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Boron Trichloride-Mediated Synthesis of Indoles *via* the Aminoboration of Alkynes

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Abstract: We describe an efficient catalyst- and metal-free aminoboration of alkynes to 3-borylated indoles using one of the least expensive boron sources, BCl_3. The major dichloro(indolyl)borane products can be used for the in situ construction of useful 3-Bpin indoles. This simple and mild method provides a novel and efficient approach for the synthesis of various 3-borylated indoles with high regioselectivity and a wide substrate scope.

Keywords: indole; cyclization; aminoboration; alkynes; catalyst-free

The indole unit is one of the most abundant and relevant heterocycles in natural products and pharmaceuticals.[1] The synthesis of indoles has been a subject of study for over 100 years, and a variety of well-established classical methods involving Fischer, Bischler, Gassman and Madelung indole syntheses are now available.[2] An important approach to the synthesis of indoles is based on the cyclization of nitrogen nucleophiles and alkyne moieties, which can be part of the same molecule or belong to two different molecules.[3] On the other hand, functionalized organoboronates are important building blocks for the construction of complex and valuable molecules, such as natural products, pharmaceuticals, and optoelectric materials. Various boronic acids and esters and their derivatives, such as trifluoroborates and MIDA boronates,[4] have been with great success. As ubiquitous synthetic building blocks, 3-borylated indoles are privileged compounds, and they have been used as precursors for Suzuki

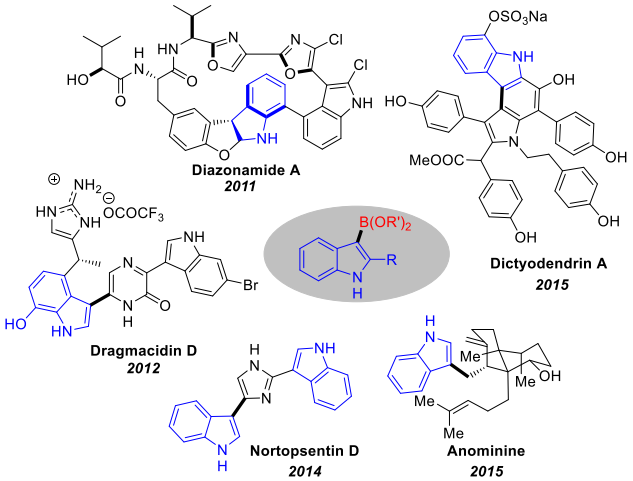

Figure 1 Total Syntheses of Indole Alkaloids Using 3-Borylated Indoles as the Building Blocks.

couplings[5] and Chan-Lam couplings[6] to synthesize a range of natural products containing indole frameworks (Figure 1).[7] As a result, considerable attention has been devoted to the effective construction of these compounds.

In 2010, Harrity et al. developed the first Pd-catalyzed borylative cyclization strategy to synthesize 3-borylated indoles using *o*-alkynylanilines as substrates and B_2Pin_2 as the boron source (Scheme 1a).[8] In 2015, Blum and coworkers uncovered a novel cascade process involving a gold-catalyzed aminoboration reaction *via* the addition of B−N σ bonds across C−C π bonds (Scheme 1b).[9] Later, the Fu group reported an example of a ClBcat-promoted borylative cyclization of *N,N*-dimethyl-2-alkynylaniline. DFT calculations

