Electronic Supplementary Material For:

Lewis acid catalyzed hydrogenation: $B(C_6F_5)_3$ mediated reduction of imines and nitriles with H_2†

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General Considerations: All experiments were performed on double manifold Schlenk $N_2(H_2)$/vacuum lines or in a N_2-filled MBraun 130-BG glove box. All glassware was heated to 140ºC overnight and either assembled and attached to the vacuum lines or placed into the glovebox while hot. Toluene, hexanes and CH_2Cl_2 were dried by passage through alumina and molecular sieves in a commercially available solvent purification system. H_2 gas (Praxair) was dried by passage through a column of 50:50 activated molecular sieves and Drierite. NMR experiments were performed on a Bruker Avance-300 spectrometer at 300K unless otherwise noted. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to $SiMe_4$ using the residual proton peak of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR spectra were referenced to 85% H_3PO_4 ($\delta = 0$), $BF_3(OEt_2)$ ($\delta = 0$), and $CFCl_3$ ($\delta = 0$), respectively. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. Commercially available imines, nitriles and 1,2,3-triphenylaziridine were purchased from Aldrich and P(2,4,6-$Me_3C_6H_2)_3$ (P(C6H2Me3)$_3$) was purchased from Strem Chemicals; all were used without further purification. $B(C_6F_5)_3$ was generously donated by NOVA corporation and used without further purification. Compounds *t*BuN=CPh_2,[1] DippN=CPh(Me),[2] DippN=C*t*Bu(Me)[3] $(C_6F_5)_3BN{\equiv}CMe$, $(C_6F_5)_3BN{\equiv}CPh$,[4] were prepared by literature methods.

Catalysis procedure, $B(C_6F_5)_3$-only

In the glovebox, substrate (1 mmol), $B(C_6F_5)_3$ (26 mg, 0.05 mmol, 5 mol%) and dry toluene (4 ml) were weighed into a 100 ml round bottomed flask equipped with a sealable Teflon tap (Kontes valve) and small magnetic stirbar. The reaction was then attached to a double manifold H_2/vacuum line and degassed (freeze-pump-thaw cycle x 3). The reaction was cooled to -196ºC (liquid N_2) and 1 atm. H_2 was introduced. The flask was sealed and warmed to room temperature. The reaction was then placed in an oil bath heated to the desired temperature and stirred at 500 rpm. At 120ºC, the H_2 pressure is ~ 5 atm. Aliquots were obtained at periodic intervals by rapidly cooling the reaction in a water bath and venting the H_2 pressure. Samples were taken by pipette in the glove box. The reaction was re-pressurized using the above procedure. Upon full conversion, the reaction was poured onto a 10 cm plug of silica (200 mesh) and eluted with 2:1 hexanes/ ethyl acetate (200 ml). If the amine was not fully soluble in the reaction mixture or the hexanes/ ethyl acetate solvent, CH_2Cl_2 (3 x 5 ml) was used to wash the reaction vessel. The collected eluent was removed *in vacuo* to obtain the product.

Catalysis procedure, $B(C_6F_5)_3$ and $P(C_6H_2Me_3)_3$:

In the glovebox, substrate (1 mmol), $B(C_6F_5)_3$ (26 mg, 0.05 mmol, 5 mol%), P(2,4,6-$Me_3C_6H_2)_3$ (19 mg, 0.05 mmol, 5 mol%) and dry toluene (4 ml) were weighed into a 100 ml round bottomed flask equipped with a sealable Teflon

[1] Moritti, I.; Torre, G. *Synthesis*, **1970**, 141.
[2] Syntheiszed via the procedure in Moritti, I.; Torre, G. *Synthesis*, **1970**, 141. For NMR see Mueller, G.; Klinga, M.; Osswald, P.; Leskelae, M.; Rieger, B. *Z. Natur. B, Chem. Sci.* **2002**, *57*, 803.
[3] Syntheiszed via the procedure in Moritti, I.; Torre, G. *Synthesis*, **1970**, 141. For NMR see Budzelaar, P.H.M.; van Oort, A.B.; Orpen, A.G. *Eur. J. Inorg. Chem.* **1998**, 1485.
[4] Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

tap (Kontes valve) and small magnetic stirbar. The reaction was then attached to a double manifold H_2/vacuum line and degassed (freeze-pump-thaw cycle x 3). The reaction was cooled to -196ºC (liquid N_2) and 1 atm. H_2 was introduced. The flask was sealed and warmed to room temperature. The reaction was then placed in an oil bath heated to the desired temperature and stirred at 500 rpm. At 120ºC, the H_2 pressure is ~ 5 atm. Aliquots were obtained at periodic intervals by rapidly cooling the reaction in a water bath and venting the H_2 pressure. Samples were taken by pipette in the glove box. The reaction was re-pressurized using the above procedure. Upon full conversion, the reaction was poured onto a 10 cm plug of silica (200 mesh) and eluted with 2:1 hexanes/ ethyl acetate (200 ml). If the amine was not fully soluble in the reaction mixture or the hexanes/ ethyl acetate solvent, CH_2Cl_2 (3 x 5 ml) was used to wash the reaction vessel. The collected eluent was removed *in vacuo* to obtain the product.

