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Merrifield resin supported phenanthroline–Cu(I): a highly efficient and recyclable catalyst for the synthesis of 2-aminobenzothiazoles via the reaction of 2-haloanilines with isothiocyanates

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ABSTRACT

A novel Merrifield resin supported phenanthroline–Cu(I) complex has been developed and used as a highly efficient and recyclable catalyst in the reaction of 2-halobenzenamines with isothiocyanates for the synthesis of 2-aminobenzothiazoles. The reactions were applicable to a variety of 2-halobenzenamines and isothiocyanates, and generated the corresponding 2-aminobenzothiazoles in good yields under mild reaction conditions. Moreover, the catalyst was quantitatively recovered from the reaction mixture by a simple filtration and reused for ten cycles with almost consistent activity.

1. Introduction

Transition-metal-catalyzed cross-coupling reactions of carbon–carbon and carbon–heteroatom bonds are important synthetic reactions in modern organic synthesis, and they have emerged as powerful tools in both academic and industrial laboratories. Among the reactions, palladium,[1] copper,[2] iron[3] and nickel[4] catalysts combined with a ligand display high activity. However, the drawbacks are the high prices of the complexes and the often laborious removal of the metals from product. From industrial and environmental points of view, the development of a cheap, efficient and environmentally benign catalyst is still desirable. Therefore, the application of reusable and recoverable heterogeneous catalysts has recently attracted much attention, for their facile isolation and reusability, which could reduce both cost and waste.[5] In the past decades, a lot of techniques to recycle metal-based heterogeneous catalysts have been developed, such as silica,[6] ionic liquids,[7] and polymers.[8] The grafting of such supports with homogeneous catalysts often provides good catalytic activity together with possible recovery of the catalyst system by simple conduction.

2-Aminobenzothiazoles, one of the important classes of heterocyclic compounds, have been found in many pharmaceuticals and agrochemicals that show prominent biological activities with applications in drug discovery since Hugerschoff's synthesis of 2-aminobenzothiazoles through a reaction of arylthioureas with liquid bromine.[9] Synthesis of 2-aminobenzothiazoles is one of the important topics in the preparation of heterocyclic compounds. Therefore, considerable effort has been made in the development of efficient strategies for their construction. The majority of efficient methods include the transition-metal-catalyzed, particularly palladium- or copper-, catalyzed intra-molecular cyclization of 2-bromobenzothiaoureas (Eq. 1, Scheme 1).[10] Castillón and coworkers reported a procedure for the synthesis of benzothiazoles using 2-bromoarylthioamide substrates and the $Pd_2(dba)_3$/(2-biphenyl)P(*t*-Bu)$_2$ catalytic system.[10c] However, both a ligand and a base are required to promote the reaction, and the substrates are not readily available. Recently, Li and Wu's groups described the practical transition-metal-catalyzed tandem reactions of 2-halobenzenamines and isothiocyanates to prepare 2-aminobenzothiozoles in the presence of CuI-phenanthroline, or FeF_3 ($FeCl_3$)-phenanthroline catalytic system (Eq. 2, Scheme 1).[11] Meanwhile, CuI/K_2CO_3 system and CuBr/TBAB system without ligand were also employed as the catalyst in this transformation, respectively (Eq. 3, Scheme 1).[12]

Although homogeneous catalysis exhibit many advantages, homogeneous catalysis suffers from the problematic separation of the expensive catalyst. In addition, homogeneous catalysis might result in heavy metal contamination of the desired isolated product.

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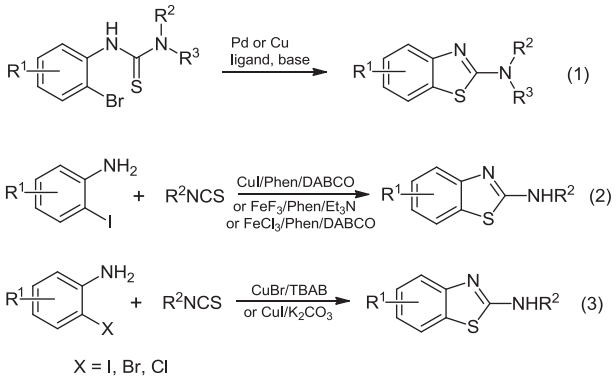
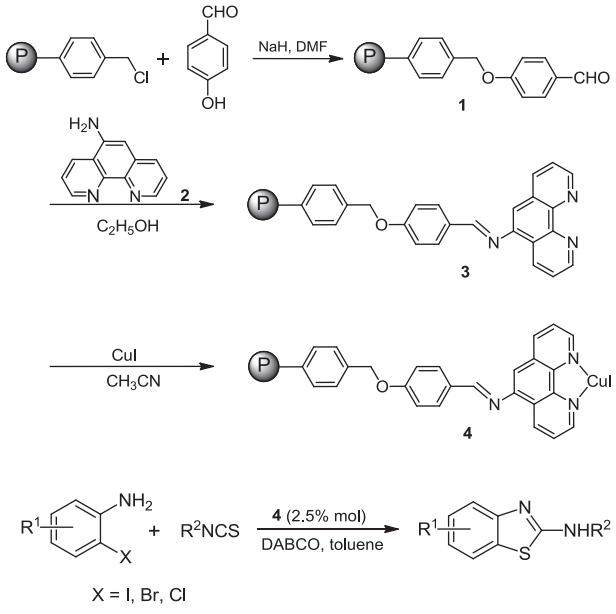


Scheme 1.

