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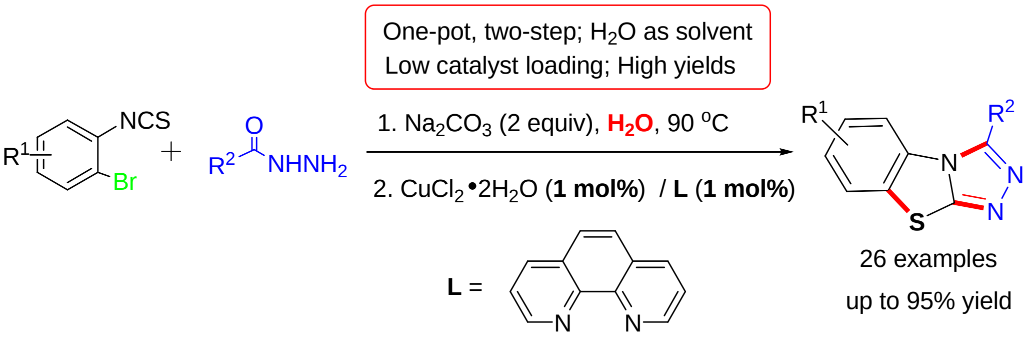
GRAPHIC ABSTRACT

A synthesis of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles has been developed from hydrazides and o-bromo-arylisothiocyanates with 1 mol % $CuCl_2 \cdot 2H_2O$ as catalyst in water.



Convenient Synthesis of Benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles with 1 mol% $CuCl_2$•$2H_2O$ as Catalyst in Water

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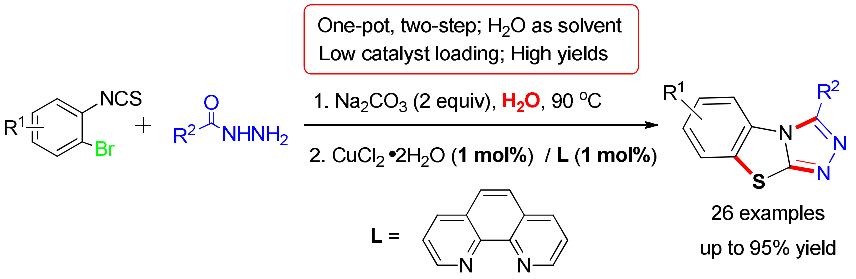


A convenient and efficient procedure for the synthesis of benzo[4,5]thiazolo [2,3-*c*][1,2,4]triazoles has been developed via a tandem intermolecular C−N bond and intramolecular C−S bond formation sequence from *o*-bromo-arylisothiocyanates and aroylhydrazides. A series of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles were provided in excellent overall yields with 1 mol % $CuCl_2 \cdot 2H_2O$/1 mol % 1,10-phenanthroline as the catalyst and water as the solvent.

Keywords: *o*-bromo-arylisothiocyanates, benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles, copper(II) catalyst, C−S bond formation

Introduction

In recent years, the research for the formation of carbon-sulfur bond in the transition-metal-catalyzed system has been the focus in organic chemistry.[1] For example, nickel,[2] palladium,[3] iron,[4] rhodium[5] and copper[6] catalysts have emerged as appealing catalysts for these reactions to overcome the drawbacks that the traditional methods suffered from, such as long reaction time and low yields. Among the various deployed metals, copper has attracted increasing attention because it is inexpensive, environmentally benign and abundant.[7] Reactions with copper catalysts usually could carry out under mild conditions and employ simple ligands at the same time.

Benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazole derivatives have been discovered to display promising activities. For example, 5-methylbenzo[4,5]thiazolo[2,3-*c*][1,2,4] triazole as a commercial compound (Figure 1, compound **I**), patented by Eli Lilly, could control some phytopathogenic fungi such as *Magnaporthe grisea*, *Colletotrichum lagenarium*, and *Colletotrichum lindemuthianum*, as well as parasites on rice, cucumber and bean.[8] For another example, 7-fluoro-*N*-phenylbenzo[4,5] thiazolo[2,3-*c*][1,2,4]triazol-8-amine (Figure 1, compound **II**) was reported to show the antimicrobial activity.[9] Also, they are active on dematiaceous human pathogenic fungi[10] and on a number of other imperfect and ascomycetous fungi.[11]

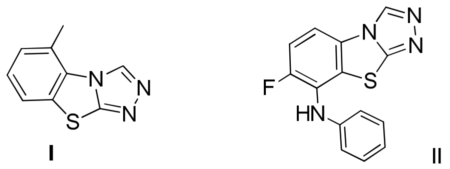


Fig. 1 Selected benzo[4,5]thiazolo[2,3-c][1,2,4]triazoles with bioactivities.

