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Three-component synthesis of 2-heteroaryl-benzothiazoles under metal-free conditions

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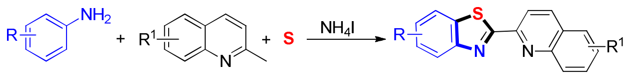
A three-component procedure for 2-heteroaryl-benzothiazole preparation from anilines, 2-methylquinolines and sulfur powder is described. The reaction was promoted by NH_4I to give the corresponding biheteroaryl products in moderate to good yields in the absence of metals.

Benzothiazole and its derivatives are privileged motif frequently found in natural products,[1] pharmaceuticals,[2] functional materials[3] and many other biologically active products. For example, 2-arylbenzothiazoles play important role in potential pharmaceutical drugs such as antitumor agents, antituberculotics, antiparasitics and calcium channel antagonists.[4] Therefore, the development of efficient methods for facile construction of various 2-aryl-subsituted benzothiazoles attracted considerable interest. The classic routes for construction of 2-arylbenzothiazoles mainly rely on the condensation of 2-aminothiophenols with aldehydes, carboxylic acids and their derivatives[5] or oxidative intramolecular cyclization of thiobenzanilides.[6] In recent years, direct arylation of preexisting benzothiazole cores has received much attention because it avoids the need to preactivate the heteroaryl coupling partner or both coupling partners.[7]

Biheteroaryls which contain two heteroaryls are an important class of organic functional compounds. The biheteroaryl structural motif is prevalent in polymers, advanced materials, liquid crystals, ligands and medicines.[8] In view of the tremendous importance of biheteroaryls, it is therefore little wonder that organic chemists have made extensive efforts to develop efficient method to construction of biheteroaryls.[9] The traditional approach has involved the transition-metal-catalyzed cross-coupling between two previously activated substrates, a heteroaryl halide and an organometallic species. Over the last decades, the activation of C-H bonds has emerged as an active field for the construction of biheteroaryls.[10] In recent years, the dehydrogenative cross-coupling of two heteroaryls have been developed for straightforward construction of biheteroaryls. This strategy obviates the need for any preactivation of the substrate. Pd,[11] Rh,[12] Ru,[13] Au,[14] Ni,[15] and Cu[16] were proved to be effective catalysts for this kind of transformation to selective afford the desired cross-coupled products. Although effective methods have been developed to synthesis of 2-heteroarylbenzothiazoles, most of them require the use of transition-metals and/or need use preactivated substrates. In addition, it is challenging to remove trace amount of transition-metals from the biheteroaryl products due to the strong adsorption between the metal and hetero atoms. Efficient method for the synthesis of 2-heteroarylbenzothiazoles from simple and readily available substrates under metal-free conditions is still highly desirable. The quinoline scaffold is particularly important as it can be found in a large variety of bioactive compounds.[17] However, efficient method for biheteroaryls containing both benzothiazole and quinoline motifs from easily access starting materials is rare.[18] General synthetic route for 2-(2-quinolyl)benzothiazole preparation using readily available starting materials under simple reaction conditions is still highly desirable. As our continuing interest in heterocycle preparation under transition-metal-free conditions,[19] we herein report a three-component synthesis of 2-heteroaryl-benzothiazoles using readily available aromatic amines, 2-methylquinolines and sulfur powder as the starting materials (Scheme 1).



Scheme 1 Three-component 2-heteroaryl-benzothiazole formation promoted by NH_4I.

We began our study by examining the reaction of 4-aminotoluene (**1a**), 2-methylquinoline (**2a**) and sulfur powder in 1,2-dichlorobenzene. When the reaction mixture was heated to 160 °C for 24 h, the desired product **3a** was observed in 6% yield as determined by GC analysis (entry 1). To improve the reaction yield, several iodide-containing additives were screened for this kind of transformation. When molecular iodine was added, the desired product was obtained in 15% yield (entry 2). Slightly higher yield

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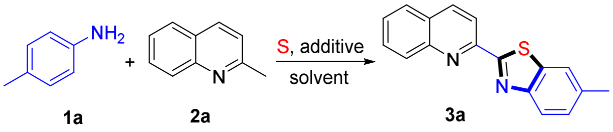
could be obtained using NH_4I as the promoter (entry 3). The use of KI and NIS both did not show better efficient and slightly lower yield was obtained (entries 4 and 5). With NH_4I as the promoter, various organic solvents were investigated. Chlorobenzene and DMF were not suitable reaction media to give the corresponding product in poor yield (entries 6 and 7). To our delight, moderate yield was observed when NMP and 1,1',2,2'-tetrachloroehtane were used (entries 8 and 9). Increased the amount of additive to two equiv. did not affect the reaction yield (entry 10). The reaction atmosphere is important to the reaction yield and similar yield was obtained when the reaction was carried out under oxygen (entry 11). However, much lower yield was obtained when the reaction was carried out under nitrogen (entry 12). Decreasing the reaction temperature significantly decreased the reaction yield (entry 13). Satisfactory yield was obtained when extended the reaction time to 40 h and the desired product was obtained in 75% yield (entry 14). According to theoretical calculation, the amount of oxygen in the reaction vessel is not adequate as the oxidant for this kind of reaction. When we used a 20 mL reaction vessel, no significant difference was observed. We speculated that both oxygen and sulfur were acted as the oxidant since H_2S could be smelled when opened the reaction vessel. Five equiv. of sulfur powder is necessary to get satisfactory yield and the desired product was obtained in 61% and 48% yield when decreasing the amount of sulfur powder to 4 and 3 equiv.

