Synthesis of 2-aminobenzothiazole *via* $FeCl_3$-catalyzed tandem reaction of 2-iodoaniline with isothiocyanate in water†

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An $FeCl_3$-catalyzed tandem reaction of 2-iodoaniline with isothiocyanate in water is described, which provides an environmentally benign, efficient, and practical route for the generation of 2-aminobenzothiazole. This present tandem process shows broad substrate scope in the presence of octadecyltrimethylammonium chloride as a phase-transfer catalyst. In addition, the reaction media can be recovered and recycled without loss of efficiency.

Introduction

The 2-aminobenzothiazole core, as a privileged scaffold, is found in many natural products and pharmaceuticals that exhibit remarkable biological activities.[1] In addition, some compounds with the skeleton, which have application in drugs for the treatment of various diseases, are found, such as tuberculosis,[2] epilepsy,[3] diabetes,[4] glutamate (*e.g.* Fig. 1, Riluzole),[5] and tumors (*e.g.* Fig. 1, R116010).[6] Therefore, many efforts continue to be given to the development of efficient strategies for their construction.[7] Usually, the classical method for the preparation of 2-aminobenzothiazoles is transition metal-catalyzed (Pd or Cu was used) intramolecular cyclization of 2-halobenzothioureas [(Scheme 1, eqn (1)].[7a–7d]

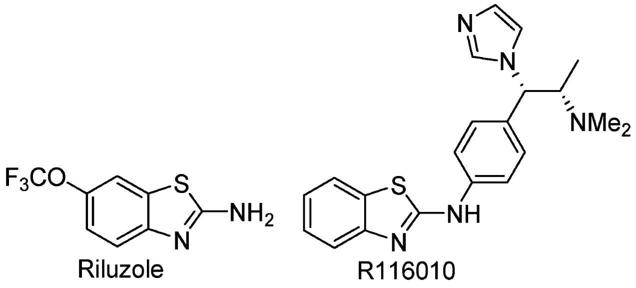
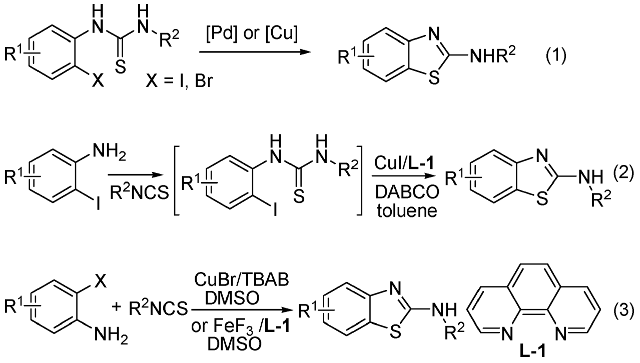


Fig. 1 Riluzole and R116010.

Tandem reactions for the efficient construction of biologically relevant heterocyclic compounds are important goals in combinatorial chemistry from the viewpoints of operational simplicity and assembly efficiency.[8,9] Tandem addition/C–S coupling reaction is another powerful strategy for construction of the 2-aminobenzothiazole core.[7e–7g] Recently, we described a novel and efficient method for the synthesis of 2-aminobenzothiazole derivatives *via* copper(I)-catalyzed tandem addition–cyclization reactions of 2-iodoanilines with isothiocyanates in toluene [(Scheme 1, eqn (2)].[7e] Subsequently, Li and co-workers reported the same transformation using FeF_3 or CuBr as catalyst [(Scheme 1, eqn (3)].[7f,7g] Although good yields can often be obtained in these methods, the use of organic solvent is always necessary but is harmful to human health. Organic reactions without the use of conventional organic solvents have attracted the attention of synthetic organic chemists, and many novel and environmentally benign modern solvents such as fluorous media,[10] $scCO_2$,[11] ionic liquid[12] and water[13] have been extensively studied recently. Organic reactions in aqueous media are definitely the best option, which have recently been found many applications in organic synthesis, due to the simple operation and avoiding the use of dry organic solvent. As part of our continuing efforts for the expeditious synthesis of biologically relevant heterocyclic compounds in a green process,[14] herein we would like to report our recent efforts towards the synthesis of diverse 2-aminobenzothiazoles *via* $FeCl_3$-catalyzed tandem reactions of 2-iodoanilines with isothiocyanates in water. The transformation proceeded smoothly under mild conditions in the presence of phase-transfer catalysis (PTC) and the corresponding products were generated in good to excellent yields.



