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Copper-Catalyzed Cascade Syntheses of 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones and Quinoxalin-2(1*H*)-ones through Capturing S and N Atom Respectively from AcSH and $TsNH_2$

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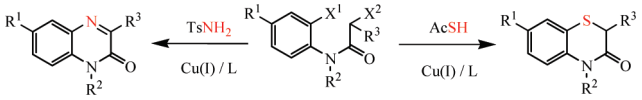

A copper-catalyzed cascade method has been developed to synthesize the 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones from 2-halo-*N*-(2-halophenyl)-acetamides **1** and AcSH via the S_N2/deacetylation/coupling process, and to synthesize the quinoxalin-2(1*H*)-ones from **1** and $TsNH_2$ via the S_N2/coupling/desulfonation process. The target products were obtained with diversity at three positions on their scaffolds.

In the past few years, copper-mediated formation of aryl C−N and C−S bonds via Ullmann-type coupling reaction has drawn considerable attention for their efficiency and low cost.[1] Recently, the copper-catalyzed coupling has been successfully applied to the assembly of various heterocyclic compounds by one-pot strategies. Many Cu(I)-catalyzed cascade methods involving *N*-arylation have been reported for the synthesis of *N*-heterocycles, including pyrrole, indole, benzimidazole, 1,3-dihydrobenzimidazol-2-one, isoquinoline, isoquinolin-1(2*H*)-one, quininazoline, quinazolinone, 3,4-dihydro-2*H*-1,4-benzoxazine, 1,4-benzodiazepin-3-one, etc.[2] However, little report was found about the construction of *S*-heterocycles via a one-pot copper-catalyzed *S*-arylation process except for benzothiazole.[3] The reason may be that the thiols are prone to be oxidized dimerization or complexed with metals, causing reduced catalytic efficiency. Therefore, searching for a new sulfur reagent to apply it to the cascade construction of *S*-heterocycles would be a research topic worthy of study.

2*H*-Benzo[*b*][1,4]thiazin-3(4*H*)-one and quinoxalin-2(1*H*)-one are important heterocycle scaffolds that display a wide range of bioorganic and medicinal activities. For example, 2*H*-benzo[*b*][1,4]-thiazin-3(4*H*)-one derivatives act as antimicrobial, anticancerous, immunostimulating, angiotensin converting enzyme, aldose reductase inhibitors, and antidiabetic, antiarrhythmic inhibitors (Figure 1).[4] Quinoxalin-2(1*H*)-ones show antithrombotic, antitumor activity (Figure 1) and are used as antimicrobial agents, kinases inhibitors, benzodiazepine receptor agonist, etc.[5]

Some methods have been developed for the syntheses of 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones[6] and quinoxalin-2(1*H*)-ones.[7] The classical synthesizing approaches of 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones are based on using 2-aminobenzenethiols or halonitrobenzenes as starting materials, which are cyclized directly by reacting with acetyl halide, or substituted by thiol acetates and reduced to form a ring system. Recently, Zuo and co-workers used 2-chlorobenzenthiols to synthesize 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones via Smiles

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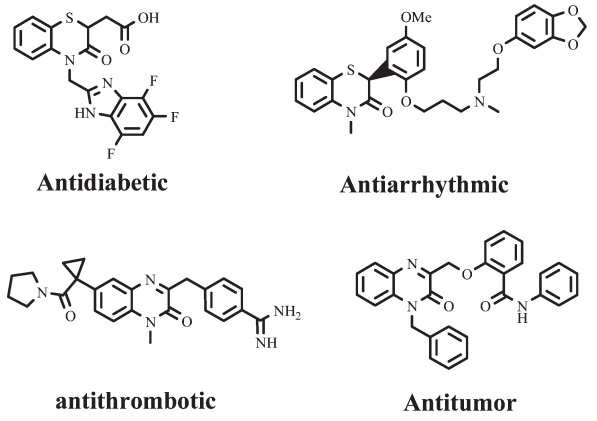


