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Metal-Free Regio- and Chemoselective Hydroboration of Pyridines Catalyzed by 1,3,2-Diazaphosphenium Triflate

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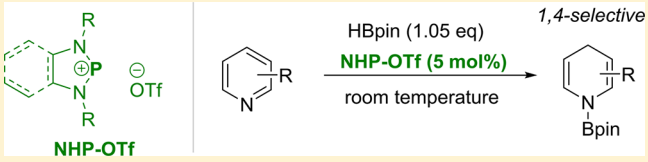
Supporting Information

ABSTRACT: N-Heterocyclic phosphenium triflates (NHP-OTf) **1** serve as efficient catalysts for the regio- and chemoselective hydroboration of pyridines under ambient condition with good functional group tolerance. Mechanistic studies indicate that a boronium salt, $[(Py)_2{\cdot}Bpin]OTf$ **4**, is generated concomitant with NHP-H **5** via hydride abstraction from HBpin by **1** in the initial reaction step. Hydride reduction of the activated pyridine in $[(Py)_2{\cdot}Bpin]OTf$ **4** by NHP-H **5** affords the 1,4-hydroboration product selectively. Thus, the phosphenium species act as a hydrogen transfer reagent in the catalytic cycle.



INTRODUCTION

Dihydropyridine (DHP) derivatives are ubiquitous in naturally occurring molecules, biologically active agents such as NADH (nicotinamide adenine dinucleotide), and pharmaceutically important molecules such as Hantzsch esters.[1] Hence, the development of efficient methodologies for the construction of a DHP skeleton has attracted considerable interest in synthetic chemistry. While the reduction of preactivated pyridines with strong reductants is utilized as the conventional synthetic approach to 1,2- or 1,4-DHP derivatives,[1e,f,2] several catalytic protocols for the direct reduction of pyridines have been described in recent years. Among them, the systems employing mild reducing reagents such as silanes and boranes instead of H_2 gas are considered to be efficacious because they may circumvent the use of highly flammable and highly pressurized hydrogen gas, as well as the obstacle of over-reduction to produce undesired piperidine derivatives (Figure 1a).[3,4]

Since the seminal work by Harrod and co-workers in 1998,[5] several catalytic hydrosilylation reactions using metal catalysts or $B(C_6F_5)_3$ have been described.[6,7] Meanwhile, the first catalytic hydroboration of pyridines (Figure 1b) was reported by the Hill group in 2011, in which the use of the magnesium catalyst **I** produced both 1,2- and 1,4-DHP derivatives.[8] Suginome and co-workers showed that 1,2-hydroboration of pyridines took place in the presence of a rhodium catalyst, **II**.[9] In 2014, pyridine hydroboration with a complete 1,2-regiospecificity was achieved by Marks and Delferro et al. with an organolanthanide catalyst, **III**.[10] For regioselective 1,4-hydroboration of pyridines, Gunanathan et al. reported that a ruthenium catalyst, **IV**, was effective.[11] Wang and Li et al. demonstrated the first metal-free 1,4-hydroboration reaction of pyridines using a bulky organoborane, $Ar^F{}_2BMe$ **V** [Ar^F = 2,4,6-tris(trifluoromethyl)phenyl].[12] Despite these pioneering studies, it is clear that an efficient catalytic system, in particular, the metal-free protocol, for regioselective hydroboration of pyridines has still remained undeveloped.