From a synthetic point of view, to date, methods for obtaining benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazole derivatives are still limited.[9,12] Ramakrishnan and co-workers[12] proposed a general photochemical synthesis of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles from 1,2,4-triazole-3-thiones by 254 nm irradiation. However, this protocol was restricted to long reaction time (15−25 h), low yields (only 34−56 %), and narrow substrate scope (7 examples). So the pursuit of inexpensive and more environmentally benign methodologies for construction of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazole motif still remains a challenge.

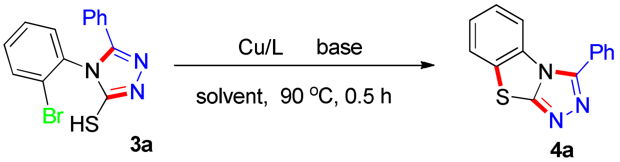
As we all know, water is the most economical and eco-friendly media in the world, and using water as solvent could also simplify the workup procedures, and enable the recycle of the catalyst as well as allow the mild conditions.[13] Moreover, taking into account the economic and environmental protection, decreasing the amount of the metal catalyst and the ligand is also of great significance.[14] In view of the points above and our ongoing research interest for the synthesis of heterocycles,[15] herein, we report an novel copper(II)-catalyzed carbon-sulfur bond formation reaction for the synthesis of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles in excellent yield in water with *o*-bromoarylisothiocyanates **1** and aroylhydrazides **2** as raw materials in a one-pot two-step process. So far, to the best of our knowledge, it is the first report on 1 mol% loading of $CuCl_2 \cdot 2H_2O$ and 1 mol% 1,10-phen as the catalyst for synthesis of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles in water.

Results and Discussion

In recent years we have witnessed great progress in the development of mild Cu-catalyzed Ullmann-type reactions.[16] We envisioned that the benzothiazole ring could be constructed by a Cu-catalyzed intramolecular C−S bond-forming reaction from 4-(2-bromoaryl)-5-aryl-4*H*-1,2,4-triazole-3-thiol compounds (**3**).

Compound **3a**, used as a test substrate for the synthesis of the target product **4a**, was synthesized in yield of 80% through the reaction of *o*-bromo-benzylisothiocyanate (**1a**) with benzohydrazide (**2a**) in the presence of NaOH in water at 90 °C.

Table 1 Reaction condition optimization of intramolecular C−S bond formation[a]

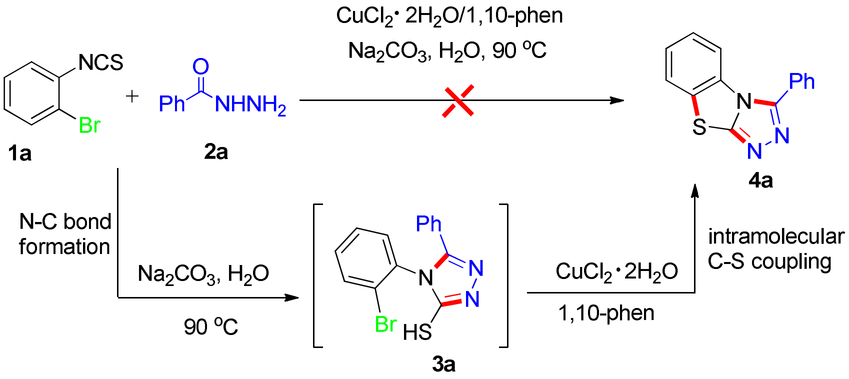


Entry	Catalyst	Ligand	Base	Solvent	Isolated Yield (%)
1	CuI	L-proline	Cs_2CO_3	DMSO	97
2	CuI	L-proline	K_2CO_3	DMSO	95
3	CuI	L-proline	Na_2CO_3	DMSO	96
4	$CuCl_2{\cdot}2H_2O$	1,10-phen	Na_2CO_3	DMSO	96
5	**$CuCl_2{\cdot}2H_2O$**	**1,10-phen**	**Na_2CO_3**	**H_2O**	**96**
6	$CuCl_2{\cdot}2H_2O$	—	Na_2CO_3	H_2O	Trace
7	—	1,10-phen	Na_2CO_3	H_2O	NR
8	$CuCl_2{\cdot}2H_2O$	1,10-phen	—	H_2O	NR

[a] Reaction conditions: **3a** (1.0 mmol), copper salt (0.1 mmol), ligand (0.1 mmol), base (2.0 mmol), solvent (2 mL).