Scheme 1 Synthesis of 2-aminobenzothiazoles.

Results and discussion

Our studies commenced with the reaction of 2-iodoaniline **1a** and phenyl isothiocyanate **2a** to optimize the reaction

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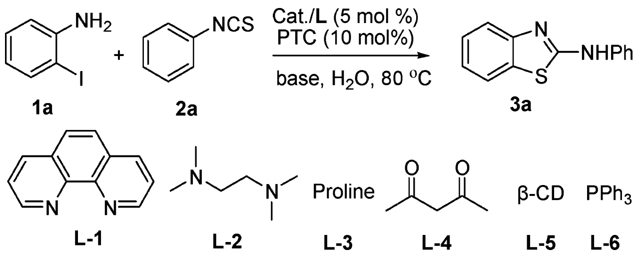
Table 1 Condition screening for [Fe]-catalyzed tandem reaction of 2-iodoaniline **1a** with phenyl isothiocyanate **2a** in water[a]



Entry	Catalyst	L	Base	PTC	Yield [%][b]
1	$FeCl_3$	L-1	Na_2CO_3	—	53
2	$FeCl_3$	L-1	$NaHCO_3$	—	60
3	$FeCl_3$	L-1	Cs_2CO_3	—	trace
4	$FeCl_3$	L-1	K_2CO_3	—	trace
5	$FeCl_3$	L-1	K_3PO_4	—	—
6	$FeCl_3$	L-1	NaOH	—	trace
7	$FeCl_3$	L-1	DBU	—	trace
8	$FeCl_3$	L-1	Et_3N	—	trace
9	$FeCl_3$	L-1	DABCO	—	75
10	$K_3Fe(CN)_6$	L-1	DABCO	—	71
11	$Fe(NO_3)_3$	L-1	DABCO	—	70
12	Fe_2O_3	L-1	DABCO	—	44
13	$Fe_2(SO_4)_3$	L-1	DABCO	—	trace
14	$FeSO_4$	L-1	DABCO	—	trace
15	$FeCl_3$	—	DABCO	—	34
16	$FeCl_3$	L-2	DABCO	—	trace
17	$FeCl_3$	L-3	DABCO	—	trace
18	$FeCl_3$	L-4	DABCO	—	trace
19	$FeCl_3$	L-5	DABCO	—	65
20	$FeCl_3$	L-6	DABCO	—	44
21	$FeCl_3$	L-1	DABCO	PTC-1[c]	88
22	$FeCl_3$	L-1	DABCO	PTC-2[c]	76
23	$FeCl_3$	L-1	DABCO	PTC-3[c]	trace
24	$FeCl_3$	L-1	DABCO	PTC-4[c]	97

[a] Reaction conditions: 2-iodoaniline **1a** (0.3 mmol), phenyl isothiocyanate **2a** (1.5 equiv), cat. (5 mol%), ligand (5 mol%), base (2.0 equiv), PTC (phase-transfer catalyst, 10 mol%), H_2O (3 mL), 80 °C, overnight. [b] Isolated yield based on 2-iodoaniline **1a**. [c] PTC-1: SDBS (sodium dodecylbenzenesulfonate), PTC-2: hexadecyldimethylbenzylammonium chloride, PTC-3: TBAB (tetrabutylammonium bromide), PTC-4: octadecyltrimethylammonium chloride.

