Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 6346

Indium-mediated annulation of 2-azidoaryl aldehydes with propargyl bromides to [1,2,3]triazolo[1,5-*a*]quinolines†

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Received 19th June 2021,
Accepted 30th June 2021

DOI: 10.1039/d1ob01183a

rsc.li/obc

An efficient indium-mediated cascade annulation reaction of 2-azidoaryl aldehydes with propargyl bromides is reported. The aromatic 5/6/6-fused heterocycles, [1,2,3]triazolo[1,5-*a*]quinoline derivatives, could be constructed in one pot in moderate yields with a broad substrate scope. Mechanistic studies indicated that the reaction proceeded through allenol formation, azide–allene [3 + 2] cycloaddition, and dehydration. The synthetic potential of the products including the denitrogenative functionalization and the Pd-catalyzed coupling reactions has also been explored.

Introduction

[1,2,3]Triazolo[1,5-*a*]quinoline is an important aromatic heterocycle with a 5/6/6-fused ring system. The existing core skeleton, which contains both the [1,2,3]triazolo[1,5-*a*]pyridine[1] and quinoline scaffolds,[2] is an essential building block and is extremely attractive for materials science and pharmaceutical chemistry (Fig. 1).[3] For example, while **Diquat** was able to interact with DNA,[3a] the 3-hydroxy-2-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-*a*]quinolinium inner salt **AZ1** was found to be a new aryl hydrocarbon receptor (AhR) agonist with exceptional potency.[3e] Moreover, the ring-chain isomerization of the cyclic triazole framework of [1,2,3]triazolo[1,5-*a*]quinolines offers new tools for the construction of functionalized quinoline derivatives *via* efficient denitrogenative ring-opening, providing potential in synthetic chemistry.[4] The development of new, efficient, and general synthetic methods for the preparation of [1,2,3]triazolo[1,5-*a*]quinolines is required and has drawn significant attention from chemists.

Typically, [1,2,3]triazolo[1,5-*a*]quinolines can be divided into *a*, *b*, and *c* rings, and efforts have been made to construct these rings by developing efficient methods. While the transition metal-catalyzed coupling reactions of 1-phenyl-1*H*-1,2,3-triazole derivatives provided general approaches for building the middle *b* ring (path a, Scheme 1),[5] the *c* ring could be constructed by the oxidative *N*–*N* bond formation of (quinolin-2-yl)methylene hydrazine derivatives directly under oxidative conditions (path b).[6] In 2017, the Nachtsheim group reported the one-pot construction of the *b* and *c* rings of [1,2,3]triazolo[1,5-*a*]quinolines through tandem Sandmeyer azide formation and subsequent intramolecular azide–alkyne cycloaddition of enynes, while the complex starting materials were prepared using iridium catalysis *via* C–H functionalization (path c).[7] Alternatively, the annulation reaction of 2-azidoaryl aldehyde/nitrile/ester with 1,3-dicarbonyl compounds offered an efficient tool for building the *b* and *c* rings of [1,2,3]triazolo[1,5-*a*]quinolines in a single step by using a strong base, typically DBU, *t*-BuOK, and NaH (path d).[8a–8d] Given that low-valent metals can mediate the allenylation reaction of propargyl bromides and aldehydes,[9,10] we proposed that the reaction of 2-azidoaryl aldehydes with propargyl bromides would proceed through metal-mediated allenylation of propargyl bro-

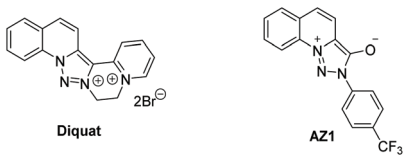

Fig. 1 Bioactive molecules with the [1,2,3]triazolo[1,5-*a*]quinoline moiety.

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†Electronic supplementary information (ESI) available. CCDC 2078447. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ob01183a

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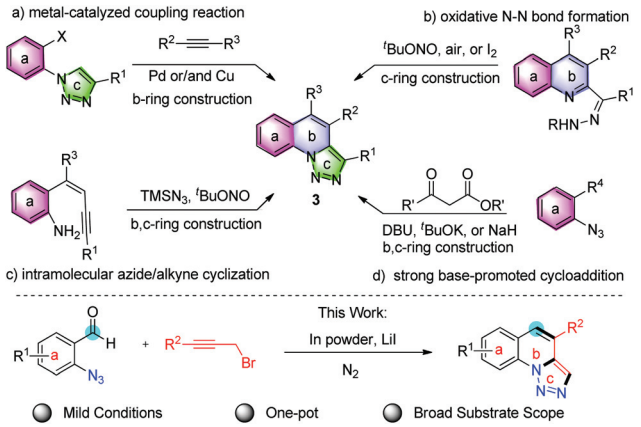


Scheme 1 Strategies for the synthesis of [1,2,3]triazole[1,5-*a*]quinolines.

