A Simple and Efficient Synthesis of (Hetero)Aryl-Substituted Benzothiazolyl or Benzoxazolyl Furan, Thiophene and *N*-methylpyrrole Derivatives through a Palladium-Catalyzed Regioselective C–H Bond Arylation

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Abstract: The synthesis of 2-(hetero)aryl-5-benzothiazol-2-yl or -benzoxazol-2-ylfuran, -thiophene, and -1-methylpyrrole derivatives was accomplished in two steps. 2-(Benzothiazol-2-yl)- or 2-benzoxazol-2-ylfuran, -thiophene, or -1-methylpyrrole were synthesized by coupling a heteroaryl aldehyde and either 2-mercaptophenol or 2-aminophenol. Then, they were successfully arylated with a wide range of aryl bromides using a phosphine-free palladium protocol; regioselective arylation at C5 of furan, thiophene, or 1-methyl-1*H*-pyrrole was observed in all cases. This reaction tolerates a wide variety of substituents on the aryl bromides as well as heteroaryl bromides.

Key words: arylation, catalysis, C–H bond activation, heterocycles, palladium

Benzothiazol-2-yl- or benzoxazol-2-yl-substituted furan, thiophene, and 1-methylpyrrole derivatives have a similar structure, which is composed of a heteroaromatic core linked to either a benzothiazole or a benzoxazole moiety. They have multiple applications, and have long been known to be biologically active (Scheme 1). As examples, benzoxazolyl-heteroaryl derivatives such as DB828 or DB320 with furan or 1-methylpyrrole frameworks, respectively, are chemotherapeutic agents for the treatment of *Trypanosoma evansi*, which causes surra, an animal pathogenic protozoan infection.[1] Similar structures could also be used for specific recognition of DNA sequences,[2] or as cysteine proteases inhibitors.[3] 2-[2-(5-Heteroarylthiophen-2-yl)benzoxazol-5-yl]propanoic acid derivatives **I** have anti-inflammatory activity.[4] The bis-substituted amidinobenzothiazoles **II** have anti-HIV activity.[5] Moreover, benzothiazolylfuran, -thiophene, or -1-methylpyrrole derivatives **III** or **IV** also have physically interesting characteristics due to their specific phosphorescence properties.[6] In addition, these structures might be used as polydentate ligands, when arylated with suitable aryls containing nitrogen or other coordinating atoms.[7]

Until now, the preparation of these derivatives involved multistep synthesis including transition-metal-catalyzed arylation from organometallic reagents earlier synthesized (e.g., Suzuki, Stille, Negishi, Kumada, Hiyama, etc.) or they were synthesized using highly functionalized starting materials.[6g,8] These procedures can not be considered as ecofriendly and they should be replaced by more sustainable chemistry.

In the last two decades, the area of the transition-metal-catalyzed direct C–H bond (hetero)arylation reactions with (hetero)aryl halides or pseudohalides, which generate less waste compared to traditional methods, has earned significant attention.[9] The direct functionalization of heteroarenes has been well studied and several protocols for the direct arylation of furans, thiophenes, or pyrroles have emerged in the literature,[10] including low catalyst loading,[11] using green solvents,[12] or less reactive aryl chlorides as coupling partners.[13] The major contribution was made using palladium chemistry, however, some reports focused on alternative metals such as copper,[14] iridium,[15] or cobalt.[16] To the best of our knowledge, to date there is no general method for the direct arylation of furans, thiophenes, and 1-methylpyrroles bearing a benzothiazole or benzoxazole substituent.

Due to the wide and interesting properties of aryl-substituted benzothiazolyl- or benzoxazolylfuran, -thiophene, and -1-methylpyrrole derivatives, the development of a simple and efficient synthesis is necessary in order to facilitate the construction of libraries of compounds. Herein, we described a convergent synthesis of these derivatives from simple and inexpensive starting materials (Scheme 1, bottom). These syntheses include regioselective C–H bond activation as the key step to build up the molecular diversity.

We started our investigation by the preparation of heteroarenes substituted by a benzothiazole or a benzoxazole (Scheme 2). Several methods for the preparation of such structures are reported in the literature.[17] The most convenient pathway is the condensation of either 2-mercaptophenol or 2-aminophenol with diverse heteroaromatic aldehydes under oxidative conditions.[18] Indeed, the ben-

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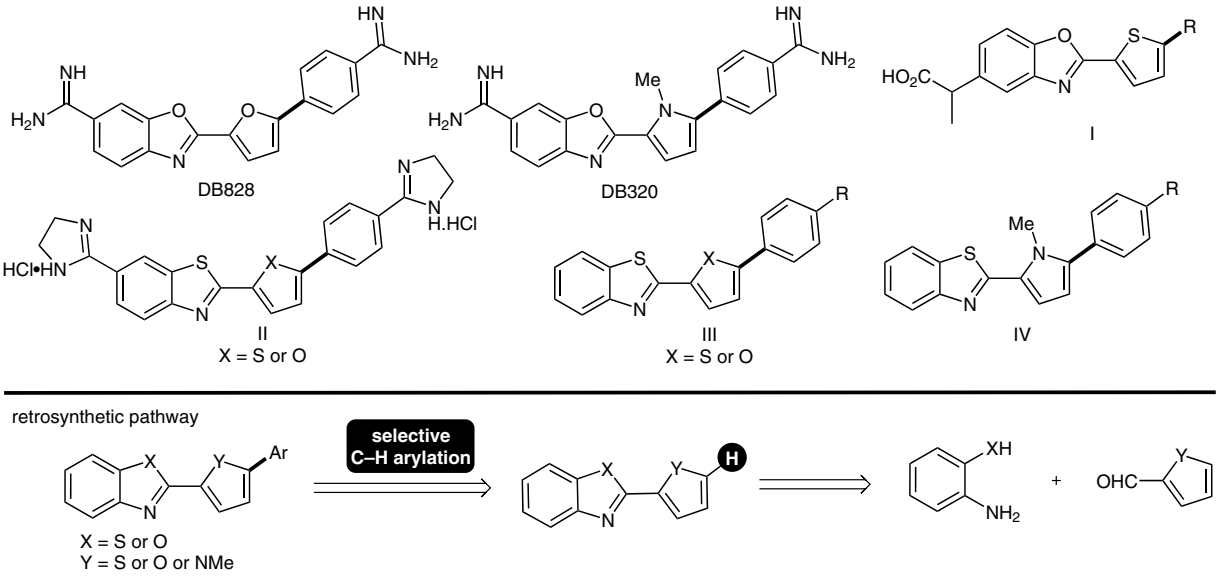
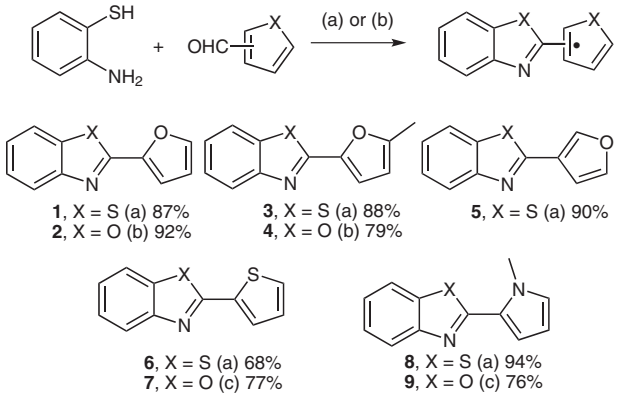


