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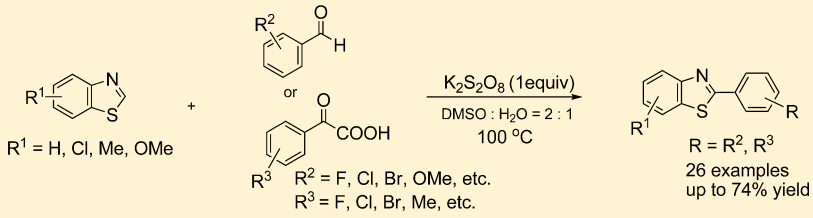
Synthesis of 2-Aryl Benzothiazoles via $K_2S_2O_8$-mediated Oxidative Condensation of Benzothiazoles with Aryl Aldehydes

Zhiyong Yang, Xiang Chen, Sizhuo Wang, Jidan Liu, Kai Xie, Anwei Wang, and Ze Tan*

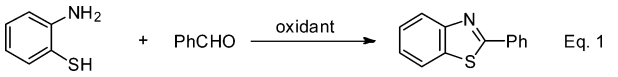
State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China

Supporting Information



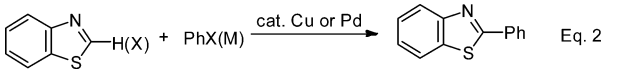
ABSTRACT: Nontransition metal-catalyzed synthesis of 2-aryl benzothiazoles was achieved through $K_2S_2O_8$-mediated oxidative condensation of benzothiazoles with aryl aldehydes. The same transformation can also be effected when the aryl aldehydes were replaced with phenylglyoxylic acids.

2-Aryl benzothiazoles are important molecules due to their use not only as medicinal agents but also as organic functional materials such as fluorescent dyes and liquid crystals.[1,2] Traditional methods for their syntheses typically involve the condensation of 2-amino thiophenols with aryl aldehydes (eq 1),[3] carboxylic acids,[4] nitriles,[4a] acyl chlorides,[4d,5] alcohols,[6] or



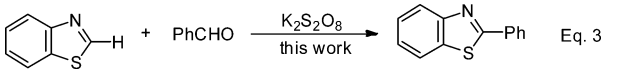
Eq. 1

through Jacobson's potassium ferricyanide mediated cyclization of thiobenzanilides.[1c,7] Alternatively, transition metal-catalyzed couplings such as Pd- or Cu-catalyzed cross coupling between benzothiazoles and aryl halides or 2-halide-substituted benzothiazoles with aryl metals have also been developed (eq 2).[8,9] Among these reports, we have shown that 2-aryl



Eq. 2

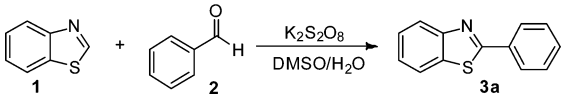
benzothiazoles can also be synthesized via Pd-catalyzed decarboxylative coupling between benzothiazoles and aryl carboxylic acids.[9] Herein we report 2-aryl benzothiazoles can be efficiently synthesized via $K_2S_2O_8$-mediated oxidative condensation of benzothiazoles with aryl aldehydes (eq 3).



Eq. 3

Inspired by recent reports that $K_2S_2O_8$ can be used to mediate the Minisci reaction between heteroaryls and phenyl boronic acids,[10] we envision a similar reaction can be effected between aryl aldehydes and benzothiazoles. When benzaldehyde (**2**) was reacted with benzothiazole (**1**) in the presence of 10 mol % of $AgNO_3$ and 1 equiv of $K_2S_2O_8$ in DMSO and H_2O at 130 °C for 12 h, we were delighted to see that our desired product, 2-phenyl benzothiazole (**3a**), was indeed formed in 57% yield (Table 1, entry 1). However, tests showed that the reaction still proceeded smoothly without the Ag catalyst