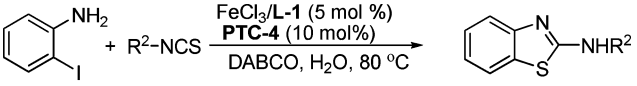
conditions, and the results are summarized in Table 1. The reaction was catalyzed by $FeCl_3$ (5 mol%) in the presence of 1,10-phenanthroline (**L-1**) and base (Na_2CO_3) in water at 80 °C. To our delight, the desired 2-aminobenzothiazole **3a** was generated in 53% yield (Table 1, entry 1). Encouraged by the result, we subsequently examined the effects of different bases (Table 1, entries 2–9). The results showed that DABCO was the best choice (Table 1, entry 9, 75% yield). Increasing the catalyst ($FeCl_3$) amount to 10 mol% gave a similar result (77% yield). Then a series of other Fe catalysts, including $K_3Fe(CN)_6$, $Fe(NO_3)_3$, $Fe_2(SO_4)_3$, $FeSO_4$, and Fe_2O_3, were evaluated (Table 1, entries 10–14), but the results were all inferior to $FeCl_3$. Subsequently, we examined the effect of ligands (Table 1, entries 16–20). The results showed that both β-CD and PPh_3 reduced the yield to some extent (entries 19, 20), and three others (TMEDA, L-proline, pentane-2,4-dione) showed no activity (Table 1, entries 16–18). A blank experiment showed that ligand **L-1** was essential to obtain a good result (Table 1, entry 15). It is well-known that PTC is widely exploited in the industry.[15] PTC as a promoter in organic reactions can make reactions faster, obtain higher conversion or yield, and fewer byproducts, eliminate the need for expensive or dangerous organic solvents and minimize waste problems. On the basis of this consideration, we chose PTC-1 (SDBS) as an additive. To our surprise, the product **3a** was generated in 88% yield (Table 1, entry 21). To examine the effects of different PTCs on the reaction, several other PTCs were applied under comparable conditions. The results showed that PTC-2 (hexadecyldimethylbenzylammonium chloride) could not improve the yield substantially (76% yield, Table 1, entry 22), PTC-3 (TBAB) did not efficiently promote the reaction (Table 1, entry 23), and PTC-4 (octadecyltrimethylammonium chloride) was unexpectedly the most efficient PTC giving an almost quantitative yield of **3a** (Table 1, entry 24). The yield (97%) was substantially higher than that of the corresponding reaction in organic solvents (88%[7e] or 86%[7f]).

With this promising result in hand, we started to investigate the scope of this reaction under the optimized conditions [$FeCl_3$ (5 mol%), 1,10-phenanthroline (L-1, 5 mol%), DABCO (2.0 equiv.), octadecyltrimethylammonium chloride (PTC-4, 10 mol%), H_2O, 80 °C]. Initially, we investigated the scope of isothiocyanates and the results are summarized in Table 2. We found that the functional groups had little effect on the phenyl ring for the tandem coupling reactions. Several substituted groups, such as methoxy, methyl, chloro, fluoro and nitro groups, on the phenyl ring of isothiocyanates were tolerated well (Table 2, entries 1–6). It was found that both electron-rich and electron-poor aryl isothiocyanates underwent the tandem coupling reaction efficiently in good to excellent yields. For instance, 2-iodoaniline **1a** reacted with 4-methoxyphenyl isothiocyanate **2b** leading to the desired product **3b** in 91% yield (Table 2, entry 2), and 98% yield of product **3d** was afforded when 4-nitrophenyl isothiocyanate **2d** was employed in the reaction (Table 2, entry 3). To our delight, alkyl isothiocyanate was also a suitable substrate in this process in moderate yield (Table 2, entries 7).

