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Synthesis of Diverse Boron-Handled N-Heterocycles via Radical Borylative Cyclization of *N*-Allylcyanamides

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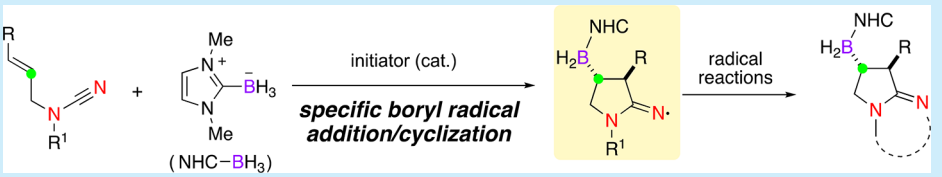
Supporting Information



ABSTRACT: A synthetic method based on radical borylation/cyclization cascades of *N*-allylcyanamides was developed to construct diverse boron-substituted N-heterocycles. In the reaction process, the N-heterocyclic carbene−boryl radical underwent a chemo- and regioselective addition to the alkene moiety, followed by cyclization with the *N*-cyano group. The resulting amide−iminyl radical intermediates underwent further reactions to afford various boron-tethered N-heterocyclic molecules. Further transformations to access synthetically useful building blocks were also demonstrated.

N-Heterocycles are prevalent in numerous natural products, pharmaceuticals, agricultural chemicals, and functional materials.[1] Among various N-heterocyclic skeletons, cyclic amidines and quinazolinones have been recognized as privileged pharmacophores in various drug molecules and candidates, bioactive molecules, and lead compounds (Figure 1).[2] Thus,

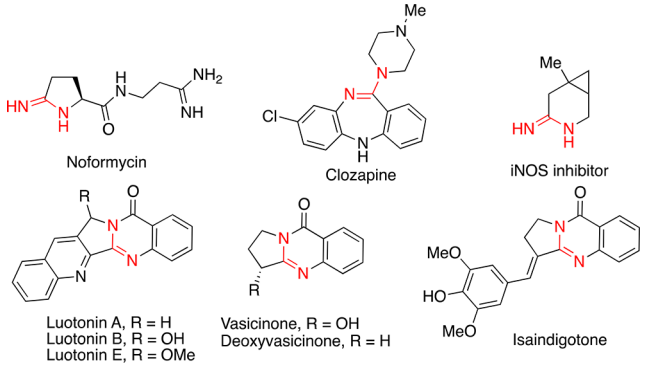


Figure 1. Bioactive molecules containing cyclic amidines and quinazolinones.

synthetic methods that enable their diverse synthesis and variable structure modifications are highly desirable in drug discovery and development. In this context, installation of a boron handle onto the cyclic framework represents a promising strategy as the versatile C−B bond can be converted to a wide range of functional groups of interest.[3] However, synthesis of these boron-substituted molecules in a chemo-, regio-, and stereocontrolled manner has been challenging.[4]

Radical cascade reactions are a powerful tool to construct N-heterocyclic skeletons.[5] Although many radical cascades and methods have been developed, the synthesis of diversified boron-handled N-heterocycles from readily available starting materials is rare. Recently, our group has reported some intriguing borylative radical cascades of 1,6-enynes and 1,6-dienes to construct boron-substituted cyclic molecules.[6] In these studies, we have investigated the reactions of N-heterocyclic carbene (NHC)−boryl radicals with alkenes and alkynes. Despite this, the reactivity and selectivity of NHC−boryl radicals with a complex system containing multiple different radical acceptors still remain elusive. Such research would be of great value to enrich boryl radical chemistry. More importantly, new findings may lead to the discovery of unprecedented synthetic approaches that may afford structurally novel and useful boron-substituted frameworks. With this in mind, we became interested in studying radical borylative cascades of *N*-allylcyanamides, from which diverse valuable boron-substituted N-heterocycles would be constructed. The challenge that needs to be addressed is how to achieve a chemoselective initial radical addition reaction between the alkene and the N−CN motifs because both functional groups may react with the NHC−boryl radical.

