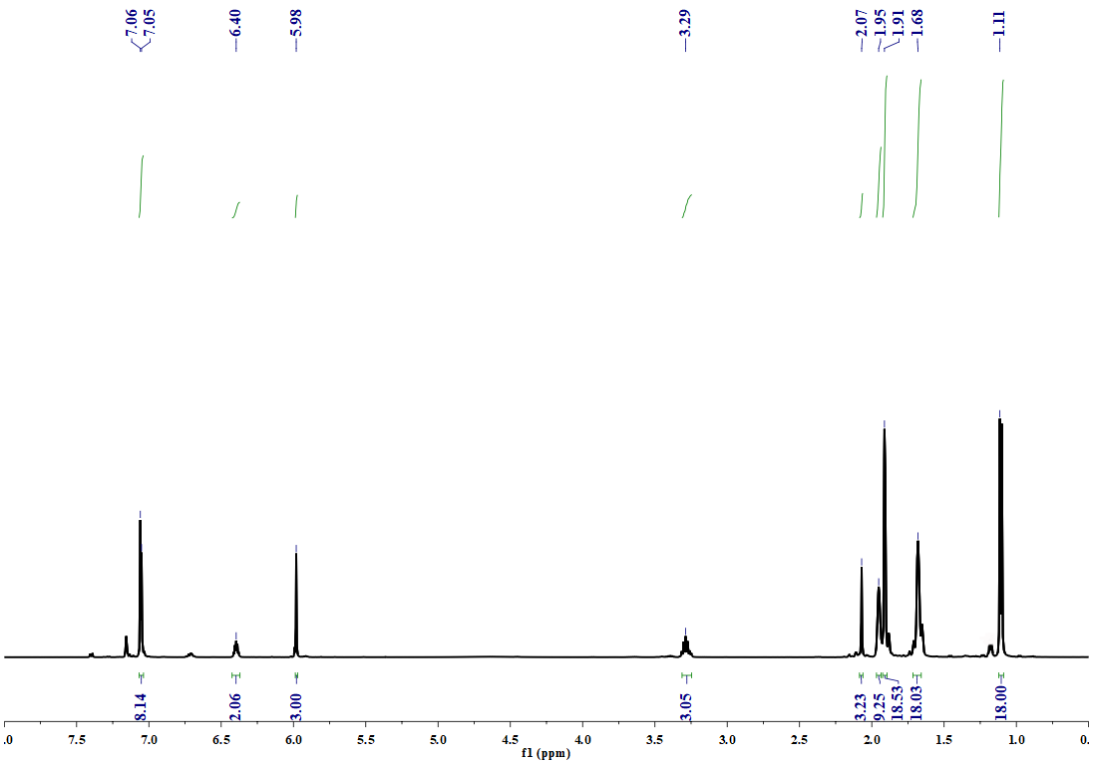

Figure S14. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca{CPh$_2$(Me)}] (**4**) in C_6D_6 at 25 ºC.

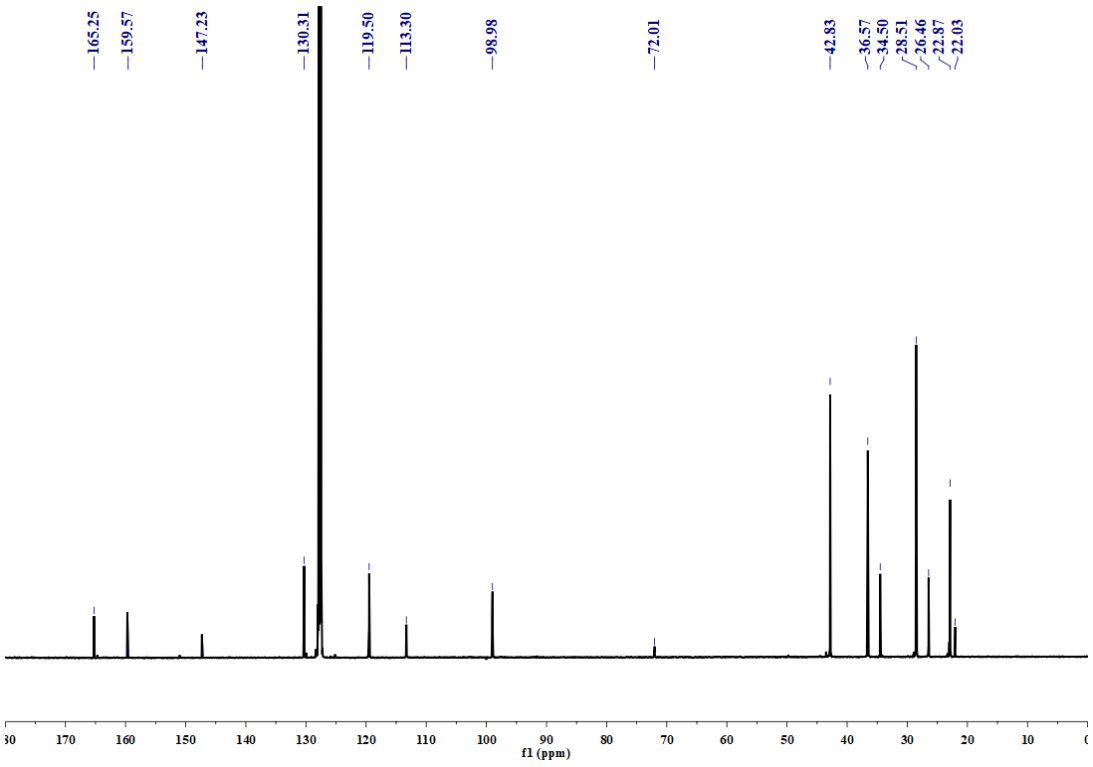

Figure S15. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca{CPh$_2$(Me)}] (**4**) in C_6D_6 at 25 ºC.

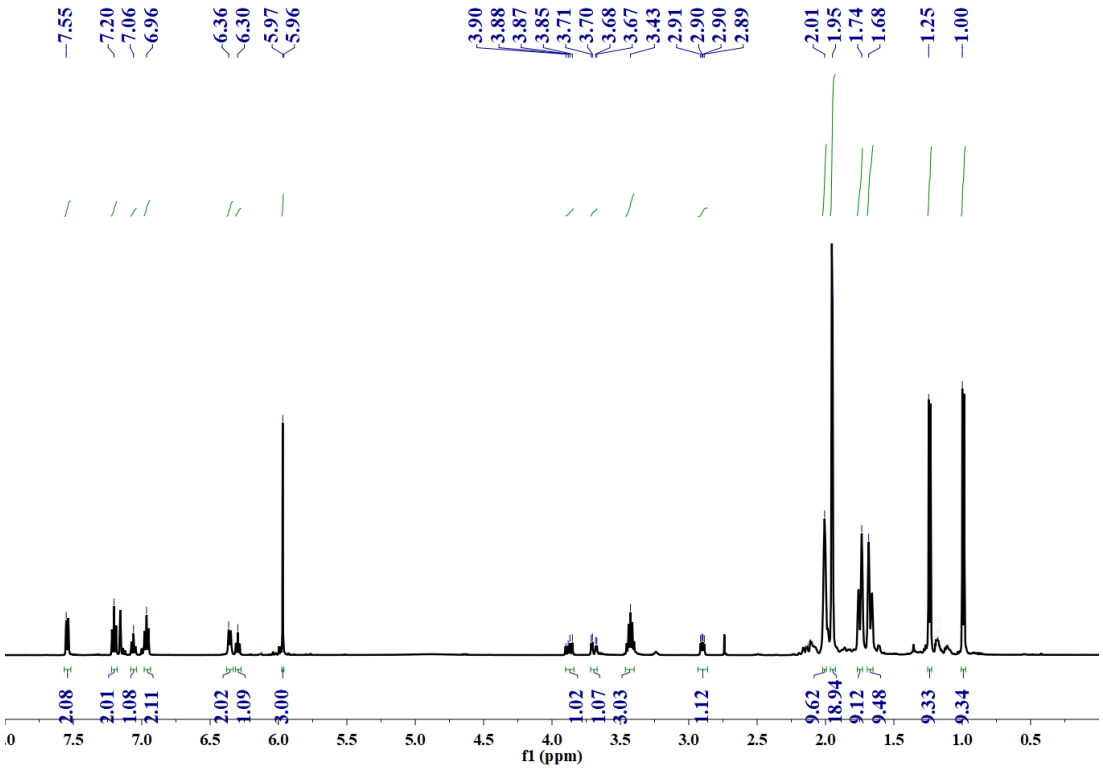

Figure S16. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca(PhCHCH$_2$Ph)] (**5**) in C_6D_6 at 25 °C.

