Supporting Information for

Imine Hydrogenation by Alkylaluminum Catalysts

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S1. Synthesis and Isolation of Compounds

General considerations

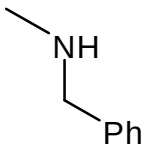
All synthetic manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an MBraun glove box and a Schlenk vacuum-line. Toluene was purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Chloroform-*d* and bromobenzene-d_5 were each dried over CaH_2, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. Toluene-d_8 and benzene-d_6 were dried over Na/benzophenone, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^{1}H, ^{13}C) or relative to an external standard (^{27}Al: $Al(NO_3)_3$). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Elemental analyses were performed in house by ANALEST on a 2400 Series II CHNS Analyzer. Diisobutylaluminum hydride (DIBAL, **1**) and commercially available substrates MeN=CHPh, (Me_3Si)N=CHPh, PhN=CHPh, (Ph_2CH)N=CHPh, *t*BuN=CHPh, (PhO_2S)N=CHPh, and 1,3,3-trimethyl-2-methyleneindoline were obtained from Sigma-Aldrich. Commercially available 1-cyclohexen-1-ylpiperidine was obtained from Alfa Aesar. Commercially available BnN=CHPh was obtained from Acros Organics. Triisobutylaluminum (TIBAL, **2**) was purchased from Strem. Liquid substrates were stored over 4 Å molecular sieves or distilled from TIBAL and stored in an inert atmosphere glovebox. Solid substrates were dried *in vacuo* and stored in an inert atmosphere glovebox. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure^{TM} gas purifier. The compound iBu$_2$AlD[1] and substrates PhN=CH(p-BrC_6H_4),[2] *t*BuN=CH(p-*t*BuC_6H_4),[3] (2,6-Me_2Ph)N=C(Me)Ph,[4] *t*BuN=CH(p-N$Me_2C_6H_4$),[5] *t*BuN=CH(m-BrC_6H_4),[6] *t*BuN=CH(p-BrC_6H_4),[7] (p-ClC_6H_4)N=CHPh[8] and *t*BuN=CH(m-OMeC_6H_4)[6] were prepared via literature methods. A series of hydrogenation experiments were performed either in a Parr Pressure reactor or a J. Young tube. Details are provided below.

General procedure for elevated pressure reductions: In a N_2 filled glove box, substrate (Entries 1, 5–8, 10–14: 0.7 mmol; Entries 2–4, 9 and 15: 0.5 mmol) was weighed in a 2 dram vial and dissolved in toluene (0.3 ml). To this was added catalyst (5 mol% of **1** (DIBAL) or 10 mol% of **2** (TIBAL)) and the imine/catalyst solution was thoroughly mixed. Seven vials were then transferred to a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged five times at 50 atm hydrogen and five times at 92 atm H_2. The reactor was sealed under 92 atm H_2, and placed on a stir plate heated to 100 °C (final pressure 102 atm H_2) for 24 h. The reactor was cooled, slowly vented and an NMR sample was taken in $CDCl_3$. Conversion of unsaturated substrate to amine product was determined by ^{1}H NMR spectroscopy.

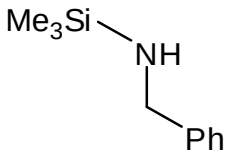
General procedure for amine isolation: The solvent was removed *in vacuo*, and the resulting oil/solid dissolved in EtOAc. To this, 2 mL of water was added, and the organic layer decanted. The aqueous layer was extracted 2 x 5 mL of EtOAc. The combined organic fractions were treated with $MgSO_4$, filtered through a plug of Celite, and dried *in vacuo*. Analysis by ^{1}H NMR spectroscopy revealed that compound *N*-benzyl(trimethylsilyl)amine decomposed upon aqueous workup. Compound *N*-benzylaniline required additional column chromatography for purification.

Product characterization data:

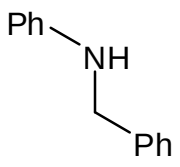
Products (isolated and crude) were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and compared to literature values where applicable.



