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Report

Frustrated Lewis pairs, B-H bond activation, Hydroboration, Stable borane adducts, Alkenes

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$B(C_6F_5)_3$-Catalyzed Hydroboration of Alkenes with *N*-Heterocyclic Carbene Boranes via B-H Bond Activation

Qiaotian Wang,[a,b] Wei Meng,[a,b] Xiangqing Feng,*[a,b] and Haifeng Du*[a,b]

[a] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190*
[b] *University of Chinese Academy of Sciences, Beijing 100049*

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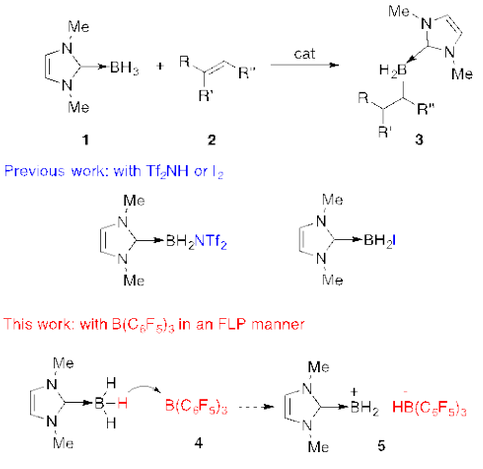
Summary of main observation and conclusion In this work, a novel mode for the activation of N-heterocyclic carbene boranes (NHC-boranes) was developed by generating the highly reactive zwitterion species through hydride abstraction with Lewis acid $B(C_6F_5)_3$ in an FLP manner. A broad range of alkenes including stilbenes, β-methylstyrenes, styrenes, and alkyl-alkenes were suitable substrates for the $B(C_6F_5)_3$-catalyzed hydroboration to furnish the desired products in good to high yields. Significantly, excellent regioselectivities were obtained in some cases. Mechanistic studies indicate that the B-H bond cleavage is likely involved in the rate-determined step. In addition, an electrophilic addition of NHC-borenium cation to alkenes and the subsequent formation of carbocation are also postulated. The current work provides a promising method for the activation of stable borane adducts, which might lead some interesting transformations in the future.

Background and Originality Content

Organoboron compounds possess an extremely broad application in synthetic chemistry, material science, life and health science, and so on.[1] The construction of C-B bonds has attracted considerable attention, and a great advance has been made in this field.[2] Notably, the hydroboration of alkenes represents one of the most efficient and straightforward approaches for the synthesis of organoboron compounds.[3] Numerous boron reagents have been well developed for the hydroboration, which can be categorized into free boranes and borane adducts with weak or strong Lewis bases. Traditional borane adducts with weak Lewis bases, such as diethyl ether, tetrahydrofuran and dimethyl sulfide, generally exhibited a high reactivity for the hydroboration of alkenes due to the easy release of borane from the complexes. However, the forming C-B bond is usually labile. A variety of stable borane complexes have been developed by means of amines, phosphines, and N-heterocyclic carbenes as Lewis bases.[4] The relatively high stability of borane complexes own and the resulting C-B bonds after hydroborations make them one class of very attractive boron reagents.

N-heterocyclic carbene boranes (NHC-boranes) are tetravalent and neutral borane complexes, which have been widely used as reactants, reagents, initiators, or catalysts in organic synthesis and polymer chemistry.[5-9] However, they are inert as boron reagents toward the hydroboration of alkenes due to their difficult decomplexation. The development of novel activation modes for NHC-boranes is therefore essential to accomplish the desired hydroboration. In 2012, Vedjes, Curran, and co-workers reported the first hydroboration of alkenes **2** with NHC-borane **1** using Tf_2NH as catalyst to furnish dihydroborated products (Scheme 1).[10] It is noteworthy that the hydroboration does not occur even under harsh conditions without catalyst. NHC-borenium cation was postulated as the reactive species, which were formed by a H_2-release reaction of NHC-borane **1** and Tf_2NH (Scheme 1). Later on, Curran and co-workers employed diiodine as activator to form covalent boryl iodide species, which was also effective for the hydroboration of alkenes to afford stable products **3** (Scheme 1).[11] Moreover, Parrain and co-workers disclosed an asymmetric intramolecular hydroboration with chiral rhodium catalysts.[12] Despite these advances, exploring new and highly efficient activation modes for NHC-boranes is still of great interest.



Scheme 1 Previous work and our proposal on the hydroboration of alkenes with NHC-boranes

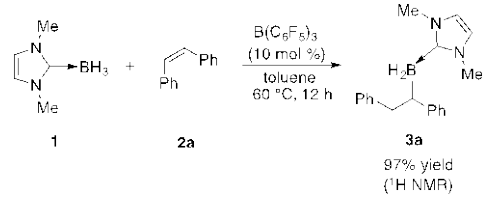
The chemistry of frustrated Lewis pairs (FLPs) has undergone a rapid growth in the past decade, which provides a powerful tool to activate a wide range of chemical bonds in a cooperative manner.[13,14] As our general interest in the FLP catalysis, we have been devoting our efforts on the activation of H-H, Si-H, and B-H bonds.[15] In 2015, our group reported a $B(C_6F_5)_3$-catalyzed transfer hydrogenation of pyridines with ammonia borane.[16] The activation of ammonia borane was supposed to be in an FLP manner. Later, Shi and co-workers reported a very similar work on the transfer hydrogenation of some N-heterocycles.[17] In 2016, Ingleson and co-workers described a $B(C_6F_5)_3$-catalyzed *trans*-hydroboration of alkynes with NHC-(9-BBN) borane.[18] Based on the previous work, we envisioned that NHC-boranes **1** might be

*E-mail: fxq@iccas.ac.cn; haifengdu@iccas.ac.cn

activated by $B(C_6F_5)_3$ with the assistance of NHC to generate zwitterion **5**, which was likely a reactive species for the hydroboration of alkenes (Scheme 1). Herein, we wish to report our efforts on this subject.

Results and Discussion

The hydroboration of *cis*-stilbene **2a** with NHC-borane **1** was initially examined with $B(C_6F_5)_3$ (10 mol %) in toluene at 60 °C for 12 h (Scheme 2). It was pleased to find that this reaction went smoothly to afford the desired borane product **3a** in 97% yield (^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard).