NHC−boryl radicals have shown versatile utility in various organic transformations.[7] For example, Curran has recently reported an NHC−boryl radical-promoted reductive decyanation reaction of organic nitriles.[8] In this transformation, the NHC−boryl radical attacked the cyano group to generate an iminyl radical intermediate, followed by a fragmentation and

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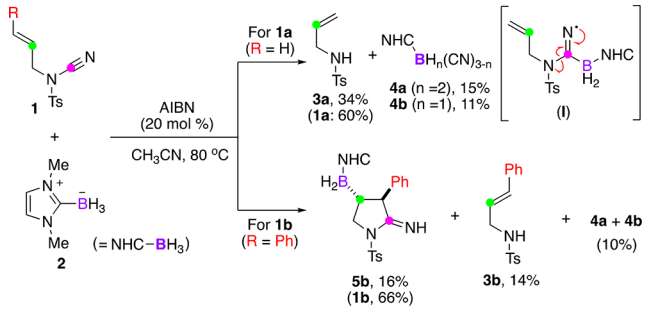
reduction to give a decyanated product. On this basis, we envisioned that an analogous addition reaction of an NHC−boryl radical to the N−CN group of *N*-allylcyanamides would also occur to give amide−iminyl radical intermediate **I** (Scheme 1), which would then lead to either decyanation or cyclization

Scheme 1. Substrate-Controlled Chemodivergent Reactions

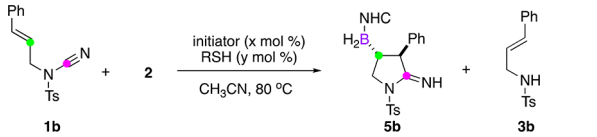


with the pendant alkene tether. To test the reactivity, we examined the reaction of *N*-allylcyanamide **1a** and 1,3-dimethylimidazol-2-ylidene borane (**2**) in the presence of AIBN as the radical initiator. As a result, the reductive decyanation product **3a** was isolated in 34% yield along with the formation of NHC−borane nitriles **4a** and **4b** in 15 and 11% yields, respectively. Meanwhile, **1a** was recovered in 60% yield. However, no cyclized product was detected at all.

Next, we attempted a cascade process that would initiate from the addition to the alkene moiety rather than the N−CN group. For this purpose, the choice of a suitable R group in *N*-allylcyanamide **1** that can render the alkene addition more favorable is crucial. Our previous studies revealed that an aryl group attached at the alkene end could promote NHC−boryl radical addition.[6] However, the reaction preference when a N−CN group was present in the substrate was unclear. To figure out the reactivity difference, the reaction of **1b** was examined. In the event, a boron-handled cyclic amidine **5b** was isolated in 16% yield as a single diastereomer with 3,4-*trans* stereochemistry. This stereochemistry was secured by X-ray crystallographic analysis.[9] Meanwhile, the reductive decyanation product **3b** was also formed in 14% yield. The process to form **5b** provides a new strategy to construct boron-tethered *N*-H cyclic amidines, which are potentially useful in medicinal chemistry but are difficult to access by the existing methods. This prompted us to optimize the reaction conditions further.

First, a control experiment was conducted in the absence of a radical initiator (Table 1, entry 1). As a result, no reaction occurred, and **1b** was fully recovered, indicating the radical reaction nature of this cascade. The following optimization revealed that the addition of RSH as a polar reversal catalyst[10] could significantly affect the product distribution and yield. For example, when 5 mol % of *tert*-dodecanethiol was added as a catalyst, the yield of **5b** was improved to 47% yield and the formation of **3b** was suppressed (entry 2). Increasing the loading of RSH catalyst led to further improvement of the yield of product **5b** (entries 3 and 4). Eventually, **5b** was isolated in 81% yield with the use of 20 mol % of *tert*-dodecanethiol (entry 4). Switching the thiol catalyst to PhSH resulted in a diminished product yield (entry 5). Using di-*tert*-butyl hyponitrite (TBHN) as the radical initiator also afforded product **5b** in a good yield (entry 6). Other NHC−boryl radical precursors bearing varied substituents on the NHC moiety gave the desired cyclized products in good yields and exclusive 3,4-*trans* stereo-

Table 1. Optimization of Reaction Conditions[a]



entry	initiator (*x* mol %)	RSH (*y* mol %)	**5b** yield (%)[b]	**3b** yield (%)[b]
1		$C_9H_{19}C(CH_3)_2SH$ (20)	ND[c]	ND
2	AIBN (20)	$C_9H_{19}C(CH_3)_2SH$ (5)	47[d]	7
3	AIBN (20)	$C_9H_{19}C(CH_3)_2SH$ (10)	75	trace
4	AIBN (20)	$C_9H_{19}C(CH_3)_2SH$ (20)	85 (81)[e]	trace
5	AIBN (20)	PhSH (20)	54	12
6[f]	TBHN (20)	$C_9H_{19}C(CH_3)_2SH$ (20)	73	trace

