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Synthesis of heteroaryl ketones via tandem reaction of 1,1-dibromoethenes

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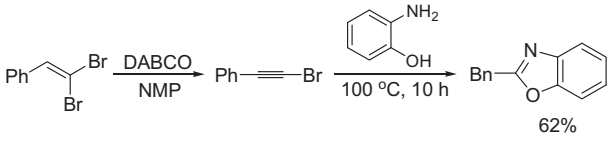
ABSTRACT

A novel method for the synthesis of heteroaryl ketones through one-pot tandem reaction of 1,1-dibromoethenes with 2-amino(thio)phenols promoted by TBAF·3H$_2$O and RuCl$_3$(5%)/air was developed. This novel method includes several reactions in one-pot and utilizes economical yet efficient reagents to generate synthetically and biologically interesting heteroaryl ketones under mild conditions with good efficiency.

1. Introduction

Heteroaryl ketones are versatile synthetic building blocks and valuable structural scaffolds of many therapeutic agents.[1–4] Therefore, their preparation is a frequently encountered mission for both organic and medicinal chemists. For this purpose, various methods, such as Friedel–Crafts acylation of heteroaromatic rings,[5,6] condensation of metalated heterocycles with nitriles,[7,8] oxidation of 1-heteroaromatic-1-alkanols,[9,10] condensation of acyl chloride with organometallics,[11] palladium-catalyzed coupling of aryl halides with organometallic agents,[12–15] C–H activation of heteroarenes,[16] and condensation of 2-aminothiophenol with 2-oxo-2-phenyl acetaldehyde,[17] have been developed. While the aforesaid methods are generally efficient and reliable, they often suffer from expensive catalysts or specially made starting materials. In addition, the use of highly reactive organometallic precursors usually precludes the presence of labile functional groups on the substrates and entails delicate reaction conditions. In this report, we present a novel method for the synthesis of heteroaryl ketones through one-pot tandem reaction of the readily available 1,1-dibromoethenes and 2-amino(thio)phenols under mild conditions.

Recently, 1,1-dibromoethenes are emerging as powerful and versatile synthetic intermediates. In addition to being widely used in various cross coupling reactions,[18–21] they are also finding increasing applications in the synthesis of heterocycles.[22–31] In this regard, Shen et al. recently reported a preparation of 2-benzyl benzoxazole through coupling of 1,1-dibromoethene with 2-aminophenol under the promotion of 1,4-diazabicyclo[2.2.2]-octane (DABCO).[32] During the formation of 2-benzyl benzoxazole, 1-(2-bromoethynyl) benzene is generated through DABCO promoted dehydrobromination of 1-(2,2-dibromovinyl) benzene and acts as a crucial intermediate (Scheme 1).



Scheme 1. Synthesis of benzoxazole from 1,1-dibromoethene with DABCO.

It is then noticed that the above process gave 2-benzyl benzoxazole only in moderate yield over long reaction period. The low efficiency is reasonably attributed to the relatively poor capability of DABCO in promoting the dehydrobromination of 1,1-dibromoethene. We reasoned that this situation should be improved with a more powerful dehydrobromination agent. In this aspect, Mori et al. recently disclosed that tetra-*n*-butylammonium fluoride (TBAF·3H$_2$O) was a mild yet efficient base for the elimination of dibromoalkenes and gave the corresponding alkynyl bromides in excellent yields.[33]

2. Results and discussion

The above-mentioned results prompted us to check the possibility of developing an improved synthesis of 2-benzyl benzoxazole

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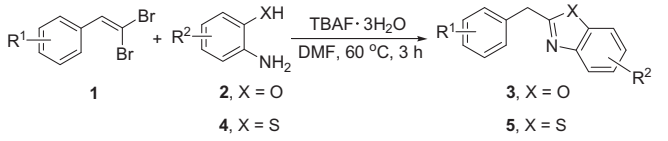
(**3**) from 1,1-dibromoethenes (**1**) and 2-aminophenols (**2**) with the promotion of TBAF·3H$_2$O (Table 1). To our delight, in the presence of TBAF·3H$_2$O, the yield and reaction time for the synthesis of **3** were considerably improved as compared to that promoted by DABCO (Table 1, entries 1–5). In addition to 2-aminophenols, this reaction was also successfully extended for the first time to 2-aminothiophenols (**4**) and afforded the corresponding 2-benzylbenzothiazoles (**5**) in good to excellent yields (Table 1, entries 6–10).

