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Palladium-Catalysed Direct C-H Activation/Arylation of Heteroaromatics: An Environmentally Attractive Access to Bi- or Polydentate Ligands

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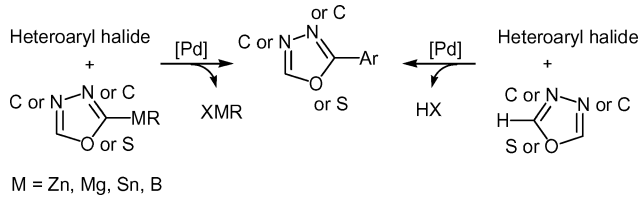
Bi- or polydentate ligands based on heterocycles can be easily prepared by palladium-catalysed C–H bond activation of heteroaromatics followed by heteroarylation with heteroaryl bromides. A variety of heteroaromatics such as furans, thiophenes, pyridines, thiazoles or oxazole derivatives have been employed and moderate to good yields were generally obtained using the air-stable complex [PdCl(dppb)(C_3H_5)] as catalyst. A range of functions such as acetyl, formyl, ester or nitrile on the heteroaromatics is tolerated.

Introduction

Bi- or polydentate ligands based on polyheteroaromatics such as bipyridines or polythiophenes are useful compounds for organometallic chemistry and catalysis or for preparation of materials due to their specific coordination and electronic properties. Palladium-catalysed Suzuki, Stille or Negishi cross-coupling reactions between 2-haloheteroarenes and organometallic derivatives of thiophenes, furans, thiazoles, oxazoles or pyridines are some of the most important methods for the synthesis of such compounds.[1–4] However, these reactions require the preparation of an organometallic derivative of the heteroaromatic and produce an organometallic salt (MX) as a by-product (Scheme 1).



Scheme 1.

Very interesting results regarding the coupling of aryl halides with heteroaromatic derivatives by C–H bond activation have been reported over the past few years. No preparation of an organometallic derivative is required for such couplings. Moreover, this reaction provides only HX associated to a base as by-product and therefore is very interesting both in terms of atom-economy and the relative inertness of the wastes (Scheme 1). This procedure could therefore provide an economic and environmentally attractive procedure for the preparation of bi- or polydentate ligands.[5] However, most of the results described so far for this reaction were obtained for the coupling of heteroaromatics with aryl halides.[5] 2-Haloheteroarenes are uncommon partners for such couplings[6–9] and only a few examples have been described with such substrates in the literature. For example, the direct heteroarylation of 5-bromo-2-furaldehyde by C–H bond activation of 2-furaldehyde has been described by McClure and co-workers, who used $PdCl_2$ in conjunction with PCy_3 as the catalyst and obtained the coupling product in 64% yield.[6] The reaction of an oxazolopyridine with 2-chloropyridine using $Pd(OAc)_2/PPh_3$ as catalyst has been reported to give 2-(pyridin-2-yl)oxazolo[4,5-*b*]pyridine in 33% yield,[7a] and an improved procedure for this reaction was recently reported by Daugulis and Chiong, who used the electron-rich and congested butyldi(1-adamantyl)phosphane ligand to obtain the coupling product in 67% yield.[7b] A coupling reaction between 2-bromothiophene and an indolizine leading to 3-(thiophen-2-yl)indolizine in 55% yield has also been reported.[8] Three examples of direct 5-heteroarylations of imidazoles via C–H activation have also been described.[9] For example, Miura and co-workers have successfully coupled 1,2-dimethyl-1*H*-imidazole with 2-bromothiazole in 41% yield using $Pd(OAc)_2/PPh_3$ as the catalyst,[9a] and 2-bromopyridine was coupled to an imidazo-pyrimidine in 55% yield under similar reaction conditions.[9b] The direct arylation of a purine at position 8 has been described by Hocek and co-workers,[9c] who used $Pd(OAc)_2$ as the catalyst, Cs_2CO_3 as the base and CuI as an additive. Although the conditions for this reaction are rather harsh (160 °C), the coupling with 2-iodopyridine gave the cross-coupling product re-

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gioselectively in 42% yield. Finally, it should be noted that homocoupling by C–H bond activation of heteroaromatics using palladium or gold catalysts has also been reported.[10]

Although a few syntheses of ligands by palladium-catalysed C–H bond activation of heteroaromatics followed by heteroarylation have been described, the scope of the reaction needs to be extended to a wider variety of heteroaromatics and also to functionalised heteroaryl halides. Moreover, higher yields for the coupling of such compounds have to be obtained using more efficient catalysts under more effective reaction conditions in order to obtain economically viable procedures.

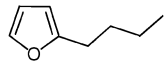
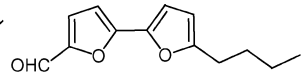
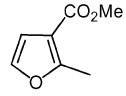
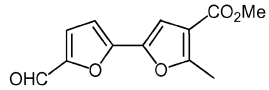
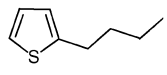
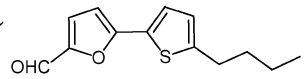
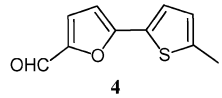
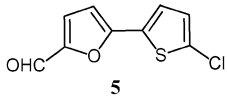
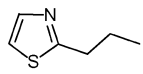
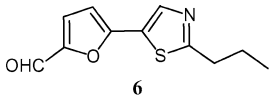
Results and Discussion

The classical palladium catalysts for C–H activation/functionalisation of heteroaromatic derivatives with aryl halides or triflates are probably ligand-less palladium complexes or palladium associated to monophosphanes,[5,11a] although bi- or polydentate phosphane ligands have also demonstrated their usefulness.[5,11b,11c,12] We therefore decided to examine the reactivity of 5-bromo-2-furaldehyde for the palladium-catalysed coupling reaction with 2-butylfuran using $Pd(OAc)_2$ or $[PdCl(C_3H_5)]_2$, DMAc (*N*,*N*-dimethylacetamide) as solvent and KOAc as base at 120 °C in the absence of ligand. The formation of unidentified side-products was observed, especially in the presence of $Pd(OAc)_2$. We have recently reported that ligand-free $Pd(OAc)_2$ is a very powerful catalyst for the direct arylation of furans, thiophenes or thiazoles − the reaction can be performed with as little as 0.01 mol-% catalyst. However, the efficiency of this catalyst is limited to the coupling of very reactive substrates such as activated aryl bromides and does not seems to be appropriate for the coupling of heteroaryl bromides.[11d]

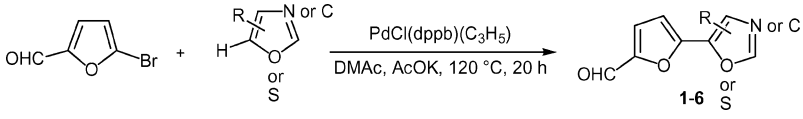
Most of the couplings of heteroaryl derivatives with aryl halides reported in the literature were performed at elevated temperature (120–150 °C),[5] where a fast decomposition of most palladium complexes generally occurs, especially when relatively high catalyst loadings are employed. The use of phosphane ligands seems to increase the stability and longevity of the catalyst in palladium-catalysed reactions, and better yields of coupling products can be expected in some cases. We therefore next performed the coupling of 5-bromo-2-furaldehyde with 2-butylfuran using $Pd(OAc)_2$ or $[PdCl(C_3H_5)]_2$ in combination with PPh_3 or dppb. A higher isolated yield of **1** was obtained using the bidentate phosphane ligand. For this reason, we have employed palladium in combination with dppb as a catalyst to study the scope and limitations of these couplings.