[a]Unless otherwise noted, the reactions were performed on a 0.2−0.3 mmol scale of **1b**, **2** (1.2 equiv), initiator (*x* mol %), and RSH (*y* mol %) in CH_3CN (2 mL) at 80 °C under a N_2 atmosphere. [b]NMR yield using tetrachloroethane as an internal standard. [c]**1b** was recovered in 94% yield. [d]**1b** was recovered in 27% yield. [e]Isolated yield. [f]The reaction was performed at 60 °C.

selectivity.[11] It should be mentioned that when **1a** was subjected to the optimized reaction conditions, the decyanation product **3a** was still obtained as the sole product, and no cyclized product was detected.

With the optimized reaction conditions in hand, we next investigated the scope and generality of this radical borylative cascades for the construction of borylated cyclic amidines **5** (Table 2). In general, *N*-allylcyanamides bearing an aryl group at the alkene end afforded the desired boron-substituted cyclic amidines **5** in good yields. Only a *trans*-diastereomer was obtained in all cases. A gram scale reaction of **1b** gave **5b** in 76% isolated yield. Various functional groups on the aryl ring were compatible (for **5c**−**5f**). Moreover, both naphthalene (for **5g**) and pyridine (for **5h**) motifs could be installed. Importantly, when the R^1 substituent was changed to *tert*-butyloxycarbonyl (for **5i**), benzyl (for **5j**), and phenyl (for **5k**) groups, good selectivity and efficiency were maintained. A range of *N*-aryl-substituted substrates bearing various functional groups were converted to borylated cyclic products in good yields (for **5l**−**5o**). In particular, heteroaryls, such as pyrimidine (for **5p**) and carbazole (for **5q**), were successfully incorporated. The present method also allowed for the construction of a boron-handled bicyclic amidine **5r** through the trapping of the resulting amide−iminyl radical intermediate with an additional intramolecular alkene tether. When an aryl group was replaced, a methyl group as the substituent R (for **1s**) was not viable to afford cyclized product, and the corresponding decynated product **3s** was formed in 9% yield. Meanwhile, **1s** was recovered in 87% yield without any *E*/*Z* isomerization, indicating that the addition of an NHC−boryl radical to a methyl-substituted alkene may not occur under the present reaction conditions. Moreover, the cascade of *N*-homoallylcyanamides **1t** to construct boron-tethered 2-iminopiperidine **5t** was unsuccessful, and the decyanated product **3t** was formed instead.

N-Acylcyanamides have been found to be competent substrates in radical cascades to construct quinazolinones[12] since the pioneering work of Malacria and Courillon.[12a] Despite the fact that various functionalized products have been prepared, the synthesis of versatile boron-substituted ones has not yet been documented. To expand the scope and generality of the present method, we next investigated reactions of *N*-benzoyl-protected allylcyanamides **6** (Scheme 2). The reaction

