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Transition Metal-Free Annulation of Enamines and Tosyl Azide Toward *N*-Heterocycle Fused and 5-Amino-1,2,3-Triazoles

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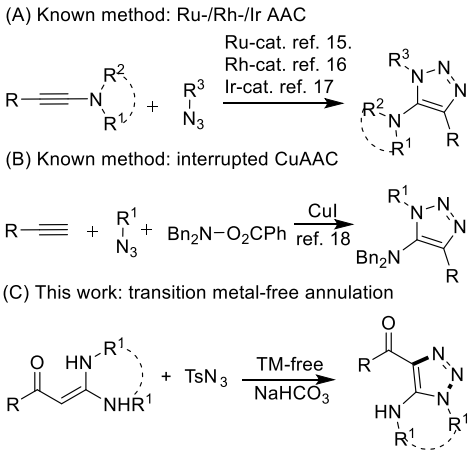
Abstract: The annulation reactions between *gem*-diamino enaminones (ketene aminals) and tosyl azide providing *N*-heterocycle fused and 5-amino side chain functionalized 1,2,3-triazoles have been developed. The synthesis of these N-side chain functionalized 1,2,3-triazoles has been executed with high efficiency and broad synthetic scope under transition metal-free conditions with the assistance of $NaHCO_3$ only.

Owing to its ubiquitous presence in molecules with biological function, organic materials as well as a variety of other application areas, the 1,2,3-triazole motif has been proven as a heterocyclic system with extraordinary importance.[1] Since the landmark works on "click"-like copper-catalyzed alkyne azide cycloaddition (CuAAC), the interest in the synthesis of 1,2,3-triazoles has received dramatic advances.[2-3] Over the recent decade, one specially notable direction in 1,2,3-triazole chemistry is the transition metal-free 1,2,3-triazole synthesis via either pure organocatalysis or other non-transition metal reagent catalyzed or promoted triazole annulation reactions.[4-5] Technically, the transition metal-free synthesis is not only more atom economical, but also better promotes application of 1,2,3-triazoles in biological research because no trace heavy metal contamination is likely to occur in the 1,2,3-triazole samples.

Among the splendid progress in the transition metal-free 1,2,3-triazole synthesis, the triazole ring formation employing enaminones or analogous stable enamines as key building blocks have been identified as particularly useful and attractive toolkit. Depending on the cleavage of different chemical bonds, highly diverse 1,2,3-triazoles, including the 1,5-disbustiuted 1,2,3-triazoles,[6] N1-H 1,2,3-triazoles,[7] ester group functionalized 1,2,3-triazoles,[8] enantiomerically pure 1,2,3-triazoles,[9] 1,4-substituted 1,2,3-triazoles,[10] fully substituted 1,2,3-triazoles[11] and sulfur side chain functionalized 1,2,3-triazoles[12] etc have been independently synthesized with efficiency. The successful application of enaminones and analogous enamines in 1,2,3-triazole synthesis, together with the versatile and featured reactivities of these stable enamines,[13] inspire us that high space remains in the designation of practical synthetic methods toward more diverse 1,2,3-triazole compounds.

On the other hand, as typical heteroatom functionalized 1,2,3-triazoles, the amino functionalized 1,2,3-triazoles have been identified to possess dramatically attractive biological relevance.[14] The synthesis of amino group substituted 1,2,3-triazoles has therefore become an important issue in 1,2,3-triazole chemistry. However, due to the low reactivity of aminoalkynes in the typical AAC reaction, synthesis of such heteroatom functionalized 1,2,3-triazoles has remined as a challenge. Only a few available synthetic methods are hitherto available. The ruthenium-catalyzed AAC reaction represents one early breakthrough in the synthesis of 5-amino-1,2,3-triazoles by employing aminoalkyne as the dipolarophile.[15] Later on, similar amino-functionalized 1,2,3-triazole synthesis have been also realized by means of rhodium catalysis[16] and iridium catalysis,[17] respectively (Scheme 1A). In addition, 5-amino-1,2,3-triazoles have been synthesized by an interesting interrupted CuAAC via the reactions of terminal alkynes, organo azides and amines (Scheme 1B).[18] Despite the success of these methods, their common feature relying on transition metal catalysis, however, has posed the urgency of developing transition metal-free approach to complement the present methodologies for the synthesis of 1,2,3-triazoles. On the basis of the amazingly diverse