Table 1
Preparation of 2-benzyl benzoxazoles (**3**) or benzothiazoles (**5**) promoted by TBAF·3H$_2$O[a]



1 **2**, X = O; **4**, X = S **3**, X = O; **5**, X = S

Entry	R^1 in **1**	R^2 in **2** or **4**, X	Product	Yield[b] (%)
1	4-Br	H, O	**3a**	80 (60)[c]
2	3-NO$_2$	H, O	**3b**	78 (53)[c]
3	3-NO$_2$	4-Me, O	**3c**	75 (52)[c]
4	4-Br	4-Cl, O	**3d**	82 (58)[c]
5	3-Br	H, O	**3e**	77 (55)[c]
6	H	H, S	**5a**	76
7	H	4-Cl, S	**5b**	78
8	H	5-Me, S	**5c**	76
9	H	3-Cl, S	**5d**	65
10	4-F	H, S	**5e**	81

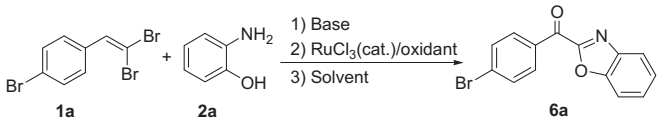
[a] Compounds **1** and **2** or **4** (1 mmol), TBAF·3H$_2$O (4 mmol), DMF (5 mL), 60 °C, 3 h.
[b] Isolated yields.
[c] Yields with literature procedure.[31]

Inspired by the above results and taking into account of the high efficiency and excellent chemoselectivity exhibited by ruthenium(III) reagents in a plethora of oxidative transformations,[34–37] we envisioned a novel route toward 2-benzoxazyl ketone from dibromoethene (**1**) and 2-aminophenol (**2**) through a one-pot tandem process including: (i) TBAF·3H$_2$O promoted dehydrobromination of **1** to give alkynyl bromide, (ii) condensation and cyclization of alkynyl bromide with **2** to give 2-benzyl benzoxazole (**3**), and (iii) benzylic oxidation of the in situ formed 2-benzyl benzoxazole (**3**) by Ru(III) to afford 2-benzoxazyl ketone (**6**).

To study the feasibility of our envisioned route, 1-bromo-4-(2,2-dibromovinyl)benzene (**1a**) and 2-aminophenol (**2a**) were used as model substrates and various solvents, bases, oxidants, and temperatures were screened (shown in Table 2). Initially, **1a** was treated with TBAF·3H$_2$O in DMF. Upon complete consumption of **1a** as monitored by TLC (60 °C, 1 h), **2a** was added together with RuCl$_3$ (5% mol) and 3 equiv of *tert*-butyl hydroperoxide (TBHP), which was used as a stoichiometric oxidant. The subsequent reaction underwent smoothly to give 2-(4-bromobenzoyl)benzoxazole (**6a**) in a yield of 59% (Table 2, entry 1). In further screening, it was found that similar yields of **6a** could be obtained with fewer amounts of TBHP, or even without TBHP (Table 2, entries 2–4). In the absence of TBHP, air is believed to act as a stoichiometric oxidant. Air's role was further confirmed by an independent experiment run under nitrogen, from which only trace amount of **6a** was formed as indicated by TLC analysis (Table 2, entry 5).

Then, the effect of different solvents was studied. In this regard, DMF was replaced by ionic liquids. It was expected that the basic property of fluoride ion in TBAF·3H$_2$O would increase in these highly polar solvents and thus accelerate the dehydrobromination process. Unfortunately, with [bmim]PF$_6$ or [bmim]BF$_4$ as the reaction medium, the dehydrobromination process was actually retarded and no alkynyl bromide was formed from **1a** as indicated by TLC (Table 2, entries 6 and 7). As for the bases, reactions with the promotion of either TBAF in THF (1 M solution) or DABCO required

Table 2
Optimization for the synthesis of **6a**[a]



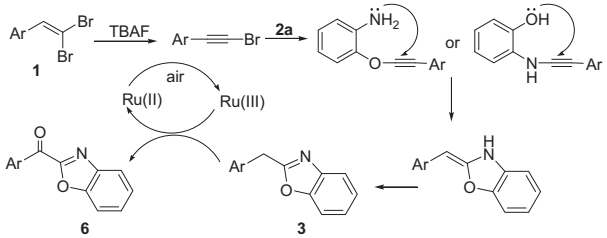
1a **2a** **6a**

Entry	Base	Oxidant (equiv)	Solvent	T (°C)	t (h)	Yield[b] (%)
1	A[c]	TBHP (3)	DMF	60	5	59
2	A	TBHP (1)	DMF	60	6	57
3	A	TBHP (0.5)	DMF	60	10	58
4	A	Air	DMF	60	10	53
5	A	N_2	DMF	60	10	Trace
6	A	Air	[bmim]PF$_6$	60	10	—
7	A	Air	[bmim]BF$_4$	60	10	—
8	B[c]	Air	DMF	60	15	41
9	C[c]	Air	DMF	60	20	37
10	*A*	*Air*	*DMF*	*80*	*10*	*61*
11	A	Air	DMF	100	10	60
12	A	Air	DMF	80	12	61

The significance of italics of entry 10 of table 2 is that with these conditions optimum yield of **6a** was obtained.
[a] Compounds **1a** and **2a** (1 mmol), DMF (5 mL) or IL (2 mL), RuCl$_3$ (0.05 mmol).
[b] Isolated yields.
[c] A for TBAF·3H$_2$O, B for TBAF in THF, C for DABCO.

much longer reaction period to complete and the yields of **6a** were lower (Table 2, entries 8 and 9) than those with TBAF·3H$_2$O. After the temperature and reaction time were optimized, the yield of **6a** was improved to 61% (Table 2, entry 10).