Table 1 Optimization of the reaction conditions[a]

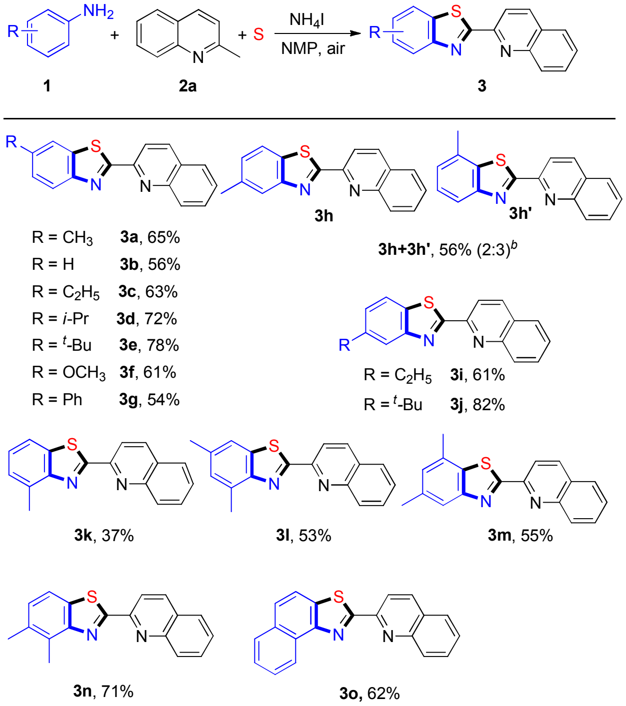


entry	additive	solvent	yield (%) [b]
1	none	1,2-dichlorobenzene	6
2	I_2	1,2-dichlorobenzene	15
3	NH_4I	1,2-dichlorobenzene	17
4	KI	1,2-dichlorobenzene	14
5	NIS	1,2-dichlorobenzene	12
6	NH_4I	PhCl	8
7	NH_4I	DMF	trace
8	NH_4I	NMP	51
9	NH_4I	$CHCl_2CHCl_2$	40
10[c]	NH_4I	NMP	50
11[d]	NH_4I	NMP	52
12[e]	NH_4I	NMP	39
13[f]	NH_4I	NMP	28
14[g]	NH_4I	NMP	**75**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), additive (0.2 mmol), solvent (0.6 mL), S (1 mmol), 160 °C, under air, 24 h. [b] GC yield. [c] NH_4I (0.4 mmol). [d] Under O_2. [e] Under N_2. [f] 150 °C. [g] Reaction 40 h.

Under the optimized reaction conditions, the scope and generality of the three-component reaction was explored (Table 2). Anilines with electron-donating groups at the *para* position were smoothly reacted with 2-methylquinoline and sulfur powder to give the corresponding products in good yields (**3b**-**3f**). Among them, the *tert*-butyl substituted aniline gave the best reaction yield (**3e**). When a phenyl substituent was presented, the desired product **3g** was obtained in moderate yield. When a methyl group was located at the meta position, **3h** and **3h'** were obtained as a mixture with 56% total yield. Interestingly, when ethyl group was located at the same position, a single product **3i** was obtained in 61% yield. High yield was obtained when a *tert*-butyl group was presented at the meta position to selectively give the corresponding product **3j** in 82% yield. The position of substituent significantly affected the reaction yield and only 37% yield was obtained when a methyl group located at the *ortho* position of aniline (**3k**). Better yields could be achieved when muti-methyl substituted anilines were used (**3l**-**3n**). When naphthalen-1-amine (**1o**) was used as the substrate, the desired product **3o** was obtained in 62% yield.

Table 2 Substrate scope with respect to the amines[a]



[a] Reaction conditions: **1** (0.6 mmol), **2a** (0.2 mmol), S (1.0 mmol), NH_4I (0.2 mmol) and solvent (0.6 mL) under air at 160 °C, 40-48 h. [b] Combined yield.

