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Versatile method for the synthesis of aminobenziodoxolones and its application to one-pot coupling of arylboronic acids with simple amines

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Hypervalent iodine(III) compounds containing transferable nitrogen functional groups, amino-λ^3-iodanes, were synthesized *via* a straightforward protocol utilizing simple amines and a benziodoxolone framework. This strategy enabled the use of a wide variety of amines, including ammonia, aliphatic and aromatic primary amines, significantly expanding the scope of accessible compounds compared to existing methods. The synthesized aminobenziodoxolones were applied to the oxidative amination of arylboronic acids, offering a practical transition-metal-free protocol for the synthesis of arylamines. To further demonstrate the synthetic utility, a one-pot process using *in situ* prepared aminobenziodoxolones was developed, allowing efficient coupling of boronic acids with various simple and pharmaceutically relevant amines. Furthermore, the method was extended to the synthesis of ^{15}N-labelled arylamines, highlighting the versatility and practical value of this approach.

Introduction

Among various methods for the synthesis of nitrogen-containing organic molecules, oxidative amination has emerged as one of the most attractive approaches, as it enables the construction of amine functionalities that are often challenging to access *via* conventional nucleophilic amination employing nitrogen-based nucleophiles.[1,2] In such transformations, electrophilic aminating reagents bearing an electron-withdrawing group, which also serves as a leaving group, on the nitrogen atom, such as *N*-haloamines, hydroxylamine derivatives, azides, nitroso compounds, and azo compounds have typically been utilized.[3–5] Additionally, trivalent hypervalent iodine reagents containing transferable nitrogen functional groups, commonly referred to as amino-λ^3-iodanes, have also been recognized as powerful tools for oxidative amination reactions, owing to the high leaving ability of their iodine(III) moieties (Scheme 1A).[6–12] To date, several amino-λ^3-iodanes have been developed, most of which possess protected nitrogen functionalities incorporating electron-withdrawing groups, such as (sulfon)amide,[13–16] bis-sulfonimide,[17–19] sulfoximidoyl,[20,21] and azide[22–25] moieties. However, the use of these reagents often necessitates laborious deprotection and further transformation steps to access the desired amine products, thereby limiting their synthetic practicality.[17,24] In addition, the use of azide reagents requires careful handling due to their inherent hazards.[25,26] To address these limitations, amino-λ^3-iodanes containing amino functionalities that can be readily converted to NH_2 group, such as phthalimide,[27–30] trifluoroacetamide,[31] and (diarylmethylene) amino groups,[32–34] have recently been developed. Nonetheless, these approaches still require a deprotection step, which hinders the direct synthesis of structurally complex amines. In this context, the development of amino-λ^3-iodanes capable of directly introducing unprotected and diverse amino groups would be highly desirable, offering a straightforward and practical route to valuable amine derivatives. Such reagents would offer a platform for the synthesis and modification of biologically active molecules and pharmaceuticals.

To address this challenge, amino-λ^3-iodanes derived from secondary[35] and benzylic primary amines[36] have recently been synthesized by incorporating a thermally stable iodoxolone framework (Scheme 1B).[7–9,37] This strategy effectively overcomes the inherent challenge that primary amines are typically sensitive to oxidants, including hypervalent iodine reagents.[38–40] In this context, we previously reported a practical approach to aminobenziodoxolones employing disilazanes as amine sources, enabling the synthesis of unprecedented reagents bearing –NH_2 and –NHR groups.[41] However, these methods require the use of *N*-silyl amines, which demand careful preparation, thereby limiting their synthetic versatility and broader applicability.[35,36,41–44] More recently, the direct use of simple alkylamines for the synthesis of amino-bis(trifluoromethyl) benziodoxoles has been reported; however, this protocol still

