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ARTICLE

Reactivity of bromofluorenes in palladium-catalysed direct arylation of heteroaromatics

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The palladium-catalysed direct arylation using bromofluorenes and heteroaromatics as the coupling partners proceed in moderate to high yields using only 0.1-0.5 mol% $Pd(OAc)_2$ or 1 mol% $PdCl(C_3H_5)(dppb)$ as the catalysts and KOAc as the base. A wide variety of heteroarenes have been successfully employed allowing to tune easily their properties. From 2,7-dibromofluorene, successive arylations allows to introduce two different heteroarenes at carbons C2 and C7.

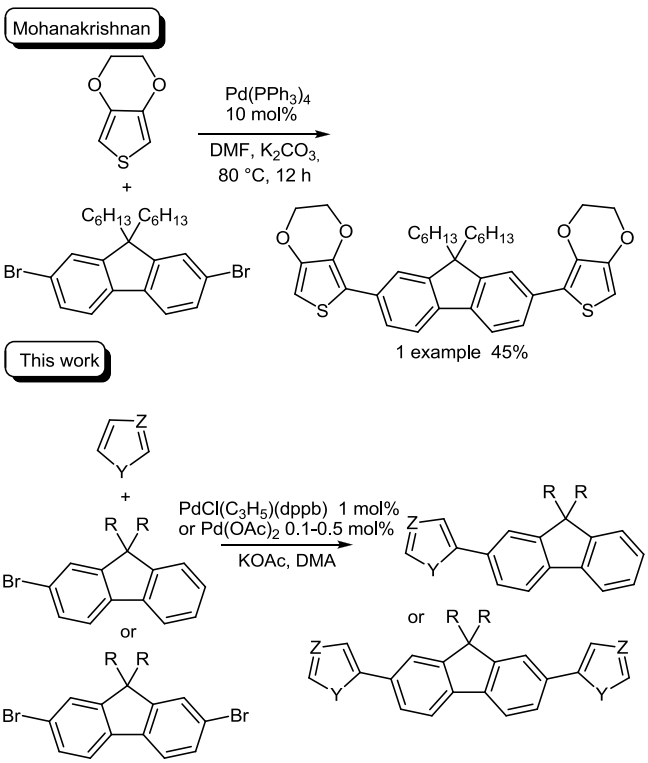
Introduction

Fluorene derivatives including fluorenes bearing heteroaromatics at C2 and C7 continue to attract the attention of synthetic organic chemists, due to their inherent physical properties.[1] Polyfluorenes have also been investigated for use as luminophores in organic light-emitting diodes.

In 1990, Ohta and co-workers reported that the 2- or 5-arylation of several heteroaromatics, including furans and thiophenes, with aryl halides proceed in moderate to good yields, via a C-H bond activation, using palladium catalysts.[2a,2b] Since these results, the palladium-catalysed so-called direct arylation[2c-2q] of heteroaromatics with aryl halides has proved to be a very powerful method for the synthesis of a wide variety of arylated heteroaromatics.[3-7] The major by-products of these reactions are a base associated to HX, instead of metallic salts produced under more classical cross-coupling procedures.

However, only a few examples of Pd-catalysed direct couplings of halo-fluorenes with heteroaromatics have been reported so far.[8-10] In most cases, heteroarylfluorenes are still prepared using more classical palladium-catalysed reactions such as Stille, Suzuki or Negishi couplings.[11] From a dibromofluorene derivative and 3,4-ethylenedioxythiophene, Mohanakrishnan and co-workers obtained the desired coupling product in 45% yield using 10 mol% $Pd(PPh_3)_4$ catalyst (Scheme 1, top).[8a] Ohe et al. reported the arylation of a furan derivative with a dibromofluorene using 5 mol% $Pd(OAc)_2$ associated to 10 mol% PPh_3.[8b] Other example of coupling of 2-halofluorenes with an imidazopyridine,[8e] a benzothiazole,[8f] a thiophene[8g] or an indolizine[8h] have also been described. For these reactions, high catalyst loadings (3-15 mol%) were generally employed and, in some cases low yields were obtained. Therefore, the substrate scope for the direct arylation of heteroaromatics with fluorene derivatives needed to be extended for accessing to a wider variety of heteroarylated fluorene derivatives. Moreover, simpler reaction conditions using low loadings of easily accessible catalyst for the couplings with such compounds have to be found, in order to provide economically viable procedures.