These problems are of particular environmental and economic concern in large-scale syntheses. To overcome these problems, the development of highly efficient and recyclable heterogeneous catalysts, such as immobilization of catalytically active metal complexes onto the surfaces of organic and inorganic supports is essential.

As a part of our continuing interest in the development of efficient heterogeneous catalysts for the organic synthesis,[13] herein we report a recoverable and efficient Merrifield resin supported phenanthroline–Cu(I) catalyst, which exhibits a high catalytic activity in the reactions of 2-halobenzenamines with isothiocyanates for the synthesis of 2-aminobenzothiazoles. In addition, the catalyst could be easily recovered from the reaction mixture by a simple filtration and reused at least 10 times without significant loss of its catalytic activity (Scheme 2).



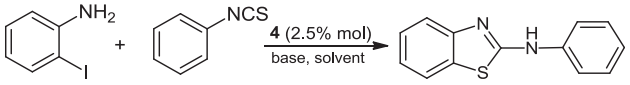
Scheme 2.

2. Results and discussion

The polystyrene-immobilized phenanthroline copper catalyst (**4**) was easily prepared starting from the commercially available Merrifield resin according to Scheme 2. Firstly, Merrifield resin reacted with 4-hydroxybenzaldehyde in the presence of sodium hydride in anhydrous DMF in 90 °C for 6 h to generate functionalized resin **1**. The above functionalized resin **1** was subsequently treated with 5-amine-1,10-phenanthrolin (**2**) in ethanol under reflux condition for 24 h. After the organics were filtered, the resin was washed with ethanol, diethyl ether and dried in vacuum, phenanthrolin-functionalized resin **3** was obtained, and then the resin **3** reacted with CuI in CH_3CN at room temperature for 4 h to generate the polystyrene-immobilized phenanthroline copper catalyst **4** as a pale-yellow powder, the copper content of the catalyst was found to be 0.25 mmol g^{-1} according to the ICP-AES measurements.

In our initial screening experiments, the reaction between 2-iodoaniline and phenyl isothiocyanate was investigated to optimize the reaction conditions, and the results are summarized in Table 1. At first, the solvent effect was examined, and a significant solvent effect was observed. It is evident that high yields were obtained when the reaction was performed in toluene, acetonitrile, and DMF (Table 1, entries 1–3), whereas 1,4-dioxane and DCE afforded moderate yields (Table 1, entries 4 and 5), so the toluene was finally selected as the solvent for the reaction.

Table 1
Reaction condition screening for the reaction of 2-iodoaniline with phenyl isothiocyanate[a]



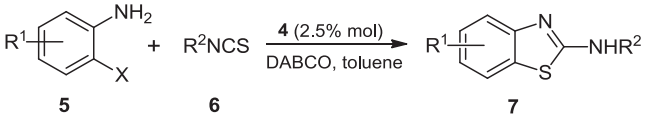
Entry	Base	Solvent	Yield (%)[b]
1	DABCO	Toluene	95
2	DABCO	DMF	92
3	DABCO	CH_3CN	93
4	DABCO	1,4-Dioxane	72
5	DABCO	DCE	76
6	Cs_2CO_3	Toluene	42
7	K_3PO_4	Toluene	52
8	Na_3PO_4	Toluene	48
9	K_2CO_3	Toluene	38
10	Na_2CO_3	Toluene	32
11	NaOAc	Toluene	20
12	Et_3N	Toluene	38
13[c]	DABCO	Toluene	81

[a] Reaction conditions: 2-iodoaniline (0.2 mmol), phenyl isothiocyanate (0.22 mmol), supported copper catalyst **4** (20 mg, containing Cu 0.005 mmol), base (0.4 mmol), solvent (1.0 mL), 60 °C for 8 h.
[b] Isolated yields.
[c] In the presence of supported copper catalyst **4** (10 mg, containing Cu 0.0025 mmol).

