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$B(C_6F_5)_3$–catalyzed C3-selective C-H Borylation of Indoles: Synthesis, Intermediates, and Reaction Mechanism

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ABSTRACT: Without addition of any additives and production of any small molecules, C3-borylated indoles and transfer hydrogenated indolines have been simultaneously achieved by $B(C_6F_5)_3$-catalyzed disproportionation reaction of a broad range of indoles with catecholborane. This catalyst system exhibit excellent catalytic performance for practical applications, such as easy scale-up under solvent free condition and long-life catalytic performance over ten sequential addition of starting materials. A combined mechanistic study through isolation and characterization of key reaction intermediate, disproportionation nature of the reaction, in-situ NMR reaction and detailed experimental data, has led to a possible reaction mechanism which illustrate pathways for the formation of both major products and byproducts. Understanding the reaction mechanism enable us to successfully suppress the side reactions by choosing appropriate substrates and adjusting the amount of catecholborane. More importantly, with elevated reaction temperature, we could achieve the convergent disproportionation reaction of indoles in which indolines were continuously oxidized to indoles for the next disproportionation catalytic cycle. Near quantitative conversions and up to 98% yields of various C3-selective borylated indoles were achieved, without any additives and H_2 acceptors.

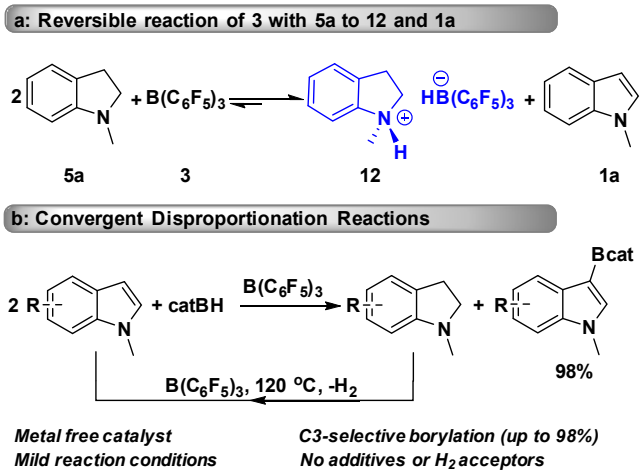
INTRODUCTION

C-H functionalization, especially C-H borylation has attracted significant attentions due to the wide application of organoboron compounds in various derivatization reaction for the synthesis of functional materials, natural products, and pharmaceuticals.[1] Compare to traditional multistep synthetic method,[1,2] transition-metal-catalyzed direct C-H borylation is more efficient and compatible to the functional group, including Rh,[3] Ir,[4] and other noble metals,[5] and inexpensive, abundant transition metals, such as Fe,[6] Co,[7] Ni,[8] Zn,[9] and even heterobimetallic complex.[10] Significant advancements have been achieved in the metal-free arene and heteroarene borylation involving stoichiometric amounts of strong electrophilic boron-derived reagents.[11] Later, several metal-free catalytic C-H borylations have been developed by using activators such as bis(trifluoromethanesulfnoyl)imide ($HNTf_2$),[12] $[Ph_3C]^+[B(C_6F_5)_4]^-$,[12a] or $[Et_3Si]^+[HCB_{11}H_5Br_6]^-$,[13] to regenerate boron electrophiles that entering into the catalytic cycle, or employing the "Frustrated Lewis Pair" catalysts for the C-H Borylation reaction.[14] Recently, in the presence of alkenes, Oestreich and co-workers succeeded in achieving the $B(C_6F_5)_3$ alone catalyed C-H borylation of various heteroarenes at room temperature. However, they discovered their method is not applied to N-methylindole.[15a] With catalytic amounts of $B(C_6F_5)_3$ and a sulfur Lewis base, Takita, Uchiyama and co-workers realized the electrophilic C-H borylation of *N*-methylindole.[15b] In 2017, Erker and co-workers successfuly employed geminal chelate bisborane as efficient catalysts for C-H borylation of arenes and heteroacreanes under mild conditions with liberation of dihydrogen.[16]

Despite these advances, there are still several unaddressed key issues in the C-H borylation of indoles. First, more examples are needed to understand the C-H borylation of indoles, as borylated indoles are of particular interest since they could sever as versatile building blocks for the construction of functional molecules.[17] Second, green and practical but highly effective synthetic strategy is needed. Third, there is only a handful of mechanistic studies related to the C-H borylation of indoles.[16] More recently, through detailed mechanistic studies, we disclosed the disproportionation nature of the $B(C_6F_5)_3$-catalyzed C-H silylation of *N*-methylindole and proposed the reaction mechanism to illustrate the formation of both major products and byproducts, which enable us to successfully realize the atom-economical, convergent disproportionation reaction and achieved near quantitative conversions and up to 99% yields of C3-silylated indoles in no presence of any additives.[18] We envisioned such method could also be applied to the C-H borylation of indoles. To this end, we represented the metal-free $B(C_6F_5)_3$-catalyzed disproportionation of C-H borylation of a variety of indoles with catecholborane at room temperature, affording C3-borylated indoles (oxidation product) and indolines (reduction product) without adding any additives and forming small molecules. This catalyst system exhibited great potentials in practical application

with features such as a low catalyst loading of 0.1 mol% under solvent free condition and long-life catalytic performance. On the basis of a series of in-situ NMR reaction and experimental details, we disclosed the isolable, key reaction intermediate, indolinium hydridoborate (complex **12**) and important reversible reaction of **3** with **5a** to yield **12** and **1a** (Scheme 1a). A possible reaction mechanism was proposed to illustrate the reaction pathways for the formation of major products and byproducts. By elevating the reaction temperature, we have successfully realized convergent disproportionation of indoles, achieving up to 98% yield of C3-selective borylation products (Scheme 1b).

Scheme 1. $B(C_6F_5)_3$-catalyzed convergent disproportionation reaction of indoles



RESULTS AND DISCUSSION

A series of electro-deficient boron catalysts (Table S1) was examined for the C-H borylation of N-methylindole (**1a**) with catecholborane (**2**), it turned out that $B(C_6F_5)_3$ (**3**) is the most effective boron source for this reaction, producing C3-borylated indole **4a** in 42% yield and corresponding transfer hydrogenation indoline product **5a** in 37% yield (Table S2, entry 1). The scope of indoles was expanded for the reaction (Table S2). It is noted that such C-H borylation also tolerates the C2-substituents in the indole substrate. With a fixed 1:0.5 indole/**2** ratio, indoles bearing electron-donating methyl group at C2, C4-C7 positions furnished C3-borylated indole **4b-4f** in 39–49% yield and transfer hydrogenated indoline **5b–5f** in 34–40% yield (Table S2, entries 2–6), respectively. While indoles bearing electron-withdrawing substituents such as halogen-containing motifs (F, Cl, Br) at C5 or C6 position afforded **4g-4l** in 39-46% yield and **5g-5l** in 34-43% yield without dehalogenation (Table S2, entries 7-12). The molecular structure of **4g** was confirmed by single–crystal X–ray diffraction analysis (Figure 1). Such borylated products containing both C-B bond and reactive halogen substituents can be employed for future derivation reaction. While for 1-methyl-5-phenyl-indole (**1m**) with a C-5 phenyl substituent, 46% yield of **4m** and 41% yield of **5m** was obtained (Table S2, entry 13). These reactions show an obvious disproportionation characteristic. However, the best conversion just reach to 96% (Table S2, entry 2) and the conversions of these indoles remained unchanged even with prolonged reaction time. These observations suggested such disproportionation of indole might be a reversible reaction and reaches equilibrium under these conditions.

