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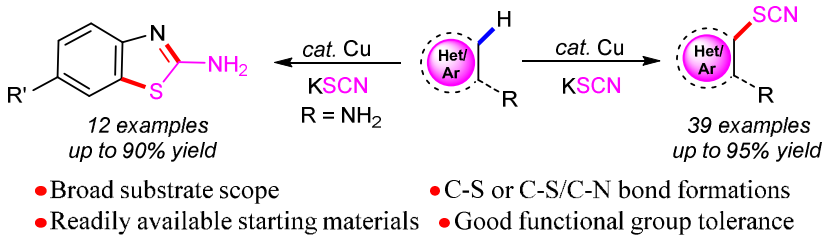
Copper-Catalyzed Aerobic Oxidative Regioselective Thiocyanation of Aromatics and Heteroaromatics

Huanfeng Jiang*, Wentao Yu, Xiaodong Tang, Jianxiao Li, and Wanqing Wu*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

Fax: (+86) 20-8711-2906; E-mail: cewuwq@scut.edu.cn, jianghf@scut.edu.cn

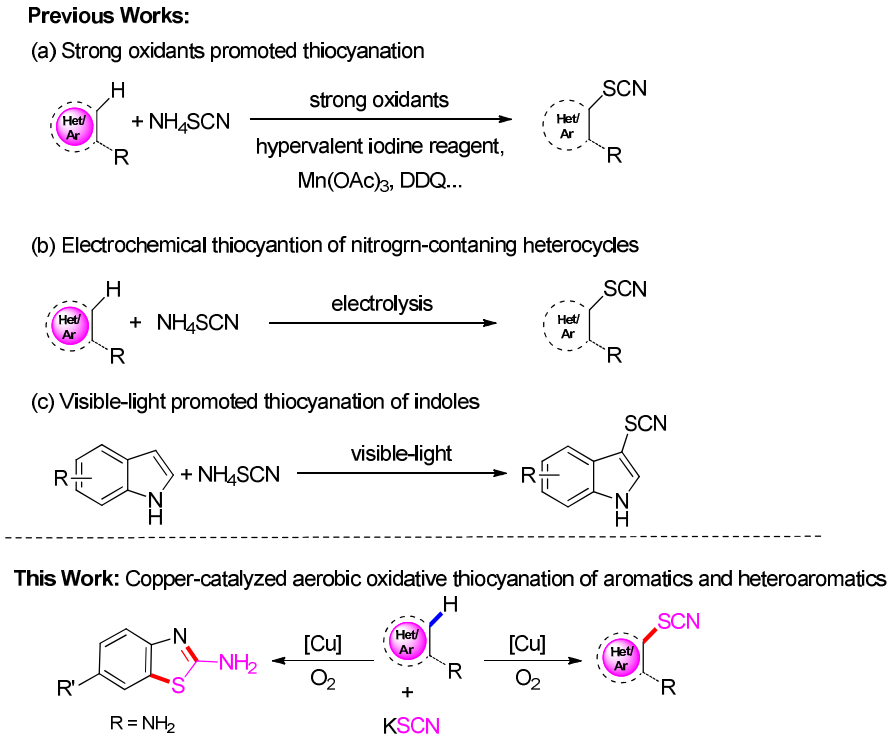


Abstract: A copper-catalyzed aerobic oxidative reaction between aromatics or heteroaromatics with KSCN is developed by using O_2 as the oxidant. The combination of $Cu(OTf)_2$, *N*,*N*,*N'*,*N'*-tetramethylethylene diamine (TMEDA) and $BF_3 \cdot Et_2O$ provides an efficient catalytic system, affording substituted thiocyanation products and 2-amino benzothiazoles in excellent yields. It also possesses a good functional group tolerance for both strong electron-withdrawing and electron-donating groups.

INTRODUCTION

Organosulfur compounds have been found in numbers of drug molecules due to their high biological activities. Hence, much effort has been devoted to the introduction of

sulfur moieties into organic carbon skeletons. Thiocyanation is one of the direct methods for the introduction of sulphur atom on the aromatic rings.[1] In addition, the thiocyanate group is a useful intermediate since it can be readily converted into other sulphur functionalities.[2] In the past few years, many efficient methods for constructing this class of compounds by using thiocyanate salts, including visible light[3], electrolysis[4], DDQ,[5] hypervalent iodine reagents,[6] oxone,[7] $Mn(OAc)_3$,[8] or others[9] have been successfully reported (Scheme 1). Despite the significance, many of these approaches still have some drawbacks and limitations, such as strong acidic or oxidation conditions, the employment of stoichiometric metal salts and narrow substrate scope.



Scheme 1. Synthetic Strategies for thiocyanation of aromatics and heteroaromatics

Substituted 2-amino benzothiazoles represent a major class of heterocycles.[10] Most of them have been extensively studied for their biological activities and medicinal

value (Figure 1, **A**-**D**) including the anti-HIV agent **A**,[11a] the antifungal compound **B**,[11c] the H_3-receptor ligand **C**[11b] and riluzole **D**[11d] (which is used to treat amyotrophic lateral sclerosis (ALS), a lethal neurodegenerative disease). Therefore, their synthesis has also attracted a broad attention from the organic chemistry community in the past decades.[12] Despite the significant advances, some of these developments suffer from certain limitations, such as prefunctionalized reactants or harsh reaction conditions which lower the synthetic efficiency and generality. Hence, the development of efficient and practical synthetic methods for the straightforward construction of this scaffold is still desirable.

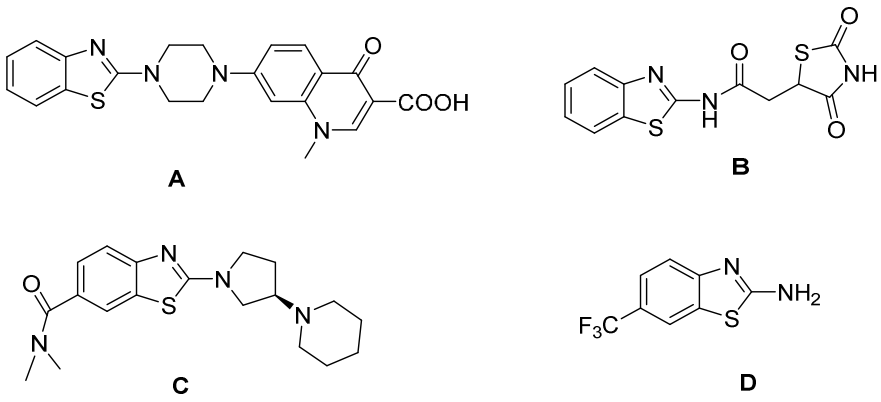


Figure 1. Several bioactive 2-*N*-substituted benzothiazole derivatives

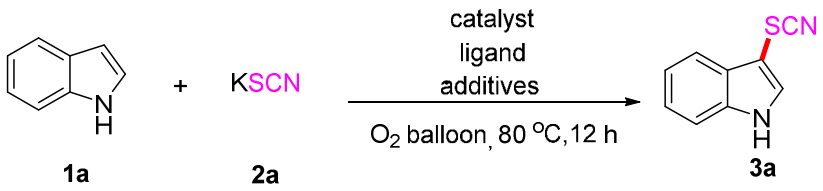
Compared to noble metal species, copper catalysts have received great attention owing to low cost and abundance in organic synthesis.[13,14] On the other hand, molecular oxygen (O_2) is a preferred ideal oxidant since it is atom-economical, environmentally benign, and abundant.[15] Therefore, combining Cu and O_2 in catalytic systems is notable due to the broad substrate suitability under mild conditions, which is known as inherently "green" processes.[16] As part of our continuous efforts on copper-catalyzed aerobic oxidative reactions,[17] herein, we report a Cu-catalyzed

aerobic oxidative regioselective thiocyanation of aromatics and heteroaromatics with O_2 as the sole oxidant.