Scheme 2 Initial study on the hydroboration of *cis*-stilbene

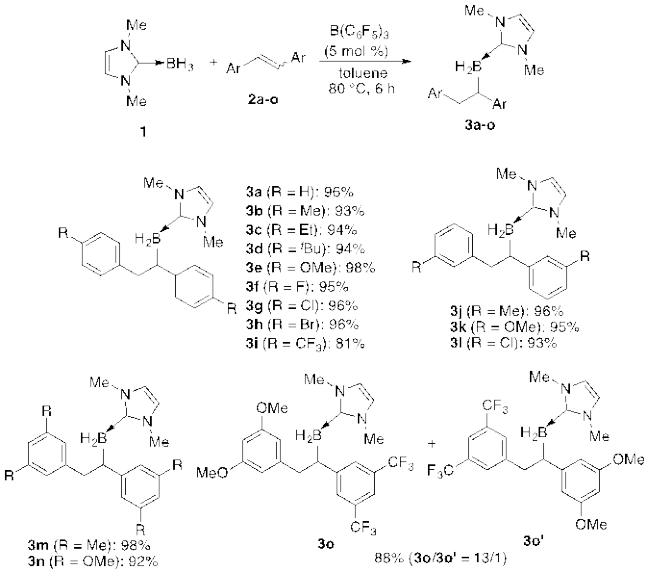
Table 1 Optimization of reaction conditions for the hydroboration of *cis*-stilbene[a].

Entry	$B(C_6F_5)_3$ (mol %)	Solvent	Conc. (M)	Temp. (°C)	Time (h)	Yield (%)[b]
1	10	toluene	0.1	60	12	97
2[c]	10	toluene	0.1	60	12	trace
3	5	toluene	0.1	60	12	47
4	5	toluene	0.1	80	12	95
5	1	toluene	0.1	80	12	trace
6	5	toluene	0.2	80	6	99
7	2.5	toluene	0.2	80	6	trace
8[d]	5	toluene	0.2	80	6	trace
9	5	DCM	0.2	80	6	39
10	5	*n*-hexane	0.2	80	6	81
11	5	cyclohexane	0.2	80	6	60

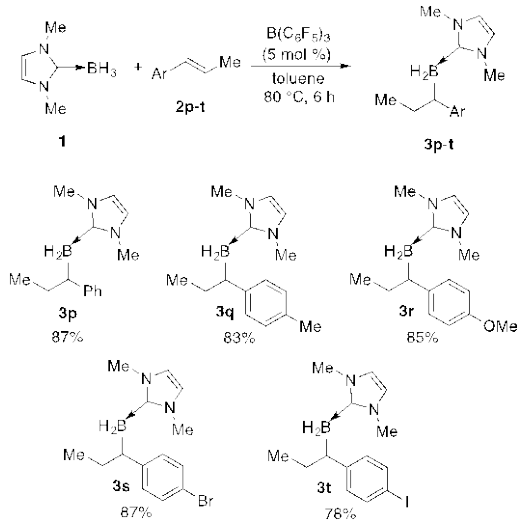
[a] (All reactions were carried out with **2a** (0.1 mmol), NHC-borane **1** (0.15 mmol), with $B(C_6F_5)_3$ (0.01 mmol) in solvent (1.0 mL) unless otherwise noted.) [b] (It was determined by crude ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.) [c] (Borane Lewis acid generated from pentafluorostyrene and $HB(C_6F_5)_2$ was used.) [d] (^{t}Bu$_3$P (5 mol %) was added as Lewis base.)

The reaction condition was next optimized. As shown in Table 1, when a borane Lewis acid generated *in situ* from pentafluorostyrene and Piers' borane $HB(C_6F_5)_2$ was employed as catalyst, no reaction occurred at all (entry 2). Lowering the loading amount of $B(C_6F_5)_3$ to 5 mol % resulted in a dramatic drop of yield (entry 3). Raising the temperature to 80 °C gave a satisfactory yield (entry 4). Further reducing the amount of catalyst to 1 mol %, no product was observed (entry 5). With the reaction concentration of 0.2 M, the reaction time can be shortened to 6 h (entry 6). Less $B(C_6F_5)_3$ (2.5 mol %) could not promote this reaction (entry 7). Additional Lewis base ^{t}Bu$_3$P (5 mol %) would inhibit the hydroboration completely by trapping $B(C_6F_5)_3$ (entry 8). Solvents were found to have an obvious influence on the reactivity, and toluene proven to be the optimal one (entries 6 vs 9-11).

Due to the similar reactivity of *cis*- and *trans*-isomers, a variety of stilbenes **2** were subjected as a mixture of *cis*- and *trans*-isomers to the $B(C_6F_5)_3$-catalyzed hydroboration with NHC borane **1** under the optimal conditions. As shown in Scheme 3, all these reactions proceeded well to produce the desired boranes **3a-n** in 81-98% yields. Both electron-donating and withdrawing substituents on the phenyl groups were well tolerated for this hydroboration. When unsymmetrical stilbene **2o** was employed as a substrate, a highly regioselective hydroboration occurred to give borane **3o** as the major product with a ratio of 13/1. The boron atom preferred to be added at the carbon atom adjacent to the electron-deficient phenyl moieties.