Scheme 1 Relevant structures in the literature and retrosynthesis analysis of benzothiazolyl- or benzoxazolylfuran, -thiophene, and -1-methylpyrrole derivatives

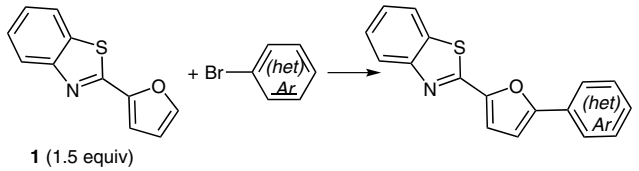
zothiazolylfuran derivatives **1**, **3**, and **5** were obtained by the condensation of 2-mercaptophenol with furfural, 3-furaldehyde, or 5-methylfurfural in dimethyl sulfoxide at high temperature, following a reported procedure.[19] All these compounds were isolated in high yields after simple recrystallization. Following the conditions reported by Reyes,[20] the corresponding benzoxazolylfurans **2** and **4** were synthesized in *N*,*N*-dimethylformamide with the assistance of one equivalent of potassium cyanide. Similar procedures were applied using thiophene-2-carbaldehyde or 1-methyl-1*H*-pyrrole-2-carbaldehyde instead of furfural to allow the formation of the desired products **6**, **8**, and **9** in high yields. Under these conditions, 2-(thiophen-2-yl)benzoxazole (**7**) was obtained in low yield, so we synthesized it from thiophene-2-carbonyl chloride in *N*-methylpyrrolidin-2-one at 200 °C, following a reported procedure.[21]



Scheme 2 Preparation of heteroarenes substituted by benzothiazole or benzoxazole. *Reagents and conditions*: (a) DMSO, 195 °C, 2 h; (b) KCN (1 equiv), DMF, r.t., 12 h; (c) corresponding acyl chloride was used instead of aldehyde, NMP, 200 °C, 12 h.

With these starting materials in hands, we started to study their palladium-catalyzed direct arylations using aryl bromides as coupling partners. We decided to employ our previous conditions, a phosphine-free palladium procedure[10b] using palladium(II) acetate at low loading (only 0.5 mol%) in the presence of potassium acetate as base (2 equiv) in *N*,*N*-dimethylacetamide (DMA) at 150 °C. Firstly, the direct arylation of 2-(furan-2-yl)benzothiazole (**1**) was investigated (Table 1). We found that the reaction proceed regioselectively at C5 of the furan and is tolerant of a wide range of functional groups on the aryl bromide (e.g., cyano, nitro, formyl, ketone, and ester) (entries 1–4 and 6). On the other hand, the reaction was completely inhibited with methoxy group in the *meta* position. This is probably due to the more difficult oxidative addition of this aryl bromide (entry 7). The reaction proceeded very well with *ortho*-substituted aryl bromide 2-bromobenzonitrile giving the desired coupling product **16** in 87% yield (entry 8). Heteroaryl bromides 3-bromopyridine, 3-bromoquinoline, and 5-bromopyrimidine also reacted with 2-(furan-2-yl)benzothiazole (**1**) to give **17**–**19** in 62%, 71%, and 72% yields, providing an efficient synthesis for new ligands with multicoordination sites (entries 9–11). Recently, we have reported the direct arylation of thiophenes,[22] benzofurans,[23] or furans[24] using benzenesulfonyl chlorides as coupling partners. The optimized conditions for this desulfitative cross-coupling, $PdCl_2(MeCN)_2$ (5 mol%) in the presence of three equivalents of lithium carbonate in dioxane at 140 °C for 40 hours, allowed the formation of the coupling product **13** between **1** and 4-nitrobenzenesulfonyl chloride (entry 5); the same regioisomer was obtained as under the previous reaction conditions, however the desired product **13** was isolated in slightly higher yield.

Table 1 Palladium-Catalyzed Direct C5-Arylation of 2-(Furan-2-yl)benzothiazole (**1**)[a]



1 (1.5 equiv)

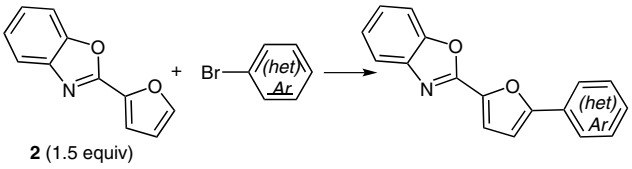
Entry	Ar	Product	Yield (%)
1	4-NCC_6H_4	**10**	67
2	4-AcC_6H_4	**11**	57
3	4-$HOCC_6H_4$	**12**	64
4	4-$O_2NC_6H_4$	**13**	59
5[b]	4-$O_2NC_6H_4$	**13**	69
6	4-$MeO_2CC_6H_4$	**14**	66
7	3-$MeOC_6H_4$	**15**	0
8	2-NCC_6H_4	**16**	87
9	pyridin-3-yl	**17**	62
10	quinolin-3-yl	**18**	71
11	pyrimidin-5-yl	**19**	72

[a] Reaction conditions: $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h.
[b] Reaction conditions: $PdCl_2(MeCN)_2$ (5 mol%), 4-$O_2NC_6H_4SO_2Cl$ (1.5 equiv), **1** (1 equiv), Li_2CO_3 (3 equiv), dioxane, 140 °C, 40 h.

We investigated next the reactivity of 2-(furan-2-yl)benzoxazole (**2**) in the palladium-catalyzed direct arylation with aryl bromides (Table 2). Again, 0.5 mol% of palladium(II) acetate was able to promote the direct arylation of **2** in the presence of two equivalents of potassium acetate in *N*,*N*-dimethylacetamide. The substrate scope of the reaction with **2** as the heteroarene was similar to the scope with compound **1**. Again, functional groups such as cyano, ester, formyl, ketone, and nitro were tolerated (entries 1–5). The *ortho*-substituted aryl bromide 2-bromobenzonitrile afforded the desired coupling product **25** in 76% yield (entry 6). The heteroaryl bromide 3-bromopyridine gave the desired coupling product **26** in high yield (entry 7).

We next explored the reactivity of 5-methylfuran bearing a benzothiazole or a benzoxazole at C2 in the palladium-catalyzed direct arylation (Scheme 3). It is important to note that with the previous substrates, the arylation took place selectively at C5, which is now blocked by a methyl substituent, hence the arylation might occur at C3 or/and C4 as we have previously shown using simpler 2,5-disubstituted furans.[25] However, using 2-(5-methylfuran-2-yl)benzothiazole (**3**) as the substrate did not give arylated product whatever the coupling partners (i.e., aryl bromide or benzenesulfonyl chloride). Using 2-(5-methylfuran-2-yl)benzoxazole (**4**) as the substrate gave only trace amounts of a monoarylated product by GC-MS analysis, which could not be isolated and identified.