RESULTS AND DISCUSSION

Indole **1a** and KSCN **2a** were initially chosen as model substrates to optimize the reaction conditions (Table 1). Treatment of **1a** with **2a** using $Cu(OTf)_2$ as catalyst in DMSO under O_2 atmosphere only gave the desired **3a** in 12% yield (entry 1). Significantly, the use of ligand (TMEDA) and additive ($BF_3 \cdot Et_2O$) improved the catalytic efficiency and the target product **3a** was afforded in 83% yield (entry 2). However, in the absence of TMEDA or $BF_3 \cdot Et_2O$, the yield of **3a** was decreased dramatically (entries 3-4). Other copper catalysts, such as CuO, $CuBr_2$, $Cu(OAc)_2$, CuCl, CuI were also examined (entries 5-9). Excitingly, $Cu(OTf)_2$ proved to be an ideal choice among the tested catalysts. Subsequently, different solvents were investigated, and DMSO gave the best results (entries 10-12). Furthermore, various ligands and Lewis acid additives were also examined (entries 13-19). It is found that the combination of *N*,*N*,*N'*,*N'*-tetramethylethylene diamine (TMEDA) and $BF_3 \cdot Et_2O$ gave the superior results than others. Control experiments revealed that copper and O_2 atmosphere are critical to this transformation (entries 20-21). Thus, the optimal reaction conditions were as follows: **1a** (0.3 mmol), **2a** (0.4 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %) and $BF_3 \cdot Et_2O$ (0.6 mmol) in DMSO at 80 ^oC with O_2 as the oxidant.

Table 1. Optimization of Reaction Conditions[a]



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

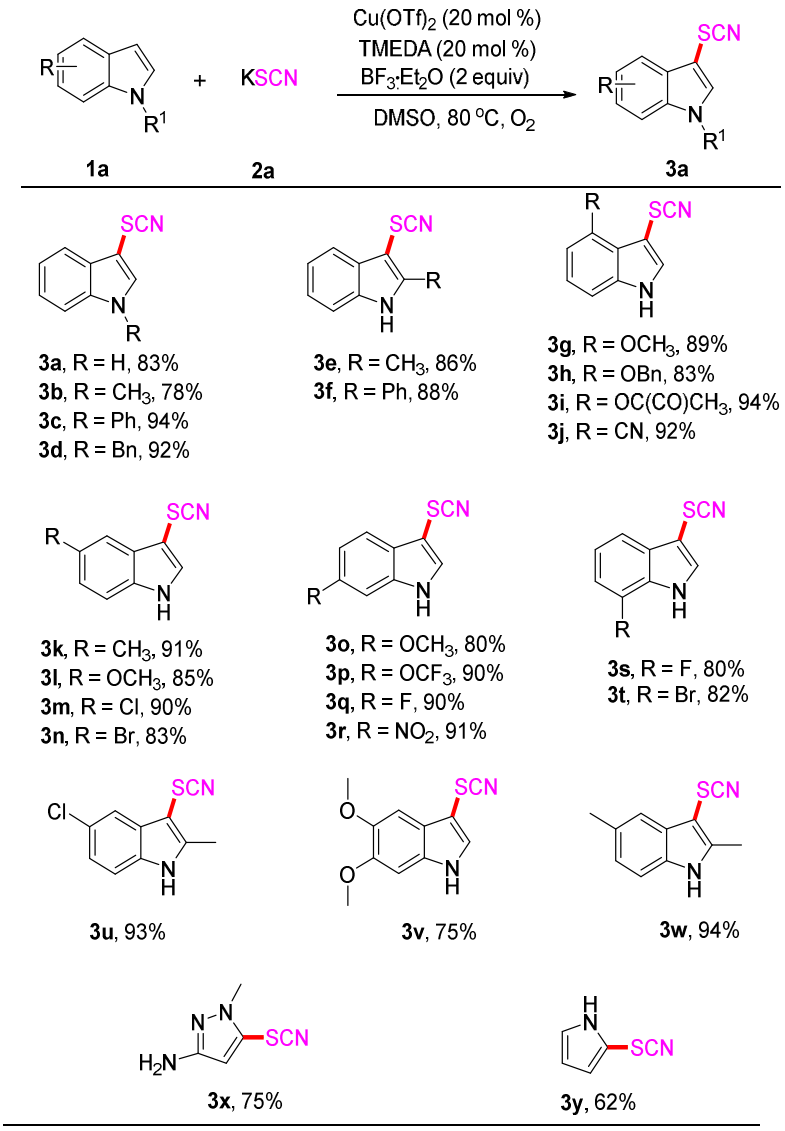
Entry	Catalyst	Ligand[b]	Additive	Solvent	Yield (%)[c]
1	$Cu(OTf)_2$	-	-	DMSO	12
2	**$Cu(OTf)_2$**	**TMEDA**	**$BF_3{\cdot}Et_2O$**	**DMSO**	**90 (83)**
3	$Cu(OTf)_2$	TMEDA	-	DMSO	45
4	$Cu(OTf)_2$	-	$BF_3{\cdot}Et_2O$	DMSO	43
5	CuO	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	70
6	$CuBr_2$	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	62
7	$Cu(OAc)_2$	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	10
8	CuCl	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	15
9	CuI	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	12
10	$Cu(OTf)_2$	TMEDA	$BF_3{\cdot}Et_2O$	Toluene	ND
11	$Cu(OTf)_2$	TMEDA	$BF_3{\cdot}Et_2O$	MeCN	NR
12	$Cu(OTf)_2$	TMEDA	$BF_3{\cdot}Et_2O$	1,4-dioxane	Trace
13	$Cu(OTf)_2$	acetylacetone	$BF_3.Et_2O$	DMSO	ND
14	$Cu(OTf)_2$	Bpy	$BF_3{\cdot}Et_2O$	DMSO	ND
15	$Cu(OTf)_2$	Phen	$BF_3{\cdot}Et_2O$	DMSO	ND
16	$Cu(OTf)_2$	TMEDA	$Eu(OTf)_3{\cdot}xH_2O$	DMSO	16
17	$Cu(OTf)_2$	TMEDA	AgOTf	DMSO	Trace
18	$Cu(OTf)_2$	TMEDA	$FeCl_3$	DMSO	18
19	$Cu(OTf)_2$	TMEDA	$ZnCl_2$	DMSO	Trace
20	-	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	NR
21[d]	$Cu(OTf)_2$	TMEDA	$BF_3{\cdot}Et_2O$	DMSO	8

[a] The reactions were carried out with **1a** (0.3mmol) , **2a** (0.4mmol) , [Cu] (20 mol %), ligand (20 mol %), and additives (0.6 mmol), in 2 mL of solvent at 80 °C under O_2 balloon for 12 h. [b]

TMEDA = *N,N,N',N'*-tetramethylethylene diamine; Bpy = 2,2'-bipyridine; Phen = 1,10-phenanthroline. [c] Determined by GC using dodecane as the internal standard. The value in parentheses is the isolated yield. [d] Under N_2 atmosphere.

With these optimized conditions in hand, we next explored the generality of the process, and the results are summarized in Table 2. For *N*-substituted indoles, such as *N*-methyl-, *N*-phenyl-, and *N*-benzyl indoles, the corresponding 3-thiocyano products were afforded in 78%, 94% and 92% yields respectively. For the indoles with a phenyl or methyl group at the C-2 position, the corresponding products were formed in excellent yields under identical conditions, indicating that the reaction was not affected by C-2 steric hindrance. The reactions with substituted indoles bearing electron-donating or electron-withdrawing groups at the phenyl ring proceeded smoothly to provide the desired products in moderate to good yields, even strong electron-withdrawing substituents, such as 4-CN, 6-NO_2, gave the corresponding 3-thiocyano indoles (**3j**, **3r**) in excellent yields. Halogen groups substituted including fluoro, chloro, and bromo, at the phenyl ring of the indoles, were well tolerated under the optimized reaction conditions. Moreover, pyrrole and 1-methy-3-aminopyrazols also transferred to the corresponding products in moderate yields (**3x**, **3y**).

