



Supporting Information

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Metal-Free Catalytic Hydrogenation**

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Materials and Methods: All experiments were performed on double manifold N₂(H₂)/vacuum lines or in a N₂-filled MBraun 130-BG glove box. Toluene was dried by passage through alumina and molecular sieves in a commercially available solvent purification system. H₂ gas (Praxair) was dried by passage through a column of 50:50 activated molecular sieves and Dririte. NMR experiments were performed on a Bruker Avance-300 spectrometer at 300K unless otherwise noted. ¹H and ¹³C {¹H} NMR spectra are referenced to SiMe₄ using the residual proton peak of the given solvent. ³¹P, ¹¹B and ¹⁹F NMR spectra were referenced to 85% H₃PO₄ (δ = 0), BF₃(OEt₂) (δ = 0), and CFC₃ (δ = 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. All imines, nitriles and 1,2,3-triphenylaziridine were purchased from Aldrich and used without further purification. Compounds (C₆F₅)₃BN(CH₂Ph)=C(H)Ph¹, (C₆F₅)₃BN≡CMe,

¹ Blackwell, J. M.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics*, **2002**, *21*, 1400.

$(\text{C}_6\text{F}_5)_3\text{BN}\equiv\text{CPh}$,² $((\text{C}_6\text{H}_2\text{Me}_3)_2\text{PH})(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ (**1**),³ $(t\text{Bu}_2\text{PH})(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ (**2**), and $(\text{C}_y\text{P})(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ ⁴ were prepared by literature methods.

Synthesis of $(\text{R}_2\text{PH})(\text{C}_6\text{F}_4)\text{B}(\text{OCH}_2\text{Ph})(\text{C}_6\text{F}_5)_2$ ($\text{R} = \text{C}_6\text{H}_2\text{Me}_3$ (6**) $t\text{Bu}$ (**7**))** These

compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of (**2**) (120 mg, 0.19 mmol) in CH_2Cl_2 (4 mL) was added a solution of benzaldehyde (20 mg, 0.19 mmol) in CH_2Cl_2 . The reaction was stirred overnight and solvent was removed *in vacuo*. The product (**7**) was isolated as a white solid; 0.138 g, 98%.

(**6**): ^1H NMR (CD_2Cl_2): δ 8.50 (d, 1H, $^1J_{\text{PH}} = 502$ Hz, *PH*), 7.38 (d, 2H, $^3J_{\text{HH}} = 7.0$ Hz, *o*-*ArH*), 7.25 (t, 2H, $^3J_{\text{HH}} = 7.0$ Hz, *m*-*ArH*), 7.14 (m, 4H, overlapping *p*-*ArH* and *MesArH*), 4.29 (s, 2H, *PhCH}_2\text{O}*), 2.35 (s, 6H, *p*-*CH}_3*), 2.27 (s, 12H, *o*-*CH}_3*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , partial): δ 148.3 (s, *p*-*ArCMe*), 148.1 (br d, $^1J_{\text{CF}} = 240$ Hz, *ArCF*), 146.5 (br d, $^1J_{\text{CF}} = 240$ Hz, *ArCF*), 144.2 (d, $^2J_{\text{CP}} = 12$ Hz, *o*-*ArCMe*), 137.0 (br d, $^1J_{\text{CF}} = 240$ Hz, *ArCF*), 132.9 (d, $^2J_{\text{CP}} = 12$ Hz, *m*-*ArCH*), 130.7 (b, *i*-*ArC-O*), 128.1 (s, *ArCH*), 126.7 (s, *ArCH*), 126.2 (s, *ArCH*), 108.6 (d, $^1J_{\text{CP}} = 87$ Hz, *i*-*ArCP*), 66.9 (s, *OCH}_2*), 22.0 (d, $^3J_{\text{CP}} = 9.9$ Hz, 2,6-*H}_3\text{CAr}*), 21.8 (4-*H}_3\text{CAr}*). ^{19}F NMR (CD_2Cl_2): δ -127.6 (br s, 2F, *ArF}_{\text{linker}}*), -134.0 (m, 4F, *o*-*ArF*), -134.3 (m, 2F, *ArF}_{\text{linker}}*), -162.8 (t, 2F, $^3J_{\text{FF}} = 20$ Hz, *p*-*ArF*), -166.9 (m, 4F, *m*-*ArF*). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -4.6 (s). ^{31}P NMR (CD_2Cl_2): δ -37.8 (d, $^1J_{\text{PH}} = 502$ Hz).

(**7**): ^1H NMR (CD_2Cl_2): 7.39 (d, 2H, $^3J_{\text{HH}} = 7.7$ Hz, *o*-*ArH*), 7.25 (t, 2H, $^3J_{\text{HH}} = 7.7$ Hz, *m*-*ArH*), 7.14 (t, 1H, $^3J_{\text{HH}} = 7.7$ Hz, *p*-*ArH*), 6.22 (d, 1H, $^1J_{\text{PH}} = 450$ Hz, *PH*), 4.30 (s, 2H, *PhCH}_2\text{O}*), 1.53 (d, 18H, $^3J_{\text{PH}} = 18$ Hz, *PC(CH}_3)_3*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 149.6 (br d, $^1J_{\text{CF}} =$, *ArCF*), 148.5 (br d, $^1J_{\text{CF}} =$, *ArCF*), 144.3 (s, *Ar*), 145.2 (br d, $^1J_{\text{CF}} = 240$ Hz,

² Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

³ Welch, G. C.; San Juan, R. R.; Masoda, J. D.; Stephan, D. W. *Science*, **2006**, *314*, 1124.