We next examined the reactivity of 5-bromo-2-furaldehyde for the palladium-catalysed coupling with a set of heteroaromatic compounds (Scheme 2, Table 1) with DMAc as solvent, KOAc as base and $[PdCl(C_3H_5)(dppb)]$[13] as catalyst. All reactions were performed at 120 °C, as partial degradation of 5-bromo-2-furaldehyde and of some of the coupling products was observed at more elevated temperatures. Complete conversion of 5-bromo-2-furaldehyde was observed under these conditions in all cases. Similar isolated yields (71–78%) of target products **2**–**6** were obtained using methyl 2-methyl-3-furancarboxylate, 2-butylthiophene, 2-methylthiophene, 2-chlorothiophene or 2-propylthiazole as reagents. The coupling is regioselective in favour of the 5-arylation in all cases. Selective 5-arylation was also observed with 2-chlorothiophene, and 5-(5-chlorothiophen-2-yl)furan-2-carbaldehyde (**5**) was obtained in 71% yield (Table 1, entry 5). The thiophene–chlorine bond of this reagent was found to be unreactive under these reaction conditions.

Table 1. Palladium-catalysed cross-coupling with 5-bromo-2-furaldehyde (Scheme 2).[a]

Entry	Heteroarene	Product	% Yield
1		 **1**	72
2		 **2**	75
3		 **3**	78
4		 **4**	75
5		 **5**	71
6		 **6**	80

[a] Conditions: $[PdCl(dppb)(C_3H_5)]$ (0.05 equiv.), 5-bromo-2-furaldehyde (1 equiv.), heteroarene (2 equiv.), KOAc (2 equiv.), DMAc, 20 h, 120 °C. The yields given are those of isolated product.

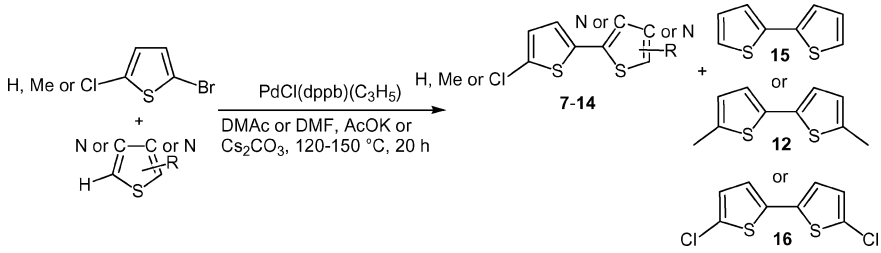


Scheme 2.

The scope and limitations of this reaction with other heteroaryl bromides were investigated next. 2-Bromothiophene or 2-bromo-5-methylthiophene were successfully coupled with 2-propylthiazole, benzoxazole, 2-chlorothiophene, 2-methylthiophene or 2-chlorothiophene (Scheme 3, Table 2). Slightly lower yields than for the coupling with 5-bromo-2-furaldehyde were obtained in some cases due to the formation of 2,2′-bithiophene (**15**), 5,5′-dimethyl-2,2′-bithiophene (**12**) or 5,5′-dichloro-2,2′-bithiophene (**16**) as side products. However, the target products **7**–**14** were obtained regioselectively in all cases. In the presence of 5-bromo-2-chlorothiophene and benzothiophene, the expected product **14** was obtained in a lower yield of 30% (Table 2, entry 8), and unidentified side products were also formed during the course of this reaction. However, these reactions generally gave a very simple access to substituted thiophenes or unsymmetrical bithiophene derivatives in one step.

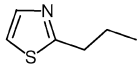
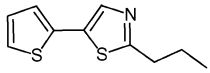
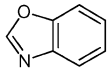
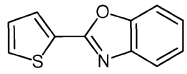
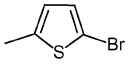
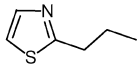
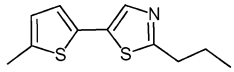
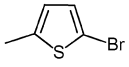
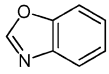
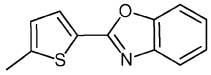
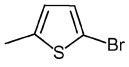
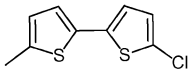
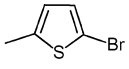
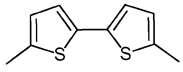
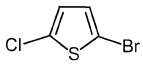
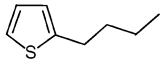
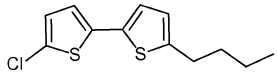
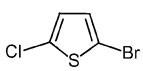
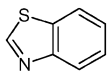
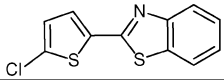
This reaction is not limited to thiophene and 2-methyl- or 2-chlorothiophenes. For example, 2-bromo-5-formylthiophene was also found to be a suitable reageant for this reaction (Table 3, Scheme 4). Again, a variety of heteroarenes weren coupled with this substrate to give the desired products **17**–**22**. Only a minor influence of the nature of the heteroarene on the yield of coupling product was observed. Thus, the highest yields of 77 and 80% were obtained using 2-butylfuran and 2-propylthiazole, respectively (Table 3, entries 1 and 6). Less reactive heteroarenes such as 2-methylthiophenes or 2-chlorothiophene gave the target products **20** and **21** in 65 and 69% yields, respectively (Table 3, entries 4 and 5). Formation of the homo-coupling product **23** from 2-bromo-5-formylthiophene was also observed in low yield during the course of these reactions.

As expected, the treatment of 2-acetyl-5-bromothiophene with electron-rich heteroarenes also gave the expected coup-



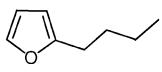
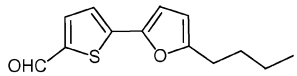
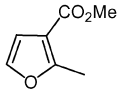
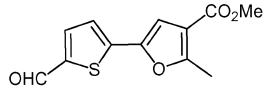
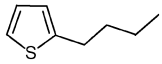
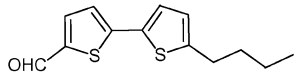
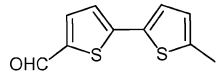
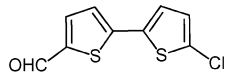
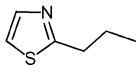
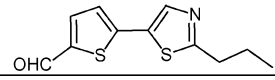
Scheme 3.