Table 1. Reaction Condition Optimization[a]



entry	oxidant (equiv)	solvent	T (°C)	yield[b] (%)
1[c]	$AgNO_3/K_2S_2O_8$	$DMSO/H_2O$	130	57
2	$K_2S_2O_8$ (1)	$DMSO/H_2O$	130	57
3	$K_2S_2O_8$ (1)	$DMSO/H_2O$	100	65
4	$K_2S_2O_8$ (1)	$DMSO/H_2O$	rt	trace
5	$K_2S_2O_8$ (1)	$DMSO/H_2O$	60	45
6	$K_2S_2O_8$ (1)	DMSO	100	38
7	$(NH_4)_2S_2O_8$(1)	$DMSO/H_2O$	100	55
8	$K_2S_2O_8$ (1)	$DMSO/H_2O$	100	60
9	$K_2S_2O_8$ (1)	DMF/H_2O	100	0
10	$K_2S_2O_8$ (1)	CH_3CN/H_2O	100	trace
11	$K_2S_2O_8$ (1)	toluene/H_2O	100	0
12[d]		$DMSO/H_2O$	100	0
13[e]	$K_2S_2O_8$ (1)	$DMSO/H_2O$	100	56

[a]Conditions: benzothiazole (1.5 mmol), aldehyde (1.0 mmol), oxidant (1.0 mmol),$DMSO/H_2O$=2 mL: 1 mL, 100 °C,3 h. [b]Yields are determined by GC. [c]$K_2S_2O_8$ (1.0 mmol), $AgNO_3$ (0.1 mmol), 12 h with $K_2S_2O_8$ in $DMSO/H_2O$. [d]No $K_2S_2O_8$ added. [e]$DMSO/H_2O$ = 1:2 mL.

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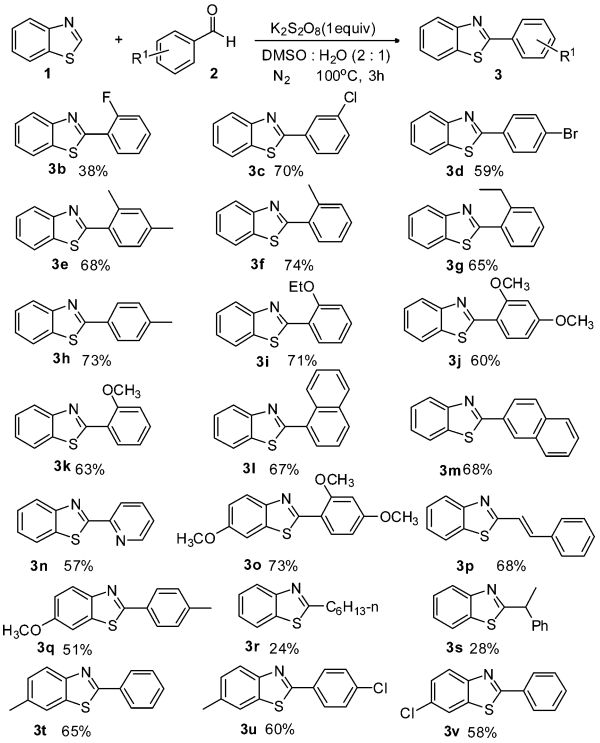
(Table 1, entry 2). Better yield (65%) was obtained when the reaction temperature was dropped to 100 °C (Table 1, entry 3) while further decrease of the reaction temperature resulted in a much slower reaction, thus leading to incomplete reactions (Table 1, entry 4 and 5). Changing the solvent to DMF/H_2O, CH_3CN/H_2O or Toluene/H_2O afforded no product whereas the use of $(NH_4)_2S_2O_8$ as the oxidant or using DMSO alone as the solvent gave inferior yields (Table 1, entries 6−11). If the ratio of DMSO against H_2O was changed from 2/1 to 1/2, the yield also dropped (Table 1, entry 13). The control experiment also showed that $K_2S_2O_8$ was necessary for the reaction to proceed (Table 1, entry 12). Extensive tests also showed that the best yield was achieved when benzothiazoles were used in excess. On the basis of these results, we decided to set heating the benzothiazoles and aryl aldehydes at 100 °C in the presence of 1 equiv of $K_2S_2O_8$ in DMSO/H_2O (2/1) as our standard condition.

