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Boryl Radicals-Triggered Selective C−H Functionalization for the Synthesis of Diverse Phenanthridine Derivatives

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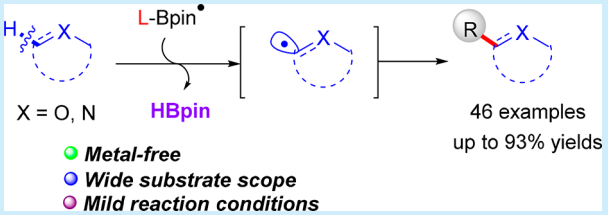
Supporting Information

ABSTRACT: A boryl radical-triggered C−H functionalization of aliphatic ethers/amines or DMF with isocyanides is developed to deliver diverse phenanthridine derivatives in good to excellent yields. The substrate scope is broad, and a wide range of functional groups are tolerated under the standard conditions. The rapid removal of HBPin species by 4-cyanopyridine 1-oxide provides the driving force for this reaction. This new method should make boryl radicals widely applicable in organic synthesis.



The chemistry of ligated boryl radicals (L−$BR_2^•$) has blossomed in the past decade.[1,2] In particular, L−BH_3 complexes have attracted great attention as precursors to boryl radicals (L−$BH_2^•$) via hydrogen atom abstraction because of their easy modification and ready availability. Due to the high bond dissociation energies (BDEs) of B−H bonds (Scheme 1),[3] the development of an efficient ligand to decrease the BDE of a B−H bond to facilitate the hydrogen atom abstraction has become a central task in this field.[4] For example, Roberts intensely investigated the first generation of amine− and phosphine−boryl radicals, and such radicals could be used in polarity-reversal catalysis in some cases.[1d] Evidence from computational studies by Rablen[4e] and later by Zipse[4a] showed the BDEs of B−H bonds in amine− and phosphine−BH_3 complexes were 94−104 kcal mol^{-1}. Lalevée and co-workers disclosed that BDEs of B−H in N-heteroaryl−BH_3 complexes could be decreased to 70−90 kcal mol^{-1} by careful selection of the substituents.[4b,c] These results were in accordance with the theoretical study by Zipse.[4a] Significantly, Fensterbank, Lacôte, Malacria, and Curran found that N-heterocyclic carbenes (NHCs) were very effective for weakening the B−H BDEs in NHC−BH_3 complexes to 74−80 kcal mol^{-1} (Scheme 1).[4d]

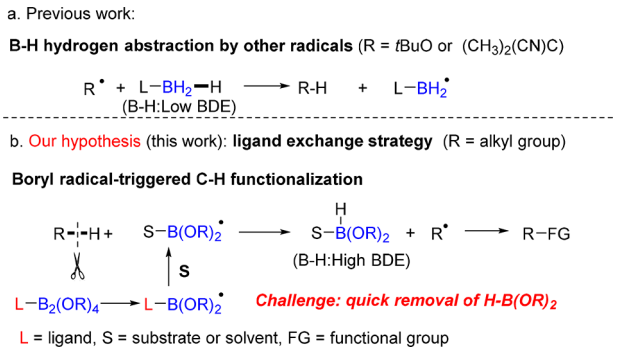
Scheme 1. Bond Dissociation Energies (BDEs) of B−H Bonds

ligand	L-BH_2-H (Kcal mol^{-1})	ref
none	106.6	3
amines or phosphines	94-104	4e
N-heteroary rings	70-90	4b
N-heterocyclic carbenes	74-80	4d
THF	103.5	4e

NHC−boryl radicals have been shown to be versatile reagents in a range of radical transformations, including in the reduction of a variety of C−X bonds,[5] such as xanthates,[4e,5e] halides,[5b−d] or CN[5a] to C−H bonds. Recently, Wang reported that thioamides could undergo desulfurative reductions or reductive radical cyclizations promoted by NHC−boryl radicals.[6] In addition to radical reductions, homolytic substitution of disulfides[7] and radical polymerizations of electron-deficient olefins[8] were developed. Furthermore, the challenging addition of boryl radicals to alkynes was also achieved.[9] Very recently, the groups of Taniguchi, Curran, and Wang reported boryl-radical initiated tandem cyclizations of 1,5-diynes[9a] and 1,6-enynes,[9b] respectively, for the facile synthesis of cyclic boron-containing compounds. Despite these achievements, the types of reactions available to boryl radicals still require further investigation (Scheme 2).

