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The Silver(I)-catalyzed Cascade Bicyclization Strategy for Synthesis of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines

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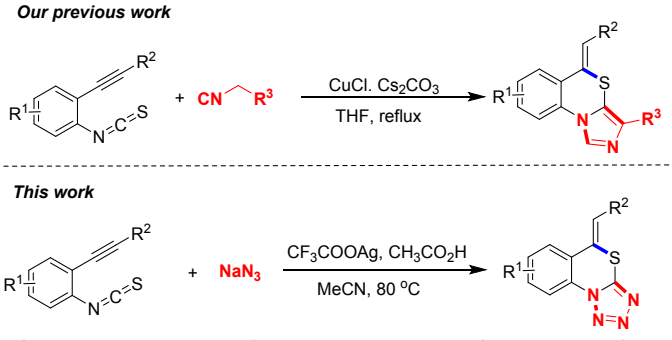
A simple and efficient protocol for silver(I)-catalyzed tandem reaction of o-alkynylphenyl isothiocyanates with sodium azide has been developed, affording a series of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines in moderate to good yields. In this transformation, a [3+2] cycloaddition reaction mechanism was involved and two new rings were formed in one-pot.

The development of efficient methods for the preparation of azoles has become one of the most important research topics in heterocyclic chemistry.[1] Among these various azoles, tetrazoles, the isostere of carboxyl acid group,[2] are one of the most promising compounds in medicinal chemistry due to its important biological activities such as antituberculosis, [3] anti-allergy,[4] antiinflammatory,[5] antitumor,[6] and other medicinal properties. Furthermore, tetrazole derivatives are also widely used as testing materials, explosives, metal coordination compounds, chemical catalysts and other aspects of materials and have attracted significant attention.[7] By far, the prevalent strategies for constructing tetrazole derivatives are the addition of azides and isothiocyanates[8] or the [3+2] cycloaddition of an azide to a nitrile by using the Lewis acid as the catalyst.[9] For instance, Hantzsch and Vagt [9a] first reported the addition of hydrazoic acid to the cyanide group resulting in the formation of 5-substituted tetrazole derivatives. In 2001, Sharpless and co-workers described a convenient, and environmentally friendly synthetic route to 5-substituted 1*H*-tetrazoles, which can be accomplished with water as a solvent and zinc salts as catalyst.[9b] On the other hand, Benzo-1,3-thiazines are very important sulfur-containing *N*-heterocyclic compounds which are found in many bioactive natural products and pharmaceuticals.[10] A common route to benzo-1,3-thiazines is via the transition-metal-catalyzed tandem 6-exo-dig cyclization reactions of 2-ethynylanilines to isothiocyanates, carbon disulfide, tetraalkylthiuram disulfides.[11] In 2014, Reddy and co-workers[12] reported the intramolecular C-O/C-S bond insertion of α-diazoesters for synthesis of a variety of 2-aryl-4H-benzo[*d*][1,3]thiazine derivatives in high yields. Although these routes can work, reports involving synthesis of the polycyclic skeleton 5*H*-benzo[*d*]tetrazolo[5,1-b][1,3]thiazine is quite rare. To the best of our knowledge, only one published example is known.[9c] Recently, a copper-catalyzed cascade bicyclization of o-alkynylphenyl isothiocyanates with isocyanides to synthesis of 5*H*-benzo[*d*]imidazo[5,1-*b*][1,3]thiazines has been reported by our group (Scheme 1)[14c]. We envisioned that sodium azide also could be applied in the reaction with o-alkynylphenyl isothiocyanates by using this Strategy[13]. As our continuous interest for the synthesis of biologically relevant heterocyclic compounds, [14]herein, we wish to introduce our recent effort for the generation of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines via the silver(I)-catalyzed cascade reaction of o-alkynylphenyl isothiocyanates with sodium azide.



