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Metal-Free Hydrogenation of *N*-Based Heterocycles

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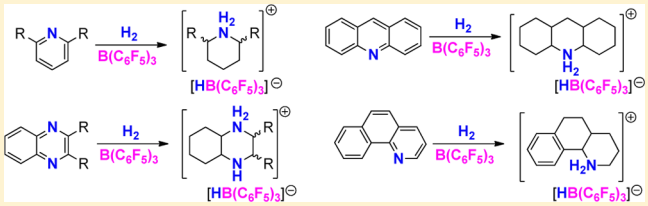
Supporting Information

ABSTRACT: Metal-free hydrogenation of substituted pyridines, quinolines, and several other *N*-heterocycles is achieved upon treatment of the nitrogen-based Lewis base with an equivalent of the Lewis acid $B(C_6F_5)_3$ and H_2 (4 atm) at 115 °C, to afford the ammonium-$[HB(C_6F_5)_3]$ salts of the reduced *N*-heterocycles.



INTRODUCTION

Homogeneous hydrogenation of unsaturated substrates began in the 1960s with the discovery of Rh[1] and Ru[2,3] catalysts by Wilkinson and co-workers. Since this seminal work, a variety of other systems have been developed.[4−10] Although unprecedented levels of activity and selectivity have been achieved through these metal systems, alternative hydrogenation strategies using non-transition-metal catalysts are being explored. For example, an initial report by Berkessel et al. described the reduction of benzophenone using KO*t*Bu and H_2 under forcing conditions.[11] Subsequently, main group systems were shown to react with H_2 under mild conditions by Power.[12,13] In 2006, we uncovered the ability of frustrated Lewis pairs (FLPs), that is, combinations of sterically encumbered Lewis acids and bases, to heterolytically split H_2.[14] Shortly thereafter we described the application of FLPs as metal-free catalysts for the hydrogenation of imines, aziridines, and nitriles.[15] The research groups of Erker,[16,17] Repo,[18−20] and Berke[21] have further broadened the scope of substrates to include enamines and silylenol ethers but perhaps more importantly have broadened the range of FLP catalysts to include a variety of P/B and N/B systems. In addition, Klankermayer and co-workers have cleverly unveiled related metal-free systems capable of asymmetric hydrogenations.[22,23] More recently, we demonstrated the utilization of weak Lewis bases in combination with $B(C_6F_5)_3$ to permit the catalytic hydrogenation of 1,1-disubstituted olefins[24] and extended such catalytic reductions to polycyclic aromatic hydrocarbons.[25] In an exciting extension of the study of these metal-free reductions, we demonstrated that stoichiometric combinations of sterically hindered anilines and $B(C_6F_5)_3$ under 4 atm of H_2 pressure effected reduction of the aromatic ring, affording cyclohexylammonium salt derivatives.[26] We have also previously communicated the partial reduction of *N*-heterocycles using catalytic conditions,[27] while Soos and co-workers[28] extended the scope of such catalytic reductions using specifically designed Lewis acids. Employing stoichiometric conditions, we sought to extend the scope of aromatic reductions beyond anilines and focused our attention on a series of substituted pyridines, quinolines, and several other *N*-based heterocycles targeting more fully reduced products.

Historically, partial homogeneous hydrogenation of quinolines using H_2 was first reported using a Ru catalyst by Fish and co-workers in 1982.[29] Since then, Rh, Ir, and Os catalysts have been developed.[30] The reported homogeneous catalysts do not effect the complete reduction of the *N*-heterocycle quinoline, although Fache et al.[31,32] found that substituted quinolines were fully reduced to decahydroquinolines using colloidal Rh on Al_2O_3 at room temperature and 50 atm of H_2. In a recent intriguing finding, Glorius et al. communicated that alteration of the catalysts allowed for unprecedented selectivity, allowing the reduction of substituted quinolines diastereoselectively to 5,6,7,8-tetrahydroquinolines or hydrogenation to decahydroquinolines.[33] Furthermore, Glorius and co-workers have also developed a homogeneous catalyst for the regioselective asymmetric hydrogenation of the carbocyclic ring of substituted quinoxalines.[34]

FLPs derived from boranes and N-based heterocycles such as sterically hindered pyridines or quinolines are known to effect the heterolytic cleavage of H_2 under mild conditions,[27,35,36] and as mentioned above, partial catalytic reduction of the *N*-heterocycle has been achieved. In this report, we explore the hydrogenation of a variety of *N*-based heterocycles employing a stoichiometric amount of $B(C_6F_5)_3$ and 4 atm of H_2. These reductions are shown to selectively reduce aromatic pyridyl- and aniline-type rings, leaving other aromatic rings untouched, thus providing a unique and metal-free route to polycarbocyclic amines.

RESULTS AND DISCUSSION

Hydrogenation of Substituted Pyridines. The combination of the Lewis base 2,6-diphenylpyridine and the Lewis acid $B(C_6F_5)_3$ does not show evidence of a donor−acceptor interaction by multinuclear NMR spectroscopy, in contrast to the observation of a reversible adduct formation for 2,6-lutidine.[35] Exposure of either the combination of 2,6-lutidine or

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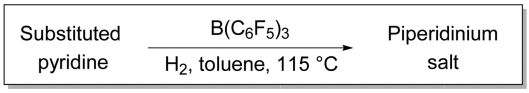
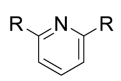
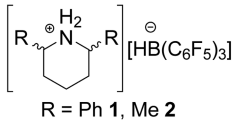
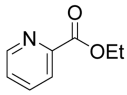
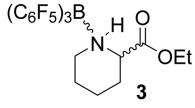
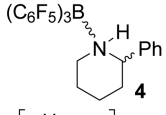
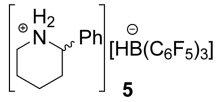
2,6-diphenylpyridine with $B(C_6F_5)_3$ has been previously reported to result in the activation of H_2 at room temperature over 16 h, affording the corresponding pyridinium−hydridoborate salt.[36] However, on heating a mixture of 2,6-diphenylpyridine and $B(C_6F_5)_3$ under H_2 (4 atm) at 115 °C for 16 h, a new product, **1**, was isolated in 92% yield (Table 1, entry 1). The NMR data for **1** in CD_2Cl_2 displayed a doublet in the ^{11}B NMR at −24.6 ppm and three resonances in the ^{19}F NMR at −134.0 (*o*), −163.4 (*m*), and −166.6 (*p*) ppm, confirming the presence of the $HB(C_6F_5)_3$ anion. The ^1H NMR data showed a broad singlet at 5.90 ppm attributed to the NH_2 group, multiplets at 4.53, 2.26, 2.12, and 1.89 ppm, and the signals assignable to the phenyl and $HB(C_6F_5)_3$ groups. These data were consistent with the formulation of **1** as the diphenylpiperidium−hydridoborate salt $[2,6\text{-}Ph_2C_5H_8NH_2][HB(C_6F_5)_3]$ (Table 1, entry 1). Furthermore, the ^1H NMR data revealed a diastereomeric excess (de) of 91% favoring the *meso*-diastereomer of **1**, an assignment that was confirmed *via* NMR spectroscopy and isolation of crystals of *meso*-$[2,6\text{-}Ph_2C_5H_8NH_2][HB(C_6F_5)_3]$ (see Supporting Information (SI)). The structure of the major product **1** was confirmed via a crystallographic study (Figure 1a). In a similar fashion, the reaction of 2,6-lutidine with $B(C_6F_5)_3$ under H_2 at 115 °C for 60 h afforded the corresponding salt $[2,6\text{-}Me_2C_5H_8NH_2][HB(C_6F_5)_3]$ (**2**) in 84% yield with a de of 80%, favoring the *meso*-diastereomer (Figure 1b). It should be noted that we have previously demonstrated the ability of $B(C_6F_5)_3$ to effect the epimerization of chiral carbons adjacent to nitrogen by a process involving hydride-abstraction and redelivery.[37] Such reactivity may account for the observed diastereoselectivity.

Ethyl 2-picolinate was also reduced under analogous conditions. In this case, the adduct of the reduced pyridine, $(2\text{-}(EtCO_2)C_5H_9NH)B(C_6F_5)_3$ (**3**), was isolated in 74% yield after 36 h (Table 1, entry 2). The ^{11}B NMR spectrum in CD_2Cl_2 showed a broadened singlet at −4.86 ppm and inequivalent ^{19}F NMR resonances that were consistent with amine−borane adduct formation in which rotation about the B−N bond was inhibited. The ^1H, $^{13}C\{^1H\}$, ^{11}B, and ^{19}F NMR of **3** displayed the presence of two diastereomers in a 1:1 ratio. Most obvious were the $^{13}C\{^1H\}$ resonances at 167.4 and 171.2 ppm attributable to the CO_2-ester carbons and the corresponding ^1H signals at 4.18 and 4.24 ppm arising from the methine protons adjacent to the ester. Furthermore, $^1H\{^1H\}$ NOESY experiments confirmed the assignment of these peaks to the respective *RS*/*SR* and *RR*/*SS* diastereomers (see SI). Interestingly, independent reaction of $B(C_6F_5)_3$ with optically pure *S*-2-$(EtCO_2)C_5H_9NH$ at low temperature (−35 °C) in CD_2Cl_2 afforded the preferential formation of the *SS*-diastereomer of **3**. However, on warming to room temperature over 18 h, racemization at nitrogen afforded a 1:1 mixture of the *SS* and *SR* diastereomers of **3**.