To explore new reaction modes of boryl radicals, our synthetic hypothesis stems from the opposite perspective. Given the high BDEs of B−H bond, it is possible to generate alkyl radicals through C−H hydrogen abstraction by boryl radicals. Our strategy is inspired by two advances in boryl radical chemistry. Very recently, a pioneering work by Li and

Scheme 2. Previous Studies on Boryl Radicals and Our New Strategy



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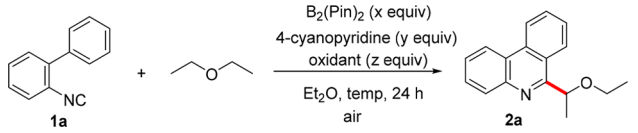
Zhu revealed that pyridine−boryl radicals, derived from the homolysis of the B−B bond in pyridine-coordinated diboranes, could reduce azo compounds and quinones, as well as sulfoxides.[10] Moreover, such pyridine−boryl radicals could also initiate radical additions/couplings of ketones or radical borylations of aryl halides or carboxylate derivatives.[11] Another elegant example using diboronate esters as boryl radical precursors was disclosed by Aggarwal for photoinduced decarboxylative borylations of carboxylic acids.[12] These reports show that ether or amide-based solvents were necessary for most of the transformations. We then envisaged that ligated boryl radicals could undergo ligand exchange with heteroatom-containing solvents or substrates, such as transition-metal catalysts. Once the ligand exchange occurs, C−H hydrogen abstraction is possible because the BDE of the B−H bond in S−B(OR)$_2$−H species (S = solvent or substrate) can increase greatly.[4e] The only challenge is the rapid removal of the in situ generated HBPin to prevent B−H hydrogen abstraction (Scheme 1b).

The α-C−H bonds of ethers,[13] amines,[14] and DMF[15] are frequently used as radical precursors because of their low BDEs.[16] On the other hand, isocyanides are excellent radical receptors, and the formation of functionalized phenanthridine derivatives is a useful technique in organic synthesis.[17] Inspired by this, we began our initial investigation with the radical cyclization of isocyanides **1** with diethyl ether.

A problem that needed to be addressed early on was the identification of a suitable oxidant that was compatible with B_2Pin_2 (bis(pinacolato)diboron) but quick to react with HBPin. First, *m*CPBA (**I**) and DDQ (**II**) were employed as the oxidants; however, the reactions were complex (Table 1, entries 1−2). Then, by reevaluating the literature precedent, 4-cyanopyridine 1-oxide was selected to be tested as the oxidant.[18] The reaction of isocyanide **1a** with Et_2O (2 mL) in the presence of B_2Pin_2 (1 equiv), 4-cyanopyridine (0.2 equiv), and 4-cyanopyridine 1-oxide (**III**, 2 equiv) provided desired product **2a** in 88% yield (Table 1, entry 3). Next, other oxidants, such as pyridine 1-oxide (**IV**), quinolone 1-oxide (**V**), and isoquinoline 2-oxide (**VI**), were investigated, but they were all less effective than **III** (Table 1, entries 4−6). Conducting the reaction at different temperatures showed that 50 °C was more suitable for this transformation (Table 1, entries 7−9). When the amount of B_2Pin_2 was decreased to 1 equiv, the yield of **2a** dropped to 46% (Table 1, entry 10). Decreasing the amount of 4-cyanopyridine also gave lower yields of the product (Table 1, entries 11−13). As the concentration was found to be important in a previous report,[11b] we conducted the reaction at high concentration, but this did not increase the efficiency (Table 1, entries 14−16). When less oxidant **III** was used, the yields of **2a** dropped to 53−59% (Table 1, entries 17−18). In the absence of 4-cyanopyridine, the reaction was very slow, but gave product **2a** in 71% yield if the reaction time was increased to 48 h (Table 1, entry 19), which suggested that 4-cyanopyridine 1-oxide could be slowly reduced to 4-cyanopyridine. In addition, no desired product **2a** was obtained in the absence of the oxidant or the radical initiator (B_2Pin_2/4-cyanopyridine) (Table 1, entries 20−21).