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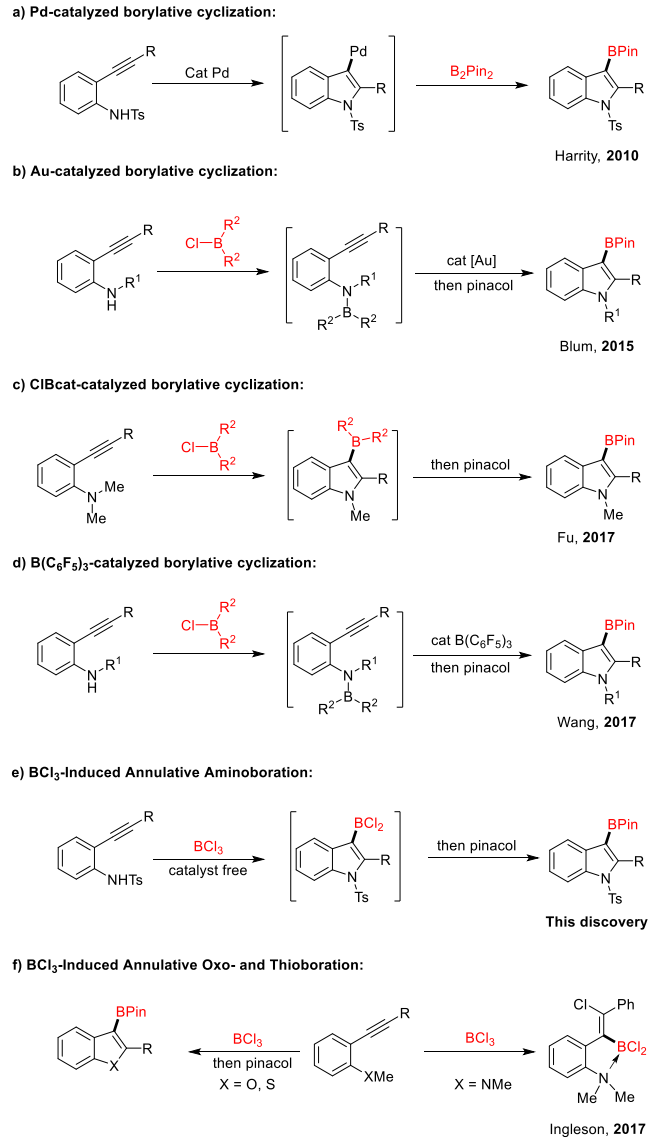

Scheme 1 Synthesis of 3-borylated indoles.

elucidated the details of the mechanism of this transformation (Scheme 1c).[10] At the same time, a facile $B(C_6F_5)_3$[11]-catalyzed *trans*-aminoboration was used to carry out a similar transformation. (Scheme 1d).[12] Despite the availability of these methods for the synthesis 3-borylated indoles, the discovery of new routes, particularly a safe and low-cost protocol, remains desirable. Herein, we demonstrate the first BCl_3-mediated annulative aminoboration of alkynes for the formation of C3-borylated indoles (Scheme 1e).

Using an alternative boron source (BCl_3) to promote the borylative cyclization enables the formation of organo-boronic acid derivatives on work-up and consequently access to the myriad of well-established transformations.[13] Recently, Ingleson et al. developed BCl_3-induced annulative oxo- and thioborations for the formation of C3-borylated benzofurans and benzothiophenes.[14] However, the addition of BCl_3 to

Table 1 Optimization the reaction conditions.[a]

entry	X	[B] (equiv)	solvent	T	Yield (%)[b]
1	Ts (**1a**)	BCl_3 (1.0)	DCM	rt	21
2	Ts (**1a**)	BCl_3 (1.2)	DCM	rt	62
3	Ts (**1a**)	BCl_3 (1.5)	DCM	rt	73
4	**Ts (1a)**	**BCl_3 (2.0)**	**DCM**	**rt**	**93 (82)**[c]
5	Boc (**1a'**)	BCl_3 (2.0)	DCM	rt	0
6	Ac (**1a"**)	BCl_3 (2.0)	DCM	rt	0
7	Ms (**1a"'**)	BCl_3 (2.0)	DCM	rt	78
8	Ts (**1a**)	BCl_3 (2.0)	DCE	rt	59
9	Ts (**1a**)	BBr_3 (2.0)	DCM	rt	trace
10	Ts (**1a**)	BF_3 (2.0)	DCM	rt	0
11	Ts (**1a**)	CatBCl (2.0)	DCM	rt	0
12	Ts (**1a**)	PinBCl (2.0)	DCM	rt	0

[a] Reaction conditions: **1a** (0.20 mmol), BCl_3 (1.0 M in DCM), in solvent (1.0 mL), 2.5 h, under Ar. [b] Determined by ^{1}H NMR analysis using dibromomethane as an internal standard. [c] Isolated yield in parentheses. CatBCl = B-chlorocatecholborane; PinBCl = 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

N,*N*-dimethyl-2-(phenylethynyl)aniline only generated an alkyne *trans*-haloboration product instead of the proposed borylated indole (Scheme 1f). The previously reported gold-catalyzed aminoboration indicated that the *N*-substituent was crucial for the transformation.[9] Inspired by Blum's result, we reasoned that a BCl_3-induced aminoboration should take place if a suitable protecting group was used instead of an NMe_2 substituent.