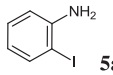
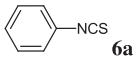
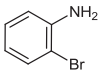
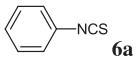
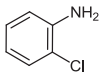
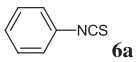
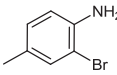
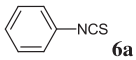
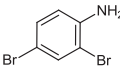
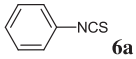
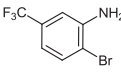
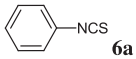
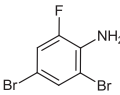
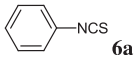
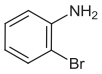
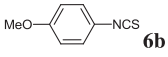
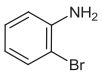
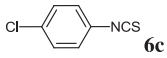
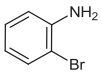
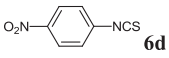
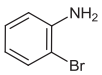
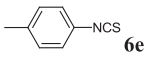
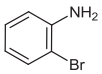
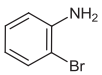
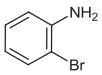
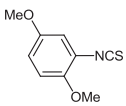
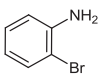
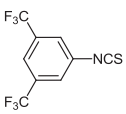
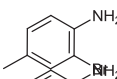
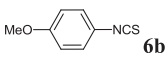
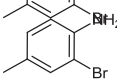
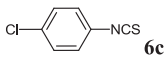
Our next studies focused on the effect of base on the model reaction. Among the bases examined, it turned out that DABCO act as an excellent base (Table 1, entry 1). While other bases, such as Cs_2CO_3, Na_2CO_3, NaOAc, Na_3PO_4, K_2CO_3, K_3PO_4 and triethylamine were substantially less effective (Table 1, entries 6–12). The effect of reaction temperature and time on the reaction was also investigated. It was found that the reaction was accomplished when it was carried out at 60 °C for 8 h. The amount of supported copper catalyst was also screened, and 2.5 mol % loading of copper was found to be optimal, a lower yield was observed when the amount of catalyst was decreased (Table 1, entry 13).

With this promising result in hand, we started to investigate the scope of this reaction under the optimized conditions. The scope of both 2-haloanilines and isothiocyanates was explored, and the results are summarized in Table 2. At the beginning of the determination of the 2-haloanilines substrate scope, phenyl isothiocyanate was used as one of the model substrate. The standard conditions were also successfully applied in the reactions of both 2-bromoaniline and 2-chloroaniline (Table 2, entries 2 and 3). For example, 2-bromoaniline underwent the reaction with phenyl isothiocyanate smoothly and generated the corresponding product in 94% yield, in addition, the reaction of the inactive 2-chloroaniline with the phenyl isothiocyanate also gave a moderate yield. Subsequently various 2-bromoanilines containing both electron-

Table 2
Merrifield resin supported phenanthroline–Cu(I) (**4**)-catalyzed reactions of 2-halobenzenamines (**5**) with isothiocyanates (**6**)[a]

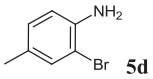
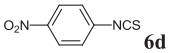
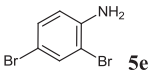
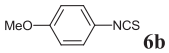
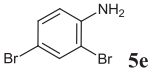
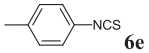
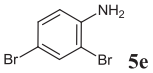


5 **6** **7**

Entry	Halobenzenamines	Isothiocyanates	Product	Yield [%][b]
1	 **5a**	 **6a**	**7a**	95
2	 **5b**	 **6a**	**7a**	94
3	 **5c**	 **6a**	**7a**	52
4	 **5d**	 **6a**	**7b**	88
5	 **5e**	 **6a**	**7c**	86
6	 **5f**	 **6a**	**7d**	71
7	 **5g**	 **6a**	**7e**	84
8	 **5b**	 **6b**	**7f**	90
9	 **5b**	 **6c**	**7g**	88
10	 **5b**	 **6d**	**7h**	98
11	 **5b**	 **6e**	**7i**	92
12	 **5b**	 **6f**	**7j**	90
13	 **5b**	 **6g**	**7k**	86
14	 **5b**	 **6h**	**7l**	78
15	 **5b**	 **6i**	**7m**	89
16	 **5d**	 **6b**	**7n**	84
17	 **5d**	 **6c**	**7o**	88

(*continued on next page*)

Table 2 (*continued*)

Entry	Halobenzenamines	Isothiocyanates	Product	Yield [%][b]
18	 **5d**	 **6d**	**7p**	69
19	 **5e**	 **6b**	**7q**	78
20	 **5e**	 **6e**	**7r**	85
21	 **5e**	 **6g**	**7s**	75

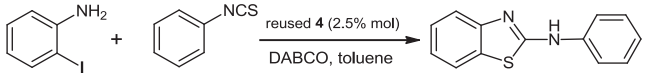
[a] Reaction conditions: 2-halobenzenamine (0.2 mmol), isothiocyanate (0.22 mmol), supported copper catalyst **4** (20 mg, containing Cu 0.005 mmol), and DABCO (0.4 mmol), toluene (1.0 mL), 60 °C for 8 h.
[b] Isolated yields.