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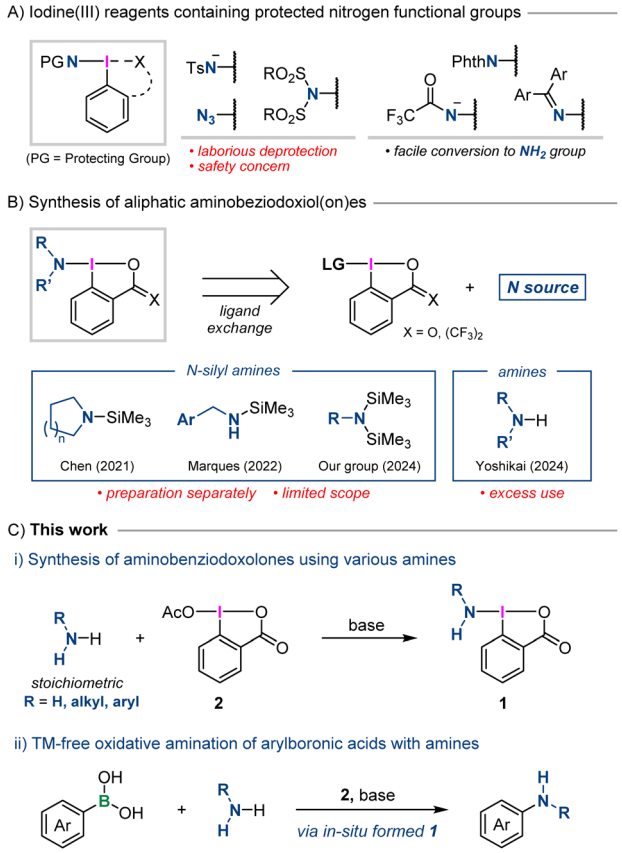
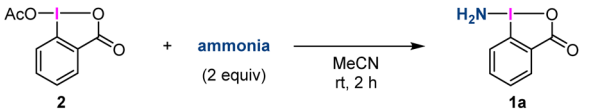


Scheme 1 (A) and (B) Overview of existing amino-λ^3-iodanes. (C) Synthesis of aminobenziodoxolones from amines and their application to oxidative amination of arylboronic acids.

necessitates an excess of amines.[45] Therefore, the development of a synthetically practical and efficient method for the preparation of amino-λ^3-iodanes employing a stoichiometric amount of amine remains an unmet and important challenge. Herein, we report the development of a general and practical strategy for the synthesis of aminobenziodoxolones using versatile, readily available simple amines, including ammonia, primary aliphatic amines, and aromatic amines (Scheme 1Ci). This method enables the synthesis of a diverse range of aminobenziodoxolones, most of which have not been accessible *via* previously reported methods. Moreover, the broad and practical synthesis of aminobenziodoxolones achieved in this study significantly expands the scope of transition-metal (TM)-free electrophilic amination of arylboronic acid derivatives to access versatile arylamines (Scheme 1Cii), which serve as valuable building blocks widely found in natural products, pharmaceuticals, agrochemicals, and organic materials.[46]

Results and discussion

We initiated our investigation into the synthesis of NH_2-substituted benziodoxolone **1a** using ammonia (Scheme 2), which offers a simpler and more practical alternative to the previously reported method using hexamethyldisilazane.[41]