To test this assumption, we added a stoichiometric amount of BCl_3 (1.0 equiv) to a solution of 4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (**1a**) in DCM. After 2.5 hours, the color of reaction mixture had turned from colorless to brown, and then the reaction was quenched carefully using a mixture of pinacol and Et_3N at low temperature under the protection of an argon atmosphere. To our delight, desired 3-borylated indole **3a** was obtained in 21% yield (Table 1, entry 1). Notably, the yield of desired product **3a** can dramatically improve to 62% by slightly increasing the amount of BCl_3 to 1.2 equivalents (Table 1, entry 2). After further screening, the optimum conditions for the annulative

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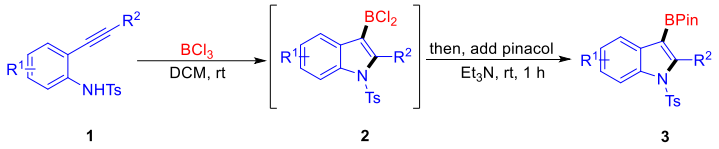
Table 2. Catalyst-free aminoboration of alkynes to indoles.[a]



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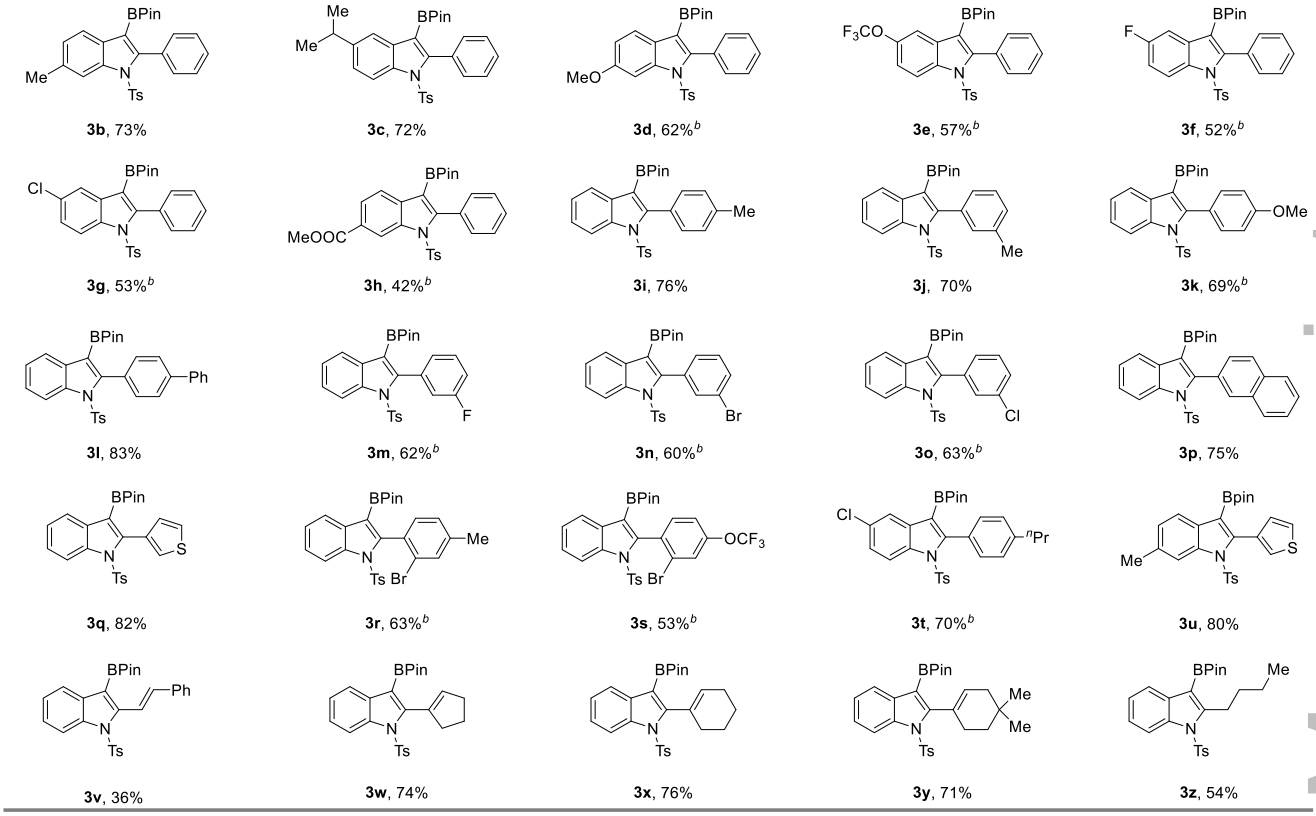


