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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c00257 • Publication Date (Web): 09 Sep 2020

Synthesis of Mesoionic *N*-Heterocyclic Olefins and Catalytic Application for Hydroboration Reactions

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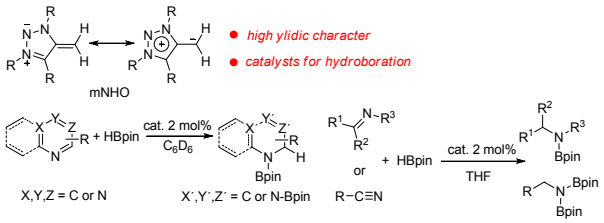


Abstract: Mesoionic *N*-heterocyclic olefins have been developed, which feature high ylidic character. These compounds have been used as efficient catalysts for hydroboration of imines, nitriles and *N*-heteroarenes.

Introduction

Breslow intermediate was firstly proposed as an active intermediate for the umpolung of aldehydes by Breslow in 1958.[1] Since then, this important species, which functions as a nucleophilic acyl anion, has held an irreplaceable position in synthetic and organocatalytic chemistry.[2] Outstanding work for isolation and characterization of Breslow intermediates and their analogous forms **A** (OR, NR_2) were reported in recent years, despite limited stability of the Breslow intermediates.[3] Apart from the Breslow intermediates **A**, their deoxy forms **B**, also called *N*-heterocyclic olefins (NHOs), were also well studied.[4-10] NHOs have been widely used as alternative and more σ-donating carbon ligands for low-valent main group elements and transition metals.[11,12] Moreover, NHOs have also been established as organocatalysts among a wide range of organic transformations, such as reduction,[13] transesterification,[14] small molecule activation[15] and polymerization.[16]

Recently, we have reported the synthesis of Breslow intermediates of mesoionic carbenes **C** featuring an elongated length of the C-C bond, which mainly due to the stronger σ-donating property of mesoionic carbenes compared with Breslow intermediates **A**.[17] Herein we report the deoxy Breslow intermediates of mesoionic carbenes **D**, which are mesoionic *N*-heterocyclic olefins (mNHOs). These compounds feature high ylidic character, and can act as efficient catalysts for hydroboration of imines, nitriles and *N*-heteroarenes. (Figure 1).[18]

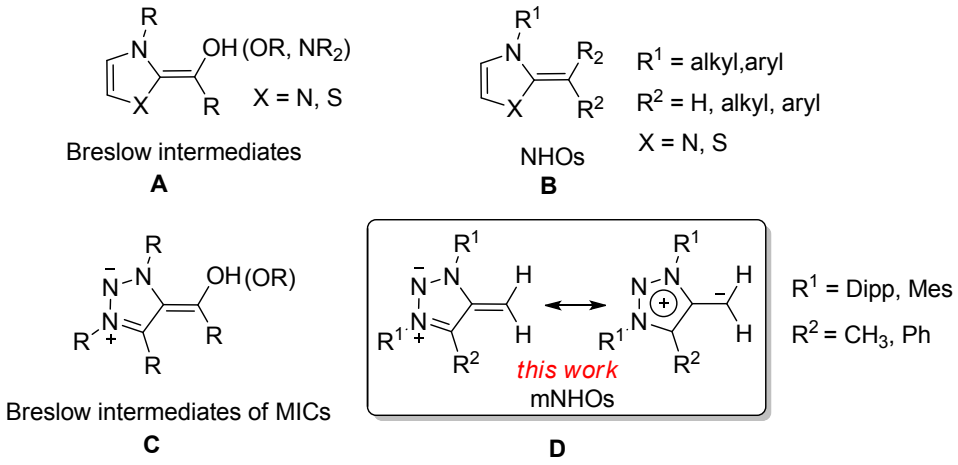


Figure 1. Breslow intermediates **A**, NHOs **B**, Breslow intermediates of MICs **C** and mNHOs **D**.

Results and discussion

Due to the stronger σ-donating property of mesoionic carbenes, we supposed mNHOs **D** would present higher ylidic property in contrast with NHOs **B**. To confirm this, DFT calculations were performed at BP86/Def2SVP level of theory (Figure 2). The highest occupied orbital (HOMO) of mNHO **D** is mainly located on the exocyclic carbon atom featuring polarized C=C π bond, which is higher in energy than that of NHO **B**, as well as NHC **E** and MIC **F**. It is noteworthy that NHOs and mNHOs feature strong polarization of the exocyclic C=C bond, leading to the hybrid of both ylidic and olefinic characters. Natural Resonance Theory (NRT) analyses at M06-2X/6-31G(d) level indicate that ylidic character and olefinic character of mNHO **D** are in an about 2:1 ratio, while the ratio is 1:2 for that of NHO **B** (Figure 3). These calculations supported the high ylidic character of mNHO **D**.

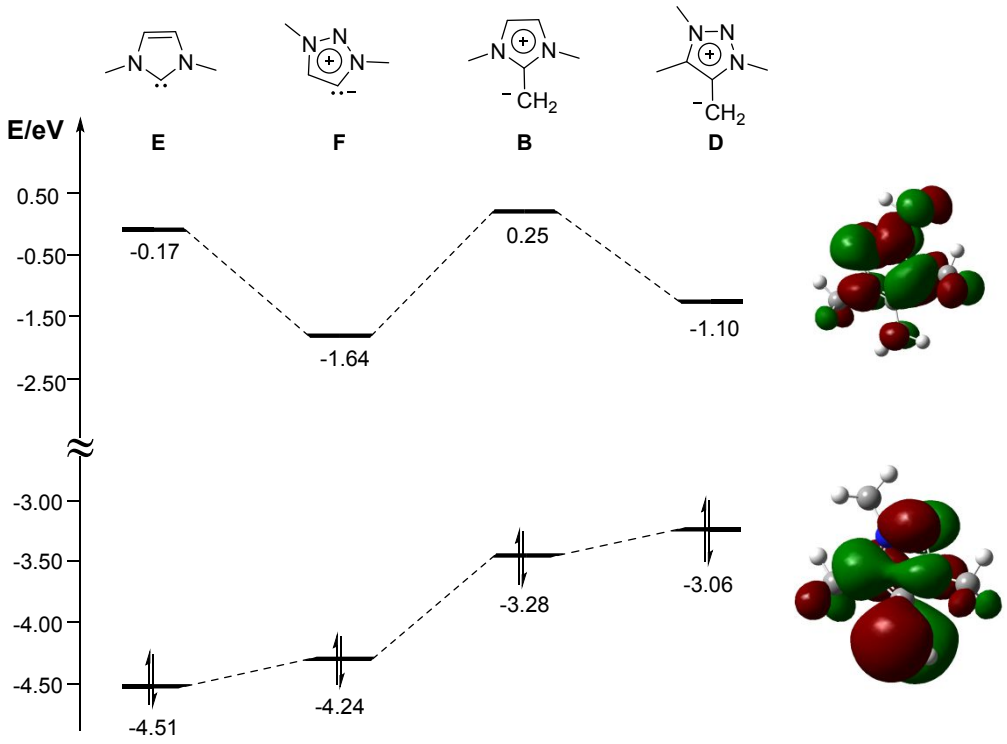


Figure 2. Energy (eV) of the HOMOs and LUMOs of NHO **B**, mNHO **D**, NHC **E**, MIC **F**, calculated at BP86/Def2SVP level of theory. The frontier orbitals of mNHO are given on the right.