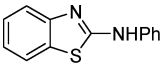
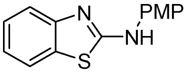
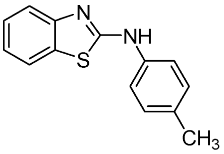
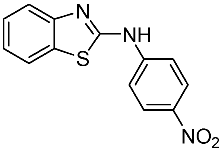
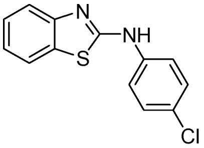
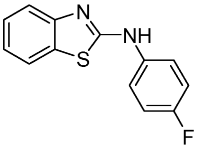
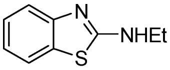
Encouraged by the above results, we further investigated the scope and the generality of the method by varying the 2-iodobenzenamine **2b–2e**, which could be facilely derived from the 4-substituted benzenamines (Table 3, entries 1–14). As showed in Table 3, generally the reactions proceeded successfully to afford the corresponding 2-aminobenzothiazole **3** in moderate to excellent yields. The results demonstrated that several functional groups, such as trifluoromethyl, fluoro, chloro, and methyl on the phenyl ring of 2-iodobenzenamine were tolerated well. For example, reaction of 2-iodo-4-trifluoromethylbenzenamine **1b** with phenyl isothiocyanate **2a** afforded the desired product **3h** in 92% yield (Table 3, entry 1). A similar result (93% yield) was obtained for the reaction of 2-iodo-4-methylbenzenamine **1e** with phenyl isothiocyanate **2a** (Table 3, entry 11). In comparison with aryl isothiocyanates, alkyl isothiocyanates seemed to have similar reactivity (Table 3, entries 8 and 14). Finally, two less active substrates, 5-bromo-2-bromobenzenamine **1f**, and 4-iodo-2-chlorobenzenamine **1g** were also tested. Unfortunately, only trace desired product was obtained when 5-bromo-2-bromobenzenamine **1f** reacted with phenyl isothiocyanate **2a** (Table 3, entry 15), and no desired product was detected with 4-iodo-2-chlorobenzenamine **1g** (Table 3, entry 16).

The efficiency of the recovered reaction media was verified with the reaction of 2-iodoaniline **1a** and phenyl isothiocyanate

Table 2 $FeCl_3$-catalyzed tandem reaction of 2-iodoaniline **1a** with isothiocyanate **2**[a]



1a **2** **3**

Entry	2/R²	Product 3	Yield [%][b]
1	**2a**/C_6H_5	 **3a**	96
2	**2b**/4-$MeOC_6H_4$	 **3b**	91
3	**2c**/4-MeC_6H_4	 **3c**	90
4	**2d**/4-$NO_2C_6H_4$	 **3d**	98
5	**2e**/4-ClC_6H_4	 **3e**	90
6	**2f**/4-FC_6H_4	 **3f**	82
7	**2g**/Et	 **3g**	65

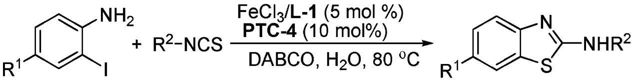
[a] Reaction conditions: 2-iodoaniline **1a** (0.3 mmol), isothiocyanate **2** (1.5 equiv), $FeCl_3$ (5 mol%), 1,10-phenanthroline (5 mol%), PTC-**4** (octadecyltrimethylammonium chloride, 10 mol%), DABCO (2.0 equiv), H_2O (3 mL), 80 °C. [b] Isolated yield based on 2-iodoaniline **1**.

2a (Table 4). Using the fresh reaction media the yield of the desired product *N*-phenylbenzo[*d*]thiazol-2-amine **3a** was 97%, while with the recovered media the yields were 96, and 80% in the next two recyclizations.

Conclusions

We have established a highly efficient $FeCl_3$-catalyzed tandem reaction of 2-iodoanilines **1** with isothiocyanates **2** for the synthesis of 2-aminobenzothiazoles **3**. The advantages of this method include simple, mild and environmentally benign reaction conditions, experimental ease, good substrate generality, and the toleration of a wide range of aromatic and aliphatic isothiocyanates. The results showed that phase-transfer catalyst PTC-**4** (octadecyltrimethylammonium chloride) could promote the reaction efficiently. The product was easily separated from the reaction mixture by filtration, and the reaction media can be recovered and recycled with good catalytic activity.