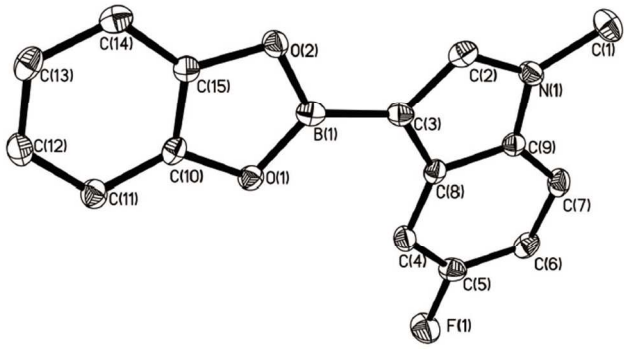
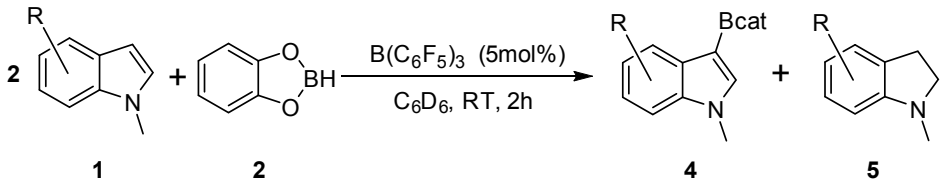


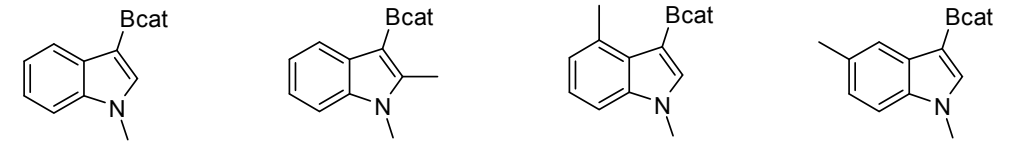
Figure 1. X–ray crystal structure of **4g**. Hydrogen atoms are omitted for clarity and ellipsoids drawn at 50% probability.

Therefore, we expected to shift equilibrium towards the right direction by adding more starting material of **2**. With increasing amount of **2**, quantitative conversions were achieved for all indoles with 1:1.5 indole/**2** ratio (Table S2, entries 14-26). The best result is obtained for 5-Ph substituted indole (**1m**), furnishing both **4m** and **5m** in 49% yield. However, the presence of excess amount of reducing agent **2** led to the formation of byproducts, such as C5-borylated indoline (**6**) and C3-borylated indoline (**7**). When the C5 position of indoles is unoccupied, byproduct **6** was detected, especially for indoles with halogen motifs at C6-position, the yield of byproduct **6** increased with the order of their electron–withdrawing ability: Br (**1l**, 7% yield of **6l**) < Cl (**1j**, 19% yield of **6j**) < F (**1h**, 24% yield of **6h**). Adding substituent to the C5-position of indoles could successfully suppress the C-5 borylation side reaction, but not affect the formation of byproduct **7**. Therefore, in order to shift equilibrium towards the right direction and suppress a series of side reactions simultaneously, we performed the reactions with a fixed 1:0.55 indole/**2** ratio at room temperature (Scheme 2). Except small amount of C5-borylated indoline byproduct was observed for **1a** (**6a**, 5%) and **1j** (**6j**, 8%), the formation of both byproducts **6** and **7** were completely suppressed for the rest of indoles, and thus high to near quantitative conversion and near 50% yield of C3-borylated indole was achieved. Such as 100% conversion and 49% yield of both C3-borylated indole **4i** and indoline **5i** is achieved for 5-Cl substituted indole (**1i**).

Scheme 2. Disproportionation Reaction of Indoles with Catecholborane.[a]



1 **2** **4** **5**

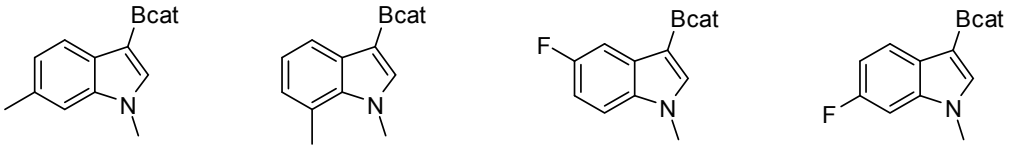


96% conversion
4a, 47% yield
5a, 42% yield

100% conversion
4b, 49% yield
5b, 48% yield

85% conversion
4c, 44% yield
5c, 37% yield

100% conversion
4d, 49% yield
5d, 46% yield

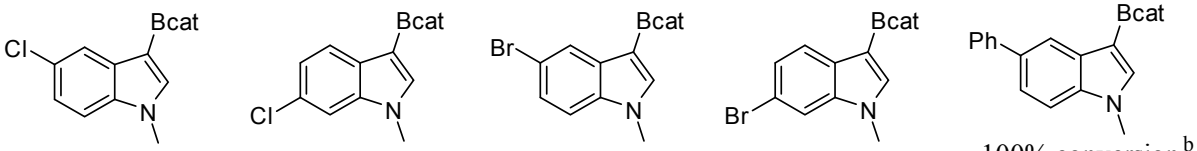


100% conversion
4e, 49% yield
5e, 46% yield

95% conversion
4f, 49% yield
5f, 43% yield

99% conversion
4g, 49% yield
5g, 48% yield

92% conversion
4h, 46% yield
5h, 44% yield



100% conversion
4i, 49% yield
5i, 49% yield

100% conversion
4j, 49% yield
5j, 42% yield

96% conversion
4k, 49% yield
5k, 47% yield

98% conversion
4l, 49% yield
5l, 48% yield

100% conversion[b]
4m, 49% yield
5m, 49% yield

[a] Yield was obtained for reaction with a 1:0.55 indole/**2** ratio. [b] Yield was obtained for reaction with a 1:1.5 indole/**2** ratio.

With the optimal reaction condition in hand, we assessed the catalytic performance of current catalyst system for practical application. The preparative-scale (1.3 g) reaction with 1:0.55 **1a**/**2** ratio was carried out under solvent–free condition with a low catalyst loading of 0.1 mol%, achieving 98% conversion of **1a** and 49% yield for both **4a** and **5a**. The separation of **4a** and **5a** is very convenient, , however, it should be noted that the isolated yield (**4a** 39%; **5a** 36%) is less than that obtained by NMR analysis. More significantly, reuse experiments initiated with a 1:0.55 **1d**/**2** reaction ratio was carried out to verify the practicability of the method (Figure 2). After each run, another batch of **1d** and **2** with 1:0.5 ratio was immediately added to the reaction system to continuously screen the catalytic activity. This process was repeated 9 times at room temperature. It turned out that such borane catalyst exhibits a long life catalytic performance, maintaining unchanged conversion of **1d** around 99% and >46% yield of both **4d** and **5d**.

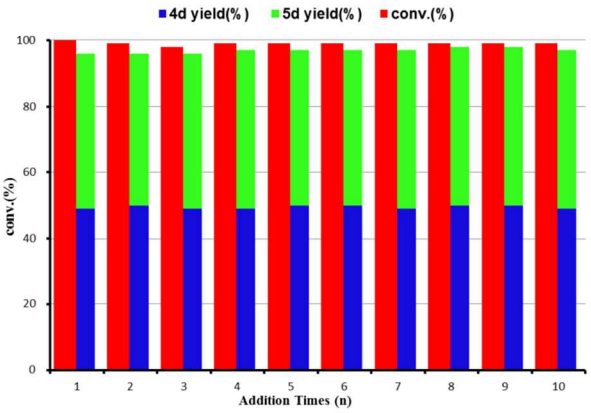


Figure 2. Reuse experiment of $B(C_6F_5)_3$–catalyzed disproportionation reaction of **1d**.