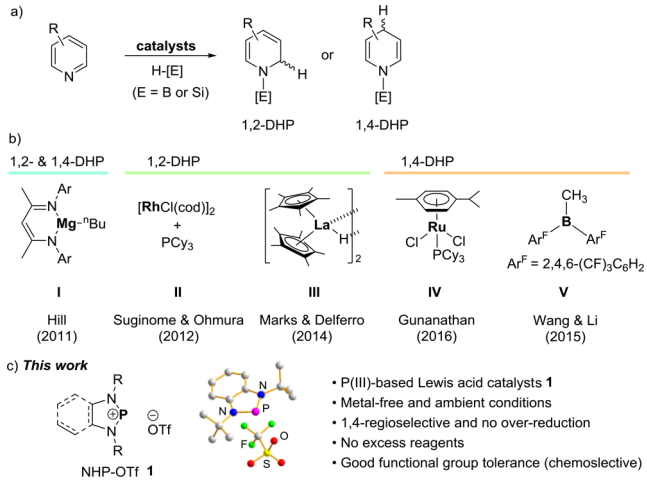


Figure 1. (a) Synthesis of 1,2- and 1,4-DHP derivatives by catalytic reduction of pyridines with boranes and silanes. (b) Examples of the reported catalysts for the hydroboration of pyridines. (c) Present work.

Recently, we have reported that N-heterocyclic phosphane (NHP-H)[13] featuring the umpolung P−H bond catalyzes various reactions involving transfer hydrogenation of unsaturated bonds with ammonia-borane, hydroboration of carbonyls, and CO_2 reduction.[14] Mechanistic studies revealed that the Lewis acidity of the P center in NHP-H as well as the property of NHP-H as a strong hydride donor is essential to achieve these catalytic reactions. We reasoned that the Lewis acidity of the P center can be enhanced in the form of phosphenium cation NHP^+,[15] which may be used as a hydride transfer reagent

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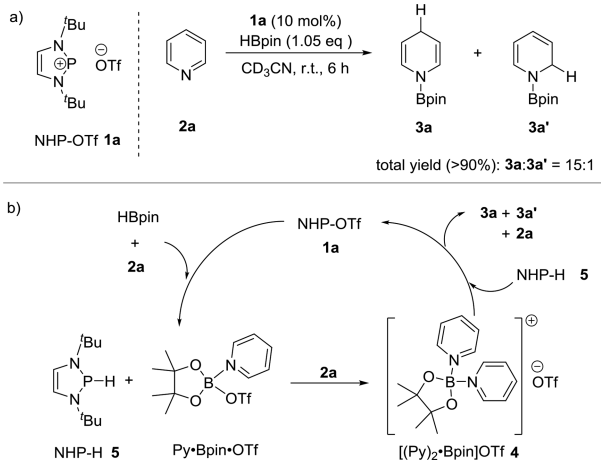
in the hydroboration reaction of pyridines. Herein we report that a catalytic amount of N-heterocyclic phosphenium triflates (NHP-OTf) **1** effectively promotes the selective hydroboration of pyridines under ambient conditions (Figure 1c).

RESULTS AND DISCUSSION

We embarked our investigation with hydroboration of pyridine **2a** employing **1a** as the catalyst, prior to which we confirmed by stoichiometric reactions that neither HBpin nor pyridine **2a** interacts with **1a** (Figures S1 and S2).[15a,b] In the presence of 10 mol % **1a**, a mixture of pyridine **2a** and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) in CD_3CN was stirred at room temperature (Scheme 1a). After 6 h, more than 90% conversion

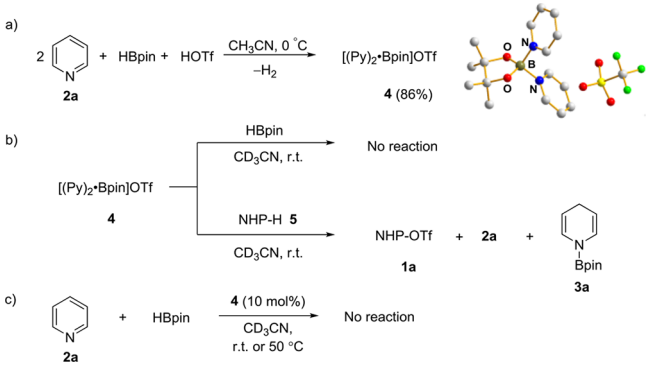
Scheme 1. (a) Hydroboration of Pyridine 2a Catalyzed by 1a; (b) Proposed Reaction Mechanism