Here, we wish to report on the reactivity of bromofluorene derivatives for coupling with a wide variety of heteroaromatics using either a phosphine-free palladium catalyst or palladium associated to the simple diphosphine ligand dppb in the presence of an inexpensive base.

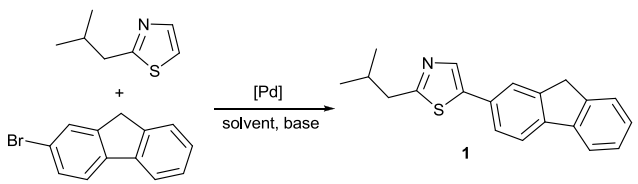


Scheme 1

Results and discussion

We initially studied the reactivity of 2-bromofluorene for coupling with 2-*i*-butylthiazole (Scheme 2, table 1). The use of 1 mol% $PdCl(C_3H_5)(dppb)$ or 0.5 mol% $PdCl_2$ and $Pd(OAc)_2$ at 150 °C led to **1** in very similar yields with high conversions of 2-bromofluorene (Table 1, entries 1-3). $Pd(OAc)_2$ associated to PPh_3 or dppb led to lower conversions of 2-bromofluorene (Table 1, entries 4 and 5). We also examined the influence of some bases. Potassium carbonate was found to be quite effective; whereas, caesium carbonate and sodium acetate led to moderate conversions of 2-bromofluorene (Table 1, entries 6-8). The influence of the nature of the solvent was also examined. The reactions performed in DMF or NMP were found to afford **1** in high yields; whereas the use of xylene and cyclopentyl methyl ether (CPME), which had been found to be an suitable solvent for the direct arylation of several heteroaromatics,[4f] was less effective (Table 1, entries 9-12). The reaction also proceed nicely at 120°C instead of 150°C using 0.5 mol% of both $PdCl(C_3H_5)(dppb)$ or $Pd(OAc)_2$ catalysts (Table 1, entries 13 and 14).

In 2003, de Vries and co-workers described extremely promising results for the Heck and Suzuki reactions using a very low loading (0.1-0.01 mol%) of ligand-free catalyst $Pd(OAc)_2$.[12a] They have demonstrated that, at elevated temperature, when $Pd(OAc)_2$ is employed as the catalyst precursor, soluble palladium(0) colloids or nanoparticles are formed, and that the Heck or Suzuki reaction takes place. We have recently reported that the use of the "de Vries conditions" allows the coupling or several heteroaromatics using ligand-free palladium catalyst.[12b] With 2-bromofluorene, a reaction using only 0.1 mol% $Pd(OAc)_2$ at 120°C also afforded the target product **1** in a very high yield of 94% (Table 1, entry 15).