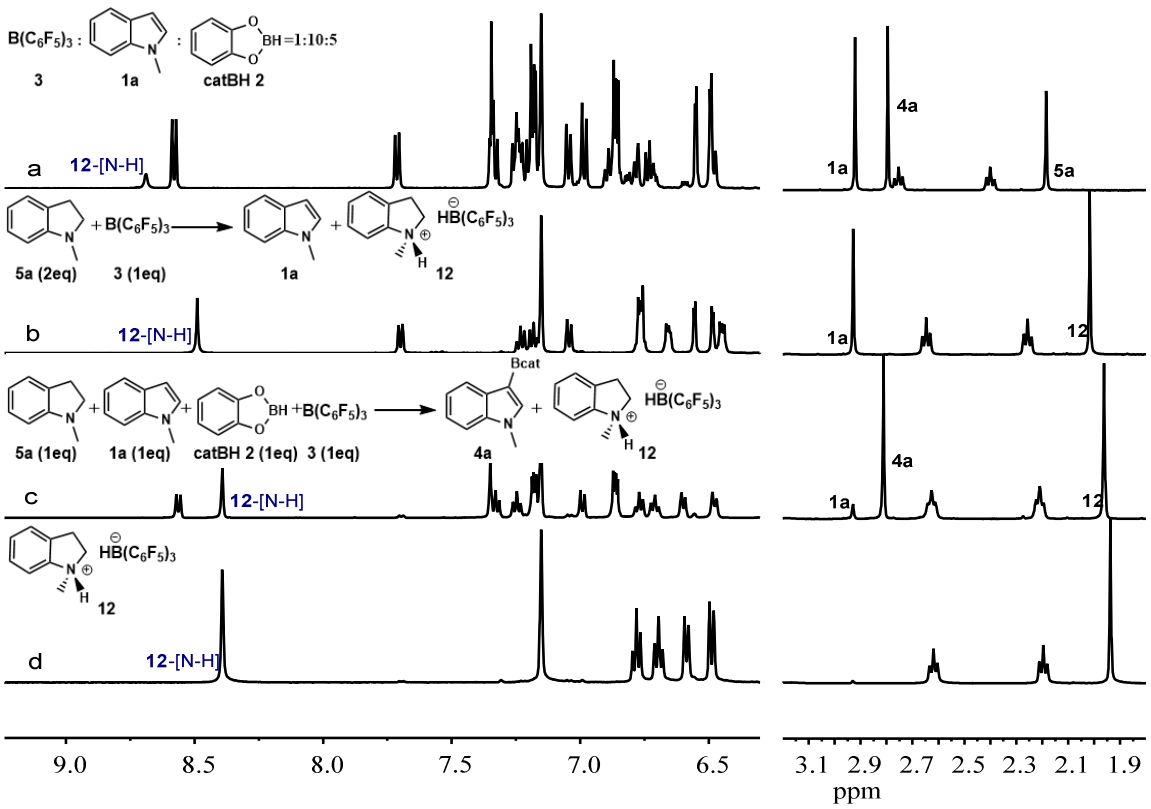


Figure 3. Overlay of ^{1}H NMR spectra for (a) reaction with 1:10:5 **3**:**1a**:**2** ratio; (b) reaction with 2:1 **5a**:**3** ratio; (c) reaction with 1:1:1:1 **5a**:**1a**:**2**:**3** ratio; (d) **12**.

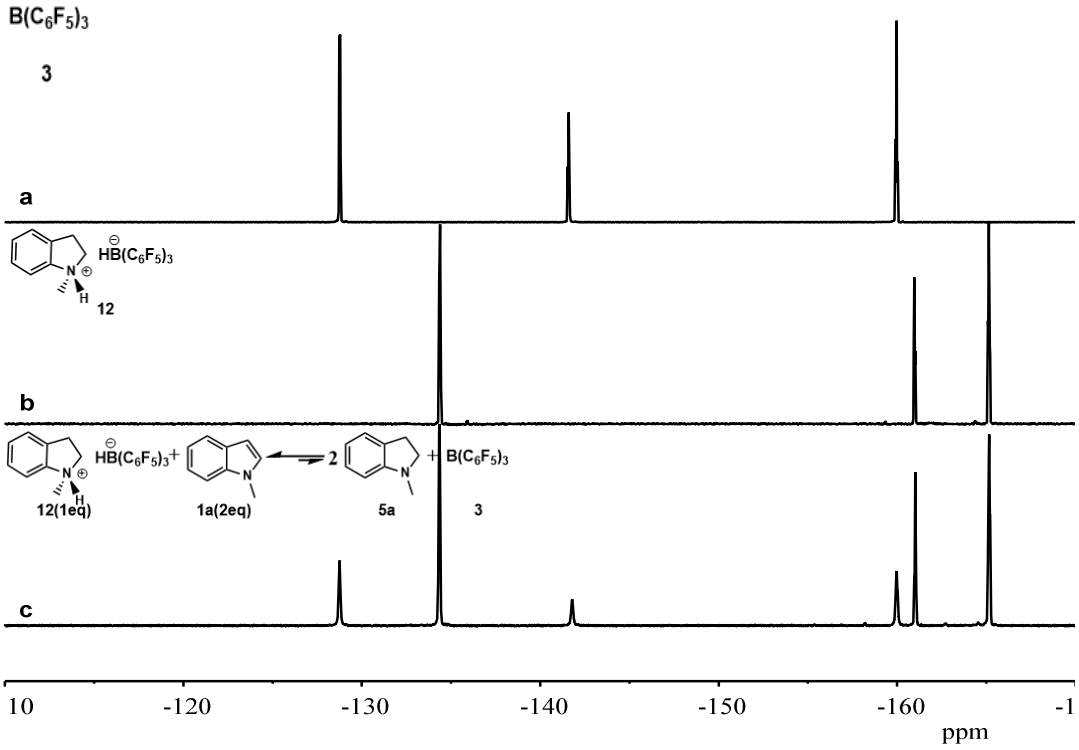
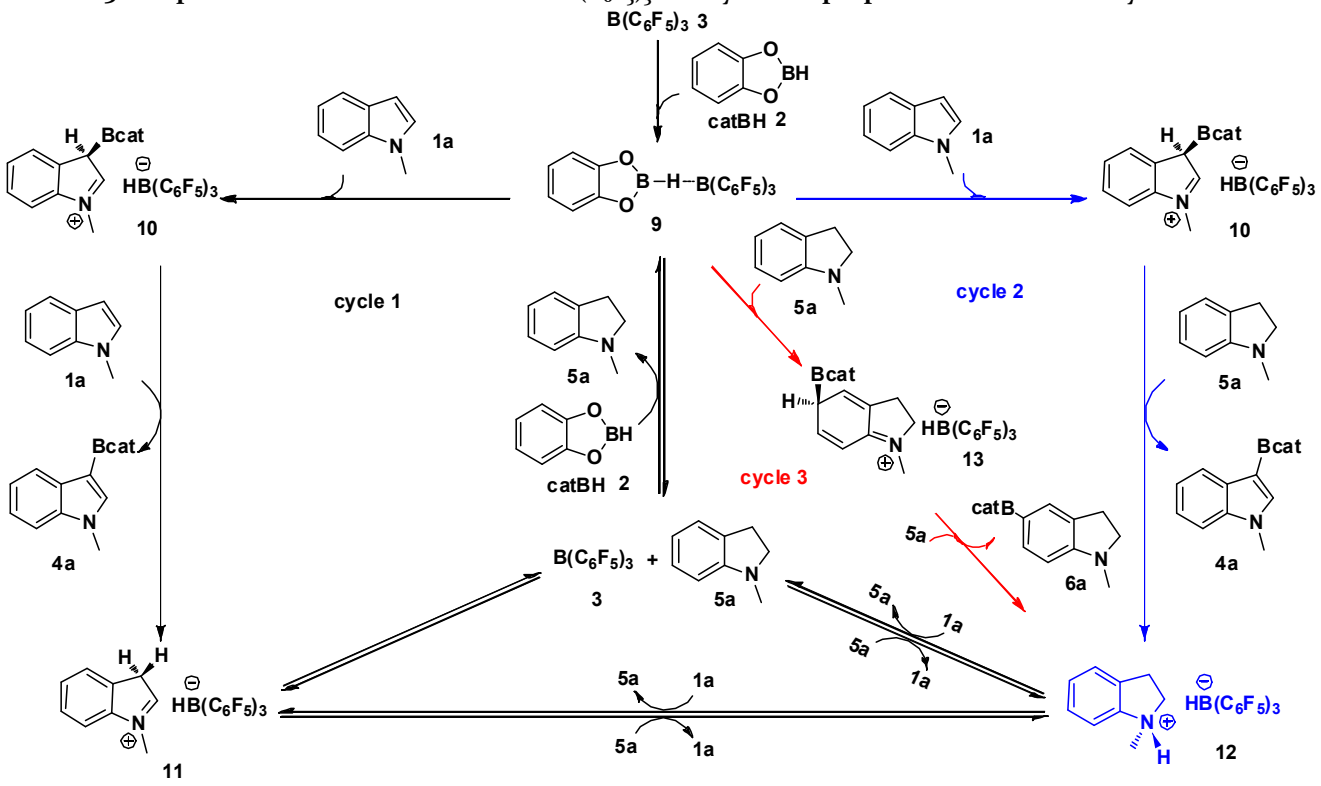