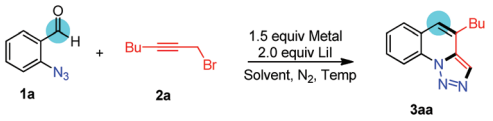
mides,[11] [3 + 2] azide–allene cycloaddition,[12] and subsequent dehydration to afford the [1,2,3]triazolo[1,5-*a*]quinoline derivatives. Herein, we report such a tandem one-pot reaction of 2-azidoaryl aldehydes with propargyl bromides. This reaction could be mediated by indium powder and the reductive condition was mild, providing a reliable and novel strategy for the synthesis of [1,2,3]triazolo[1,5-*a*]quinolines.

Results and discussion

To verify the feasibility of the design, the reaction of 2-azidobenzaldehyde (**1a**) and 1-bromohept-2-yne (**2a**) was first conducted in the presence of 1.5 equiv. of indium and 2.0 equiv. of LiI in DME at room temperature (rt) under a N_2 atmosphere. The reaction proceeded smoothly and the desired product **3aa** was obtained in 71% yield based on isolation (entry 1). The reaction conditions were then optimized (Table 1). First, the indium powder was proven to be important for the transformation.[11] Other related metals, such as Mn and Zn, did not promote the reaction, while Fe powder only led to a low yield (entries 2–4). The solvent effect was also surveyed. Other ether solvents, such as THF, MTBE, and 1,4-dioxane, gave relatively lower yields (66%, 53%, and 32%, respectively) (entries 5–7), while chlorinated solvents, such as DCE and DCM, afforded the desired products in only 25–33% yields (entries 8 and 9). The reaction in DMA gave a result similar to that with DME (entry 10). Other polar solvents, such as DMSO, DMF, and MeCN, afforded the product only in 15–52% yields (entries 11–13). Interestingly, the reaction could be conducted in a protic solvent (MeOH) with a lower yield (entry 14). Moreover, when the reaction temperature was increased to 60 or 100 °C, the yields decreased significantly (entries 15 and 16).

With the optimized conditions in hand, the scope of the reaction was first tested using various propargyl bromides (Table 2). 3-Alkyl, alkenyl, or aryl substituted propargyl bromides were tolerated under the standard reaction conditions and the corresponding 4-substituted [1,2,3]triazolo[1,5-*a*]quinolines were obtained in moderate yields. Electron-donating groups, such as *t*-Bu (**3ae**) and OMe (**3af**), or electron-withdrawing groups, such as CF_3 (**3ag**) and COOMe (**3ah**), on the phenyl group were tolerated well and the products were iso-

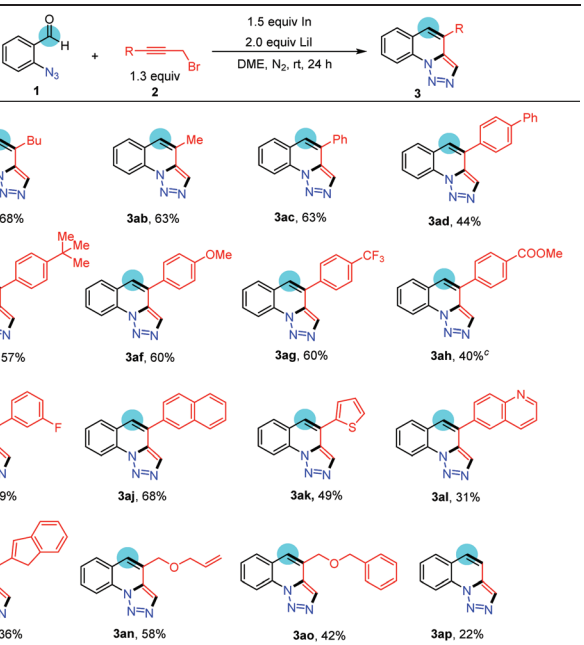
Table 1 Optimization of the reaction conditions[a]



