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TBHP/KI-Promoted Annulation of Anilines, Ethers and Elemental Sulfur: Access to 2-Aryl, 2-Heteroaryl or 2-Alkyl Substituted Benzothiazoles

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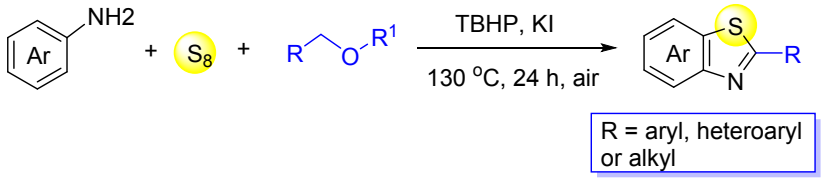


ABSTRACT: An efficient TBHP/KI-promoted annulation of anilines with ethers and elemental sulfur has been developed through the selective C-O bond cleavage of ethers under transition-metal-free conditions. A wide range of 2-aryl, 2-heteroaryl and 2-alkyl substituted benzothiazoles were easily prepared with satisfactory yields and good functional group compatibility.

■ INTRODUCTION

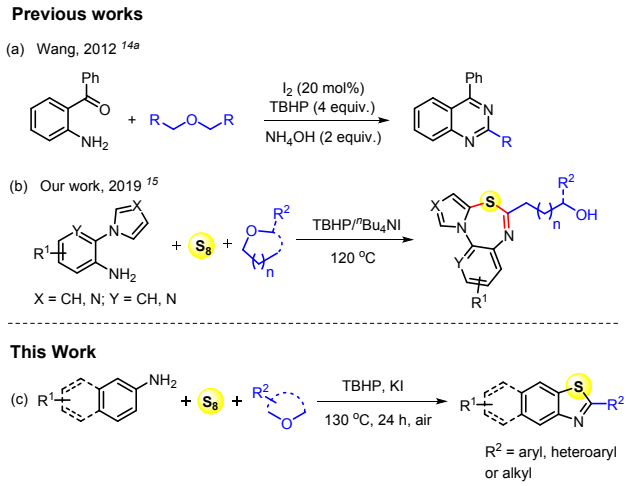
Benzothiazole and its derivatives are one class of important heterocyclic compounds due to their diverse application in pharmaceuticals,[1a-c] organic light-emitting diodes (OLEDs)[1d] and fluorescent probes,[1e] *etc*. For example, some 2-substituted benzothiazoles show a variety of pharmacological properties, such as antitumor,[2] antimicrobial[3] and anticonvulsant activities[4]. In general, prefunctionalized substrates, such as 2-aminobenzenethiol,[5] thiobenzanilides or *N*-arylthiourea,[6] 2-haloanilines[7] and 2-halonitroarenes[8] are used as precursors to synthesize 2-substituted benzothiazoles. Besides, many efforts have been paid on the direct C–H arylation or alkylation at the 2-position of simple benzothiazoles.[9] However, these prefunctionalized substrates and benzothiazoles are not readily available, resulting in limited synthetic applications in some ways. Therefore, it is of great importance for the development of efficient methods to construct benzothiazoles from more simple starting materials.

In recent years, the combination of simple anilines and elemental sulfur was synthetically attractive for one-pot generation of 2-substituted benzothiazoles through three-component reaction. In 2012, Wei and co-workers described the direct construction of 2-substituted benzothiazoles from anilines or naphthylamine, sulfur and methylaromatics in absence of catalysts, but a high reaction temperature (275 °C) was needed.[10] In 2017, Deng et al. reported a NH_4I or KI-catalyzed reaction of aromatic amines, sulfur powder and benzaldehydes at 150 °C, providing 2-arylbenzothiazoles and 2-arylnaphtho[2,1-*d*]thiazoles in good to excellent yields.[11] More recently, Chen et al. established an efficient I_2-promoted reaction of aromatic amines, sulfur powder and acetophenones for the synthesis of 2-aryl benzothiazoles.[12] Though these methods were successfully applied to generate 2-aryl benzothiazoles, aliphatic aldehydes and ketones were incompatible so that 2-alkyl benzothiazoles could not be obtained.

Ethers, such as diethyl ether, THF, *etc*. are cheap and readily available solvents in most labs, and are versatile building blocks in organic synthesis.[13] During recent years, ethers have been reported as sources of alkyls through the C–O bond cleavage of ethers, but the application in the construction of heterocycles is still rare (Scheme 1a).[14] In 2019, we developed an efficient three-component reaction of 1-(2-aminoaryl)pyrroles, elemental sulfur and ethers for constructing 1,3,6-benzothiadiazepines, and found it easy to introduce both aryl and alkyl to the heterocyclic skeleton (Scheme 1b).[15] Along this lines, we envisioned that aryl, heteroaryl or alkyl species generated from the C–O bond cleavage of ethers would be an alternative

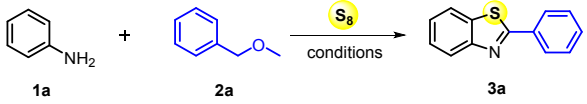
source to 2-aryl, 2-heteroaryl or 2-alkyl substituted benzothiazoles (Scheme 1c).

Scheme 1. Synthesis of Heterocycles through the C–O Bond Cleavage of Ethers



Initially, we commenced the three-component reaction of aniline (**1a**), benzyl methyl ether (**2a**) and sulfur powder (S_8) in the presence of an organic or inorganic oxidant and a catalytic amount of iodide compound (Table 1). To our delight, when the substrates was conducted with *tert*-butyl-hydroperoxide (TBHP) (4 equiv, 70% aqueous solution) and ^{n}Bu$_4$NI (20 mol %) in DMSO at 130 °C for 24 h, the desired product 2-phenylbenzo[*d*]thiazole (**3a**) was obtained in 62% yield (entry 1). A screen with peroxides such as di-*tert*-butyl peroxide (DTBP), benzoyl peroxide (BPO), dicumyl peroxide (DCP) and $K_2S_2O_8$ indicated TBHP to be optimal for this transformation (entries 2–5). The reaction did not occur in the absence of a catalyst (entry 6). Thus, a series of catalysts including iodides (NH_4I, KI, I_2), ^{n}Bu$_4$NBr and ^{n}Bu$_4$NCl were tested, and KI was proved to be the best one (entries 1, 7–11). Further screen of the amount of TBHP (entries 12 and 13), KI (entries 14 and 15), benzyl methyl ether (entry 16) and sulfur powder (entry 17) showed that the most appropriate amounts of these reagents were 4 equiv TBHP, 20 mol % KI, 4 equiv **2a** and 2 equiv $\mathbf{S_8}$. Increase or decrease of the temperature might reduce the yield (entry 18). In addition, no desired product was obtained when 2 equiv Na_2S or CS_2 was used instead of elemental sulfur.

