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Note

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Selective Construction of 2-Substituted Benzothiazoles from *o*-Iodoaniline Derivatives, S_8 and *N*-Tosylhydrazones

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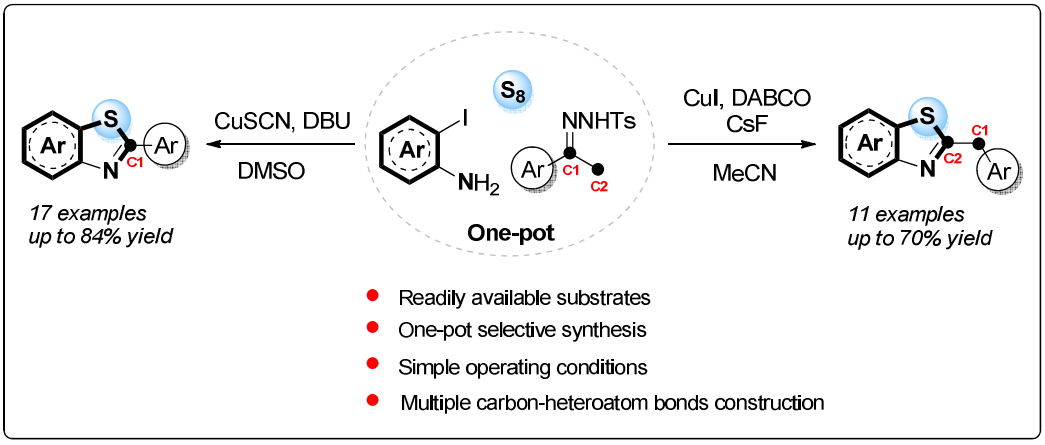
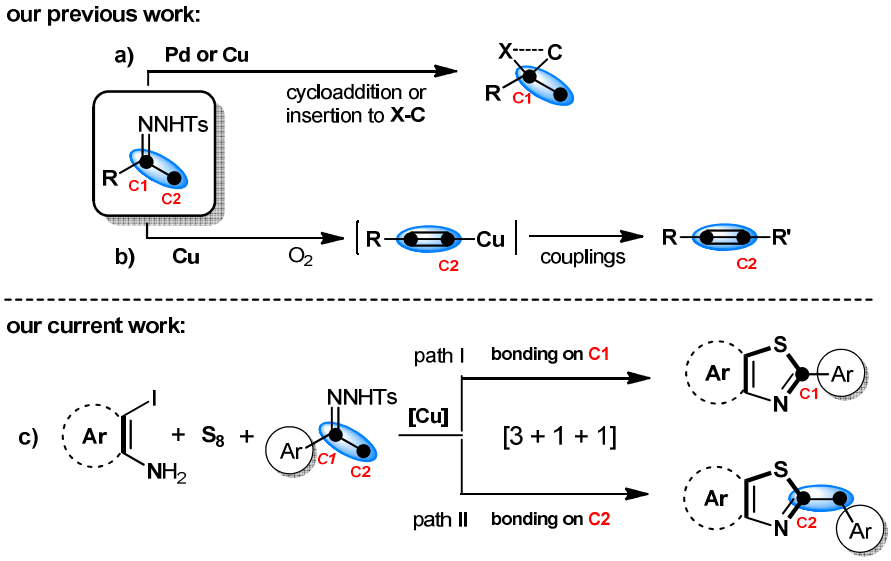


Abstract: A selective construction of 2-substituted benzothiazoles from *o*-iodoaniline derivatives, S_8 and *N*-tosylhydrazone *via* copper-promoted [3+1+1]-type cyclization reaction has been realized. In the protocol, the carbon atom on *N*-tosylhydrazone could be regulated to construct benzothiazole by changing the reaction system. Furthermore, the transformation has achieved the construction of multiple carbon-heteroatom bonds.

Carbon-heteroatom bonds such as C-S, C-O and C-N bonds are basic fragments of functional heterocyclic molecules. The development of novel and effective protocols to construct these chemical bonds is a significant issue in organic synthesis,[1] especially in the research of biologically active molecules, drugs and agrochemicals. *N*-Tosylhydrazones, as readily available and stable substrates, can be used as metal carbene precursors after generating diazo compounds *in situ* under basic conditions. As a result of the high concern, using metal carbene species to construct carbon-heteroatom bonds has received considerable attention. In the respect, the insertions of metal carbenes into X-H **(**X = B, N, O, S, Si, *etc.***)** bonds,[2] cyclization reactions,[3] difunctionalization[4] and multicomponent reactions of metal-carbene[5] have displayed versatile applications in the constructions of carbon-heteroatom bonds. In recent years, our group has successfully achieved a series of conversion reactions of *N*-tosylhydrazones to build carbon-heteroatom bonds in transition metal-catalyzed systems.[4a,6] For example, the cyanothiolation of copper-carbene to incorporate a sulfur-substituted quaternary carbon center,[4a] and the synthesis of oxiranes through the construction of carbonyl ylides from palladium carbenes.[6a] Similarly, two different bonds was built on the carbon atom of metal carbene (C1) (Scheme 1a). Furthermore, copper-catalyzed oxidative transformations of *N*-tosylhydrazones as alkyne precusors have been applied in the cross-coupling reactions,[6e] where C2 was the bonding site (Scheme 1b). Based on previous studies, we intend to construct diverse heterocyclic molecules by using different bonding sites of *N*-tosylhydrazones.