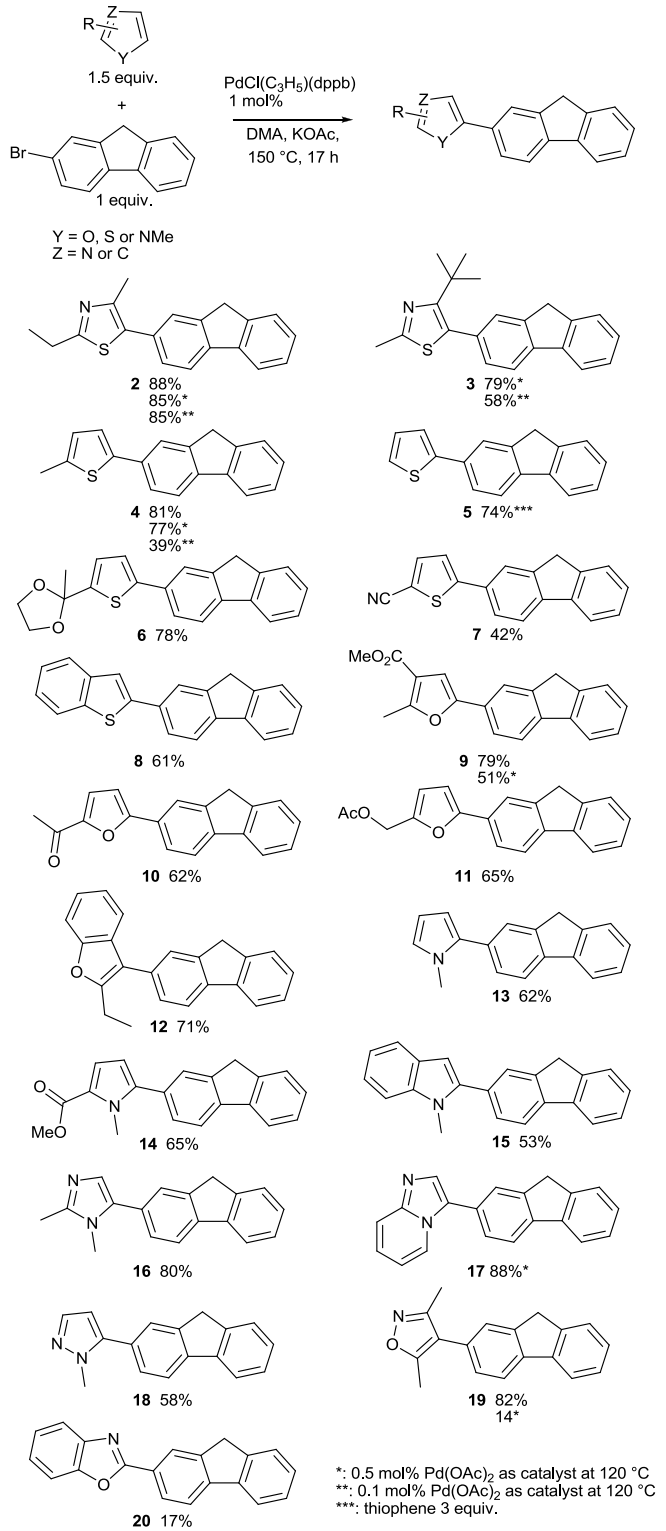
Scheme 2: Coupling of 2-*i*-butylthiazole with 2-bromofluorene

Table 1: Arylation of 2-*i*-butylthiazole with 2-bromofluorene, influence of the reaction conditions (Scheme 2)

Entry	Solvent	Base	Catalyst (mol%)	Temp. (°C)	Conv. (%)	Yield in **1** (%)
1	DMA	KOAc	$PdCl(C_3H_5)(dppb)$ (1)	150	91	80
2	DMA	KOAc	$PdCl_2$ (0.5)	150	87	77
3	DMA	KOAc	$Pd(OAc)_2$ (0.5)	150	86	80
4	DMA	KOAc	$Pd(OAc)_2$ (1) / PPh_3 (2)	150	69	
5	DMA	KOAc	$Pd(OAc)_2$ (1) / dppb (1)	150	71	
6	DMA	K_2CO_3	$PdCl(C_3H_5)(dppb)$ (1)	150	90	76
7	DMA	Cs_2CO_3	$PdCl(C_3H_5)(dppb)$ (1)	150	76	
8	DMA	NaOAc	$PdCl(C_3H_5)(dppb)$ (1)	150	71	
9	DMF	KOAc	$PdCl(C_3H_5)(dppb)$ (1)	150	85	78
10	NMP	KOAc	$PdCl(C_3H_5)(dppb)$ (1)	150	94	82
11	xylene	KOAc	$PdCl(C_3H_5)(dppb)$ (1)	150	62	
12	CPME	KOAc	$PdCl(C_3H_5)(dppb)$ (1)	120	61	
13	DMA	KOAc	$Pd(OAc)_2$ (0.5)	120	93	84
14	DMA	KOAc	$PdCl(C_3H_5)(dppb)$ (0.5)	120	100	93
15	DMA	KOAc	$Pd(OAc)_2$ (0.1)	120	100	94