Previously reported amines were identified by comparison of ^{1}H NMR spectra to literature values:

E1; HN(*t*Bu)CH_2Ph: Froyen, P.; Juvvik, P. *Tetrahedron Lett.* **1995**, *36*, 9555.

E2; HN($CHPh_2$)CH_2Ph: Mehrotra, K. N.; Giri, B. P. *Synthesis* **1977**, 470.

E3, **E8**; HN(SO_2Ph)CH_2Ph: Nyasse, B.; Grehn, L.; Ragnarsson, U.; Maia, H. L. S.; Monteiro, L. S.; Leito, I.; Koppel, I.; Koppel, J. *J. Chem. Soc. Perkin Trans. 1*, **1995**, 2025.

E4; HN(*t*Bu)$CHPh_2$: Cliffe, I.A.; Crossley, R.; Shepard, R.G. *Synthesis*, **1985**, 1138.

E5; HN(Dipp)CHPh(Me): **^{1}H NMR** (C_6D_6, 500 MHz): 7.16 (br, 4H, Ar*H*), 7.11 (t, 1H, $^3J_{HH}$ = 6.7 Hz), 7.09 (s, 3H, Ar*H*), 4.12 (d of q, 1H, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*Ph(Me), 3.22 (heptet, 2H, $^3J_{HH}$ = 7.0 Hz, C*H*Me_2), 3.14 (d, 1H, $^3J_{HH}$ = 9.3 Hz, N*H*), 1.39 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CHPh(CH_3)), 1.19 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)), 1.05 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)). **^{13}C{^{1}H} NMR** (C_6D_6): δ 145.6 (s, *ipso* Ar*C*), 143.3 (s, *ipso* Ar*C*), 142.5 (s, *ipso* Ar*C*), 129.0 (s, Ar*C*H), 127.6 (s, Ar*C*H), 127.0 (s, Ar*C*H), 124.6 (s, Ar*C*H), 124.3 (s, Ar*C*H), 60.8 (s, N*C*HPh(Me)), 28.4 (overlapping s, 2 x *i*Pr CH*C*H_3), 22.4 (NC*C*H_3). *Anal. Calc'd:* C 85.35 H 9.67 N 4.98; *Found:* C 84.98 H 9.93 N 5.08.

E6: no product obtained

E7; HN(Ph)C(Ph)CH_2Ph: Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2001**, 4411.

E9; $EtNH_2B(C_6F_5)_3$: Chase, P.A.; Welch, G.C.; Jurca, T.; Stephan, D.W. *Angew. Chem. Int. Ed.* **2007,** *45*, 8050.

E10; $PhCH_2NH_2B(C_6F_5)_3$: Mountford, A.J.; Lancaster, S.J.; Coles, S.J.; Horton, P.N.; Hursthouse, M.B.; Light, M.E. *Inorg. Chem.* **2005**, *44*, 5921.

Partial NMR data for $PhCH_2$(*t*Bu)NH-$B(C_6F_5)_3$ (2):

^{1}H NMR (C_6D_5Br): δ 7.18 (br s, 5H, Ar*H*), 6.20 (v br, 1H, PhCH_2), 4.60 (m, 1H, N*H*), 4.16 (v br, 1H, PhCH_2), 0.93 (s, 9H, C(CH_3)$_3$). **^{19}F NMR** (C_6D_5Br): δ -122.8 (d, 1F, $^3J_{FF}$ = 23.3 Hz, *o*-Ar*F*), -126.7 (d, 1F, $^3J_{FF}$ = 22.0 Hz, *o*-Ar*F*), -127.9 (t, 1F, $^3J_{FF}$ = 23.3 Hz, *o*-Ar*F*), -130.0 (t, 1F, $^3J_{FF}$ = 29.1 Hz, *o*-Ar*F*), -131.9 (m, 1F, *o*-Ar*F*), -134.0 (m, 1F, *o*-Ar*F*), -154.4 (t, 1F, $^3J_{FF}$ = 21.3 Hz, *p*-Ar*F*), -155.8 (t, 1F, $^3J_{FF}$ = 21.3 Hz, *p*-Ar*F*), -157.1 (t, 1F, $^3J_{FF}$ = 21.3 Hz, *p*-Ar*F*), -161.1 (m, 1F, *m*-Ar*F*), -161.9 (m, 1F, *m*-Ar*F*), -162.6 (m, 1F, *m*-Ar*F*), -162.9 (m, 1F, *m*-Ar*F*), -163.4 (m, 1F, *m*-Ar*F*), -163.8 (m, 1F, *m*-Ar*F*).. **^{11}B NMR** (C_6D_5Br): δ -4.5 (br s).

