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# Palladium-Catalysed Direct Monoarylation of Bithiophenyl Derivatives or Bis(thiophen-2-yl)methanone with Aryl Bromides

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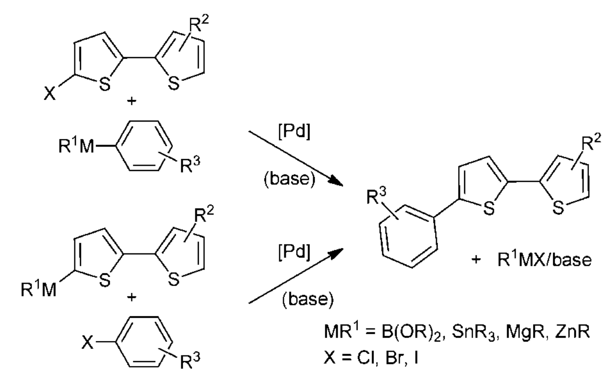
**Keywords:** Arylation / Heterocycles / Homogeneous catalysis / C-H activation / Palladium

Arylated bithiophenes, which are useful compounds due to their coordination and/or physical properties, can be easily prepared by palladium-catalysed C–H bond activation of heteroaromatics followed by arylation using electron-deficient aryl bromides. A variety of 5-arylated 2,2′-bithiophenyl derivatives have been prepared. Good yields were generally obtained by using the air-stable [PdCl(dppb)($C_3H_5$)] complex as catalyst. A range of functions on the aryl bromide, such as acetyl, formyl, ester, nitrile, trifluoromethyl, fluoro and hydroxyalkyl, are tolerated.

## Introduction

The search for an easy access to a variety of arylated bithiophene derivatives is an important field of research in organometallic and materials chemistry due to the coordination and/or physical properties of some of these compounds.[1,2] Palladium-catalysed Suzuki, Stille and Negishi cross-coupling reactions between 5-halo-2,2′-bithiophenyl derivatives and organometallic derivatives or between organometallic bithiophenyls and aryl halides are some of the most important methods for the synthesis of such compounds.[3–6] However, these reactions require the preparation of an organometallic derivative of the (hetero)aromatics and provide an organometallic salt (MX) as a byproduct (Scheme 1).

Ohta et al. reported in 1990 that the direct 2- or 5-arylation of several heteroaromatics, including thiophenes, with aryl halides proceeds in moderate to good yields by using [$Pd(PPh_3)_4$] as the catalyst.[7] Since then, the palladium-catalysed direct arylation of heteroaryl derivatives with aryl halides has proved to be a very powerful method for the synthesis of a wide range of arylated heteroarenes.[8,9] The direct arylation of quite simple thiophene derivatives has been widely explored,[10] whereas the palladium-catalysed direct arylation of polythiophenes has attracted less attention.[11] Some examples of the preparation of 5,5′-diarylated bithiophenyls have been described. For example, Miura and co-workers reported the 5′-arylation of 5-aryl-2,2′-bithiophenes in 51–91% yields using 10 mol-% $Pd(OAc)_2$ in combination with 20 mol-% P(biphenyl-2-yl)($t$Bu)$_2$ as the catalyst and $Cs_2CO_3$ as the base.[11a] Similarly, the arylation of 5-(4-methoxyphenyl)-2,2′-bithiophenyl with ethyl 4-iodobenzoate gave the 5′-arylated product in 33% yield by using [$PdCl_2(PPh_3)_2$], $AgNO_3$/KF and DMSO.[11c] An example of the diarylation of 2,2′-bithiophenyl at C-5 and C-5′ has also been reported by Fagnou and co-workers.[11e] On the other hand, very few examples of the preparation of monoarylated bithiophenyls by direct arylation reactions have been reported. To prepare push–pull systems, the reaction of 3,4-ethylenedioxythiophene with 4-iodoanisole gave the monoarylated bithiophenyl in 30% yield.[11d]




Scheme 1.

We now report the conditions for the direct monoarylation at C-5 of 2,2′-bithiophenyl derivatives and Bis(thiophen-2-yl)methanone with *para*-, *meta*- and *ortho*-substituted aryl bromides as well as heteroaryl bromides using a relatively low loading of an air-stable catalyst.

## Results and Discussion

To determine the reactivity of 2,2′-bithiophenyl in palladium-catalysed direct arylation reactions, a series of direct

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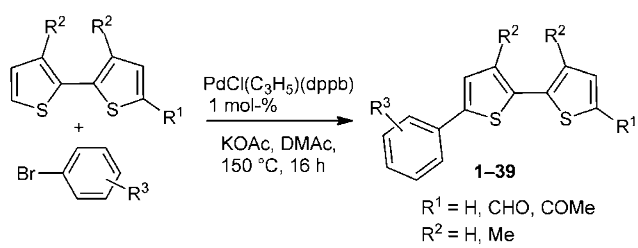
arylations in the presence of 4-bromobenzonitrile as the coupling partner were carried out under several reaction conditions. Our objective was to obtain the monoarylated compound **1** (Scheme 2). We first explored the activity of [PdCl($C_3H_5$)(dppb)] as we have recently demonstrated that it is one of the best catalysts for the direct arylation of some furans, thiophenes and thiazoles.[9d,10i] However, the formation of 5,5′-diarylated 2,2′-bithiophenyl in this reaction is possible. To minimize the formation of this side-product, we employed an excess of 2,2′-bithiophenyl. Thus, the yields of the reactions are based on the molar amount of the aryl bromide used. As 2,2′-bithiophenyl is stable, the excess can be recovered at the end of the reaction. We observed that by using 3 equiv. of 2,2′-bithiophenyl in the presence of only 1 mol-% of this catalyst with KOAc as the base and DMAc as the solvent, compound **1** was obtained in 74% yield. As expected, the use of a smaller excess of 2,2′-bithiophenyl (1.5–2 equiv.) led to the formation of larger amounts of the 5,5′-diarylated product.



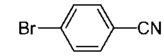
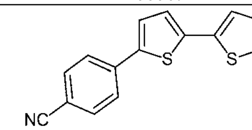
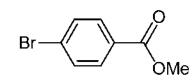
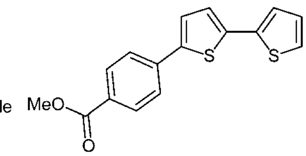
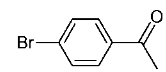
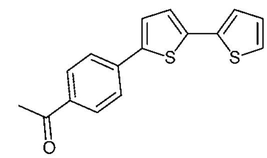
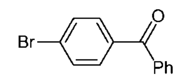
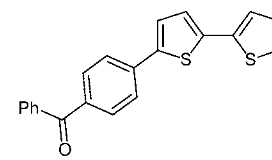
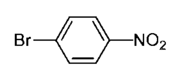
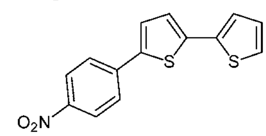
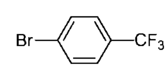
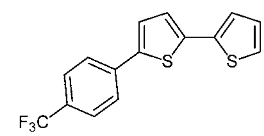
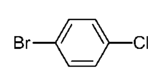
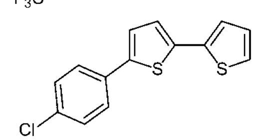
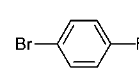
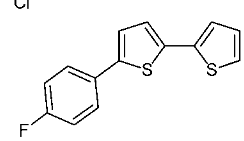
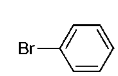
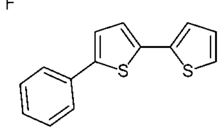
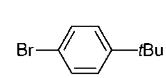
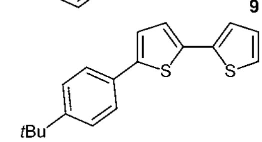

Scheme 2. Coupling of 2,2′-bithiophenyls with aryl bromides.

