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Copper-catalyzed tri- or tetrafunctionalization of alkenylboronic acids to prepare tetrahydrocarbazol-1-ones and indolo[2,3-*a*]carbazoles†

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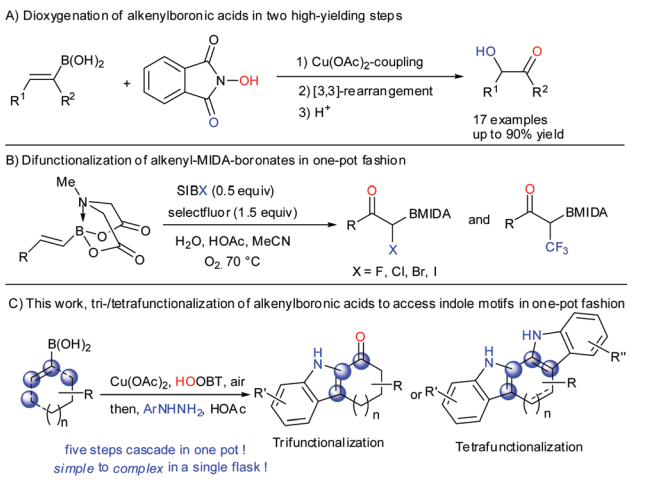
We describe a cascade strategy for tri- or tetrafunctionalization of alkenylboronic acids to prepare diverse tetrahydrocarbazol-1-ones and indolo[2,3-*a*]carbazoles in good yields with *N*-hydroxybenzotriazin-4-one (HOOBT) and arylhydrazines as oxygen and nitrogen sources, respectively. Mechanistic studies reveal that the domino reaction undergoes the copper-catalyzed Chan–Lam reaction, [2,3]-rearrangement, nucleophilic substitution, oxidation and sequential [3,3]-rearrangement over five steps in a one-pot reaction. The reaction shows a broad substrate scope and tolerates a wide range of functional groups. More importantly, the reaction is easily performed at gram scales and the product is purified by simple extraction, washing, and recrystallization without flash column chromatography. The present protocol features easily available starting materials, high site-marked functionalization, five-step cascade in one pot, multiple C–C/C–O/C–N bond formation, and diversity of indole motifs.

Introduction

The cascade reaction serves as one of the most important synthetic strategies to access nitrogen heterocycles of great complexity, and has attracted much attention because of its advantage of multiple bond formation from simple or easily available starting materials in a single step.[1] It improves the synthetic efficiency, simplifies operations, reduces waste generation, and saves time, labor and energy, which have great significance for green and sustainability issues of synthetic chemistry.[2] Organoboron compounds are highly reactive intermediates and versatile building blocks with numerous synthetic applications, primarily attributed to their versatility of the efficient construction of novel C–C and C–heteroatom bonds in the metal-catalyzed cross-coupling reaction.[3] In particular, alkenylboron reagents have received much attention towards the preparation of complex molecules due to the rich transformations of the double bond in the coupling products.[4] Functionalization of alkenes is a powerful and efficient tool for organic synthesis, which can introduce two groups into an alkene in one step to access more complex functional architectures.[5] Although the use of alkenylboron reagents toward the construction of various new bonds is well established, direct functionalization of alkenylboron reagents would be a facile strategy to access diverse functionalized molecules.[6] In 2012, Anderson and co-workers developed a powerful dioxygenation of alkenylboronic acids to prepare α-oxygenated ketones through a copper-mediated etherification, [3,3]-rearrangement and hydrolysis sequence (Scheme 1A).[7] In 2016, Wang and



Scheme 1 Regio-controlled functionalization of alkenylboron reagents.

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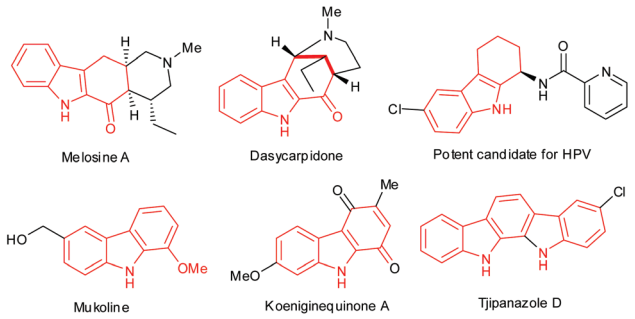


Fig. 1 Selected examples of indole alkaloids.

