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Ruthenium-Catalyzed Selective Hydroboration of Nitriles and Imines

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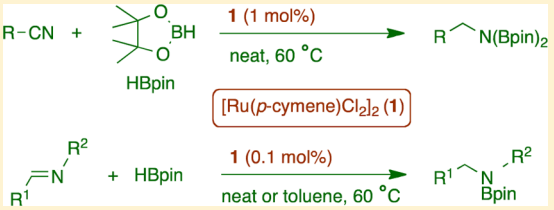
Supporting Information

ABSTRACT: Ruthenium-catalyzed hydroboration of nitriles and imines is attained using pinacolborane with unprecedented catalytic efficiency. Chemoselective hydroboration of nitriles over esters is also demonstrated. A simple $[Ru(p\text{-cymene})Cl_2]_2$ complex (**1**) is used as a catalyst precursor, which upon reaction with pinacolborane *in situ* generates the monohydrido-bridged complex $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-H-}\mu\text{-Cl})]$ **2**. Further oxidative addition of pinacolborane to intermediate **2** leading to the formation of mononuclear ruthenium hydride species is suggested. Mass spectral analysis of the reaction mixture and independent experiments with phosphine-ligated ruthenium complexes indicated the involvement of mononuclear ruthenium intermediates in the catalytic cycle. Consecutive intramolecular 1,3-hydride transfers from the ruthenium center to coordinated nitrile and boronate imine ligands, leading to the reduction and resulting in the formation of diboronate amines, are proposed as a plausible reaction mechanism.



INTRODUCTION

Catalytic hydroelementation processes such as hydroboration and hydrosilylation are the fundamental transformations with academic and industrial importance as these reactions are employed in the production of commodity and agrochemicals and material synthesis and are also often encountered in chemical synthesis of complex molecules.[1] Aliphatic primary and secondary amines and their derivatives are prevalently present in nature, and they are important compounds in chemistry and biology.[2] Amines are also extensively used in the synthesis of agrochemicals, polymers, dyestuffs, pigments, and textiles and act as protectants against damage from γ radiation.[3] Thus, reduction of nitriles to primary amines by hydrogenation,[4] pyrophoric alkali metal hydrides,[5] and electron transfer processes[6] is developed. However, these methods suffer from the requirement of a high-pressure setup[7] and exceedingly excess amounts of reagents,[5c,6] generation of inorganic waste as byproducts, and poor selectivity.[5b,8] Hydroboration and hydrosilylation of nitriles can be beneficial over the hydrogenation and other processes of reduction as they generate further functionality in the resultant amines.[9] While the catalytic hydrosilylation leads to the formation of both monosilylated imine and disilylamine products,[10] hydroboration provides diboronate amines selectively.

Although catalytic hydroboration of various unsaturated functional groups has been extensively explored, hydroboration of nitriles remain scarcely studied.[11−13] Nikonov's group disclosed the hydroboration of acetonitrile and benzonitrile with catecholborane using the Mo(IV) complex as a catalyst (5 mol %), which provided the corresponding dioboronate amines.[11] Szymczak and Geri have reported a proton-switchable bifunctional ruthenium pincer complex (5 mol %), which catalyzed the nitrile hydroboration.[12] Hill and co-workers have recently demonstrated a Mg(II)-catalyzed (10 mol %) hydroboration of nitriles.[13] Synthesis of secondary amines from the reduction of imine C═N bonds is an attractive synthetic method. Like the reduction of other unsaturated functionalities, reduction of imines can also be attained using the reagents such as $LiAlH_4$ or $NaBH_4$, but these reagents remain unattractive due to their poor yields and product selectivity.[14] Hydrogenation of imines using transition metal catalysts has been extensively explored.[15] Thus, hydroboration of imines can serve as an important transformation for the synthesis of secondary amines, provided an efficient catalytic method for the hydroboration of imines is developed. However, catalytic hydroboration of imines was scarcely studied in the literature with very limited substrate scope. Baker and Westcott et al. reported the first metal-catalyzed hydroboration of imines using bidentate phosphine ligated gold(I) complexes (5 mol %) and catecholborane in 1995.[16] Since then, we were aware of only a few reports for the hydroboration of imines.[17] Thus, development of an efficient catalytic method for the hydroboration of imines is desirable. We have reported the highly efficient chemoselective hydroboration of carbonyl compounds[18] using simple and commercially available $[Ru(p\text{-cymene})Cl_2]_2$ (**1**) as a precatalyst in which we have uncovered the involvement of a new reaction intermediate,[19] monohydrido-bridged complex $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-H-}\mu\text{-Cl})]$ (**2**). Recently, we have also developed ruthenium(II)-catalyzed regioselective 1,4-hydroboration of pyridine compounds using complex **1** and other *mono*-nuclear ruthenium complexes, which established a facile intramolecular 1,5-hydride transfer process.[20] In continuation of our efforts in developing efficient hydroelementation reactions,[18−20] herein we report facile hydroboration of nitriles and imines with unprecedented catalytic efficiency using pinacolborane with 1 mol % and 0.1 mol % of **1**, respectively.

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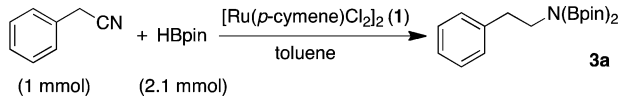
RESULTS AND DISCUSSION

At first, we performed the reaction of benzyl nitrile (1 mmol) with pinacolborane (2.1 mmol) using complex **1** (0.5 mol %) at room temperature where ^{1}H NMR analysis of the reaction mixture indicated 25% formation of the product, 1,1-bis(boryl)phenethylamine. For optimization, several reactions were performed (Table 1). Initially, catalyst load was increased

Table 1. Hydroboration of Nitrile: Optimization of Reaction Conditions



entry	load of **1** (mol %)	temp. (°C)	time (h)	yield of **3a** (%)[a]
1	0.5	rt	24	25
2	1	rt	24	40
3	1	60	24	>99
4	0.2	60	22	25
5	0.5	60	22	75

[a]Based on ^{1}H NMR (400 MHz) analysis of the reaction mixtures.

to 1 mol %, and the reaction was carried out at room temperature for 24 h (entry 2, Table 1), which resulted in a slight improvement in product formation (40%). Further, reaction with same load of catalyst (1 mol %) at 60 °C for 24 h was performed, which provided quantitative conversion of benzyl nitrile to product as inferred from ^{1}H NMR analysis. To verify the reaction progress at 60 °C under low loading of catalyst, the reactions were carried out with 0.2 and 0.5 mol % of **1** (entries 4 and 5, Table 1), which resulted in incomplete hydroboration. Thus, 1 mol % of **1** with mild heating at 60 °C was found to be an optimized condition for the hydroboration of nitriles.