Scheme 1 Methods for the synthesis of 5-amino-1,2,3-triazoles

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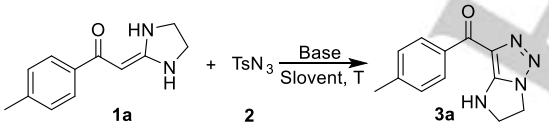
reactivity and synthetic applications of enaminones disclosed by us and others,[19] we have made extensive efforts in establishing a practical protocol toward the synthesis of 5-amino-1,2,3-triazoles via transition metal-free operation. Although some *N*-heterocycle fused 1,2,3-triazoles have been previously synthesized by employing specific fluoroalkyl functionalized sulfonyl azide or observed as side products from the cycloaddition reactions of enamines with organoazides,[20] a generally selective and applicable method for the transition metal-free synthesis of 5-amino functionalized 1,2,3-triazoles using conventional enamines is yet unavailable. Herein, we report a new transition metal-free method for synthesis of both *N*-heterocycle fused and acyclic 5-amino side chain functionalized 1,2,3-triazoles by employing *gem*-diamino enaminones and tosyl azide, wherein $NaHCO_3$ is only used to promote the reactions (Scheme 1C).

To start the work, the reaction of enamine substrate **1a** and tosyl azide **2** was investigated under different conditions. First, performing this reaction in a series of different medium, including water, DMF, DMSO, MeCN, and toluene by heating at 120 °C or reflux in the presence of tetramethyl ethylene diamine (TMEDA) proved that DMSO was amongst the most favourable reaction medium (entries 1-5, Table 1) in providing *N*- heterocycle fused 1,2,3-triazole **3a**. Afterwards, the species of base additive was screened by using NaOH, *t*-BuONa, $NaHCO_3$ and DBACO, respectively. The results indicated that $NaHCO_3$ was the best additive by affording target product with evidently higher yield (entries 6-9, Table 1). While modifying the centration of the reaction led to slight improvement on the result (entries 10-11, Table 1), the variation on the base loading led to the observation that 1.5 equiv base in the reaction provided product **3a** with further enhanced yield (entries 12-13, Table 1). The reaction conducted at different temperature, however, led to not further improved result (entries 14-16, Table 1).

Table 1. Optimization on reaction conditions[a]

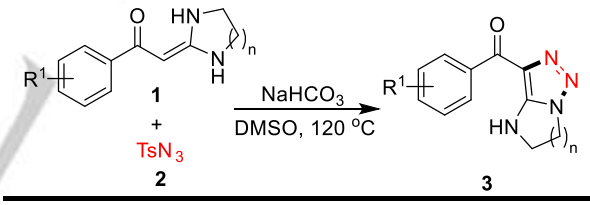


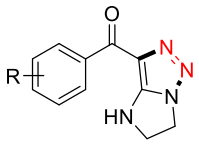
Entry	Base	Solvent	T (°C)	Yield (%)[b]
1	TMEDA	H2O	reflux	38
2	TMEDA	DMF	120	42
3	TMEDA	DMSO	120	44
4	TMEDA	MeCN	reflux	39
5	TMEDA	toluene	reflux	20
6	NaOH	DMSO	120	41
7	*t*-BuONa	DMSO	120	63
8	$NaHCO_3$	DMSO	120	74
9	DABCO	DMSO	120	55
10[c]	$NaHCO_3$	DMSO	120	77
11[d]	$NaHCO_3$	DMSO	120	59
12[c,e]	$NaHCO_3$	DMSO	120	85
13[c,f]	$NaHCO_3$	DMSO	120	66
14[c,e]	$NaHCO_3$	DMSO	130	78
15[c,e]	$NaHCO_3$	DMSO	110	71
16[c,e]	$NaHCO_3$	DMSO	100	66

[a] General conditions: **1a** (0.2 mmol), **2** (0.3 mmol), base (0.4 mmol), in solvent (2 mL) and stirred for 12 h. [b] Isolated yield. [c] In 2.5 mL DMSO. [d] In 3 mL DMSO. [e] With $NaHCO_3$ (0.3 mmol). [f] With $NaHCO_3$ (0.6 mmol).

