Photoinduced Deaminative Borylation of Unactivated Aromatic Amines Enhanced by CO_2

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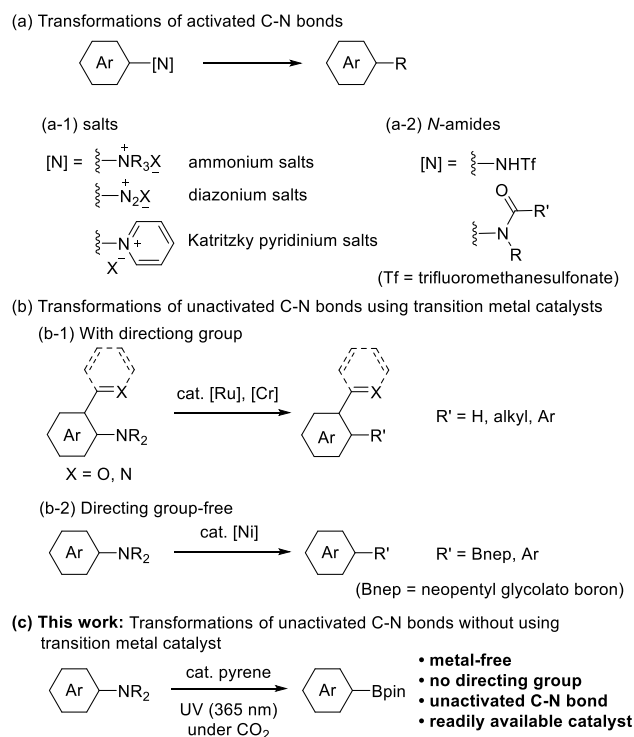
ABSTRACT: Herein, direct unactivated C-N borylation of aromatic amines by a photocatalyst was achieved under mild and metal-free conditions. The C-N borylation of aromatic amines with bis(pinacolato)diboron (B_2pin_2) proceeded in the presence of a pyrene catalyst under light irradiation ($\lambda = 365$ nm) to afford desired borylated products and aminoborane as a byproduct. The yield of borylated product improved under a CO_2 atmosphere. Reactions conducted in the presence of a stoichiometric amount of aminoborane under N_2 or CO_2 indicated that CO_2 reduced the inhibitory effect of aminoborane. Optimal reaction conditions were applied to a variety of aromatic amines. Mechanistic studies suggested that the C-N bond cleavage and C-B bond formation proceeded via a concerted pathway.

Transformation via C-N bond cleavage is a promising protocol for synthetic applications, since a wide variety of natural and industrial products contain amino groups. In particular, arylamine moieties are common among bioactive natural products, pharmaceuticals, and organic functional materials. However, cleavage of aromatic C-N bonds is challenging owing to their high bond dissociation energies.[1] To overcome this problem, several strategies for C-N bond transformation have been developed. Typically, highly reactive species, such as quaternary ammonium salts ([Ar-NR3]+) and diazonium salts ([Ar-N2]+X-), are prepared from arylamines in advance or in situ, and their C-N bonds are consequently converted to various functional groups (Scheme 1, a-1).[2-5] The C-N bonds of Katritzky pyridinium salts, which are readily prepared from anilines, are also transformed by a photoredox or Lewis base catalyst (Scheme 1, a-1).[6-9] For other methods, nickel-catalyzed reduction and borylation of *N*-aryl amides[10] and coupling reactions of *N*-arylsulfonamides[11] and *N*-aryl amides[12] via C–N bond cleavage were developed (Scheme 1, a-2). In these reactions, the C-N bonds are more reactive than those of the corresponding amino groups because of the electron-withdrawing effect of the acyl or sulfonyl groups. Furthermore, direct transformations of unreactive aromatic C-N bonds have been investigated.[13-19] For example, Kakiuchi et al. have recently developed directing-group-assisted ruthenium-catalyzed C-N bond functionalization of *N,N*-dimethyl aniline derivatives, and they reported hydrodeamination, alkyldeamination, and coupling reactions with the arylboronic acid ester of *o*-acylanilines (Scheme 1, b-1).[13-15] In a similar study, Zeng et al. reported arylation and alkylation of arylamines via chromium-catalyzed C-N bond cleavage, with imino groups as directing groups (Scheme 1, b-1).[16,17] Although effective direct transformations of aromatic C-N bonds were achieved in the abovementioned reaction systems, they can only be applied to substrates with a directing group. The first example of C–N transformation without the use of a directing group was reported by Shi et al. (Scheme 1, b-2). They developed Ni-catalyzed direct C-N borylation[20] and arylation[21] of tertiary anilines. Direct C-N transformations have generally been catalyzed by transition metal complexes via oxidative addition of the C-N bonds to the metal center.[22,23] However, metal-free direct transformations of unactivated aromatic C–N bonds are yet to be developed.

