A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition Chemie

GDCh

www.angewandte.org

Accepted Article

Title: Synergistic Photoredox and Organocatalysis for Inverse Hydroboration of Imines

Authors: Jin Xie

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201800421
Angew. Chem. 10.1002/ange.201800421

Link to VoR: http://dx.doi.org/10.1002/anie.201800421
http://dx.doi.org/10.1002/ange.201800421

WILEY-VCH

10.1002/anie.201800421

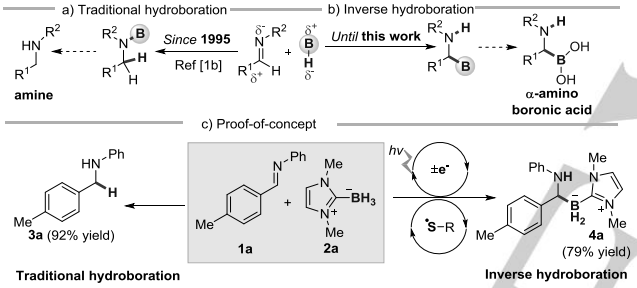
WILEY-VCH

Synergistic Photoredox and Organocatalysis for Inverse Hydroboration of Imines

Nengneng Zhou, Xiang-Ai Yuan, Yue Zhao, Jin Xie* and Chengjian Zhu*

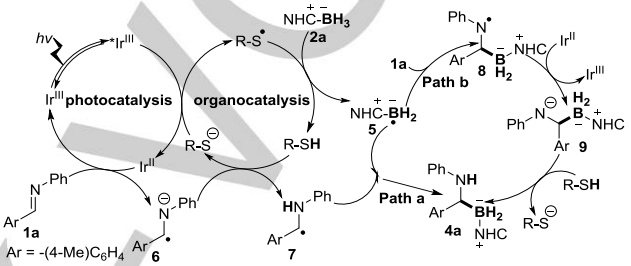
Abstract: The first catalytic inverse hydroboration of imines with *N*-heterocyclic carbene boranes has been realized by means of cooperative organocatalysis and photocatalysis. This catalytic combination brings a promising platform to promote NHC-boryl radical chemistry under sustainable and radical initiator free conditions. The highly important functional group compatibility and possible application in late-stage hydroboration represent an important step-forward to an enhanced α-amino organoboron lead library.

Hydroboration of C=N bonds with organoboranes or borohydrides is a workhorse reaction for the mild reduction of imines into amines (Scheme 1a).[1] In this fundamental transformation, the addition of B-H bond to C=N bond typically results in nitrogen-bound boryl intermediates. Its exclusive regioselectivity derives from the favorable interaction of B-H bond with positively polarized carbon atom on C=N bond. Since 1995, no catalytic inverse hydroboration has been reported.



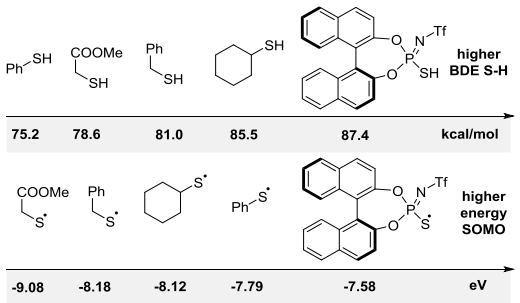
Scheme 1. Selective hydroboration of imines and our design.

α-Amino organoborons are versatile building blocks in organic synthesis and potent protease inhibitors in medicinal chemistry.[2] Although transition-metal-catalyzed diborylation of C=N bond has been reliable to access,[3] the limited flexibility and moderate functional group tolerance compromise their late-stage applications in complex bioactive molecules. To further enhance α-amino organoboron lead library, the development of catalytic inverse hydroboration of imines with organoboranes is highly desirable, which can afford a general and practical strategy to one class of unprecedented α-aminoboron compounds (Scheme 1b). During the last five years, the development of B-centered radical synthetic chemistry has gained increasing momentum.[4],[5] Thus, we rationalized that radical hydroboration of imines with organoboranes could potentially realize inverse hydroboration to deliver α-aminoboryl products instead of the existing intermediates with N-B bond.



Scheme 2. Mechanistic hypothesis.