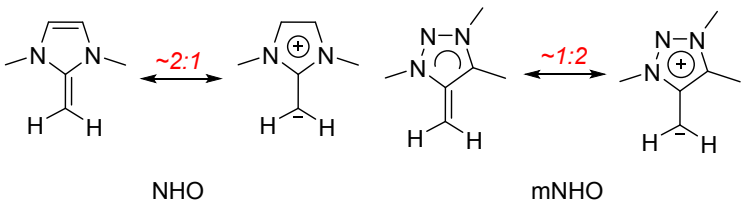
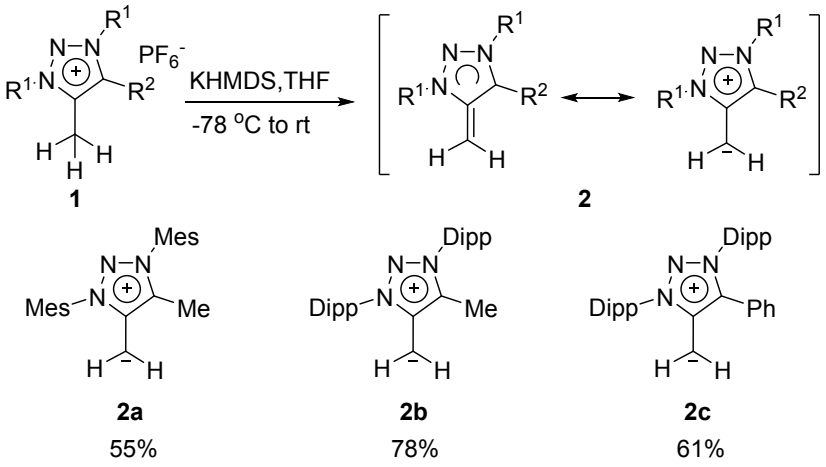


Figure 3. The ylidic and olefinic character resonance forms of NHO and mNHO. Natural Resonance Theory (NRT) analyses were carried out at M06-2X/6-31G(d) level of theory to give the corresponding proportion.

Experimentally, mNHOs were prepared by α-deprotonation of 4-methyl-1,2,3-triazolium **1a-c** by potassium bis(trimethylsilyl)amide (KHMDS) in THF under -78 °C.[19] After removing the solvent, the remaining solids were extracted with toluene and the corresponding mNHOs **2a-c** were obtained in 55%-78% yields (Scheme 1). Besides, similar products were also formed by using potassium *tert*-butoxide as the base, but no reaction occurred when amidines were employed, which suggested the pKa of C-H in **1** was between alcohol and amidinium.



Scheme 1. Synthesis of mNHO **2a-c**.

It should be mentioned that the ^{1}H NMR of **2a** and **2b** feature broadened signals, which we supposed a rapid hydrogen transfer between methylene and methyl (Figure 4). However, different from **2a** and **2b**, ^{1}H NMR signal of **2c** presents two broad peaks of CH_2, with the chemical shifts of 3.68 and 2.85. The single crystals of **2a** and **2b** were obtained by slow evaporation of the corresponding toluene solution at room temperature in the glovebox, and the ORTEP of single-crystal X-ray diffraction of **2a** and **2b** are showed in SI. X-ray structures of the mNHOs **2a** and **2b** present an equal length of the exocyclic C-C bonds, which is due to disorder between the two $–CH_3/=CH_2$ sites in the solid state.

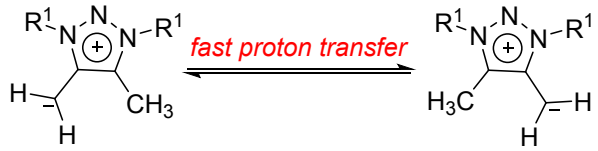
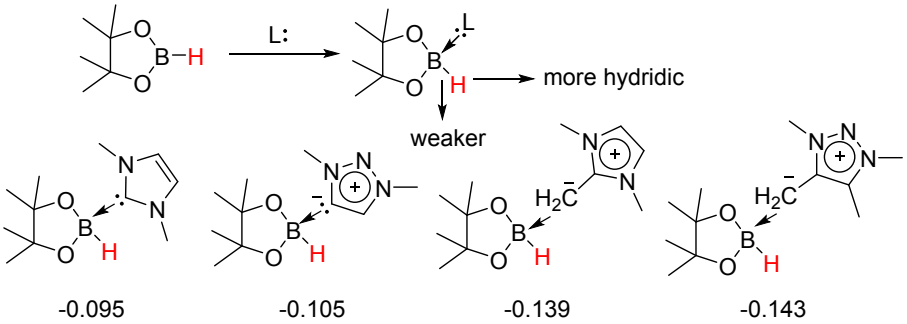


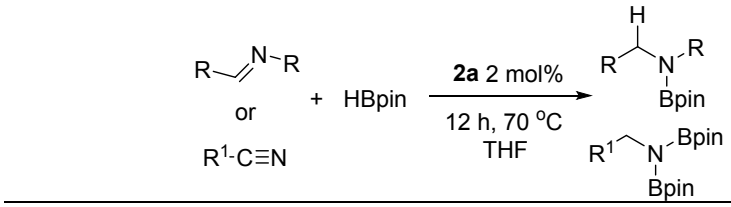
Figure 4. Fast proton transfer of **2a** and **2b** in solution.