Scheme 1. Transition Metal-Catalyzed Conversions of *N*-Tosylhydrazones

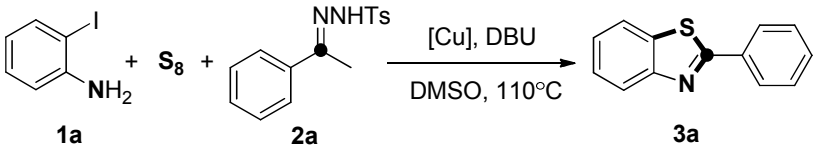


As an important class of heterocyclic scaffold, benzothiazoles are widely found in biologically active molecules, clinically drugs, and application materials. The common approaches for the assembly of 2-substituted benzothiazoles are based on the condensations of 2-aminothiophenols with carboxylic acids, aldehydes, nitriles and etc,[7] where the preparation of readily oxidized 2-aminothiophenols is a major problem. The other accesses to synthesize 2-substituted benzothiazoles include C-H functionalization/C-S bond formation,[8] cyclization of *ortho*-halobenzo-thiourea,[9] and etc.[10] Normally, the benzothioureas used in such methods require further conversion of the corresponding amides. Despite the diversification of synthetic methods, we are still eager to develop a novel method to synthesize benzothiazoles with readily-available raw materials. Hence, we propose a copper-promoted multi-component tandem cyclization for the selective construction of 2-substituted benzothiazoles from *o*-iodoaniline derivatives, S_8 and *N*-tosylhydrazones (Scheme 1c). In the protocol, by changing the reaction system, C1 or C2 is used selectively as a

binding site to achieve the construction of carbon-heteroatom bonds.

In order to increase the yield and selectivity of products **3a** and **4a**, the reaction conditions for each product were optimized individually. As shown in Table 1, the reaction was initially carried out in the presence of CuTC (5 mol %), DBU (2 equiv) and DMSO (1.5 mL) at 110 °C under air for 10 h to produce **3a** in 40% yield (entry 1). Then, differ copper catalysts (CuI, CuCl, CuSCN, $Cu(OAc)_2$, *etc.*), as well as the amount of copper catalyst and DBU were investigated, and the use of 10 mol % of CuSCN and 3 equiv of DBU was found to be suitable to form **3a** (entry 7). The reaction proceeded better when conducted under N_2, which delivered **3a** in 72% isolated yield (entry 8). Notably, the reaction did not occur without a copper salt (entry 9).

Table 1. Optimization of the Reaction Conditions to Construct 3a [a]



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

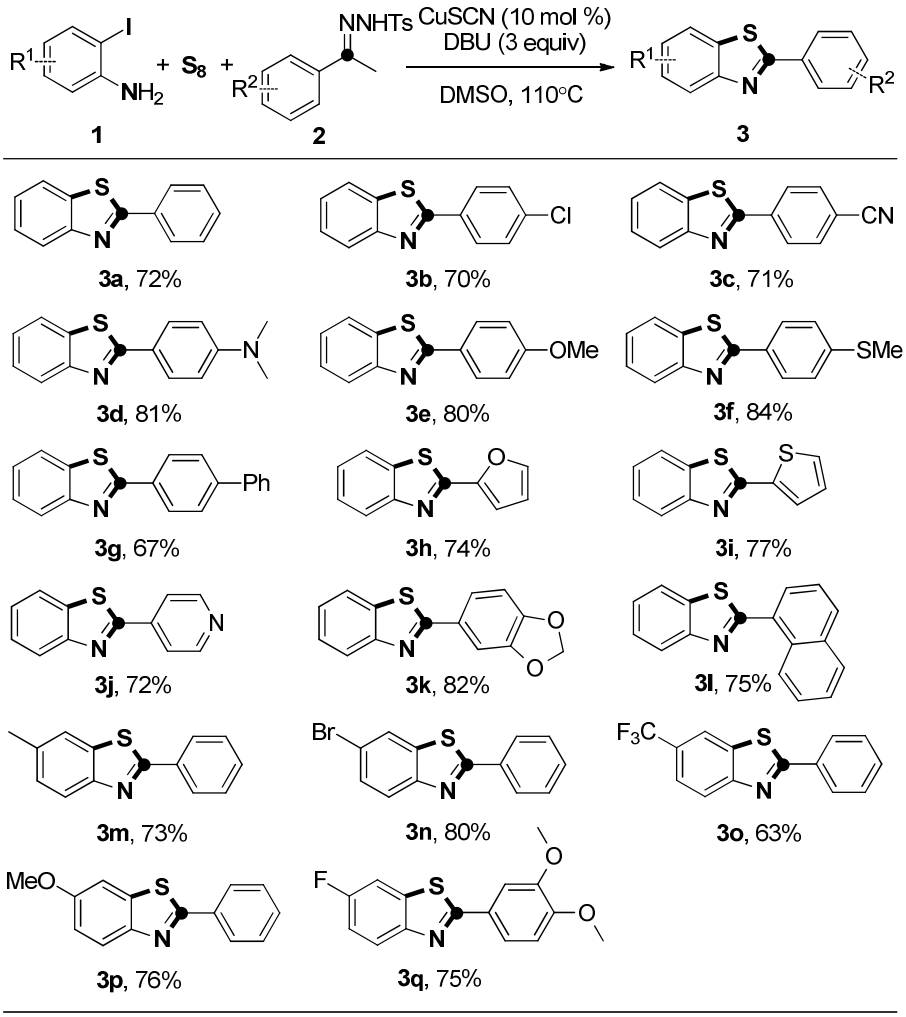
Entry	[Cu]	Base	Yield [b](%) of 3a
1	CuTC (5)	DBU (2)	40
2	CuI (5)	DBU (2)	36
3	CuSCN (5)	DBU (2)	49
4	$Cu(OAc)_2$ (5)	DBU (2)	n.d.
5	CuSCN (10)	DBU (2)	58
6	CuSCN (20)	DBU (2)	56
7	CuSCN (10)	DBU (3)	69

8 [c]	**CuSCN (10)**	**DBU (3)**	**76 (72)**
9	-	DBU (3)	n.d.

