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Oxidant/Solvent-Controlled I_2-Catalyzed Domino Annulation for Selective Synthesis of 2-Aroylbenzothiazoles and 2-Arylbenzothiazoles under Metal-Free Conditions

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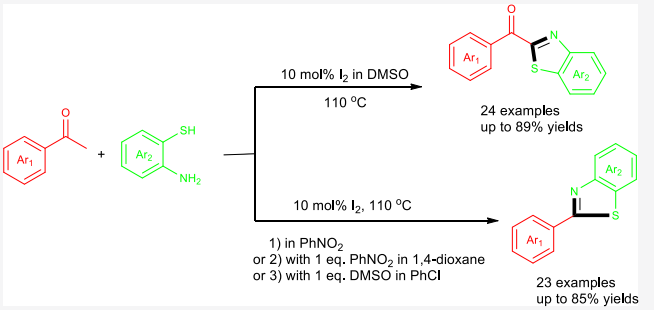
ABSTRACT: A simple and practical domino protocol for the selective synthesis of 2-aroylbenzothiazoles and 2-aryl benzothiazoles catalyzed by I_2 is developed under metal-free conditions. The reaction outcomes are exclusively controlled by the reaction oxidant/medium. With DMSO employed as both the solvent and the oxidant, an oxidation of aromatic methyl ketones takes precedence over the condensation with 2-aminobenzenethiols. On the other hand, when the reaction was carried out in $PhNO_2$ or in 1,4-dioxane containing $PhNO_2$, the condensation of aromatic methyl ketones with 2-aminobenzenethiols has priority to form imines which is followed by an oxidation of the methyl group from ketones to afford 2-arylbenzothiazoles as a sole product. The $PhNO_2/I_2$ co-catalytic system is proposed first time.



INTRODUCTION

Benzothiazoles represent an important and abundant class of fused heterocycles. Compounds containing the benzothiazole motif have their wide occurrence in diverse pharmacological agents,[1] natural products,[2] and synthetic intermediates.[3] In addition, the benzothiazole scaffold has been found frequently in other molecules such as industrial dyes[2a,4] and functional materials.[5] Consequently, the development of effective methods for constructing the benzothiazole skeleton has attracted considerable attention, and a number of versatile methods have been developed in recent years. There are two conventional synthetic methods adopted for the preparation of this building block: one involves a condensation and annulation of 2-aminobenzenethiol with aromatic alcohol,[6] aldehydes,[7] aromatic methyl ketones,[8] benzoic acids/benzoates/benzoic anhydrides,[9] or nitriles[10] (Scheme 1a); another is a metal-catalyzed intramolecular annulation of arylthiobenzamide analogues (Scheme 1b).[11] However, these existing methods suffer from the disadvantages of multistep processes, use of stoichiometric oxidants, or low yields, all of which limit their application in industrial production. Therefore, development of practical and efficient procedures for the preparation of 2-substituted benzothiazoles in a user-friendly manner is highly desirable.

In 2009, Ma *et al.* reported a practical synthesis of substituted benzothiazoles from 2-haloanilides with sulfides using CuI as the catalyst under mild conditions.[12] Deng's group used 2-aminobenzenethiol and aryl ketones to synthesize 2-arylbenzothiazoles promoted by molecular oxygen.[8d] Recently, Tan *et al.* developed a one-pot tandem procedure for the synthesis of 2-substituted benzothiazoles under an I_2/TBHP system.[13] For the synthesis of 2-aroylbenzothiazole, the Wu's group developed an I_2/IBX-mediated domino strategy from 2-aminobenzenethiol with arylethenes, arylacetylene, 2-hydroxy-aromatic ketones, or carbinols *via* phenylglyoxal intermediates.[14] His group also constructed a 2-aroylbenzothiazole skeleton from aromatic methyl ketones and 2-aminobenzenethiols in the presence of an excess of I_2.[8b] However, most likely, a mixture of 2-aryl and 2-aroyl benzothiazole was generated in dimethyl sulfoxide (DMSO) from these two starting materials.[6e,8c,d] Intrigued by these findings, we attempted the reaction of 2-aminobenzenethiols and aromatic methyl ketones to synthesize 2-aroyl and 2-aryl benzothiazoles selectively. Interestingly, 2-aroylbenzothiazoles were selectively afforded with a catalytic amount of I_2 in DMSO, while 2-aryl analogues were formed in nitrobenzene catalyzed by I_2 (Scheme 1c). To the best of our knowledge, the $PhNO_2$-mediated I_2-catalyzed strategy has never been reported. Herein, we would like to disclose our preliminary results in this aspect.

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Scheme 1. Literature Reports and the Present Work for the Synthesis of 2-Substituted Benzothiazoles

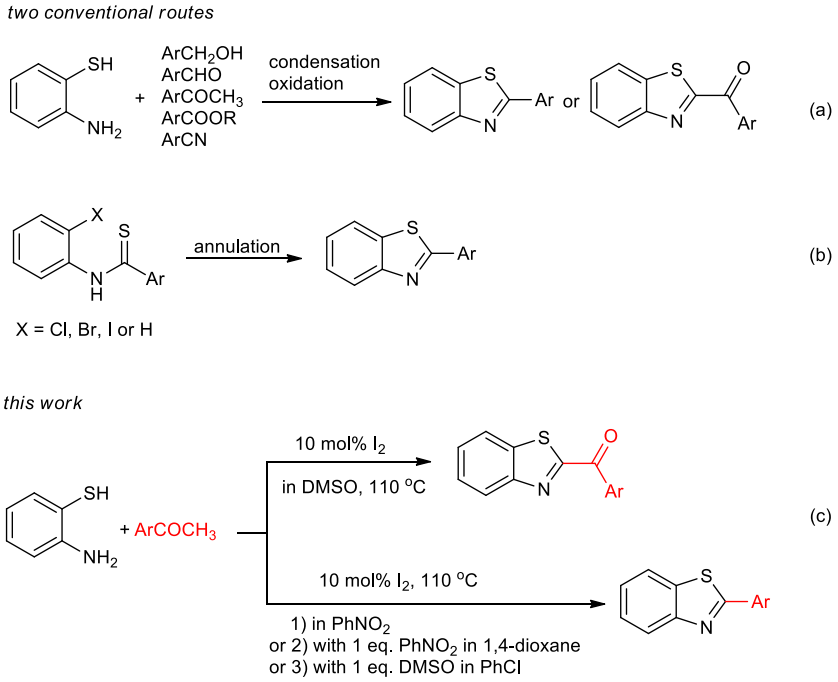
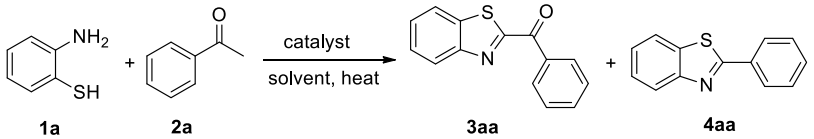


Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa** **4aa**

Entry	solvent	I_2 (equiv)	temp. (°C)	yield (%) 3aa	yield (%) 4aa
1	DMSO	1	110	82	0
2	EtOH	1	80	0	0
3	MeOH	1	65	0	0
4	THF	1	65	0	0
5	DMF	1	110	0	0
6	DMA	1	110	0	0
7	$PhCH_3$	1	110	0	0
8	1,4-dioxane	1	110	0	0
9	PhCl	1	110	0	0
10	$PhNO_2$	1	110	0	80
11	$PhNO_2$	0.3	110	0	77
12	**$PhNO_2$**	**0.1**	**110**	**0**	**78**
13	**DMSO**	**0.1**	**110**	77	**0**
14[b]	$PhNO_2$	0.1	110	0	75
15	DMSO or $PhNO_2$	0	110	0	0
16	**1,4-dioxane + $PhNO_2$**[c]	**0.1**	**110**	**0**	**80**
17	PhCl + $PhNO_2$[c]	0.1	110	0	15
18	DMF + $PhNO_2$[c]	0.1	110	0	0
19	DMA + $PhNO_2$[c]	0.1	110	0	0
20	PhCl + DMSO[d]	0.1	110	0	48
21	1,4-dioxane + DMSO[d]	0.1	110	0	15
22	1,4-dioxane + $PhNO_2$[c]	0.1	80	0	0
23	DMSO	0.1	80	51	0
24	DMSO	0.1	60	42	0

[a]Reaction conditions: **1a** (1.5 mmol), **2a** (1 mmol), solvent (2 mL), and iodine at the indicated amount in a reaction vessel at the indicated temperature for 2−8 h. [b]Reaction under the N_2 atmosphere. [c]$PhNO_2$ at 1 mmol (1 equiv). [d]DMSO at 1 mmol (1 equiv).

