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Transition-Metal-Free Cyclization of Propargylic Alcohols with Aryne: Synthesis of 3-Benzofuranyl-2-oxindole and 3-Spirooxindole Benzofuran Derivatives[⊥]

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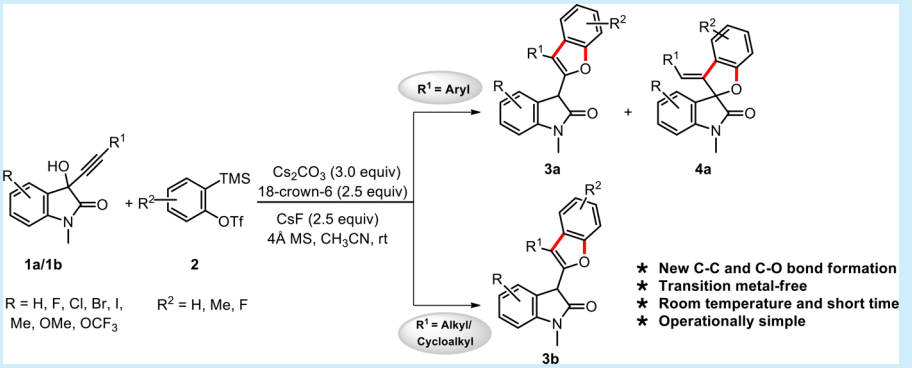
Supporting Information



ABSTRACT: An unprecedented base-mediated cyclization of propargylic alcohols with aryne is reported, providing a novel method for the synthesis of 3-benzofuranyl-2-oxindole and 3-spirooxindole benzofuran scaffolds via a propargyl Claisen rearrangement/cycloaddition pathway. The nature of the substituent on acetylene group of propargylic alcohol influences the outcome of the reaction. The protocol offers a transition-metal-free and operationally simple methodology with broad substrate scope as a ready access to complex oxindole-linked heterocyclic compounds.

The development of novel synthetic methodologies is an interesting and challenging proposition for organic chemists when complex scaffolds are to be built from simpler precursors. Over the past decade, arynes have emerged as the favored species that facilitated the construction of new chemical bonds toward the ready access to functionalized chemical entities.[1] The transient and high reactivity of aryne has paved the way to a manifold of reactions such as multicomponent reactions (MCR),[1d] pericyclic reactions,[1g] insertion reactions,[2] and many more.[1a,e,i,j] Among them, cycloaddition and insertion reactions of arynes allow the insertion of benzene ring through the formation of new C−C and C-X (X = H, O, N, S, etc.) bond in one step, and such a manifestation prompted its varied exploitation.[1k,2,3] The resurgence of aryne chemistry was made possible mainly because of the mild and expedient method developed by Koyabashi[4] in 1983, for the *in situ* generation of arynes from the *o*-silylaryl triflates by fluoride-induced *β*-elimination reaction at ambient temperatures, which tolerated a wide range of functional groups.

On the other hand, the complexity and structural diversity of oxindole derivatives have gained prominence, because of their presence as structural subunits of bioactive natural products and pharmaceutical ingredients.[5] Interestingly, furan and oxindole derivatives are ubiquitous scaffolds that display diverse pharmacological activities.[5−7] For instance, while Amiodarone **I** is an antiarrhythmic agent,[7a,b] compound **II** exhibited antiproliferative activity,[7a] Obovaten **III** displayed antitumor activity,[7d] and (−)-BPAP **IV** is an antidepressant drug.[7e] In addition, oxindole-linked spirocyclic compounds are privileged scaffolds, and, because of their unique three-dimensional structures, possess broad biological activities in several natural products and pharmacologically relevant drugs.[5d,8] For example, XEN907 **V**, which is a tetracyclic 3-spirooxindole benzoether, is a unique $hNa_v1.7$ blocker used for the treatment of chronic pain[8e] and 3-spirooxindole ether **VI** is a CB2 receptor antagonist[8f] (see Figure 1).