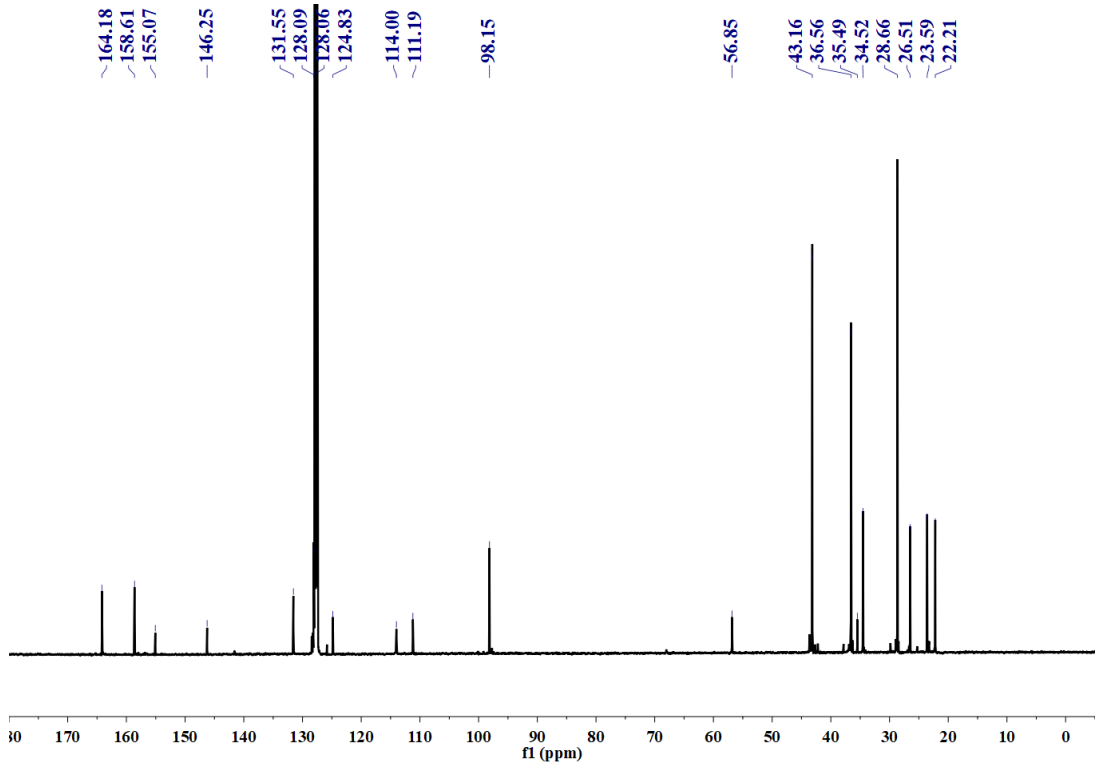

Figure S17. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca(PhCHCH$_2$Ph)] (**5**) in C_6D_6 at 25 °C.

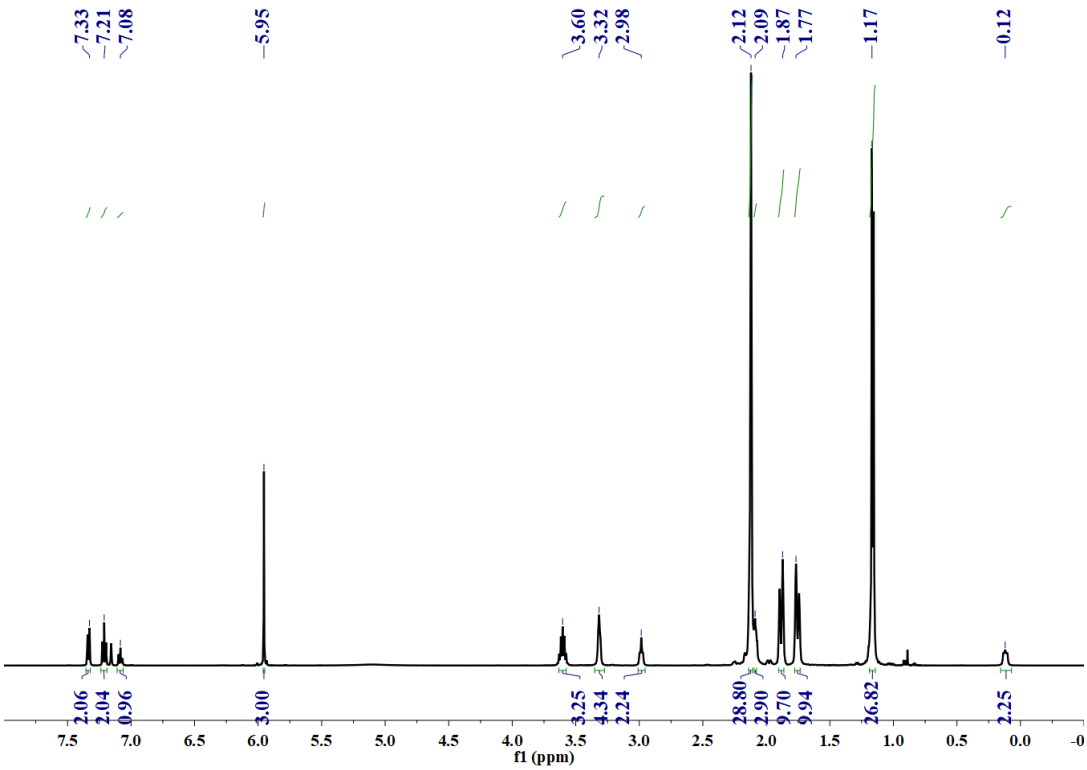

Figure S18. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca{$(CH_2)_4$Ph}(THP)] (**6**) in C_6D_6 at 25 ^{o}C

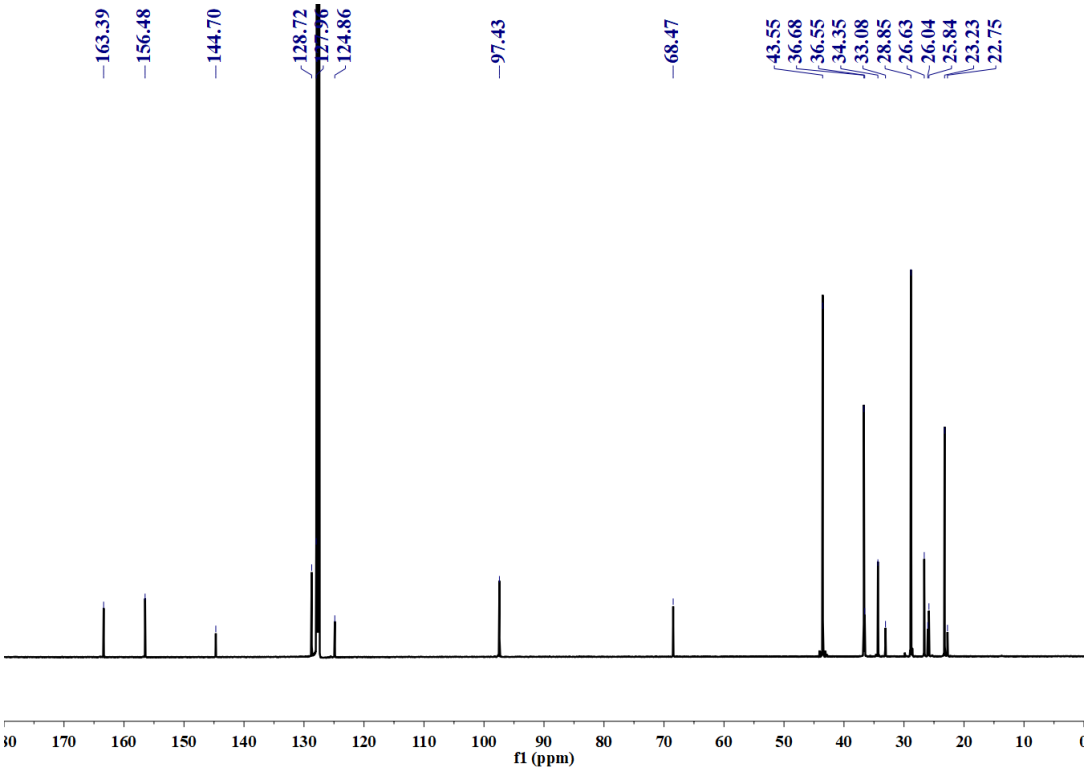

Figure S19. ^{13}C{^{1}H} NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ca{$(CH_2)_4$Ph}(THP)] (**6**) in C_6D_6 at 25 ^{o}C.