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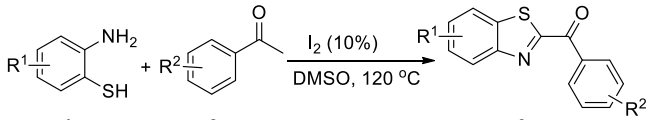
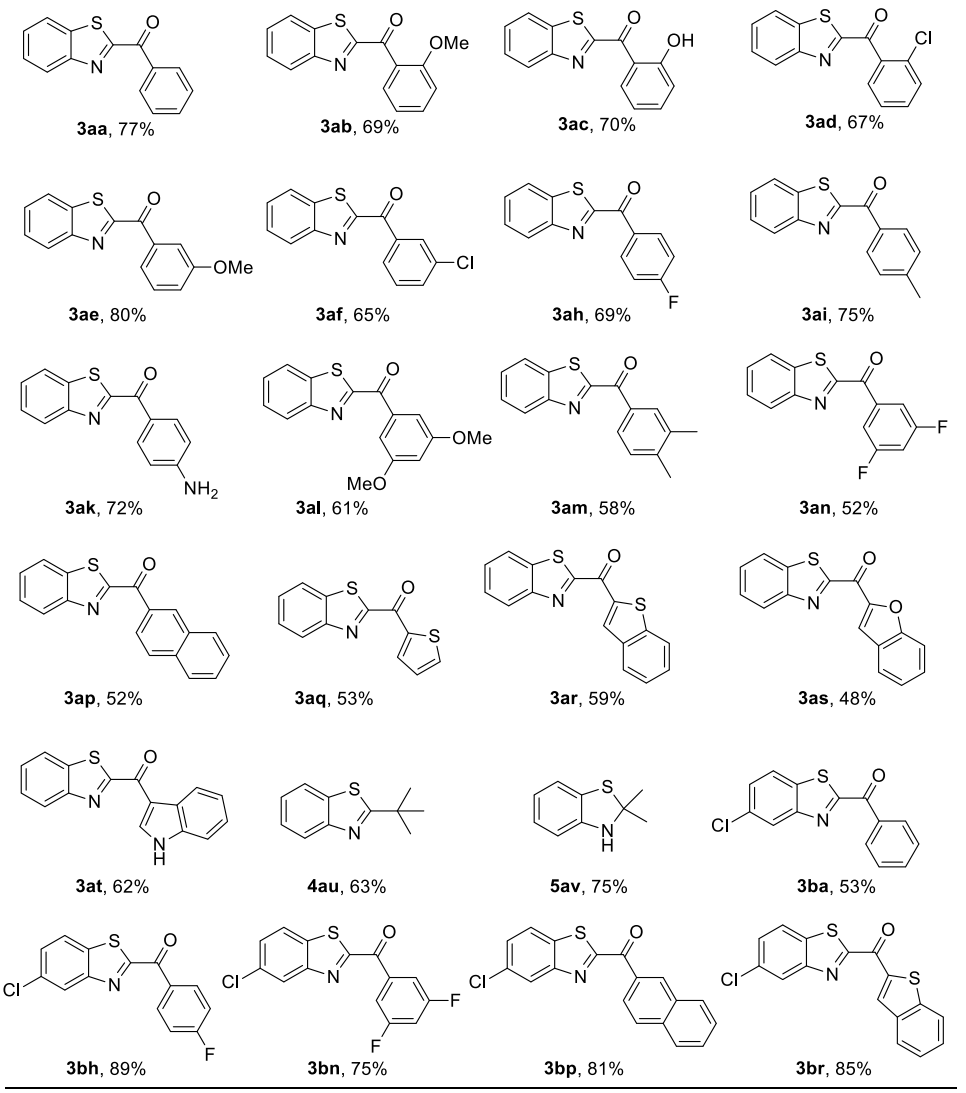
J. Org. Chem. XXXX, XXX, XXX−XXX

Table 2. Reaction of 2-Aminobenzenethiols with Various Ketones Mediated by DMSO[a]





[a]Reaction conditions: **1** (1.5 mmol), **2** (1 mmol), DMSO (2 mL), and iodine (10 mol %) in a reaction vessel at 110 °C for 2 h.

RESULTS AND DISCUSSION

We began our study by choosing 2-aminobenzenethiol (**1a**) and acetophenone (**2a**) as the initial starting materials and investigating the effect of solvents on the product yield. Similar to Wu's work,[8b] when acetophenone reacted with 1.5 equiv of 2-aminobenzenethiol in DMSO in the presence of 1 equiv of I_2 at 110 °C, 82% yield of the 2-aroylbenzothiazole (**3aa**) was achieved (Table 1, entry 1). In contrast to DMSO, other solvents such as ethanol, methanol, tetrahydrofuran (THF), dimethylformamide (DMF), *N*,*N*-dimethylaniline (DMA), toluene, 1,4-dioxane, and chlorobenzene failed to facilitate the reaction and the desired product was not obtained (entries 2−9). Surprisingly, when the reaction was carried out in nitrobenzene, the expected 2-aroylbenzothiazole was not afforded. Instead, a good yield of 2-aryl analogue (**4aa**) was achieved, which was characterized by NMR and MS methods (entry 10). Upon decreasing the dose of I_2 to 30 and 10%, the yield of **4aa** was not markedly influenced (entries 11−12). Based on this finding, we attempted to reduce the dose of I_2 to 10% for the reaction of acetophenone and 2-aminobenzenethiol in DMSO. To our delight, 77% yield of **3aa** was afforded, which is not significantly different from that of I_2 at 1 equiv (entry 13 *vs* 1). The reaction in $PhNO_2$ was also successively carried out under a N_2 atmosphere, without significant loss of the product yield, indicating that oxygen from air was not involved in the oxidation process (entry 14). In the absence of I_2, the reaction did not proceed either in DMSO or in $PhNO_2$, suggesting that I_2 played a crucial role in this transformation (entry 15). Because $PhNO_2$ possesses a high boiling point and is difficult to be removed by a routine rotary evaporation, we attempted to use 1,4-dioxane with 1 equiv of $PhNO_2$ to replace $PhNO_2$ as the reaction medium and satisfactorily a slightly