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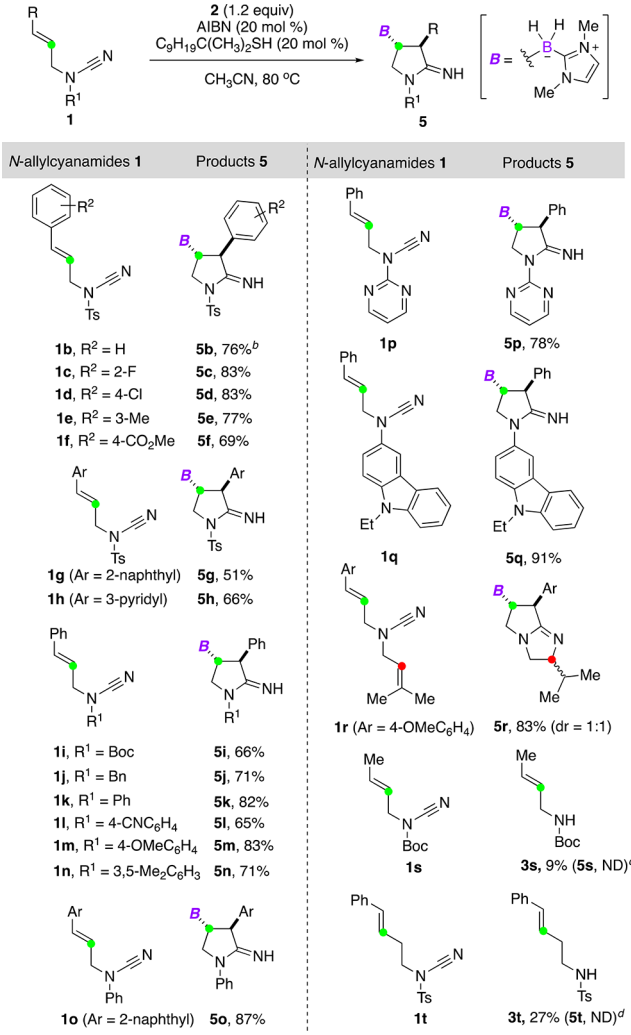
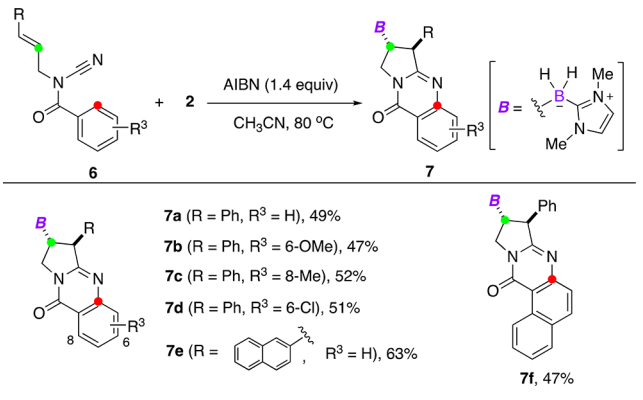
Table 2. Scope of Radical Borylative Cyclizations of *N*-Allylcyanamides[a]



[a]Unless otherwise noted, the reactions were performed on a 0.2−0.4 mmol scale of **1**, **2** (1.2 equiv), AIBN (20 mol %), and $C_9H_{19}C(CH_3)_2SH$ (20 mol %) in CH_3CN (4 mL) at 80 °C under a N_2 atmosphere. [b]Isolated yield of a gram scale reaction of **1b**. [c]**1s** was recovered in 87% yield. [d]**1t** was recovered in 57% yield.

Scheme 2. Synthesis of Boron-Substituted Quinazolinones[a]

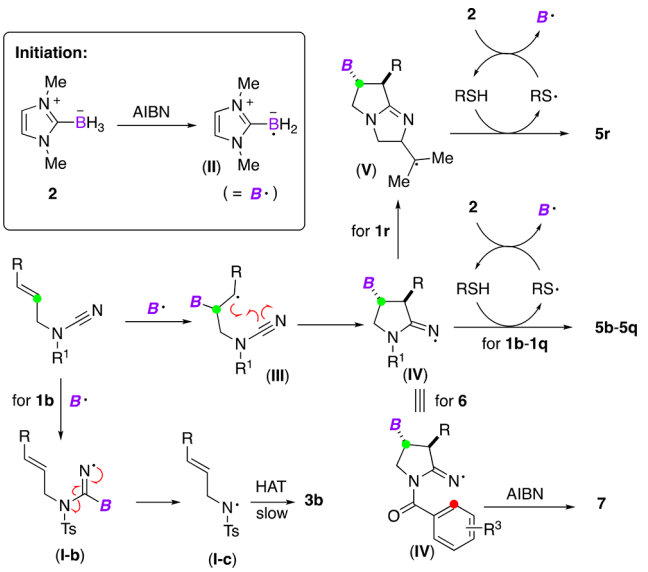


[a]Unless otherwise noted, the reactions were performed on a 0.3−0.4 mmol scale of **6**, **2** (1.2 equiv), and AIBN (1.4 equiv, added in several portions) in CH_3CN (3 mL) at 80 °C under a N_2 atmosphere.

proceeded smoothly in the presence of 1.4 equiv of AIBN, affording boron-substituted quinazolinones **7** in moderate yields with the tolerance of a variety of functional groups.