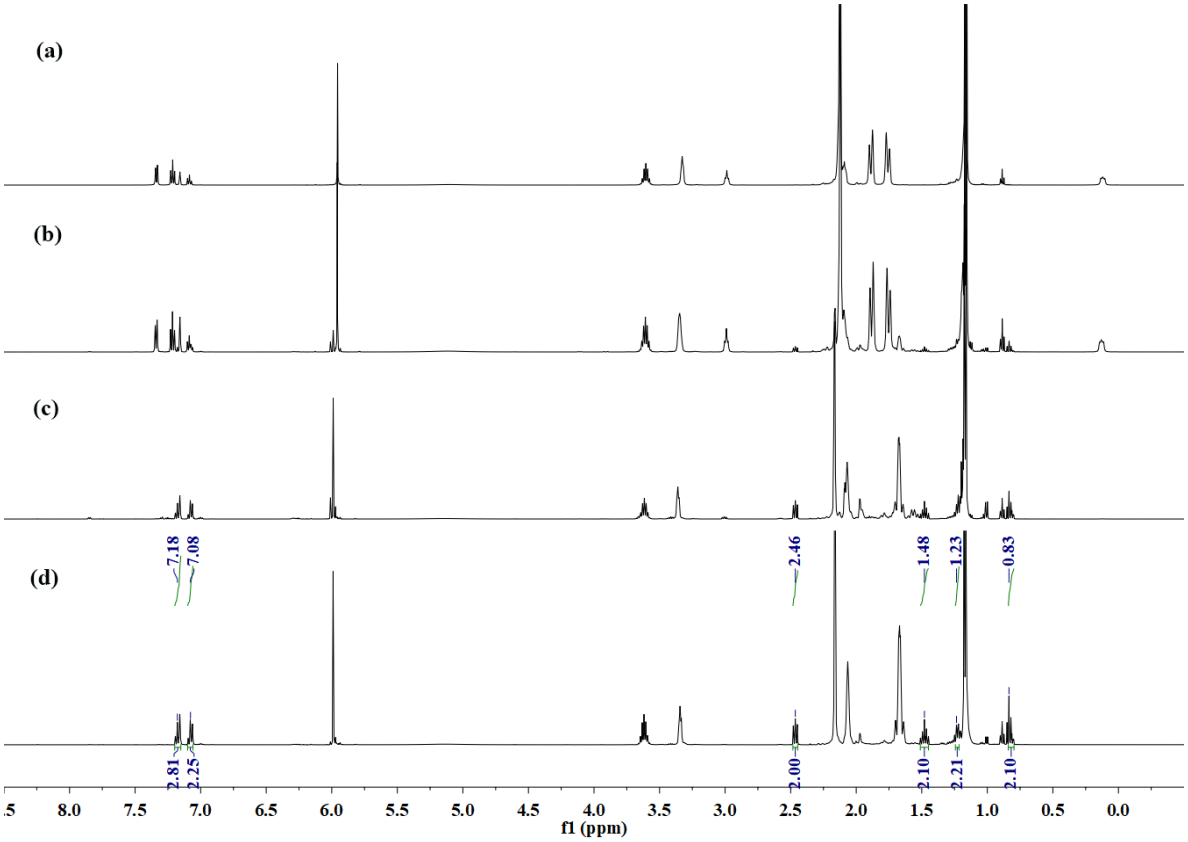

Figure S20. Stacked ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ca{$(CH_2)_4$Ph}(THP)] (**6**) in C_6D_6 at varied temperatures. (a)10 minutes at 25 °C; (b)12 hours at 25 °C; (c) 2 hours at 60 °C; (d) 8 hours at 60 °C. There is no corresponding evidence for the precursor $Ph(CH_2)_3CH_2{=}CH_2$, obtained *via* *β*-hydride elimination. The signals of $Ph(CH_2)_3CH_2D$ are assigned: 7.18, 7.08 (5H, Ar), 2.46 (2H, PhC*H*$_2$), 1.48 (2H, $PhCH_2CH_2$), 1.23 (2H, $PhCH_2CH_2CH_2$), 0.83 (2H, $PhCH_2CH_2CH_2CH_2D$), in accord with the result of $Ph(CH_2)_3CH_3$ in **Figure S28**.

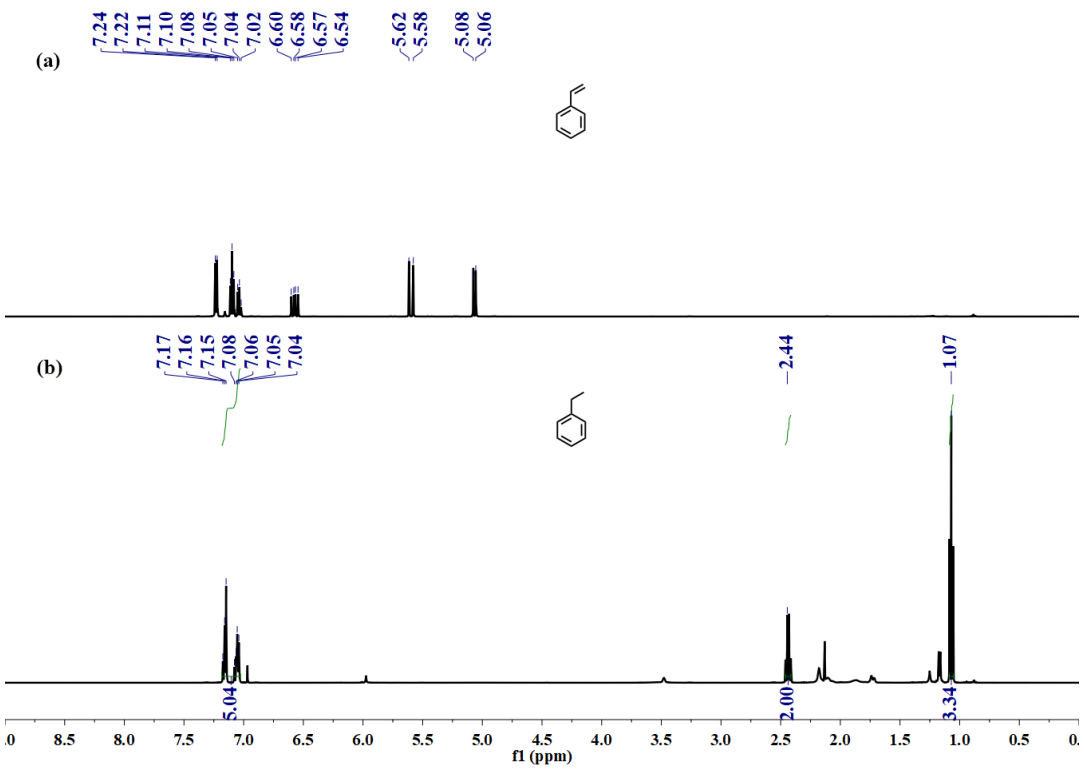

Figure S21. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 °C) of (a) styrene and (b) ethylbenzene after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 1).

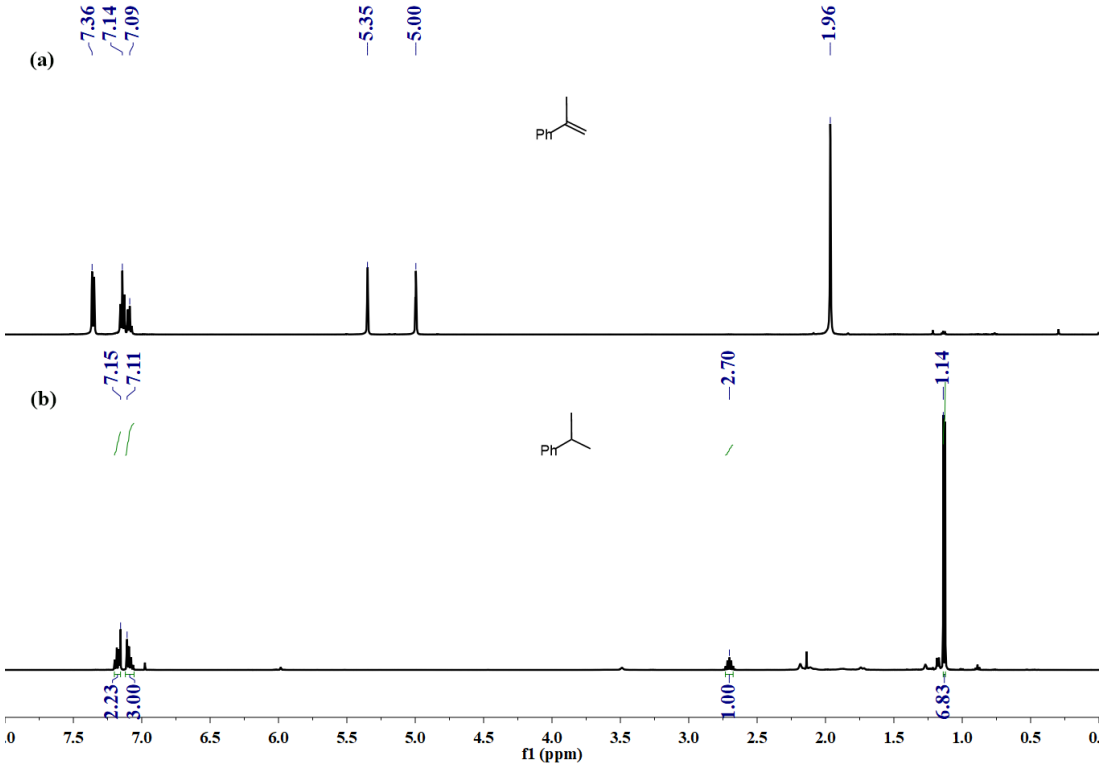

Figure S22. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 °C) of (a) α-methyl styrene and (b) isopropylbenzene after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 2).

