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Full Paper

$RuCl_3 \cdot 3H_2O$ Catalyzed Tandem Reaction of Alkynylbromides with 2-Aminothiophenols in Water: A Convenient Synthesis of 2-Benzoylbenzothiazoles

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$RuCl_3 \cdot 3H_2O$ catalyzed tandem reaction of alkynyl bromides with 2-aminothiophenols mediated by water is shown to represent a convenient synthesis of 2-benzoylbenzothiazoles. In addition, the Ru(III) catalyst could be readily recovered and efficiently reused together with water up to three times.

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Introduction

Heteroaryl ketones are valuable synthetic synthons and frequent structural units of many therapeutic agents.[1–5] To date, various methods, such as Friedel–Crafts acylation of heteroaromatic rings,[6] condensation of metalated heterocycles with nitriles,[7] oxidation of 1-heteroaromatic-1-alkanols,[8–9] reaction of acyl chlorides with organometallic reagents,[10] Pd-catalyzed carbonylative coupling of aryl halides with organometallic reagents,[11] and Pd-catalyzed carbonylation of heteroarenes,[12] have been developed for the synthesis of heteroaryl ketones. While these methods are generally efficient and reliable, some of them still suffer from the need to use 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 so mild reaction conditions are usually required. Further, the solvents used are often volatile and relatively toxic and not well suited to industrial settings. As a result, there would be widespread interest in developing more practical and sustainable methods to produce heteroaryl ketones.

As a sustainable solvent, water is considered as one of the most desirable since it is abundant, inexpensive and safe. To develop synthetic procedures mediated by water is therefore a common and important aim of green and sustainable chemistry.[13,14]

Based on the above observations and as a continuation of our interests in developing new synthetic strategies for the preparation of heterocyclic compounds by using water as the reaction medium[15] or by using $RuCl_3 \cdot 3H_2O$ as an efficient and selective oxidative catalyst,[16] we envisioned a new route towards heteroaryl ketones, specifically here benzoylbenzothiazoles, via water mediated, $RuCl_3 \cdot 3H_2O$ promoted coupling of alkynyl bromides with 2-aminothiophenols and benzylic oxidation of the *in situ* formed 2-benzylbenzothiazole. Alkynyl bromides attracted our attention because they are highly versatile synthetic building blocks and have been used in the synthesis of a plethora of biologically and synthetically interesting compounds, such as alkynylselenides,[17] alkynylsulfonamides,[18] heterocycles,[19–20] ynamides,[21] and enynes,[22] etc.

Herein, we report our preliminary results in this regard.

Results and Discussion

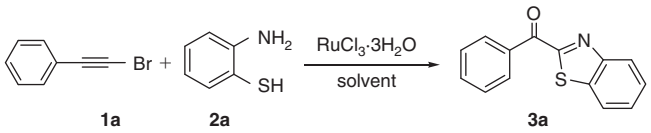
To check the feasibility of our envisioned route, several experiments were carried out by using 1-(2-bromoethynyl) benzene (**1a**) and 2-aminothiophenol (**2a**) as model substrates (Scheme 1).

Initially, **1a** and **2a** were treated with 0.05 equiv of $RuCl_3 \cdot 3H_2O$ in water. It turned out that **3a** could be obtained in 55 % yield after the mixture of **1a** and **2a** was stirred at 40°C for 15 h (Table 1, entry 1). Higher reaction temperatures resulted in shorter reaction times and higher yields (entries 2–4). It was also observed that increasing the amount of $RuCl_3 \cdot 3H_2O$ to 0.1 equiv improved the yield of **3a** to 81 % (entry 5). On the other hand, in the absence of either $RuCl_3 \cdot 3H_2O$ or air, only trace amount of **3a** were formed according to TLC analysis, indicating that both $RuCl_3 \cdot 3H_2O$ (cat.) and air are indispensable for the formation of **3a** (entries 7 and 8). It is worth noting that with a catalytic amount of $RuCl_3 \cdot 3H_2O$, air is actually acting as a stoichiometric oxidant for this tandem reaction.

In order to compare the applicability of water with that of routinely used organic solvents as medium for this tandem process, the reaction of **1a** and **2a** was tried in THF, CH_2Cl_2, or CH_3CN. It followed that these organic solvents afforded **3a** in lower yields even though the reaction systems were completely homogeneous (Table 1, entries 9–11). This does not necessarily prove that water is the best solvent, as longer reaction times for these lower boiling organic solvents may lead to an increased yield. However, the aqueous conditions that we have discovered to be effective are far more preferable from the perspective of green chemistry.