Based on our previous mechanistic studies on the NHC−boryl radical reaction with alkenes,[6] we proposed plausible reaction pathways as depicted in Scheme 3 for the formation of

Scheme 3. Proposed Reaction Pathways for Cascade Products



cascade products. Initially, the NHC−boryl radical (**II**) is generated by hydrogen atom abstraction from **2** in the presence of AIBN as the radical initiator.[13] Boryl radical **II** then undergoes chemo- and regioselective addition to the phenyl-substituted alkene moiety, affording a resonance-stabilized radical intermediate **III**, which then cyclizes with the intramolecular N−CN group to form amide−iminyl radical intermediate **IV**. For the reaction of **1b**−**1q**, hydrogen atom transfer from the thiol catalyst (RSH) occurs to give products **5b**−**5q** with the generation of a sulfur radical (RS•), which in turn abstracts a hydrogen atom from **2** to regenerate RSH and boryl radical **II**.[10] As shown in Table 1, the RSH catalyst has played an important role in the product distribution and yield. When an RSH catalyst was present, the hydrogen atom transfer (**IV** to **5b**) was dramatically enhanced because of the matching polarity between the nucleophilic amide−iminyl radical **IV** and the thiol catalyst.[14] In contrast, such a polarity effect was not obvious for electrophilic aminyl radical **I-c**. As a consequence, the radical chain process to afford product **5b** was facilitated, and the pathway to form **3b** was inhibited. When another allyl group is installed on the nitrogen atom (for **1r**), the resulting amide−iminyl radical **IV** can be trapped to assemble a bicyclic framework. In this domino process, the propagation of a radical chain reaction is also achieved using a thiol catalyst. In addition, for the reaction of **6**, the radical intermediate **IV** is capable of performing aromatic homolytic substitutions[15] with intramolecular *N*-benzoyl groups, leading to boron-substituted quinazolinones **7**. In this case, an excess amount of AIBN is required to facilitate the rearomatization step.[12c,e,16]

The synthetic utility of borylated N-heterocycles was demonstrated (Scheme 4). The NHC−borane-tethered *N*-H amidine **5n** was treated with tosyl chloride in the presence of NaH as the base, giving *N*-tosyl-protected product **8**. The

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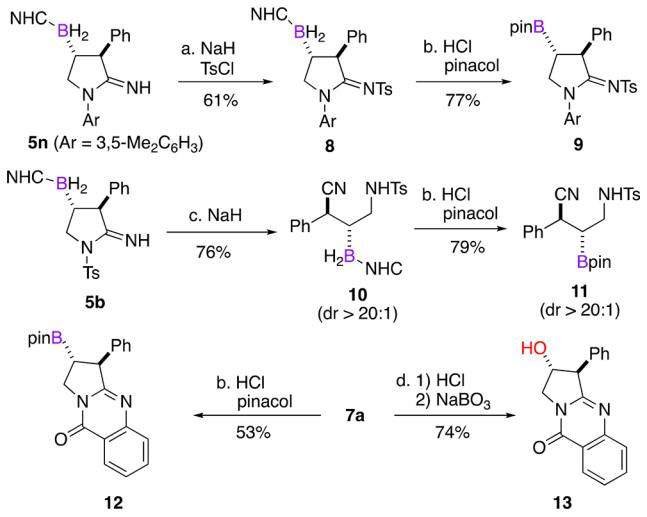
Scheme 4. Transformations of Borylated Products[a]



[a]Reagents and conditions: (a) TsCl (1.2 equiv), NaH (1.5 equiv), THF, 30 °C, 4 h; (b) aq HCl (2 M, 2.6 equiv), pinacol (2 equiv), CH_3CN, 30 °C, 2 h; (c) NaH (1.2 equiv), THF, 30 °C, 10 min; (d) (1) aq HCl (2 M, 2.6 equiv), CH_3CN, 30 °C, 2 h, (2) $NaBO_3$ (3 equiv), THF/H_2O, 30 °C, 1 h.

following treatment with HCl[17] and pinacol afforded synthetically useful pinacol boronic ester **9**. Interestingly, treatment of **5b** with NaH led to *β*-boryl-*γ*-cyanoamine **10**[9] with the maintenance of excellent diastereoselectivity. The corresponding pinacol boronic ester **11** was also obtained in a good yield. The NHC−borane-substituted quinazolinone **7a** was converted to pinacol boronic ester **12** and hydroxylated product **13** in 53 and 74% yields, respectively.