Table 2. Scope of the thiocyanation reaction of substituted indoles [a]

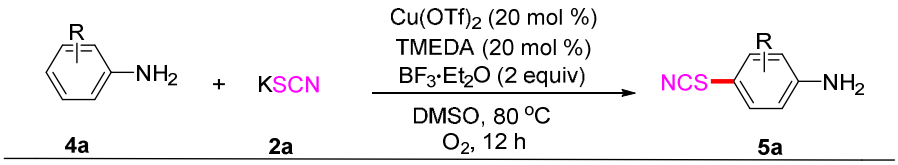


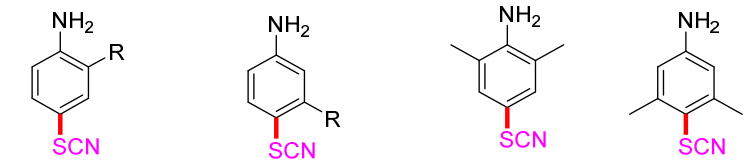
[a] Standard reaction conditions: **1a** (0.3 mmol), **2a** (0.4 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %), $BF_3 \cdot Et_2O$ (0.6 mmol), DMSO (2 mL), O_2 (1 balloon), 80 °C, 12 h.

In the past decade, few examples in the *para* aromatic C-H functionalization have been reported, in which it has remained extremely difficult.[18] Herein, we reported the *para*-thiocycnation of anilines under the optimized conditions. With increasing of KSCN from 0.4 to 0.6 mmol, various anilines were converted into the respective

4-thiocyanatoanilines **5a-5n** in moderate to excellent yields in Table 3. *meta*-Substitution relative to the newly formed C-S bond was well tolerated bearing electron-withdrawing (**5d, 5e, 5f**) or electron-donating substituents (**5b**). Interestingly, for the *meta*-substituted anilines, the reaction could afford the corresponding products regiospecifically in excellent yields (**5g-5j**). As for *N*-methylaniline and *N,N*-dimethylaniline, they were also well tolerated under the optimized reaction conditions (**5m**, **5n**).

Table 3. Scope of the thiocyanation of 4-thiocyanation of anilines [a]





5a, R=H, 78%

5b, R=CH_3, 69%

5c, R=F, 72%

5d, R=Cl, 91%

5e, R=Br, 90%

5f, R=CN, 95%

5g, R=CH_3, 80%

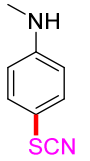
5h, R=Br, 83%

5i, R=COOEt, 83%

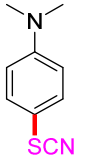
5j, R=CF_3, 88%

5k, 89%

5l, 77%



5m, 76%



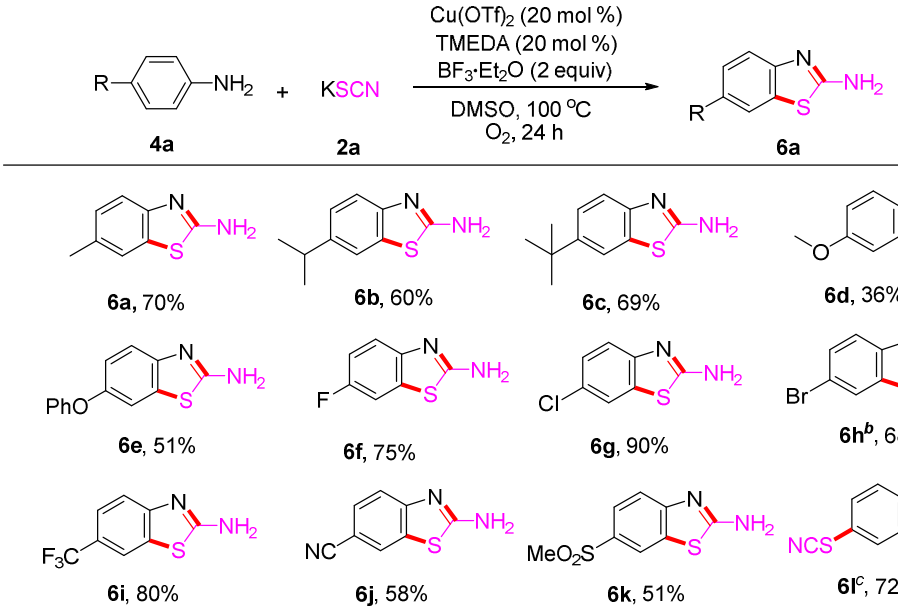
5n, 80%

[a] Standard reaction conditions: **4a** (0.3 mmol), **2a** (0.6 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %), $BF_3 \cdot Et_2O$ (0.6 mmol), DMSO (2 mL), O_2 balloon, 80 °C, 12 h.

When the 4-substituted anlinines were chosen for the reactant, various 1,3-benzothiazol-2-amines were produced (Table 4). The reaction conditions were compatible with alkyl, fluoro, chloro, bromo, and trifluoromethyl groups (**6a-6c, 6f-6i**). However, the product yields decreased when the substituents were -OMe,

-OBn, -CN and -SO_2Me (**6d, 6e, 6j, 6k**). Obviously, the electronic effect plays an important role, and both strong electron-rich and electron-poor substituents on the benzene ring disfavored the transformation. Noteworthily, the generation of 6-thiocyanato-1,3-benzothiazol-2-amine from aniline requires the stronger reaction conditions (**6l**).

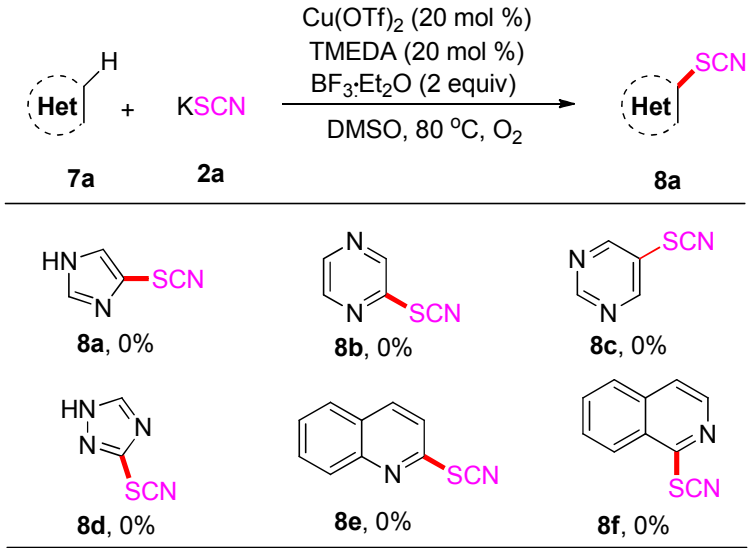
Table 4. Scope of the thiocyanation reaction of 4-substituted anilines [a]



[a] Standard reaction conditions: **4a**(0.3 mmol), **2a**(0.6 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %), $BF_3 \cdot Et_2O$ (0.6 mmol), DMSO (2 mL), O_2 balloon, 100 °C, 12 h. [b] 80 °C. [c] **2a** (0.9 mmol), 110 °C.

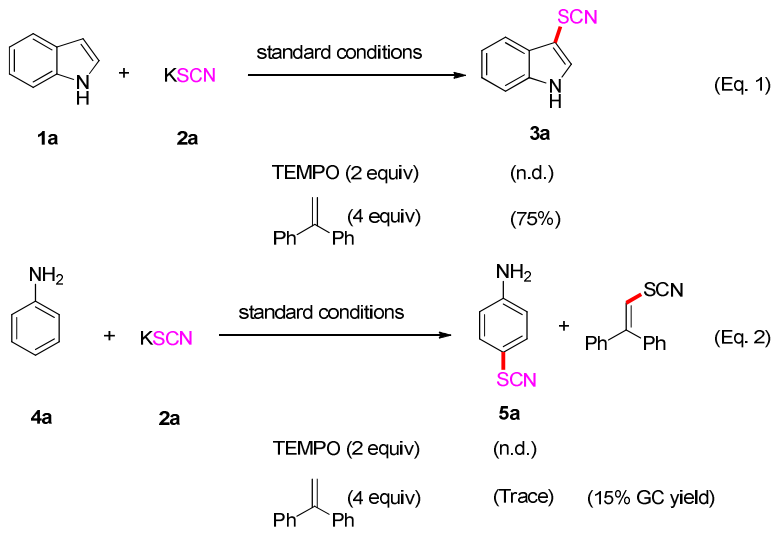
As the success of these methods in indoles and anilines, we next applied the optimized conditions to other *N*-heterocyclic compounds. Unfortunately, it is failed when we tried to use other *N*-heterocyclic substrates to produce the thiocyanation products (Table 5).