Table 2. Palladium-catalysed cross-coupling with 2-bromothiophene, 2-bromo-5-methylthiophene or 2-bromo-5-chlorothiophene (Scheme 3).[a]

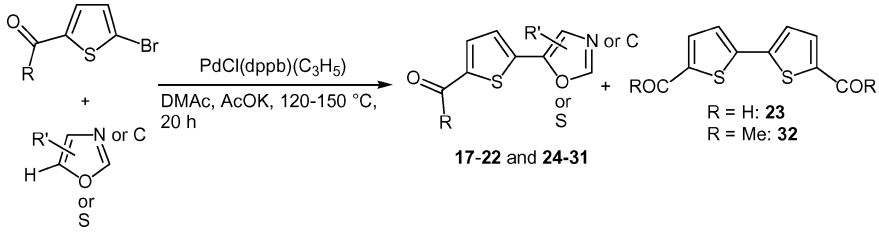
Entry	Heteroaryl bromide	Heteroarene	Temperature / °C	Product		% Yield
1			150		**7**	56
2			150		**8**	73[b,d,e]
3			150		**9**	63[c]
4			150		**10**	80[c,d]
5			150		**11**	51[c]
6			120		**12**	78
7			120		**13**	61[f]
8			120		**14**	30[d,f]

[a] Conditions: [PdCl(dppb)(C_3H_5)] (0.05 equiv.), 2-bromothiophene, 2-bromo-5-methylthiophene or 2-bromo-5-chlorothiophene (1 equiv.), heteroarene (2 equiv.), KOAc (2 equiv.), DMAc, 20 h. The yields given are those of isolated product. [b] The formation of 2,2′-bithiophene (**15**) was also observed. [c] The formation of 5,5′-dimethyl-2,2′-bithiophene (**12**) was also observed. [d] Cs_2CO_3 was used as base and DMF as solvent. [e] 1 mol-% of [PdCl(dppb)(C_3H_5)]. [f] The formation of 5,5′-dichloro-2,2′-bithiophene (**16**) was also observed.

Table 3. Palladium catalysed cross-coupling with 2-bromo-5-formylthiophene (Scheme 4).[a]

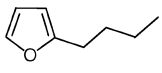
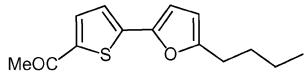
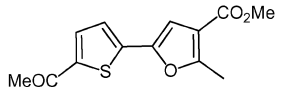
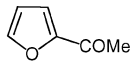
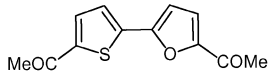
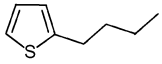
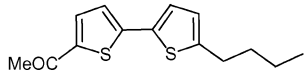
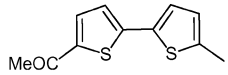
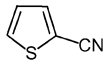
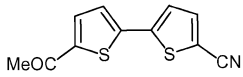
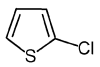
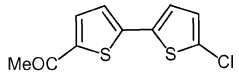
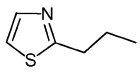
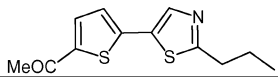
Entry	Heteroarene	Temperature / °C	Product		% Yield
1		150		**17**	77
2		120		**18**	57
3		150		**19**	67
4		120		**20**	65
5		120		**21**	69
6		150		**22**	80

[a] Conditions: [PdCl(dppb)(C_3H_5)] (0.05 equiv.), 2-bromo-5-formylthiophene (1 equiv.), heteroarene (2 equiv.), KOAc (2 equiv.), DMAc, 20 h. The yields given are those of isolated product. The formation of 2,2′-bithiophene-5,5′-dicarbaldehyde (**23**) was also observed.



Scheme 4.

Table 4. Palladium-catalysed cross-coupling with 2-acetyl-5-bromothiophene (Scheme 4).[a]

Entry	Heteroarene	Temperature / °C	Product		% Yield
1		150		**24**	62
2		120		**25**	53
3		120		**26**	32
4		120		**27**	83
5		120		**28**	67
6		120		**29**	64
7		120		**30**	57
8		150		**31**	56

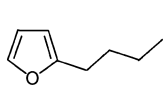
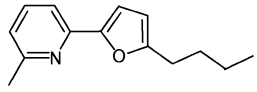
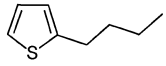
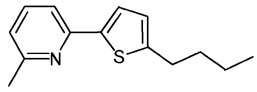
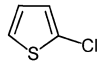
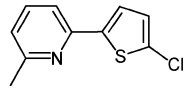
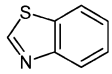
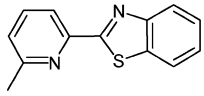
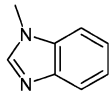
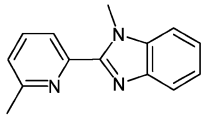
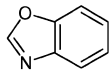
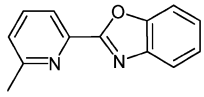
[a] Conditions: [PdCl(dppb)(C_3H_5)] (0.05 equiv.), 2-acetyl-5-bromothiophene (1 equiv.), heteroarene (2 equiv.), KOAc (2 equiv.), DMAc, 20 h. The yields given are those of isolated product. The formation of 1-(5′-acetyl-2,2′-bithiophene-5-yl)ethanone (**32**) was also observed.

ling products **24**–**31** together with a small amount of the homo-coupling product **32** (Table 4, Scheme 4). Thus, the reaction of 2-butylfuran or methyl 2-methyl-3-furancarboxylate gave **24** and **25** in 62 and 53% yields, respectively, whereas **26** was obtained from 2-acetylfuran in a lower yield due to the formation of unidentified side-products (Table 4, entries 1–3). The coupling with four thiophene derivatives was also tested with this substrate; they gave the expected substituted bithiophenes **27**–**30** in good yields (Table 4, entries 4–7). For example, the reaction of 2-acetyl-5-bromothiophene with thiophene-2-carbonitrile gave 5′-acetyl-2,2′-bithiophene-5-carbonitrile (**29**) in 64% yield (Table 4, entry 6). Again, a selective 5-arylation of 2-propylthiazole was observed with 2-acetyl-5-bromothiophene to give **31** in 56% yield (Table 4, entry 8).

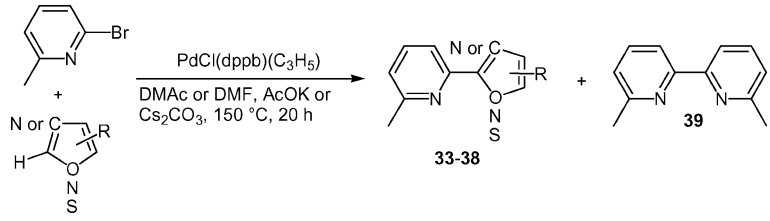
Palladium chemistry involving heterocycles has several unique characteristics that stem from the heterocycles' inherently different structural and electronic properties in comparison to the corresponding carbocyclic aryl compounds. Pyridines, for example, are π-electron deficient, while thiophenes or furans are π-electron rich. Thus, if the oxidative addition of the aryl halide to the palladium complex is the rate-limiting step of the reaction with this catalyst, the reactions should be slower with thiophenes or furans than with pyridines. In fact, we generally obtained better yields of coupling products with thiophenes or furans than with pyridines (Table 5, Scheme 5). Using 2-bromo-5-methylpyridine, the formation of the homo-coupling side-product 6,6′-dimethyl-2,2′-bipyridinyl (**39**) was observed in moderate to large amounts therefore only low to moderate yields of the expected coupling products **33**–**38** were obtained. The oxidative addition to palladium is probably relatively fast with this substrate but the coupling with the heteroarenes is apparently slower than with 2-bromofurans or thiophenes. This means that the side reaction that gives the homo-coupling bipyridine product **39** is predominant in some cases. With 2-bromo-5-methylpyridine, the best yields of coupling products were obtained using benzothiazole or benzoxazole as coupling partners (Table 5, entries 4 and 6, respectively).

