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Phosphine-Free Palladium Catalytic System for the Selective Direct Arylation of Furans or Thiophenes bearing Alkenes and Inhibition of Heck-Type Reaction

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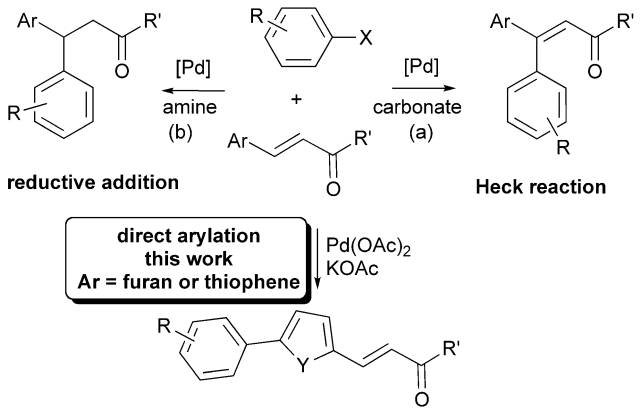
Abstract: Palladium acetate associated to potassium carbonate as catalytic system has been found to efficiently catalyse the direct 5-arylation of furans or thiophenes bearing enal, enone or acrylate functions at carbon C-2, and to inhibit the Heck-type reaction. The nature of the base is crucial to control the selectivity of the arylation. In the presence of electron-deficient aryl bromides and potassium carbonate as the base, the direct arylation is favoured, whereas the use of potassium fluoride gave selectively the Heck-type product, and tri-*n*-butylamine the reductive addition product.

Keywords: atom-economy; catalysis; C–H activation; heteroarenes; palladium

Introduction

Mixed bi(hetero)aryl derivatives display a set of bioactive or physical properties and their preparation constitutes an active field of research in organic chemistry.[1] Several methods for the preparation of these products have been described. The palladium-catalysed direct arylation of some heteroaromatics *via* a C–H bond activation using aryl halides has led to successes in recent years.[2] For such direct coupling reactions, no preparation of an organometallic derivative is required, and this is a tremendous advantage as compared to the more classical cross-coupling procedures arising from more costly Suzuki–Miyaura, Stille, or Negishi reactions. Moreover, the direct arylation reaction provides only an acid (HX) associated to a required base as by-product and therefore presents advantages both in terms of atom-economy and relatively inert wastes. However, although this procedure has been widely applied in recent years for the synthesis of arylthiophenes,[3] arylfurans,[4] arylpyrroles,[5] or other arylated heteroaromatics,[6–8] relatively few arylated heteroaromatics bearing a functional alkene as substituent have been prepared by direct C–H bond functionalisation.[9,10] This is due to the possible competitive Heck reaction[11,12c] or the reductive addition on the alkene in the presence of amines[12] (Scheme 1). Heck reactions with benzalacetone, cinnamates or chalcone, proceed nicely in the presence of carbonates as the base in DMF (a);[13–17] whereas tertiary amines produces the reductive addition products (b).[12d]



Scheme 1.

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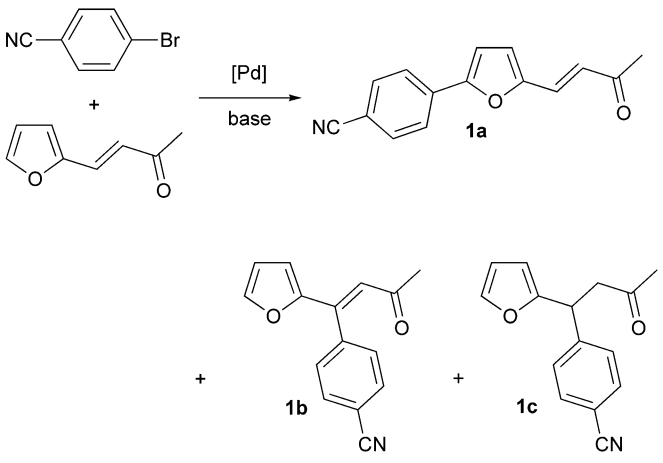
The control of the direct arylation of heteroaromatics bearing an alkene, without formation of competitive Heck-type products, would offer a strong potential in organic synthesis since it would provide a more environmentally and economically attractive access to conjugated compounds useful as materials due to their optical properties such as for dye sensitized solar cells.[18] So far, only a few examples of palladium-catalysed intramolecular cyclisations of 2-alkenyl-substituted *N*-(*o*-iodobenzyl)pyrroles employing thallium acetate as the base,[9] and the direct arylation of thiophenes bearing trisubstituted alkenes [2-(2,2-diarylvinyl)-thiophenes][10] have been reported. To the best of our knowledge, the general intermolecular direct arylation of heteroaromatics such as thiophenes or furans bearing enal, enone or acrylate functions has not been described.

We now report that $Pd(OAc)_2$ catalyst in the presence of KOAc as the base controls the intermolecular direct 5-arylation with aryl bromides of furans or thiophenes bearing enal, enone or acrylate functions at carbon C-2 with inhibition of Heck-type reactions.

Results and Discussion

As the nature of the base has been found in recent years to be a crucial factor to promote efficiently palladium-[9,19] or ruthenium-catalysed[20] direct arylations, we could expect a drastic influence of the nature of the base, associated with that of the ligand, on the selectivity for the reaction of heteroaromatics bearing electron-poor alkenes with aryl bromides.

First, we have considered the reaction of (*E*)-4-furan-2-ylbut-3-en-2-one for the palladium-catalysed coupling reaction with 4-bromobenzonitrile to reach the formation of C-5 arylated product **1a** (Scheme 2). As this substrate is similar to benzalacetone,[13] the formation of Heck-type product **1b** is possible.



Scheme 2.