Entry	Metal	Solvent	Temperature	Yield[b] (%)
1	In	DME	rt	71 (68)[c]
2	Mn	DME	rt	0
3	Zn	DME	rt	0
4	Fe	DME	rt	9
5	In	THF	rt	66
6	In	MTBE	rt	53
7	In	1,4-Dioxane	rt	32
8	In	DCE	rt	25
9	In	DCM	rt	33
10	In	DMA	rt	69
11	In	DMSO	rt	32
12	In	DMF	rt	52
13	In	MeCN	rt	15
14	In	MeOH	rt	50
15	In	DME	60 °C	58
16	In	DME	100 °C	36

[a] The reactions were conducted with **1a** (0.2 mmol), **2a** (0.26 mmol), metal (0.3 mmol), and LiI (0.4 mmol) under N_2 for 24 h. [b] All yields are based on isolation. [c] The yield in parentheses is based on isolation of the reaction product at the 0.5 mmol scale.

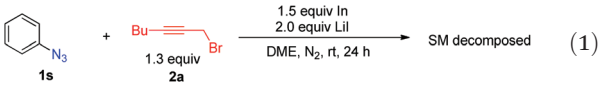
Table 2 Scope of propargyl bromides[a,b]



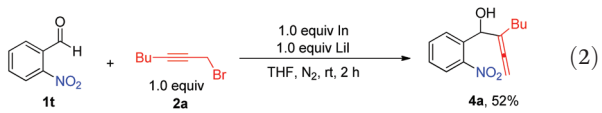
[a] The reactions were conducted with **1a** (0.5 mmol), **2** (0.65 mmol), In (0.75 mmol), and LiI (1.0 mmol) in DME (5 mL) at room temperature under N_2 for 24 h. [b] All yields are based on isolation. [c] The reaction temperature was 60 °C.

lated in 40–60% yields. While the electron-donating or electron-withdrawing groups did not affect the reaction significantly, the variation in the yield of these transformations is probably dependent on the stability of substrate **2** under these conditions. The reaction of **1a** with 3-(2-naphthyl)-propargyl bromide occurred smoothly and provided the corresponding product in 68% yield (**3aj**). Intriguingly, when propargyl bromides containing heteroaryl groups, such as thiophen-2-yl and quinolin-6-yl groups, were treated with **1a**, the corresponding cyclization products were obtained successfully with only slightly lower yields (**3ak** and **3al**). While the ether group was tolerated in the reaction (**3an** and **3ao**), the simple propargyl bromide afforded the corresponding product **3ap** in only 22% yield. The structure of **3ab** was further confirmed by single crystal X-ray diffraction (Fig. 2).[13]

The scope of the functionalized 2-azidoaryl aldehydes **1** was next investigated with **2a** under the standard reaction conditions (Table 3). When substrates **1** bearing a methyl group were used, the reaction proceeded well to afford the corresponding product (**3ba**). The highly strained cyclopropane ring was unreactive under the standard conditions and remained intact during the transformation (**3ca**). The carbon–halogen bonds (**3da** and **3ea**) were also tolerated well although a higher reaction temperature (60 °C) was required to facilitate higher yields. All the reactions proceeded smoothly to afford the corresponding products when substituted phenyl groups with either an electron-donating group, such as OMe (**3ga**), or an electron-withdrawing group, such as CF_3 (**3ha**) or CN (**3ia**), were used. Moreover, heteroaryl groups, such as pyridin-2-yl (**3ja**), furan-2-yl (**3ka**), or thiophen-2-yl (**3la**), were also tolerated. While the simple ester groups were able to remain (**3ma** and **3na**), interestingly, substrates bearing complex scaffolds, such as (L)-menthol, dehydroepiandrosterone, and cholesterol derivatives, also gave moderate yields (**3oa**, **3pa**, and **3qa**). Notably, when 1-(2-azidophenyl)propan-1-one **1r** was prepared and subjected to the reaction with **2a** under the standard conditions, the desired product **3ra** was not detected but only the reduction product of the starting material was obtained.