Table 1. Hydrogenation of Substituted Pyridines



Entry	Substrate	Product(s)	Time Isolated Yield
1		 R = Ph **1**, Me **2**	**1**: 16 h, 92 % **2**: 60 h, 84 %
2		 **3**	**3**: 36 h, 74 %
3		 **4**  **5**	**4**[a]: 48 h, 54 %

[a]The isolated product mixture consisted of **4** and **5** in a 4:1 ratio. Reactions were carried out at 4 atm of H_2.

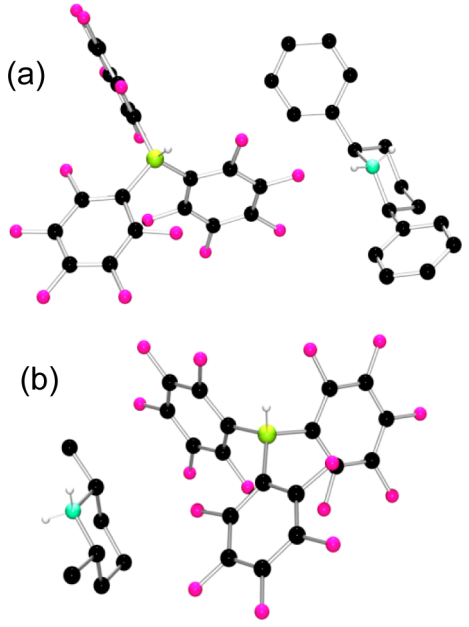


Figure 1. POV-ray depiction of the molecular structure of (a) **1** and (b) **2**. Hydrogen atoms, except for BH and NH_2 atoms, are omitted for clarity.

In the case of 2-phenylpyridine and $B(C_6F_5)_3$, a mixture of two products of reduction was obtained after 48 h under H_2 (4 atm). The mixture was isolated in 54% overall yield. A broad ^{11}B NMR signal was seen at −3.91 ppm, together with a doublet at −24.0 ppm, in a 4:1 ratio, consistent with the presence of B−N adduct $(2\text{-}PhC_5H_9NH)B(C_6F_5)_3$ (**4**) and $[2\text{-}PhC_5H_9NH_2][HB(C_6F_5)_3]$ (**5**), respectively (Table 1, entry 3). The formulation of **4** is further supported by the observation of ^{19}F signals and ^1H NMR resonances resulting from the $B(C_6F_5)_3$ adduct of 2-phenylpiperidine. These NMR data, together with the two distinctively broad NH singlets in the ^1H NMR at 5.55 and 5.81 ppm, were attributable to a 7:1 ratio of the two diastereomers of **4**. The *RS*/*SR* diastereomer **4** was the more abundant form, as evidenced by NMR and X-ray crystallographic data (Figure 2). Presumably, the favored *RS*/*SR* diastereomer results from intramolecular $\pi-\pi$ stacking interactions of the C_6H_5 and C_6F_5 groups in addition to the interactions between the $C-H\cdots F_{ortho}$ and $N-H\cdots F_{ortho}$, which are evidenced by $^1H\{^{19}F\}$ HOESY NMR spectroscopy (see SI).

Hydrogenation of Substituted *N*-Heterocycles. Exposure of a stoichiometric mixture of 2-methylquinoline and $B(C_6F_5)_3$ to H_2 (4 atm) at 115 °C for 48 h was found to effect

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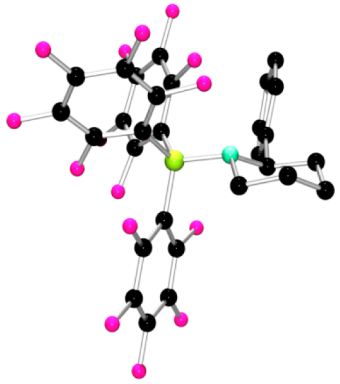
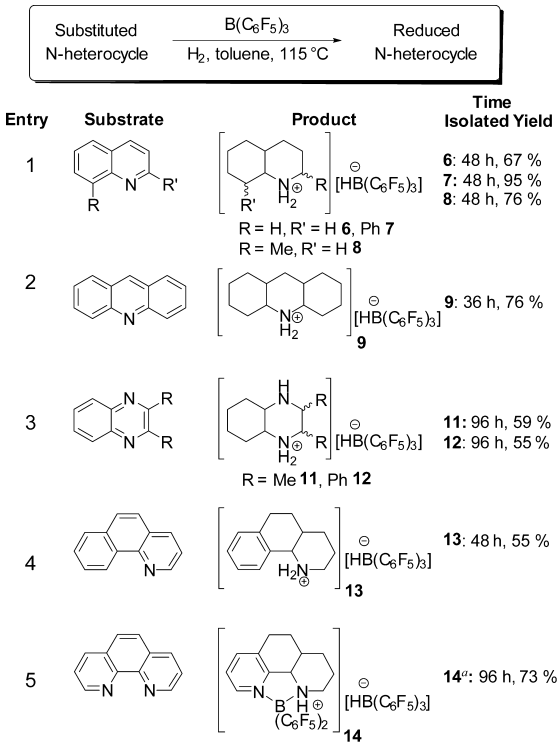


Figure 2. POV-ray depiction of the molecular structure of **4**. Hydrogen atoms are omitted for clarity. B–N: 1.66(5) Å.

the hydrogenation of the *N*-hetero- and carbocyclic rings to yield $[2\text{-}MeC_9H_{15}NH_2][HB(C_6F_5)_3]$ (**6**) in 67% yield (Table 2, entry 1). In a similar fashion, 2-phenylquinoline was reduced after 48 h to give $[2\text{-}PhC_9H_{15}NH_2][HB(C_6F_5)_3]$ (**7**) in 95% yield. ^{1}H NMR spectroscopy for **6** and **7** exhibits characteristic chemical shifts corresponding to the NH_2, methine, and methylene groups. Both compounds **6** and **7** were produced as mixtures of diastereomers, although in both cases the major isomer was crystallized and found to comprise 60% and 73% of the isolated products, respectively. X-ray methods (Figure 3a,b) showed that the isolated diastereomers of **6** and **7** exhibited *SSS/RRR* stereochemistries, in which one of the ring junctions adopts an equatorial disposition, while the other is axially disposed. Analogous treatment of 8-methylquinoline with H_2 and $B(C_6F_5)_3$ in toluene for 48 h yielded $[8\text{-}MeC_9H_{15}NH_2][HB(C_6F_5)_3]$ (**8**) in 76% yield (Table 2, entry 1). ^{1}H and $^{13}C\{^1H\}$ NMR data showed only the presence of the *RRR/SSS* diastereomers (Figure 3c). The corresponding reduction of acridine results in the isolation of the fully reduced tricyclic species in 76% yield (Table 2, entry 2). The isolated product is obtained as a mixture of two isomers, one of which was characterized crystallographically as the salt $[C_{13}H_{22}NH_2][HB(C_6F_5)_3]$ (**9**), in which the ring junctions in the cation are all equatorially positioned (Figure 3d) and thus the *SRSR/RSRS* diastereomers. Interestingly, a second product, **10**, was isolated from the pentane wash. Crystallographic data demonstrated it to be the Lewis acid–base adduct $(C_{13}H_{22}NH)B(C_6F_5)_3$ (Figure 4); however in this case the stereochemistry of the ring junctions alpha to nitrogen are inverted, affording the *RRSS/SSRR* diastereomers of the reduced acridine heterocycle. Compound **10** was also independently synthesized in 73% yield from a mixture of isomers of the neutral amine, $C_{13}H_{22}NH$, and $B(C_6F_5)_3$.

Table 2. Hydrogenation of Substituted *N*-Heterocycles[a]



[a]Two equivalents of $B(C_6F_5)_3$. Reactions were carried out at 4 atm of H_2.

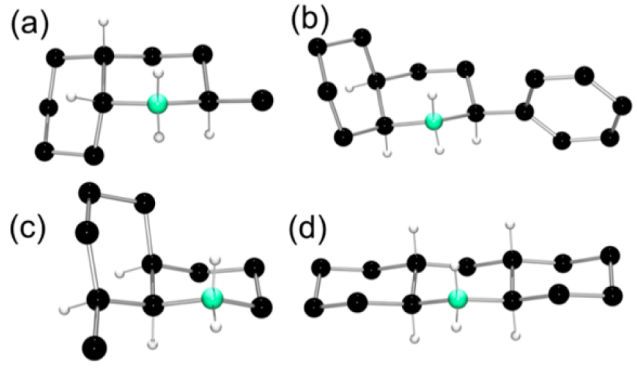


Figure 3. POV-ray depiction of the molecular structures of the cations (a) **6**, (b) **7**, (c) **8**, and (d) **9**. Selected hydrogen atoms are shown.

