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# IRON-CATALYZED TANDEM REACTIONS OF *ORTHO*-AMINOBENZENETHIOLS WITH ISOTHIOCYANATES LEADING TO 2-AMINOBENZOAZOLES UNDER LIGAND- AND SOLVENT-FREE CONDITIONS

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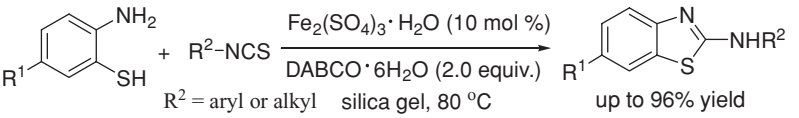
## GRAPHICAL ABSTRACT




**Abstract** *An efficient route to synthesize a variety of 2-aminobenzoazoles has been discovered. It involves the reaction of* ortho*-aminobenzenethiols with isothiocyanates via iron-catalyzed tandem addition-annulations process under ligand and solvent free conditions on silica gel surface.*

**Keywords** 2-Aminobenzoazoles; iron-catalyzed; isothiocyanate; tandem reaction

## INTRODUCTION

2-Aminobenzothiazoles have attracted considerable attention because of their chemical properties and biological activity.[1,2] A number of general and efficient methods for the preparation of this kind of compounds have been developed.[3–10] In this area, transition metal–catalyzed intramolecular cyclization of 2-bromobenzothioureas is one of the most efficient methods.[3–6] For example, Benedí et al. first reported the Pd-catalyzed intramolecular cyclization of 2-bromobenzothioureas to form 2-aminobenzothiazoles in the presence of *o*-biphenylP($t$Bu)$_2$ and $Cs_2CO_3$.[3] Batey and co-workers also reported the same transformation using ligand-accelerated Cu- or Pd-catalyzed intramolecular cyclizations

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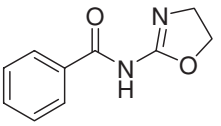


**Figure 1** *N*-(4,5-Dihydrooxazol-2-yl)benzamide.

of *ortho*-halobenzanilides (using 1,10-phenanthroline or *N*,*N*′-dimethylethylenediamine as ligands).[4,5] Recently, Wang et al. described a practical Cu-catalyzed intramolecular cyclization process for the synthesis of 2-aminobenzothiazoles employing *N*-(4,5-dihydrooxazol-2-yl)benzamide (Figure 1) as a novel and efficient ligand.[6]

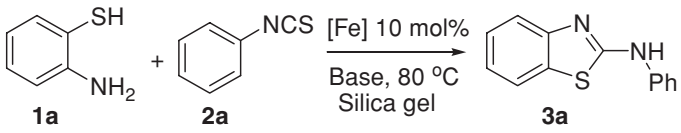
Very recently, a tandem addition/C—S coupling reaction was presented as another powerful strategy for the construction of the 2-aminobenzothiazole framework.[7–10] We have previously described a novel and efficient method for the preparation of this class of compounds *via* copper(I)-catalyzed tandem addition-cyclization reactions of 2-iodoanilines with isothiocyanates in toluene.[7] In addition, on the basis of current criteria of green chemistry, we carried out the transformation in the presence of 1,10-phenanthroline as ligand in water.[8] In our work, phase-transfer catalysis (octadecyltrimethylammonium chloride) was employed as a key additive to enhance the catalytic efficiency. Although there are many powerful methods to prepare 2-aminobenzothiazoles, most of them are transition metal–catalyzed using an expensive ligand. Hence, the development of efficient and environmental benign approaches under ligand-free conditions is still desirable.

In recent years the use of solid-phase organic synthesis to simplify and improve classical organic reactions has become a very popular method.[11,12] Solvent-free organic synthesis using silica-supported reagents for the preparation of heterocycles has received considerable importance as an environmentally benign approach.[13] In addition, commercially available and unmodified silica gel (TLC grade) has been used as an efficient source of solid support for a variety of organic reactions.[14–17] Very recently, we have described a highly efficient tandem addition-cyclization reactions for 2,4-dihydro-*1H*-benzo[*d*][1,3]thiazine promoted by silica gel.[14] Basu et al. reported silica-promoted acylation and alkylation of aromatic and aliphatic thiols[15] and highly selective *N*-alkylation of amines.[16] In continuation of our work on transition metal–catalyzed tandem annulations for heterocyclic compounds,[18–23] we now report a new solid phase synthetic method, which could be used for generation of 2-aminobenzothiazole libraries. In this article, we describe a practical approach to 2-aminobenzothiazole based on parallel diversity-oriented synthesis catalyzed by $Fe_2(SO_4)_3 \cdot H_2O$ under ligand-free conditions on a silica gel surface.