(1)



(2)

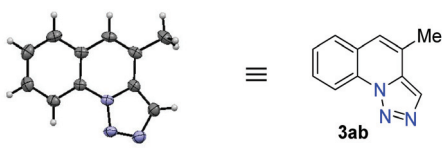
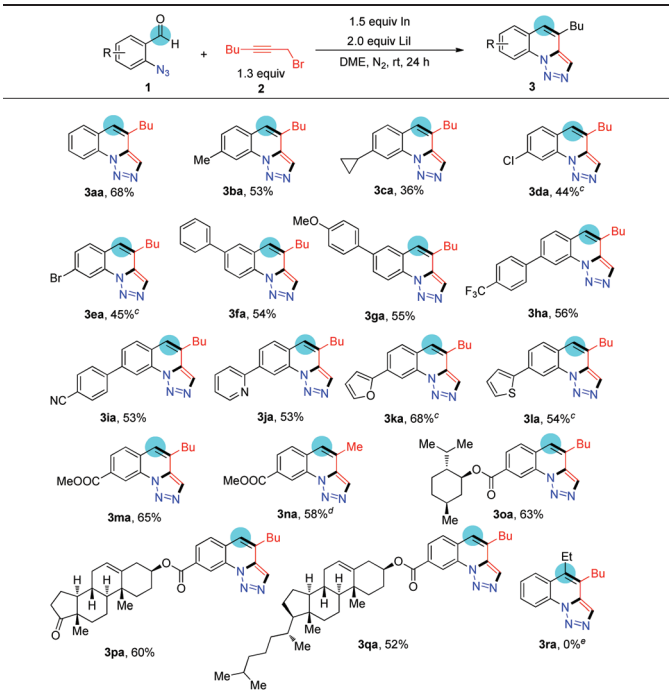
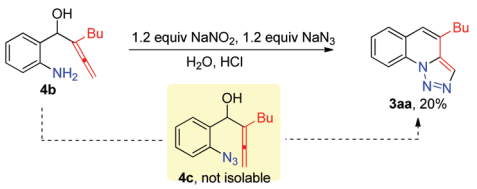


Fig. 2 The crystal structure of compound **3ab**. Atoms are presented as thermal ellipsoids at 50% probability level.

Table 3 Scope of 2-azidoaryl aldehydes[a,b]



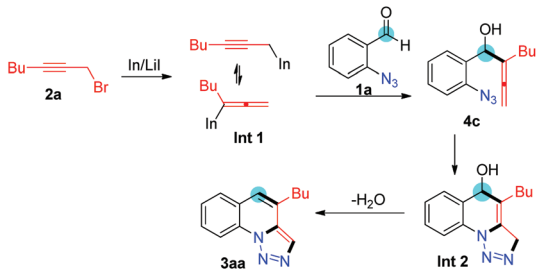
[a] The reactions were conducted with **1** (0.5 mmol), **2a** (0.65 mmol), In (0.75 mmol), and LiI (1.0 mmol) in DME at room temperature under N_2 for 24 h. [b] All yields are based on isolation. [c] The reaction temperature was 60 °C. [d] 1-Bromo-2-butyne **2b** was used. [e] 1-(2-Azidophenyl) propan-1-one was used.



(3)

For understanding the reaction process, a series of experiments were conducted. First, while the reaction of azidobenzene **1s** with **2a** under the standard conditions failed to afford the triazole product (eqn (1)), the reaction of 2-nitrobenzaldehyde **1t** with **2a** produced allenol **4a** in 52% yield (eqn (2)). These results indicated that the reaction between aldehyde and propargyl bromide at the beginning is crucial for the transformation. Second, when 2-aminophenyl allenol **4b** was prepared and subjected to the Sandmeyer azidation, the desired product 2-azidophenyl allenol **4c** was not isolated but only the cyclization product **3aa** was obtained in 20% yield (eqn (3)), indicating that the azide–allene cycloaddition and the subsequent dehydration are highly driven to produce the [1,2,3]triazolo[1,5-*a*]quinoline product even in the absence of indium.