The *N*-heterocyclic carbene (NHC) boranes are bench-stable, nontoxic, easy available and convenient to handle organoboranes.[6] The seminal work from Curran, Fensterbank, Lacôte and Malacria have revealed a fruitful chemical space for NHC-boryl radicals,[7] including radical deoxygenation of xanthates, radical reduction of halides, radical reductive decyanation etc. More recently, Wang's group[8] reported an elegant radical borylation and subsequent cyclization of 1,6-enynes with NHC-boranes in the presence of radical initiators. Despite this great progress, the exploitation of NHC-boranes for radical C-B bond formation is still of great importance to enrich boron-containing libraries and currently its application in highly polarized C=N-π bond is scarcely studied owing to competing reduction pathway. The proof-of-concept for radical inverse hydroboration of imines was shown in Scheme 1c.



Scheme 3. Calculated BDEs and SOMO energies.

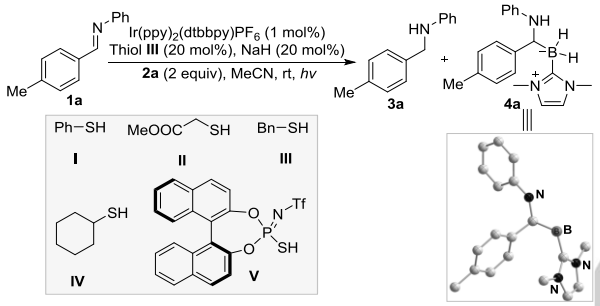
Usually, the generation of NHC-boryl radical requires the use of potentially toxic radical initiators (e.g., 2,2'-azoisobutyronitrile, di-*tert*-butyl hyponitrite and di-*tert*-butyl peroxoide).[7] The recent efforts on synergetic photocatalysis

[*] N. Zhou, Dr Y. Zhao, Prof. Dr J. Xie, and Prof. Dr C. Zhu
State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023 (P. R. China)
Email: xie@nju.edu.cn or cjzhu@nju.edu.cn
Homepage: http://hysz.nju.edu.cn/xie/
http://hysz.nju.edu.cn/cjzhu/
Dr. X.-A. Yuan
School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165 (P. R. China)
Prof. Dr C. Zhu
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032 (P. R. China)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:

and thiol catalysis demonstrated that photoexcited *Ir(ppy)$_2$(dtbbpy)PF$_6$ ($E_{1/2}^{*III/II}$ = + 0.66 V vs SCE; τ= 557 ns) could readily accept one electron from thiol to give reactive thiyl radical.[9] As our ongoing interests in photocatalysis,[10] we wondered if the thiyl radical generated *in situ* via such a photocatalytic synergistic mode is capable of accomplishing the inverse regioselectivity in hydroboration of imines under mild conditions. After an insight into photocatalytic radical C-C functionalization of imines,[11] two possible pathways for inverse hydroboration were depicted in Scheme 2. In path a, it is likely to undergo single electron transfer (SET) reduction of imine first with strongly reductive Ir^{II} species ($E_{1/2}^{III/II}$ = - 1.51 V vs SCE)[9a] followed by radical-radical C-B cross-coupling of NHC-boryl radical **5** and α-aminobenzyl radical **7**. In path b, NHC-boryl radical addition to imine **1a** occurs at first followed by SET reduction of nitrogen-centered radical **8**.

***Table 1*:** Optimization of reaction conditions.



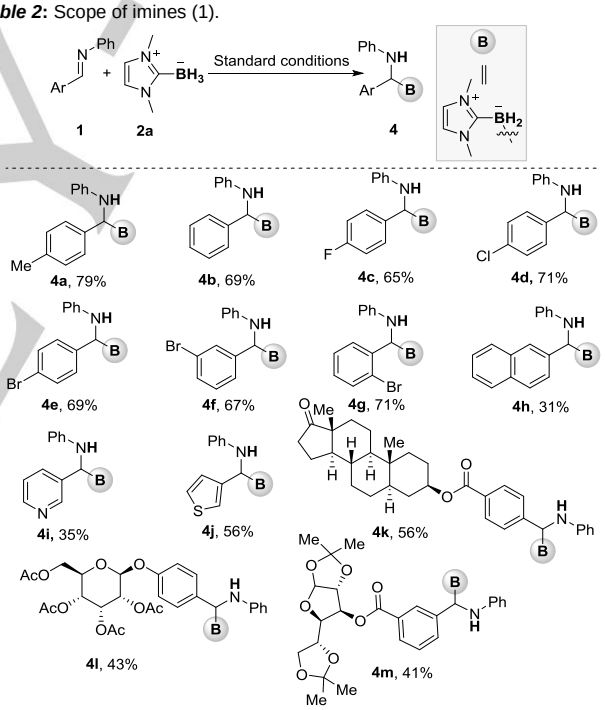
Entry	Variation of standard conditions	Yield:**4a**[a]	Yield:**3a**[a]
1	None	79%	9%
2	Ru(bpy)$_3$Cl$_2$ as photocatalyst	0	91%
3	*fac*-Ir(ppy)$_3$ as photocatalyst	0	93%
4	Thiol **I** or **V** instead of **III** or no thiol	0	91%
5	Thiol **II** instead of **III**	23%	43%
6	Thiol **IV** instead of **III**	49%	31%
7	Blue LEDs instead of CFL	57%	27%
8	No photocatalyst	0	92%
9	No light	0	91%