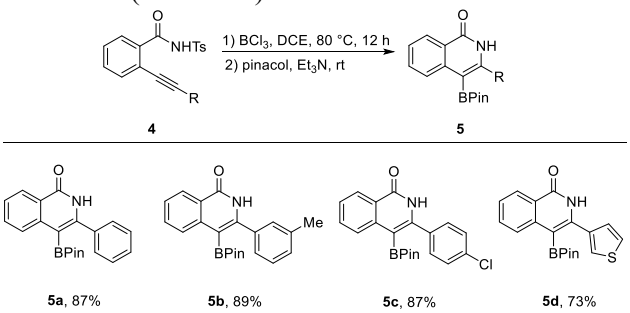
[a] Reaction conditions: **1a** (0.20 mmol), BCl_3 (0.4 mL, 1.0 M in DCM), in solvent (1.0 mL), 2.5 h, room temperature, under Ar. [b] Extended to 5 hours.

aminoboration reaction were identified as DCM at room temperature with 2.0 equivalents BCl_3 give indole **3a** in 82% isolated yield (Table 1, entries 3-4). Among the different *N*-protecting groups tested on the starting materials, the *N*-Boc substituted substrate only furnished deprotected cyclized 2-phenyl-1*H*-indole as the product (Table 1, entry 5). Whereas the *N*-acetyl-protected substrate failed with quantitative recovery (Table 1, entry 6). Switching the *N*-protecting group for a Ms substituent also afforded indole product **3a'''** in moderate yield (Table 1, entry 7). The use of other solvents such as DCE resulted in reduced yields (Table 1, entry 8). Notably, other boron sources such as BBr_3, BF_3, CatBCl or PinBCl failed to yield borylated indole **3a** (Table 1, entries 9-12).

With the optimized reaction conditions in hand, we next turned our attention to investigating the scope of o-alkynylanilines (Table 2). Substrates bearing electron-neutral and electron-donating substituents including methyl (**3b**), isopropyl (**3c**), and methoxy (**3d**) groups underwent facile cyclization to generate the corresponding products. Substrates containing halogen motifs (OCF_3, F, and Cl) work well under the optimized reaction conditions (**3e**–**3g**). An aniline substrate bearing an ester group (**1h**) was also compatible, and it afforded desired product **3h** in moderate yield. Meanwhile, aromatic groups with various substitution patterns can be effectively converted to the corresponding *o*-alkynyl groups regardless of their electronic profile (**3i-3o**). Naphthalene- and thiophene-containing products **3p** and **3q** were also generated good yields. Ortho bromo-substituted aryl derivatives lead to moderate yields (**3r-3s**), suggesting that the increased steric congestion does not affect the reactivity. Notably, *ortho*-enynyl-substituted amines were compatible with the reaction system, and the products were isolated in modest to good yields (**3v-3y**). In addition, the reaction system was found to be tolerant of alkyl substituents, and compound **3z** was obtained in 54% yield.