With the optimal reaction conditions in hand (Table 1, entry 3), we next evaluated the substrate scope of the reaction by varying the structure of isocyanides **1** (Scheme 3). It was found that several substrates with different *para*-R^2 substituents were all suitable for this cyclization and gave corresponding products **2b**−**2g** in good to excellent yields, and the electronic properties of R^2 had no significant effect on the reaction outcome. For a substrate with a *meta*-MeO substituent (R^2), the reaction delivered **2h** as the sole product in lower yield, probably because a strong electron-donating MeO does not favor

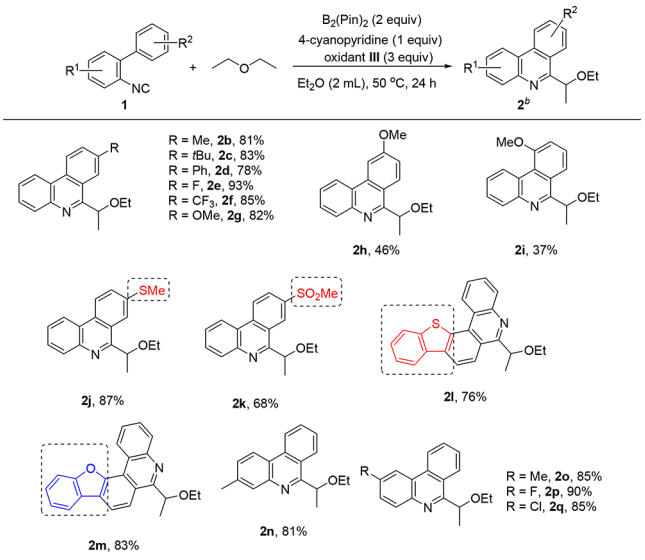
Table 1. Optimization of the Reaction Conditions



entry	*x*/*y*/*z*	oxidant	temp (°C)	yield (%)[a]
1	2/1/3	**I**	50	trace
2	2/1/3	**II**	50	trace
3	2/1/3	**III**	50	88
4	2/1/3	**IV**	50	70
5	2/1/3	**V**	50	37
6	2/1/3	**VI**	50	22
7	2/1/3	**III**	40	78
8	2/1/3	**III**	60	83
9	2/1/3	**III**	70	82
10	1/1/3	**III**	50	46
11	2/0.5/3	**III**	50	80
12	2/0.4/3	**III**	50	73
13	2/0.2/3	**III**	50	70
14	2/0.3/3	**III**	50	64[b]
15	2/0.4/3	**III**	50	65[b]
16	2/0.4/3	**III**	50	49[c]
17	2/0.5/2	**III**	50	59
18	2/0.5/1	**III**	50	53
19	2/0/3	**III**	50	71[d]
20	2/1/0	–	50	–[e]
21	0/0/3	**III**	50	–[e]

[a]Reaction conditions: 0.2 mmol scale. The reaction tube was well-sealed and heated at the indicated temperature. [b]Et_2O (1 mL). [c]Et_2O (0.5 mL). [d]The reaction time was 48 h. [e]**2a** was not detected. **I**: *m*CPBA (3-chloroperoxybenzoic acid). **II**: DDQ (2,3-dicyano-5,6-dichlorobenzoquinone). **III**: 4-cyanopyridine 1-oxide. **IV**: pyridine 1-oxide. **V**: quinoline 1-oxide. **VI**: isoquinoline 2-oxide.

Scheme 3. Substrate Scope of Radical Cyclization of 1 with Et_2O[a]



[a]All reactions were carried out on a 0.2 mmol scale. [b]Isolated yields.

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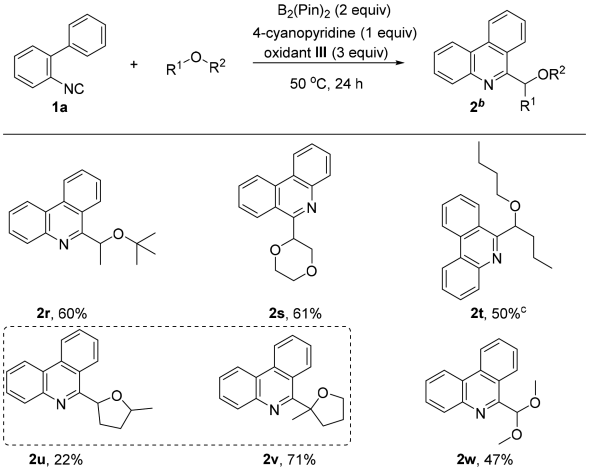
nucleophilic radical attack at its *para*-position. In addition, a substrate with an *ortho*-MeO (R^2) only gave corresponding product **2i** in 37% yield, perhaps because of steric hindrance. Notably, heteroatom-containing functional groups were well-tolerated in this reaction and provided corresponding products **2j**−**2m** in 68%−87% yields. Moreover, substrates with different R^1 groups were also subjected to the reaction and furnished **2n**−**2q** in 81%−90% yields.