Table 5. Scope of the thiocyanation reaction of *N*-heterocyclic substrates [a]



[a] Standard reaction conditions: **7a** (0.3 mmol), **2a** (0.4 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %), $BF_3 \cdot Et_2O$ (0.6 mmol), DMSO (2 mL), O_2 (1 balloon), 80 °C, 12 h.

To understand more insight into the reaction mechanism, we conducted several experiments (Scheme 2). First, by addition of radical inhibitor TEMPO to the process, no thiocyanation product was detected. However, when 4 equiv of 1,1-diphenylethylene was added to the standard conditions, the 3-thiocyanation product **3a** was obtained in 75% isolated yield and only a trace amount of 4-thiocyanatoaniline **5a** was obtained. These results suggested that free radical might be involved in the reaction of anilines instead of indoles.[19]

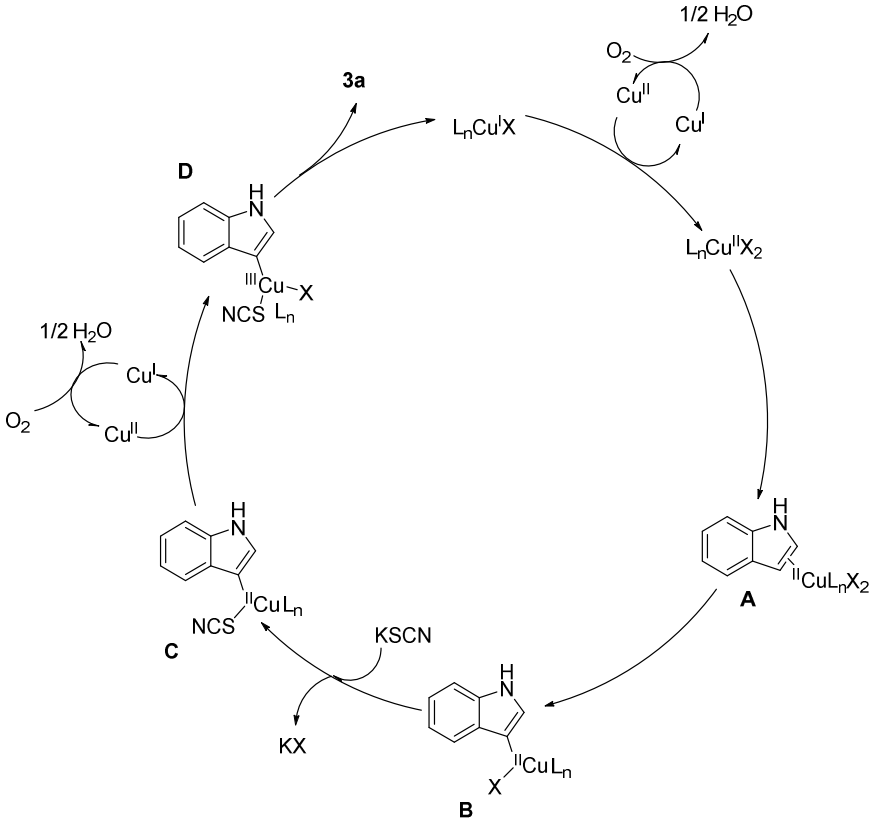


Scheme 2. Control Experiments

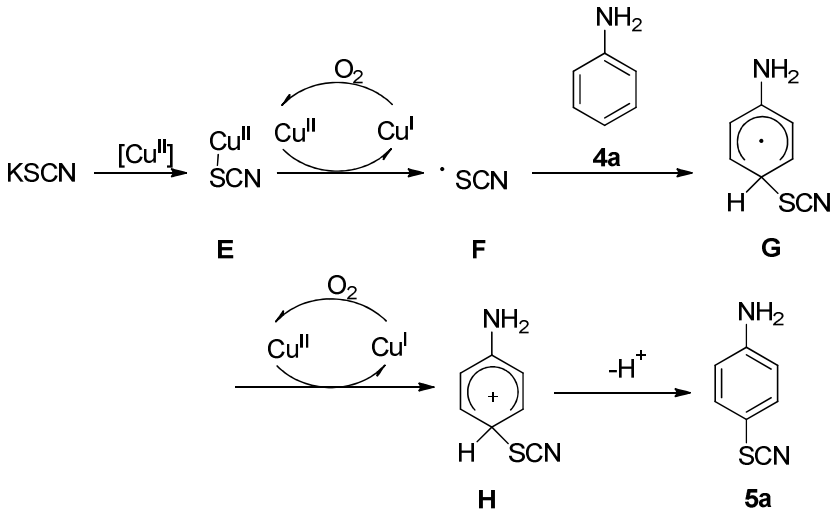
According to the above results, plausible mechanisms are proposed. For indoles case, we suspect that an organometallic pathway should be involved in this transformation (Scheme 3). The catalytic cycle would start with the activation of the Cu^{II} species. Cu^{II} gains the ability to associate with the indole through π-coordination to form copper complex **A**.[21a] Then, a molecule of HX is lost to generate copper complex **B**.[21b] Next, interchange of the anion between copper complex **B** and the potassium thiocyanate occurs to form copper complex **C**.[21b,c] The complex **C** would be oxidized to Cu^{III} complex **D** and the product **3a** is produced followed by the reductive elimination.[21b,d] As for $BF_3{\cdot}Et_2O$, we suggested that it may played as a Lewis acid in the formation of the iodolium intermediate to activate C3 position of indole.[22]

For aniline case, the above experiments imply the generation of SCN radical (Scheme 4). The reaction is initiated by the copper-mediated single electron transfer (SET) in Cu^{II}-SCN **E** generates the SCN radical **F**.[8,23] Then, the radical **F** reacts with

the electron-rich site of aniline **4a** to deliver intermediate **G** which is further oxidized to the aromatic cation **H**.[23e] Finally, the desired product is afforded by proton elimination of **H**.[23f] Meanwhile, the Cu^{I} can be oxidized by DMSO or O_2 to generate the Cu^{II} species.[20] As for 4-substituted aniline, when the *o*-anline was generated, it could be cyclized immediately to form 2-amino benzothiazoles *via N*-attack.[12]



Scheme 3. Possible mechanism



Scheme 4. Possible mechanism

CONCLUSION

In conclusion, we have developed a Cu-catalyzed aerobic oxidative thiocyanation of aromatics and heteroaromatics, which are ubiquitous structural units in a number of biologically active compounds. This method exhibits a good functional group tolerance even with strong electron-withdrawing groups. Moreover, this reaction provides an attractive practical synthetic strategy for the direct C-S bond formation and a new method for the synthesis of 2-amino benzothiazoles. Meanwhile, the use of molecular oxygen as the oxidant makes the overall chemical transformation sustainable and practical.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in 10 mL tubes under O_2 balloon. TLC was performed by using commercially prepared 100−400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. Unless otherwise noted, all reagents

were purchased as reagent grade and used without further purification. Melting points were measured with a micromelting point apparatus. NMR spectra were recorded in $CDCl_3$, acetone-d_6 or DMSO-d_6 on a 400 MHz spectrometer. Chemical shifts were reported in parts per million (δ) relative to TMS (0.00 ppm) for ^1H NMR data and $CDCl_3$ (77.00 ppm), Acetone (206.68, 29.92) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR data. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared Fourier spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer.

General Procedure for Thiocyanation of Indoles: Indole (0.3 mmol), potassium thiocyanate (0.4 mmol), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %) and $BF_3 \cdot Et_2O$ (0.6 mmol) were mixed in DMSO to stir under O_2 balloon at 80 ^oC. Upon completion, the reaction mixture was washed by saturated NaCl aqueous solution (2×10 mL) and then extracted with ethyl acetate (2×10 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was separated by column chromatography (petroleum ether/ethyl acetatet, 8/1 to 5/1) give the pure products.