Table 1. Optimization of the Reaction Conditions[a]

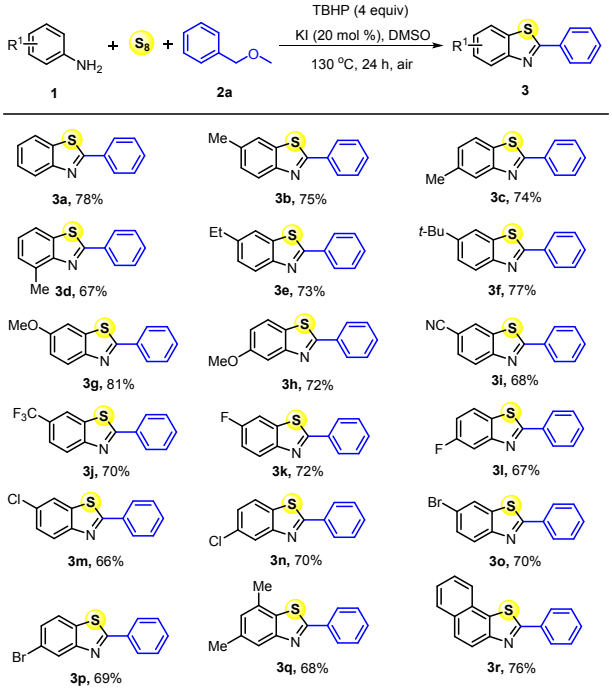


Entry	Oxidant (equiv)	Catalyst (mol %)	Yield (%)
1	TBHP (4)	^{n}Bu$_4$NI (20)	62
2	DTBP (4)	^{n}Bu$_4$NI (20)	46
3	BPO (4)	^{n}Bu$_4$NI (20)	32
4	DCP (4)	^{n}Bu$_4$NI (20)	29
5	$K_2S_2O_8$ (4)	^{n}Bu$_4$NI (20)	0
6	TBHP (4)	—	0
7	TBHP (4)	NH_4I (20)	69
8	**TBHP (4)**	**KI (20)**	**78**
9	TBHP (4)	I_2 (20)	63
10	TBHP (4)	^{n}Bu$_4$NBr (20)	0
11	TBHP (4)	^{n}Bu$_4$NCl (20)	0
12	TBHP (3)	KI (20)	65
13	TBHP (5)	KI (20)	77
14	TBHP (4)	KI (10)	60
15	TBHP (4)	KI (30)	75
16	TBHP (4)	KI (20)	65[b], 77[c]
17	TBHP (4)	KI (20)	55[d], 76[e]
18	TBHP (4)	KI (20)	61[f], 73[g]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol, 4 equiv), $\mathbf{S_8}$ (0.4 mmol, 2 equiv), oxidant, catalyst and DMSO (1 mL) were stirred in a sealed tube at 130 °C under air for 24 h. [b]**2a** (0.6 mmol, 3 equiv). [c]**2a** (1.0 mmol, 5 equiv). [d]$\mathbf{S_8}$ (0.2 mmol). [e]$\mathbf{S_8}$ (0.6 mmol). [f]120 °C. [g]140 °C.

With the optimized reaction conditions in hand, the substrate scope of anilines **1** was investigated (Scheme 2). In general, anilines **1** bearing an electron-donating (Me, Et, ^{t}Bu and MeO) or electron-withdrawing group (CN, CF_3 and F) at different positions of the benzene ring were all effective, and delivered the corresponding products **3a–3l** in 67% to 81% yield. The potential coupling groups Cl and Br at the *para*- or *meta*-position did not show obvious influences and furnished the desired products **3m–3p** in satisfactory yields. It was worth noting that for the *meta*-substituted anilines, only trace amounts of regioisomers were detected, presumably owing to the steric effect. In addition, the 3,5-dimethyl substituted substrate **1q** could also smoothly react with benzyl methyl ether and sulfur powder to give the product **3q** in 68% yield. Notably, when 2-naphthylamine (**1r**) was used under the optimized conditions, the cyclization product **3r** was obtained in high yield (76%).

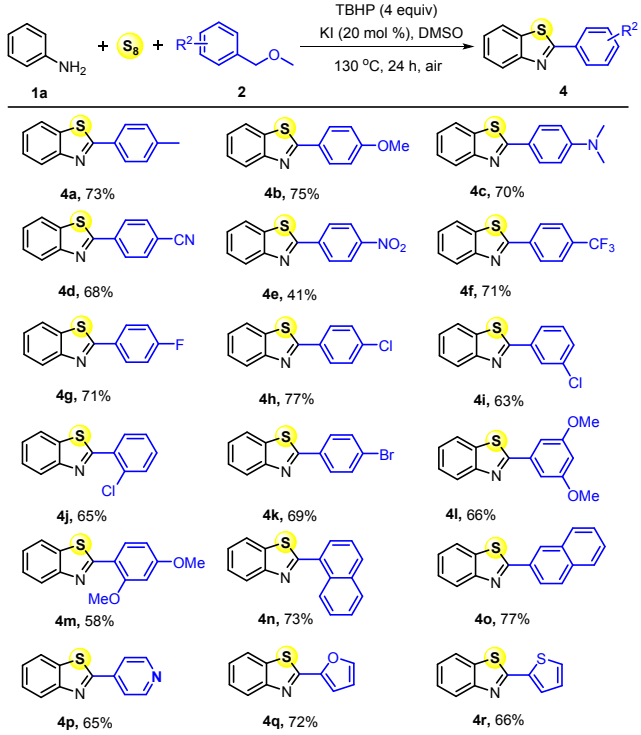
Scheme 2. Reaction Scope of Anilines 1[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.8 mmol), S_8 (0.4 mmol), TBHP (0.8 mmol), KI (20 mol %), DMSO (1 mL), 130 °C, 24 h, under air.