With the optimized reaction conditions, the scope and limitations of this reaction were explored. The results included

in Table 2 show that aryl substituted alkynyl bromides with either electron-withdrawing or electron-donating groups on the aryl ring underwent this tandem process efficiently (entries 1–16). On the other hand, benzyl substituted alkynyl bromides gave



Scheme 1.

Table 1. Optimization study for the synthesis of 3a[A]

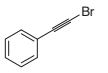
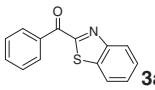
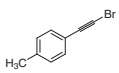
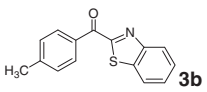
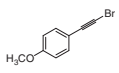
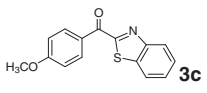
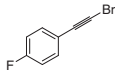
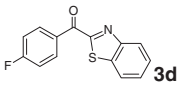
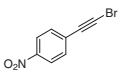
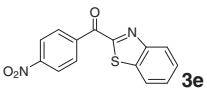
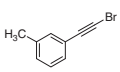
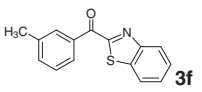
Entry	Solvent	$RuCl_3·3H_2O$ [equiv]	Temp. [°C]	Time [h]	**3a** [%][B]
1	H_2O	0.05	40	15	55
2	H_2O	0.05	60	9	67
3	H_2O	0.05	80	6	75
4	H_2O	0.05	100	6	73
5	**H_2O**	**0.1**	**80**	**6**	**81**
6	H_2O	0.2	80	6	81
7	H_2O	–	80	6	Trace
8	H_2O	0.1	80	6	Trace[C]
9	THF	0.1	Reflux	6	71
10	CH_2Cl_2	0.1	Reflux	6	72
11	CH_3CN	0.1	Reflux	6	64

[A]**1a** and **2a** (1 mmol), H_2O (5 mL), other solvents (10 mL).
[B]Isolated yields.
[C]Under N_2.

2-phenethyl benzothiazoles without benzylic oxidation (entries 17–18), indicating that under these mild conditions the benzylic oxidation was highly chemoselective and only occurred with methylene groups immediately between two aromatic moieties. As for the 2-aminothiophenol substrates, reactions with 3-chloro-2-aminothiophenol (entries 10–13) were less effective than those with 2-aminothiophenol, 4-chloro- or 5-methyl-2-aminothio phenol, probably due to steric hindrance. In addition, it was observed that various functional groups, such as methyl, methoxy, nitro, and halides, were compatible with the reaction conditions.

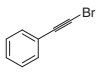
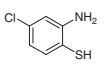
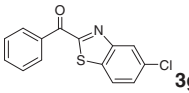
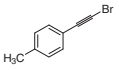
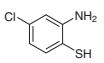
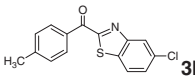
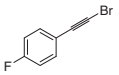
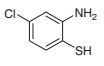
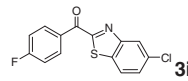
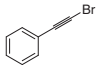
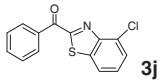
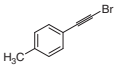
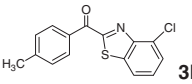
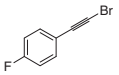
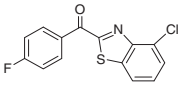
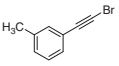
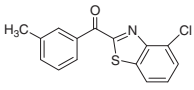
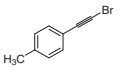
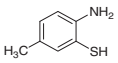
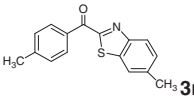
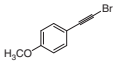
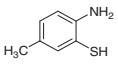
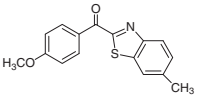
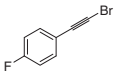
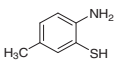
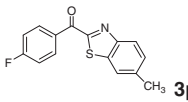
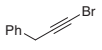
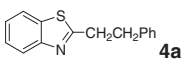
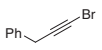
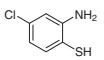
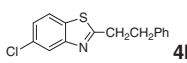
This is the first report of benzothiazol-2-yl ketones prepared from tandem reactions of alkynyl bromides with *o*-aminothiophenols by using water as the reaction medium. Recently, we have reported that 2-benzoyl benzothiazoles could be obtained from the condensation of *o*-aminothiophenol and phenyl acetaldehyde under the promotion of $FeCl_3·6H_2O$ in $[bmim]BF_4$,[23] or of 1,1-dibromoethenes with 2-amino(thio) phenols promoted by $TBAF·3H_2O$ and $RuCl_3$ by using DMF as the reaction medium.[24] To our knowledge, phenyl acetaldehyde derivatives are usually obtained through the Darzens condensation between benzaldehydes and α-halo esters to give α,β-epoxy esters and subsequent saponification of α,β-epoxy esters followed by decarboxylation. This sequence of reactions is hard to deal with and the yields of phenyl acetaldehydes are low. Alkynyl bromides used in this protocol, on the other hand, can be efficiently prepared from the condensation of aldehydes with tetra-bromomethane followed by base promoted dehydrobromination.[25] In addition to readily available starting materials, the synthetic strategy developed in this paper features another advantage over our previously reported protocols in that