Synthesis of [*t*BuNH_2(CH_2Ph)][$HB(C_6F_5)_3$] (3):

$B(C_6F_5)_3$ (0.360g, 0.70 mmol) and *t*BuN=CPh(H) (0.117g, 0.71 mmol) were weighted into a 50 ml glass bomb and dissolved in dry toluene (10 ml). The reaction was degassed (freeze-pump-thaw x 3) and the flask was immersed in LN_2. H_2

gas was introduced, the flask sealed and allowed to warm to room temperature. The reaction was heated to 120ºC for 30 minutes and stirred for 16 hours at room temperature. In the glovebox, dry hexanes (30 ml) was added to the turbid solution and a white solid precipitated. The solid was filtered, washed with hexanes (3 x 10 ml) and dried *in vacuo*. Yield 0.411 g (87%). X-ray quality crystals were obtained at room temperature by layering hexanes onto a solution of product in CH_2Cl_2. **^{1}H NMR** (CD_2Cl_2): δ 7.44 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-Ar*H*), 7.35 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-Ar*H*), 7.20 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-Ar*H*), 6.06 (v br m, 2H, NH_2), 4.28 (m, 2H, NCH_2Ph), 3.32 (br q, 1H, $^1J_{HB}$ = 82 Hz, B*H*), 1.57 (s, 9H, C(CH_3)$_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.6 (br d, *o*-Ar*C*F, $^1J_{CF}$ = 240 Hz), 138.9 (br d, *p*-Ar*C*F, $^1J_{CF}$ = 246 Hz), 137.2 (br d, *m*-Ar*C*F, $^1J_{CF}$ = 243 Hz), 131.3 (s, Ar*C*H), 130.5 (s, Ar*C*H), 129.7 (s, *ipso* Ar*C*), 129.4 (s, Ar*C*H), 62.7 (s, N*C*(CH$_3$)$_3$) 48.5 (s, N*C*H$_2$Ph), 26.7 (s, NC(*C*H$_3$)$_3$). **^{11}B NMR** (CD_2Cl_2): δ -21.4 (d, $^1J_{BH}$ = 82 Hz). **^{19}F NMR** (CD_2Cl_2): δ -131.9 (d, 6F, $^3J_{FF}$ = 21 Hz, *o*-Ar*F*), -160.3 (t, 4F, $^3J_{FF}$ = 21 Hz, *p*-Ar*F*), -163.9 (m, 6F, *m*-Ar*F*). *Anal. Calc'd*: C 51.43 H 2.83 N 2.07; *Found*: C 51.22 H 2.87 N 2.51.

NMR scale generation of [DippNH=C*t*Bu(Me)][HB(C_6F_5)$_3$] (4):

In a J-Young NMR tube, B(C_6F_5)$_3$ (8 mg, 15 μmol) and DippN=C*t*Bu(Me) (4 mg, 15 μmol) were weighed and then dissolved in C_6D_5Br (0.5 ml). The tube was placed on an H_2/vacuum line and degassed (freeze-pump-thaw cycle x 3). The reaction was cooled to -196ºC (liquid N_2) and 1 atm H_2 was introduced. The tube was sealed and allowed to warm to room temperature. The reaction was heated to 80ºC for 3 days. **^{1}H NMR** (C_6D_5Br): δ 10.50 (br, 1H, NH^+), 7.07 (br, 3H, overlapping Ar*H*), 3.85 (v. br, 1H, B*H*), 2.31 (br, 2H, C*H*Me$_2$), 1.82 (br, 3H, CH_3), 1.08 (br, 12H, CH(CH_3)$_2$), 0.97 (br, 9H, *t*Bu*H*). **^{19}F NMR** (C_6D_5Br): δ -132.9 (m, 6F, *o*-Ar*F*), -162.7 (br m, 3F, *p*-Ar*F*), -166.0 (m, 6F, *m*-Ar*F*). **^{11}B NMR** (C_6D_5Br): δ -24.4 (d, $^1J_{BH}$ = 80 Hz).