Standard conditions: Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%), thiol **III** (20 mol%), NaH (20 mol%), **1a** (0.2 mmol), **2a** (0.4 mmol), MeCN (1.0 mL), 33 W compact fluorescent light (CFL) bulb, 24 h, room temperature. [a] Isolated yield.

It is worthy of noting that the background reaction of imine **1a** and NHC-borane **2a** furnishes secondary amine **3a** in almost quantitative yield without synergistic catalytic cycle at room temperature (Scheme 1c). To significantly suppress this pathway, the resulting thiyl radical should have a high enough potential to rapidly abstract one hydrogen atom from NHC-borane **2a** (BDE of B-H bond = 74.5 kcal/mol) to generate NHC-boryl radical **5** (calculated SOMO energy = - 4.59 eV). Polar kinetic effects aside,[7d] to some extend, the use of thermodynamically matched thiol would be another possible tunability for intermolecular H-atom abstraction manifestation. Therefore, we performed density functional theory (DFT) calculations on the BDE of S-H bond in thiols and SOMO energy of corresponding thiyl radicals (Scheme 3). We are glad to find that varied thiols show significant variation on both factors, and these variable reactivities indicate possible tunability for the H-atom transfer step.

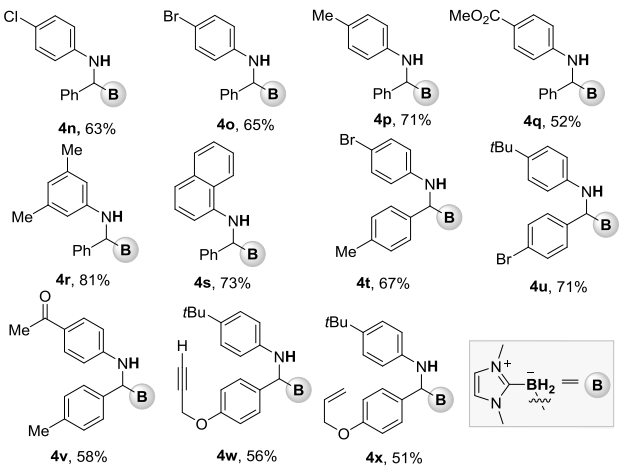
We commenced to investigate the inverse hydroboration model reaction of imine **1a** and NHC-borane **2a** (Table 1). The optimized conditions were determined to be 1 mol% Ir(ppy)$_2$(dtbbpy)PF$_6$ as photocatalyst and 20 mol% phenyl-methanethiol **III** as organocatalyst together with 20 mol% NaH as inorganic base in MeCN under the irradiation with 33 W CFL at room temperature (Table 1, entry 1). Replacing Ir(ppy)$_2$(dtbbpy)PF$_6$ with Ru(bpy)$_3$Cl$_2$ or *fac*-Ir(ppy)$_3$ did not give product **4a** (Table 1, entries 2 and 3). To our delight, consistent with DFT calculation results, the use of suitable thiol was vital for success (Table 1, entries 4-6). When thiols **I** and **V** were employed, no desired product was detected; other aliphatic thiols **II** and **IV** instead of thiol **III** delivered moderate yields (Table 1, entries 5 and 6). Change the light source from CFL to blue LEDs, the yield of **4a** decreased to 57% with a significant amount of byproduct **3a** (Table 1, entry 7). The better yield for CFL might be due to the thermal factor. The control experiments demonstrated that photocatalyst, thiol and light were three essential factors (Table 1, entries 4, 8 and 9).