Then the scope of the monoarylation of 2,2′-bithiophenyl was investigated by using 1 mol-% [PdCl($C_3H_5$)(dppb)] as the catalyst and 3 equiv. of 2,2′-bithiophenyl with other aryl bromides (Scheme 2, Tables 1, 2 and 3).

First, we studied the reactivities of *para*-substituted aryl bromides (Table 1). In the presence of electron-deficient aryl bromides such as 4-bromoacetophenone, methyl 4-bromobenzoate, 4-bromobenzonitrile or 1-bromo-4-(trifluoromethyl)benzene and 1 mol-% of catalyst, the products **2**–**6** were obtained in 69–73% yields (Table 1, Entries 2–6). Products **2** and **6** have previously been prepared in 65 and 69% yields by Stille or Suzuki coupling of (2,2′-bithiophenyl-5-yl)boronic acid or 2-(tributylstannyl)thiophene with aryl bromides.[2d,4a]

Note that even 1-bromo-4-chlorobenzene could be employed to give **7** in 67% yield. In the course of this reaction, no cleavage of the C–Cl bond was observed, allowing for further transformations (Table 1, Entry 7). 1-Bromo-4-fluorobenzene was also successfully coupled with 2,2′-bithiophenyl to give **8** in a slightly lower yield of 64% due to an incomplete conversion of this aryl bromide (Table 1, Entry 8). A moderate yield of 52% of **9** was obtained in the presence of the non-activated aryl bromide bromobenzene (Table 1, Entry 9). On the other hand, with the electron-rich 1-bromo-4-*tert*-butylbenzene as coupling partner, the expected product **10** was not detected (Table 1, Entry 10). Therefore, this procedure is limited to the use of electron-poor or neutral aryl bromides.

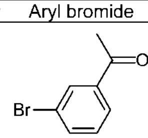
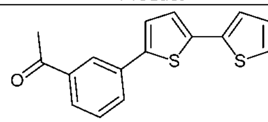
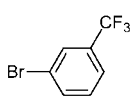
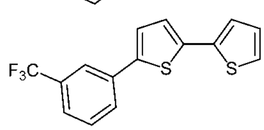
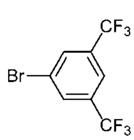
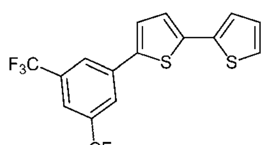
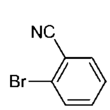
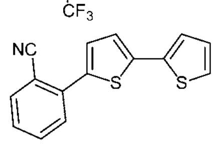
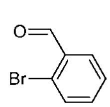
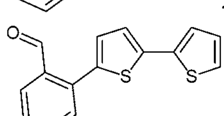
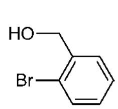
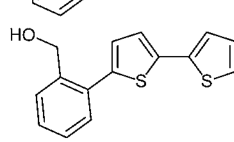
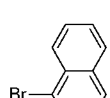
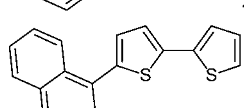
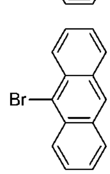
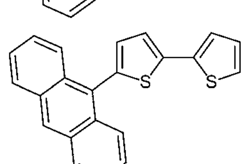
Table 1. Palladium-catalysed coupling of 2,2′-bithiophenyl with *para*-substituted aryl bromides (Scheme 2).[a]

| Entry | Aryl bromide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **1** | 74 |
| 2 |  |  **2** | 70 |
| 3 |  |  **3** | 72 |
| 4 |  |  **4** | 73 |
| 5 |  |  **5** | 69 |
| 6 |  |  **6** | 70 |
| 7 |  |  **7** | 67 |
| 8 |  |  **8** | 64 |
| 9 |  |  **9** | 52 |
| 10 |  |  **10** | 0 |

[a] Reagents and conditions: [PdCl($C_3H_5$)(dppb)] (0.01 equiv.), 2,2′-bithiophenyl (3 equiv.), aryl bromide (1 equiv.), KOAc (2 equiv.), DMAc, 150 °C, 16 h. [b] Isolated yields.

A similar reactivity was observed in the presence of *meta*-substituted aryl bromides (Table 2). The coupling reactions with 3-bromoacetophenone, 1-bromo-3-(trifluoromethyl)-benzene and 1-bromo-3,5-bis(trifluoromethyl)benzene gave **11**–**13** in 70–74% yields (Table 2, Entries 1–3). The reactions of 2,2′-bithiophenyl with *ortho*-substituted aryl bromides were also examined. Palladium-catalysed reactions with such aryl bromides are sometimes more difficult due to the steric or coordination properties of the *ortho* substituent. Good yields were obtained in the presence of 2-bromobenzonitrile or 1-bromonaphthalene (Table 2, Entries 4 and 7). On the other hand, the coupling reactions with 2-bromobenzaldehyde and (2-bromophenyl)methanol led to **15** and **16**, respectively, in lower yields due to the formation of unidentified side-products (Table 2, Entries 5 and 6). Note that even 9-bromoanthracene could be coupled successfully to give **18** in good yield (Table 2, Entry 8). Such coupling reactions with anthracene derivatives should allow the preparation of very useful compounds for materials chemistry.[12]

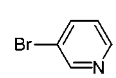
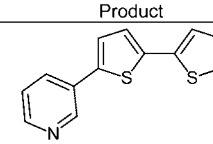
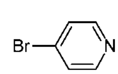
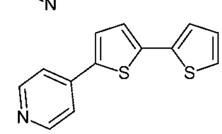
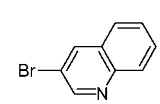
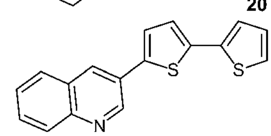
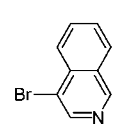
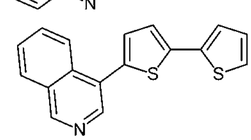
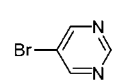
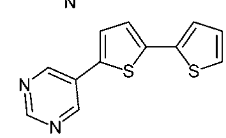
Table 2. Palladium-catalysed coupling of 2,2′-bithiophenyl with *meta*- or *ortho*-substituted aryl bromides (Scheme 2).[a]

| Entry | Aryl bromide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **11** | 74 |
| 2 |  |  **12** | 71 |
| 3 |  |  **13** | 70 |
| 4 |  |  **14** | 71 |
| 5 |  |  **15** | 63 |
| 6 |  |  **16** | 58 |
| 7 |  |  **17** | 73 |
| 8 |  |  **18** | 67 |

[a] Reagents and conditions: $[PdCl(C_3H_5)(dppb)]$ (0.01 equiv.), 2,2′-bithiophenyl (3 equiv.), aryl bromide (1 equiv.), KOAc (2 equiv.), DMAc, 150 °C, 16 h. [b] Isolated yields.