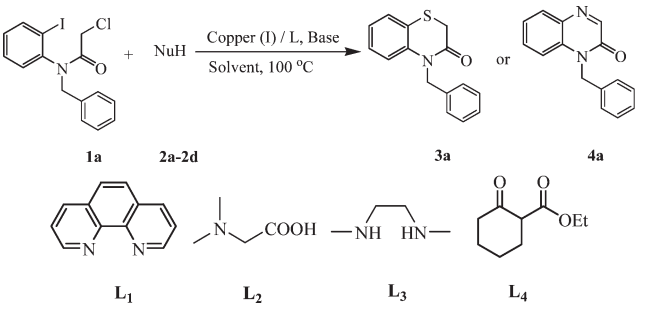
FIGURE 1. Structures of some pharmaceutically important 2*H*-benzo- [*b*][1,4]thiazin-3(4*H*)-one and quinoxalin-2(1*H*)-one derivatives.

rearrangement. Quinoxalin-2(1*H*)-ones can be obtained through condensing substituted *o*-phenylenediamine with α-ketone acids, α-aldehyde acids, α-ketone acid esters, or α-aldehyde acid esters. Although these methods for the synthesis of the title heterocycles are feasible, they have two common disadvantages: (i) The substituted group diversification of products is limited, for example, it is difficult to synthesize *N*-aryl substituted products. (ii) The substituted products were obtained in low yields because of multistep reaction or multiple byproduct. Therefore, it is highly desirable to search for more convenient and efficient approaches for these two heterocycles.

AcSH and $TsNH_2$ are the common nucleophilic reagents, which are prone to S_N2 reaction. Ac and Ts groups are also the leaving groups. Therefore, they can provide S and imine N atoms for building heterocycles. However, to the best of our knowledge, there is no report about the formation of *N*- or *S*-heterocycle via copper-catalyzed one-pot strategies using this idea. As a part of our ongoing research in developing copper-catalyzed tandem reaction methods for the syntheses of heterocycles,[8] we were further interested in developing new protocols for the syntheses of 2*H*-benzo[*b*]-[1,4]thiazin-3(4*H*)-ones and quinoxalin-2(1*H*)-ones in one pot. Herein, we report a Cu(I)-catalyzed domino strategy, which employs 2-halo-*N*-(2-halophenyl)acetamides as precursors to react with AcSH to synthesize 2*H*-benzo[*b*]-[1,4]thiazin-3(4*H*)-ones via the S_N2/deacetylation/coupling process, or to react with $TsNH_2$ to synthesize quinoxalin-2(1*H*)-ones via the S_N2/coupling/desulfonation process. The target products were obtained with diversity at three positions on their scaffold.

The reaction between *N*-benzyl-2-chloro-*N*-(2-iodophenyl)-acetamide (**1a**) and AcSH (**2a**) or $TsNH_2$ (**2b**) was investigated to optimize the reaction conditions, including bases, solvents, ligands, and catalysts. The results are summarized in Table 1. Initially, according to our previously reported experiment for the synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones,[8d] we adopted the same reaction condition (10 mol % CuI, 20 mol % 1,10- phenanthroline, Cs_2CO_3 in dioxane) to

TABLE 1. Optimization of the Reaction Conditions for Synthesis of 4-Benzyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one or 1-Benzylquinoxalin-2(1*H*)-one[a]



entry	NuH	cat.	L	base	solvent	yield (%)
1	AcSH (**2a**)	CuI	L_1	Cs_2CO_3	dioxane	83
2	AcSH	CuI	L_1	K_2CO_3	dioxane	40
3	AcSH	CuI	L_1	Cs_2CO_3	toluene	72
4	AcSH	CuI	L_1	Cs_2CO_3	DMF	55
5	AcSH	CuI	L_1	Cs_2CO_3	dioxane	23[b]
6	$TsNH_2$ (**2b**)	CuI	L_1	Cs_2CO_3	dioxane	89[c]
7	$TsNH_2$	CuI	L_2	Cs_2CO_3	dioxane	52[c]
8	$TsNH_2$	CuI	L_3	Cs_2CO_3	dioxane	73[c]
9	$TsNH_2$	CuI	L_4	Cs_2CO_3	dioxane	70[c]
10	$TsNH_2$	CuBr	L_1	Cs_2CO_3	dioxane	83[c]
11	$TsNH_2$	Cu_2O	L_1	Cs_2CO_3	dioxane	81[c]
12	$TsNH_2$	$Cu(OAc)_2$	L_1	Cs_2CO_3	dioxane	62[c]
13	$BocNH_2$ (**2c**)	CuI	L_1	Cs_2CO_3	dioxane	-[c]
14	$PhCONH_2$ (**2d**)	CuI	L_1	Cs_2CO_3	dioxane	-[c]
15	$BnNH_2$ (**2e**)	CuI	L_1	Cs_2CO_3	dioxane	-[c]

