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Denitrogenative Suzuki and Carbonylative Suzuki Coupling Reactions of Benzotriazoles with Boronic Acids†

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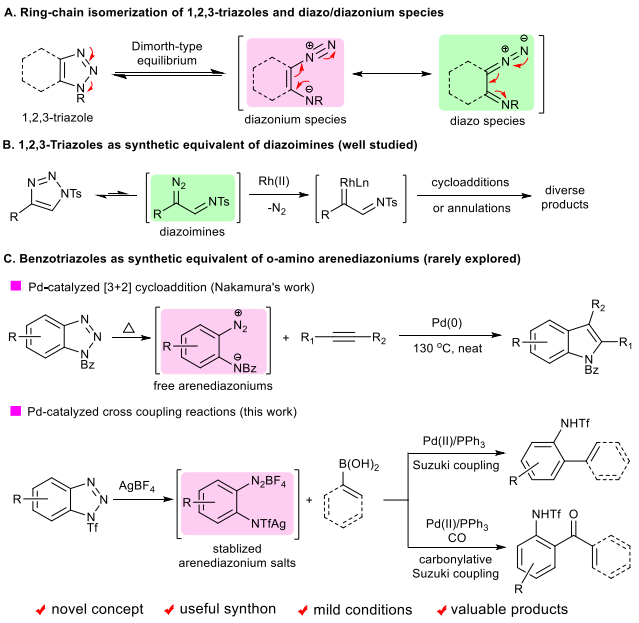
The unprecedented palladium-catalyzed denitrogenative Suzuki and carbonylative Suzuki coupling reactions of benzotriazoles with boronic acids have been realized, which afforded structurally diverse ortho-amino-substituted biaryl and biaryl ketone derivatives. Key to the success relies on a rationally designed strategy to achieve the ring opening of benzotriazoles with a synergistic activating-stabilizing effect, which enables in situ generation of the corresponding ortho-amino-arenediazonium species. The present work opens a new avenue to utilize benzotriazoles as synthetic equivalent of ortho-amino-arenediazoniums, which otherwise could not be directly accessed by existing synthetic methods.

Introduction

1,2,3-Triazoles are among the most important structural elements in modern chemical, biological and material sciences.[1] As one of their unique chemical properties, they could undergo ring-chain isomerization to form the corresponding diazonium or diazo species via Dimorth-type equilibrium (Scheme 1A).[2] Considerable efforts have been devoted to the development of novel transformations based on this unique reactivity. As a paradigm, recently significant advances have been made on the applications of 1-sulfonyl-1,2,3-triazoles as synthetic equivalents of diazoimines in a broad range of intriguing reactions (Scheme 1B).[3] In contrast, the ring-opening chemistry of benzotriazoles, a subset of 1,2,3-triazoles well known for their versatile reactivity,[4] has remained underdeveloped, mainly due to their high stability and innate reluctance to the ring-opening process.[5] Historically, it was reported that benzotriazoles could undergo ring opening followed by denitrogenative cyclization upon photolysis[6] or pyrolysis,[7] however, those transformations suffer from forcing conditions, narrow substrate scope and moderate efficiency, and thus have rarely found applications in organic synthesis.

In 2009, Nakamura and co-workers reported a novel palladium-catalyzed denitrogenative formal [3+2] cycloaddition of *N*-aroylbenzotriazoles with internal alkynes (Scheme 1C).[8] It was assumed that the reaction proceeded via an *ortho*-amino-arenediazonium intermediate in situ generated through the ring opening of *N*-aroylbenzotriazole. This seminal discovery shed



Scheme 1 Ring-opening chemistry of 1,2,3-triazoles and benzotriazoles.

light on the feasibility of implementing the ring opening of benzotriazoles and transition-metal-catalyzed denitrogenative transformations in one pot. However, such potential has been overlooked by synthetic community over the past several years, probably because that both the demanding reaction conditions and moderate efficiency of the reaction make it less attractive from a practical point of view. Thus, the development of a more general, efficient and robust method to achieve the ring-opening chemistry of benzotriazoles remains an unmet challenge.