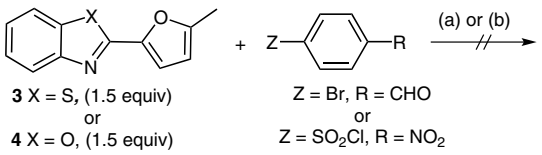
Table 2 Palladium-Catalyzed Direct C5-Arylation of 2-(Furan-2-yl)benzoxazole (**2**)[a]



2 (1.5 equiv)

Entry	Ar	Product	Yield (%)
1	4-NCC_6H_4	**20**	77
2	4-$MeO_2CC_6H_4$	**21**	52
3	4-$HOCC_6H_4$	**22**	68
4	4-AcC_6H_4	**23**	64
5	4-$O_2NC_6H_4$	**24**	58
6	2-NCC_6H_4	**25**	76
7	pyridin-3-yl	**26**	71

[a] Reaction conditions: $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h.



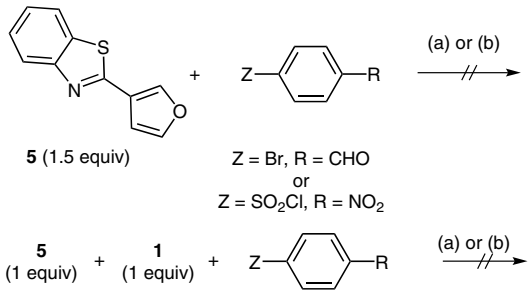
3 X = S, (1.5 equiv)
or
4 X = O, (1.5 equiv)

Z = Br, R = CHO
or
Z = SO_2Cl, R = NO_2

Scheme 3 Reactivity of 2-(5-methylfuran-2-yl)benzoxazothizole (**3**) and 2-(5-methylfuran-2-yl)benzoxazole (**4**) in palladium-catalyzed direct arylations. *Reagents and conditions*: (a) ArBr (1 equiv), $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h; (b) $ArSO_2Cl$ (1.5 equiv), $PdCl_2(MeCN)_2$ (5 mol%), Li_2CO_3 (3 equiv), dioxane, 140 °C, 40 h.

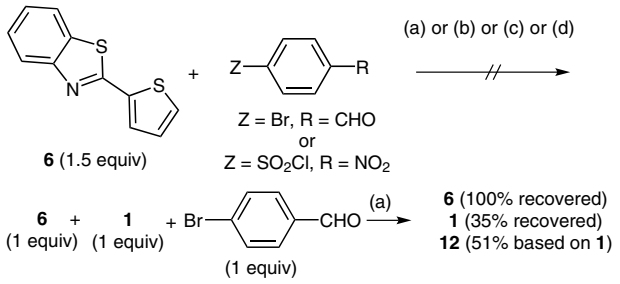
Having successfully arylated 2-(furan-2-yl)benzothiazole (**1**) using different aryl bromides, we attempted to extend the scope of the reaction to 3-substituted furans such as 2-(furan-3-yl)benzothiazole (**5**). However, **5** was completely unreactive under our conditions with both an aryl bromide and an arenesulfonyl chloride as the coupling partners; only starting materials were recovered at the end of the reaction (Scheme 4, top). In order to get more information on the reactivity of **5**, we performed a competitive reaction between one equivalent of both 2-(furan-3-yl)benzothiazole (**5**) and 2-(furan-2-yl)benzothiazole (**1**) in the presence of one equivalent of 4-bromobenzaldehyde or one equivalent of 4-nitrobenzenesulfonyl chloride; no reaction occurred, and even **1** was not arylated (Scheme 4, bottom). This result suggests that **5** is a poisoning agent for the palladium catalyst.

Next, we turned our attention to the reactivity of thiophene derivatives. Firstly, we attempted to arylate 2-(thiophen-2-yl)benzothiazole (**6**) with 4-bromobenzaldehyde



Scheme 4 Reactivity of 2-(furan-3-yl)benzothiazole (**5**) in palladium-catalyzed direct arylations. *Reagents and conditions*: (a) $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h; (b) $ArSO_2Cl$ (1.5 equiv), $PdCl_2(MeCN)_2$ (5 mol%), Li_2CO_3 (3 equiv), dioxane, 140 °C, 16 h.

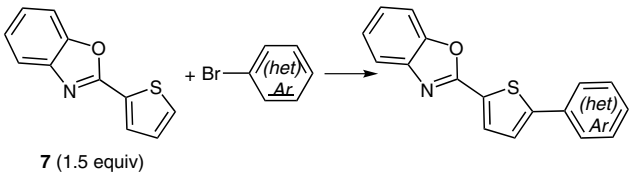
as the coupling partner. However, no reaction occurred using the previous palladium catalytic system (Scheme 5, top). Other conditions, such as higher catalyst loading [2 mol% of $Pd(OAc)_2$], or with other sources of palladium such as PdCl(allyl)(dppb) (2 mol%), were also unsuccessful in this transformation. A competitive reaction between 2-(furan-2-yl)benzothiazole (**1**) and 2-(thiophen-2-yl)benzothiazole (**6**) gave the arylated product **12** in 51% yield, while **6** was fully recovered at the end of the reaction (Scheme 5, bottom). This result suggested that **6** does not poison the catalytic system but its reactivity is poor in this palladium-catalyzed direct arylation.



Scheme 5 Reactivity of 2-(thiophen-2-yl)benzothiazole (**6**) in palladium-catalyzed direct arylations. *Reagents and conditions*: (a) ArBr (1 equiv), $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h; (b) $ArSO_2Cl$ (1.5 equiv), $PdCl_2(MeCN)_2$ (5 mol%), Li_2CO_3 (3 equiv), dioxane, 140 °C, 40 h; (c) ArBr (1 equiv), $Pd(OAc)_2$ (2 mol%), KOAc (2 equiv), 150 °C, 16 h; (d) ArBr (1 equiv), PdCl(allyl)(dppb) (2 mol%), KOAc (2 equiv), 150 °C, 16 h.

In contrast to the thiophene bearing a benzothiazole moiety at C2, the thiophene derivative **7**, which has a benzoxazole moiety, reacted well in direct arylations using aryl bromides as coupling partners (Table 3). Under the previous conditions, a wide variety of 5-arylated 2-(thiophen-2-yl)benzoxazole derivatives were synthesized in moderate to high yields (entries 1, 2, and 4–7). The direct arylation via desulfitative coupling from 4-nitrobenzenesulfonyl chloride was also tested. However, no arylated product was observed, and only the starting materials were recovered (entry 3).

Table 3 Palladium-Catalyzed Direct C5-Arylation of 2-(Thiophen-2-yl)benzoxazole (**7**)[a]



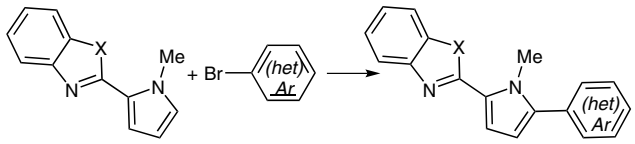
Entry	Ar	Product	Yield (%)
1	4-$OHCC_6H_4$	**27**	54
2	4-$O_2NC_6H_4$	**28**	48
3[b]	4-$O_2NC_6H_4SO_2Cl$	**28**	0
4	2-NCC_6H_4	**29**	63
5	pyrimidin-5-yl	**30**	71
6	pyridin-3-yl	**31**	73
7	quinolin-3-yl	**32**	67

[a] Reaction conditions: (a) $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h.
[b] $PdCl_2(MeCN)_2$ (5 mol%), 4-$O_2NC_6H_4SO_2Cl$ (1.5 equiv), **7** (1 equiv) Li_2CO_3 (3 equiv), dioxane, 140 °C, 40 h.