Based on the above observations, a plausible pathway for the formation of **6** was depicted in Scheme 2. While the procedure is thought to follow the route as envisioned above, air's role as a stoichiometric oxidant to oxidize the in situ formed Ru(II) back to Ru(III) is worth to be noted. The use of a cost-free oxidant (air) makes this tandem procedure toward heteroaryl ketones remarkably sustainable.

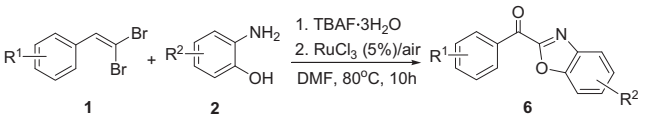


Scheme 2. Tandem pathway for the formation of **6**.

Next, the scope of this reaction with various dibromoethenes (**1**) and 2-aminophenols (**2**) was evaluated under the optimized conditions determined above (as shown in Table 3). In general, all the reactions were efficient and 2-benzoxazyl aryl ketone derivatives (**6**) were obtained in moderate to good yields. For 2-aminophenols with either electron-withdrawing or electrondonating groups, the tandem process proceeded efficiently. In addition, various functional groups, such as nitro, cyano, and halides, on the aromatic ring of dibromoethenes were tolerated under the reaction conditions.

The above process was then extended to the synthesis of 2-benzothiazyl ketones (**7**) by using 2-aminothiophenols (**4**) to react with dibromoethenes. With 2-aminothiophenol as a fixed substrate, we carried out the reaction with various dibromoethenes (Table 4, entries 1–4, 7, and 13). It turned out that all the aromatic substituted dibromoethenes reacted with 2-aminothiophenol smoothly and 2-benzothiazyl ketones (**7**) were isolated in good yields. It was also noted that the electronic effect of the substituents on the aromatic rings affected the yields of **7** and the presence of electron-withdrawing group gave better yields than that of

Table 3
Scope of the reaction leading to 2-benzoxazyl ketones (**6**)[a]

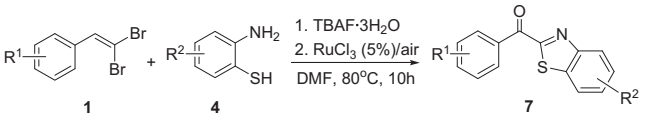


1 2 6

Entry	R^1 in **1**	R^2 in **2**	Product	Yield[b] (%)
1	4-Br	H	**6a**	61
2	4-Br	4-Me	**6b**	58
3	4-Br	4-Cl	**6c**	54
4	4-NO_2	H	**6d**	63
5	4-NO_2	4-Me	**6e**	62
6	3-Br	H	**6f**	61
7	3-Br	4-Me	**6g**	58
8	3-Br	H	**6h**	57
9	3-Br	4-Cl	**6i**	53
10	4-CN	H	**6j**	65

[a] Compounds **1** and **2** (1 mmol), TBAF·$3H_2O$ (4 mmol), $RuCl_3$ (0.05 mmol), DMF (5 mL), 80 °C, 10 h.
[b] Isolated yields.

Table 4
Scope of the reaction leading to 2-benzothiazyl ketones (**7**)[a]

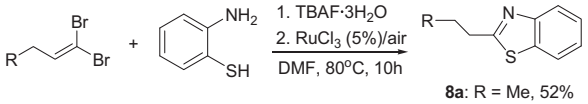


1 4 7

Entry	R^1 in **1**	R^2 in **4**	Product	Yield[b] (%)
1	4-Br	H	**7a**	72
2	4-Me	H	**7b**	65
3	4-OMe	H	**7c**	56
4	4-NO_2	H	**7d**	75
5	H	4-Cl	**7e**	63
6	4-Me	4-Cl	**7f**	64
7	H	H	**7g**	65
8	4-F	4-Cl	**7h**	68
9	H	3-Cl	**7i**	57
10	4-Me	3-Cl	**7j**	56
11	4-Me	5-Me	**7k**	58
12	4-OMe	5-Me	**7l**	53
13	3-Me	H	**7m**	59

[a] Compounds **1** and **4** (1 mmol), TBAF·$3H_2O$ (4 mmol), $RuCl_3$ (0.05 mmol), DMF (5 mL), 80 °C, 10 h.
[b] Isolated yields.

electrondonating group. Additionally, nitro, methyl, methoxy, and halide groups are well compatible with the reaction conditions. On the other hand, aliphatic group-substituted dibromoethenes gave 2-substituted benzothiazoles (**8a** and **8b**) without benzylic oxidation (Scheme 3), indicating that under these mild conditions the benzylic oxidation was highly chemoselective and only occurred with methylene groups immediately between two aromatic moieties.