We also attempted to perform the diarylation of 2,5-dibromothiophene as this reaction would give a very simple access to tridentate ligands. We observed that the expected 2,5-diarylated thiophenes **40** and **41** were obtained directly in the presence of benzoxazole or 2-butylthiophene (Schemes 6 and 7). Finally, we tried to diarylate 1,2-dibro-

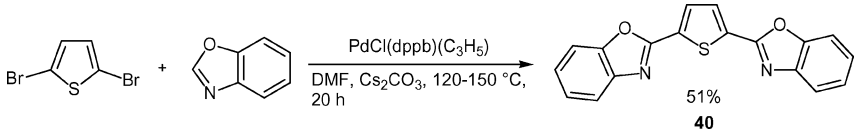
Table 5. Palladium-catalysed cross-coupling with 2-bromo-5-methylpyridine (Scheme 5).[a]

Entry	Heteroarene	Product	% Yield
1		 **33**	32
2		 **34**	34
3		 **35**	37
4		 **36**	54[b]
5		 **37**	31
6		 **38**	78[b]

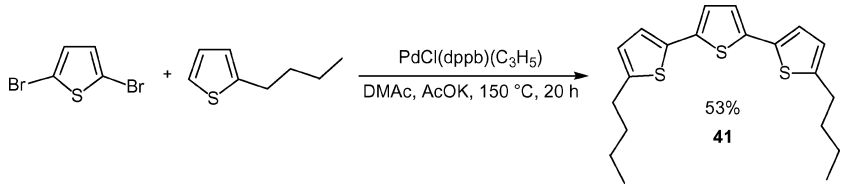
[a] Conditions: [PdCl(dppb)(C_3H_5)] (0.05 equiv.), 2-bromo-5-methylpyridine (1 equiv.), heteroarene (2 equiv.), KOAc (2 equiv.), DMAc, 20 h, 150 °C. The yields given are those of isolated product. The formation of 6,6′-dimethyl-2,2′-bipyridinyl (**39**) was also observed. [b] Cs_2CO_3 was used as base and DMF as solvent.



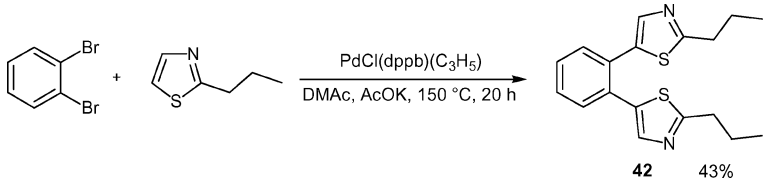
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

mobenzene as this reaction would also allow access to another class of useful ligands in one step. The coupling with 2-propylthiazole afforded **42** in 43% yield (Scheme 8).

Conclusions

In summary, a wide variety of bi- or polydentate ligands can be prepared easily in moderate to good yields by the direct heteroarylation of 2-halogenated heteroaromatic derivatives. Better results were generally obtained using 2-bromothiophenes or a 2-bromofuran than a 2-bromopyridine derivative. Several heteroaromatics can be employed as coupling partners, and good yields were generally obtained using substituted furans, thiophenes, thiazoles or oxazoles. *N*-Methylbenzimidazole was found to be less reactive. It should be noted that a range of functions such as acetyl, formyl, ester or nitrile are tolerated. This procedure is very simple, economically attractive and uses commercially available substrates. The air-stability of the catalyst also makes this procedure very convenient. A large number of the products prepared by this method have never been described so far, thus indicating that this procedure provides a convenient access to compounds which cannot be prepared easily by more classical cross-coupling methods. Moreover, due to environmental considerations, such atom-economic procedures that produce inert wastes (acetic acid and potassium bromide in most cases) should become increasingly important for industrial processes.

Experimental Section

General Remarks: All reactions were prformed under argon in Schlenk tubes on a vacuum line. Analytical grade *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) were used as received. Potassium acetate and caesium carbonate (99%) were obtained commercially. Commercial heteroaryl halides and heteroaryl derivatives were used without purification. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 200 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.25 for ^{1}H and 77.0 ppm for ^{13}C). Flash chromatography was performed on silica gel (230–400 mesh).

Preparation of the [PdCl(dppb)(C_3H_5)] Catalyst:[13] 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 an argon atmosphere. Anhydrous dichloromethane (10 mL) was then added and the resulting solution stirred at room temperature for twenty minutes. The solvent was removed in vacuo and the resulting yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 19.3 (s) ppm.

General Procedure for Coupling Reactions: In a typical experiment, the heteroaryl bromide (1 mmol), heteroaryl (2 mmol), KOAc (0.196 g, 2 mmol) or Cs_2CO_3 (0.650 g, 2 mmol; see tables) and [PdCl(C_3H_5)(dppb)] (0.030 g, 0.05 mmol) were dissolved in DMAc or DMF (5 mL; see tables) under argon and the reaction mixture stirred at 120–150 °C (see tables) for 20 h. The solution was diluted with water or with a 1 M H_2O/KOH solution (20 mL) for products containing a pyridine, benzoxazole or benzimidazole moiety. The product was then extracted three times with CH_2Cl_2. The combined organic layers weres dried with $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by silica gel column chromatography.

5′-Butyl-2,2′-bifuranyl-5-carbaldehyde (1): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), 2-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **1** in 72% (0.157 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.60 (s, 1 H), 7.31 (d, J = 3.5 Hz, 1 H), 6.83 (d, J = 3.5 Hz, 1 H), 6.67 (d, J = 3.5 Hz, 1 H), 6.15 (d, J = 3.5 Hz, 1 H), 2.71 (t, J = 7.5 Hz, 2 H), 1.72 (quint, J = 7.4 Hz, 2 H), 1.45 (sext, J = 7.4 Hz, 2 H), 0.93 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.7, 159.0, 151.9, 151.2, 143.1, 123.9, 110.7, 107.5, 106.4, 29.9, 27.8, 22.2, 13.7 ppm. $C_{13}H_{14}O_3$ (218.25): calcd. C 71.54, H 6.47; found C 71.41, H 6.57. HRMS (EI) calcd. for $[M]^+$: m/z 218.0943; found 218.0941.