## RESULTS AND DISCUSSION

We have chosen 2-aminobenzenethiol **1a** and phenyl isothiocyanate **2a** as the standard substrates to optimize the catalysis conditions, including optimization of the Fe salt catalysts and bases (Table 1). Several Fe salts were evaluated as catalysts for the model reaction. The results showed that all Fe catalysts investigated could catalyze the reaction and afford the desired products in good to excellent yields (Table 1, entries 1–6). Among them, $Fe_2(SO_4)_3 \cdot H_2O$ catalyzed the reaction with the best yield under the employed reaction conditions. On the other hand in the absence of Fe salt catalyst, the product was obtained only in 48% yield (Table 1, entry 7). Decreasing the temperature to r.t. slowed down the reaction and also decreased the yield (Table 1, entry 8). Only 45% of the corresponding product was

**Table 1** Condition screening for Fe-catalyzed tandem reaction of 2-aminobenzenethiol **1a** with phenyl isothiocyanate **2a** on silica gel surface[a]




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

| Entry | Catalyst | Base | Yield (%)[b] |
|---|---|---|---|
| 1 | $FeCl_3$ | DABCO · $6H_2O$ | 70 |
| 2 | $Fe(NO_3)_3 \cdot 9H_2O$ | DABCO · $6H_2O$ | 82 |
| 3 | $FeSO_4 \cdot 7H_2O$ | DABCO · $6H_2O$ | 78 |
| 4 | $Fe(NH_4)_2(SO_4)_2 \cdot H_2O$ | DABCO · $6H_2O$ | 83 |
| 5 | $Fe(acac)_3$ | DABCO · $6H_2O$ | 75 |
| 6 | $Fe_2(SO_4)_3 \cdot H_2O$ | DABCO · $6H_2O$ | 96 |
| 7 | – | DABCO · $6H_2O$ | 48 |
| 8[c] | $Fe_2(SO_4)_3 \cdot H_2O$ | DABCO · $6H_2O$ | 70 |
| 9[d] | $Fe_2(SO_4)_3 \cdot H_2O$ | DABCO · $6H_2O$ | 45 |
| 10 | $Fe_2(SO_4)_3 \cdot H_2O$ | – | 70 |
| 11 | $Fe_2(SO_4)_3 \cdot H_2O$ | $NaHCO_3$ | 85 |
| 12 | $Fe_2(SO_4)_3 \cdot H_2O$ | $Na_2CO_3$ | 80 |
| 13 | $Fe_2(SO_4)_3 \cdot H_2O$ | $K_2CO_3$ | 80 |
| 14 | $Fe_2(SO_4)_3 \cdot H_2O$ | NaOH | 75 |
| 15 | $Fe_2(SO_4)_3 \cdot H_2O$ | DBU | 57 |
| 16 | $Fe_2(SO_4)_3 \cdot H_2O$ | $Et_3N$ | 38 |

[a]Reaction conditions: 2-aminobenzenethiol **1a** (0.3 mmol), phenyl isothiocyanate **2a** (1.5 equiv), [Fe] (10 mol %), base (2.0 equiv.), silica gel (300 mg), 80°C, overnight.

[b]Isolated yield based on 2-aminobenzenethiol **1a**.

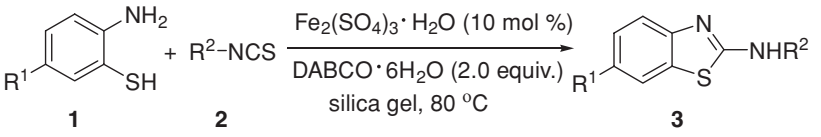
[c]r.t., 48 h.