Finally, we investigated the direct arylation of 1-methyl-1*H*-pyrrole substituted by either benzothiazole or benzoxazole at C2 (Table 4). In the case of 2-(1-methyl-1*H*-pyrrol-2-yl)benzothiazole (**8**), the regioselective arylation at C5 proceeded smoothly with a wide range of aryl bromides including quite sensitive functional groups such as ketone or cyano and also with heteroaryl bromide derivatives (entries 1–4). With 2-(1-methyl-1*H*-pyrrol-2-yl)benzoxazole (**9**), the desired arylated products were obtained in moderate to high yields. Again, nitro, aldehyde, or cyano functional groups were tolerated (entries 5–7). Heteroaryl bromides such as 3-bromoquinoline or 5-bromopyrimidine allowed the formation of the desired coupling products **40** and **41** in 56% and 61% yields, respectively (entries 8 and 9).

In summary, we report here a very efficient method for the synthesis of C5-(hetero)arylated furan, thiophene, and 1-methylpyrrole derivatives bearing benzothiazolyl or benzoxazolyl moieties at C2. These syntheses involve two steps from inexpensive and commercially available starting materials. The C–H bond functionalization key step proceeds with ligand-free palladium(II) acetate catalyst and potassium acetate as base in *N*,*N*-dimethylacetamide, and affords regioselectively the C5-arylated furans, thiophenes, and 1-methylpyrroles. This procedure tolerates a wide variety of substituents on the aryl bromides such as nitro, cyano, ester, ketone, formyl, and also pyridines derivatives. Generally, the heteroarenes substituted by a benzoxazole moiety display better reactivity than those substituted by a benzothiazole unit. Moreover, palladium-catalyzed desulfitative arylations of furan derivatives have been also demonstrated. Thirty new products have

Table 4 Palladium-Catalyzed Direct C5-Arylation of 2-(1-Methyl-1*H*-pyrrol-2-yl)benzothiazole (**8**) and 2-(1-Methyl-1*H*-pyrrol-2-yl)benzoxazole (**9**)[a]



8 X = S, (1.5 equiv)
9 X = O, (1.5 equiv)

Entry	X	Ar	Product	Yield (%)
1	S	4-AcC_6H_4	**33**	65
2	S	2-NCC_6H_4	**34**	77
3	S	pyridin-3-yl	**35**	64
4	S	pyrimidin-5-yl	**36**	53
5	O	4-$O_2NC_6H_4$	**37**	62
6	O	4-HOCC_6H_4	**38**	67
7	O	2-NCC_6H_4	**39**	83
8	O	quinolin-3-yl	**40**	56
9	O	pyrimidin-5-yl	**41**	61

[a] Reaction conditions: (a) $Pd(OAc)_2$ (0.5 mol%), KOAc (2 equiv), 150 °C, 16 h.

been synthesized by this procedure, which could find further applications in diverse fields of chemistry such as medicine, or materials chemistry.

DMA (99%) was purchased from Acros. KOAc (99%) and $Pd(OAc)_2$ (98%) were purchased from Alfa Aesar. These compounds were not purified before use.

2-Heteroarylbenzothiazoles; General Procedure
A mixture of aldehyde (10 mmol), 2-aminothiophenol (13 mmol), and DMSO (27 mL) was heated at 195 °C for 2 h. The mixture was cooled to 50 °C and then poured into cold water, and the precipitate was collected. The pale-brown solid was obtained after column chromatography.

2-(Furan-2-yl)benzothiazole (1)
Following the general procedure from 2-aminothiophenol (1.63 g, 13 mmol) and furfural (0.80 mL, 10 mmol) gave **1** (1.74 g, 87%). This is a known compound and the spectral data are identical to those reported in the literature.[26]

2-(5-Methylfuran-2-yl)benzothiazole (3)
Following the general procedure from 2-aminothiophenol (1.63 g, 13 mmol) and 5-methylfurfural (1 mL, 10 mmol) gave **3** (1.89 g, 88%). This is a known compound and the spectral data are identical to those reported in the literature.[27]

2-(Furan-3-yl)benzothiazole (5)
Following the general procedure from 2-aminothiophenol (1.63 g, 13 mmol) and 3-furaldehyde (0.86 mL, 10 mmol) gave **5** (1.81 g, 90%). This is a known compound and the spectral data are identical to those reported in the literature.[27]

2-(Thiophen-2-yl)benzothiazole (6)
Following the general procedure from 2-aminothiophenol (1.63 g, 13 mmol) and thiophene-2-carbaldehyde (0.92 mL, 10 mmol) gave **6** (1.47 g, 68%). This is a known compound and the spectral data are identical to those reported in the literature.[26]

2-(1-Methyl-1*H*-pyrrol-2-yl)benzothiazole (8)
Following the general procedure from 2-aminothiophenol (1.63 g, 13 mmol) and 1-methyl-1*H*-pyrrole-2-carbaldehyde (0.92 mL, 10 mmol) gave **8** (2.01 g, 94%) as a white solid; mp 62–66 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.0 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.88 (td, *J* = 2.0, 4.0 Hz, 1 H), 6.85 (t, *J* = 2.0 Hz, 1 H), 6.26 (ddd, *J* = 1.5, 2.5, 4.0 Hz, 1 H), 4.19 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.2, 154.1, 133.7, 127.7, 126.3, 125.6, 124.2, 122.2, 120.8, 114.6, 108.5, 36.9.

Anal. Calcd for $C_{12}H_{10}N_2S$ (214.29): C, 67.26; H, 4.70. Found: C, 67.47; H, 4.33.

2-Heteroarylbenzoxazoles; General Procedure
A mixture of 2-aminophenol (10 mmol), aldehyde (10 mmol), and KCN (10 mmol) in DMF (25 mL) was stirred at r.t. Once the reaction was complete, the mixture was diluted with water (30 mL) and extracted with EtOAc (2 × 30 mL). The extracts were combined and the solvent was removed under reduced pressure. The obtained solid was then recrystallized (boiling EtOH–H_2O, 50:50) to give the pure compound.

2-(Furan-2-yl)benzoxazole (2)
Following the general procedure from 2-aminophenol (1.09 g, 10 mmol) and furfural (0.80 mL, 10 mmol) gave **2** (1.70 g, 92%). This is a known compound and the spectral data are identical to those reported in the literature.[28]

2-(5-Methylfuran-2-yl)benzoxazole (4)
Following the general procedure from 2-aminophenol (1.09 g, 10 mmol) and 5-methylfurfural (1 mL, 10 mmol) gave **4** (1.57 g, 79%) as an orange solid; mp 68–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72 (d, *J* = 7.0 Hz, 1 H), 7.53–7.50 (m, 1 H), 7.33–7.30 (m, 2 H), 7.15 (d, *J* = 4.0 Hz, 1 H), 6.19 (d, *J* = 4.0 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.1, 156.1, 150.6, 142.3, 141.4, 125.4, 125.2, 120.4, 116.1, 110.9, 109.2, 14.4.

Anal. Calcd for $C_{12}H_9NO_2$ (199.21): C, 72.35; H, 4.55. Found: C, 71.98; H, 4.87.