Figure 4. Overlay of ^{19}F NMR spectra for (a) **3**, (b) **12** and (c) reaction with a 1:2 **12:1a** ratio (C_6D_6, 471 MHz).

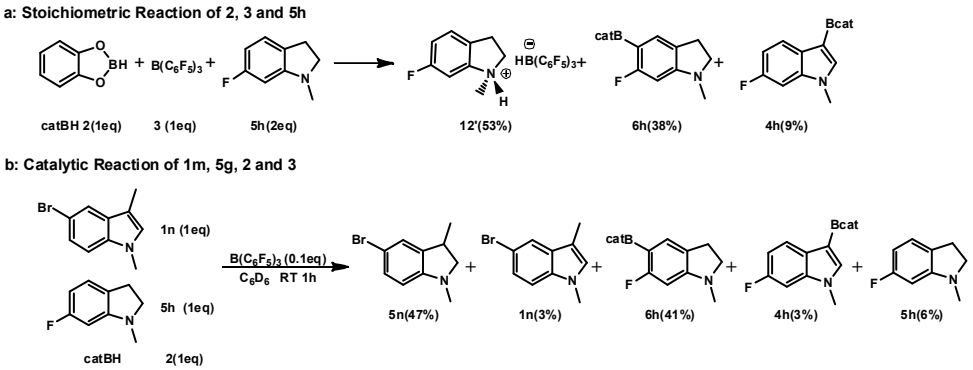
Scheme 3. Proposed reaction mechanism for $B(C_6F_5)_3$–catalyzed disproportionation C-H borylation of indoles



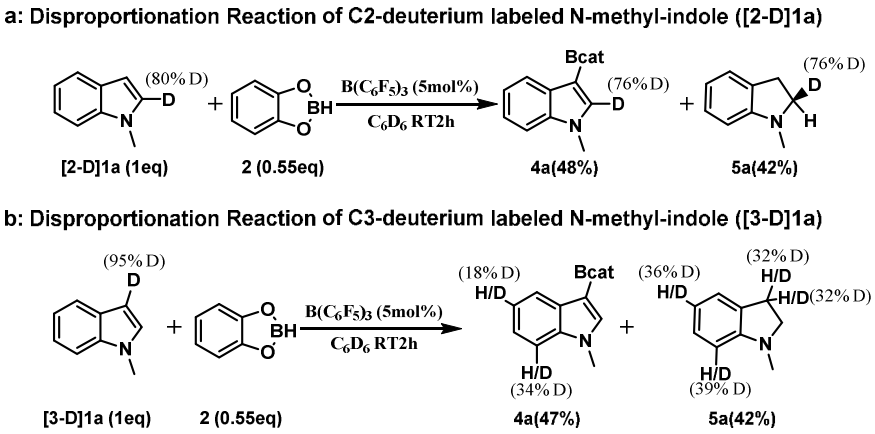
To gain deeper insight into the disproportionation of C-H borylation, we first examined the reaction with a 10:5:1 **1a**/**2**/**3** ratio and observed a stable species with the similar amount to **3** (Figure 3a), in addition to the disproportionation product **4a** and **5a**. The characteristic [N-*H*] resonance peak of indoline at δ 8.69 ppm in ^{1}H NMR spectrum (Figure 3a) and typical signals for a four-coordinated borohydride analogue in ^{19}F NMR spectrum (Figure S4) could be attributed to the indolinium hydridoborate previously reported by Grimme and Paradises.[19] It should be noted that we observed this species in all in-situ NMR reactions investigated for the reaction mechanism. We could successfully prepare and isolate such indolinium hydridoborate, complex **12**, through the reaction with a 1:2 **3**/**5a** ratio (Figure 3b), which turned out to be highly effective for the disproportionation of indoles (Figure S13), suggesting that complex **12** is the real active, isolable intermediate for the reaction. Next a stoichiometric reaction with 1:1:1:1 **1a**/**2**/**3**/**5a** ratio afforded **12** and C3-borylated indole **4a** as product (Figure 3c, see also cycle 2 in scheme 3), further confirmed **12** is a very important reaction intermediate. To realize the catalytic C-H borylation of indoles, the reaction of **3** with **5a** to produce complex **12** and **1a** need to be reversible such that complex **12** could be continuously converted to **3** for the catalytic cycle. If so, the addition of more starting materials should shift the equilibrium existing in the reversible reaction. Therefore, we performed the following control experiment with a 2:1 **1a**/**12** ratio to verify its reversibility. As indicated in the ^{19}F NMR spectra (Figure 4), in the presence of excess amount of **1a**, partial of complex **12** was converted to **5a** and **3**, which perfectly confirmed that the reaction of **3** with **5a** to produce complex **12** and **1a** is a reversible reaction.

On the basis of the disproportionation nature and the above-mentioned experimental details, we proposed a possible reaction pathway for the disproportionation of C-H borylation: the reaction was initiated with activation of **2** by **3** through a B···H interaction to form the weak adduct **9**, which was nucleophilic attacked by the electron–rich indole **1a** to generate highly Brønsted–acidic Wheland complex **10** along with a borohydride. The subsequent attack of **10** by another molecule of **1a** yielded C3-borylated indole **4a** and the Wheland complex **11**, which could produce indoline **5a** and regenerate **3** after transferring hydride onto **11** (cycle 1, Scheme 3). Once the formation of **5a**, the catalytic C-H borylation will follow the reaction pathway as shown in cycle 2 of scheme 3. **3** would activate **2** to reform **9**, which was attacked by **1a** to generate **10**. The subsequent attack of **5a** eventually afforded C-3 borylated indole **4a** and intermediate **12**. In the presence of **1a**, **12** could be converted to **5a** and **3**, which enters the next catalytic cycle (cycle 2, blue). C5-borylated indoline is a common byproduct observed in the C-H borylation of indole, its formation could also be explained by the proposed reaction mechanism (cycle 3, red, Scheme 3). During the reaction, if **9** was attacked by **5a** instead of **1a**, a wheland complex **13** is formed, the subsequent attack by another molecule of **5a** yielded intermediate **12** and C5-