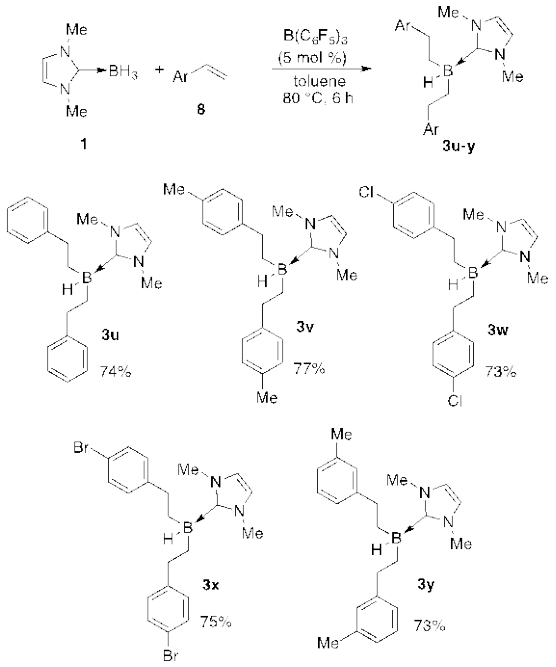
Scheme 3 $B(C_6F_5)_3$-catalyzed hydroboration of stilbenes



Scheme 4 $B(C_6F_5)_3$-catalyzed hydroboration of β-methylstyrenes

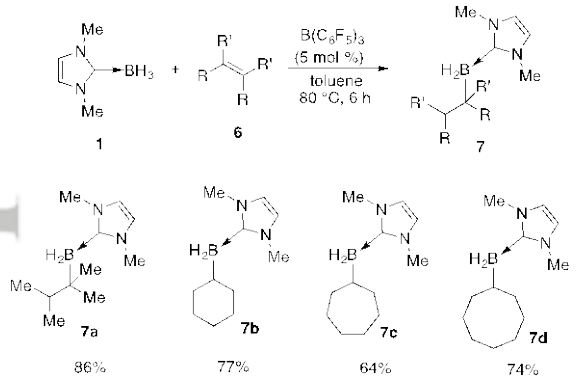
β-Methylstyrenes **2p-t** were next employed as substrates for the hydroboration. As shown in Scheme 4, all these reactions went smoothly to afford products **3p-t** in 78-87% yields. Interestingly, the hydroboration occurred with excellent regioselectivities and the other isomers were not observed. A preliminary DFT calculation suggests that compounds **3p-t** were thermodynamic products (see Supporting Information). We then turned our attention to the hydroboration of styrenes **2u-y** (Scheme 4). Distinct from the aforementioned substrates, a dihydroboration reaction occurred to give the corresponding products **3u-y** in 73-77% yields. In comparison with the unstable dihydroborated products obtained in the reported work[10], the obtained dihydroborated products were stable enough and could

be isolated through chromatography on silica gel.



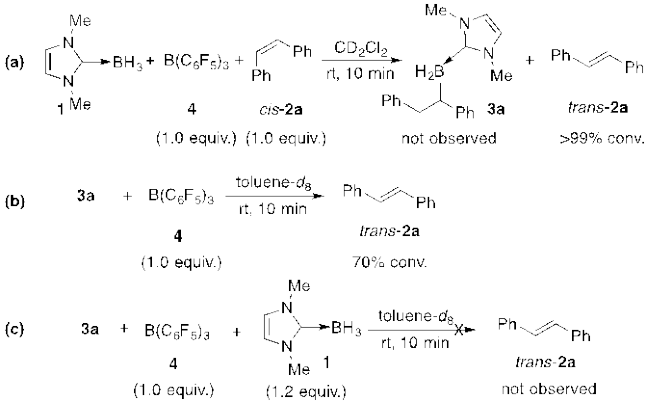
Scheme 5 $B(C_6F_5)_3$-catalyzed hydroboration of styrenes

In addition, alkyl-alkenes were also investigated for the hydroboration reaction. As shown in Scheme 6, tetramethylethene (**6a**) was an effective substrate for this reaction to afford the desired product **7a** in 86% yield. The hydroboration of cyclic alkenes **6b-d** also proceeded well to furnish products **7b-d** in 64-77% yields.

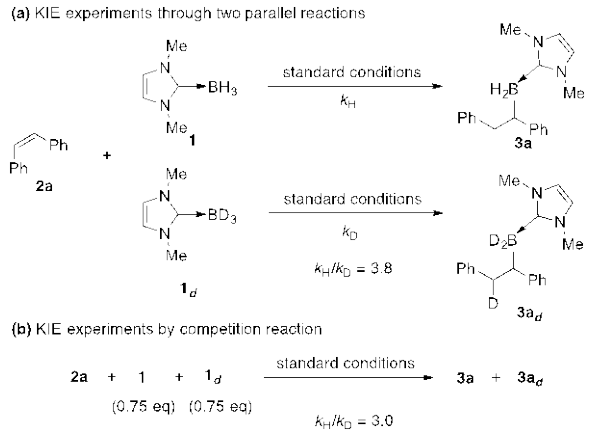


Scheme 6 $B(C_6F_5)_3$-catalyzed hydroboration of alkyl olefins

The mixture of $B(C_6F_5)_3$ and NHC-BH_3 (**1**) (1 equiv.) in 0.5 mL CD_2Cl_2 was heated at 80 °C for 6 h, to which one equivalent amount of *cis*-stilbene (*cis*-**2a**) was added, to our surprise, instead of the desired hydroboration, an isomerization reaction occurred rapidly to afford *trans*-stilbene (*trans*-**2a**) (Scheme 7a). A further ^1H NMR study was therefore performed by mixing compound **3a** and $B(C_6F_5)_3$ together in toluene-d_8. It was found that a retrohydroboration reaction happened to afford *trans*-stilbene (Scheme 7b). Interestingly, when NHC-borane **1** was introduced to the mixture, the retrohydroboration process was inhibited (Scheme 7c). These results indicate that $B(C_6F_5)_3$ likely promotes the retrohydroboration reaction and the excess amount of NHC-borane probably inhibits this process through an interaction with $B(C_6F_5)_3$.[19]



Scheme 7 Control experiments on the hydroboration of *cis*-stilbene



Scheme 8 KIE studies on the hydroboration of *cis*-stilbene

Kinetic studies were next performed to understand the hydroboration process. Significant kinetic isotope effects (KIE, k_H/k_D = 3.8 and 3.0, respectively) were observed for the hydroboration of *cis*-stilbene (**2a**) with NHC-boranes **1** and $\mathbf{1}_d$ through both parallel and completion reactions (Scheme 8), suggesting that the B-H bond cleavage is probably involved in the rate-determining step.[20]

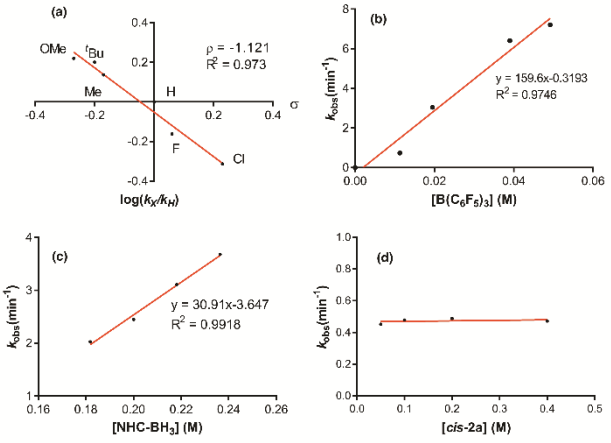


Figure 1 Kinetic studies.