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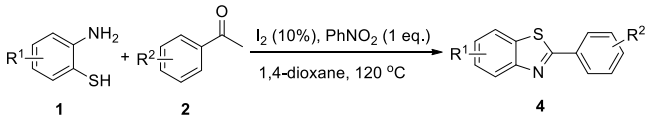
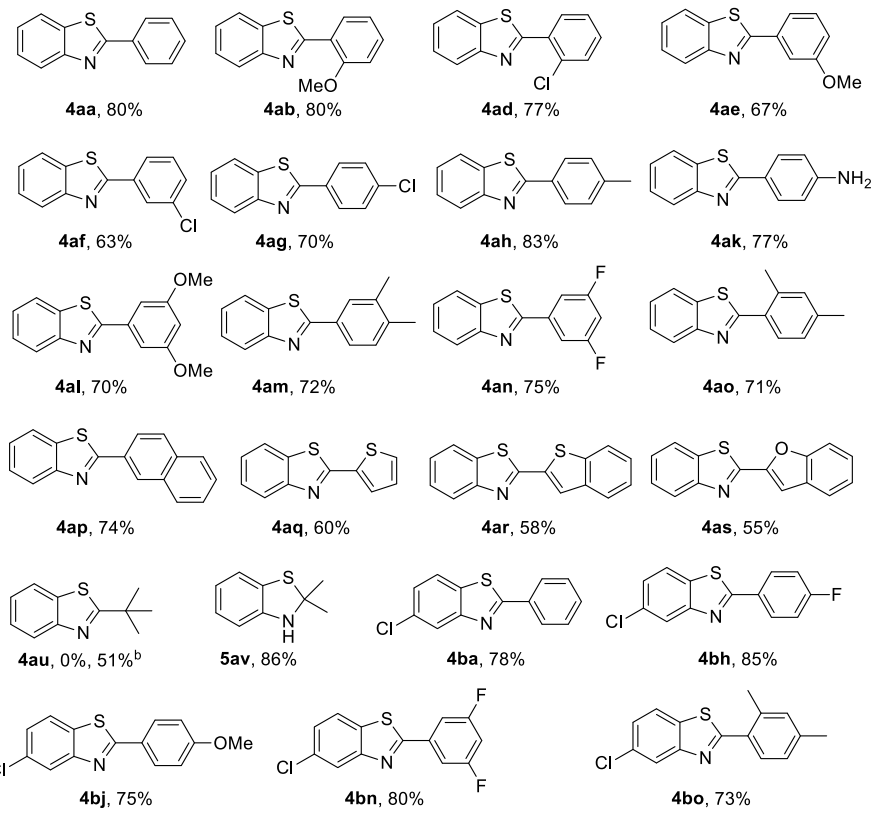
Table 3. Reaction of 2-Aminobenzenethiols with Various Ketones Mediated by $PhNO_2$[a]





[a]Reaction conditions: **1** (1.5 mmol), **2** (1 mmol), $PhNO_2$ (1 mmol), 1,4-dioxane (2 mL), and iodine (10 mol %) in a reaction vessel at 110 °C for 4−8 h. [b]The reaction was carried out in the same conditions but with 1 equiv of I_2.

higher yield of **4aa** was obtained (entry 16 *vs* 12). However, other solvents such as PhCl, DMF, and DMA failed to facilitate the reaction (entries 17−19). On the other hand, the reaction in PhCl or in 1,4-dioxane mediated by DMSO gave **4aa** at 48 and 15% yields, respectively, and surprisingly, **3aa** was not detected in these conditions (entries 20−21). The reaction temperature was also examined. The reaction mediated by $PhNO_2$ did not proceed at 80 °C (entry 22). On the other hand, lower yields of **3aa** were afforded when the temperature of the reaction in DMSO decreased (entries 23−24). Based on these studies, the optimal reaction conditions for the production of **3aa** were established as listed in entry 13 and the optimal reaction conditions for **4aa** were set up as described in entry 16.

With the optimized reaction conditions in hand, the substrate scope and generality of the reaction mediated by DMSO were explored (Table 2). Various substituted aromatic methyl ketones containing both electron-donating group (EDG) and electron-withdrawing group (EWG) were examined. Acetophenones, bearing either an EDG, such as methoxy and methyl group or an EWG, such as fluoro and chloro group on the aromatic ring, underwent the reaction smoothly to afford the corresponding 2-aroylbenzothiazoles in moderate to good yields (**3aa**−**3an**). It was found that the positions of both EDG and EWG on the aromatic ring had no appreciable influence on the product yield, while the electronic nature of the aryl moiety slightly affected the yield. Acetophenones containing an EDG gave moderately higher yield by compared with those containing an EWG (**3ab** *vs* **3ad**, **3ae** *vs* **3af**, **3ai** *vs* **3ah**, and **3an**). It is worth noting that the hydroxyl and amino-containing acetophenones were also well tolerable for the transformation (**3ac** and **3ak**). In addition, 2-acetonaphthone (**2p**) and several heterocyclic ketones (**2q**−**2t**) were also investigated for this transformation, and all of them were found to be smoothly converted to the corresponding 2-aroylbenzothiazoles (**3ap**−**3at**) in 48−62% yields. To further expand the substrate scope, two aliphatic ketones such as pinacolone (**2u**) and acetone (**2v**) were also investigated. Unfortunately, the desired 2-aroyl-substituted products were not afforded. Instead, 63% yield of 2-(*tert*-butyl)benzothiazole (**4au**) and 75% yield of 2,2-dimethyl-2,3-dihydrobenzothiazole (**5av**) were given from pinacolone and acetone, respectively. Furthermore, 2-amino-4-chlorobenzenethiol (**1b**) was also successfully reacted with acetophenones (**2**) to give the corresponding 2-aroylbenzothiazoles in 53−89% yields, which are better than those from **1a** (**3bh** *vs* **3ah**, **3bn** *vs* **3an**, **3bp** *vs* **3ap**, and **3br** *vs* **3ar**).

Having established an efficient synthesis of 2-aroylbenzothiazoles (**3**) from 2-aminobenzenethiols (**1**) and acetophenones (**2**) in DMSO catalyzed by I_2, we then turned our

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J. Org. Chem. XXXX, XXX, XXX−XXX

attention to explore the substrate scope and generality of the reaction mediated by $PhNO_2$ (Table 3). Similar to the results mentioned above, all of the investigated substrates were tolerable to this transformation and gave good yields of the corresponding 2-aryl-substituted benzothiazoles, regardless of the electronic nature and the position of the substituted group (**4aa**−**4ao**). It is worthy to be noted that **4ak**, which contains an amino group, can be further conjugated with a ligand as antitumor agents or imaging probes.[15] In addition, 2-acetonaphthone (**2p**) was also successfully converted into the corresponding product **4ap** in a good yield, and heterocyclic ketones (**2q**−**2s**) gave moderate yields of **4aq**−**4as**. When an aliphatic ketone such as pinacolone was examined for the reaction mediated by $PhNO_2$, the desired product **4au** was not observed. However, a moderate yield of **4au** was achieved when increasing the dose of I_2 to 1 equiv. In other cases, the same product (**5av**) as that mediated by DMSO was observed in a good yield when acetone was examined for the reaction. Again, 4-chloro-substituted 2-aminobenzenethiol (**1b**) was also tolerated to the reaction, and 73−85% yields of the expected products **4ba**−**4bo** were isolated.

In order to demonstrate the relationship between the product yield and the dose of the oxidant, the reaction was performed in 1,4-dioxane with different doses of DMSO or $PhNO_2$, and the result is presented in Figure 1. It can be seen

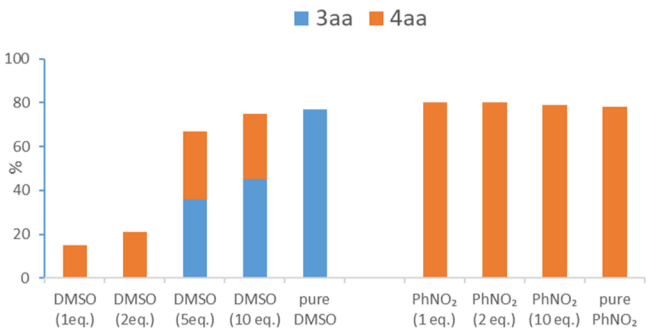

Figure 1. Relationship between the yield of **3aa** and **4aa** with the dose of DMSO or $PhNO_2$. The reaction of **1a** (1.5 mmol), **2a** (1 mmol), and I_2 (10%) in 1,4-dioxane with DMSO or $PhNO_2$ at the indicated dose in a reaction vessel was carried out at 110 °C for 2 h.

that only **4aa** at a low yield was obtained when DMSO at 1−2 equiv was applied. When the dose of DMSO was increased up to 10 equiv, the yield of **4aa** was improved, being accompanied by the production of **3aa** at a moderate yield. However, only **3aa** was afforded in a good yield when the reaction was performed by using DMSO as the sole solvent. In contrast, the reaction in 1,4-dioxane with different doses of $PhNO_2$ gave **4aa** only at good yields.