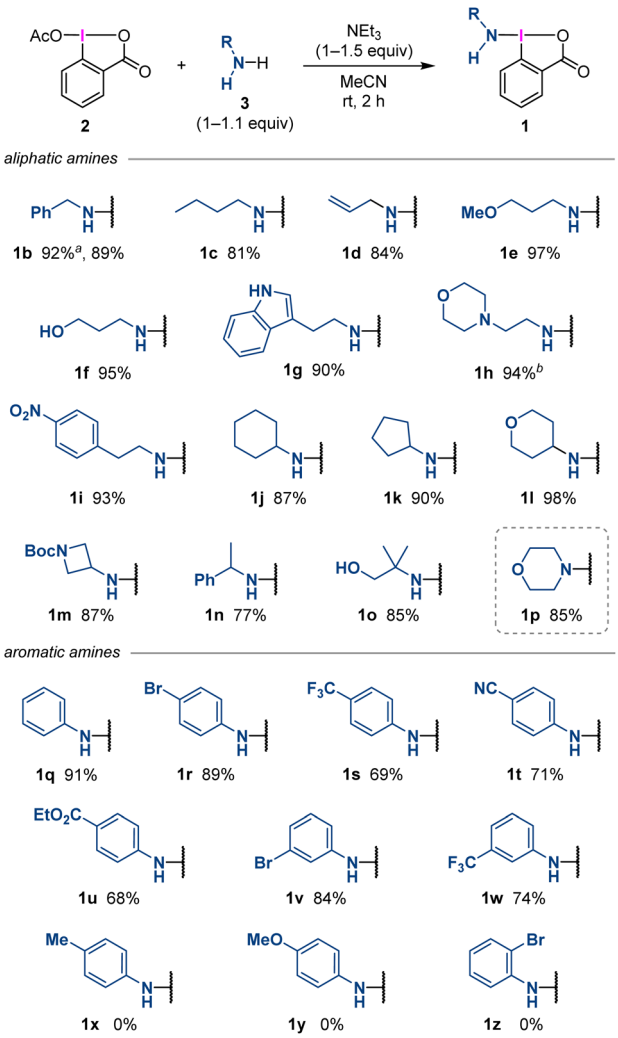
Entry	Ammonia source	Yield (%) 1a	Yield (%) 4
1	NH_3, 28% in water	61	27 (**4a**)
2	NH_3, 2 M in MeOH	87 (75)	10 (**4b**)
3	NH_3, 0.4 M in 1,4-dioxane	22	-
4	gaseous NH_3 (1 atm)	>95 (92)	-
5	$H_2NCO_2NH_4$ (1 equiv)	88 (88)	-

byproduct
R = H (**4a**)
Me (**4b**)

Scheme 2 Synthesis of NH_2-substituted benziodoxolone **1a** using ammonia. Yields were determined by ^{1}H NMR analysis of the crude product on a 0.1–0.2 mmol scale. Values in parentheses are isolated yields on 0.5 mmol (entry 2), 2 mmol (entry 4), and 1 mmol (entry 5) scales.

Gratifyingly, treatment of 1-acetoxy-1,2-benzodioxol-3-(1*H*)-one (**2**) with aqueous ammonia (2 equivalents of NH_3) underwent ligand exchange at the iodine center to furnish the desired product **1a** in 61% yield (entry 1). However, the presence of water also generated hydroxy-benziodoxolone **4a**, hindering the isolation of **1a** due to their low solubility in common organic solvents. Switching to a methanolic ammonia solution improved the yield of **1a** to 87%, albeit with minor formation of methoxy-benziodoxolone **4b** (entry 2). In this case, simple washing of the crude mixture with chloroform allowed for isolation of pure **1a** in 75% yield. To suppress undesired side reactions derived from protic solvents, a 1,4-dioxane solution of ammonia was examined; however, this resulted in a low conversion of **2** and a low yield of **1a** (entry 3). We then turned our attention to the use of gaseous ammonia. Conducting the reaction in acetonitrile under an ammonia atmosphere proved highly effective, delivering **1a** in 92% isolated yield (entry 4). In addition, ammonium carbamate, a bench-stable and inexpensive ammonia equivalent, was also found to be applicable.[47] Employing 1 equivalent of ammonium carbamate, corresponding to 2 equivalents of ammonia, furnished **1a** in high yield (entry 5). In contrast, other common ammonium salts, such as NH_4Cl and NH_4OAc, were ineffective.[48] It should be noted that attempts to synthesize the corresponding NH_2-substituted benziodoxoles were unsuccessful (see SI, Scheme S1), highlighting that the iodoxolone framework is essential for the successful preparation of NH_2-substituted reagents. The reagent **1a** has been demonstrated to serve as an electrophilic aminating reagent, enabling the efficient synthesis of a broad range of primary amines.[41] This practical and operationally simple method thus provides a new synthetic platform for utilization of ammonia in primary amine synthesis.