Next, the scope of benzyl methyl ethers was investigated to test the generality and limitations of this three-component reaction. As shown in Scheme 3, benzyl methyl ethers **2** substituted with a variety of electron-donating (Me, MeO, and NMe_2) or electron-withdrawing groups (CN, NO_2, CF_3 and F) at the *para*-position of the phenyl ring were well tolerated and generated the corresponding products **4a**–**4g** in moderate to good yields (41%–75%). It should be noted that a lower yield (41%) and conversion (52%) were observed when the substrate **2e** possessing a nitro group was used (**4e**). Moreover, substrates **2** with moderately electron-deficient (Cl and Br) substituents at the *para*- (**2h**, **2k**), *meta*- (**2i**) and *ortho*-position (**2j**) also reacted well and afforded the 2-substituted benzothiazoles in good yields (**4h**–**4k**). The electron-rich 3,5-dimethoxy and 2,4-dimethoxy substituted benzyl methyl ethers (**2l**, **2m**) were also suitable for this transformation and produced **4l** and **4m** in 66% and 58% yields, respectively. We were pleased to find that α-naphthyl, β-naphthyl, 4-pyridyl, 2-furanyl and 2-thienyl substituted ethers readily furnished benzothiazole products **4n**–**4r** in good yields (65–77%).

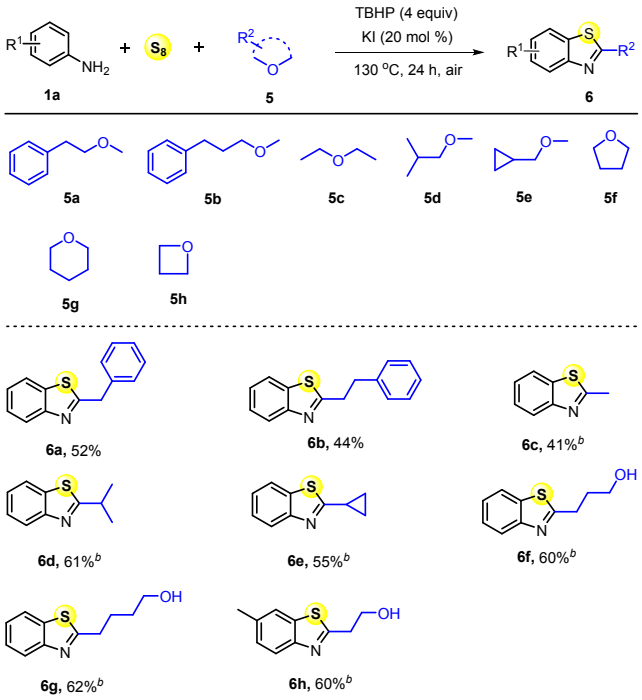
Scheme 3. Reaction Scope of Benzyl Methyl Ethers 2[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.8 mmol), S_8 (0.4 mmol), TBHP (0.8 mmol), KI (20 mol %), DMSO (1 mL), 130 °C, 24 h, under air.

To expand the general applicability of the method, we tested a set of ethers (Scheme 4). To our delight, linear ethers functionalized with a phenyl (**5a**, **5b**) were applicable for this reaction, and the products **6a** and **6b** were obtained in 52% and 44% yields, respectively. The reaction of ethers **5c**-**5h** which have low boiling points also gave the corresponding products **6c**-**6h** when 1 mL ether was used as both reagent and solvent. Interestingly, in the case of cyclic ethers (**5f**-**5h**), ring opening occurred to yield the products **6f**-**6h** in 60-62% yields. For the ether with a cyclopropyl substituent (**5e**), no ring-opening product was detected. Compared with the benzylic ethers, these unbenzylic ethers (**5**) showed lower reactivity, maybe due to the low stability of the reaction intermediates.

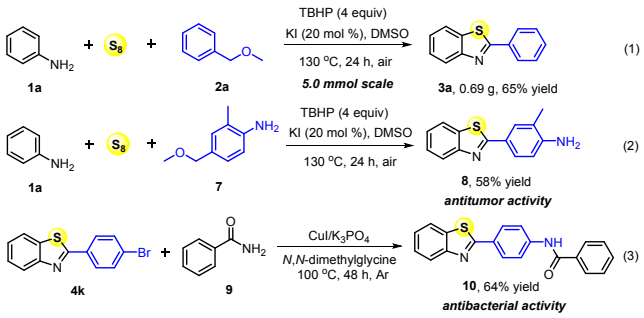
Scheme 4. Reaction Scope of Ethers 2[a]



[a]Reaction conditions: **1** (0.2 mmol), **5** (0.8 mmol), S_8 (0.4 mmol), TBHP (0.8 mmol), KI (20 mol %), DMSO (1 mL), 130 °C, 24 h, under air. [b]**5** (1 mL) was used instead of DMSO.

