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# Photoredox Controlled β-Regioselective Radical Hydroboration of Activated Alkenes with NHC-Boranes

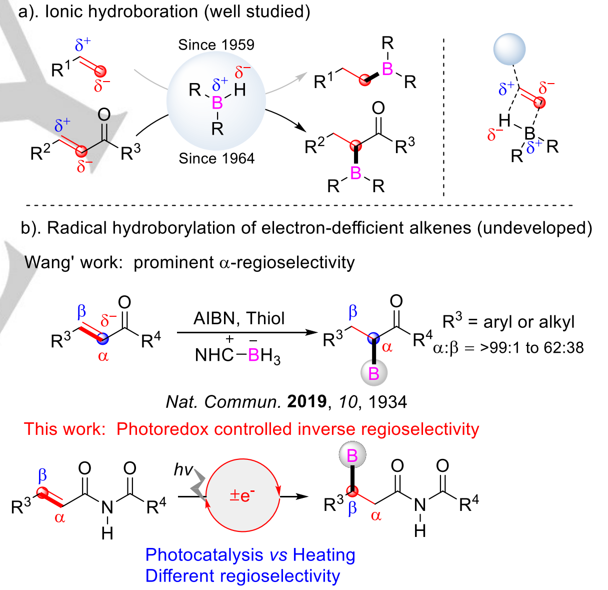
Congjun Zhu, Jie Dong, Xueting Liu, Liuzhou Gao, Yue Zhao, Jin Xie*, Shuhua Li*, and Chengjian Zhu*

Dedicated to the 70th anniversary of Shanghai Institute of Organic Chemistry

**Abstract:** In this communication, we report an unprecedented β-regioselective radical inverse hydroboration (compared with ionic hydroboration) of α, β-unsaturated amides with NHC-$BH_3$ enabled by the photoredox catalysis. The density functional theory (DFT) calculations show that the unique photoredox cycle is a key factor to control the β-regioselective radical hydroboration, which makes the energy barrier is lower than other pathways. This protocol provides a general and convenient route to construct a wide range of structurally diverse β-borylated amides in synthetically useful yields under mild conditions.

The organoboron are versatile building blocks for cross-coupling in synthetic chemistry and also important structural motifs in medicine and materials.[1] The direct hydroboration of alkenes with boranes has been esteemed as a direct and efficient method for the construction of C-B bonds although these compounds are always regarded as the reactive intermediates for the preparation of alcohols.[2] In general, the regioselectivity for hydroboration of olefin should meet the electronic demand in the transition states, in which the boron motif adds to the relatively less electronic-rich position (Scheme 1a).

N-heterocyclic carbene (NHC) boranes are air-stable and easily handling organoborane reagents.[3] During the past decade, the groups of Curran, Malacria, Fensterbank, Lacôte and Wang, have successfully shown the promising chemical space in the exploration of NHC-boryl radicals in both organic synthesis and main-group element radical chemistry.[4-10] In 2018, our group developed the first inverse radical hydroboration of imines with NHC-ligated boranes to construct α-amino organoboron.[11a] In the ionic hydroboration of activated alkenes, the α-borylated products are always obtained due to the matched electronic demand in the transition state. As our continuing efforts in radical borylation, we wondered if the generated NHC-boryl radical by mild photoredox catalysis can be used for inverse radical hydroboration of electron-deficient alkenes to furnish synthetically valuable β-borylated compounds (compared with ionic hydroboration, Scheme 1b, lower part). During the process of this work, Wang and co-workers reported an elegant radical α-borylation of α,β-unsaturated carbonyl compounds with NHC-boranes using azodi-*iso*-butyronitrile (AIBN) as the radical initiators at 80 °C (Scheme 1b).[12] However, in some case, a significant amount of regioisomeric products can be formed dependent on the electronic effect of substituents (α: β ranges from >99:1 to 62:38).