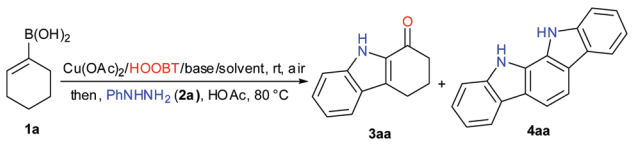
co-workers reported a novel one-pot difunctionalization of alkenyl-MIDA-boronates to synthesize halogenated and trifluoromethylated α-boryl ketones (Scheme 1B).[8] Both these strategies have shown their attractive and powerful efficiencies toward the preparation of functionalized molecules, but simple target molecules were obtained. Therefore, tri- or tetra-functionalization of alkenylboronic acids to more complex targets in one pot is still challenging and desirable to be explored.

N–O bond compounds have attracted much attention recently because they efficiently serve as *O*- or *N*-reagents in the oxidation reaction,[9] C–H amination[10] and aminoxygenation of alkenes.[11] During the studies of N–O bond coupling with alkenylboronic acids by the Chan–Lam reaction[12] and N–O bond rearrangement in our group,[13,14] we proposed an efficient cascade strategy for tri-/tetrafunctionalization of alkenylboronic acids to access indole scaffolds using HOOBT or arylhydrazines as O- or N-sources, respectively, through copper-catalyzed cross-coupling, [2,3]-rearrangement, nucleophilic substitution, oxidation and [3,3]-rearrangement over five steps in a one-pot reaction (Scheme 1C). Moreover, the functionalization can be easily controlled since indole alkaloids are formed in a site-marked process which are not easily obtained from traditional strategies, such as condensation of diketones with arylhydrazines[15] and condensation of β-keto-acids or α-hydroxymethylene ketones with aryl diazonium salts by the Japp–Klingermann reaction.[16] Meanwhile, indole and carbazole are normally occurring scaffolds in a variety of indole alkaloids and pharmaceuticals (Fig. 1).[17] Consequently, the development of a new cascade strategy to prepare these important indole heterocycles in a green manner is valuable.[18]

Results and discussion

Our investigations started with cyclohexenylboronic acid **1a** as the model substrate and HOOBT and phenylhydrazine **2a** as O- and N-sources, respectively (Table 1). A 36% yield of the trifunctionalized product tetrahydrocarbazol-1-one **3aa** was obtained using $Cu(OAc)_2$ as a catalyst and pyridine (pyr) as a base in 1,2-dichloroethane (DCE) under air for 24 h, and then followed with **2a** and HOAc at 80 °C for 18 h (Table 1, entry 1). However, other copper(II) or copper(I) salts, such as $CuCl_2$, $CuSO_4$, $Cu(OTf)_2$, and CuI, afforded **3aa** in lower yields (Table 1, entries 2–5). Solvent screening showed that toluene, THF, MeOH, and DMSO delivered product **3aa** in less than 28% yield (Table 1, entries 6–9). Pleasingly, the yield of **3aa** was dramatically improved to 68% in MeCN (Table 1, entry 10). Decreasing the amount of $Cu(OAc)_2$ to 10 mol% reduced the yield of **3aa** to 52% (Table 1, entry 11). The influence of the base was also investigated (Table 1, entries 12–14). Using either organic bases, such as NEt_3 and DMAP, or inorganic bases, such as Cs_2CO_3, in the reaction did not give **3aa** in higher yields than using pyridine. When the reaction was performed using 1.5 equiv. of pyridine, **3aa** was obtained in 60% yield (Table 1, entry 15). Compared to entry 10, an obvious increase in the yield of **3aa** was observed in the presence of Na_2SO_4 (Table 1, entry 16). The yield of **3aa** decreased to 10% under N_2 instead of air (Table 1, entry 17). Interestingly, when the amount of phenylhydrazine **2a** was increased to 2.0 equiv., the yield of **3aa** was only 20% accompanied by the tetrafunctionalized product indolo[2,3-*a*]carbazole **4aa** in 40% yield (Table 1, entry 18). Further increasing the amount of **2a** to 3.0 equiv. selectively afforded **4aa** in 66% yield without the observation of **3aa** (Table 1, entry 19). Therefore, the optimal conditions for trifunctionalization of alkenylboronic acid **1a** to prepare tetrahydrocarbazol-1-one **3aa** were $Cu(OAc)_2$ (20 mol%) and pyr (3.0 equiv.) with Na_2SO_4 as an additive in MeCN at room temperature under air for 18 h, and then adding phenyl-