***Table 2*:** Scope of imines (1).



Under the optimal reaction conditions, we investigated the imine scope with respect to aldehyde-derived moiety (Table 2). In general, this protocol combines excellent chemo- and regioselectivities with good functional group compatibility despite of multiple reactive sites on imines. Only monohydroboration products were obtained and no di- or tri-hydroboration was observed. Aromatic rings bearing both electron- donating and electron-withdrawing substituents could smoothly undergo inverse hydroboration (**4a-j**). The position of substituents on phenyl ring seemed to have no effect on the transformation (**4e-g**). Additionally, heteroaromatic aldehyde-derived imines were good coupling partners (**4i** and **4j**).

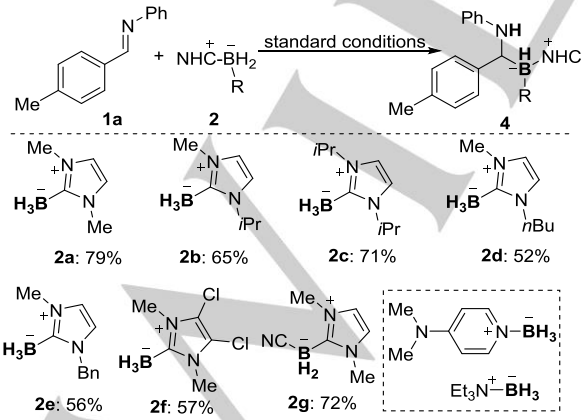
To demonstrate the practice of inverse hydroboration, we applied this protocol to late-stage radical borylation of a series of biologically important compounds, such as estrone, helicid and diacetone-D-glucose derivatives (**4k-m**). Meanwhile, the reactive ketone unit remained intact, underlying its synthetic advantages in organic synthesis.



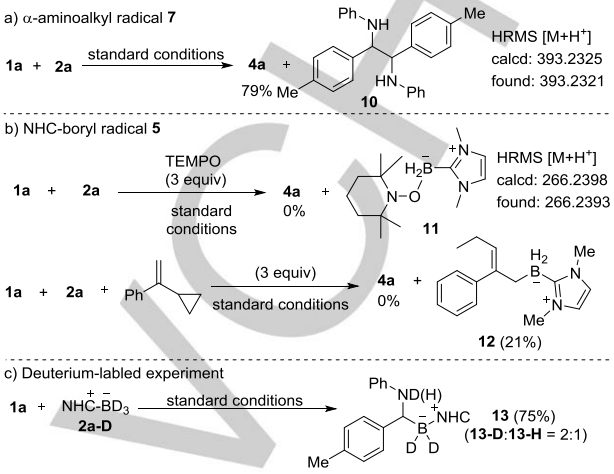
Scheme 4. Scope of imines (2).

We then turned our attention to examine the effect of *N*-aryl part on aldimines (Scheme 4). It was found that the aromatic rings of *N*-aryl bearing either electron-rich (-Me, -^{t}Bu) or electron-poor groups (-Cl, -Br, -Ac, -COOMe etc.) could uniformly proceed inverse hydroboration (**4n-x**). Naphthyl-amine-derived aldimines was also successful (**4s**, 73%). Varying the substituents on both aromatic rings simultaneously was also viable and **4t-x** were obtained in satisfying yields. A broad range of versatile functional groups, such as ester group (**4q**), acyl group (**4v**), alkynyl group (**4w**) and alkenyl group (**4x**) were well compatible, thus complementing the known protocols because the metal-catalyzed diborylation of these unsaturated bonds are known.[3f]

Table 3: Reaction scope with respect to NHC-boranes.



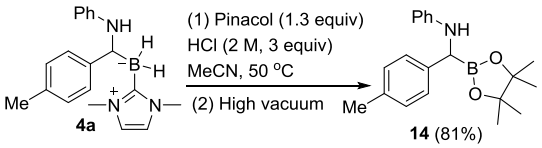
Next, the scope with respect to NHC-boranes was explored (Table 3). Several kinds of NHC-boranes **2a-f** could participate in the inverse hydroboration to afford the desired products in 52%-79% yields. The CN-substituted borane **2g** was also a good reaction partner. However, besides NHC-boranes, 4-dimethylaminopyridine-boranes and triethyl amine-boranes failed.



Scheme 5. Mechanistic studies.

