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Graphical Abstract

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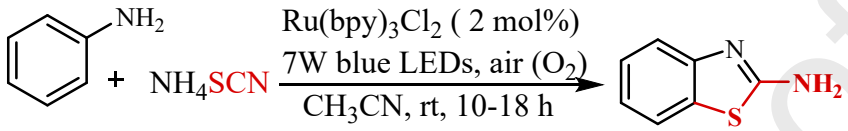

17 examples
74-96 % yields

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Visible-light photoredox catalytic approach for the direct synthesis of 2-aminobenzothiazoles from anilines

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ABSTRACT

A novel, highly efficient and convenient approach for the visible-light-promoted direct synthesis of 2-aminobenzothiazoles from anilines and ammonium thiocyanate is presented. The reaction involves addition/cyclization cascade of SCN radical and anilines under photoredox catalysis with $Ru(bpy)_3Cl_2$. The salient features of the protocol include the utilization of atmospheric oxygen and visible light as clean, inexpensive and sustainable resources at room temperature.

Keywords:
Visible light
Photoredox catalysis
Cyclization
2-Aminobenzothiazoles

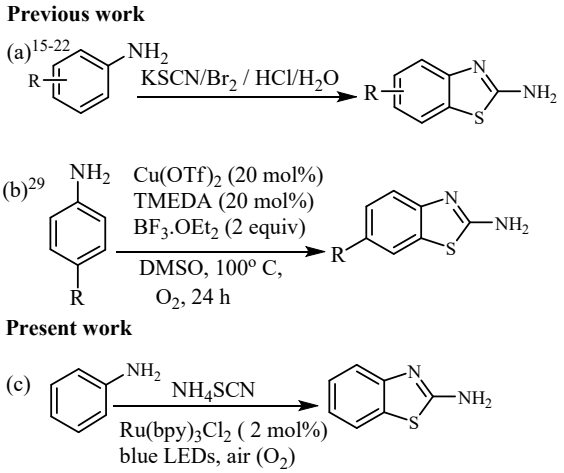
Visible-light has great prospects for the development of sustainable methods for organic synthesis because sunlight is a clean, inexpensive and unending natural energy source.[1–5] In fact the success of this methodology has been basically derived from the pioneering work of the research groups of MacMillan,[1] Yoon[2] and Stephenson,[3] who efficiently utilized $Ru(bpy)_3Cl_2$ (bpy=2,2'-ipyridine) and $Ir(drbbpy)_3Cl_2$ as efficient photoredox catalysts. Advantageously, visible light photoredox catalysis has enabled the utilization of atmospheric oxygen in organic synthesis. In this process atmospheric oxygen oxidatively regenerates photocatalysts from their radical anion to complete the catalytic cycle with concomitant formation of superoxide radical ($O_2^{\bullet -}$), which have also been utilized in situ for various oxidative functionalizations.[1e, 2b, 3, 6, 7]

The 2-aminobenzothiazole moiety features in many natural products and bioactive molecules possessing a broad spectrum of medicinal and pharmaceutical activities such as, antitumor,[8] antibacterial[9a] and antirotaviral,[9b] ubiquitin ligase inhibitor[10] nuclear hormone[11] and the adenosine receptor.[12] The diverse use of biologically active 2-aminobenzothiazoles has prompted the development of their synthetic methods with enhanced efficiency, generality, scope and cost effectiveness. Accordingly, many efficient strategies were established for the synthesis of 2-aminobenzothiazoles.[13–14] Tradtionally, 2-minobenzothiazoles are synthesized from anilines using KSCN and molecular bromine as reagents (Scheme 1a).[15-22]

However, because of its highly hazardous nature, the use of molecular bromine has been restricted in organic synthesis. In 2017, Fan and coworkers have been reported an elegant synthesis of 2-aminobenzothiazoles via iodine-catalyzed and oxygen-promoted cascade reaction of isothiocyanatobenzenes with amines.[23]