Under the optimized condition an assortment of nitriles were subjected to the hydroboration reactions, which delivered diboronate amines in good yields (Table 2). Formation of diboronate amine products was calculated from the ^{1}H NMR analysis of the reaction mixtures, which were in the range of 73% to >99%. Aromatic nitriles embedded with electron-donating and electron-withdrawing groups were well tolerated, and quantitative formations of products were observed (Table 2, entries 2−6). Representatively, a single-crystal structure of a diboronate amine **4g** was solved (entry 7, Table 2; Figure 1), which clearly established the dihydroboration of nitrile to diboronate amine. ^{1}H NMR analysis also confirmed the absence of monoborylimine products in the reaction mixture. Hydroboration of aliphatic nitriles provided good to quantitative conversions (entries 7−11, Table 2). Notably, acetonitrile and deuterated acetonitrile also underwent catalytic hydroboration and provided quantitative and 88% yields of products, respectively (entries 12−13, Table 2). Under similar experimental conditions, efficient formation of bis(diboronate amine) products from dinitrile substrates is also attained in 24 h (entries 14 and 15, Table 2). Gratifyingly, hydroboration of all these nitriles catalyzed by **1** proceeded very well under solventless conditions.

Upon monitoring the catalytic hydroboration of 4-methoxy benzonitrile using ^{1}H NMR, a singlet signal that corresponds to monoborylimine (δ = 8.45 ppm) was observed after 7 h. Affirmed from the above in situ observation and literature that the reduction of nitrile to amine proceeds via the imine formation, hydroboration of imines catalyzed by complex **1** was tested.[7] Upon reaction of complex **1** (0.1 mol %) with (*E*)-*N*-benzylidene-1-phenylmethanamine (1 mmol) and pinacolborane (1 mmol) for 15 h at 60 °C, hydroboration of imine proceeded efficiently, and the ^{1}H NMR analysis of the reaction mixture indicated the quantitative conversion of imines to boronate amines (TON > 990). Imines that are derived from both aliphatic amines and arylamines underwent quantitative hydroboration (as inferred from ^{1}H NMR analysis of the reaction mixture) to provide the corresponding boronate amines. Both electron-withdrawing and electron-donating functionalities as well as aryl halides were tolerated on imine substrates. Hydrolysis of boronate amines by using silica gel in methanol for 6 h at 50 °C provided the respective secondary amines, which were isolated through column chromatography in good yields (Table 3).

In an attempt to expand the synthetic scope of this efficient hydroboration, we have tested the chemoselective hydroboration of nitriles. Competitive intermolecular catalytic hydroboration of 4-methoxybenzonitrile with phenethyl benzoate resulted in exclusive hydroboration of nitrile (Scheme 1a, ^{1}H NMR). Further, substrates containing both nitrile and ester functionalities within the molecule (**6**, **7**) were also subjected to the catalytic hydroboration (**1**, 1 mol %, HBpin (2.1 equiv)), which established chemoselective hydroboration only at the nitrile functionality, and the ester motifs remained intact in the products **8** and **9**, respectively (Scheme 1b).[21]

In situ ^{1}H NMR monitoring of the reaction progress for 4-methoxybenzonitrile hydroboration with pinacolborane catalyzed by **1** indicated the involvement of first-order kinetics (Figure 2). Further, ^{1}H NMR analysis of the stoichiometric reaction between complex **1** and pinacolborane had shown only a singlet resonance in the metal-hydride region at δ_{Ru-H} = −10.18 ppm, and the result is comparable to that of hydroboration of carbonyl compounds catalyzed by **1**, which confirmed the formation of monohydrido-bridged complex $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-H-}\mu\text{-Cl})]$ **2**.[18,19] Formation of ClBpin was inferred from ^{11}B NMR.[18] Upon reaction with pinacolborane, complex **2** splits into mononuclear unobserved intermediate **I**, which may involve the intermediacy of Ru(0) species and the B−H activation.[22] The common intermediate **I** reacts with both nitriles and in situ formed imines leading to the formation of coordination complexes (Scheme 2). The nitrile-ligated intermediate **II** undergoes intramolecular 1,3-hydride transfer resulting in the reduction of nitrile to imine, providing **III**. Oxidative addition of pinacolborane with **III** provides Ru(IV)-diboryl-ligated intermediate **IV**.[23,24] Boryl and imide ligands in **IV** undergo reductive elimination to liberate boronate imine and regenerate **I**. The in situ formed boronate imine was observed in ^{1}H NMR of the reaction mixture, which resonated a characteristic imine singlet signal at δ 8.45 ppm in the hydroboration of 4-methoxy benzonitrile. Further, intermediate **I** undergoes similar catalytic cycle with an in situ formed boronate imine, which leads to the formation of diboronate amine products. Reaction of **I** with boronate imine provides **II′**, which undergoes 1,3-hydride transfer in order to reduce the unsaturated imine functionality to amine (**III′**). Reaction of **III′** with pinacolborane and subsequent reductive elimination from intermediate **IV′** result in diboronate amine products and regeneration of intermediate **I** to close one loop in catalytic cycles. In an attempt to identify the transient ruthenium intermediates involved in the catalytic cycles, electrospray ionization mass spectrometric (ESI-MS) analysis

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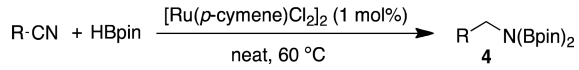
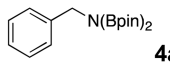
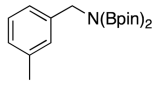
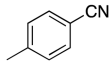
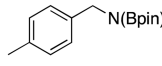
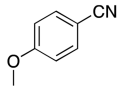
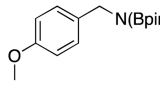
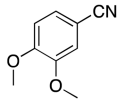
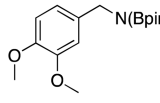
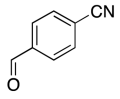
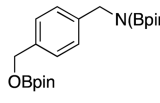
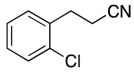
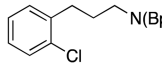
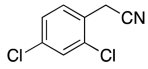
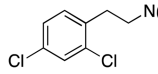
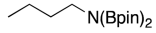
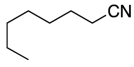
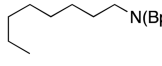
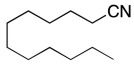
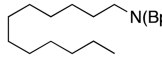
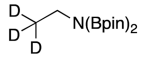
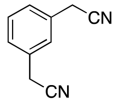
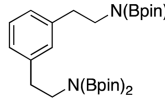
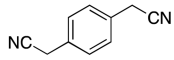
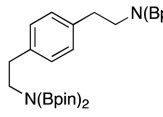
Table 2. Catalytic Hydroboration of Nitriles to Diboryl Amines[a]