Based on the above research background, we focused on a metal-free direct C–N borylation, because it is a powerful protocol for various organic syntheses.[24,25] The resulting C-B bonds can be transformed into diverse substituents and functional groups.[26] In this study, we report the first example of a metal-free direct C-N borylation of unactivated aromatic amines by a photocatalyst under UV irradiation (Scheme 1c). In this reaction, readily available pyrene served as a photocatalyst,[27,28] and a significant effect of CO_2 on the efficient promotion of C-N borylation was demonstrated.
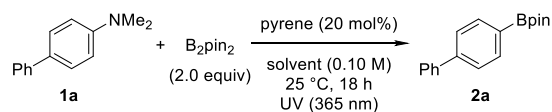
Scheme 1. Transformations via Cleavage of C-N Bond in Aromatic Amines

(a) Transformations of activated C-N bonds

(a-1) salts

[N] = $-\overset{+}{N}R_3\underline{X}$ ammonium salts

$-\overset{+}{N_2}\underline{X}$ diazonium salts

$-N\overset{+}{\underset{X^-}{\bigcirc}}$ Katritzky pyridinium salts

(a-2) N-amides

[N] = $-NHTf$

$-\overset{O}{\underset{R}{N}}-R'$

(Tf = trifluoromethanesulfonate)

(b) Transformations of unactivated C-N bonds using transition metal catalysts

(b-1) With directiong group

R' = H, alkyl, Ar

X = O, N

(b-2) Directing group-free

R' = Bnep, Ar

(Bnep = neopentyl glycolato boron)

(c) **This work:** Transformations of unactivated C-N bonds without using transition metal catalyst

• metal-free
• no directing group
• unactivated C-N bond
• readily available catalyst

Table 1. Optimization of Reaction Conditions

entry[a]	solvent	atmosphere	conv (%)[b,c]	yield (%)[c]
1	CH$_2$Cl$_2$	N$_2$ (close)	37	0
2	DMF	N$_2$ (close)	49	0
3	MeCN	N$_2$ (close)	68	0
4	C$_6$H$_6$	N$_2$ (close)	59	50
5	THF	N$_2$ (close)	80	58
6	1,4-di-oxane	N$_2$ (close)	71	66
7	CPME	N$_2$ (close)	85	67
8	CPME	CO$_2$ (close)	90	82
9	CPME	CO$_2$ (balloon)	97	93
10[d]	CPME	CO$_2$ (balloon)	90	88 (80)[e]
11[f]	CPME	N$_2$ (close)	13	13
12[f]	CPME	CO$_2$ (close)	15	15

[a]**1a** (0.0600 mmol), B$_2$pin$_2$ (0.120 mmol), pyrene (0.0120 mmol), CPME (0.60 mL). [b]Conversion of **1a**. [c]Determined by GC. [d]**1a** (0.15 mmol), B$_2$pin$_2$ (0.300 mmol), pyrene (0.0300 mmol), CPME (1.5 mL). [e]Isolated yield is described in parentheses. [f]Without pyrene. THF, tetrahydrofuran; DMF, dimethylformamide; CPME, cyclopentyl methyl ether.

We began our investigation of direct C–N bond borylation of N,N-dimethyl-4-biphenylamine (**1a**) with 2.0 equiv of B$_2$pin$_2$ in the presence of 20 mol% pyrene upon photoirradiation at 365 nm under N$_2$ atmosphere (Table 1). Solvent screening revealed that the desired 4-biphenylboronic acid pinacol ester (**2a**) was not formed in CH$_2$Cl$_2$, DMF, or MeCN (entries 1–3), but was formed in benzene and ethers (entries 4–7). The best result was obtained with cyclopentyl methyl ether (CPME), and the corresponding product **2a** was obtained in 67% yield (entry 7).[28] Surprisingly, CO$_2$ atmosphere significantly improved the yield of **2a** to 82% (entry 8). Moreover, under CO$_2$ atmosphere in a balloon, the yield of **2a** reached 93% (entry 9). Product **2a** was isolated in 80% yield in a slightly larger scale reaction (entry 10). The reaction conducted without the use of pyrene afforded **2a** in low yields both in the presence or absence of CO$_2$ (entries 11 and 12).