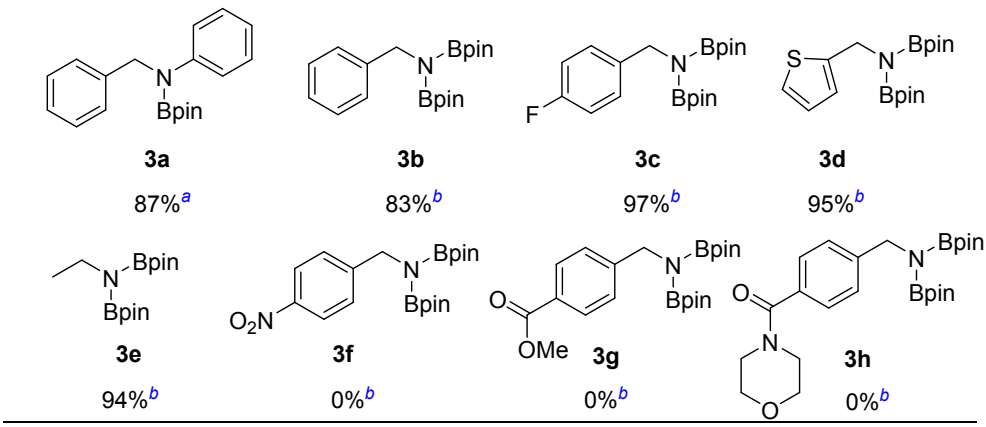
With the property of high HOMO energy and high ylidic character in mind, we started to investigate the catalytic application of mNHOs. We envisioned that mNHOs could interact with HBpin to form Lewis adducts, leading to weakening the B-H bonds and enhancing the hydridic character to promote the hydroboration of unsaturated substrates.[20] Natural bond orbital (NBO) analyses of HBpin-base adducts were performed at M06-2X/Def2tzvp. Among typical strong Lewis bases, such as NHC, MIC, NHO, and mNHO, the HBpin-mNHO adducts show the most negative

charge at H-(Bpin) (Scheme 2). To show the superior catalytic activity of mNHOs, aldehydes and ketones were employed for hydroboration. The results revealed that mNHO gave higher yields with low catalyst loading compared with NHO (For details see SI, Figure S11). And then we started to test more challenging work about hydroboration of imines and nitriles (Scheme 3). To our delight, the catalytic hydroboration of aldimines furnished the corresponding product **3a** in 87% yield with only 2 mol% of **2a**.[21] Hydroboration of ketimines catalyzed by **2a** failed which might be due to the steric hindrance. When arylnitriles were employed as substrates, the corresponding products **3b-d** were obtained in high yields. Moreover, not only aromatic nitriles but also aliphatic nitriles were tolerated. Hydroboration of acetonitrile afforded the corresponding product **3e** in 94% yield. Unfortunately, ester, amide and nitro groups were not tolerated and no products were detected (**3f-h**), of which was due to decomposition of catalyst by these functional groups. It is noteworthy that the catalytic hydroboration of imines[22] and nitriles[23] without metals have not often been reported. Our protocol not only avoided the use of large amounts of catalysts but also gave almost full conversion of substrates when compared with Al, Mg-based catalytic system.[23b,d] For further comparison, NHO was also employed as catalyst in hydroboration of imines and nitriles under the same conditions, while lower yields were obtained (75% for **3a** and 72% for **3c**, for details see SI, Figure S11). Besides, excellent intramolecular chemoselective hydroboration on aldimine rather than nitrile was realized for substrate containing both cyano group and imino group, the corresponding product (**3i**) was obtained with high isolated yield (Scheme 4).

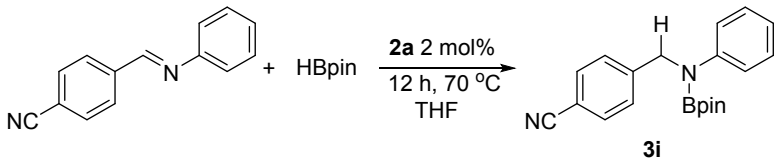


Scheme 2. NBO analyses of HBpin-base Adducts. Selected NBO Charges of H-(Bpin) are Given in the Units. The Optimized Structures of HBpin-base Complexes at M06-2X/Def2tzvp Level of Theory.





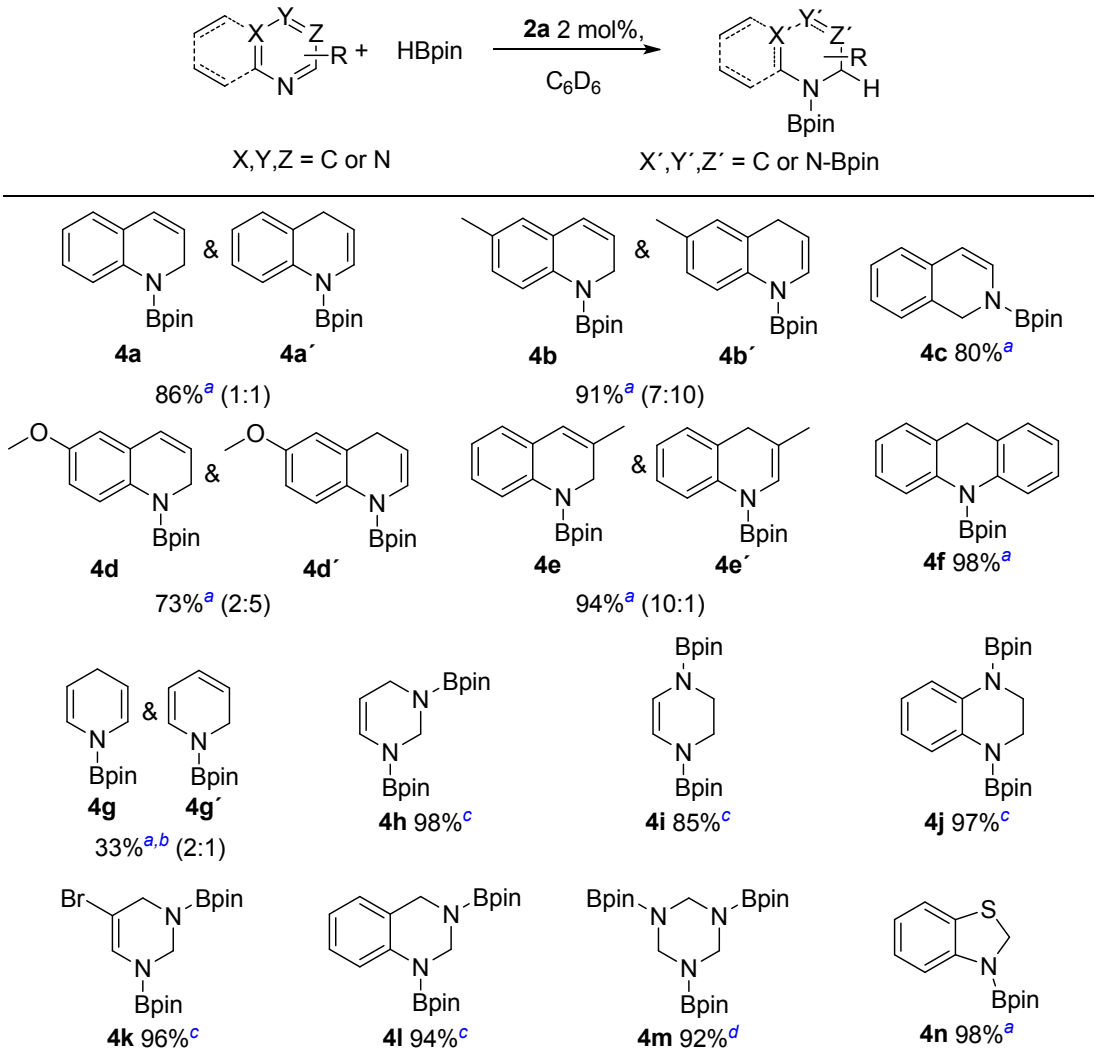
Scheme 3. Hydroboration of Imine and Nitriles Catalyzed by **2a**. [a]Reaction condition: imine (0.50 mmol), HBpin (0.55 mmol), mNHO **2a** (2 mol%), THF (1.5 mL), 70 °C in sealed tube. [b]Reaction condition: nitriles (0.50 mmol), HBpin (1.1 mmol), mNHO **2a** (2 mol%), THF (1.5 mL), 70 °C in sealed tube.