Recently, Bollikolla and coworkers have reported the synthesis of 2-arylaminobenzothiazoles through copper catalyzed domino C–N cross-coupling reactions of arylisothioureas with aryl iodide.[24] Most of the protocols available for the synthesis of 2-aminobenzothiazoles, suffer from one or more drawbacks, such as the use of harsh reaction conditions, high temperature, strong acids, toxic reagents and hazardous liquid bromine. Some of these drawbacks were overcome by cross-coupling reactions using transition metals such as Cu,[25] Pd,[26] Ru[27] and Fe[28] under comparatively milder reaction conditions. Recently, Wu and co-workers have reported $Cu(OTf)_2$-catalyzed synthesis of 2-aminobenzothiazoles from anilines using a strong Lewis acid $BF_3.OEt_2$ as an additive (Scheme 1b).[29] However, the development of more convenient environmentally and economically more sustainable synthetic strategies for 2-aminobenzothiazoles are still highly desirable. In view of the above discussion and our continued research efforts focused on the development of new synthetic methods employing visible light photoredox catalysis,[30] herein we report the visible-light photoredox catalytic synthesis of 2-

an
1c).

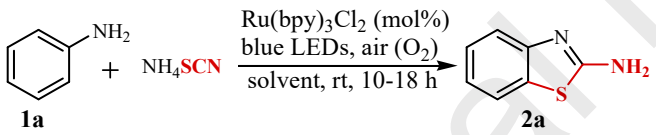


Scheme 1. Synthesis of 2-aminobenzothiazoles from anilines.

To optimize the reaction conditions, a model reaction of aniline **1a** with NH_4SCN was performed using ruthenium as a photoredox catalyst in a solvent under irradiation with blue LEDs [λ = 475.5 nm] in an air atmosphere at room temperature (Table 1). We obtained the desired product **2a** in 90% yield (Table 1, entry 1). Now, the control experiments were conducted, which show that a photocatalyst, air (O_2) and light all are essential for the reaction, because in the absence of any of the reagents/reaction parameters the product was not detected/formed in traces (Table 1, entries 4, 10 and 11).

Table 1

Optimization of reaction conditions[a]



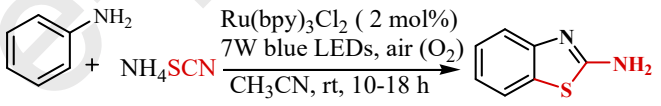
Entry	Catalyst	air	Solvent	Time (h)	Yield (%)[b]
1	$Ru(bpy)_2Cl_2$ (2 mol%)	+	CH_3CN	10	90
2	Eosin Y (2 mol%)	+	CH_3CN	10	76
3	Rose Bengal (2 mol%)	+	CH_3CN	10	65
4	-	+	CH_3CN	10	n. d.[c]
5	$Ru(bpy)_2Cl_2$ (2 mol%)	O_2	CH_3CN	10	90[d]
6	$Ru(bpy)_2Cl_2$ (1 mol%)	+	CH_3CN	10	59
7	$Ru(bpy)_2Cl_2$ (3 mol%)	+	CH_3CN	10	90
8	$Ru(bpy)_2Cl_2$ (2 mol%)	+	THF	10	62
9	$Ru(bpy)_2Cl_2$ (2 mol%)	+	DMF	18	72
10	$Ru(bpy)_2Cl_2$ (2 mol%)	+	CH_3CN	18	traces[e]
11	$Ru(bpy)_2Cl_2$ (2 mol%)	N_2	CH_3CN	10	traces[f]
12	$Ru(bpy)_2Cl_2$ (2 mol%)	+	CH_3CN	18	traces[g]