[d]Silica gel–free conditions.

generated in the absence of silica gel (Table 1, entry 9), which shows the importance of silica gel in this tandem addition-cyclization reaction. A blank experiment shows that DABCO · $6H_2O$ can notably enhance the yield of the product (Table 1, entry 10). Subsequently, the base effect was investigated and DABCO · 6 $H_2O$ was found to provide the best result (Table 1, entry 6) as compared to $NaHCO_3$, $Na_2CO_3$, $K_2CO_3$, NaOH, DBU, or $Et_3N$ (Table 1, entries 11–16).

The applicability of the Fe-catalyzed tandem addition-cyclization reaction of 2-aminobenzenethiol **1** with isothiocyanates **2** on silica gel surface was explored under the optimized conditions [10 mol% $Fe_2(SO_4)_3 \cdot H_2O$ as catalyst, 2.0 equiv. DABCO · $6H_2O$ as base, 1.0 g/mmol silica gel, 80°C]. As shown in Table 2, the tandem reactions worked quite well for all the substrates examined, and the desired 2-aminobenzothiazoles were obtained in moderate to excellent yields. Isothiocyanates with an electron-withdrawing or electron-donating group attached to the aromatic ring were good substrates in this transformation. For example, 4-fluorophenyl isothiocyanate **2c** reacted with 2-aminobenzenethiol **1a** leading to the corresponding product **3c** in 83% yield (Table 2, entry 3), and 78% yield of product **3f** was obtained when 4-methylphenyl isothiocyanate **2f** was used in the reaction (Table 2, entry 6). However, isothiocyanates having a strong electron-withdrawing group (nitro group) display moderate activity (Table 2, entry 2). Alkyl isothiocyanates **2g** and **2h** were also good partners for this one-pot tandem reaction, giving good yields (Table 2,

**Table 2** Iron-catalyzed tandem reaction of 2-aminobenzenethiol **1** with isothiocyanate **2**[a]




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

| Entry | **1**/$R^1$ | **2**/$R^2$ | Product **3** | Yield [%][b] |
|---|---|---|---|---|
| 1 | **1a**/H | **2a**/$C_6H_5$ | **3a** | 96 |
| 2 | **1a**/H | **2d**/4-$NO_2C_6H_4$ | **3b** | 60 |
| 3 | **1a**/H | **2c**/4-$FC_6H_4$ | **3c** | 83 |
| 4 | **1a**/H | **2d**/4-$ClC_6H_4$ | **3d** | 70 |
| 5 | **1a**/H | **2e**/4-$MeOC_6H_4$ | **3e** | 71 |
| 6 | **1a**/H | **2f**/4-$MeC_6H_4$ | **3f** | 78 |
| 7 | **1a**/H | **2g**/Et | **3g** | 88 |
| 8 | **1a**/H | **2h**/Cyclohexyl | **3h** | 76 |
| 9 | **1b**/MeO | **2a**/$C_6H_5$ | **3i** | 91 |
| 10 | **1b**/MeO | **2d**/4-$ClC_6H_4$ | **3j** | 71 |
| 11 | **1b**/MeO | **2f**/4-$MeC_6H_4$ | **3k** | 86 |
| 12 | **1c**/Br | **2a**/$C_6H_5$ | **3l** | 85 |
| 13 | **1c**/Br | **2d**/4-$ClC_6H_4$ | **3m** | 75 |
| 14 | **1c**/Br | **2f**/4-$MeC_6H_4$ | **3n** | 78 |
| 15 | **1d**/I | **2a**/$C_6H_5$ | **3o** | 74 |
| 16 | **1d**/I | **2d**/4-$ClC_6H_4$ | **3p** | 72 |
| 17 | **1d**/I | **2f**/4-$MeC_6H_4$ | **3q** | 71 |

[a]Reaction conditions: 2-aminobenzenethiol **1** (0.3 mmol), isothiocyanate **2** (1.5 equiv), $Fe_2(SO_4)_3 \cdot H_2O$ (10 mol %), DABCO · $6H_2O$ (2.0 equiv), silica gel (300 mg), 80°C, overnight.