We first explored the activity of $PdCl(C_3H_5)(dppb)$ as we recently demonstrated that it was one of the best catalysts for the direct arylation of some furans, thiophenes or thiazoles.[3c,h] Using 1 mol% of $PdCl(C_3H_5)(dppb)$ as the catalyst precursor, DMAc as the solvent and KOAc or CsOAc as the base at 130 °C, the desired 5-arylation product **1a** was obtained in 96% selectivity (Scheme 2, Table 1, entries 2 and 3). The Heck type product **1b** was only produced in 4% selectivity, and the reductive addition product **1c** was not detected. On the other hand, surprisingly the use of NaOAc led mostly to the Heck-type product **1b** (Table 1, entry 1). This difference of selectivity might come from a stronger interaction of the acetate anion with Na^+ cation than with K^+ or Cs^+ in DMAc. Consequently, the transfer of the acetate to the palladium(II) would be faster with KOAc or CsOAc than with NaOAc and this should favour a concerted metallation deprotonation mechanism.[19b] In the presence of carbonates as the bases, complete conversions of 4-bromobenzonitrile were observed, but only traces of product **1a** were detected (Table 1, entries 4–6). As KF was shown to favour Heck-type reactions and to inhibit reductive addition,[12c] it has also been evaluated. With this base, the Heck-type product **1b** was predominantly formed and isolated in 40% yield (Table 1, entry 7).

The nature of the solvent often modifies the catalyst activity in cross-coupling reactions, thus we observed that DMF gave **1a** in high selectivity, but the formation of 15% of biphenyl-4,4′-dicarbonitrile was also observed (Table 1, entry 8). NMP gave a mixture of several unidentified products (Table 1, entry 9), and dioxane and toluene led to poor conversions of 4-bromobenzonitrile and to equimolar mixtures of products **1a** and **1b** (Table 1, entries 10 and 11). We then evaluated the influence of the palladium source. Interestingly, $Pd(OAc)_2$ and $[PdCl(C_3H_5)]_2$ gave very selectively **1a** (Table 1, entries 13 and 14). A few reactions were also performed using palladium associated to other phosphine ligands, and showed that the presence of such phosphines for the coupling with 4-bromobenzonitrile was found to be useless, as the selectivities in favour of the formation of **1a** and the conversions of 4-bromobenzonitrile were not improved (Table 1, entries 15–19). It should be noted that the use of $(n\text{-}Bu)_3N$ as the base led to the predominant formation of the reductive addition product **1c** in moderate yield (Table 1, entry 20). Thus it clearly appears that although $PdCl(C_3H_5)(dppb)$ 1 mol% leads with KOAc in DMAc (Table 1, entry 3) to a decent yield of **1a**, the phosphine-free $Pd(OAc)_2$ catalyst (1 mol%) appears to be the most efficient for the production of **1a**. Moreover, the use of only 0.1 mol% $Pd(OAc)_2$ gave **1a** in 96% selectivity and in 74% yield (Table 1, entry 21).

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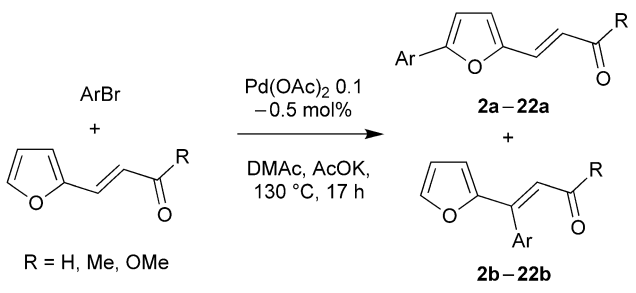
Table 1. Influence of the reaction conditions for palladium-catalysed coupling of (*E*)-4-furan-2-ylbut-3-en-2-one with 4-bromobenzonitrile (Scheme 2).[a]

Entry	[Pd] (mol%)	Temp. [°C]	Solvent	Base	Conv. [%]	Ratio **1a**:**1b**	Yield in **1a** [%]
1	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	NaOAc	100	29:71	–
2	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	CsOAc	100	96:4[b]	–
3	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	KOAc	100	96:4	72
4	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	Na_2CO_3	100	5:95[b]	–
5	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	K_2CO_3	100	mixture[c,d]	–
6	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	Cs_2CO_3	100	mixture[c,d]	–
7	$PdCl(C_3H_5)(dppb)$ (1)	130	DMAc	KF	100	3:97[b,c]	40[e]
8	$PdCl(C_3H_5)(dppb)$ (1)	130	DMF	KOAc	100	96:4[b]	–
9	$PdCl(C_3H_5)(dppb)$ (1)	130	NMP	KOAc	57	mixture[c]	–
10	$PdCl(C_3H_5)(dppb)$ (1)	130	dioxane	KOAc	46	50:50	–
11	$PdCl(C_3H_5)(dppb)$ (1)	130	toluene	KOAc	41	48:52	–
12	$PdCl(C_3H_5)(dppb)$ (1)	100	DMAc	KOAc	48	93:7	–
13	$Pd(OAc)_2$ (1)	130	DMAc	KOAc	100	96:4	–
14	0.5 $[PdCl(C_3H_5)]_2$ (1)	130	DMAc	KOAc	100	96:4[d]	–
15	0.5 $[PdCl(C_3H_5)]_2$/2 PPh_3 (1)	130	DMAc	KOAc	100	92:8[d]	–
16	$Pd(OAc)_2$/dppe	130	DMAc	KOAc	100	96:4[d]	–
17	$Pd(OAc)_2$/dppm	130	DMAc	KOAc	100	78:22	–
18	$Pd(OAc)_2$/dppb	130	DMAc	KOAc	100	94:6[d]	–
19	$PdCl(C_3H_5)(dppb)$ (0.1)	130	DMAc	KOAc	100	92:8	
20	$PdCl(C_3H_5)(dppb)$ (2)	150	DMAc	$N(n\text{-}Bu)_3$	88	–	47[f]
21	$Pd(OAc)_2$ (0.1)	130	DMAc	KOAc	100	96:4	74

[a] *Conditions:* 4-bromobenzonitrile (1 equiv.), (*E*)-4-furan-2-ylbut-3-en-2-one (2 equiv.), base (2 equiv.), 17 h, GC and NMR conversion of 4-bromobenzonitrile, yields of isolated product.
[b] The formation of 10–20% of biphenyl-4,4′-dicarbonitrile was also observed.
[c] The formation of several products was observed.
[d] The formation of more than 20% of biphenyl-4,4′-dicarbonitrile was also observed.
[e] Product **1b** was isolated in 40% yield.
[f] **1a** not detected, product **1c** was isolated in 47% yield.