To gain insight into the mechanism, several mechanistic experiments were carried out. The frequent detection of imine dimerization byproduct **10** indicated that α-aminobenzylic radical **7** might be involved (Scheme 5a). Interestingly, the NHC-boryl radical intermediate **5** was successfully trapped by 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO). A competing radical-clock experiment with (1-cyclopropylvinyl)benzene was further designed to validate the involvement of NHC-boryl radical (Scheme 5b). Replacing NHC-BH_3 **2a** with NHC-BD_3, the desired inverse hydroboration product was obtained in 75% yield with a ratio of **13-D**:**13-H** = 2:1 (Scheme 5c).[12] The DFT calculation results demonstrated that the total Gibbs' free-energy change (ΔG) of path a and path b shown in Scheme 2 were comparable (See Supporting Information for details). At present, although both radical intermediates (**5** and **7**) have been detected (Scheme **5a** and **5b**), both the radical-radical C-B cross-coupling (path a) driven by persistent radical effect[13] and the B-centered radical addition to imines (path b) are possible. However, a radical chain pathway is less likely as the quantum yield of model reaction was determined as 0.35.

As *N*-aryl α-amino acid serves as one core motif in a great number of bioactive compounds,[14] the isoelectronic *N*-aryl α-aminoboronic acid potentially hold promising bioactivities. However, no general access to *N*-aryl α-aminoboronic acids was available.[15] To our delight, the inverse hydroboration products are good precursors to *N*-aryl α-aminoboronates after hydrolysis (Scheme 6).



Scheme 6. Conversion to *N*-aryl α-aminoboronates.

In conclusion, we have developed an unprecedented inverse hydroboration transformation of imines with organoboranes by means of photoredox and phenylmethanethiol cooperative catalysis. The experimental and DFT calculation results demonstrate that matched thiol organocatalyst is one key factor, as it not only expedites the generation of boryl radical but also significantly depresses the classical ionic reduction pathway. Several impressive features, such as mild reaction conditions, radical initiator-free, good functional group tolerance and late-stage hydroboration, make this protocol practical to access medically important *N*-aryl α-aminoboron compounds. A novel radical-radical C-B coupling is likely based on mechanistic studies. The exploration of inverse hydroboration strategy for the synthesis of enantiopure *N*-aryl α-aminoborons is currently ongoing in our lab.

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (21702098, 21732003, 21703118 and 21672099), "1000-Youth Talents Plan" and Shandong Provincial Natural Science Foundation (No. ZR2017MB038) for financial support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: imines • hydroboration • visible-light photoredox catalysis • radical • C-B coupling

[1] For pioneering and selected work: a) H. C. Brown, B. C. Subba Rao, *J. Am. Chem. Soc.* **1956**, *78*, 5694; b) R. T. Baker, Calabrese, J. C. Westcott, S. A. *J. Organomet. Chem.* **1995**, *498,* 109; c) C. H. Tien, M. R. Adams, M. J. Ferguson, E. R. Johnson, A. W. H. Speed, *Org. Lett.* **2017**, *19*, 5565; d) M. R. Adams, C.-H. Tien, R. Mcdonald, A. W. H. Speed, *Angew. Chem. Int. Ed.* **2017**, *56*, 16660; e) P. Eisenberger, A. B. Bailey, C. M. Crudden, *J. Am. Chem. Soc.* **2012**, *134*, 17384; f) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050; g) M. R. Adams, C. H. Tien, B. S. N. Huchenski, M. J. Ferguson, A. W. H. Speed, *Angew. Chem. Int. Ed.* **2017**, *56*, 6268; h) C. C. Chong, R. Kinjo, *ACS Catal.* **2015**, *5*, 3238; i) T. Liu, L. Chen, Z. Sun, *J. Org. Chem.* **2015**, *80*,11441.

[2] a) R. Smoum, A. Rubinstein, V. M. Dembitsky, M. Srebnik, *Chem. Rev.* **2012**, *112*, 4156; b) P. Andrés, G. Ballano, M. I. Calaza, C. Cativiela, *Chem. Soc. Rev.* **2016**, *45*, 2291; c) J. C. Tellis, C. B. Kelly, D. N. Primer, M. Jouffroy, N. R. Patel, G. A. Molander, *Acc. Chem. Res.* **2016**, *49*, 1429; Selected recent examples: d) K. Miyazawa, T. Koike, M. Akita, *Adv. Synth. Catal.* **2014**, *356*, 2749; e) M. E. Khatib, R. Serafim, G. A. Molander, *Angew. Chem. Int. Ed.* **2016**, *55*, 254.