Subsequently, the generality of ethers was investigated with isocyanide **1a** as a model substrate. As shown in Scheme 4,

Scheme 4. Substrate Scope of Different Ethers[a]



[a]All reactions were carried out on a 0.2 mmol scale in 2 mL of the ether. [b]Isolated yields. [c]Other complex isomers were observed.

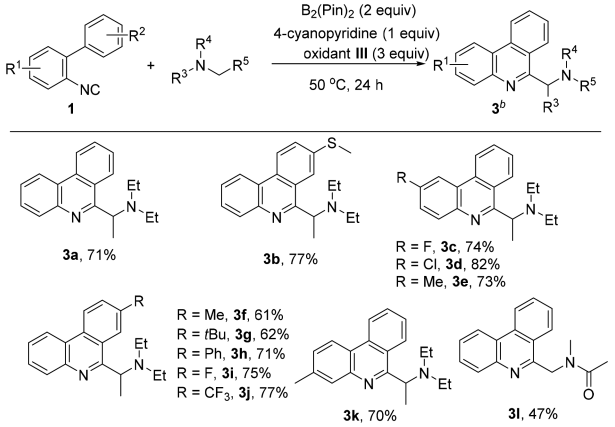
several commercially available ethers were tested in the reaction, and all were suitable for this cyclization, delivering corresponding products **2r**−**2w** in moderate to good yields. Notably, with *n*-butyl ether, the reaction furnished desired product **2t**, together with other complex isomers, indicating unactivated C−H bonds can also undergo hydrogen abstraction.

Unactivated tertiary aliphatic amines such as triethylamine are frequently used as precursors of α-amino radicals.[14] The radical cyclizations of **1** with aliphatic amines have not yet been reported. Fortunately, under the standard reaction conditions, the reactions of **1** with amines proceeded smoothly and furnished desired products **3a**−**3k** in moderate to good yields (Scheme 5). When DMA (*N*,*N*-dimethylacetamide) was used as a reagent and solvent, **3l** was obtained in 47% yield (Scheme 5).

The reactivities of different **1** with DMF (*N*,*N*-dimethylformamide) were also studied.[15] As seen in Scheme 6, all the reactions gave the corresponding products (**4a**−**4l**) in moderate to good yields and good chemoselectivities. The C−H bond in the carbonyl group is weaker than that in the NCH_2−H moiety,[16] so the formation of an acyl radical is fast, causing this transformation to be highly chemoselective.

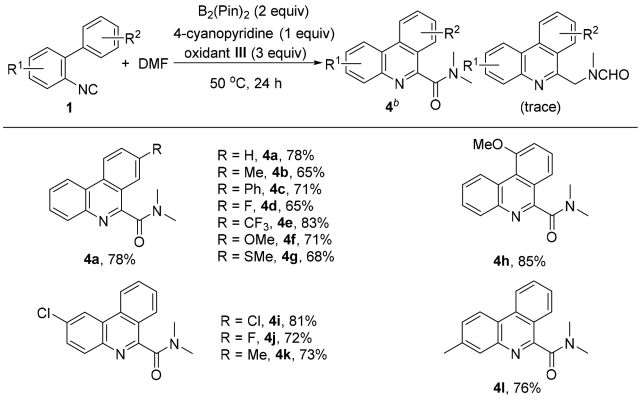
To probe the reaction mechanism, several control experiments were performed. With 1 equiv of TEMPO, the reaction of **1a** gave desired product **2a** in 72% yield, but only a trace amount of **2a** was obtained when 5 equiv of TEMPO were added, indicating that the reaction probably proceeds through a radical pathway (Scheme 7, eq 1). The intermolecular competing kinetic isotopic effect (KIE) study revealed that C−H bond cleavage might not be the rate-determining step

Scheme 5. Substrate Scope of Unactivated Tertiary Aliphatic Amines[a]



[a]All reactions were carried out on a 0.2 mmol scale in 2 mL of the amine. [b]Isolated yields.