Methyl 5′-Formyl-5-methyl-2,2′-bifuranyl-4-carboxylate (2): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), methyl 2-methyl-3-furancarboxylate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **2** in 75% (0.176 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.65 (s, 1 H), 7.31 (d, J = 3.5 Hz, 1 H), 7.13 (s, 1 H), 6.73 (d, J = 3.5 Hz, 1 H), 3.87 (s, 3 H), 2.68 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.0, 163.7, 160.7, 151.7, 150.3, 142.6, 123.0, 115.0, 109.9, 107.7, 51.6, 13.9 ppm. $C_{12}H_{10}O_5$ (234.20): calcd. C 61.54, H 4.30;

found C 61.59, H 4.21. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 234.0528; found 234.0518.

5-(5-Butylthiophen-2-yl)furan-2-carbaldehyde (3): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), 2-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **3** in 78% (0.183 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.60 (s, 1 H), 7.37 (d, J = 3.5 Hz, 1 H), 7.27 (d, J = 3.5 Hz, 1 H), 6.80 (d, J = 3.5 Hz, 1 H), 6.60 (d, J = 3.5 Hz, 1 H), 2.86 (t, J = 7.5 Hz, 2 H), 1.72 (quint, J = 7.4 Hz, 2 H), 1.47 (sext, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.5, 155.2, 151.1, 149.0, 128.8, 126.1, 125.3, 123.0, 106.6, 33.4, 29.7, 22.0, 13.7 ppm. $C_{13}H_{14}O_2S$ (234.32): calcd. C 66.64, H 6.02; found C 66.50, H 6.10. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 234.0715; found 234.0719.

5-(5-Methylthiophen-2-yl)furan-2-carbaldehyde (4): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), 2-methylthiophene (0.196 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **4** in 75% (0.144 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 7.34 (d, J = 3.5 Hz, 1 H), 7.27 (d, J = 3.5 Hz, 1 H), 6.77 (d, J = 3.5 Hz, 1 H), 6.59 (d, J = 3.5 Hz, 1 H), 2.54 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.1, 155.6, 151.1, 143.7, 129.7, 127.0, 126.9, 124.0, 107.2, 15.9 ppm. $C_{10}H_8O_2S$ (192.24): calcd. C 62.48, H 4.19; found C 62.34, H 4.07. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 192.0245; found 192.0250.

5-(5-Chlorothiophen-2-yl)furan-2-carbaldehyde (5): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), 2-chlorothiophene (0.237 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **5** in 71% (0.151 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.62 (s, 1 H), 7.30 (m, 2 H), 6.94 (d, J = 4.0 Hz, 1 H), 6.63 (d, J = 3.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.8, 153.5, 151.5, 132.5, 130.1, 127.3, 125.3, 123.4, 107.5 ppm. $C_9H_5ClO_2S$ (212.65): calcd. C 50.83, H 2.37; found C 50.71, H 2.51. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 211.9699; found 211.9698.

5-(2-Propylthiazol-5-yl)furan-2-carbaldehyde (6): The reaction of 5-bromo-2-furaldehyde (0.175 g, 1 mmol), 2-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **6** in 80% (0.177 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.64 (s, 1 H), 8.05 (s, 1 H), 7.30 (d, J = 3.5 Hz, 1 H), 6.69 (d, J = 3.5 Hz, 1 H), 3.03 (t, J = 7.5 Hz, 2 H), 1.85 (sext, J = 7.5 Hz, 2 H), 1.05 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C (50 MHz, $CDCl_3$): δ = 177.4, 173.4, 152.6, 152.3, 141.2, 123.7, 118.3, 109.3, 35.9, 23.7, 14.0 ppm. $C_{11}H_{11}NO_2S$ (221.28): calcd. C 59.71, H 5.01; found C 59.94, H 4.87. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 221.0510; found 221.0507.

2-Propyl-5-(thiophen-2-yl)thiazole (7): The reaction of 2-bromothiophene (0.163 g, 1 mmol), 2-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **7** in 56% (0.117 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.24 (d, J = 5.2 Hz, 1 H), 7.14 (m, 1 H), 7.05 (m, 1 H), 2.97 (t, J = 7.5 Hz, 2 H), 1.86 (sext, J = 7.5 Hz, 2 H), 1.04 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.7, 138.3, 133.9, 131.9, 128.2, 125.7, 125.5, 35.9, 23.7, 14.1 ppm. $C_{10}H_{11}NS_2$ (209.33): calcd. C 57.38, H 5.30; found C 57.48, H 5.30. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 209.0333; found 209.0330.

2-(Thiophen-2-yl)benzoxazole (8):[12b] The reaction of 2-bromothiophene (0.163 g, 1 mmol), benzoxazole (0.238 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2 mmol) at 150 °C in dry DMF (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (6.1 mg, 0.01 mmol) afforded **8** in 73% (0.147 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.88 (d, J = 3.6 Hz, 1 H), 7.75 (m, 1 H), 7.55 (m, 2 H), 7.37 (m, 2 H), 7.18 (t, J = 4.1 Hz, 1 H) ppm.

5-(5-Methylthiophen-2-yl)-2-propylthiazole (9): The reaction of 2-bromo-5-methylthiophene (0.177 g, 1 mmol), 2-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **9** in 63% (0.141 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.63 (s, 1 H), 6.93 (d, J = 4.5 Hz, 1 H), 6.68 (d, J = 4.5 Hz, 1 H), 2.97 (t, J = 7.5 Hz, 2 H), 2.50 (s, 3 H), 1.86 (sext, J = 7.5 Hz, 2 H), 1.04 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C (50 MHz, $CDCl_3$): δ = 169.6, 139.9, 137.2, 131.9, 131.1, 125.9, 125.1, 35.4, 23.3, 15.3, 13.6 ppm. $C_{11}H_{13}NS_2$ (223.36): calcd. C 59.15, H 5.87; found C 59.07, H 5.94. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 223.0489; found 223.0490.

2-(5-Methylthiophen-2-yl)benzoxazole (10):[14] The reaction of 2-bromo-5-methylthiophene (0.177 g, 1 mmol), benzoxazole (0.238 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2 mmol) at 150 °C in dry DMF (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **10** in 80% (0.172 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.72 (m, 2 H), 7.53 (m, 1 H), 7.34 (m, 2 H), 6.85 (m, 1 H), 2.59 (s, 3 H). ^{13}C (50 MHz, $CDCl_3$): δ = 159.0, 150.3, 145.7, 142.0, 130.2, 127.0, 126.7, 124.7, 124.5, 119.5, 110.2, 15.6 ppm.

5′-Chloro-5-methyl-2,2′-bithiophene (11): The reaction of 2-bromo-5-methylthiophene (0.177 g, 1 mmol), 2-chlorothiophene (0.238 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **11** in 51% (0.109 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.90 (d, J = 3.2 Hz, 1 H), 6.86 (d, J = 3.2 Hz, 1 H), 6.82 (d, J = 3.2 Hz, 1 H), 6.68 (d, J = 3.2 Hz, 1 H), 2.50 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.6, 136.4, 134.1, 127.9, 127.2, 126.4, 124.2, 122.5, 15.8 ppm. $C_9H_7ClS_2$ (214.74): calcd. C 50.34, H 3.29; found C 50.51, H 3.52. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 213.9678; found 213.9670.