Table 1 Optimization of the reaction conditions[a]



Entry	Cat.	Solvent	Base	**3aa** Yield %[b]	**4aa** Yield %[b]
1	$Cu(OAc)_2$	DCE	Pyr	36	<5
2	$CuCl_2$	DCE	Pyr	12	<5
3	$CuSO_4$	DCE	Pyr	5	<5
4	$Cu(OTf)_2$	DCE	Pyr	16	<5
5	CuI	DCE	Pyr	9	<5
6	$Cu(OAc)_2$	Toluene	Pyr	16	<5
7	$Cu(OAc)_2$	THF	Pyr	9	<5
8	$Cu(OAc)_2$	MeOH	Pyr	10	<5
9	$Cu(OAc)_2$	DMSO	Pyr	28	<5
10	$Cu(OAc)_2$	MeCN	Pyr	68	<5
11[c]	$Cu(OAc)_2$	MeCN	Pyr	52	<5
12	$Cu(OAc)_2$	MeCN	NEt_3	12	<5
13	$Cu(OAc)_2$	MeCN	DMAP	43	<5
14	$Cu(OAc)_2$	MeCN	Cs_2CO_3	<5	<5
15[d]	$Cu(OAc)_2$	MeCN	Pyr	60	<5
16[e]	$Cu(OAc)_2$	MeCN	Pyr	79	<5
17[e,f]	$Cu(OAc)_2$	MeCN	Pyr	10	<5
18[e,g]	$Cu(OAc)_2$	MeCN	Pyr	20	40
19[e,h]	$Cu(OAc)_2$	MeCN	Pyr	<5	66

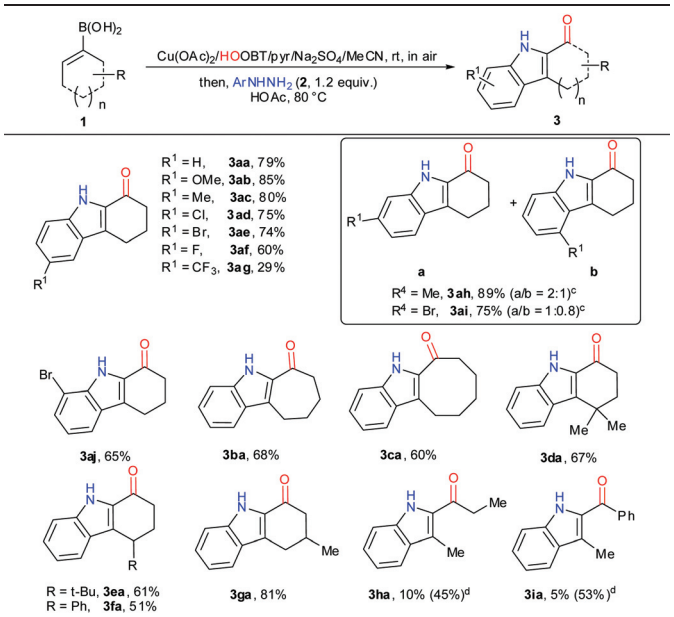
[a] Reaction conditions: **1a** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), cat. (20 mol%, unless noted otherwise), base (3.0 equiv.), solvent (3.0 mL), rt, 18–24 h, under air; then adding **2a** (0.36 mmol, 1.2 equiv.) and HOAc (5 mL), 80 °C, 10–24 h. [b] Isolated yield. [c] $Cu(OAc)_2$ (10 mol%), 36 h. [d] Pyr (1.5 equiv.). [e] Na_2SO_4 (400 mg). [f] Performed under N_2 instead of air. [g] **2a** (2.0 equiv.). [h] **2a** (3.0 equiv.).

hydrazine **2a** (1.2 equiv.) and HOAc at 80 °C for 12 h (Table 1, entry 16). The optimal conditions for preparing the tetrafunctionalized product indolo[2,3-*a*]carbazole **4aa** included increasing the amount of phenylhydrazine **2a** to 3.0 equiv. (Table 1, entry 19).