Next, we investigated the substrate scope of the aromatic amines using optimal reaction conditions (Scheme 2). To simplify product purification, the resulting aryl boronic acid pinacol esters were transformed to aryl trifluoroborates by treating the reaction mixtures with KHF$_2$. N,N-Dimethyl-4-biphenylamines with an electron-donating substituent at the para-position of the aniline ring were borylated to afford the corresponding 4-biphenyltrifluoroborate **3b**–**3d** in good to excellent yields. The cyclopropyl groups of **3d** were tolerated under the reaction conditions. Halogen atoms (F and Cl) were also left intact, and the corresponding halo-4-biphenyltrifluoroborates **3e** and **3f** were produced in high yields. Furthermore, the alkynyl group was tolerated without dimerization or polymerization, and product **3g** was obtained in 72% yield. The trimethylsilyl group was

also tolerated under the reaction conditions, giving the corresponding product **2h** in 53% yield. 4-Mesityl-N,N-dimethylaniline with fully twisted aromatic rings or N,N-dimethyl-2-amine fluorene-fused aromatic rings were smoothly converted to their corresponding 4-biphenyltrifluoroborate **3i** and fluorenyl trifluoroborate **3j** in 78% yield and 81% yield, respectively. The methoxycarbonyl group, which is an electron-withdrawing group, was applied, and the corresponding product **3k** was obtained in 70% yield. In the case of 2,4-bis(dimethylamino)biphenyl, the C–N bond at the 4-position was selectively borylated, giving the corresponding aryl trifluoroborate **3l** in 57% yield. The borylation of N,N-dimethylaniline with a phenyl group at the meta-position also gave product **3m** in 52% yield, but the borylation of N,N-dimethyl-2-biphenylamines bearing a substituent at the ortho-position of the aniline ring failed, probably because of steric repulsion (Figure S3). The reaction system was not limited to the biphenyl derivatives, and the deaminative borylation of N,N-dimethyl-4-(thiophen-2-yl)aniline afforded the borylated product **3n** in 54% yield. In addition, N,N-dimethyl-cyclohexenylaniline and N,N-dimethyl-naphthylamines were successfully transformed into the corresponding aryl trifluoroborate **3o**–**3q**.

Scheme 2. Direct Borylation of Aromatic Amines by Cleavage of Unactivated C-N Bond
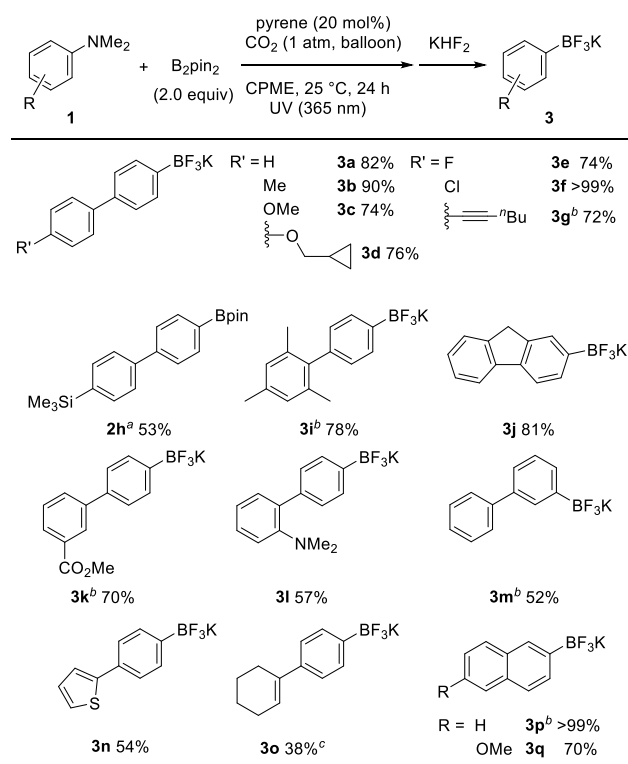
^{a}Isolated yield as pinacol ester without the treatment with KHF$_2$ is described in parentheses. ^{b}B$_2$pin$_2$ (3.0 equiv), pyrene (30 mol%), 36 h. ^{c}12 h.