Scheme 4. Chemoselective Hydroboration of Cyano-substituted Aldimine.

The metal-free catalytic hydroboration of *N*-heteroarenes[24] were also investigated (Scheme 5). When quinoline, substituted quinolines, isoquinoline and acridine were employed, the corresponding products, 1,2-addition products and/or 1,4-addition products, **4a-f** were obtained in 73%-98% yields. Besides, we also noticed the 1,2-additon product was the main product when 3-methylquinoline was employed for hydroboration, which we supposed the steric hindrance affected the selectivity. Meanwhile, when 2-methylquinoline was employed, no product was detected. Hydroboration of pyridine afforded the products in low yields (**4g/4g´**, 33%), which

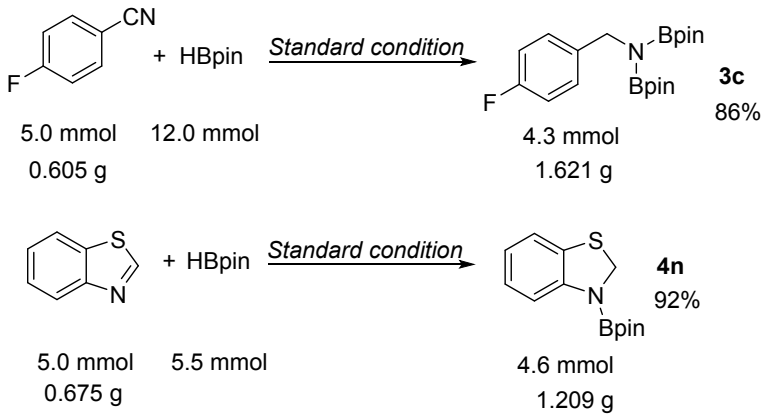
was mainly due to the high resonance stabilization of pyridine compounds. Moreover, pyrazine, pyrimidine, quinazoline and quinoxaline were double-hydroborated in high yields with only 2 mol% catalyst (**4h-l**). And 1,3,5-triazine was triple-hydroborated with almost full conversion (**4m**). Besides, hydroboration of benzothiazole gave the corresponding product **4n** in 98% yield. For comparison, no product was obtained by using NHO as catalyst (For details see Figure S11). It should be noted that NHC-catalyzed 1,2-selective hydroboration of quinolines has been developed recently.[24g]



Scheme 5. Hydroboration of *N*-heteroarenes catalyzed by **2a**. [a]*N*-heteroarenes (0.50 mmol), HBpin (0.55 mmol), mNHO **2a** (2 mol%), C_6D_6 (1.5 mL). [b]The solvent was replaced by THF. [c]*N*-heteroarenes (0.50 mmol), HBpin (1.1 mmol),

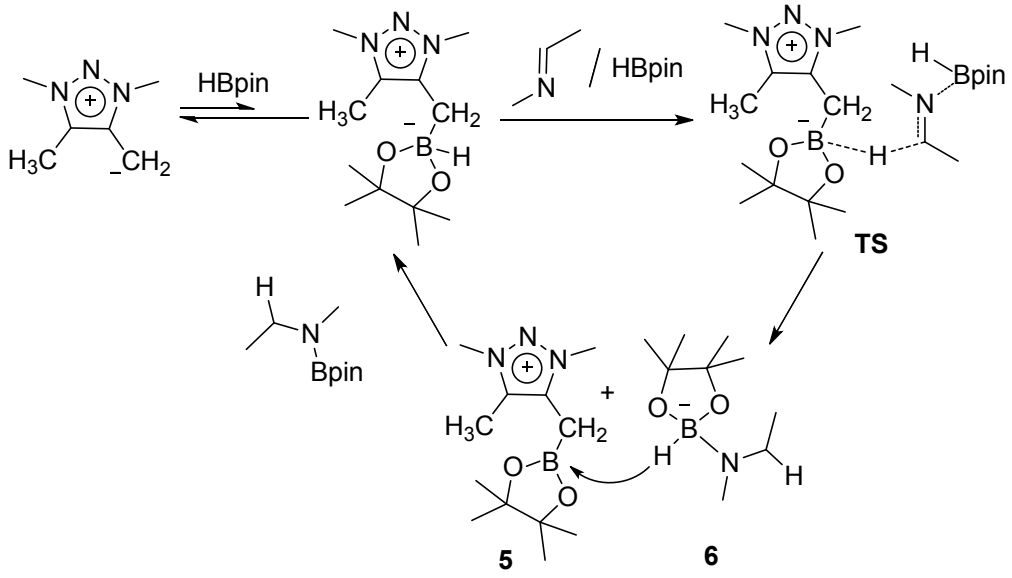
mNHO **2a** (2 mol%), C_6D_6 (1.5 mL). [d]1,3,5-triazine (0.50 mmol), HBpin (1.65 mmol), mNHO **2a** (2 mol%), C_6D_6 (1.5 mL).