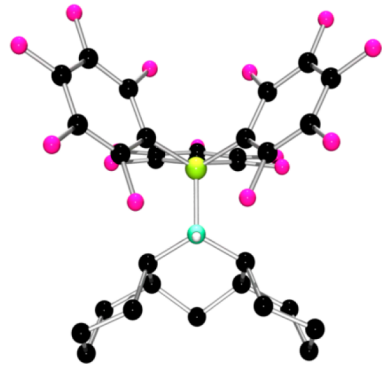


Figure 4. POV-ray depiction of the molecular structure of **10**. Hydrogen atoms except for NH are omitted for clarity. B–N: 1.66(6) Å.

Reductions of the additional substrates 2,3-dimethyl- and 2,3-diphenylquinoxaline yielded the piperazinium derivatives $[(C_4H_6Me)_2NHNH_2][HB(C_6F_5)_3]$ (**11**) and $[(C_4H_6Ph)_2NHNH_2][HB(C_6F_5)_3]$ (**12**) in 59% and 55% yield, respectively (Table 2, entry 3). In the case of **11**, a single set of diastereomers was observed and the NMR data were consistent with ring junctions and methyl groups adopting equatorial dispositions. In contrast, the isolated product **12** was comprised of two diastereomers. One of these was crystallographically characterized (Figure 5) and shown to be the diastereomer in which the phenyl rings adopt equatorial

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positions, while the ring junctions are axial and equatorially disposed (Figure 5a).

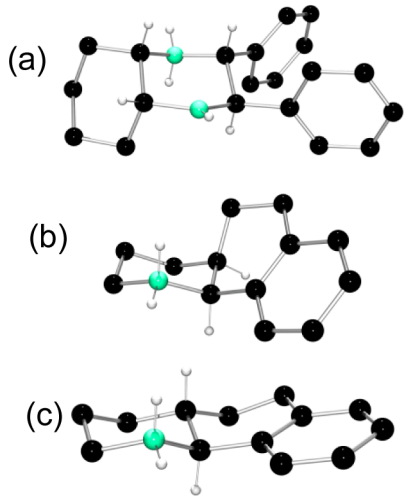

Figure 5. POV-ray depiction of the molecular structures of the cations (a) **12**, (b) **13a**, and (c) **13b**. Selected hydrogen atoms are shown.

It is noteworthy that while the aromatic ring of the quinoxaline fragment is fully reduced, the phenyl substituents remain intact. In a similar situation reduction of 7,8-benzoquinoline resulted in the formation of $[(C_6H_4)\text{-}C_7H_{12}NH_2][HB(C_6F_5)_3]$ (**13**) in 55% yield (Table 2, entry 4). The product was comprised of a 4:1 mixture of two diastereomers, as evidenced by ^{1}H NMR spectroscopy. X-ray crystallography was used to unambiguously confirm that in both isomers reduction of the pyridine and adjacent ring was achieved while aromaticity of the ring remote from the N atom was retained. The dominant diastereomer **13a** was found to be the *SR/RS* diastereomers (Figure 5b), while the less abundant diastereomer **13b** showed *SS/RR* stereochemistry (Figure 5c).

Finally, efforts to reduce the heterocycle 1,10-phenanthroline were undertaken employing two equivalents of $B(C_6F_5)_3$. This resulted in the isolation of product **14** in 73% yield after 96 h at 115 °C (Table 2, entry 5). The ^{11}B NMR spectrum revealed the presence of two four-coordinate boron centers with resonances at 3.91 and −25.4 ppm. The latter ^{11}B NMR signal together with the three corresponding ^{19}F resonances arises from the $[HB(C_6F_5)_3]$ anion. The second boron species exhibited six inequivalent fluorine atoms, as evidenced by the ^{19}F NMR spectrum, inferring the presence of two inequivalent fluoroarene rings. X-ray crystallography confirmed the formulation of **14** as the *SRS/RSR* diastereomer of $[(C_5H_3N)\text{-}(CH_2)_2(C_5H_8NH)B(C_6F_5)_2][HB(C_6F_5)_3]$. The reported major diastereomer was present as 65% of the isolated reaction mixture. In the cationic fragment of compound **14**, the boron center is bound to two perfluoroarene rings and is chelated by a pyridine and amine nitrogen atoms of a partially reduced 1,10-phenanthroline (Figure 6). The B−N distances in the cation were found to be 1.61(6) Å for $B(1)\text{−}N(1)_{amine}$ and 1.59(8) Å for $B(1)\text{−}N(2)_{py}$. In this unique case, presumably as the reduction of the heterocycle proceeds, the relative disposition of the two nitrogen atoms results in the preferential loss of C_6F_5H from $B(C_6F_5)_3$ and chelation of the partially reduced phenanthroline to boron, thus affording the cation of **14**.

The reductions described above demonstrate the ability of $B(C_6F_5)_3$ to mediate the complete aromatic reduction of a

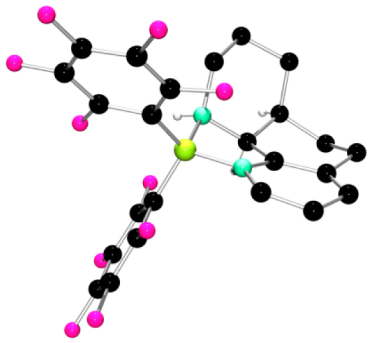

Figure 6. POV-ray depiction of the cation of **14**. Selected hydrogen atoms are shown. Selected bond distances (Å) and angles (deg): B(1)−N(1) 1.61(6), B(1)−N(2) 1.59(8), N(1)−B(1)−N(2) 96.6(3). (NB: N(1) in heterocyclic amine, N(2) in pyridyl ring.)

number of N-heterocycles. It is clear that the products arise from reduction of pyridyl- and/or aniline-type rings. In some cases, the observation of a preferred set of diastereomers is consistent with the known ability of $B(C_6F_5)_3$ to effect epimerization of chiral centers alpha to nitrogen.[37] Efforts to monitor several of the mixtures over the course of the reactions failed to provide unambiguous mechanistic insight. Nonetheless, it is known that *N*-heterocycles in combination with $B(C_6F_5)_3$ effect the heterolytic cleavage of H_2 under mild conditions. By analogy with previous computational studies for aniline hydrogenations, the need for elevated temperatures presumably reflects the fact that hydride delivery from $[HB(C_6F_5)_3]$ to the heterocycle is energetically uphill; however once this is achieved, there is an exothermic route to the saturated amine.[26] Subsequent activation of H_2 by the product amine and borane affords the corresponding ammonium salt, which is irreversible under the reaction conditions. This latter reaction sequesters the borane and thus precludes further catalytic reduction. While the reactions are nominally stoichiometric in N and B, multiple turnovers of H_2 delivery are achieved in these reductions. For example, eight equivalents of H_2 are taken up by acridine in the formation of **9**. The reaction stoichiometry also facilitates product isolation and purification, as the product salts readily crystallize from solution.

■ CONCLUSIONS

The reduction of a variety of pyridyl- and aniline-type rings in N-containing compounds is readily achieved upon heating a mixture of the substrate precursor with an equivalent of $B(C_6F_5)_3$ under H_2 (4 atm) at 115 °C. We are continuing to develop FLP systems capable of such reductions and to explore their utility in synthetic applications.

■ EXPERIMENTAL SECTION

General Considerations. All preparations were performed under an atmosphere of dry, oxygen-free N_2 by means of both standard Schlenk line and glovebox techniques (MBraun glovebox equipped with a −40 °C freezer). Pentane and toluene (Aldrich) were dried employing a Grubbs-type column system (Innovative Technology), degassed, and stored over molecular sieves (4 Å) in the glovebox. Molecular sieves (4 Å) were purchased from Aldrich Chemical Co. and dried at 140 °C under vacuum for 24 h prior to use. Dichloromethane-d_2 and bromobenzene-d_5 were purchased from Cambridge Isotope Laboratories, dried over CaH_2, and distilled under N_2 prior to use. Tetrahydrofuran-d_8 was purchased from Cambridge Isotope Laboratories and distilled under N_2 from Na/

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benzophenone. All substituted quinolines, pyridines, and other N-heterocycles were purchased from Sigma-Aldrich or Alfa Aesar. The oils were distilled over CaH_2, and solids were sublimed under high vacuum prior to use. $B(C_6F_5)_3$ was purchased from Boulder Scientific and sublimed at 80 °C under high vacuum before use. Nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance III 400 MHz or a Varian 400 MHz spectrometer equipped with an HFX AutoX triple resonance indirect probe (used for $^{13}C\{^1H, ^{19}F\}$ experiments), and spectra were referenced to residual solvent of C_6D_5Br (^1H = 7.28 ppm for *meta*-proton; ^{13}C = 122.4 ppm for *ipso*-carbon), CD_2Cl_2 (^1H = 5.32 ppm; ^{13}C = 53.84 ppm), THF-d_8 (^1H = 1.72 ppm for CH_2(3,4); ^{13}C = 25.31 ppm for CH_2(3,4)), or externally (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$). Chemical shifts (δ) are reported in ppm, and the absolute values of the coupling constants (J) are in Hz. NMR assignments are supported by additional 2D and DEPT-135 experiments. Elemental analyses (C, H, N) were performed in-house employing a Perkin-Elmer 2400 Series II CHNS analyzer. H_2 (grade 5.0) was purchased from Linde and dried through a Nanochem Weldassure purifier column prior to use.