***Scheme 1.*** The state-of-the-art of ionic and radical hydroboration of alkenes with boranes.

A series of electron-deficient alkenes were initially investigated by means of synergistic photocatalysis and thiol catalysis based on the success of our inverse hydroborylation of imines (Scheme 2).[11] Much to our surprise, the highly electron-deficient alkenes, such as (vinylsulfonyl)benzene (**1a**) and 2-benzylidenemalononitrile (**3a**), cannot occur the radical hydroboration process. The use of ethyl (*E*)-but-2-enoate (**4a**) also failed to give the desired product under our photoredox conditions, which is indeed a competent substrate in Wang's reaction conditions despite of moderate regioselectivity.[12a] Fortunately, when α,β−unsaturated amide (**7a**) was employed, the β-borylated amide can be obtained in 62% yield.[13] It is

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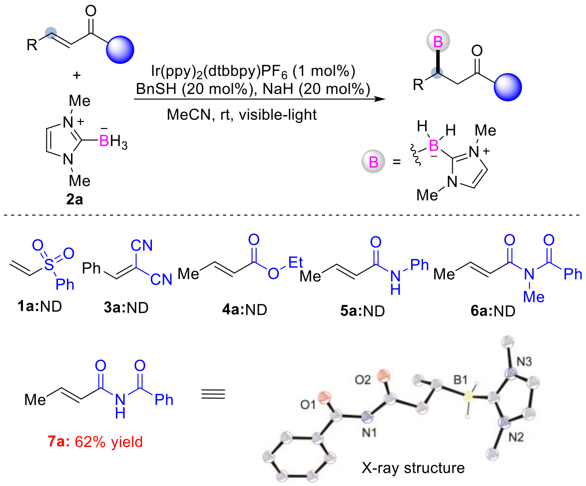
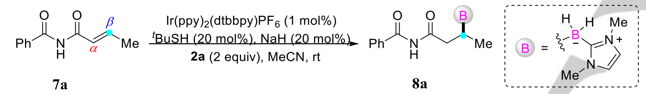
Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate)) interesting to find that this kind of NH-free amide functional group (**7a**) is a crucial factor for a successful radical hydroboration.



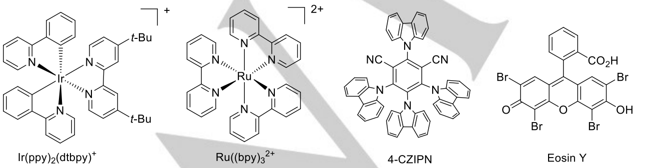
***Scheme 2.*** Initial investigation of radical hydroboration of electron-deficient alkenes. Bn = benzylic group

***Table 1:*** Optimization of reaction conditions.[a]

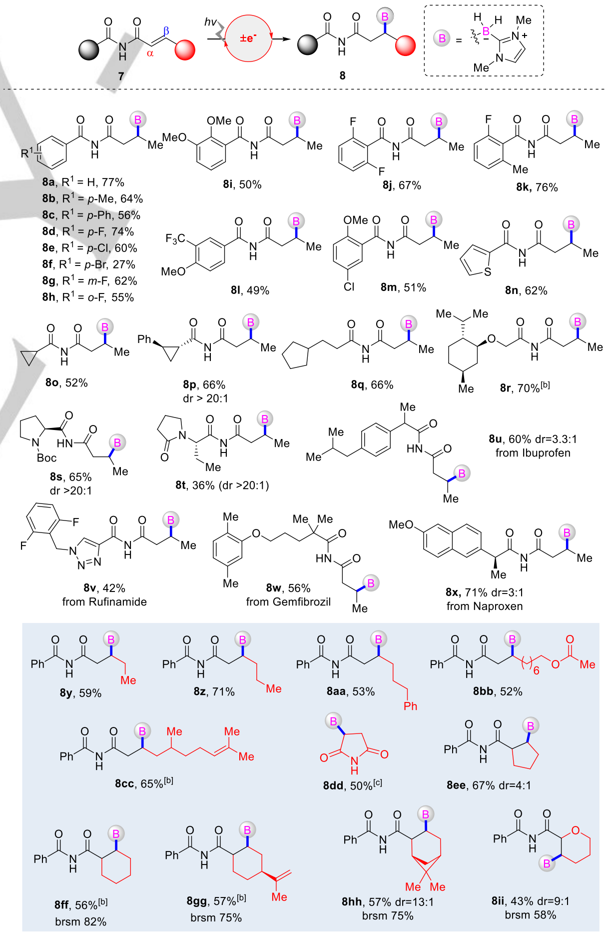


| Entry | Variation of standard conditions | Yield [%][b] |
|---|---|---|
| **1** | **None** | **77** |
| 2 | Ru(bpy)$_3$Cl$_2$ | ND |
| 3 | 4CZIPN | ND |
| 4 | Eosin Y | trace |
| 5 | blue LEDs instead CFL | 25 |
| 6 | without $^t$BuSH | 27 |
| 7 | without light | ND |
| 8 | Without photocatalyst | ND |