With the optimized conditions for the formation of tetrahydrocarbazol-1-ones in hand, we turned to study the scope of trifunctionalization of alkenylboronic acids with various arylhydrazines. As shown in Table 2, a wide range of arylhydrazines **2** were subjected to the trifunctionalization conditions and they smoothly afforded diverse tetrahydrocarbozol-1-ones **3ab–3aj** in moderate to good yields. Arylhydrazines with electron-donating groups at the *para*-position gave better yields than those with electron-withdrawing groups (**3ab** and **3ac** *vs.* **3af** and **3ag**). Unfortunately, arylhydrazines with strong electron-withdrawing groups at the *para*-position, such as NO_2, CO_2Me, and CN (not shown in the table), did not afford the corresponding tetrahydrocarbozol-1-ones even though the temperature was increased to 120 °C or 1.0 equiv. of PPA was added as an additive. When arylhydrazine **2h** with a 3-methyl group and **2i** with a 3-bromo group were subjected to the trifunctionalization conditions, products **3ah** and **3ai** were obtained in 89% and 75% yields with 2 : 1 and 1 : 1 regioselectivity of [3,3]-rearrangement, respectively. Various alkenylboronic acids **1** were compatible for the trifunctionalization protocol affording the corresponding desired products, tolerating both six- to eight-membered rings and various substituents on the six-membered rings (**3ba–3ga**). The structure of compound **3** was determined by X-ray diffraction analysis of **3ga**.[19] Linear alkenylboronic acids **1h** and **1i** were reacted under the trifunctionalization conditions delivering indole products **3ha** and **3ia** in only 10% and 5% yields, respectively. To our delight, adding 1.0 equiv. of polyphosphoric acid (PPA) under the standard conditions furnished **3ha** and **3ia** in 45% and 53% yields, respectively. Most of these scaffolds were not easily obtained by conventional condensation of unsymmetrical 1,2-diketones with phenylhydrazine *via* the Fischer indole synthesis.

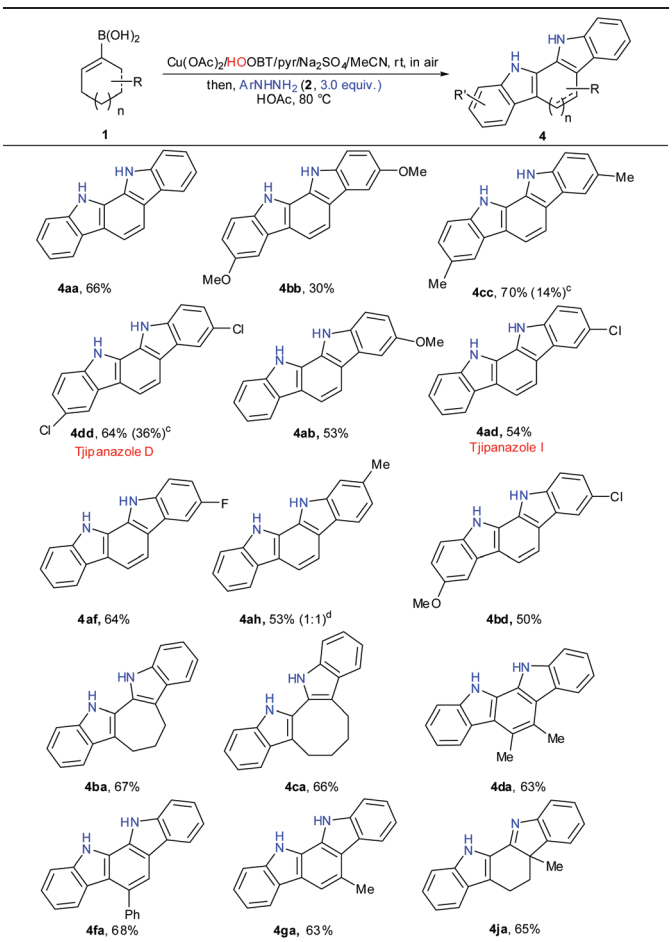
Next, the scope of tetrafunctionalization of alkenylboronic acids to prepare indolo[2,3-*a*]carbazoles was also investigated. As shown in Table 3, symmetrical indolo[2,3-*a*]carbazoles **4bb–4dd** with methoxy, methyl, and chloro groups were obtained in moderate to good yields when a single arylhydrazine was used. Compared to the traditional strategy by condensation of cyclo-

Table 2 Substrate scope for the trifunctionalization to prepare tetrahydrocarbazol-1-ones **3** [a,b]



[a] Reaction conditions: **1** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), Cu(OAc)$_2$ (20 mol%), pyr (0.9 mmol, 3.0 equiv.), MeCN (3.0 mL), Na_2SO_4 (400 mg), rt, under air, 18–24 h; then, adding arylhydrazine **2** (0.36 mmol, 1.2 equiv.), HOAc (5 mL), 80 °C, 10–24 h. [b] Isolated yield. [c] Regioselectivity of [3,3]-rearrangement. [d] PPA (1.0 equiv.) was added.