With the optimized protocol in hand, we next set out to explore the scope and limitation of the reaction (Table 2). We found that the reaction worked very well for a wide variety of substituted benzaldehydes, affording the desired 2-aryl substituted benzothiazoles in yields ranging from 38 to 74%. Substituents such as methyl, ethyl, chloro, bromo, fluoro as well as methoxy groups were well tolerated. The reaction of 1- or 2-naphthyl aldehyde also worked well, furnishing the 2-naphthyl substituted benzothiazoles in good yields. 2-Pyridine aldehyde, a heteroaryl aldehyde, was also a viable partner, affording the 2-pyridine-substituted benzothiazole in 57% yield. Methoxy, methy and chloro substituted benzothiazoles gave no problem, showing that this reaction is not very sensitive to the electronic effects of the substituents. In addition, under the standard condition, the reaction of cinnamon aldehyde with benzothiazole produced the 2-styryl-substituted benzothiazole **3p** in 68% yield. While the results of aryl aldehydes were all favorable, the reactions of aliphatic aldehydes were messy, only producing the desired products in low yields. For example, the reaction of 1-heptanal with benzothiazole only gave the desired product in 24% yield.

Since glyoxylic acids are known to form aldehydes at a relative elevated temperature,[11] we next tested the possibility of synthesizing 2-aryl benzothiazoles from glyoxylic acids and benzothiazoles. After a series of investigations, we found that this transformation can be effected in a two-step/one-pot fashion. Specifically, 1 equiv of glyoxylic acid and 1.5 equiv of benzothiazole were heated at 100 °C in DMSO/H_2O for 1 h, then 1 equiv of $K_2S_2O_8$ was added and the reaction was reacted for another 3 h. After stopping the reaction and regular work up, the desired 2-aryl benzothiazole can be isolated. Using this method, various 2-aryl-substituted benzothiazoles can be synthesized in 35−62% yields starting from various glyoxylic acids, and the results are summarized in Table 3. Surprisingly, directly mixing glyoxylic acid, benzothiazole and $K_2S_2O_8$ together in DMSO/H_2O did not produce any desired 2-substituted benzothizaole and the reason is still unknown.

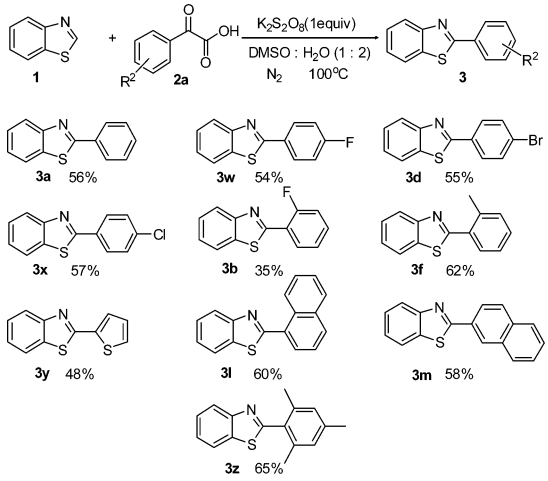
Though the exact mechanism is still not clear at present, we believe that the reaction is actually not a Minisci type reaction. This is supported by the control reaction that almost all of the benzaldehyde remained intact when benzaldehyde was heated in DMSO/H_2O with 1 equiv of $K_2S_2O_8$ whereas benzothiazole was completely consumed under the same reaction condition (eq 4 and 5). Since 2-amino thiophenol and CO_2 were detected

Table 2. Synthesis of 2-Aryl Benzothiazoles from Benzothiazoles and Aryl Aldehydes[a]

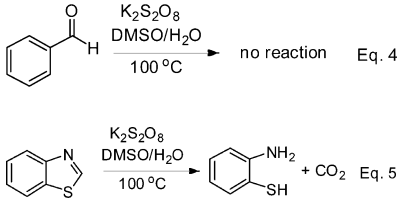


[a]Conditions: benzothiazole (1.5 mmol), aldehyde (1.0 mmol), oxidant (1.0 mmol), DMSO/H_2O = 2:1 mL, 100 °C, 3 h.

Table 3. Synthesis of 2-Aryl Benzothiazoles from Benzothiazoles and Glyoxylic Acids[a]



[a]Conditions: benzothiazole (1.5 mmol), glyoxylic acid (1.0 mmol), DMSO/H_2O = 1:2 mL, 100 °C, 1 h; then oxidant (1.0 mmol), another 3 h.



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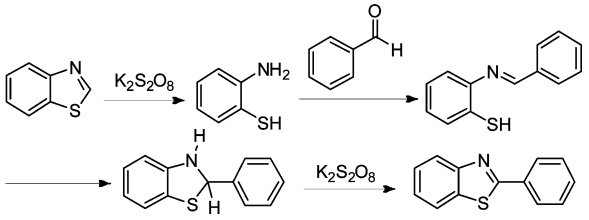
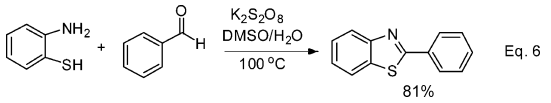
in the reaction of benzothiazole with $K_2S_2O_8$, a more likely mechanism seems to involve the oxidative opening of the thiazole ring and oxidative condensation of the resultant 2-amino thiophenol with the aldehyde (Scheme 1).