⁴ Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton*, **2007**, accepted (DOI 10.1039).

ArCF), 139.0 (br d, $^1J_{CF} = 240$ Hz, ArCF), 137.0 (br d, $^1J_{CF} = 240$ Hz, ArCF), 127.9 (s, Ar), 126.6 (s, Ar), 126.0 (s, Ar), 123.7 (vbr s, BC) 89.0 (d of t, PC_{ArF}) 66.6 (s, PhCH₂O), 36.5 (d, $^1J_{PC} = PC(CH_3)_3$), 28.1 (s, $PC(CH_3)_3$). ^{19}F NMR (CD₂Cl₂): δ -126.5 (m, overlapping 3F, ArF_{linker}), -133.0 (m, 1F, ArF_{linker}), -134.1 (m, 4F, *o*-ArF), -162.8 (t, 2F, $^3J_{FF} = 20$ Hz, *p*-ArF), -166.9 (m, 4F, *m*-ArF). $^{11}B\{^1H\}$ NMR (CD₂Cl₂): δ -4.6 (s). ^{31}P NMR (CD₂Cl₂): δ 34.1 (d, $^1J_{PH} = 450$ Hz). *Anal.* Calcd: C 53.11, H 3.51. Found: 53.78, H 3.62.

Synthesis of (C₆F₅)₃BN≡C(CH₂)₄C≡NB(C₆F₅)₃: To a solution of B(C₆F₅)₃ (1.024 g, 2 mmol) in CH₂Cl₂ (6 ml) was added a solution of N≡C(CH₂)₄C≡N (0.108g, 1 mmol) in CH₂Cl₂ (2 ml). Some white precipitate formed upon mixing and the reaction was stirred overnight. All volatiles were removed *in vacuo* to obtain the product as a white solid. Yield: 1.120 g, 99%. 1H NMR (C₆D₅Br, 393K): δ 2.34 (br s, 4H, NCCH₂), 1.52 (br s, 4H, CH₂). $^{13}C\{^1H\}$ NMR (C₆D₅Br, 393K): δ 147.9 (d of m, $^1J_{CF} = 245$ Hz, *o*-ArCF), 141.2 (d of m, $^1J_{CF} = 260$ Hz, *p*-ArCF), 137.3 (d of m, $^1J_{CF} = 255$ Hz, *m*-ArCF), 114.7 (s, CN), 22.5 (s, NCCH₂), 16.1 (s, CH₂). ^{19}F NMR (C₆D₅Br, 393K): -132.8 (br s, 12F, *o*-ArF), -152.5 (br s, 6F, *p*-ArF), -161.9 (br s, 12F, *m*-ArF) δ . $^{11}B\{^1H\}$ NMR (C₆D₅Br, 393K): δ 10.5 (v br). *Anal.* Calcd: C 44.56, H 0.71, N 2.47, Found: C 44.34, H 0.63, N 2.27.

Typical Catalysis Procedure:

Pressurized Reactions: Each catalytic run was performed in duplicate and the yields reported are the averages between the two runs. In the glove box, a 100 ml glass bomb equipped with a small stirbar and a teflon screw tap was charged with imine (1 mmol), catalyst (0.05 mmol, 5 mol%) and dry toluene (4 ml). The reaction was transferred to the vacuum/H₂ line and was degassed three times with a freeze/pump/thaw cycle. The reaction flask was cooled to -196°C, 1 atm. of H₂ was introduced and the flask then sealed and

warmed to room temperature. The reaction was placed in a preheated oil bath and stirred at 500 rpm; at 120 °C, this gives an H₂ pressure of ~5 atm. To take aliquots, the reaction is cooled rapidly in an ice bath, vented to release the H₂ pressure and taken into the glovebox. Reactions were periodically monitored by ¹H NMR until complete. In all cases, the crude mixtures of the completed reactions were pure to the limits of NMR spectroscopy.

Atmospheric Pressure Reactions: Each catalytic run was performed in duplicate and the yields reported are the averages between the two runs. In the glove box, the catalyst (0.05 mmol) was weighed into a 50 ml round bottomed Schlenk flask and slurried in toluene (2 ml). The reaction was attached to a vacuum/ H₂ line and freeze-pump-thaw cycled three times. The slurry was then allowed to equilibrate at the desired temperature under an atmosphere of H₂ with rapid stirring (500 rpm). A solution of substrate (1.0 mmol) in toluene (2 ml) was added via syringe. The reaction was monitored periodically by ¹H NMR until complete. In all cases, the crude mixtures of the completed reactions were pure to the limits of NMR spectroscopy.