Scheme 3. Reaction of aliphatic dibromoethenes with 2-aminothiophenol.

It is noted herein that this is the first report that heteroaryl ketones were prepared directly from tandem reaction of *o*-aminothiophenol or *o*-aminophenol with 1,1-dibromoethenes. Recently, we have reported that 2-benzoyl benzothiazoles could be obtained from the condensation of *o*-aminothiophenol and phenyl acetaldehyde under the promotion of $FeCl_3·6H_2O$.[38] To our knowledge, phenyl acetaldehyde derivatives are scarcely commercially available. They are usually obtained through the Darzens condensation between benzaldehydes and α-halo ester to give α,β-epoxy ester and subsequent saponification of α,β-epoxy ester followed by decarboxylation. This sequence of reactions is hard to deal with and the yields of phenyl acetaldehydes are low. On the other hand, 1,1-dibromoetheres used in this protocol can be easily prepared from aldehydes and tetrabromomethane with excellent yields. Therefore, it is reasonable to state that the present study has not only developed new chemistry of 1,2-dibromoethene, but also provided a more practical and sustainable synthetic pathway toward heteroaryl ketones.

3. Conclusion

In summary, TBAF·$3H_2O$ and $RuCl_3$(5%)/air promoted one-pot tandem reaction of 1,1-dibromoethenes with 2-amino(thio)phenols was found to be a promising approach toward the synthetically and pharmaceutically interesting heteroaryl ketones. To the best of our knowledge, this is the first report in which heteroaryl ketones are synthesized directly from 1,1-dibromoethenes. This novel method includes several reactions in one-pot and utilizes economical yet efficient reagents to generate molecular complexity under mild conditions. It is also worth to be noted that it is compatible with various functional groups, which are not tolerated with literature methods utilizing highly reactive organometallic reagents. With the above-mentioned merits, this novel protocol should be valuable for the construction of these kinds of heterocycles with biological and medicinal interests. Biological evaluation of the heteroaryl ketones obtained in this work is currently underway.

4. Experimental section

4.1. General information

Dibromoethenes were prepared through reaction of aldehydes with carbon tetrabromide based on literature procedure.[39] Other reagents and solvents were purchased from commercial suppliers and used without further purification. The ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. Chemical shifts were reported in parts per million from tetramethylsilane (TMS) as internal standard in $CDCl_3$ solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. and coupling constants are given in hertz. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F_{254} 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

4.2. Typical procedure for the preparation of 2-(4-bromo benzyl)benzoxazole (3a)

To a solution of 1-(2,2-dibromovinyl)-4-bromobenzene (1 mmol) in DMF (5 mL) was added TBAF·$3H_2O$ (4 mmol). The mixture was stirred at 60 °C for 1 h. 2-Aminophenol (1 mmol) was added and the mixture was stirred at 60 °C for 2 h. Upon completion, the reaction mixture was cooled to room temperature and diluted with diethyl ether (60 mL). The organic phase was washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (3–5%) to give **3a**. Other 2-benzyl benzoxazoles (**3b**–**e**) and 2-benzylbenzothiazoles (**5a**–**e**) were prepared in a similar manner.

*4.2.1. 2-(4-Bromobenzyl)benzoxazole (**3a**)*[32]. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.22 (s, 2H), 7.24–7.27 (m, 2H), 7.29–7.31 (m, 2H), 7.45–7.48 (m, 3H), 7.67–7.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.6, 110.4, 119.8, 121.4, 124.3, 124.9, 130.7, 131.9, 133.7, 141.2, 151.0, 164.5. MS: *m*/*z* 288 $(MH)^+$.

*4.2.2. 2-(3-Nitrobenzyl)benzoxazole (**3b**).* Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.38 (s, 2H), 7.31–7.33 (m, 2H), 7.47–7.49 (m, 1H), 7.53 (t, *J*=8.0 Hz, 1H), 7.68–7.70 (m, 1H), 7.73 (d, *J*=8.0 Hz, 1H), 8.16 (dd, *J*1=8.0 Hz, *J*2=1.2 Hz, 1H), 8.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.8, 110.5, 120.0, 122.5, 124.1, 124.5, 125.1, 129.8, 135.2, 136.6, 141.1, 148.4, 151.0, 163.6. MS: *m*/*z* 255 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{11}N_2O_3$: 255.077 [M+H], found: 255.0775.