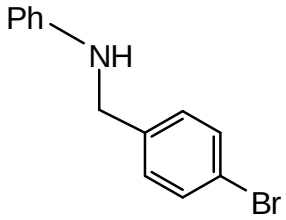
***N*-benzylmethylamine (entry 1)**: ref[9] (colourless oil, 81 mg, 95 % isolated yield) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35-7.31 (m, 5H, C_6H_5); 3.75 (s, 2H, CH_2); 2.46 (s, 3H, CH_3). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 139.2, 128.5, 128.4 and 128.3 (Ph–*C*); 56.3 (CH_2); 36.2 (CH_3).



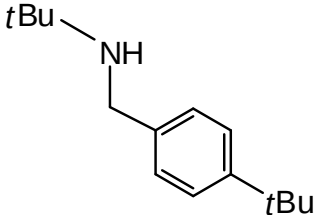
***N*-benzyl(trimethylsilyl)amine (entry 2)**: ref[10] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (m, 3H, C_6H_5); 7.36 (m, 3H, C_6H_5); 3.94 (d, 2H, CH_2, $^3J_{HH}$ = 8.3 Hz); 0.11 (s, 9H, $Si(CH_3)_3$). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 139.4, 128.7, 128.1 and 127.1 (Ph–*C*); 49.2 (CH_2); 2.1 (s with Si satellites, Si–CH_3, $^1J_{CSi}$ = 58 Hz).



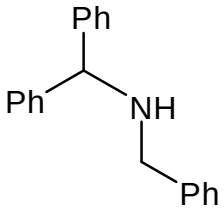
***N*-benzylaniline (entry 3)**: ref[11] (white solid, 80 mg, 87 % isolated yield) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.3 (m, 4H, C_6H_5); 7.23 (m, 1H, *p*-C_6H_5); 7.12 (dd, 2H, C_6H_5, $^3J_{HH}$ = 8, 6.7 Hz); 6.68 (t, 1H, *p*-C_6H_5, $^3J_{HH}$ = 6.7 Hz); 6.56 (d, 2H, *o*-C_6H_5, $^3J_{HH}$ = 8.8 Hz); 4.23 (s, 2H, CH_2); 3.90 (br, 1H, N*H*). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 148.2, 139.5, 129.3, 128.7, 127.5, 127.2, 117.6 and 112.9 (Ph–*C*); 48.3 (CH_2).



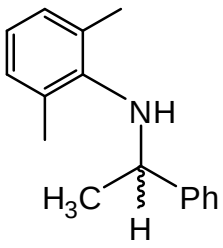
***N*-(4-bromobenzyl)aniline (entry 4)**: ref[12] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, 2H, C_6H_5, $^3J_{HH}$ = 8 Hz) 7.25-7.18 (m, 3H, C_6H_5); 6.72 and 6.62 (d, 4H, *p*-BrC_6H_4, $^3J_{HH}$ = 8.7 Hz); 4.29 (d, 2H, CH_2, $^3J_{HH}$ = 6.9 Hz); 4.03 (br m, 1H, N*H*). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):** δ 147.0, 138.1, 129.9, 129.2, 129.1, 118.2 and 113.4 (Ph–*C*); 47.9 (CH_2).



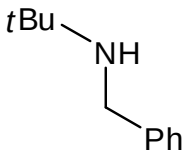
***N*-(4-*tert*-butylbenzyl)-*tert*-butylamine (entry 5)**: (white solid, 149 mg, 97 % isolated yield) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 and 7.36 (d, 4H, *p*-*t*BuC_6H_4, $^3J_{HH}$ = 7 Hz); 3.65 (d, 2H, CH_2, $^3J_{HH}$ = 7.7 Hz); 1.34 (s, 9H, *p*-*t*Bu–CH_3); 1.17 (s, 9H, *t*Bu–CH_3); 0.81 (br t, 1H, N*H*). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):** δ 144.1, 139.2, 132.9 and 126.8 (Ph–*C*); 57.5 and 50.6 (*t*Bu–*C*); 46.6 (CH_2); 29.6 and 29.1 (*t*Bu–CH_3).