Entry	Nitrile	Product	Time (h)	Yield (%)[b]
1[c]		 **4a**	15	96
2		 **4b**	15	>99
3		 **4c**	15	>99
4		 **4d**	15	>99
5		 **4e**	15	>99
6[d]		 **4f**	15	>99
7[f]		 **4g**	24	73 (69)[e]
8[f]		 **4h**	24	>99
9[f]		 **4i**	24	>99
10[f]		 **4j**	24	74
11		 **4k**	36	>99
12	CH_3CN	 **4l**	15	>99
13[c]	CD_3CN	 **4m**	15	88
14[f]		 **4n**	24	91
15		 **4o**	24	>99

[a]Conditions: nitrile (1 mmol), pinacolborane (2.1 mmol), and $[Ru(p\text{-cymene})Cl_2]_2$ **1** (1 mol %) were charged in a screw-capped vial under nitrogen atmosphere, and the reaction mixture was heated at 60 °C. [b]Calculated on the basis of ^1H NMR (400 MHz) integration of a characteristic product signal present in the reaction mixtures. [c]Anisole was used as an internal standard. [d]3.1 mmol of pinacolborane was used. [e]Isolated yield. [f]Traces of unknown ipurity observed (<1%, based on ^1H NMR (400 MHz) integration).

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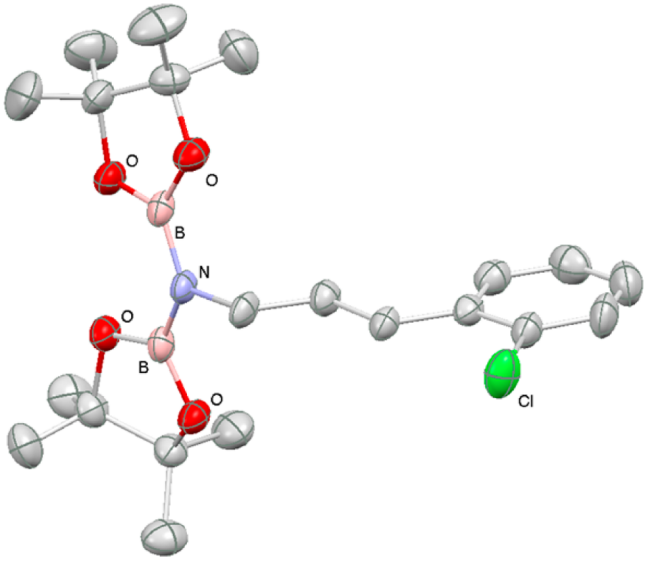

Figure 1. Single-crystal structure of a diboronate amine **4g** from 3-(2-chlorophenyl)propanenitrile. Thermal ellipsoids in the ORTEP diagram are drawn at 50% probability.

of the reaction mixture corresponding to hydroboration of 4-methoxy benzonitrile was performed in which m/z 673 and 753 ions correspond to intermediates **IV** or **II′** (both intermediates have same molecular mass), and **IV′**, respectively, was observed, indicating the involvement of mononuclear ruthenium complexes in the catalytic cycles (Scheme 2).

To further confirm the involvement of mononuclear metal complexes in the catalytic cycles, phosphine-ligated mononuclear ruthenium complexes **10a** and **10b** were prepared from $[Ru(p\text{-cymene})Cl_2]_2$ (**1**).[20] Upon performing the reaction of pinacolborane with 4-methoxy benzonitrile catalyzed by **10a** (2 mol %), the corresponding diboronate amine was obtained in 55% yields. Perhaps, the strongly bound electron-rich phosphine ligand (PCy_3; Cy = cyclohexyl) retarded the reaction. Thus, the similar reaction was performed with triphenylphosphine-ligated **10b** (2 mol %), which provided the product in 85% yields (Scheme 3).[25] These experimental evidences strongly suggest the involvement of mononuclear metal complexes in the catalytic hydroboration of nitriles catalyzed by complex **1**.

CONCLUSION

In summary, an efficient catalytic hydroboration of nitriles to the corresponding diboronate amines is developed. The reactions proceed via the in situ formation of imines. Thus, highly efficient (catalyst load: 0.1 mol % of **1**, TON, >990) hydroboration of imines to boronate amines and their further hydrolysis to secondary amines are also demonstrated. Among the few catalysts reported for the hydroboration of nitriles and imines, complex **1** offers the most efficient catalytic hydroboration, and the reactions are highly chemoselective; exclusive hydroboration of nitrile functionality over esters is demonstrated in both inter- and intramolecular fashion. Experimental observations confirmed the immediate formation of a monohydrido-bridged dinuclear complex $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-H-}\mu\text{-Cl})]$ **2** in the reaction mixture. Further oxidative addition of pinacolborane leading to the formation of mononuclear ruthenium hydride intermediates is proposed. ESI-MS analysis of the reaction mixture and independent catalytic experiments with phosphine-ligated mononuclear ruthenium complexes suggest the involvement of mononuclear ruthenium complexes in the catalytic cycles. Successive intramolecular 1,3-hydride transfers to coordinated nitrile and borylimine ligands on mononuclear ruthenium intermediates are suggested to be operative, resulting in reduction of nitrile motif to diboronate amines.

EXPERIMENTAL SECTION

General Information. All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere glovebox. Catalyst $[Ru(p\text{-cymene})Cl_2]_2$ (**1**) and pinacolborane were purchased from Sigma-Aldrich. Dry solvents were prepared according to standard procedures. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded using 400, 100.6, and 96.3 MHz magnetic fields, respectively. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were reported in ppm downfield from tetramethylsilane. Multiplicity is abbreviated as s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplet; br, broad. IR spectra were recorded in an FT-IR spectrometer by using KBr pellets. Mass spectra were recorded on a micrOTOF-Q II spectrometer.

Experimental Procedure. *General Procedure for Catalytic Hydroboration of Nitrile to Diboronate Amines.* Nitrile (1 mmol), pinacolborane (2.1 mmol), and $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol %) [toluene (0.5 mL) was used for inhomogeneous reaction mixture] were charged in a PTFE screw-capped reaction vial with a magnetic bead under nitrogen atmosphere. The reaction mixture was heated at 60 °C with stirring. Progress of the reaction was monitored by ^1H NMR, which indicated the completion of the reaction in 15−24 h. The diboronate amine products are air and moisture sensitive. All experimental procedures were carried out under nitrogen atmosphere, and NMR samples were prepared inside the glovebox using dry $CDCl_3$. The solid products can be isolated after filtering the reaction mixture through a short plug of Celite under nitrogen atmosphere. The crude products can be further purified by crystallization in dichloromethane/hexane solution.