Scheme 6. Substrate Scope of 1[a]



[a]All reactions were carried out on a 0.2 mmol scale in 2 mL of DMF. [b]Isolated yields.

(Scheme 7, eq 2). Treatment of 4-cyanopyridine 1-oxide (1 equiv) with BPin−H (0.1 equiv), and then immediately analyzing the reaction mixture by GC showed that 4-cyanopyridine was rapidly formed, indicating the oxidation is fast (Scheme 7, eq 3) (see Supporting Information for detailed information). Moreover, the intermolecular competition reactions revealed that the reactivities of Et_2O and Et_3N are similar, but they are both less reactive than DMF (Scheme 7, eq 4), and these results are in good agreement with the corresponding BDEs of their C−H bonds.[16]

Based on the control experiments, a plausible mechanism was proposed as shown in Scheme 8. Initially, pyridine-boryl radical **A** is generated by homolysis of the B−B bond. Then, ligand exchange occurs to generate diethyl ether-coordinated boryl radical **B**, which can abstract a hydrogen from ether to furnish α-radical intermediate **C**.[19] Finally, isocyanide insertion to form intermediate **D** and subsequent oxidative aromatization will give the final products. The rapid removal of L−BPinH (L: Et_2O or 4-cyanopyridine) provides the driving force for this reaction.

In summary, we have developed a novel C−H functionalization of aliphatic ethers/amines and DMF through boryl radical-enabled hydrogen abstraction under mild conditions. The substrate scope is broad, and a variety of functional groups are

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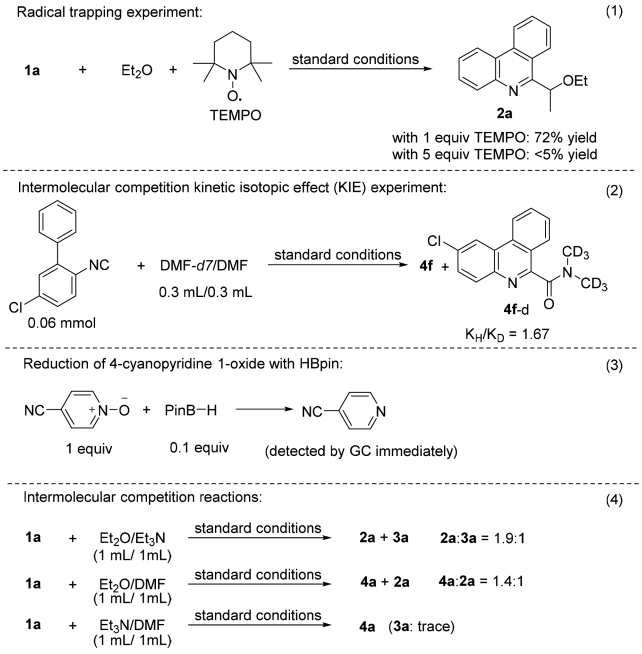
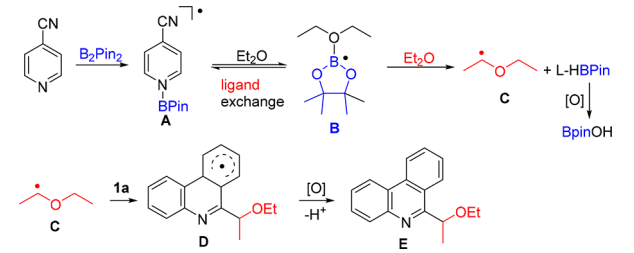
Scheme 7. Control Experiments



Scheme 8. Proposed Mechanism



compatible with this reaction. A plausible mechanism has been proposed based on control experiments and a KIE study. We believe this transition-metal-like property of boryl radicals can provide new opportunities for transition-metal-free C−H functionalizations. Further mechanistic studies and evaluations of the applicability of this ligand-exchange strategy are currently underway in our laboratory and will be published in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00642.

Experimental procedures, characterization data for all new compounds, selected NMR spectra and GC traces (PDF)

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Notes

The authors declare no competing financial interest.

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