Encouraged by the successful synthesis of **1a** using ammonia, we next sought to expand the scope of the method for the synthesis of aminobenziodoxolones from simple amines (Scheme 3). As expected, the reaction with 2 equivalents of benzylamine (**3b**) afforded the corresponding product **1b** in high yield. To reduce the amount of amine substrates required, we screened bases capable of scavenging the *in situ* generated acetic acid. Among those tested, triethylamine proved effective,

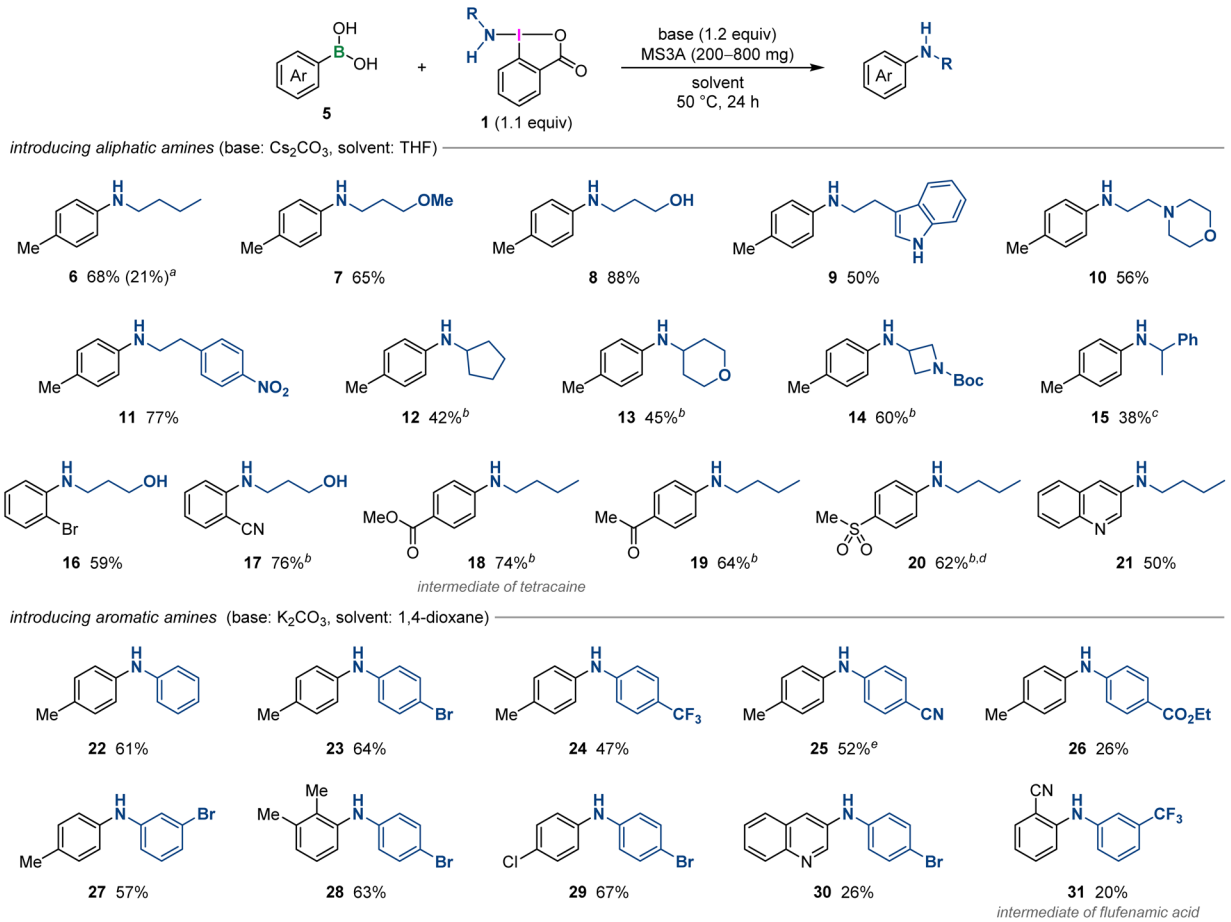


Scheme 3 Synthesis of aminobenziodoxolones using amines. Yields represent isolated yields. [a]Benzylamine (2 equiv.) was used without NEt_3. [b]1,4-Diazabicyclo[2.2.2]octane (DABCO) was used instead of NEt_3.