(a) Hammett plot of different stilbenes. (b) Plot of kobs against the concentration of $B(C_6F_5)_3$. (c) Plot of kobs against the concentration of NHC-borane **1**. (d) Plot of kobs against the concentration of *cis*-stilbene

(**2a**).

Hammett studies were further carried out, and a negative slope (ρ = -1.121) was obtained (Figure 1a). It is indicated that the electrophilic addition of NHC-borenium cation to alkenes and the subsequent formation of carbocation are likely involved in the hydroboration. The plot of k_{obs} against [$B(C_6F_5)_3$] or [NHC-BH_3] was found to be a straight line as shown in Figures 1b and 1c, suggesting the hydroboration is first-order kinetics in both $B(C_6F_5)_3$ catalyst and NHC-borane. In addition, as shown in Figure 1d, hydroborations with different amounts of *cis*-stilbene were found to have similar reaction rates, indicating zero-order kinetics in substrate **2a**. These kinetic results provide an additional support for the involving of the B-H bond cleavage in the rate-determined step.

Based on all the experimental and mechanistic results, a plausible catalytic cycle is outlined in Figure 2. In cycle **A**, Lewis acid $B(C_6F_5)_3$ (**4**) activates NHC-borane **1** through a hydride abstraction in an FLP manner to form zwitterion **5**. An electrophilic addition of NHC-borenium cation to alkenes occurs to generate zwitterion **8** composed of carbocation and $HB^-(C_6F_5)_3$. After the hydride transfer, product **3** is formed, and $B(C_6F_5)_3$ catalyst is regenerated to complete the catalytic cycle. An alternative pathway via the direct hydride-transfer from NHC-borane **1** to zwitterion **8** is also proposed (cycle **B**), in which $B(C_6F_5)_3$ acts as an initiator instead of a catalyst. A control experiment for the hydroboration of *cis*-stilbene **2a** with [Ph_3C][$B(C_6F_5)_4$] (5 mol %) gave the desired product in a full conversion, which provides a support for this pathway.[21]

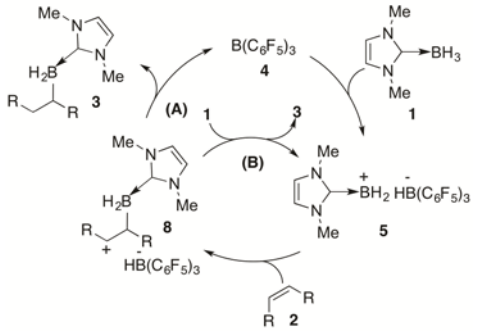


Figure 2 Plausible catalytic cycle.

Conclusions

A hydroboration of alkenes with stable NHC-borane has been achieved using $B(C_6F_5)_3$ as catalyst. A quite wide range of alkenes, including stilbenes, β-methylstyrenes, styrenes, and alkyl-alkenes, were all suitable substrates for the hydroboration to furnish the desired products in 64-98% yields. Notably, excellent regioselectivities were obtained for the hydroboration of β-methylstyrenes, and dihydroboration occurred for the styrene substrates. Mechanistic studies indicate that the activation of NHC-borane with $B(C_6F_5)_3$ is likely through a hydride abstraction in an FLP manner to form the reactive zwitterion species. KIE and kinetic studies suggest that the B-H cleavage is probably involved in the rate-determined step, and the electrophilic addition of borenium cation to alkenes and the formation of carbocation may be involved in the hydroboration. The current work provides a novel mode for the activation of stable borane adducts. Further efforts on the activation of B-H bond and the asymmetric hydroboration with chiral boron Lewis acids are underway in our laboratory.

Experimental

General information

All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on Bruker AV 400 and Bruker AV 500 at ambient temperature with $CDCl_3$, CD_2Cl_2 and toluene-d_8 as solvent and TMS as internal standard. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of TMS (0) or to the carbon resonance of the $CDCl_3$ (77.23). Coupling constants (*J*) were given in Hertz (Hz). All solvents were purified by conventional methods, distilled before use. Commercially available reagents were used without further purification. All the substrates were synthesized according to reported method.

General procedure for the hydroboration of stilbenes or alkyl olefins (Scheme 3 or 6)

To a sealed-tube were added stilbenes **2** or alkyl olefins **6** (0.5 mmol), $B(C_6F_5)_3$ (0.0128 g, 0.025 mmol), NHC-BH_3 (**1**) (0.0825 g, 0.75 mmol) and dry toluene (2.5 mL) in a nitrogen atmosphere glovebox. After being sealed, the resulting mixture was stirred at 80 °C for 6 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under vacuum. The crude residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (10/1, v/v) as the fluent to give the desired products **3a-o** and **7**.

General procedure for the hydroboration of β-methylstrenes (Scheme 4)

To a sealed-tube were added β-methylstrenes **2p-t** (0.6 mmol), $B(C_6F_5)_3$ (0.0128 g, 0.025 mmol), NHC-BH_3 (**1**) (0.0550 g, 0.5 mmol) and dry toluene (2.5 mL) in a nitrogen atmosphere glovebox. After being sealed, the resulting mixture was stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. The crude residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (10/1, v/v) as the fluent to give the desired products **3p-t**.

General procedure for the hydroboration of styrenes (Scheme 5)

To a sealed-tube were added styrenes **2u-y** (1.2 mmol), $B(C_6F_5)_3$ (0.0128 g, 0.025 mmol), NHC-BH_3 (**1**) (0.0550 g, 0.5 mmol) and dry toluene (2.5 mL) in a nitrogen atmosphere glovebox. After being sealed, the resulting mixture was stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. The crude residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (10/1, v/v) as the fluent to give the desired products **3u-y**.