To elucidate the reaction mechanism, some controlled experiments were undertaken (Scheme 2). First, it was found that 8% yield of phenylglyoxal was achieved when **2a** was heated at 110 °C for 2 h in DMSO in the presence of I_2 (10%) (eq 1). In contrast, **2a** was fully recovered when the reaction was performed in 1,4-dioxane in the presence of $PhNO_2$ (eq 2). In the absence of DMSO or $PhNO_2$, the reaction of **1a** and **2a** gave 2,3-dihydrobenzothiazole (**5aa**), a key intermediate for the production of 2-arylbenzothiazoles (eq 3). **5aa** can be further converted into the desired product **4aa** in 1,4-dioxane with an excellent yield in the presence of I_2 (10%) and $PhNO_2$ (1 equiv) (eq 4). In contrast, a 2:1 molar ratio of **3aa**:**4aa** was detected when the reaction catalyzed by I_2 was carried out in DMSO (eq 5). This result indicates that the production of **5aa** from **1a** and **2a** (eq 3) in DMSO is reversible. Considering that $PhNO_2$ in the reaction was used as an oxidant and its reduced form aniline was detected by gas chromatography−mass spectrometry (GC−MS), we attempted to investigate **2w** which contains one nitro group as both a substrate and an oxidant for this conversion in the absence of $PhNO_2$. Unfortunately, the expected product **4** was not successfully afforded. Instead, compound **5aw** was given in a moderate yield (eq 6). Further conversion of **5aw** into **4aw** under the standard conditions failed, mostly likely due to the strong electron-withdrawing property of the nitro group.

On the basis of these preliminary experimental results and previous literature reports,[8b,d,16] a possible reaction mechanism is proposed as follows using 2-aminobenzenethiol (**1a**) and acetophenone (**2a**) as an example (Scheme 3). Initially, acetophenone **2a** was promoted by I_2 to afford **A** in the presence of DMSO, which was further converted into phenylglyoxal **B** by Kornblun oxidation. Intermediate **B** condenses with 2-aminobenzenethiol **1a** to furnish an imine **C**, and one molecule of water is removed. The intermediate **C** undergoes spontaneous cyclization, followed by oxidation catalyzed by iodine in the presence of DMSO. Elimination of HI from intermediate **E** affords the final 2-aroylbenzothiazoles **3aa**. When the reaction of **1a** and **2a** was performed in the presence of nitrobenzene or 1,4-dioxane, condensation was carried out prior to the oxidation of **2a** to generate the corresponding imine **F**, which is spontaneously cyclized to afford an intermediate **5aa**. Oxidation of the methyl group by iodine generates intermediate **G**. In this process, the byproduct HI could be oxidized by nitrobenzene to regenerate iodine. Subsequently, intermediate **G** could be oxidized with $PhNO_2$ to form its oxo derivative **H**, which has been detected successfully by GC−MS after 1 h reaction of **1a** and **2a** under the standard conditions. Aromatization of the intermediate **H** with an elimination of formaldehyde produces the final 2-phenyl benzothiazole **4aa**.

CONCLUSIONS

In conclusion, we have developed an I_2-catalyzed domino annulation of aromatic methyl ketones and 2-aminobenzenethiols under metal-free conditions. Under the optimal reaction conditions, the versatile synthetic approach can not only produce 2-aroyl benzothiazoles but also afford 2-aryl benzothiazoles selectively by altering the oxidant/solvent. Using DMSO as the oxidant/solvent, 2-aroyl benzothiazoles were selectively achieved while the reaction mediated by $PhNO_2$ gave 2-aryl benzothiazoles only. The operational simplicity, insensitivity to air and moisture, the reaction selectivity, and generality of the present protocol render the method attractive. Further application of this novel $PhNO_2/I_2$ co-catalytic system is currently undergoing in our lab.

EXPERIMENTAL SECTION

General Methods. All the starting materials, reagents, and solvents were purchased from commercial sources and used as received. ^1H and ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively. High-resolution mass spectra (HRMS) of new compounds were recorded on a Waters SYNAPT G2-Si mass spectrometer with quadrupole time-of-flight tandem mass spectrometry analysis. High performance liquid chromatography analyses were

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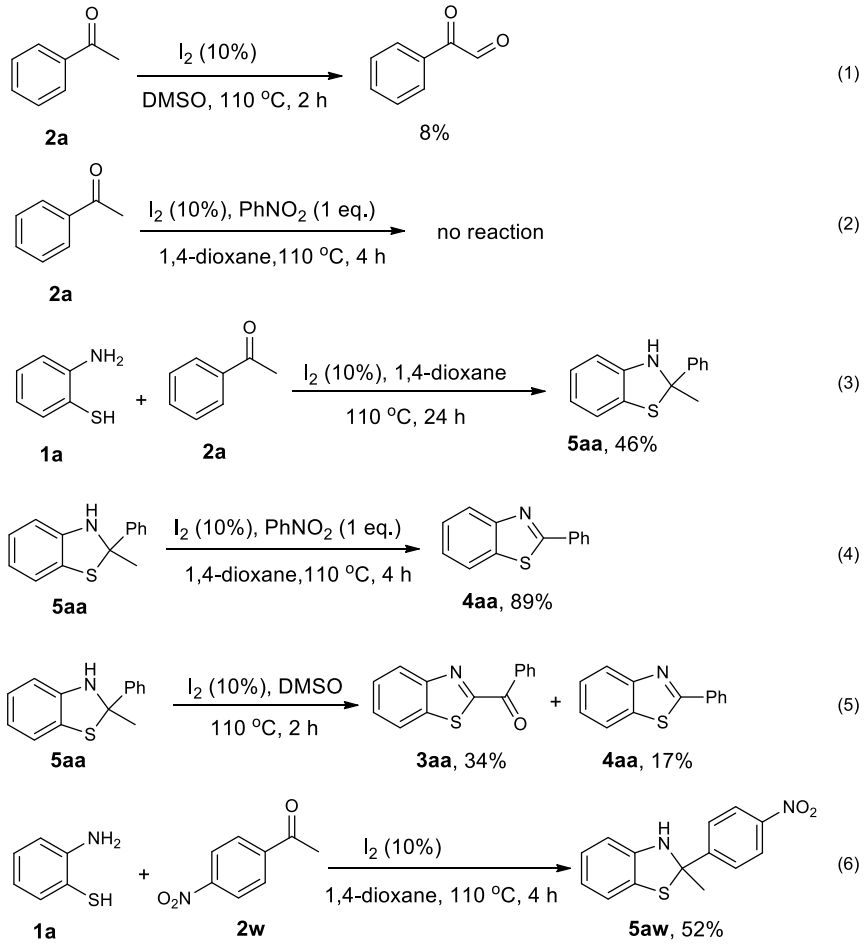
J. Org. Chem. XXXX, XXX, XXX−XXX

Scheme 2. Control Experiments



carried out on an Agilent 1260 Infinity II instrument. Melting points were determined using an X-4 digital micro melting point apparatus. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254).

General Procedure for the Synthesis of 3 (3aa as an Example). The reaction in a reaction vessel was carried out with **1a** (1.5 mmol, 1.5 equiv), **2a** (1 mmol, 1 equiv), and iodine (0.1 mmol, 0.1 equiv) in DMSO (2 mL) at 110 °C in an oil bath for 2 h. After disappearance of the reactant (monitored by TLC), water (10 mL) was added, and the mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with 10% $Na_2S_2O_3$ solution (20 mL) and brine (20 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel to afford the desired **3aa** (184 mg, 77%).

General Procedure for the Synthesis of 4 (4aa as an Example). The reaction in a reaction vessel was carried out with **1a** (1.5 mmol, 1.5 equiv), **2a** (1 mmol, 1 equiv), $PhNO_2$ (1 mmol, 1 equiv), and iodine (0.1 mmol, 0.1 equiv) in 1,4-dioxane (2 mL) at 110 °C in an oil bath for 4−8 h. After disappearance of the reactant (monitored by TLC), water (10 mL) was added and the mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with 10% $Na_2S_2O_3$ solution (20 mL) and brine (20 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel to afford the desired **4aa** (169 mg, 80%).

