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IRON-CATALYZED ONE-POT SYNTHESIS OF 2-AMINOBENZOTHAZOLES FROM 2-AMINOBENZETHIOLS AND ISOTHIOCYANATES UNDER LIGAND-FREE CONDITIONS IN WATER

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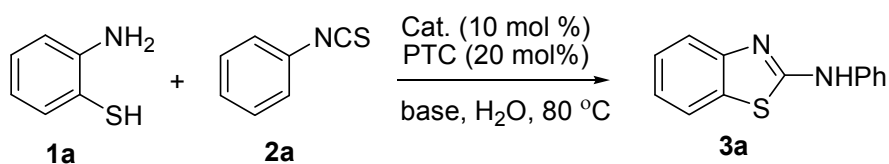
Abstract – A practical and efficient method for the synthesis of 2-aminobenzothiazoles has been developed via an iron-catalyzed one-pot tandem reaction. Various 2-aminobenzothiazoles were conveniently synthesized in moderate to excellent yields. It is highlighted that the reaction is conducted under ligand-free conditions in water.

2-Aminobenzothiazole derivatives are an important class of common heterocyclic compounds that exhibit a wide range of biological activities and medicinal properties. Some 2-aminobenzothiazoles are potential drugs for tuberculosis,¹ epilepsy,² diabetes,³ antitumor (e.g. R116010),⁴ and glutamate (e.g. Riluzole).⁵ Due to the importance of 2-aminobenzothiazoles, many synthetic methods have been reported over the last decade. The transition metal-catalyzed intramolecular cyclization of 2-bromophenylthioureas is one of the most efficient methods.⁶ One-pot strategies for the synthesis of various useful heterocyclic compounds have been received much attention because of their more convenient manipulations and good efficiencies during the past decade. Recently, 2-aminobenzothiazoles as a significant *N*- and *S*-heterocyclic compounds have been reported *via* one-pot strategies.⁷ Among the strategies, we described a novel and efficient *via* Cu(I)-catalyzed one-pot tandem intermolecular addition-intramolecular cyclization reactions to prepare 2-aminobenzothiazole derivatives.^{7a} Subsequently, FeF₃ or

CuBr-catalyzed one-pot tandem methods were reported by Li and co-workers.^{7b and 7c} Although powerful methods to prepare 2-aminobenzothiazoles have been emerged, the transition metal combined with a ligand and using organic solvent were essential to obtain good result.^{6,7} From environmental points of view, the development of a cheap and efficient catalyst under ligand-free conditions in aqueous medium is still desirable. As a part of our continuing interest in the use of transition metal-catalyzed one-pot multicomponent tandem cyclization for benz-fused heterocycle synthesis,⁸ herein we report the successful realization the synthesis of 2-aminobenzothiazoles using ligand-free iron-catalyzed one-pot tandem strategy in water. To the best of our knowledge, there is no report about the formation of 2-aminobenzothiazoles *via* one-pot iron-catalyzed coupling process under ligand-free conditions in water. Although we recently reported a very efficient method for the synthesis of such compounds *via* FeCl₃-catalyzed tandem reaction of 2-iodoaniline with isothiocyanate in water, 1,10-phenanthroline as ligand was essential to obtain a good result.^{8a}

Preliminary studies were performed by treatment of 2-aminobenzenethiol **1a** and phenyl isothiocyanate **2a** in water in the presence of a catalytic amount of various Fe or Cu catalysts (Table 1). To our delight, we found that the desired product **3a** could be afforded in 70% yield when Fe₂(SO₄)₃·H₂O (10 mol%) was utilized as catalyst under ligand- and base-free conditions (Table 1, entry 1). Blank experiment showed that Fe₂(SO₄)₃·H₂O was essential to obtain good result (Table 1, entry 2), although Pazdera reported the similar reaction in organic solvent without catalyst in moderate to good yield.⁹ The yield (86%) was greatly enhanced in the presence of Na₂CO₃ (Table 1, entry 3). Several other bases were examined meanwhile, and Na₂CO₃ showed as the best one. Subsequently, five other Fe salts [Fe(NO₃)₃·9H₂O, FeSO₄·7H₂O, Fe(NH₄)₂(SO₄)₂·H₂O, FeCl₃ and FeS] and four Cu salts (CuI, CuCl, CuBr, CuO) catalysts were evaluated, and the results showed that Fe(NO₃)₃·9H₂O was the best choice (Table 1, entry 9). Further investigation showed that sodium dodecylbenzenesulfonate (SDBS) as an additive (phase-transfer catalysts) can improve the yield (96%) of product to some extent (Table 1, entry 18). Therefore, the optimized conditions were to use a combination of Fe(NO₃)₃·9H₂O (10 mol%) and SDBS (20 mol%) in the presence of Na₂CO₃ as base in water at 80 °C.