The scope of the coupling of (*E*)-4-furan-2-ylbut-3-en-2-one using other aryl bromides was investigated using low amounts of $Pd(OAc)_2$ catalyst (Scheme 3, Table 2). These reactions were performed using DMAc, AcOK, 130 °C and 0.5–0.1 mol% $Pd(OAc)_2$. First, we studied the reactivity of *para*-substituted aryl bromides. In the presence of electron-deficient aryl bromides such as ethyl 4-bromobenzoate or 4-bromonitrobenzene, the products **2a** and **3a** were isolated in 52% and 57% yields, respectively (Table 2, entries 1 and 2). A similar reactivity and regioselectivity was observed in the presence of the *meta*-substituted aryl bromides, 3-bromoacetophenone, 3-bromonitrobenzene or 3-bromobenzonitrile. With these aryl bromides, the direct arylation products **4a**–**6a** were produced in 83–90% selectivity and isolated in 49–73% yields (Table 2, entries 4–6). On the other hand, in the presence of the electron-rich aryl bromide, 4-bromoanisole, an inversion of the regioselectivity of the arylation in favour of the Heck-type coupling product **8b** was observed (Table 2, entry 8). It is likely that with donating groups on arenes, the more nucleophilic aryl group interacts first with the electrophilic carbon of the enone. By contrast, with electrophilic ArPd(OAc) moieties, the interaction with the furan HC-5=C-4 bond is favoured to lead to the C–H bond deprotonation by acetate.[19] Although an electrophilic aromatic-type substitution cannot be ruled out,[2b] however, the assistance of carboxylate ligand on palladium for the arylation of heterocycles has been demonstrated by Fagnou.[19b] As we have observed a strong influence of the acetate with very small amounts of $Pd(OAc)_2$, the concerted metallation deprotonation mechanism is preferred in these examples.



Scheme 3.

The influence of the nature of the double bond substituents on the selectivity and activity also needed to be evaluated. The reactivity of cinnamaldehyde in the

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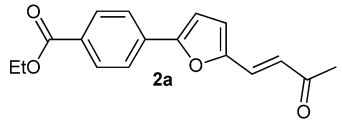
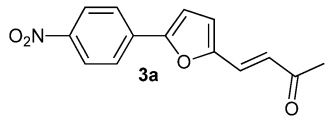
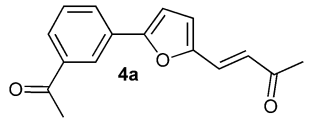
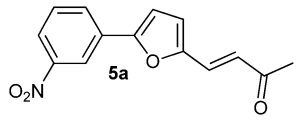
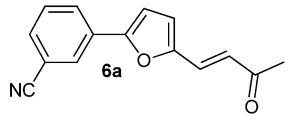
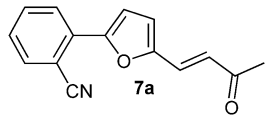
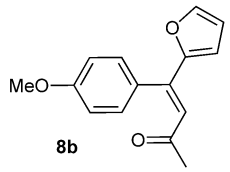
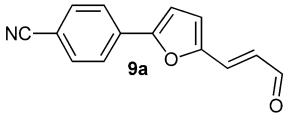
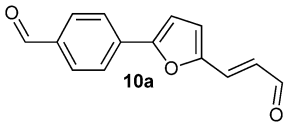
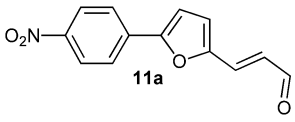
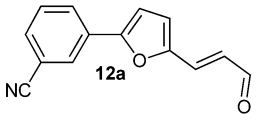
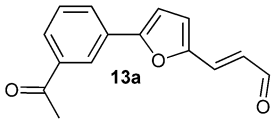
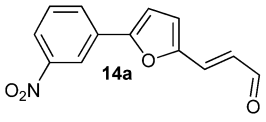
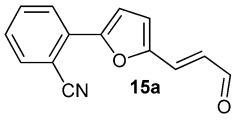
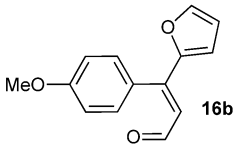
Table 2. Palladium-catalysed direct coupling of (*E*)-4-furan-2-ylbut-3-en-2-one with aryl bromides (Scheme 3).[a]

Entry	Ratio **a**:**b**	Major product	Yield of **a** [%]
1	77:23	 **2a**	52
2	91:9	 **3a**	57[b]
3	92:8		75[c]
4	83:17	 **4a**	51
5	90:10	 **5a**	73
6	88:12	 **6a**	49[b]
7	94:6	 **7a**	71
8	–	 **8b**	25[d]

[a] *Conditions:* $Pd(OAc)_2$ (0.001 equiv.), aryl bromide (1 equiv.), (*E*)-4-furan-2-ylbut-3-en-2-one (2 equiv.), AcOK (2 equiv.), DMAc, 17 h, 130 °C.
[b] $Pd(OAc)_2$ (0.005 equiv.).
[c] $PdCl(C_3H_5)(dppb)$ (0.01 equiv.).
[d] Yield of isomer **8b**.