Scheme 1. Possible Reaction Mechanism

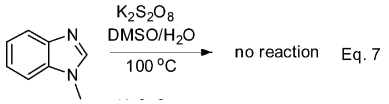


To support this, 2-amino thiophenol was reacted with benzaldehyde in the presence of $K_2S_2O_8$ under the standard reaction condition, and we found that 2-phenyl benzothiazole was indeed formed in 81% yield (eq 6). This proposed

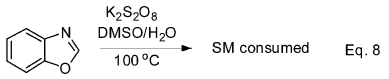


Eq. 6

mechanism also explains why 4,5-dimethyl thiazole did not afford any desired product, yet the starting materials were completely consumed because in this case, once the ring is opened, it can not be reformed. The reactions of aliphatic aldehydes are messy because they are more easily oxidized by $K_2S_2O_8$ to produce carboxylic acids, which are not able to react with 2-amino thiophenol to produce the desired substituted benzothiazoles under the reaction condition. Unfortunately, benzoxazoles and benzimidazoles can not participate in the reaction and experiments showed that benzimidazoles remained intact under the reaction condition whereas benzoxazoles were completely consumed in the reaction (eqs 7 and 8). The failure

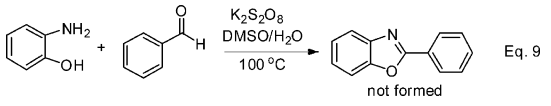


Eq. 7



Eq. 8

of the benzoxazole might be due to the fact that 2-amino phenol was found not to be able to undergo oxidative condensation with aryl aldehydes to form 2-aryl benzoxazoles under the standard reaction condition (eq 9). In addition, attempts to extend this reaction to carboxylic acid in place of benzaldehyde also met with failure.



Eq. 9

In summary, a novel way of synthesizing 2-aryl benzothiazoles from benzothiazoles and aryl aldehydes was developed. By treating benzothiazoles and aryl aldehydes with $K_2S_2O_8$ in DMSO and H_2O, the benzothiazoles were found to undergo oxidation to produce 2-amino thiophenols in situ, which subsequently underwent oxidative cyclization with the aryl aldehydes to give a variety of 2-aryl benzothiazoles in yields ranging from 38 to 74%. The reaction also worked well when aryl aldehydes were replaced with phenylglyoxylic acids. Since this protocol obviates the need to spend an extra step to convert the benzothiazoles into 2-amino thiophenols, it is more efficient in terms of step economy than the classical condensation approach in cases where substituted benzothiazoles are readily available. It also could be complementary to the Cu- or Pd-catalyzed cross coupling protocols provided that the aryl aldehydes are more readily accessible than the corresponding aryl halides.

EXPERIMENTAL SECTION

General Experimental Methods. Benzothiazole, aldehydes and DMSO were purchased commercially and used without further purification. Methoxy, methy, chloro-substituted benzothiazoles were prepared from the corresponding substituted 2-amino benzothiazoles.[12] α-Oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[13] ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature. The chemical-shifts scale is based on internal TMS.

Procedure for the Synthesis of 2-Aryl Benzothiazoles via $K_2S_2O_8$-mediated Oxidative Condensation of Benzothiazoles with Aryl Aldehydes. A 25-mL round-bottom flask was charged with Benzothiazole (1.5 mmol), aryl aldehydes (1.0 mmol), $K_2S_2O_8$ (1.0 mmol) and DMSO/$H_2$0 (2:1 mL). The reaction was stirred at 100 °C under N_2 for 3 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with H_2O and extracted with dichloromethane (30 mL × 3). The organic layers were combined, washed with brine, dried over Mg_2SO_4, and filtered. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, gradient eluent of EtOAc in *n*-pentane: 2%, v/v) to yield the product as a colorless (yellow) solid (oil).