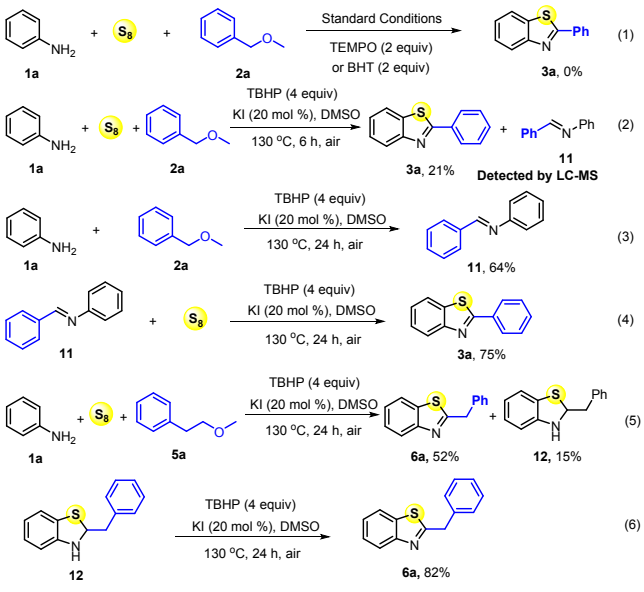
To demonstrate the scalability and synthetic utility of the method, we performed a gram-scale reaction of **1a** (5 mmol) with **2a** and sulfur powder (Scheme 5, eqn (1)). Gratifyingly, the efficiency of this transformation was not obviously affected, and the desired product **3a** was obtained in 65% yield. The current procedure provided an efficient pathway to synthesize the antitumor agent 4-(benzo[*d*]thiazol-2-yl)-2-methylaniline (**8**) in one step (Scheme 5, eqn (2)). Upon treatment of **4k** with benzamide (**9**) in the presence of CuI/K_3PO_4/*N*,*N*-dimethylglycine in DMF, an antibacterial active coupling product *N*-(4-(benzo[*d*]thiazol-2-yl)phenyl) benzamide (**10**) was delivered in 64 % yield (Scheme 5, eqn (3)).[1a, 21b]

Scheme 5. Synthetic Application and Product Transformations



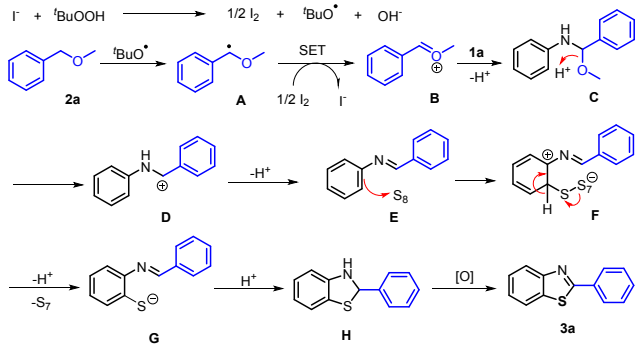
In order to gain mechanistic insights into this transformation, several control experiments were performed. When radical inhibitor 2,2,6,6-tetramethylpiper-idine-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) (2 equiv) was added to the reaction mixture, no desired product **3a** was observed (Scheme 6, eqn (1)). These results indicated that a radical pathway might be involved in this process. When the model reaction was performed for 6 h, imine **11** could be detected by LC-MS (Scheme 6, eqn (2)). Treating **1a** with **2a** in the absence of sulfur powder, imine **11** was isolated in 64% yield (Scheme 6, eqn (3)). Moreover, imine **11** could be converted to the product **3a** in 75% yield under standard reaction conditions (Scheme 6, eqn (4)). Besides, when we performed the reaction with substrate **5a**, the desired product **6a** was obtained in 52% yield, accompanied by a 15% yield of the thiazoline **12** (Scheme 6, eqn (5)). **12** could also be easily converted to the final product **6a** in 82% yield (Scheme 6, eqn (6)). These results indicated that imine **11** and thiazoline **12** might be the probable reaction intermediates.

Scheme 6. Control Experiments



Based on the aforementioned experimental results and related reports, a plausible reaction mechanism was depicted in Scheme 7. Initially, ^{t}BuO· probably generated through the reaction of TBHP and KI, followed by regioselective hydrogen abstraction from **2a** to produce carbon radical **A**. Next, a single electron transfer (SET) process between radical **A** and I_2 led to the oxonium **B**.[16] The intermolecular nucleophilic addition of **1a** to **B** as well as selective C–O bond cleavage of **C** occurred in sequence, and resulted in cation intermediate **D** (when cylic ethers such as tetrahydrofuran **5f** was used, C–O bond cleavage and ring-opening occurred in the process). Deprotonation of cation **D** formed the imine **E**,[15,17] which attacked sulfur powder (S_8) to give **F**. Subsequent elimination of $\mathbf{S_7}$ and deprotonation, sulfurated imine **G** was formed.[11,18] Finally, the intramolecular cyclization of intermediate **G** delivered thiazoline **H**, followed by oxidative aromatization to construct the desired product **3a**.

Scheme 7. Proposed Mechanism



In summary, we have developed a novel three-component reaction of anilines, ethers and elemental sulfur to synthesize benzothiazole derivatives under transition-metal-free conditions. The annulation of anilines was initiated from the selective C(sp^3)-H bond cleavage of ethers in the presence of TBHP and KI. The synthetic utility of our method was further reflected by the synthesis of two heterocyclic compounds with antitumor activity. Thus, this convenient protocol for constructing benzothiazoles may find applications in organic and pharmaceutical synthesis.

■ EXPERIMENTAL SECTION

1. General Information

All reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography. Column chromatography was performed using silica gel (300–400 mesh). The NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ using TMS as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. High-resolution mass spectra were obtained by ESI on a TOF mass analyzer. Melting points are uncorrected.

2. Experimental Procedures

2.1. General Procedure for the Preparation of 3, 4, 6a, 6b and 8

To a sealed tube were added anilines (0.2 mmol, 1.0 equiv), S_8 (12.8 mg, 0.4 mmol, 2.0 equiv), ether (0.8 mmol, 4.0 equiv), KI (6.6 mg, 0.04 mmol, 20 mol %), TBHP (112 μL, 0.8 mmol, 4.0 equiv, 70% aqueous solution) and DMSO (1 mL). The reaction mixture was stirred at 130 °C in oil bath for 24 h under air. After cooled to room temperature, the resulting solution was diluted with EtOAc (10 mL). The

organic layer was washed with water (10 mL). The aqueous phase was extracted with EtOAc (5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacum, and the resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1) as eluent to afford the desired products.