Scheme 1 Comparison between previous and present work

The starting *o*-alkynylphenyl isothiocyanates were prepared via Sonogashira coupling of 2-iodoanilines with terminal alkynes,[15] followed by the treatment with thiophosgene according to the literature procedure[16]. At the outset, we used

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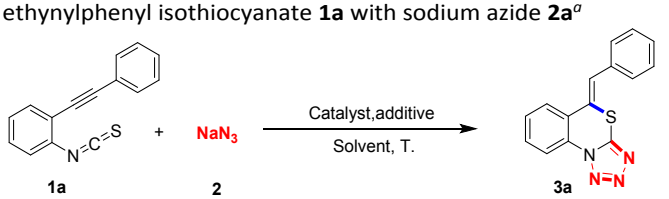
o-phenylethynylphenyl isothiocyanate **1a** and sodium azide **2** as the substrates in a model reaction to optimize the conditions, and the results are summarized in Table 1. The reaction was carried out in the presence of CuI (20 mol%), and HCl (2.0 equiv.) in THF (2mL) at 80 °C for 20 h. To our delight, the desired product **3a** was successfully isolated in 43% yield (Table 1, entry 1). Other metal salts used as catalysts in the reaction were then screened (Table 1, entries 1-5). Silver sources were found to be more effective than copper salts and CF_3CO_2Ag gave the best results (Table 1, entry 5). Subsequently, we examined the acid effect on the reaction. It is evident that CH_3CO_2H was the best choice, leading to the desired product **3a** in 79% yield (Table 1, entry 9). Lower yields were observed when other protonic acid such as HNO_3, TsOH, PivOH, $NaHCO_3$ were employed, whereas H_2SO_4 failed to promote the reaction (Table 1, entries 6-11). It is worth noting that only 15% yield of product was obtained in the absence of acid (Table 1, entry 12). We next examined the solvent effect (Table 1, entries 13−18). When MeCN was employed as the solvent, the highest yield of 84% was obtained. Finally, we examined the effect of temperature on the reaction. When the reaction temperature was reduced to 60 °C, the reaction was completed with a yield of 40% (Table 1, entry 19). Rising the reaction temperature to 100 °C and 120 °C resulted in a diminished yield (Table 1, entries 20-21).

Table 1 Initial studies for the tandem reaction of o-phenyl ethynylphenyl isothiocyanate **1a** with sodium azide **2a**[a]



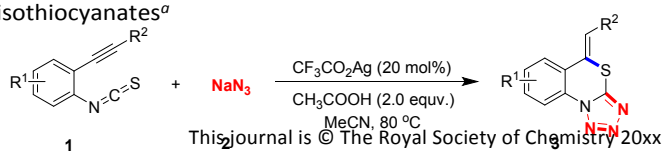
1a **2** **3a**

Entry	Catalyst	Additive	Solvent	Temp.	Yield (%) [b]
1	CuI	HCl	THF	80 °C	43
2	$Pd(OAc)_2$	HCl	THF	80 °C	Trace
3	Ag_2CO_3	HCl	THF	80 °C	50
4	$AgSO_3F_3$	HCl	THF	80 °C	48
5	AgO_2CCF_3	HCl	THF	80 °C	60
6	$AgOOCCF_3$	H_2SO_4	THF	80 °C	NR
7	$AgOOCCF_3$	HNO_3	THF	80 °C	45
8	$AgOOCCF_3$	TsOH	THF	80 °C	48
9	$AgOOCCF_3$	CH_3CO_2H	THF	80 °C	79
10	$AgOOCCF_3$	PivOH	THF	80 °C	72
11	$AgOOCCF_3$	$NaHCO_3$	THF	80 °C	75
12	$AgOOCCF_3$	/	THF	80 °C	15
13	**$AgOOCCF_3$**	**CH_3CO_2H**	**MeCN**	**80 °C**	**84**
14	$AgOOCCF_3$	CH_3CO_2H	DMF	80 °C	52
15	$AgOOCCF_3$	CH_3CO_2H	DMSO	80 °C	62
16	$AgOOCCF_3$	CH_3CO_2H	Toluene	80 °C	NR
17	$AgOOCCF_3$	CH_3CO_2H	DCM	80 °C	trace
18	$AgOOCCF_3$	CH_3CO_2H	DCE	80 °C	NR
19	$AgOOCCF_3$	CH_3CO_2H	MeCN	60 °C	40
20	$AgOOCCF_3$	CH_3CO_2H	MeCN	100°C	65
21	$AgOOCCF_3$	CH_3CO_2H	MeCN	120°C	60
22[c]	$AgOOCCF_3$	CH_3CO_2H	MeCN	80 °C	45
23[d]	$AgOOCCF_3$	CH_3CO_2H	MeCN	80 °C	80

