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Syntheses of quinazolinones from 2-iodobenzamides and enaminones *via* copper-catalyzed domino reactions†

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N-Substituted 2-iodobenzamides and enaminones undergo cascade transformations to achieve quinazolinones *via* a copper-catalyzed Ullmann-type coupling, a Michael addition and a retro-Mannich reaction. A unique stereochemical feature of this domino process was that *Z*-enaminones reacted without external ligands, whereas *E*-enaminones required the assistance of ligands.

Transition metal-catalyzed domino reactions have been one of the most selective tools for synthesizing complex organic molecules.[1] Especially, the copper-catalyzed Ullmann N-arylation[2] has been a powerful strategy for constructing N-containing heterocycles.[3] Quinazolinones are one of the most important N-containing heterocyclic compounds due to their common occurrence in alkaloid natural products.[4] Furthermore, they also show a variety of biological activities.[5] Therefore, a number of methodologies have been developed towards quinazolinone synthesis.[6]

Recently, Fu described a remarkable domino synthesis of quinazolinone derivatives *via* an Ullmann-type coupling followed by aerobic oxidation, starting from 2-halobenzamides and amines.[7] This system provided a powerful synthetic tool to synthesize aromatic-substituted quinazolinones (Fig. 1a). Later, Ma also reported the elegant domino reactions of 2-bromobenzamides and amides catalyzed by Cu(I), to facilitate aryl amidation followed by dehydration.[8] In Ma's system, a variety of substituted quinazolinones were possible. However, cyclization with the use of HMDS/$ZnCl_2$ was required (Fig. 1b). We have undertaken studies aimed specifically at copper-catalyzed domino reactions to produce N-containing heterocyclic compounds under mild and simple reaction conditions. During our studies, we found that N-substituted 2-iodobenzamides and enaminones could undergo domino processes in the presence of CuI to furnish quinazolinone derivatives (Fig. 1c). In our catalytic system, the enaminone serves as a stable surrogate of an unstable imine equivalent, to construct the quinazolinone core structure in one cascade process. We believe that the enaminone could be a synthetically useful coupling partner in Ullmann-type reactions for the synthesis of N-containing heterocyclic molecules. Furthermore, a variety of enaminones have been readily prepared from the condensation reactions of nitrogen sources and 1,3-diketone compounds.[9]

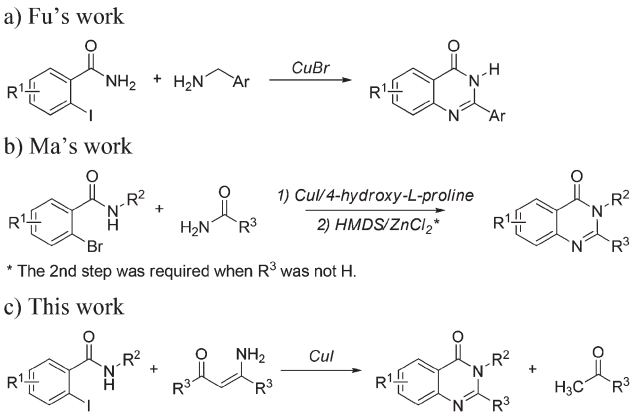

Fig. 1 Copper-catalyzed domino reactions for quinazolinone synthesis.

To investigate our reaction, we initially began with reaction optimization. *N*-Benzyl-2-iodobenzamide (**1a**), (*Z*)-4-aminopent-3-en-2-one (**2a**), and the use of CuI as the catalyst were selected as the model system (Table 1). The reaction's outcome depended on the nature of the base, and the use of K_2CO_3 gave no reaction (entry 1). However, quinazolinone **3** was obtained in 14% yield by changing the base from K_2CO_3 to Cs_2CO_3 under otherwise identical conditions (entry 2). 2-Iodobenzamide **1a** was completely consumed when the reaction was carried out at 90 °C, and gave the highest yield (entry 3). The effects of the solvent were also investigated, and CH_3CN was chosen as the optimal solvent (entries 3–5). An investigation for finding the optimal source of copper was undertaken (entries 3, 6, 7 and 8), revealing that CuI was the most suitable for this domino transformation. Interestingly, in the presence