Table 3. Palladium-catalysed direct coupling of (*E*)-3-furan-2-ylpropenal with aryl bromides (Scheme 3).[a]

Entry	Base	Ratio **a**:**b**	Major product	Yield of **a** (%)
1	KOAc	96:4	 **9a**	64
2	KOAc	96:4	 **10a**	68
3	KOAc	97:3	 **11a**	74
4	KOAc	96:4	 **12a**	66
5	KOAc	78:22	 **13a**	52
6	KOAc	93:7	 **14a**	70
7	KOAc	95:5	 **15a**	73[b]
8	KOAc	0:100	 **16b**	35[c]
9	$NaHCO_3$	0:100		41[d]

[a] *Conditions:* $Pd(OAc)_2$ (0.001 equiv.), aryl bromide (1 equiv.), (*E*)-3-furan-2-ylpropenal (2 equiv.), AcOK or $NaHCO_3$ (2 equiv.), DMAc, 17 h, 130 °C.
[b] $PdCl(C_3H_5)(dppb)$ (0.01 equiv.).
[c] 41 h, Ratio of Heck-type products *Z*:*E* 19:81, yield of **16b**.
[d] Ratio of Heck-type products *Z*:*E* 22:78, yield of **16b**.

presence of aryl halides has already been described, and in that case, the Heck-type products were easily obtained.[14] We observed that the coupling of (*E*)-3-furan-2-ylpropenal with electron-deficient aryl bromides, under the activation by $Pd(OAc)_2$/KOAc, gave the direct arylation products **9a**–**12a**, **14a** and **15a** with high selectivities, and that in several cases, higher selectivities than for the coupling with (*E*)-4-furan-2-ylbut-3-en-2-one were observed (Table 3). Again, the electron-rich aryl bromide, 4-bromoanisole, gave the Heck type product **16b** selectively (Table 3, entries 8 and 9). From the *E* isomer, a mixture of *Z* and *E* isomers was obtained in 22:78 ratio.

The reaction of methyl (*E*)-3-furan-2-yl acrylate with aryl bromides in the presence of $Pd(OAc)_2$ was found to give the direct arylation products **17a**–**22a** in extremely high selectivity in several cases. This result was quite surprising as the Heck reaction with cinnamates is known to be relatively easy. For example, the reaction of ethyl cinnamate with 4-bromotoluene in the presence of only 0.1 mol% of $[PdCl(C_3H_5)]_2$/tetra-

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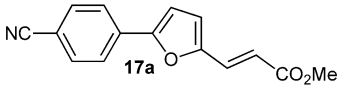
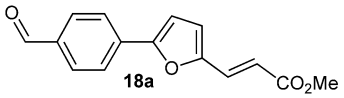
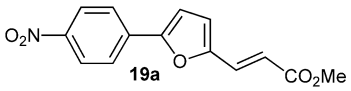
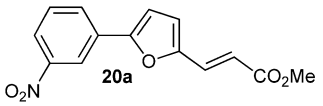
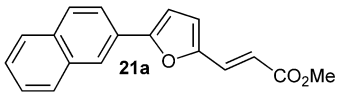
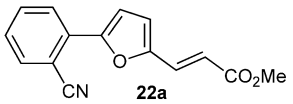
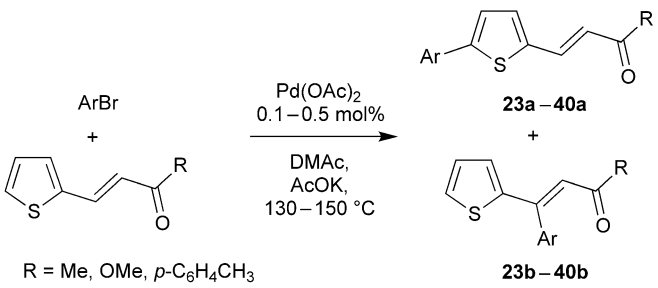
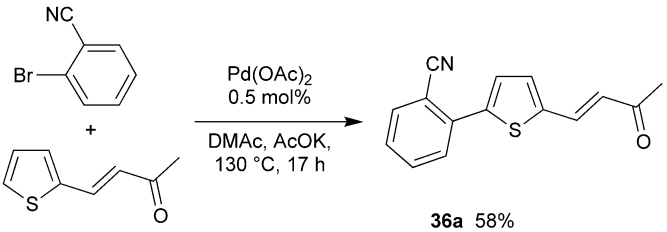
Table 4. Palladium-catalysed direct coupling of methyl (*E*)-3-furan-2-yl acrylate with aryl bromides (Scheme 3).[a]

Entry	Ratio **a**:**b**	Major product	Yield of **a** [%]
1	95:5	 **17a**	81
2	91:9	 **18a**	67
3	97:3	 **19a**	82
4	86:14	 **20a**	65
5	83:17	 **21a**	62
6	96:4	 **22a**	66

[a] *Conditions:* $Pd(OAc)_2$ (0.005 equiv.), aryl bromide (1 equiv.), methyl (*E*)-3-furan-2-yl acrylate (2 equiv.), AcOK (2 equiv.), DMAc, 17 h, 150 °C.



Scheme 4.



Scheme 5.

phosphine as the catalyst, K_2CO_3 as the base in DMF gives the Heck product in 91% yield.[13b] In the presence of methyl (*E*)-3-furan-2-yl acrylate, and 0.5 mol% $Pd(OAc)_2$, the reaction of 4-bromonitrobenzene, 2- or 4-bromobenzonitrile or 1-bromobenzaldehyde gave more than 90% of the 5-arylated furans **17a**–**19a** and **22a**, and only traces of the Heck-type products were detected (Table 4, entries 1–3 and 6). With 3-bromonitrobenzene or 1-bromonaphthalene, the arylated furans **20a** and **21a** were obtained in 86% and 83% selectivities, respectively (Table 4, entries 4 and 5). Again, the phosphine-free $Pd(OAc)_2$/KOAc system with electron-deficient aryl bromides appears to be the best catalyst to prevent the Heck-type reaction to the profit of C-5 arylation.

