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AN EFFICIENT ROUTE FOR THE SYNTHESIS OF 2-ARYLBENZOTHIAZOLES IN AN IONIC LIQUID, USING ULTRASOUND IRRADIATION

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Abstract – The condensation of 2-aminothiophenol and aromatic aldehydes promoted by an ionic liquid of [*n*-HexylNEt$_3$][HSO$_4$] results 2-arylbenzothiazoles in high yields under ultrasound irradiation.

2-Arylbenzothiazoles exhibit unique biological and pharmaceutical properties, including antifungal and antiviral activity, rendering them suitable as, e.g., anticancer agents and caspase inhibitors.[1] Thus, 2-arylbenzothiazoles have received attention in the fields of chemistry, biology, and medicine.

Two main routes for the synthesis of 2-arylbenzothiazoles have been reported. The first synthesis route couples benzothiazole to an aromatic ring via the loss of a leaving group, while employing metal catalysts such as iron(III) nitrate nonahydrate,[2] NiBr$_2$(DME) (DME = 1,2-dimethoxyethane),[3] palladium diacetate,[4] and nickel(II) acetate tetrahydrate.[5] This method has been reported for the synthesis of Cu$_2$ (4,4'-oxybis(4,4'-oxybis(benzoate)))$_2$(4,4'-bipyridine) [Cu$_2$(OBA)$_2$(BPY)].[6] The second synthesis route involves a cyclic reaction of 2-aminothiophenol with aromatic aldehydes, catalyzed by a Lewis acid such as scandium tris(trifluoromethanesulfonate),[7] vanadium(IV)-salen complex,[8] ceric(IV) ammonium nitrate,[9] or nano-crystalline sulfated zirconia.[10] The first route involves the use of expensive metals such as palladium and nickel, which potentially remain in the product and cannot be recycled, thus causing considerable environmental pollution. The second route presents similar environmental dangers due to the use of metal-containing catalysts.

Environmentally friendly chemicals and less harmful synthesis routes have therefore become attractive alternatives to the abovementioned routes in synthetic organic chemistry.

In this paper, we describe an efficient and harmless synthesis of 2-arylbenzothiazoles, involving the direct reaction of aryl aldehydes with 2-aminothiophenol in an ionic liquid upon ultrasonic irradiation.

Ultrasonic irradiation is increasingly used in the organic synthesis[11] of natural products,[12] nucleic acids,[13] pyrimidine derivatives,[14] pyridine derivatives,[15] and pyrazoles derivatives.[16] While traditional kettle reactions generate energy by heat radiation and exchange, ultrasonic irradiation generates energy at lower temperatures, is easier to control, and facilitates higher yields over shorter reaction times.[17] Ionic liquids are also widely used, i.e., as solvents,[18] and in chemical processes,[19] such as separations,[20] homogeneous catalysis,[21] and polymerizations.[22]

A few organic reactions using both ultrasound and ionic solutions have been reported.[23] In this study, 2-arylbenzothiazoles was synthesized using an effective metal-free catalytic method. There is no metal residue, and 2-arylbenzothiazoles are synthesized efficiently.

The synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones with the [Et_3NH][HSO_4] ionic liquid via the Biginelli reaction has been reported.[24] We used this procedure to synthesize 2-arylbenzothiazole; however, the product yield was low (56.1%, Entry 1 in Table 1). During the reaction, *p*-methylbenzaldehyde, 2-aminothiophenol, and the triethylamine sulfate ionic liquid initially mixed well; however, coagulation occurred, thereby forming solid particles that could not be dissolved even when vigorously stirred with a glass rod. The low solubility of 2-arylbenzothiazole in the ionic liquid led to the formation of an undissolved product, inhibiting further reaction and resulting in a low product yield.