Palladium chemistry involving heterocycles has its own unique characteristics stemming from the inherently different coordination and electronic properties of heterocycles in comparison to the corresponding carbocyclic aryl compounds. Pyridines and quinolines are both π-electron-deficient, and the oxidative addition of bromopyridines and -quinolines to palladium complexes is generally not the rate-limiting step for most palladium-catalysed reactions. We observed that the reactions of 3- and 4-bromopyridines, 3-bromoquinoline, 4-bromoisoquinoline and 5-bromopyrimidine in the presence of 1 mol-% $[PdCl(C_3H_5)(dppb)]$ gave **19**–**23** in 70–75% yields without poisoning of the catalyst by coordination of the nitrogen atom to the palladium catalyst (Table 3). Note that the products **19** and **20** have previously been prepared by Kumada coupling by using (2,2′-bithiophenyl-5-yl)magnesium bromide with 3- and 4-bromopyridine, respectively, as the coupling partners.[6c] However, low to moderate yields of 51 and 14%, respectively, were obtained. Moreover, **22** was obtained in only 35% yield by Stille coupling of 4-bromisoquinoline with 2-(tributylstannyl)thiophene.[5a]

Table 3. Palladium-catalysed coupling of 2,2′-bithiophenyl with heteroaryl bromides (Scheme 2).[a]

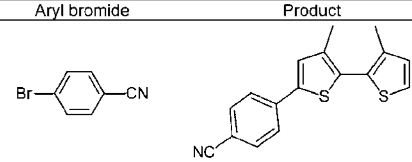
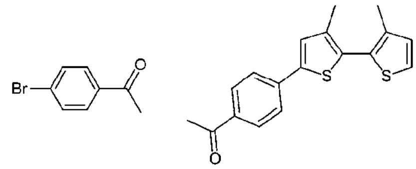
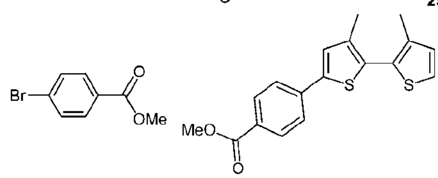
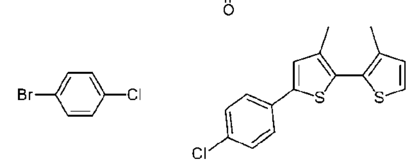
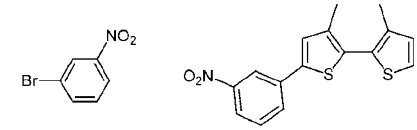
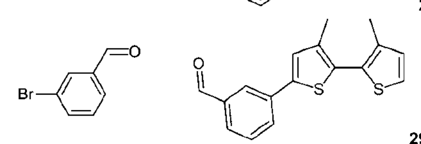
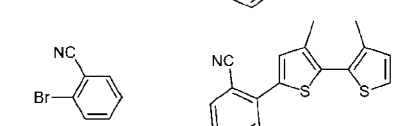
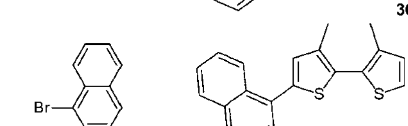
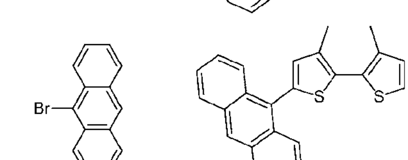
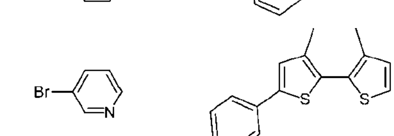
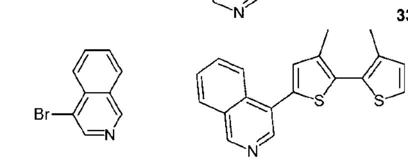
| Entry | Aryl bromide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **19** | 73 |
| 2 |  |  **20** | 75 |
| 3 |  |  **21** | 73 |
| 4 |  |  **22** | 74 |
| 5 |  |  **23** | 70 |

[a] Reagents and conditions: $[PdCl(C_3H_5)(dppb)]$ (0.01 equiv.), 2,2′-bithiophenyl (3 equiv.), heteroaryl bromide (1 equiv.), KOAc (2 equiv.), DMAc, 150 °C, 16 h. [b] Isolated yields.

The presence of substituents at C-3 and C-3′ of the bithiophenyls is known to be useful for materials chemistry.[13] To the best of our knowledge the direct arylation of 3,3′-dimethyl-2,2′-bithiophenyl has never been reported. Therefore, we examined the reactivity of this substrate with a series of aryl bromides. The presence of such methyl substituents on bithiophenyl has only a minor influence on the reaction, and yields very similar to those obtained with 2,2′-bithiophenyl were obtained (Table 4). Again, we em-

Table 4. Palladium-catalysed coupling of 3,3′-dimethyl-2,2′-bithiophenyl with aryl bromides (Scheme 2).[a]

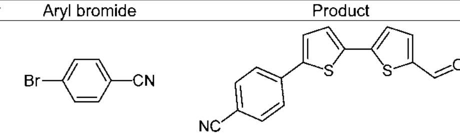
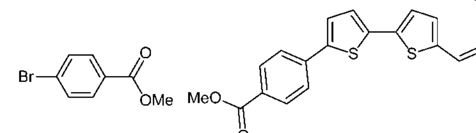
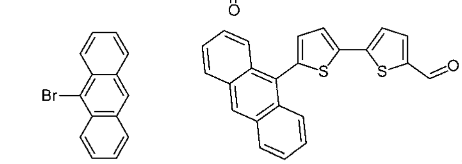
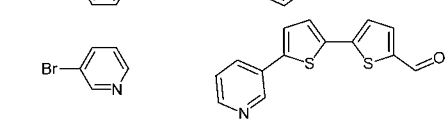
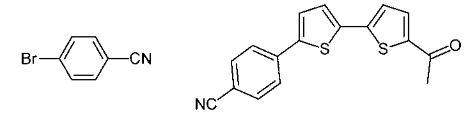
| Entry | Aryl bromide / Product | Yield (%)[b] |
|---|---|---|
| 1 |  **24** | 73 |
| 2 |  **25** | 74 |
| 3 |  **26** | 70 |
| 4 |  **27** | 62 |
| 5 |  **28** | 69 |
| 6 |  **29** | 81 |
| 7 |  **30** | 71 |
| 8 |  **31** | 62 |
| 9 |  **32** | 67 |
| 10 |  **33** | 74 |
| 11 |  **34** | 75 |

[a] Reagents and conditions: $[PdCl(C_3H_5)(dppb)]$ (0.01 equiv.), 3,3′-dimethyl-2,2′-bithiophenyl (3 equiv.), aryl bromide (1 equiv.), KOAc (2 equiv.), DMAc, 150 °C, 16 h. [b] Isolated yields.

ployed a variety of *para*-, *meta*- and *ortho*-substituted aryl bromides and also heteroaryl bromides. In all cases the desired coupling products were obtained in good yields. Even the coupling of the sterically very congested aryl bromide 9-bromoanthracene proceeded smoothly to give **32** in 67% yield (Table 4, Entry 9).