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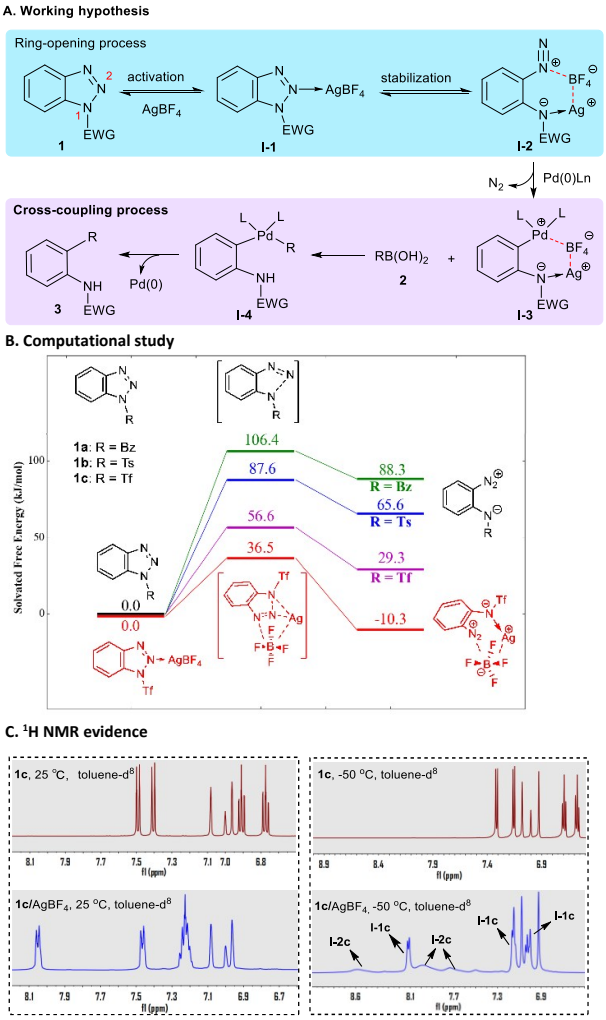
Our laboratory has been working on the development of novel reactions based on the ring-opening chemistry of 1,2,3-triazoles.[9] Given that such type of chemistry remained underdeveloped for benzotriazoles, we initiated a program to confront this challenge. Notably, when our manuscript was in preparation, Glorius disclosed an elegant work on the subject, wherein the first visible-light-promoted denitrogenative functionalization of benzotriazoles via aryl radical intermediates was realized.[10] We herein report a different strategy to achieve the ring opening of benzotriazoles with a synergistic activating-stabilizing effect, which enables in situ generation of an *ortho*-amino-arenediazonium species. As proof-of-concept cases, the palladium-catalyzed denitrogenative Suzuki and carbonylative Suzuki coupling reactions of benzotriazoles with boronic acids have been developed, giving rise to diverse *ortho*-amino-substituted biaryl and biaryl ketone derivatives. The present work opens a new avenue to utilize benzotriazoles as synthetic equivalent of *ortho*-amino-arenediazoniums, which otherwise could not be accessed by existing synthetic methods.[11]