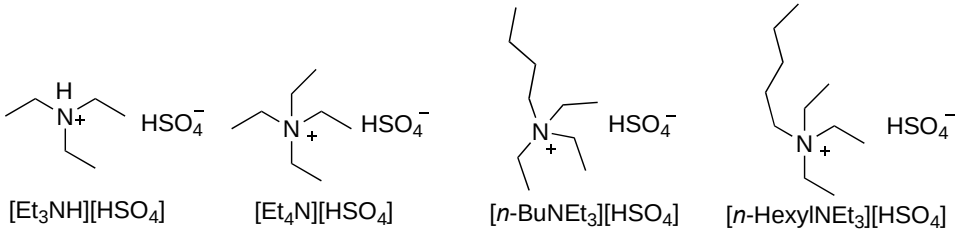
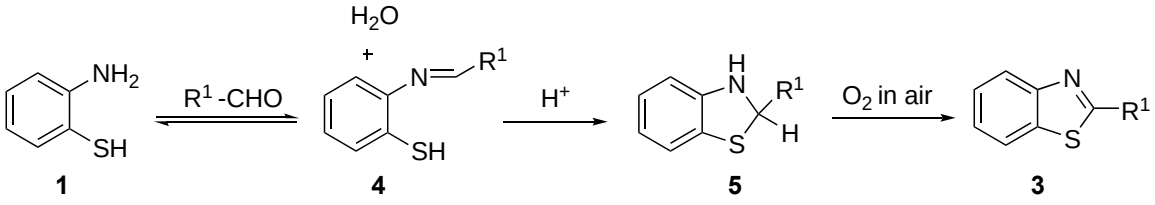


Figure 1. Various structures of ionic liquid

We then replaced the [Et_3NH][HSO_4] ionic liquid with [Et_4N][HSO_4] and [*n*-$BuNEt_3$][HSO_4]; however, the solution became sticky in both cases (Entries 2 and 3). Slightly higher yields were achieved with [*n*-$BuNEt_3$][HSO_4] (80.5%, Entry 3 in Table 1) than those with [Et_4N][HSO_4] (79.3%, Entry 2 in Table 1). We attributed the seemingly superior compatibility between [*n*-$BuNEt_3$][HSO_4] and 2-arylbenzothiazole to the presence of the four-carbon alkyl substituent group of [*n*-$BuNEt_3$][HSO_4]. Exploiting the advantage of longer chains, we synthesized an [*n*-$HexylNEt_3$][HSO_4] for use as the ionic liquid in further experiments. Long alkyl chains have better solubility with benzothiazole, making the reaction mixture more homogeneous. Non-uniformity of the reaction is avoided, and the reaction is carried out better. At 80 °C, according to TLC detection, no raw material was observed after 8 h of reaction, and subsequent reactions were set at 8 h. At 8 h reaction, yields reached 50.0% (frequency of ultrasound, 25 kHz, Entry 4), 92.1% (40 kHz, Entry 6), and 92.0% (59 kHz, Entry 5) respectively. In order to reduce energy

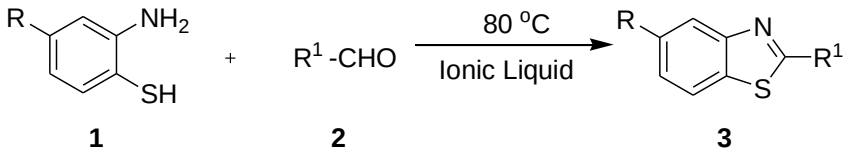
consumption, a 40 KHZ ultrasonic instrument was selected. We performed the reaction at different reaction temperatures of 20 ℃, 50 ℃, 80 ℃, and 100 ℃ and obtained yields of 20.1%, 30.1%, 92.1%, and 50.3%, respectively. The yield of 92.1%, obtained at 80 ℃, was higher than the reported values (85.7%).[25] While the yields increased with temperature, a decrease was observed at 100 °C. We attributed this to the possible decomposition of the ionic liquid. A yield of 75.2% was obtained when ultrasonic cleaner was replaced by mechanical agitation at 80 ℃ for 8 h.

A summary of the reaction parameters has been included in Table 1. These show the yields for 2-arylbenzothiazoles when synthesized in an ionic liquid upon ultrasonic irradiation, using various aromatic aldehydes and 2-aminothiophenol. High yields were obtained for both aromatic aldehydes with electron-withdrawing and electron-donating groups. Yields for aromatic aldehydes with strong electron-withdrawing groups -NO_2 (4-O_2N, 75.1%; 3-O_2N, 71.2%; 2-O_2N, 50.6%;) and -CF_3 (4-CF_3, 85.2%; 3-CF_3, 83.0%; 2-CF_3, 83.2%) are displayed in entries 14-19. According to reported reaction mechanisms, amines and aldehydes first form unstable imines. The double bond of these imines is then attacked by the thiophenol nucleus, followed by oxidation, to form the thermodynamically stable benzopyrazole.[26]



Scheme 1. Reaction mechanism

Table 1. Synthesis of 2-arylbenzothiazoles using an ionic liquid[a]