Table 2. Preparation of various benzothiazol-2-yl ketones[A]

Entry	1	2	3	Yield [%][B]
1			 **3a**	**81**
2			 **3b**	**80**
3			 **3c**	**78**
4			 **3d**	**82**
5			 **3e**	**86**
6			 **3f**	**75**

(*Continued*)

Table 2. (Continued)

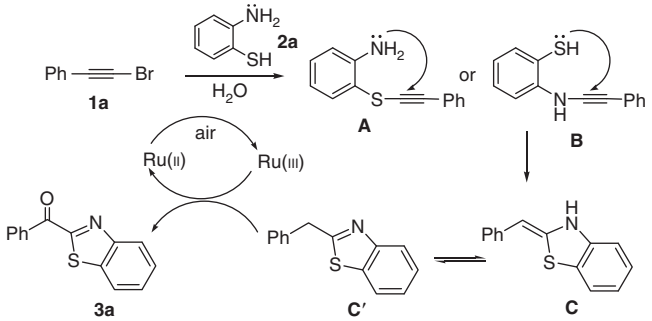
Entry	1	2	3	Yield [%][B]
7			 **3g**	**81**
8			 **3h**	**73**
9			 **3i**	**80**
10			 **3j**	**65**
11			 **3k**	**66**
12			 **3l**	**62**
13			 **3m**	**60**
14			 **3n**	**79**
15			 **3o**	**77**
16			 **3p**	**80**
17			 **4a**	**73**
18			 **4b**	**76**

[A]**1** and **2** (1 mmol), $RuCl_3 \cdot 3H_2O$ (0.1 mmol), H_2O (5 mL), 80°C, 6 h.
[B]Isolated yields.

water is used as an environmentally sustainable and efficiency-enhancing reaction medium.

Based on the above observations, a plausible pathway for the formation of **3a** is depicted in Scheme 2. First, condensation of **1a** and **2a** affords an alkynylthiophenyl amine (**A**) or alkynylaminothiophenol (**B**), followed by *intramolecular* cyclization to give 2-benzylbenzothiazole (**C′**). Ru(III)/air promoted oxidation of the benzylic methylene moiety of **C′** affords 2-benzothiazyl ketone (**3a**) to conclude the tandem process. Meanwhile, the in situ formed Ru(II) could be oxidized back to Ru(III) by air to complete the catalytic cycle.

Finally, the recovery and reuse of $RuCl_3$ together with water was studied by using **1a** and **2a** as model substrates. Upon completion of the reaction, the resulting mixture was extracted with diethyl ether (10 mL × 3) to remove the product and the remaining aqueous phase was ready for reuse. The recovered Ru(III)/H_2O was reused three times and gave **3a** in yields of 80, 78, and 70 %, respectively, for each reuse.



Scheme 2.

In summary, an efficient and environmentally sustainable preparation of 2-benzoylbenzothiazoles was developed. To our knowledge, this is the first report in which heteroaryl ketones have been synthesized from alkynyl bromides through a Ru(III)/air promoted tandem process mediated by water. In addition, the Ru(III) catalyst could be readily recovered and efficiently reused together with water up to 3 times. Current studies are in progress to extend the synthetic potential of this novel procedure.

Experimental Section

Thin-layer chromatography (TLC) was carried out with silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with a UV lamp. NMR spectra were recorded using TMS as internal standard and peak multiplicities are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; td, triplet of doublets. Chemical shifts (δ) were expressed in ppm downfield from the internal standard tetramethylsilane and coupling constants *J* were given in Hz.