enabling the formation of **1b** in high yield with 1.1 equivalents of **3b**. This strategy not only avoids the preparation of disilazanes but also circumvents the need for an excess amount of valuable amine substrates.[41] With the practical method in hand, we subsequently explored the substrate scope for the synthesis of diverse aminobenziodoxolones from primary amines. Simple aliphatic primary amines, such as *n*-butyl and allylamine, were suitable, furnishing **1c** and **1d** in high yields, respectively. The method also proved applicable to amines bearing functional groups such as methoxy (**1e**), hydroxy (**1f**, **1o**), NH-indolyl (**1g**), morpholine (**1h**), nitro (**1i**), tetrahydropyran (**1l**), and *N*-Boc-azetidine (**1m**) moieties, affording previously inaccessible compounds.[36,41,45] Steric hindrance of amines had little effect on the ligand exchange, enabling the use of amines bearing α-secondary and tertiary carbon centers (**1j–o**), as well as a secondary amine (**1p**). Owing to the mild reaction conditions and inherent stability of the benziodoxolones, the method was further applicable to typically oxidation-sensitive aromatic amines.[39,40] Various arylamines bearing electron-withdrawing groups such as bromo (**1r**, **1v**), trifluoromethyl (**1s**, **1w**), cyano (**1t**), and ethoxycarbonyl (**1u**) groups underwent smooth conversion to the corresponding aminobenziodoxolones. In contrast, more oxidizable electron-rich arylamines (**1x**, **1y**) than aniline were not compatible, resulting in the formation of complex mixtures containing azo compounds.[40,49] Additionally, attempts to synthesize aminobenziodoxolones derived from *ortho*-substituted arylamine (**1z**) were also unsuccessful, affording complex mixtures including *o*-iodobenzoate and recovering a small amount of unreacted **3z**. Although several limitations remain, we have developed a general and practical method for the synthesis of aminobenziodoxolones using simple amines, including substrates that have been challenging to access by existing methods.[36,41,45] The developed method considerably broadens the range of accessible aminobenziodoxolones, which are promising reagents in oxidative amination reactions.

TM-free oxidative amination of arylboronic acid derivatives with electrophilic aminating reagents has been recognized as a valuable strategy for the synthesis of arylamines. However, existing methods have been predominantly limited to the synthesis of primary arylamines,[50–59] largely due to the scarcity of suitable aminating reagents that enable efficient access to secondary amines.[60–62] Although several protocols employing nitro(so) compounds have been reported, they typically require harsh reaction conditions, which limit their synthetic utility and functional group compatibility.[63–67] Previously, we demonstrated that aminobenziodoxolones serve as suitable reagents for the oxidative amination of various arylboronic acid derivatives.[41] Nevertheless, their application to secondary arylamine synthesis has remained limited due to the restricted availability of aminobenziodoxolones.