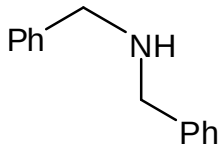
***N*-benzyl-diphenylmethylamine (entry 6)**: ref[13] (pale yellow solid, 186 mg, 97 % isolated yield) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32-7.10 (m, 15H, C_6H_5); 4.88 (d, 1H, C*H*, $^3J_{HH}$ = 3.8 Hz); 3.76 (d, 1H, CH_2, $^3J_{HH}$ = 7.6 Hz); 1.85 (m, 1H, N*H*). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):** δ 144.1, 140.6, 128.4, 128.3, 128.2, 127.4, 127.1 and 127.0 (Ph–*C*); 66.5 (*C*H); 51.9 (CH_2).



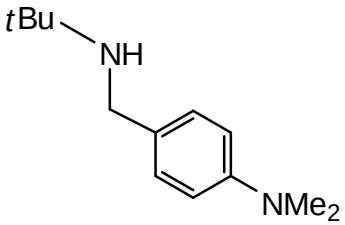
***rac*-2,6-dimethyl-*N*-(1-phenylethyl)aniline (entry 7)**: (pale yellow solid, 151 mg, 94 % isolated yield) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 and 7.20 (m, 5H, C_6H_5); 7.02 (d, 2H, *m*-(2,6-Me_2)C_6H_3, $^3J_{HH}$ = 8 Hz); 6.88 (t, 1H, *p*-(2,6-Me_2)C_6H_3, $^3J_{HH}$ = 8 Hz); 4.35 (dq, 1H, C*H*, $^3J_{HH}$ = 10.3, 6.8 Hz); 3.20 (d, 1H, N*H*, $^3J_{HH}$ = 10.3 Hz); 2.20 (s, 6H, (2,6-CH_3)$_2$Ph); 1.52 (s, 3H, CH_3, $^3J_{HH}$ = 6.8 Hz). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):** δ 145.3, 145.0, 129.1, 128.4, 128.2, 127.0, 126.1 and 121.7 (Ph–*C*); 56.8 (*C*H); 22.6 (CH_3); 18.9 (2,6–CH_3).



***N*-benzyl-*tert*-butylamine (entry 8)**: ref[14] **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.25 and 7.23 (m, 4H, *o* and *m*–Ph–*H*); 7.15 (tt, 1H, *p*–Ph–*H*, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz); 3.65 (s, 2H, CH_2); 1.11 (s, 9H, *t*Bu–CH_3). **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz):** δ 141.4, 128.2, 128.1 and 126.6 (Ph–*C*); 50.5 (*t*Bu–*C*); 47.1 (CH_2); 29.0 (*t*Bu–CH_3).

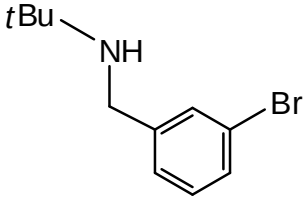


Dibenzylamine (entry 9): **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39-7.33 (m, 10H, C_6H_5); 3.79 (d, 2H, CH_2, $^3J_{HH}$ = 6.5 Hz); 1.51 (br t, 1H, N*H*). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):** δ 140.4, 129.1, 128.4 and 127.0 (Ph–*C*); 53.2 (CH_2).