2-(Thiophen-2-yl)benzoxazole (7)
A mixture 2-aminophenol (1.09 g, 10 mmol) and thiophene-2-carbonyl chloride (1.1 mL, 10 mmol) was stirred in NMP (10 mL) at 200 °C for 2 h. Once the reaction was complete, the mixture was diluted with water (30 mL) and extracted with EtOAc (2 × 30 mL). The extracts were combined and the solvent was removed under reduced pressure. The obtained solid was then recrystallized (boiling EtOH–H_2O, 50:50) to give pure **7** (1.55 g, 77%). This is a known compound and the spectral data are identical to those reported in the literature.[29]

2-(1-Methyl-1*H*-pyrrol-2-yl)benzoxazole (9)
A mixture 2-aminophenol (1.09 g, 10 mmol) and 1-methyl-1*H*-pyrrole-2-carbonyl chloride (1.16 mL, 10 mmol) was stirred in NMP (10 mL) at 200 °C for 2 h. Once the reaction was complete, the mixture was diluted with water (30) and extracted with EtOAc (2 × 30 mL). The extracts were combined and the solvent was removed under reduced pressure. The obtained solid was then recrystallized (boiling EtOAc–H_2O, 50:50) to give pure **9** (1.50 g, 76%) as a brown solid; mp 90–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.36–7.32 (m, 2 H), 7.12 (d, *J* = 3.0 Hz, 1 H), 6.89 (br s, 1 H), 6.29 (d, *J* = 3.0 Hz, 1 H), 4.18 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.4, 149.1, 141.9, 128.0, 123.7, 120.2, 118.8, 114.6, 109.5, 108.3, 36.5.

Anal. Calcd for $C_{12}H_{10}N_2O$ (198.23): C, 72.71; H, 5.09. Found: C, 72.44; H, 5.28.

Direct Arylation Reaction; General Procedure

A mixture of aryl bromide (1 mmol), benzothiazolyl- or benzoxazolyl-substituted furan, thiophene, or 1-methyl-1*H*-pyrrole derivatives (1.5 mmol), and KOAc (0.196 g, 2 mmol) in DMA (2 mL) in the presence of $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) was heated at 150 °C for 16 h under argon to afford the arylation product after evaporation of the solvent and filtration (silica gel).

2-[5-(4-Cyanophenyl)furan-2-yl]benzothiazole (10)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 4-bromobenzonitrile (0.80 g, 1 mmol) gave **10** (0.202 g, 67%) as an orange solid; mp 190–194 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (d, *J* = 8.0 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 8.5 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 3.5 Hz, 1 H), 7.00 (d, *J* = 3.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.0, 154.1, 154.0, 149.8, 134.6, 133.7, 133.0, 132.9, 127.0, 125.8, 124.8, 123.5, 119.0, 113.8, 111.7, 111.0.

Anal. Calcd for $C_{18}H_{10}N_2OS$ (302.35): C, 71.51; H, 3.33. Found: C, 71.68; H, 3.17.

2-[5-(4-Acetylphenyl)furan-2-yl]benzothiazole (11)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 4-bromoacetophenone (0.199 g, 1 mmol) gave **11** (0.182 g, 57%) as a yellow solid; mp 170–174 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.06 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.5 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 3.5 Hz, 1 H), 6.97 (d, *J* = 3.5 Hz, 1 H), 2.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 198.0, 157.8, 155.6, 154.7, 150.0, 127.2, 135.3, 134.4, 129.8, 127.4, 126.2, 125.0, 124.0, 122.4, 114.4, 110.8, 27.4.

Anal. Calcd for $C_{19}H_{13}NO_2S$ (319.38): C, 71.45; H, 4.10. Found: C, 71.62; H, 4.33.

2-[5-(4-Formylphenyl)furan-2-yl]benzothiazole (12)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) gave **12** (0.195 g, 64%) as an orange solid; mp 180–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.03 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.95 (s, 4 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 3.5 Hz, 1 H), 7.02 (d, *J* = 3.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.6, 157.1, 154.7, 154.1, 149.6, 135.9, 135.0, 134.6, 130.6, 126.9, 125.7, 124.8, 123.4, 121.8, 113.8, 110.9.

Anal. Calcd for $C_{18}H_{11}NO_2S$ (305.35): C, 70.80; H, 3.63. Found: C, 71.04; H, 3.59.

2-[5-(4-Nitrophenyl)furan-2-yl]benzothiazole (13)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 1-bromo-4-nitrobenzene (0.202 g, 1 mmol) gave **13** (0.190 g, 59%) as a brown solid; mp 230–234 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.31 (d, *J* = 8.0 Hz, 2 H), 8.08 (d, *J* = 8.5 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 3 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 3.5 Hz, 1 H), 7.05 (d, *J* = 3.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.9, 154.2, 153.8, 150.2, 147.4, 135.5, 134.7, 127.1, 125.9, 125.0, 124.7, 123.6, 121.97, 114.0, 111.7.

Anal. Calcd for $C_{17}H_{10}N_2O_3S$ (322.34): C, 63.35; H, 3.13. Found: C, 63.28; H, 2.94.

2-{5-[4-(Methoxycarbonyl)phenyl]furan-2-yl}benzothiazole (14)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and methyl 4-bromobenzoate (0.215 g, 1 mmol) gave **14** (0.221 g, 66%) as a yellow solid; mp 174–178 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.11 (d, *J* = 8.0 Hz, 2 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 2 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 3.5 Hz, 1 H), 6.97 (d, *J* = 3.5 Hz, 1 H), 3.95 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.8, 157.3, 155.1, 154.1, 149.2, 134.6, 133.7, 130.4, 129.8, 126.8, 125.6, 124.3, 123.4, 121.8, 113.8, 110.1, 52.4.

Anal. Calcd for $C_{19}H_{13}NO_3S$ (335.38): C, 68.05; H, 3.91. Found: C, 67.98; H, 4.12.

2-[5-(2-Cyanophenyl)furan-2-yl]benzothiazole (16)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 2-bromobenzonitrile (0.181 g, 1 mmol) gave **16** (0.263 g, 87%) as a pale yellow solid; mp 178–182 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.07 (dd, *J* = 8.0, 11.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.77 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.69 (ddd, *J* = 1.5, 7.5, 8.0 Hz, 1 H), 7.52 (ddd, *J* = 1.5, 7.0, 8.0 Hz, 1 H), 7.47 (d, *J* = 4.0 Hz, 1 H), 7.42 (dt, *J* = 5.0, 8.0 Hz, 2 H), 7.36 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.9, 154.0, 151.6, 149.3, 134.6, 134.5, 133.2, 132.1, 128.2, 126.7, 126.6, 125.5, 123.3, 121.8, 118.8, 113.4, 112.9, 107.5.

Anal. Calcd for $C_{18}H_{10}N_2OS$ (302.35): C, 71.51; H, 3.33. Found: C, 71.68; H, 3.67.

2-[5-(Pyridin-3-yl)furan-2-yl]benzothiazole (17)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 3-bromopyridine (96 μL, 1 mmol) gave **17** (0.172 g, 62%) as a brown solid; mp 182–186 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.03 (s, 1 H), 8.55 (d, *J* = 4.5 Hz, 1 H), 8.07–8.03 (m, 2 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.40–7.33 (m, 2 H), 7.29 (d, *J* = 3.5 Hz, 1 H), 6.91 (d, *J* = 3.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.4, 153.3, 152.4, 148.5, 148.4, 145.2, 134.0, 130.7, 126.0, 125.3, 124.7, 123.0, 122.6, 121.0, 112.8, 108.5.