Procedure for the Synthesis of 2-Aryl Benzothiazoles via $K_2S_2O_8$-mediated Oxidative Condensation of Benzothiazole with α-Oxocarboxylic Acids. A 25-mL round-bottom flask was charged with Benzothiazole (1.5 mmol), α-oxocarboxylic acids (1.0 mmol) and DMSO/$H_2$0 (1:2 mL). The reaction flask was stirred at 100 °C under N_2 for 1 h, then $K_2S_2O_8$ (1.0 mmol) was added and resultant mixture was stirred for another 3 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with H_2O and extracted with dichloromethane (30 mL × 3). The organic layers were combined, washed with brine, dried over Mg_2SO_4, and filtered. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, gradient eluent of EtOAc in *n*-pentane: 2%, v/v) to yield the product as a colorless (yellow) solid (oil).

*2-Phenylbenzothiazole (**3a**)..*[8e,14,18] The product was isolated as a colorless solid in 65% yield (137 mg), mp = 98.1−100.7 °C, TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.6 Hz, 1H), 7.45−7.50 (m, 4H), 7.87 (d, J = 7.6 Hz, 1H), 8.06−8.09 (m, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.6, 123.1, 125.2, 126.2, 127.5 (2C), 128.9 (2C), 130.9, 133.5, 134.9, 154.0, 168.0; FTIR (film, cm^{-1}): 1477, 1444, 757, 670; HRMS (EI) m/z calcd for $C_{13}H_9NS$: 211.0456, found 211.0445; Anal. Calcd for $C_{13}H_9NS$ Elemental Analysis: C, 73.90; H, 4.29; N, 6.63; Found: C, 73.98; H, 4.41; N, 6.50.

*2-(2-Fluorophenyl)benzothiazole (**3b**).*[15] The product was isolated as a colorless solid in 38% yield (87 mg), mp = 110.2−112.3 °C, TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.42−7.52 (m, 3H), 7.95 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.42 (t, J = 7.6 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 116.3 (d, J_{C-F} = 21.3 Hz), 121.4, 123.2, 124.6, 124.7, 125.3, 126.3, 129.7, 132.1 (d, J_{C-F} = 8.4 Hz), 135.7 (d, J_{C-F} = 7.7 Hz), 152.5, 160.1 (d, J_{C-F} = 183.7 Hz), 161.8; HRMS (EI) m/z calcd for $C_{13}H_8NFS$: 229.0361, found 229.0361; Anal. Calcd for $C_{13}H_8NFS$ Elemental Analysis: C, 68.10; H, 3.52; N, 6.11; Found: C, 68.22; H, 3.61; N, 6.00.

*2-(3-Chlorophenyl)benzothiazole (**3c**).*[16] The product was isolated as a colorless solid in 70% yield (170 mg), mp = 112.3−114.2 °C, TLC

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R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.46 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.7, 123.4, 125.5, 125.6, 126.5, 127.3, 130.2, 130.8, 135.0, 135.1, 135.2, 153.9, 166.2; HRMS (EI) m/z calcd for $C_{13}H_8ClNS$: 245.0066, found 245.0060.

*2-(4-Bromophenyl)benzothiazole (**3d**).*[17] The product was isolated as a colorless solid in 59% yield (132 mg), mp = 105.3−107.1 °C, TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.6, 123.2, 125.4, 126.5, 128.8 (2C), 132.2 (2C), 132.4, 135.0, 154.0, 166.7; MS (m/z) 289 (M^+).

*2-(2,4-Dimethylphenyl)benzothiazole (**3e**).* The product was isolated as a colorless solid in 68% yield (164 mg), mp = 111.1−113.0 °C, TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.64 (s, 3H), 7.09 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.2, 21.3, 121.2, 123.1, 124.8, 126.0, 126.8, 130.2, 130.5, 132.3, 135.4, 137.0, 140.1, 153.7, 168.1; HRMS (EI) m/z calcd for $C_{15}H_{13}NS$: 239.0769, found 239.0764.

*2-(2-Methylphenyl) benzothiazole (**3f**)..*[8e,14] The product was isolated as a colorless solid in 74% yield (167 mg), mp = 56.2−57.7 °C, TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H), 7.29−7.35 (m, 3H), 7.38 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.3, 121.3, 123.3, 125.0, 126.0, 126.1, 129.9, 130.5, 131.5, 133.0, 135.5, 137.2, 153.7, 167.9; FTIR (film, cm^{-1}): 2926, 1453, 955, 758, 721; HRMS (EI) m/z calcd for $C_{14}H_{11}NS$: 225.0612, found 225.0606; Anal. Calcd for $C_{14}H_{11}NS$ Elemental Analysis: C, 74.63; H, 4.92; N, 6.22; Found: C, 74.75; H, 5.01; N, 6.02.