2.2. General Procedure for the Preparation of 6c–6h

To a sealed tube were added anilines (0.2 mmol, 1.0 equiv), S_8 (12.8 mg, 0.4 mmol, 2.0 equiv), ether (1 mL), KI (6.6 mg, 0.04 mmol, 20 mol %) and TBHP (112 μL, 0.8 mmol, 4.0 equiv, 70% aqueous solution). The reaction mixture was stirred at 130 °C in oil bath for 24 h under air. After cooled to room temperature, the resulting solution was diluted with EtOAc (10 mL). The organic layer was washed with water (10 mL). The aqueous phase was extracted with EtOAc (5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacum, and the resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1) as eluent to afford the desired products.

2.3. Procedure for the Preparation of 10

A mixture of **4k** (57.8 mg, 0.2 mmol, 1.0 equiv), benzamide **9** (29.1 mg, 0.24 mmol, 1.2 equiv), CuI (7.6 mg, 20 mol %), K_3PO_4 (106.1 mg, 0.5 mmol, 2.5 equiv) and *N*,*N*-dimethylglycine (4.1 mg, 20 mol %, 0.2 equiv) in DMF (2 mL) was stirred at 100 °C for 48 h in oil bath under Ar. After cooling to room temperature, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacum, and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to produce the desired product **10**.

2.4. ^{1}H and ^{13}C NMR data of the products

2-Phenylbenzo[d]thiazole (3a).[7f] White soild (32.9 mg, 78% yield). mp 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16–8.11 (m, 3H), 7.94–7.92 (m, 1H), 7.55–7.51 (m, 4H), 7.44–7.40 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1, 154.1, 135.0, 133.6, 131.0, 129.0, 127.6, 126.4, 125.2, 123.2, 121.6.

6-Methyl-2-phenylbenzo[d]thiazole (3b).[7f] Light yellow solid (33.8 mg, 75% yield). mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12–8.05 (m, 2H), 7.97 (d, J = 8.3 Hz, 1H), 7.67 (s, 1H), 7.51–7.46 (m, 3H), 7.32–7.28 (m, 1H), 2.49 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.5, 151.8, 134.8, 134.8, 133.3, 130.2, 128.5, 127.4, 126.9, 122.3, 120.9, 21.1.

5-Methyl-2-phenylbenzo[d]thiazole (3c).[7f] White soild (33.3 mg, 74% yield). mp 146–148 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.09 (dd, J = 6.8, 3.0 Hz, 2H), 7.89 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.50–7.48 (m, 3H), 7.22 (d, J = 7.8 Hz, 1H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.5, 154.6, 136.2, 133.7, 132.0, 130.7, 128.9, 127.4, 126.7, 123.2, 121.0, 21.4.

4-Methyl-2-phenylbenzo[d]thiazole (3d).[12] White soild (30.2 mg, 67% yield). mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13–8.11 (m, 2H), 7.53–7.28 (m, 3H), 7.44 (d, J = 1.8 Hz, 1H), 7.40–7.34 (m, 1H), 7.24–7.22 (m, 1H), 2.79 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.7, 152.3, 135.3, 134.0, 133.1, 129.6, 129.0, 128.9, 128.6, 127.5, 119.6, 18.6.

6-Ethyl-2-phenylbenzo[d]thiazole (3e).[11] Light yellow solid (34.9 mg, 73% yield). mp 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12–8.10 (m, 2H), 8.02 (d, J = 8.3 Hz, 1H), 7.74 (s, 1H), 7.54–7.50 (m, 3H), 7.37 (d, J = 8.4 Hz, 1H), 2.82 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.2, 152.3, 141.8, 135.2, 133.7, 130.8, 129.0, 127.5, 126.9, 122.8, 120.2, 29.0, 15.9.

6-(tert-Butyl)-2-phenylbenzo[d]thiazole (3f).[11] White solid (41.1 mg, 77% yield). mp 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14–8.10 (m, 2H), 8.04 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 2.1 Hz, 1H), 7.61–7.58 (m 1H), 7.53–7.50 (m, 3H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5, 152.1, 148.7, 135.1, 133.8, 130.8, 129.0, 127.5, 124.6, 122.6, 117.7, 35.1, 31.6.

6-Methoxy-2-phenylbenzo[d]thiazole (3g).[7f] White solid (39.1 mg, 81% yield). mp 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09–8.06 (m, 2H), 7.99 (d, J = 8.9 Hz, 1H), 7.52–7.48 (m, 3H), 7.37 (d, J = 2.6 Hz, 1H), 7.13–7.11 (m 1H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 165.6, 157.8, 148.6, 136.4, 133.7, 130.6, 129.0, 127.3, 123.7, 115.7, 104.1, 55.8.

5-Methoxy-2-phenylbenzo[d]thiazole (3h).[19a] White soild (34.7 mg, 72% yield). mp 63–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (dd, J = 6.8, 3.1 Hz, 2H), 7.74 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.49–7.48 (m, 3H), 7.04 (dd, J = 8.9, 2.4 Hz, 1H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.3, 159.2, 155.4, 133.7, 130.9, 129.0, 127.4, 126.9, 121.8, 115.5, 105.6, 55.6.

2-Phenylbenzo[d]thiazole-6-carbonitrile (3i).[19a] White solid (32.1 mg, 68% yield). mp 193–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.54 (s, 1H), 8.66 (dd, J = 6.5, 3.1 Hz, 2H), 8.34 (s, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 2.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 163.3, 160.9, 151.9, 137.0, 134.7, 133.4, 131.7, 130.3, 128.9, 122.8, 117.9, 110.8.

2-Phenyl-6-(trifluoromethyl)benzo[d]thiazole (3j).[7f] Light yellow soild (39.1 mg, 70% yield). mp 150–152 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.67 (s, 1H), 8.24–8.12 (m, 3H), 7.84 (d, J = 8.7 Hz, 1H), 7.63–7.58 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 171.7, 156.2 (d, J = 1.2 Hz), 135.4, 132.8, 132.6, 130.0, 128.8, 128.0, 126.1 (q, J = 270.3 Hz), 124.0, 123.8 (q, J = 3.2 Hz), 121.1 (q, J = 4.0 Hz).