*4.2.3. 2-(3-Nitrobenzyl)-5-methylbenzoxazole (**3c**).* Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 4.36 (s, 2H), 7.12 (d, *J*=8.0 Hz, 1H), 7.34 (d, *J*=8.0 Hz, 1H), 7.47 (s, 1H), 7.52 (t, *J*=8.0 Hz, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 8.15 (d, *J*=8.0 Hz, 1H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 34.8, 109.9, 119.9, 122.5, 124.1, 126.2, 129.7, 134.3, 135.2, 136.7, 141.3, 148.4, 149.2, 163.6. MS: *m*/*z* 269 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_{13}N_2O_3$: 269.0927 [M+H], found: 269.0929.

*4.2.4. 2-(4-Bromobenzyl)-5-chlorobenzoxazole (**3d**).* Pale yellow solid, mp 76–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.21 (s, 2H), 7.23–7.29 (m, 3H), 7.38 (d, *J*=8.8 Hz, 1H), 7.47–7.50 (m, 2H), 7.66 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.6, 111.2, 119.9, 121.5, 125.2, 129.8, 130.7, 132.0, 133.2, 142.3, 149.6, 165.9. MS: *m*/*z* 322 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{10}BrClNO$: 321.9635 [M+H], found: 321.9625.

*4.2.5. 2-(3-Bromobenzyl)benzoxazole (**3e**).* Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.24 (s, 2H), 7.22–7.24 (m, 1H), 7.31–7.33 (m, 3H), 7.42 (d, *J*=8.0 Hz, 1H), 7.47–7.49 (m, 1H), 7.54 (s, 1H), 7.69–7.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.8, 110.5, 119.9, 122.8, 124.3, 124.9, 127.7, 130.3, 130.5, 132.0, 136.9, 141.2, 151.0, 164.3. MS: *m*/*z* 288 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{11}BrNO$: 288.0025 [M+H], found: 288.0019.

*4.2.6. 2-Benzylbenzothiazole (**5a**)*[38]. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.45 (s, 2H), 7.29–7.39 (m, 6H), 7.46 (td, *J*1=7.6 Hz, *J*2=0.8 Hz, 1H), 7.79 (d, *J*=8.0 Hz, 1H), 8.01 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 40.6, 121.5, 122.8, 124.8, 125.9, 127.3, 128.8, 129.1, 135.7, 137.2, 153.2, 171.2. MS: *m*/*z* 226 $(MH)^+$.

*4.2.7. 2-Benzyl-5-chlorobenzothiazole (**5b**)*[38]. Pale yellow solid, mp 74–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.43 (s, 2H), 7.29–7.37 (m, 6H), 7.67 (d, *J*=8.4 Hz, 1H), 7.98 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 40.6, 122.2, 122.6, 125.3, 127.5, 128.9, 129.2, 131.9, 133.9, 136.8, 154.1, 173.3. MS: *m*/*z* 260 $(MH)^+$.

*4.2.8. 2-Benzyl-6-methylbenzothiazole (**5c**)*[38]. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 4.41 (s, 2H), 7.24–7.36 (m, 6H), 7.57 (s, 1H), 7.86 (d, *J*=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 40.5, 121.2, 122.2, 127.2, 127.5, 128.8, 129.1, 134.8, 135.8, 137.3, 151.3, 170.0. MS: *m*/*z* 240 $(MH)^+$.

*4.2.9. 2-Benzyl-4-chlorobenzothiazole (**5d**)*[38]. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.50 (s, 2H), 7.24–7.37 (m, 6H), 7.47 (d, *J*=7.6 Hz, 1H), 7.66 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 40.8, 120.1, 125.3, 126.2, 127.4, 127.5, 128.9, 129.3, 136.9, 137.1, 150.2, 173.0. MS: *m*/*z* 260 $(MH)^+$.

*4.2.10. 2-(4-Fluorobenzyl)benzothiazole (**5e**)*[38]. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.41 (s, 2H), 7.04 (t, *J*=8.4 Hz, 1H), 7.31–7.36 (m, 3H), 7.46 (t, *J*=7.6 Hz, 1H), 7.80 (d, *J*=7.6 Hz, 1H), 7.99 (d, *J*=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.7, 115.6, 115.8, 121.5, 122.8, 124.9, 126.0, 126.1, 130.6, 130.7, 135.5, 153.2, 170.8. MS: *m*/*z* 244 $(MH)^+$.

4.3. Typical procedure for the preparation of 2-(4-bromo benzoyl) benzoxazole (6a)

To a solution of 1-bromo-4-(2,2-dibromovinyl)benzene (1 mmol) in DMF (5 mL) was added TBAF·$3H_2O$ (4 mmol). The mixture was stirred at 80 °C for 1 h. 2-Aminophenol (1 mmol) and $RuCl_3$ (0.05 mmol) were then added. The mixture was stirred at 80 °C for 9 h. Upon completion, the reaction mixture was cooled to room temperature and diluted with diethyl ether (60 mL). The organic phase was washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (3–5%) to give **6a**. Other 2-benzoylbenzoxazoles (**6b**–**j**) and 2-benzoyl benzothiazoles (**7a**–**m**) were prepared in a similar manner.