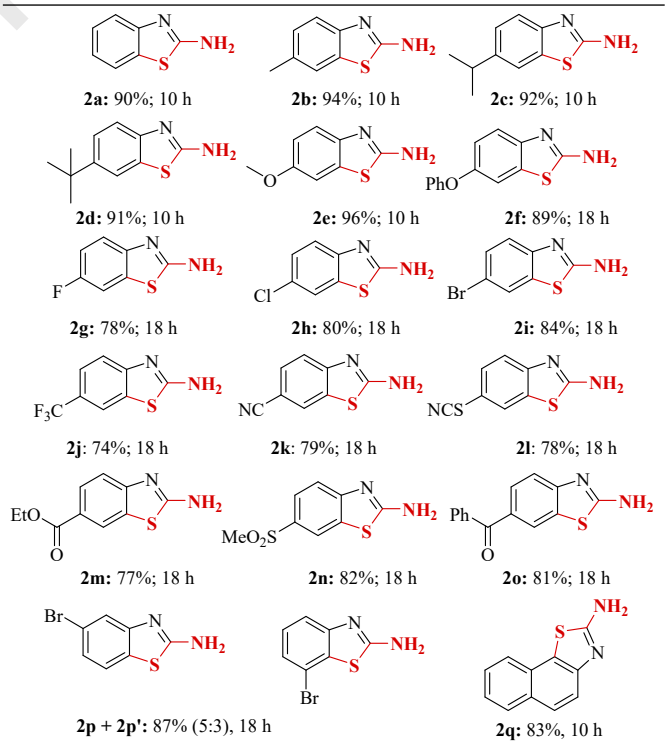
[a]Reaction conditions: aniline **1a** (1.0 mmol), NH_4SCN (1.0 mmol), $Ru(bpy)_3Cl_2$ (2 mol%), base (2 equiv), solvent (3 mL), open to air (without bubbling air) irradiation at rt through the flask's bottom side using Liuxeon Rebel high power blue LEDs (4.45 W , λ max = 447.5 nm).
[c]Reaction was carried out without catalyst; n.d.= not detected.
[d]O_2 balloon was used.
[e]Reaction was performed in the dark.
[f] Reaction was performed under N_2
[g]Reaction was quenched with TEMPO (2 equiv).

It was also noted that the same result was obtained on using O_2 balloon instead of an air atmosphere (Table 1, entry 1 vs 5). The use of another photocatalysts such as Eosin Y and Rose Bengal was not so effective in terms of the reaction time and yield in comparison to $Ru(bpy)_3Cl_2$ (Table 1, entries 1 vs 2 and 3). The optimum amount of catalyst loading required for the maximum yield in the shortest reaction time was 2 mol%. On decreasing the amount of photocatalyst from 2 mol% to 1 mol%, the yield was significantly decreased (Table 1, entry 1 vs 6), whereas on increasing the amount of catalyst loading from 2 mol% to 3 mol% the yield remained unchanged (Table 1, entry 1 vs 7). Next, we optimized the reaction with different solvents and noted that CH_3CN was the best among THF, DMF and CH_3CN, hence it was used throughout the present study (Table 1, entry 1 vs 8 and 9). The reaction was quenched with 2, 2, 6, 6-tetramethylpiperidyl-1-oxyl (TEMPO) (2 equiv), which indicates that a radical intermediate involved in the reaction (Table 1, entry 12).

Table 2

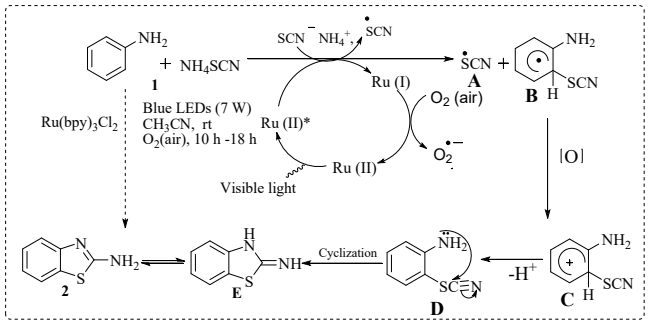
Substrate scope for the synthesis of 2-aminobenzothiazoles[a]





[a]For experimental procedure, see ref. 32
[b]All compounds are known and were characterized by comparison of their spectral data with those reported in the literature.[33]
[c]Yields of isolated pure compounds **2**.