Entry	Product	R	R^1	Yield, % (lit.)[b]	MP °C (lit.)
1	**3a**	H	4-MeC_6H_5	56.1[c]	-
2	**3a**	H	4-MeC_6H_5	79.3[d]	-
3	**3a**	H	4-MeC_6H_5	80.5[e]	-
4	**3a**	H	4-MeC_6H_5	50.0[f]	-
5	**3a**	H	4-MeC_6H_5	92.0[g]	-
6	**3a**	H	4-MeC_6H_5	92.1(85.7)[25]	82-85(85-86)[27]
7	**3b**	H	3-MeC_6H_5	90.3(89.0)[28]	66-69(66.7-67.5)[29]
8	**3c**	H	2-MeC_6H_5	83.2(80.0)[30]	50-53 (51.1-52)[29]
9	**3d**	H	C_6H_5	91.5(85.0)[25]	111-113(112-114) [31]
10	**3e**	H	4-ClC_6H_5	92.3(86.0)[25]	113-116(114)[27]

11	**3f**	H	4-BrC_6H_5	90.1(90.0)[28]	129-131(130)[32]
12	**3g**	H	4-FC_6H_5	89.6(97.0)[28]	99-101(99-100)[33]
13	**3h**	H	4-$MeOC_6H_5$	90.5(81.4)[25]	123-124(121)[27]
14	**3i**	H	4-$CF_3C_6H_5$	85.2(80.0)[34]	157-159(156.5-157.1)[35]
15	**3j**	H	3-$CF_3C_6H_5$	83.0(75)[35]	92-94 (93.3-93.8)[35]
16	**3k**	H	2-$CF_3C_6H_5$	83.2(82)[35]	Liquid
17	**3l**	H	4-$O_2NC_6H_5$	75.1(53)[36]	234-236 (234-236)[37]
18	**3m**	H	3-$O_2NC_6H_5$	71.2(33.4)[25]	184-186(183-185)[38]
19	**3n**	H	2-$O_2NC_6H_5$	50.6(30.0)[39]	235-237(234-236)[40]
20	**3o**	H	4-(1-Naphthyl)	90.5(60.0)[41]	77-79(78-79)[41]
21	**3p**	H	4-(2-Naphthyl)	93.4(85.0)[28]	128-130(129-130)[42]
22	**3q**	Me	C_6H_5	94.5(81)[43]	145-146(144.2-145.7)[29]
23	**3r**	CF_3	C_6H_5	83.8(79.0)[44]	130-132(131-133)[45]

[a] Reaction condition: arylaldehyde (1.2 mmol), 2-aminothiophenol (1.2 mmol), and the ionic liquid = [*n*-HexylNEt$_3$][HSO_4] (20 mL), at 80 ^oC, 8 h, Frequency of ultrasound, 40 kHz; [b] Isolated yields; [C] ionic liquid = [Et_3NH][HSO_4]; [d] ionic liquid = [Et_4N][HSO_4]; [e] ionic liquid = [*n*-BuNEt$_3$][HSO_4]; [f] Frequency of ultrasound, 25 kHz; [g] Frequency of ultrasound, 59 kHz

In conclusion, we successfully developed a simple and efficient method for the synthesis of 2-arylbenzothiazoles by a reaction of arylaldehydes and 2-aminothiophenol in an ionic liquid upon ultrasonic irradiation. The results show that the longer the alkyl group in the ionic solution, the better the reaction effect, and the best effect is observed. The method makes use of simple raw materials, does not require the addition of a metal catalyst or other organic solvents, and is easily controlled with the use of an ultrasonic cleaner.

EXPERIMENTAL

Liquid aldehydes and 2-aminothiophenol were purified by distillation in an inert gas. Solid aldehydes were stored in an inert gas atmosphere. An AVANCE 400 MHz Superconducting Fourier Nuclear Magnetic Resonance Spectrometer was used, with tetramethylsilane as the internal standard and either $CDCl_3$ or dimethyl sulfoxide (DMSO) as the solvent. Ultrasonic cleaners were purchased from Skymen Cleaning Equipment Shenzhen Co., Ltd. Triethylammonium sulfate was purchased from Shanghai Titan Technology Co., LTD, while triethylammonium hydrogen sulfate, *n*-butyltriethylamonium hydrogen sulfate, and *n*-hexyltriethylamonium hydrogen sulfate were synthesized according to a previously reported method.[46]

Arylaldehyde (1.2 mmol), 2-aminothiophenol (1.2 mmol), and the ionic liquid (20 mL) were successively added to a flat-bottomed reaction bottle and gently mixed. Synthesis was allowed to proceed at a temperature of 80 °C, a frequency of 40 KHz. The reaction bottles were placed into the ultrasonic cleaner, with reactant levels always slightly below the water level in the tank. The reaction bottle was open so that the mixture came into contact with the air. After 480 min, the mixture was separated directly by column chromatography (EtOAc: petroleum ether = 1:40). The ionic liquid was washed out firstly. The eluted

product was analyzed through nuclear magnetic resonance (NMR) spectroscopy. Product identity and purity were confirmed on the basis of published data.