The reaction is not limited to the direct arylation of furans. Three thiophenes bearing electron-deficient alkenes have also been successfully arylated (Scheme 4 and Scheme 5 and Table 5). Methyl (*E*)-3-thiophen-2-yl acrylate was arylated at carbon 5 of thiophene with very high regioselectivities and yields (Table 5). Moreover, the reaction proceeded using only 0.1 mol% $Pd(OAc)_2$ as the catalyst. Thus, alkenyl-furans and thiophenes react similarly towards direct arylation at C-5 in the presence of phosphine-free catalyst. A range of electron-deficient aryl bromides was successfully employed. Even 1-bromonaphthalene was found to be a suitable reactant for this reaction (Table 5, entry 10). It is noteworthy that 3-bromopyridine, 3-bromoisoquinoline or 4-bromoisoquinoline led to 73–83% of direct arylation products **33a**–**35a** without poisoning of the catalyst by coordination of the pyridine group (Table 5, entries 11–13). However, with these three substrates 0.5 mol% catalyst had to be employed in order to reach full conversions of these aryl bromides.

On the other hand, the coupling of 2-bromobenzonitrile with (*E*)-4-thien-2-ylbut-3-en-2-one gave the target compound **36a** in only 58% yield due to the formation of unidentified products (Scheme 5).

Four aryl bromides have been reacted with (*E*)-3-thiophen-2-yl-1-*p*-tolylpropenone (Scheme 6). The arylation took place selectively at C-5 of thiophene. The use of only 0.5 mol% catalyst led to a complete conversion of the aryl bromides and the desired compounds **37a**–**40a** were obtained in good yields.

The use of a furan bearing a trisubstituted alkene led only to the direct arylation products (Scheme 7). The Heck reaction with similar trisubstituted alkenes is known to be very challenging due to a slow insertion of such congested alkenes into the Ar–Pd bonds.[17] A wide range of aryl bromides has been employed, and in all cases, using only 0.1 mol% $Pd(OAc)_2$ as the catalyst, a regioselective arylation at carbon 5 of furan was observed. Moreover, from the (*E*)-3-furan-2-yl-2-methylpropenal, the (*E*)-3-(5-arylfuran-2-yl)-2-methylpropenals **41**–**60** were obtained without isomerisation of the alkenyl bond. It should be noted that with this reactant, the coupling with the

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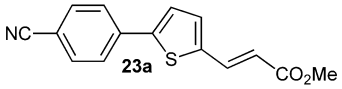
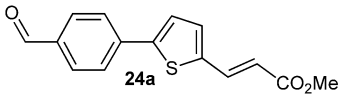
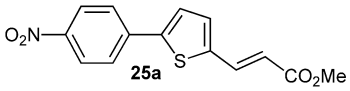
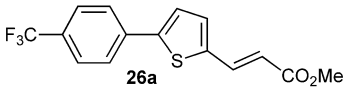
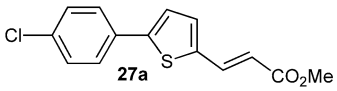
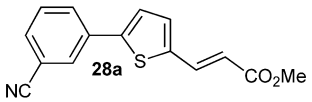
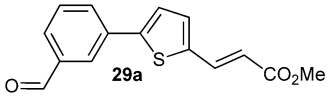
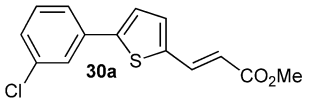
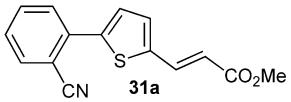
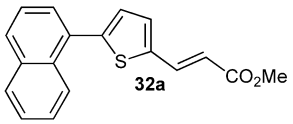
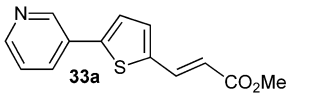
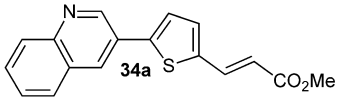
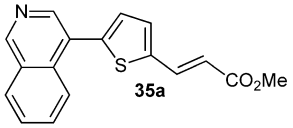
Table 5. Palladium-catalysed direct coupling of methyl (*E*)-3-thiophen-2-yl acrylate with aryl bromides (Scheme 4).[a]

Entry	Ratio **a**:**b**	Major product	Yield of **a** [%]
1	98:2	 **23a**	80
2	98:2	 **24a**	81
3	99:1	 **25a**	79
4	98:2	 **26a**	77
5	91:9	 **27a**	70
6	98:2	 **28a**	77
7	90:10	 **29a**	68
8	94:6	 **30a**	68
9	98:2	 **31a**	84
10	98:2	 **32a**	81[b]
11	97:3	 **33a**	78[b]
12	97:3	 **34a**	73[c]
13	98:2	 **35a**	83[d]

[a] *Conditions:* $Pd(OAc)_2$ (0.001 equiv.), aryl bromide (1 equiv.), methyl (*E*)-3-thiophen-2-yl acrylate (2 equiv.), AcOK (2 equiv.), DMAc, 17 h, 130 °C.
[b] $Pd(OAc)_2$ (0.005 equiv.), 27 h, 150 °C.
[c] $Pd(OAc)_2$ (0.005 equiv.), 41 h, 150 °C.
[d] $Pd(OAc)_2$ (0.005 equiv.), 46 h, 150 °C.

electron-rich 4-bromoanisole also proceeded nicely to give only the arylated furan at C-5 **47a** in 83% yield. Thus, the trisubstituted alkene itself disfavours the Heck-type reaction. This property should be used to prevent the Heck type reaction with electron-rich aryl bromides.

Conclusions

We have shown that the $Pd(OAc)_2$/KOAc catalyst system without any phosphine ligand, promotes the direct arylation of heteroaromatics and inhibits the Heck reaction with 1,2-disubstituted alkenes. The nature of the base was found to be crucial to control the selectivity in favour of the arylation. This reaction allows the synthesis in one step of a wide variety of 5-arylated five-membered heteroarenes bearing enone, enal or acrylates at carbon 2. These couplings can be performed using low catalyst loadings (0.5–0.1 mol%) of a commercially available, air-stable and phosphine-free catalyst. A wide range of functions such as acetyl, formyl, ester, nitro, trifluoromethyl, fluoro or nitrile on the aryl bromide is tolerated. It should be noted that a variety of new bis(hetero)aryl derivatives have been prepared, indicating that this procedure provides a convenient access to compounds which cannot be very easily synthesised using more classical coupling methods. Finally, due to environmental considerations, the advantage of such an inert wastes procedure (formation of acetic acid and potassium bromide) should become increasingly important for industrial processes.