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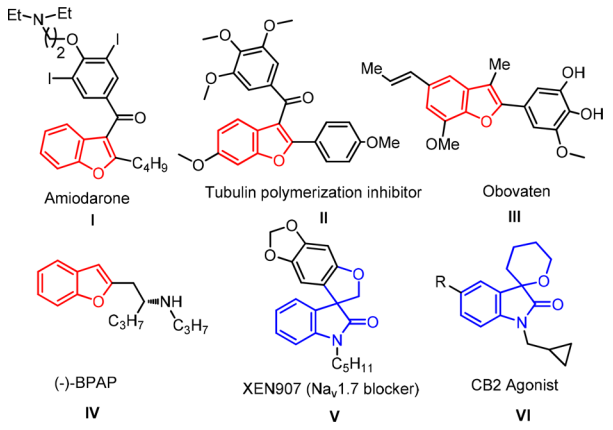
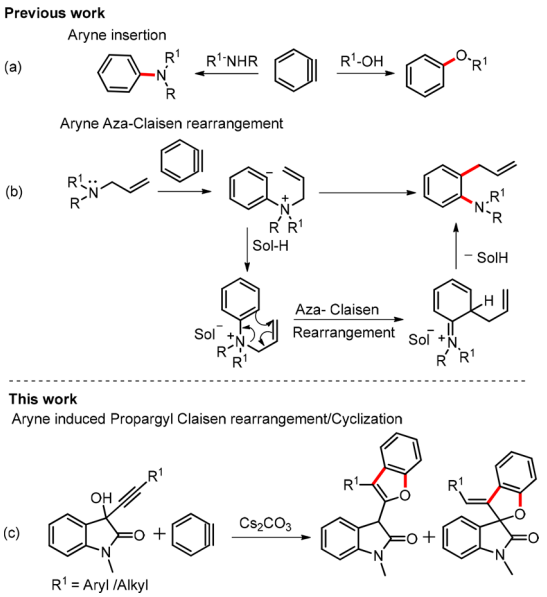


Figure 1. Representative bioactive benzofuran and spirooxindole scaffolds.

Because of the aforementioned importance, numerous emerging protocols provide viable alternatives to conventional techniques, or sometimes offer direct construction of heterocyclic systems via domino/cascade/tandem transformations.[9a−d] Moreover, some synthetic methodologies were reported for the preparation of furan-containing heterocyclic derivatives through transition-metal/noble-metal catalysts,[9,10] Lewis/Brønsted acids,[11] and base-promoted cyclizations[12] using propargylic alcohols or their derivatives as starting materials. However, accessing such preferred scaffolds using aryne chemistry is less known.[13] Recently, Larock and coworkers described the synthesis of diaryl ethers and aryl esters by the aryne insertion into the O−H bond of phenols and carboxylic acids under transition-metal free conditions. In addition, amines were also amenable to aryne insertion to produce corresponding aryl amines (see Scheme 1a).[2a,b] More recently, Biju et al. developed a temperature-dependent reaction of aryne with aliphatic alcohols for the synthesis of alkylaryl ethers via aryne insertion, followed by multicomponent coupling (MCC).[2c,d] Interestingly, Greany's group developed aryne-induced aza-Claisen rearrangement of arynes with tertiary allylamine to afford functionlized aniline derivatives (see Scheme 1b).[2e] Thus, tuning aryne chemistry for the synthesis of architecturally diverse heterocyclic derivatives is worth exploring. We have a long-standing interest in developing novel synthetic protocols for functionalized heterocyclic compounds.[14] In continuation, herein, we report a novel and efficient protocol for the synthesis of 3-benzofuranyl-2-oxindoles and 3-spiroox-indole benzofuran motifs from propargylic alcohols and aryne under mild and transition-metal-free conditions (see Scheme 1c).