*2-(2-Ethylphenyl)benzothiazole (**3g**).*[17] The product was isolated as a colorless oil in 65% yield (154 mg), TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 7.6 Hz, 3H), 3.03 (q, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.36−7.44 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 15.7, 26.7, 121.4, 123.4, 125.1, 126.0, 126.1, 129.8, 130.2, 130.8, 132.7, 135.7, 143.4, 153.8, 167.9; MS (m/z) 239 (M^+).

*2-(4-Methylphenyl)benzothiazole (**3h**).*[18] The product was isolated as a colorless solid in 73% yield (162 mg), mp = 110.3−112.7 °C, TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.28 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.97 (t, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.5, 121.5, 123.0, 125.0, 126.2, 127.4 (2C), 129.7 (2C), 130.9, 134.9, 141.4, 154.1, 168.2; FTIR (film, cm^{-1}): 2913, 1477, 1433, 839, 757; HRMS (EI) m/z calcd for $C_{14}H_{11}NS$: 225.0612, found 225.0606.

*2-(2-Ethoxyphenyl)benzothiazole (**3i**).*[19] The product was isolated as a colorless solid in 71% yield (181 mg), mp = 123.5−126.1 °C, TLC R_f = 0.36 (petroleum ether/ethyl acetate, 8/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64 (t, J = 6.8 Hz, 3H), 4.27 (q, J = 6.8 Hz, 2H), 7.02 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 7.6 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.9, 64.9, 112.2, 120.9, 121.2, 122.2, 122.7, 124.5, 125.8, 129.4, 131.7, 136.1, 152.0, 156.6, 163.2; MS (m/z) 255 (M^+).

*2-(2,4-Dimethoxyphenyl)benzothiazole (**3j**).*[20] The product was isolated as a colorless solid in 60% yield (162 mg), mp = 125.6−127.3 °C, TLC R_f = 0.35 (petroleum ether/ethyl acetate, 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 4.01 (s, 3H), 6.56 (s, 1H), 6.66 (d, J = 8.8 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 8.8 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 55.5, 55.6, 98.4, 105.8, 115.5, 121.1, 122.2, 124.1, 125.7, 130.7, 135.6, 152.1, 158.5, 162.8, 163.3; MS (m/z) 271 (M^+).

*2-(2-Methoxyphenyl)benzothiazole (**3k**).*[18] The product was isolated as a colorless solid in 63% yield (152 mg), mp = 120.2−121.8 °C, TLC R_f = 0.40 (petroleum ether/ethyl acetate, 8/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.04 (d, J = 8.4 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.44−7.48 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 55.6, 111.5, 121.1, 121.2, 122.1, 122.7, 124.5, 125.8, 129.4, 131.7, 136.0, 152.0, 157.1, 163.1; FTIR (film, cm^{-1}): 2994, 1603, 1481, 831, 757; HRMS (EI) m/z calcd for $C_{14}H_{11}NOS$: 241.0561, found 241.0552.

*2-(Naphthalen-1-yl)benzothiazole (**3l**).*[18] The product was isolated as a yellow oil in 67% yield (174 mg), TLC R_f = 0.55 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J = 7.6 Hz, 1H), 7.52−7.57 (m, 3H), 7.61 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.96 (t, J = 8.4 Hz, 2H), 8.19 (d, J = 8.0 Hz, 1H), 8.93 (d, J = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.3, 123.5, 124.9, 125.2, 125.8, 126.2, 126.5, 127.6, 128.4, 129.3, 130.5, 130.7, 131.0, 133.9, 135.4, 154.1, 167.6; HRMS (EI) m/z calcd for $C_{17}H_{11}NS$: 261.0612, found 261.0604.

*2-(Naphthalen-2-yl)benzothiazole (**3m**).*[15] The product was isolated as a colorless solid in 68% yield (177 mg), mp = 99.2−101.7 °C, TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, J = 7.6 Hz, 1H), 7.48−7.56 (m, 3H), 7.85−7.96 (m, 4H), 8.11 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 120.6, 122.2, 123.4, 124.2, 125.3, 125.8, 126.4, 126.5, 126.8, 127.8 (2C), 129.9, 132.1, 133.5, 134.0, 153.1, 167.1; MS (m/z) 261 (M^+).