Next, the borylation of biphenylamines bearing different substituents on the nitrogen atom was investigated (Scheme 3). The reaction system was applied to cyclic amines with pyrrolidyl or piperidyl groups, **1r** and **1s**, to afford trifluoroborate **3a** in 46% and 75% yields, respectively. Surprisingly, the borylation of *N*-methylamine **1t** proceeded to give **3a** in 77% yield.[30,31]

## Scheme 3. Direct Borylation of Aromatic Amines with Other Amino Groups
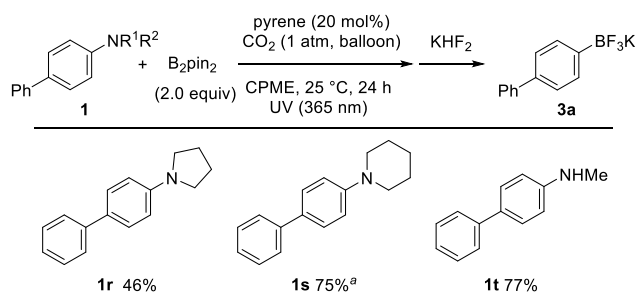
^{a}B$_2$pin$_2$ (3.0 equiv), pyrene (30 mol%), 36 h.

We next initiated mechanistic studies to elucidate the reaction mechanism of direct C–N bond borylation. The tolerance of cyclopropyl group of **3d** under the reaction conditions, as shown in Scheme 2, can be attributed to the fact

that the C–N bond cleavage in anilines did not proceed via a radical intermediate.[32,33] To investigate our hypothesis, borylation was conducted in the presence of 1,1-diphenylethylene or 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical trapping reagent (Scheme 4). Therefore, the borylation of **1a** proceeded smoothly and product **2a** was obtained in 81% and 62% yields, respectively. Furthermore, radical addition products derived from arylamine **1a** were not observed by GC-MS (Scheme 4).[34] In the reaction with 10 equiv of MeOH, **2a** was obtained in 46% yield, but Ar-OMe was not detected at all (Table S7, entry 5). The results indicated that the borylation did not involve generation of α-amino methyl radicals, aryl radicals, or aryl cations, which suggested that both the C–N bond cleavage and the C–B bond formation presumably proceeded via a concerted mechanism.
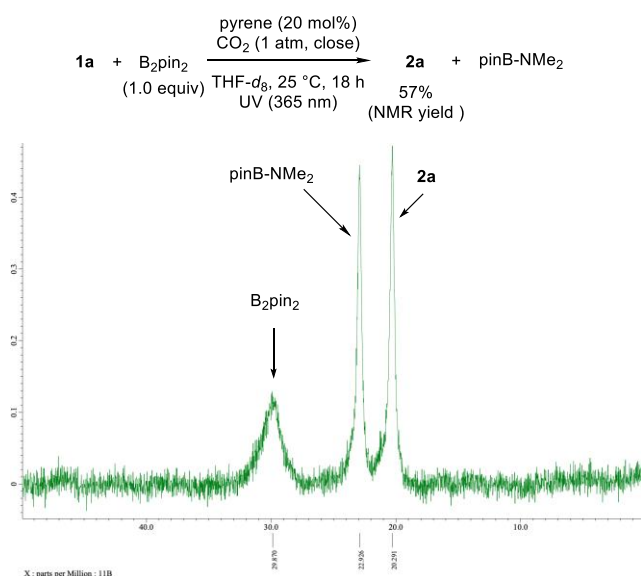
Scheme 4. Borylation Reactions in the Presence of Radical Trap Reagent