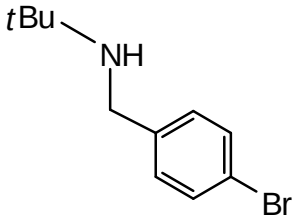


***N*-(4-dimethylaminobenzyl)-*tert*-butylamine (entry 10)**: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 and 7.45 (d, 4H, *p*-$NMe_2C_6H_4$, $^3J_{HH}$ = 9.1 Hz); 3.65 (d, 2H, CH_2, $^3J_{HH}$ = 7.7 Hz); 2.38 (s, 6H,

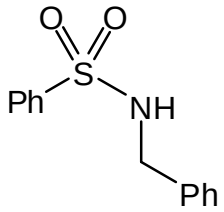
N(CH_3)$_2$); 1.20 (s, 9H, *t*Bu–CH_3). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 136.2, 131.5, 130.0 and 120.5 (Ph–*C*); 50.8 (*t*Bu–*C*); 46.7 (*C*H$_2$); 29.7 (NCH_3); 29.2 (*t*Bu–CH_3).



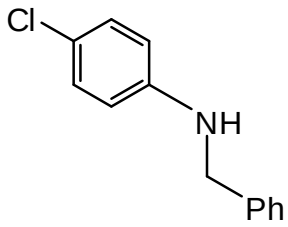
***N*-(3-bromobenzyl)-*tert*-butylamine (entry 11)**: **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41–7.30, 7.23 and 7.18 (m, 4H, C$_6H_5$); 3.73 (br s, 2H, C*H*$_2$); 1.21 (s, 9H, *t*Bu–CH_3). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 138.5, 133.7, 128.4, 128.1, 127.9 and 125.4 (Ph–*C*); 50.4 (*t*Bu–*C*); 46.8 (*C*H$_2$); 29.1 (*t*Bu–*C*H$_3$).



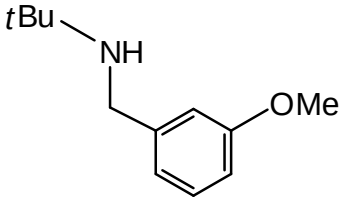
***N*-(4-bromobenzyl)-*tert*-butylamine (entry 12)**: **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.43 and 7.21 (d, 4H, *p*-BrC$_6H_4$, $^3J_{HH}$ = 8.3 Hz); 3.65 (d, 2H, C*H*$_2$, $^3J_{HH}$ = 7.8 Hz); 1.18 (s, 9H, *t*Bu–CH_3); 0.89 (br t, 1H, N*H*). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 140.7, 131.4, 130.0 and 120.4 (Ph–*C*); 50.7 (*t*Bu–*C*); 46.6 (*C*H$_2$); 29.2 (*t*Bu–*C*H$_3$).



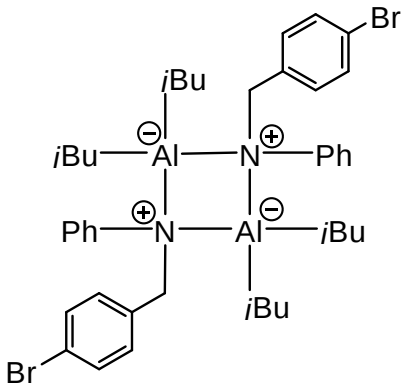
***N*-benzylbenzenesulfonamide (entry 13)**: ref[15] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.05 (d, 2H, SO$_2$C$_6H_5$, $^3J_{HH}$ = 8 Hz); 7.89 (m, 3H, SO$_2$C$_6H_5$); 7.57-7.48 (m, 5H, C$_6H_5$); 5.33 (t, 1H, N*H*, $^3J_{HH}$ = 6 Hz); 4.13 (d, 2H, C*H*$_2$, $^3J_{HH}$ = 6 Hz). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 140.3, 136.5, 129.3, 128.7, 127.9 and 127.3 (Ph–*C*); 47.5 (*C*H$_2$).