of **2a** was confirmed, and 1,4-DHP **3a** was formed as the major product concomitant with a trace amount of 1,2-DHP **3a′**. When the reaction was monitored by NMR spectroscopy (Figure S3), we detected a set of resonances at 8.87 ppm (4H), 8.32 ppm (2H), 7.85 ppm (4H), and 1.09 ppm (12H) in the ^{1}H NMR spectrum, as well as a singlet at 7.26 ppm in the ^{11}B NMR spectrum, which should correspond to the activated pyridine intermediate. Because the phosphenium moiety of **1a** does not form the Lewis adduct with pyridine **2a** (Figure S2), we envisaged that the activated pyridine intermediate is the borane-pyridine complex **4** in the form of a boronium.[16] Hence, we propose a B−H bond activation mechanism (Scheme 1b), in which the initial step is the formation of Py·Bpin·OTf and NHP-H **5** via the activation of the B−H bond of HBpin by **1a** and **2a**. After immediate complexation of Py·Bpin·OTf with the second Py to afford the boronium $[(Py)_2\cdot Bpin]OTf$ **4**, one of the activated pyridines in **4** would be reduced via the H transfer from NHP-H **5** to furnish **3a**/**3a′** along with the release of **1a** and **2a**. Note that the catalytic organic reactions involving phosphenium species are extremely rare,[17] and to the best of our knowledge, this result represents not only the first phosphenium catalysis but also the first selective pyridine hydroboration using a phosphorus-based catalyst.

In order to support the proposed reaction mechanism, we performed several control reactions. First, we attempted the preparation and isolation of **4**. While Li and Wang et al. described that boronium $[(Py)_2\cdot Bpin]^+$ with $[HB(Me)Ar^F{}_2]^-$ [Ar^F = 2,4,6-tris(trifluoromethyl)phenyl] as the counterion decomposed at room temperature to yield pyridine **2a** and **3a** in addition to $B(Me)Ar^F{}_2$,[12] we straightforwardly prepared **4** from pyridine, HBpin, and triflic acid in CD_3CN, and the solid-state structure was determined by X-ray diffraction analysis (Scheme 2a). The ^{1}H and ^{11}B NMR data of **4** are identical to

Scheme 2. (a) Synthesis and the Solid-State Structure of 4; (b) Stoichiometric Reactions between 4 and HBpin or 5; (c) Attempt of Hydroboration of 2a in the Presence of 10 mol % 4



those observed during the reaction (Figure S3), confirming that **4** is generated as a key intermediate in the catalytic reaction. The presence of **4** during the reaction was further confirmed in the HRMS (Figure S3). Boronium **4** did not react with HBpin, whereas treatment of **4** with a stoichiometric amount of NHP-H **5** at room temperature afforded NHP-OTf **1a** and hydroboration product **3a** quantitatively (Scheme 2b). Since no direct reaction takes place between Py **2a** and NHP-H **5** (Figure S5), the pyridine in boronium **4** must be activated. Crudden et al. demonstrated that a borenium catalyst promotes hydroboration of imines with HBpin and proposed that the boron-activated iminium ion $[(imine)\cdot Bpin]^+$ is reduced by HBpin with assistance from the Lewis base DABCO.[18] In order to check whether a similar process is involved in our catalytic cycle, the reaction of Py **2a** and HBpin in the presence of 10 mol % **4** was examined. Even at 50 °C, no reaction was observed, confirming that boronium **4** itself does not serve as the catalyst to promote the hydroboration of pyridine (Scheme 2c). We have also confirmed that a similar reaction proceeded between $[(2\text{-}PhPy)_2\cdot Bpin]OTf$ and NHP-H **5** to afford the corresponding hydroboration product 1-Bpin-2-phnyldihydropyridine (Figure S8), suggesting that irrespective of the bulkiness of the pyridine substrates, the borane-bis(pyridine) species is a key intermediate in the catalytic cycle.