[a] Reaction conditions: **1a** (0.1 mmol), $\mathbf{S_8}$ (0.12 mmol), **2a** (0.12 mmol), [Cu] (mol %), DBU (equiv) in DMSO (1.5 mL) at 110 °C under air for 10 h unless otherwise noted. [b] GC yield with *n*-dodecane as internal standard. n.d. = not detected. The number in the parentheses is isolated yield. [c] Under N_2.

The substrate scope for the construction of benzothiazoles **3** was shown in Table 2. Various *N*-tosylhydrazones containing different functional groups, especially electron-rich groups (NMe_2, OMe and SMe), at the *para*-position of benzene ring worked well to afford the desired benzothiazoles **3** in moderate to good yields (**3a**-**3g**). Heterocycles derived *N*-tosylhydrazones were good substrates and the corresponding products were delivered in good yields (**3h**-**3j**). The reaction performed with sterically hindered substrates gave the corresponding products in the yields of 82% (**3k)** and 75% (**3l)**, respectively. 2-Iodoanilines containing various groups including Me, Br, CF_3 and OMe at 4-position of aromatic ring also worked well, and the reactions delivered the desired products in good yields (**3m**-**3p**). In addition, when 4-fluoro-*2*-iodoaniline and 3,4-dimethoxyacetophenone derived *N*-tosylhydrazones were used as substrates, the reaction gave **3q** in 75% yield.

Table 2. Synthesis of Substituted Benzothiazoles 3 [a]

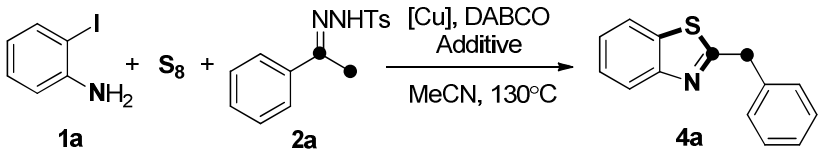


[a] Reaction conditions: **1** (0.2 mmol), S_8 (0.24 mmol), **2** (0.24 mmol), CuSCN (10 mol%), DBU (3 equiv) in DMSO (2.5 mL) at 110 °C under N_2 for 10 h unless otherwise noted. Yields refer to the isolated yields.

Next, we went on optimizing the reaction conditions to promote the formation of **4a**. As shown in Table 3, the reaction was carried out with DABCO as base in 1.5 mL of MeCN at 130 °C under nitrogen atmosphere, and various types of copper catalysts were then examined. When using 10 mol% of CuI, the better selectivity and higher yield for **4a** were observed (entry 2). Reducing the amount of DABCO to 1 equivalent,

the yield was maintained (entry 5). Subsequently, we conducted the reaction by adding different fluoride ion-containing additives. It is found that the addition of 2 equivalent of CsF was effective and the yield of **4a** increased to 53% (entry 6). The reaction appeared to proceed more smoothly when increasing CuI loading (entries 9-10), whereas the reaction was hindered when 1 equivalent of CuI was used (entry 11). Notably, the presence of oxygen could inhibit the production of **4a** (entry 12). Similarly, the reaction did not occur without a copper salt (entry 13).

Table 3. Optimization of Reaction Conditions to Construct 4a [a]



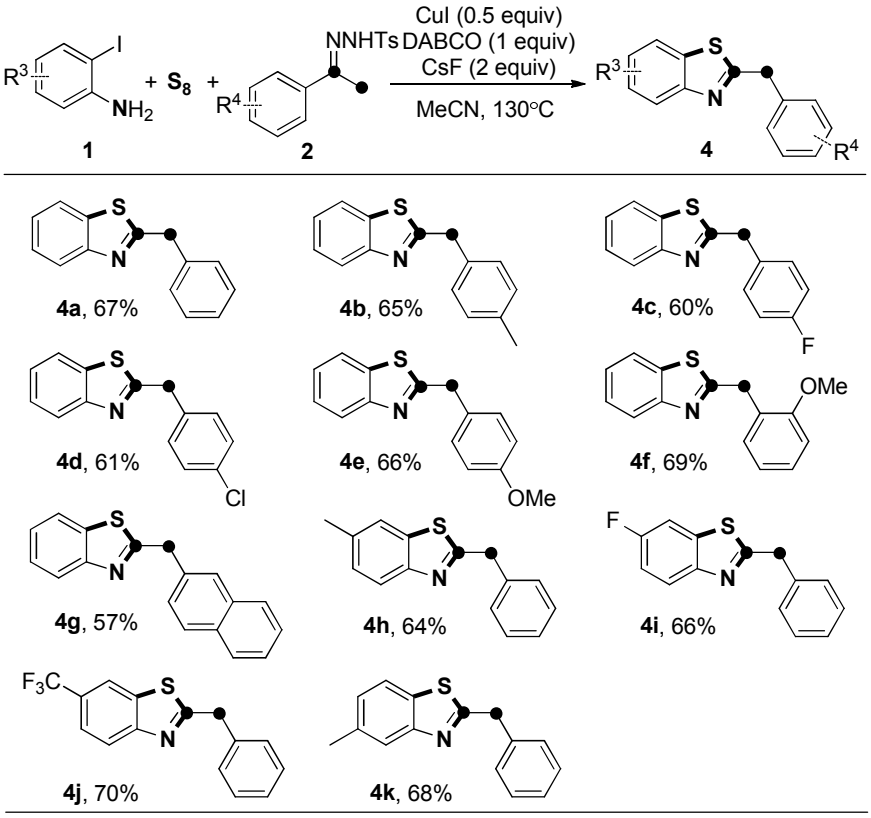
Entry	[Cu]	Base	Additive	Yield [b](%) of 4a
1	CuTC (10)	DABCO (2)	-	30
2	CuI (10)	DABCO (2)	-	41
3	CuCl (10)	DABCO (2)	-	27
4	CuSCN (10)	DABCO (2)	-	13
5	CuI (10)	DABCO (1)	-	42
6	CuI (10)	DABCO (1)	CsF (2)	53
7	CuI (10)	DABCO (1)	TBAF (2)	50
8	CuI (10)	DABCO (1)	KF (2)	43
9	CuI (30)	DABCO (1)	CsF (2)	65
10	**CuI (50)**	**DABCO (1)**	**CsF (2)**	**69 (67)**
11	CuI (100)	DABCO (1)	CsF (2)	32