Initially, we employed the classic CuI/L-proline/Cs_2CO_3 catalyst system in DMSO at 90 °C to prepare the ring-close product **4a**, and the reaction gave an excellent yield of 97% within 30 min (Table 1, entry 1). Next, other inexpensive bases such as K_2CO_3 and Na_2CO_3 were tested and also gave similar yields as Cs_2CO_3 (Table 1, entries 2 and 3). These results promoted us to use cheaper $CuCl_2{\cdot}2H_2O$/1,10-phen/Na_2CO_3 catalyst system to conduct this reaction. To our delight, the reaction proceeded well affording the same yield (Table 1, entry 4). Considering the requirement of green chemistry, water also was attempted as the reaction medium. More gratifyingly, this reaction system favored water (Table 1, entry 5). The control experiments confirmed that a copper catalyst, a ligand, and a base were necessary for this coupling reaction (Table 1, entries 6-8).

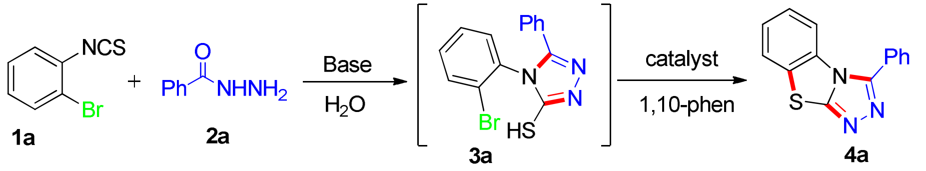
With this promising result above in hand, we focused on whether through a tandem process from the substrates *o*-bromoarylisothiocyanates **1** and aroylhydrazides **2** as starting materials in one-pot operation to prepare the products **4**. Based on the above successful experimental results of copper(II)-catalyzed intramolecular ring closure from **3** to **4**, we performed directly the reaction of **1a** and **2a** with $CuCl_2 \cdot 2H_2O$/1,10-phen/Na_2CO_3 as the catalyst in H_2O at 90 °C to prepare the target compound **4a**. Disappointingly, however, **4a** was not observed after 8 h, and **3a** was the only product as indicated by TLC. Next, we changed the strategy, the above model reaction was first carried out in the presence of Na_2CO_3 in water at 90 °C for 2 h without adding any metal catalyst. Consequently, the precursor **3a** was provided directly and smoothly. Then without isolating **3a**, $CuCl_2 \cdot 2H_2O$ and 1,10-phen were directly added to the reaction system and continued to stir for 2 h. Gratifyingly, in this case, the target product **4a** was obtained in an excellent total yield of 95% after two steps (Scheme 1).



Scheme 1 One-pot reaction design for the synthesis of **4a**.

The other copper(II) salts such as $CuSO_4 \cdot 5H_2O$, $Cu(OAc)_2 \cdot H_2O$ also were tested and gave similar results as $CuCl_2 \cdot 2H_2O$ (Table 2, entries 1 and 2). Whereas other more inexpensive transition metal salt such as $FeCl_3 \cdot 6H_2O$ was less effective for this coupling reaction (Table 2, entry 3). Finally, the catalyst load was investigated. To our delight, when 1 mol% $CuCl_2 \cdot 2H_2O$ and 1,10-phen were used, the same excellent yield was obtained (Table 2, entries 4−7).

Table 2 Reaction condition optimization for the tandem reaction[a]