To gain insight into the features of the reaction intermediates, we performed a theoretical study using a DFT method (Scheme 3). The calculated free energy shows that formation of Py·Bpin·OTf from $Py\cdot Bpin^+$ is exergonic with ΔG = −8.3 kcal·mol^{-1}. $[(Py)_2\cdot Bpin]OTf$ **4** formed by coordination of the second pyridine to Py·Bpin·OTf is found to be slightly more stable than Py·Bpin·OTf, which is in line with our NMR observation (Figure S3). Natural bond orbital (NBO) analysis reveals that the charges at the *para* position of the activated pyridines in Py·Bpin·OTf and $[(Py)_2\cdot Bpin]OTf$ **4** are comparable, although they are slightly more electronegative than that in $Py\cdot Bpin^+$. Because of the small free energy gap between Py·Bpin·OTf and $[(Py)_2\cdot Bpin]OTf$ **4**, as well as the comparable electrophilic nature of their activated pyridine moieties, the reaction pathway via a hydride transfer from NHP-H **5** to Py·Bpin·OTf may also be plausible in the actual

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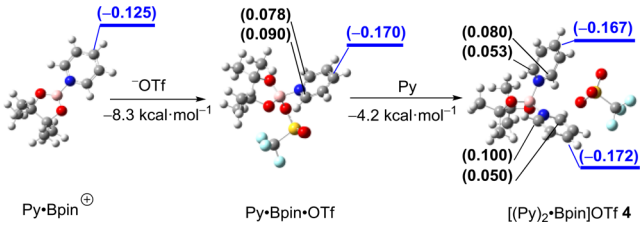
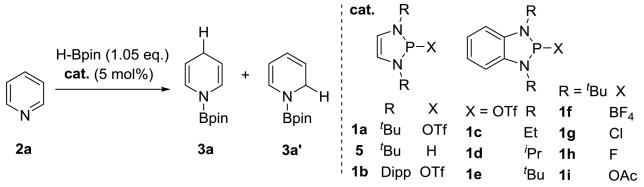
Scheme 3. Calculated Free Energy Differences (ΔG) in Py·Bpin$^+$, Py·Bpin·(OTf), and [(Py)$_2$·Bpin]OTf 4 and the Charges (in Parentheses) at the Selected *para*- and *ortho*-Carbon Atoms of the Activated Pyridines



catalytic reaction. The charges at the *ortho* carbon atoms in both Py·Bpin·(OTf) and [(Py)$_2$·Bpin]OTf **4** are more positive compared with those at the *para* position, suggesting that the selective formation of 1,4-DHP derivative **3a** is most likely due to steric factors rather than electronic effects. A kinetic study confirms that the reaction is *first* order for catalyst **1a** but *zeroth* order for both HBpin and pyridine **2a** (Figures S9−S14).

Having a mechanistic understanding in mind, we briefly investigated the reaction conditions (Table 1). Without any catalysts, no reaction was observed (entry 1). The use of a polar solvent such as CD_3CN gave the best result with high yield and good product selectivity, whereas the catalytic process was remarkably inhibited in nonpolar C_6D_6 (entries 2−4). When NHP-H **5** was employed, only a trace amount of product was detected after 24 h at room temperature (entry 5). While no reaction proceeded with catalyst **1b** at room temperature, **3a** was selectively formed in good yield under heating conditions at 70 °C, probably due to the steric effect of bulky Dipp groups on the N atoms in **1b** (entries 6 and 7). We also examined the catalytic activity of benzannulated NHP-OTf (**1c**−**1e**). With **1c** bearing small ethyl groups, formation of 1,2-DHP product **3a′** was apparently increased (entry 8). By contrast, the employment of **1d** and **1e** led to highly selective reactions, and **1e** was found to be the best catalyst for the reaction (entries 9 and 10). Note that the solid-state structure of **1e** determined by an X-ray diffractometry reveals the ion-separated form of **1e**, confirming the pronounced phosphenium ($\sigma^2\lambda^3$) feature rather than tricoordinate phosphorus triflate ($\sigma^3\lambda^3$) (see the SI). We have also investigated the effect of the X group of the catalysts using **1f**−**1i** bearing BF_4, Cl, F, and OAc, respectively (entries 11−14). While **1f** (X = BF_4) exhibited a similar catalytic activity to that of **1e** (X = OTf), the reaction with **1g** (X = Cl) required a longer reaction time. No reactions at all were observed with **1h** (X = F) and **1i** (X = OAc), demonstrating the significant effect of the X group of the catalyst.