[b]Isolated yield based on 2-aminobenzenethiol **1**.

entries 7 and 8). Other substituted 2-aminobenzenethiols **1b–d** were also effective in this kind of reaction and good yields of products were afforded.

In conclusion, we have successfully developed a novel, facile, and practical method for the synthesis of 2-aminobenzothiazoles from substituted 2-aminobenzenethiols in moderate to excellent yields using a Fe(III)-catalyzed tandem addition-cyclization. It is noteworthy that the reaction is carried out under ligand-free conditions in solid phase.

## EXPERIMENTAL

All reactions were performed in test tubes. Analytical thin-layer chromatography was performed using glass plates precoated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Commercially available reagents were used as received. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AV 400 instrument operating at 400 MHz and 100 MHz, respectively, at 293 K. The chemical shifts are given on the delta scale ($\delta$) and are referenced to tetramethylsilane (0 ppm). Melting points are uncorrected.

### $Fe_2(SO_4)_3 \cdot H_2O$-Catalyzed One-Pot Tandem Reaction of 2-Aminobenzenethiols 1 with Isothiocyanates 2: General Procedure

A mixture of the 2-aminobenzenethiol **1** (0.30 mmol), the isothiocyanate **2** (0.45 mmol, 1.5 equiv.), DABCO · 6 $H_2O$ (2.0 equiv), silica gel (300 mg), and $Fe_2(SO_4)_3 \cdot H_2O$

(0.03 mmol, 10 mol%) was stirred at 80°C under $N_2$. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature and then passed through a small plug of silica to obtain pure 2-aminobenzothizole **3**.

### *N*-Phenylbenzo[*d*]thiazol-2-amine[7,9] (3a)

White solid, mp 158–160°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$–$7.19$ (m, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 9.0 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 118.7$, 119.9, 120.3, 121.9, 123.9, 125.6, 129.1, 129.3, 129.5, 150.7, 164.5.

### *N*-(4-Nitrophenyl)benzo[*d*]thiazol-2-amine[7] (3b)

Yellow solid, mp 230–231°C (lit. mp 225–227°C); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.24$ (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 8.10 (d, $J = 9.2$ Hz, 2H), 8.27 (d, $J = 9.2$ Hz, 2H), 11.2 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 117.6$, 120.5, 121.9, 123.7, 125.9, 126.7, 130.8, 141.4, 146.9, 152.0, 161.2.

### *N*-(4-Fluorophenyl)benzo[*d*]thiazol-2-amine[8] (3c)

White solid, mp 216–217°C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.14$ (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 8.8$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.77–7.82 (m, 3H), 10.52 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 116.0$ ($\delta$, $^2J_{CF} = 22$ Hz), 119.7 ($\delta$, $^2J_{CF} = 18$ Hz), 119.8, 121.5, 122.8, 126.3, 130.3, 137.4, 152.4, 157.9 ($\delta$, $^1J_{CF} = 237$ Hz), 162.0.

### *N*-(4-Chlorophenyl)benzo[*d*]thiazol-2-amine[8] (3d)

White solid, mp 208–209°C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.19$ (t, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 119.1$, 119.3, 121.0, 122.4, 125.4, 125.9, 128.8, 129.9, 139.5, 151.9, 162.2.

### *N*-(4-Methoxyphenyl)benzo[*d*]thiazol-2-amine[8] (3e)

White solid, mp 153–155°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3H), 6.96 (d, $J = 8.8$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.38-7.48 (m, 3H), 7.57 (d, $J = 8.0$ Hz, 1H), 9.77 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 55.5$, 114.8, 118.8, 120.8, 121.9, 124.2, 126.0, 129.7, 133.0, 151.6, 157.4, 167.3.

### *N*-*p*-Tolylbenzo[*d*]thiazol-2-amine[8] (3f)

White solid, mp 178–179°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.37$ (s, 3H), 7.13 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 20.9$, 119.1, 120.8, 121.2, 122.1, 126.0, 129.8, 130.1, 134.6, 137.4, 151.5, 165.9.

### *N*-Ethylbenzo[*d*]thiazol-2-amine[8] (3g)

White solid, mp 114–116°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.32$ (t, $J = 7.2$ Hz, 3H), 3.45 (q, $J = 7.2$ Hz, 2H), 6.23 (br, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.9$, 40.4, 118.7, 120.8, 121.4, 126.0, 130.2, 152.3, 167.7.