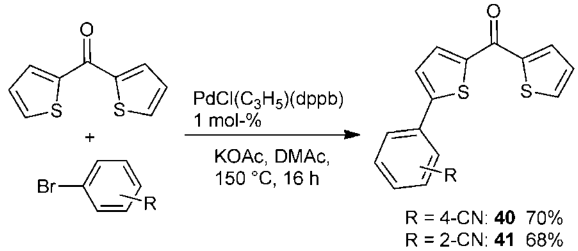
The reactivities of two 5-substituted 2,2′-bithiophenyls were also examined. Miura and Mori and their co-workers previously reported the 5′-arylation of 5-aryl-2,2′-bithiophenyl by using either expensive bases or large amounts of an air-sensitive and expensive catalyst.[11a,11c] To access more functionalized compounds we decided to employ 2,2′-bithiophenyls bearing either formyl or acetyl functions at C-5. The reaction of 1.5 equiv. of 2,2′-bithiophenyl-5-carbaldehyde with 1 equiv. of 4-bromobenzonitrile and methyl 4-bromobenzoate by using only 1 mol-% of $[PdCl(C_3H_5)(dppb)]$ and KOAc as base gave the target 5′-arylated products **35** and **36** in 66 and 60% yields, respectively (Table 5, Entries 1 and 2). Even the congested substrate 9-bromoanthracene could be coupled to 2,2′-bithiophenyl-5-carbaldehyde with this catalytic system to give **37** in 62% yield (Table 5, Entry 3). The reactivity of 2,2′-bithiophenyl substituted at C-5 by an acetyl group was found to be similar. Its coupling with 4-bromobenzonitrile produced **39** in 66% yield (Table 5, Entry 5).

Table 5. Palladium-catalysed coupling of 5-substituted 2,2′-bithiophenyls with aryl bromides (Scheme 2).[a]

| Entry | Aryl bromide / Product | Yield (%)[b] |
|---|---|---|
| 1 |  **35** | 66 |
| 2 |  **36** | 60 |
| 3 |  **37** | 62 |
| 4 |  **38** | 65 |
| 5 |  **39** | 66 |

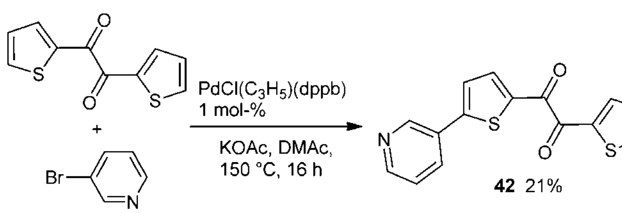
[a] Reagents and conditions: $[PdCl(C_3H_5)(dppb)]$ (0.01 equiv.), 5-substituted 2,2′-bithiophenyls (1.5 equiv.), aryl bromide (1 equiv.), KOAc (2 equiv.), DMAc, 150 °C, 16 h. [b] Isolated yields.

Then the reactivity of bis(thiophen-2-yl)methanone was examined (Scheme 3). Because the formation of diarylated compounds was possible, we employed 3 equiv. of this thiophene derivative. In the presence of 4- or 2-bromobenzonitrile and 1 mol-% of [PdCl($C_3H_5$)(dppb)], the 5-arylation products **40** and **41** were obtained in 70 and 68% yields, respectively.




Scheme 3. Coupling of bis(thiophen-2-yl)methanone with aryl bromides.

Finally, the coupling of 3-bromopyridine with 1,2-bis(thiophen-2-yl)ethane-1,2-dione was studied (Scheme 4). However, a low yield of **42** was obtained due to the formation of several unidentified products. This might be a result of the moderate thermal stability of these dithiophenes.




Scheme 4. Coupling of 1,2-bis(thiophen-2-yl)ethane-1,2-dione with 3-bromopyridine.

## Conclusion

These results demonstrate that a low loading (1 mol-%) of an air-stable catalyst in combination with a cheap and non-toxic base can be employed for the palladium-catalysed direct arylation of 2,2′-bithiophenyl derivatives and bis(thiophen-2-yl)methanone. The use of an excess of these thiophenes allows the formation of compounds monoarylated at C-5 in good yields. This procedure compares favourably with previously reported procedures as similar or higher yields were obtained and there was no need to prepare boron, tin or magnesium derivatives of the bithiophenyls. The major drawback of this procedure is the use of an excess of the bithiophenyl derivatives. However, in large-scale reactions it is possible to recycle most of the excess of the bithiophenyls. By our procedure, satisfactory results were obtained in the presence of electron-deficient aryl bromides and with congested aryl bromides. A wide range of functions on the aryl bromide, such as acetyl, benzoyl, formyl, ester, nitro, nitrile, trifluoromethyl, chloro, fluoro and hydroxyalkyl, are tolerated. The major by-products of these coupling reactions are AcOH/KBr instead of the metallic salts obtained by more classical coupling procedures. For these reasons this reaction should give an economically viable and environmentally attractive access to arylated bithiophene derivatives useful as ligands or in materials chemistry.

## Experimental Section

**General:** *N*,*N*-Dimethylacetamide (DMAc; 99%) was purchased from Acros. KOAc (99%), [Pd($C_3H_5$)Cl]$_2$ (56.5%), and 1,4-bis(diphenylphosphanyl)butane (dppb; 98%) were purchased from Alfa Aesar. These compounds were not purified before use. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker 300 MHz spectrometer.

**Preparation of the [PdCl($C_3H_5$)(dppb)] Catalyst:** An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar was charged with [Pd($C_3H_5$)Cl]$_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol) under argon. Anhydrous dichloromethane (10 mL) was added, and then the solution was stirred at room temperature for 20 min. The solvent was removed in vacuo. The yellow powder was used without purification. $^{31}$P NMR (81 MHz, $CDCl_3$): $\delta$ = 19.3 (s) ppm.

**General Procedure for the Coupling Reactions:** In a typical experiment, the aryl bromide (1 mmol), heteroaryl derivative (1.5–3 mmol; see Tables 1, 2, 3, 4, 5), base (2 mmol) and [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) were dissolved in DMAc (5 mL) under argon. The reaction mixture was stirred at 150 °C for 16 h. Then the solvent was evaporated, and the product was purified by silica gel column chromatography.

**4-(2,2′-Bithiophenyl-5-yl)benzonitrile (1):**[11a] The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **1** in 74% (0.198 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.60 (m, 4 H), 7.36 (d, *J* = 3.8 Hz, 1 H), 7.30–7.22 (m, 2 H), 7.18 (d, *J* = 3.8 Hz, 1 H), 7.07 (dd, *J* = 4.8, 3.8 Hz, 1 H) ppm.

**Methyl 4-(2,2′-Bithiophenyl-5-yl)benzoate (2):** The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **2** in 70% (0.210 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.07 (d, *J* = 8.3 Hz, 2 H), 7.67 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 3.8 Hz, 1 H), 7.35–7.25 (m, 2 H), 7.20 (d, *J* = 3.8 Hz, 1 H), 7.07 (dd, *J* = 4.8, 3.8 Hz, 1 H), 3.95 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 166.7, 141.6, 138.4, 138.3, 137.1, 130.3, 128.8, 127.9, 125.2, 125.1, 124.8, 124.7, 124.1, 52.1 ppm. $C_{16}H_{12}O_2S_2$ (300.40): calcd. C 63.97, H 4.03; found C 64.11, H 3.89.