Table 1. Condition screening for Fe- or Cu-catalyzed tandem reaction of 2-aminobenzenethiol **1a** with phenyl isothiocyanate **2a** in water^a

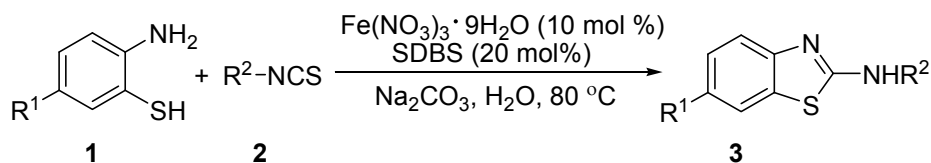


Entry	Catalyst	Base	PTC	Yield ^b (%)
1	Fe ₂ (SO ₄) ₃ ·H ₂ O	-	-	70
2	-	-	-	55 ^c
3	Fe ₂ (SO ₄) ₃ ·H ₂ O	Na ₂ CO ₃	-	86
4	Fe ₂ (SO ₄) ₃ ·H ₂ O	K ₂ CO ₃	-	70
5	Fe ₂ (SO ₄) ₃ ·H ₂ O	NaHCO ₃	-	78
6	Fe ₂ (SO ₄) ₃ ·H ₂ O	DBU	-	52
7	Fe ₂ (SO ₄) ₃ ·H ₂ O	Et ₃ N	-	83
8	Fe ₂ (SO ₄) ₃ ·H ₂ O	DABCO	-	78
9	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	-	89
10	FeSO ₄ ·7H ₂ O	Na ₂ CO ₃	-	88
11	Fe(NH ₄) ₂ (SO ₄) ₂ ·H ₂ O	Na ₂ CO ₃	-	78
12	FeCl ₃	Na ₂ CO ₃	-	63
13	FeS	Na ₂ CO ₃	-	68
14	CuCl	Na ₂ CO ₃	-	70
15	CuBr	Na ₂ CO ₃	-	83
16	CuI	Na ₂ CO ₃	-	87
17	Cu ₂ O	Na ₂ CO ₃	-	86
18	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC1 ^d	96
19 ^e	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC1 ^d	76
20	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC2 ^d	90
21	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC3 ^d	80
22	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC4 ^d	93
23	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PTC5 ^d	92
24	Fe(NO ₃) ₃ ·9H ₂ O	Na ₂ CO ₃	PEG-400	trace

a) Reaction conditions: 2-aminobenzenethiol **1a** (0.3 mmol), phenyl isothiocyanate **2a** (1.2 equiv), Cat. (10 mol%), base (2.0 equiv), PTC (phase-transfer catalysis, 20 mol %), H₂O (3 mL), 80 °C, overnight. b) Isolated yield based on 2-aminobenzenethiol **1a**. c) 72 h. d) PTC1: sodium dodecylbenzenesulfonate (SDBS), PTC2: hexadecyldimethylbenzylammonium chloride, PTC3: tetrabutylammonium bromide (TBAB), PTC4: octadecyltrimethylammonium chloride, PTC5: sodium dodecylsulfonate. e) rt, 48 h.