Experimental Section

General Remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. DMAc analytical grade was not distilled before use. Potassium acetate (99%) was used. Commercial aryl halides and heteroarene derivatives were used without purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker 300 or 500 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.25 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

General Procedure for Coupling Reactions

In a typical experiment, the aryl bromide (1 mmol), heteroaryl derivative (2 mmol), base (2 mmol) and [Pd] (see Tables) were dissolved in DMAc (3 mL) under an argon atmosphere. The reaction mixture was stirred at 130–150 °C (see Tables) for 17–46 h. Then, the solvent was evaporated and the isomeric products were separated by silica gel column chromatography.

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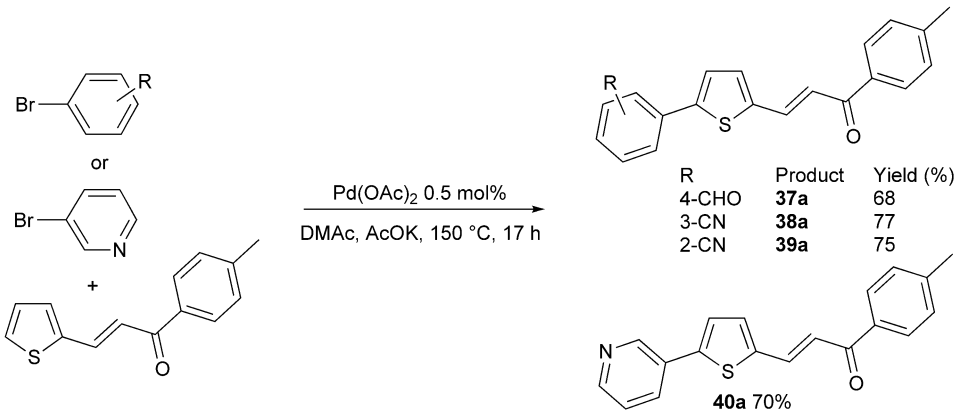
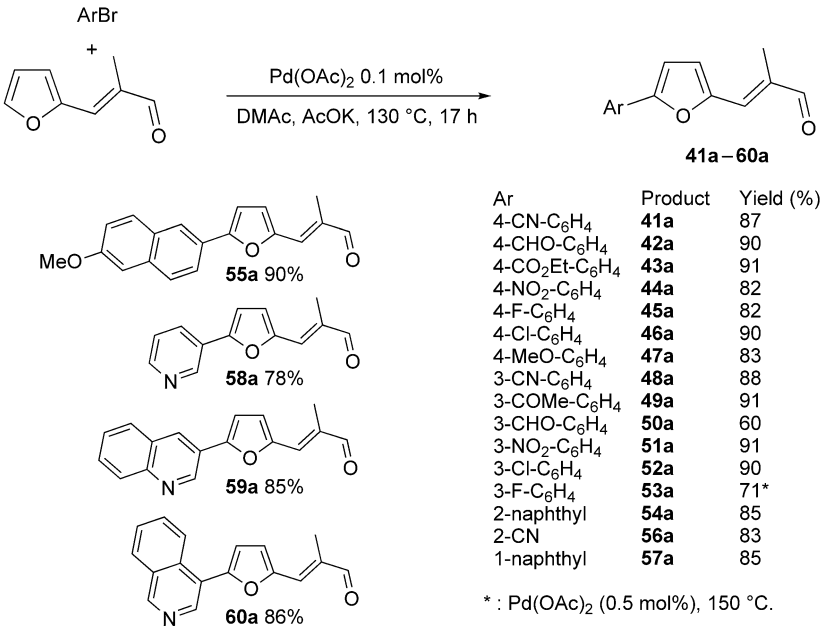


Scheme 6.



Scheme 7.

4-{5-[(*E*)-3-Oxobut-1-enyl]-furan-2-yl}-benzonitrile (1a): From 4-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **1a** was obtained; yield: 0.176 g (74%).

(*E*)-4-(1-Furan-2-yl-3-oxobut-1-enyl)-benzonitrile (1b): From 4-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and KF (0.116 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) product **1b** was obtained; yield: 0.095 g (40%).

4-(1-Furan-2-yl-3-oxobutyl)-benzonitrile (1c): From 4-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and $(n\text{-}Bu)_3N$ (0.740 g, 4 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) product **1c** was obtained; yield: 0.112 g (47%).

Ethyl 4-{5-[(*E*)-3-oxobut-1-enyl]-furan-2-yl}-benzoate (2a): From ethyl 4-bromobenzoate (0.229 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **2a** was obtained; yield: 0.148 g (52%).

(*E*)-4-[5-(4-Nitrophenyl)-furan-2-yl]-but-3-en-2-one (3a): From 4-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) product **3a** was obtained; yield: 0.193 g (75%).

(*E*)-4-[5-(3-Acetylphenyl)-furan-2-yl]-but-3-en-2-one (4a): From 3-bromoacetophenone (0.199 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **4a** was obtained; yield: (0.130 g (51%).

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(*E*)-4-[5-(3-Nitrophenyl)-furan-2-yl]-but-3-en-2-one (5a): From 3-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **5a** was obtained; yield: 0.188 g (73%).

3-{5-[(*E*)-3-Oxobut-1-enyl]-furan-2-yl}-benzonitrile (6a): From 3-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **6a** was obtained; yield: 0.116 g (40%).

2-{5-[(*E*)-3-Oxobut-1-enyl]-furan-2-yl}-benzonitrile (7a): From 2-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **7a** was obtained; yield: 0.168 g (71%).

(*E*)-4-Furan-2-yl-4-(4-methoxyphenyl)-but-3-en-2-one (8b): From 4-bromoanisole (0.187 g, 1 mmol), (*E*)-4-furan-2-ylbut-3-en-2-one (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **8b** was obtained; yield: 0.060 g (25%). The formation of Heck-type *Z* isomer was also observed.