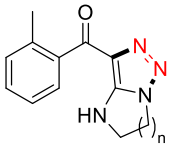
With the optimized parameters, the scope on the synthesis of the *N*-heterocycle fused 1,2,3-triazoles **3** was then examined by using diversely functionalized enamines of type **1** to react with tosyl azide **2** under the optimized conditions. As outlined in Table 2, the synthesis of fused 1,2,3-triazoles **3** via this transition metal-free annulation was identified with good application scope and generally good to excellent product yields. The enamines **1** featuring the five-membered heterocycle reacted with tosyl azide to provide corresponding products bearing alkyl, alkoxyl, halogen atom as well as trifluoromethyl substitution in the phenyl ring (**3a**-**3h**, Table 2), and strong electron withdrawing or donating group in the phenyl ring of **1** led to relatively lower product yield (**3c** and **3g**, Table 2). Analogously, the reactions employing six-membered heterocycle-based enamines could also be smoothly employed for the synthesis of six-membered hetero-ring fused 1,2,3-triazoles (**3i**, **3k**-**3q**, Table 2). Notably, alongside the fine reactions using those enamines functionalized with variously substituted phenyl ring, the fused aryl such naphthyl (**3j**-**3k**, Table 2) and heteroaryl ring (**3q**, Table 2) functionalized enamines could also take part in the synthesis of the 1,2,3-triazole products.

Table 2 Scope on the enaminone-based synthesis of N-heterocycle fused 1,2,3-triazoles[a,b]

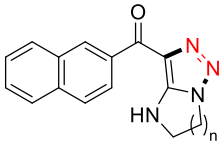




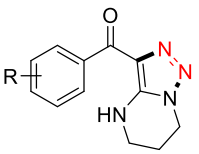
3a, R = 4-Me, 85%
3b, R = H, 77%
3c, R = 4-OMe, 51%
3d, R = 4-F, 71%
3e, R = 4-Cl, 74%
3f, R = 4-Br, 73%
3g, R = 4-CF_3, 55%



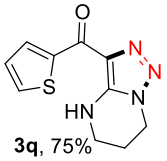
3h, n = 1, 74%
3i, n = 2, 89%



3j, n = 1, 66%
3k, n = 2, 72%



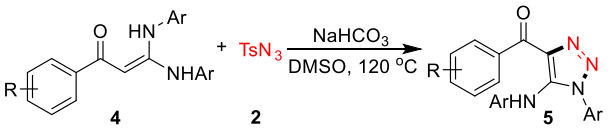
3l, R = H, 83%
3m, R = 4-Me, 80%
3n, R= 4-F, 85%
3o, R = 4-Cl, 70%
3p, R = 4-Br, 79%



3q, 75%

[a] General conditions: **1** (0.2 mmol), **2** (0.3 mmol), $NaHCO_3$ (0.3 mmol) in DMSO (2.5 mL), stirred at 120 °C for 12h. [b] Yield of isolated prouducts based on **1**.

Encouraged by the successful synthesis of the heterocycle fused 1,2,3-triazoles, we then turned to extend the synthetic scope of the reaction by employing acyclic diamino functionalized enamines **4** as alternative substrates of **1**. Delightfully, the reactions of **4** with tosyl azide proceeded efficiently under the standard conditions to provide 5-amino functionalized 1,2,3-triazoles **5**. As shown in Scheme 2, the synthesis of 1,2,3-triazoles **5** containing a series of different functional groups such as methyl, methoxyl, halogen and nitro group in the *N*-aryl or the ketone aryl segment were provided with moderate to good yield, further illustrating the advantageous application of this transition metal-free protocol in the synthesis of nitrogen side chain functionalized 1,2,3-triazoles with exceptional product diversity. According to the present data, the substituent in both the ketone aryl and the aryl ring connected to the amino group didn't show regular influence to the reaction results.