Spectral Data of Diboronate Amines. *4,4,5,5-Tetramethyl-N-phenethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**3a**).* IR (DCM): 2977, 2928, 1455, 1372, 1272, 1217, 1147, 1065, 952, 852, 747, 699, 675 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.24 (d, 2H, J = 8 Hz), 7.15−7.19 (m, 3H), 3.28−3.31 (m, 2H), 2.71 (t, 2H, J = 8 Hz), 1.17 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.6, 129.4, 128.2, 125.7, 82.2, 45.3, 39.5, 24.6. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25.4 (s, *B*-N). HRMS (EI) m/z calcd for C_8H_9 (Fragment): $(M-C_{12}H_{24}B_2NO_4)^+$: 105.0704, found: 105.0705.

*N-Benzyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**4a**).*[13] IR (DCM): 2977, 1454, 1372, 1272, 1216, 1147, 1061, 1009, 981, 943, 924, 852, 785, 750, 698, 676 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.30 (d, 2H, J = 8 Hz), 7.22−7.26 (m, 2H), 7.14−7.17 (m, 1H), 4.23 (s, 2H), 1.19 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.2, 127.9, 127.6, 126.2, 82.4, 47.4, 24.6. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25.8 (s, *B*-N). HRMS (EI) m/z calcd for $C_7H_{10}N$: $(M+H-C_{12}H_{24}B_2NO_4)^+$: 108.0813, found: 108.0796.

*4,4,5,5-Tetramethyl-N-(3-methylbenzyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**4b**).*[13] IR (DCM): 2982, 2894, 1462, 1354, 1264, 1210, 1053, 952, 921, 764, 652 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.15 (d, 2H, J = 4 Hz), 7.12 (d, 1H, J = 4 Hz), 6.98 (d, 1H, J = 8 Hz), 4.21 (s, 2H), 2.31 (s, 3H), 1.21 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.0, 137.3, 128.4, 127.8, 126.8, 124.6, 82.4, 47.2, 24.6, 21.5. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25.3 (s, *B*-N). HRMS (EI) m/z calcd for C_8H_9 (Fragment): $(M-C_{12}H_{24}B_2NO_4)^+$: 105.0704, found: 105.0682.

*4,4,5,5-Tetramethyl-N-(4-methylbenzyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**4c**).* IR (DCM): 2977, 2891, 1451, 1378, 1217, 1079, 918, 747, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.24 (d, 2H, J = 8 Hz), 7.11 (d, 1H, J = 8 Hz), 4.24 (s, 2H), 2.35 (s, 3H), 1.21 (s, 24). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.2, 135.5, 128.6, 127.6, 82.4, 47.0, 24.6, 21.2. $^{11}B\{^1H\}$ NMR

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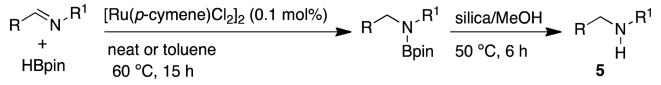
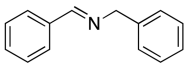
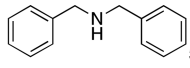
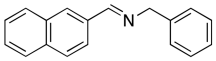
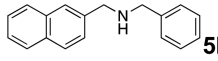
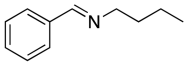
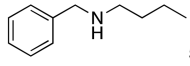
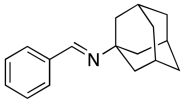
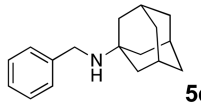
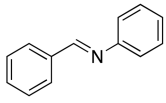
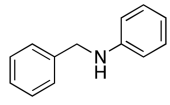
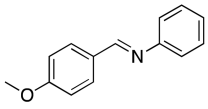
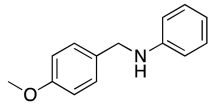
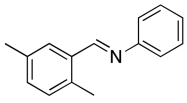
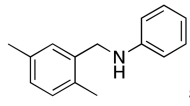
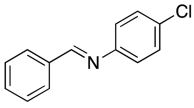
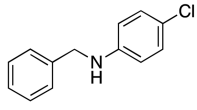
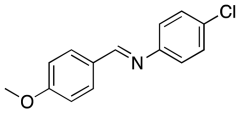
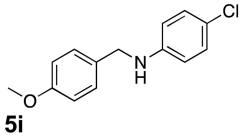
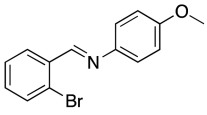
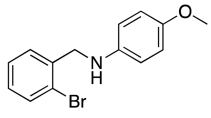
Table 3. Hydroboration of Imines Catalyzed by 1 and the Conversion of Amine Boronates to Secondary Amines[a]



Entry	Imine	Yield (%)[b]	2° amine	Yield (%)[c]
1		>99	 **5a**	87
2		n.c	 **5b**	85
3		>99	 **5c**	89
4[d]		>99	 **5d**	91
5		>99	 **5e**	91
6[d]		n.c	 **5f**	92
7		n.c	 **5g**	88
8[d]		n.c	 **5h**	91
9[d]		>99	 **5i**	88
10[d]		>99	 **5j**	83

[a]Conditions: imine (1 mmol), pinacolborane (1 mmol), and complex **1** (0.1 mol %) were charged in a screw-capped vial under nitrogen atmosphere, and the reaction mixture was stirred at 60 °C for 15 h. [b]Based on ^{1}H NMR (400 MHz) analysis of the reaction mixture. [c]Isolated yields. [d]Toluene was used as solvent. n.c.: not calculated.

($CDCl_3$): δ 25.3 (s, *B*-N). HRMS (EI) *m*/*z* calcd for C_8H_9 (Fragment): $(M-C_{12}H_{24}B_2NO_4)^+$: 105.0704, found: 105.0681.

*N-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**4d**).*[13] IR (DCM): 2976, 2932, 1459, 1374, 1252, 1218, 1168, 1147, 1059, 924, 739, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.23 (d, 2H, *J* = 12 Hz), 6.78 (d, 2H, *J* = 8 Hz), 4.15 (s, 2H), 3.77 (s, 3H), 1.20 (s, 24H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 158.1, 135.6, 128.9, 113.3, 82.4, 55.3, 46.7, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.8 (s, *B*-N). HRMS (EI) *m*/*z* calcd for C_8H_9O (Fragment): $(M-C_{12}H_{24}B_2NO_4)^+$: 121.0653, found: 121.0663.