Scheme 4. Control Experiment for the Formation of C5-borylated indoline (cycle 3 in the Scheme 3)



Scheme 5. Isotope-labeled Experiments



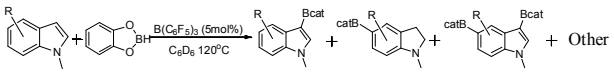
-borylated indoline **6a** (cycle 3, red). The formation of **6a** could be confirmed by the following stoichiometric reaction of **2**, **3** and 1-methyl-6-fluoroindoline (**5h**) with a 1:1:2 **2**/**3**/**5h** ratio at room temperature: as expected, **3** reacted with **5h** to produce complex **12**' in 53% yield and **6h** in 38% yield. (Scheme 4a, Figure S18 and S19). We also verified the cycle 3 through the following catalytic reaction of 5-bromo-1,3-dimethylindole (**1n**), **5h**, **2** and **3** with a 1:1:1:0.1 ratio at room temperature for one hour: similar to cycle 3, most of **5h** underwent the C5-borylation to furnish **6h** in 41% yield, while **1n** was reduced to indoline **5n** in 47% yield(Scheme 4b, Figure S20). Therefore, by choosing appropriate reactants, we have successfully verified all the reaction pathways as shown in the proposed mechanism.

To gain more information on the reaction mechanism, we also ran the isotope-labeled experiment as followed. Through the employment of a C2-deuterium labeled N-methyl-indole (**[2-D]1a**) or C3-deuterium labeled N-methyl-indole (**[3-D]1a**) as starting materials, we investigated 5 mol% of **3** catalyzed in-situ NMR reaction with a 1:0.55 **indole**/**2** ratio. The analysis of these corresponding disproportionation products by ^{1}H NMR spectroscopy revealed that **[2-D]1a** afforded the normal disproportionation product C2-deuterated C3-borylated indole in 48% yield and C2-deuterated indoline in 42% yield (Scheme 5a, Figure S21), without isotope scrambling; while for **[3-D]1a**, C5-borylated indole and indoline was obtained in 47% and 42% yield, respectively. Interestingly, the deuterium signal was observed for the C5, C7 position of C3-borylated indole and C3, C5, C7 position of indoline (Scheme 5b, Figure S22), which is different from previous study reported by Erker[17] but similar to that reported by Werner.[20] These observations implied there existed fast hydrogen exchange in the reaction, which led to the substantial H/D isotope scrambling effects in the end. As seen from the reaction mechanism, such hydrogen exchange should only occur in the reversible reaction of **3** with **5a** to yield **12** and **1a** as shown in the bottom triangle of scheme 3. To test our hypothesis, we added 2 equiv. of **[3-D]1a** to **12** at room temperature (Figure S23 and S24). As expected, we also observed the deuterium signals at C3, C5, C7 position of indole, C3, C5, C7-position of indoline and N1, C3, C5, C7 position of **12**. These observations not only clearly indicated that the hydrogen is quickly exchanged between N1 (only for **12**), C3, C5, C7 position of the products during the reaction, but also further confirmed that the reaction of **3** with **5a** to yield **12** and **1a** is reversible.

After the mechanistic study, we focused our attention on improving the atom economy of the reaction, since it is not very good for disproportionation reaction in general. To achieve convergent disproportionation with an ideal atom-economy, one of the resulted disproportionation products needs to be continuously converted back to starting materials, such that which could subsequently enter the next catalytic cycle of the disproportionation reaction.[21] More recently, our group has achieved up to 99% excellent yield of C3-silylated indole in the $B(C_6F_5)_3$ catalyzed convergent disproportionation of C-H silylation of indole by elevating reaction temperature,[18] as indoline could be oxidized to indole in excellent yield at 120 °C.[19, 22] We envisioned such method should also be applied to the C-H borylation of indoles.

As indicated by the disproportionation of indole, adding more **2** could shift the equilibrium to improve the conversion of indole, therefore, we examined the reaction with a fixed 1:1.5 indole/**2** ratio at 120 °C for two hours (Table 1). The satisfactory result was achieved when the C5 position of indoles is occupied. Near quantitative conversion and excellent yield of C3-borylated indole in the range of 92–98% were achieved for all C5-substituted indoles (**4d**, 98%; **4g**, 96%; **4i**, 96%; **4k**, 92%; and **4m**, 95%) (Table 1, entries 4, 7, 9, 11 and 13). While for indoles with C5 position unoccupied, in addition to the high yield of C3-borylated indole (**4b**, 73%; **4c**, 76%; **4e**, 91%; **4f**, 81%; **4j**, 79%; **4l**, 78%), we also observed the formation of several byproducts, such as C5-borylated indoline (**6**) resulted from the C5-borylation of indolines and C3,C5-diborylated indole (**8**) generated from the subsequent dehydrogenation of **6** and then followed by C3-borylation. Up to 14% yield of byproduct **6** is produced for indoles with halogen motifs at C6-position while up to 31% yield of byproduct **8** was observed for all indoles without C-5 substituents. Obviously, the presence of excess amount of reducing agent **2** resulted in the generation of byproduct **6**, which led to the further formation byproduct **8**. In order to shift equilibrium toward the right direction but prevent the formation of a series of byproducts simultaneously, we performed the reaction with a fixed 1:1.05 indole/**2** ratio at 120 °C. It is delightful to see that near quantitative conversion and excellent yield of C3-borylated indole in the range of 92–95% was achieved for all C5-substituted indoles (**4d**, 95%; **4g**, 93%; **4i**, 92%; **4k**, 92%; **4m**, 94%) (Table 1, entries 17, 20, 22, 24 and 26). The formation of byproduct **6** and **8** were clearly suppressed to a great extent for indoles with unoccupied C5-position, especially for indoles with halogen motifs at C6-position. For example, the yields of C3-borylated indole products obtained for the reaction with 1:1.05 raio were significantly enhanced than those obtained for the reaction with 1:1.5 raio (**1b**, 82% vs 73%; **1h**, 70% vs 52%; **1j**, 93% vs 79%; **1l**, 92% vs 78%).

Table 1. Convergent Disproportionation Reaction of Indoles [a]



1 **2** **4** **6** **8**

Entry	1	Conv. (%)[b]	Yield of **4** (%)[b]	Yield of **6** or **8** (%)[b]
1	**1a**, R = H	100	**4a**, 69	**8a**, 29
2	**1b**, R = 2–Me	100	**4b**, 73	**8b**, 24
3	**1c**, R = 4–Me	100	**4c**, 76	**8c**, 19
4	**1d**, R = 5–Me	100	**4d**, 98	0
5	**1e**, R = 6–Me	100	**4e**, 91	**8e**, 6
6	**1f**, R = 7–Me	100	**4f**, 81	**8f**, 19
7	**1g**, R = 5–F	100	**4g**, 96	0
8	**1h**, R = 6–F	100	**4h**, 52	**6h**, 14; **8h**, 31
9	**1i**, R = 5–Cl	100	**4i**, 96	0
10	**1j**, R = 6–Cl	100	**4j**, 79	**6j**, 12; **8j**, 3
11	**1k**, R = 5–Br	98	**4k**, 92	0
12	**1l**, R = 6–Br	98	**4l**, 78	**6l**, 9; **8l**, 2
13	**1m**, R = 5–Ph	100	**4m**, 95	0
14	**1a**, R = H	95	**4a**, 71	**8a**, 11
15	**1b**, R = 2–Me	100	**4b**, 82	**8b**, 10
16	**1c**, R = 4–Me	90	**4c**, 80	**6c**, 5; **8c**, 5
17	**1d**, R = 5–Me	100	**4d**, 95	0
18	**1e**, R = 6–Me	100	**4e**, 95	**8e**, 5
19[c]	**1f**, R = 7–Me	95	**4f**, 81	**8f**, 7
20	**1g**, R = 5–F	100	**4g**, 93	0
21[c]	**1h**, R = 6–F	97	**4h**, 70	**6h**, 5; **8h**, 14
22	**1i**, R = 5–Cl	100	**4i**, 92	0
23	**1j**, R = 6–Cl	100	**4j**, 93	**6j**, 2; **8j**, 4
24	**1k**, R = 5–Br	95	**4k**, 92	0
25	**1l**, R = 6–Br	100	**4l**, 92	**6l**, 5; **8l**, 2
26	**1m**, R = 5–Ph	100	**4m**, 94	0

[a] Entry 1–13, [**1**]/[**2**] = 1:1.5 , Entry 14–26, [**1**]/[**2**] = 1:1.05 ; [b] Conversion and yield was determined by ^{1}H NMR analysis ; [c] The reaction time was prolonged to 8h.