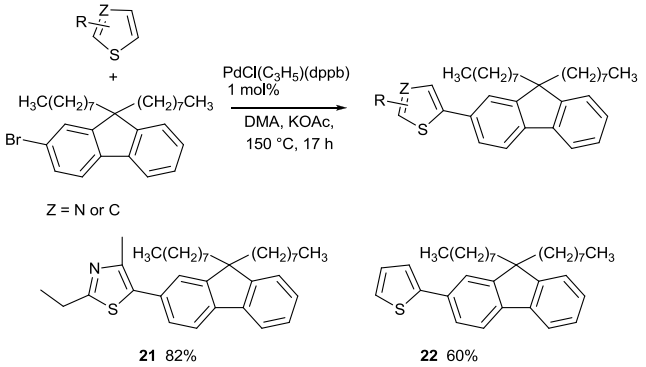
Conditions: [Pd], 2-bromofluorene (1 eq.), 2-*i*-butylthiaziole (1.5 eq.), base (2 eq.), 17 h, conversions of 2-bromofluorene determined by GC and NMR, isolated yields.

Then, we studied the scope of this reaction with various heteroaromatics using either 1 mol% $PdCl(C_3H_5)(dppb)$ or 0.1-0.5 mol% $Pd(OAc)_2$ as the catalysts, KOAc as the base in DMA at 150°C or at 120°C (Scheme 3). Coupling of 2-bromofluorene with 2-ethyl-4-methylthiazole or 2-methyl-4-*tert*-butylthiazole proceed nicely to afford **2** and **3** in 85% and 79% yields, respectively using 0.5 mol% $Pd(OAc)_2$ (Scheme 3, top). A high yield in **2** was also obtained with only 0.1 mol% $Pd(OAc)_2$; whereas, under these conditions, with more congested 2-methyl-4-*tert*-butylthiazole, a moderate yield in **3** was obtained due to a partial conversion of 2-bromofluorene. From 2-methylthiophene, **4** was also obtained in good yields using 1 mol% $PdCl(C_3H_5)(dppb)$ or 0.5 mol% $Pd(OAc)_2$ catalysts. Again, the use of only 0.1 mol% $Pd(OAc)_2$ was ineffective with this substrate. In the presence of a larger excess of thiophene (3 equiv.), **5** was obtained in 74% yield. A few thiophene derivatives bearing useful functional groups at C2 were also employed. From 2-methyl-2-thiophen-2-yl-[1,3]dioxolane, the target product **6** was isolated in 78% yield; whereas, from 2-acetylthiophene degradation products were observed. The reaction of thiophene-2-carbonitrile with 2-bromofluorene, using similar reaction conditions, gave **7** in lower yield. A regioselective arylation at carbon C2 of benzothiophene affords **8** in 61% yield. Then, four furan derivatives were employed. In all cases, the desired products **9**-**12** were obtained in relatively good yields. Even 2-acetylfuran reacts nicely without significant degradation of the acetyl function to give **9** in 62% yield. As expected, the reaction with benzofuran led to a mixture of mono- and di-arylation products, as both carbons C2 and C3 of benzofuran display quite similar reactivity for Pd-catalysed direct arylation.[3h] On the other hand, 2-ethylbenzofuran selectively affords the C3 arylation product **12** in 71% yield. Moderate yields of **13**-**15** (53-65%) were obtained from 1-methylpyrrole, methyl 1-methylpyrrole-2-carboxylate and 1-methylindole. It should be noted that with 1-methylindole the formation of a mixture of C2 and C3 arylated products was observed (ratio C2:C3 = 72:28). Both 1,2-dimethylimidazole and an imidazopyridine affords the expected products **16** and **17** in high yields. In all cases, with these thiophene, furan, pyrrole, imidazole and imidazopyridine derivatives (except benzofuran and 1-methylindole) a regioselective arylation was observed. On the other hand, from 1-methylpyrazole a lower yield in **18** was obtained due to some formation of the 4-arylated product. The formation of mixtures of 4- and 5-arylation products in the course of the arylation of pyrazoles is known.[7h] 3,5-Dimethylisoxazole reacts nicely to give the C4 arylated isoxazole **19** in 82% yield. On the other hand, the coupling of benzoxazole with 2-bromofluorene was found to afford **20** in only 17% yield due to the formation of several unidentified side-products.