donating and electron-withdrawing groups, such as methyl, fluoro, bromo and trifluoromethyl groups on the benzene rings **5d**–**g** were investigated to react with isothiocyanates under the standard conditions. As showed in Table 2, generally the reactions proceeded successfully to afford the corresponding 2-aminobenzothiazoles in moderate to excellent yields. For example, reaction of 2-bromo-4-methylaniline (**5d**) with phenyl isothiocyanate afforded the desired product **7b** in 88% yield (Table 2, entry 4). A similar result (86% yield) was obtained for the reaction of 2,4-dibromoaniline (**5e**) with phenyl isothiocyanate (Table 2, entry 5). In addition, a less active substrate, such as 2-bromo-5-trifluoromethylaniline (**5f**), also displayed high activity for the tandem reaction with phenyl isothiocyanate in 71% yield (Table 2, entry 6). Finally, it should be worth noting that for the hindered 2,4-dibromo-6-fluoroaniline (**5h**), a good yield was also obtained (Table 2, entry 7).

Encouraged by the above results, the scope and the generality of the reaction by varying the isothiocyanates were further investigated. We were pleased to find that the standard conditions were compatible with various isothiocyanates **6b**–**i** bearing methoxy, chloro, methyl, nitro and trifluoromethyl groups. It was found that both electron-rich and electron-poor aryl isothiocyanates underwent the tandem reaction efficiently and generated the corresponding products in good to excellent yields. For example, substrate **6b** and **6c** with 4-methoxy and 4-chloro groups on phenyl isothiocyanate underwent the reaction with 2-bromoaniline (**5b**), smoothly and the desired products were isolated in good yields (Table 2, entries 8 and 9). Meanwhile, almost quantitative yield of 2-aminobenzothiazole **7h** was obtained when 4-nitrophenyl isothiocyanate (**6d**) was used as a replacement (Table 2, entry 10). 4-Methylphenyl isothiocyanate (**6e**), was treated with 2-bromoaniline (**5b**) to afford the target product **7i** in 92% yield (Table 2, entry 11), and 3-methylphenyl isothiocyanate (**6f**) provided the corresponding product **7j** in 90% yield (Table 2, entry 12). Substrate **6g**, bearing a 2-methylphenyl group, could also react with 2-bromoaniline (**5b**) smoothly and the product was isolated in 86% yield (Table 2, entry 13). On the other hand, the reactions of 2-bromoaniline with substituted groups, such as methyl, and bromo groups on the benzene rings with various substituted isothiocyanates, afforded the corresponding products also in good yields (Table 2, entries 16–21).

For a heterogeneous catalyst, it is important to examine its ease of separation, good of recoverability and reusability. The recyclability of the polystyrene-immobilized phenanthroline–Cu(I) catalyst **4** was also investigated. After carrying out the reaction, the catalyst was separated by simple filtration and washed with diethyl ether (2×2.5 mL). After being air-dried, it can be reused directly without further purification. The recovered catalyst was used in the next run, and almost consistent activity was observed for ten consecutive cycles (Table 3, entries 1–10). In addition, copper leaching in the supported catalyst was also determined. ICP analysis of the clear filtrates found that Cu content less than 0.20 ppm.

Table 3
Successive runs by using recovered polystyrene-immobilized phenanthroline–Cu(I) catalyst **4**[a]



Cycle	Yield [%][b]	Cycle	Yield [%][b]
1	95	2	95
3	93	4	92
5	91	6	90
7	88	8	87
9	86	10	86

[a] Reaction conditions: 2-iodoaniline (00.2 mmol), phenyl isothiocyanate (0.22 mmol), DABCO (0.4 mmol), supported copper catalyst **4** (2.5 mol %), toluene (1.0 mL), nitrogen, 60 °C for 8 h.
[b] Isolated yields.

3. Conclusion

In summary, we have successfully developed a novel, practical and environmentally friendly method for the synthesis of 2-aminobenzothiazoles through the reaction of 2-halobenzenamines with isothiocyanates by using polystyrene-immobilized phenanthroline–Cu(I) **4** as catalyst (2.5 mol %) under mild reaction conditions. The reactions generated the corresponding 2-aminobenzothiazoles in high yields and were applicable to various 2-halobenzenamines and isothiocyanates. In addition, this methodology offers the competitiveness of recyclability of the catalyst without significant loss of catalytic activity, and the catalyst could be readily recovered and reused for 10 cycles, thus making this procedure environmentally more acceptable.

4. Experimental

4.1. Physical measurements and materials

General: all ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively). Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard. The C, H and N analyses were performed with a Vario El III elementar. The Cu content was determined with a Jarrell-Ash 1100 ICP analysis. 5-amine-1,10-phenanthrolin (**2**) was prepared according to the literature.[14] Products were purified by flash column chromatography on 230–400 mesh silica gel, SiO_2.