**1-[4-(2,2′-Bithiophenyl-5-yl)phenyl]ethanone (3):**[14] The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **3** in 72% (0.205 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.99 (d, *J* = 8.3 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 3.8 Hz, 1 H), 7.35–7.25 (m, 2 H), 7.20 (d, *J* = 3.8 Hz, 1 H), 7.07 (dd, *J* = 4.8, 3.8 Hz, 1 H), 2.60 (s, 3 H) ppm.

**[4-(2,2′-Bithiophenyl-5-yl)phenyl](phenyl)methanone (4):** The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **4** in 73% (0.253 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.95–7.75 (m, 4 H), 7.75–7.45 (m, 5 H), 7.39 (d, *J* = 3.8 Hz, 1 H), 7.35–7.24 (m, 2 H), 7.21 (d, *J* = 3.8 Hz, 1 H), 7.07 (dd, *J* = 4.8, 3.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 196.3, 142.4, 138.8, 138.3, 138.1, 137.4, 136.5, 132.8, 131.4, 130.4, 128.7, 128.4, 125.7, 125.4, 125.3, 125.2, 124.5 ppm. $C_{21}H_{14}OS_2$ (346.47): calcd. C 72.80, H 4.07; found C 73.04, H 4.18.

**5-(4-Nitrophenyl)-2,2′-bithiophenyl (5):**[2d] The reaction of 1-bromo-4-nitrobenzene (0.202 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **5** in 69% (0.198 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.26 (d, $J$ = 8.7 Hz, 2 H), 7.74 (d, $J$ = 8.7 Hz, 2 H), 7.42 (d, $J$ = 3.8 Hz, 1 H), 7.35–7.25 (m, 2 H), 7.22 (d, $J$ = 3.8 Hz, 1 H), 7.09 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**5-[4-(Trifluoromethyl)phenyl]-2,2′-bithiophenyl (6):**[4a] The reaction of 1-bromo-4-(trifluoromethyl)benzene (0.225 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **6** in 70% (0.217 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.71 (d, $J$ = 8.7 Hz, 2 H), 7.65 (d, $J$ = 8.7 Hz, 2 H), 7.40–7.20 (m, 4 H), 7.09 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**5-(4-Chlorophenyl)-2,2′-bithiophenyl (7):** The reaction of 1-bromo-4-chlorobenzene (0.191 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **7** in 67% (0.185 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.54 (d, $J$ = 8.2 Hz, 2 H), 7.37 (d, $J$ = 8.2 Hz, 2 H), 7.30–7.10 (m, 4 H), 7.05 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.6, 137.2, 133.3, 132.6, 129.1, 127.9, 126.7, 124.7, 124.6, 123.8, 123.3 ppm. $C_{14}H_9ClS_2$ (276.81): calcd. C 60.75, H 3.28; found C 60.59, H 3.40.

**5-(4-Fluorophenyl)-2,2′-bithiophenyl (8):** The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **8** in 64% (0.166 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.58 (dd, $J$ = 8.8, 3.5 Hz, 2 H), 7.30–7.05 (m, 7 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 162.8 (d, $J$ = 237.5 Hz), 142.4, 137.7, 137.1, 130.8, 128.3, 127.7 (d, $J$ = 8.1 Hz), 125.0, 124.9, 124.1, 124.0, 116.3 (d, $J$ = 21.8 Hz) ppm. $C_{14}H_9FS_2$ (260.35): calcd. C 64.59, H 3.48; found C 64.70, H 3.61.

**5-Phenyl-2,2′-bithiophenyl (9):**[11b] The reaction of bromobenzene (0.157 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **9** in 52% (0.126 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.63–7.58 (m, 2 H), 7.43–7.36 (m, 2 H), 7.33–7.12 (m, 5 H), 7.04 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**1-[3-(2,2′-Bithiophenyl-5-yl)phenyl]ethanone (11):** The reaction of 3-bromoacetophenone (0.199 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **11** in 74% (0.210 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19 (s, 1 H), 7.87 (d, $J$ = 7.7 Hz, 1 H), 7.78 (d, $J$ = 7.8 Hz, 1 H), 7.49 (t, $J$ = 7.8 Hz, 1 H), 7.31 (d, $J$ = 3.8 Hz, 1 H), 7.30–7.20 (m, 2 H), 7.18 (d, $J$ = 3.8 Hz, 1 H), 7.06 (dd, $J$ = 4.8, 3.8 Hz, 1 H), 2.62 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 198.2, 142.1, 138.1, 137.9, 137.5, 135.0, 130.3, 129.6, 128.4, 127.7, 125.5, 125.1, 125.0, 124.9, 124.3, 27.2 ppm. $C_{16}H_{12}OS_2$ (284.40): calcd. C 67.57, H 4.25; found C 67.41, H 4.14.

**5-[3-(Trifluoromethyl)phenyl]-2,2′-bithiophenyl (12):**[11a] The reaction of 1-bromo-3-(trifluoromethyl)benzene (0.225 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **12** in 71% (0.220 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.86 (s, 1 H), 7.77 (d, $J$ = 7.0 Hz, 1 H), 7.60–7.10 (m, 6 H), 7.07 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**5-[3,5-Bis(trifluoromethyl)phenyl]-2,2′-bithiophenyl (13):** The reaction of 1-bromo-3,5-bis(trifluoromethyl)benzene (0.293 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **13** in 70% (0.265 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.00 (s, 2 H), 7.78 (s, 1 H), 7.38 (d, $J$ = 3.8 Hz, 1 H), 7.33–7.22 (m, 2 H), 7.21 (d, $J$ = 3.8 Hz, 1 H), 7.07 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 139.2, 139.0, 136.5, 136.1, 132.4 (q, $J$ = 33.2 Hz), 128.0, 125.9, 125.2, 125 (m), 124.8, 124.4, 123.4 (q, $J$ = 272.9 Hz), 120.6 (sept, $J$ = 3.2 Hz) ppm. $C_{16}H_8F_6S_2$ (378.36): calcd. C 50.79, H 2.13; found C 50.70, H 2.04.

**2-(2,2′-Bithiophenyl-5-yl)benzonitrile (14):** The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **14** in 71% (0.190 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.75 (d, $J$ = 8.6 Hz, 1 H), 7.70–7.55 (m, 3 H), 7.50–7.35 (m, 1 H), 7.30–7.15 (m, 3 H), 7.06 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 139.3, 137.8, 137.0, 136.6, 134.4, 133.0, 129.2, 128.3, 127.9, 127.5, 125.1, 124.7, 124.3, 118.8, 109.5 ppm. $C_{15}H_9NS_2$ (267.37): calcd. C 67.38, H 3.39; found C 67.31, H 3.32.

**2-(2,2′-Bithiophenyl-5-yl)benzaldehyde (15):** The reaction of 2-bromobenzaldehyde (0.185 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **15** in 63% (0.170 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.27 (s, 1 H), 8.02 (d, $J$ = 8.6 Hz, 1 H), 7.70–7.00 (m, 6 H), 6.97 (dd, $J$ = 4.8, 3.8 Hz, 1 H), 6.91 (d, $J$ = 3.6 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 192.3, 139.9, 138.0, 137.8, 137.0, 134.5, 134.1, 131.4, 130.8, 128.7, 128.5, 128.4, 125.5, 124.7, 124.6 ppm. $C_{15}H_{10}OS_2$ (270.37): calcd. C 66.63, H 3.73; found C 66.70, H 3.79.