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	T (°C)	time (h)	yield (%) ratio[b]
1		CD_3CN	28	24	0
2	**1a**	CD_3CN	28	6	90 (15:1)
3	**1a**	$CDCl_3$	28	18	80 (11:1)
4	**1a**	C_6D_6	28	24	10
5	**5**	CD_3CN	28	24	<5
6	**1b**	CD_3CN	28	12	0
7	**1b**	CD_3CN	70	12	91(>20:1)
8	**1c**	CD_3CN	28	12	78 (5:1)
9	**1d**	CD_3CN	28	12	92 (>20:1)
10	**1e**	CD_3CN	28	12	96 (>20:1)
11	**1f**	CD_3CN	28	12	94 (>20:1)
12	**1g**	CD_3CN	28	24	92 (15:1)
13	**1h**	CD_3CN	28	48	0
14	**1i**	CD_3CN	28	48	0

[a]Reaction conditions: pyridine (0.20 mmol), HBpin (0.21 mmol), solvent (0.40 mL). Catalyst loading is 5 mol % relative to pyridine. [b]Yields and **3a**/**3a′** ratio were determined by ^{1}H NMR spectroscopy using methyltriphenylsilane as an internal standard.

Having the optimized conditions in hand, we examined the scope of the catalytic reaction with various pyridine substrates (Table 2). Pyridines bearing either a methyl or phenyl group at the *meta* position afforded single products in high yields (**3b** 99%, **3c** 96%, **3d** 91%). Electron-withdrawing substituents such as ester, acetyl, cyano, and amide groups greatly promoted the reaction rate, and hydroboration completed within 1 h to afford the corresponding 1,4-DHP products in high yields (**3e** 99%, **3f** 90%, **3g**/**3g′**/**3g″** 98%, **3h** 95%). Note that these unsaturated functional groups were tolerated under the reaction conditions despite their potentially reducible property.[8,14b,19] Thus, the hydroboration reaction proceeded with a remarkable chemoselectivity. Halogen (Cl, Br, I) groups were also well tolerated to afford the products in good yields (**3i**/**3i′** 94%, **3j**/**3j′** 98%, **3k**/**3k′** 99%), in which a slight formation of 1,2-DHP products was observed. When treating 3,5-dicholoropyridine **2l**, a single product (**3l**) was obtained in 94% yield, and the solid-state structure was confirmed by X-ray diffractometry. Pyridine substrates with alkynyl and akenyl groups could also smoothly generate 1,4-DHP products (**3m** 96%, **3n** 98%, **3o** 98%). Interestingly, when 3-methoxyl and amino pyridine **2p** and **2q** were employed, 1,4-DHP and 1,2-DHP products were obtained in 1:2 and 1:4 ratios, respectively. The reversed regioselectivity is probably due to the strong electron-donating property of the methoxy and amino groups.[10] It is salient to mention that Lewis acidic borane B(Me)Ar$^F_2$ could not promote the hydroboration reaction of 3-methoylpyridine **2p**.[12] Moreover, while it has been concluded in previous reports that with the ruthenium and organolanthanide catalysts,[10,11] 2-substituted pyridines did not undergo hydroboration because of steric hindrance, 2-picoline **2r** and 2,3-dimethylpyridine **2s** were readily transformed to the corresponding 1,4-DHP products with our system (**3r** 90%, **3s** 91%). Significantly, NHP-OTf **1e** exhibited catalytic activity for hydroboration of 2-arylpyridines **2t** and **2u** to generate **3t**/**3t′** (95%) and **3u**/**3u′** (97%), respectively. This result is in stark contrast to Crudden's rhodium catalysis, in which 2-arylpyrindes afforded *o*-C−H borylation products via dehydrogenation.[20] Note that the Ru catalyst **IV** did not promote the hydroboration of 2-substituted pyridines.[11] In addition, the substrates **2c**, **2p**, and **2t** did not undergo hydroboration with the B-based catalyst **V**.[12] With benzannulated substrate quinoline **2v**, 1,2-DHP product **3v′** was formed as the major product. When 4-(pyridin-3-yl)benzaldehyde **2w** was employed, single 1,4-DHP **3w** was obtained in 94% yield via hydroboration of both aldehyde and pyridine moieties. Double hydroboration of pyrimidine **2x** proceeded cleanly, and **3x** was obtained in 91% yield. We observed no reactions with 2-substitued pyridines with a strong electron-withdrawing group