3-Thiocyanato-*1H*-indole (3a):[3] Red solid (43 mg, 83 %), m.p. = 70 - 71 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.89 - 7.71 (m, 1H), 7.41 (m, 2H), 7.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 131.0, 127.6, 123.8, 121.9, 118.7, 112.0, 111.9, 92.2 ppm; ν_{max}(KBr)/cm^{-1} 3315, 3116, 2154, 1714, 1504, 1466, 1234, 745; MS (EI, 70 eV): m/z (%) = 174 $[M]^+$, 142, 120, 87, 77.

1-Methyl-3-thiocyanato-1*H*-indole (3b):[3] Yellow solid (44 mg, 78 %), m.p. = 95 - 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 1H), 7.41-7.30 (m, 4H), 3.79 (d, J = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.0, 128.4, 123.4, 121.5, 118.9, 111.8, 110.2, 89.8, 33.3 ppm; ν_{max}(KBr)/cm^{-1} 3112, 3055, 2942, 2152, 1510, 1459, 1330, 1242, 745; MS (EI, 70 eV): m/z (%) = 188 $[M]^+$, 173, 155, 120, 94, 77.

1-Phenyl-3-thiocyanato-*1H*-indole (3c):[3] Red solid (71 mg, 94 %), m.p. = 54 - 55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 1H), 7.65 (s, 1H), 7.56 (m, 3H), 7.47 (d, J = 7.8 Hz, 3H), 7.42 - 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.5, 133.8, 129.8, 128.6, 127.9, 124.6, 124.1, 122.3, 119.1, 111.3, 111.2, 93.1 ppm; ν_{max}(KBr)/cm^{-1} 3157, 3056, 2154, 1595, 1507, 1458, 1318, 1225, 749; MS (EI, 70 eV): m/z (%) = 250 $[M]^+$, 249, 218, 146, 111, 77.

1-Benzyl-3-thiocyanato-*1H*-indole (3d):[3] Yellow solid (73 mg, 92 %), m.p. = 102 - 103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.83 (m, 1H), 7.43 (s, 1H), 7.40 - 7.32 (m, 6H), 7.20 - 7.15 (m, 2H), 5.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.6, 134.2, 128.9, 128.5, 128.1, 127.0, 123.5, 121.7, 119.0, 111.6, 110.6, 90.7, 50.6 ppm; ν_{max}(KBr)/cm^{-1} 3109, 3047, 2930, 2151, 1504, 1462, 1161, 738; MS (EI, 70 eV): m/z (%) = 264 $[M]^+$, 204, 173, 91, 63.

2-Methyl-3-thiocyanato-*1H*-indole (3e):[9i] Yellow solid (49 mg, 87 %), m.p. = 87 - 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.22 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 135.1, 128.6, 122.9, 121.5, 117.9, 112.1, 111.2, 88.6, 11.9 ppm; ν_{max}(KBr)/cm^{-1} 3391, 3324, 3056, 2922, 2148,

1716, 1544, 1404, 1226, 740; MS (EI, 70 eV): m/z (%) = 188 $[M]^+$, 173, 161, 155, 118, 77.

2-Phenyl-3-thiocyanato-*1H*-indole (3f): Yellow solid (66 mg, 88 %), m.p. = 70-71 ^oC; ^1H NMR (400 MHz, DMSO) δ 12.40 (s, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.73 (d, J = 7.1 Hz, 1H), 7.63 (m, 2H), 7.55 (m, 2H), 7.35 - 7.27 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ 143.6, 136.3, 130.5, 129.8 129.7, 129.4, 129.3, 123.9, 121.9, 118.5, 113.0, 112.8, 87.6 ppm; ν_{max}(KBr)/cm^{-1} 3336, 3063, 2151, 1718, 1549, 1403, 1222, 741; HRMS-ESI (m/z): calcd for $C_{15}H_{10}N_2NaS$, $[M+Na]^+$: 273.0465, found 273.0457.

4-Methoxy-3-thiocyanato-*1H*-indole (3g): Brown solid (54 mg, 89 %), m.p. = 143 - 144 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.32 (d, J = 2.7 Hz, 1H), 7.18 (t, J = 8.1 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.62 (d, J = 7.9 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 137.9, 128.7, 124.9, 117.0, 113.0, 105.0, 101.7, 92.4, 55.6 ppm; ν_{max}(KBr)/cm^{-1} 3309, 3108, 2928, 2842, 2154, 1587, 1510, 1252, 1084, 731; HRMS-ESI (m/z): calcd for $C_{10}H_8N_2NaOS$, $[M+Na]^+$: 227.0259, found 227.0250.

4-(Benzyloxy)-3-thiocyanato-*1H*-indole (3h):[3] Brown solid (70 mg, 83 %), m.p. = 107 - 109 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 7.10 (t, J = 8.1 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.9, 136.9, 129.3, 128.5, 127.8, 127.3, 124.7, 117.1, 113.2, 105.3, 102.9, 91.9, 70.2 ppm; ν_{max}(KBr)/cm^{-1} 3404, 3118, 3039, 2922, 2154, 1584, 1506, 1243, 1076, 731; MS (EI, 70 eV): m/z (%) = 280 $[M]^+$, 149, 132, 91, 71.

4-Acetoxy-3-thiocyanato-*1H*-indole (3i): Black solid (66 mg, 94 %), m.p. = 117 - 118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.11 (t, J = 7.9 Hz, 1H), 7.03 (m, 2H), 6.89 (d, J = 7.6 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 142.9, 138.0, 132.9, 123.6, 119.4, 114.5, 112.4, 110.7, 88.5, 21.1 ppm; ν_{max}(KBr)/cm^{-1} 3353, 3123, 2924, 2156, 1752, 1207, 1045, 738; HRMS-ESI (m/z): calcd for $C_{11}H_8N_2NaO_2S$, $[M+Na]^+$: 255.0200, found 255.0199.

4-Cyano-3-thiocyanato-*1H*-indole (3j): Yellow solid (55 mg, 92 %), m.p. = 177 - 178 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 11.45 (s, 1H), 7.99 (s, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.26 (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ 138.0, 137.3, 129.0, 127.6, 124.0, 118.9, 118.0, 112.5, 102.8, 92.1 ppm; ν_{max}(KBr)/cm^{-1} 3299, 3114, 2912, 2221, 1715, 1541, 1346, 745; HRMS-ESI (m/z): calcd for $C_{10}H_5N_3NaS$, $[M+Na]^+$: 222.0103, found 222.0096.

5-Methyl-3-thiocyanato-*1H*-indole (3k):[3] Yellow solid (51 mg, 91 %), m.p. = 94 - 95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.46 (s, 1H), 7.25 (s, 1H), 7.17 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 134.3, 131.4, 131.1, 127.8, 125.4, 118.0, 112.4, 111.8, 90.8, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 3327, 3120, 3036, 2920, 2154, 1480, 1414, 1235, 794; MS (EI, 70 eV): m/z (%) = 188 $[M]^+$, 155, 128, 130, 91, 80.

5-Methoxy-3-thiocyanato-*1H*-indole (3l):[3] Yellow solid (52 mg, 85 %), m.p. = 128 - 129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.31 (s, 1H), 7.18 (d, J = 9.0 Hz, 1H), 7.08 (s, 1H), 6.83 (d, J = 8.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 131.5, 130.8, 128.4, 114.3, 113.1, 112.2, 99.7, 91.0, 55.8 ppm;

ν_{max}(KBr)/cm^{-1} 3327, 3120, 2938, 2154, 1625, 1582, 1434, 1292, 1209, 806; MS (EI, 70 eV): m/z (%) = 204 $[M]^+$, 188, 178, 161, 134, 76.