5,5′-Dimethyl-2,2′-bithiophene (12):[15] The reaction of 2-bromo-5-methylthiophene (0.177 g, 1 mmol), 2-methylthiophene (0.196 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **12** in 78% (0.152 g) isolated yield. This compound was also obtained as side product of the reactions with 2-bromo-5-methylthiophene and 2-propylthiazole, 2-chlorothiophene or benzoxazole. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.89 (d, J = 3.2 Hz, 2 H), 6.65 (d, J = 3.2 Hz, 2 H), 2.49 (s, 6 H) ppm.

5′-Butyl-5-chloro-2,2′-bithiophene (13): The reaction of 2-bromo-5-chlorothiophene (0.198 g, 1 mmol), 2-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **13** in 61% (0.157 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.92 (d, J = 3.7 Hz, 1 H), 6.86 (d, J = 3.7 Hz, 1 H), 6.82 (d, J = 3.7 Hz, 1 H), 6.69 (d, J = 3.7 Hz, 1 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.65 (quint, J = 7.4 Hz, 2 H), 1.42 (sext, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.2, 137.0, 134.2, 127.2, 125.2, 124.0, 122.5, 122.4, 34.1, 30.3, 22.6, 14.3 ppm. $C_{12}H_{13}ClS_2$ (256.82): calcd. C 56.12, H 5.10; found C 56.31, H 5.24. HRMS (EI) calcd. for $[M]^+$: *m*/*z* 256.0147; found 256.0150.

2-(5-Chlorothiophen-2-yl)benzothiazole (14):[16] The reaction of 2-bromo-5-chlorothiophene (0.198 g, 1 mmol), benzothiazole

(0.270 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2 mmol) at 120 °C in dry DMF (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **14** in 30% (0.076 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.3 Hz, 1 H), 7.86 (d, J = 8.3 Hz, 1 H), 7.55–7.30 (m, 3 H), 6.97 (d, J = 3.8 Hz, 1 H) ppm.

2,2′-Bithiophene (15): This compound was obtained as a side product from several reactions with 2-bromothiophene. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.16 (d, J = 5.2 Hz, 2 H), 7.15 (d, J = 3.7 Hz, 2 H), 6.97 (dd, J = 5.2 and 3.7 Hz, 2 H) ppm.

5,5′-Dichloro-2,2′-bithiophene (16):[17] This compound was obtained as a side product from the reactions with 2-bromo-5-chlorothiophene. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.87 (d, J = 3.8 Hz, 2 H), 6.83 (d, J = 3.8 Hz, 2 H) ppm.

5-(5-Butylfuran-2-yl)thiophene-2-carbaldehyde (17): The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), 2-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **17** in 77% (0.181 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 7.67 (d, J = 4.0 Hz, 1 H), 7.23 (d, J = 4.0 Hz, 1 H), 6.67 (d, J = 2.9 Hz, 1 H), 6.12 (d, J = 2.9 Hz, 1 H), 2.70 (t, J = 7.5 Hz, 2 H), 1.69 (quint, J = 7.4 Hz, 2 H), 1.45 (sext, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 182.5, 158.5, 146.4, 143.4, 140.6, 137.4, 121.8, 109.8, 107.7, 29.9, 27.7, 22.2, 13.7 ppm. $C_{13}H_{14}O_2S$ (234.32): calcd. C 66.64, H 6.02; found C 66.80, H 5.89. HRMS (EI) calcd. for $[M]^+$: m/z 234.0715; found 234.0719.

Methyl 5-(5-Formylthiophen-2-yl)-2-methylfuran-3-carboxylate (18): The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), methyl 2-methyl-3-furancarboxylate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **18** in 57% (0.143 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 7.67 (d, J = 4.0 Hz, 1 H), 7.29 (d, J = 4.0 Hz, 1 H), 6.94 (s, 1 H), 3.85 (s, 3 H), 2.64 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.0, 164.1, 160.6, 146.5, 142.2, 142.0, 137.6, 123.6, 116.2, 109.5, 52.1, 14.4 ppm. $C_{12}H_{10}O_4S$ (250.27): calcd. C 57.59, H 4.03; found C 57.67, H 3.94. HRMS (EI) calcd. for $[M]^+$: m/z 250.0300; found 250.0303.

5′-Butyl-2,2′-bithiophene-5-carbaldehyde (19): The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), 2-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **19** in 67% (0.168 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.84 (s, 1 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.19 (d, J = 3.9 Hz, 1 H), 7.17 (d, J = 3.9 Hz, 1 H), 6.75 (d, J = 3.6 Hz, 1 H), 2.83 (t, J = 7.5 Hz, 2 H), 1.72 (quint, J = 7.4 Hz, 2 H), 1.45 (sext, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 182.4, 148.6, 147.8, 140.9, 137.5, 133.3, 125.9, 125.4, 123.3, 33.5, 29.8, 22.0, 13.7 ppm. $C_{13}H_{14}OS_2$ (250.38): calcd. C 62.36, H 5.64; found C 62.10, H 5.81. HRMS (EI) calcd. for $[M]^+$: m/z 250.0486; found 250.0481.

5′-Butyl-2,2′-bithiophene-5-carbaldehyde (20):[18] The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), 2-methylthiophene (0.196 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **20** in 65% (0.135 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 7.66 (d, J = 3.9 Hz, 1 H), 7.19 (d, J = 3.9 Hz, 1 H), 7.17 (d, J = 3.9 Hz, 1 H), 6.75 (d, J = 3.6 Hz, 1 H), 2.52 (s, 3 H) ppm.

5′-Chloro-2,2′-bithiophene-5-carbaldehyde (21): The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), 2-chlorothiophene (0.237 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **21** in 69% (0.158 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.67 (d, J = 4.0 Hz, 1 H), 7.17 (d, J = 4.0 Hz, 1 H), 7.13 (d, J = 3.9 Hz, 1 H), 6.90 (d, J = 3.9 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 182.4, 145.9, 141.9, 137.2, 134.5, 131.7, 127.4, 125.2, 124.2 ppm. $C_9H_5ClOS_2$ (228.72): calcd. C 47.26, H 2.20; found C 47.02, H 2.31. HRMS (EI) calcd. for $[M]^+$: m/z 227.9470; found 227.9479.

5-(2-Propylthiazol-5-yl)thiophene-2-carbaldehyde (22): The reaction of 2-bromo-5-formylthiophene (0.191 g, 1 mmol), 2-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **22** in 80% (0.190 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.88 (s, 1 H), 7.88 (s, 1 H), 7.69 (d, J = 3.9 Hz, 1 H), 7.24 (d, J = 3.9 Hz, 1 H), 3.00 (t, J = 7.6 Hz, 2 H), 1.84 (sext, J = 7.6 Hz, 2 H), 1.05 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C (50 MHz, $CDCl_3$): δ = 182.9, 173.1, 143.7, 142.8, 140.6, 137.5, 130.9, 126.1, 36.0, 23.7, 14.1 ppm. $C_{11}H_{11}NOS_2$ (237.34): calcd. C 55.67, H 4.67; found C 55.78, H 4.80. HRMS (EI) calcd. for $[M]^+$: m/z 237.0282; found 237.0287.