**[2-(2,2′-Bithiophenyl-5-yl)phenyl]methanol (16):** The reaction of (2-bromophenyl)methanol (0.187 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **16** in 58% (0.158 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.59 (d, $J$ = 8.6 Hz, 1 H), 7.52 (d, $J$ = 8.6 Hz, 1 H), 7.45–7.35 (m, 2 H), 7.30–7.20 (m, 2 H), 7.19 (d, $J$ = 3.8 Hz, 1 H), 7.13 (d, $J$ = 3.8 Hz, 1 H), 7.06 (dd, $J$ = 4.8, 3.8 Hz, 1 H), 4.83 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 140.5, 138.4, 137.8, 137.2, 133.3, 130.6, 129.1, 128.4, 128.0, 127.9, 127.7, 124.5, 124.1, 123.8, 63.5 ppm. $C_{15}H_{12}OS_2$ (272.39): calcd. C 66.14, H 4.44; found C 66.21, H 4.37.

**5-(1-Naphthyl)-2,2′-bithiophenyl (17):**[11a] The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **17** in 73% (0.213 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.50–8.40 (m, 1 H), 8.05–7.90 (m, 2 H), 7.80–7.50 (m, 4 H), 7.40–7.20 (m, 4 H), 7.12 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**5-(9-Anthryl)-2,2′-bithiophenyl (18):**[12a] The reaction of 9-bromoanthracene (0.257 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **18** in 67% (0.229 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.57 (s, 1 H), 8.20–8.10 (m, 4 H), 7.60–7.45 (m, 4 H), 7.44 (d, $J$ = 3.6 Hz, 1 H), 7.35–7.25 (m, 2 H), 7.15 (d, $J$ = 3.6 Hz, 1 H), 7.12 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**3-(2,2′-Bithiophenyl-5-yl)pyridine (19):**[6c] The reaction of 3-bromopyridine (0.158 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of $[PdCl(C_3H_5)(dppb)]$ (6.8 mg, 0.01 mmol) afforded **19** in 73% (0.177 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.90 (s, 1 H), 8.54 (d, $J$ = 4.2 Hz, 1 H), 7.88 (d, $J$ = 8.2 Hz, 1 H), 7.40–7.20 (m, 5 H), 7.07 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**4-(2,2′-Bithiophenyl-5-yl)pyridine (20):**[6c] The reaction of 4-bromopyridine hydrochloride (0.194 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **20** in 75% (0.182 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.60 (d, $J$ = 6.0 Hz, 2 H), 7.44 (d, $J$ = 6.0 Hz, 2 H), 7.41 (d, $J$ = 3.8 Hz, 1 H), 7.30–7.22 (m, 2 H), 7.18 (d, $J$ = 3.8 Hz, 1 H), 7.05 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**3-(2,2′-Bithiophenyl-5-yl)quinoline (21):** The reaction of 3-bromoquinoline (0.208 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **21** in 73% (0.214 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.18 (s, 1 H), 8.20 (s, 1 H), 8.10 (d, $J$ = 8.2 Hz, 1 H), 7.80 (d, $J$ = 7.8 Hz, 1 H), 7.69 (t, $J$ = 8.0 Hz, 1 H), 7.55 (t, $J$ = 8.0 Hz, 1 H), 7.40–7.10 (m, 4 H), 7.07 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 148.5, 147.6, 139.6, 138.5, 137.4, 131.2, 129.8, 129.7, 128.4, 128.3, 128.2, 127.7, 127.6, 125.4, 125.3, 125.2, 124.5 ppm. $C_{17}H_{11}NS_2$ (293.41): calcd. C 69.59, H 3.78; found C 69.51, H 3.64.

**4-(2,2′-Bithiophenyl-5-yl)isoquinoline (22):**[5a] The reaction of 4-bromoisoquinoline (0.208 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **22** in 74% (0.217 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.25 (s, 1 H), 8.66 (s, 1 H), 8.32 (d, $J$ = 8.2 Hz, 1 H), 8.05 (d, $J$ = 7.7 Hz, 1 H), 7.76 (t, $J$ = 8.0 Hz, 1 H), 7.70 (t, $J$ = 8.0 Hz, 1 H), 7.35–7.20 (m, 4 H), 7.07 (dd, $J$ = 4.8, 3.8 Hz, 1 H) ppm.

**5-(2,2′-Bithiophenyl-5-yl)pyrimidine (23):** The reaction of 5-bromopyrimidine (0.159 g, 1 mmol), 2,2′-bithiophenyl (0.498 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **23** in 70% (0.171 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.12 (s, 1 H), 8.95 (s, 2 H), 7.40–7.20 (m, 4 H), 7.10–7.00 (m, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 156.1, 151.9, 138.4, 135.3, 133.4, 127.3, 127.0, 124.9, 124.3, 123.8, 123.5 ppm. $C_{12}H_8N_2S_2$ (244.34): calcd. C 58.99, H 3.30; found C 59.14, H 3.32.

**4-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)benzonitrile (24):** The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **24** in 73% (0.215 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.60 (m, 4 H), 7.33 (d, $J$ = 5.1 Hz, 1 H), 7.28 (s, 1 H), 6.97 (d, $J$ = 5.1 Hz, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 140.7, 138.4, 138.0, 136.9, 132.7, 131.7, 130.3, 128.7, 128.2, 125.6, 125.5, 118.9, 110.4, 15.0, 14.9 ppm. $C_{17}H_{13}NS_2$ (295.42): calcd. C 69.11, H 4.44; found C 68.89, H 4.35.

**1-[4-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)phenyl]ethanone (25):** The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **25** in 74% (0.231 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.94 (d, $J$ = 8.3 Hz, 2 H), 7.57 (d, $J$ = 8.3 Hz, 2 H), 7.28 (d, $J$ = 5.1 Hz, 1 H), 7.27 (s, 1 H), 6.96 (d, $J$ = 5.1 Hz, 1 H), 2.63 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 192.2, 140.6, 137.5, 136.7, 135.7, 134.6, 129.9, 129.2, 128.1, 127.9, 126.6, 124.3, 124.2, 25.5, 13.9, 13.8 ppm. $C_{18}H_{16}OS_2$ (312.45): calcd. C 69.19, H 5.16; found C 69.17, H 5.34.

**Methyl 4-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)benzoate (26):** The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **26** in 70% (0.230 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.05 (d, $J$ = 8.3 Hz, 2 H), 7.66 (d, $J$ = 8.3 Hz, 2 H), 7.32 (d, $J$ = 5.1 Hz, 1 H), 7.28 (s, 1 H), 6.96 (d, $J$ = 5.1 Hz, 1 H), 3.95 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 166.8, 141.8, 138.4, 137.8, 136.8, 130.7, 130.3, 130.2, 129.0, 128.7, 127.5, 125.3, 125.1, 52.1, 15.0, 14.9 ppm. $C_{18}H_{16}O_2S_2$ (328.45): calcd. C 65.82, H 4.91; found C 65.98, H 4.97.