[3] a) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091; b) M. A. Beenen, C. An, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 6910; c) K. Wen, H. Wang, J. Chen, H. Zhang, X. Cui, C. Wei, E. Fan, Z. Sun, *J. Org. Chem.* **2013**, *78*, 3405; d) D. Wang, P. Cao, B. Wang, T. Jia, Y. Lou, M. Wang, J. Liao, *Org. Lett.* **2015**, *17*, 2420; e) K. Hong, J. P. Morken, *J. Am. Chem. Soc.* **2013**, *135*, 9252; f) G. Mann, K. D. John, R. T. Baker, *Org. Lett.* **2000**, *2*, 2105; g) C. Solé, H. Gulyás, E. Fernández, *Chem. Commun.* **2012**, *48*, 3769; h) M. M. Hansmann, R. L. Melen, M. Rudolph, F. Rominger, H. Wadepohl, D. W. Stephan, A. S. K. Hashmi, *J. Am. Chem. Soc.* **2015**, *137,* 15469.

[4] For recent reviews: a) G. Yan, D. Huang, X. Wu, *Adv. Synth. Catal.* Doi:10.1002/adsc.201701030; b) G. Duret, R. Quinlan, P. Bisseret, N. Blanchard, *Chem. Sci.* **2015**, *6*, 5366.

[5] Our work: G. Wang, H. Zhang, J. Zhao, W. Li, J. Cao, C. Zhu, S. Li, *Angew. Chem. Int. Ed.* **2016**, *55*, 5985.

[6] D. P. Curran, A. Solovyev, M. M. Brahmi, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem. Int. Ed.* **2011**, *50*, 10294.

[7] Selected examples: a) S. Ueng, M. M. Brahmi, É. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082; b) S. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacôte, M. Malacria, M. Newcomb, J. C. Walton, D. P. Curran, *J. Am. Chem. Soc.* **2009**, *131*, 11256; c) J. C. Walton, M. M. Brahmi, L. Fensterbank, E. Lacôte, M. Malacria, Q. Chu, S. Ueng, A. Solovyev, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 2350; d) X. Pan, E. Lacôte, J. Lalevée, D. P. Curran, *J. Am. Chem. Soc.* **2012**, *134*, 5669; e) J. Lalevée, S. Telitel, M. A. Tehfe, J. P. Fouassier, D. P. Curran, E. Lacôte, *Angew. Chem. Int. Ed.* **2012**, *51*, 5958; f) T. Kawamoto, S. Geib, D. P. Curran, *J. Am. Chem. Soc.* **2015**, *137*, 8617; g) X. Pan, A.-L. Vallet, S. Schweizer, K. Dahbi, B. Delpech, N. Blanchard, B. Graff, S. J. Geib, D. P. Curran, J. Lalevée, E. Lacôte, *J. Am. Chem. Soc.* **2013**, *135*, 10484; h) S. Telitel, A.-L. Vallet, S. Schweizer, B. Delpech, N. Blanchard, F. Morlet-Savary, B. Graff, D. P. Curran, M. Robert, E. Lacôte, J. Lalevée, *J. Am. Chem. Soc.* **2013**, *135*, 16938; i) T. Watanabe, D. Hirose, D. P. Curran, T. Taniguchi, *Chem. –Eur. J.* **2017**, *23*, 5404.

[8] a) S. Ren, F. Zhang, J. Qi, Y. Huang, A. Xu, H. Yan, Y. Wang, *J. Am. Chem. Soc.* **2017**, *139,* 6050; b) Y. Yu, F. Zhang, J. Cheng, J. Hei, W. Deng, Y. Wang, *Org. Lett.* **2018**, *20*, 24; Another early impressive radical hydroborylation case: c) M. Tehfe, M. M. Brahmi, J.-P. Fouassier, D. P. Curran, M. Malacria, L. Fensterbank, Lacôte, J. Lalevée, *Macromolecules* **2010**, *43*, 2261.

[9] For reviews about photoredox catalysis: a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; b) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828. For photoredox and thiol catalysis: c) K. Qvortrup, D. A. Rankic, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 626; d) W. Li, Y. Duan, M. Zhang, J. Cheng, C. Zhu, *Chem. Comm.* **2016**, *52*, 7596; e) J. Liu, J. Xie, C. Zhu, *Org. Chem. Front.* **2017**, *4*, 2433.