Reduction Procedure. These compounds were prepared in a similar fashion; thus only one preparation is detailed and only specific variations are presented below. In the glovebox, a 50 mL Teflon screw cap glass bomb equipped with a stirbar was charged with a solution of $B(C_6F_5)_3$ (0.379 g, 0.740 mmol) and the respective N-heterocycle in toluene (5 mL). The reaction tube was degassed three times through a freeze−pump−thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at −196 °C. After the addition of H_2 the reaction tube was placed in a 115 °C oil bath for the indicated reaction time. The solvent was then removed under reduced pressure, and the crude product was washed with pentane to yield the product as a solid.

Synthesis of [2,6-$Ph_2C_5H_8NH_2$][$HB(C_6F_5)_3$] (1). 2,6-Diphenylpyridine (171 mg, 0.740 mmol), reaction time 16 h, white solid, 92% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at −40 °C over 36 h. Isomer ratio *meso* 91%, *rac* 9%.

[meso-2,6-$Ph_2C_5H_8NH_2$][$HB(C_6F_5)_3$]. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.34 (tt, 2H, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.4 Hz, *p*-Ph), 7.26 (m, 8H, *o*,*m*-Ph), 5.90 (br, 2H, NH_2), 4.53 (m, 2H, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 2.4 Hz, C(*H*)(Ph), 3.39 (br q, 1H, $^1J_{HB}$ = 90 Hz, BH), 2.26 (br m, 3H, $^{B,A}CH_2$), 2.12 (m, 2H, $^BCH_2$), 1.89 (m, 1H, $^ACH_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 148.3 (dm, $^1J_{CF}$ = 237 Hz, C_6F_5), 138.0 (dm, $^1J_{CF}$ = 244 Hz, C_6F_5), 136.7 (dm, $^1J_{CF}$ = 246 Hz, C_6F_5), 133.8 (*ipso*-Ph), 131.3 (*p*-Ph), 127.1 (Ph), 126.4 (Ph), 124.1 (*ipso*-C_6F_5), 65.7 (C(H)(Ph)), 29.7 ($^BCH_2$), 23.3 ($^ACH_2$). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −134.0 (m, 2F, *o*-C_6F_5), −163.4 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −166.6 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −24.6 (d, $^1J_{HB}$ = 90 Hz, BH). Anal. Calcd (%) for $C_{35}H_{21}BF_{15}N$: C 55.95; H 2.82; N 1.86. Found: C 55.47; H 3.03; N 1.86.

Synthesis of [2,6-$Me_2C_5H_8NH_2$][$HB(C_6F_5)_3$] (2). 2,6-Dimethylpyridine (79.3 mg, 0.740 mmol), reaction time 60 h, white solid, 84% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of bromobenzene/pentane at −40 °C over 48 h. Isomer ratio *meso* 80%, *rac* 20%.

[meso-2,6-$Me_2C_5H_8NH_2$][$HB(C_6F_5)_3$]. ^1H NMR (400 MHz, C_6D_5Br): δ 5.08 (br, 2H, NH_2), 3.45 (br q, $^1J_{HB}$ = 83 Hz, BH), 2.68 (m, 2H, NCH), 1.37 (m, 4H, CH_2), 0.86 (d, 6H, $^3J_{HH}$ = 6.4 Hz, Me), 0.77 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 148.5 (dm, $^1J_{CF}$ = 235 Hz, CF), 138.5 (dm, $^1J_{CF}$ = 246 Hz, CF), 137.0 (dm, $^1J_{CF}$ = 249 Hz, CF), 123.6 (*ipso*-C_6F_5), 56.7 (NCH), 30.3 (CH_2), 22.0 (CH_2), 19.3 (Me). ^{19}F NMR (377 MHz, C_6D_5Br): δ −134.1 (m, 2F, *o*-C_6F_5), −161.7 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −165.5 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −23.8 (d, $^1J_{HB}$ = 83 Hz, BH). Anal. Calcd (%) for $C_{25}H_{17}BF_{15}N$: C 47.87; H 2.73; N 2.23. Found: C 47.64; H 2.90; N 2.22.

Independent Synthesis of [*meso*-2,6-$Me_2C_5H_8NH_2$][$HB(C_6F_5)_3$]. *Synthesis of meso-2,6-$Me_2C_5H_8NH$·HCl.* A 4 dram vial with a magnetic stirbar was charged with 2,6-lupetidine (500 mg, 4.4 mmol) in pentane (ca. 3 mL) followed by the dropwise addition of HCl (1.4 mL, 4 M in 1,4-dioxane, 5.7 mmol, 1.3 equiv). The formation of a white precipitate was gradually observed in the vial. The precipitate was washed with pentane (3 × 5 mL) and placed under vacuum in a Schlenk flask at 50 °C for 2 h to give *meso*-2,6-$Me_2C_5H_8NH$·HCl in 98% yield.

Synthesis of [meso-2,6-$Me_2C_5H_8NH_2$][$HB(C_6F_5)_3$]. A 4 dram vial with a magnetic stirbar was charged with a slurry of $NaHB(C_6F_5)_3$ (341 mg, 0.64 mmol) in dicholormethane (10 mL) and *meso*-2,6-$Me_2C_5H_8NH$·HCl (95 mg, 0.64 mmol) in dichloromethane (5 mL). The mixture was stirred for 16 h at room temperature and filtered through a pad of Celite. The solvent was removed under vacuum to yield 74% of the product as a white solid.

Synthesis of [2-(CO_2Et)$C_5H_9NHB(C_6F_5)_3$] (3). Ethyl 2-picolinate (112 mg, 0.740 mmol), reaction time 36 h, white solid, 74% isolated yield. The isolated product consisted of a 1:1 ratio of both isomers. Anal. Calcd (%) for $C_{26}H_{15}BF_{15}NO_2$: C 46.67; H 2.26; N 2.09. Found: C 46.60; H 2.47; N 2.11.

*[RS/SR-2-(CO_2Et)$C_5H_9NHB(C_6F_5)_3$] (**3a**).* ^1H NMR (400 MHz, CD_2Cl_2): δ 5.90 (m, 1H, NH), 4.30 (m, 1H, C*H*(H)NH), 4.18 (br m, 1H, C*H*CO_2Et), 3.93 (dq, 1H, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_2), 3.73 (dq, 1H, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_2), 3.20 (dm, 1H, $^2J_{HH}$ = 12.6 Hz, CH(*H*)NH), 2.17 (m, 2H, CH_2), 2.04 (dm, 1H, $^2J_{HH}$ = 13.4 Hz, CH_2), 1.84 (m, 1H, CH_2), 1.75 (m, 1H, CH_2), 1.19 (t, 3H, $^3J_{HH}$ = 7.2 Hz, Me), 1.03 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 167.4 (CO_2), 63.6 (OCH_2), 56.8 ($CHCO_2Et$), 44.5 (CH(H)NH), 30.5 (CH_2), 20.8 (CH_2), 18.1 (CH_2), 13.4 (Me). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −126.4 (m, 1F, *o*-C_6F_5), −128.0 (m, 1F, *o*-C_6F_5), −129.5 (m, 1F, *o*-C_6F_5), −129.7 (m, 1F, *o*-C_6F_5), −140.4 (m, 1F, *o*-C_6F_5), −143.3 (m, 1F, *o*-C_6F_5), −155.5 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −157.3 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −157.5 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −161.6 (m, 1F, *m*-C_6F_5), −162.1 (m, 1F, *m*-C_6F_5), −162.8 (m, 1F, *m*-C_6F_5), −163.1 (m, 1F, *m*-C_6F_5), −164.0 (m, 1F, *m*-C_6F_5), −164.9 (m, 1F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −4.86 (s, BNH).