*N-(3,4-Dimethoxybenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**4e**).* IR (DCM): 2978, 1459, 1375, 1343, 1265, 1243, 1167, 1147, 1055, 924, 766, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.90 (d, 1H, *J* = 1.6 Hz), 6.85 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2 Hz), 6.74 (d, 1H, *J* = 8 Hz), 4.14 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 1.20 (s, 24H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 148.4, 147.4, 136.1, 112.0, 111.3, 110.7, 82.4, 55.9, 55.7, 47.0, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.9 (s, *B*-N). HRMS (EI) *m*/*z*

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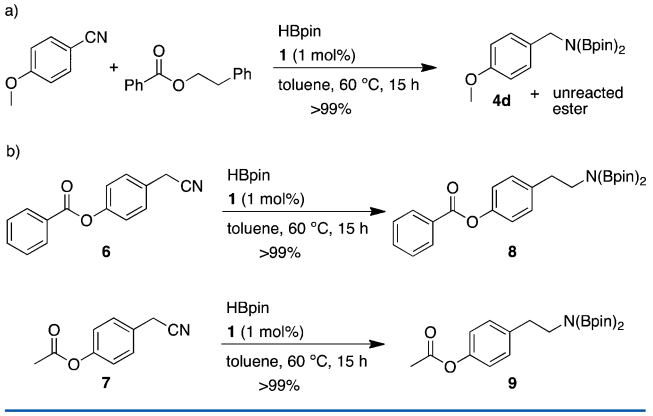
Scheme 1. Chemoselective Hydroboration of Nitrile to Diboronate Amines



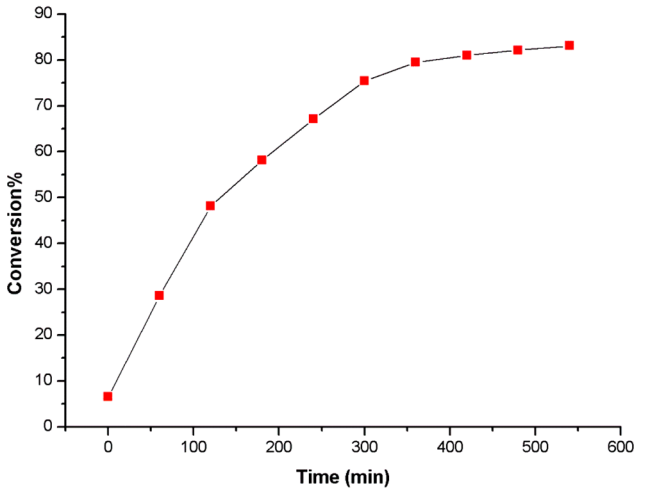


Figure 2. ^{1}H NMR monitoring of the reaction progress: 4-methoxybenzonitrile (0.25 mmol), pinacolborane (0.55 mmol), **1** (0.0025 mmol), and C_6D_6 were charged in a screw cap NMR tube and monitored at regular interval. % Conversion is determined from integration of ^{1}H NMR.

calcd for $C_{15}H_{23}BNO_4Na$ (Fragment): $(M-C_6H_{12}BO_2+Na)^+$ 315.1618, found: 315.1639.

4,4,5,5-Tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzyl)-1,3,2-dioxaborolan-2-amine ***(4f)***. IR (DCM): 2977, 1454, 1371, 1273, 1217, 1167, 1146, 1057, 981, 944, 924, 852, 699, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24−7.30 (m, 4H), 4.90 (s, 2H), 4.24 (s, 2H), 1.28 (s, 12 H), 1.21 (s, 24H).^{13}C {^{1}H} NMR ($CDCl_3$): δ 142.4, 137.0, 127.5, 126.5, 83.0, 82.4, 66.8, 47.1, 24.7, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.9 (s, *B*-N), 25.8 (s, *B*-O). HRMS (EI) *m*/*z* calcd for $C_{14}H_{20}BO_3$ (Fragment): (M- $C_{12}H_{24}B_2NO_4)^+$: 247.1506, found: 247.1491.

N-(3-(2-Chlorophenyl)propyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine ***(4g)***. The compound **4g** was isolated by crystallization (hexane/DCM) of the crude solid obtained from filtration through a Celite pad. Yield 290 mg, 69%. IR (DCM): 2976, 2930, 1475, 1453, 1372, 1272, 1217, 1167, 1055, 1009, 924, 852, 752, 699, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.32−7.34 (m, 1H), 7.26−7.28 (m, 1H), 7.19−7.21 (m, 1H), 7.12−7.15 (m, 1H), 3.17 (t, 2H, *J* = 8 Hz), 2.68−2.74 (m, 2H), 1.76 (t, 2H, *J* = 8 Hz), 1.25 (s, 24H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.6, 134.1, 130.1, 129.4, 127.0, 126.7, 82.2, 43.6, 32.8, 30.9, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.9 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_{15}H_{22}BClNO_2$: $(M-C_6H_{12}BO_2)^+$: 294.1432, found: 294.1425.

N-(2,4-Dichlorophenethyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine ***(4h)***. IR (DCM): 2977, 1455, 1372, 1273, 1216, 1146, 1060, 1009, 943, 924, 852, 743, 701, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.31 (d, 1H, *J* = 4 Hz), 7.12 (d, 1H, *J* = 4 Hz), 7.10 (s, 1H), 3.29−3.32 (m, 2H), 2.80−2.83 (m, 2H), 1.16 (s, 24H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 136.8, 135.3, 132.4, 132.1, 129.0, 126.7, 82.2, 43.2, 36.2, 24.5. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.7 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_8H_{10}Cl_2N$ (Fragment): $(M-C_{12}H_{24}B_2O_4+H)^+$ 190.0186, found: 190.0156.

N-Butyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine ***(4i)***.[26] IR (DCM): 2973, 2937, 1462, 1454, 1274, 1170, 1059, 963, 941, 765, 750, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.00 (t, 2H, *J* = 8 Hz), 1.32−1.37 (m, 4H), 1.20 (s, 24H), 0.86 (t, 3H, *J* = 8 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 82.0, 43.3, 35.4, 24.6, 19.7, 14.1. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.6 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_4H_{11}NNa$: $(M-C_{12}H_{24}B_2O_4+Na)^+$: 96.0784, found: 96.0781.

4,4,5,5-Tetramethyl-N-octyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine ***(4j)***. IR (DCM): 2922, 1453, 1371, 1271, 1166, 1069, 1009, 941, 723, 702, 678 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.99−3.00 (m, 2H), 1.22−1.25 (m, 12H), 1.20 (s, 24H), 0.85 (t, 3H, *J* = 8 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 82.1, 43.7, 33.1, 32.0, 29.6, 29.4, 26.7, 24.6, 22.8, 14.2. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.6 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_8H_{20}N$ (Fragment): $(M-C_{12}H_{24}B_2O_4+H)^+$ 130.1596, found: 130.1587.