5-Chloro-3-thiocyanato-*1H*-indole (3m): Black solid (57 mg, 90 %), m.p. = 123 - 124 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 11.10 (s, 1H), 7.82 (d, J = 2.8 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.14 (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ 135.2, 134.2, 129.1, 126.9, 123.5, 117.4, 114.3, 111.0, 90.8 ppm; ν_{max}(KBr)/cm^{-1} 3319, 3316, 2923, 2150, 1691, 1567, 1467, 792; HRMS-ESI (m/z): calcd for $C_9H_5ClN_2NaS$, $[M+Na]^+$: 230.9744, found 230.9754.

5-Bromo-3-thiocyanato-*1H*-indole (3n):[3] Red solid (63 mg, 83 %), m.p. = 175 - 176 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 11.24 (s, 1H), 7.95 (m, 1H), 7.91 (s, 1H), 7.54 (m, 1H), 7.45 - 7.38 (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ 135.5, 134.0, 129.6, 126.1, 120.5, 114.6, 114.4, 111.1, 90.7 ppm; ν_{max}(KBr)/cm^{-1} 3328, 3111, 2149, 1696, 1563, 1453, 868, 792; MS (EI, 70 eV): m/z (%) = 253 $[M]^+$, 251, 173, 146, 129.

6-Methoxy-3-thiocyanato-*1H*-indole (3o):[3] Red solid (49 mg, 80 %), m.p. = 113 - 114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.37 (s, 1H), 6.99 - 6.82 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 137.0, 129.9, 121.7, 119.2, 112.2, 112.0, 95.3, 91.8, 55.6 ppm; ν_{max}(KBr)/cm^{-1} 3323, 3129, 2918, 2160, 1627, 1511, 1243, 809; MS (EI, 70 eV): m/z (%) = 204 $[M]^+$, 189, 178, 161, 134, 76.

6-(Trifluoromethoxy)-3-thiocyanato-*1H*-indole (3p): Yellow solid (70 mg, 90 %), m.p. = 51 - 52 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.54 (d, J = 2.2 Hz, 1H), 7.31 (s, 1H), 7.19 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 146.2, 135.7, 132.3, 126.2, 120.6 (q, J = 255.3 Hz), 119.6, 116.0, 111.7 (q, J = 7.6 Hz), 105.2, 92.6 (q, J =10.6 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3108, 2927, 1716, 1515, 1258, 1159, 961, 888; HRMS-ESI (m/z): calcd for $C_{10}H_5F_3N_2NaOS$, $[M+Na]^+$: 280.9967, found 280.9974.

6-Fluoro-3-thiocyanato-*1H*-indole (3q):[3] Red solid (52 mg, 90 %), m.p. = 106 - 107 ^oC; ^1H NMR (400 MHz, DMSO) δ 12.07 (s, 1H), 8.00 (s, 1H), 7.70 - 7.65 (m, 1H), 7.36 (d, J = 9.7 Hz, 1H), 7.13 (t, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 159.5 (d, J = 235.5 Hz), 136.3 (d, J = 12.9 Hz), 133.9, 124.1, 119.0 (d, J = 10.2 Hz), 112.1, 109.7 (d, J = 24.8 Hz), 98.9 (d, J = 25.9 Hz), 89.9 ppm; ν_{max}(KBr)/cm^{-1} 3313, 3121, 2923, 2154, 1727, 1506, 1231, 801; MS (EI, 70 eV): m/z (%) = 192 $[M]^+$, 172, 166, 138, 107, 95.

6-Nitro-3-thiocyanato-*1H*-indole (3r): Yellow solid (60 mg, 91 %), m.p. = 179 - 180 ^oC; ^1H NMR (400 MHz, Acetone) δ 11.52 (s, 1H), 8.37 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 2.8 Hz, 1H), 8.01 (m, 1H), 7.75 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, Acetone) δ 149.5, 143.1, 140.5, 137.5, 123.7, 121.5, 116.0, 114.7, 97.9 ppm; ν_{max}(KBr)/cm^{-1} 3355, 3110, 2920, 2154, 1722, 1508, 1328, 665; HRMS-ESI (m/z): calcd for $C_9H_5N_3NaO_2S$, $[M+Na]^+$: 241.9996, found 241.9995.

7-Fluoro-3-thiocyanato-*1H*-indole (3s): Red solid (46 mg, 80 %), m.p. = 113 - 114 ^oC; ^1H NMR (400 MHz, Acetone) δ 7.93 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.22 (m, 1H), 7.07 - 7.01 (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ 150.9 (d, J = 244 Hz), 134.5, 132.6 (d, J = 4.9 Hz), 125.9 (d, J = 14.3 Hz), 123.0 (d, J = 7.8 Hz), 115.3, 112.0, 109.2 (d, J = 16.2 Hz), 93.5 (d, J = 3.4 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3272, 3124,

2159, 1578, 1423, 1232, 784, 685; HRMS-ESI (m/z): calcd for $C_9H_5FN_2NaS$, $[M+Na]^+$: 215.0055, found 215.0050.

7-Bromo-3-thiocyanato-*1H*-indole (3t): Yellow solid (62 mg, 82 %), m.p. = 155 - 157 ^oC; ^1H NMR (400 MHz, Acetone) δ 11.14 (s, 1H), 7.84 (s, 1H), 7.62 (m, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.10 (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ 136.2, 134.5, 130.4, 127.0, 123.8, 118.8, 111.9, 106.3, 93.8 ppm; ν_{max}(KBr)/cm^{-1} 3264, 2155, 1708, 1567, 1194, 774; HRMS-ESI (m/z): calcd for $C_9H_5BrN_2NaS$, $[M+Na]^+$: 274.9249, found 274.9245.

2-Methyl-5-chloro-3-thiocyanato-*1H*-indole (3u): Yellow solid (62 mg, 93 %), m.p. = 170 - 171 ^oC; ^1H NMR (400 MHz, Acetone) δ 10.94 (s, 1H), 7.43 (s, 1H), 7.27 (d, J = 8.6 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, Acetone) δ 144.7, 134.2, 130.0, 126.5, 122.6, 116.8, 113.2, 110.9, 87.9, 11.2 ppm; ν_{max}(KBr)/cm^{-1} 3296, 2925, 2852, 2156,1717, 1549, 1454, 938, 860, 798; HRMS-ESI (m/z): calcd for $C_{10}H_7ClN_2NaS$, $[M+Na]^+$: 244.9912, found 244.9911.

5,6-Dimethoxy-3-thiocyanato-*1H*-indole (3v): Red solid (53 mg, 75 %), m.p. = 142 - 143 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.33 (d, J = 2.8 Hz, 1H), 7.15 (s, 1H), 6.87 (s, 1H), 3.98 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.6, 130.2, 129.3, 120.8, 112.1, 99.7, 95.1, 91.2, 56.3, 56.1 ppm; ν_{max}(KBr)/cm^{-1} 3328, 3122, 2939, 2154, 1484, 1318, 1211,1157, 1020, 842; HRMS-ESI (m/z): calcd for $C_{11}H_{10}N_2NaO_2S$, $[M+Na]^+$: 257.0355, found 257.0359.

2,5-Dimethyl-3-thiocyanato-*1H*-indole (3w): Yellow solid (57 mg, 94 %), m.p. = 135 - 136 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.47 (s, 1H), 7.19 (d, J =

8.2 Hz, 1H), 7.08 - 7.02 (m, 1H), 2.49 (d, J = 2.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.3, 131.1, 128.9, 124.4, 117.7, 112.2, 110.8, 88.2, 21.4, 12.0 pm; ν_{max}(KBr)/cm^{-1} 3285, 3031, 2921, 2152, 1722, 1542, 1459, 1408, 1298, 1222, 798; HRMS-ESI (m/z): calcd for $C_{11}H_{10}N_2NaS$, $[M+Na]^+$: 225.0457, found 225.0457.

1-Methyl-3-amine-5-thiocyanato-*1H*-pyrazol (3x): Yellow solid (35 mg, 75 %), m.p. = 103 - 104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 3.93 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 135.6, 110.9, 81.3, 39.2 ppm; ν_{max}(KBr)/cm^{-1} 3302, 3120, 2929, 2154, 1725, 1607, 1541; HRMS-ESI (m/z): calcd for $C_5H_6N_4NaS$, $[M+Na]^+$: 177.0205, found 177.0203.