surveyed the scope of the present protocol across a series of anilines **1** incorporating various substitutents, such as CH_3, *i*-Pr, *t*-Bu, OCH_3, PhO, F, Cl, Br, CF_3, CN, SCN, CO_2Et, MeO_2S and PhCO. The reaction worked well in all the cases, affording the corresponding 2-aminobenzothiazoles **2** in moderate to excellent yields (Table 2). Anilines **1** bearing an electron-donating group appeared to react faster and to afford slightly higher yields of 2-aminobenzothiazoles compared with anilines **1** having an electron-withdrawing group (**2b-e** vs **2g-o**). The regioselectivity of the present intramolecular cyclization was investigated with a aniline bearing a *m*-bromo group, and the reaction afforded a mixture of regioisomers **2p** and **2p′** in a ratio of 5:3, respectively. The reaction is also compatible with a fused ring system such as 2-naphthylamine (**2q**).



Scheme 3. A plausible mechanism for the formation of 2-aminobenzothiazoles.

On the basis of the above observations and the literature reports,[30a, 31a,b] a plausible mechanism for the formation of 2-aminobenzothiazoles **2** from anilines **1** and NH_4SCN is depicted in Scheme **3**. On irradiation with visible light Ru(II) undergoes excitation to Ru(II)* followed by single electron transfer (SET) with SCN^- to afford the SCN radical **A** and Ru(I). The photoredox cycle is completed by the oxidation of Ru(I) to Ru(II) with atmospheric oxygen. The formation of superoxide radical anion ($O_2^{\bullet-}$) was confirmed by a test with KI/starch indicator. The thiocyanate radical generated in situ attacks aniline **1** to form the radical intermediate **B**, which is oxidized to give cationic intermediate **C**. The deprotonation of **C** forms intermediate **D**. Then, the intramolecular cyclization involving the attack of nucleophilic amino group on the thiocyanate group produces the desired product **2**.

In summary, we have developed a highly efficient, operationally convenient strategy for the direct synthesis of 2-aminobenzothiazoles from anilines and ammonium thiocyanate. The tandem reactions successfully afforded the corresponding 2-aminobenzothiazoles in moderate to excellent yields under visible light photoredox catalysis with Ru(II) and an air atmosphere. Advantageously, the protocol utilizes visible light and atmospheric oxygen as green and sustainable natural resources at room temperature.

Acknowledgments

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32. *General procedure for the synthesis of 2-aminobenzothiazoles* ***2****:* A mixture of aniline **1** (1 mmol), NH_4SCN **2** (1.0 mmol), ruthinium (2 mol%), and CH_3CN (3 mL) was taken in a flask open to air and stirred at rt for 10-18 h (Table 2). After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate (4:1) as eluent to afford an analytically pure sample of product **2**. All the compounds **2** are known and were characterized by comparison of their spectral data with those reported in the literature.[33] Characterization data of representative compounds **2** are given below with relevant reference:
Compound **2a**:[33b] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.31(t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.67 (bs, 2H, NH_2), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 152.3, 131.8, 126.3, 122.5, 121.2, 119.5. HRMS (EI) Calcd for $C_7H_6N_2S$: 150.0252, found, 150.0256.
Compound **2f**: [33a] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 8.7 Hz, 1H), 7.33 (dt, *J* = 10.6, 5.1 Hz, 3H), 7.07 (t, *J* = 7.4Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 3H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 159.9, 152.7, 150.8, 134.1, 131.1, 123.9, 120.4, 119.0, 118.9,113.3 HRMS (EI) Calcd for $C_{13}H_{10}N_2OS$: 242.0514, found, 242.0511.
Compound **2h**:[33a] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 1.8 Hz, 1H), 7.79 (m, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.33 (s, 2H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 158.5, 135.1, 133.5, 126.5, 122.2, 119.5, 45.5. HRMS (EI) Calcd for $C_8H_8N_2OS$: 228.0027, found, 228.0031.
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Highlights

- Photocatalytic approach to 2-aminobenzothiazoles.
- Visible-light-promoted radical reactions.
- Addition/cyclization cascade of thiocyanate and anilines.
- Utilization of atmospheric oxygen as an oxidant.