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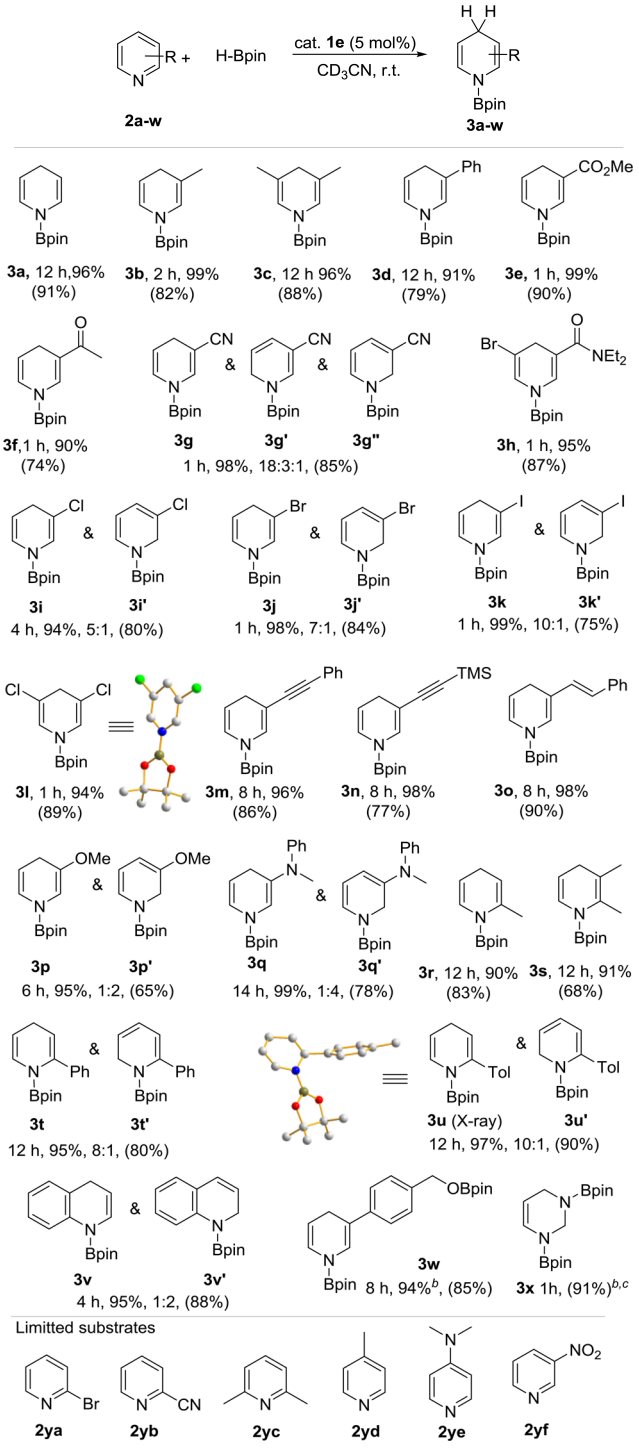
Table 2. Scope of Pyridine Substrates[a]