12 [c]	CuI (50)	DABCO (1)	CsF (2)	trace
13	-	DABCO (1)	CsF (2)	n.d

[a] Reaction conditions: **1a** (0.1 mmol), $\mathbf{S_8}$ (0.12 mmol), **2a** (0.12 mmol), [Cu] (mol %), DABCO (equiv), additive (equiv) in MeCN (1.5 mL) at 130 °C under N_2 for 10 h unless otherwise noted. [b] GC yield with *n*-dodecane as internal standard. n.d = not detected. The number in the parentheses is isolated yield. [c] 1 atm of O_2.

The substrate scope for the synthesis of benzothiazoles **4** was shown in Table 4. Different substituents on the aromatic ring of *N*-tosylhydrazones have little effect on the reaction, and the corresponding products were obtained in moderate yields (**4a-4e**). Altering the position of the substituent on the aromatic ring had little effect on the yield (**4e-4f**). Sterically hindered acetylnaphthalene derived *N*-tosylhydrazones also reacted smoothly, and the desired product was obtained in 57% yield (**4g**). Additionally, various substituted 2-iodoanilines worked well under the optimal conditions, and afforded the corresponding products in moderate to good yields (**4h-4k**).

Table 4. Synthesis of Substituted Benzothiazoles 4 [a]

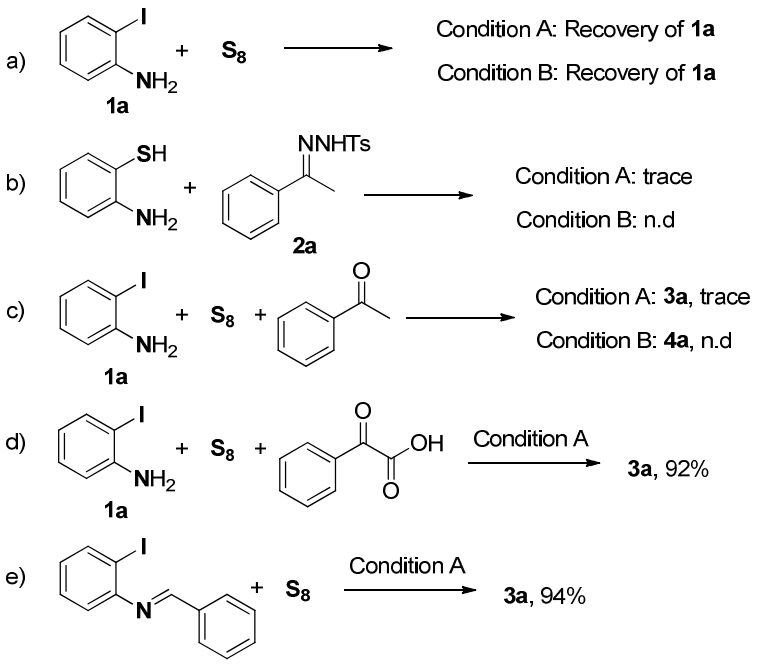


[a] Reaction conditions: **1** (0.2 mmol), S_8 (0.24 mmol), **2** (0.24 mmol), CuI (0.5 equiv), DABCO (1 equiv), CsF (2 equiv) in MeCN (2.5 mL) at 130 °C under N_2 for 10 h unless otherwise noted. Yields refer to the isolated yields.

To further clarify the mechanism, some control experiments were conducted (Scheme 2). Initially, in order to determine whether the reactions were initiated by the formation of *o*-aminobenzenethiol,[7a-7c] we mixed *o*-iodoaniline and elemental sulfur under condition A and condition B, respectively. After the reaction, *o*-iodoaniline in each reaction system was completely recovered (Eqn. a). Subsequently, we performed the reactions using *o*-aminobenzenethiol and **2a** as substrates (Eqn. b), and the results further indicated that *o*-aminobenzenethiol should not be an intermediate in both reaction systems. Because acetophenone was detected as a by-product, we next used

acetophenone as a substrate to react with *o*-iodoaniline and $\mathbf{S_8}$ under two different conditions (Eqn. c). We could infer from the results that acetophenone was not a possible intermediate, and the reactions might be achieved *via* the formation of active copper carbene intermediates. Under Condition A, benzoylformic acid could be well converted, which required the release of CO_2, and the reaction gave **3a** in 92% yield (Eqn. d). Moreover, the cyclization of imine and $\mathbf{S_8}$ went smoothly to give **3a** in 94% yield (Eqn. e), where imine was considered to be a probable reaction intermediate.