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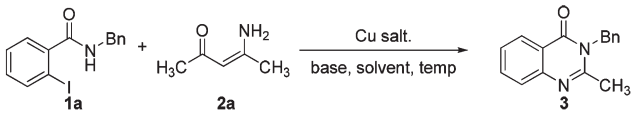
Table 1 Copper-catalyzed domino reactions of *N*-benzyl 2-iodobenzamide (**1a**) and enaminone (**2a**): optimization of reaction conditions[a]



Entry	Cu salt	Base	Solvent	Temp (°C)	Yield[b] (%)
1	CuI	K_2CO_3	CH_3CN	60	0
2	CuI	Cs_2CO_3	CH_3CN	60	14
3	CuI	Cs_2CO_3	CH_3CN	90	78
4	CuI	Cs_2CO_3	DMSO	90	49
5	CuI	Cs_2CO_3	DMF	90	56
6	CuCl	Cs_2CO_3	CH_3CN	90	62
7	CuBr	Cs_2CO_3	CH_3CN	90	50
8	$Cu(OAc)_2$	Cs_2CO_3	CH_3CN	90	46
9	CuI + (L-proline)[c]	Cs_2CO_3	CH_3CN	90	51

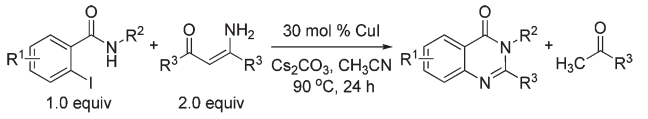
[a] Reaction conditions: all reactions were performed with 0.3 mmol of **1a**, 30 mol% of Cu salt, 2.0 equiv. of **2a**, 2.5 equiv. of base, and 3.0 mL of solvent, for 24 h. [b] Isolated yield. [c] Reaction was performed with 30 mol% of L-proline.

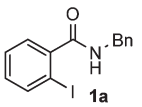
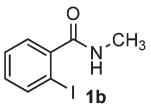
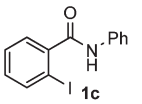
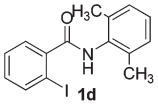
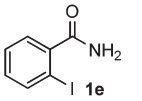
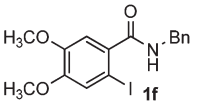
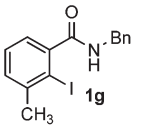
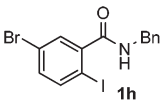
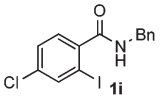
of L-proline as a ligand, the reaction gave a lower yield (entry 9). Based on this result, we believe that **2a** played not only the role of a substrate but also as a ligand for this transformation, corresponding to a recent finding from Liu.[10] Note that, 2.0 equiv. of **2a** were crucial to promoting the highest product yields. The use of 1.0 equiv. of **2a** with 30 mol% L-proline and without L-proline under the optimal conditions gave 31% and 36% yields respectively.

After the optimized conditions had been established, the scope of the substrates in the copper-catalyzed domino reactions was investigated. A variety of N-substituted benzamides and enaminones were applicable for the copper-catalyzed domino reactions (Table 2). As the size of the substituents on the enaminones increased, the yields of corresponding quinazolinones were dramatically diminished (entry 1, compounds **3–5**), demonstrating that steric hindrance, especially the substituents on the enaminones, played a crucial role in determining the product yields.

On the other hand, the enaminones with aryl substituents were efficiently converted to the corresponding quinazolinones (entry 1, compounds **6** and **7**). *N*-Phenyl substituted benzamides (**1c** and **1d**) gave low yields due to their low nucleophilicities for Michael additions. In addition, the comparable yields of **12** and **14** suggested that the steric hindrance of the *N*-phenyl substituted benzamides had a minor impact on the reactions (entries 3 and 4). Moreover, the moderate yield from the reaction of **1e**, a naked amide, and a phenyl-substituted enaminone suggested that the nucleophilicity of the amide nitrogen dictated the product yield (entry 5). *N*-Benzyl-2-iodobenzamide (**1f**), with electron-donating substituents on the aromatic ring, was compatible in the domino reaction (entry 6). However, the reaction of *N*-benzyl-3-methyl-2-iodobenzamide (**1g**) gave a low yield (entry 7). The results indicated that accessibility to the C–I bond was vital. The Br-substituted quinazolinones, derived from *N*-benzyl-5-bromo-2-iodobenzamide