^{a}NMR yield, ^{b}GC yield.
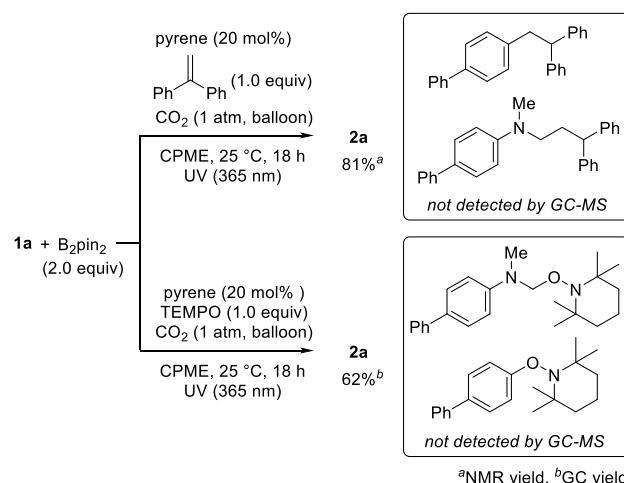
Next, the rate orders of each component (**1a**, B$_2$pin$_2$, and pyrene) were determined by kinetic analyses (Figures S6–8).[35] The reaction rates were found to be first-order in both **1a** and B$_2$pin$_2$(Figures S6 and S7). Interestingly, a negative correlation between pyrene concentration and initial reaction rate was observed (Figure S8). This is probably due to pyrene excimer formation at high concentrations of pyrene, which suppresses electron transfer via the pyrene monomer.[36]

To gain insight into the reaction mechanism, we conducted an NMR experiment on the borylation of **1a**, B$_2$pin$_2$ (1.0 equiv), and pyrene (20 mol%) in THF-d_8 under CO$_2$ atmosphere (Scheme 5). As a result, two new signals at 20.3 ppm and 22.9 ppm were observed in the ^{11}B NMR spectrum, which were assigned to **2a** and *N,N*-dimethylaminopinacolborane (pinB-NMe$_2$),[37] respectively (Scheme 5). The results proved that borylation proceeded and pinB-NMe$_2$ was generated as a byproduct.

Scheme 5. Observation of pinB-NMe₂ Species by ¹¹B NMR Experiment

$$\text{1a} + \text{B}_2\text{pin}_2 \xrightarrow[\substack{\text{THF-}d_8, \text{ 25 °C, 18 h} \\ \text{UV (365 nm)}}]{\substack{\text{pyrene (20 mol\%)} \\ \text{CO}_2 \text{ (1 atm, close)}}} \text{2a} + \text{pinB-NMe}_2$$

(1.0 equiv)   57%
                              (NMR yield)

Control experiments were conducted (Scheme 6) to investigate whether the gradual generation of pinB-NMe₂ inhibited the borylation of **1a**. Indeed, the addition of 1.0 equiv of pinB-NMe₂ into the reaction system under N₂ atmosphere decreased the yield of **2a** from 67% (Table 1, entry 1) to 35%. This result indicated that pinB-NMe₂ acts as a reaction inhibitor. Next, we investigated the effect of CO_2 on the reaction; we assumed that CO_2 weakened the inhibitory effect of pinB-NMe₂. Based on the above assumption, borylation with 1.0 equiv of pinB-NMe₂ under CO_2 atmosphere was conducted, resulting in a higher yield than that under N₂ atmosphere (Scheme 6). To investigate its effect, the borylations under N₂ and CO_2 atmospheres were monitored (Figure S11). Initial reaction rates show a similar tendency, whereas at a later stage, the reaction under N₂ atmosphere was slower than that under CO_2 atmosphere. This result suggested that CO_2 reduced the inhibition by pinB-NMe₂[38] rather than activated aromatic amines, which agrees with the result that the pyrene-free reactions with or without CO_2 afforded similar product yields (Table 1, entries 11 and 12).

Scheme 6. Examinations of Inhibition Effect by pinB-NMe₂

| atmosphere	additive	yield[a]
N₂	none	67%
	pinB-NMe₂ (1.0 equiv)	35%
CO₂	pinB-NMe₂ (1.0 equiv)	45%
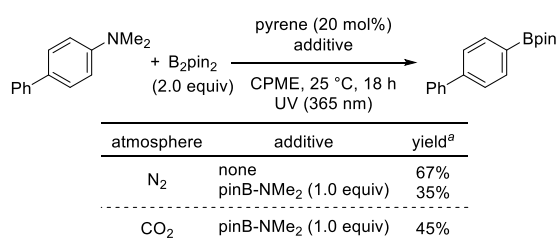
[a]Determined by GC.