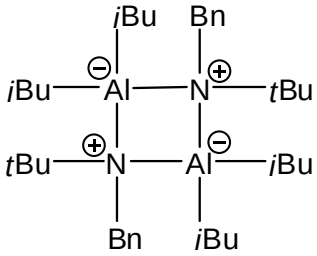
***N*-benzyl-4-chloroaniline (entry 14)**: ref[12] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.33-7.26 (m, 5H, C$_6H_5$); 7.10 and 6.43 (d, 4H, *p*-ClC$_6H_4$, $^3J_{HH}$ = 8.3 Hz); 4.15 (d, 2H, C*H*$_2$, $^3J_{HH}$ = 7.7 Hz); 3.95 (br, 1H, N*H*). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 146.6, 138.8, 129.2, 128.8, 127.5, 122.1 and 113.9 (Ph–*C*); 48.2 (*C*H$_2$).



***N*-(3-methoxybenzyl)-*tert*-butylamine (entry 15)**: ref[16] **^{1}H NMR (CDCl$_3$, 400 MHz):** δ 7.22 (dd, 1H, 5–Ph–*H*, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz); 6.93 (s, 1H, 2–Ph–*H*); 6.93 (m, 1H, 4–Ph–*H*); 6.78 (dd, 1H, 6–Ph–*H*, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 2.2 Hz); 3.80 (s, 1H, OCH_3); 3.71 (s, 2H, C*H*$_2$); 1.17 (s, 9H, *t*Bu–CH_3). **^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz):** δ 158.7, 141.8, 128.4, 119.6, 121.8, and 111.4 (Ph–*C*); 54.1 (O*C*H$_3$); 49.9 (*t*Bu–*C*); 46.2 (*C*H$_2$); 28.0 (*t*Bu–*C*H$_3$).



Synthesis of [*i*Bu$_2$AlN(Ph)(*p*-BrBn)]$_2$ (3). A 1.0 M solution of DIBAL in toluene (0.35 mL, 0.35 mmol) was added to the imine PhN=CH(*p*-BrC$_6$H$_4$) (91 mg, 0.35 mmol) in a vial. The red solution was left on the shelf at room temperature overnight, whereupon colourless X-ray quality crystals precipitated from the solution. The supernatant was decanted, the crystals washed with a small amount of cold pentane, then dried *in vacuo* yielding a white solid (131 mg, 92% yield).
^{1}H NMR (400 MHz, C$_6$D$_5$Br): δ 7.11 (d, 4H, *m*-C$_6$*H*$_4$Br, $^3J_{HH}$ = 8.8 Hz); 7.04 (m, 8H, *o*/*m*-C$_6$*H*$_5$); 6.83 (t, 2H, *p*-C$_6$*H*$_5$, $^3J_{HH}$ = 6.8 Hz); 6.72 (d, 4H, *o*-C$_6$*H*$_4$Br, $^3J_{HH}$ = 8.8 Hz); 4.47 (s, 4H, Bn-C*H*$_2$); 2.01 and 1.84 (m, 4H, *i*Bu-C*H*); 1.09, 1.06, 0.99 and 0.95 (d, 24H, *i*Bu-C*H*$_3$, $^3J_{HH}$ = 6.6 Hz); 0.40, 0.38, 0.24 and 0.23 (d, 8H, *i*Bu-C*H*$_2$, $^3J_{HH}$ = 7.6, 7.3, 7 Hz). **^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_5$Br):** δ 145.8, 139.6, 130.9, 129.2, 128.6, 128.2, 123.9 and 123.6 (Ar-*C*); 53.3 (*C*H$_2$); 27.9, 27.6, 27.5 and 27.4 (*i*Bu-*C*H$_3$); 25.9 and 25.6 (*i*Bu-*C*H$_2$); 21.4 and 21.0 (*i*Bu-*C*H). **^{27}Al NMR (104 MHz, C$_6$D$_5$Br):** δ 67.6 (br s, $W_{1/2}$ = 4076 Hz). **Anal. Calcd.** for C$_{42}$H$_{58}$Al$_2$Br$_2$N$_2$: C 62.69%, H 7.26%, N 3.48%. Found C 62.31%, H 6.99%, N 3.51%.