[a]Reaction conditions: *N*-benzyl-2-chloro-*N*-(2-iodophenyl)acetamide **1a** (0.5 mmol), **2a**−**e** (0.6 mmol), copper source (0.05 mmol), ligand (0.1 mmol), and base (2.0 mmol) in solvent (2.0 mL) under N_2 at 100 °C for 13 h. [b]50 °C, 36 h. [c]18 h.

study the synthesis of 4-benzyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one **3a**. Luckily, a satisfactory result was found, and the yield of product **3a** reached 83% (entry 1). Both base and solvent were tested. The yield was decreased greatly as the base K_2CO_3 was selected (entry 2). The other solvents, toluene and DMF, were also inferior to dioxane. Subsequently, we investigated the optimum reaction condition for the synthesis of 1-benzylquinoxalin-2(1*H*)-one **4a**. Except that the reaction time was extended to 18 h, the same reaction condition also provides the highest yield of product **4a** (89%, entry 6). Despite the good result, three other ligands (L_2−L_4), including *N*,*N*-dimethylglycine, DMEDA, and ethyl 2-oxocyclohexanecarboxylate, were evaluated (entries 7−9), and 1,10-phenanthroline was proved to be the most effective. Cu-catalysts were also examined (entries 10−12), and the others (CuBr, Cu_2O, $Cu(OAc)_2$) were poorer than CuI. Finally, the reactions between **1a** and different NuH reagents were investigated, but no target products were observed (entries 13−15).

We then investigated the scope of copper-catalyzed coupling of the substituted 2-halo-*N*-(2-halophenyl)acetamide with AcSH for the synthesis of 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones under the optimized conditions determined above. As shown in Table 2, most of the substrates examined provided good to excellent yields. For the variation of *N*-substituted group R^2 in 2-chloro-*N*-(2-iodophenyl)acetamide, we found allyl and methyl groups did not significantly affect the yield of target products, compared with benzyl group (entries 1 and 2), but phenyl and H groups gave the corresponding

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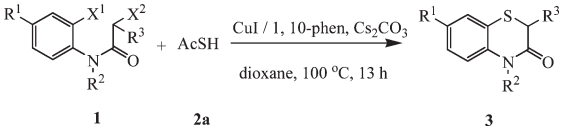
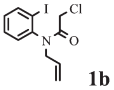
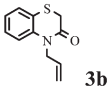
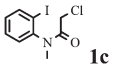
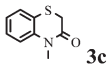
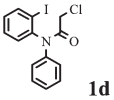
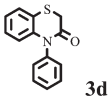
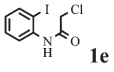
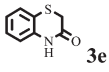
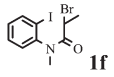
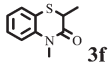
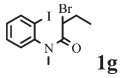
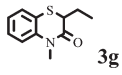
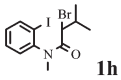
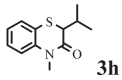
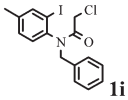
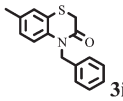
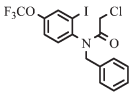
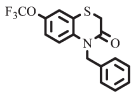
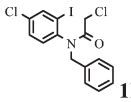
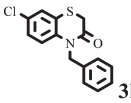
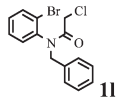
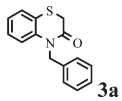
TABLE 2. CuI-Catalyzed One-Pot Synthesis of 2*H*-Benzo[*b*][1,4]thiazin-3(4*H*)-one from 2-Halo-*N*-(2-halophenyl)acetamide and AcSH[a]