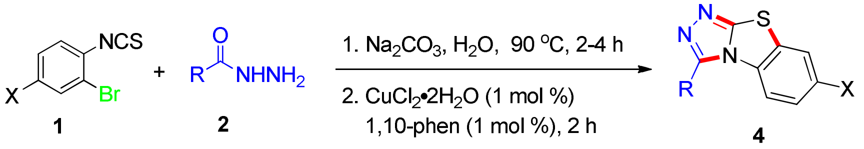


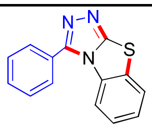
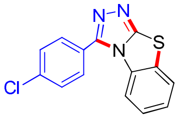
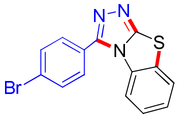
Entry	Cat. (equiv)	1,10-Phen (equiv)	Base	Time (h)	Yield (%)[b]
1	$CuSO_4·5H_2O$ (0.01)	0.01	Na_2CO_3	2+2	90
2	$Cu(OAc)_2·H_2O$ (0.01)	0.01	Na_2CO_3	2+2	91
3	$FeCl_3·6H_2O$ (0.01)	0.01	Na_2CO_3	2+2	30
4	$CuCl_2·2H_2O$ (0.05)	0.05	Na_2CO_3	2+2	94
5	$CuCl_2·2H_2O$ (0.02)	0.02	Na_2CO_3	2+2	93
6	$CuCl_2·2H_2O$ (0.01)	0.01	Na_2CO_3	2+2	94
7	$CuCl_2·2H_2O$ (0.005)	0.005	Na_2CO_3	2+2	25[c]

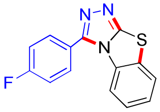
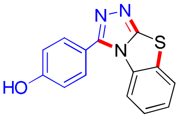
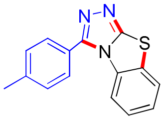
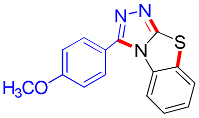
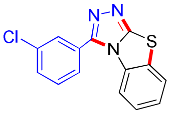
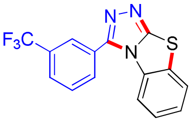
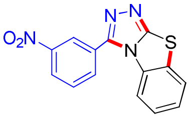
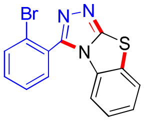
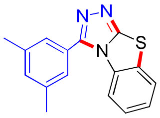
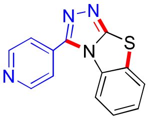
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), base (2.0 mmol), water (2 mL), 90 °C. [b] Yields of the pure product after washing with water. [c] 4 mmol scale.

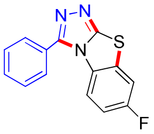
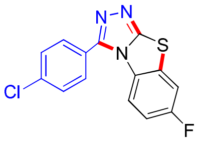
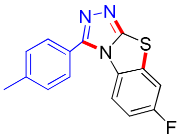
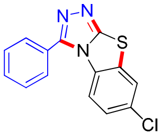
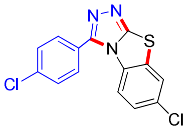
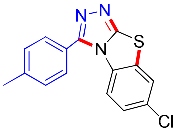
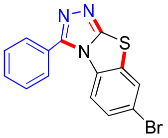
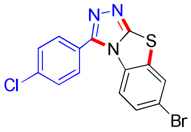
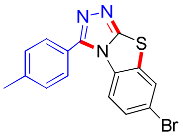
With this promising result in hand, the scope of this reaction was investigated under the optimized conditions (1 mol% $CuCl_2·2H_2O$ and 1,10-phen, Na_2CO_3 (2.0 equiv) in H_2O at 90 °C). Various isothiocyanates **1** and hydrazides **2** were examined, and the results were summarized in Table 3.

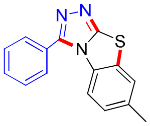
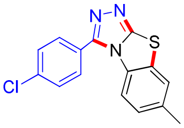
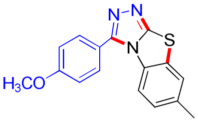
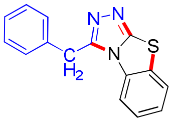
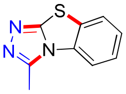
Table 3 Investigation on the substrate scope of one-pot copper-catalyzed synthesis of **4**[a].



Entry	X	R	**4**	Time (h)	Yield (%) [b]
1	H	C_6H_5	 **4a**	2+2	94 (lit.[12] 41)
2	H	$4\text{-}ClC_6H_4$	 **4b**	2+2	95
3	H	$4\text{-}BrC_6H_4$	 **4c**	2+2	95

4	H	4-FC_6H_4	 **4d**	2+2	94
5	H	4-OHC_6H_4	 **4e**	2+2	95
6	H	4-$CH_3C_6H_4$	 **4f**	2+2	94 (lit.[12] 40)
7	H	4-$OCH_3C_6H_4$	 **4g**	2+2	93 (lit.[12] 56)
8	H	3-ClC_6H_4	 **4h**	2+2	95
9	H	3-$CF_3C_6H_4$	 **4i**	2+2	94
10	H	3-$NO_2C_6H_4$	 **4j**	2+2	95
11	H	2-BrC_6H_4	 **4k**	2+2	90
12	H	3,5-$(CH_3)_2C_6H_3$	 **4l**	2+2	95
13	H	4-pyridinyl		2+2	92