CONCLUSIONS

To summarize, we disclosed the disproportionation nature for the $B(C_6F_5)_3$-catalyzed C-H borylation of indoles, affording various C3-selective borylated indoles and transfer hydrogenated indoline products at room temperature, without adding any additives and releasing small molecules. A systematic investigation into the disproportionation reaction as well as experimental details provided significant insights into reaction mechanism, which illustrated reaction pathways for the formation of both major products and byproduct. By choosing appropriate substrates and adjusting the amount of **2**, we could inhibit the formation of byproducts. More importantly, the convergent disproportionation reaction of indole was achieved by heating at 120 °C, which allow the continuous conversion of indoline products back to indoles, and then proceed with disproportionation reaction to produce C3-borylated indole and indoline for the next catalytic cycle, and thus achieving C3-borylated indoles in up to 98% excellent yield. Such highly effective

method enabled us to synthesize more regioselective borylated products for future derivation purpose. Relevant research work is in progress.

EXPERIMENTAL SECTION

General Information. All manipulations and syntheses of air- or moisture–sensitive materials were carried out in flamed Schlenk–type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. Benzene, hexane and toluene were refluxed over sodium/potassium alloy or CaH_2 and distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. C_6D_6 and $CDCl_3$ was dried over molecular sieves 4 Å. NMR spectra were recorded on a Varian Inova 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or Bruker Avance II 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C; 471 MHz, ^{19}F; 160 MHz, ^{11}B) instrument at room temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent, whereas ^{19}F NMR spectra were referenced to external $CFCl_3$. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes. It should be noted that all new compounds reported in the Experimental section were characterized by both ^{1}H and ^{13}C NMR spectroscopy without HRMS or elemental analyses, due to their extreme air and moisture-sensitive properties.

Catecholborane (catBH) were purchased from Adamas and distilled prior to use. 5-phenyl-1H-indole, 1,2-dimethyl-indole and 5-bromo-3-methyl-1H-indole were purchased from J&K. Cyclohexane, Et_3N (TEA) and methyl tert-butyl ether (TBME) were purchased from Titan. Boron trichloride (1.0 M solution in hexanes), 4-methyl-1H-indole, 5-methyl-1H-indole, 6-methyl-1H-indole, 7-methyl-1H-indole, 5-fluoro-1H-indole, 6-fluoro-1H-indole, 5-chloro-1H-indole, 6-chloro-1H-indole, 5-bromo-1H-indole and 6-bromo-1H-indole were purchased from Energy Chemical. 1-methylindole were purchased from Alfa Aesar. All of Chemicals were used as received unless otherwise specified as follows. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was prepared according to literature procedures.[23] Methylindole was prepared according to literature procedures. [19a]

Molecular Structure and X-Ray Data of compound 4g

Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10^{-6} Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on F^2 for all reflections (*SHELXTL*, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions (Sheldrick, G. M. *Acta Crystallogr., Sect. A.* **1990**, *46*, 467–473 & **2008**, *64*, 112–122.).

Typical Procedure for Disproportionation Reaction of Indoles

Method A: In a glovebox, indole (0.2 mmol) was added to a $B(C_6F_5)_3$ (**3**) (10 μmol) solution of 0.5 mL C_6D_6 in a 2-mL NMR tube. Then the catecholborane (**2**) (0.1 mmol or 0.11 mmol or 0.3 mmol) was added. After completion of the reaction and measurement of NMR, the reaction mixture was concentrated under vacuum, the solid was obtained after crystallization. The solid was collected by filtration, then washed with hexane and dried in vacuo to afford the C3-borylated indole. The filtrate was concentrated in vacuo and the residue was further purified by flash column chromatography on silica gel using cyclohexane/TBME/Et_3N (100/1/1) as eluent to give the indoline.

Typical Procedure for Convergent Disproportionation Reaction of Indoles

Method B: In a glovebox, indole (0.1 mmol) was added to a $B(C_6F_5)_3$ (**3**) (5 μmol) solution of 0.5 mL C_6D_6 in a J. Young-type NMR tube. Then the catecholborane (0.105 mmol or 0.15 mmol) was added to resulting mixture. The NMR tube was taken out of the glovebox and the reaction mixture was heated to 120°C. After completion of the reaction and measurement of NMR, the reaction mixture was concentrated under vacuum and the solid was obtained after crystallization. The solid was collected by filtration, then washed with hexane and dried in vacuo to afford the C3-borylated indole.

Preparative-scale Synthesis of 4a and 5a. In a glove box, 1-methylindole (**1a**) (1.31 g 10 mmol), $B(C_6F_5)_3$ (**3**) (5.1 mg, 0.01 mmol,) and Catecholborane (**2**) (0.66 g 5.5 mmol) were mixed in a 20 mL reaction flask. The reaction was stirred in neat condition at ambient temperature for 2h, a sample was taken from the reaction mixture and characterized by NMR experiments, conversion is 98% (Yield: **4a** 49%; **5a** 49%). Then 10 mL toluene and 20 mL hexane was added to the reaction system, after stirred for 10 min and filtered to give white solid. The solid was washed with hexane several times and dried in vacuo to afford the 3-(1,3,2-Benzodioxaborol-2-yl)-1-methylindole (**4a**) (0.96 g, 39% yield). The filtrate was concentrated in vacuo and the residue was further purified by flash column chromatography (hexane) on silica gel to afford pure **5a** (0.48g , 36% yield).

Reuse Experiment of The Disproportionation Reaction. In a glovebox, the reaction was carried out with $B(C_6F_5)_3$ (0.005mmol, 2.6mg) was dissolved in 600μL in a J. Young-type NMR tube. At the first time, **1d** (0.1 mmol, 14.5mg) and **2** (0.055mmol, 6.6mg) in 1:0.55 **1d**/**2** ratio were added. After each run, another batch of **1d** (0.1 mmol, 14.5mg) and **2** (0.5mmol, 6.0mg) with 1:0.5 **1d**/**2** ratio were immediately added to the reaction system for the

continuous screening of the catalytic activity. This process was repeated 9 times.

Preparation of Complex 12. In a glove box, 1-methylindoline (**5a**) (53.3mg, 0.4mmol) was dissolved in 1mL hexane, then $B(C_6F_5)_3$ (**3**) (102.4mg, 0.2mmol) was added. The reaction was stirred vigorously at ambient temperature for 10min. The pale yellow solid was collected by filtration, then washed with hexane and dried in vacuo to afford the indolinium hydridoborate **12** (112.1mg, 87% yield). ^{1}H NMR (500 MHz, C_6D_6) δ 8.39 (s, 1H), 6.78 (t, *J* = 7.5Hz, 1H), 6.69 (t, *J* = 7.6Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 3.74-3.08 (m, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.94 (s, 3H). ^{19}F NMR (471 MHz, C_6D_6) δ -134.31 (m), -161.28(m), -165.34(m). ^{11}B NMR (160 MHz, C_6D_6) δ -24.2 (d, *J* = 73.6 Hz).