*[RR/SS-2-(CO_2Et)$C_5H_9NHB(C_6F_5)_3$] (**3b**).* ^1H NMR (400 MHz, CD_2Cl_2): δ 7.43 (br m, 1H, NH), 4.40 (dq, 1H, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_2), 4.38 (dq, 1H, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_2), 4.24 (br m, 1H, C*H*CO_2Et), 3.50 (ddd, 1H, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 4.9 Hz, C*H*(H)NH), 3.33 (dm, 1H, J_{HH} = 13.3 Hz, CH(*H*)NH), 2.18 (m, 1H, CH_2), 2.08 (m, 1H, CH_2), 1.85 (m, 1H, CH_2), 1.54 (m, 1H, CH_2), 1.51 (m, 1H, CH_2), 1.35 (t, 3H, $^3J_{HH}$ = 7.1 Hz, Me), 1.24 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2,): δ 171.2 (CO_2), 61.6 (OCH_2), 58.1 ($CHCO_2Et$), 45.7 (CH(H)NH), 25.9 (CH_2), 23.5 (CH_2), 17.1 (CH_2), 13.9 (Me). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −127.6 (m, 1F, *o*-C_6F_5), −128.5 (m, 2F, *o*-C_6F_5), −129.1 (m, 1F, *o*-C_6F_5), −137.1 (m, 1F, *o*-C_6F_5), −142.1 (m, 1F, *o*-C_6F_5), −154.9 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −157.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −157.8 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −161.8 (m, 1F, *m*-C_6F_5), −162.6 (m, 1F, *m*-C_6F_5), −162.8 to −163.2 (m, 3F, *m*-C_6F_5),), −163.3 (m, 1F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −4.86 (s, BNH).

Independent Synthesis of [*SS*-2-(CO_2Et)$C_5H_9NHB(C_6F_5)_3$] (3b). *Synthesis of (S)-Piperidine-2-carboxylic Acid Ethyl Ester.* A 4 dram vial with a magnetic stirbar was charged with (*S*)-piperidine-2-carboxylic acid ethyl ester hydrochloride (491 mg, 2.53 mmol) and dichloromethane (3 mL). To the slurry was added in portions potassium *tert*-butoxide (296 mg, 264 mmol) over 5 min and allowed to mix for 8 h. The mixture was filtered through a pad of Celite, and the solvent was removed under vacuum to give a yellow oil in 65% yield.

*Synthesis of [SS-2-(CO_2Et)$C_5H_9NHB(C_6F_5)_3$] (**3b**).* In a vial, (*S*)-piperidine-2-carboxylic acid ethyl ester (11.6 mg, 0.074 mmol) and d_2-dichloromethane (0.25 mL) were cooled to −35 °C. To the vial was added a cooled (−35 °C) solution of $B(C_6F_5)_3$ (37.9 mg, 0.074 mmol) in d_2-dichloromethane (0.25 mL), and the multinuclear NMR of **3b** was obtained within 10 min of the reaction.

Synthesis of [2-(Ph)$C_5H_9NHB(C_6F_5)_3$] (4) and [2-(Ph)-$C_5H_9NH_2$][$HB(C_6F_5)_3$] (5). 2-Phenylpyridine (115 mg, 0.740 mmol), reaction time 48 h, white solid, 54% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at −40 °C over 1 week. The isolated product consisted of **4a** (70%), **4b** (10%), and **5** (20%) Anal. Calcd (%) for

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$C_{29}H_{17}BF_{15}N$: C 51.58; H 2.54; N 2.09. Found: C 52.09; H 2.58; N 2.10.

*[RS/SR-2-(Ph)C$_5$H$_9$NHB(C$_6$F$_5$)$_3$] (**4a**).* ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.27 (m, 2H, Ph), 7.14 (m, 3H, Ph), 5.55 (br s, 1H, NH), 4.15 (ddd, 1H, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 9.38 Hz, $^3J_{HH}$ = 3.6 Hz, C*H*Ph), 3.56 (dm, 1H, $^2J_{HH}$ = 13.2 Hz, C*H*(H)NH), 2.57 (ddd, 1H, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 3.1 Hz, CH(*H*)NH), 1.99–1.35 (m, 6H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 138.5 (*ipso*-Ph), 129.7 (*p*-Ph), 129.1 (Ph), 128.5 (Ph), 64.6 (*C*HPh), 52.1 (NCH_2), 35.5 (CH_2), 24.8 (CH_2), 21.9 (CH_2). ^{19}F NMR (377 MHz, C_6D_5Br): δ −121.6 (m, 1F, *o*-C_6F_5), −123.6 (m, 1F, *o*-C_6F_5), −127.4 (m, 1F, *o*-C_6F_5), −128.6 (m, 1F, *o*-C_6F_5), −131.2 (m, 1F, *o*-C_6F_5), −142.6 (m, 1F, *o*-C_6F_5), −153.4 (t, 1F, $^3J_{HH}$ = 22 Hz, *p*-C_6F_5), −156.6 (t, 2F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −156.7 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −161.5 (m, 2F, *m*-C_6F_5), −162.0 (m, 3F, *m*-C_6F_5), −162.4 (m, 1F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −3.91 (s, BN).

*[SS/RR-2-(Ph)C$_5$H$_9$NHB(C$_6$F$_5$)$_3$] (**4b**).* ^{1}H NMR (400 MHz, C_6D_5Br): δ 7.10–6.81 (m, 5H, Ph), 5.81 (br s, 1H, NH), 4.49 (m, 1H, C*H*Ph), 3.47 (dm, 1H, $^2J_{HH}$ = 12.5 Hz, C*H*(H)NH), 3.21 (m, 1H, $^2J_{HH}$ = 12.5 Hz, CH(*H*)NH), 1.85 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.28 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 136.5 (*ipso*-Ph),129.4 (*p*-Ph), 128.3 (Ph), 125.6 (Ph), 62.9 (*C*HPh), 45.4 (NCH_2), 35.0 (CH_2), 29.7 (CH_2), 26.0 (CH_2). ^{19}F NMR (377 MHz, C_6D_5Br): δ −124.9 (m, 1F, *o*-C_6F_5), −126.3 (m, 1F, *o*-C_6F_5), −126.8 (m, 1F, *o*-C_6F_5), −128.7 (m, 1F, *o*-C_6F_5), −139.0 (m, 1F, *o*-C_6F_5), −143.1 (m, 1F, *o*-C_6F_5), −155.5 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −155.9 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −156.2 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −159.8 (m, 1F, *m*-C_6F_5), −161.0 (m, 1F, *m*-C_6F_5), −161.7 (m, 1F, *m*-C_6F_5), −162.0 (m, 1F, *m*-C_6F_5), −162.2 (m, 1F, *m*-C_6F_5), −164.3 (m, 1F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −3.9 (s, BN).

*[2-(Ph)C$_5$H$_9$NH$_2$][HB(C$_6$F$_5$)$_3$] (**5**).* ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.10 − 6.81 (m, 5H, Ph), 5.57 (br s, 2H, NH_2), 3.55 (dd, 1H, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 2.8 Hz, C*H*Ph), 3.30 (br q, 1H, $^1J_{HB}$ = 86 Hz, BH), 2.95 (dm, 1H, J_{HH} = 12.4 Hz, C*H*(H)NH_2), 2.44 (td, 1H, J_{HH} = 12.4 Hz, $^3J_{HH}$ = 3.0 Hz, CH(*H*)NH_2), 1.86 (m, 2H, $^{B,C}CH_2$), 1.65 (m, 1H, $^ACH_2$), 1.57 (m, 1H, $^CCH_2$), 1.41 (m, 1H, $^BCH_2$), 1.37 (m, 1H, $^ACH_2$);. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 139.9 (*ipso*-Ph), 129.7 (Ph), 129.5 (*p*-Ph), 126.7 (Ph), 62.5 (*C*HPh), 47.1 (NCH_2), 32.7 ($^CCH_2$), 24.2 ($^BCH_2$), 24.0 ($^ACH_2$). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −134.4 (m, 2F, *o*-C_6F_5), −161.0 (t, 1F, $^3J_{HH}$ = 20 Hz, *p*-C_6F_5), −166.7 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −24.8 (d, $^1J_{HB}$ = 86 Hz, BH).

Synthesis of [2-MeC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$] (6). 2-Methylquinoline (106 mg, 0.740 mmol), reaction time 48 h, white solid, 67% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at −40 °C over 36 h. Sixty percent of the isolated reaction product consisted of the *SSS/RRR* diastereomer.