Benzo[d]thiazol-2-yl(phenyl)methanone (***3aa***).[8b] Petroleum ether/ethyl acetate = 3:1; a white solid (184 mg, 77%), mp: 98−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 7.2 Hz, 2H), 8.25 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.63−7.52 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.65, 127.0, 125.8, 122.2; ESI-MS: m/z [M + 1]$^+$, 240.

Benzo[d]thiazol-2-yl(2-methoxyphenyl)methanone (***3ab***).[17] Petroleum ether/ethyl acetate = 3:1; a white solid (186 mg, 69%); mp: 107−110 °C; 1H NMR (400 MHz, $CDCl_3$): δ 8.14−8.17 (m, 1H), 7.98−8.02 (m, 1H), 7.77 (dd, J = 7.6, 1.8 Hz, 1H), 7.50−7.58 (m, 3H), 7.10 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.1, 167.3, 158.8, 153.7, 137.2, 133.7, 131.2, 127.5, 126.8, 126.3, 125.7, 122.3, 120.4, 112.1, 56.0; ESI-MS: m/z [M + 1]$^+$, 270.

Benzo[d]thiazol-2-yl(2-hydroxyphenyl)methanone (***3ac***).[18] Petroleum ether/ethyl acetate = 1:1; a yellow solid (179 mg, 70%); mp: 77−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.10 (s, 1H), 9.26 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.54−7.62 (m, 3H), 7.02−7.08 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.65, 167.10, 164.17, 153.69, 137.53, 136.72, 134.07, 127.86, 127.13, 125.70, 122.11, 119.55, 118.43, 118.14; ESI-MS: m/z [M + 1]$^+$, 256.

Benzo[d]thiazol-2-yl(2-chlorophenyl) methanone (***3ad***).[17] Petroleum ether/ethyl acetate = 3:1; a white solid (183 mg, 67%); mp: 76−78 °C; 1H NMR (400 MHz, $CDCl_3$): δ 8.15−8.18 (m, 1H), 8.00−8.04 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.50−7.58 (m, 4H), 7.41−7.45 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.6, 165.9, 153.7, 137.4, 136.0, 132.6, 132.4, 130.8, 130.6, 128.0, 127.1, 126.5, 126.0, 122.4; ESI-MS: m/z [M + 1]$^+$, 274.

Benzo[d]thiazol-2-yl(3-methoxyphenyl)methanone (***3ae***).[17] Petroleum ether/ethyl acetate = 3:1; a white solid (215 mg, 80%); mp: 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22−8.26 (m, 2H), 8.01−8.06 (m, 2H), 7.53−7.61 (m, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.22 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.1, 167.1, 159.6, 153.9, 137.0, 136.1, 129.6,

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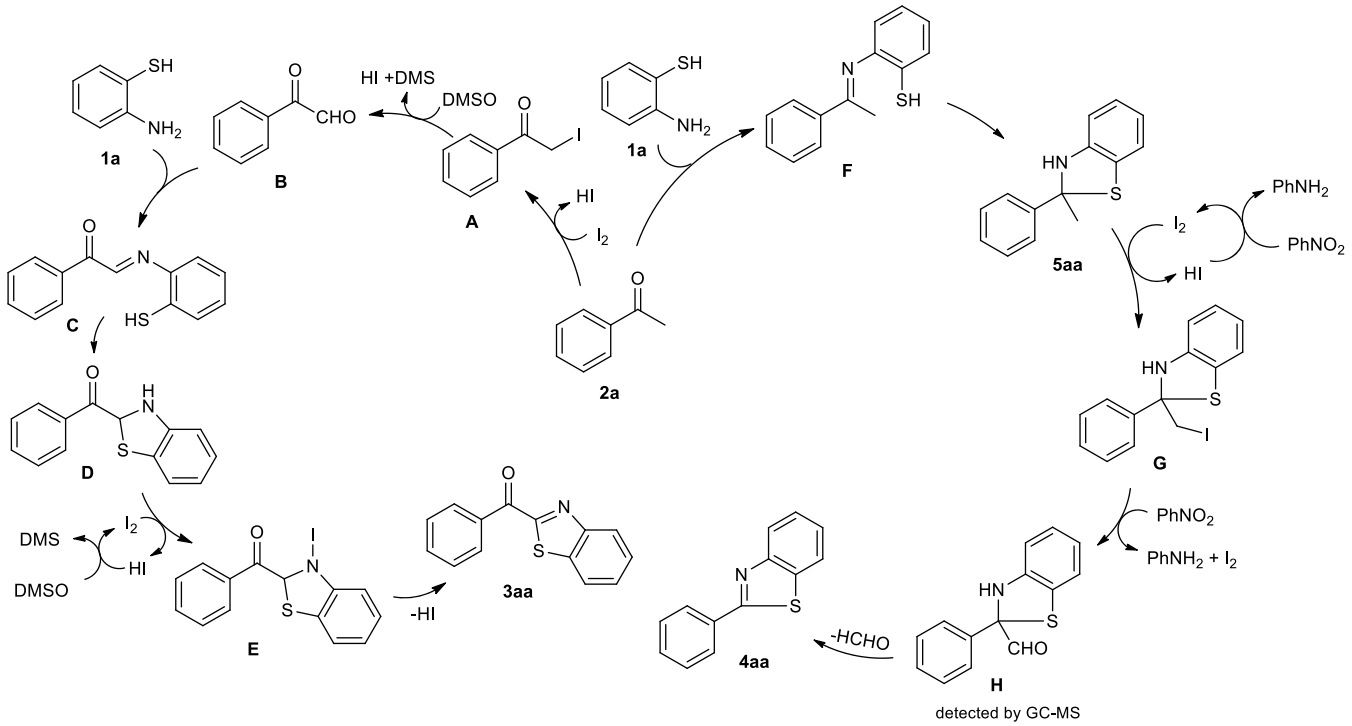
Scheme 3. Plausible Reaction Mechanism



plausible reaction mechanism

127.7, 127.0, 125.8, 124.2, 122.2, 120.6, 115.3, 55.5; ESI-MS: m/z [M + 1]$^+$, 270.

Benzo[d]thiazol-2-yl(3-chlorophenyl)methanone (**3af**).[17] Petroleum ether/ethyl acetate = 3:1; a white solid (177 mg, 65%); mp: 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.48 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.55−7.66 (m, 3H), 7.51 (t, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.0, 166.4, 153.8, 137.1, 136.4, 134.7, 133.8, 131.2, 129.8, 129.5, 127.9, 127.1, 125.9, 122.2; ESI-MS: m/z [M + 1]$^+$, 274.

Benzo[d]thiazol-2-yl(4-fluorophenyl)methanone (**3ah**).[17] Petroleum ether/ethyl acetate = 3:1; a red solid (177 mg, 69%); mp: 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, J = 8.6, 5.5 Hz, 2H), 8.24 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.6, 167.0, 166.4 (d, J = 255 Hz), 153.8, 137.0, 134.2 (d, J = 9.4 Hz), 131.3 (d, J = 3.0 Hz), 127.7, 127.0, 125.7, 122.2, 115.8 (d, J = 21.7 Hz); ESI-MS: m/z [M + 1]$^+$, 258.

Benzo[d]thiazol-2-yl(p-tolyl)methanone (**3ai**).[8b] Petroleum ether/ethyl acetate = 3:1; a white solid (190 mg, 75%); mp: 79−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.0 Hz, 2H), 8.23 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.51−7.59 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.9, 167.3, 153.9, 145.0, 137.0, 132.4, 131.4, 129.3, 127.5, 126.9, 125.7, 122.2, 21.9; ESI-MS: m/z [M + 1]$^+$, 254.