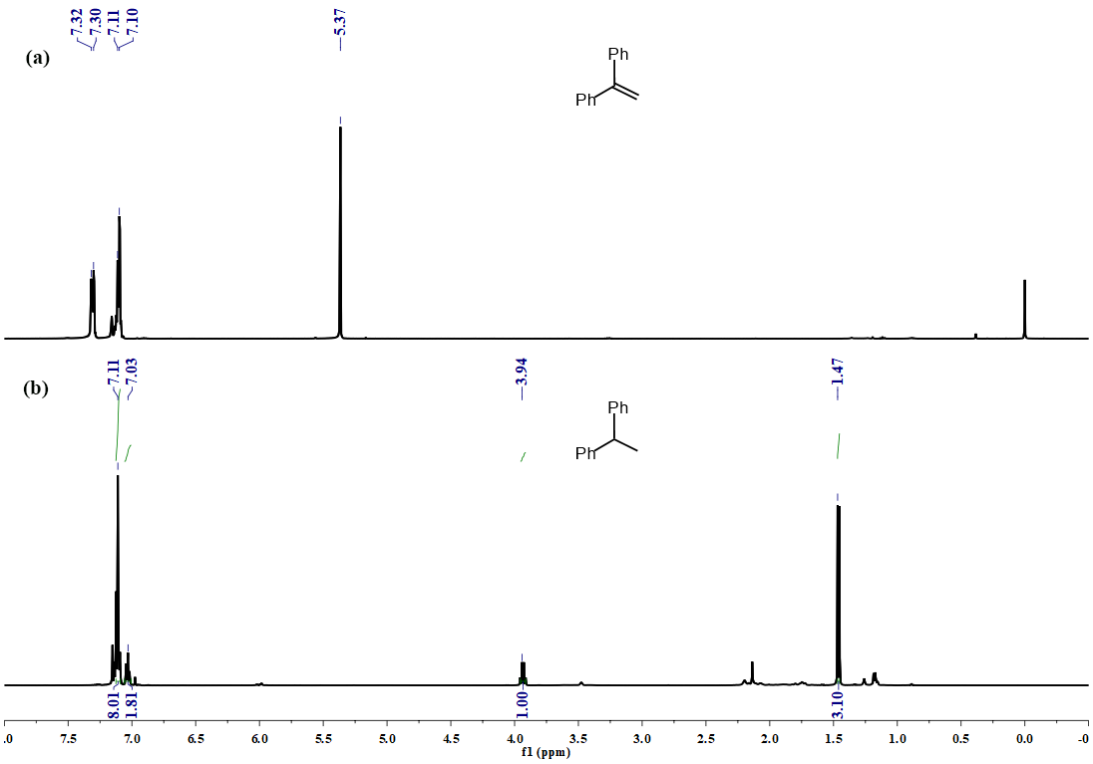

Figure S23. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 1,1-diphenylethylene and (b) 1,1-diphenylethane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 3).

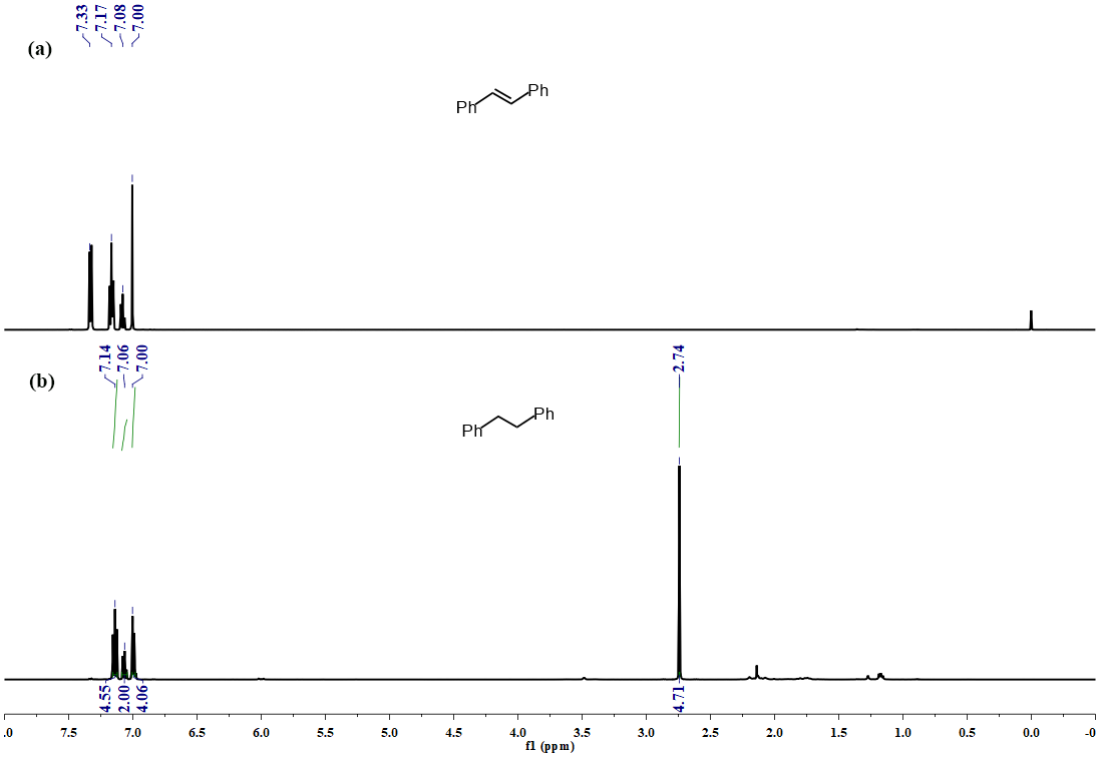

Figure S24. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 1,2-diphenylethylene and (b) 1,2-diphenylethane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 4).

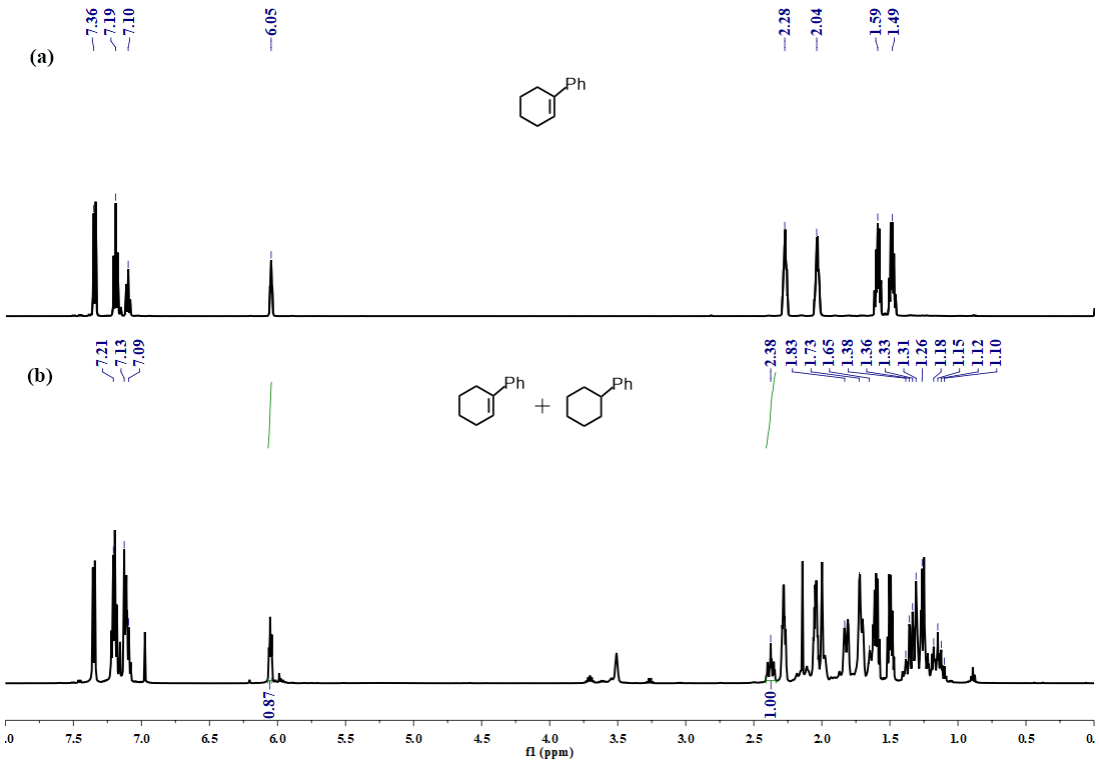

Figure S25. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 1-phenylcyclohexene and (b) 1-phenylcyclohexane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 5).

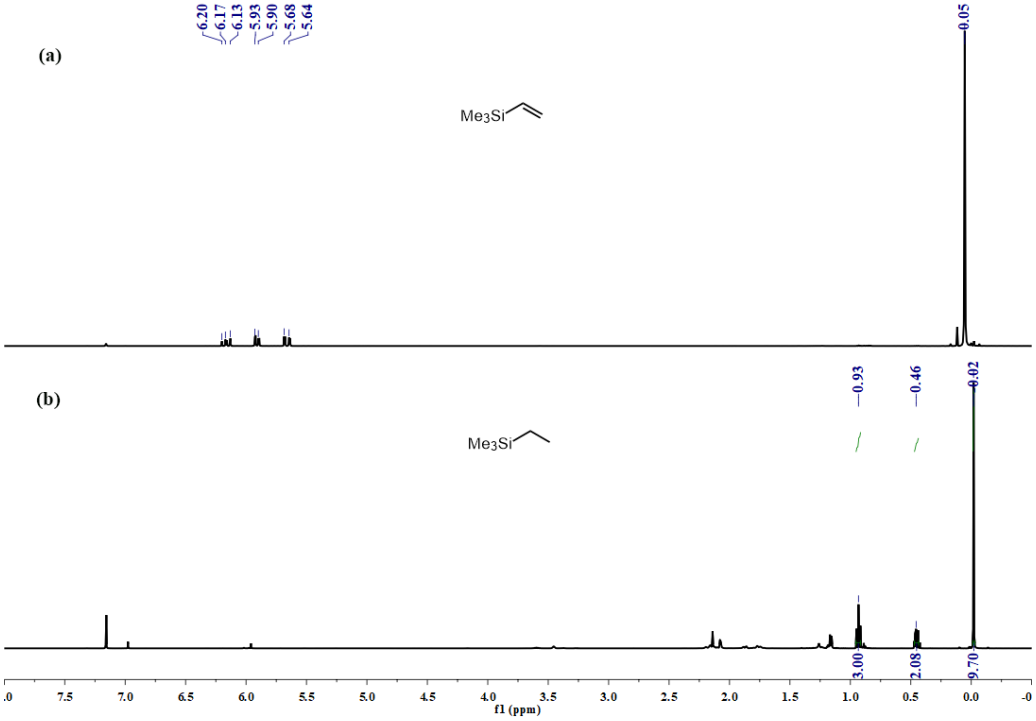

Figure S26. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) trimethylsilylethylene and (b) trimethylsilylethane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 6).