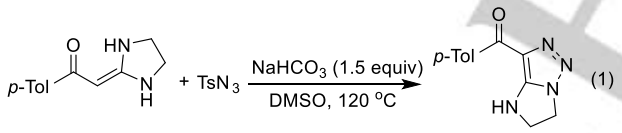


4 2 5

5a, R = 4-Me, Ar = Ph, 74% **5b**, R = H, Ar = p-tolyl, 80%
5c, R = H, Ar = 3-MeC_6H_4, 62% **5d**, R = H, Ar = 4-MeOC_6H_4, 69%
5e, R = H, Ar = 4-ClC_6H_4, 75% **5f**, R = H, Ar = 4-BrC_6H_4, 66%
5g, R = 4-Me, Ar = 4-$NO_2C_6H_4$, 45%

Scheme 2 Scope on the metal-free synthesis of 5-amino-1,2,3-triazoles

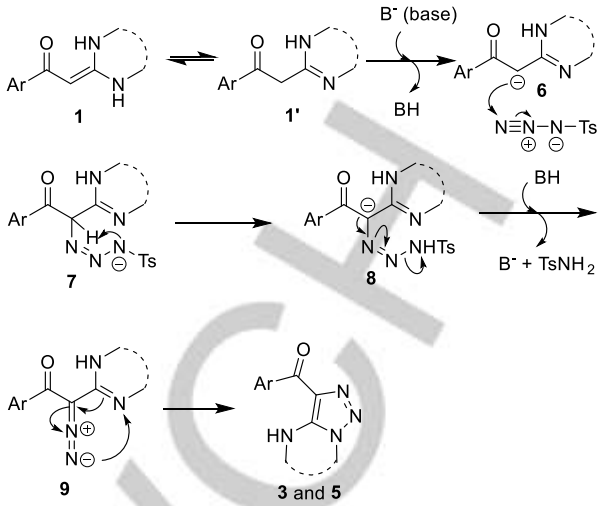
Following the work in scope examination, the gram scale synthesis on the model reaction was carried out. Notably, the 5 mmol scale reaction under the standard reaction condition led to the synthesis of **3a** with high yield of 70% (Eq 1), proving the applicability of the present method in the synthesis of the functional 1,2,3-triazoles with large amount.



5 mmol, 1.01 g 7.5 mmol, 1.48 g **3a**, 0.8 g, 70 %

Based on the results from the experiments, the possible mechanism of this 1,2,3-triazole annulation is proposed. As presented in Scheme 3, the reaction of enamine **1** and a base provides cation intermediate **6** via the isomeric form **1'**. The addition of **6** to tosyl azide gives rise to intermediate **7** which can further transform into **8** via proton migration. A typical Regitz diazo transfer[21] taking place on **8** in the presence of base then affords diazo intermediate **9**. The N-N bond formation initiated intramolecular annulation on **9** then leads to the production of 1,2,3-triazoles **3** and **5**.

In conclusion, by employing the readily available diamino functionalized enamines to react with tosyl azide, the annulation leading to 1,2,3-triazole ring has been realized with only $NaHCO_3$ promotion based on a featured Regitz diazo transfer process. This synthetic method involving the C(sp^2)-N and N-N bond formation



Scheme 3 The proposed reaction mechanism

has exhibited broad application scope in the synthesis of both *N*-heterocycle fused 1,2,3-triazoles and 5-amino-1,2,3-triazoles. Besides offering a reliable transition metal-free route the useful 1,2,3-triazole scaffolds, the present work discloses further the high potential of enamines in the designation of valuable and sustainable methods of synthesis.

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Keywords: enamine • tosyl azide • transition metal-free • *N*-side chain • 1,2,3-triazole

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1,2,3-Triazole synthesis

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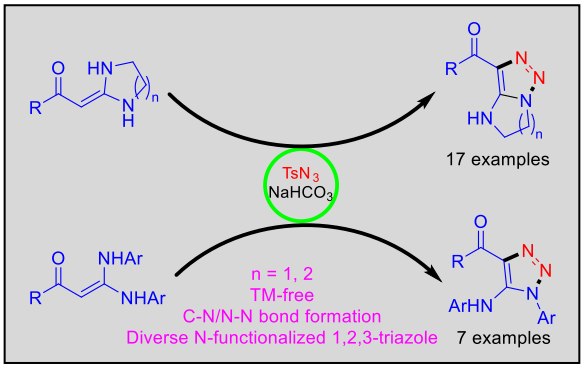

The synthesis of versatile 5-amino functionalized 1,2,3-triazoles, both in the forms of N-heterocycle fused and acyclic amino group functionalized forms, have been realized via the annulation reactions of *gem*-diamino enaminones and tosyl azide under transition metal-free conditions.