[SSS/RRR-2-MeC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$]. ^{1}H NMR (400 MHz, C_6D_5Br): δ 6.02 (br, 1H, NH_2), 4.60 (br d, 1H, NH_2), 3.36 (br q, 1H, $^1J_{BH}$ = 83 Hz, BH), 3.15 (dt, 1H, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 5.2 Hz, NCH), 2.76 (m, 1H, C*H*Me), 1.45–0.96 (m, 8H, CH_2), 1.10 (m, 1H, *CH*CHN), 0.93–0.67 (m, 4H, CH_2), 0.81 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 148.4 (dm, $^1J_{CF}$ = 234 Hz, CF), 138.4 (dm, $^1J_{CF}$ = 246 Hz, CF), 136.9 (dm, $^1J_{CF}$ = 249 Hz, CF), 123.3 (*ipso*-C_6F_5), 57.7 (NCH), 49.3 (*C*HMe), 32.2 (*C*HCHN), 28.1 (CH_2), 27.2 (CH_2), 25.5 (CH_2), 24.0 (CH_2), 23.6 (CH_2), 21.1 (CH_2), 18.9 (Me). ^{19}F NMR (377 MHz, C_6D_5Br): δ −133.5 (m, 2F, *o*-C_6F_5), −160.7 (t, 1F, $^3J_{FF}$ = 22 Hz, *p*-C_6F_5), −164.6 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.1 (d, $^1J_{BH}$ = 83 Hz, BH). Anal. Calcd (%) for $C_{28}H_{21}BF_{15}N$: C 50.40; H 3.17; N 2.10. Found: C 50.21; H 3.31; N 2.12.

Synthesis of [2-PhC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$] (7). $B(C_6F_5)_3$ (289 mg, 0.564 mmol), 2-phenylquinoline (116 mg, 0.564 mmol), reaction time 48 h, white solid, 95% isolated yield. Seventy-three percent of the reaction mixture consisted of the reported *SSS/RRR* diastereomer.

[SSS/RRR-2-PhC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$]. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.33 (tm, 1H, $^3J_{HH}$ = 7.3 Hz, *p*-Ph), 7.26 (tm, 2H, $^3J_{HH}$ = 7.3 Hz, *m*-Ph), 7.20 (dm, 2H, $^3J_{HH}$ = 7.3 Hz, *o*-Ph), 6.46 (br, 1H, NH_2), 5.01 (br t, 1H, NH_2), 4.33 (dm, 1H, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 3.3 Hz, C(*H*)Ph), 3.80 (br m, 1H, $CH_2C(H)NH_2$), 3.20 (br q, 1H, $^1J_{BH}$ = 87 Hz, BH), 2.18–1.08 (m, 13H, $CH_2C(H)CH_2$ and CH_2). $^{13}C\{1H\}$ NMR (101 MHz, CD_2Cl_2): δ 134.2 (*ipso*-Ph), 131.2 (*p*-Ph), 130.1 (*m*-Ph), 126.9 (*o*-Ph), 64.7 ($CH_2C(H)NH_2$), 60.1 (C(H)Ph), 34.5 ($CH_2C(H)CH_2$), 29.1 (CH_2), 28.5 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 24.8 (CH_2), 19.7 (CH_2). ^{19}F NMR (377 MHz, C_6D_5Br): δ −133.4 (m, 2F, *o*-C_6F_5), −161.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −164.7 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.2 (d, $^1J_{BH}$ = 87 Hz, BH). Anal. Calcd (%) for $C_{33}H_{23}BF_{15}N$: C 54.34; H 3.18; N 1.92. Found: C 54.31; H 3.31; N 1.92.

Synthesis of [8-MeC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$] (8). 8-Methylquinoline (106 mg, 0.740 mmol), reaction time 48 h, white solid, 76% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at −40 °C over 48 h. Only the reported *SSS/RRR* diastereomer was observed.

[SSS/RRR-8-MeC$_9$H$_{15}$NH$_2$][HB(C$_6$F$_5$)$_3$]. ^{1}H NMR (400 MHz, C_6D_5Br): δ 5.55 (br, 1H, NH_2), 4.97 (br, 1H, NH_2), 3.52 (br q, 1H, $^1J_{BH}$ = 80 Hz, BH), 3.27 (dm, 1H, $^2J_{HH}$ = 12.1 Hz, $NH_2CH(H)$), 2.63 (dm, 1H, $^3J_{HH}$ = 11.2 Hz coupling to NH_2 is observed in ^{1}H,^{1}H-COSY, *CH*N) 2.52 (qt, 1H, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 2.7 Hz, $NH_2CH(H)$, 1.41–1.33 (br m, 2H, CH_2), 1.34 (m, 1H, CH_2CHCH_2), 1.25–1.14 (br m, 4H, CH_2), 1.22 (m, 1H, *CH*Me), 1.02 (m, 1H), 0.89 (m, 2H), 0.63 (d, 3H, $^3J_{HH}$ = 7.5 Hz, Me), 0.58 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 148.4 (dm, $^1J_{CF}$ = 234 Hz, CF), 138.3 (dm, $^1J_{CF}$ = 246 Hz, CF), 136.8 (dm, $^1J_{CF}$ = 249 Hz, CF), 123.7 (br, *ipso*-C_6F_5), 63.2 (CHN), 47.8 ($NH_2CH(H)$), 33.9 (CH_2CHCH_2), 33.7 (CHMe), 27.1 (CH_2), 26.8 (CH_2), 24.3 (CH_2), 23.1 (CH_2), 17.8 (CH_2), 16.3 (Me). ^{19}F NMR (377 MHz, C_6D_5Br): δ −134.3 (m, 2F, *o*-C_6F_5), −161.8 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −165.6 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.2 (d, $^1J_{BH}$ = 80 Hz, BH). Anal. Calcd (%) for $C_{28}H_{21}BF_{15}N$: C 50.40; H 3.17; N 2.10. Found: C 50.26; H 3.30; N 2.09.

Synthesis of [C$_{13}$H$_{22}$NH$_2$][HB(C$_6$F$_5$)$_3$] (9). Acridine (132 mg, 0.740 mmol), reaction time 36 h, white solid, 76% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of bromobenzene/pentane at 25 °C over 16 h. The isolated product is a mixture of the *SRSR/RSRS* and *RRSS/SSRR* isomers in a 1:1 ratio. The *SRSR/RSRS* diastereomer was separated by crystallization.

[SRSR/RSRS-C$_{13}$H$_{22}$NH$_2$][HB(C$_6$F$_5$)$_3$]. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.26 (br m, 1H, NH_2), 5.13 (br m, 1H, NH_2), 3.27 (br q, 1H, $^1J_{BH}$ = 86 Hz, BH), 2.85 (ddt, 2H, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 4.0 Hz, C*H*N), 1.82 (m, 2H, NH_2CHCH_2), 1.76 (m, 2H, $^{Cy}CH_2$), 1.75 (m, 1H, $CHCH_2CH$), 1.71 (m, 2H, $^{Cy}CH_2$), 1.67 (m, 2H, $^{Cy}CH_2$), 1.44 (qt, 2H, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 4.0 Hz, CH_2CHCH_2), 1.23 (m, 2H, $^{Cy}CH_2$), 1.22 (m, 2H, NH_2CHCH_2), 1.18 (m, 2H, $^{Cy}CH_2$), 1.01 (m, 2H, $^{Cy}CH_2$), 1.00 (m, 1H, $CHCH_2CH$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) partial: δ 63.9 (*CH*N), 40.6 (CH_2CHCH_2), 37.1 ($CHCH_2CH$), 31.8 ($^{Cy}CH_2$), 30.7 (NH_2CHCH_2), 24.9 ($^{Cy}CH_2$), 24.8 ($^{Cy}CH_2$). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −134.5 (m, 2F, *o*-C_6F_5), −162.7 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −166.3 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −24.4 (d, $^1J_{BH}$ = 86 Hz, BH). Anal. Calcd (%) for $C_{31}H_{25}BF_{15}N$: C 52.64; H 3.56; N 1.98. Found: C 52.14; H 3.58; N 1.96.

Synthesis of *RRSS/SSRR* and *SRSR/RSRS* Tetradecahydroacridine. In a 4 dram vial, compound **9** (278 mg, 0.393 mmol) was dissolved in toluene (5 mL), and potassium bis(trimethylsilyl)amide (78.4 mg, 0.393 mmol) was added in small portions over 5 min. The reaction was allowed to mix for 1 h at room temperature, and the solvent was removed. The reaction mixture was washed with pentane (3 × 5 mL) and filtered through a pad of Celite. The filtrate was collected, and pentane was removed under vacuum to yield a white solid, which was collected and sublimed under dynamic vacuum at 40 °C for 5 h to give the product in 91% yield.

RRSS/SSRR-Tetradecahydroacridine. ^{1}H NMR (400 MHz, CD_2Cl_2) partial: δ 2.79 (ddd, 2H, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 3.1 Hz, NCH), 1.73 (ddm, 2H, J_{HH} = 13.0 Hz, $^3J_{HH}$ = 3.8 Hz, NH_2CHCH_2), 1.45 (m, 2H, CH_2CHCH_2), 1.20 (m, 2H,

dx.doi.org/10.1021/om4000727 | *Organometallics* XXXX, XXX, XXX–XXX

NH_2CHCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) partial: δ 55.8 (NCH), 37.0 (CH_2CHCH_2), 26.7 (NH_2CHCH_2).