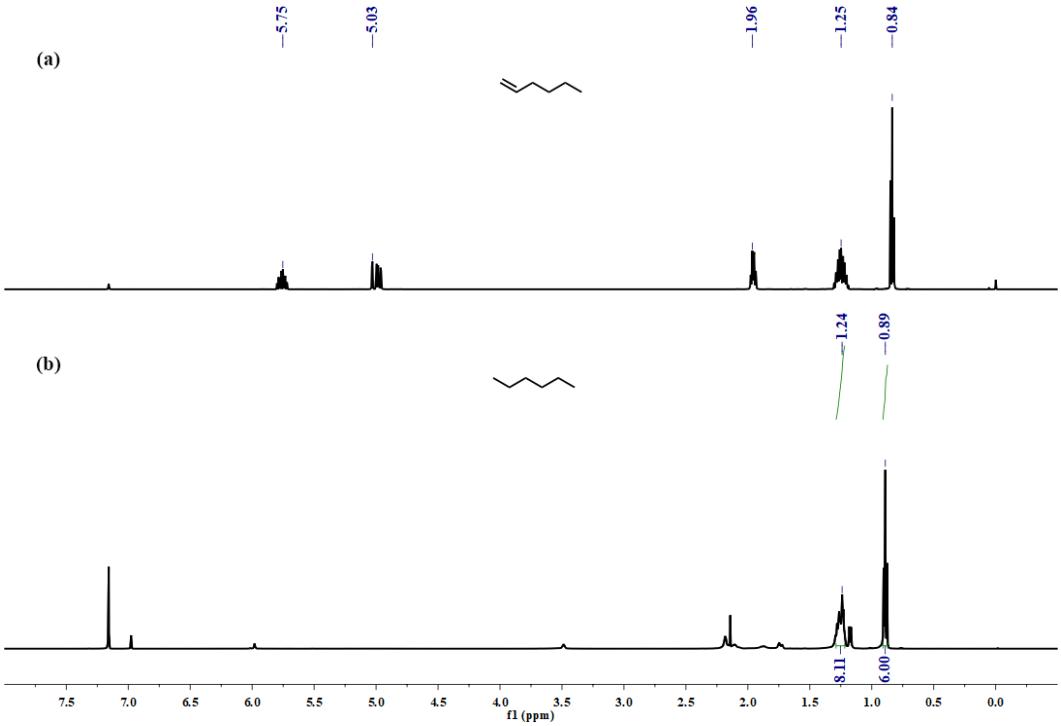

Figure S27. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 1-hexene and (b) hexane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 7).

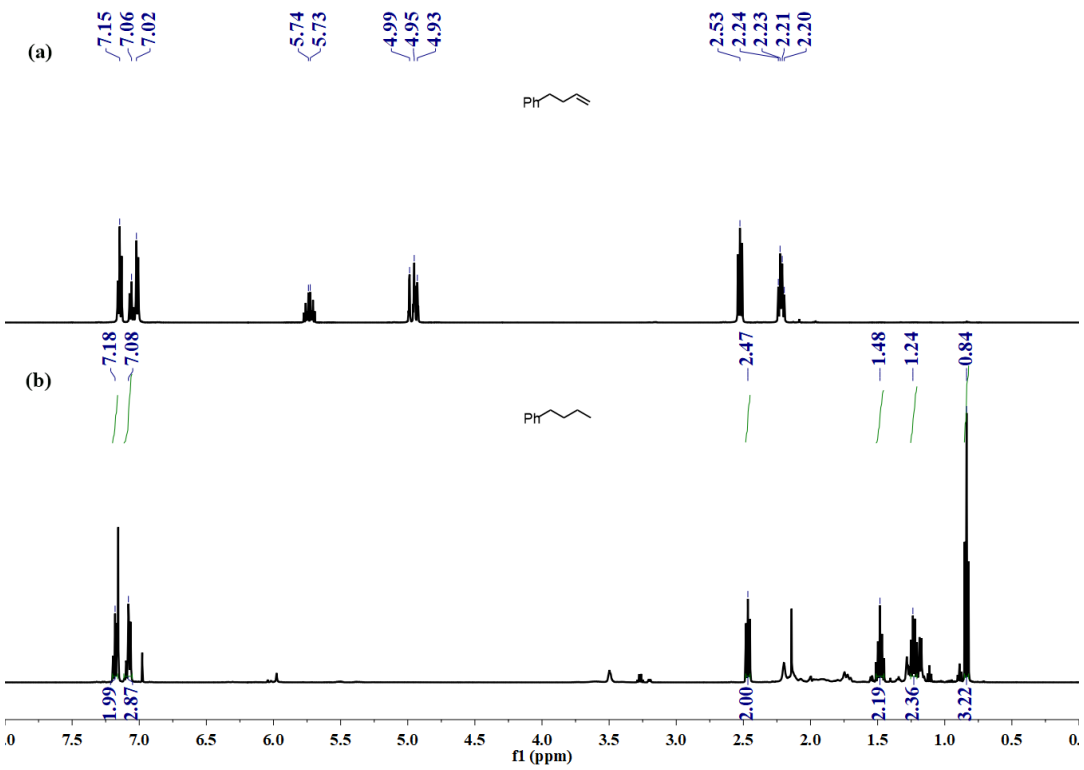

Figure S28. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 4-phenyl-1-butene and (b) 1-butylbenzene after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 8).

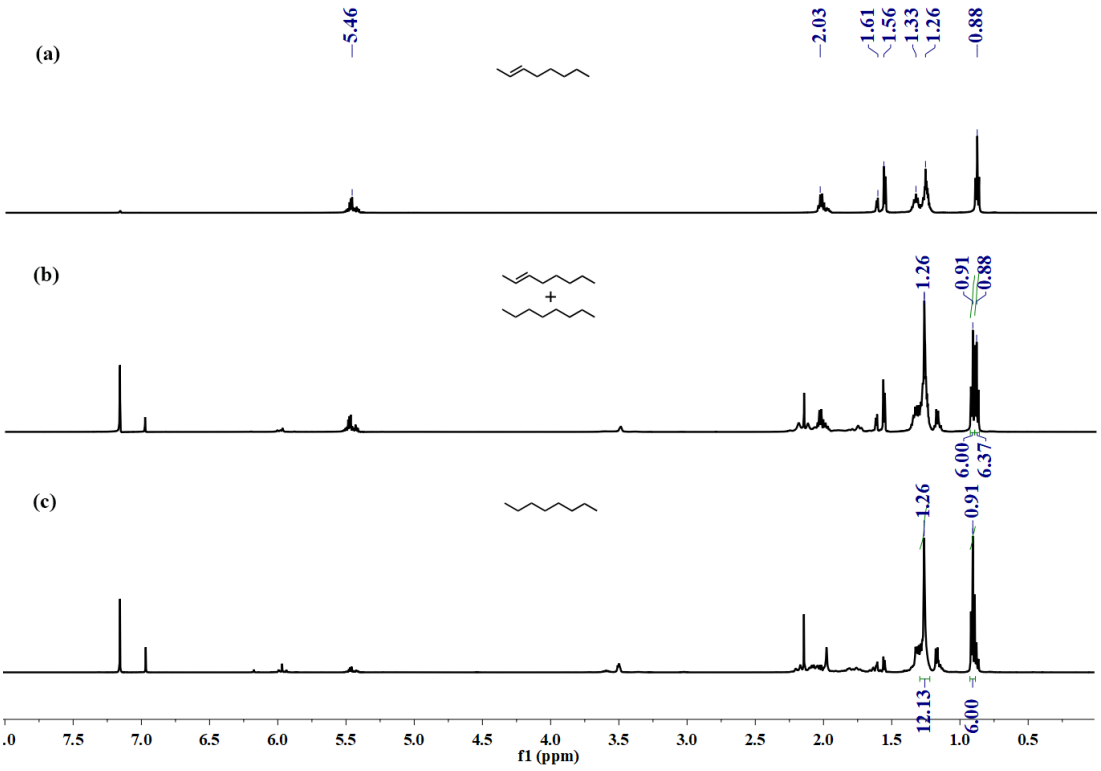

Figure S29. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 2-octene and catalytic hydrogenation of 2-octene mediated by **2-THP** (5 mol%) with H_2 (10 atm) after (b) 24 hours and (c) 72 hours at 40 °C (entry 9).