Synthesis of [*i*Bu$_2$Al(N(*t*Bu)Bn)]$_2$, (4). A 1.0 M solution of DIBAL in toluene (0.35 mL, 0.35 mmol) was added to the imine *t*BuN=CH(Ph) (57 mg, 0.35 mmol) in a vial. The colourless solution was allowed to react for 1 h and the solvent removed *in vacuo* yielding a colourless oil. (101 mg, 95% yield).
^{1}H NMR (400 MHz, tol-*d*$_8$): δ 7.12 (d, 4H, *o*-C$_6$*H*$_4$Br, $^3J_{HH}$ = 8.4 Hz); 7.02 and 6.95 (m, 6H, *m*/*p*-C$_6$*H*$_5$); 4.19 (s, 4H, Bn-C*H*$_2$); 2.07 (m, 4H, *i*Bu-C*H*); 1.11 and 1.10 (d, 24H, *i*Bu-C*H*$_3$, $^3J_{HH}$ = 6.6 Hz); 0.53 (m, 8H, *i*Bu-C*H*$_2$). **^{13}C{^{1}H} NMR (101 MHz, tol-*d*$_8$):** δ 141.0, 128.5, 128.2 and 127.4 (Ar-*C*); 58.2 (*C*H$_2$); 53.2 (*t*Bu–*C*); 31.6 (*t*Bu−*C*H$_3$); 28.5 and 28.2 (*i*Bu-*C*H$_3$); 28.2 and 28.1 (*i*Bu-*C*H$_2$); 26.9 (*i*Bu-*C*H). **^{27}Al NMR (104 MHz, tol-*d*$_8$):** δ 74.2 (br s, $W_{1/2}$ = 3388 Hz).

S2. Mechanism

Activation of dihydrogen by 3. In an inert atmosphere glovebox, [*i*Bu$_2$AlN(Ph)(*p*-BrBn)]$_2$ (0.35 mmol) was dissolved in C$_6$D$_5$Br and placed in a J. Young NMR tube. The tube was sealed and subjected to three freeze-pump-thaw cycles. The tube was then frozen, evacuated and backfilled with 4 atm H$_2$ gas. The tube was thawed and heated to 100 °C. Analysis of the crude reaction mixture after 10 h by ^{1}H NMR spectroscopy revealed the presence of unreacted **3** and free amine PhNHCH$_2$(*p*-BrC$_6$H$_4$). The reaction was allowed to continue overnight at 100 °C. The solvent was removed *in vacuo* and the residue redissolved in CDCl$_3$. The ^{1}H NMR spectra below depict the change in CH$_2$ chemical shift over time:

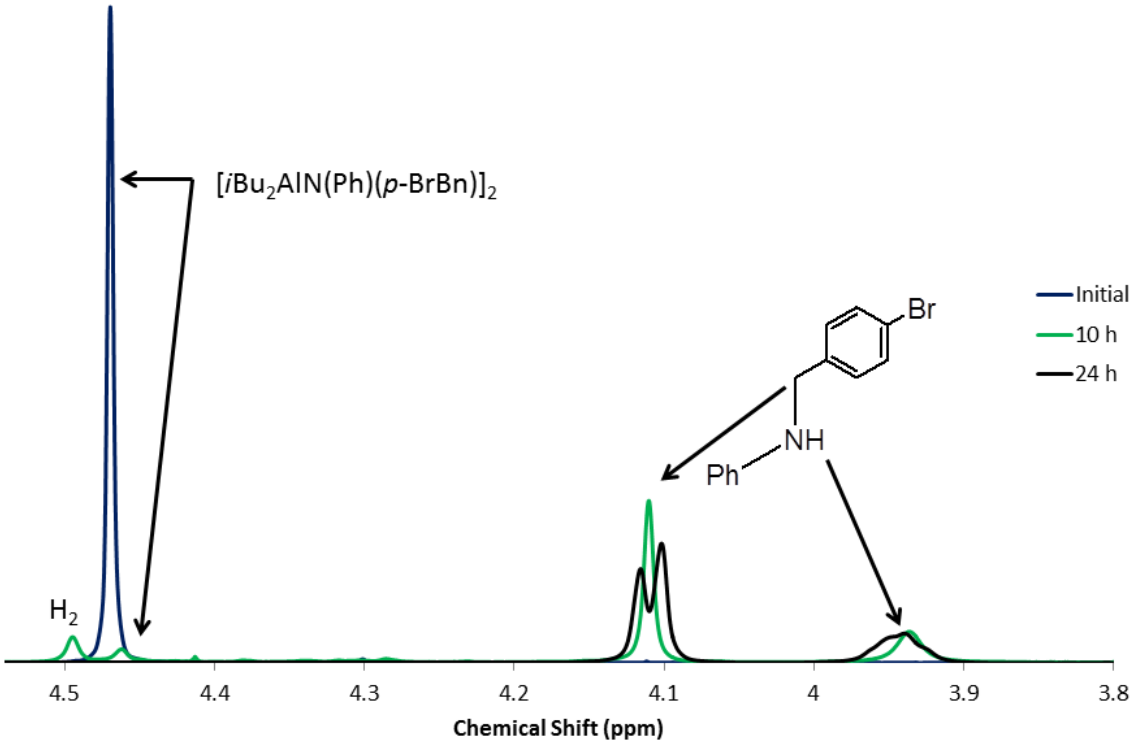


Figure S2 – ^{1}H NMR spectra (400 MHz) showing the change in CH_2 chemical shift over time for the reaction of [*i*Bu_2AlN(Ph)(*p*-BrBn)]$_2$ (**3**) with H_2 at 100 °C in C_6D_5Br overnight.

Activation of D_2 by 3. The activation of D_2 was carried out in an analogous manner to that reported above for the activation of H_2; however, deuterium gas was used in place of hydrogen gas, and C_6H_5Br was used in place of C_6D_5Br. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed a broad singlet for the CH_2 protons at δ 4.11, but no distinguishable resonance at δ 3.95 associated with NH of the corresponding amine. The ^{2}H NMR spectrum displayed a weak, broad peak at δ 4 with no resolved coupling. These data support the formation of PhNDCH$_2$(*p*-BrBn).

The reaction was allowed to proceed for 1 week at 100 °C. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed a broad multiplet for the CH_2 protons at δ 4.11 accompanied with a decreased intensity, and a new broad, unresolved multiplet at δ 3.9 associated with NH of the corresponding amine. The ^{2}H NMR spectrum displayed two weak, broad peaks at δ 4.1 and 4.0 with no resolved coupling These data support a reversible mechanism enabling deuterium scrambling resulting in a mixture of products: PhN(H/D)CH$_2$(*p*-BrBn), PhN(H/D)CHD(*p*-BrBn) and PhNDCD$_2$(*p*-BrBn).

Stoichiometric reaction of *i*Bu_2AlD, (2,6-Me_2Ph)N=C(Me)Ph and H_2. In a N_2 filled glove box, (2,6-Me_2Ph)N=C(Me)Ph (63 mg, 0.3 mmol) was weighed in a 2 dram vial dissolved in toluene (0.3 ml). To this was added *i*Bu_2AlD (40 mg, 0.3 mmol) and the solution was thoroughly

mixed. Initial analysis by ^{2}H NMR spectroscopy revealed a weak multiplet with 5 lines at δ 4.6 with a $^{3}J_{DH}$ value of 2.6 Hz (Figure S3) indicative of CD coupling to CH_3 (partial 1:3:6:7:6:3:1 septet). The corresponding 1:1:1 triplet in the ^{1}H NMR could not be located as it coincides with the resonance associated with diethyl ether (*vide infra*).