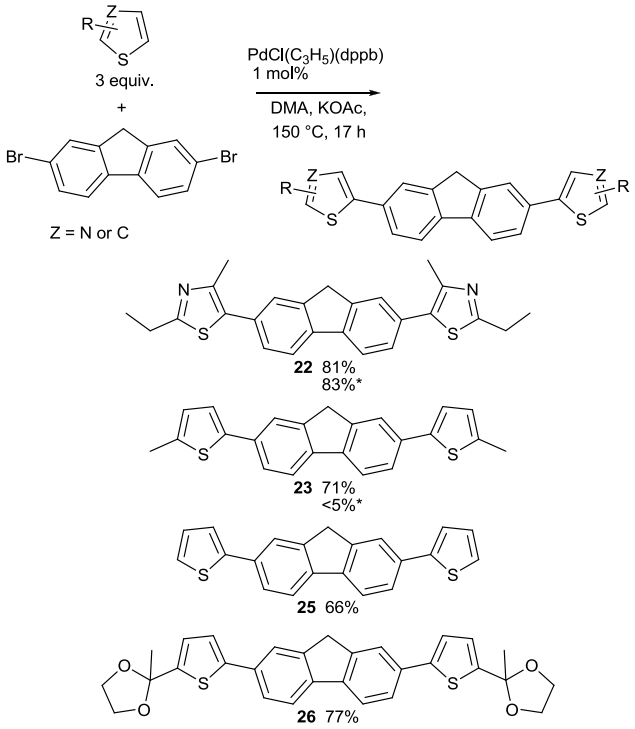
Scheme 3: Direct arylation of heteroaromatics with 2-bromofluorene.

The presence of alkyl chains at carbon 9 of 2-bromofluorene, which are often employed as fluorene substituents for the preparation of materials, only has a minor influence of the yields (Scheme 4). From 2-bromo-9,9-dioctylfluorene and 2-ethyl-4-methylthiazole or thiophene as the coupling partners, the expected products **21** and **22** were obtained in 82% and 60% yields, respectively.



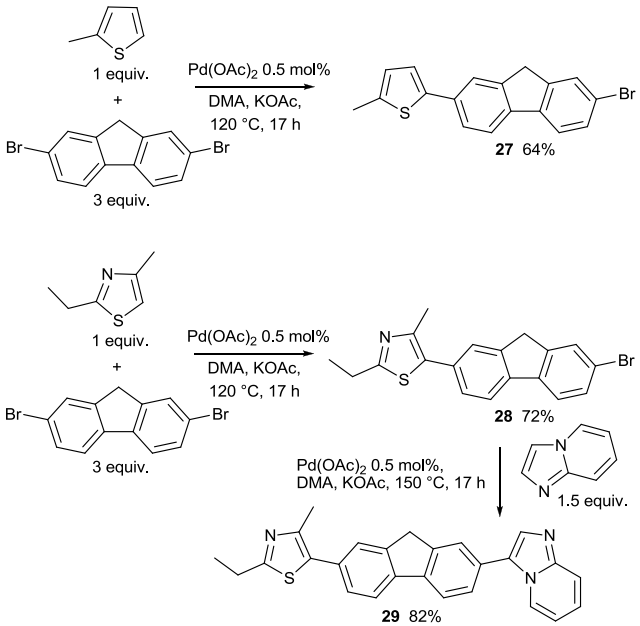
Scheme 4: Direct arylation of heteroaromatics with 2-bromofluorene derivatives.