[a] Standard reaction conditions: Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%), $^t$BuSH (20 mol%), NaH (20 mol%), **1a** (0.2 mmol), **2a** (0.4 mmol), MeCN (1.0 mL), 36 W CFL bulb, 24 h, ambient temperature. [b] Yield of isolated product. ND means not detected; CFL means compact fluorescent lamps; LEDs means light emitting diode strips.



After getting these initial results, we focused our attention on optimizing the reaction conditions (See Supporting Information for details). The optimized reaction conditions include of 1 mol% of Ir[ppy]$_2$(dtbbpy)PF$_6$ as the photocatalyst, 20 mol% of 2-methylpropane-2-thiol ($^t$BuSH) as the hydrogen-atom transfer (HAT) organocatalyst together with 20 mol% NaH as the base and MeCN as the solvent under the irradiation of 36 W compact fluorescent light (CFL) at room temperature (Table 1, entry 1). The desired product (**8a**) can be obtained in 77% yield under the standard conditions. The use of other photocatalysts decreased the reaction yield (entries 2-4, Table 1). Switching the light source from CFL to blue LEDs led to a significant lower yield (entry 5, Table 1). Interestingly, without $^t$BuSH still 27% yield can be obtained (entry 6, Table 1). We speculated that in this case the amide motif in **7a** may act as HAT catalyst role. Provided by stronger bond dissociation energies (BDE) of N-H (**7a**) than S-H bonds,[14] we performed the density functional theory calculations and it was found that electrophilic thiyl radical was slightly easier than amidyl radical to abstract one hydrogen atom from NHC-BH$_3$ (6.3 kcal mol$^{-1}$ versus 7.7 kcal mol$^{-1}$), giving rise to the corresponding NHC-boryl radical (See Supporting Information for details). According to initial investigation, if protected amide substrate (**6a** in Scheme 2) was employed, the reaction did not occur (See Supporting Information for details). The control experiments indicated that both light and photocatalyst were important factors for the reaction (entries 7 and 8, Table 1).



***Scheme 3.*** Reaction scope with regard to α,β-unsaturated alkenes. [a] Standard conditions: Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%), $^t$BuSH (20 mol%), NaH (20 mol%), **1a** (0.2 mmol), **2a** (0.4 mmol), MeCN (1.0 mL), 36 W CFL bulb, 24 h, ambient temperature. [b] The diastereoselectivity of product cannot be determined by NMR due to the complex peak overlap. [c] BnSH instead $^t$BuSH. brsm means the isolated yields are calculated based on the recovered starting materials.