Anal. Calcd for $C_{16}H_{10}N_2OS$ (278.33): C, 69.05; H, 3.62. Found: C, 68.87; H, 4.01.

2-[5-(Quinolin-3-yl)furan-2-yl]benzothiazole (18)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 3-bromoquinoline (136 μL, 1 mmol) gave **18** (0.233 g, 71%) as a dark red solid; mp 128–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.25 (s, 1 H), 8.89 (s, 1 H), 8.50 (d, *J* = 8.5 Hz, 1 H), 8.06 (dd, *J* = 8.0, 12.0 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.83 (t, *J* = 7.5 Hz, 1 H), 7.68 (t, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.42–7.37 (m, 2 H), 7.00 (d, *J* = 3.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.4, 154.1, 153.5, 153.3, 149.6, 142.7, 134.6, 132.6, 131.7, 128.7, 128.5, 127.8, 126.8, 125.5, 124.6, 123.4, 121.8, 121.5, 113.2, 112.8.

Anal. Calcd for $C_{20}H_{12}N_2OS$ (328.39): C, 73.15; H, 3.68. Found: C, 72.98; H, 3.99.

2-[5-(Pyrimidin-5-yl)furan-2-yl]benzothiazole (19)

Following the general procedure from **1** (0.302 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) gave **19** (0.201 g, 72%) as a yellow solid; mp 212–216 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.18 (s, 1 H), 9.13 (s, 2 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0

Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 3.0 Hz, 1 H), 7.01 (d, *J* = 3.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.7, 156.5, 153.8, 152.3, 150.0, 149.8, 134.4, 126.8, 125.6, 124.2, 123.3, 121.7, 113.2, 110.5.

Anal. Calcd for $C_{15}H_9N_3OS$ (279.32): C, 64.50; H, 3.25. Found: C, 64.38; H, 3.51.

2-[5-(4-Cyanophenyl)furan-2-yl]benzoxazole (20)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 4-bromobenzonitrile (0.182 g, 1 mmol) gave **20** (0.220 g, 77%) as a yellow solid; mp 222–226 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.80 (d, *J* = 8.5 Hz, 2 H), 7.68 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.47 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.29–7.24 (m, 3 H), 6.87 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 154.7, 154.6, 150.2, 143.1, 141.6, 133.2, 132.6, 125.6, 125.0, 124.8, 120.2, 118.4, 116.4, 111.7, 110.6, 110.1.

Anal. Calcd for $C_{18}H_{10}N_2O_2$ (286.28): C, 75.52; H, 3.52. Found: C, 75.38; H, 3.79.

2-{5-[4-(Methoxycarbonyl)phenyl]furan-2-yl}benzoxazole (21)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and methyl 4-bromobenzoate (0.215 g, 1 mmol) gave **21** (0.166 g, 52%) as a pale yellow solid; mp 208–212 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.09 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 2 H), 7.78 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.57 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.38–7.34 (m, 3 H), 6.95 (d, *J* = 3.5 Hz, 1 H), 3.93 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.8, 156.1, 155.2, 150.4, 142.8, 141.9, 133.5, 130.4, 130.0, 125.7, 125.2, 124.5, 120.4, 116.7, 110.8, 109.5, 52.4.

Anal. Calcd for $C_{19}H_{13}NO_4$ (319.31): C, 71.47; H, 4.10. Found: C, 71.69; H, 4.33.

2-[5-(4-Formylphenyl)furan-2-yl]benzoxazole (22)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) gave **22** (0.196 g, 68%) as a yellow solid; mp 188–192 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.0 (s, 1 H), 7.97 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 2 H), 7.79–7.77 (m, 1 H), 7.57–7.55 (m, 1 H), 7.37–7.33 (m, 3 H), 6.89 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.7, 155.8, 155.1, 150.5, 143.3, 142.0, 136.1, 134.9, 130.6, 125.9, 125.3, 125.1, 120.5, 116.8, 110.9, 110.4.

Anal. Calcd for $C_{18}H_{11}NO_3$ (289.28): C, 74.73; H, 3.83. Found: C, 75.02; H, 3.79.

2-[5-(4-Acetylphenyl)furan-2-yl]benzoxazole (23)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 4-bromoacetophenone (0.199 g, 1 mmol) gave **23** (0.194 g, 64%) as a brown solid; mp 185–189 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.03 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.82–7.78 (m, 1 H), 7.60–7.57 (m, 1 H), 7.39–7.37 (m, 3 H), 6.99 (d, *J* = 4.0 Hz, 1 H), 2.63 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 197.4, 156.2, 155.3, 150.6, 143.2, 142.1, 137.1, 133.8, 129.3, 125.8, 125.2, 124.9, 120.5, 116.8, 110.8, 109.8, 31.1.

Anal. Calcd for $C_{19}H_{13}NO_3$ (303.31): C, 75.24; H, 4.32. Found: C, 75.52; H, 3.99.

2-[5-(4-Nitrophenyl)furan-2-yl]benzoxazole (24)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 1-bromo-4-nitrobenzene (0.202 g, 1 mmol) gave **24** (0.177 g, 58%) as a yellow solid; mp 240–244 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.31 (d, *J* = 8.0 Hz, 2 H), 8.00 (d, *J* = 8.0 Hz, 2 H), 7.81 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.61 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.41–7.39 (m, 3 H), 7.07 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.0, 154.8, 150.6, 147.6, 143.9, 142.0, 135.3, 126.1, 125.5, 125.3, 124.7, 120.7, 116.8, 111.2, 111.0.

Anal. Calcd for $C_{17}H_{10}N_2O_4$ (306.27): C, 66.67; H, 3.29. Found: C, 66.34; H, 3.41.

2-[5-(2-Cyanophenyl)furan-2-yl]benzoxazole (25)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 2-bromobenzonitrile (0.181 g, 1 mmol) gave **25** (0.217 g, 76%) as a pale yellow solid; mp 159–163 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.20 (d, *J* = 8.0 Hz, 1 H), 7.81–7.79 (m, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.70 (t, *J* = 8.0 Hz, 1 H), 7.61–7.59 (m, 1 H), 7.50 (d, *J* = 4.0 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 4.0 Hz, 1 H), 7.40–7.38 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 154.8, 152.5, 150.3, 142.8, 141.8, 134.3, 133.2, 132.0, 128.4, 126.9, 125.7, 125.1, 120.4, 118.7, 116.5, 112.6, 110.7, 107.8.

Anal. Calcd for $C_{18}H_{10}N_2O_2$ (286.28): C, 75.52; H, 3.52. Found: C, 75.87; H, 3.41.

2-[5-(Pyridin-3-yl)furan-2-yl]benzoxazole (26)
Following the general procedure from **2** (0.277 g, 1.5 mmol) and 3-bromopyridine (96 μL, 1 mmol) gave **26** (0.186 g, 71%) as a dark red solid; mp 127–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.05 (s, 1 H), 8.56 (br s, 1 H), 8.10 (d, *J* = 7.5 Hz, 1 H), 7.77 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.57–7.53 (m, 1 H), 7.38–7.30 (m, 4 H), 6.92 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.0, 154.2, 150.3, 149.5, 146.1, 142.8, 141.8, 131.8, 125.8, 125.6, 125.1, 123.8, 120.3, 116.5, 110.7, 108.8.