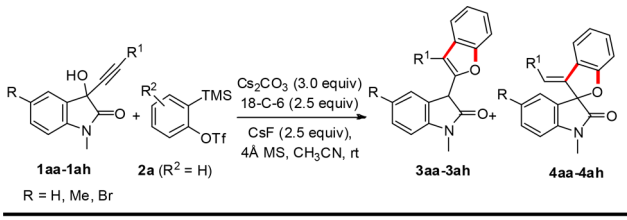
Scheme 1. Previous and Present Approaches



Our investigation began by reacting propargylic alcohol (**1aa**) as the model substrate with Koyabashi precursor (**2a**), using CsF and 18-crown-6 as additive in the presence of Cs_2CO_3 in anhydrous CH_3CN at room temperature. A smooth transformation under these conditions led to chromatographically separable products 3-benzofuranyl-2-oxindole **3aa** and 3-spirooxindole benzofuran **4aa** derivative in yields of 48% and 23%, respectively. Next, we screened several bases, solvents, F^- sources, and various reaction conditions (equivalents, time, and temperature) to increase the yield of products. The optimization results are presented in the Supporting Information (SI).[15]

With the optimized reaction conditions in hand, we explored the substrate scope and versatility of this protocol. Generally, substrates with aryl substituent on the propargylic alcohol afforded a separable mixture of corresponding products. A wide variety of propargylic alcohols with aryl substituents were examined in the reaction, and the results are summarized in Scheme 2. Broadly, this strategy displayed good functional group tolerance. Accordingly, the reaction of propargylic alcohol possessing different substituents at the *para* position of the phenyl ring **1aa**−**1ae** with aryne **2a** produced an isolable mixture of corresponding products **3aa**−**3ae** and **4aa**−**4ae** in moderate to good yields. Furthermore, the structures of **3ac** and **4aa** have been unequivocally corroborated by single X-ray crystallographic analysis (see the SI). The effect of the electron-rich substituent at the *para* position of benzene ring like *p*-Me exhibited minimal reactivity. The reaction of *p*-OMe phenyl substrate (**1af**) provided the compound **3af** (56%) and the corresponding **4af** could not be obtained in pure form. Moreover, the halo group such as 4-Cl (**1ad**) underwent the reaction in 2 h to yield **3ad** (34%) and **4ad** (17%). Next, we

Scheme 2. Substrate Scope When R^1 = Aryl[a]



3aa (R = H, R^3 = H), 48%
3ab (R = H, R^3 = Me), 37%
3ac (R = H, R^3 = Et), 48%
3ad (R = H, R^3 = Cl), 34%
3ae (R = H, R^3 = Ph), 36%
3af (R = H, R^3 = OMe), 56%
3ag (R = Me, R^3 = Et), 41%
3ah (R = Br, R^3 = Et), 36%

4aa (R = H, R^3 = H), 23%
4ab (R = H, R^3 = Me), 24%
4ac (R = H, R^3 = Et), 23%
4ad (R = H, R^3 = Cl), 17%
4ae (R = H, R^3 = Ph), 19%
4af (R = H, R^3 = OMe), trace
4ag (R = Me, R^3 = Et), 19%
4ah (R = Br, R^3 = Et), 18%

[a]Reaction was carried out with **1a** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (3.0 mmol), CsF (2.5 mmol) and 18-crown-6 (2.5 mmol) and 4 Å MS (60 mg) in CH_3CN (2.0 mL) at room temperature for 1−2 h; isolated yields were reported.

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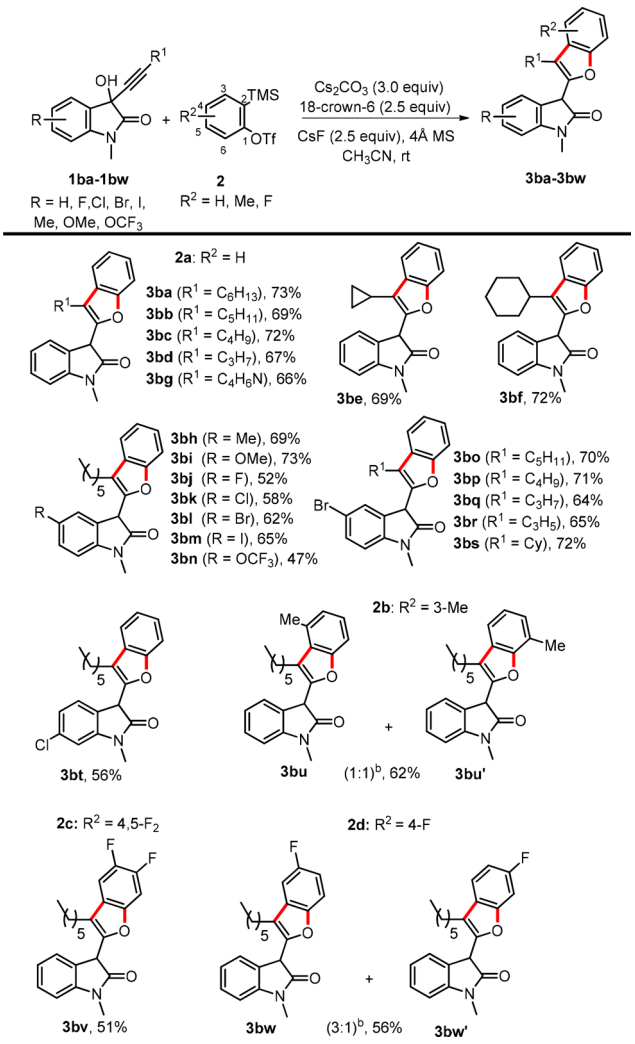
examined the electronic effects of substituents (−Me and −Br) at the C5-position of the oxindole scaffold, which, under established reaction conditions, provided the corresponding products **3ag**−**3ah** and **4ag**−**4ah** in decent yields.