*4.3.1. 2-(4-Bromobenzoyl)benzoxazole (**6a**)*[16]. Colorless solid, mp 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.38 (m, 2H), 7.57–7.59 (m, 1H), 7.67 (d, *J*=8.8 Hz, 2H), 7.76–7.78 (m, 1H), 8.12 (d, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.6, 120.1, 124.7, 125.4, 126.1, 126.2, 129.0, 132.2, 142.0, 150.7, 162.1, 177.5. MS: *m*/*z* 302 $(MH)^+$.

*4.3.2. 2-(4-Bromobenzoyl)-5-methylbenzoxazole (**6b**).* Yellow solid, mp 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3H), 7.17 (d, *J*=8.4 Hz, 1H), 7.44 (d, *J*=8.4 Hz, 1H), 7.54 (s, 1H), 7.66 (d, *J*=8.4 Hz, 2H), 8.10 (d, *J*=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 110.0, 119.9, 126.0, 126.2, 126.5, 128.9, 132.2, 134.6, 142.1, 148.9, 162.2, 178.9. MS: *m*/*z* 316 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_{11}BrNO_2$: 315.9974 [M+H], found: 315.9981.

*4.3.3. 2-(4-Bromobenzoyl)-5-chlorobenzoxazole (**6c**).* Pale yellow crystals, mp 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.35 (m, 1H), 7.48–7.50 (m, 1H), 7.67 (d, *J*=8.0 Hz, 2H), 7.74 (s, 1H), 8.09 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 119.8, 120.0, 125.6, 126.7, 129.1, 130.2, 132.3, 143.1, 149.3, 163.4, 182.0. MS: *m*/*z* 336 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_8BrClNO_2$: 335.9428 [M+H], found: 335.9426.

*4.3.4. 2-(4-Nitrobenzoyl)benzoxazole (**6d**).* Brown solid, mp 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (t, *J*=8.4 Hz, 1H), 7.62 (t, *J*=8.4 Hz, 1H), 7.75 (d, *J*=8.4 Hz, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 8.42 (d, *J*=8.8 Hz, 2H), 8.78 (d, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.0, 122.6, 123.6, 126.2, 129.2, 132.1, 139.5, 140.6, 150.5, 150.8, 156.4, 178.8. MS: *m*/*z* 269 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_9N_2O_4$: 269.0563 [M+H], found: 269.0568.

*4.3.5. 5-Methyl-2-(4-nitrobenzoyl)benzoxazole (**6e**).* Colorless solid, mp 188–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 7.24–7.25 (m, 1H), 7.50 (d, *J*=8.0 Hz, 1H), 7.60 (s, 1H), 8.36–8.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 110.3, 120.4, 124.2, 127.5, 128.3, 131.0, 135.1, 142.1, 149.2, 160.7, 184.5. MS: *m*/*z* 283 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_{11}N_2O_4$: 283.072 [M+H], found: 283.0711.

*4.3.6. 2-(3-Nitrobenzoyl)benzoxazole (**6f**).* Pink solid, mp 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.44 (m, 2H), 7.63–7.66 (m, 1H), 7.76 (t, *J*=8.0 Hz, 1H), 7.81–7.83 (m, 1H), 8.38–8.41 (m, 1H), 8.58–8.61 (m, 1H), 9.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.0, 110.9, 120.5, 122.5, 125.1, 125.8, 126.1, 130.1, 133.0, 141.8, 150.8, 160.5, 184.7. MS: *m*/*z* 269 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_9N_2O_4$: 269.0563 [M+H], found: 269.0561.

*4.3.7. 5-Methyl-2-(3-nitrobenzoyl)benzoxazole (**6g**).* Pink solid, mp 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 7.22 (d,

J=8.4 Hz, 1H), 7.49 (d, J=8.4 Hz, 1H), 7.58 (s, 1H), 7.72 (t, J=8.0 Hz, 1H), 8.35–8.38 (m, 1H), 8.55–8.57 (m, 1H), 9.06 (t, J=1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 110.2, 120.3, 122.4, 125.6, 127.2, 129.1, 130.1, 132.9, 135.0, 141.9, 148.6, 149.1, 160.6, 180.6. MS: m/z 283 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_{11}N_2O_4$: 283.072 [M+H], found: 283.0729.

*4.3.8. 2-(3-Bromobenzoyl)benzoxazole (**6h**).* Yellow solid, mp 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.52 (m, 2H), 7.58 (t, J=8.0 Hz, 1H), 7.72 (d, J=8.0 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.96 (d, J=8.0 Hz, 1H), 8.55 (d, J=8.0 Hz, 1H), 8.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.9, 122.5, 122.8, 125.9, 128.8, 129.7, 130.2, 133.7, 136.6, 137.1, 140.6, 150.4, 156.6, 179.0. MS: m/z 302 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_9BrNO_2$: 301.9817 [M+H], found: 301.9811.