Spectral Data for products. 3-(1,3,2-Benzodioxaborol-2-yl)-1-methylindole (**4a**)[16]: This product was obtained according to Method B in a 52% yield (12.9 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.59 (d, *J* = 7.9 Hz, 1H, H_{Ar}), 7.37 – 7.32 (m, 2H, H_{Ar}), 7.25 (t, *J* = 7.3 Hz, 1H, H_{Ar}), 7.19 (m, 2H, H_{Ar}), 6.98 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 6.88 – 6.83 (m, 2H, H_{Ar}), 2.79 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ148.8, 139.3, 138.1, 132.5, 128.0, 122.7, 122.3, 122.2, 121.1, 112.1, 110.0, 31.8.

3-(1,3,2-Benzodioxaborol-2-yl)-1,2-dimethylindole (**4b**)[16]: This product was obtained according to Method B in a 71% yield (18.7 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.63 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 7.37 (t, *J* = 7.4 Hz, 1H, H_{Ar}), 7.25 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 7.21 – 7.16 (m, 2H, H_{Ar}), 6.95 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 6.88-6.82 (m, 2H, H_{Ar}), 2.67 (s, 3H, NCH_3), 2.33 (s, 3H, CH_3).^{13}C NMR (126 MHz, C_6D_6) δ 148.7, 148.5, 138.2, 132.5, 128.0, 122.2, 121.9, 121.3, 120.9, 112.1, 108.9, 28.4, 12.2.

3-(1,3,2-Benzodioxaborol-2-yl)-1,4-dimethylindole (**4c**): This product was obtained according to Method B in a 47% yield (12.4 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 (s, 1H, H_{Ar}), 7.22 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 7.15 – 7.11 (m, 3H, H_{Ar}), 6.89 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 6.85 (m, 2H, H_{Ar}), 3.15 (s, 3H, NCH_3), 2.82 (s, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 149.0, 141.3, 138.7, 132.8, 130.8, 128.0, 122.6, 122.4, 122.2, 112.0, 107.3, 32.0, 21.3.

3-(1,3,2-Benzodioxaborol-2-yl)-1,5-dimethylindole (**4d**): This product was obtained according to Method B in a 91% yield (23.9 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.41 (s, 1H, H_{Ar}), 7.35 (s, 1H, H_{Ar}), 7.20 (m, 2H, H_{Ar}), 7.11 (d, *J* = 8.1, 1H, H_{Ar}), 6.93 (d, *J* = 8.3 Hz, 1H, H_{Ar}), 6.88 – 6.82 (m, 2H, H_{Ar}), 2.81 (s, 3H, NCH_3), 2.46 (s, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.9, 139.4, 136.6, 132.8, 130.2, 128.0, 123.8, 122.5, 122.2, 112.1, 109.2, 31.9, 21.3.

3-(1,3,2-Benzodioxaborol-2-yl)-1,6-dimethylindole (**4e**): This product was obtained according to Method B in a 78% yield (20.5 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.50 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 7.19 (m, 3H, H_{Ar}), 6.88 – 6.83 (m, 3H, H_{Ar}), 2.83 (s, 3H, NCH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.9, 138.9, 138.5, 131.7, 130.3, 128.0, 122.8, 122.3, 122.2, 112.1, 109.6, 31.9, 21.6.

3-(1,3,2-Benzodioxaborol-2-yl)-1,7-dimethylindole (**4f**): This product was obtained according to Method B in a 58% yield (15.3 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.49 (d, *J* = 7.9 Hz, 1H, H_{Ar}), 7.28 (s, 1H, H_{Ar}), 7.24 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 7.21 – 7.16 (m, 2H, H_{Ar}), 6.92 (d, *J* = 7.1, 1H, H_{Ar}), 6.88 – 6.84 (m, 2H, H_{Ar}), 3.02 (s, 3H, NCH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.9, 140.9, 136.8, 133.6, 128.0, 124.9, 122.2, 121.3, 121.2, 120.9, 112.1, 36.0, 19.0 .

3-(1,3,2-Benzodioxaborol-2-yl)-5-fluoro-1-methylindole (**4g**): This product was obtained according to Method B in a 87% yield (23.1 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.26 (dd, *J* = 9.5, 2.5 Hz, 1H, H_{Ar}), 7.24 (s, 1H, H_{Ar}), 7.16 – 7.11 (m, 2H, H_{Ar}), 6.96 (td, ^3J = 9.0 Hz, ^4J = 2.5Hz, 1H, H_{Ar}), 6.88 – 6.83 (m, 2H, H_{Ar}), 6.63 (dd, ^3J = 8.8 Hz, ^4J = 4.3Hz, 1H, H_{Ar}) , 2.69 (s, 3H, NCH_3). ^{19}F NMR (471 MHz, C_6D_6) δ -123.00 – -123.08 (m). ^{13}C NMR (126 MHz, C_6D_6) δ 159.3 (d, *J* = 236.3 Hz), 148.7, 140.4, 134.5 (d, *J* = 4.0 Hz), 133.1 (d, *J* = 10.5 Hz), 128.0, 127.6, 122.3, 110.4 (d, *J* = 26.3 Hz), 110.2 (d, *J* = 9.8 Hz), 107.6 (d, *J* = 23.6 Hz), 32.0.

3-(1,3,2-Benzodioxaborol-2-yl)-6-fluoro-1-methylindole (**4h**): This product was obtained according to Method B in a 51% yield (13.6 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.31 (dd, *J* = 8.7, 5.4 Hz, 1H, H_{Ar}), 7.25 (s, 1H, H_{Ar}), 7.18 (m, 2H, H_{Ar}), 7.07 (m, 1H, H_{Ar}), 6.87 (m, 2H, H_{Ar}), 6.69 (dd, ^3J = 9.5 Hz, ^4J = 2.3Hz, 1H, H_{Ar}), 2.63 (s, 3H, NCH_3). ^{19}F NMR (471 MHz, C_6D_6) δ -120.15 – -120.21 (m). ^{13}C NMR (126 MHz, C_6D_6) δ 160.3 (d, *J* = 238.6 Hz), 148.7, 139.8 (d, *J* = 3.1 Hz), 123.4 (d, *J* = 9.9 Hz), 122.4, 122.5 (d, *J* = 11.5 Hz), 112.2, 110.0 (d, *J* = 24.1 Hz), 96.2 (d, *J* = 26.2 Hz), 31.8.

3-(1,3,2-Benzodioxaborol-2-yl)-5-chloro-1-methylindole (**4i**)[16]: This product was obtained according to Method B in a 90% yield (25.5 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.62 (d, *J* = 1.9 Hz, 1H, H_{Ar}), 7.23 (dd, *J* = 8.7, 2.0 Hz, 1H, H_{Ar}), 7.20 (s, 1H, H_{Ar}), 7.13(m, 2H, H_{Ar}), 6.85 (m, 2H, H_{Ar}), 6.62 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 2.64 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 140.2, 136.3, 133.4, 128.0, 127.2, 122.5, 122.4, 122.0, 112.2, 110.5, 31.9.