4,4,5,5-Tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-undecyl-1,3,2-dioxaborolan-2-amine ***(4k)***. IR (DCM): 2931, 1444, 1370, 1259, 1179, 1061, 978, 757, 663 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.96−2.99 (m, 2H), 1.20−1.23 (m, 20H), 1.18 (s, 24H), 0.83−0.86 (m, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 82.0, 43.6, 33.1, 32.0, 29.8, 29.7, 29.6, 29.4, 26.6, 24.5, 22.7, 14.2. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.6 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_{12}H_{28}N$ (Fragment): $(M-C_{12}H_{24}B_2O_4+H)^+$ 186.2222, found: 186.2201.

N-Ethyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine ***(4l)***. IR (DCM): 2972, 1453, 1372, 1220, 1165, 1093, 1059, 943, 922, 678 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.06 (quat, 2H, *J* = 8 Hz), 1.22 (s, 24H), 1.03 (t, 3H, *J* = 8 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 82.1, 38.7, 24.6, 18.7. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.6 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_{14}H_{30}B_2NO_4$: $(M+H)^+$ 298.2361, found: 298.2378.

N-Ethyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine-d$_3$ ***(4m)***. IR (DCM): 2972, 1446, 1385, 1272, 1162, 1061, 1003, 944, 917, 681 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.05 (s, 2H, CH_2), 1.24 (s, 24H, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 81.94 (quat-C), 38.35 (CH_2), 24.50 (CH_3), 17.30−17.74 (m, CD_3). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.69 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_8H_{13}D_3BNO_2$: $(M-C_6H_{12}BO_2-H)^+$ 172.1458, found: 172.1462.

N,N′-(1,3-Phenylenebis(ethane-2,1-diyl))bis(4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine) ***(4n)***. IR (DCM): 2975, 1591, 1454, 1372, 1272, 1217, 1147, 1060, 981, 924, 852, 792, 736, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.11−7.12 (m, 2H), 6.97−6.99 (m, 2H), 3.27 (t, 4H, *J* = 8 Hz), 2.65−2.68 (m, 4H), 1.19 (s, 48H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.2, 130.0, 127.9, 126.6, 82.1, 45.3, 39.6, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.5 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_{10}H_{17}N_2$: $(M-C_{12}H_{24}B_2O_4+5H)^+$ 165.1392, found: 165.1382.

N,N′-(1,4-Phenylenebis(ethane-2,1-diyl))bis(4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine) ***(4o)***. IR (DCM): 2979, 1453, 1373, 1288, 1169, 1056, 981, 945, 924, 852, 784, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.07 (s, 4H), 3.23 (t, 4H, *J* = 8 Hz), 2.64 (t, 4H, *J* = 8 Hz), 1.18 (s, 48H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 137.8, 129.0, 82.1, 45.5, 39.3, 24.6. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 25.5 (s, *B*-N). HRMS (EI) *m*/*z* calcd for $C_{10}H_{17}N_2$ (Fragment): $(M-C_{12}H_{24}B_2O_4+H)^+$ 165.1392, found: 165.1381.

General Procedure for Imine Hydroboration. Imine (1 mmol), pinacolborane (1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.1 mol %) [toluene (0.5 mL) for solid substrates], and a magnetic bead were charged in a PTFE screw-capped reaction vial under nitrogen atmosphere. The reaction mixture was heated to 60 °C for 15 h. Progress of the reaction was monitored by ^{1}H NMR. Upon completion, the reaction mixture was treated with silica gel (500 mg, 100−200 mesh) and methanol at 50 °C for 6 h. The completion of hydrolysis was monitored by TLC.

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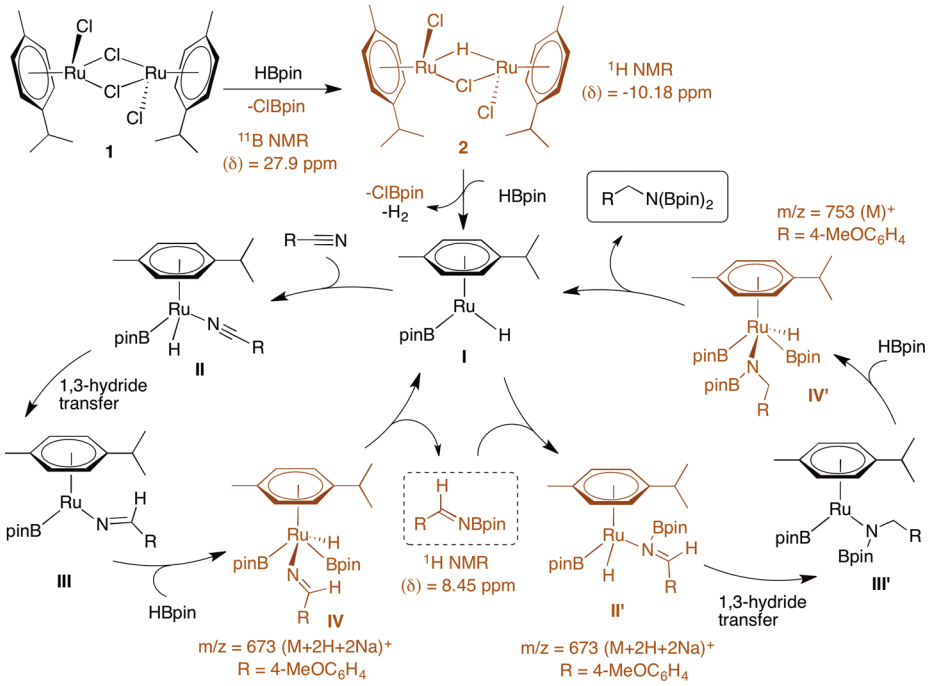
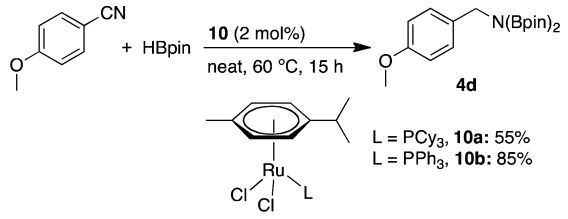
Scheme 2. Proposed Mechanism for the Catalytic Hydroboration of Nitriles to Diboronate Amines



Scheme 3. Catalytic Hydroboration of Nitriles Using Mononuclear Ru Complexes



The reaction mixture was filtered and evaporated, and residue was purified by column chromatography over silica gel (100−200 mesh) with ethyl acetate/hexane (1:5).