2-(*p*-Tolyl)benzothiazole (3a):[25,27] Yellow solid. mp 82 - 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.7 Hz, 2H), 7.72 (m, 1H), 7.51 (m, 1H), 7.31(s, 4H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 154.2, 141.1, 135.1, 131.3, 130.1, 127.5, 126.4, 125.2, 123.1, 121.5, 21.4. HRMS (ESI): calculated for $C_{14}H_{12}NS$ $(M+H)^+$: 226.07, found: 226.05.

2-(*m*-Tolyl)benzothiazole (3b):[28,29] White solid. mp 66 - 69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.05 (d, *J* = 8.1 Hz, 1H), 7.91 (s, 1H), 7.87 - 7.82 (m, 2H), 7.47 - 7.43 (t, *J* = 8.1 Hz, 1H), 7.33 (m, 2H), 7.25 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.2, 154.1, 138.7, 135.0, 133.5, 131.6, 128.7, 128.2, 126.2, 125.0, 124.8, 123.0, 121.4, 21.3. HRMS (ESI): calculated for $C_{14}H_{12}NS$ $(M+H)^+$: 226.07, found: 226.08.

2-(*o*-Tolyl)benzothiazole (3c):[29,30] White solid. mp 50 - 53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.50 (m, 1H), 7.3 - 7.26 (m, 4H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.1, 153.8, 137.4, 135.5, 133.0, 131.4, 130.5, 130.1, 126.2, 125.2, 123.3, 121.3, 21.2. HRMS (ESI): calculated for $C_{14}H_{12}NS$ $(M+H)^+$: 226.07, found: 226.06.

2-Phenylbenzothiazole (3d):[25] White solid. mp 111 - 113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 - 8.07 (m, 3H), 7.88 (dd, *J* = 8.1, 0.4 Hz, 1H), 7.51 - 7.47 (m, 4H), 7.38 (td, *J* = 7.7, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.0, 154.1, 135.1, 133.6, 131.2, 129.1, 127.5, 126.3, 125.1, 123.3, 121.6. HRMS (ESI): calculated for $C_{13}H_{10}NS$ $(M+H)^+$: 212.05, found: 212.05.

2-(4-Chlorophenyl)benzothiazole (3e):[25,47] White solid. mp 113 - 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 155.2, 139.1, 134.0, 131.1, 128.7, 127.3, 126.0, 125.2, 120.2, 120.5. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8ClNS$: 245.01; found: 245.05.

2-(4-Bromophenyl)benzothiazole (3f):[28] Yellow solid. mp 129 - 131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.54 - 7.52 (m, 3H), 7.46 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.4, 154.8, 136.7, 134.6, 131.7, 128.6, 126.5, 125.0, 122.8, 122.4. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8BrNS$: 290.2; found: 290.3.

2-(4-Fluorophenyl)benzothiazole (3g):[28] White solid. mp 99 - 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.08 - 8.04 (m, 3H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.48 (m, 1H), 7.36 (m, 1H), 7.22 - 7.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.7, 165.4, 163.0, 153.8, 134.6, 129.8, 129.7, 129.3, 129.2, 126.3, 125.0, 123.2, 121.7, 116.2, 116.0. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8FNS$: 229.3; found: 229.2.

2-(4-Methoxyphenyl)benzothiazole (3h):[25] White solid. mp 123 - 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 3H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.4

Hz, 2H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.6, 151.1, 130.4, 128.8, 124.2, 121.4, 120.3, 119.5, 117.7, 113.1, 53.3. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{14}H_{11}NOS$: 241.06; found: 241.07.

2-[4-(Trifluoromethyl)phenyl]benzothiazole (3i):[34,35] White solid. mp 157 - 159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 154.4, 135.8, 134.0, 130.2 (q, *J* = 32 Hz), 125.4, 126.4, 125.3 (q, *J* = 3.5 Hz), 122.8 (q, *J* = 271 Hz), 122.2, 120.1. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{14}H_8F_3NS$: 279.03; found: 279.05.