Then, we examined the reactivity of 2,7-dibromofluorene for the preparation of 2,7-di(heteroaryl)fluorenes (Scheme 5). Using 3 equiv. of 2-ethyl-4-methylthiazole and 2-methylthiophene, in the presence of 1 mol% $PdCl(C_3H_5)(dppb)$, the desired products **23** and **24** were selectively obtained in 81% and 71% yields, respectively. Again, the use of only 0.5 mol% $Pd(OAc)_2$ catalyst at 120 °C was also very effective with 2-ethyl-4-methylthiazole as the coupling partner, as **23** was obtained in 83% yield. It should be noted that no significant amounts of the monoheteroarylated products were detected in the crude mixtures. The reaction of 6 equiv. of thiophene allows to prepare **25** in 66% yield. A high yield in **26** was also obtained from 2-methyl-2-thiophen-2-yl-[1,3]dioxolane.



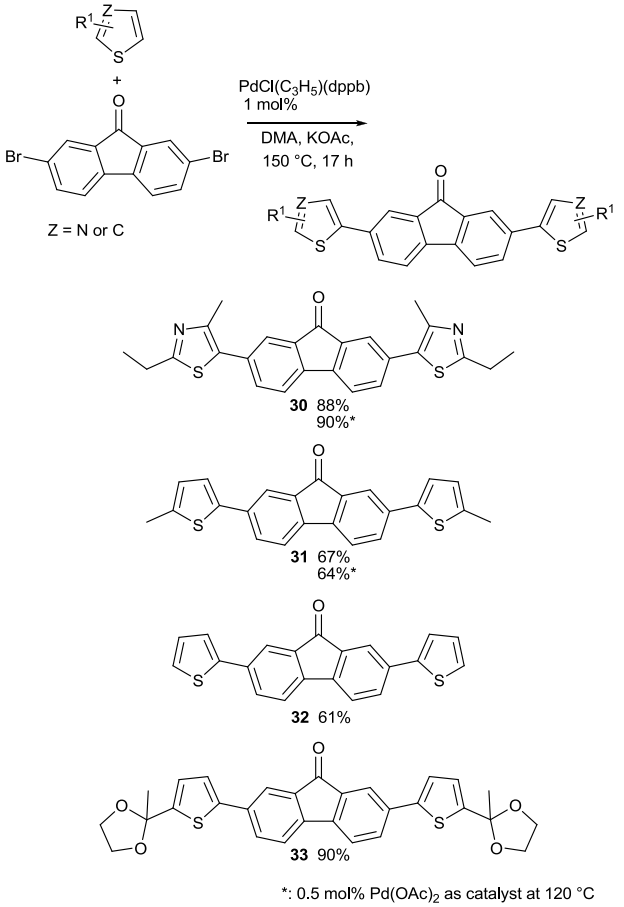
Scheme 5: Direct arylation of heteroaromatics with 2,7-dibromofluorene.