Table 3 $FeCl_3$-catalyzed tandem reaction of 2-iodobenzenamine **1** with isothiocyanate **2**[a]



1 **2** **3**

Entry	1/R¹/X	2/R²	Product 3	Yield [%][b]
1	**1b**/4-CF_3/I	**2a**/C_6H_5	**3h**	92
2	**1b**/4-CF_3/I	**2b**/4-$MeOC_6H_4$	**3i**	65
3	**1b**/4-CF_3/I	**2d**/4-$NO_2C_6H_4$	**3j**	58
4	**1b**/4-CF_3/I	**2e**/4-ClC_6H_4	**3k**	86
5	**1c**/4-F/I	**2a**/C_6H_5	**3l**	91
6	**1c**/4-F/I	**2c**/4-MeC_6H_4	**3m**	73
7	**1c**/4-F/I	**2d**/4-$NO_2C_6H_4$	**3n**	73
8	**1c**/4-F/I	**2g**/Et	**3o**	77
9	**1d**/4-Cl/I	**2a**/C_6H_5	**3p**	91
10	**1d**/4-Cl/I	**2c**/4-MeC_6H_4	**3q**	78
11	**1e**/4-CH_3/I	**2a**/C_6H_5	**3r**	93
12	**1e**/4-CH_3/I	**2b**/4-$MeOC_6H_4$	**3s**	97
13	**1e**/4-CH_3/I	**2d**/4-$NO_2C_6H_4$	**3t**	78
14	**1e**/4-CH_3/I	**2g**/Et	**3u**	73
15	**1f**/5-Br/Br	**2a**/C_6H_5	**3v**	trace
16	**1g**/4-I/Cl	**2a**/C_6H_5	**3w**	—

[a] Reaction conditions: 2-iodoaniline **1** (0.3 mmol), isothiocyanate **2** (1.5 equiv), $FeCl_3$ (5 mol%), 1,10-phenanthroline (5 mol%), PTC-**4** (octadecyltrimethylammonium chloride, 10 mol%), DABCO (2.0 equiv), H_2O (3 mL), 80 °C. [b] Isolated yield based on 2-iodoaniline **1**.

Table 4 Efficiency of the recovered reaction media

no. of cycles	cycle I	cycle II	cycle III
yield [%]	97	96	80

Experimental section

General experimental

All reactions were performed in test tubes under air. Flash column chromatography was performed using silica gel (200–300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at 25–35 °C. Commercial reagents and solvents were used as received.

Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz and 100 MHz respectively at 293 K. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and referenced to tetramethylsilane (0 ppm).

Synthesis of 2-aminobenzothiazoles

A mixture of 2-iodoaniline **1** (0.3 mmol), isothiocyanate **2** (0.45 mmol, 1.5 equiv), DABCO (0.6 mmol, 2 equiv), FeCl$_3$ (0.015 mmol, 5 mol%), 1,10-phenanthroline **L-1** (0.015 mmol, 5 mol%), and octadecyltrimethylammonium chloride PTC-**4** (0.03 mmol, 10 mol%) was stirred in water (3 mL) at 80 °C. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature. The mixture was washed with saturated brine, and extracted with ethyl acetate. The organic layer was dried with anhydrous MgSO$_4$ and the solvent was evaporated under vacuum, and then the residue was purified by flash column chromatography on silica gel to provide the corresponding pure product **3**. Selected example: *N*-phenylbenzo[*d*]thiazol-2-amine (**3a**):[16] white solid, mp 158–160 °C (lit. mp 157.2–159.4 °C); IR (prism, KBr, cm^{-1}) 3468, 1627; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13–7.19 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 118.7, 119.9, 120.4, 121.9, 123.9, 125.6, 129.1, 129.3, 139.4, 150.7, 164.5.

Acknowledgements

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