Characterization of products

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1,2-diphenylethyl)dihydroborate (**3a**): white solid, 0.1408 g, 96% yield, m.p. 106-109 °C; IR (film): 3020, 2920, 2850, 2286, 1596, 1488 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.19-7.08 (m, 4H), 7.05-6.95 (m, 3H), 6.89-6.77 (m, 2H), 6.62 (s, 2H), 3.33 (s, 6H), 3.24-3.04 (m, 2H), 2.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 153.6, 145.5, 128.9, 127.6, 127.5, 126.8, 124.6, 122.5, 119.9, 42.7, 35.5; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.6 (t, J_{B-H} = 86.9 Hz); HRMS (ESI) calcd. for $C_{19}H_{23}N_2BNa$ [M+Na]$^+$: 313.1847, Found: 313.1850.

(1,2-Di-*p*-tolylethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3b**): white solid, 0.1493 g, 93% yield, m.p. 81-83 °C; IR (film): 2920, 2286, 1508, 1265, 1065 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.04 (d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 2H), 3.34 (s, 6H), 3.17-2.95 (m, 2H), 2.25 (s, 1H), 2.22 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 150.4, 142.4, 133.6, 131.3, 128.7, 128.3, 128.1, 126.6, 119.9, 42.3, 35.5, 21.0, 20.9; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.7 (t, J_{B-H} = 86.7 Hz); HRMS (ESI) calcd. for

$C_{21}H_{27}N_2BNa$ [M+Na]$^+$: 341.2160, Found: 341.2159.

(1,2-Bis(4-ethylphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydrobor-ate (**3c**): white solid, 0.1641 g, 94% yield, m.p. 101-103 °C; IR (film): 2961, 2920, 2289, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.09 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.60 (s, 2H), 3.31 (s, 6H), 3.21-2.99 (m, 2H), 2.60-2.40 (m, 4H), 2.27 (s, 1H), 1.23-1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.8, 142.8, 140.1, 138.1, 128.7, 127.1, 126.9, 126.6, 119.9, 42.2, 35.4, 28.4, 28.3, 16.1, 15.7; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.7 (t, J_{B-H} = 89.3 Hz); HRMS (ESI) calcd. for $C_{23}H_{31}N_2BNa$ [M+Na]$^+$: 369.2473, Found: 369.2473.

(1,2-Bis(4-(*tert*-butyl)phenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)di-hydroborate (**3d**): white solid, 0.1897 g, 94% yield, m.p. 79-82 °C; IR (film): 3449, 2961, 2286, 1477, 1267, 1066 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.17-7.00 (m, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.42 (s, 2H), 3.15 (s, 6H), 3.13-2.88 (m, 2H), 2.20 (s, 1H), 1.16 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.8, 145.9, 143.9, 141.5, 127.4, 125.0, 123.4, 123.2, 118.8, 40.7, 34.2, 33.1, 33.0, 30.6, 30.4; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.5 (t, J_{B-H} = 86.2 Hz); HRMS (ESI) calcd. for $C_{27}H_{38}N_2B$ [M-H]$^-$: 401.3134, Found: 401.3126.

(1,2-Bis(4-methoxyphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate (**3e**): yellow oil, 0.1719 g, 98% yield, IR (film): 3448, 1652, 1264, 1119 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.04 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 3.68(9) (s, 3H), 3.68(6) (s, 3H), 3.36 (s, 6H), 3.02 (d, *J* = 7.5 Hz, 2H), 2.19 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 156.8, 155.5, 145.6, 137.7, 129.6, 127.5, 120.0, 113.0, 112.9, 55.2, 55.1, 42.3, 35.5; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.9 (t, J_{B-H} = 86.5 Hz); HRMS (ESI) calcd. for $C_{21}H_{27}O_2N_2BNa$ [M+Na]$^+$: 373.2058, Found: 373.2055.

(1,2-Bis(4-fluorophenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate (**3f**): yellow solid, 0.1561 g, 95% yield, m.p. 103-106 °C; IR (film): 2921, 2849, 2286, 1503, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.12-6.97 (m, 2H), 6.85-6.67 (m, 6H), 6.66 (s, 2H), 3.39 (s, 6H), 3.15-2.93 (m, 2H), 2.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.2 (d, J_{C-F} = 118.7 Hz), 158.8 (d, J_{C-F} = 116.5 Hz), 148.6 (d, J_{C-F} = 2.9 Hz), 140.7, 129.9 (d, J_{C-F} = 7.4 Hz), 127.7 (d, J_{C-F} = 7.1 Hz), 120.1, 114.2 (d, J_{C-F} = 20.6 Hz), 114.0 (d, J_{C-F} = 20.3 Hz), 42.4, 35.5; ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -119.6, -119.2; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -23.0 (t, J_{B-H} = 86.9 Hz); HRMS (APCI) calcd. for $C_{19}H_{22}N_2BF_2$ [M+H]$^+$: 327.1839, Found: 327.1839.

(1,2-Bis(4-chlorophenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate (**3g**): white solid, 0.1727 g, 96% yield, m.p. 113-115 °C; IR (film): 2920, 2850, 2286, 1488, 1265, 1090 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.13-7.01 (m, 4H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 2H), 3.39 (s, 6H), 3.17-2.86 (m, 2H), 2.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.7, 143.5, 130.2, 130.1, 128.1, 127.8, 127.7, 127.5, 120.1, 42.2, 35.6; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.8 (t, J_{B-H} = 88.0 Hz); HRMS (ESI) calcd. for $C_{19}H_{20}N_2BCl_2$ [M-H]$^-$: 357.1102, Found: 357.1099.