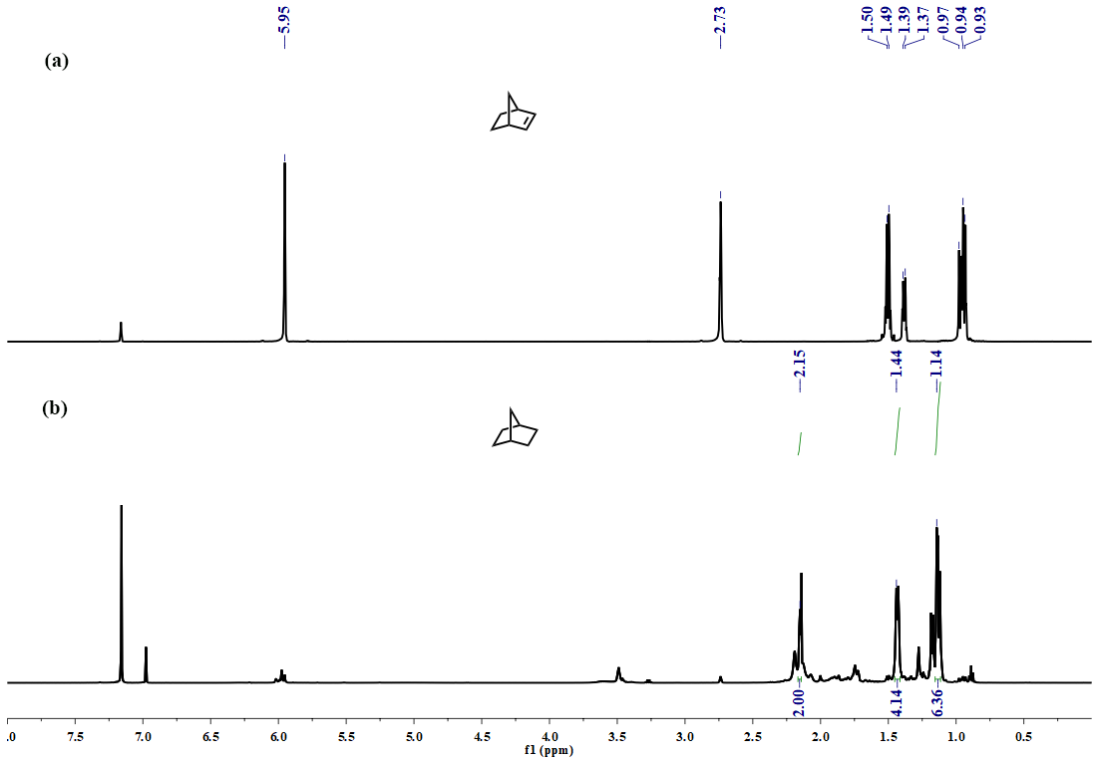

Figure S30. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) norbornene and (b) norbornane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 10).

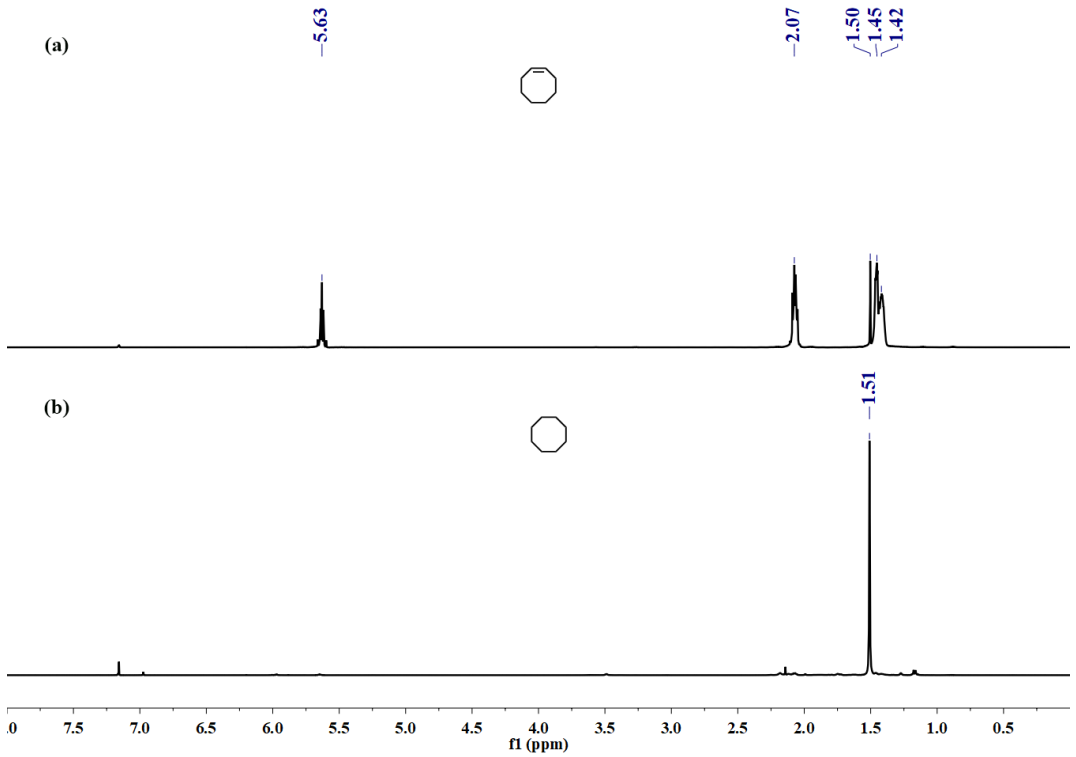

Figure S31. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) cyclooctene and (b) cyclooctane after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 11).

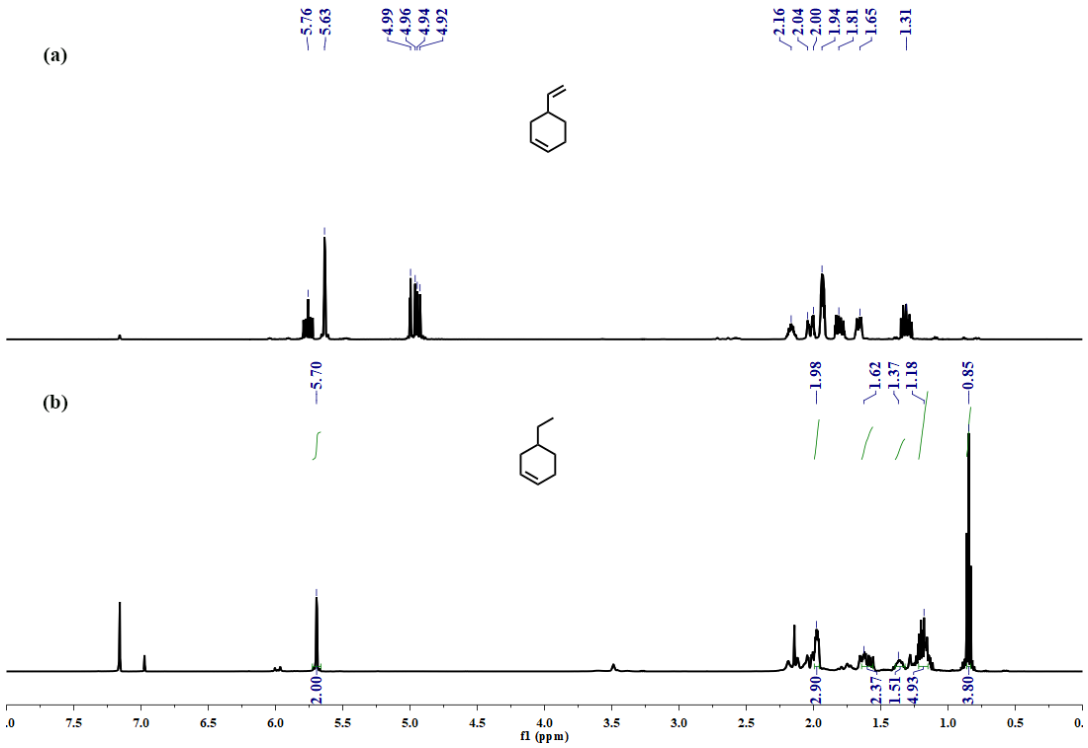

Figure S32. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) 4-ethenylcyclohexene and (b) 4-ethylcyclohexene after catalytic hydrogenation with **2-THP** (5 mol%) and H_2 (10 atm) at 40 °C (entry 12).