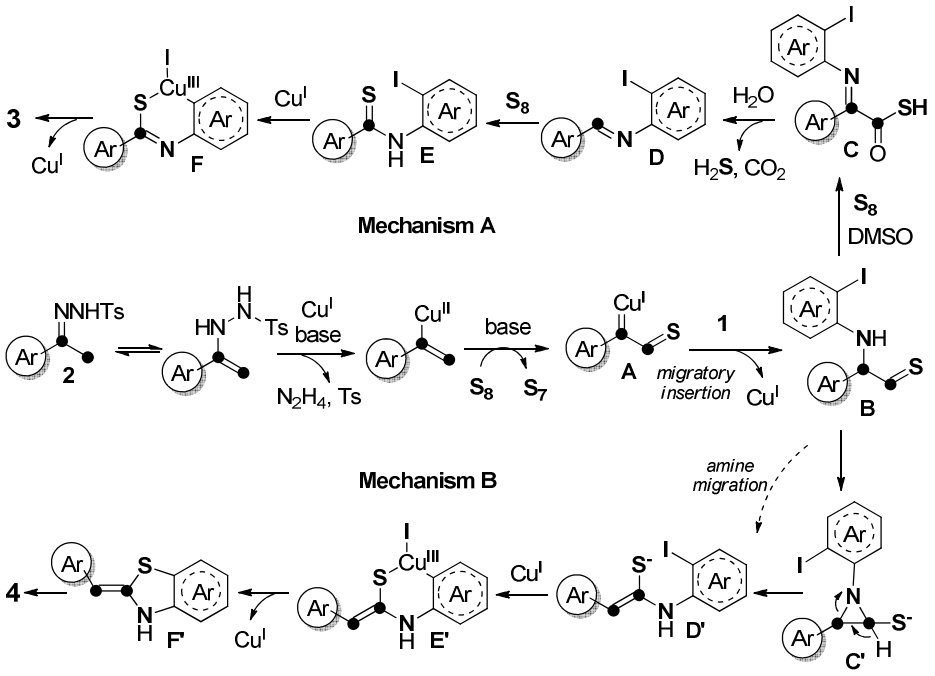
Scheme 2. Control Experiments [a,b]



[a] Condition A: Reaction conditions: CuSCN (10 mol %), DBU (3 equiv) in DMSO (1.5 mL) at 110 °C under N_2 for 10 h. Condition B: CuI (0.5 equiv), DABCO (1 equiv), CsF (2 equiv) in MeCN (1.5 mL) at 130 °C under N_2 for 10 h. [b] GC yield with *n*-dodecane as internal standard. n.d = not detected.

Based on our previous research and the results of control experiments above, we proposed the possible mechanisms for the formation of **3** and **4** (Scheme 3). Initially, the *N*-tosylhydrazone isomerized, followed by the release of N_2H_2 and Ts to provide vinyl copper(II) complex,[11] which subsequently might undergo the reaction with $\mathbf{S_8}$ and the migratory insertion process to form intermediate **B**. The product **3** could be constructed through Mechanism A and the product **4** could be constructed through Mechanism B. In Mechanism A, intermediate **B** might be oxidized under the action of $\mathbf{S_8}$[12] and DMSO[13] to form intermediate **C**, which could subsequently convert to imine intermediate **D** after releasing H_2S and CO_2.[14] Imine intermediate **D** underwent an attack of $\mathbf{S_8}$[15] and a copper-catalyzed intramolecular cyclization process[16] to finally generate product **3**. In Mechanism B, *α*-aminovinyl intermediate **D'** might be formed *via* the process of amine migration,[17] which subsequently underwent the copper-catalyzed intramolecular cyclization and the electron rearrangement to generate the desired product **4**.

Scheme 3. Proposed Reaction Mechanisms



In conclusion, a copper-promoted [3+1+1]-type cyclization reaction to construct 2-substituted benzothiazoles selectively from *o*-iodoaniline derivative, S_8 and *N*-tosylhydrazone has been realized. In the protocol, by changing the reaction system, the carbon atom on *N*-tosylhydrazone was used selectively as a binding site to achieve the construction of multiple carbon-heteroatom bonds. Remarkably, simple operations, inexpensive metal catalyst and readily available substrates made this reaction more valuable. Further applications of the synthesis are currently undergoing in our laboratory.

EXPERIMENTAL SECTION

General Information.

Melting points were determined with a Buchi Melting Point B-545 instrument. ^{1}H and

^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification.

General procedures for the synthesis of reaction substrates: (I) The preparation of *N*-tosylhydrazones **2**: A mixture of ketone compounds (5.0 mmol) and *p*-toluenesulfonhydrazide (5.0 mmol) in 7.5 mL MeOH was stirred at 70 ^{o}C for 0.5-3 h to afford the corresponding *N*-tosylhydrazone **1** as white precipitate. After that, the precipitate was washed and filtered with petroleum ether twice and dried under vacuum to provide the pure compounds. (II) The preparation of *o*-iodoaniline derivatives **1** could be carried out according to the literature procedure.[18]

General procedure A: the synthesis of benzo[*d*]thiazole products 3: A 25 mL Schlenk tube equipped with a magnetic stirring bar was added *o*-iodoaniline **1** (0.2 mmol), $\mathbf{S_8}$ (0.24 mmol), *N*-tosylhydrazone **2** (0.24 mmol), CuSCN (10 mol %), DBU

(3 equiv), DMSO (2.0 mL) under argon atmosphere. The resulting mixture was vigorously stirred at 90 °C in an oil bath. After 10 h, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 10:1–30:1) as the eluent to afford the desired product.

General procedure B: the synthesis of benzo[*d*]thiazole products 4: A 25 mL Schlenk tube equipped with a magnetic stirring bar was added *o*-iodoaniline **1** (0.2 mmol), $\mathbf{S_8}$ (0.24 mmol), *N*-tosylhydrazone **2** (0.24 mmol), CuI (0.5 equiv), DABCO (1 equiv), CsF (2 equiv), MeCN (2.5 mL) under argon atmosphere. The resulting mixture was vigorously stirred at 90 °C in an oil bath. After 10 h, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 10:1–30:1) as the eluent to afford the desired product.