The scope of the process was studied under the optimized reaction conditions. From Table 2, for most cases, the transformation proceeded smoothly with a wide range of isothiocyanates and 2-aminobenzenethiols leading to the corresponding products **3** in moderate to good yields. As expected, the reaction of 2-aminobenzenethiol **1a** and 4-nitrophenyl isothiocyanate **2b** gave rise to the desired product **3b** in 84% yield (Table 2, entry 2). Similar or better yield was generated when 4-fluorophenyl isothiocyanate **2c** or 4-chlorophenyl isothiocyanate **2d** was used as a partner in the reaction (Table 2, entries 3 and 4). 4-Methylphenyl isothiocyanate **2e** also furnished the corresponding product in good yield using 2-aminobenzenethiol **1a** (Table 2, entry 5). To our delight, alkyl isothiocyanate was also good substrate for this one-pot tandem reaction in moderate yield (Table 2, entry 6). Methoxy-, bromo- or iodo-substituted 2-aminobenzenethiols **1b**, **1c** and **1d** were examined meanwhile, and the desired products were obtained in moderate to excellent yields (Table 2, entries 7-12).

Table 2. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -catalyzed one-pot tandem reaction of 2-aminobenzenethiol **1** with isothiocyanate **2**^a



Entry	1/R ¹	2/R ²	Yield of 3 (%) ^b	Entry	1/R ¹	2/R ²	Yield of 3 (%) ^b
1	1a /H	2a /C ₆ H ₅	3a , 96	7	1b /OMe	2a /C ₆ H ₅	3g , 94
2	1a /H	2b /4-NO ₂ C ₆ H ₄	3b , 84	8	1b /OMe	2e /4-MeC ₆ H ₄	3h , 77
3	1a /H	2c /4-FC ₆ H ₄	3c , 70	9	1b /OMe	2d /4-ClC ₆ H ₄	3i , 72
4	1a /H	2d /4-ClC ₆ H ₄	3d , 91	10	1c /Br	2e /4-MeC ₆ H ₄	3j , 57
5	1a /H	2e /4-MeC ₆ H ₄	3e , 75	11	1d /I	2a /C ₆ H ₅	3k , 65
6	1a /H	2f /Cyclohex.	3f , 65	12	1d /I	2d /4-ClC ₆ H ₄	3l , 80

a) Reaction conditions: 2-aminobenzenethiol **1** (0.3 mmol), isothiocyanate **2** (1.2 equiv), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (10 mol %), Na_2CO_3 (2.0 equiv.), SDBS (20 mol %), H_2O (3 mL), 80 °C. b) Isolated yield based on 2-aminobenzenethiol **1**

In conclusion, we have described a practical and efficient route for generation of diverse 2-aminobenzothiazoles *via* $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -catalyzed one-pot tandem addition/cyclization reaction of 2-aminobenzenethiol and isothiocyanate. It is noteworthy that the reaction is conducted under ligand-free conditions in water. We believe that this methodology may become a very useful tool in organic synthesis.

EXPERIMENTAL

General procedure for $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -catalyzed one-pot tandem reaction of 2-aminobenzenethiol **1** with isothiocyanate **2**: A mixture of 2-aminobenzenethiol **1** (0.30 mmol), isothiocyanate **2** (0.36 mmol, 1.2 equiv.), Na_2CO_3 (0.6 mmol, 2.0 equiv.), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.03 mmol, 10 mol%), SDBS (0.06 mmol, 20 mol%) was stirred in water (3.0 mL) at 80 °C under air. After completion of the reaction as indicated by TLC, the reaction mixture was cooled in ice bath. The solid was filtered off and washed with saturated brine, then washed with water, and dried under vacuum. Then the solid was washed with petroleum ether, and the product **3** was obtained in almost pure form (except for **3b** needing to pass through a small plug of silica).

***N*-Phenylbenzo[*d*]thiazol-2-amine (3a)**,^{7a} white solid, mp 158-160 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.13-7.19 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 9.0 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 118.7, 119.9, 120.3, 121.9, 123.9, 125.6, 129.1, 129.3, 129.5, 150.7, 164.5.

***N*-(4-Nitrophenyl)benzo[*d*]thiazol-2-amine (3b)**,^{7a} yellow solid, mp 230-231 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.24 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 2H), 8.27 (d, *J* = 9.2 Hz, 2H), 11.2 (br, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 117.6, 120.5, 121.9, 123.7, 125.9, 126.7, 130.8, 141.4, 146.9, 152.0, 161.2.