Table 2 CuI-catalyzed domino syntheses of quinazolinones from 2-iodobenzamides and *Z*-enaminones[a]

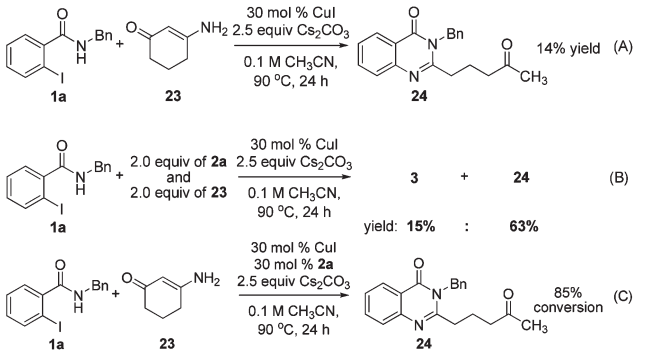


Entry	2-Iodobenzamides	Quinazolinones (% yield)[b]
1	 **1a**	**3**: $R^3 = CH_3$ (78%) **4**[c]: $R^3 = i$-Pr (30%) **5**[d]: $R^3 = i$-Bu (35%) **6**: R^3 = Ph (71%) **7**: $R^3 = p$-OCH_3-Ph (50%)
2	 **1b**	**8**[c]: $R^3 = i$-Pr (25%) **9**: R^3 = Ph (70%) **10**: $R^3 = p$-OCH_3-Ph (65%)
3	 **1c**	**11**[c]: $R^3 = i$-Pr (34%) **12**: R^3 = Ph (30%)
4	 **1d**	**13**: $R^3 = CH_3$ (53%) **14**: R^3 = Ph (35%)
5	 **1e**	**15**: R^3 = Ph (48%)
6	 **1f**	**16**: $R^3 = CH_3$ (38%) **17**[c]: $R^3 = i$-Pr (35%) **18**: R^3 = Ph (73%)
7	 **1g**	**19**: R^3 = Ph (34%)
8	 **1h**	**20**: $R^3 = CH_3$ (20%) **21**: R^3 = Ph (45%)
9	 **1i**	**22**[d]: $R^3 = i$-Bu (54%)

[a] Reaction conditions: all reactions were carried out with 0.5 mmol of 2-iodobenzamides, and 2.5 equiv. of Cs_2CO_3, in 0.1 M CH_3CN. [b] Isolated yield. [c] 3-Amino-4-methyl-1-phenylpent-2-en-1-one was used. [d] 3-Amino-5-methyl-1-phenylhex-2-en-1-one was used.

(**1h**), were isolated in low to moderate yields, showing that **1h** was fairly tolerant of this catalytic system (entry 8). It is noteworthy that the Cl-substituted quinazolinone (**22**), a precursor of the Ispinesib synthesis reported by Holland,[11] was generated smoothly and in a moderate yield (entry 9).

Next, we turned our interest to the effects of the geometries of the enaminones. *E*-Enaminones would serve as better nitrogen nucleophiles than *Z*-enaminones, since they lack intramolecular H-bonding. Surprisingly, when 3-aminocyclohex-2-enone (**23** as the *E*-enaminone representative) was subjected to the reaction conditions, the corresponding quinazolinone was



Scheme 1 (A) The CuI-catalyzed domino reaction of **1a** and **23**. (B) The comparison reaction between **2a** and **23**. (C) The CuI-catalyzed domino reaction with **2a** as a ligand.

obtained in low yield (Scheme 1, (A)). The results gave us a clue about the geometrically-dependant reactivities of the two types of enaminones.

Interestingly, exposure of **1a** with a mixture of enaminones, **2a** and **23** (2.0 equiv. each), under standard conditions, gave quinazolinones **3** and **24** in 15% and 63% yields respectively (Scheme 1, (B)). Based on the results, the *E*-enaminone exhibited a better reactivity than the *Z*-enaminone in the cascade process, demonstrating that the domino reaction of the 2-iodobenzamides and the *E*-enaminones required the assistance of the *Z*-enaminone, in which we believe that **2a** played the role of a ligand. To emphasize the ligand requirement, 30 mol% of **2a** was used as a ligand, resulting in the facile domino transformation of **1a** and **23** to afford **24** with 85% conversion (Scheme 1, (C)).