2-Phenylbenzo[*d*]thiazole (3a). White solid, yield 30 mg (72%), mp 112-113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.49 (m, 4H), 7.38 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 154.2, 135.1, 133.7, 131.0, 129.0, 127.6, 126.4, 125.2, 123.3, 121.6. IR (KBr, cm^{-1}): 3066, 2925, 1475, 961, 761. HRMS (ESI) (m/z): calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0528, found: 212.0534.

2-(4-Chlorophenyl)benzo[*d*]thiazole (3b). White solid, yield 34 mg (70%), mp

114-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.0, 137.1, 135.0, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7. IR (KBr, cm^{-1}): 3055, 2920, 1472, 967, 826, 756. HRMS (ESI) (m/z): calcd for $C_{13}H_9ClNS$ $[M+H]^+$: 246.0139, found: 246.0148.

4-(Benzo[*d*]thiazol-2-yl)benzonitrile (3c). White solid, yield 34 mg (71%), mp 172-173 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.54 (m, 1H), 7.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 154.0, 137.5, 135.3, 132.8, 127.9, 126.8, 126.1, 123.8, 121.8, 118.3, 114.2. IR (KBr, cm^{-1}): 2920, 2854, 1636, 834, 761. HRMS (ESI) (m/z): calcd for $C_{14}H_9N_2S$ $[M+H]^+$: 237.0481, found: 237.0472.

4-(Benzo[*d*]thiazol-2-yl)-N,N-dimethylaniline (3d). Yellow solid, yield 41 mg (81%), mp 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 3H), 7.84 (dd, J = 7.9, 0.5 Hz, 1H), 7.44 (m, 1H), 7.30 (m, 1H), 6.75 (d, J = 8.9 Hz, 2H), 3.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 154.4, 152.2, 134.6, 128.9, 126.0, 124.2, 122.3, 121.4, 121.4, 111.7, 40.2. IR (KBr, cm^{-1}): 2919, 2854, 1608, 815, 754. HRMS (ESI) (m/z): calcd for $C_{15}H_{15}N_2S$ $[M+H]^+$: 255.0950, found: 255.0951.

2-(4-Methoxyphenyl)benzo[*d*]thiazole (3e). White solid, yield 39 mg (80%), mp 120-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 3H), 7.86 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.0, 154.1, 134.8, 129.2, 126.4, 126.2, 124.8, 122.8, 121.5, 114.4, 55.5. IR (KBr, cm^{-1}): 2918, 2847, 1598, 830, 756.

HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$: 242.0634, found: 242.0639.

2-(4-(Methylthio)phenyl)benzo[*d*]thiazole (3f). White solid, yield 43 mg (84%), mp 142-143 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 154.0, 142.9, 134.8, 130.0, 127.8, 126.4, 126.0, 125.1, 123.0, 121.6, 15.2. IR (KBr, cm^{-1}): 2919, 2850, 1427, 812, 755. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS_2$ $[M+H]^+$: 258.0406, found: 258.0399.

2-([1,1'-Biphenyl]-4-yl)benzo[*d*]thiazole (3g). Yellow solid, yield 38 mg (67%), mp 190-191 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.49 (m, 3H), 7.40 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.1, 143.8, 140.1, 135.0, 132.4, 129.0, 128.0, 128.0, 127.7, 127.1, 126.4, 125.2, 123.2, 121.6. IR (KBr, cm^{-1}): 2920, 2852, 965, 757. HRMS (ESI) (m/z): calcd for $C_{19}H_{14}NS$ $[M+H]^+$: 288.0841, found: 288.0846.

2-(Furan-2-yl)benzo[d]thiazole (3h). Brown solid, yield 30 mg (74%), mp 101-102 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 3.3 Hz, 1H), 6.57 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 153.7, 148.7, 144.7, 134.3, 126.5, 125.2, 123.1, 121.6, 112.6, 111.5. IR (KBr, cm-1): ν = 3123, 2921, 1500, 746. HRMS (ESI) calcd for $C_{11}H_8NOS$ [M+H]+: 202.0321, found: 202.0313.

2-(Thiophen-2-yl)benzo[*d*]thiazole (3i). White solid, yield 33 mg (77%), mp 99-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.87 (dd, J = 8.0, 0.5 Hz, 1H), 7.68 (dd, J = 3.7, 1.0 Hz, 1H), 7.51 (m, 2H), 7.39 (m, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 153.7, 137.3, 134.7, 129.3, 128.7, 128.1, 126.5, 125.2, 123.0, 121.5. IR (KBr, cm^{-1}): 3061, 2922, 1421, 908, 706. HRMS (ESI) (m/z): calcd for $C_{11}H_8NS_2$ $[M+H]^+$: 218.0093, found: 218.0099.

2-(Pyridin-4-yl)benzo[*d*]thiazole (3j). White solid, yield 31 mg (72%), mp 123-124 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.12 (d, J = 8.1 Hz, 1H), 7.93 (m, 3H), 7.53 (m, 1H), 7.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 165.0, 154.0, 150.7, 140.5, 135.2, 126.8, 126.2, 123.9, 121.9, 121.3. IR (KBr, cm^{-1}): 3658, 3038, 2920, 1408, 758. HRMS (ESI) (m/z): calcd for $C_{12}H_9N_2S$ $[M+H]^+$: 213.0481, found: 213.0486.