In addition, mNHO-catalyzed hydroboration reaction could be scaled up. For example, gram-scale hydroboration of *p*-fluorobenzonitrile and benzothiazole afforded the corresponding products **3c** and **4n** in 86% and 92% yields, respectively (Scheme 6).



Scheme 6 Gram-Scale Hydroboration of *p*-Fluorobenzonitrile and Benzothiazole.

For further investigation of the mechanism, we tried stoichiometric reaction between mNHO and HBpin. However, no obvious adduct was observed by both ^{1}H NMR and ^{11}B NMR. DFT calculation showed that the mNHO-HBpin adduct was ~10 kcal/mol higher in energy. We supposed there is an equilibrium between mNHO/HBpin and their adduct. Based on the experimental results and calculation, we proposed a plausible mechanism for mNHO catalyzed hydroboration reaction. Firstly, reaction of HBpin with mNHO afforded the adduct mNHO-HBpin in equilibrium, which presented increased hydridic character of B-H bond. Then nucleophilic B-H bond attacked C atom of C=N bond, while the N atom reacted with another HBpin, leading to the formation of boryl-substituted triazolium **5** and amido-HBpin anion **6**. The transition state was calculated by DFT with an energy barrier of 27.8 kcal/mol (For details of the calculated reaction pathways, see Figure S8).[27] Hydride transfer between **5** and **6** led to formation of mNHO-HBpin adduct as well as hydroboration product (Scheme 7).



Scheme 7. Plausible Mechanism for mNHO-Catalyzed Hydroboration Reaction.

Conclusion

In summary, mesoionic *N*-Heterocyclic olefins (mNHOs) have been developed, which feature high ylidic character caused by the polarization of the exocyclic carbon-carbon bond, suggesting superior σ-donating property compared with NHOs. Our study indicates that mNHOs show efficient catalytic activity for hydroboration of imines, nitriles and *N*-heteroarenes. Research in our laboratory is currently underway to broaden the catalytic application.

EXPERIMENTAL SECTION

General Information. All reagents were obtained from commercial suppliers and used directly without further purification, unless otherwise noted. Solvents were obtained directly from solvent purification system to get rid of moisture and oxygen. For NMR solvents C_6D_6 and $CDCl_3$ were dried up with activated molecular sieve and further degassed with nitrogen, then moved to glovebox for further use. All air sensitive synthetic manipulations were performed in glovebox or carried out in flame-dried glassware equipped with magnetic agitators under nitrogen atmosphere using Schlenk techniques. All reactions that required heating were carried out under oil bath conditions. NMR spectra were recorded on Bruker 400 MHz and 600 MHz

spectrometers. The chemical shift data for each signal were given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the residual solvent resonances. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* were given in Hz. High-resolution mass spectra were acquired on Thermo Q Exactive Focus Hybrid Quadrupole-Orbitrap mass spectrometer using electrospray ionization mode (ESI).

Synthesis of compounds 1a-c.

1,3-dimesityl-4,5-dimethyl-1*H*-1,2,3-triazolium hexafluorophosphate (1a). A 250 mL Schlenk flask was charged with 1,3-dimesityltriazene[19] (2.80 g, 10.0 mmol), potassium hexafluorophosphate (1.84 g, 10.0 mmol) and 2-butyne (950 μL ,12.0 mmol). And dichloromethane (20 mL) was added to the flask in the dark at -78 °C. Then *tert*-butyl hypochlorite (1.30 mL, 12.0 mmol) was added to the mixture. The mixture was stirred overnight and slowly warmed to room temperature. The contents were filtered with celite, and the solid was washed with dichloromethane (20 mL × 3). All the filtrate was collected, and solvent was removed under reduced pressure. Then residual solid was washed with diethyl ether to obtain white solid (4.01 g, 84%). **1a** was further purified after recrystallization by diffusion of diethyl ether in an acetone solution at room temperature. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11 (s ,4H), 2.40 (s, 6H), 2.38 (s, 6H), 2.06 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 142.8(trz-*C*), 140.6(aryl-*C*), 134.8(aryl-*C*), 130.1(aryl-*C*), 129.3(aryl-*C*), 21.2(Ar*C*H_3), 16.8(Ar*C*H_3), 8.6(trz-*C*H_3). HRMS (ESI) m/z: $[M - PF_6]^+$ Calcd. for $C_{22}H_{28}N_3$ 334.2283; Found 334.2270.

1,3-Bis(2,6-diisopropyphenyl)-4,5-dimethyl-1*H*-1,2,3-triazolium hexafluorophosphate (1b). A 250 mL Schlenk flask was charged with 1,3-bis(2,6-diisopropyphenyl)triazene[19,25] (3.65 g, 10.0 mmol), potassium hexafluorophosphate (1.84 g, 10.0 mmol) and 2-butyne (950 μL ,12.0 mmol). And dried dichloromethane (20 mL) was added to the flask in the dark at -78 °C. Then *tert*-butyl hypochlorite (1.30 mL, 12.0 mmol) was added to the mixture. The mixture was stirred overnight and slowly warmed to room temperature. The contents were

filtered with celite, and the solid was washed with dichloromethane (20 mL × 3). All the filtrate was collected and solvent was removed under reduced pressure. Then residual solid was washed with diethyl ether to obtain white solid (5.34 g, 95%). **1b** was further purified after recrystallization by diffusion of diethyl ether in an acetone solution at room temperature. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.66 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 4H), 2.42 (s, 6H), 2.22 (sept, *J* = 6.8 Hz, 4H), 1.30 (d, *J* = 6.7 Hz, 12H), 1.13 (d, *J* = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 145.8(trz-*C*), 141.1(Aryl-*C*), 133.1(Aryl-*C*), 128.5(Aryl-*C*), 125.1(Aryl-*C*), 29.0(*C*H(CH_3)$_2$), 25.1(*C*H_3), 23.1(*C*H_3), 9.1(trz-*C*H_3). HRMS (ESI) m/z: $[M - PF_6]^+$ Calcd. for $C_{28}H_{40}N_3$ 418.3217; Found 418.3211.