Spectral Data for Imine Hydroboration. *Dibenzylamine (**5a**).*[27] Yield 172 mg, 87%. IR (DCM): 3457, 3028, 2925, 2802, 1602, 1493, 1452, 1366, 1247, 1120, 973, 744, 699, 623 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.48 (d, 4H, *J* = 8 Hz), 7.38 (t, 4H, *J* = 8 Hz), 7.29 (t, 2H, *J* = 8 Hz), 3.63 (s, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.8, 128.9, 128.4, 127.0, 58.0. HRMS (EI) *m*/*z* calcd for $C_{14}H_{16}N$: $(M+H)^+$ 198.1283, found: 198.1265.

*N-Benzyl-1-(naphthalen-2-yl)methanamine (**5b**).*[28] Yield 210 mg, 85%. IR (DCM): 3336, 3059, 2923, 1597, 1453, 1396, 1264, 1114, 969, 777, 736, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.15 (d, 1H, *J* = 8 Hz), 7.91−7.93 (m, 1H), 7.84 (d, 1H), 7.53−7.59 (m, 3H), 7.49−7.51 (m, 1H), 7.39−7.47 (m, 4H), 7.32−7.35 (m, 1H), 4.31 (s, 2H), 3.98 (s, 2H), 2.48 (br s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.3, 135.8, 134.0, 131.9, 128.8, 128.5, 128.3, 127.9, 127.1, 126.2, 126.1, 125.7, 125.4, 123.8, 53.7, 50.7. HRMS (EI) *m*/*z* calcd for $C_{18}H_{18}N$: $(M+H)^+$: 248.1439, found: 248.1412.

*N-Benzylbutan-1-amine (**5c**).*[29] Yield 145 mg, 89%. IR (DCM): 3132, 2924, 2852, 1493. 1463, 1308, 1114, 987, 704, 672 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34 (d, 4H, *J* = 4 Hz), 7.25−7.29 (m, 1H), 3.81 (s, 2H), 2.65 (t, 2H, *J* = 8 Hz), 1.82 (br s, 1H), 1.49−1.56 (m, 2H), 1.34−1.40 (m, 2H), 0.93 (t, 3H, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.5, 128.4, 128.2, 126.9, 54.1, 49.2, 32.3, 20.6, 14.1. HRMS (EI) *m*/*z* calcd for $C_{11}H_{16}NNa$: $(M-H+Na)^+$ 185.1180, found: 185.1161.

*N-Benzyladamantan-1-amine (**5d**).* Yield 219 mg, 91%. IR (DCM): 3410, 2910, 2847, 1558, 1453, 1252, 1147, 1098, 1073, 862, 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38−7.40 (m, 2H), 7.32−7.36 (m, 2H), 7.26−7.28 (m, 1H), 3.81 (s, 2H), 3.14 (br s, 1H), 2.13 (br s, 3H), 1.75−1.77 (m, 7H), 1.66−1.71 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.9, 128.5, 128.5, 126.9, 51.5, 45.0, 42.5, 36.8, 29.7. HRMS (EI) *m*/*z* calcd for $C_{17}H_{24}N$: $(M+H)^+$ 242.1909, found: 242.1932.

*N-Benzylaniline (**5e**).*[30] Yield 167 mg, 91%. IR (DCM): 3452, 2993, 2882, 1608, 1508, 1324, 1162, 1035, 847, 757, 640 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.36−7.42 (m, 4H), 7.29−7.33 (m, 1H), 7.21 (t, 2H, *J* = 8 Hz), 6.75 (t, 1H, *J* = 8 Hz), 6.67 (d, 2H, *J* = 8 Hz), 4.36 (s, 1H), 4.05 (br s, 1H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 148.3, 139.6, 129.4, 128.8, 127.6, 127.3, 117.7, 113.0, 48.4. HRMS (EI) *m*/*z* calcd for $C_{13}H_{14}N$: $(M+H)^+$ 184.1126, found: 184.1131.

*N-(4-Methoxybenzyl)aniline (**5f**).*[31] Yield 196 mg, 92%. IR (DCM): 3420, 2985, 2861, 1567, 1509, 1425, 1301, 1016, 941, 826, 748, 652 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34 (d, 2H, *J* = 8 Hz), 7.23 (t, 2H, *J* = 8 Hz), 6.93 (d, 2H, *J* = 8 Hz), 6.76−6.80 (m, 1H), 6.70 (d, 2H), 4.29 (s, 2H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.0, 148.0, 131.3, 129.3, 129.0, 117.8, 114.1, 113.2, 55.3, 48.0. HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}NO$: $(M-H)^+$ 212.1075, found: 212.1088.

*N-(2,5-Dimethylbenzyl)aniline (**5g**).*[32] Yield 186 mg, 88%. IR (DCM): 3414, 3047, 2920, 1602, 1504, 1378, 1318, 1270, 1179, 1066, 992, 810, 748, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.21−7.29 (m, 3H), 7.14 (d, 1H, *J* = 8 Hz), 7.07 (d, 1H, *J* = 4 Hz), 6.78 (t, 1H, *J* = 8 Hz), 6.70 (d, 2H, *J* = 8 Hz), 4.28 (s, 2H), 3.84 (br s, 1H), 2.38 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 148.5, 136.9, 135.7, 133.3, 130.4, 129.4, 129.2, 128.2, 117.5, 112.8, 46.6, 21.1, 18.5. HRMS (EI) *m*/*z* calcd for $C_{15}H_{18}N$: $(M+H)^+$ 212.1439, found: 212.1410.

*N-Benzyl-4-chloroaniline (**5h**).*[33] Yield 197 mg, 91%. IR (DCM): 3358, 2920, 2892, 1594, 1358, 1250, 1126, 995, 867, 815, 732, 673 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (s, 4H), 7.21 (t, 2H, *J* = 8 Hz), 6.79 (t, 1H, *J* = 8 Hz), 6.68 (d, 2H, *J* = 8 Hz), 4.34 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.3, 137.6, 133.1, 129.4, 129.0, 128.9, 118.5, 113.5, 48.1. MS (EI) *m*/*z* calcd for $C_{13}H_{12}ClN$: $(M)^+$ 217, found: 217.