6-Fluoro-2-phenylbenzo[d]thiazole (3k).[7f] Light yellow soild (33.0 mg, 72% yield). mp 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09–8.02 (m, 3H), 7.60 (dd, J = 8.1, 2.6 Hz, 1H), 7.53–7.51 (dt, J = 4.9, 1.8 Hz, 3H), 7.28–7.23 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8 (d, J = 3.3 Hz), 160.5 (d, J = 246.1 Hz), 150.7 (d, J = 1.8 Hz), 136.0 (d, J = 11.4 Hz), 133.3, 131.1, 129.1, 127.5, 124.1 (d, J = 9.2 Hz), 115.0 (d, J = 24.9 Hz), 107.9 (d, J = 26.8 Hz).

5-Fluoro-2-phenylbenzo[d]thiazole (3l).[12] White soild (30.7 mg, 67% yield). mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09–8.05 (m, 2H), 7.81–7.73 (m, 2H), 7.51–7.47 (m, 3H), 7.18–7.11 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 170.45, 161.92 (d, J = 242.7 Hz), 155.05 (d, J = 12.2 Hz), 133.36, 131.18, 130.43 (d, J = 2.2 Hz), 129.01, 127.49, 122.2 (d, J = 9.8 Hz), 113.78 (d, J = 24.9 Hz), 109.32 (d, J = 23.2 Hz).

6-Chloro-2-phenylbenzo[d]thiazole (3m).[19b] White solid (32.3 mg, 66% yield). mp 155–157 °C. ^{1}H NMR (400

MHz, $CDCl_3$) δ (ppm) 8.10–8.08 (m, 2H), 8.00 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 2.0 Hz, 1H), 7.54–7.51 (m, 3H), 7.47 (dd, J = 8.7, 2.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.6, 152.6, 136.2, 133.1, 131.3, 131.1, 129.1, 127.6, 127.2, 123.9, 121.3.

5-Chloro-2-phenylbenzo[d]thiazole (3n).[12] White soild (34.3 mg, 70% yield). mp 137–139 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14–8.04 (m, 3H), 7.81 (d, J = 8.5 Hz, 1H), 7.51–7.50 (m, 3H), 7.37–7.35 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.4, 154.5, 132.8, 132.8, 131.8, 130.8, 128.6, 127.1, 125.1, 122.6, 121.8.

6-Bromo-2-phenylbenzo[d]thiazole (3o).[7f] White soild (40.5 mg, 70% yield). mp 154–156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11–8.08 (m, 2H), 8.00 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 2.1 Hz, 1H), 7.56–7.50 (m, 3H), 7.48-7.46 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.6, 152.6, 136.2, 133.2, 131.3, 129.1, 127.5, 127.2, 123.9, 121.3, 121.2.

5-Bromo-2-phenylbenzo[d]thiazole (3p).[12] White soild (39.9 mg, 69% yield). mp 134–136 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (s, 1H), 8.09–8.07 (m, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.51–7.48 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.6, 155.2, 133.8, 133.1, 131.2, 129.0, 128.1, 127.5, 126.0, 122.5, 119.8.

5,7-Dimethyl-2-phenylbenzo[d]thiazole (3q).[11] Light yellow solid (32.5 mg, 68% yield). mp 87–89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14–8.12 (m, 2H), 7.76 (s, 1H), 7.51 (dd, J = 5.1, 1.8 Hz, 3H), 7.05 (s, 1H), 2.58 (s, 3H), 2.51 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 154.3, 136.6, 133.9, 132.5, 131.1, 130.8, 129.0, 127.5, 127.1, 120.7, 21.5, 21.3.

2-Phenylnaphtho[2,1-d]thiazole (3r).[11] White soild (39.7 mg, 76% yield). mp 100–102 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20–8.14 (m, 3H), 8.07 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.66–7.58 (m, 2H), 7.55–7.52 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.3, 152.0, 133.6, 132.1, 131.1, 130.8, 129.1, 129.0, 128.1, 127.5, 127.4, 127.1, 126.1, 125.2, 121.7.

2-(p-Tolyl)benzo[d]thiazole (4a).[7f] White soild (32.9 mg, 73% yield). mp 86–88 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 7.9 Hz, 1H), 7.53–7.49 (m, 1H), 7.42–7.38 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.3, 154.1, 141.5, 134.9, 130.9, 129.7, 127.5, 126.3, 125.0, 123.0, 121.6, 21.5.

3-(2-Methylbenzo[4,5][1,3,6]thiadiazepino[3,2-a]indol-6-yl)propan-1-ol (4b).[7f] White soild (36.2 mg, 75% yield). mp 119–121 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08–8.05 (m, 3H), 7.89 (d, J = 7.9 Hz, 1H), 7.52–7.48 (m, 1H), 7.40–7.36 (m, 1H), 7.04–7.00 (m, 2H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 162.0, 154.1, 134.8, 129.1, 126.4, 126.2, 124.8, 122.8, 121.5, 114.4, 55.5.

4-(Benzo[d]thiazol-2-yl)-N,N-dimethylaniline (4c).[7g] Yellow soild (35.6 mg, 70% yield). mp 169–171 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03–7.97 (m, 3H), 7.86 (d, J = 7.8 Hz, 1H), 7.48–7.44 (m, 1H), 7.35–7.31 (m, 1H), 6.78–6.75 (m, 2H), 3.07 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.9, 154.3, 152.2, 134.5, 128.9, 126.0, 124.2, 122.2, 121.4, 121.3, 111.7, 40.2.

4-(Benzo[d]thiazol-2-yl)benzonitrile (4d).[7f] White solid (32.1 mg, 68% yield). mp 168–170 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20–8.18 (m, 2H), 8.12 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.58–7.54 (m, 1H), 7.49–7.45 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 165.3, 153.9, 137.4, 135.3, 132.8, 127.9, 126.9, 126.1, 123.8, 121.8, 118.3, 114.1.