With the diverse range of reagents derived from primary amines now in hand, we sought to explore their potential for secondary arylamine synthesis *via* oxidative amination of arylboronic acids, probably proceeds through the formation of a tetravalent borate complex with a B–N dative bond that is followed by 1,2-aryl migration (Scheme 4).[41] The reaction of 4-methylphenylboronic acid (**5a**) with aminobenziodoxolone **1c** was carried out in THF at 50 °C in the presence of Cs_2CO_3 and molecular sieves 3A (MS3A) was found to furnish the desired secondary arylamine **6** in 68% yield.[68] However, the corresponding boronic acid pinacol ester showed low reactivity to afford **6** in only 21% yield. A range of secondary arylamines were synthesized in good to high yields using reagents bearing functionalized amino groups, including methoxy, hydroxy, NH-indolyl, morpholino, and nitro moieties (**7–11**). Furthermore, amino groups possessing α-secondary carbon centers could also be successfully installed (**12–15**), whereas reagents derived from α-tertiary primary amine (**1o**) and secondary amine (**1p**) were unsuitable under the reaction conditions. The amination proved effective for arylboronic acids bearing electron-withdrawing substituents, such as bromo, cyano, carbonyl, and sulfonyl groups at either the *ortho*- or *para*-position (**16–20**), which are typically less reactive in electrophilic amination reactions.[50–62] This method was also successfully extended to