***N*-(4-Fluorophenyl)benzo[*d*]thiazol-2-amine (3c)**,^{8a} white solid, mp 216-217 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.14 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.77-7.82 (m, 3H), 10.52 (br, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 116.0 (d, ²*J*_{CF} = 22 Hz), 119.7 (d, ²*J*_{CF} = 18 Hz), 119.8, 121.5, 122.8, 126.3, 130.3, 137.4, 152.4, 157.9 (d, ¹*J*_{CF} = 237 Hz), 162.0.

***N*-(4-Chlorophenyl)benzo[*d*]thiazol-2-amine (3d)**,^{8a} white solid, mp 208-209 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.19 (t, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 119.1, 119.3, 121.0, 122.4, 125.4, 125.9, 128.8, 129.9, 139.5, 151.9, 162.2.

***N*-*p*-Tolylbenzo[*d*]thiazol-2-amine (3e)**,^{8a} white solid, mp 178-179 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.37 (s, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 119.1, 120.8, 121.2, 122.1, 126.0, 129.8, 130.1, 134.6, 137.4, 151.5, 165.9.

***N*-Cyclohexylbenzo[*d*]thiazol-2-amine (3f)** ¹H NMR (400 MHz, CDCl₃) δ 1.18-1.45 (m, 5H), 1.61-1.77 (m, 3H), 2.11-2.13 (m, 3H), 3.5 (br, 1H), 5.79 (br, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 24.8, 25.4, 33.2, 54.6, 118.6, 120.7, 121.2, 125.8, 130.3, 152.4, 166.9; HRMS Calcd for C₁₃H₁₇N₂S [M+H]⁺: 233.1112. Found: 233.19.

6-Methoxy-*N*-phenylbenzo[*d*]thiazol-2-amine (3g) white solid, mp 131-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (s, 3H), 6.91 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.47 (t, *J* = 8.8 Hz, 2H), 8.40 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.9, 105.3, 114.0, 119.9, 120.0, 123.9, 129.4, 131.1, 140.2, 145.8, 155.9, 162.6; HRMS Calcd for C₁₄H₁₃N₂OS [M+H]⁺: 257.0749. Found: 257.0739.

6-Methoxy-*N*-*p*-tolylbenzo[*d*]thiazol-2-amine (3h) white solid, mp 164-165 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 3.80 (s, 3H), 6.90 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 8.35 (br, 1H); ¹³C NMR (100 MHz,

CDCl₃) δ 20.2, 55.4, 104.8, 113.3, 119.2, 120.1, 129.5, 130.6, 133.5, 137.1, 145.4, 155.2, 162.9; HRMS Calcd for C₁₅H₁₅N₂OS [M+H]⁺: 271.0905. Found: 271.0909.

N-(4-Chlorophenyl)-6-methoxybenzo[d]thiazol-2-amine (3i) white solid, mp 179-181 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.83 (s, 3H), 6.95 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 56.0, 105.3, 114.2, 120.5, 120.6, 128.7, 129.5, 131.4, 138.7, 146.0, 156.3, 161.9; HRMS Calcd for C₁₄H₁₂ClN₂OS [M+H]⁺: 291.0359. Found: 291.0375.

6-Bromo-N-p-tolylbenzo[d]thiazol-2-amine (3j) yellow solid, mp 202-203 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (s, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 2H), 7.70 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 114.6, 120.3, 121.0, 123.3, 129.3, 130.2, 131.7, 134.9, 136.8, 150.6, 165.5; HRMS Calcd for C₁₄H₁₂BrN₂S [M+H]⁺: m/z 318.9905. Found: 318.9917.

6-Iodo-N-phenylbenzo[d]thiazol-2-amine (3k) white solid, mp 184-186 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.89 (s, 1H), 8.50 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 120.3, 121.1, 124.7, 129.1, 129.5, 129.6, 135.1, 139.4, 151.8; HRMS Calcd for C₁₃H₁₀IN₂S [M+H]⁺: 352.9609. Found: 352.9615.

N-(4-Chlorophenyl)-6-iodobenzo[d]thiazol-2-amine (3l) white solid, mp 214-215 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.35-7.38 (m, 3H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 8.15 (s, 1H), 10.67 (br, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 85.2, 119.3, 121.2, 125.7, 128.8, 129.0, 132.5, 134.5, 139.0, 151.4, 161.6; HRMS Calcd for C₁₃H₉ClIN₂S [M+H]⁺: 386.9220. Found: m/z 386.9230.

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