1,3-Bis(2,6-diisopropyphenyl)-4-phenyl,5-methyl-1*H*-1,2,3-triazolium hexafluorophosphate (1c). A 250 mL Schlenk flask was charged with 1,3-bis(2,6-diisopropyphenyl)triazene[19,25] (3.65 g, 10.0 mmol), potassium hexafluorophosphate (1.84 g, 10.0 mmol) and 1-phenylprop-1-yne (1250 μL ,10.0 mmol). And dried dichloromethane (20 mL) was added to the flask in the dark at -78 ^{o}C. Then *tert*-butyl hypochlorite (1.30 mL, 12.0 mmol) was added to the mixture. The mixture was stirred overnight and slowly warmed to room temperature. The contents were filtered with celite, and the solid was washed with dichloromethane (20 mL × 3). All the filtrate was collected and solvent was removed under reduced pressure. Then residual solid was washed with diethyl ether to obtain white solid (5.75 g, 92%). **1c** was further purified after recrystallization by diffusion of diethyl ether in an acetone solution at room temperature. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (t, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.53 (s, 3H), 2.37 – 2.27 (sept, *J* = 6.8 Hz, 4H), 1.36 (d, *J* = 6.7 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.05 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 145.7(trz-*C*), 145.5(trz-*C*), 142.8(Aryl-*C*), 140.7(Aryl-*C*), 133.4(Aryl-*C*), 133.2(Aryl-*C*), 131.9(Aryl-*C*), 129.7(Aryl-*C*), 129.6(Aryl-*C*), 129.1(Aryl-*C*), 128.4(Aryl-*C*), 125.3(Aryl-*C*), 125.1(Aryl-*C*), 121.2(Aryl-*C*), 29.4(*C*H(CH_3)$_2$), 29.3(*C*H(CH_3)$_2$), 25.6(*C*H_3), 25.2(*C*H_3), 23.1(*C*H_3), 22.3(*C*H_3),

9.8(trz-*C*H_3). HRMS (ESI) m/z: [M − PF_6]$^+$ Calcd. for $C_{33}H_{42}N_3$ 480.3373; Found 480.3372.

General procedure for the preparation of mNHOs.

A 100 mL Schlenk flask was charged with a magnetic agitator, triazolium salt (1.0 mmol, 1.0 equiv) and potassium bis(trimethylsilyl)amide (1.1 mmol, 1.1 equiv). Then dried THF (10 mL) was added to the flask under -78 °C. The mixture was stirred about 2 h and slowly warmed to room temperature. Then solvent was removed under reduce pressure, and the residual solid was extracted with dried toluene (20 mL). Solvent was removed again under reduce pressure to afford mNHOs **2**.

(2a) Brownish red solid (183.3 mg, 55%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.72 (br, 4H), 2.25-2.06 (br, 23H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 139.4(trz-*C*), 135.7(Aryl-*C*), 134.3(Aryl-*C*), 132.8(Aryl-*C*), 129.3(Aryl-*C*), 128.9(Aryl-*C*), 20.8(*C*H_3), 17.6(*C*H_3). 16.7(*C*H_3). HRMS (ESI) m/z: [M + H]$^+$ Calcd. for $C_{22}H_{27}N_3$ 334.2283; Found 334.2285.

(2b) Brownish solid (325.6 mg, 78%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.31- 6.88 (m, 6H), 3.60-2.27 (br, 4H), 1.38-0.93 (br, 29H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 130.2(Aryl-*C*), 127.9(Aryl-*C*), 124.0(Aryl-*C*), 28.5(*C*H(CH_3)$_2$), 24.6(*C*H_3), 23.1(*C*H_3), 22.6(*C*H_3). HRMS (ESI) m/z: [M + H]$^+$ Calcd. for $C_{28}H_{40}N_3$ 418.3217; Found 418.3219.

(2c) Dark blue solid (292.8 mg, 61%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.42 (br, 2H), 7.31-7.29 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.13-7.12 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 3.68 (br, 1H), 3.54 (br, 2H), 3.15 (sept, *J* = 6.6 Hz, 2H), 2.85 (br, 1H), 1.45 (d, *J* = 6.6 Hz, 6H), 1.28 (d, *J* = 6.6 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 148.2(trz-*C*), 147.0(trz-*C*), 145.7(Aryl-*C*), 132.9(Aryl-*C*), 132.7(Aryl-*C*), 130.7(Aryl-*C*), 130.1(Aryl-*C*), 125.7(Aryl-*C*), 125.4(Aryl-*C*), 124.5(Aryl-*C*), 124.2(Aryl-*C*), 45.5(*C*H_2), 29.8(*C*H(CH_3)$_2$), 28.7(*C*H(CH_3)$_2$), 25.5(*C*H_3), 24.2(*C*H_3), 23.3(*C*H_3), 22.3(*C*H_3). HRMS (ESI) m/z: [M + H]$^+$ Calcd. for $C_{33}H_{42}N_3$ 480.3373; Found 480.3372.

General procedure for hydroboration of imines and nitriles. A 25 mL Schlenk flask was charged with a magnetic agitator, aldimine or nitriles (0.50 mmol, 1.0 equiv) and mNHO **2a** (0.0040 mmol, 0.020 equiv). Then dried THF (1.5 mL) was slowly added to the flask. After that HBpin was added based on the [C=N]/[HBpin]=1:1.1. The reaction mixture was stirred at 70 °C for 12 h under oil bath conditions. After being allowed to cool to room temperature, solvent was removed under reduce pressure, and the products were washed with pentane (2 × 0.5 mL) for further purification. (Besides, the blank control experiments were tried under the same conditions in the absence of **2a**. The results showed imines were hydroborated in low yields, and the corresponding products **3a** and **3i** were obtained in 37% and 45% yields. But no products were detected for nitriles, for details see Table S7)

(3a)[22b, e] Colorless oil (134.4 mg, 87% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.14-7.00 (m, 6H), 4.78 (s, 2H), 1.08 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 146.5(Aryl-*C*), 140.7(Aryl-*C*), 126.4(Aryl-*C*), 121.5(Aryl-*C*), 120.7(Aryl-*C*), 82.7(*C*$(CH_3)_2$), 51.2(N(*C*H_2)), 24.4(C(*C*$H_3)_2$).

(3b)[23d] Colorless solid (148.9 mg, 83% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.6 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.14-7.10 (m, 1H), 4.62 (s, 2H), 1.03 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 143.5(Aryl-*C*), 131.8(Aryl-*C*), 131.7(Aryl-*C*), 82.3(*C*$(CH_3)_2$), 47.6(N(*C*H_2)), 24.4(C(*C*$H_3)_2$).

(3c)[23c] Colorless solid (355.5 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H), 6.93-6.90 (m, 2H), 4.17 (s, 2H), 1.19 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.5 (d, $^1J_{C\text{-}F}$ = 243.0 Hz, Aryl-*C*), 138.8(Aryl-*C*), 129.2 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, Aryl-*C*), 114.5 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, Aryl-*C*), 82.3(*C*$(CH_3)_2$), 46.5(N(*C*H_2)), 24.5(C(*C*$H_3)_2$).