4.2. Preparation of benzaldehyde functionalized resin 1

Into a 100-mL round-bottom flask were introduced successively anhydrous DMF (40.0 mL), 4-hydroxybenzaldehyde (1.17 g) and sodium hydride (0.44 g). After the solution was stirred at room temperature for 2 h, the Merrifield resin (4.0 g) was added and the solution was refluxed in 90 °C for 6 h. The solution was filtered, and the solid was washed subsequently with DMF (5.0 mL), dichloromethane (5.0 mL), diethyl ether (5.0 mL) and dried under reduced pressure to yield 4.4 g of benzaldehyde functionalized resin **1**. IR (KBr, cm^{-1}): 3436, 3057, 3024, 2919, 2849, 1671 ($\nu_{C=O}$), 1599, 1508, 1492, 1419, 1384, 1250, 1157, 1066, 1017.

4.3. Preparation of phenanthroline functionalized resin 3

5-Amine-1,10-phenanthrolin (**2**) (0.41 g, 5.0 mmol) and benzaldehyde functionalized resin **1** (2.0 g) were mixed in ethanol (25.0 mL) in a round-bottom flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered, and the solid was washed with ethanol (5.0 mL), diethyl ether (5.0 mL), and dried under vacuum to yield 2.08 g of phenanthroline functionalized resin **3** as a yellow powder. The loading of the phenanthroline functionalized resin **3** was quantified by CHN microanalysis and found to be 0.76 mmol g^{-1} based on the N content. IR (KBr, cm^{-1}): 3057, 3023, 2918, 1601 ($\nu_{C=O}$), 1573, 1507, 1492, 1451, 1419, 1374, 1300, 1221, 1163, 1109, 1002.

4.4. Preparation of the polystyrene-immobilized phenanthroline–Cu(I) catalyst 4

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), phenanthroline functionalized resin **3** (1.0 g) and CH_3CN (5.0 mL) were added. The resulting suspension was stirred at room temperature under nitrogen for 6 h. Then the solution was filtered, and the solid was washed with CH_3CN (5.0 mL), diethyl ether (5.0 mL) and dried under vacuum. The polystyrene-immobilized phenanthroline–Cu(I) catalyst **4** was obtained as a yellow powder (1.06 g). The copper content of the catalyst was found to be 0.25 mmol g^{-1} based on ICP analysis. IR (KBr, cm^{-1}): 3081, 3057, 3023, 2919, 2849, 1675 ($\nu_{C=O}$), 1601, 1508, 1492, 1419, 1392, 1302, 1244, 1165, 1017.

4.5. Typical experimental procedure for synthesis of 2-aminobenzothiazole

A mixture of 2-iodoaniline (0.20 mmol), phenyl isothiocyanate (0.22 mmol), DABCO (0.40 mmol, 2.0 equiv) and polystyrene-immobilized phenanthroline–Cu(I) catalyst **4** (20 mg, containing Cu 0.005 mmol) and toluene (1.0 mL) was stirred at 60 °C for 8 h. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature and Et_2O (5.0 mL) was added and the mixture stirred for 10 min to ensure product removal from catalyst. As supported catalyst **4** was precipitated to the bottom of the flask, the organic layer was decanted and the residue was washed with Et_2O (2×5.0 mL). The combined organic layers were concentrated, and then the residue was purified by flash chromatography on silica gel to provide the corresponding pure product **7a** in 95% yield.

*4.5.1. N-Phenylbenzo[d]thiazol-2-amine (**7a**).* White solid, mp 158–159 °C (lit.[11a] mp 158.1–159.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.63 (d, J=7.6 Hz, 2H), 7.51 (d, J=7.6 Hz, 2H), 7.41 (t, J=7.6 Hz, 2H), 7.34 (t, J=7.6 Hz, 1H), 7.14–7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.8, 151.3, 139.9, 129.6, 129.3, 126.1, 124.4, 122.4, 120.8, 120.3, 119.3. IR (KBr, cm^{-1}): 3212, 3074, 2930, 2869, 1629, 1610, 1581, 1480, 1457, 1448, 1386, 1319, 1270, 1177, 1122.

*4.5.2. 6-Methyl-N-phenylbenzo[d]thiazol-2-amine (**7b**).* White solid, mp 157–159 °C (lit.[12a] mp 157–160 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.80 (s, 1H), 7.51–7.47 (m, 3H), 7.45 (s, 1H), 7.41 (t, J=8.0 Hz, 2H), 7.14–7.19 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.1, 149.1, 140.0, 132.2, 129.9, 129.5, 127.4, 124.1, 120.9, 120.1, 118.9, 21.3. IR (KBr, cm^{-1}): 3216, 2871, 1631, 1611, 1580, 1482, 1458, 1450, 1388, 1320, 1272, 1174, 1125.