In order to probe if the substituents on the distal end of acetylene group of propargylic alcohol have any bearing on the product outcome, we selected substrates possessing alkyl/cycloalkyl groups on the alkynyl carbon (see Scheme 3). First,

Scheme 3. Substrate Scope When R^1 = Alkyl/Cycloalkyl[a] and R^2 = Variation of Arynes



[a]Reactions were carried out with **1ba** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (3.0 mmol), CsF (2.5 mmol) and 18-crown-6 (2.5 mmol), and 4 Å MS (60 mg) in CH_3CN (2.0 mL) at room temperature for 1−2 h; isolated yields were reported. [b]The ratio of regioisomers were determined by ^1H NMR.

1ba (containing hexyl group) was chosen as the test substrate and the reaction was conducted under established conditions to afford **3ba** as an exclusive product in 73% yield. To evoke more understanding, the cycloalkyl analogue **1bf** (cyclohexyl group) was selected as the next example to give **3bf** as a sole product in matching yields (72%). We next sought to evaluate the scope of similar substrates such as *n*-pentyl (**1bb**), *n*-butyl (**1bc**), and *n*-propyl (**1bd**), which furnished corresponding products **3bb**−**3bd** in varying yields (69%−72%). Gratifyingly, the cyclopropyl-group-bearing substrate (**1be**) was also well-tolerated under these conditions, retaining the cyclopropane ring. The substrate with propyl cyanide group (**1bg**) gave **3bg** in 66% yield. To expand the generality of the reaction, we set out to explore both electron-rich (−Me and −OMe) and electron-deficient (−F, −Cl, −Br, −I, and $-OCF_3$) effects at the 5-position of the oxindole moiety. The results indicated that, while **1bh** and **1bi** gave **3bh** and **3bi** in 69% and 73% yields, respectively, their counterparts **1bj**−**1bn** gave corresponding products **3bj**−**3bn** in the range of 47%−65% yields. The structure of the product **3bk** was unambiguously confirmed by X-ray analysis (see the SI). The alkyl/cycloalkyl groups on substrates containing alkynyl carbon of the 5-Br-oxindole moiety were subsequently investigated and found that the reaction worked equally well on **1bo**−**1bs** to afford respective products **3bo**−**3bs** in moderate to good yields. Furthermore, the 6-Cl-oxindole derivative **1bt** provided **3bt** in 56% yield. These results demonstrate that very negligible electronic effects were observed, irrespective of their position.

Finally, we investigated the regioselectivity and substituent effects on substituted aryne precursors **2** with **1ba** under the optimal conditions (Scheme 3). Thus, the reaction of unsymmetrical 3-methyl aryne precursor **2b** with **1ba** gave an inseparable mixture of regioisomers **3bu** and **3bu′** in a ratio of 1:1 (62% yield). Moreover, the symmetrical 4,5-difluoro aryne **2c** with **1ba** resulted in **3bv** as the sole product in 51% yield. Next, we selected 4-fluoro aryne (from **2d**), which produced a mixture of regioisomers **3bw** and **3bw′** in 3:1 ratio in a combined yield of 56%. In addition, we performed the reaction with substrates containing tertiary propargylic alcohol systems such as 2-methyl-4-phenylbut-3-yn-2-ol (**5**) and1-(phenyethynyl)-cyclopentanol (**7**) with aryne precursor (**2a**) to afford the corresponding aryl ethers **6** (25%) and **8** (30%).[16]