3-(1,3,2-Benzodioxaborol-2-yl)-6-chloro-1-methylindole (**4j**): This product was obtained according to Method B in a 79% yield (22.3 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.27 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 7.31 (dd, *J* = 8.5, 1.9 Hz, 1H, H_{Ar}), 7.16 (m, 3H, H_{Ar}), 7.02 (d, *J* = 1.7 Hz, 1H, H_{Ar}), 6.88 – 6.84 (m, 2H, H_{Ar}), 2.59 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.7, 139.9, 138.4, 130.8, 128.3, 128.0, 123.4, 122.4, 121.6, 112.2, 109.9, 31.8.

3-(1,3,2-Benzodioxaborol-2-yl)-5-bromo-1-methylindole (**4k**) [16]: This product was obtained according to Method B in a 82% yield (26.8 mg) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.72 (d, *J* = 1.7 Hz, 1H, H_{Ar}), 7.33 (dd, *J* = 8.6, 1.8 Hz, 1H, H_{Ar}), 7.14 (s, 1H, H_{Ar}), 7.11 (m, 2H, H_{Ar}), 6.84 (m, 2H, H_{Ar}), 6.54 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 2.64 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 140.0, 136.5, 134.0, 128.0, 127.6, 125.0, 122.4, 114. 8, 112.2, 111.0, 31.9.

3-(1,3,2-Benzodioxaborol-2-yl)-6-bromo-1-methylindole (**4l**): This product was obtained according to Method B in a 72% yield (23.6 mg) as a white solid. ^{1}H NMR (500 MHz,

C_6D_6) δ 8.21 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 7.44 (dd, *J* = 8.4, 1.7 Hz, 1H, H_{Ar}), 7.19 (d, *J* = 1.6 Hz, 1H, H_{Ar}), 7.17 – 7.14 (m, 3H, H_{Ar}), 6.88 – 6.84 (m, 2H, H_{Ar}), 2.57 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 139.8, 138.8, 131.1, 128.0, 124.2, 123.8, 122.4, 115.9, 112.9, 112.2, 31.8.

3-(1,3,2-Benzodioxaborol-2-yl)-5-phenyl-1-methylindole (**4m**): This product was obtained according to Method B in a 82% yield (26.6 mg) as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 8.86 (d, *J* = 1.2 Hz, 1H, H_{Ar}), 7.81 – 7.75 (m, 2H, H_{Ar}), 7.58 (dd, *J* = 8.5, 1.7 Hz, 1H, H_{Ar}), 7.38 (s, 1H, H_{Ar}), 7.28 (t, *J* = 7.6 Hz, 2H, H_{Ar}), 7.20 – 7.16 (m, 3H, H_{Ar}), 7.01 (d, *J* = 8.5 Hz, 1H, H_{Ar}), 6.84 (m, 2H, H_{Ar}), 2.82 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 148.8, 142.7, 140.0, 137.6, 135.0, 133.0, 128.7, 128.0, 127.6, 126.4, 122.3, 122.2, 121.2, 112.2, 109.8, 32.0.

5-bromo-1,3-dimethylindoline **(5n):** This product was obtained according to Method A in a 40% yield (18.1 mg) as a colorless oil. ^1H NMR (500 MHz, C_6D_6) δ 7.18 (dd, J = 8.3, 1.3 Hz, 1H, H_{Ar}), 7.06 (s, 1H, H_{Ar}), 5.97 (d, J = 8.3 Hz, 1H, H_{Ar}), 2.97 (t, J = 8.4 Hz, 1H, NCH), 2.86 – 2.80 (m, 1H, CH), 2.35 (t, J = 8.3 Hz, 1H, NCH), 2.24 (s, 3H, NCH_3), 0.89 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 152.0, 137.4, 130.1, 126.1, 109.5, 108.3, 63.5, 35.1, 35.0, 17.8.

5-(1,3,2-Benzodioxaborol-2-yl)-6-fluoro-1-methylindoli-ne (**6h**): Prepared from 6-fluoro-1-methylindoline (**5h**) (30.2 mg, 0.2 mmol, 1 equiv), catecholborane(**2**) (119.9 mg, 1.0 mmol, 5 equiv) and $B(C_6F_5)_3$ (**3**) (10 μmol) similar to Method B in a 70% yield (37.7 mg) as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 7.65 (d, *J* = 6.0 Hz, 1H, H_{Ar}), 7.13 – 7.10 (m, 2H, H_{Ar}), 6.82 – 6.78 (m, 2H, H_{Ar}), 5.94 (d, *J* = 10.7 Hz, 1H, H_{Ar}), 2.75 (t, *J* = 8.4 Hz, 2H, NCH_2), 2.45 – 2.40 (t, *J* = 8.4 Hz, 2H, CH_2) , 2.10 (s, 3H, NCH_3). ^{19}F NMR (471 MHz, C_6D_6) δ -101.79 – -101.91 (m). ^{13}C NMR (126 MHz, C_6D_6) δ 170.4 (d, *J* = 250.4 Hz), 158.4 (d, *J* = 12.8 Hz), 148.9, 130.7 (d, *J* = 10.2 Hz) , 125.1 (d, *J* = 1.5 Hz), 122.3, 112.4 (d, *J* = 21.5 Hz), 112.2, 93.5 (d, *J* = 29.0 Hz), 54.9, 33.3, 26.9.

3,5-bis(1,3,2-Benzodioxaborol-2-yl)-1-methylindole (**8a**): Prepared from 1-methylindole (**2a**) (26.2 mg, 0.2 mmol, 1 equiv), catecholborane(**2**) (119.9 mg, 1.0 mmol, 5 equiv) and $B(C_6F_5)_3$ (**3**) (10 μmol) according to the similar process to Method B in a 32% yield (23.5 mg) as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 9.51 (s, 1H, H_{Ar}), 8.22 (d , *J* = 8.2 Hz, 1H, H_{Ar}), 7.29 (s, 1H, H_{Ar}), 7.16 – 7.09 (m, 4H, H_{Ar}), 6.99 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 6.84 (m, 4H, H_{Ar}), 2.75 (s, 3H, NCH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 149.1, 148.8, 140.5, 139.9, 132.2, 130.9, 128.5, 128.0, 127.6, 122.4, 122.3, 112.4, 112.3, 109.7, 31.8.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Additional experimental details, NMR spectra, crystal data, bond lengths and angles, and further tabular data (PDF)
Cif data for **4g** ($C_{15}H_{11}BFNO_2$) (CIF)

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Notes

The authors declare no competing financial interest.

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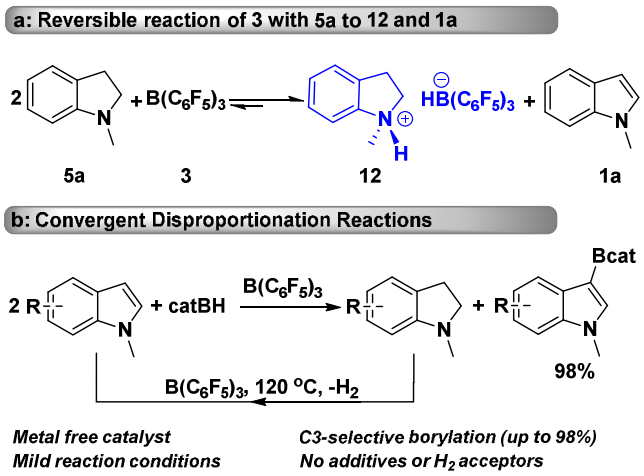
a: Reversible reaction of 3 with 5a to 12 and 1a
2
+ B(C6F5)3
HB(C6F5)3 +
5a
3
12
1a
b: Convergent Disproportionation Reactions
2 R
+ catBH
B(C6F5)3
R
+ R
Bcat
98%
B(C6F5)3, 120 °C, -H2
Metal free catalyst
Mild reaction conditions
C3-selective borylation (up to 98%)
No additives or H2 acceptors