(3d)[23c] Colorless oil (173.3 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 4.9 Hz, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 6.87 (dd, *J* = 4.9, 3.6 Hz, 1H), 4.37 (s, 2H), 1.22 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.8(Aryl-*C*), 126.1(Aryl-*C*), 124.5(Aryl-*C*), 123.5(Aryl-*C*), 82.5(*C*$(CH_3)_2$), 42.1(N(*C*H_2)), 24.5(C(*C*$H_3)_2$).

(3e)[23c] Colorless solid (139.5 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (q, *J* = 7.0 Hz, 2H), 1.21 (s, 24H), 1.02 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 81.9(*C*$(CH_3)_2$), 38.5(N(*C*H_2)), 24.5(C(*C*$H_3)_2$), 18.6(CH_2(*C*H_3)).

(3i) Colorless solid (160.3 mg, 96% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.13-7.09 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.84-6.82 (m, 3H), 4.52 (s, 2H), 1.06 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 145.8(Aryl-*C*), 131.9(Aryl-*C*), 128.8(Aryl-*C*), 126.8(Aryl-*C*), 121.9(Aryl-*C*), 118.7(*C*N), 112.8(Aryl-*C*), 110.7(Aryl-*C*), 83.0(*C*$(CH_3)_2$), 50.8(N(*C*H_2)), 24.3(C(*C*$H_3)_2$).

General procedure for the hydroboration of *N*-heteroarenes. General procedure for the hydroboration products **4a**-**4e**: A 25 mL dried Schlenk flask was charged with a magnetic agitator, *N*-heteroarenes (0.50 mmol, 1.0 equiv) and mNHO **2a** (0.0040 mmol, 0.020 equiv). Then dried C_6D_6 (1.5 mL) was slowly added to the flask. After that HBpin was added based on the [C=N]/[HBpin] = 1:1.1. The reaction mixture was stirred at room temperature for 12 h. Then solvent was removed under reduce pressure, and the products were washed with pentane (2 × 0.5 mL) for further purification. (Besides, the blank control experiments for *N*-heteroarenes were tried under the same conditions in the absence of **2a**, and no products were detected, for details see Table S7).

The mixture of **4a** and **4a´** were obtained as yellow oil (110.5 mg, 86% yield). (**4a)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.14-6.75 (m, 3H), 6.26 (d, *J* = 9.6 Hz, 1H), 5.57 (dt, *J* = 9.4, 4.2 Hz, 1H), 4.16 (dd, *J* = 4.2 Hz, 1.7 Hz 2H), 1.04 (s, 12H). (**4a´)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.14-6.75 (m, 4H), 4.82 (m,1H), 3.32 (m, 2H), 1.02 (s, 14H).

The mixture of **4b** and **4b´** were obtained as yellow oil (123 mg, 91% yield). (**4b)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 7.71 (d, *J* = 8.2 Hz, 1H), 6.66-6.64 (m, 2H), 6.27 (d, *J* = 9.5 Hz, 1H), 5.64-5.59 (m, 1H), 4.16 (dd, *J* = 4.2, 1.7 Hz, 2H), 1.10 (s, 3H), 1.05 (s, 12H). (**4b´)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 8.07 (d, *J* = 8.4 Hz, 1H), 6.95-6.92 (m, 3H), 4.86-4.83 (m, 1H), 3.34 (d, *J* = 3.3 Hz, 2H), 1.10 (s, 3H), 1.02 (s, 12H).

(4c)[26a] Colorless solid (102 mg, 80% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 7.02-6.98 (m, 1H), 6.91-6.81 (m, 3H), 6.73 (d, *J* = 7.4 Hz, 1H), 5.63 (d, *J* = 7.5 Hz,

1H), 4.64 (s, 2H), 1.03 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 133.3(N(*C*H)), 132.6(Aryl-*C*), 132.0(Aryl-*C*), 128.7(Aryl-*C*), 125.9(Aryl-*C*), 125.2(Aryl-*C*), 123.5(Aryl-*C*), 105.9(CH(*C*H)), 83.1(*C*$(CH_3)_2$), 46.0(N(*C*H_2)), 24.4(C(*C*$H_3)_2$).

4d and **4d´** were obtained as yellow oil (104.7 mg, 73% yield). (**4d)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 7.69 (d, *J* = 8.2 Hz, 1H), 6.88-6.85 (m, 1H), 6.55 (d, *J* = 2.9 Hz, 1H), 6.23 (d, *J* = 9.5 Hz, 1H), 5.66-5.61 (m, 1H), 4.14 (dd, *J* = 4.2, 1.7 Hz, 2H), 3.34 (s, 3H), 1.06 (s, 12H). (**4d´)**[26a]: ^{1}H NMR (400 MHz, C_6D_6): δ 8.09 (d, *J* = 9.2 Hz, 1H), 6.95 (dt, *J* = 8.1, 1.7 Hz, 1H), 6.73 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.49 (d, *J* = 3.1 Hz, 1H), 4.80 (dt, *J* = 8.1, 1.7 Hz, 1H), 3.35 (s, 2H), 3.34 (s, 3H), 1.07 (s, 12H).

4e and **4e´** were obtained as yellow oil (127.3 mg, 94% yield). (**4e)**[26b]: ^{1}H NMR (400 MHz, C_6D_6): δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.12-7.08 (m, 1H), 6.90-6.82 (m, 2H), 6.01 (s, 1H), 4.09 (s, 2H), 1.50 (s, 3H), 1.06 (s, 12H). (**4e´)**[26b]: ^{1}H NMR (400 MHz, C_6D_6): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.12-7.08 (m, 1H), 6.90-6.82 (m, 3H), 3.20 (s, 2H), 1.53 (s, 3H), 1.01 (s, 12H).

General procedure for the hydroboration products **4f-4n**: A 25 mL Schlenk flask was charged with a magnetic agitator, *N*-heteroarenes (0.50 mmol, 1.0 equiv) and mNHO **2a** (0.0040 mmol, 0.020 equiv). Then dried C_6D_6 or THF (1.5 mL) was slowly added to the flask. After that HBpin was added based on the [C=N]/[HBpin]=1:1.1. The reaction mixture was stirred at 70 ^{o}C (oil bath) for 12 h (**4g-4n**) or 18 h (**4f**). After being allowed to cool to room temperature, solvent was removed under reduce pressure. The products were washed with pentane (2 × 0.5 mL) for further purification.