*4.5.3. 6-Bromo-N-phenylbenzo[d]thiazol-2-amine (**7c**).* White solid, mp 185–187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.57 (s, 1H), 8.04 (s, 1H), 7.76 (d, J=8.0 Hz, 2H), 7.51 (d, J=8.4 Hz, 1H), 7.44 (d, J=8.4 Hz, 1H), 7.36 (t, J=8.0 Hz, 2H), 7.02 (t, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=162.7, 151.8, 140.8, 132.6, 129.5, 129.2, 124.0, 122.8, 121.1, 118.3, 114.2. IR (KBr, cm^{-1}): 3214, 3077, 2870, 1632, 1612, 1580, 1484, 1458, 1453, 1389, 1320, 1273, 1175, 1128. HRMS (ESI): calcd for $C_{13}H_9BrN_2S$ [M]$^+$ 303.9670; found 303.9671.

*4.5.4. 5-Trifluoromethyl-N-phenylbenzo[d]thiazol-2-amine (**7d**).* White solid; mp 199–200 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.77 (s, 1H), 8.03 (d, J=8.0 Hz, 1H), 7.87 (s, 1H), 7.79 (d, J=8.0 Hz, 2H), 7.45 (d, J=8.4 Hz, 1H), 7.37 (t, J=8.0 Hz, 2H), 7.05 (t, J=7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=163.8, 152.6, 140.7, 135.0, 129.5, 127.1, 125.0 (q, $^1J_{CF}$=270.4 Hz), 122.8 (q, $^2J_{CF}$=44.1 Hz), 118.8, 118.7, 118.5, 115.7. IR (KBr, cm^{-1}): 3198, 2958, 1627, 1572, 1467, 1458, 1426, 1329, 1308, 1148, 1112. HRMS (ESI): calcd for $C_{14}H_9F_3N_2S$ [M]$^+$ 294.0439; found 294.0440.

*4.5.5. 6-Bromo-4-fluoro-N-phenylbenzo[d]thiazol-2-amine (**7e**).* White solid, mp 194–196 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.77 (s, 1H), 7.89 (s, 1H), 7.75 (d, J=8.0 Hz, 2H), 7.45 (d, J=10.4 Hz, 1H), 7.37 (t, J=8.0 Hz, 2H), 7.95 (t, J=7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=163.1, 152.5 (d, $^1J_{CF}$=252.1 Hz), 140.5, 140.0 (d, $^3J_{CF}$=12.5 Hz), 134.7, 129.5, 120.4, 118.5, 115.9 (d, $^2J_{CF}$=21.4 Hz), 118.8, 113.2. IR (KBr, cm^{-1}): 3259, 3200, 3075, 1613, 1561, 1527, 1496, 1446, 1316, 1278, 1243, 1191. HRMS (ESI): calcd for $C_{13}H_8BrFN_2S$ [M]$^+$ 321.9576; found 321.9578.

*4.5.6. N-(4-Methoxyphenyl)benzo[d]thiazol-2-amine (**7f**).* White solid, mp 154–156 °C (lit.[11a] mp 154.4–155.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59 (d, J=7.6 Hz, 1H), 7.44–7.42 (m, 3H), 7.28 (t, J=7.6 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 6.98 (d, J=8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.5, 157.4, 151.6, 133.0, 129.7, 126.0, 124.3, 121.8, 120.8, 118.7, 114.8, 55.5. IR (KBr, cm^{-1}): 3201, 2957, 1629, 1577, 1472, 1453, 1420, 1321, 1300, 1142, 1112.

*4.5.7. N-(4-Chlorophenyl)benzo[d]thiazol-2-amine (**7g**).* White solid, mp 203–205 °C (lit.[11a] mp 204.2–206.5 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.61 (s, 1H), 7.83–7.81 (m, 3H), 7.61 (d, J=7.2 Hz, 1H), 7.40 (d, J=8.0 Hz, 2H), 7.32 (t, J=7.2 Hz, 1H), 7.16 (t, J=7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=161.7, 152.4,

140.0, 130.4, 129.3, 126.4, 125.8, 122.9, 121.6, 119.8, 119.6. IR (KBr, cm^{-1}): 3199, 2960, 1625, 1574, 1470, 1454, 1422, 1325, 1300, 1145, 1110.

*4.5.8. N-(4-Nitrophenyl)benzo[d]thiazol-2-amine (**7h**).* Yellow solid, mp 224–227 °C (lit.[11a] mp 225.2–227.2 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=11.22 (s, 1H), 8.26 (d, J=8.8 Hz, 2H), 8.00 (d, J=8.8 Hz, 2H), 7.88 (d, J=8.0 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.39 (t, J=8.0 Hz, 1H), 7.24 (d, J=7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=161.1, 151.9, 146.9, 141.3, 130.8, 126.7, 125.9, 123.7, 121.8, 120.5, 117.6. IR (KBr, cm^{-1}): 3337, 1612, 1592, 1569, 1533, 1497, 1489, 1318, 1302, 1288, 1256, 1247, 1170, 1161, 1145, 1112.