*4.3.9. 2-(3-Bromobenzoyl)-5-chlorobenzoxazole (**6i**).* Colorless crystals, mp 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (t, J=8.0 Hz, 1H), 7.54 (d, J=8.0 Hz, 1H), 7.65 (d, J=8.4 Hz, 1H), 7.82 (d, J=8.0 Hz, 1H), 7.95 (d, J=2.0 Hz, 1H), 8.53 (d, J=8.0 Hz, 1H), 8.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.7, 122.2, 122.9, 129.2, 129.6, 130.2, 131.5, 133.7, 136.3, 137.3, 141.6, 148.9, 157.5, 178.6. MS: m/z 336 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_8BrClNO_2$: 335.9428 [M+H], found: 335.9421.

*4.3.10. 2-(4-Cyanobenzoyl)benzoxazole (**6j**).* Colorless solid, mp 184–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.43 (m, 2H), 7.61–7.64 (m, 1H), 7.82–7.84 (m, 3H), 8.37 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.9, 114.7, 120.5, 125.1, 126.1, 127.9, 128.8, 131.1, 132.7, 141.8, 150.9, 160.9, 179.6. MS: m/z 249 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_9N_2O_2$: 249.0665 [M+H], found: 249.0664.

*4.3.11. 2-(4-Bromobenzoyl)benzothiazole (**7a**)[17].* Pale yellow solid, mp 121–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.62 (m, 2H), 7.69–7.73 (m, 2H), 8.02–8.04 (m, 1H), 8.23–8.25 (m, 1H), 8.46–8.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.2, 125.7, 127.0, 127.8, 129.5, 131.8, 132.7, 133.6, 137.0, 153.8, 166.7, 184.3. MS: m/z 318 $(MH)^+$.

*4.3.12. 2-(4-Methylbenzoyl)benzothiazole (**7b**)[17].* Colorless crystals, mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H, CH3), 7.36 (d, J=8.0 Hz, 2H), 7.53–7.58 (m, 2H), 7.99 (t, J=8.4 Hz, 1H), 8.24 (d, J=8.0 Hz, 1H), 8.48 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 122.2, 125.7, 126.9, 127.4, 127.5, 129.3, 129.7, 131.4, 132.3, 136.9, 145.0, 153.9, 167.4, 184.9. MS: m/z 254 $(MH)^+$.

*4.3.13. 2-(4-Methoxylbenzoyl)benzothiazole (**7c**)[40].* Colorless solid, mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.93 (s, 3H), 7.05 (d, J=8.8 Hz, 2H), 7.52–7.61 (m, 2H), 8.02 (d, J=8.0 Hz, 1H), 8.24 (d, J=8.0 Hz, 1H), 8.65 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.6, 113.9, 122.1, 125.5, 126.8, 127.4, 127.7, 133.8, 136.8, 153.9, 164.4, 167.9, 183.5. MS: m/z 270 $(MH)^+$.

*4.3.14. 2-(4-Nitrobenzoyl)benzothiazole (**7d**).* Yellow solid, mp 171–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59–7.63 (m, 2H), 8.04–8.06 (m, 1H), 8.25–8.28 (m, 1H), 8.40 (d, J=8.8 Hz, 2H), 8.74 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.3, 123.5, 124.3, 125.9, 127.3, 128.3, 132.3, 137.2, 139.7, 153.8, 165.8, 183.9. MS: m/z 285 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_9N_2O_3S$: 285.0335 [M+H], found: 285.0332.

*4.3.15. 2-Benzoyl-5-chlorobenzothiazole (**7e**)[38].* Colorless crystals, mp 133–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.59 (m, 3H), 7.69 (t, J=7.6 Hz, 1H), 7.95 (d, J=7.6 Hz, 1H), 8.24 (d, J=2.0 Hz, 1H), 8.55 (d, J=7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.0, 125.2, 128.2, 128.6, 131.3, 133.0, 134.1, 134.6, 135.2, 154.6, 168.9, 185.0. MS: m/z 274 $(MH)^+$.

*4.3.16. 5-Chloro-2-(4-methylbenzoyl)benzothiazole (**7f**)[38].* Yellow solid, mp 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 7.36 (d, J=8.4 Hz, 2H), 7.51 (dd, $J1$=8.4 Hz, $J2$=1.6 Hz, 1H), 7.93 (d, J=8.4 Hz, 1H), 8.22 (d, J=1.6 Hz, 1H), 8.46 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 122.9, 125.1, 128.1, 129.3, 131.4, 132.0, 132.9, 135.1, 145.3, 154.6, 169.2, 184.4. MS: m/z 288 $(MH)^+$.