**5-(4-Chlorophenyl)-3,3′-dimethyl-2,2′-bithiophenyl (27):** The reaction of 1-bromo-4-chlorobenzene (0.191 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **27** in 62% (0.189 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.53 (d, $J$ = 8.2 Hz, 2 H), 7.36 (d, $J$ = 8.2 Hz, 2 H), 7.31 (d, $J$ = 5.1 Hz, 1 H), 7.16 (s, 1 H), 6.97 (d, $J$ = 5.1 Hz, 1 H), 2.26 (s, 3 H), 2.22 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.9, 137.6, 136.7, 133.2, 132.7, 130.2, 129.5, 129.1, 129.0, 126.7, 126.5, 125.2, 15.0, 14.9 ppm. $C_{16}H_{13}ClS_2$ (304.86): calcd. C 63.04, H 4.30; found C 63.17, H 4.47.

**3,3′-Dimethyl-5-(3-nitrophenyl)-2,2′-bithiophenyl (28):** The reaction of 1-bromo-3-nitrobenzene (0.202 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **28** in 69% (0.217 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.45 (s, 1 H), 8.14 (d, $J$ = 8.3 Hz, 1 H), 7.88 (d, $J$ = 8.3 Hz, 1 H), 7.57 (t, $J$ = 7.8 Hz, 1 H), 7.28 (d, $J$ = 5.1 Hz, 1 H), 7.27 (s, 1 H), 6.96 (d, $J$ = 5.1 Hz, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 147.7, 139.1, 136.8, 136.0, 134.8, 130.0, 129.2, 128.9, 128.8, 126.7, 124.4, 123.9, 120.7, 118.9 ppm. $C_{16}H_{13}NO_2S_2$ (315.41): calcd. C 60.93, H 4.15; found C 60.98, H 4.04.

**3-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)benzaldehyde (29):** The reaction of 3-bromobenzaldehyde (0.185 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **29** in 81% (0.241 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.07 (s, 1 H), 8.10 (s, 1 H), 7.85 (d, $J$ = 8.2 Hz, 1 H), 7.80 (d, $J$ = 8.2 Hz, 1 H), 7.56 (t, $J$ = 8.0 Hz, 1 H), 7.31 (d, $J$ = 5.1 Hz, 1 H), 7.27 (s, 1 H), 6.97 (d, $J$ = 5.1 Hz, 1 H), 2.26 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 192.5, 141.8, 138.1, 137.3, 137.2, 135.6, 131.6, 130.6, 130.0, 129.0, 127.5, 126.7, 125.7, 15.4, 15.3 ppm. $C_{17}H_{14}OS_2$ (298.42): calcd. C 68.42, H 4.73; found C 68.57, H 4.60.

**2-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)benzonitrile (30):** The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **30** in 71% (0.210 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.73 (d, $J$ = 8.2 Hz, 1 H), 7.60–7.20 (m, 5 H), 6.98 (d, $J$ = 5.1 Hz, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 138.4, 137.7, 137.3, 136.9, 134.5, 133.0, 131.9, 130.4, 130.2, 129.3, 128.6, 127.4, 125.5, 118.9, 109.5, 15.0, 14.9 ppm. $C_{17}H_{13}NS_2$ (295.42): calcd. C 69.11, H 4.44; found C 68.97, H 4.57.

**3,3′-Dimethyl-5-(1-naphthyl)-2,2′-bithiophenyl (31):** The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **31** in 62% (0.198 g) yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.45–8.35 (m, 1 H), 8.00–7.75 (m, 2 H), 7.65–7.45 (m, 4 H), 7.32 (d, $J$ = 5.1 Hz, 1 H), 7.15 (s, 1 H), 6.99 (d, $J$ = 5.1 Hz, 1 H), 2.31 (s, 3 H), 2.29 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 137.0, 136.9, 134.3, 132.7, 132.0, 130.8, 130.6, 130.2, 128.8, 128.7, 128.3, 126.8, 126.4, 126.2, 125.7, 125.5, 125.4, 15.4, 15.3 ppm. $C_{20}H_{16}S_2$ (320.47): calcd. C 74.96, H 5.03; found C 75.08, H 5.12.

**5-(9-Anthryl)-3,3′-dimethyl-2,2′-bithiophenyl (32):** The reaction of 9-bromoanthracene (0.257 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **32** in 67% (0.248 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.54 (s, 1 H), 8.06 (d, $J$ = 7.5 Hz, 4 H), 7.55–7.45 (m, 4 H), 7.34 (d, $J$ = 5.1 Hz, 1 H), 7.02 (s, 1 H), 7.00 (d, $J$ = 5.1 Hz, 1 H), 2.36 (s, 3 H), 2.35 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 136.8, 135.0, 134.9, 131.0, 130.3, 129.9, 129.4, 128.8, 128.1, 127.4, 127.0, 126.6, 125.5, 124.7, 124.1, 123.8, 17.0, 16.9 ppm. $C_{24}H_{18}S_2$ (370.53): calcd. C 77.80, H 4.90; found C 77.97, H 5.01.

**3-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)pyridine (33):** The reaction of 3-bromopyridine (0.158 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **33** in 74% (0.201 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.86 (s, 1 H), 8.48 (d, $J$ = 4.7 Hz, 1 H), 7.80 (d, $J$ = 8.0 Hz, 1 H), 7.40–7.10 (m, 3 H), 6.93 (d, $J$ = 5.1 Hz, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 147.4, 145.6, 138.2, 136.7, 135.7, 131.5, 129.3, 129.1, 127.8, 126.1, 124.3, 122.6, 13.9, 13.8 ppm. $C_{15}H_{13}NS_2$ (271.40): calcd. C 66.38, H 4.83; found C 66.27, H 4.94.

**4-(3,3′-Dimethyl-2,2′-bithiophenyl-5-yl)isoquinoline (34):** The reaction of 4-bromoisoquinoline (0.208 g, 1 mmol), 3,3′-dimethyl-2,2′-bithiophenyl (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **34** in 75% (0.241 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.25 (s, 1 H), 8.67 (s, 1 H), 8.35 (d, $J$ = 8.2 Hz, 1 H), 8.03 (d, $J$ = 7.7 Hz, 1 H), 7.73 (t, $J$ = 8.0 Hz, 1 H), 7.71 (t, $J$ = 8.0 Hz, 1 H), 7.30 (d, $J$ = 5.1 Hz, 1 H), 7.19 (s, 1 H), 6.96 (d, $J$ = 5.1 Hz, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 152.8, 143.7, 137.5, 137.4, 137.1, 134.4, 131.4, 131.3, 130.7, 129.3, 128.8, 128.4, 127.8, 126.6, 125.7, 125.1, 15.4, 15.3 ppm. $C_{19}H_{15}NS_2$ (321.46): calcd. C 70.99, H 4.70; found C 71.12, H 4.85.

**4-(5′-Formyl-2,2′-bithiophenyl-5-yl)benzonitrile (35):** The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2,2′-bithiophenyl-5-carbaldehyde (0.291 g, 1.5 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **35** in 66% (0.195 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.91 (s, 1 H), 7.75–7.70 (m, 5 H), 7.45–7.20 (m, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 181.5, 145.1, 142.2, 141.2, 136.6, 136.3, 131.9, 131.6, 126.2, 125.2, 125.0, 123.7, 117.6, 110.2 ppm. $C_{16}H_9NOS_2$ (295.38): calcd. C 65.06, H 3.07; found C 65.24, H 3.14.