In order to have access to fluorenes derivatives bearing two different heteroarene units at carbons C2 and C7, we studied the influence of the ratio of 2,7-dibromofluorene and 2-methylthiophene or 2-ethyl-4-methylthiazole on the products formation (Scheme 6). From 1 equiv. of the thiophene or thiazole derivative and 3 equiv. of 2,7-dibromofluorene, the desired mono-heteroarylated fluorenes **27** and **28** were obtained in 64% and 72% yields, respectively. Then, the reaction of **28** with imidazo[1,2-a]pyridine, using again 0.5 mol% $Pd(OAc)_2$ catalyst, affords **29** in 82% yield.



Scheme 6: Direct arylation of heteroaromatics with 2,7-dibromofluorene.

Finally, the reactivity of 2,7-dibromofluorenone was examined using again 1 mol% $PdCl(C_3H_5)(dppb)$, or 0.5 mol% $Pd(OAc)_2$ catalysts (Scheme 7). The product **30** was obtained in 88-90% yields using 3 equiv. of 2-ethyl-4-methylthiazole as coupling partner. 2-Methylthiophene, thiophene and 2-methyl-2-thiophen-2-yl-[1,3]dioxolane also afforded the diheteroarylated fluorenones **31**-**33** in good yields.



Scheme 7: Direct arylation of heteroaromatics with 2,7-dibromofluorenone.

Conclusion

In summary, we demonstrated that 2-bromofluorene derivatives including a fluorenone can be employed as coupling partners for palladium-catalysed direct arylations with a very wide variety of heteroarenes. Bromofluorenes reacts nicely in the presence of 1 mol% $PdCl(C_3H_5)(dppb)$ or 0.1-0.5 mol% $Pd(OAc)_2$ catalysts and KOAc as the base. Moreover, sequential C-H bond activations allow to introduce two different heteroaryl units at carbons C2 and C7 of fluorenes. This procedure is economically and environmentally attractive as the major by-products of these couplings are AcOH / KBr instead of metallic salts with more classical coupling procedures such as Suzuki, Negishi or Stille reactions, and as it reduces the number of steps to prepare these compounds compared to other types of couplings (the method avoids the preliminary preparation of a requisite organometallic).

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Experimental section

DMA (99%), 2-bromofluorene (97%) and 2,7-dibromofluorene (99%) were purchased from Acros. $Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$, 1.4-bis(diphenylphosphino)butane (98%) and KOAc (99%), 2,7-dibromo-9-fluorenone (96%) were purchased from Alfa Aesar. These compounds were not purified before use.

Preparation of the $PdCl(C_3H_5)$(dppb) catalyst:[13] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane was added, then the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

General procedure for the synthesis of compounds 1-33
In a typical experiment, the bromofluorene derivative (1 mmol), heteroarene (1.5-6 mmol, see tables or schemes), KOAc (2-4 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) or $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) or were dissolved in DMA (4 mL) under an argon atmosphere. The reaction mixture was stirred at 120 or 150 °C for 17h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography.

5-(Fluoren-2-yl)-2-isobutylthiazole (1)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-isobutylthiazole (0.211 g, 1.5 mmol), **1** was obtained in 84% (0.256 g) yield as a white solid (mp: 142-147 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.45)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 3.91 (s, 2H), 2.90 (d, *J* = 7.5 Hz, 2H), 2.17 (m, 1H), 1.05 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 144.0, 143.3, 141.6, 141.0, 138.9, 137.3, 130.0, 126.9, 126.8, 125.4, 125.0, 123.1, 120.2, 119.9, 42.5, 36.8, 29.8, 22.3. Elemental analysis: calcd (%) for $C_{20}H_{19}NS$ (305.44): C 78.65, H 6.27; found: C 78.78, H 6.10.

2-Ethyl-5-(fluoren-2-yl)-4-methylthiazole (2)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **2** was obtained in 88% (0.256 g) yield as a white solid (mp: 86-91 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.40)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 3.83 (s, 2H), 2.93 (q, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.32 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 146.9, 143.9, 143.6, 141.5, 141.3, 131.7, 130.9, 128.2, 127.2, 127.1, 126.0, 125.3, 120.3, 120.2, 37.1, 27.1, 16.4, 14.6. Elemental analysis: calcd (%) for $C_{19}H_{17}NS$ (291.41): C 78.31, H 5.88; found: C 78.44, H 5.99.