2-(Benzo[*d*][1,3]dioxol-5-yl)benzo[*d*]thiazole (3K). Brown solid, yield 42 mg (82%), mp 120-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.59 (m, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 167.6, 154.0, 150.2, 148.4, 134.8, 128.0, 126.3, 125.0, 122.9, 122.6, 121.5, 108.6, 107.6, 101.7. IR (KBr, cm^{-1}): 2917, 1471, 1249, 1034, 755. HRMS (ESI) (m/z): calcd for $C_{14}H_{10}NO_2S$ $[M+H]^+$: 256.0427, found: 256.0429.

2-(Naphthalen-1-yl)benzo[*d*]thiazole (3l). White solid, yield 39 mg (75%), mp 124-125 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, J = 8.3 Hz, 1H), 8.35 (t, J = 6.8 Hz, 1H), 7.98 (m, 4H), 7.71 (dd, J = 10.6, 3.5 Hz, 1H), 7.61 (m, 3H), 7.48 (t, J = 7.6

Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.4, 135.6, 134.2, 131.2, 130.9, 130.8, 129.6, 128.6, 127.8, 126.6, 126.4, 126.2, 125.4, 125.1, 123.7, 121.6. IR (KBr, cm^{-1}): 3054, 1503, 934, 765. HRMS (ESI) (m/z): calcd for $C_{17}H_{12}NS$ $[M+H]^+$: 262.0685, found: 262.0689.

6-Methyl-2-phenylbenzo[*d*]thiazole (3m). Yellow solid, yield 33 mg (73%), mp 125-126 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 6.6, 2.9 Hz, 2H), 7.95 (d, J = 8.3 Hz, 1H), 7.67 (s, 1H), 7.47 (dd, J = 4.9, 1.6 Hz, 3H), 7.29 (d, J = 8.3 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 152.2, 135.4, 135.2, 133.7, 130.8, 129.0, 128.0, 127.5, 122.7, 121.4, 21.6. IR (KBr, cm^{-1}): 2919, 1442, 965, 810, 759, 685. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0687.

6-Bromo-2-phenylbenzo[*d*]thiazole (3n). White solid, yield 46 mg (80%), mp 156-157 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 8.03 (d, J = 1.9 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.59 (dd, J = 8.7, 1.9 Hz, 1H), 7.49 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 152.9, 136.6, 133.1, 131.4, 129.9, 129.1, 127.6, 124.3, 124.2, 118.8. IR (KBr, cm^{-1}): 3660, 2920, 1475, 964, 817, 757, 681. HRMS (ESI) (m/z): calcd for $C_{13}H_9BrNS$ $[M+H]^+$: 289.9634, found: 289.9641.

2-Phenyl-6-(trifluoromethyl)benzo[*d*]thiazole (3o). Yellow solid, yield 35 mg (63%), mp 151-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.11 (dd, J = 7.4, 2.1 Hz, 2H), 7.73 (d, J = 8.6 Hz, 1H), 7.52 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 156.1, 135.1, 133.1, 131.7, 129.2, 127.8, 127.3 (q, J = 31.3 Hz), 124.2 (q, J = 270.0 Hz), 123.5, 123.3 (q, J = 3.7 Hz), 119.32 (q, J = 4.2 Hz). IR (KBr, cm^{-1}): 3658, 2921, 1318, 1115, 839. HRMS (ESI) (m/z): calcd for

$C_{14}H_9F_3NS$ $[M+H]^+$: 280.0402, found: 280.0410.

6-Methoxy-2-phenylbenzo[*d*]thiazole (3p). White solid, yield 37 mg (76%), mp 116-117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.98 (d, J = 8.9 Hz, 1H), 7.48 (dd, J = 5.3, 1.7 Hz, 3H), 7.34 (d, J = 1.9 Hz, 1H), 7.11 (dd, J = 8.9, 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 157.8, 148.7, 136.5, 133.8, 130.5, 129.0, 127.3, 123.7, 115.7, 104.2, 55.8. IR (KBr, cm^{-1}): 2930, 1470, 1269, 1023, 823. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$: 242.0634, found: 242.0637.

2-(3,4-Dimethoxyphenyl)-6-fluorobenzo[*d*]thiazole (3q). Yellow solid, yield 43 mg (75%), mp 153-155 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.9, 4.8 Hz, 1H), 7.65 (d, J = 1.4 Hz, 1H), 7.52 (dd, J = 8.2, 2.0 Hz, 2H), 7.18 (td, J = 8.9, 2.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6 (d, J = 3.1 Hz), 160.3 (d, J = 245.4 Hz), 151.7, 150.7 (d, J = 1.4 Hz), 149.4, 135.9 (d, J = 11.3 Hz), 126.4, 123.6 (d, J = 9.3 Hz), 121.1, 114.8 (d, J = 24.6 Hz), 111.1, 109.7, 107.8 (d, J = 26.8 Hz), 56.1, 56.0. IR (KBr, cm^{-1}): 2919, 1449, 1242, 1014, 802. HRMS (ESI) (m/z): calcd for $C_{15}H_{13}FNO_2S$ $[M+H]^+$: 290.0646, found: 290.0652.

2-Benzylbenzo[*d*]thiazole (4a). Brown oil, yield 30 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.38 (m, 6H), 4.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 153.2, 137.2, 135.7, 129.2, 128.9, 127.4, 126.0, 124.9, 122.8, 121.6, 40.6. IR (KBr, cm^{-1}): 3063, 2923, 1648, 1490, 1284, 760, 705. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0676.

2-(4-Methylbenzyl)benzo[*d*]thiazole (4b). Brown oil, yield 31 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 4.44 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 153.3, 137.0, 135.7, 134.2, 129.6, 129.1, 126.0, 124.8, 122.8, 121.6, 40.3, 21.2. IR (KBr, cm^{-1}): 3023, 2920, 1511, 1436, 756. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0846.