We were delighted to find that L-proline was a compatible ligand, albeit we have not thoroughly explored a variety of ligands. After further optimization of the reaction of **1a** and **23**, the use of 10 mol% CuI, 20 mol% L-proline, and 2.5 equiv. Cs_2CO_3, in 0.1 M CH_3CN, with a reaction temperature of 90 °C were identified as the optimal conditions.

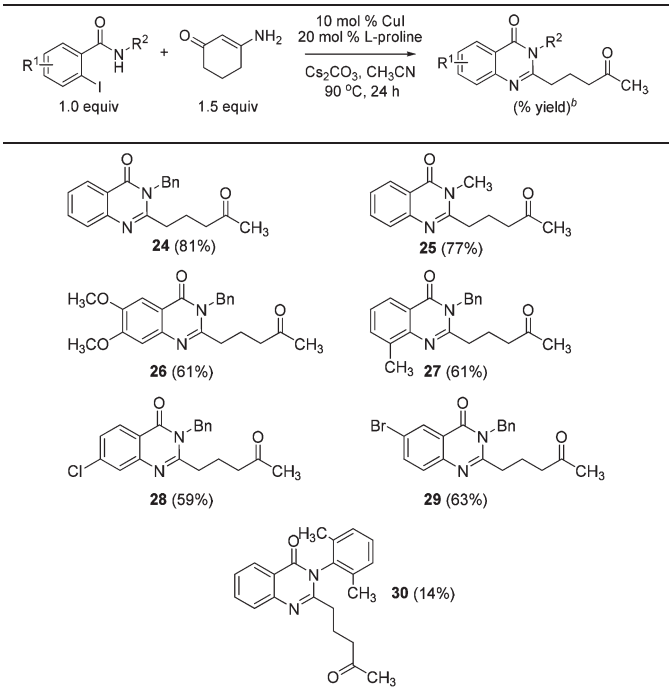
As we expected, better nucleophiles allowed us to lower the catalyst loading to 10 mol%, along with the amount of enaminones. Although we have not exhaustively explored the scope for this reaction, we found that **23** could be coupled with a variety of *N*-substituted 2-iodobenzamides with moderate to good yields (Table 3, compounds **24–29**). The results showed that the electronic effects of the aromatic rings of the 2-iodobenzamides had only a minor impact on the reactions. On the other hand, the reaction of **1d** and **23** gave a low yield (Table 3, compound **30**), indicating that steric hindrance and the effect of the aryl substituent greatly affected the reaction. We were pleased to discover that the domino transformation of **23** was possible, as being a surrogate of a hydrocarbon chain, with a ketone functionality, it could be further functionalized.

The possible mechanism of the quinazolinone syntheses from 2-iodobenzamides and enaminones was postulated *via* a domino process, an Ullmann-type coupling, an intramolecular Michael addition, and a retro-Mannich reaction. The last two steps were proposed according to the condensation of anthranilamides and 1,3-diketones.[12] Along with the mechanistic study of copper-catalyzed arylation of nucleophiles,[13] the complexation of ligands and Cu(I) was crucial, allowing the coupling reaction to occur smoothly at a low temperature.[14] Our initial mechanism involves the association of Cu(I) and the *Z*-enaminone to generate the active Cu(I) complex **I**,[10] which undergoes an Ullmann-type coupling to form the N-arylation intermediate, **III**, under relatively mild coupling conditions due to the *ortho*-substitution effect performed by the N-substituent.[15] Subsequently, the intramolecular Michael addition of **III** takes place to form the dihydroquinazolinone intermediate **IV**, followed by the retro-Mannich reaction to produce the quinazolinone and to expel acetone (Scheme 2A).