Thus, it was observed that the substituents on the alkynyl carbon decided the outcome of the reaction. If the distal end of the propargylic alcohol is substituted by an alkyl group (R^1), then 3-benzofuranyl-2-oxindole derivatives were the sole products. Conversely, if aryl groups are the substituents (R^1), then both propargyl Claisen rearrangement and cycloaddition products were obtained in one pot via 5-*exo*-*dig* cyclization. In the case of the aryl group that is present at the distal end of the triple bond, the cycloaddition process is the competing reaction that is mainly facilitated because of the extended conjugation.

Based on the experimental results and the literature precedence[2e−g,3,17,18] a tentative mechanism for the reaction is depicted in Scheme 4. Initially, propargylic oxyanion **A** is generated by abstraction of the proton from the propargylic alcohol **1a**/**1b** by Cs_2CO_3. The intermolecular nucleophilic attack of O^- in **A** onto aryne (**2a**) results in the intermediate **B**, which undergoes intramolecular nucleophilic addition on alkyne moiety, followed by protonation to produce **4a** via cycloaddition pathway. On the other hand, the intermediate **B** can transform to the allene intermediate **C** by propargyl Claisen rearrangement, followed by 5-*exo*-*dig* cyclization to generate the intermediate **D**, which, upon subsequent protonation, affords the product **3a**/**3b**. The reaction pathway involves a domino transformation of intermolecular C−O and subsequent intramolecular C−C/C-O bond formation.

In summary, we have demonstrated an efficient Cs_2CO_3-mediated propargyl Claisen rearrangement/cycloaddition reaction between 3-alkynyl-3-hydroxy oxindole derivatives and aryne, leading to the formation of 3-benzofuranyl-2-oxindole and 3-spirooxindol benzofuran derivatives in one pot.

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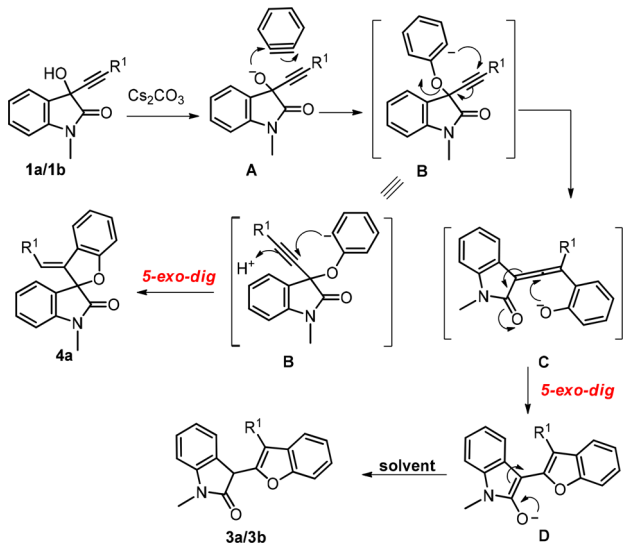
Scheme 4. Proposed Reaction Mechanism



The nature of substituent on alkynyl carbon of propargyl alcohol decides the outcome of the reaction. The salient features of this protocol are operational simplicity, broad substrate scope, short reaction times, and mild conditions. Further scope of this strategy including mechanistic studies and synthetic applications are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01414.

Typical experimental procedures, detailed screening of the reaction conditions, preparations and characterizations of compounds and spectroscopic data for **4aa**, **3ac**, and **3bk** (PDF)

Accession Codes

CCDC 1821924−1821926 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

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The authors declare no competing financial interest.

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(15) For details, please see Table 1 in the Supporting Information.
(16) For experimental details on the insertion reaction of 2-methyl-4-phenylbut-3-yn-2-ol (**5**) and 1-(phenylethynyl)cylcopentanol (**7**) with aryne precursor (**2a**), please see the Supporting Information.
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