Anal. Calcd for $C_{16}H_{10}N_2O_2$ (262.26): C, 73.27; H, 3.84. Found: C, 73.61; H, 3.99.

2-[5-(4-Formylphenyl)thiophen-2-yl]benzoxazole (27)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) gave **27** (0.165 g, 54%) as a yellow solid; mp 186–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.0 (s, 1 H), 7.91 (d, *J* = 7.5 Hz, 2 H), 7.88 (d, *J* = 4.0 Hz, 1 H), 7.79 (d, *J* = 7.5 Hz, 2 H), 7.75–7.72 (m, 1 H), 7.54–7.52 (m, 1 H), 7.48 (d, *J* = 4.0 Hz, 1 H), 7.36–7.34 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.2, 158.4, 150.5, 147.1, 142.0, 138.9, 135.9, 130.9, 130.6, 130.5, 126.3, 125.9, 124.4, 124.9, 120.0, 110.5.

Anal. Calcd for $C_{18}H_{11}NO_2S$ (305.35): C, 70.80; H, 3.63. Found: C, 71.03; H, 3.42.

2-[5-(4-Nitrophenyl)thiophen-2-yl]benzoxazole (28)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 1-bromo-4-nitrobenzene (0.202 g, 1 mmol) gave **28** (0.154 g, 48%) as a yellow solid; mp 198–202 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.31 (d, *J* = 9.0 Hz, 2 H), 7.94 (d, *J* = 4.0 Hz, 1 H), 7.83 (d, *J* = 9.0 Hz, 2 H), 7.80–7.77 (m, 1 H), 7.56 (d, *J* = 4.0 Hz, 1 H), 7.51 (dd, *J* = 2.0, 9.0 Hz, 1 H), 7.41–7.39 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.6, 145.7, 142.0, 139.4, 131.1, 130.9, 130.0, 129.9, 126.5, 126.4, 125.6, 125.0, 124.6, 120.0, 110.6.

Anal. Calcd for $C_{17}H_{10}N_2O_3S$ (322.34): C, 63.35; H, 3.13. Found: C, 63.67; H, 3.49.

2-[5-(2-Cyanophenyl)thiophen-2-yl]benzoxazole (29)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 2-bromobenzonitrile (0.181 g, 1 mmol) gave **29** (0.190 g, 63%) as a pale yellow solid; mp 151–155 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.94 (d, *J* = 4.0 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.77–7.65 (m, 4 H), 7.59–7.56 (m, 1 H), 7.48 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.37 (dd, *J* = 3.0, 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.9, 151.1, 144.3, 142.5, 136.9, 135.1, 133.8, 131.5, 131.2, 130.3, 129.15, 129.1, 126.0, 125.5, 120.5, 119.0, 111.1, 110.8.

Anal. Calcd for $C_{18}H_{10}N_2OS$ (302.35): C, 71.51; H, 3.33. Found: C, 71.22; H, 3.19.

2-[5-(Pyrimidin-5-yl)thiophen-2-yl]benzoxazole (30)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) gave **30** (0.198 g, 71%) as a yellow solid; mp 228–232 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.18 (s, 1 H), 9.01 (s, 2 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.76–7.73 (m, 1 H), 7.57–7.55 (m, 1 H), 7.47 (d, *J* = 4.0 Hz, 1 H), 7.36 (dd, *J* = 3.0, 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.0, 153.5, 150.4, 141.8, 140.4, 130.9, 130.7, 127.7, 126.1, 135.5, 124.9, 124.7, 119.9, 110.5.

Anal. Calcd for $C_{15}H_9N_3OS$ (279.32): C, 64.50; H, 3.25. Found: C, 64.38; H, 3.56.

2-[5-(Pyridin-3-yl)thiophen-2-yl]benzoxazole (31)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 3-bromopyridine (96 μL, 1 mmol) gave **31** (0.203 g, 73%) as a yellow solid; mp 179–183 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.92 (d, *J* = 2.5 Hz, 1 H), 8.56 (dd, *J* = 1.5, 5.0 Hz, 1 H), 7.88 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.86 (d, *J* = 4.0 Hz, 1 H), 7.72 (dd, *J* = 3.0, 6.0 Hz, 1 H), 7.54–7.50 (m, 1 H), 7.39 (d, *J* = 4.0 Hz, 1 H), 7.35–7.31 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.6, 150.6, 149.6, 147.2, 145.1, 142.1, 133.2, 131.0, 129.8, 129.6, 125.5, 125.3, 125.0, 124.0, 120.0, 110.6.

Anal. Calcd for $C_{16}H_{10}N_2OS$ (278.33): C, 69.05; H, 3.62. Found: C, 68.79; H, 3.85.

2-[5-(Quinolin-3-yl)thiophen-2-yl]benzoxazole (32)
Following the general procedure from **7** (0.302 g, 1.5 mmol) and 3-bromoquinoline (136 μL, 1 mmol) gave **32** (0.220 g, 67%) as a yellow solid; mp 198–202 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.25 (d, *J* = 2.5 Hz, 1 H), 8.36 (d, *J* = 2.5 Hz, 1 H), 8.13 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 4.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.77–7.72 (m, 2 H), 7.62–7.54 (m, 3 H), 7.39–7.35 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.7, 150.7, 148.3, 148.0, 145.5, 142.3, 132.2, 131.2, 130.2, 129.9, 129.6, 128.3, 128.0, 127.8, 126.8, 125.6, 125.5, 125.1, 120.1, 110.7.

Anal. Calcd for $C_{20}H_{12}N_2OS$ (328.39): C, 73.15; H, 3.68. Found: C, 73.47; H, 3.31.

2-[5-(4-Acetylphenyl)-1-methyl-1*H*-pyrrol-2-yl]benzothiazole (33)
Following the general procedure from **8** (0.321 g, 1.5 mmol) and 4-bromoacetophenone (0.199 g, 1 mmol) gave **33** (0.216 g, 65%) as a pale yellow solid; mp 163–167 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.05 (d, *J* = 8.0 Hz, 2 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 6.91 (d, *J* = 4.0 Hz, 1 H), 6.4 (d, *J* = 4.0 Hz, 1 H), 4.14 (s, 3 H), 2.65 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 197.6, 160.4, 154.4, 139.3, 137.0, 136.0, 134.0, 129.3, 128.9, 128.7, 126.2, 124.8, 122.7, 121.3, 115.2, 110.1, 35.6, 26.7.

Anal. Calcd for $C_{20}H_{16}N_2OS$ (332.10): C, 72.26; H, 4.85. Found: C, 72.47; H, 4.90.

2-[5-(2-Cyanophenyl)-1-methyl-1*H*-pyrrol-2-yl]benzothiazole (34)
Following the general procedure from **8** (0.321 g, 1.5 mmol) and 2-bromobenzonitrile (0.181 g, 1 mmol) gave **34** (0.243 g, 77%) as a pale yellow solid; mp 175–179 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.80 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.67 (dt, *J* = 1.5, 8.0 Hz, 1 H), 7.50 (dt, *J* = 1.0, 7.0 Hz, 2 H), 7.45 (dt, *J* = 1.0, 7.0 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 6.93 (d, *J* = 4.0 Hz, 1 H), 6.50 (d, *J* = 4.0 Hz, 1 H), 4.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.4, 154.4, 136.1, 135.5, 134.2, 133.8, 132.7, 131.3, 129.1, 128.5, 126.2, 124.9, 122.9, 121.4, 118.3, 115.0, 113.4, 112.4, 35.4.