-2,2′-Bithiophene-5,5′-dicarbaldehyde (23):[10c] This compound was obtained as a side product from the reactions with 2-bromo-5-formylthiophene. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.94 (s, 2 H), 7.75 (d, J = 3.9 Hz, 2 H), 7.44 (d, J = 3.9 Hz, 2 H) ppm.

1-[5-(5-Butylfuran-2-yl)thiophen-2-yl]ethanone (24): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **24** in 62% (0.154 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58 (d, J = 4.0 Hz, 1 H), 7.16 (d, J = 4.0 Hz, 1 H), 6.58 (d, J = 2.9 Hz, 1 H), 6.08 (d, J = 2.9 Hz, 1 H), 2.67 (t, J = 7.5 Hz, 2 H), 2.53 (s, 3 H), 1.67 (quint, J = 7.4 Hz, 2 H), 1.42 (sext, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.3, 157.9, 146.6, 142.1, 141.2, 133.3, 121.7, 108.9, 107.5, 29.9, 27.7, 26.4, 22.1, 13.7 ppm. $C_{14}H_{16}O_2S$ (248.34): calcd. C 67.71, H 6.49; found C 67.78, H 6.68. HRMS (EI) calcd. for $[M]^+$: m/z 248.0871; found 248.0876.

Methyl 5-(5-Acetylthiophen-2-yl)-2-methylfuran-3-carboxylate (25): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), methyl 2-methyl-3-furancarboxylate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **25** in 53% (0.140 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60 (d, J = 4.0 Hz, 1 H), 7.22 (d, J = 4.0 Hz, 1 H), 6.90 (s, 1 H), 3.86 (s, 3 H), 2.65 (s, 3 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.3, 163.7, 159.7, 146.2, 142.5, 140.3, 133.1, 123.1, 115.5, 108.2, 51.5, 26.5, 13.8 ppm. $C_{13}H_{12}O_4S$ (264.30): calcd. C 59.08, H 4.58; found C 59.20, H 4.49. HRMS (EI) calcd. for $[M]^+$: m/z 264.0456; found 264.0452.

1-[5-(5-Acetylfuran-2-yl)thiophen-2-yl]ethanone (26): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **26** in 32% (0.075 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65 (d, J = 4.0 Hz, 1 H), 7.47 (d, J = 4.0 Hz, 1 H), 7.27 (d, J = 3.7 Hz, 1 H), 7.79 (d, J = 3.7 Hz, 1 H), 2.59 (s, 3 H), 2.54 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.9, 186.8, 152.7, 151.9, 144.8, 139.7, 133.4, 126.0, 119.5, 110.2, 27.2, 26.5 ppm. $C_{12}H_{10}O_3S$ (234.27): calcd. C 61.52, H 4.30; found C 61.30, H 4.21. HRMS (EI) calcd. for $[M]^+$: m/z 234.0351; found 234.0347.

1-(5′-Butyl-2,2′-bithiophene-5-yl)ethanone (27): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **27** in 83% (0.219 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54 (d, J = 4.0 Hz, 1 H), 7.11 (d, J = 3.6 Hz, 1 H), 7.05 (d, J = 4.0 Hz, 1 H), 6.70 (d, J = 3.6 Hz, 1 H), 2.79 (t, J = 7.5 Hz, 2 H), 2.51 (s, 3 H), 1.62 (quint, J = 7.4 Hz, 2 H), 1.43 (sext, J = 7.4 Hz, 2 H), 0.94 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.1, 147.7, 146.3, 141.4, 133.5, 133.3, 125.3, 125.1, 123.1, 33.4, 29.7, 26.2, 22.0, 13.6 ppm. $C_{14}H_{16}OS_2$ (264.41): calcd. C 63.59, H 6.10; found C 63.40, H 6.21. HRMS (EI) calcd. for $[M]^+$: m/z 264.0643; found 264.0651.

1-(5′-Methyl-2,2′-bithiophene-5-yl)ethanone (28):[19] The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-methylthiophene (0.196 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **28** in 67% (0.149 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.56 (d, J = 4.0 Hz, 1 H), 7.11 (d, J = 3.6 Hz, 1 H), 7.07 (d, J = 4.0 Hz, 1 H), 6.71 (d, J = 3.6 Hz, 1 H), 2.53 (s, 3 H), 2.51 (s, 3 H) ppm.

5′-Acetyl-2,2′-bithiophene-5-carbonitrile (29):[19] The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), thiophene-2-carbonitrile (0.218 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **29** in 64% (0.149 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.63 (d, J = 4.0 Hz, 1 H), 7.57 (d, J = 4.0 Hz, 1 H), 7.28 (m, 2 H), 2.58 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.8, 145.2, 143.6, 142.7, 138.8, 133.6, 126.8, 125.7, 114.1, 109.9, 27.1 ppm.

1-(5′-Chloro-2,2′-bithiophene-5-yl)ethanone (30): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-chlorothiophene (0.237 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **30** in 57% (0.138 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58 (d, J = 4.0 Hz, 1 H), 7.09 (m, 2 H), 6.88 (d, J = 4.0 Hz, 1 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.3, 144.5, 142.7, 134.8, 133.2, 131.0, 127.3, 124.7, 124.1, 26.5 ppm. $C_{10}H_7ClOS_2$ (242.75): calcd. C 49.48, H 2.91; found C 49.60, H 2.87. HRMS (EI) calcd. for $[M]^+$: m/z 241.9627; found 241.9627.

1-[5-(2-Propylthiazol-5-yl)thiophen-2-yl]ethanone (31): The reaction of 2-acetyl-5-bromothiophene (0.205 g, 1 mmol), 2-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **31** in 56% (0.141 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.58 (d, J = 4.0 Hz, 1 H), 7.12 (d, J = 4.0 Hz, 1 H), 2.97 (t, J = 7.5 Hz, 2 H), 2.54 (s, 3 H), 1.83 (sext, J = 7.4 Hz, 2 H), 1.03 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 190.2, 171.9, 143.0, 141.7, 139.5, 133.0, 130.6, 125.4, 35.4, 26.4, 23.1, 13.5 ppm. $C_{12}H_{13}NOS_2$ (251.37): calcd. C 57.34, H 5.21; found C 57.34, H 5.30. HRMS (EI) calcd. for $[M]^+$: m/z 251.0439; found 251.0434.

1-(5′-Acetyl-2,2′-bithiophene-5-yl)ethanone (32):[10c] This compound was obtained as a side product from the reactions with 2-acetyl-5-bromothiophene. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.59 (d, J = 3.2 Hz, 2 H), 7.32 (d, J = 3.2 Hz, 2 H), 2.58 (s, 6 H) ppm.