Purification of unprotected amines: All volatiles were removed *in vacuo* and the product was purified by trap to trap vacuum distillation or filtration through a small plug of silica (~ 30 cm) with hexanes/ ethyl acetate (3:1, 200ml) eluent to removed residual catalyst. The B(C₆F₅)₃ protected amines were not purified from residual catalyst.

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

E1, E2; HN(*t*Bu)CH₂Ph: Froyen, P.; Juvvik, P. *Tetrahedron Lett.* **1995**, *36*, 9555.

E3, E4; HN(SO₂Ph)CH₂Ph: 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.

E5; HN(CHPh₂)CH₂Ph: Mehrotra, K. N.; Giri, B. P. *Synthesis* **1977**, 470.

E6; HN(CH₂Ph)₂: Chandrasekhar, S.; Reddy, M. V.; Chandraiah, L. *Synth. Comm.* **1999**, 29, 3981.

E7, E9; (C₆F₅)₃B-NH(CH₂Ph)₂, (C₆F₅)₃B-NH₂CH₂Ph: Mountford, A. J.; Lancaster, S. J.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hursthouse, M. B.; Light, M. E. *Inorg. Chem.* **2005**, 44, 5921.

E11; HN(Ph)C(Ph)CH₂Ph: Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2001**, 4411.

Characterization data for new amines:

E8; (C₆F₅)₃B-NH₂Et: ¹H NMR (CD₂Cl₂): δ 4.91 (br s, 2H, NH), 2.76 (m, 2H, NCH₂), 1.36 (t, ³J_{HH} = 7.3 Hz, 3H CH₃). ¹³C{¹H} NMR (CD₂Cl₂, partial): δ 41.2 (s, CH₂), 15.6 (s, CH₃). ¹⁹F NMR (CD₂Cl₂): δ -133.1 (d, 6F, ³J_{FF} = 23 Hz, *o*-ArF), -154.9 (t, ³J_{FF} = 23 Hz, 3F, *p*-ArF), -161.5 (m, 6F, *m*-ArF). ¹¹B{¹H} NMR (CD₂Cl₂): δ -7.4 (br s).

E10; (C₆F₅)₃BNH₂(CH₂)₆NH₂B(C₆F₅)₃: ¹H NMR (CD₂Cl₂): δ 4.94 (br, 4H, NH₂), 2.66 (br, 4H, NCH₂), 1.63 (br, 4H, CH₂), 1.30 (br, 4H, CH₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 148.5 (d of m, *o*-C₆F₅), 141.1 (d of m, *p*-C₆F₅), 137.9 (d of m, *m*-C₆F₅), 45.6 (s, NCH₂), 30.3 (s, CH₂), 26.4 (s, CH₂). ¹⁹F NMR (CD₂Cl₂): δ -133.1 (m, 12F, *o*-C₆F₅), -154.5 (overlapping t, 6F, *p*-C₆F₅), -161.4 (m, 12F, *m*-C₆F₅). ¹¹B{¹H} NMR (CD₂Cl₂): δ -6.4 (br s).

In situ reactions between **2** and *t*BuN=CPh(H): In the glovebox, (*t*Bu₂PH)(C₆F₄)BH(C₆F₅)₂ (**2**) (21 mg, 33 μmol) was weighted into a J-Young NMR tube. A solution of *t*BuN=CPh(H)

(5 mg, 31 μmol) in $\text{C}_6\text{D}_5\text{Br}$ (0.5 ml) was added and the solution turned yellow. The tube was attached to a H_2 /vacuum line and freeze/pump/thaw cycled three times. The reaction was cooled to -198°C and 1 atm. of H_2 was introduced. The reaction was allowed to warm to room temperature then was heated to 110°C for 1 hour during which time the colour discharged. **^1H NMR** ($\text{C}_6\text{D}_5\text{Br}$): δ 7.09 (br s, 5H, ArH), 4.00 (br s, 2H, NH_2), 3.75, (br m, 1H, BH). 3.66 (s, 2H, CH_2Ph), 1.12 (d, 9H $^3J_{\text{PH}} = 13.7$ Hz, PCCH_3), 1.05 (s, 9H, NCCH_3). **^{19}F NMR** ($\text{C}_6\text{D}_5\text{Br}$): δ -124.6 (s, 1F, ArF linker), -131.5 (d, 1F, $^3J_{\text{FP}} = 96$ Hz, ArF linker), -132.7 (m, 2F, ArF linker), -133.5 (d, 4F, $^3J_{\text{FF}} = 23$ Hz, *o*- C_6F_5) -162.4 (t, 2F, $^3J_{\text{FF}} = 23$ Hz, *p*- C_6F_5), -165.9 (m, 4F, *m*- C_6F_5). **^{31}P NMR** ($\text{C}_6\text{D}_5\text{Br}$): δ 20.4 (d of m, $^3J_{\text{PF}} = 93$ Hz). **^{11}B NMR** ($\text{C}_6\text{D}_5\text{Br}$): δ -24.3 (d, $^1J_{\text{BH}} = 73$ Hz).