**Methyl 4-(5′-Formyl-2,2′-bithiophenyl-5-yl)benzoate (36):** The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol), 2,2′-bithiophenyl-5-carbaldehyde (0.291 g, 1.5 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **36** in 60% (0.197 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.90 (s, 1 H), 8.09 (d, $J$ = 8.3 Hz, 2 H), 7.75–7.68 (m, 3 H), 7.41 (d, $J$ = 4.0 Hz, 1 H), 7.38 (d, $J$ = 4.0 Hz, 1 H), 7.32 (d, $J$ = 4.0 Hz, 1 H), 3.96 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 182.5, 166.6, 146.6, 144.5, 142.0, 137.6, 137.3, 136.5, 130.4, 129.5, 127.2, 125.6, 125.5, 124.4, 52.3 ppm. $C_{17}H_{12}O_3S_2$ (328.41): calcd. C 62.17, H 3.68; found C 62.27, H 3.60.

**5′-(9-Anthryl)-2,2′-bithiophenyl-5-carbaldehyde (37):** The reaction of 9-bromoanthracene (0.257 g, 1 mmol), 2,2′-bithiophenyl-5-carbaldehyde (0.291 g, 1.5 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **37** in 62% (0.230 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.91 (s, 1 H), 8.58 (s, 1 H), 8.09 (d, $J$ = 8.0 Hz, 2 H), 7.96 (d, $J$ = 8.0 Hz, 2 H), 7.71 (d, $J$ = 3.5 Hz, 1 H), 7.58 (d, $J$ = 3.6 Hz, 1 H), 7.57–7.40 (m, 4 H), 7.32 (d, $J$ = 3.6 Hz, 1 H), 7.17 (d, $J$ = 3.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 182.6, 147.0, 141.7, 141.2, 137.4, 137.3, 131.6, 131.2, 130.8, 128.6, 128.5, 127.2, 126.4, 126.3, 126.2, 125.4, 124.3 ppm. $C_{23}H_{14}OS_2$ (370.49): calcd. C 74.56, H 3.81; found C 74.67, H 3.87.

**5′-Pyridin-3-yl-2,2′-bithiophenyl-5-carbaldehyde (38):** The reaction of 3-bromopyridine (0.158 g, 1 mmol), 2,2′-bithiophenyl-5-carbaldehyde (0.291 g, 1.5 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **38** in 65% (0.176 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.86 (s, 1 H), 8.87 (s, 1 H), 8.55 (d, $J$ = 4.7 Hz, 1 H), 7.85 (d, $J$ = 8.0 Hz, 1 H), 7.68 (d, $J$ = 4.0 Hz, 1 H), 7.45–7.30 (m, 4 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 182.4, 149.1, 146.8, 146.4, 142.0, 141.8, 137.2, 136.4, 132.8, 129.5, 127.1, 125.3, 124.4, 123.7 ppm. $C_{14}H_9NOS_2$ (271.36): calcd. C 61.97, H 3.34; found C 62.10, H 3.41.

**4-(5′-Acetyl-2,2′-bithiophenyl-5-yl)benzonitrile (39):** The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-(2,2′-bithiophenyl-5-yl)-ethanone (0.312 g, 1.5 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **39** in 66% (0.204 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.73–7.66 (m, 4 H), 7.62 (d, $J$ = 4.0 Hz, 1 H), 7.38 (d, $J$ = 4.0 Hz, 1 H), 7.33 (d, $J$ = 4.0 Hz, 1 H), 7.24 (d, $J$ = 4.0 Hz, 1 H), 2.58 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 189.7, 144.1, 142.4, 141.9, 137.1, 137.0, 132.7, 132.2, 126.1, 125.5, 125.2, 124.0, 118.0, 110.4, 25.9 ppm. $C_{17}H_{11}NOS_2$ (309.41): calcd. C 65.99, H 3.58; found C 65.87, H 3.41.

**4-[5-(Thiophen-2-ylcarbonyl)thiophen-2-yl]benzonitrile (40):** The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), bis(thiophen-2-yl)methanone (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **40** in 70% (0.207 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.93 (d, $J$ = 3.8 Hz, 1 H), 7.90 (d, $J$ = 4.0 Hz, 1 H), 7.79 (d, $J$ = 8.0 Hz, 2 H), 7.71 (d, $J$ = 8.0 Hz, 2 H), 7.80–7.70 (m, 1 H), 7.48 (d, $J$ = 4.0 Hz, 1 H), 7.22 (dd, $J$ = 4.8, 4.0 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 178.3, 149.3, 143.5, 142.4, 137.4, 134.0, 133.9, 133.2, 132.9, 128.1, 126.7, 125.6, 118.4, 112.2 ppm. $C_{16}H_9NOS_2$ (295.38): calcd. C 65.06, H 3.07; found C 65.14, H 3.20.

**2-[5-(Thiophen-2-ylcarbonyl)thiophen-2-yl]benzonitrile (41):** The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), bis(thiophen-2-yl)methanone (0.582 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **41** in 68% (0.201 g) yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.95 (d, $J$ = 3.8 Hz, 1 H), 7.91 (d, $J$ = 4.0 Hz, 1 H), 7.80–7.45 (m, 6 H), 7.22 (dd, $J$ = 4.8, 4.0 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 178.6, 147.0, 144.2, 142.6, 136.5, 134.7, 134.1, 133.8, 133.6, 133.5, 130.1, 129.1, 128.4, 128.3, 118.5, 110.5 ppm. $C_{16}H_9NOS_2$ (295.38): calcd. C 65.06, H 3.07; found C 65.01, H 3.22.

**1-(5-Pyridin-3-ylthiophen-2-yl)-2-(thiophen-2-yl)ethane-1,2-dione (42):** The reaction of 3-bromopyridine (0.158 g, 1 mmol), 1,2-bis(thiophen-2-yl)ethane-1,2-dione (0.666 g, 3 mmol) and KOAc (0.196 g, 2 mmol) in the presence of [PdCl($C_3H_5$)(dppb)] (6.8 mg, 0.01 mmol) afforded **42** in 21% (0.063 g) yield. $^1$H NMR

(300 MHz, $CDCl_3$): $\delta$ = 9.00 (s, 1 H), 8.65 (d, $J$ = 4.7 Hz, 1 H), 8.14 (d, $J$ = 4.0 Hz, 1 H), 8.11 (d, $J$ = 4.0 Hz, 1 H), 7.99 (d, $J$ = 8.2 Hz, 1 H), 7.89 (d, $J$ = 4.9 Hz, 1 H), 7.47 (d, $J$ = 4.0 Hz, 1 H), 7.41 (dd, $J$ = 8.2, 4.7 Hz, 1 H), 7.26 (t, $J$ = 4.0 Hz, 1 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 181.9, 181.7, 152.2, 150.3, 147.4, 138.4, 138.2, 138.1, 137.8, 137.5, 133.6, 129.1, 128.7, 125.5, 123.9 ppm. $C_{15}H_9NO_2S_2$ (299.37): calcd. C 60.18, H 3.03; found C 60.31, H 3.10.

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