Results and discussion

At the outset of our study, we were cognizant of two challenges associated with the project: 1) how to effect the ring opening of benzotriazoles under mild conditions; 2) how to combine the ring-opening process with other synthetically useful transformations? In terms of the first question, it has been known that an electron-withdrawing *N1*-substituent could facilitate the ring opening of benzotriazoles.[12] For examples, Ziegler reported that 1-nonafluorobutanesulfonyl-benzotriazole[12c] and l-nitrobenzotriazole[12f] could undergo ring opening upon treatment with strong nucleophiles such as amines and deprotonated phenols. Nakamura[8] and Glorius[10] employed 1-aroylbenzotriazoles as effective substrates in their studies. To get deeper insight into the role of the *N1*-substituent, we conducted a computational study with three representative benzotriazoles (**1a**-**c**) as model substrates (Scheme 2B). It revealed that the electron-withdrawing *N1*-substituent exerts a beneficial effect on the ring opening of benzotriazoles by lowering both the activation free energy ($\Delta G^{\neq}$) and Gibbs free energy difference (ΔG). Not surprisingly, such activating effect positively correlates to the electron-withdrawing capability of *N1*-substituents (Tf > Ts > Bz). Nevertheless, in all cases, the ring opening of benzotriazoles is a thermodynamically unfavorable process, and thus the resulting zwitterionic diazoniums readily return to their ring-closing forms. To overcome this problem, we planned to use an additive such as $AgBF_4$ to further promote the ring-opening process of benzotriazole by 1) activating the *N1-N2* bond through formation of a complex of benzotriazole-$AgBF_4$ (**I-1**), and 2) stabilizing the ring-opening product through formation of an arenediazonium tetrafluoroborate species (**I-2**). Encouragingly, the synergistic activating-stabilizing effect of $AgBF_4$ was supported by the calculation result with **1c** as model substrate. Indeed, both $\Delta G^{\neq}$ and ΔG of the ring-opening process notably decreased in the presence of $AgBF_4$. As a result, the ring-opening/ring-closing equilibrium shifted to the desired direction. More convincing evidence was obtained from the extensive spectroscopic study performed by us. As shown in Scheme 2C, the chemical shifts of **1c** (toluene-d^8, 25 °C) notably move to downfield in the presence of equimolar $AgBF_4$, implying that there exists a strong coordination effect between $AgBF_4$



Scheme 2 A) Working hypothesis; B) Computational study; C) NMR evidence.

and **1c**. Moreover, the variable temperature ^{1}H NMR experiments showed that a new group of broad signals appeared when the ^{1}H NMR was recorded at -50 °C, which might be correlated to the putative ring-opening species **I-2c**. Of note, similar phenomenon was also observed in the variable temperature ^{19}F NMR experiments (for details, see Supporting Information).

As to the second question, we envisaged that since arenediazonium tetrafluoroborates have proved to be versatile precursors in organic synthesis,[13] it was feasible to combine the ring-opening chemistry of benzotriazoles with various other synthetically useful transformations, such as the palladium-catalyzed denitrogenative Suzuki coupling reaction.

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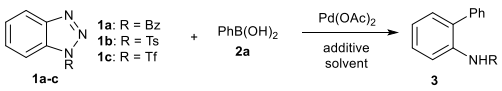
Indeed, Bohle *et al.* proved that the ring-opening forms of benzotriazoles could be trapped by coordination to a suitable organometallic complex.[14] In the current scenario, the in situ formed *ortho*-amino-arenediazonium tetrafluoroborate (**I-2**) would undergo oxidative addition with Pd(0) to give an organopalladium complex (**I-3**), which, after transmetalation with boronic acid (**2**) and reductive elimination, could advance to the final product (**3**) (Scheme 2A).

Table 1 Condition optimization[a,b]