(4-Aminophenyl)(benzo[d]thiazol-2-yl)methanone (**3ak**).[19] Petroleum ether/ethyl acetate = 2:1; a yellow solid (183 mg, 72%); mp: 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 8.4 Hz, 2H), 8.21 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 6.73 (d, J = 8.4 Hz, 2H), 4.32 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.6, 168.6, 153.9, 152.2, 136.8, 134.2, 127.1, 126.6, 125.4, 125.0, 122.1, 113.8; ESI-MS: m/z [M + 1]$^+$, 255.

Benzo[d]thiazol-2-yl(3,5-dimethoxyphenyl)methanone (**3al**). Petroleum ether/ethyl acetate = 4:1; a grey solid (182 mg, 61%); mp: 105−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 2.4 Hz, 2H), 7.53−7.610 (m, 2H), 6.77 (d, J = 2.4 Hz, 2H), 3.89 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.9, 167.0, 160.7, 153.8, 137.0, 136.5, 127.7, 126.9, 125.8, 122.3, 109.0, 106.7, 55.7; HRMS (ESI): calcd for $C_{16}H_{14}NO_3S$ m/z [M + H]$^+$, 300.0689; found, 300.0681.

Benzo[d]thiazol-2-yl(3,4-dimethylphenyl)methanone (**3am**).[17] Petroleum ether/ethyl acetate = 4:1; colorless oil (155 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, J = 7.9, 1.8 Hz, 1H), 8.22−8.26 (m, 2H), 8.01 (d, J = 7.2 Hz, 1H), 7.51−7.61 (m, 2H), 7.31 (d, J = 8.0 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.3, 167.6, 153.9, 143.9, 137.0 (2C), 132.8, 132.1, 129.8, 129.3, 127.5, 126.8, 125.7, 122.2, 19.9 ppm; ESI-MS: m/z [M + 1]$^+$, 268.

Benzo[d]thiazol-2-yl(3,5-difluorophenyl)methanone (**3an**). Petroleum ether/ethyl acetate = 4:1; a white solid (143 mg, 52%); mp: 89−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 6.0 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.09−7.14 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.5, 166.0, 162.7 (dd, J = 248, 11.9 Hz), 153.8, 137.4 (t, J = 8.6 Hz), 137.1, 128.1, 127.3, 126.0, 122.2, 114.3 (dd, J = 19.3, 7.5 Hz), 109.2 (t, J = 25.2 Hz); HRMS (ESI): calcd for $C_{14}H_8F_2NOS$ m/z [M + H]$^+$, 276.0289; found, 276.0294.

Benzo[d]thiazol-2-yl(naphthalen-2-yl)methanone (**3ap**).[8b] Petroleum ether/ethyl acetate = 3:1; a white solid (150 mg, 52%); mp: 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.53−7.66 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.1, 167.4, 154.0, 137.1, 136.0, 134.4, 132.5, 132.2, 130.3, 129.1, 128.4, 127.8, 127.6, 127.0, 126.8, 125.8, 125.8, 122.2; ESI-MS: m/z [M + 1]$^+$, 290.

Benzo[d]thiazol-2-yl(thiophen-2-yl)methanone (**3aq**).[8b] Petroleum ether/ethyl acetate = 2:1; a yellow solid (130 mg, 53%); mp: 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 3.2 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 4.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 4.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 177.0, 166.6, 153.7,

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J. Org. Chem. XXXX, XXX, XXX−XXX

139.7, 137.4, 137.0, 136.8, 128.5, 127.6, 127.0, 125.6, 122.3; ESI-MS: m/z $[M + 1]^+$, 246.

Benzo[b]thiophen-2-yl(benzo[d]thiazol-2-yl)methanone (**3ar**). Petroleum ether/ethyl acetate = 3:1; a yellow solid (174 mg, 59%); mp: 147−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.63 (dt, J = 1.2, 7.6 Hz, 1H), 7.57 (dt, J = 1.2, 7.6 Hz, 1H), 7.52 (dt, J = 1.2, 7.6 Hz, 1H), 7.45 (dt, J = 1.2, 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.4, 166.3, 153.8, 143.8, 139.6, 139.3, 137.0, 135.4, 128.1, 127.7, 127.1, 126.9, 125.7, 125.1, 122.8, 122.3; HRMS (ESI): calcd for $C_{16}H_{10}NOS_2$ m/z $[M + H]^+$, 296.0198; found, 296.0191.

Benzo[d]thiazol-2-yl(benzofuran-2-yl)methanone (**3as**).[8b] Petroleum ether/ethyl acetate = 4:1; a white solid (134 mg, 48%); mp: 179−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.64 (td, J = 7.2, 1.2 Hz, 1H), 7.53−7.60 (m, 2H), 7.37 (td, J = 7.6, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 174.0, 165.9, 156.4, 153.8, 149.8, 137.0, 129.3, 127.8, 127.4, 127.2, 125.6, 124.2, 122.3, 121.1, 112.7; ESI-MS: m/z $[M + 1]^+$, 280.

Benzo[d]thiazol-2-yl(1H-indol-3-yl)methanone (**3at**).[8b] Petroleum ether/ethyl acetate = 4:1; a yellow solid (172 mg, 62%); mp: 252−254 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.38 (s, 1H), 9.26 (s, 1H), 8.19−8.38 (m, 3H), 7.56−7.69 (m, 3H), 7.28−7.33 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 178.3, 170.0, 153.9, 138.7, 136.9, 136.3, 127.5, 127.3, 126.9, 125.3, 124.0, 123.1, 123.0, 122.0, 113.1, 113.1; ESI-MS: m/z $[M + 1]^+$, 279.

(5-Chlorobenzo[d]thiazol-2-yl)(phenyl)methanone (**3ba**).[8b] Petroleum ether/ethyl acetate = 3:1; a red solid (145 mg, 53%); mp: 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 1.9 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.53 (dd, J = 8.8, 1.9 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.9, 168.9, 154.6, 135.2, 134.7, 134.1, 133.0, 131.3, 128.6, 128.2, 125.3, 123.0; ESI-MS: m/z $[M + 1]^+$, 274.

(5-Chlorobenzo[d]thiazol-2-yl)(4-fluorophenyl)methanone (**3bh**).[14] Petroleum ether/ethyl acetate = 4:1; a red solid (259 mg, 89%); mp: 139−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, J = 5.4, 8.4 Hz, 2H), 8.24 (d, J = 1.6 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 1.6 Hz, 1H), 7.24 (t, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.1, 168.8, 166.5 (d, J = 256 Hz), 154.6, 135.2, 134.2 (d, J = 9.4 Hz), 133.1, 131.0 (d, J = 3.0 Hz), 128.3, 125.2, 123.0, 115.8 (d, J = 21.7 Hz); ESI-MS: m/z $[M + 1]^+$, 292.

(5-Chlorobenzo[d]thiazol-2-yl)(3,5-difluorophenyl)methanone (**3bn**). Petroleum ether/ethyl acetate = 3:1; a yellow solid (232 mg, 75%); mp: 164−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 2.0 Hz, 1H), 8.15−8.20 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 8.4, 2.0 Hz, 1H), 7.13 (tt, J = 8.4, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.2, 167.7, 162.8 (dd, J = 249, 11.7 Hz), 154.5, 137.1 (t, J = 8.8 Hz), 135.3, 133.4, 128.7, 125.5, 123.0, 114.3 (dd, J = 19.3, 7.5 Hz), 109.4 (t, J = 25.2 Hz); HRMS (ESI): calcd for $C_{14}H_7ClF_2NOS$ m/z $[M + H]^+$, 309.9899; found, 309.9912.