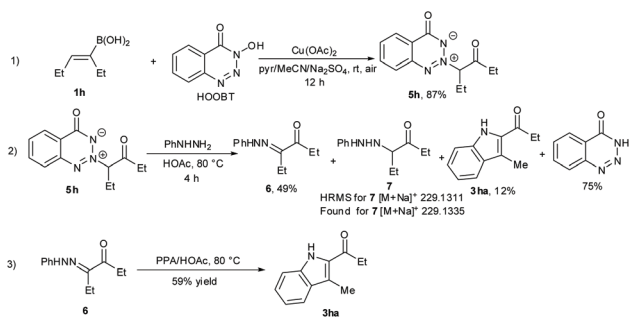
Table 3 Substrate scope for tetrafunctionalization to prepare indolo[2,3-*a*]carbazoles **4** [a,b]



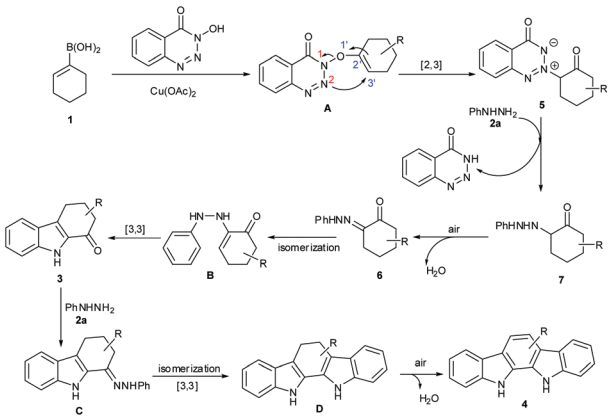
[a] Reaction conditions: **1** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), Cu(OAc)$_2$ (20 mol%), pyr (0.9 mmol, 3.0 equiv.), MeCN (3.0 mL), Na_2SO_4 (400 mg), rt, 18–24 h; then adding $ArNHNH_2$ **2** (0.9 mmol, 3.0 equiv.), HOAc (5 mL), 80 °C, 10–24 h under air or adding Ar^1NHNH_2 (0.45 mmol, 1.5 equiv.) and Ar^2NHNH_2 (0.45 mmol, 1.5 equiv.). [b] Isolated yield. [c] Prepared by condensation of cyclohexane-1,2-dione with arylhydrazines. [d] Regioselectivity of [3,3]-rearrangement.

hexane-1,2-dione with arylhydrazines in a one-pot process, the yields of **4cc** and **4dd** were only 14% and 46%, respectively. We were pleased to find that two different arylhydrazines were added in sequence in a one-pot process affording unsymmetrical indolo[2,3-*a*]carbazoles **4ab**, **4ad**, **4af**, **4ah** and **4bd** in good yields ranging from 50% to 64%, which are difficult to be achieved by traditional methods. It is noteworthy that compounds **4dd** and **4ad** were the natural products, *Tjipanazole* D and *Tjipanazole* I, which were prepared in lower yields from commercial cyclohexenylboronic acid **1a** with the corresponding arylhydrazines in one pot. When cycloheptenylboronic acid **1b** and cyclooctenylboronic acid **1c** were reacted with **2a** under the tetrafunctionalization conditions, products **4ba** and **4ca** were obtained in 67% and 66% yields, respectively, which were prepared for the first time. When substituted cyclohexenylboronic acids **1d**, **1f**, **1g**, and **1j** were reacted under the tetrafunctionalization conditions, the obtained products were dependent on the substituted groups of six-membered ring. Cyclohexenylboronic acid **1d** with two methyl groups at the 4-position of the six-membered ring furnished product **4da** in 63% yield, suggesting that the reaction involved a 1,2-rearrangement of the methyl group. Cyclohexenylboronic acid **1f** with a phenyl group at the 4-position and **1g** with a methyl group at the 5-position resulted in products **4fa** and **4ga** in 68% and 63% yields, respectively. However, cyclohexenylboronic acid **1j** with a 6-methyl group afforded product **4ja** containing a quaternary carbon center in 65% yield. This tetrafunctionalization provides a facile approach to access indolo[2,3-*a*]carbazoles or analogs in a one-pot reaction from commercial cyclic alkenylboronic acids.