*4.5.9. N-(p-Tolyl)benzo[d]thiazol-2-amine (**7i**).* White solid, mp 177–178 °C (lit.[11a] mp 177.0–177.5 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=10.36 (s, 1H), 7.77 (d, J=7.6 Hz, 1H), 7.65 (d, J=8.0 Hz, 2H), 7.56 (d, J=7.6 Hz, 1H), 7.30 (t, J=7.6 Hz, 1H), 7.16–7.10 (m, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=162.1, 152.6, 138.7, 131.4, 130.4, 129.8, 126.3, 122.5, 121.4, 119.5, 118.3, 20.9. IR (KBr, cm^{-1}): 3215, 2959, 1628, 1598, 1573, 1478, 1328, 1300, 1286, 1253, 1172, 1110.

*4.5.10. N-(m-Tolyl)benzo[d]thiazol-2-amine (**7j**)[12a].* White solid, mp 116–117 °C. ^1H NMR (400 MHz, DMSO-d_6): δ=10.41 (s, 1H), 7.78 (d, J=7.6 Hz, 1H), 7.65–7.56 (m, 3H), 7.31 (t, J=8.0 Hz, 1H), 7.23 (t, J=7.6 Hz, 1H), 7.13 (t, J=7.6 Hz, 1H), 6.83 (d, J=7.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=162.1, 152.6, 141.0, 138.7, 130.4, 129.3, 126.3, 123.3, 122.7, 121.4, 119.6, 118.7, 115.5, 21.8. IR (KBr, cm^{-1}): 3200, 1629, 1599, 1560, 1515, 1467, 1415, 1400, 1355, 1341, 1294, 1255, 1066.

*4.5.11. N-(o-Tolyl)benzo[d]thiazol-2-amine (**7k**).* White solid, mp 121–123 °C (lit.[11a] mp 121.1–123.2 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=9.66 (s, 1H), 7.86 (d, J=8.0 Hz, 1H), 7.73 (d, J=7.6 Hz, 1H), 7.48 (d, J=8.0 Hz, 1H), 7.29–7.21 (m, 3H), 7.11–7.06 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=164.6, 152.4, 139.2, 131.2, 130.9, 130.8, 127.0, 126.2, 125.0, 123.5, 122.2, 121.5, 119.1, 18.5. IR (KBr, cm^{-1}): 3210, 2958, 1625, 1594, 1571, 1477, 1455, 1325, 1302, 1288, 1256, 1170, 1145, 1111.

*4.5.12. N-(2,4-Dimethoxyphenyl)benzo[d]thiazol-2-amine (**7l**).* White solid, mp 120–121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ=8.10 (s, 1H), 7.89 (br s, 1H), 7.72 (d, J=7.6 Hz, 1H), 7.67 (d, J=7.2 Hz, 1H), 7.38 (t, J=6.8 Hz, 1H), 7.19 (t, J=6.8 Hz, 1H), 6.82 (d, J=8.4 Hz, 1H), 6.55 (d, J=7.2 Hz, 1H), 3.86 (br, s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.7, 154.1, 152.0, 141.9, 130.4, 130.1, 126.1, 122.7, 120.7, 120.1, 110.7, 106.2, 105.0, 56.3, 55.8. IR (KBr, cm^{-1}): 3205, 2965, 1634, 1569, 1475, 1451, 1422, 1319, 1298, 1145, 1114. HRMS (ESI): calcd for $C_{15}H_{14}N_2O_2S$ $[M]^+$ 286.0776; found 286.0779.

*4.5.13. N-(3,5-Ditrifluoromethylphenyl)benzo[d]thiazol-2-amine (**7m**)[11b].* White solid, mp 117–779 °C. ^1H NMR (400 MHz, $CDCl_3$): δ=8.06 (s, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.58 (s, 1H), 7.40 (t, J=7.2 Hz, 1H), 7.25 (t, J=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.9, 150.5, 141.5, 132.8 (q, $^2J_{CF}$=33.3 Hz), 129.7, 126.6, 124.4, 123.6 (q, $^1J_{CF}$=271.1 Hz), 121.1, 120.0, 118.5, 116.6. IR (KBr, cm^{-1}): 3210, 2968, 1637, 1561, 1478, 1455, 1424, 1320, 1300, 1148, 1112.