2-Thiocyanato-*1H*-pyrrol (3y):[9d] black liquid (23mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 6.99 (s, 1H), 6.65 (s, 1H), 6.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 120.1, 111.2, 110.7, 103.0 ppm; ν_{max}(KBr)/cm^{-1} 3309, 3121, 2159, 1713, 1535, 1024, 740; MS (EI, 70 eV): m/z (%) = 124 $[M]^+$, 98, 71, 70, 79.

4-Thiocyanatoaniline (5a):[9d] Brown solid (35 mg, 78 %), m.p. = 75 - 76 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.8 Hz, 2H), 6.66 (d, J = 7.8 Hz, 2H), 3.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 134.4, 116.0, 112.4, 109.4 ppm; ν_{max}(KBr)/cm^{-1} 3372, 3218, 3045, 2150, 1721, 1582, 1493, 1294, 822; MS (EI, 70 eV): m/z (%) = 150$[M]^+$, 123, 118, 106, 96, 80, 65.

2-Methyl-4-thiocyanatoaniline (5b):[8] Yellow solid (34 mg, 69 %), m.p. = 69 - 70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 2H), 6.64 (d, J = 8.3 Hz, 1H), 3.75 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 135.0, 132.0, 123.8, 115.7, 112.5,

109.2, 17.1 ppm; ν_{max}(KBr)/cm^{-1} 3379, 3037, 2927, 2150, 1729, 1567, 1491, 1292, 882, 813; MS (EI, 70 eV): m/z (%) = 164 $[M]^+$, 138, 131, 104, 77.

2-Fluoro-4-thiocyanatoaniline (5c): Brown solid (36 mg, 72 %), m.p. = 33 - 34 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 1H), 7.16 (m, 1H), 6.77 (t, J = 8.7 Hz, 1H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (d, J = 242.8 Hz), 137.4 (d, J = 12.6 Hz), 129.7 (d, J = 3.3 Hz), 119.7 (d, J = 20.7 Hz), 111.6, 109.4 (d, J = 7.3 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3376, 3061, 2926, 2153, 1623, 1502, 1302, 1206, 877, 811; HRMS-ESI (m/z): calcd for $C_7H_5FN_2NaS$, $[M+Na]^+$: 191.0050, found, 191.0041.

2-Chloro-4-thiocyanatoaniline (5d):[8] Yellow solid (50 mg, 91 %), m.p. = 51 - 52 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 2.0 Hz, 1H), 7.28 - 7.24 (m, 1H), 6.75 (d, J = 8.5 Hz, 1H), 4.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 133.7, 132.5, 119.5, 116.3, 111.7, 109.7 ppm; ν_{max}(KBr)/cm^{-1} 3480, 3072, 3065, 2152, 1614, 1487, 1309, 872, 813; MS (EI, 70 eV): m/z (%) = 184 $[M]^+$, 152, 149, 122, 105, 90, 63.

2-Bromo-4-thiocyanatoaniline (5e): Yellow solid (62 mg, 90 %), m.p. = 57 - 59 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.59 (m, 1H), 7.32 - 7.27 (m, 1H), 6.74 (m, 1H), 4.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 136.8, 133.2, 116.1, 111.7, 110.0, 109.1 ppm; ν_{max}(KBr)/cm^{-1} 3476, 3370, 3063, 2152, 1614, 1483, 1308, 875, 812; HRMS-ESI (m/z): calcd for $C_7H_5B_rN_2NaS$, $[M+Na]^+$: 250.9249, found, 250.9246.

2-Cyano-4-thiocyanatoaniline (5f): Brown solid (49 mg, 95 %), m.p. = 126 - 127 ^oC; ^1H NMR (400 MHz, DMSO) δ 7.82 (d, J = 2.2 Hz, 1H), 7.58 (m, 1H), 6.89 (d, J = 8.9 Hz, 1H), 6.72 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 153.7, 139.0, 138.6, 117.5, 117.1, 112.9, 107.4, 95.0 ppm; ν_{max}(KBr)/cm^{-1} 3441, 3362, 2216, 2151, 1729, 1636,

1583, 1486, 896, 824; HRMS-ESI (m/z): calcd for $C_8H_5N_3NaS$, $[M+Na]^+$: 198.0096, found, 198.0100.

3-Methyl-4-thiocyanatoaniline (5g):[8] Brown solid (39 mg, 80 %), m.p. = 56-58 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 2.5 Hz, 1H), 6.49 (m, 1H), 3.93 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 142.9, 136.2, 117.2, 113.6, 112.0, 108.9, 20.8 ppm; ν_{max}(KBr)/cm^{-1} 3373, 3225, 2928, 2149, 1590, 1480, 1319, 1254, 858, 812; MS (EI, 70 eV): m/z (%) = 164 $[M]^+$, 149, 131, 94, 77.

3-Bromo-4-thiocyanatoaniline (5h):[8] Brown solid (57 mg, 83 %), m.p. = 63 - 65 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 1H), 6.97 - 6.91 (m, 1H), 6.61 (m, 1H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 134.9, 127.5, 119.3, 115.0, 111.2, 110.8 ppm; ν_{max}(KBr)/cm^{-1} 3371, 3064, 2152, 1712, 1580, 1107, 856; MS (EI, 70 eV): m/z (%) = 228 $[M]^+$, 198, 149, 123, 105, 90, 63.

3-Ethoxyformyl-4-thiocyanatoaniline (5i): Yellow solid (56 mg, 83 %), m.p. = 143 - 144 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 2.7 Hz, 1H), 6.91 (m, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.89 (s, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 146.3, 129.4, 127.9, 120.3, 117.3, 116.3, 112.6, 62.0, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3461, 3369, 3237, 2921, 2146, 1683, 1273, 813, 773; HRMS-ESI (m/z): calcd for $C_{10}H_{10}N_2NaO_2S$, $[M+Na]^+$: 245.0355, found, 245.0358.

3-Trifluoromethyl-4-thiocyanato-aniline (5j): Yellow solid (58 mg, 88 %), m.p. = 58 - 59 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 2.6 Hz, 1H), 6.78 (m, 1H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 138.2,

133.6 (q, J = 30.8 Hz), 122.8 (q, J = 272.3 Hz), 117.9, 113.7 (q, J = 5.5 Hz), 111.5, 106.5 ppm; ν_{max}(KBr)/cm^{-1} 3378, 3070, 2156, 1732, 1596, 1329, 1263, 1126, 877, 824; HRMS-ESI (m/z): calcd for $C_8H_6F_3N_2S$, $[M+H]^+$: 219.0198, found, 219.0200.

2,6-Dimethyl-4-thiocyanatoaniline (5k): Yellow solid (48 mg, 89 %), m.p. = 82 - 83 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 3.77 (s, 2H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.8, 123.1, 112.6, 108.4, 17.3 ppm; ν_{max}(KBr)/cm^{-1} 3419, 3344, 3246, 2962, 2151, 1638, 1456, 871; HRMS-ESI (m/z): calcd for $C_9H_{10}N_2NaS$, $[M+Na]^+$: 201.0457, found, 201.0459.

3,5-Dimethyl-4-thiocyanatoaniline (5l): Black solid (43 mg, 77 %), m.p. = 123 - 124 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 6.46 (s, 2H), 3.82 (s, 2H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 144.5, 115.1, 111.8, 109.1, 22.0 ppm; ν_{max}(KBr)/cm^{-1} 3480, 3387, 3216, 2930, 2141, 1588, 1463, 1336, 851; HRMS-ESI (m/z): calcd for $C_9H_{10}N_2NaS$, $[M+Na]^+$: 201.0457, found, 201.0460.

4-Thiocyanato-*N*-methylaniline (5m):[8] Black liquid (37 mg, 76 %), ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 2H), 6.57 (d, J = 7.9 Hz, 2H), 4.02 (s, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 134.6, 113.3, 112.6, 107.3, 30.1 ppm; ν_{max}(KBr)/cm^{-1} 3410, 2927, 2149, 1594, 1510, 1327, 814; MS (EI, 70 eV): m/z (%) = 164 $[M]^+$, 149, 131, 105, 81, 63.