In summary, we have developed a radical borylation method of *N*-allylcyanamides to construct diverse boron-handled N-heterocycles. The reactions were initiated by a chemo- and regioselective addition of an NHC−boryl radical to the aryl-substituted alkene moiety, followed by varied cascade processes to assemble various boron-tethered N-heterocyclic frameworks. Further transformations of borylated N-heterocyclic products to valuable synthetic building blocks have been accomplished. The present method offers a conceptually new strategy to access valuable boron-functionalized bioactive N-heterocycles, and it would find important applications in medicinal chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03303.

Experimental details (PDF)

Accession Codes

CCDC 1869820−1869821 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected recent reviews, see: (a) Costantino, L.; Barlocco, D. *Curr. Med. Chem.* **2006**, *13*, 65. (b) Welsch, M. E.; Snyder, S. A.; Stockwell, B. R. *Curr. Opin. Chem. Biol.* **2010**, *14*, 347. (c) Thomas, G. L.; Johannes, C. W. *Curr. Opin. Chem. Biol.* **2011**, *15*, 516. (d) Taylor, R. D.; MacCoss, M.; Lawson, A. D. G. *J. Med. Chem.* **2014**, *57*, 5845.

(2) For selected recent reviews, see: Oehlrich, D.; Prokopcova, H.; Gijsen, H. J. M. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 2033. (b) Edwards, P. D.; Albert, J. S.; Sylvester, M.; Aharony, D.; Andisik, D.; Callaghan, O.; Campbell, J. B.; Carr, R. A.; Chessari, G.; Congreve, M.; Frederickson, M.; Folmer, R. H. A.; Geschwindner, S.; Koether, G.; Kolmodin, K.; Krumrine, J.; Mauger, R. C.; Murray, C. W.; Olsson, L.-L.; Patel, S.; Spear, N.; Tian, G. *J. Med. Chem.* **2007**, *50*, 5912. (c) Shankaran, K.; Donnelly, K. L.; Shah, S. K.; Guthikonda, R. N.; MacCoss, M.; Humes, J. L.; Pacholok, S. G.; Grant, S. K.; Kelly, T. M.; Wong, K. K. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4539. (d) Kshirsagar, U. A. *Org. Biomol. Chem.* **2015**, *13*, 9336.

(3) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2011.

(4) For a recent review on transition-metal-catalyzed borylative cyclization reactions, see: Buñuel, E.; Cárdenas, D. J. *Eur. J. Org. Chem.* **2016**, *2016*, 5446.

(5) For selected recent reviews, see: (a) Baralle, A.; Baroudi, A.; Daniel, M.; Fensterbank, L.; Goddard, J.-P.; Lacôte, E.; Larraufie, M.-H.; Maestri, G.; Malacria, M.; Ollivier, C. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; John Wiley & Sons, Ltd: Chichester, U.K., 2012. (b) Wille, U. *Chem. Rev.* **2013**, *113*, 813. (c) Albert, M.; Fensterbank, L.; Lacôte, E.; Malacria, M. *Top Curr. Chem.* **2006**, *264*, 1. (d) Dhimane, A.-L.; Fensterbank, L.; Malacria, M. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley: Weinheim, Germany, 2008; Vol. 2, p 350. (e) Xuan, J.; Studer, A. *Chem. Soc. Rev.* **2017**, *46*, 4329.

(6) (a) Ren, S.-C.; Zhang, F.-L.; Qi, J.; Huang, Y.-S.; Xu, A.-Q.; Yan, H.-Y.; Wang, Y.-F. *J. Am. Chem. Soc.* **2017**, *139*, 6050. (b) Qi, J.; Zhang, F.-L.; Huang, Y.-S.; Xu, A.-Q.; Ren, S.-C.; Yi, Z.-Y.; Wang, Y.-F. *Org. Lett.* **2018**, *20*, 2360.