[a]Reaction was performed with **1a** (0.2 mmol), **2** (0.4 mmol), catalyst (0.04mmol), acid (0.4 mmol) in solvent (2mL) for 20 h. [b]Isolated yield based on *o*-phenylethynylphenyl isothiocyanate **1a**. [c] The reaction time was 12 h. [d] The reaction time was 24 h.

To further demonstrate the substrate scope and flexibility of the present optimized conditions, different *o*-alkynyl phenyl isothiocyanates were then explored, the results are summarized in Table 2. All reactions proceeded smoothly, leading to the desired 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines in moderate to good yields. For example, the substituents on the R^2 position of *o*-alkynylphenyl isothiocyanates showed obvious electronic effects on the reaction. When R^2 group in the substrates **1** was an electron-deficient aryl, such as *p*-FC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, the reactions with **2** proceeded smoothly to afford the corresponding products **3b-3d** in lower yields compared with the reactions of substrates **1** with an electron-rich aryl group such as *p*-$MeOC_6H_4$, *p*-MeC_6H_4 at the R^2 position, which afforded the corresponding products **3e** and **3f** in 85% and 87% yields, respectively. Surprisingly, no desired products were obtained when the R^2 group in the substrate *o*-alkynylphenyl isothiocyanates **1** was an alkyl group, such as *n*-butyl, *t*-butyl, *n*-hexyl. This may be due to the fact that the alkyl group cannot conjugate with anacetylenic bond and activate it. However, when the R^2 group in the substrate *o*-alkynylphenyl isothiocyanates **1** was the cyclopropyl group , the desired 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazine was not obtained, and an unexpected seven-member-ring compound **4a** was isolated instead. The structure of **4a** was further confirmed using X-ray diffraction analysis (see Fig. 2 in the ESI†). The other two substitution products **4b, 4c** also were obtained successfully under standard conditions. In addition, the reactions of *o*-alkynylphenyl isothiocyanates bearing various substituents such as fluoro, chloro, bromo, trifluoromethyl and methyl groups on the aryl rings, regardless of their electronic properties and substitution positions, gave the desired products **3g-3l** in moderate to good yields. Similarly, (Z)-7-fluoro-5-(4-fluorobenzylidene)-5H-benzo[*d*]tetrazolo[5,1-*b*][1,3] thiazine **3m** and (Z)-5-(4-fluorobenzylidene)-7-(trifluoromethyl) -5H-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazine **3n** could also be conventiently obtained in good yields by the silver-catalyzed cascade bicyclization reaction under the same reaction conditions. The structure of **3n** was further confirmed using X-ray diffraction analysis (see Fig. 2 in the ESI†). All products were uniformly formed as the Z-isomer, which might be due to a kinetic effect according to Baldwin's rules and smaller steric effect compared to the E-isomer.[17]

Table 2 Synthesis of 5*H*-benzo[*d*]imidazo[5,1-*b*][1,3]thiazines via the silver(I)-promoted tandem reaction of *o*-alkynylphenyl isothiocyanates[a]