2-(4-Fluorobenzyl)benzo[*d*]thiazole (4c). Brown oil, yield 29 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.46 (m, 1H), 7.34 (m, 3H), 7.04 (m, 2H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 162.2 (d, J = 246.0 Hz), 153.1, 135.5, 132.9 (d, J = 3.3 Hz), 130.7 (d, J = 8.1 Hz), 126.1, 125.0, 122.8, 121.6, 115.8 (d, J = 21.5 Hz), 39.7. IR (KBr, cm^{-1}): 3061, 2922, 1506, 1225, 830, 758. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}FNS$ $[M+H]^+$: 244.0591, found: 244.0589.

2-(4-Chlorobenzyl)benzo[*d*]thiazole (4d). Brown oil, yield 32 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.31 (s, 4H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 153.0, 135.6, 135.5, 133.4, 130.5, 129.0, 126.2, 125.0, 122.8, 121.6, 39.8. IR (KBr, cm^{-1}): 3067, 2921, 1491, 1091, 812, 757. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}ClNS$ $[M+H]^+$: 260.0295, found: 260.0293.

2-(4-Methoxybenzyl)benzo[*d*]thiazole (4e). Brown oil, yield 34 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.7

Hz, 1H), 7.29 (m, 3H), 6.87 (d, J = 8.5 Hz, 2H), 4.36 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 159.0, 153.4, 135.7, 130.3, 129.3, 126.0, 124.8, 122.8, 121.5, 114.3, 55.3, 39.8. IR (KBr, cm^{-1}): 3063, 2931, 1511, 1249, 761. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791, found: 256.0798.

2-(2-methoxybenzyl)benzo[d]thiazole (4f). Brown oil, yield 35 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 7.23 (t, J = 7.6 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.42 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 157.4, 153.3, 135.8, 130.9, 129.0, 125.8, 125.8, 124.6, 122.65, 121.5, 120.8, 110.8, 55.4, 35.2. IR (KBr, cm^{-1}): 3064, 2938, 1595, 1501, 1247, 756. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791, found: 256.0795.

2-(Naphthalen-2-ylmethyl)benzo[*d*]thiazole (4g). Brown oil, yield 31 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.9 Hz, 4H), 7.78 (d, J = 8.0 Hz, 1H), 7.48 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 4.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 153.3, 135.7, 134.6, 133.6, 132.6, 128.7, 127.9, 127.8, 127.8, 127.2, 126.3, 126.0, 126.0, 124.9, 122.8, 121.6, 40.8. IR (KBr, cm^{-1}): 3689, 2920, 1509, 966, 751. HRMS (ESI) (m/z): calcd for $C_{18}H_{14}NS$ $[M+H]^+$: 276.0841, found: 276.0846.

2-Benzyl-6-methylbenzo[*d*]thiazole (4h). Brown oil, yield 31 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 1H), 7.60 (s, 1H), 7.38 (m, 4H), 7.33 (d, J = 3.2 Hz, 1H), 7.28 (s, 1H), 4.46 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 151.3, 137.3, 135.9, 134.9, 129.2, 128.9, 127.6, 127.3, 122.3, 121.3, 40.6, 21.5.

IR (KBr, cm^{-1}): 3685, 3054, 2920, 1507, 1228, 1028, 690. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0843.

2-Benzyl-6-fluorobenzo[*d*]thiazole (4i). Brown solid, yield 32 mg (66%), mp 57-58 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, J = 8.7, 4.3 Hz, 1H), 7.46 (dd, J = 4.9, 3.0 Hz, 1H), 7.39 (d, J = 4.3 Hz, 4H), 7.33 (m, 1H), 7.20 (m, 1H), 4.43 (d, J = 3.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (d, J = 3.2 Hz), 160.3 (d, J = 245.0 Hz), 149.9, 137.0, 136.6 (d, J = 11.3 Hz), 129.2, 129.0, 127.5, 123.7 (d, J = 9.4 Hz), 114.6 (d, J = 24.7 Hz), 107.8 (d, J = 26.7 Hz), 40.6. IR (KBr, cm^{-1}): 3067, 2922, 1453, 1249, 817, 701. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}FNS$ $[M+H]^+$: 244.0591, found: 244.0597.

2-Benzyl-6-(trifluoromethyl)benzo[*d*]thiazole (4j). Brown oil, yield 41 mg (70%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.5 Hz, 2H), 7.69 (m, 1H), 7.38 (d, J = 4.4 Hz, 4H), 7.33 (m, 1H), 4.47 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 155.3, 136.6, 135.8, 129.2, 129.0, 127.6, 127.1 (q, J = 32.0 Hz), 124.2 (q, J = 273.4 Hz), 123.2, 123.0 (q, J = 3.4 Hz), 119.2 (q, J = 4.2 Hz), 40.8. IR (KBr, cm^{-1}): 3029, 2924, 1320, 1124, 650. HRMS (ESI) (m/z): calcd for $C_{15}H_{11}F_3NS$ $[M+H]^+$: 294.0559, found: 294.0552.

2-Benzyl-5-methylbenzo[*d*]thiazole (4k). Yellow solid, yield 33 mg (68%), mp 79-81 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.31 (m, 5H), 7.13 (m, 1H), 4.40 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 153.7, 137.3, 136.0, 132.7, 129.2, 128.9, 127.3, 126.4, 122.9, 121.0, 40.7, 21.5. IR (KBr, cm^{-1}): 3060, 2921, 1647, 1486, 1283, 863, 703. HRMS (ESI) (m/z): calcd

for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0849.

ASSOCIATED CONTENT

Supporting Information

NMR spectra of the products. The Supporting Information is available free of charge *via* the Internet at http://pubs.acs.org.

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