2-(4-Nitrophenyl)benzo[d]thiazole (4e).[19c] White solid (21.0 mg, 41% yield). mp 220–222 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.39–8.37 (m, 2H), 8.31–8.28 (m, 2H), 8.17–8.15 (m, 1H), 8.00–7.97 (m, 1H), 7.61–7.56 (m, 1H), 7.52–7.47 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9, 154.1, 149.0, 139.2, 135.5, 128.2, 127.0, 126.3, 124.3, 123.9, 121.9.

2-(4-(Trifluoromethyl)phenyl)benzo[d]thiazole (4f).[19b] White soild (33.6 mg, 71% yield). mp 162–164 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, J = 8.1 Hz, 2H), 8.14 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.58–7.54 (m, 1H), 7.48–7.44 (m, 1H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 153.9, 136.8, 135.2, 132.5 (q, J = 32.6 Hz), 127.8, 126.7, 126.0 (q, J = 3.7 Hz), 125.8, 123.6 (q, J = 273.4 Hz), 122.5, 121.8.

2-(4-Fluorophenyl)benzo[d]thiazole (4g).[19b] White solid (32.5 mg, 71% yield). mp 99–101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13–8.08 (m, 3H), 7.92 (d, J = 8.4 Hz, 1H), 7.52 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.42 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.24–7.18 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.8, 164.5 (d, J = 252.0 Hz), 154.0, 135.0, 129.9 (d, J = 3.2 Hz), 129.6 (d, J = 8.7 Hz), 126.5, 125.3, 123.2, 121.7, 116.2 (d, J = 22.1 Hz).

2-(4-Chlorophenyl)benzo[d]thiazole (4h).[7f] White solid (37.7 mg, 77% yield). mp 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 8.2 Hz, 1H), 8.07–8.02 (m, 2H), 7.92 (d, J = 7.7 Hz, 1H), 7.55–7.51 (m, 1H), 7.50–7.47 (m, 2H), 7.44–7.40 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.6, 154.0, 137.1, 135.0, 132.0, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7.

2-(3-Chlorophenyl)benzo[d]thiazole (4i).[19c] White solid (30.9 mg, 63% yield). mp 95–97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15–8.14 (m, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.99–7.96 (m, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.56–7.52 (m, 1H), 7.50–7.42 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.3, 153.9, 135.2, 135.0, 130.9, 130.3, 127.4, 126.6, 126.5, 125.7, 125.6, 123.4, 121.7.

2-(2-Chlorophenyl)benzo[d]thiazole (4j).[19b] White solid (31.9 mg, 65% yield). mp 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27–8.17 (m, 1H), 8.18 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.48–7.43 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 164.2, 152.4, 136.1, 132.7, 132.2, 131.8, 131.2, 130.8, 127.2, 126.4, 125.5, 123.5, 121.4.

2-(4-Bromophenyl)benzo[d]thiazole (4k).[19c] White solid (39.9 mg, 69% yield). mp 130–132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.92 (dd, J = 8.1, 1.5 Hz, 1H), 7.66–7.63 (m, 2H), 7.55–7.51 (m, 1H), 7.44–7.40 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.7, 154.0, 135.0, 132.5, 132.2, 128.9, 126.5, 125.5, 125.5, 123.3, 121.7.

2-(3,5-Dimethoxyphenyl)benzo[d]thiazole (4l).[19b] White solid (35.8 mg, 66% yield). mp 85–87 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.44–7.39 (m, 1H), 7.29 (d, J = 2.3 Hz, 2H), 6.62 (t, J = 2.3 Hz, 1H), 3.92 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0, 161.1,

153.9, 135.3, 135.0, 126.4, 125.3, 123.2, 121.6, 105.5, 103.5, 55.7.

2-(2,4-Dimethoxyphenyl)benzo[d]thiazole (4m).[20a] White solid (31.4 mg, 58% yield). mp 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.51 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.51–7.47 (m, 1H), 7.38–7.34 (m 1H), 6.70 (dd, J = 8.8, 2.4 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 4.05 (s, 3H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 163.3, 162.9, 158.6, 152.1, 135.6, 130.8, 125.8, 124.2, 122.3, 121.1, 115.5, 105.9, 98.5, 55.7, 55.6.

2-(Naphthalen-1-yl)benzo[d]thiazole (4n).[19b] White solid (38.1 mg, 73% yield). mp 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.98 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.04–7.96 (m, 4H), 7.69–7.58 (m, 4H), 7.51–7.47(m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 167.7, 154.1, 135.5, 134.0, 131.2, 130.8, 130.7, 129.5, 128.5, 127.7, 126.6, 126.4, 125.9, 125.4, 125.0, 123.6, 121.5.

2-(Naphthalen-2-yl)benzo[d]thiazole (4o).[7f] White solid (40.2 mg, 77% yield). mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62–8.58 (m, 1H), 8.24 (dd, J = 8.5, 1.8 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.01–7.89 (m, 4H), 7.60–7.53 (m, 3H), 7.45–7.41 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 168.2, 154.1, 135.1, 134.6, 133.2, 130.9, 128.9, 128.9, 127.9, 127.6, 127.5, 126.9, 126.5, 125.3, 124.4, 123.2, 121.7.

2-(Pyridin-4-yl)benzo[d]thiazole (4p).[19b] White solid (27.6 mg, 65% yield). mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.78 (d, J = 5.6 Hz, 2H), 8.14 (d, J = 8.2 Hz, 1H), 7.97–7.94 (m, 3H), 7.58–7.53 (m, 1H), 7.49–7.44 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 165.1, 153.9, 150.7, 140.5, 135.2, 126.8, 126.2, 123.9, 121.9, 121.2.

2-(Furan-2-yl)benzo[d]thiazole (4q).[19b] White solid (28.9 mg, 72% yield). mp 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 1.5 Hz, 1H), 7.53–7.49 (m, 1H), 7.42–7.38 (m, 1H), 7.23 (d, J = 3.4 Hz, 1H), 6.62 (dd, J = 3.5, 1.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 157.6, 153.6, 148.7, 144.8, 134.2, 126.5, 125.2, 123.1, 121.6, 112.6, 111.6.