(5-Chlorobenzo[d]thiazol-2-yl)(naphthalen-2-yl)methanone (**3bp**). Petroleum ether/ethyl acetate = 4:1; a yellow solid (262 mg, 81%); mp: 150−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.41 (dd, J = 8.7, 1.7 Hz, 1H), 8.29 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.53 (dd, J = 8.6, 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.6, 169.2, 154.7, 136.1, 135.2, 134.5, 133.0, 132.4, 131.9, 130.3, 129.2, 128.4, 128.2, 127.8, 126.9, 125.7, 125.3, 123.0; HRMS (ESI): calcd for $C_{18}H_{11}ClNOS$ m/z $[M + H]^+$, 324.0244; found, 324.0231.

Benzo[b]thiophen-2-yl(5-chlorobenzo[d]thiazol-2-yl)methanone (**3br**). Petroleum ether/ethyl acetate = 3:1; a yellow solid (280 mg, 85%); mp: 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.28 (d, J = 2.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.49−7.53 (m, 2H), 7.44 (td, J = 8.1 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.0, 168.1, 154.5, 143.9, 139.4, 139.2, 135.6, 135.2, 133.2, 128.3, 128.3, 126.9, 125.2 (2C), 123.0, 122.8; HRMS (ESI): calcd for $C_{14}H_7ClF_2NOS$ m/z $[M + H]^+$, 309.9899; found, 309.9893.

2-Phenylbenzo[d]thiazole (**4aa**).[8d] Petroleum ether/ethyl acetate = 3:1; a yellow solid (169 mg, 80%); mp: 100−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.12 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.48−7.52 (m, 4H), 7.39 (td, J = 8.0, 0.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.1, 154.2, 135.1, 133.6, 131.0, 129.1, 127.6, 126.4, 125.2, 123.3, 121.7; ESI-MS: m/z $[M + 1]^+$, 212.

(2-Methoxyphenyl)benzo[d]thiazole (**4ab**).[8d] Petroleum ether/ethyl acetate = 3:1; a red solid (193 mg, 80%); mp: 99−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, J = 7.9, 1.8 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.44−7.51 (m, 2H), 7.37 (td, J = 8.0, 0.8 Hz, 1H), 7.14 (td, J = 8.1, 1.1 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 4.06 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 163.1, 157.2, 152.1, 136.1, 131.8, 129.6, 125.9, 124.6, 122.8, 122.3, 121.2, 121.2, 111.7, 55.7; ESI-MS: m/z $[M + 1]^+$, 242.

(2-Chlorophenyl)benzo[d]thiazole (**4ad**).[8d] Petroleum ether/ethyl acetate = 4:1; a yellow solid (189 mg, 77%); mp: 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20−8.22 (m, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.51−7.55 (m, 2H), 7.40−7.45 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.2, 152.5, 136.1, 132.7, 132.3, 131.8, 131.2, 130.8, 127.2, 126.3, 125.5, 123.5, 121.4; ESI-MS: m/z $[M + 1]^+$, 246.

2-(3-Methoxyphenyl)benzo[d]thiazole (**4ae**).[20] Petroleum ether/ethyl acetate = 3:1; a white solid (161 mg, 67%); mp: 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.1, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.66−7.68 (m, 1H), 7.63 (td, J = 7.6, 1.2 Hz, 1H), 7.48 (td, J = 7.2, 1.2 Hz, 1H), 7.34−7.39 (m, 2H), 7.02 (dd, J = 8.0, 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.0, 160.1, 154.1, 135.1, 130.1, 126.3, 125.3, 123.3, 121.6, 120.3, 117.4, 112.0, 55.5; ESI-MS: m/z $[M + 1]^+$, 242.

2-(3-Chlorophenyl)benzo[d]thiazole (**4af**).[21] Petroleum ether/ethyl acetate = 3:1; a white solid (154 mg, 63%); mp: 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (t, J = 1.6 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.92 (dt, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.49 (td, J = 7.2, 1.2 Hz, 1H), 7.36−7.45 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.3, 154.0, 135.3, 135.2, 135.1, 130.9, 130.3, 127.4, 126.6, 125.7, 125.6, 123.5, 121.7; ESI-MS: m/z $[M + 1]^+$, 246.

2-(4-Chlorophenyl)benzo[d]thiazole (**4ag**).[8d] Petroleum ether/ethyl acetate = 3:1; a red solid (172 mg, 70%); mp: 98−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 9.2 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.6, 154.1, 137.0, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7; ESI-MS: m/z $[M + 1]^+$, 246.

2-(p-Tolyl)benzo[d]thiazole (**4ah**).[8d] Petroleum ether/ethyl acetate = 3:1; a white solid (187 mg, 83%); mp: 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.9 Hz, 1H), 7.47 (td, J = 8.3, 1.2 Hz, 1H), 7.36 (td, J = 8.0, 1.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.3, 154.2, 141.5, 135.0, 131.0, 129.8, 127.5, 126.3, 125.0, 123.1, 121.6, 21.6; ESI-MS: m/z $[M + 1]^+$, 226.

4-(Benzo[d]thiazol-2-yl)aniline (**4ak**).[22] Petroleum ether/ethyl acetate = 2:1; a white solid (174 mg, 77%); mp: 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 4.00 (br s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.5, 154.3, 149.2, 134.6, 129.2, 126.1, 124.5, 124.0, 122.5, 121.4, 114.8; ESI-MS: m/z $[M + 1]^+$, 227.

2-(3,5-Dimethoxyphenyl)benzo[d]thiazole (**4al**).[23] Petroleum ether/ethyl acetate = 2:1; colorless oil (190 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.074 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.49 (td, J = 7.6, 1.3 Hz, 1H), 7.38 (td, J = 7.6, 0.8 Hz, 1H), 7.25 (d, J = 2.4 Hz, 2H), 6.59 (t, J = 2.3 Hz, 1H), 3.88 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.0, 161.1, 154.0, 135.4, 135.1, 126.3, 125.3, 123.3, 121.6, 105.5, 103.4, 55.6; ESI-MS: m/z $[M + 1]^+$, 272.

2-(3,4-Dimethylphenyl)benzo[d]thiazole (**4am**).[24] Petroleum ether/ethyl acetate = 4:1; a white solid (172 mg, 72%); mp: 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.0 Hz, 1H), 7.88 (s,

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J. Org. Chem. XXXX, XXX, XXX−XXX

1H), 7.86 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.5, 154.2, 140.2, 137.4, 135.0, 131.3, 130.3, 128.5, 126.2, 125.2, 124.9, 123.0, 121.6, 19.9, 19.7; ESI-MS: m/z $[M + 1]^+$, 240.

*2-(3,5-Difluorophenyl)benzo[d]thiazole (**4an**).*[25] Petroleum ether/ethyl acetate = 3:1; a white solid (185 mg, 75%); mp: 104−106 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 7.6, 2.4 Hz, 2H), 7.53 (td, J = 7.6, 1.3 Hz, 1H), 7.43 (td, J = 7.8, 1.2 Hz, 1H), 6.93 (tt, J = 7.6, 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.1 (t, J = 3.6 Hz), 163.3 (dd, J = 248, 12.6 Hz), 153.8, 136.6 (t, J = 9.8 Hz), 135.1, 126.7, 125.90, 123.7, 121.8, 110.5 (dd, J = 19.3, 7.8 Hz), 106.1 (t, J = 25.2 Hz); ESI-MS: m/z $[M + 1]^+$, 248.

*2-(2,4-Dimethylphenyl)benzo[d]thiazole (**4ao**).*[26] Petroleum ether/ethyl acetate = 4:1; a pink solid (170 mg, 71%); mp: 31−33 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.15 (s, 1H), 7.11 (d, J = 7.6 Hz, 1H), 2.64 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.2, 153.9, 140.2, 137.1, 135.5, 132.4, 130.6, 130.3, 126.9, 126.1, 124.9, 123.3, 121.3, 21.4, 21.3; ESI-MS: m/z $[M + 1]^+$, 240.