To better understand the formation mechanism of tetrahydrocarbozol-1-ones **3** and indolo[2,3-*a*]carbazoles **4** from alkenylboronic acids, control experiments were performed (Scheme 2). Alkenylboronic acid **1h** was reacted with HOOBT for 12 h affording product **5h** in 87% yield (Scheme 2-1), which might be formed by the Chan–Lam reaction and sequential 2,3-rearrangement. When compound **5h** was reacted with phenylhydrazine **2a** in HOAc at 80 °C for 4 h, in addition to hydrazone **6** that was afforded in 49% yield, compound **7** was detected by HRMS and indole **3ha** was obtained in 12% yield accompanied by benzotriazin-4-one in 75% yield (Scheme 2-2). These results showed that compound **7** might be the intermediate in the formation of hydrazone **6**. When



Scheme 2 Mechanistic studies.



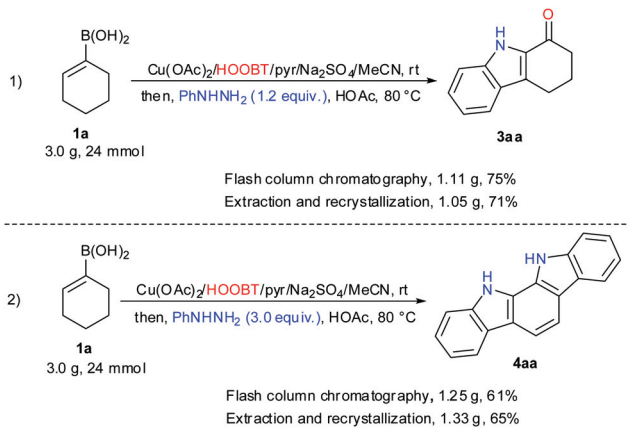
Scheme 3 Proposed mechanism.

hydrazone **6** was subjected to PPA/HOAc conditions, the desired product **3ha** was obtained in 59% yield (Scheme 2-3), which was in accordance with the yield of **3ha** in Table 2.

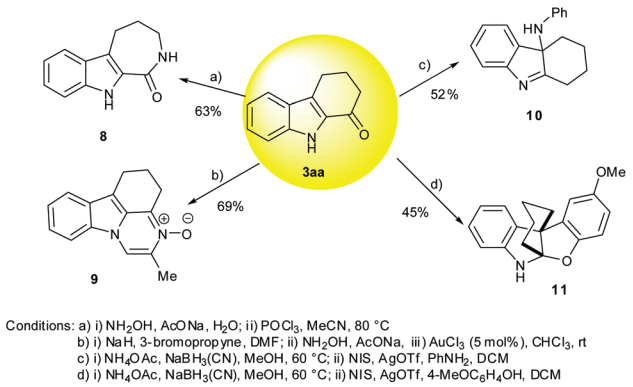
Based on the experimental results, a possible mechanism for the formation of tetrahydrocarbazol-1-one **3** and indolo[2,3-*a*]carbazole **4** was proposed (Scheme 3). Initially, a copper-mediated cross-coupling reaction of HOOBT with alkenylboronic acids **1** affords O-vinylation intermediate **A**, which facilitates a [2,3]-rearrangement to produce α-nitrogenated ketone **5**.[20] Compound **5** is attacked by phenylhydrazine **2a** and undergoes nucleophilic substitution, affording compound **7** and releasing benzotriazinone. Further oxidation of **7** by air under heating conditions yields hydrazone **6**, which undergoes isomerization and [3,3]-rearrangement *via* intermediate **B** to afford tetrahydrocarbazol-1-one **3**. Alternatively, compound **3** could also undergo condensation with excess phenylhydrazine **2a**, isomerization and [3,3]-rearrangement *via* intermediate **C** to give intermediate **D**. Finally, oxidation of **D** by air results in compound **4**. It is worth noting that α-nitrogenated ketone **5** shows a high site-marked reactivity for nucleophilic substitution instead of condensation with the ketone group.