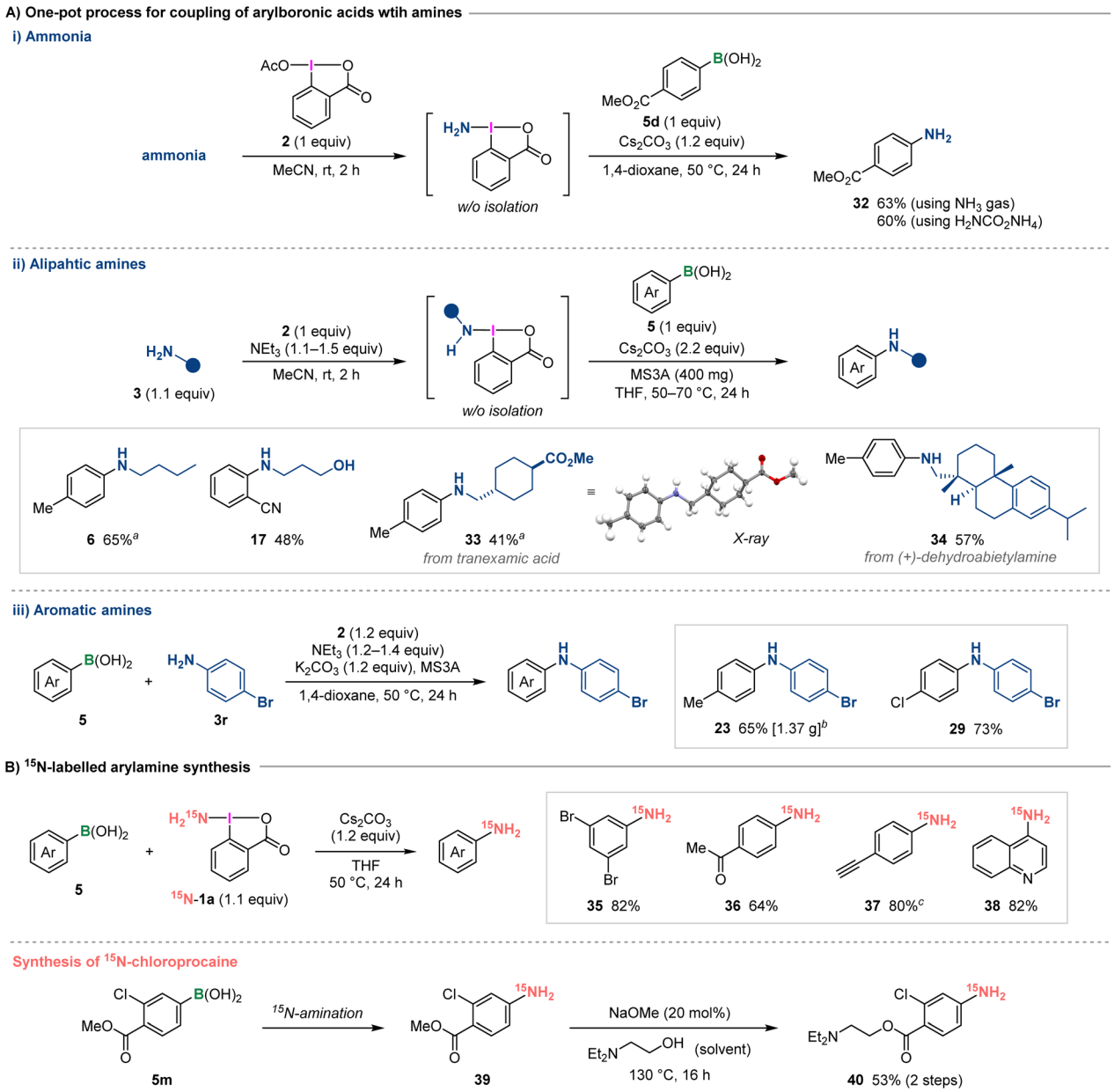


Scheme 4 The scope of amination of arylboronic acids with aminobenziodoxolones. Reactions were performed on a 0.2–0.4 mmol scale. [a]The corresponding pinacol boronic acid ester was used as a substrate. The yield was determined by ^{1}H NMR analysis of the crude product. [b]The reaction was conducted at 70 °C. [c]The reaction was conducted at 80 °C in 1,4-dioxane. [d]**1c** (1.5 equiv.) was used. [e] KO*t*-Bu was used instead of K_2CO_3.

heteroarylboronic acid, as exemplified by the amination of quinoline boronic acid to afford **21**.

Diarylamine synthesis *via* electrophilic amination of arylboronic acids has been quite limited, with existing methods requiring the use of hazardous arylazides[60] or nitro(so)arenes[63,64,66] under harsh reaction conditions. It is noteworthy that arylamine-derived reagents **1q–w** were successfully applied to oxidative amination to provide the corresponding diarylamines. Following a brief optimization of the reaction conditions, the use of K_2CO_3 as a base in 1,4-dioxane proved to be effective for diarylamine synthesis (see SI, Scheme S4). This method enables the synthesis of a variety of unsymmetrical diarylamines with good functional group compatibility, including bromo, trifluoromethyl, cyano, and ethoxycarbonyl groups (**22–27**). Sterically demanding diarylamine (**28**) and diarylamine bearing two different halogen substituents (**29**) could also be synthesized, which would be challenging to access *via* TM-catalyzed amination reactions.[46,69–71] Furthermore, electron-deficient arylboronic acids could also be applied, albeit in relatively lower efficiency (**30**, **31**). This approach enables the TM-free synthesis of a diverse array of secondary arylamines under mild reaction conditions, offering a practical tool for accessing pharmaceutical intermediates, such as tetracaine (**18**) and flufenamic acid (**31**).[72,73] For a complementary approach to the synthesis of arylamines, the arylation of amines with diaryliodonium salts has been reported.[74,75] A key feature of these methods is the synthesis of tertiary arylamines using secondary amines, which has not yet been achieved with the present method. In contrast, the present method uses readily available arylboronic acids, offering a broader scope in terms of aryl moieties.

Building upon the highly efficient method for the preparation of aminobenziodoxolones from amines, we next aimed to develop a direct oxidative amination of arylboronic acids using amines *via* the *in situ* preparation of aminobenziodoxolones, offering a TM-free alternative to the Chan–Lam–Evans coupling (Scheme 5A).[76,77] Gaseous ammonia was first employed for the *in situ* preparation of NH_2-substituted benziodoxolone **1a**, which was subsequently reacted with arylboronic acid **5d** to afford the target primary amine **32** in 63% yield – comparable to the reaction using isolated **1a** (Scheme 5Ai).[41] In addition, ammonium carbamate was also used in the one-pot process, affording **32** in comparable yield. Although the process requires the replacement of solvent and reaction atmosphere, the



Scheme 5 Synthetic applications. The yields are isolated. (A) One-pot amination of arylboronic acids with amines *via in situ* preparation of aminobenziodoxolones. (B) Synthesis of ^{15}N-labelled arylamines. [a]Both steps were performed in 1,4-dioxane. [b]The reaction was conducted on an 8 mmol scale. [c]The corresponding pinacol boronic acid ester was used as a substrate.