*2-(Pyridin-2-yl)benzothiazole (**3n**).*[8e] The product was isolated as a yellow solid in 57% yield (121 mg), mp = 132.8−134.1 °C, TLC R_f = 0.41 (petroleum ether/ethyl acetate, 8/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 6.0 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.83 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.68 (d, J = 4.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 120.7, 122.0, 123.5, 125.3, 125.6, 126.3, 136.1, 137.0, 149.6, 151.3, 154.2, 169.3; FTIR (film, cm^{-1}): 1564, 1433, 979, 758, 728, 720; HRMS (EI) m/z calcd for $C_{12}H_8N_2S$: 212.0408, found 212.0411; Anal. Calcd for $C_{12}H_8N_2S$ Elemental Analysis: C, 67.90; H, 3.80; N, 13.20; Found: C, 68.00; H, 3.93; N, 13.05.

*2-(2,4-Dimethoxyphenyl)-5-methoxybenzothiazole (**3o**).*[8h] The product was isolated as a yellow solid in 73% yield (220 mg), mp = 115.8−117.6 °C, TLC R_f = 0.26 (petroleum ether/ethyl acetate, 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 3.85 (s, 3H), 3.97 (s, 3H), 6.52 (s, 1H), 6.63 (d, J = 8.8 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 7.32 (s, 1H), 7.91 (d, J = 8.8 Hz, 1H), 8.83 (d, J = 8.4 Hz, 1H).; ^{13}C NMR(100 MHz, $CDCl_3$): δ 55.4, 55.5, 55.6, 98.2, 103.3, 105.7, 115.0, 115.5, 122.7, 130.2, 136.8, 146.6, 156.8, 158.0, 160.9, 162.3; MS (m/z) 301 (M^+).

*2-Styrylbenzothiazole (**3p**).*[8e] The product was isolated as a yellow solid in 68% yield (162 mg), mp = 98.2−100.1 °C, TLC R_f = 0.45 (petroleum ether/ethyl acetate, 8/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.43 (m, 5H), 7.47−7.59 (m, 4H), 7.85 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H)); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.5, 122.0, 122.9, 125.3, 126.3 (2C), 127.3 (2C), 128.9, 129.4, 134.2, 135.3, 137.6, 153.8, 167.0; HRMS (EI) m/z calcd for $C_{15}H_{11}NS$: 237.0612, found 237.0606.

*5-Methoxy-2-(p-tolyl)benzothiazole (**3q**).*[21] The product was isolated as a colorless solid in 51% yield (131 mg), mp = 99.2−101.4 °C, TLC R_f = 0.36 (petroleum ether/ethyl acetate, 8/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.87 (s, 3H), 7.07 (d, J = 9.2 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.33 (s, 1H), 7.91−7.94 (m, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.4, 55.7, 104.1, 115.4, 123.4, 127.1 (2C), 129.6 (2C), 131.0, 136.2, 140.8, 148.6, 157.5, 165.7; HRMS (EI) m/z calcd for $C_{15}H_{13}NOS$: 255.0718, found 255.0712.

*2-Hexylbenzothiazole (**3r**).*[17] The product was isolated as a yellow oil in 24% yield (52 mg), TLC R_f = 0.59 (petroleum ether/ethyl acetate, 12/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 8.0 Hz, 3H), 1.31−1.33 (m, 4H), 1.34−1.35 (m, 2H), 1.85−1.87 (m, 2H), 3.12 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H); ^{13}C NMR(100

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MHz, $CDCl_3$): δ 14.0, 22.5, 28.8, 29.7, 31.4, 34.3, 121.4, 122.4, 124.6, 125.8, 135.1, 153.1, 172.5; MS (*m*/*z*) 219 (M^+).

2-(1-Phenylethyl)benzothiazole (**3s**).[22] The product was isolated as a yellow oil in 28% yield (66 mg), TLC R_f = 0.60 (petroleum ether/ethyl acetate, 12/1); ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (d, *J* = 7.2 Hz, 3H), 4.58 (q, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.32−7.40 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.2, 44.8, 121.4, 122.8, 124.7, 125.8, 127.3, 127.6 (2C), 128.7 (2C), 135.2, 143.0, 153.0, 176.3; FTIR (film, cm^{-1}): 3062, 3002, 2975, 2929, 1513, 1494, 1454, 1437, 1125, 1058, 1026, 1014, 758, 729, 699; MS (*m*/*z*) 239 (M^+).