To further examine the scope and limitations of the reaction, we tested various methyl arenes for this kind of reaction (Table 3). The reaction selectively occurred at the ortho position of the nitrogen atom when 2,6-dimethylquinoline (**2b**) was used as the substrate to give **3p** as the single product. Methoxy and hydroxyl groups were well tolerated at the optimized reaction conditions to give the corresponding products **3q** and **3r** in good yields. Besides 2-methylquinolines, 3-methylbenzo[f]quinoline (**2e**) and 2-methylquinoxaline (**2f**) were also could be used as substrates for this kind of reaction. When 4-*tert*-butyl aniline (**1e**) was used as the amine substrate,

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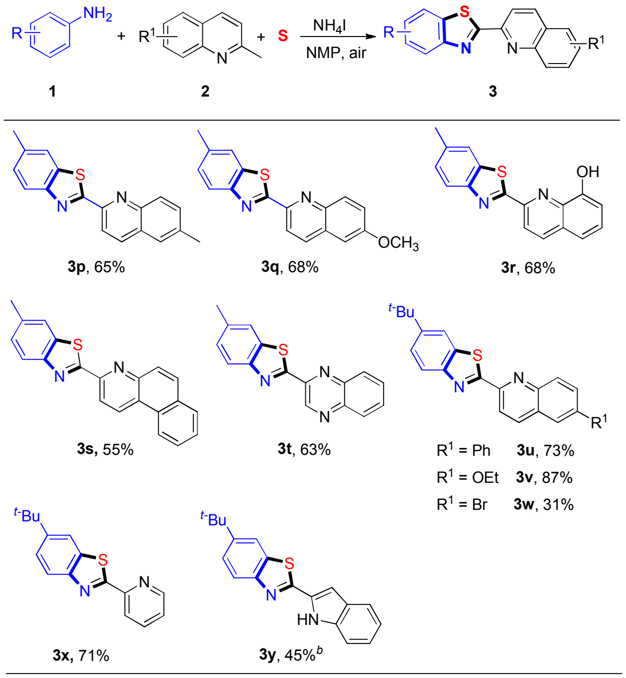
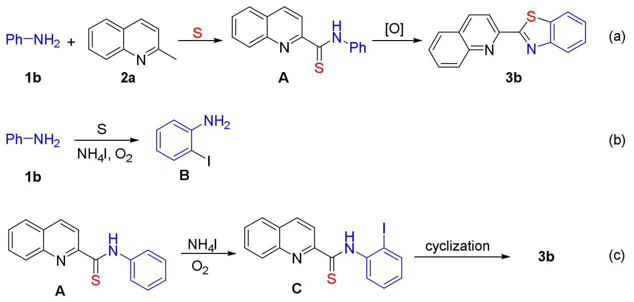
the corresponding products **3u** and **3v** were obtained in 73% and 87% yields, respectively. However, much lower yield was obtained when a bromo substituent was presented at the same position of 2-methylquinoline (**3w**). To our delight, good yield was obtained when less reactive 2-methylpyridine (**2j**) was used as the substrate to give **3x** in 71% yield. 2-Methyl-1H-indole (**2k**) also could participate this kind of reaction to give the desired product **3y** in 45% yield. This strategy provided a new route for biheteroaryls contain a benzothiazole motif and an indole motif from readily available starting materials in the absence of metal-catalyst.

Table 3 Substrate scope of sulfur with various amines and 2-methyl-arenes[a]



[a] Reaction conditions: **1** (0.6 mmol), **2** (0.2 mmol), S (1.0 mmol), NH$_4$I (0.2 mmol) and solvent (0.6 mL) under air at 160 °C, 40-48 h. [b] 72 h.

According to the literature,[18] the benzothiazole product should be obtained via a two-step process (Scheme 2). The reaction of aniline, 2-methylquinoline and sulfur powder yields a thioanilide intermediate (**A**). This key intermediate then can be converted into the final product via oxidative cyclization procedure (Scheme 2, (a)). However, efficiency for the second step is not satisfactory even in the presence of excess oxidant and strong base. In our reaction, we observed small amount of 2-iodoaniline (**B**) when the reaction was carried out in the absence of 2-methylquinoline substrate (Scheme 2, (b)). This can give a reasonable explanation why the addition of NH$_4$I could improve the reaction yield even without the aid of strong oxidant and base since more reactive iodized intermediate was possibly formed (Scheme 2, (c)). Although the exact reaction mechanism is still not clear, this method could provide the benzothiazole products in moderate to good yields in a mild reaction conditions.



Scheme 2 Possible reaction pathway.

In summary, we have developed a novel approach for the synthesis of biheteroaryls from anilines, 2-methylquinolines and sulfur powder under metal-free conditions. According to this strategy, a series of 2-(quinolin-2-yl)benzo[d]thiazoles were synthesized in moderate to good yields in the absence of transition-metal catalyst under oxygen atmosphere. The addition of NH$_4$I could significantly improve the reaction yield. This method affords a simple approach for biheteroaryls from readily available starting materials. The mechanism and the further synthetic applications of this reaction are in progress in our laboratory.

ACKNOWLEDGMENT

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Three-component synthesis of 2-heteroaryl-benzothiazoles under metal-free conditions

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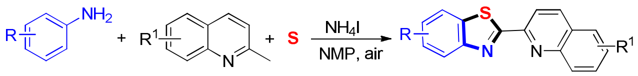

2-Heteroaryl-benzothiazole derivatives were selectively prepared from anilines, 2-methylquinolines and elemental sulfur under metal-free conditions.