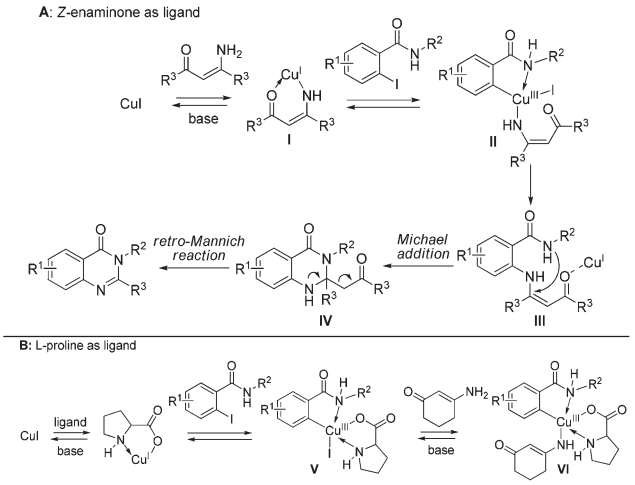
Although the geometries of the enaminones affect the reactions, we believe that both geometries undergo domino processes with the same reaction mechanisms. *Z*-Enaminones are promoted with the possible mechanism shown in Scheme 2A. On the other hand, in the case of *E*-enaminones (Scheme 2B), L-proline plays the role of a ligand in the copper-catalyzed Ullmann-type coupling, as remarkably described by Ma.[16] The *E*-enaminone, **23**, acts as the nitrogen nucleophile to form complex **VI**, and then undergoes reductive elimination to generate the N-arylation intermediate followed by the sequential mechanisms described in Scheme 2A, revealing the pendant ketone functionality.

In order to explore the sequence of the reactions, attempts to detect the intermediates described in the proposed mechan-

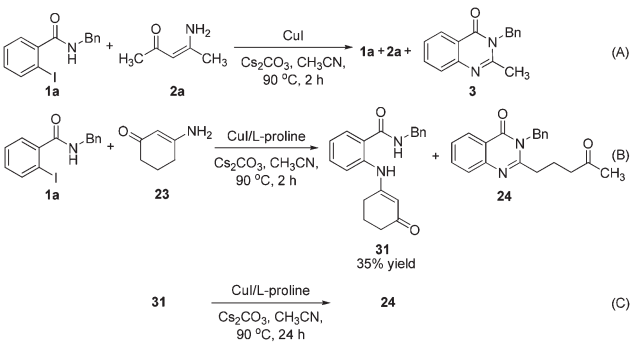
Table 3 CuI-catalyzed domino syntheses of quinazolinones from 2-iodobenzamides and 3-aminocyclohex-2-enone[a]



[a] Reaction conditions: all reactions were carried out with 0.5 mmol of 2-iodobenzamides, and 2.5 equiv. of Cs_2CO_3, in 0.1 M CH_3CN. [b] Isolated yield.



Scheme 2 Possible mechanism for the domino syntheses of quinazolinones *via* CuI-catalyzed Ullmann-type coupling.



Scheme 3 Mechanism investigation experiments.

ism were applied. Stopping the reaction of **1a** and **2a** prior to completion revealed a 1 : 1 ratio of **1a** and **3** (Scheme 3, (A)), as identified by the ^{1}H NMR spectrum of the crude mixture. None of the expected intermediates were obtained. In contrast, the exposure of **1a** and **23** to the standard reaction conditions for 2 h resulted in a complete consumption of **1a**, and the N-arylation intermediate **31** was isolated in a 35% yield (Scheme 3, (B)). **31** was then smoothly converted to **24** under the standard conditions (Scheme 3, (C)), indicating that the first transformation of the domino process was the copper-catalyzed N-arylation, supporting our proposed mechanism. Although we did not perform a study of the isotope effects, based on our findings, the detection of a stable intermediate, which accumulated after the Ullmann-type coupling, implied that the rate-determining step of the domino reaction of **1a** and **23** was possibly the intramolecular Michael addition.

Conclusions

We have demonstrated domino syntheses of quinazolinone derivatives *via* a copper-catalyzed Ullmann-type coupling, an intramolecular Michael addition and a retro-Mannich reaction, under mild and simple reaction conditions. The geometry of the double bonds in the enaminones played an important role in the reactions. *Z*-Enaminones could undergo sequential reactions without the addition of any external ligands. On the other hand, *E*-enaminones showed better reactivity, but required the assistance of ligands. Furthermore, the two major contributions to the reaction were the steric hindrance of the enaminones and the nucleophilicities of the amide nitrogens. Although the product yields suffered from steric hindrance, our method provides a variety of quinazolinones from one-pot syntheses using simple enaminones. Further applications of the reaction and a study of the reaction mechanism are ongoing.

Acknowledgements

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