1 2a 3

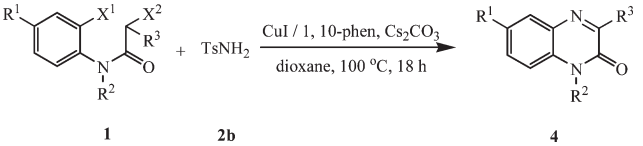
Entry	1	Product	Yield (%)
1	 **1b**	 **3b**	86
2	 **1c**	 **3c**	92
3	 **1d**	 **3d**	60
4	 **1e**	 **3e**	51
5	 **1f**	 **3f**	93
6	 **1g**	 **3g**	94
7	 **1h**	 **3h**	89
8	 **1i**	 **3i**	86
9	 **1j**	 **3j**	81
10	 **1k**	 **3k**	78
11	 **1l**	 **3a**	55[b]

[a]Reaction conditions: 2-halo-*N*-(2-halophenyl)acetamide **1** (0.5 mmol), AcSH **2a** (0.6 mmol), CuI (0.05 mmol), ligand (0.1 mmol), and Cs_2CO_3 (2.0 mmol) in dioxane (2.0 mL) under N_2 at 100 °C for 13 h. [b]At reflux.

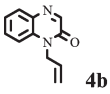
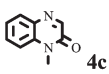
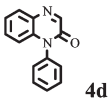
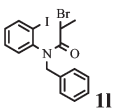
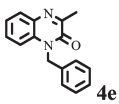
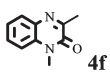
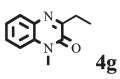
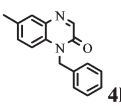
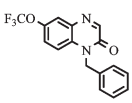
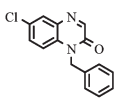
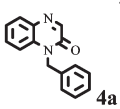
products in moderate yield (entries 3 and 4, 60% and 51%, respectively). In the presence of R^3 (Me, Et, *i*-Pr) groups, the yields of **3f**, **3g**, and **3h** were also excellent (entries 5−7). The substrates with an electron-donating group on the phenyl ring exhibited higher reactivity than the others with electron-withdrawing groups (entries 8−10). In addition, *N*-benzyl-2-chloro-*N*-(2-bromophenyl)acetamide **1l** could react with AcSH to give the product **3a** in moderate yield.

The scope of the copper-catalyzed cascade synthesis of quinoxalin-2(1*H*)-ones from substituted 2-halo-*N*-(2-halophenyl)acetamide with $TsNH_2$ was also investigated (Table 3, entries 1−10). Most of the quinoxalin-2(1*H*)-ones could be obtained in good yields under the optimized conditions (10 mol % CuI, 20 mol % 1,10-phenanthroline, Cs_2CO_3 in dioxane, 100 °C, 18 h). Among the examination of the *N*-substituted group of 2-chloro-*N*-(2-iodophenyl)acetamide, the *N*-allyl substrate gave lower yield of product than the others (entries 1−3). Comparing the yield of **4c** with that of **4f** and **4g**, it was obvious that the R^3 group showed a little stereohindrance effect. The electronic effect of the substituents on the aromatic rings of 2-halo-*N*-(2-halophenyl)acetamide was also investigated. The presence of an electron-donating group provided better yield

TABLE 3. CuI-Catalyzed One-Pot Synthesis of Quinoxalin-2(1*H*)-ones from 2-Halo- *N*-(2-halophenyl)acetamide and $TsNH_2$[a]

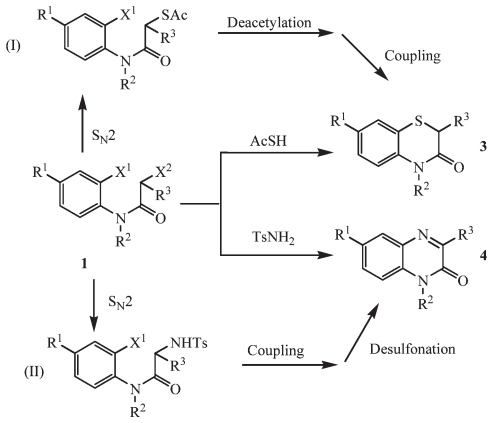


1 2b 4

Entry	1	Product	Yield (%)
1	**1b**	 **4b**	72
2	**1c**	 **4c**	86
3	**1d**	 **4d**	81
4	 **1l**	 **4e**	52
5	**1f**	 **4f**	72
6	**1g**	 **4g**	75
7	**1i**	 **4h**	85
8	**1j**	 **4i**	76
9	**1k**	 **4j**	45
10	**1l**	 **4a**	78[b]