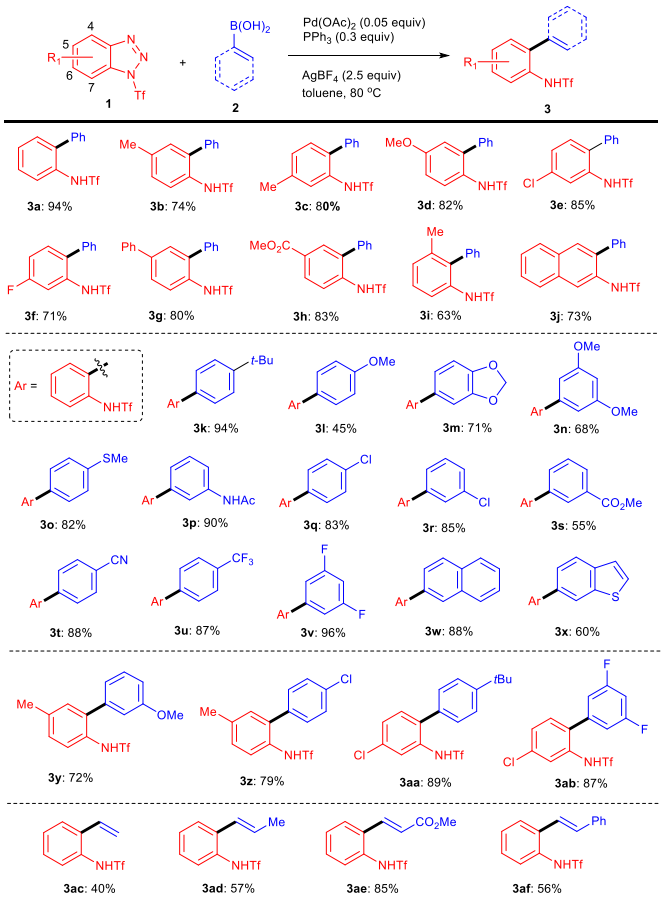
entry	triazole	solvent	additive	T (°C)	Yield of **3**
1	**1a**	toluene	$AgBF_4$	100	n.r.
2	**1b**	toluene	$AgBF_4$	100	n.r.
3	**1c**	toluene	$AgBF_4$	100	58%
4	**1c**	toluene	$LiBF_4$	100	n.r.
5	**1c**	toluene	$AgSbF_6$	100	18%
6	**1c**	toluene	AgOTf	100	27%
7	**1c**	CH_3CN	$AgBF_4$	100	17%
8	**1c**	1,4-dioxane	$AgBF_4$	100	25%
9	**1c**	DMF	$AgBF_4$	100	n.r.
10	**1c**	toluene	$AgBF_4$/PPh_3	100	92%
11	**1c**	toluene	$AgBF_4$/dppf	100	39%
12[c]	**1c**	toluene	$AgBF_4$/PPh_3	100	68%
13	**1c**	toluene	$AgBF_4$/PPh_3	80	94%
14[d]	**1c**	toluene	$AgBF_4$/PPh_3	80	22%
15	**1c**	toluene	PPh_3	80	13%

[a]Reaction conditions: **1a** (0.30 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (0.015 mmol), PPh_3 (0.09 mmol) and $AgBF_4$ (0.75 mmol) in the solvent (3.0 mL). [b]Isolated yield. [c]$Pd(PPh_3)_4$ (5 mol%) was used. [d]1.0 equiv. of $AgBF_4$ (0.30 mmol) was used. n.r. = no reaction. Bz = benzoyl, Ts = *p*-toluenesulfonyl, Tf = trifluoromethanesulfonyl, dppf = 1,1′-bis(diphenylphosphino)ferrocene.

We commenced the study by treating 1-benzoylbenzotriazole (**1a**) and phenylboronic acid (**2a**) with $AgBF_4$ (2.5 equiv.) and $Pd(OAc)_2$ (0.05 equiv.) in toluene at 100 °C for 12 h. To our disappointment, no reaction occurred under the conditions (entry 1, Table 1). We further evaluated benzotriazoles **1b** and **1c** in the reaction. Gratifyingly, while **1b** also failed to give promising result (entry 2), **1c** displayed superior reactivity by affording the desired product **3a** in 58% isolated yield (entry 3). Encouraged by this outcome, we moved to optimize the reaction with **1c** as substrate. First of all, several other additives including $LiBF_4$, $AgSbF_6$ and AgOTf were employed in the reactions, however, none of them gave improved results than $AgBF_4$ (entries 4-6), which indicated that both of the counter ions of $AgBF_4$ played a crucial role for promoting the reaction. Next, a simple evaluation of the solvent effect was conducted, however, it failed to give promising outcomes (entries 7-9). Gratifyingly, we found that the usage of PPh_3 as additive could notably improve the reaction by affording **3a** in an excellent yield (entry 10). Comparably, the other commonly used phosphine ligand dppf afforded only moderate yield (entry 11). Interestingly, although $Pd(PPh_3)_4$ was proved to be effective catalyst for the transformation, it only gave a decreased yield (entry 12). Of note, lowering the reaction temperature to 80 °C had no side-effect on the reaction (entry 6). However, a poor yield of **3a** was obtained when the reaction was performed with reduced equivalents of or in the absence of $AgBF_4$ (entries 14-15).