(4f)[26b] Colorless solid (150.4 mg, 98% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.18-6.93 (m, 6H), 3.54 (s, 2H), 1.06 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 142.4(Aryl-*C*), 130.3(Aryl-*C*), 127.2(Aryl-*C*), 126.2(Aryl-*C*), 123.4(Aryl-*C*), 122.6(Aryl-*C*), 83.0(*C*$(CH_3)_2$), 33.8(*C*H_2), 24.4(C(*C*$H_3)_2$).

4g and **4g´**were obtained as yellow oil (NMR yield 33%, CH_2Br_2 was used as internal standard). (**4g)**[26c]: ^{1}H NMR (400 MHz, C_6D_6): δ 6.56 (dt, *J* = 8.4, 1.6 Hz, 2H), 4.55-4.60 (m, 2H), 2.82 (tt, *J* = 3.2, 1.6 Hz, 2H), 0.96 (s, 12H). (**4g´)**[26c]: ^{1}H NMR (400

MHz, C_6D_6): δ 6.74 (d, *J* = 7.6 Hz, 1H), 5.77-5.83 (m, 1H), 5.04-5.14 (m, 2H), 4.18 (dd, *J* = 4.0, 1.6 Hz, 2H), 1.00 (s, 12H).

(4h)[26d] Colorless solid (164.6 mg, 98% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 6.72 (d, *J* =8.2 Hz, 1H), 4.72 (s, 2H), 4.62-4.58 (m, 1H), 3.75 (s, 2H), 1.04 (s, 12H), 1.01 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 129.3(N(*C*H)), 102.2(CH(*C*H)CH_2), 82.5(*C*$(CH_3)_2$), 82.0(*C*$(CH_3)_2$), 55.8(N(*C*H_2)N)), 41.8(N(*C*H_2)), 24.6(C(*C*$H_3)_2$), 24.4(C(*C*$H_3)_2$).

(4i)[26d] Colorless solid (142.8 mg, 85% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 6.06 (s, 2H), 3.44 (s, 4H), 1.04 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 110.8(N(*C*H)), 82.4(*C*$(CH_3)_2$), 42.1(N(*C*H_2)), 24.5(C(*C*$H_3)_2$).

(4j) Colorless solid (187.2 mg, 97% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 8.14-8.11 (m, 2H), 6.96-6.94 (m, 2H), 3.61 (s, 4H), 1.06 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 133.0((Aryl-*C*)), 121.2(Aryl-*C*), 120.8(Aryl-*C*), 82.4(*C*$(CH_3)_2$), 43.9(N(*C*H_2)), 24.4(C(*C*$H_3)_2$). HRMS (ESI) m/z: [M+H+2H_2O-2HOBpin] Calcd. for $C_8H_{11}N_2$ 135.0917; Found 135.0912.

(4k)[26d] Colorless solid (198.7 mg, 96% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 7.03 (s, 1H), 4.54 (s, 2H), 3.96 (s, 2H), 1.00 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 130.4(N(*C*H)), 96.4(Br*C*), 83.0(*C*$(CH_3)_2$), 82.5(*C*$(CH_3)_2$), 55.1(N(*C*H_2)N), 48.8(N(*C*H_2)), 24.5(C(*C*$H_3)_2$), 24.3(C(*C*$H_3)_2$).

(4l)[26d] Colorless solid (181.4 mg, 94% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 8.00-7.98 (m, 1H), 7.11-7.06 (m, 1H), 6.78-6.73 (m, 2H), 4.86 (s, 2H), 4.44 (s, 2H), 1.09 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 141.9(Aryl-*C*), 126.5(Aryl-*C*), 124.3(Aryl-*C*), 121.0(Aryl-*C*), 120.8(Aryl-*C*), 82.5(*C*$(CH_3)_2$), 82.2(*C*$(CH_3)_2$), 57.5(N(*C*H_2)N), 45.9(N(*C*H_2)), 24.6(C(*C*$H_3)_2$), 24.4(C(*C*$H_3)_2$).

(4m)[26d] Colorless solid (213.9 mg, 92% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 4.62 (s, 6H), 1.07 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 81.9(*C*$(CH_3)_2$), 58.7(N(*C*H_2)), 24.5(C(*C*$H_3)_2$).

(4n)[26d] Colorless solid (128.8 mg, 98% yield): ^{1}H NMR (400 MHz, C_6D_6): δ 7.61 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 4.92 (s, 2H), 1.01 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ

144.5(Aryl-*C*), 130.2(Aryl-*C*), 125.2(Aryl-*C*), 122.0(Aryl-*C*), 121.8(Aryl-*C*), 114.3(Aryl-*C*), 83.1(*C*(CH_3)$_2$), 52.6(N(*C*H_2)), 24.4(C(*C*H_3)$_2$).

Gram scale hydroboration of *p*-fluorobenzonitrile and benzothiazole

A 25 mL Schlenk flask was charged with a magnetic agitator, *p*-fluorobenzonitrile (5.0 mmol, 1.0 equiv) and mNHO **2a** (0.0040 mmol, 0.020 equiv). Then dried THF (5.0 mL) was added to the flask. After that HBpin was slowly added to the mixture (12 mmol, 2.4 equiv). The reaction mixture was stirred at 70 °C (oil bath) for 12 h. After being allowed to cool to room temperature, solvent was removed under reduce pressure. The product was washed with pentane (2 × 1.0 mL) for further purification and **3c** was obtained as colorless solid (1.621 g, 4.3 mmol).

A 25 mL Schlenk flask was charged with a magnetic agitator, benzothiazole (5.0 mmol, 1.0 equiv) and mNHO **2a** (0.0040 mmol, 0.020 equiv). Then dried C_6D_6 (5.0 mL) was added to the flask. After that HBpin was slowly added to the mixture (5.5 mmol, 1.1 equiv). The reaction mixture was stirred at 70 °C (oil bath) for 12 h. After being allowed to cool to room temperature, solvent was removed under reduce pressure. The product was washed with pentane (2 × 1.0 mL) for further purification and **4n** was obtained as colorless solid (1.209 g, 4.6 mmol).

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for all compounds, the calculation details and X-ray crystallography details of compound **2a**, **2b** (CIF).

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (21602249), the Fundamental Research Funds for the Central Universities and the Research Funds of Renmin University of China (Program 20XNLG20), and Public Computing Cloud Platform, Renmin University of China. We also thank professor Guy Bertrand and professor Jean Bouffard for sharing their unpublished works.

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