6-Methyl-2-phenylbenzothiazole (**3t**).[23] The product was isolated as a white solid in 65% yield (146 mg), TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); mp = 126−127 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.46−7.49 (m, 3H), 7.67 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.05−8.08 (m, 2H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.5, 121.3, 122.7, 127.4 (2C), 127.9, 128.9 (2C), 130.7, 133.7, 135.2, 135.3, 152.2, 167.0; HRMS (EI) *m*/*z* calcd for $C_{15}H_{13}NOS$: 225.0612, found 225.0614.

2-(4-Chlorophenyl)-6-methylbenzothiazole (**3u**).[18] The product was isolated as a yellow oil in 60% yield (156 mg), TLC R_f = 0.58 (petroleum ether/ethyl acetate, 12/1); mp = 136−138 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 2H), 7.67 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.5, 121.4, 122.7, 128.1, 128.5 (2C), 129.2 (2C), 132.2, 135.2, 135.6, 136.7, 152.2, 165.5; MS (*m*/*z*) 259 (M^+).

6-Chloro-2-phenylbenzothiazole (**3v**).[23] The product was isolated as a yellow oil in 58% yield (141 mg), TLC R_f = 0.58 (petroleum ether/ethyl acetate, 12/1); mp = 160−161 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.8 Hz, 1H), 7.47−7.49 (m, 3H), 7.84 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 8.03−8.06 (m, 2H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.2, 123.9, 127.1, 127.5 (2C), 129.0 (2C), 131.0, 131.2, 133.2, 136.2, 152.6, 165.8; MS (*m*/*z*) 245 (M^+).

2-(4-Fluorophenyl)benzothiazole (**3w**).[18] The product was isolated as a colorless solid in 54% yield (124 mg), mp = 110.1−112.6 °C, TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 8.04−8.08 (m, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 116.1 (d, J_{C-F} = 22.1 Hz), 121.5, 123.1, 125.2, 126.3, 129.4 (d, J_{C-F} = 8.4 Hz), 129.8, 135.0, 154.0, 164.4 (d, J_{C-F} = 250.2 Hz), 166.7; HRMS (EI) *m*/*z* calcd for $C_{13}H_8NFS$: 229.0361, found 229.0366.

2-(4-Chlorophenyl)benzothiazole (**3x**).[18] The product was isolated as a colorless solid in 57% yield (139 mg), mp = 110.3−112.5 °C, TLC R_f = 0.56 (petroleum ether/ethyl acetate, 12/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 8.57 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.6, 123.2, 125.4, 126.5, 128.7 (2C), 129.2 (2C), 132.0, 135.0, 137.0, 154.0, 166.6; HRMS (EI) *m*/*z* calcd for $C_{13}H_8ClNS$: 245.0066, found 245.0061.

2-(Thiophen-2-yl)benzothiazole (**3y**)..[4d,18] The product was isolated as a yellow solid in 48% yield (103 mg), mp = 113.2−114.7 °C, TLC R_f = 0.47 (petroleum ether/ethyl acetate, 12/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (t, *J* = 4.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 5.2 Hz, 1H), 7.54 (d, *J* = 3.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 121.4, 122.9, 125.2, 126.4, 128.0, 128.6, 129.3, 134.6, 137.3, 153.6, 161.4; HRMS (EI) *m*/*z* calcd for $C_{11}H_7NS_2$: 217.0020, found 217.0030; Anal. Calcd for $C_{11}H_7NS_2$ Elemental Analysis: C, 60.80; H, 3.25; N, 6.45; Found: C, 60.92; H, 3.34; N, 6.32.

2-Mesitylbenzothiazole (**3z**).[8g] The product was isolated as a colorless solid in 65% yield (165 mg), mp = 115.3−116.7 °C, TLC R_f = 0.53 (petroleum ether/ethyl acetate, 12/1); ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 6H), 2.34 (s, 3H), 6.96 (s, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.1 (2C), 21.2, 121.5, 123.3, 125.0, 125.9, 128.3 (2C), 130.6, 136.3, 137.1 (2C), 139.4, 153.4, 167.7; MS (*m*/*z*) 253 (M^+).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*ztanze@gmail.com

Notes

The authors declare no competing financial interest.

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