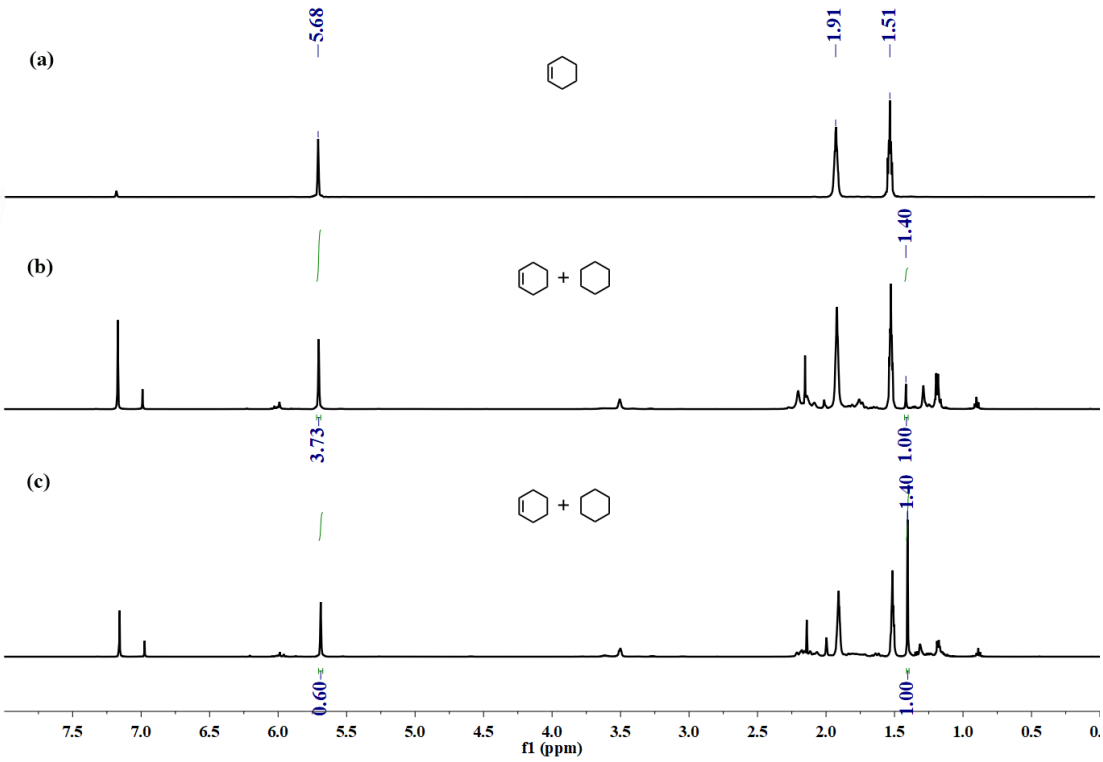

Figure S33. Stacked ^{1}H NMR spectrum (500 MHz, C_6D_6, 25 ^{o}C) of (a) cyclohexene and catalytic hydrogenation of cyclohexene mediated by **2-THP** (5 mol%) with H_2 (10 atm) after (b) 24 hours and (c) 120 hours at 40 °C (entry 13).

X-ray Crystallographic Studies

Single crystals suitable for X-ray analysis were obtained as described in the preparation. The crystals were manipulated in the glovebox under a microscope in the glovebox, Data collection was performed at -80 ^{o}C on a Bruker SMART APEX (or D8 Venture, for complex **3**) diffractometer with a CCD area detector, using graphite monochromated Mo K_{α} radiation (λ = 0.71073 Å). The determination of the crystal class and unit cell parameters was carried out by the SMART program packages[2]. The raw frame data were processed using SAINT[3] and absorption corrections using SADABS[4] to yield the reflection data file. The structures were solved by using SHELXS-2018[5] or SUPERFLIP[6-7] in the WinGX program package[8]. Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method using SHELXL-2018 program.

Refinement of **2**: There are two independent molecules in the unit cell. One ^{i}Pr group in the $Tp^{Ad,iPr}$ ligand was disordered. C161~C163 and C261~C263 disordered over two sites with occupancies 0.492:0.508.

Refinement of **3**: Over several batches of X-Ray diffraction experiments, the resulting structures were always shown to contain small proportions of isostructural calcium compound, tentatively assigned as calcium hydroxide species [($Tp^{Ad,iPr}$)Ca(OH)(THP)] (**3***) (Figure **S36**). Complexes **3** and **3*** share the same steric requirements and shape, but dramatically differ in electron density. In this case, the terminal hydride (H1) and the oxygen atom (O2) of were located by difference Fourier syntheses and refined, and disordered over two sites with occupancies 0.805:0.195.

Refinement of **6**: One of the three adamantyl groups in the $Tp^{Ad,iPr}$ ligand was highly disordered. C27~C35 and C27'~C35' disordered over two sites with occupancies 0.872:0.128.

Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and analysis results are listed in **Table S1-5**.

CCDC number 1967134 (**2**), 1967136 (**4**), 1967137 (**5**) and 1967138 (**6**) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for complex **2**

Identification code	C157
CCDC number	1967134
Empirical formula	$C_{120}H_{174}B_2N_{12}O_2Ca_2$
Formula weight	1918.48
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2/c
a	15.552(3) Å
b	15.578(3) Å
c	45.215(10) Å
α	90 °
β	90.580(4) °
γ	90 °
Volume	10953(4) $Å^3$
Z, Calculated density	4, 1.163 Mg/m^3
Absorption coefficient	0.160 mm^{-1}
F(000)	4176
Crystal size	0.250 x 0.210 x 0.160 mm
Theta range for data collection	1.383 to 24.999 ^{o}
Limiting indices	-15<=h<=18, -18<=k<=18, -51<=l<=53
Reflections collected / unique	53094 / 19243 [R(int) = 0.1639]
Completeness to theta	(24.999 ^{o}) 99.6 %
Absorption correction	Empirical
Max. and min. transmission	0.975 and 0.961
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19243 / 3 / 1167
Goodness-of-fit on F^2	0.982
Final R indices [I>2sigma(I)]	R1 = 0.0911, wR2 = 0.1914
R indices (all data)	R1 = 0.2307, wR2 = 0.2495
Largest diff. peak and hole	0.878 and -0.506 e. $Å^{-3}$

Table S2. Crystal data and structure refinement for complex **3/3***(80:20)

Identification code	Shi04
CCDC number	1967135
Empirical formula	$C_{53}H_{81}B_1N_6O_{1.20}Ca_1$
Formula weight	872.20
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.6853(4) Å
b	14.2781(6) Å
c	16.8887(7) Å
α	76.4060(10) °
β	87.4920(10) °
γ	67.6630(10) °
Volume	2530.07(17) $Å^3$
Z, Calculated density	2, 1.145 Mg/m^3
Absorption coefficient	0.167 mm^{-1}
F(000)	951
Crystal size	0.210 x 0.140 x 0.120 mm
Theta range for data collection	1.887 to 24.998 °
Limiting indices	-13<=h<=13, -16<=k<=16, -20<=l<=20
Reflections collected / unique	65672 / 8835 [R(int) = 0.0637]
Completeness to theta	(24.998) 99.4 %
Absorption correction	Empirical
Max. and min. transmission	0.980 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8835 / 37 / 563
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1371
R indices (all data)	R1 = 0.0702, wR2 = 0.1493
Largest diff. peak and hole	0.726 and -0.482 e. $Å^{-3}$

Table S3. Crystal data and structure refinement for complex **4**

Identification code	D004
CCDC number	1967136
Empirical formula	$C_{62}H_{83}B_1N_6Ca_1$
Formula weight	963.23
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.7488(13) Å
b	15.0579(15) Å
c	15.7679(17) Å
α	96.695(2) °
β	94.947(2) °
γ	101.734(3) °
Volume	2695.2(5) $Å^3$
Z, Calculated density	2, 1.187 Mg/m^3
Absorption coefficient	0.162 mm^{-1}
F(000)	1044
Crystal size	0.230 x 0.150 x 0.120 mm
Theta range for data collection	1.776 to 24.997 º
Limiting indices	-10<=h<=13, -17<=k<=17, -18<=l<=18
Reflections collected / unique	13974 / 9305 [R(int) = 0.0495]
Completeness to theta	(24.997) 98.0 %
Absorption correction	Empirical
Max. and min. transmission	0.981 and 0.971
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9305 / 0 / 636
Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1195
R indices (all data)	R1 = 0.1296, wR2 = 0.1489
Largest diff. peak and hole	0.242 and -0.279 e. $Å^{-3}$

Table S4. Crystal data and structure refinement for complex **5**

Identification code	G094
CCDC number	1967137
Empirical formula	$C_{62}H_{83}B_1N_6Ca_1$
Formula weight	963.23
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.9771(8) Å
b	14.8686(10) Å
c	16.6034(11) Å
α	99.7570(10) °
β	99.7770(10) °
γ	104.4060(10) °
Volume	2751.9(3) $Å^3$
Z, Calculated density	2, 1.162 Mg/m^3
Absorption coefficient	0.158 mm^{-1}
F(000)	1044
Crystal size	0.210 x 0.170 x 0.120 mm
Theta range for data collection	1.800 to 25.000 °
Limiting indices	-14<=h<=14, -16<=k<=17, -11<=l<=19
Reflections collected / unique	14196 / 9486 [R(int) = 0.0324]
Completeness to theta	(25.000) 97.8 %
Absorption correction	Empirical
Max. and min. transmission	0.981 and 0.968
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9486 / 0 / 639
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0558, wR2 = 0.1160
R indices (all data)	R1 = 0.0850, wR2 = 0.1316
Largest diff. peak and hole	0.251 and -0.201 e. $Å^{-3}$