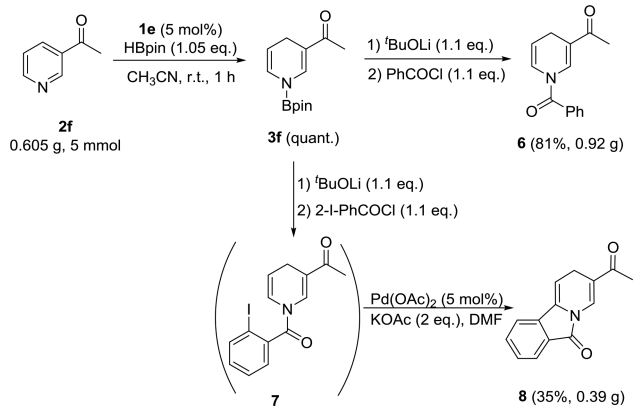


[a]Reaction conditions: pyridine substrates (0.20 mmol), HBpin (0.21 mmol), CD_3CN (0.40 mL), **1e** (5 mol %). NMR yields and ratios of regioisomers (1,4-DHP:1,2-DHP) are determined by ^1H NMR spectroscopy using methyltriphenylsilane as an internal standard. Isolated yield is in parentheses. [b]0.42 mmol of HBpin was used. [c]Due to the poor solubility of the product **3x** in CD_3CN, only the isolated yield was determined.

2ya,b, 2,6-lutidine **2yc**, 4-picoline **2yd**, and 4-dimethylaminopyridine **2ye**, which was probably on account of the electronic and steric factors on the pyridine skeleton and in line with the trends observed in previous reports.[10−12] With substrates **2yf**, no hydroboration product was obtained presumably due to the intolerance of the nitro group.

To demonstrate the robustness of our catalytic process, we performed the reaction with 5 mmol of pyridine **2f** at the standard conditions (Scheme 4). After 1 h, **3f** was formed

Scheme 4. Further Transformation of 3f



nearly quantitatively, which was further treated with ^{t}BuOLi followed by benzoyl choloride in a one-pot manner to afford *N*-benzoyl-1,4-dihydropydine **6** in 81% yield (0.92 g).[9,21] Moreover, by acylation with 2-iodobenzoyl chloride to give the crude product **7** and subsequent intramolecular Heck reaction, a new heterocyclic product **8** was obtained in 35% total yield from **2f**. These results demonstrate that our catalysis may provide a straightforward synthetic approach to functionalize 1,4-DHP derivatives from pyridine substrates under mild conditions.[1d]

CONCLUSIONS

After more than 50 years since the discovery of dicoordinate phosphorus species by Dimroth and Hoffmann,[22] we have demonstrated that phosphenium species can be utilized as a catalyst. We have shown the unique performance of NHP-OTf **1** as a regio- and chemoselective catalyst for hydroboration of pyridines. The reaction has been achieved under metal-free and ambient conditions, and various pyridine substrates involving those not available in previous reports were well tolerated in our system. Mechanistic studies suggest that (i) the initial step involves the hydride transfer from HBpin to NHP cation to generate a boronium, $[(Py)_2{\cdot}Bpin]OTf$ **4**, the structure of which was decisively confirmed by X-ray diffraction analysis, and (ii) the second step is reduction of the activated pyridine in **4** by NHP-H **5**. Thus, diazaphophenium plays a pivotal role as a hydride transfer reagent during the selective pyridine hydoboration reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09754.

Experimental section (PDF)
Crystallographic data in CIF format (CIF)
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Notes

The authors declare no competing financial interest.

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