transformation could be carried out through sequential one-pot operations. This protocol was further extended to the synthesis of secondary amines using primary amines (Scheme 5Aii). In this manner, secondary arylamines **6** and **17** were obtained from 1.1 equivalents of the corresponding aliphatic primary amines with comparable efficiencies to those achieved with isolated reagents **1** (*cf.* Scheme 4). Notably, pharmaceutically relevant amines, such as tranexamic acid and dehydroabietylamine, also participated smoothly in the oxidative amination (**33**, **34**).[78] When employing aliphatic amines, conducting the reaction by mixing all the reagents at once led to diminished yield. In contrast, reactions involving aniline derivatives proceeded efficiently upon single-step mixing of reagents, without the need for prior *in situ* preparation of aminobenziodoxolones (Scheme 5Aiii). Notably, this operationally simple method was successfully applied to the gram-scale synthesis of **23**, further demonstrating its synthetic utility.

As an extension of the method for the synthesis of NH_2-substituted benziodoxolone from ammonia, we next focused on the preparation of ^{15}N-labelled analogue ^{15}N-**1a**, which is a promising reagent for the synthesis of ^{15}N-labelled compounds. Such compounds are of considerable significance for detailed structural analysis and bioimaging studies of nitrogen-containing molecules in the field of organic chemistry

and medicinal chemistry, owing to the favorable magnetic properties of the ^{15}N nucleus (Scheme 5B).[79–81] Gratifyingly, the desired ^{15}N-**1a** could be synthesized using a separately prepared methanolic solution of ammonia-^{15}N (see SI).[82] The resulting ^{15}N-**1a** was then applied to the oxidative amination of arylboronic acids or pinacol boronic acid esters, furnishing ^{15}N-labelled aniline derivatives bearing bromo, acetyl, alkyne, and ester functionalities (**35–37**, **39**). Moreover, the method proved applicable to the synthesis of ^{15}N-labelled quinoline derivative **38**. Furthermore, ^{15}N-labelled chloroprocaine **40**, an analogue of a clinically used local anesthetic, was synthesized from **5m** *via* sequential ^{15}N-amination and transesterification. Conventionally, ^{15}N-labelled arylamines are synthesized by the Hofmann rearrangement of ^{15}N-benzamides[83,84] or TM-catalyzed coupling reactions.[85–87] The present method would offer a good alternative, featuring broad functional group tolerance under mild reaction conditions.

Conclusions

In conclusion, we have developed a versatile method for the synthesis of aminobenziodoxolones from simple amines. This protocol is widely applicable to ammonia, a variety of aliphatic and aromatic primary amines, and even secondary amines, substantially expanding the scope of synthetically accessible aminobenziodoxolones. The synthesized reagents were applied to the oxidative amination of arylboronic acids, enabling the efficient synthesis of pharmaceutically and synthetically valuable secondary amines under TM-free mild reaction conditions. Furthermore, a one-pot protocol integrating the *in situ* preparation of aminobenziodoxolones and subsequent oxidative amination was established. As a further demonstration of the synthetic utility, ^{15}N-labelled arylamines were also synthesized using a^{15}N-labelled aminating reagent. We anticipate that the aminobenziodoxolones developed in this study will find broad application in oxidative amination reactions and serve as valuable tools for amine synthesis in both organic synthesis and medicinal chemistry.

Author contributions

K. K. and S. N. performed the experiments. K. K., and K. K. wrote the draft of the manuscript, participated in compound characterization, and SI preparation. S. M. supervised the research. All authors discussed the results and prepared the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2471676 contains the supplementary crystallographic data for this paper.[88]

Supplementary information: Experimental procedures, compound characterization data, crystal data, and NMR spectra can be found in SI. See DOI: https://doi.org/10.1039/d5sc06301a.

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