4-{5-[(*E*)-3-Oxopropenyl]-furan-2-yl}-benzonitrile (9a): From 4-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **9a** was obtained; yield: 0.143 g (64%).

4-{5-[(*E*)-3-Oxopropenyl]-furan-2-yl}-benzaldehyde (10a): From 4-bromobenzaldehyde (0.185 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **10a** was obtained; yield: 0.154 g (68%).

(*E*)-3-[5-(4-Nitrophenyl)-furan-2-yl]-propenal (11a): From 4-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **11a** was obtained; yield: 0.180 g (74%).

3-{5-[(*E*)-3-Oxopropenyl]-furan-2-yl}-benzonitrile (12a): From 3-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **12a** was obtained; yield: 0.147 g (66%).

(*E*)-3-[5-(3-Acetylphenyl)-furan-2-yl]-propenal (13a): From 3-bromoacetophenone (0.199 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **13a** was obtained; yield: (0.125 g (52%).

(*E*)-3-[5-(3-Nitrophenyl)-furan-2-yl]-propenal (14a): From 3-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **14a** was obtained; yield: 0.170 g (70%).

2-{5-[(*E*)-3-Oxopropenyl]-furan-2-yl}-benzonitrile (15a): From 2-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) product **15a** was obtained; yield: 0.163 g (73%).

(*E*)-3-Furan-2-yl-3-(4-methoxyphenyl)-propenal (16b): From 4-bromoanisole (0.187 g, 1 mmol), (*E*)-3-furan-2-ylpropenal (0.244 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **16b** was obtained; yield: 0.93 g (41%).

Methyl (*E*)-3-[5-(4-cyanophenyl)-furan-2-yl]-acrylate (17a): From 4-bromobenzonitrile (0.182 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **17a** was obtained; yield: 0.205 g (81%).

Methyl (*E*)-3-[5-(4-formylphenyl)-furan-2-yl]-acrylate (18a): From 4-bromobenzaldehyde (0.185 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **18a** was obtained; yield: 0.172 g (67%).

Methyl (*E*)-3-[5-(4-nitrophenyl)-furan-2-yl]-acrylate (19a): From 4-bromonitrobenzene (0.202 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **19a** was obtained; yield: 0.224 g (82%).

Methyl (*E*)-3-[5-(3-nitrophenyl)-furan-2-yl]-acrylate (20a): From 3-bromonitrobenzene (0.202 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **20a** was obtained; yield: 0.178 g (65%).

Methyl (*E*)-3-(5-naphthalen-2-ylfuran-2-yl)-acrylate (21a): From 2-bromonaphthalene (0.207 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **21a** was obtained; yield: (0.172 g (62%).

Methyl (*E*)-3-[5-(2-cyanophenyl)-furan-2-yl]-acrylate (22a): From 2-bromobenzonitrile (0.182 g, 1 mmol), methyl (*E*)-3-furan-2-yl acrylate (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **22a** was obtained; yield: (66%).

Methyl (*E*)-3-[5-(4-cyanophenyl)-thiophen-2-yl]-acrylate (23a): From 4-bromobenzonitrile (0.182 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **23a** was obtained; yield: 0.215 g (80%).

Methyl (*E*)-3-[5-(4-formylphenyl)-thiophen-2-yl]-acrylate (24a): From 4-bromobenzaldehyde (0.185 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **24a** was obtained; yield: 0.220 g (81%).

Methyl (*E*)-3-[5-(4-nitrophenyl)-thiophen-2-yl]-acrylate (25a): From 4-bromonitrobenzene (0.202 g, 1 mmol), methyl

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(*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **25a** was obtained; yield: 0.228 g (79%).

Methyl (*E*)-3-[5-(4-trifluoromethylphenyl)-thiophen-2-yl]-acrylate (26a): From the reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **26a** was obtained; yiield: (0.240 g (77%).

Methyl (*E*)-3-[5-(4-chlorophenyl)-thiophen-2-yl]-acrylate (27a): The reaction of 4-chlorobromobenzene (0.191 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **27a** was obtained; yield: 0.195 g (70%).

Methyl (*E*)-3-[5-(3-cyanophenyl)-thiophen-2-yl]-acrylate (28a): From 3-bromobenzonitrile (0.182 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **28a** was obtained; yield: 0.207 g (77%).

Methyl (*E*)-3-[5-(3-formylphenyl)-thiophen-2-yl]-acrylate (29a):From 3-bromobenzaldehyde (0.185 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **29a** was obtained; yield: 0.185 g (68%).

Methyl (*E*)-3-[5-(3-chlorophenyl)-thiophen-2-yl]-acrylate (30a): The reaction of 3-chlorobromobenzene (0.191 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **30a** was obtained; yield: 0.189 g (68%).

Methyl (*E*)-3-[5-(2-cyanophenyl)-thiophen-2-yl]-acrylate (31a): From 2-bromobenzonitrile (0.182 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **31a** was obtained; yield: 0.226 g (84%).

Methyl (*E*)-3-(5-naphthalen-1-yl-thiophen-2-yl)-acrylate (32a): From 1-bromonaphthalene (0.207 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 27 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **32a** was obtained; yield: 0.238 g (81%).

Methyl (*E*)-3-(5-pyridin-3-ylthiophen-2-yl)-acrylate (33a): From 3-bromopyridine (0.158 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 27 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **33a** was obtained; yield: 0.191 g (78%).

Methyl (*E*)-3-(5-quinolin-3-ylthiophen-2-yl)-acrylate (34a): From 3-bromoquinoline (0.208 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 41 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **34a** was obtained; yield: 0.215 g (73%).

Methyl (*E*)-3-(5-isoquinolin-4-yl-thiophen-2-yl)-acrylate (35a): From 4-bromoisoquinoline (0.208 g, 1 mmol), methyl (*E*)-3-thiophen-2-yl acrylate (0.336 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 46 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **35a** was obtained; yield: 0.245 g (83%).