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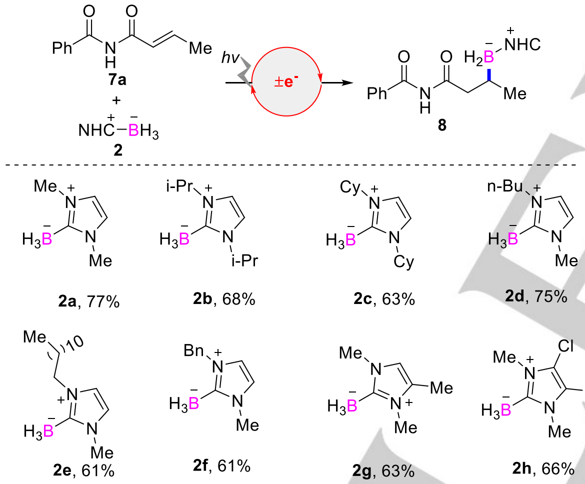
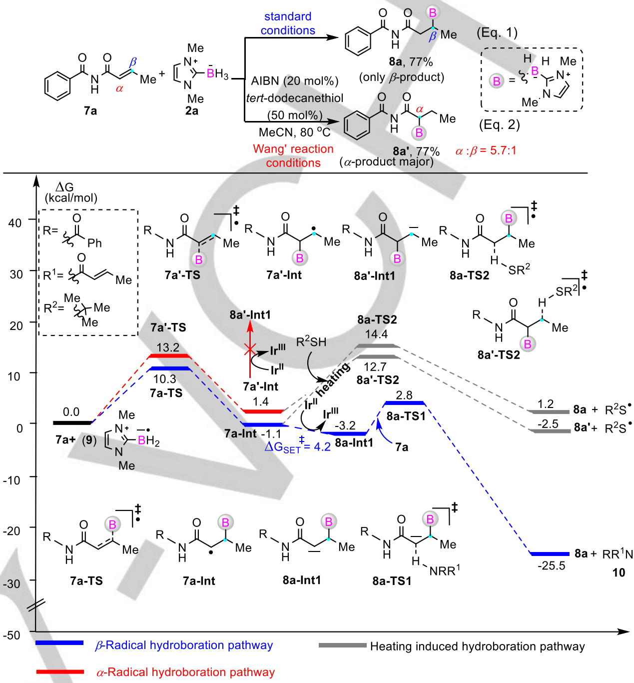
In general, a wide array of amide bearing substituents with different electronic and steric properties are competent substrates (Scheme 3). The electron-donating and electron-withdrawing substituents on *ortho*-, *meta*- and *para*-positions of phenyl rings could smoothly occur this radical hydroboration in exclusive regioselectivity (**8a**–**n**). The position of substituents on phenyl ring have little influence on the yield (**8d, 8g, 8h**). The alkyl substituted amide can also deliver the desired products in synthetically useful yield and excellent regioselectivity (**8o**–**x**). Importantly, the introduction of heterocyclic motif into the amides can tolerate the reaction conditions well (**8n**, **8s**, **8t**, **8v**). A series of biologically important compounds derived amides were subjected to this protocol and they can readily proceed the regioselective hydroboration process (**8u**–**x**). Subsequently, a wide range of readily available unsaturated alkenes were evaluated. It has a very broad scope (**8y**–**ii**) independent of the substitution structures and electronic effect. The long-chain alkyl-substituted (**8y**–**cc**) unsaturated amides can give rise to the desired products in moderate yield. Interestingly, 1H-pyrrole-2,5-dione is also a good substrate for radical hydroboration (**8dd**). Besides, the cyclic unsaturated amides can occur this transformation to afford the desired β-borylated amides in moderate yields and diastereoselectivity (**8ee**–**ii**). Of note, the terminal alkene motif hardly influences the reaction selectivity and it can keep intact well during the reaction process (**8gg**).



***Scheme 4.*** Scope with respect to the NHC-boranes. Standard conditions: Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%), $^t$BuSH (20 mol%), NaH (20 mol%), **1a** (0.2 mmol), **2a** (0.4 mmol), MeCN (1.0 mL), 36 W CFL bulb, 24 h, ambient temperature.

Finally, different kinds of NHC-boranes were explored and the results are summarized in Scheme 4. Excitingly, the substituents on NHC have little effect on the reaction efficiency. The NHC-boranes (**2a**–**f**) tested could provide the β-borylated products in 61–77% yields.