*4.3.17. 2-Benzoylbenzothiazole (**7g**)[40].* Pale yellow solid, mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.63 (m, 4H), 7.69 (t, J=7.2 Hz, 1H), 8.04 (d, J=7.2 Hz, 1H), 8.27 (d, J=7.2 Hz, 1H), 8.58 (d, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.2, 125.7, 126.9, 127.6, 128.5, 131.3, 133.9, 134.9, 137.0, 153.9, 167.1, 185.4. MS: m/z 240 $(MH)^+$.

*4.3.18. 5-Chloro-2-(4-fluorobenzoyl)benzothiazole (**7h**)[38].* Pink solid, mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.26 (m, 2H), 7.53 (dd, $J1$=8.8 Hz, $J2$=2.0 Hz, 1H), 7.94 (d, J=8.8 Hz, 1H), 8.23 (d, J=1.6 Hz, 1H), 8.64–8.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.7, 115.9, 123.0, 125.2, 128.3, 130.9, 133.1, 134.2, 134.3, 135.2, 154.5, 165.2, 168.8, 183.1. MS: m/z 292 $(MH)^+$.

*4.3.19. 2-Benzoyl-4-chlorobenzothiazole (**7i**)[38].* Pale yellow crystals, mp 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (t, J=8.0 Hz, 1H), 7.57–7.71 (m, 4H), 7.92 (d, J=8.0 Hz, 1H), 8.68 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 120.6, 127.0, 128.0, 128.5, 130.6, 131.5, 134.1, 134.6, 138.4, 151.0, 167.8, 184.5. MS: m/z 274 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_9ClNOS$: 274.0094 [M+H], found: 274.0099.

*4.3.20. 4-Chloro-2-(4-methylbenzoyl)benzothiazole (**7j**)[38].* Colorless solid, mp 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 7.38 (d, J=8.0 Hz, 2H), 7.47 (t, J=8.0 Hz, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.91 (d, J=8.0 Hz, 1H), 8.59 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 120.6, 127.0, 127.9, 129.4, 130.5, 131.7, 132.0, 138.4, 145.3, 151.1, 167.5, 184.1. MS: m/z 288 $(MH)^+$.

*4.3.21. 6-Methyl-2-(4-methylbenzoyl)benzothiazole (**7k**)[38].* Pale yellow solid, mp 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 2.54 (s, 3H), 7.34–7.40 (m, 3H), 7.80 (s, 1H), 8.11 (d, J=8.4 Hz, 1H), 8.46 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.8, 121.7, 125.1, 128.7, 129.2, 131.3, 132.5, 137.2, 138.1, 144.8, 152.1, 166.4, 185.0. MS: m/z 268 $(MH)^+$.

*4.3.22. 2-(4-Methoxybenzoyl)-6-methylbenzothiazole (**7l**)[38].* Colorless solid, mp 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 3.92 (s, 3H), 7.04 (d, J=8.8 Hz, 2H), 7.39 (d, J=8.4 Hz, 1H), 7.79 (s, 1H), 8.10 (d, J=8.4 Hz, 1H), 8.63 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.8, 55.5, 113.8, 121.7, 125.0, 127.9, 128.6, 133.8, 137.2, 138.0, 152.1, 164.2, 166.8, 183.5. MS: m/z 284 $(MH)^+$.

*4.3.23. 2-(3-Methylbenzoyl)benzothiazole (**7m**)[38].* Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 7.44–7.50 (m, 2H), 7.54–7.62 (m, 2H), 8.03 (d, J=8.0 Hz, 1H), 8.25–8.28 (m, 2H), 8.38 (d, J=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 122.2, 125.7, 126.9, 127.6, 128.4, 128.6, 131.4, 134.8, 134.9, 137.0, 138.3, 153.8, 167.2, 185.7. MS: m/z 254 $(MH)^+$.

*4.3.24. 2-Propylbenzothiazole (**8a**).* Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (t, J=7.6 Hz, 3H), 1.90–1.96 (m, 2H), 3.11 (t, J=7.6 Hz, 2H), 7.35 (t, J=7.6 Hz, 1H), 7.46 (t, J=7.6 Hz, 1H), 7.85 (d, J=8.0 Hz, 1H), 7.98 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 23.1, 36.2, 121.4, 122.5, 124.6, 125.8, 126.6, 126.8, 135.1, 153.2, 172.2. MS: m/z 178 $(MH)^+$.

*4.3.25. 2-Phenethylbenzothiazole (**8b**)[17].* Colorless solid, mp 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.22 (t, J=8.0 Hz, 2H), 3.44 (t, J=8.0 Hz, 2H), 7.21–7.38 (m, 6H), 7.46 (t, J=8.0 Hz, 1H), 7.83 (d, J=8.0 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ:

35.5, 36.0, 121.5, 122.6, 124.7, 125.9, 126.4, 128.4, 128.6, 135.1, 140.2, 153.1, 170.9. MS: m/z 240 $(MH)^+$.

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Supplementary data

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