*4.5.14. N-(4-Methoxyphenyl)-6-methylbenzo[d]thiazol-2-amine (**7n**).* White solid, mp 160–161 °C (lit.[12a] mp 160 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=10.19 (s, 1H), 7.66 (d, J=8.8 Hz, 2H), 7.54 (s, 1H), 7.42 (d, J=8.4 Hz, 1H), 7.09 (d, J=8.4 Hz, 1H), 6.93 (d, J=8.8 Hz, 2H), 3.72 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=161.7, 155.0, 150.6, 134.6, 131.6, 130.4, 127.3, 121.3, 119.9, 119.0, 114.6, 55.6, 21.3. IR (KBr, cm^{-1}): 3177, 2930, 1611, 1573, 1555, 1511, 1462, 1450, 1268, 1246, 1182, 1166, 1034.

*4.5.15. N-(4-Chlorophenyl)-6-methylbenzo[d]thiazol-2-amine (**7o**).* White solid, mp 196–197 °C (lit.[12a] mp 197 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=10.50 (s, 1H), 7.80 (d, J=8.4 Hz, 2H), 7.59 (s, 1H), 7.49 (d, J=8.0 Hz, 1H), 7.38 (d, J=8.8 Hz, 2H), 7.13 (d, J=8.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=160.9, 140.1, 132.3, 130.5, 129.3, 129.3, 127.5, 127.5, 125.6, 121.4, 119.5, 21.3. IR (KBr, cm^{-1}): 3165, 2943, 1618, 1577, 1559, 1521, 1452, 1366, 1320, 1265, 1241, 1185, 1146, 1114.

*4.5.16. 6-Methyl-N-(4-nitrophenyl)benzo[d]thiazol-2-amine (**7p**)[11c].* Yellow solid, mp 265–267 °C. ^1H NMR (400 MHz, DMSO-d_6): δ=11.09 (br s, 1H), 8.23 (d, J=8.8 Hz, 2H), 7.97 (d, J=9.2 Hz, 2H), 7.65 (s, 1H), 7.58 (d, J=8.4 Hz, 1H), 7.18 (t, J=8.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=160.2, 149.9, 146.7, 141.2, 133.1, 130.8, 127.8, 125.9, 121.6, 120.1, 117.4, 21.4. IR (KBr, cm^{-1}): 3317, 1610, 1595, 1574, 1540, 1498, 1484, 1325, 1304, 1260, 1181, 1155, 1111.

*4.5.17. 6-Bromo-N-(4-methoxyphenyl)benzo[d]thiazol-2-amine (**7q**).* White solid, mp 207–209 °C. ^1H NMR (400 MHz, DMSO-d_6): δ=10.35 (s, 1H), 8.00 (s, 1H), 7.64 (d, J=8.8 Hz, 2H), 7.43 (d, J=6.8 Hz, 2H), 6.94 (d, J=8.8 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=163.2, 155.3, 152.0, 134.1, 132.6, 129.1, 123.9, 120.7, 120.3, 114.7, 113.8, 55.7. IR (KBr, cm^{-1}): 3327, 1615, 1598, 1577, 1544, 1500, 1485, 1325, 1300, 1257, 1183, 1165, 1114. HRMS (ESI): calcd for $C_{14}H_{11}BrN_2OS$ $[M]^+$ 333.9775; found 333.9778.

*4.5.18. 6-Bromo-N-(p-tolyl)benzo[d]thiazol-2-amine (**7r**).* White solid, mp 202–203 °C. ^1H NMR (400 MHz, DMSO-d_6): δ=10.47 (s, 1H), 8.03 (s, 1H), 7.62 (d, J=8.4 Hz, 2H), 7.48 (d, J=8.8 Hz, 1H), 7.42 (d, J=8.4 Hz, 1H), 7.15 (d, J=8.0 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=162.8, 151.9, 138.4, 132.6, 131.8, 129.9, 129.2, 123.9, 120.9, 118.5, 114.0, 20.9. IR (KBr, cm^{-1}): 3232, 3182, 2917, 1624, 1613, 1585, 1568, 1552, 1445, 1401, 1334, 1258, 1244, 1226, 1085. HRMS (ESI): calcd for $C_{14}H_{11}BrN_2S$ $[M]^+$ 317.9826; found 317.9828.

*4.5.19. 6-Bromo-N-(o-tolyl)benzo[d]thiazol-2-amine (**7s**).* White solid, mp 198–199 °C. ^1H NMR (400 MHz, DMSO-d_6): δ=9.76 (s, 1H), 7.98 (s, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.39–7.37 (m, 2H), 7.26–7.21 (m, 2H), 7.09 (t, J=7.2 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=165.4, 151.7, 138.9, 132.9, 131.2, 131.1, 129.1, 127.0, 125.4, 123.9, 123.7, 120.6, 113.6, 18.4. IR (KBr, cm^{-1}): 3178, 3063, 2850, 1615, 1595, 1563, 1494, 1445, 1328, 1295, 1260, 1188, 1110, 1080, 1044. HRMS (ESI): calcd for $C_{14}H_{11}BrN_2S$ $[M]^+$ 317.9826; found 317.9828.

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Supplementary data

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