[a]Reaction conditions: 2-halo-*N*-(2-halophenyl)acetamide **1** (0.5 mmol), $TsNH_2$ **2b**(0.6 mmol), CuI (0.05 mmol), ligand (0.1 mmol), and Cs_2CO_3 (2.0 mmol) in dioxane (2.0 mL) under N_2 at 100 °C for 18 h. [b]At reflux

SCHEME 1. Proposed Reaction Pathways for the One-Pot Syntheses of 2*H*-Benzo[*b*][1,4]thiazin-3(4*H*)-ones and Quinoxalin-2(1*H*)-ones



than the presence of electron-withdrawing groups (entries 7−9). Additionally, 1-benzylquinoxanlin-2(1*H*)-one could be obtained from the reaction of *N*-benzyl-2-chloro-*N*-(2-bromophenyl)-acetamide **1l** with $TsNH_2$ in good yield (entry 10).

The possible formation pathways for 2*H*-benzo[*b*]-[1,4]thiazin-3(4*H*)-ones and quinoxalin-2(1*H*)-ones are proposed in Scheme 1 on the basis of the reported literature[9] and our previous reports for syntheses of 2*H*-1,4-benzoxazin-3-(4*H*)-ones and quinoxalin-2(1*H*)-ones.[8d,e] First, the S_N2 reaction happened between 2-halo-*N*-(2-halophenyl)acetamide **1** and AcSH or $TsNH_2$, and the intermediates **I** or **II** would be formed. Subsequently, 2*H*-benzo[*b*][1,4]-thiazin-3(4*H*)-ones were achieved through the deacetylation and intramolecular coupling process, while quinoxalin-2(1*H*)-ones were formed through the intramolecular coupling and desulfonation process.

In summary, we have developed a domino method to synthesize the 2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-ones via the S_N2/deacetylation/coupling process, and to synthesize the quinoxalin-2(1*H*)-ones via the S_N2/coupling/desulfonation process. The method could give the target products of diversifying groups at three positions on their scaffold and obtain good to excellent yields of product. The method should be valuable for the construction of these kinds of heterocycles with biological and medicinal activities.

Experimental Section

General Experimental Procedures for the Cu(I)-Catalyzed One-Pot Synthesis of 2*H*-Benzo[*b*][1,4]thiazin-3(4*H*)-ones or Quinoxalin-2(1*H*)-ones. An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, CuI (10 mg, 0.05 mmol, 10 mol %), Cs_2CO_3 (652 mg, 2.0 mmol), 1,10-phenanthroline (20 mg, 0.10 mmol, 20 mol %), and 2-halo-*N*-(2-halophenyl)acetamide **1** (0.5 mmol). The tube was evacuated and backfilled with N_2 (this procedure was repeated 3 times). Under a counter flow of N_2, AcSH (48 mg, 0.6 mmol) and dioxane (2.0 mL) were added by syringe ($TsNH_2$ was added before the tube was capped), and the mixture was prestirred for about 15 min at room temperature.Then the reaction was stirred at 100 °C. After the reaction was completed, the mixture was directly passed through Celite and rinsed with 30 mL of CH_2Cl_2. The combined filtrate was concentrated and purified by column chromatography on silica gel to give the pure product.

4-Benzyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one(3a): yellow solid;[10] mp 85−86 °C; IR (neat) ν_{max}/cm^{-1} 3065, 2918, 1660, 1579, 1476, 1377, 1145, 910, 749, 659 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 3H), 7.24−7.19 (m, 3H), 7.11−7.07 (m, 1H), 7.00−6.95 (m, 2H), 5.22 (s, 2H), 3.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.7, 136.6, 128.7, 128.3, 127.2, 126.3, 123.7, 123.6, 118.2, 48.4, 31.5 ppm.

1-Benzylquinoxalin-2(1*H*)-one(4a): yellow solid;[8e] mp 120−122 °C; IR (neat) ν_{max}/cm^{-1} 3061, 2979, 1649, 1596, 1448, 1365, 1072, 924, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.47−7.43 (m, 1H), 7.32−7.23 (m, 7H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 150.2, 134.9, 133.6, 132.5, 131.0, 130.6, 128.9, 127.7, 126.8, 123.8, 114.6, 45.5 ppm.

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Supporting Information Available: Experimental procedures along with copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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