1 **2** **3**

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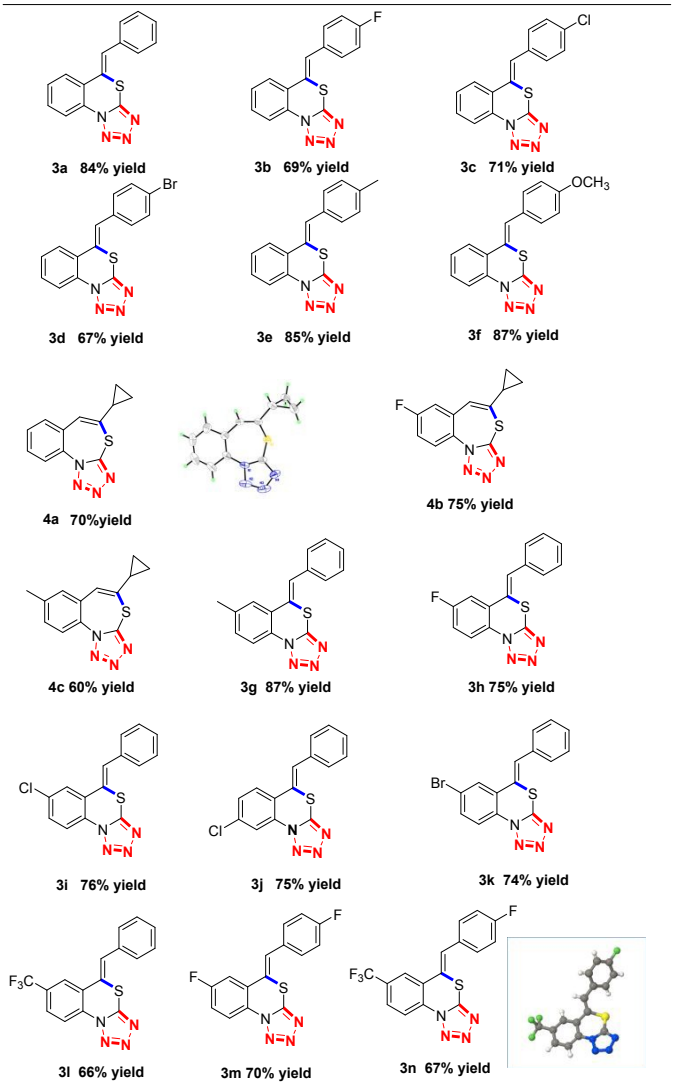
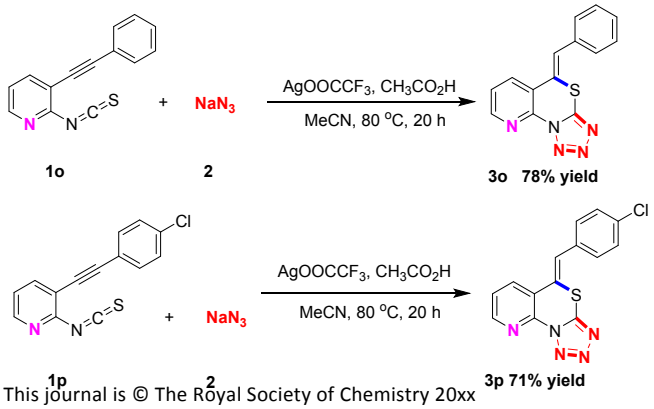


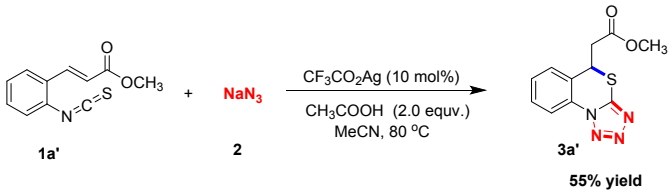
[a]Reaction was performed with *o*-alkynylphenyl isothiocyanate **1** (0.2 mmol), sodium azide **2** (0.4 mmol), CH_3COOH (0.4 mmol), $AgOOCCF_3$ (0.04 mmol) in MeCN (2 mL) under 80 ^oC for 20 h.

In order to further expand the substrate scope, we examined the reaction of 2-isothiocyanato-3-(phenylethynyl)pyridine and 3-((4-chlorophenyl)ethynyl)-2-isothiocyanatopyridine with **2** under the standard conditions (Scheme 2), the corresponding products (*Z*)-5-benzylidene-5H-pyrido[2,3-*d*]tetrazolo[5,1-*b*][1,3]thiazine (**3o**) and (Z)-5-(4-chlorobenzylidene)-5H-pyrido[2,3-*d*]tetrazolo[5,1-*b*][1,3]thiazine (**3p**) were obtained in 78% and 71% yields, respectively.