The vial was then transferred to a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged five times at 50 atm hydrogen and five times at 92 atm H_2. The reactor was sealed under 92 atm H_2, and placed on a stir plate heated to 100 °C (final pressure 102 atm H_2) for 2 h. The reactor was cooled, slowly vented and an NMR sample was taken. Conversion of unsaturated substrate to amine product was determined by ^{1}H NMR spectroscopy to be quantitative. The ^{1}H NMR spectrum displayed a broad 1:1:1 triplet at δ 3.2 for the NH proton coupled to CD with a $^{3}J_{HD}$ value of 1.6 Hz. This fails to integrate properly with the CH_3 resonance, presumably due to H/D scrambling. A broad resonance can be located in the baseline at δ 4.6 due to CH. The ^{2}D NMR spectrum revealed a weak, broad resonance at δ 4.6 for CD.

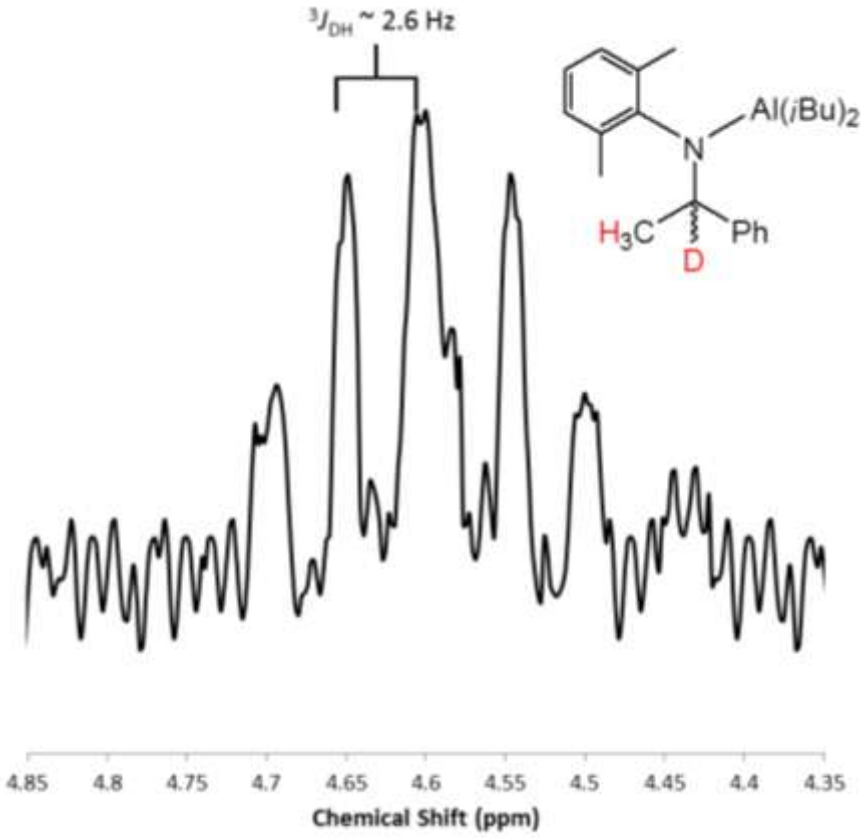


Figure S3 – ^{2}H NMR spectrum (61.4 MHz) showing 5 lines of a 1:3:6:7:6:3:1 septet ($^{3}J_{DH}$ ~ 2.6 Hz) for the stoichiometric reaction of *i*Bu_2AlD and (2,6-Me_2Ph)N=C(Me)Ph in toluene before H_2 addition.

Stoichiometric reaction of *i*Bu_2AlD, *t*BuN=CHPh and H_2. This reaction was carried out in an analogous manner to that reported above for (2,6-Me_2Ph)N=C(Me)Ph; however *t*BuN=CHPh (45 mg, 0.3 mmol) was used as the substrate. The ^{1}H NMR spectrum displayed a broad singlet at δ 3.6 for the CH_2 protons. The ^{2}D NMR spectrum was silent.

Note: The above reactions with *i*Bu_2AlD took place in the presence of diethyl ether that could not be removed following its synthesis, even after repetitive distillations. This displays catalyst tolerance toward ether functionalities.

S3. References

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