Having secured the optimal conditions, we next investigated the substrate scope of the reaction. First, a variety of substituted benzotriazoles were evaluated with **2a** as reaction partner. Pleasingly, all of the examined benzotriazoles bearing either electron-donating or -withdrawing substituents were proved to be suitable substrates by affording the corresponding products (**3b**-**3i**, Table 2) in good to excellent yields. Generally, the 5- and 6-substituted benzotriazoles gave a slightly higher yields than the 4-substituted one (e.g. **3b** and **3c** vs **3i**). Moreover, the naphtha[2,3-*d*]-1,2,3-triazole was also amenable to the reaction, indicating that it could be extended to other aromatic ring-fused 1,2,3-triazole derivatives. Next, the scope of boronic acids was evaluated with **1c** as reaction partner. As shown, an array of substituted phenylboronic acids worked well to give the corresponding products in good efficiency, regardless of the steric or electronic bias imposed by the substrates. Of note, the functional groups of ester, amide and cyano remained unchanged during the reactions, demonstrating its good functionality tolerance. Some other aryl boronic acids were also amenable to the reactions, as witnessed by the cases leading to **3w** and **3x**. Not surprisingly, the transformation could be applied to the synthesis of biaryl

Table 2 Substrate scope of Suzuki reaction[a,b]

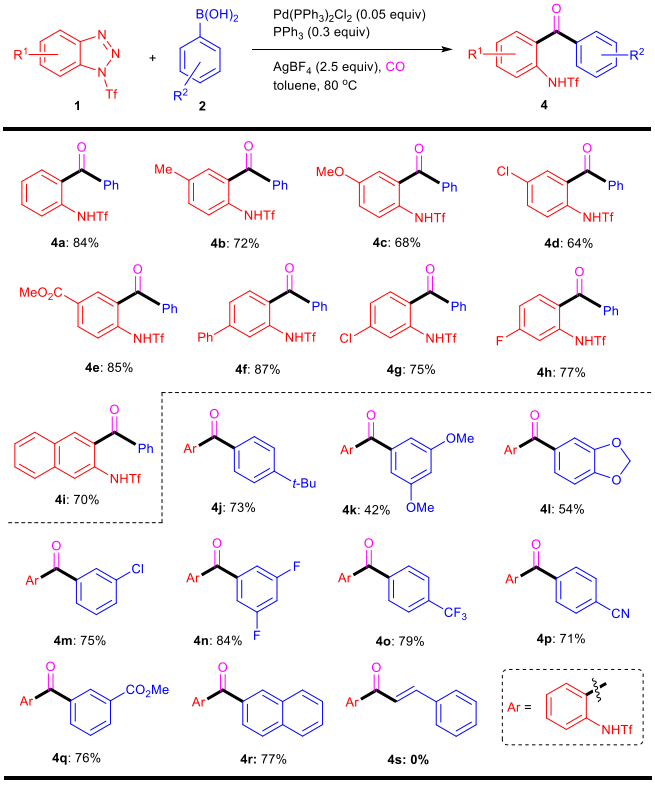


[a] Condition A: **1** (0.30 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (0.015 mmol), PPh_3 (0.09 mmol) and $AgBF_4$ (0.75 mmol) in toluene (3.0 mL). [b] Isolated yield.

derivatives containing two substituted aromatic rings (e.g. **3y**-**ab**). Last but not least, vinylboronic acids also proved to be effective substrates for the reactions (**3ac**-**af**), thus expending its synthetic application to *ortho*-amino-substituted styrene derivatives.