(7) For recent reviews, see: (a) Walton, J. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1726. (b) Curran, D. P.; Solovyev, A.; Makhlouf Brahmi, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 10294. For a leading report, see: (c) Ueng, S.-H.; Makhlouf Brahmi, M.; Derat, É.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 10082. For selected recent examples, see: (d) Lalevée, J.; Telitel, S.; Tehfe, M. A.; Fouassier, J. P.; Curran, D. P.; Lacôte, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 5958. (e) Pan, X.; Vallet, A.-L.; Schweizer, S.; Dahbi, K.; Delpech, B.; Blanchard, N.; Graff, B.; Geib, S. J.; Curran, D. P.; Lalevée, J.; Lacôte, E. *J. Am. Chem. Soc.* **2013**, *135*, 10484. (f) Watanabe, T.; Hirose, D.; Curran, D. P.; Taniguchi, T. *Chem. - Eur. J.* **2017**, *23*, 5404. (g) Yu, Y.-J.; Zhang, F.-L.; Cheng, J.; Hei, J.-H.; Deng, W.-T.; Wang, Y.-F. *Org. Lett.* **2018**, *20*, 24. (h) Shimoi, M.; Watanabe, T.; Maeda, K.; Curran, D. P.; Taniguchi, T. *Angew. Chem.,*

DOI: 10.1021/acs.orglett.8b03303
Org. Lett. XXXX, XXX, XXX−XXX

Int. Ed. **2018**, *57*, 9485. (i) Zhou, N.; Yuan, X.-A.; Zhao, Y.; Xie, J.; Zhu, C. *Angew. Chem., Int. Ed.* **2018**, *57*, 3990.
(8) Kawamoto, T.; Geib, S. J.; Curran, D. P. *J. Am. Chem. Soc.* **2015**, *137*, 8617.
(9) The structures of compounds **5b** and **10** were secured by X-ray crystallographic analysis; see Supporting Information.
(10) Pan, X.; Lacôte, E.; Lalevée, J.; Curran, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 5669.
(11) The electronic properties and the structure of the NHC moiety may not have significant impact on the stereoselectivity of the cyclization. For detailed results, see Supporting Information.
(12) For a leading report, see: (a) Servais, A.; Azzouz, M.; Lopes, D.; Courillon, C.; Malacria, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 576. For recent examples, see: (b) Beaume, A.; Courillon, C.; Derat, E.; Malacria, M. *Chem. - Eur. J.* **2008**, *14*, 1238. (c) Larraufie, M.-H.; Courillon, C.; Ollivier, C.; Lacôte, E.; Malacria, M.; Fensterbank, L. *J. Am. Chem. Soc.* **2010**, *132*, 4381. (d) Larraufie, M. H.; Ollivier, C.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem., Int. Ed.* **2010**, *49*, 2178. (e) Larraufie, M.-H.; Malacria, M.; Courillon, C.; Ollivier, C.; Fensterbank, L.; Lacôte, E. *Tetrahedron* **2013**, *69*, 7699. (f) Han, Y.-Y.; Jiang, H.; Wang, R.; Yu, S. *J. Org. Chem.* **2016**, *81*, 7276. (g) Zheng, J.; Deng, Z.; Zhang, Y.; Cui, S. *Adv. Synth. Catal.* **2016**, *358*, 746. (h) Zheng, J.; Zhang, Y.; Wang, D.; Cui, S. *Org. Lett.* **2016**, *18*, 1768. (i) Liu, X.; Qian, P.; Wang, Y.; Pan, Y. *Org. Chem. Front.* **2017**, *4*, 2370. (j) Qian, P.; Deng, Y.; Mei, H.; Han, J.; Zhou, J.; Pan, Y. *Org. Lett.* **2017**, *19*, 4798.
(13) (a) Walton, J. C.; Brahmi, M. M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 2350. (b) Walton, J. C.; Brahmi, M. M.; Monot, J.; Fensterbank, L.; Malacria, M.; Curran, D. P.; Lacôte, E. *J. Am. Chem. Soc.* **2011**, *133*, 10312.
(14) Dénès, F.; Pichowicz, M.; Povie, G.; Renaud, P. *Chem. Rev.* **2014**, *114*, 2587.
(15) Bowman, W. R.; Storey, J. M. D. *Chem. Soc. Rev.* **2007**, *36*, 1803.
(16) (a) Curran, D. P.; Yu, H.; Liu, H. *Tetrahedron* **1994**, *50*, 7343. (b) Curran, D. P.; Liu, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, *1*, 1377. (c) Beckwith, A. L. J.; Bowry, V. W.; Bowman, W. R.; Mann, E.; Parr, J.; Storey, J. M. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 95. (d) Curran, D. P.; Keller, A. I. *J. Am. Chem. Soc.* **2006**, *128*, 13706.
(17) Solovyev, A.; Chu, Q.; Geib, S. J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 15072.

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