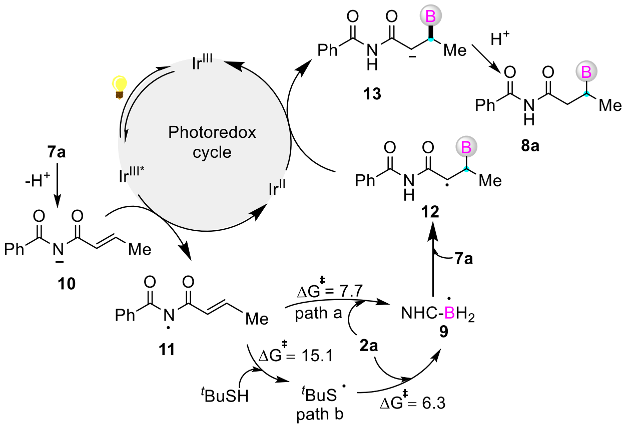
The 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) and 1,4-dinitrobenzene can completely inhibit the hydroboration, suggesting that a radical process may be likely. Both the NHC-boryl radical and amidyl radical can be successfully trapped by TEMPO (See Supporting Information for details).[15] In addition, in our radical hydroboration process, a full β-regioselectivity was obtained (Scheme 5a). However, for the same substrate (Scheme 5, Eq. 1), when it was subjected to Wang's reaction conditions in the presence of AIBN and thiol with heating conditions,[12a] the overwhelming α-regioselectivity (α:β=5.7:1) was detected (Eq. 2).



***Scheme 5.*** DFT studies: Gibbs free energy (in kcal mol$^{-1}$) profile for the reaction between the radical **9** and **7a**.

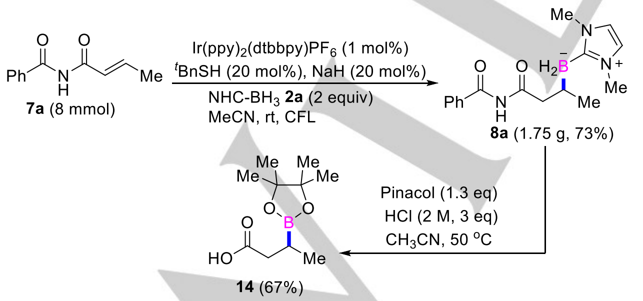
To gain more insight into this selectivity, DFT calculations with the M06 functional[16] was performed, for the model reaction between the NHC-boryl radical **9** and **7a** (computatisonal details are provided in the supporting information). Our DFT calculations indicated that the addition of the NHC-boryl radical to the β-position of **7a** requires a lower activation energy (10.3 kcal mol$^{-1}$) than that to the α-position (13.2 kcal mol$^{-1}$). The subsequent photoreduction of the β-addition intermediate (**7a**–**Int** to **8a**–**Int1**) is readily feasible with an single-electron transfer (SET) energy barrier as low as 4.2 kcal mol$^{-1}$. The following protonation step to form the product **8a** involves a free energy barrier of 6.0 kcal mol$^{-1}$, and is exothermic by 22.3 kcal mol$^{-1}$. This result indicates that the β-addition pathway under photoredox condition is both thermodynamically and kinetically favorable. In contrast, our theoretical study suggests that the photoreduction of α-addition intermediate (**7a'**–**Int** to **8a'**–**Int1**) is thermodynamically unfavorable. The calculated results are in accord with the observed β-regioselectivity under photoredox catalysis (Scheme 5, Eq. 1).

Our calculations also showed that under thermal (radical chain process) conditions,[12a] the β-addition step is slightly favorable than the α-addition step, but the subsequent hydrogen-atom transfer (HAT) of the β-addition intermediate from thiol involves a barrier of 14.4 kcal mol$^{-1}$. In contrast, the HAT of the α-addition intermediate involves a free energy barrier of 12.7 kcal mol$^{-1}$. Thus, under thermal conditions, the formation of α–addition product **8a** is kinetically more favorable, which is consistent with the experimental result (α:β = 5.7:1, Scheme 5, Eq. 2).