2-(Thiophen-2-yl)benzo[d]thiazole (4r).[7f] White solid (28.6 mg, 66% yield). mp 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 3.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.41–7.37 (m, 1H), 7.17–7.15 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 161.4, 153.6, 137.3, 134.7, 129.4, 128.7, 128.1, 126.5, 125.3, 123.0, 121.5.

2-Benzylbenzo[d]thiazole (6a).[7f] Yellow oil (30.6 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.51–7.46 (m, 1H), 7.43–7.30 (m, 6H), 4.48 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 171.3, 153.2, 137.2, 135.7, 129.2, 128.9, 127.4, 126.0, 124.9, 122.8, 121.6, 40.7.

2-Phenethylbenzo[d]thiazole (6b).[20b] Light yellow solid (30.1 mg, 63% yield). mp 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.52–7.48 (m, 1H), 7.41–7.25 (m, 6H), 3.50–3.45 (m, 2H), 3.27–3.23 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 171.2, 152.9, 140.1, 135.0, 128.6, 128.5, 126.5, 126.1, 124.9, 122.5, 121.6, 36.0, 35.6.

2-Methylbenzo[d]thiazole (6c).[20c] Yellow oil (12.2 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.48–7.44 (m, 1H), 7.37–7.33 (m, 1H), 2.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 166.9, 153.3, 135.6, 125.9, 124.7, 122.4, 121.4, 20.1.

2-Isopropylbenzo[d]thiazole (6d).[20b] Yellow oil (21.6 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 3.45 (m, 1H), 1.51 (dd, J = 6.9, 0.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 178.7, 153.1, 134.7, 125.7, 124.6, 122.6, 121.6, 34.1, 22.9.

2-Cyclopropylbenzo[d]thiazole (6e).[19b] Yellow oil (19.3 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.46–7.41 (m, 1H), 7.34–7.30 (m, 1H), 2.44–2.38 (m, 1H), 1.26–1.22 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 174.6, 153.3, 134.1, 125.9, 124.3, 122.0, 121.4, 15.3, 11.8.

3-(Benzo[d]thiazol-2-yl)propan-1-ol (6f).[6f] Yellow oil (23.2 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94–7.92 (m, 1H), 7.88–7.85 (m, 1H), 7.48–7.48 (m, 1H), 7.38–7.34 (m, 1H), 3.86 (t, J = 5.7 Hz, 2H), 3.44 (t, J = 6.6 Hz, 2H), 2.26–2.20 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 174.5, 153.3, 134.1, 125.9, 124.3, 122.0, 121.3, 61.3, 32.8, 30.9.

4-(Benzo[d]thiazol-2-yl)butan-1-ol (6g). Yellow oil (25.7 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92–7.91 (m, 1H), 7.84–7.82 (m, 1H), 7.51–7.41 (m, 2H), 3.73 (t, J = 6.2 Hz, 2H), 3.11 (t, J = 7.3 Hz, 2H), 2.10–2.03 (m, 2H), 1.81–1.74 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 172.3, 157.0, 135.4, 129.1, 127.1, 125.9, 125.2, 61.9, 34.4, 32.4, 23.6. HRMS (ESI) m/z calcd for $C_{11}H_{14}NOS^+$ $[M+H]^+$ 208.0791, found 208.0794.

2-(6-Methylbenzo[d]thiazol-2-yl)ethanol (6h). Yellow solid (23.2 mg, 60% yield). mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88–7.75 (m, 2H), 7.24–7.22 (m, 1H), 4.22 (t, J = 5.4 Hz, 2H), 3.23 (t, J = 5.4 Hz, 2H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 170.5, 155.0, 137.7, 129.0, 126.5, 122.4, 121.2, 60.5, 35.2, 21.8. HRMS (ESI) m/z calcd for $C_{10}H_{12}NOS^+$ $[M+H]^+$ 194.0634, found 194.0638.

4-(Benzo[d]thiazol-2-yl)-2-methylaniline (8).[21a] Light yellow solid (27.8 mg, 58% yield). mp 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.54–7.50 (m, 1H), 7.45–7.40 (m, 2H), 7.18 (dd, J = 7.6, 1.9 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 5.25 (s, 2H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 168.7, 154.1, 147.9, 134.6, 131.7, 131.1, 126.9, 125.6, 125.5, 123.0, 122.6, 115.4, 112.3, 18.0.

N-(4-(Benzo[d]thiazol-2-yl)phenyl)benzamide (10).[21b] White solid (42.3 mg, 64% yield). mp 124–126 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.58 (s, 1H), 8.13–8.10 (m, 3H), 8.06–8.00 (m, 5H), 7.63–7.60 (m, 1H), 7.59–7.52 (m, 3H), 7.46–7.42 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 167.5, 166.4, 154.3, 142.6, 135.1, 134.8, 132.3, 128.9, 128.4, 128.3, 128.3, 127.0, 125.7, 123.1, 122.7, 120.9.

N-benzylideneaniline (11).[21c] Light yellow solid (23.2 mg, 64% yield). mp 50–52 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.50 (s, 1H), 7.96 (dd, J = 6.6, 3.1 Hz, 2H), 7.53–7.51 (m, 3H), 7.44 (t, J = 7.7 Hz, 2H), 7.30–7.26 (m,

3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 152.0, 136.2, 131.5, 129.2, 128.9, 128.8, 126.0, 120.9.

2-Benzyl-2,3-dihydrobenzo[d]thiazole (12).[22] White solid (6.8 mg, 15% yield). mp 98–100 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.37 (m, 2H), 7.34–7.30 (m, 1H), 7.28–7.25 (m, 2H), 7.12 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.96 (td, *J* = 7.7, 1.3 Hz, 1H), 6.79 (td, *J* = 7.5, 1.2 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.43 (dd, *J* = 8.1, 5.7 Hz, 1H), 4.07 (s, 1H), 3.24–3.10 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 145.9, 137.0, 129.4, 128.8, 127.1, 126.4, 125.4, 122.2, 120.7, 110.5, 68.9, 45.0.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
^1H NMR and ^{13}C NMR spectra of compounds **3**, **4**, **6**, **8**, **10**, **11** and **12** (PDF)

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Notes

The authors declare no competing financial interest.

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