(1,2-Bis(4-bromophenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate (**3h**): white solid, 0.2157 g, 96% yield, m.p. 135-137 °C; IR (film): 3056, 2307, 1485, 1266 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 6.68 (s, 2H), 3.39 (s, 6H), 3.15-2.90 (m, 2H), 2.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 152.2, 143.9, 130.6, 130.5, 130.4, 128.6, 120.1, 118.4, 115.7, 42.1, 35.6; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.8 (t, J_{B-H} = 88.6 Hz); HRMS (ESI) calcd. for $C_{19}H_{20}N_2BBr_2$ [M-H]$^-$: 445.0092, Found: 445.0101.

(1,2-Bis(4-(trifluoromethyl)phenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3i**): white solid, 0.1730 g, 81% yield, m.p. 121-123 °C; IR (film): 3389, 2920, 2848, 2325, 1325, 1109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.33-7.14 (m, 4H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.70 (s, 2H), 3.37 (s, 6H), 3.20 (d, *J* = 7.6 Hz, 2H), 2.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 157.8, 148.9, 128.9, 127.1 (q, J_{C-F} = 32.1 Hz), 126.6, 125.0 (q, J_{C-F} = 32.0 Hz), 124.8 (q, J_{C-F} = 271.7 Hz), 124.7 (q, J_{C-F} = 272.2 Hz), 124.6 (q, J_{C-F} = 3.8 Hz),124.4 (q, J_{C-F} = 3.5 Hz), 120.2, 42.2, 35.5; ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -61.7, -62.1; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -22.6 (t, J_{B-H} = 87.4 Hz); HRMS (ESI) calcd. for $C_{21}H_{20}N_2BF_6$ [M-H]$^-$: 425.1629, Found: 425.1639.

(1,2-Di-*m*-tolylethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3j**): white solid, 0.1544 g, 96% yield, m.p. 75-77 °C; IR (film): 3021, 2920, 2286, 1601, 1481, 1265 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.96-6.85 (m, 3H), 6.84-7.77 (m, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.0 Hz, 1H), 6.57-6-51 (m, 2H), 6.46 (s, 2H), 3.21 (s, 6H), 3.11-2.86 (m, 2H), 2.18 (s, 1H), 2.15 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 153.7, 145.5, 136.8, 136.5, 129.8, 127.7, 127.5, 127.4, 125.9, 125.4, 123.8, 123.2, 119.9, 42.6, 35.4, 21.5(7), 21.5(5); ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.9 (t, J_{B-H} = 86.9 Hz); HRMS (ESI) calcd. for $C_{21}H_{27}N_2BNa$ [M+Na]$^+$: 341.2160, Found: 341.2159.

(1,2-Bis(3-methoxyphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate (**3k**): colorless oil, 0.1669 g, 95% yield, IR (film): 2920, 2850, 2288, 1596, 1482, 1264, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.01-6.97 (m, 1H), 6.94-6.85 (m, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 6.57 (s, 2H), 6.56-6.52 (m, 2H), 6.47-6.34 (m, 3H), 3.65 (s, 3H), 3.63 (s, 3H), 3.32 (s, 6H), 3.17-3.00 (m, 2H), 2.29 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 159.2, 159.1, 155.4, 147.1, 128.5, 128.2, 121.4, 120.0, 119.6, 114.4, 112.3, 110.2, 108.0, 55.0, 54.9, 42.8, 35.5; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.7 (t, J_{B-H} = 87.2 Hz); HRMS (ESI) calcd. for $C_{21}H_{27}O_2N_2Na$ [M+Na]$^+$: 373.2058, Found: 373.2058.

(1,2-Bis(3-chlorophenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl) dihydro-borate (**3l**): yellow oil, 0.1675 g, 93% yield, IR (film): 3057, 2928, 2850, 2286, 1076 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.05 (s, 1H), 7.00-6.88 (m, 3H), 6.88-6.81 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.55 (s, 2H), 3.29 (s, 6H), 2.98 (d, *J* = 7.6 Hz, 2H), 2.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.6, 147.0, 133.4, 133.2, 128.9, 128.8, 128.7, 127.1, 126.7, 125.0, 124.9, 122.7, 120.2, 42.3, 35.5; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -23.0 (t, J_{B-H} = 87.7 Hz); HRMS (APCI) calcd. for $C_{19}H_{22}N_2BCl_2$ [M+H]$^+$: 359.1248, Found: 359.1249.

(1,2-Bis(3,5-dimethylphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl) dihydroborate (**3m**): white solid, 0.1705 g, 98% yield, m.p. 129-131 °C; IR (film): 2914, 2285, 1595, 1479, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.80 (s, 2H), 6.66 (s, 1H), 6.59 (s, 2H), 6.51 (s, 1H), 6.45 (s, 2H), 3.33 (s, 6H), 3.13-2.88 (m, 2H), 2.24 (s, 1H), 2.20 (s, 6H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.8, 142.8, 140.1, 138.1, 128.7, 127.1, 126.9, 126.6, 119.9, 42.2, 35.4, 28.4, 28.3, 16.1, 15.7; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -23.0 (t, J_{B-H} = 86.8 Hz); HRMS (ESI) calcd. for $C_{23}H_{31}N_2BNa$ [M+Na]$^+$: 369.2473, Found: 369.2475.

(1,2-Bis(3,5-dimethoxyphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl) dihydroborate (**3n**): yellow oil, 0.1906 g, 92% yield, IR (film): 2937, 2316, 1591, 1147 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.63 (s, 2H), 6.35 (s, 2H), 6.14 (s, 1H), 6.04 (s, 2H), 6.01 (s, 1H), 3.66 (s, 6H), 3.62 (s, 6H), 3.39 (s, 6H), 3.16-2.94 (m, 2H), 2.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.1, 156.4, 147.8, 120.0, 106.9, 104.8, 97.0, 95.1, 55.0(9), 55.0(7), 43.0, 35.5; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.9 (t, J_{B-H} = 85.5 Hz); HRMS (ESI) calcd. for $C_{23}H_{31}O_4N_2BNa$ [M+Na]$^+$: 433.2269, Found: 433.2266.