Table S5. Crystal data and structure refinement for complex **6**

Identification code	MA001
CCDC number	1967138
Empirical formula	$C_{63}H_{93}B_1N_6O_1Ca_1$
Formula weight	1001.32
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	14.5913(16) Å
b	14.6823(16) Å
c	15.1498(16) Å
α	61.123(2) °
β	82.567(2) °
γ	88.425(2) °
Volume	2815.9(5) $Å^3$
Z, Calculated density	2, 1.181 Mg/m^3
Absorption coefficient	0.158 mm^{-1}
F(000)	1092
Crystal size	0.180 x 0.150 x 0.120 mm
Theta range for data collection	1.585 to 25.000 ^{o}
Limiting indices	-17<=h<=10, -17<=k<=17, -18<=l<=16
Reflections collected / unique	13854 / 9656 [R(int) = 0.0284]
Completeness to theta	(25.000) 97.4 %
Absorption correction	Empirical
Max. and min. transmission	0.981 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9656 / 51 / 633
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1155
R indices (all data)	R1 = 0.0752, wR2 = 0.1288
Largest diff. peak and hole	0.389 and -0.265 e. $Å^{-3}$

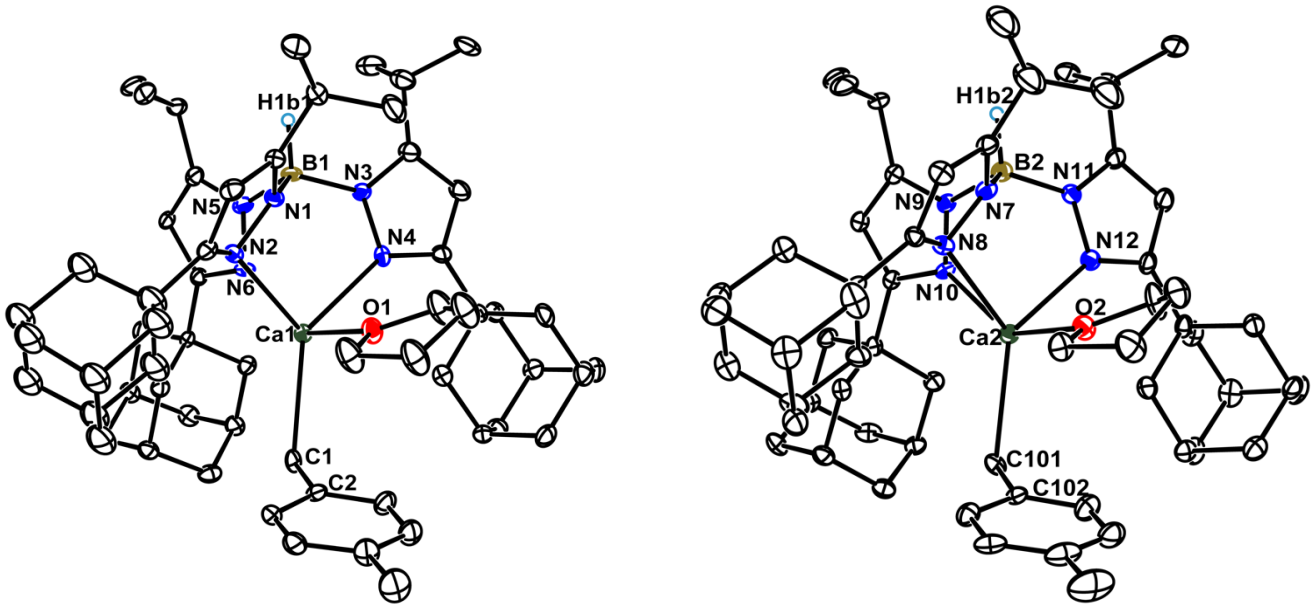

Figure S34. ORTEP drawing of [(Tp^{Ad,iPr})Ca(*p*-$CH_2C_6H_4$-Me)(THF)] (**2**) with thermal ellipsoids drawn at the 20% probability level. Two independent molecules were found in the unit cell. Except H1b1 and H1b2, all the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Ca1—C1 2.610(6), Ca1—O1 2.407(4), Ca1—N2 2.448(5), Ca1—N4 2.434(5), Ca1—N6 2.491(5), C1—C2 1.466(8), Ca1—C1—C2 107.2(4); Ca2—C101 2.573(6), Ca2—O2 2.422(4), Ca2—N8 2.425(5), Ca2—N10 2.502(5), Ca2—N12 2.421(5), C101—C102 1.430(8), Ca1—C101—C102 111.1(4).

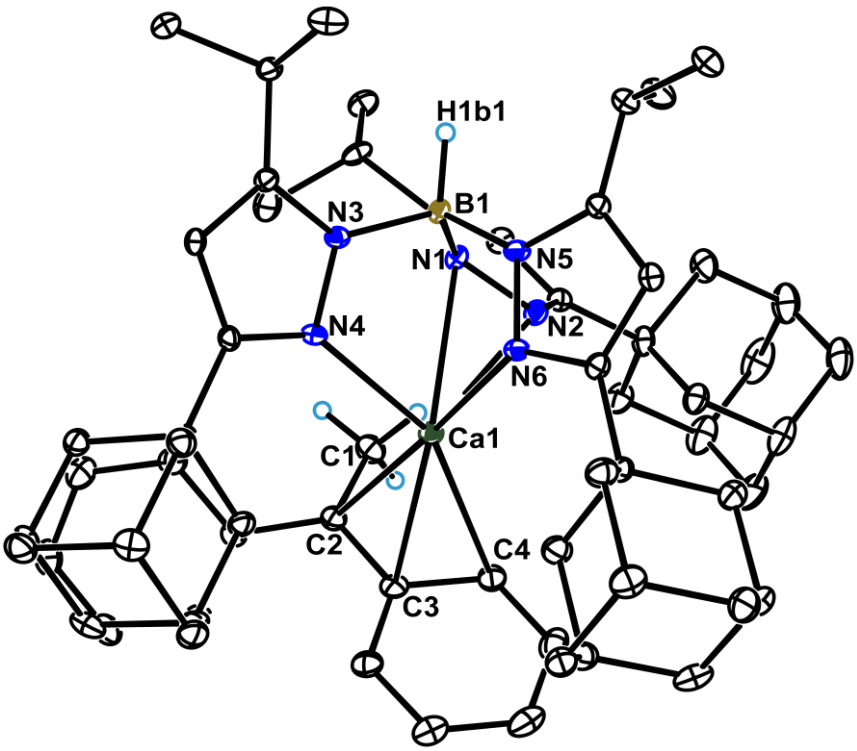

Figure S35. ORTEP drawing of [(Tp^{Ad,iPr})Ca{CPh$_2$(Me)}] (**4**) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms in pyrazoles and phenyl groups are omitted for clarity. Selected interatomic distances [Å]: Ca1—C2 2.675(3), Ca1—C3 2.672(3), Ca1—C4 2.779(3), Ca1—N1 2.691(3), Ca1—N2 2.538(3), Ca1—N4 2.419(3), Ca1—N6 2.422(3), C1—C2 1.530(5), C2—C3 1.415(5), C3—C4 1.441(5).

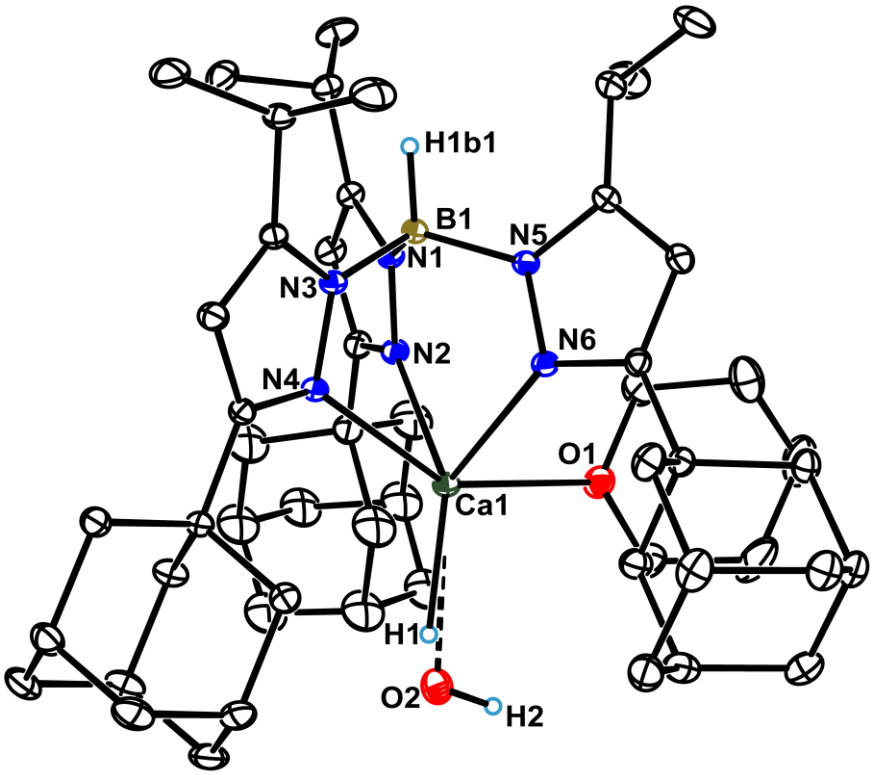

Figure S36. ORTEP drawing of [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**) / [(Tp^{Ad,iPr})Ca(OH)(THP)] (**3***) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms in pyrazoles and THP are omitted for clear.

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