Anal. Calcd for $C_{19}H_{13}N_3S$ (315.39): C, 72.36; H, 4.15. Found: C, 72.55; H, 4.47.

2-[1-Methyl-5-(pyridin-3-yl)-1*H*-pyrrol-2-yl]benzothiazole (35)
Following the general procedure from **8** (0.321 g, 1.5 mmol) and 3-bromopyridine (96 μL, 1 mmol) gave **35** (0.186 g, 64%) as an orange solid; mp 138–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.76 (br s, 1 H), 8.62 (dd, *J* = 1.5, 5.0 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.79 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.46 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.40 (dd, *J* = 5.0, 7.5 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 6.91 (d, *J* = 4.0 Hz, 1 H), 6.37 (d, *J* = 4.0 Hz, 1 H), 4.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.6, 154.5, 150.0, 148.9, 136.8, 136.4, 134.1, 129.0, 128.8, 126.3, 124.9, 123.6, 122.8, 121.4, 115.2, 111.0, 35.4.

Anal. Calcd for $C_{17}H_{13}N_3S$ (291.37): C, 70.08; H, 4.50. Found: C, 69.89; H, 4.88.

2-[1-Methyl-5-(pyrimidin-5-yl)-1*H*-pyrrol-2-yl]benzothiazole (36)
Following the general procedure from **8** (0.321 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) gave **36** (0.155 g, 53%) as a yellow solid; mp 214–218 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.22 (s, 1 H), 8.88 (s, 2 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.47 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.93 (d, *J* = 4.0 Hz, 1 H), 6.43 (d, *J* = 4.0 Hz, 1 H), 4.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.1, 157.6, 156.3, 154.4, 134.2, 132.8, 130.0, 127.1, 126.4, 125.2, 123.0, 121.4, 115.3, 111.8, 35.3.

Anal. Calcd for $C_{16}H_{12}N_4S$ (292.36): C, 65.73; H, 4.14. Found: C, 65.36; H, 4.23.

2-[1-Methyl-5-(4-nitrophenyl)-1*H*-pyrrol-2-yl]benzoxazole (37)
Following the general procedure from **9** (0.297 g, 1.5 mmol) and 1-bromo-4-nitrobenzene (0.202 g, 1 mmol) gave **37** (0.198 g, 62%) as a yellow solid; mp 185–189 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.34 (dd, *J* = 8.5, 12.5 Hz, 2 H), 7.78 (d, *J* = 9.0 Hz, 1 H), 7.73–7.70 (m, 1 H), 7.64 (d, *J* = 9.0 Hz, 2 H), 7.56–7.53 (m, 1 H), 7.34–7.32 (m, 1 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.48 (d, *J* = 4 Hz, 1 H), 4.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.6, 149.9, 147.2, 142.4, 138.8, 138.5, 129.4, 128.6, 124.7, 124.6, 124.3, 119.8, 115.5, 112.0, 110.4, 35.6.

Anal. Calcd for $C_{18}H_{13}N_3O_3$ (319.31): C, 67.71; H, 4.10. Found: C, 67.88; H, 4.31.

2-[5-(4-Formylphenyl)-1-methyl-1*H*-pyrrol-2-yl]benzoxazole (38)
Following the general procedure from **9** (0.297 g, 1.5 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) gave **38** (0.202 g, 67%) as an orange solid; mp 177–181 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.14 (s, 1 H), 8.05 (d, *J* = 8.0 Hz, 2 H), 7.80–7.76 (m, 1 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.62–7.59 (m, 2 H), 7.41–7.39 (m, 1 H), 7.26 (d, *J* = 4.0 Hz, 1 H), 6.53 (d, *J* = 4.0 Hz, 1 H), 4.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.8, 157.7, 149.8, 142.4, 139.5, 138.3, 135.5, 130.2, 129.5, 124.8, 124.6, 123.7, 119.6, 115.4, 111.5, 110.3, 35.6.

Anal. Calcd for $C_{19}H_{14}N_2O_2$ (302.33): C, 75.48; H, 4.67. Found: C, 75.66; H, 4.89.

2-[5-(2-Cyanophenyl)-1-methyl-1*H*-pyrrol-2-yl]benzoxazole (39)
Following the general procedure from **9** (0.297 g, 1.5 mmol) and 2-bromobenzonitrile (0.181 g, 1 mmol) gave **39** (0.248 g, 83%) as a white solid; mp 159–163 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.79 (d, *J* = 7.5 Hz, 1 H), 7.71–7.65 (m, 2 H), 7.53–7.47 (m, 3 H), 7.30 (t, *J* = 4.0 Hz, 2 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.50 (d, *J* = 4.0 Hz, 1 H), 3.97 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.1, 150.2, 142.8, 136.4, 136.3, 134.2, 133.1, 131.8, 129.1, 125.1, 124.9, 123.6, 120.0, 118.6, 115.5, 114.0, 112.6, 110.7, 35.5.

Anal. Calcd for $C_{19}H_{13}N_3O$ (299.33): C, 76.24; H, 4.38. Found: C, 76.59; H, 4.22.

2-[1-Methyl-5-(quinolin-3-yl)-1*H*-pyrrol-2-yl]benzoxazole (40)
Following the general procedure from **9** (0.297 g, 1.5 mmol) and 3-bromoquinoline (136 μL, 1 mmol) gave **40** (0.182 g, 56%) as a yellow solid; mp 122–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.76 (br s, 1 H), 8.63 (d, *J* = 4.0 Hz, 1 H), 7.79 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.73–7.69 (m, 1 H), 7.53 (d, *J* = 9.0 Hz, 1 H), 7.41 (dd, *J* = 5.0, 8.0 Hz, 1 H), 7.37–7.34 (m, 1 H), 7.34–7.30 (m, 2 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.99 (s, 1 H), 6.41 (d, *J* = 4.0 Hz, 1 H), 4.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ =173.6, 157.8, 152.3, 150.1, 149.8, 149.1, 142.3, 137.1, 136.4, 128.5, 125.0, 124.7, 124.6, 123.6, 123.2, 119.6, 115.3, 114.2, 111.0, 110.3, 35.4.

Anal. Calcd for $C_{21}H_{15}N_3O$ (325.36): C, 77.52; H, 4.65. Found: C, 77.24; H, 4.98.

2-[1-Methyl-5-(pyrimidin-5-yl)-1*H*-pyrrol-2-yl]benzoxazole (41)
Following the general procedure from **9** (0.297 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) gave **41** (0.168 g, 61%) as a pale yellow solid; mp 190–194 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.22 (s, 1 H), 8.87 (s, 2 H), 7.73–7.69 (m, 1 H), 7.55–7.51 (m, 1 H), 7.35–7.30 (m, 2 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.46 (d, *J* = 4.0 Hz, 1 H), 4.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.4, 157.1, 156.1, 149.5, 142.0, 133.0, 126.7, 124.7, 124.4, 123.9, 119.5, 115.1, 111.4, 110.1, 34.9.

Anal. Calcd for $C_{16}H_{12}N_4O$ (276.29): C, 69.55; H, 4.38. Found: C, 69.31; H, 4.11.

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