(1-(3,5-Bis(trifluoromethyl)phenyl)-2-(3,5-dimethoxyphenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3o**): colorless oil, 0.2147 g, 88% yield, IR (film): 2955, 2839, 2294, 1595, 1277, 1128 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39 (s, 1H), 7.26 (s, 2H), 6.70 (s, 2H), 6.26 (s, 2H), 6.16 (s, 1H), 3.66 (s, 6H),

3.42 (s, 6H), 3.14-3.00 (m, 2H), 2.48 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 159.3, 155.4, 145.5, 129.2 (q, J_{C-F} = 32.9 Hz), 125.7, 122.8 (q, J_{C-F} = 270.9 Hz), 119.3, 115.1 (q, J_{C-F} = 3.8 Hz), 105.7, 96.4, 54.0, 41.5, 34.5; ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -62.7; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.5 (t, J_{B-H} = 90.2 Hz); HRMS (ESI) calcd. for $C_{23}H_{24}BF_6N_2O_2$ $[M-H]^-$: 485.1841, Found: 485.1826.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-phenylpropyl)dihydroborate (**3p**): white solid, 0.0995 g, 87% yield, m.p. 81-84 °C; IR (film): 3448, 2306, 1617, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.03-6.89 (m, 2H), 6.86-6.76 (m, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 2H), 3.28 (s, 6H), 1.84-1.63 (m, 3H), 0.83 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.6, 127.5, 126.7, 122.2, 119.9, 35.4, 29.3, 14.8; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -23.0 (t, J_{B-H} = 86.5 Hz); HRMS (ESI) calcd. for $C_{14}H_{21}N_2BNa$ $[M+Na]^+$: 251.1690, Found: 251.1691.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(*p*-tolyl)propyl)dihydroborate (**3q**): yellow oil, 0.1005 g, 83% yield, IR (film): 3449, 2951, 2275, 1266 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.85 (d, *J* = 7.5 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 2H), 6.67 (s, 2H), 3.37 (s, 6H), 2.23 (s, 3H), 1.87-1.67 (m, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 150.2, 130.2, 127.1, 125.5, 118.8, 34.5, 28.4, 19.8, 13.7; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -23.1 (t, J_{B-H} = 86.1 Hz); HRMS (ESI) calcd. for $C_{15}H_{23}N_2BNa$ $[M+Na]^+$: 265.1847, Found: 265.1845.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(4-methoxyphenyl)propyl)dihydro-borate (**3r**): yellow oil, 0.1101 g, 85% yield, IR (film): 3446, 2275, 1636, 1266 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.71 (d, *J* = 8.5 Hz, 2H), 6.67 (s, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 3.85-3.71 (m, 1H), 3.74 (s, 3H), 3.40 (s, 6H), 1.75 (s, 2H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 154.4, 145.6, 126.3, 118.8, 112.0, 54.3, 34.5, 28.7, 13.7; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -23.2 (t, J_{B-H} = 86.1 Hz); HRMS (ESI) calcd. for $C_{15}H_{23}ON_2BNa$ $[M+Na]^+$: 281.1796, Found: 281.1795.

(1-(4-Bromophenyl)propyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3s**): white solid, 0.1329 g, 87% yield, m.p. 101-103 °C; IR (film): 3449, 2951, 2342, 1641, 1265 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 2H), 6.69 (d, *J* = 7.0 Hz, 4H), 3.40 (s, 6H), 1.85-1.65 (m, 3H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 152.8, 129.3, 127.5, 119.0, 114.2, 34.5, 28.3, 13.6; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -23.0 (t, J_{B-H} = 86.9 Hz); HRMS (ESI) calcd. for $C_{14}H_{20}BrN_2BNa$ $[M+Na]^+$: 329.0795, Found: 329.0792.

(1-(4-Iodophenyl)propyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3t**): yellow solid, 0.1389 g, 78% yield, m.p. 85-87 °C; IR (film): 3167, 2948, 2855, 2287, 1479, 1109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 6.51 (d, *J* = 8.4 Hz, 4H), 3.23 (s, 6H), 1.79-1.57 (m, 3H), 0.78 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 153.6, 135.2, 128.1, 119.0, 84.9, 34.5, 28.2, 13.6; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -22.9 (t, J_{B-H} = 86.9 Hz); HRMS (ESI) calcd. for $C_{14}H_{19}N_2BI$ $[M-H]^-$: 353.0681, Found: 353.0677.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)diphenethylhydroborate (**3u**): colorless oil, 0.1177 g, 74% yield, IR (film): 3402, 2329, 1645, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.22-7.15 (m, 2H), 7.15-7.01 (m, 2H), 7.09-7.02 (m, 1H), 7.02-6.94 (m, 2H), 6.88-6.81 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.55 (s, 2H), 3.39 (s, 6H), 2.68-2.50 (m, 1H), 2.23-2.06 (m, 1H), 2.06-1.92 (m, 1H), 1.41-1.28 (m, 3H), 1.20-0.97 (m, 1H), 0.93-0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.4, 148.1, 127.9(3), 127.9(0), 127.3, 125.9, 124.5, 122.2, 120.3, 37.9, 36.0, 20.9; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -14.2 (d, J_{B-H} = 84.4 Hz); HRMS (ESI) calcd. for $C_{21}H_{27}N_2BNa$ $[M+Na]^+$: 341.2160, Found: 341.2161 .

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)bis(4-methylphenethyl)hydroborate (**3v**): colorless oil, 0.1336 g, 77% yield, IR (film): 3374, 2920, 2850, 1645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.09-6.96 (m, 4H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 6.57 (s, 2H), 3.41 (s, 6H), 2.62-2.45 (m, 1H), 2.27 (s, 3H), 2.19 (s, 3H), 2.15-2.04 (m, 1H), 2.02-1.87 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.17-0.95 (m, 1H), 0.93-0.66 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 153.1, 145.2, 133.8, 131.2, 128.6, 127.9, 127.8, 125.9, 120.2, 37.4, 36.0, 21.2, 21.0, 20.8; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -14.3 (d, J_{B-H} = 83.3 Hz); HRMS (ESI) calcd. for $C_{23}H_{31}N_2BNa$ $[M+Na]^+$: 369.2473, Found: 369.2473.