*2-(Naphthalen-2-yl)benzo[d]thiazole (**4ap**).*[20] Petroleum ether/ethyl acetate = 2:1; a yellow solid (193 mg, 74%); mp: 110−112 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 1.2 Hz, 1H), 8.22 (dd, J = 8.6, 1.8 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.93−7.99 (m, 3H), 7.87−7.90 (m, 1H), 7.49−7.58 (m, 3H), 7.41 (td, J = 8.0, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.1, 154.2, 135.1, 134.6, 133.2, 131.0, 128.9 (2C), 127.9, 127.6, 127.5, 126.9, 126.4, 125.3, 124.5, 123.2, 121.7; ESI-MS: m/z $[M + 1]^+$, 262.

*2-(Thiophen-2-yl)benzo[d]thiazole (**4aq**).*[8d] Petroleum ether/ethyl acetate = 2:1; a yellow solid (130 mg, 60%); mp: 99−101 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 3.6 Hz, 1H), 7.50 (d, J = 5.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.14 (t, J = 4.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 153.7, 137.3, 134.7, 129.3, 128.6, 128.1, 126.5, 125.3, 123.0, 121.5; ESI-MS: m/z $[M + 1]^+$, 218.

*2-(Benzo[b]thiophen-2-yl)benzo[d]thiazole (**4ar**).*[27] Petroleum ether/ethyl acetate = 4:1; a yellow solid (155 mg, 58%); mp: 185−188 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 1H), 7.81−7.86 (m, 4H), 7.49 (td, J = 7.8, 1.2 Hz, 1H), 7.36−7.42 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.5, 153.7, 140.8, 139.6, 137.2, 135.0, 126.6, 126.2, 125.6, 125.3, 125.0, 124.6, 123.4, 122.6, 121.6; ESI-MS: m/z $[M + 1]^+$, 268.

*2-(Benzofuran-2-yl)benzo[d]thiazole (**4as**).*[28] Petroleum ether/ethyl acetate = 4:1; a yellow solid (138 mg, 55%); mp: 189−191 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 8.4, 0.9 Hz, 1H), 7.54 (d, J = 0.8 Hz, 1H), 7.53 (td, J = 7.6, 1.2 Hz, 1H), 7.39−7.45 (m, 2H), 7.31 (td, J = 7.6, 0.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 157.6, 155.5, 153.9, 149.8, 134.7, 128.2, 126.7, 126.5, 125.7, 123.8, 123.5, 122.1, 121.7, 111.9, 107.6; ESI-MS: m/z $[M + 1]^+$, 252.

*(tert-Butyl)benzo[d]thiazole (**4au**).*[21] Petroleum ether/ethyl acetate = 3:1; colorless liquid (120 mg, 63%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 1.52 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 181.8, 153.3, 135.0, 125.7, 124.5, 122.7, 121.5, 38.3, 30.8; ESI-MS: m/z $[M + 1]^+$, 192.

*5-Chloro-2-phenylbenzo[d]thiazole (**4ba**).*[8d] Petroleum ether/ethyl acetate = 2:1; a white solid (191 mg, 78%); mp: 140−142 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03−8.08 (m, 3H), 7.79 (d, J = 8.4 Hz, 1H), 7.47−7.51 (m, 3H), 7.35 (dd, J = 8.4, 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.9, 155.0, 133.3, 133.3, 132.3, 131.4, 129.1, 127.6, 125.7, 123.1, 122.3; ESI-MS: m/z $[M + 1]^+$, 246.

*5-Chloro-2-(4-fluorophenyl)benzo[d]thiazole (**4bh**).*[29] Petroleum ether/ethyl acetate = 2:1; a red solid (223 mg, 85%); mp: 139−142 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03−8.09 (m, 3H), 7.81 (t, J = 7.2 Hz, 1H), 7.36 (dd, J = 8.4, 2.0 Hz, 1H), 7.19 (t, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.6, 164.7 (d, J = 251 Hz), 155.0, 133.3, 132.4, 129.6 (d, J = 8.6 Hz), 129.6, 125.7, 123.0, 122.3, 116.3 (d, J = 22.0 Hz); ESI-MS: m/z $[M + 1]^+$, 264.

*5-Chloro-2-(4-methoxyphenyl)benzo[d]thiazole (**4bj**).*[30] Petroleum ether/ethyl acetate = 2:1; a yellow solid (206 mg, 75%); mp: 142−145 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 2H), 7.99 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.31 (dd, J = 8.4, 1.6 Hz, 1H), 6.99 (t, J = 8.8 Hz, 2H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.7, 162.2, 155.1, 133.1, 132.2, 129.2, 126.1, 125.2, 122.6, 122.2, 114.4, 55.5; ESI-MS: m/z $[M + 1]^+$, 276.

*5-Chloro-2-(3,5-difluorophenyl)benzo[d]thiazole (**4bn**).* Petroleum ether/ethyl acetate = 2:1; a white solid (225 mg, 80%); mp: 155−157 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 1.6 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 6.0 Hz, 2H), 7.39 (dd, J = 8.6, 2.0 Hz, 1H), 6.95 (tt, J = 7.6, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.9 (t, J = 3.5 Hz), 163.2 (dd, J = 249, 12.5 Hz), 154.6, 136.1 (t, J = 9.9 Hz), 133.3, 132.8, 126.4, 123.4, 122.4, 110.5 (dd, J = 19.4, 7.9 Hz), 106.4 (t, J = 25.3 Hz); HRMS (ESI): calcd for $C_{13}H_7ClF_2NS$ m/z $[M + H]^+$, 281.9950; found, 281.9932.

*5-Chloro-2-(2,4-dimethylphenyl)benzo[d]thiazole (**4bo**).* Petroleum ether/ethyl acetate = 3:1; a yellow solid (199 mg, 73%); mp: 104−106 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 8.4, 1.6 Hz, 1H), 7.16 (s, 1H), 7.12 (d, J = 7.6 Hz, 1H), 2.64 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.1, 154.7, 140.6, 137.2, 133.7, 132.5, 132.0, 130.6, 129.9, 127.0, 125.4, 123.0, 122.0, 21.5, 21.3; HRMS (ESI): calcd for $C_{15}H_{13}ClNS$ m/z $[M + H]^+$, 274.0452; found, 274.0463.

*2-Methyl-2-phenyl-2,3-dihydrobenzo[d]thiazole (**5aa**).*[31] Petroleum ether/ethyl acetate = 3:1; colorless liquid (104 mg, 46%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.21 (dd, J = 7.6, 0.8 Hz, 1H), 7.15 (td, J = 7.6, 1.2 Hz, 1H), 6.96 (td, J = 7.6, 1.2 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 4.44 (br s, 1H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 146.1, 145.8, 128.6, 128.0, 127.5, 125.8, 125.6, 122.1, 121.2, 111.2, 78.5, 31.7; ESI-MS: m/z $[M + 1]^+$, 228.

*2,2-Dimethyl-2,3-dihydrobenzo[d]thiazole (**5av**).*[32] Petroleum ether/ethyl acetate = 3:1; colorless liquid (124 mg, 75%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.05 (dd, J = 7.6, 0.8 Hz, 1H), 6.90 (td, J = 7.6, 1.2 Hz, 1H), 6.75 (td, J = 7.6, 0.8 Hz, 1H), 6.65 (dd, J = 7.6, 0.8 Hz, 1H), 3.91 (br s, 1H), 1.71 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.8, 128.5, 125.1, 122.1, 121.0, 111.5, 74.7, 31.7; ESI-MS: m/z $[M + 1]^+$, 166.

*2-Methyl-2-(4-nitrophenyl)-2,3-dihydrobenzo[d]thiazole (**5aw**).*[31] Petroleum ether/ethyl acetate = 3:1; colorless liquid (141 mg, 52%); ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 6.97−7.04 (m, 2H), 6.81−6.85 (m, 2H), 4.33 (br s, 1H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 153.8, 147.1, 145.1, 127.9, 126.5, 125.7, 123.6, 122.1, 121.9, 112.2, 77.4, 30.8. ESI-MS: m/z $[M + 1]^+$, 273.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02095.

^1H NMR and ^{13}C NMR spectra (PDF)

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J. Org. Chem. XXXX, XXX, XXX−XXX

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Notes

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