SRSR/RSRS-Tetradecahydroacridine. ^1H NMR (400 MHz, CD_2Cl_2): partial: δ 2.02 (ddd, 2H, $^3J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 3.6, NCH), 1.43 (m, 2H, NH_2CHCH_2), 1.11 (m, 2H, CH_2CHCH_2), 1.06 (m, 2H, NH_2CHCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) partial: δ 63.5 (NCH), 37.6 (CH_2CHCH_2), 33.5 (NH_2CHCH_2).

Synthesis of [*RRSS/SSRR* and *SRSR/RSRS*-($C_{13}H_{22}NH$)$B(C_6F_5)_3$] (10). In a 4 dram vial, tetradecahydroacridine (36.6 mg, 0.189 mmol) was dissolved in pentane (5 mL) at room temperature. To the vial was added $B(C_6F_5)_3$ (96.5 mg, 0.189 mmol) at once and allowed to mix for 2 min. The solution was filtered through a bed of Celite to yield a colorless solution. The vial was placed in a −35 °C freezer for 3 h, and colorless crystals were collected in 73% yield.

The isolated mixture of compound **10** consisted of a 1:1 mixture of *RRSS/SSRR* and *SRSR/RSRS* ($C_{13}H_{22}NH$)$B(C_6F_5)_3$, and only the diagnostic resonances of *RRSS/SSRR*-($C_{13}H_{22}NH$)$B(C_6F_5)_3$ have been reported.

[RRSS/SSRR-($C_{13}H_{22}NH$)$B(C_6F_5)_3$]. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.03 (br, 1H, NH), 3.53 (dm, 2H, $^3J_{HH}$ = 12.3 Hz, NCH), 2.14 (dm, 2H, J_{HH} = 12.3 Hz, NH_2CHCH_2), 1.96−1.60 (m, 6H, CH_2), 1.88 (m, 2H, CH_2CHCH_2), 1.77 (m, 4H, NH_2CHCH_2 and $CHCH_2CH$), 1.49−1.11 (m, 6H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) partial: δ 63.0 (NCH), 35.9 ($CHCH_2CH$), 35.6 (CH_2CHCH_2), 29.9 (NH_2CHCH_2). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −127.0 (m, 1F, *o*-C_6F_5), −127.7 (m, 1F, *o*-C_6F_5), −128.1 (m, 1F, *o*-C_6F_5), −129.1 (m, 2F, *o*-C_6F_5), −130.2 (m, 1F, *o*-C_6F_5), −155.8 (t, 1F, $^3J_{HH}$ = 20 Hz, *p*-C_6F_5), −157.9 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −158.9 (t, 1F, $^3J_{HH}$ = 21 Hz, *p*-C_6F_5), −162.4 (m, 1F, *m*-C_6F_5), −163.6 to −163.8 (m, 3F, *m*-C_6F_5), −164.1 8 (m, 1F, *m*-C_6F_5), −164.4 8 (m, 1F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −3.18 (s, BN). Anal. Calcd (%) for $C_{31}H_{23}BF_{15}N$: C 52.79; H 3.29; N 1.99. Found: C 52.66; H 3.28; N 1.96.

Synthesis of [*SRSS/RSRR*-(C_4H_6Me)$_2$$NHNH_2$][$HB(C_6F_5)_3$] (11). 2,3-Dimethylquinoxaline (0.117 g, 0.740 mmol), reaction time 96 h, white solid, 59% isolated yield. Only the reported diastereomer was observed. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.43 (br, 1H, NH_2), 5.92 (br, 1H, NH_2), 3.49 (dm, 1H, $^3J_{HH}$ = 12.8 Hz, CH_2CHN), 3.34 (br q, 1H, $^1J_{BH}$ = 94 Hz, BH), 3.26 (br m, 2H, $NCHMe$, CH_2CHN), 2.81 (dq, 1H, $^3J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 6.4 Hz, $NCHMe$), 2.23 (dm, 1H, J_{HH} = 12.8 Hz, CH_2), 1.89 (dm, 1H, J_{HH} = 13.4 Hz, CH_2), 1.79 (dm, 1H, J_{HH} = 13.4 Hz, CH_2), 1.62 (dm, 2H, J_{HH} = 13.4 Hz, CH_2), 1.47 (m, 1H, CH_2), 1.31 (m, 1H, CH_2), 1.28 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me), 1.21 (d, 3H, $^3J_{HH}$ = 6.2 Hz, Me), 1.20 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 148.1 (dm, $^1J_{C-F}$ = 234 Hz, C_6F_5), 138.4 (dm, $^1J_{C-F}$ = 246 Hz, C_6F_5), 136.8 (dm, $^1J_{C-F}$ = 247 Hz, C_6F_5), 123.2 (*ipso*-C_6F_5), 57.6 (CH_2CHN), 56.3 (NCHMe), 54.1 ($NCHMe$), 51.9 (CH_2CHN), 30.4 (CH_2), 24.2 (CH_2), 22.4 (CH_2), 18.5 (CH_2), 17.8 (Me), 15.1 (Me). ^{19}F NMR (377 MHz, C_6D_5Br): δ −133.6 (m, 2F, *o*-C_6F_5), −160.7 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −164.6 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.1 (d, $^1J_{BH}$ = 94 Hz, BH). Anal. Calcd (%) for $C_{28}H_{22}BF_{15}N$: C 49.29; H 3.25; N 4.11. Found: C 49.09; H 3.33; N 4.21.

Synthesis of [2,3-$Ph_2C_8H_{12}NHNH_2$][$HB(C_6F_5)_3$] (12). 2,3-Dimethylquinoxaline (117 mg, 0.740 mmol), reaction time 96 h, white solid, 59% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at ambient temperature over 1 week. Diastereomers **12a** and **12b** are present in equal ratios. The obtained structures were supported with the through-space distances derived from ^1H,^1H NOESY NMR spectra. Anal. Calcd (%) for $C_{28}H_{22}BF_{15}N$: C 49.29; H 3.25; N 4.11. Found: C 49.09; H 3.33; N 4.21.

*(SRSS/RSRR) (**12a**).* ^1H NMR (400 MHz, C_6D_5Br): δ 7.63 (m, 2H, Ph), 6.99−6.84 (m, 3H, Ph), 5.72 (br, 2H, NH_2), 4.76 (d, 1H, $^3J_{HH}$ = 3.4 Hz, CHPh), 4.41 (d, 1H, $^3J_{HH}$ = 3.4 Hz, CHPh), 4.07 (br, 1H, NH), 3.56 (br q, 1H, $^1J_{BH}$ = 82 Hz, BH), 3.14 (td, 1H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 3.4 Hz, CH_2CHN), 2.60 (m, 1H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 3.4 Hz, CH_2CHN), 1.67 (m, 1H, CH_2), 1.59 (m, 1H, CH_2), 1.53 (m, 1H, CH_2), 1.29 (m, 1H, CH_2), 1.22 (m, 2H, CH_2), 1.21 (m, 1H, CH_2), 0.86 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 148.3 (dm, $^1J_{CF}$ = 235 Hz, CF), 138.5 (dm, $^1J_{CF}$ = 246 Hz, CF), 136.7 (dm, $^1J_{CF}$ = 248 Hz, CF), 136.2 (*ipso*-Ph), 131.3 (Ph), 130.1 (Ph), 126.7 (Ph), 63.7 (CHPh), 61.9 (CHPh), 59.7 (CH_2CHN), 56.1 (CH_2CHN), 31.4 (CH_2), 28.2 (CH_2), 24.2 (CH_2), 23.3 (CH_2). ^{19}F NMR (377 MHz, C_6D_5Br): δ −133.1 (m, 2F, *o*-C_6F_5), −160.6 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −164.3 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −23.8 (d, $^1J_{BH}$ = 82 Hz, BH).

*(RRRS/SSSR) (**12b**).* ^1H NMR (500 MHz, CD_2Cl_2): δ 7.29−7.08 (m, 10H, Ph), 6.57 (br, 2H, NH_2), 4.51 (dm, 1H, $^3J_{HH}$ = 10.2 Hz, CHPh), 4.29 (dm, 1H, $^3J_{HH}$ = 10.2 Hz, CHPh), 3.86 (dm, 1H, $^3J_{HH}$ = 10.7 Hz, CH_2CHN), 3.66 (br, 1H, NH), 3.28 (br q, 1H, $^1J_{BH}$ = 82 Hz, BH), 2.68 (dm, 1H, $^3J_{HH}$ = 10.7 Hz CH_2CHN), 2.05 (m, 1H, CH_2), 1.88 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 1.57 (m, 1H, CH_2), 1.45 (m, 1H, CH_2), 1.30 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 147.9 (dm, $^1J_{CF}$ = 235 Hz, CF), 138.2 (dm, $^1J_{CF}$ = 246 Hz, CF), 136.6 (dm, $^1J_{CF}$ = 248 Hz, CF), 131.4 (*ipso*-Ph), 130.4 (Ph), 130.1 (*ipso*-Ph), 129.3 (Ph), 129.0 (Ph), 128.6 (Ph), 127.7 (Ph), 127.4 (Ph), 122.6 (*ipso*-C_6F_5), 65.5 (CHPh), 62.1 (CHPh), 58.1 (CH_2CHN), 52.6 (CH_2CHN), 30.8 (CH_2), 24.5 (CH_2), 22.9 (CH_2), 18.8 (CH_2). ^{19}F NMR (377 MHz, C_6D_5Br): δ −133.1 (m, 2F, *o*-C_6F_5), −160.6 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −164.3 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −23.8 (d, $^1J_{BH}$ = 82 Hz, BH).