[10] a) J. Xie, H. Jin, A. S. K. Hashmi, *Chem. Soc. Rev.* **2017**, *46*, 5193; b) W. Li, W. Xu, J. Xie, S. Yu, C. Zhu, *Chem. Soc. Rev.* DOI: 10.1039/C7CS00507E; c) J. Xie, Q. Xue, H. Jin, H. Li, Y. Cheng, C. Zhu, *Chem. Sci.* **2013**, *4*, 1281; d) J. Xie, H. Li, J. Zhou, Y. Cheng, C. Zhu, *Angew. Chem. Int. Ed.* **2012**, *51*, 1252; e) P. Xu, G. Wang, Y. Zhu, W. Li, Y. Cheng, S. Li, C. Zhu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2939; f) P. Xu, W. Li, J. Xie, C. Zhu, *Acc. Chem. Res.* DOI: 10.1021/acs.accounts.7b00565.

[11] a) L. Qi, Y. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 13312; b) D. Hager, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 16986; c) M. Nakajima, E. Fava, S. Loescher, Z. Jiang, M. Rueping, *Angew. Chem. Int. Ed.* **2015**, *54*, 8828; d) E. Fava, A. Millet, M. Nakajima, S. Loescher, M. Rueping, *Angew. Chem. Int. Ed.* **2016**, *55*, 6776; e) H. Zhang, S. Yu, *J. Org. Chem.* **2017**, *82*, 9995; f) C. Wang, J. Qin, X. Shen, R. Riedel, K. Harms, E. Meggers, *Angew. Chem. Int. Ed.* **2016**, *55*, 685; g) D. Uraguchi, N. Kinoshita, T. Kizu, T. Ooi, *J. Am. Chem. Soc.* **2015**, *137*, 13768; h) J. Jeffrey, F. R. Petronijević, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2016**, *137*, 8404.

[12] As the hydrogen of NH is reactive, hydrogen−deuterium exchange is easy to occur from solvent. Indeed, even we could observe **13-D** compound by HRMS analysis, only **13-H** was obtained after normal work-up on silica gel column chromatography.

[13] a) A. Studer, *Chem. -Eur. J.* **2001**, *7*, 1159; b) H. Fischer, *Chem. Rev.* **2001**, *101*, 3581; c) A. Studer, *Chem. Soc. Rev.* **2004**, *33*, 267; d) A. Studer, D. P. Curran, *Angew. Chem. Int. Ed.* **2016**, *55*, 58; e) J. Xuan, T.-T. Zeng, Z.-J. Feng, Q.-H. Deng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao,

H. Alper, *Angew. Chem. Int. Ed.* **2015**, *54*, 1625; f) J. Xie, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2017**, *56*, 7266; g) J. Xie, S. Shi, T. Zhang, N. Mehrkens, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 6046; h) J. Xie, J. Yu, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2016**, *55*, 9416; i) W.-J. Zhou, G.-M. Cao, G. Shen, X. Zhu, Y. Gui, J. Ye, L. Sun, L. Liao, J. Li, D.-G. Yu, *Angew. Chem. Int. Ed.* **2017**, *56*, 15683.

[14] D. Ma, J. Yao, *Tetrahedron: Asymmetry* **1996**, *7*, 3075.

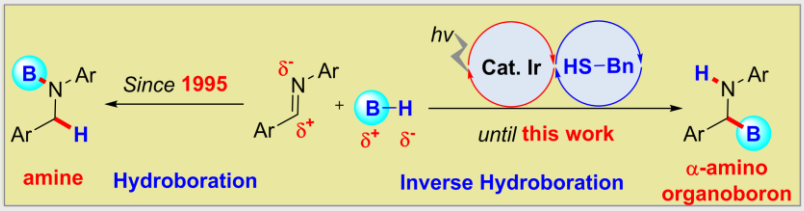
[15] The reported Cu-catalyzed diborylation of *N*-Ar imines failed to give *N*-aryl α-aminoboronates, see SI for details.

10.1002/anie.201800421

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



N. Zhou, X.-A. Yuan, Y. Zhao, J. Xie and C. Zhu**

Page No. – Page No.
Synergistic Photoredox and Organocatalysis for Inverse Hydroboration of Imines

Unprecedented Inversion: The first catalytic inverse hydroboration of imines with *N*-heterocyclic carbene boranes has been realized by means of cooperative organocatalysis and photocatalysis. The nature of thiol is a vital choice for inverse hydroboration. This protocol represents an important step-forward to enhanced α-amino organoboron lead libraries.