2-(5-Butylfuran-2-yl)-6-methyl-pyridine (33): The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), 2-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **33** in 32% (0.069 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58 (t, J = 7.6 Hz, 1 H), 7.45 (d, J = 8.2 Hz, 1 H), 7.00 (m, 2 H), 6.12 (d, J = 2.9 Hz, 1 H), 2.77 (t, J = 7.5 Hz, 2 H), 2.58 (s, 3 H), 1.67 (quint, J = 7.4 Hz, 2 H), 1.42 (sext, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.7, 158.2, 152.5, 149.6, 137.1, 121.4, 115.7, 109.7, 107.7, 30.5, 28.4, 25.1, 22.7, 14.3 ppm. $C_{14}H_{17}NO$ (215.29): calcd. C 78.10, H 7.96; found C 78.23, H 7.81. HRMS (EI) calcd. for $[M]^+$: m/z 215.1310; found 215.1307.

2-(5-Butylthiophen-2-yl)-6-methyl-pyridine (34): The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), 2-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **34** in 34% (0.079 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54 (t, J = 7.6 Hz, 1 H), 7.43 (d, J = 8.2 Hz, 1 H), 7.40 (d, J = 2.8 Hz, 1 H), 6.97 (d, J = 8.2 Hz, 1 H), 6.79 (d, J = 2.8 Hz, 1 H), 2.86 (t, J = 7.5 Hz, 2 H), 2.58 (s, 3 H), 1.70 (quint, J = 7.4 Hz, 2 H), 1.42 (sext, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.6, 152.7, 148.6, 142.8, 137.1, 125.5, 124.6, 121.3, 115.8, 34.2, 30.5, 25.0, 22.6, 14.3 ppm. $C_{14}H_{17}NS$ (231.36): calcd. C 72.68, H 7.41; found C 72.71, H 7.50. HRMS (EI) calcd. for $[M]^+$: m/z 231.1082; found 231.1086.

2-(5-Chlorothiophen-2-yl)-6-methylpyridine (35): The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), 2-chlorothiophene (0.237 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **35** in 37% (0.078 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.56 (t, J = 7.6 Hz, 1 H), 7.37 (d, J = 8.2 Hz, 1 H), 7.29 (d, J = 3.9 Hz, 1 H), 7.02 (d, J = 8.2 Hz, 1 H), 6.91 (d, J = 3.9 Hz, 1 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.9, 151.5, 144.3, 137.2, 132.4, 127.5, 123.6, 122.2, 115.4, 24.9 ppm. $C_{10}H_8ClNS$ (209.70): calcd. C 57.28, H 3.85; found C 57.40, H 3.91. HRMS (EI) calcd. for $[M]^+$: m/z 209.0066; found 209.0063.

2-(6-Methylpyridin-2-yl)benzothiazole (36): The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), benzothiazole (0.270 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2 mmol) at 150 °C in dry DMF (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **36** in 54% (0.122 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.0 Hz, 1 H), 8.11 (d, J = 8.0 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 1 H), 7.26 (d, J = 8.0 Hz, 1 H), 2.67 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.2, 154.8, 151.1, 137.6, 136.6, 126.6, 125.9, 125.4, 123.9, 122.5, 122.4, 118.2, 24.8 ppm. HRMS (EI) calcd. for $[M]^+$: m/z 226.0565; found 226.0564.

1-Methyl-2-(6-methylpyridin-2-yl)-1*H*-benzimidazole (37):[20] The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), *N*-methylbenzimidazole (0.264 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **37** in 31% (0.069 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.0 Hz, 1 H), 7.80 (m, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.44 (m, 1 H), 7.32 (m, 2 H), 7.23 (d, J = 8.0 Hz, 1 H), 4.30 (s, 3 H), 2.67 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 157.4, 150.5, 142.5, 137.2, 137.0, 123.2, 123.1, 122.4, 122.0, 121.7, 119.9, 109.8, 32.7, 24.5 ppm.

2-(6-Methylpyridin-2-yl)benzoxazole (38):[12b] The reaction of 2-bromo-5-methylpyridine (0.172 g, 1 mmol), benzoxazole (0.238 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2 mmol) at 150 °C in dry DMF (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **38** in 78% (0.164 g) isolated yield. ^{1}H NMR (200 MHz,

$CDCl_3$): δ = 8.14 (d, J = 8.0 Hz, 1 H), 7.80 (m, 1 H), 7.73 (t, J = 8.0 Hz, 1 H), 7.64 (m, 1 H), 7.37 (m, 2 H), 7.10 (d, J = 8.0 Hz, 1 H), 2.70 (s, 3 H) ppm.

6,6′-Dimethyl-2,2′-bipyridine (39): This compound was obtained as a side product from the reactions with 2-bromo-5-methylpyridine. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.2 Hz, 2 H), 7.70 (t, J = 7.6 Hz, 2 H), 7.16 (d, J = 8.2 Hz, 2 H), 2.64 (s, 6 H) ppm.

2,5-Bis(benzoxazole)thiophene (40):[12b] The reaction of 2,5-dibromothiophene (0.242 g, 1 mmol), benzoxazole (0.476 g, 4 mmol) and Cs_2CO_3 (1.300 g, 4 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **40** in 51% (0.162 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98 (s, 2 H), 7.80 (m, 2 H), 7.60 (m, 2 H), 7.42 (m, 4 H) ppm.

5,5′′-Dibutyl[2,2′;5′,2′′]terthiophene (41): The reaction of 2,5-dibromothiophene (0.242 g, 1 mmol), 2-butylthiophene (0.560 g, 4 mmol) and KOAc (0.392 g, 4 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **41** in 53% (0.191 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.01 (s, 4 H), 6.72 (s, 2 H), 2.84 (t, J = 7.5 Hz, 4 H), 1.72 (quint, J = 7.4 Hz, 4 H), 1.44 (sext, J = 7.4 Hz, 4 H), 1.00 (t, J = 7.5 Hz, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 145.7, 136.6, 135.1, 125.2, 123.9, 123.6, 34.2, 30.3, 22.7, 14.3 ppm. $C_{20}H_{24}S_3$ (360.60): calcd. C 66.61, H 6.71; found C 66.45, H 6.92. HRMS (EI) calcd. for $[M]^+$: m/z 360.1040; found 360.1042.

1,2-Bis(2-propylthiazol-5-yl)benzene (42): The reaction of 1,2-dibromobenzene (0.236 g, 1 mmol), 2-propylthiazole (0.508 g, 4 mmol) and KOAc (0.392 g, 4 mmol) at 150 °C in dry DMAc (5 mL) in the presence of [PdCl(dppb)(C_3H_5)] (30.5 mg, 0.05 mmol) afforded **42** in 43% (0.141 g) isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.30 (m, 6 H), 2.93 (t, J = 7.6 Hz, 4 H), 1.81 (sext, J = 7.6 Hz, 4 H), 1.00 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.3, 141.0, 135.6, 130.9, 128.5, 124.9, 35.3, 23.2, 13.5 ppm. HRMS (EI) calcd. for $[M]^+$: m/z 328.1068; found 328.1083.

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