Synthesis of [(C_6H_4)$C_7H_{12}NH_2$][$HB(C_6F_5)_3$] (13). 7,8-Benzoquinoline (133 mg, 0.740 mmol), reaction time 48 h, white solid, 55% isolated yield. Crystals of the *SR/RS* isomer suitable for X-ray diffraction were grown from a layered solution of bromobenzene/pentane at −40 °C over 16 h. Crystals of the *SS/RR* isomer suitable for X-ray diffraction were grown from a layered solution of dichloromethane/pentane at −40 °C over 1 week. Isomer ratio *SR/RS* 80% (pale orange crystals), *SS/RR* 20% (colorless crystals).

*[SR/RS-(C_6H_4)$C_7H_{12}NH_2$][$HB(C_6F_5)_3$] (**13a**).* ^1H NMR (400 MHz, CD_2Cl_2): δ 7.25 (td, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, C_6H_4), 7.15 (d, 1H, $^3J_{HH}$ = 7.7 Hz, C_6H_4), 7.07 (d, 1H, $^3J_{HH}$ = 7.7 Hz, C_6H_4), 7.00 (t, 1H, $^3J_{HH}$ = 7.7 Hz, C_6H_4), 5.97 (br, 2H, NH_2), 4.40 (d, 1H, $^3J_{HH}$ = 3.8 Hz, NCH), 3.61 (dt, 1H, J_{HH} = 13.1 Hz, $^3J_{HH}$ = 3.5 Hz, $NCH(H)$), 3.28 (m, 1H, $NCH(H)$), 3.14 (br q, 1H, $^1J_{BH}$ = 80 Hz, BH), 2.94 (dm, 1H, $^2J_{HH}$ = 17.2 Hz, C_6H_4-$CH(H)$), 2.85 (dm, 1H, $^2J_{HH}$ = 17.2 Hz, C_6H_4-$CH(H)$), 2.39 (m, 1H, CH_2CHCH_2), 2.00−1.88 (br m, 6H, $^{Piperidine,Cy}CH_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 148.3 (dm, $^1J_{CF}$ = 235 Hz, CF), 138.3 (dm, $^1J_{CF}$ = 246 Hz, CF), 137.8 (quaternary C for C_6H_4-CHN), 136.8 (dm, $^1J_{CF}$ = 248, CF), 131.1 (C_6H_4), 130.7 (C_6H_4), 129.2 (C_6H_4), 128.8 (quaternary C for C_6H_4-CH_2), 127.7 (C_6H_4), 123.4 (*ipso*-C_6F_5), 60.5 (NCH), 47.9 (NCH_2), 32.0 (CH_2CHCH_2), 28.6 (C_6H_4-CH(H)), 27.4 ($^{Piperidine}CH_2$), 22.5 ($^{Cy}CH_2$), 18.4 ($^{Piperidine}CH_2$). ^{19}F NMR (377 MHz, C_6D_5Br): δ −134.5 (m, 2F, *o*-C_6F_5), −162.1 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −165.7 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.1 (d, $^1J_{BH}$ = 80 Hz, BH). Anal. Calcd (%) for $C_{31}H_{21}BF_{15}N$: C 52.94; H 3.01; N 1.99. Found: C 53.47; H 2.91; N 2.09.

*[SS/RR-(C_6H_4)$C_7H_{12}NH_2$][$HB(C_6F_5)_3$] (**13b**).* ^1H NMR (400 MHz, C_6D_5Br) partial: δ 7.01 (m, 1H, C_6H_4), 6.99 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 6.75 (d, 1H, $^3J_{HH}$ = 7.7 Hz, C_6H_4), 3.50 (d, 1H, $^3J_{HH}$ = 10.4 Hz, NCH), 3.24 (br dm, 1H, J_{HH} = 12.4 Hz, $NCH(H)$), 2.79 (m, 1H, $NCH(H)$), 2.54 (m, 1H, C_6H_4-$CH(H)$), 2.42 (m, 1H, C_6H_4-$CH(H)$), 1.42 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 1.05 (m, 1H, CH_2CHCH_2), 0.83 (m, 2H, CH_2); (not observed NH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): δ 137.0 (quaternary C for C_6H_4-CHN), 130.4 (C_6H_4), 129.1 (C_6H_4), 128.4 (quaternary C for C_6H_4-CH_2), 126.4 (C_6H_4), 122.6 (C_6H_4), 62.9 (NCH), 47.4 (NCH_2), 37.8 (CH_2CHCH_2), 29.1 (CH_2), 28.8 (C_6H_4-CH(H)), 27.6 (CH_2), 22.9 (CH_2).

Synthesis of [(C_5H_3N)$(CH_2)_2$(C_5H_8NH)$B(C_6F_5)_2$][$HB(C_6F_5)_3$] (14). 1,10-Phenanthroline (66.7 mg, 0.370 mmol), reaction time 96 h, white solid, 73% isolated yield. Crystals suitable for X-ray diffraction were grown from a layered solution of tetrahydrofuran/pentane at −40 °C over 1 week. Sixty-five percent of the reaction mixture consisted of the *SRS/RSR* diastereomer. ^1H NMR (400 MHz, CD_2Cl_2): δ 9.44 (br s, 1H, NH), 8.50 (dd, 1H, J_{HH} = 4.7 Hz, J_{HH} = 1.5 Hz, C_5H_3N), 7.44 (dd, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.5 Hz, C_5H_3N), 7.22 (dd, 1H, J_{HH} = 7.8

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Hz, J_{HH} = 4.7 Hz, C_5H_3N), 4.42 (d, 1H, $^3J_{HH}$ = 4.3 Hz, ^{Cy}NCH), 3.42 (br, 1H BH), 3.22 (dm, 1H, $^2J_{HH}$ = 13.8 Hz, NC(H)*H*), 2.91 (ddd, 1H, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 5.3 Hz, NC(*H*)H), 2.76–2.72 (m, 2H, C_6H_4-C*H*(*H*)), 2.12 (dp, 1H, $^3J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 3.8 Hz, CH_2CHCH_2), 1.96 (m, 1H, CH_2), 1.88 (m, 1H, CH_2), 1.73 (m, 1H, CH_2), 1.32 (dt, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 3.2 Hz, CH_2), 0.91 (qd, 1H, J_{HH} = 13.1 Hz, $^3J_{HH}$ = 3.8 Hz, CH_2), 0.71 (qt, 1H, J_{HH} = 13.7 Hz, $^3J_{HH}$ = 4.0 Hz, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 148.4 (quaternary C for C_5H_3N), 146.6 (quaternary C for C_5H_3N), 144.8 (C_5H_3N), 135.4 (C_5H_3N), 126.0 (C_5H_3N), 58.1 (^{Cy}NCH), 45.1 (NC(H)H), 29.6 ($CH_2C(H)CH_2$), 24.1 (CH_2), 21.8 (CH_2), 21.0 (CH_2), 20.6 (CH_2). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −128.9 (m, 2F, $^{B(C6F5)2}o$-C_6F_5), −134.3 (m, 6F, $^{HB(C6F5)3}o$-C_6F_5), −134.8 (m, 2F, $^{B(C6F5)2}o$-C_6F_5), −149.1 (t, 1F, $^3J_{FF}$ = 20 Hz, $^{B(C6F5)2}p$-C_6F_5), −151.1 (t, 1F, $^3J_{FF}$ = 20 Hz, $^{B(C6F5)2}p$-C_6F_5), −159.6 (m, 4F, $^{B(C6F5)2}m$-C_6F_5), −164.5 (t, 3F, $^3J_{FF}$ = 20 Hz, $^{HB(C6F5)3}p$-C_6F_5), −167.6 (m, 6F, $^{HB(C6F5)3}m$-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 3.43 (br s, BN). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 3.91 (s, BN), −25.4 (d, $^1J_{BH}$ = 93 Hz, BH). Anal. Calcd (%) for $C_{42}H_{17}B_2F_{25}N_2$: C 48.22; H 1.64; N 2.68. Found: C 47.83; H 1.97; N 2.69.

X-ray Data Collection, Reduction, Solution, and Refinement. Single crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under an N_2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) or 293(±2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[38] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors (see Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

Synthetic, spectroscopic, and crystallographic data are deposited. See CCDC 917790–917798. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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