2-[5-((*E*)-3-Oxobut-1-enyl)-thiophen-2-yl]-benzonitrile (36a): From 2-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-4-thien-2-ylbut-3-en-2-one (0.304 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **36a** was obtained; yield: 0.147 g (58%).

(*E*)-4-[5-(3-Oxo-3-*p*-tolylpropenyl)-thiophen-2-yl]-benzaldehyde (37a): From 4-bromobenzaldehyde (0.185 g, 1 mmol), (*E*)-3-thiophen-2-yl-1-*p*-tolylpropenone (0.256 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **37a** was obtained; yield: 0.226 g (68%).

(*E*)-3-[5-(3-Oxo-3-*p*-tolylpropenyl)-thiophen-2-yl]-benzonitrile (38a): From 3-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-thiophen-2-yl-1-*p*-tolylpropenone (0.256 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **38a** was obtained; yield: 0.253 g (77%).

(*E*)-2-[5-(3-Oxo-3-*p*-tolylpropenyl)-thiophen-2-yl]-benzonitrile (39a): From 2-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-thiophen-2-yl-1-*p*-tolylpropenone (0.256 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **39a** was obtained; yield: 0.247 g (75%).

(*E*)-3-(5-Pyridin-3-ylthiophen-2-yl)-1-*p*-tolylpropenone (40a): From 3-bromopyridine (0.158 g, 1 mmol), (*E*)-3-thiophen-2-yl-1-*p*-tolylpropenone (0.256 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **40a** was obtained; yield: 0.213 g (70%).

(*E*)-4-[5-(2-Methyl-3-oxopropenyl)-furan-2-yl]-benzonitrile (41a): From 4-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **41a** was obtained; yield: 0.206 g (87%).

(*E*)-4-[5-(2-Methyl-3-oxopropenyl)-furan-2-yl]-benzaldehyde (42a): From 4-bromobenzaldehyde (0.185 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **42a** was obtained; yield: 0.216 g (90%).

Ethyl (*E*)-4-[5-(2-methyl-3-oxopropenyl)-furan-2-yl]-benzoate (43a): From ethyl 4-bromobenzoate (0.229 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **43a** was obtained; yield: 0.259 g (91%).

(*E*)-2-Methyl-3-[5-(4-nitrophenyl)-furan-2-yl]-propenal (44a): From 4-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **44a** was obtained; yield: 0.211 g (82%).

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(*E*)-3-[5-(4-Fluorophenyl)-furan-2-yl]-2-methylpropenal (45a): From 4-bromofluorobenzene (0.175 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **45a** was obtained; yield: 0.189 g (82%).

(*E*)-3-[5-(4-Chlorophenyl)-furan-2-yl]-2-methylpropenal (46a): From 4-chlorobromobenzene (0.191 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **46a** was obtained; yield: 0.222 g (90%).

(*E*)-3-[5-(4-Methoxyphenyl)-furan-2-yl]-2-methylpropenal (47a): From 4-bromoanisole (0.187 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **47a** was obtained; yield: 0.201 g (83%).

(*E*)-3-[5-(2-Methyl-3-oxopropenyl)-furan-2-yl]-benzonitrile (48a): From 3-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **48a** was obtained; yield: 0.209 g (88%).

(*E*)-3-[5-(3-Acetylphenyl)-furan-2-yl]-2-methylpropenal (49a): From 3-bromoacetophenone (0.199 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **49a** was obtained; yield: 0.231 g (91%).

(*E*)-3-[5-(2-Methyl-3-oxopropenyl)-furan-2-yl]-benzaldehyde (50a): From 3-bromobenzaldehyde (0.185 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **50a** was obtained; yield: 0.144 g (60%).

(*E*)-2-Methyl-3-[5-(3-nitrophenyl)-furan-2-yl]-propenal (51a): From 3-bromonitrobenzene (0.202 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **51a** was obtained; yield: 0.234 g (91%).

(*E*)-3-[5-(3-Chlorophenyl)-furan-2-yl]-2-methylpropenal (52a): The reaction of 3-chlorobromobenzene (0.191 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **52a** was obtained; yield: 0.222 g (90%).

(*E*)-3-[5-(3-Fluorophenyl)-furan-2-yl]-2-methylpropenal (53a): From 3-bromofluorobenzene (0.175 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) product **53a** was obtained; yield: 0.163 g (71%).

(*E*)-2-Methyl-3-(5-naphthalen-2-ylfuran-2-yl)-propenal (54a): From 2-bromonaphthalene (0.207 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **54a** was obtained; yield: 0.218 g (83%).

(*E*)-3-[5-(6-Methoxynaphthalen-2-yl)-furan-2-yl]-2-methylpropenal (55a): From 2-bromo-6-methoxynaphthalene (0.237 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **55a** was obtained; yield: 0.263 g (90%).

(*E*)-2-[5-(2-Methyl-3-oxopropenyl)-furan-2-yl]-benzonitrile (56a): From 2-bromobenzonitrile (0.182 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **56a** was obtained; yield: (0.197 g (83%).

(*E*)-2-Methyl-3-(5-naphthalen-1-ylfuran-2-yl)-propenal (57a): From 1-bromonaphthalene (0.207 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **57a** was obtained; yield: 0.223 g (85%).

(*E*)-2-Methyl-3-(5-pyridin-3-ylfuran-2-yl)-propenal (58a): From 3-bromopyridine (0.158 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **58a** was obtained; yield: 0.166 g (78%).

(*E*)-2-Methyl-3-(5-quinolin-3-ylfuran-2-yl)-propenal (59a): From 3-bromoquinoline (0.208 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **59a** was obtained; yield: 0.224 g (85%).

(*E*)-3-(5-Isoquinolin-5-ylfuran-2-yl)-2-methylpropenal (60a): From 4-bromoisoquinoline (0.208 g, 1 mmol), (*E*)-3-furan-2-yl-2-methylpropenal (0.272 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 130 °C in DMAc (3 mL) for 17 h in the presence of $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) product **60a** was obtained; yield: 0.226 g (86%).

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