4-Thiocyanato-*N,N*-dimethylaniline (5n):[9d] Brown solid (43 mg, 80 %), m.p. = 67 - 68 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 2.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 134.4, 129.4, 113.1, 112.5,

106.4, 40.0 ppm; ν_{max}(KBr)/cm^{-1} 3338, 3061, 2925, 2152, 1447, 742, 683; MS (EI, 70 eV): m/z (%) = 178 $[M]^+$, 145, 118, 104, 89, 81.

6-Methyl-1,3-benzothiazol-2-amine (6a):[11f] Yellow solid (34 mg, 70 %), m.p. = 129-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 5.53 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 149.7, 131.9, 131.4, 127.1, 120.9, 118.5, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 3392, 3288, 3045, 2932, 1636, 1535, 1460, 1113, 813; MS (EI, 70 eV): m/z (%) = 164 $[M]^+$, 136, 110, 77, 69.

6-Isopropyl-1,3-benzothiazol-2-amine (6b): Green solid (35 mg, 60 %), m.p. = 121 - 122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.3 Hz, 1H), 5.78 (s, 2H), 2.95 (m, 1H), 1.27 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 150.0, 143.2, 131.7, 124.6, 118.7, 118.3, 33.9, 24.2 ppm; ν_{max}(KBr)/cm^{-1} 3436, 3088, 2955, 1632, 1531, 1462, 822; HRMS-ESI (m/z): calcd for $C_{10}H_{13}N_2S$, $[M+H]^+$: 193.0794, found, 193.0796.

6-Tert-butyl-1,3-benzothiazol-2-amine (6c): Black solid (46 mg, 69 %), m.p. = 141 - 142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 1.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.34 (m, 1H), 5.74 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 149.6, 145.5, 131.5, 123.6, 118.4, 117.3, 34.7, 31.6 ppm. ν_{max}(KBr)/cm^{-1} 3434, 3279, 3082, 2957, 1634, 1527, 1464, 1309, 1109, 822 cm$^{-1;}$ HRMS-ESI (m/z): calcd for $C_{11}H_{15}N_2S$, $[M+H]^+$: 207.0950; found, 207.0955.

6-Methoxy-1,3-benzothiazol-2-amine (6d):[11f] Black solid (19 mg, 36 %), m.p. = 158 - 159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 6.90 (m, 1H), 5.15 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1,

155.7, 146.0, 132.5, 119.6, 113.7, 105.4, 55.9 ppm; ν_{max}(KBr)/cm^{-1} 3383, 3295, 3095, 2925, 1543, 1461, 1269, 1205, 807; MS (EI, 70 eV): m/z (%) = 180 $[M]^+$, 165, 137, 110, 80 ,69.

6-Phenoxy-1,3-benzothiazol-2-amine (6e):[11f] Green solid (52 mg, 71 %), m.p. = 168 - 169 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 7.41 (d, J = 8.7 Hz, 1H), 7.34 (dt, J = 10.6, 5.1 Hz, 3H), 7.06 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 8.5 Hz, 3H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, Acetone) δ 167.5, 159.9, 152.6, 150.9, 134.0, 131.0, 123.9, 120.3, 119.0, 118.9, 113.3 ppm; ν_{max}(KBr)/cm^{-1} 3429, 3069, 1536, 1466, 1221, 867, 854, 726; MS (EI, 70 eV): m/z (%) = 242 $[M]^+$, 165, 137, 110, 77.

6-Fluoro-1,3-benzothiazol-2-amine (6f):[11f] Green solid (38 mg, 75 %), m.p. = 183 - 184 ^{o}C; ^{1}H NMR (400 MHz, DMSO) δ 7.59 (m, 1H), 7.47 (s, 2H), 7.32 (m, 1H), 7.09 - 7.01 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ 166.8, 157.6 (d, J = 234.7 Hz), 149.9, 132.4 (d, J = 11.1 Hz), 118.6 (d, J = 8.8 Hz), 113.2 (d, J = 23.5 Hz), 108.2 (d, J = 26.9 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3299, 2086, 2923, 1719, 1539, 1480, 917, 846, 805; MS (EI, 70 eV): m/z (%) = 167 $[M]^+$, 141, 114, 84, 70.

6-Chloro-1,3-benzothiazol-2-amine (6g):[11f] Yellow solid (50 mg, 90 %),m.p. = 200 - 201 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 7.56 (s, 1H), 7.23 (d, J = 8.6 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.88 (s, 2H); ^{13}C NMR (100 MHz, Acetone) δ 168.1, 153.1, 134.3, 126.7, 126.7, 121.3, 120.2 ppm; ν_{max}(KBr)/cm^{-1} 3456, 3282, 3100, 1714, 1529, 1443, 852, 798; MS (EI, 70 eV): m/z (%) = 184 $[M]^+$, 156, 149, 122, 93, 62.

6-Bromo-1,3-benzothiazol-2-amine (6h):[12f] Yellow solid (44 mg, 65 %), m.p. = 214 - 215 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 7.82 (d, J = 1.9 Hz, 1H), 7.37 (m, 1H), 7.31

(d, J = 8.5 Hz, 1H), 6.99 (s, 2H); ^{13}C NMR (100 MHz, Acetone) δ 168.0, 153.3, 134.7, 129.5, 124.1, 120.7, 113.9 ppm; ν_{max}(KBr)/cm^{-1} 3452, 3287, 3099, 2923, 1712, 1628, 1526, 1442; MS (EI, 70 eV): m/z (%) = 227[M]$^+$, 200, 149, 122, 95, 63.

6-Trifluoromethyl-1,3-benzothiazol-2-amine (6i): Yellow solid (52 mg, 80 %), m.p. = 109 - 110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.53 (s, 2H), 6.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 154.4, 131.4, 124.4 (q, J = 270.1 Hz), 124.3 (q, J = 32.5 Hz), 123.2 (q, J = 3.6 Hz), 118.6, 118.4 (q, J =4.0 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3297, 3112, 1526, 1320, 1117, 884, 822; HRMS-ESI (m/z): calcd for $C_8H_6F_3N_2S$, $[M+H]^+$: 219.0198, found, 219.0198.

6-Cyano-1,3-benzothiazol-2-amine (6j): Yellow solid (34 mg, 58 %), m.p. = 204 - 206 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 7.96 (s, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.23 (s, 2H); ^{13}C NMR (100 MHz, Acetone) δ 170.9, 157.6, 130.5, 125.9, 120.0, 119.5, 104.6 ppm; ν_{max}(KBr)/cm^{-1} 3360, 3076, 2918, 2215, 1520, 1465, 1303, 814; HRMS-ESI (m/z): calcd for $C_8H_6N_3S$, $[M+H]^+$: 176.0277, found, 176.0275.

6-Methylsulfonyl-1,3-benzothiazol-2-amine (6k): Yellow solid (35 mg, 51 %), m.p. = 224 - 225 ^{o}C; ^{1}H NMR (400 MHz, Acetone) δ 8.23 (d, J = 1.8 Hz, 1H), 7.79 (m, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.34 (s, 2H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, Acetone) δ 171.4, 158.4, 135.0, 133.5, 126.4, 122.1, 119.4, 45.4 ppm; ν_{max}(KBr)/cm^{-1} 3360, 3114, 2922, 1717, 1520, 1288, 1142, 956; HRMS-ESI (m/z): calcd for $C_8H_9N_2O_2S_2$, $[M+H]^+$: 229.0100, found, 229.0095.

6-Thiocyanato-1,3-benzothiazol-2-amine (6l): Yellow solid (43 mg, 72 %), m.p. = 214 - 217 ^{o}C; ^{1}H NMR (400 MHz, DMSO) δ 8.06 (s, 1H), 7.84 (s, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 168.7, 154.6, 132.9, 129.9, 125.2, 118.8, 113.3, 112.5 ppm; ν_{max}(KBr)/cm^{-1} 3304, 3100, 1720, 1532, 958; HRMS-ESI (m/z): calcd for $C_8H_6N_3S_2$, $[M+H]^+$: 207.9998, found, 207.9999.

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Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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