Bis(4-chlorophenethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (**3w**): colorless oil, 0.1405 g, 73% yield, IR (film): 3442, 1636, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 2H), 3.42 (s, 6H), 2.59-2.44 (m, 1H), 2.20-2.08 (m, 1H), 2.01-1.90 (m, 1H), 1.33-1.23 (m, 3H), 1.15-0.95 (m, 1H), 0.84-0.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.9, 145.3, 129.0, 128.2, 126.8, 126.4, 126.2, 119.4, 36.0, 35.0, 19.9; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -14.4 (d, J_{B-H} = 85.0 Hz); HRMS (ESI) calcd. for $C_{21}H_{24}N_2BCl_2$ $[M-H]^-$: 385.1415, Found: 385.1419.

Bis(4-bromophenethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (**3x**): colorless oil, 0.1783 g, 75% yield, IR (film): 3349, 2921, 1645, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 2H), 3.40 (s, 6H), 2.59-2.39 (m, 1H), 2.19-2.05 (m, 1H), 2.00-1.87 (m, 1H), 1.37-1.17 (m, 3H), 1.16-0.91 (m, 1H), 0.85-0.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.5, 145.8, 129.7, 129.1, 128.7, 126.7, 119.4, 117.0, 114.2, 36.1, 35.0, 19.8; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -14.4 (d, J_{B-H} = 84.7 Hz); HRMS (ESI) calcd. for $C_{21}H_{24}N_2BBr_2$ $[M-H]^-$: 473.0405, Found: 473.0402.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)bis(3-methylphenethyl)hydroborate (**3y**): colorless oil, 0.1258 g, 73% yield, IR (film): 3057, 2357, 1265 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.12-7.05 (m, 1H), 6.97-6.91 (m, 2H), 6.90-6.84 (m, 2H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 6.57 (s, 2H), 6.56 (d, *J* = 7.5 Hz, 2H), 3.40 (s, 6H), 2.62-2.49 (m, 1H), 2.28 (s, 3H), 2.16 (s, 3H), 2.15-2.06 (m, 1H), 2.00-1.91 (m, 1H), 1.39-1.28 (m, 3H), 1.16-0.97 (m, 1H), 0.87-0.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 155.2, 147.1, 136.2, 135.3, 127.7, 126.8, 126.1, 125.7, 124.3, 123.9, 121.9, 121.8, 119.1, 36.8, 34.9, 20.4, 19.8; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -14.2 (d, J_{B-H} = 84.6 Hz); HRMS (ESI) calcd. for $C_{23}H_{31}N_2BNa$ $[M+Na]^+$: 369.2473, Found: 369.2469.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)dihydroborate (**7a**): colorless oil, 0.0834 g, 86% yield, IR (film): 2949, 2849, 2275, 1457, 1323, 1139 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.82 (s, 2H), 3.78 (s, 6H), 0.89 (d, *J* = 6.8 Hz, 6H), 0.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.3, 39.8, 36.7, 28.3, 19.0; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -23.8 (t, J_{B-H} = 83.7 Hz); HRMS (ESI) calcd. for $C_6H_{13}O_3N_2BNa$ $[M+Na]^+$: 195.0922, Found: 195.0920.

Cyclohexyl(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**7b**): colorless oil, 0.0738 g, 77% yield, IR (film): 3160, 3111, 2909, 2243, 1479 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.80 (s, 2H), 3.77 (s, 6H), 1.84-0.93 (m, 12H), 0.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 120.0, 36.2, 36.1, 29.1, 27.7; ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ -24.1 (t, J_{B-H} = 83.2 Hz); HRMS (ESI) calcd. for $C_{11}H_{21}N_2BNa$ $[M+Na]^+$: 215.1690, Found: 215.1690.

Cycloheptyl(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**7c**): yellow solid, 0.0663 g, 64% yield, m. p. 63-66 °C; IR (film): 3462, 2906, 2253, 1264 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.74 (s, 2H), 3.70 (s, 6H), 1.67-0.97 (m, 14H), 0.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 120.0, 37.4, 36.1, 29.6, 28.8; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -23.8 (t, J_{B-H} = 83.6 Hz); HRMS (ESI) calcd. for $C_{12}H_{23}N_2BNa$ $[M+Na]^+$: 229.1847, Found: 229.1848.

Cycloctyl(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**7d**): white solid, 0.0818 g, 74% yield, m.p. 48-51 °C; IR (film): 2920, 2275, 1752, 1266, 1086 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.73 (s, 2H), 3.70 (s, 6H), 1.81-1.07 (m, 16H), 0.72 (s, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$, ppm) δ 120.0, 36.1, 34.8, 28.0, 27.7, 26.9; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ -23.7 (t, J_{B-H} = 83.7 Hz); HRMS (ESI) calcd. for $C_{13}H_{24}N_2B$ [M-H]$^-$: 219.2038, Found: 219.2032.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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[21] This possible pathway was raised by one of the reviewers, thanks for this suggestion.

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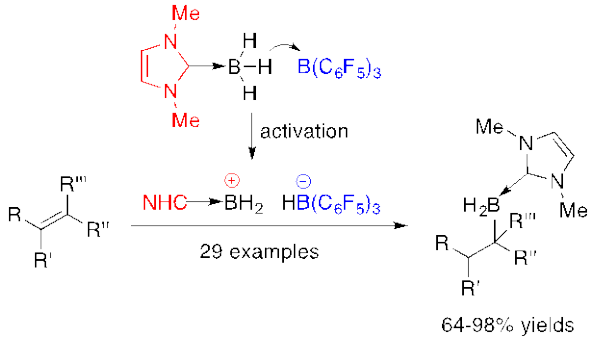
Entry for the Table of Contents

Page No.

$B(C_6F_5)_3$-Catalyzed Hydroboration of Alkenes with N-Heterocyclic Carbene Boranes Via B-H Bond Activation



Qiaotian Wang; Wei Meng; Xiangqing Feng*; Haifeng Du*

$B(C_6F_5)_3$-catalyzed hydroboration of alkenes with N-heterocyclic carbene boranes (NHC-boranes) was successfully realized by the activation of NHC-boranes in an FLP manner for generating the highly reactive zwitterion species to furnish the desired organoboron products in good to high yields.

[a] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190
E-mail: fxq@iccas.ac.cn; haifengdu@iccas.ac.cn

[b] University of Chinese Academy of Sciences, Beijing 100049