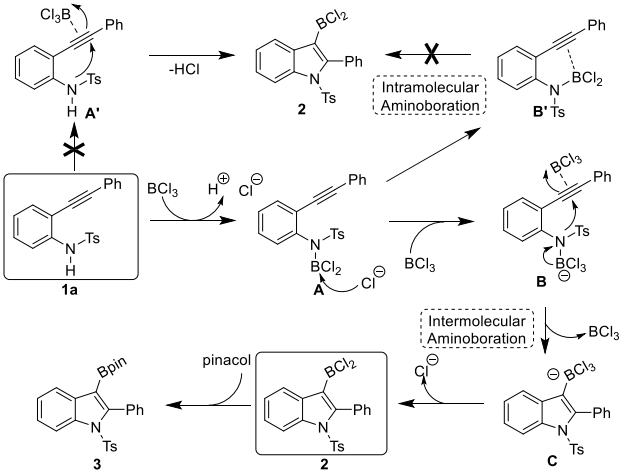
Substituted isoquinolone molecular motifs are also common in functional molecules.[15] Therefore,

synthetic routes to prepare isoquinolones including traditional methods [16] and modern synthetic methods[17] have been explored. To further demonstrate the utility of this borylative cyclization, we evaluated the cyclization of 2-(alkynyl)-*N*-tosylbenzamides **4** to generate various borylated isoquinolones **5** in good yields. Interestingly, the Ts group was immediately hydrolyzed probably due to the instability of the imides generated under acidic conditions (Scheme 2).



Scheme 2 Synthesis of 4-borylated isoquinolin-1(*2H*)-one.

We proposed a mechanism for this tandem process as shown in Scheme 3. According to a previously reported result, when BCl_3 is mixed with the substrate, it immediately interacts with the nitrogen atom of the sulfonamide to form *N*-BCl_2 intermediate **A**.[11b] We consider that another molecule of BCl_3 playing a similar role as the gold catalyst in Blum's reaction[9a] can associate with the newly formed tetracoordinate borane to generate intermediate **B**. Then, intermediate **B** undergoes B−N bond activation and *trans* aminoboration, releasing one molecule of BCl_3 and anion **C**. Subsequent Cl^- dissociation from **C** can produce product **2**. The alternative pathways, including BCl_3 acting as a Lewis acid-promoted cyclization *via* intermediate **A'** and intramolecular aminoboration of intermediate **B'**, can directly generate product **2**. However, these two results are not consistent with 1.2 equivalents of BCl_3 dramatically improving the reaction outcome



Scheme 3 Mechanistic considerations.

compared to 1.0 equivalent of BCl_3. We currently think this process, in which BCl_3 serves a dual role, is more reasonable. Once dichloro(indoyl)borane **2** is formed, the nucleophilic pinacol then interacts with the BCl_2 group to form final products **3**.

In summary, we have presented a mild BCl_3-mediated strategy for the direct cyclization of various *o*-alkynylanilines to form substituted indole derivatives. This discovery complements the recently reported gold- or $B(C_6F_5)_3$-catalyzed alkyne aminoboration reactions, which is of great importance because such procedures obviate the need for removing the catalysts from the reaction residues and eliminating traces of metals from the final compounds.

Experimental Section

General Procedure for the BCl_3-Mediated Synthesis of Indoles *via* the Aminoboration of Alkynes:

A flame-dried 10-mL Schlenk tube was filled with argon, 4-methyl-*N*-(2-(phenylethynyl)phenyl) benzenesulfonamide (**1a**) (69.4 mg, 0.20 mmol) and dry DCM (1 mL) taken directly from a solvent purification system. BCl_3 (1 M in DCM) (0.4 mL) was slowly added in a glovebox. The reaction mixture was stirred for 2.5 hours at room temperature and then was transferred to a liquid nitrogen-acetone bath. A solution of pinacol (59.0 mg, 0.5 mmol) and dry Et_3N (0.42 mL, 3 mmol) in dry DCM (1 mL) was slowly added with a syringe under an argon atmosphere. The solution was then slowly warmed to room temperature and continued to stir for another two hours. The solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (200-300 mesh) (eluent: DCM / PE from 1:4 to 1:2) to afford the corresponding product.

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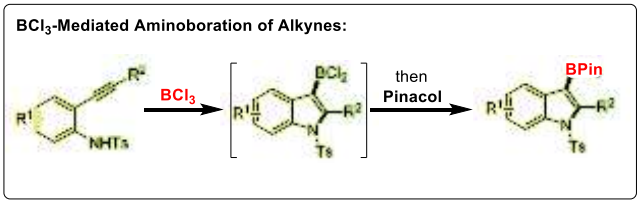

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