14	4-F	C_6H_5	**4m** 	2+2	91
15	4-F	$4\text{-}ClC_6H_4$	**4n** 	2+2	92
16	4-F	$4\text{-}CH_3C_6H_4$	**4o** 	2+2	90
17	4-Cl	C_6H_5	**4p** 	2+2	91
18	4-Cl	$4\text{-}ClC_6H_4$	**4q** 	4+2	85
19	4-Cl	$4\text{-}CH_3C_6H_4$	**4r** 	4+2	86
20	4-Br	C_6H_5	**4s** 	2+2	94
21	4-Br	$4\text{-}ClC_6H_4$	**4t** 	2+2	89
22	4-Br	$4\text{-}CH_3C_6H_4$	**4u** 	2+2	90

			4v		
23	4-CH_3	C_6H_5	 **4w**	2+2	95
24	4-CH_3	4-ClC_6H_4	 **4x**	2+2	93
25	4-CH_3	4-$OCH_3C_6H_4$	 **4y**	2+2	94
26	H	Bn	 **4z**	2+2	95
27	H	CH_3	 **4zz**	2+2	Trace

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), $CuCl_2 \cdot 2H_2O$ (0.01 mmol), 1,10-phen (0.01 mmol), Na_2CO_3 (2.0 mmol). [b] Yields of the pure products after washing with water.

As can be seen from Table 3, various isothiocyanates **1** and hydrazides **2** were smoothly transformed to the corresponding target products **4** in excellent yields. For the substrates **2**, the substituted hydrazides both bearing electron-donating groups and electron-withdrawing groups at 2-, 3-, or 4- as well as 3,5-positions all gave the satisfactory yields (Table 3, entries 1−12). However, compared to 3- and 4-positions, the substituent at 2-position seemed to have slight effect on the results, which might be subject to steric hindrance. For example, 2-bromobenzohydrazide could afford only 90% yield (Table 3, entry 11). A heretocyclic hydrazide such as isonicotinohydrazide was also investigated, which could provide 92% yield (Table 3, entry 13). For the substrates **1**, the various isothiocyanates bearing different substituents did not display obvious difference in reactivity (Table 3, entries 14−25). However, when benzyl hydrazide or an aliphatic hydrazide such as acetohydrazide was employed in this tandem reaction, they performed quite differently. Benzyl hydrazide provided very high yield of 95%, whereas acetohydrazide only gave the trace product (Table 3, entries 26 and 27).

The structures of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles **4** were identified by their IR, ^{1}H NMR, ^{13}C NMR, HRMS spectra, and ascertained by the single-crystal X-ray diffraction analysis of **4h** (Figure 2).

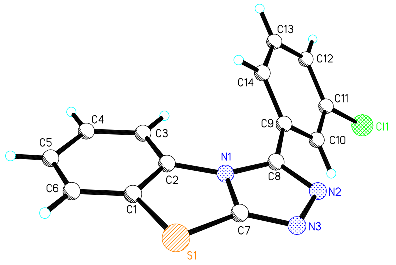
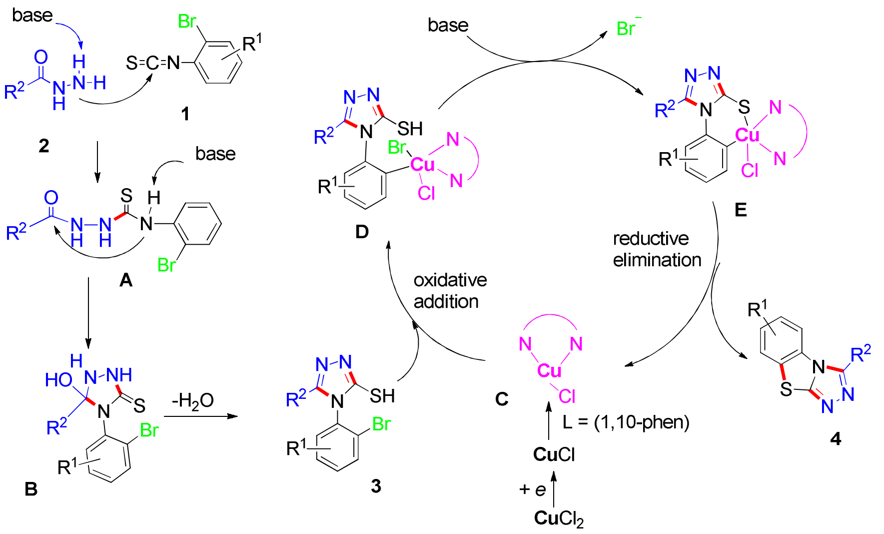


Fig. 2 X-ray structure of **4h**.