*Typical Procedure for the Preparation of **3a***

A mixture containing 1-(2-bromoethynyl)benzene (**1a**, 1 mmol), 2-aminothiophenol (**2a**, 1 mmol) and $RuCl_3 \cdot 3H_2O$ (0.1 mmol) in water (5 mL) was stirred at 80°C for 6 h. Upon completion, the mixture was extracted with diethyl ether (5 mL × 3). The combined organic phases were concentrated under vacuum. The crude product was purified by column chromatography eluting with ethyl acetate/hexane (3–5 %) to give **3a** in a yield of 81 %. **3b**-**3q** were obtained in a similar manner.

*2-Benzoylbenzothiazole (**3a**)*[26]

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 $(MH)^+$.

*2-(4-Methylbenzoyl)benzothiazole (**3b**)*[26]

Colourless crystals, mp 94–96°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H, CH_3), 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 $(MH)^+$.

*2-(4-Methoxylbenzoyl)benzothiazole (**3c**)*[27]

Colourless 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 $(MH)^+$.

*2-(4-Fluorobenzoyl)benzothiazole (**3d**)*[27]

Colourless solid, mp 116–118°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22–7.26 (m, 2H), 7.56–7.61 (m, 2H), 8.02–8.04 (m, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 8.65–8.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.6, 115.9, 122.2, 125.7, 127.0, 127.7, 131.2, 134.1, 134.2, 136.9, 153.8, 167.0, 183.6. MS: *m/z* 258 $(MH)^+$.

*2-(4-Nitrobenzoyl)benzothiazole (**3e**)*[27]

Yellow solid, mp 177–178°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 $(MH)^+$.

*2-(3-Methylbenzoyl)benzothiazole (**3f**)*[23]

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 $(MH)^+$.

*2-Benzoyl-5-chlorobenzothiazole (**3g**)*[23]

Colourless 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 $(MH)^+$.

*5-Chloro-2-(4-methylbenzoyl)benzothiazole (**3h**)*[23]

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, J_1 = 8.4 Hz, J_2 = 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 $(MH)^+$.

*5-Chloro-2-(4-fluorobenzoyl)benzothiazole (**3i**)*[23]

Pink solid, mp 149–151°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.26 (m, 2H), 7.53 (dd, J_1 = 8.8 Hz, J_2 = 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 $(MH)^+$.

*2-Benzoyl-4-chlorobenzothiazole (**3j**)*[23]

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 $(MH)^+$.

*4-Chloro-2-(4-methylbenzoyl)benzothiazole (**3k**)*[23]

Colourless 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-Chloro-2-(4-fluorobenzoyl)benzothiazole (**3l**)*[23]

Colourless solid, mp 121–123°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.28 (m, 2H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 8.76–8.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.8, 116.0, 120.7, 127.1, 128.2, 130.6, 134.4, 134.5, 138.4, 150.9, 167.6, 182.8. MS: *m/z* 292 $(MH)^+$.

*4-Chloro-2-(3-methylbenzoyl)benzothiazole (**3m**)*[23]

Colourless solid, mp 128–130°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 7.45–7.51 (m, 3H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 8.43 (s, 1H), 8.52 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 120.7, 127.0, 128.0, 128.6, 128.9, 130.6, 131.8, 134.5, 135.0, 138.3, 138.4, 151.0, 167.9, 184.7. MS: *m/z* 288 $(MH)^+$.

*6-Methyl-2-(4-methylbenzoyl)benzothiazole (**3n**)*[23]

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 $(MH)^+$.

*2-(4-Methoxybenzoyl)-6-methylbenzothiazole (**3o**)*[23]

Colourless 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 $(MH)^+$.

*6-Methyl-2-(4-fluorobenzoyl)benzothiazole (**3p**)*[23]

Colourless solid, mp 133–135°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.55 (s, 3H), 7.22 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.81 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 8.64–8.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.8, 115.6, 115.8, 121.7, 125.2, 128.9, 131.4, 134.1, 134.1, 137.3, 138.4, 152.0, 166.0, 180.5. MS: *m/z* 272 $(MH)^+$.

*2-Phenethylbenzothiazole (**4a**)*[26]

Colourless 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 $(MH)^+$.

*5-Chloro-2-phenethylbenzothiazole (**4b**)*

Pale brown solid, mp 93–95°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.20 (t, $J = 8.0$ Hz, 2H), 3.42 (t, $J = 8.0$ Hz, 2H), 7.21–7.34 (m, 6H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.4, 36.0, 122.2, 122.5, 125.2, 126.5, 128.4, 128.6, 132.0, 133.4, 139.9, 154.1, 172.9. MS: *m/z* 274 $(MH)^+$. HRMS (FAB) calcd for $C_{15}H_{13}ClNS$: 274.0458 [M+H], found: 274.0451.

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