To show the utility of this tri-/tetrafunctionalization of alkenylboronic acids, gram-scale reactions were performed. As shown in Scheme 4-1, 3.0 g of **1a** (24 mmol) was reacted with 1.3 g of HOOBT (8 mmol) and phenylhydrazine **2a** (1.0 g, 9.6 mmol) under the trifunctionalization conditions affording **3aa** in 75% yield (1.11 g) by flash column chromatography. Interestingly, the purification of compound **3aa** could also be achieved through extraction, washing and sequential recrystallization without flash column chromatography to afford 1.05 g of **3aa** in 71% yield. As shown in Scheme 4-2, indolo[2,3-*b*]carbazole **4aa** was obtained in 61% yield (1.2 g) by flash column chromatography under the tetrafunctionalization conditions while the extraction, washing, and sequential recrystallization procedure delivered **4aa** in 65% yield (1.33 g). This easy purification procedure shows a green approach to access tetrahydrocarbozol-1-ones and indolo[2,3-*a*]carbazoles.

To demonstrate the advantages of the current approach for preparing tetrahydrocarbozol-1-ones, an array of indole, indo-



Scheme 4 Gram-scale preparation of **3aa** and **4aa**.



Scheme 5 Applications of **3aa** to diverse indole scaffolds. Conditions: [a](i) NH_2OH, AcONa, H_2O, (ii) $POCl_3$, MeCN, 80 °C; [b](i) NaH, 3-bromopropyne, DMF, (ii) NH_2OH, AcONa, (iii) $AuCl_3$ (5 mol%), $CHCl_3$, rt; [c](i) NH_4OAc, $NaBH_3(CN)$, MeOH, 60 °C, (ii) NIS, AgOTf, $PhNH_2$, DCM; [d](i) NH_4OAc, $NaBH_3(CN)$, MeOH, 60 °C, (ii) NIS, AgOTf, 4-$MeOC_6H_4OH$, DCM.

line, and indolenine scaffolds was prepared. As shown in Scheme 5, azepine amide **8** was afforded in 63% yield by a two-step synthetic sequence involving condensation and Beckmann rearrangement. An alkylation/condensation/gold-catalyzed 6-*exo*-*dig* cyclization sequence on **3aa** delivered tricyclic indole-fused pyrazine *N*-oxide **9** in 69% yield. Reduction of the carbonyl group in **3aa** with $NaBH_3CN$ and NH_4OAc, followed by indole oxidation and $PhNH_2$ attack on the C3-position afforded indolenine **10** in 52% yield. Similarly, furo[2,3-*b*]indoline **11** was obtained in 45% yield when $PhNH_2$ was replaced by 4-methoxyphenol.

Conclusions

We have identified an efficient one-pot cascade process of tri- or tetrafunctionalization of alkenylboronic acids with HOOBT and arylhydrazines as oxygen and nitrogen sources, respectively, through the Chan–Lam reaction/2,3-rearrangement/nucleophilic substitution/oxidation/[3,3]-rearrangement over five steps that can be a facile strategy to access various tetrahydrocarbozol-1-ones and indolo[2,3-*a*]carbazoles in good yields. The reaction showed a broad substrate scope and tolerated various functional groups. Moreover, the reaction was easily performed at gram scales with a simple purification procedure and the tetrahydrocarbozol-1-one can be converted into various indole, indoline, and indolenine scaffolds. We anticipate that this high site-marked indole formation from alkenylboronic acids compared with conventional Fischer indole synthesis substrates could offer a new approach to indole scaffold design.

Experimental

General procedure for preparing tetrahydrocarbozol-1-ones 3

A 25 mL reaction flask was charged with alkenylboronic acids **1** (0.9 mmol, 3.0 equiv.) *N*-hydroxybenzotriazin-4-one (HOOBT) (0.3 mmol), $Cu(OAc)_2$ (5.4 mg, 20 mol%) and Na_2SO_4 (400 mg) under an air atmosphere, MeCN (3.0 mL) and pyridine (72 μL, 0.9 mmol, 3.0 equiv.) were then added. The reaction mixture was stirred vigorously at room temperature for 18–24 h until HOOBT disappeared (monitored by TLC). Then, arylhydrazine **2** (0.36 mmol, 1.2 equiv.) and HOAc (5 mL) were added to the reaction mixture and stirred at 80 °C for 10–24 h. After this, the reaction was quenched with H_2O (10 mL) and the reaction mixture was extracted with EtOAc (3 × 10 mL). Then, the combined organic layers were washed with $NaHCO_3$ (10 mL) and brine (10 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compound **3**.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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