It is noteworthy that all of the products only need washing with water rather than column chromatography or recrystallization. This easy purification makes this methodology facile, practical, and rapid to execute.

In order to justify the mechanism, CuCl/1,10-phen catalyst was employed in this tandem reaction. First the reaction of **1a** and **2a** was conducted in the presence of Na_2CO_3 in H_2O at 90 °C for 2 h, then CuCl/1,10-phen was added in the reaction system under N_2 atmosphere. The product **4a** was obtained within 1 h in 95% yield, which suggested the key catalytic species is Cu(I).

Based on the above experimental results, a possible mechanism for the tandem reaction for the synthesis of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles **4** is depicted in Scheme 2. First, isothiocyanates **1** and hydrazides **2** take place intermolecular nucleophilic addition reaction to provide an thiourea intermediate **A** in presence of a base, followed by an intramolecular nucleophilic addition reaction to give **B**, which eliminates a molecule of water to afford cyclization product **3**. Next, **3** undergoes an oxidative addition reaction with the active copper(I) species **C**, which is generated by the reduction process of the copper(II) salt,[17] to yield copper(III) intermediate **D**. Then **D** undergoes an intramolecular cyclization in the presence of a base via **E** to give cross-coupling products **4**, completing the catalytic cycle by the reductive elimination.



Scheme 2 Proposed reaction mechanism.

Conclusion

In conclusion, we have developed a general, convenient, and environmentally benign method for the preparation of benzo[4,5]thiazolo[2,3-*c*][1,2,4]triazoles in excellent yields from *o*-bromoarylisothiocyanates and aroylhydrazides by a one-pot two-step procedure with cheap and air stable $CuCl_2 \cdot 2H_2O$/1,10-phen as the catalyst in water. The low loading of the catalyst (1 mol %) and easy purification of products (by simple washing with water) make this methodology facile, practical, and rapid to execute. For these reasons, this novel process should show environmental and economic advantages over previously reported protocols.

Experimental

General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. 1,4-dioxane was dried over CaH_2 and distilled prior to use. All reagents were weighed and handled in air at room temperature. Melting points were recorded on a RY-1 microscopic melting apparatus and uncorrected. ^1H NMR spectra were recorded on 500 MHz and ^{13}C NMR spectra were recorded on 125 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer and only major peaks are reported in cm^{-1}. Mass spectra were performed on an Ultima Global spectrometer with an ESI source. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument.

*General procedure for 2-bromo-1-isothiocyanatobenzenes **1***

A 100 mL round-bottom flask was charged with a mixture of *o*-bromo-aniline (5 mmol) and 10 mL of 1,4-dioxane in an ice bath. Then NaH (15 mmol, 60% dispersion in mineral oil) was added to the flask, and CS_2 (20 mmol) was added dropwise to the reactor slowly. When CS_2 addition was complete, the reaction was stirred at room temperature for 5 hours. Then the reaction system was refluxed. After completion of the reaction (nearly 24 hours), the reaction solution was cooled to room temperature, filtered and the solid was dissolved in 30 mL water, and extracted with ethyl acetate (3×30 mL). The combined filtrate and the organic layer was dried over anhydrous magnesium sulfate, rotary evaporated under reduced pressure and purified by silica gel column chromatography to obtain products **1**.

*General procedure for the thiazolo[2,3-c][1,2,4]triazoles **4***

A 25 mL round-bottom flask was charged with a mixture of hydrazides **2** (1.0 mmol), o-bromo-2-isothiocyanatobenzenes **1** (1.0 mmol), sodium carbonate (2 mmol), and the mixture was stirred in 2 mL of water at 90 ºC for 2 h. Then cupric chloride dihydrate (0.01 mmol) and 1,10-phen (0.01mmol) were added when the starting materials were completely consumed. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and filtered. The solid was washed with water (3×10 mL) to give the pure products **4**.

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