***Scheme 6.*** Proposed mechanism. Gibbs free energy (in kcal mol$^{-1}$)

Base on our DFT calculations and control experiments (results are provided in the SI), a plausible mechanism is proposed in Scheme 6. First, the photoexcited *Ir[ppy]$_2$(dtbbpy)PF$_6$ undergoes single-electron oxidation of nitrogen anion (**10**) to form an amidyl radical (**11**),[17] which can abstract one hydrogen atom from NHC-BH$_3$ (**2a**) (ΔG$^‡$= 7.7 kcal mol$^{-1}$) to form the NHC-boryl radical species (**9**) (path a). On the other hand, the resulting amidyl radical (**11**) can also abstract one hydrogen atom from $^t$BuSH (ΔG$^‡$= 15.1 kcal mol$^{-1}$) to generate electrophilic thiyl radical, and the thiyl radical subsequently abstracts one hydrogen atom from NHC-BH$_3$ (**2a**) (ΔG$^‡$= 6.3 kcal mol$^{-1}$) to form the NHC-boryl radical species (**9**) (path b).[10b,11a] Two paralleled pathways may account for a higher yield in the presence of thiol (27% vs 77%). Subsequently, the radical addition of the NHC-boryl radical to the unsaturated carbon-carbon double bond can afford radical intermediate (**12**), which further accepts one electron from Ir(II) to complete the photoredox cycle and generates intermediate (**13**), which can get one proton from (**7a**) or $^t$BuSH to afford the desired product **8a**. Indeed, the photoredox catalysis is a key factor to achieve β-regioselective radical hydroborylation of unsaturated amides compared to Wang's work.[12a]



**Scheme 7.** Gram scale experiment and synthetic application to synthesize β-boronate carboxylic acid.

The β-boronate carboxylic acid serves as one important structural motif in a great number of bioactive compounds.[18] 1.75 grams desired products (**8a**) can be obtained under standard conditions without compromise the reaction efficiency. To our delight, treatment of product (**8a**) with 2 M HCl in the presence of pinacol can afford β-boronate carboxylic acid (**14**) in 67% yields (Scheme 7).

In conclusion, an unprecedented photoredox radical hydroboration of α,β-unsaturated amides with NHC-BH$_3$ has been developed by means of photoredox catalysis. The DFT calculation are performed to explain the corresponding β- or α-regioselectivity under photoredox catalysis or normal radical chain conditions. Interestingly, we found that the photoredox catalysis is an important factor to control β-regioselective radical hydroborylation compared to previous work. This protocol provides a general and convenient route to construct a wide range of structurally diverse β-borylated amides in synthetically useful yields under mild conditions. The excellent functional group compatibility, exclusive regioselectivity and mild reaction conditions enable a promising protocol in radical boron chemistry. Further application of this strategy and the exploration of inverse hydroboration strategy for the synthesis of enantiopure β-borylated amides is underway in our laboratory.

## Acknowledgements

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**Keywords:** Regioselective hydroboration • Photoredox catalysis • Radical borylation • Umpolung

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[17] Although, 2-methylpropane-2-thiolate ($^t$BuS$^-$) holds a similar oxidation potential with nitrogen anion (**10**) (0.52 V versus 0.53 V vs SCE), the concentration of intermediate **10** in the reaction solution is higher than 2-methylpropane-2-thiolate. We guessed that the intermediate **10** was first oxidized by the photocatalyst.

[18] a) R. C. Gardner, S. J. Assinder, G. Christie, G. G. Mason, R. Markwell, H. Wadsworth, M. McLaughlin, R. King, M. C. Chabot-Fletcher, J. J. Breton, D. Allsop, A. J. Rivett, *Biochem. J.* **2000**, *346*, 447; b) R. C. Kane, P. F. Bross, A. T. Farrell, R. Pazdur, *Oncologist*, **2003**, *8*, 508.

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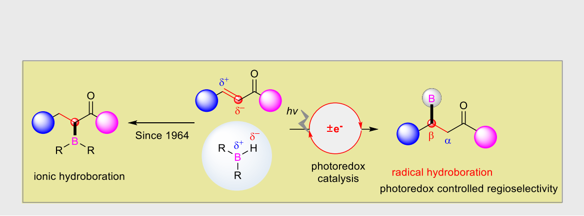
## COMMUNICATION



**Light Does Different:** An unprecedented photoredox-controlled regioselective radical inverse hydroboration (compared with ionic hydroboration) of α, β-unsaturated amides with NHC-BH$_3$ has been developed. This protocol provides a general and convenient route to construct a wide range of structurally diverse β-borylated amides in synthetically useful yields under mild conditions.

*Congjun Zhu, Jie Dong, Xueting Liu, Liuzhou Gao, Yue Zhao, Jin Xie*, Shuhua Li* and Chengjian Zhu**

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**Photoredox Controlled β-Regioselective Radical Hydroboration of Activated Alkenes with NHC-Boranes**

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