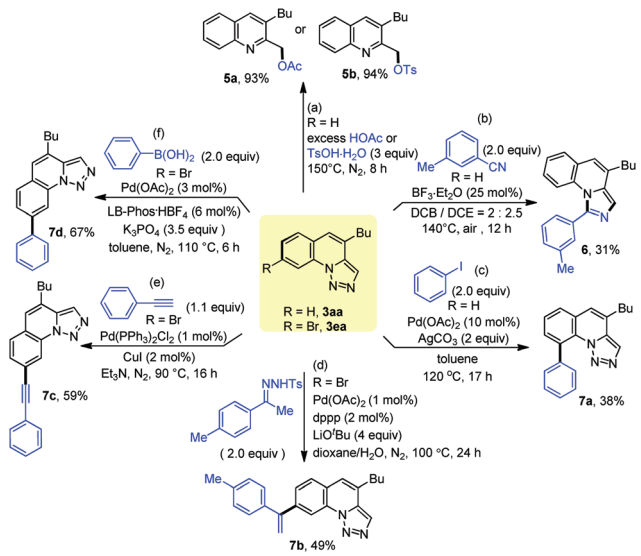
Based on the mechanistic studies, a plausible mechanism was proposed (Scheme 2). First, the reaction of propargyl bromide **2a** in the presence of indium formed intermediate **Int 1**, which underwent 1,2-addition with 2-azidobenzaldehyde **1a** to afford allenol **4c**. The fast intramolecular azide–allene



Scheme 2 Plausible mechanism.

[3 + 2] cycloaddition and subsequent dehydration led to the final product **3aa**.

Finally, the synthetic potential of the prepared [1,2,3]triazolo[1,5-*a*]quinoline was examined (Scheme 3). First, the product **3aa** served as the quinolin-2-yl carbene precursor to react with an excess amount of HOAc or 3.0 equiv. of $TsOH{\cdot}H_2O$ under reflux for 8 hours to afford (quinolin-2-yl) methyl acetate **5a** or (quinolin-2-yl)methyl 4-methylbenzenesulfonate **5b** (route a).[14a] The Brønsted acid-promoted dinitrogen liberation of the triazole moiety was followed by addition of acetic acid or $TsOH{\cdot}H_2O$, leading to the final product in 93% or 94% yield, respectively. In addition, the [5 − 2 + 2] cycloaddition product substrate **6** was obtained by treating product **3aa** with 3-methylbenzonitrile in the presence of 25 mol% of $BF_3{\cdot}Et_2O$ in DCB and DCE at 140 °C for 12 hours (route b). The denitrogenation provided the strong driving force for the transformation.[6c] The C–H arylation product **7a** was obtained by treating **3aa** with iodobenzene in the presence of 10 mol% of $Pd(OAc)_2$ and 2 equiv. of Ag_2CO_3 under air for 17 hours (route c).[14b] Moreover, the coupling reaction of compound **3ea** with 4-methyl-*N*′-(1-(*p*-tolyl)ethylidene)benzenesulfonohydrazide in the presence of 1 mol% of $Pd(OAc)_2$, 2 mol% of dppp, and 4 equiv. of *t*-BuOLi occurred smoothly to afford the alkenylation product **7b** in 49% yield (route d).[14c] The Sonogashira coupling reaction of substrate **3ea** with phenylacetylene proceeded smoothly to generate the internal alkyne **7c** in 59% yield (route e).[14d] Substrate **3ea** underwent the Suzuki coupling reaction with phenylboronic acid in the presence of $Pd(OAc)_2$ and LBphos to produce the corresponding product **7d** in a moderate yield (route f).[14e–14g]



Scheme 3 Synthetic potential of [1,2,3]triazole[1,5-*a*]quinolines.

Conclusions

In summary, we have developed a one-pot synthesis of [1,2,3]triazolo[1,5-*a*]quinolines by an annulation reaction of 2-azidoaryl aldehydes and propargyl bromides in moderate yields. A stoichiometric amount of indium powder promoted the transformation, which was proposed to proceed by a tandem procedure involving allenol formation, azide–allene [3 + 2] cycloaddition, and subsequent dehydration. The reaction scope was broad when functional groups, such as esters, alkenes, and ethers, were well tolerated. In addition, the synthetic potential, including Suzuki coupling, Sonogashira coupling, directed C–H arylation, and the denitrogenative ring-opening of the corresponding products, was studied.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

R.Z. is grateful for the financial support from the National Natural Science Foundation of China (21901197), the Natural Science Basic Research Plan in Shaanxi Province of China (2019JM093), the Guangdong Provincial Key Laboratory of Catalysis (2020B121201002), and the start-up funds from Xi'an Jiaotong University (XJTU). We thank the Instrument Analysis Center of XJTU for assistance with HRMS analysis.

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