*4-Chloro-N-(4-methoxybenzyl)aniline (**5i**).*[34] Yield 217 mg, 88%. IR (DCM): 3412, 3052, 2806, 1583, 1458, 1362, 1258, 1132, 1028, 942, 818, 742, 623 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (s, 4H), 6.81 (d, 2H, *J* = 8 Hz), 6.62 (d, 2H, *J* = 8 Hz), 4.28 (s, 2H), 3.86 (br s, 1H) 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.6, 141.8, 138.1, 132.9, 128.9, 128.8, 115.0, 114.5, 55.8, 48.7. HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}ClNO$: $(M+Na)^+$ 270.0662, found: 270.0689

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*N-(2-Bromobenzyl)-4-methoxyaniline (**5j**).*[35] Yield 241 mg, 83%. IR (DCM): 3416, 3027, 2930, 2831, 1513, 1464, 1316, 1235, 1180, 1026, 818, 751, 661 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.60 (d, 1H, J = 8 Hz), 7.45 (d, 1H, J = 8 Hz), 7.29 (t, 1H, J = 8 Hz), 7.14−7.18 (m, 1H), 6.80−6.82 (m, 2H), 6.61−6.64 (m, 2H), 4.40 (s, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.3, 141.9, 138.5, 132.8, 129.3, 128.7, 127.6, 123.3, 115.0, 114.3, 55.8, 49.3. HRMS (EI) m/z calcd for $C_{14}H_{15}BrNO$: $(M+H)^+$ 292.0329, found: 292.0299.

Substrate Preparation for Intramolecular Chemoselectivity Study. *Synthesis and Spectral Data of 4-(Cyanomethyl)phenyl Benzoate (**6**).*[36] In an oven-dried 50 mL RB flask 4-hydroxyphenylacetonitrile (3 mmol, 399 mg) and sodium hydroxide (3.5 mmol, 140 mg) were dissolved in 5 mL of THF under nitrogen atmosphere and stirred at room temperature for 1 h. Benzoyl chloride (3 mmol, 350 μL) was dissolved in 5 mL of THF and added dropwise to the RB flask containing aliquot and allowed to stir at room temperature for 10 h. After completion of the reaction the solvent was evaporated and extracted from water and dichloromethane. The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. After that the crude reaction mixture was purified by column chromatography using *n*-hexane and ethyl acetate as an eluant. Yield (82%, 583 mg). ^1H NMR ($CDCl_3$): δ 8.21 (d, 2H, J = 8 Hz), 7.66 (t, 1H, J = 8 Hz), 7.53 (t, 2H, J = 8 Hz), 7.41 (d, 2H), 7.26 (d, 2H, J = 12 Hz), 3.79 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.2, 150.9, 133.9, 130.3, 129.4, 129.2, 128.8, 127.6, 122.7, 117.8, 23.9.

*Synthesis and Spectral Data of 4-(Cyanomethyl)phenyl Acetate (**7**).*[37] In an oven-dried 50 mL RB flask, 4-hydroxyphenylacetonitrile (3 mmol, 399 mg) and sodium hydroxide (3.5 mmol, 140 mg) were dissolved in 5 mL of THF under nitrogen atmosphere and stirred at room temperature for 1 h. Acetyl chloride (3 mmol, 210 μL) was dissolved in 5 mL of THF and added dropwise to the RB flask containing aliquot and allowed to stir at room temperature for 10 h. After completion of the reaction the solvent was evaporated and extracted from water and dichloromethane. The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. After that the crude reaction mixture was purified by column chromatography using *n*-hexane and ethyl acetate as an eluant. Yield (80%, 420 mg). ^1H NMR ($CDCl_3$): δ 7.30 (d, 2H, J = 8 Hz), 7.08 (d, 2H, J = 8 Hz), 3.69 (s, 2H), 2.28 (s, 3H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.2, 150.3, 129.0, 127.5, 122.3, 117.7, 22.9, 20.9.

Procedure for Intermolecular Chemoselective Catalytic Hydroboration. 4-Methoxy benzonitrile (1 mmol), pinacolborane (2.1 mmol), phenethyl benzoate (1 mmol), and $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol %, 0.01 mmol, 6.1 mg) were taken in a PTFE screw-capped reaction vial equipped with a magnetic bar, and the reaction mixture was stirred at 60 °C for 15 h. Reaction progress was monitored by ^1H NMR analyses, which clearly indicated the complete conversion of nitrile to diboryl amines and the presence of unreacted phenethyl benzoate.

*Synthesis and Spectral Data of 4-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)amino)ethyl)phenyl Benzoate (**8**).* 4-(Cyanomethyl)phenyl benzoate (1 mmol), pinacolborane (2.1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol %), and toluene (1 mL) were taken in a PTFE screw-capped reaction vial equipped with a magnetic bar, and the reaction mixture was stirred at 60 °C for 15 h. Progress of the reaction was monitored by ^1H NMR. IR (DCM): 2972, 1733, 1423, 1364, 1226, 1198, 1126, 967, 902, 852, 729, 652 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.19−8.21 (m, 2H), 7.63 (t, 1H, J = 8 Hz), 7.51 (t, 3H, J = 8 Hz), 7.25 (d, 1H, J = 4 Hz), 7.23 (s, 1H), 7.10 (d, 2H, J = 8 Hz), 3.31 (t, 2H, J = 8 Hz), 2.74 (t, 2H, J = 8 Hz), 1.20 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.3, 149.2, 138.3, 133.5, 130.3, 130.3, 128.6, 121.3, 82.3, 45.2, 39.0, 24.6. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25.1 (s, *B*-N). HRMS (EI) m/z calcd for $C_{15}H_{16}NO_2$: $(M+H^+)$ 242.1181, found: 242.1173.

*Synthesis and Spectral Data of 4-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)amino)ethyl)phenyl Acetate (**9**).* 4-(Cyanomethyl)phenyl acetate (1 mmol), pinacolborane (2.1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol %, 0.01 mmol, 6 mg), and toluene (1 mL) were taken in a PTFE screw-capped reaction vial equipped with a magnetic bar, and the reaction mixture was stirred at 60 °C for 15 h. Progress of the reaction was monitored by ^1H NMR. IR (DCM): 2983, 2873, 1741, 1449, 1363, 1259, 1138, 1032, 995, 752, 721, 653 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.26−7.30 (m, 4H), 3.31−3.34 (m, 2H), 2.72−2.75 (m, 2H), 2.29 (s, 3H), 1.21 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.7, 148.9, 137.6, 130.2, 125.4, 82.2, 45.1, 38.8, 24.6, 21.2. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 24.9 (s, *B*-N). HRMS (EI) m/z calcd for $C_{10}H_{11}O_2$ (Fragment): $(M\text{-}C_{12}H_{24}B_2O_4)^+$ 163.0759, found: 163.0741.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02122

Single-crystal X-ray data and ORTEP diagram of diboronate amine **4g** (CCDC 1477230) (CIF)

Copies of NMR (^1H and ^{13}C) spectra of compounds **4a−4o**, **5a−5j**, **6−9**, mass spectra of compounds **4a−4o**, **5a−5j**, **8−9**, and reaction intermediates **IV**/**II′** and **IV′** (PDF)

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Notes

The authors declare no competing financial interest.

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