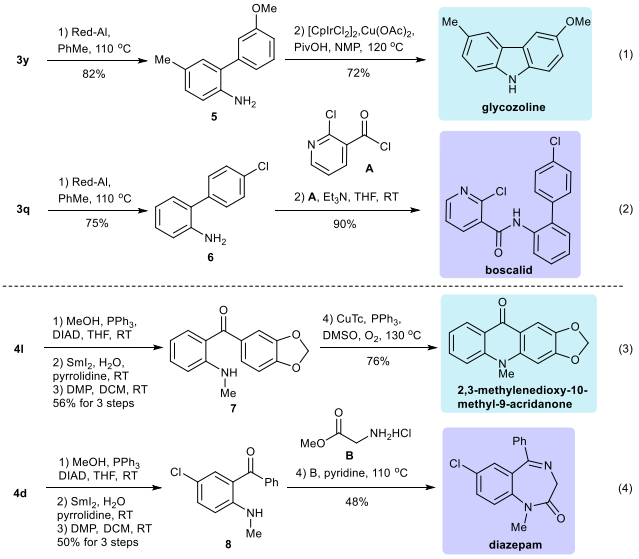
To further showcase of the synthetic utility of the ring-opening chemistry, we successfully developed an intriguing carbonylative Suzuki coupling reaction, which provided a new method to access *ortho*-amino-substituted biaryl ketone derivatives. As shown in Table 3, a slightly different catalytic system ($AgBF_4$, $Pd(PPh_3)_2Cl_2$, toluene, CO, 80 °C) was employed in the carbonylative Suzuki coupling reactions (Table 3). Generally, the transformations exhibited fair substrate scopes with regard to both benzotriazoles and aryl boronic acid reaction partners. Most of the reactions proceeded smoothly to furnish the corresponding products in good to excellent yields, regardless of the electronic properties and substituent patterns of the substrates. However, different from the above-mentioned Suzuki coupling reactions, the vinyl boronic acids failed to give the desired products (e.g. **4s**) under the examined conditions.

Table 3 Scope of carbonylative Suzuki coupling reaction[a,b]



[a] Condition A: **1** (0.30 mmol), **2** (0.45 mmol), $Pd(PPh_3)_2Cl_2$ (0.015 mmol), PPh_3 (0.09 mmol) and $AgBF_4$ (0.75 mmol) in toluene (3.0 mL) with a CO balloon (1 atm). [b] Isolated yield.

To exemplify the power of the above reactions, we converted some of the resulting products into bioactive natural products and drugs. For examples, the Suzuki coupling product **3y** could undergo deprotection (Red-Al, toluene, reflux, 82%) followed by an intramolecular Ir-catalyzed annulation[15] to give the carbazole alkaloid glycozoline,[16] which exhibits antibiotic and antifungal properties (eq. 1, Scheme 3). Similarly, **3q** could undergo sequential deprotection and condensation with 2-chloronicotinoyl chloride to provide boscalid,[17] a fungicide marketed by BASF company (eq. 2). For carbonylative Suzuki coupling product **4l**, it could be converted to **7** in three steps (methylation, SmI_2 mediated reductive deprotection and Dess-Martin oxidation), which then underwent a Cu-catalyzed intramolecular C-H bond activation/C-N bond formation[18] to give the alkaloid 2,3-methylenedioxy-10-methyl-9-acridanone (eq. 3).[19] The same protocol was also employed to convert **4d** to **8**, which, after condensation with glycine methyl ester, gave diazepam, a well-known drug for treating anxiety and epilepsy (eq. 4).[20]



Scheme 3 Applications in natural product and drug synthesis.

Conclusions

In summary, we developed a new strategy to achieve the ring opening of benzotriazole with a synergistic activating-stabilizing effect, which enables the facile generation of a versatile *ortho*-amino-arenediazonium species. As proof-of-concept cases, palladium-catalyzed denitrogenative Suzuki and carbonylative Suzuki coupling reactions of benzotriazoles with boronic acids have been achieved. The great synthetic potential of the developed chemistry was demonstrated by its application in the synthesis of bioactive natural products and drugs. We anticipated that the novel concept presented in this work may inspire the development of more mechanistically interesting and synthetically useful transformations. Related studies on this subject are currently underway in our laboratory and the progress will be communicated in due course.

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