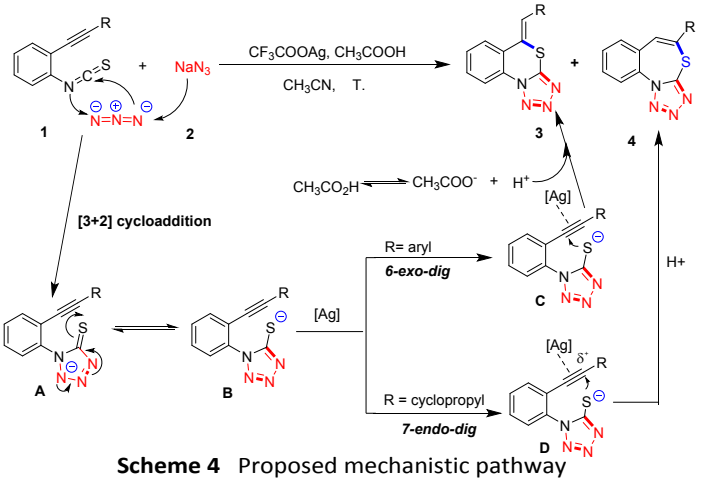
Scheme 2 Reaction of -2-isothiocyanatopyridines with **2**

Afterwards, we also examined the reaction of methyl (*E*)-3-(2-isothiocyanatophenyl)acrylate **1a'** with **2** under the standard conditions (Scheme 3). Unsuspensefully, the more activated acrylate fragment can also be carried into the reaction and the corresponding product methyl (R)-2-(5H-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazin-5-yl)acetate **3a'** was obtained in 55% yield.



Scheme 3 Reaction methyl (*E*)-3-(2-isothiocyanatophenyl) acrylate with **2**

We next focus our attention on the different cyclization modes of **1**, and a possible mechanism was proposed in Scheme 4. Firstly, the formal [3+2] cycloaddition of azido anion **2** to an isothiocyanate moiety in compound **1** would occur first to produce the intermediate **A**. Intermediate **A** could then undergo isomerization to afford intermediate **B**. Then, it appears that **R** is critical in determining the regioselectivity. When **R** was an aryl group, 6-exo-dig mode is favourable. The sulfur anion would attack the triple bond which is activated by coordination of the alkynyl moiety of **B** to the silver salt to produce the Intermediate **C.** However, when **R** was the cyclopropyl group, the electronic bias on the triple bond favours 7-endo-dig cyclization to generate Intermediate **D**. Finally, the protonation of intermediate **C** and **D** would happen to give the target products **3** and **4**.



Scheme 4 Proposed mechanistic pathway

Conclusions

In summary, we have developed an efficient method for the synthesis of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines via the silver(I)-catalyzed tandem bicyclization of o-alkynylphenyl isothiocyanates and sodium azide. Different kinds of 5*H*-benzo[*d*]tetrazolo[5,1-b][1,3]thiazines could be synthesized in

good yields. In this reaction, a [3+2] cycloaddition reaction mechanism was involved and two new rings were formed in one-pot. This present cascade bicyclization strategy represented an effective way to construct small molecular *N, S*-heterocycles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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The Silver(I)-catalyzed Cascade Bicyclization Strategy for Synthesis of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3] thiazines

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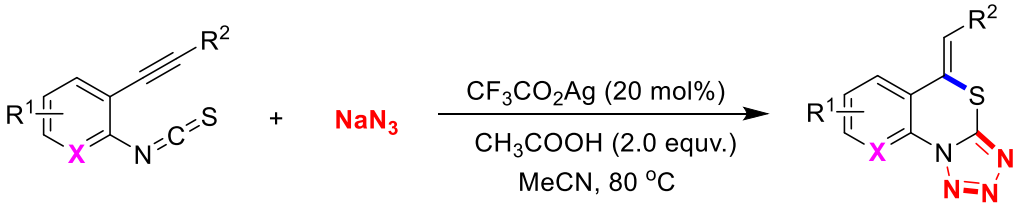

18 examples;
55%~87% yield ;
***X* = C, N;**

An efficient method for the synthesis of 5*H*-benzo[*d*]tetrazolo[5,1-*b*][1,3]thiazines via the silver(I)-catalyzed tandem bicyclization of o-alkynylphenyl isothiocyanates and sodium azide.