2-[3-(Trifluoromethyl)phenyl]benzothiazole (3j):[35] Gray solid. mp 92 - 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.48 - 7.63 (m, 1H), 7.48 - 7.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 154.0, 135.1, 134.4, 131.9, 131.7, 131.5, 131.2, 130.7, 129.6, 127.4, 126.7, 126.5, 125.7, 124.7, 124.3, 123.5, 122.9, 121.8. HRMS (ESI) *m*/*z*: $[M + H]^+$ calculated for 280.04, found for 280.05.

2-[2-(Trifluoromethyl)phenyl]benzothiazole (3k):[35] Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.11 (s, 1H), 7.98 (s, 1H), 7.84 (d, *J* = 25 Hz, 3H), 7.64 - 7.57 (m, 1H), 7.57 - 7.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 153.4, 136.1, 133.2, 132.9, 132.4, 131.4, 127.8, 127.7, 127.5, 127.2, 126.3, 125.1, 123.8, 123.1, 122.6. HRMS (ESI) *m*/*z*: $[M + H]^+$: calculated for 280.04, found for 280.04.

2-(4-Nitrophenyl)benzothiazole (3l):[36] Yellow solid. mp 234 - 236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.1 Hz, 2H), 8.31 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 154.4, 149.7, 139.2, 136.1, 127.2, 128.03, 127.2, 125.7, 122.7, 122.7. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8N_2O_2S$: 256.3; found: 256.2.

2-(3-Nitrophenyl)benzothiazole (3m):[25] Yellow solid. mp 184 - 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.35 (dd, 1H, *J* = 8.2 Hz, *J* = 1.4 Hz), 8.14 (d, *J* = 8.1 Hz, 1H), 7.97(d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 164.8, 153.8, 148.7, 135.4, 135.3, 133.1, 130.0, 126.9, 126.1, 125.2, 123.8, 122.2, 121.9. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8N_2O_2S$: 256.3; found: 256.1.

2-(2-Nitrophenyl)benzothiazole(3n):[39] Yellow solid. mp 235 - 237 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.45 (m, 1H), 7.47 - 7.57 (m, 1H), 7.65 (td, *J* = 8.0 Hz, *J* = 2.3 Hz, 1H), 7.71 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.78 - 7.83 (m, 1H), 7.93 - 7.95 (m, 2H), 8.08 - 8.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.4, 123.8, 124.6, 125.7, 126.4, 128.0, 130.8, 131.7, 132.1, 135.7, 148.7, 153.6, 162.4. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{13}H_8N_2O_2S$: 256.3; found: 256.2.

2-(Naphthalen-2-yl)benzothiazole (3o):[41] Yellow solid. mp 77 - 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.91 (m, 3H), 7.86 (m, 1H), 7.54 (m,

2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 153.0, 133.0, 132.5, 131.5, 130.2, 128.8, 127.6, 126.8, 126.6, 126.1, 125.6, 124.4, 124.1, 122.8, 122.2, 120.8. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{17}H_{11}NS$: 261.06; found: 261.07.

2-(Naphthalen-3-yl)benzothiazole (3p):[28] White solid. mp 128 - 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.96 (m, 4H), 7.55 (m, 3H), 7.28 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.2, 136.3, 135.3, 131.1, 129.9, 128.1, 127.5, 126.5, 125.7, 123.0, 122.6, 122.1, 121.2, 120.4, 119.8, 119.1. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{17}H_{11}NS$: 261.06; found: 261.08.

5-Methyl-2-phenylbenzo[*d*]thiazole (3q):[43] White solid. mp 145 - 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 - 8.13 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.81 (s, 1H), 7.70 (s, 1H), 7.50 - 7.56 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 152.4, 135.2, 132.9, 131.4, 129.1, 127.6, 127.8, 126.4, 125.9, 122.8, 122.3, 121.9, 21.7. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{14}H_{13}NS$: 225.06; found: 225.06.

5-(Trifluoromethyl)-2-phenylbenzo[*d*]thiazole (3r):[44] Yellow solid. mp 130 - 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 8.07 - 8.11 (m, 3H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.48 - 7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 154.1, 138.6, 133.2, 130.8, 129.4, 128.9 (q, *J* = 33 Hz), 127.9, 122.2, 121.7, 121.5, 120.7 (q, *J* = 4 Hz). HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{14}H_{11}F_3NS$: 280.04; found: 280.05.

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