The proposed mechanism for C-N borylation, derived from the above mechanistic studies, is depicted in Scheme 7: (1) photoinduced single electron transfer from the

excited pyrene occurs upon UV light photoexcitation to form a complex of the arylamino radical cation with B₂pin₂; (2) C-N bond cleavage C–B bond formation of the resulting radical cation species occur by a concerted pathway; the aminoboryl radical cation generates as a byproduct; and (3) electron transfer from the pyrene radical anion to the aminoboryl radical cation resulting in pyrene and aminoborane, which might interact with CO_2.

Scheme 7. Proposed Reaction Mechanism
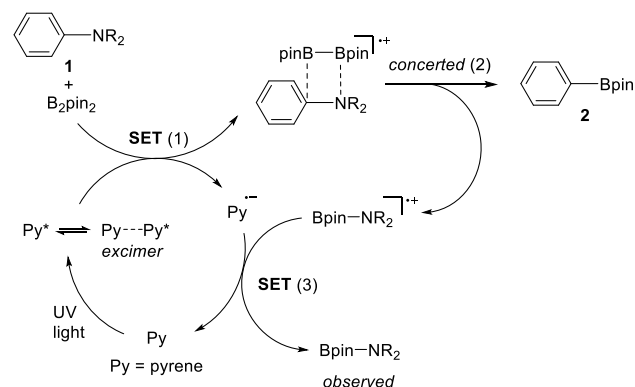
In summary, to the best of our knowledge, this is the first study to develop a photoinduced metal-free direct borylation of aromatic amines via unactivated C–N bonds cleavage. We found that the yields of the borylated products improved dramatically under CO_2 atmosphere. The reaction system was applied to various aromatic amines, efficiently producing the corresponding borylated products. In the mechanistic study, the demonstration of radical trap experiments suggested that both the C–N bond cleavage and the C–B bond formation proceeded via a concerted mechanism. Moreover, the results of the ¹¹B NMR experiment and the reactions in the presence of aminoborane, which was a byproduct, indicated that aminoborane had an inhibitory effect, which was reduced by CO_2. The elucidation of a more detailed reaction mechanism is underway in our group. We believe that this study will shed light on a new strategy for transformation via of unactivated C–N bonds cleavage.

ASSOCIATED CONTENT

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

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Notes

The authors declare no competing financial interest.

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(29) For the screening of other photosensitizers, such as benzophenone and 9,10-diphenylanthracene, see Table S4 in the Supporting Information.

(30) It is significant that the borylation of 4-aminobiphenyl also proceeded to give the borylated product **3a** whereas the yield was low (16% GC yield).

(31) The borylation of *N*-biphenylpyrrole used in the previous literature reported by Shi group[20] was failed. The reaction conditions were not suitable to substrates bearing steric congested amino groups and moderate-to-strong electron-withdrawing substituents. See Figure S3.

(32) The reaction of *N,N*-dimethylaniline excited by a photosensitizer generally includes the formation of α-amino radical intermediate. See: Yang, S.; Li, P.; Wang, Z.; Wang, L. Photoinduced Oxidative Formylation of *N,N*-Dimethylanilines with Molecular Oxygen without External Photocatalyst. *Org. Lett.* **2017**, *19*, 3386–3389.

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(34) The borylated compound of 1,1-diphenylethylene was obtained in 65% yield. See the Supporting Information for the detail (Scheme S1).

(35) See the Supporting Information for exact details of reaction conditions.

(36) The Stern–Volmer experiments suggested that a quench of excited pyrene monomer (λ= 394 nm) is more favorable than that of pyrene excimer (λ= 480 nm). See Figures S9 and S10.

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(38) We assumed that an adduct between CO_2 and pinB-NMe$_2$ formed, or pinB-NMe$_2$ was transformed by CO_2. However, it is not clear so far. For the transformation of aminoboranes with CO_2, see: Cragg, R. H.; Lappert, M. F.; Niith, H.; Schweizer, P.; Tilley, B. P. Die Aminoborierung von Kohlendioxid und Kohlenstoffdisulfid. *Chem. Ber.* **1967**, *100*, 2377–2382.
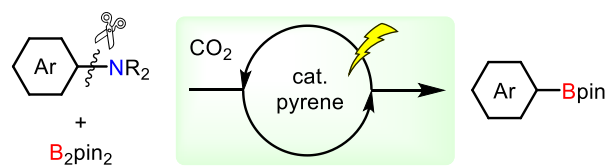
✓metal-free ✓unactivated C-N bond
✓easily available catalyst