### *N*-Cyclohexylbenzo[*d*]thiazol-2-amine[7] (3h)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.18$–1.45 (m, 5H), 1.61–1.77 (m, 3H), 2.11–2.13 (m, 3H), 3.5 (br, 1H), 5.79 (br, 1H), 7.05 (t, $J = 7.2$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 24.8$, 25.4, 33.2, 54.6, 118.6, 120.7, 121.2, 125.8, 130.3, 152.4, 166.9.

### 6-Methoxy-*N*-phenylbenzo[*d*]thiazol-2-amine (3i)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H), 6.91 (dd, $J = 2.4$, 8.8 Hz, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 2.4$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 2H), 7.44 (s, 1H), 7.47 (t, $J = 8.8$ Hz, 2H), 8.40 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 55.9$, 105.3, 114.0, 119.9, 120.0, 123.9, 129.4, 131.1, 140.2, 145.8, 155.9, 162.6.

### 6-Methoxy-*N*-p-tolylbenzo[*d*]thiazol-2-amine (3j)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.34$ (s, 3H), 3.80 (s, 3H), 6.90 (dd, $J = 2.4$, 8.8 Hz, 1H), 7.12 (d, $J = 2.8$ Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 8.35 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 20.2$, 55.4, 104.8, 113.3, 119.2, 120.1, 129.5, 130.6, 133.5, 137.1, 145.4, 155.2, 162.9.

### *N*-(4-Chlorophenyl)-6-methoxybenzo[*d*]thiazol-2-amine (3k)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.83$ (s, 3H), 6.95 (dd, $J = 2.4$, 8.8 Hz, 1H), 7.16 (d, $J = 1.6$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 56.0$, 105.3, 114.2, 120.5, 120.6, 128.7, 129.5, 131.4, 138.7, 146.0, 156.3, 161.9.

### 6-Bromo-*N*-phenylbenzo[*d*]thiazol-2-amine (3l)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (t, $J = 6.8$ Hz, 1H), 7.38-7.44 (m, 4H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.73 (s, 1H), 7.54 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 114.9$, 120.2, 120.6, 123.3, 124.7, 129.4, 129.6, 131.7, 139.3, 150.5, 164.0.

### 6-Bromo-*N*-*p*-tolylbenzo[*d*]thiazol-2-amine (3m)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.36$ (s, 3H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.40 (s, 2H), 7.70 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 20.9$, 114.6, 120.3, 121.0, 123.3, 129.3, 130.2, 131.7, 134.9, 136.8, 150.6, 165.5.

### 6-Bromo-*N*-(4-chlorophenyl)benzo[*d*]thiazol-2-amine (3n)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 8.8$ Hz, 2H), 7.46–7.49 (m, 4H), 7.75 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 115.3$, 120.8, 121.1, 123.4, 124.0, 129.5, 129.6, 131.7, 137.9, 150.4, 163.5.

### 6-Iodo-*N*-phenylbenzo[*d*]thiazol-2-amine (3o)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.17$ (t, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.59 (dd, $J = 1.6$, 8.4 Hz, 1H), 7.89 (s, 1H), 8.50 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 120.3$, 121.1, 124.7, 129.1, 129.5, 129.6, 135.1, 139.4, 151.8.

### 6-Iodo-*N*-p-tolylbenzo[*d*]thiazol-2-amine (3p)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.36$ (s, 3H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.25 (s, 1H), 7.33 (d, $J = 7.6$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.87 (s, 1H), 8.75 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 20.9$, 84.3, 120.7, 121.3, 129.0, 130.2, 132.1, 135.0, 136.9, 151.1, 165.8.

### *N*-(4-Chlorophenyl)-6-iodobenzo[*d*]thiazol-2-amine (3q)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.35$–7.38 (m, 3H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.76 (d, $J = 7.6$ Hz, 1H), 8.15 (s, 1H), 10.67 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 85.2$, 119.3, 121.2, 125.7, 128.8, 129.0, 132.5, 134.5, 139.0, 151.4, 161.6.

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