4-*tert*-Butyl-5-(fluoren-2-yl)-2-methylthiazole (3)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-methyl-4-*tert*-butylthiazole (0.232 g, 1.5 mmol), **3** was obtained in 79% (0.252 g) yield as a yellow solid (mp: 180-185 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.75)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.40-7.25 (m, 3H), 3.93 (s, 2H), 2.67 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 158.6, 143.2, 142.4, 141.3, 140.9, 131.8, 129.9, 129.6, 127.5, 126.8, 126.6, 124.9, 119.8, 118.8, 36.6, 36.1, 31.3, 18.8. Elemental analysis: calcd (%) for $C_{21}H_{21}NS$ (319.46): C 78.95, H 6.63; found: C 79.14, H 6.55.

2-(Fluoren-2-yl)-5-methylthiophene (4)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), **4** was obtained in 81% (0.212 g) yield as a white solid (mp: 208-213 °C). (Column chromatography: pentane, Rf: 0.55)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.70 (m, 3H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 143.1, 142.2, 141.1, 140.5, 139.0, 133.1, 126.6, 126.4, 126.0, 124.8, 124.1, 122.5, 121.8, 119.9, 119.6, 36.7, 15.3. Elemental analysis: calcd (%) for $C_{18}H_{14}S$ (262.37): C 82.40, H 5.38; found: C 82.21, H 5.47.

2-(Fluoren-2-yl)-thiophene (5)[14]
From 2-bromofluorene (0.245 g, 1 mmol) and thiophene (0.252 g, 3 mmol), **5** was obtained in 74% (0.183 g) yield as a white solid (mp: 200-205 °C). (Column chromatography: pentane, Rf: 0.52)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.75 (m, 3H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.40-7.25 (m, 4H), 7.13-7.09 (m, 1H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 143.9, 143.3, 141.2, 141.1, 132.9, 128.0, 126.8, 126.7, 125.0, 124.8, 124.5, 122.8, 122.5, 120.2, 119.9, 36.9.

2-[5-(Fluoren-2-yl)-thiophen-2-yl]-2-methyl-[1,3]dioxolane (6)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-methyl-2-thiophen-2-yl-[1,3]dioxolane (0.255 g, 1.5 mmol), **6** was obtained in 78% (0.260 g) yield as a white solid (mp: 230-235 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.31)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.70 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 4.12-4.00 (m, 4H), 3.93 (s, 2H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 153.4, 144.1, 143.6, 142.8, 142.7, 140.9, 133.5, 131.7, 127.3, 127.0, 125.2, 125.1, 123.6, 122.8, 120.4, 120.2, 36.9, 26.6. Elemental analysis: calcd (%) for $C_{21}H_{18}O_2S$ (334.43): C 75.42, H 5.43; found: C 75.55, H 5.31.

5-(Fluoren-2-yl)thiophene-2-carbonitrile (7)
From 2-bromofluorene (0.245 g, 1 mmol) and thiophene-2-carbonitrile (0.164 g, 1.5 mmol), **7** was obtained in 42% (0.115 g) yield as a yellow solid (mp: 160-165 °C). (Column chromatography: Et_2O:pentane 1:9, Rf: 0.58)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.65-7.55 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 3.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 144.2, 143.5, 143.1, 140.7, 138.4, 130.6, 127.5, 127.0, 125.4, 125.2, 123.0, 122.9, 120.5, 120.3, 114.5, 107.7, 36.9. Elemental analysis:

calcd (%) for $C_{18}H_{11}NS$ (273.35): C 79.09, H 4.06; found: C 79.21, H 4.00.

2-(Fluoren-2-yl)benzo[b]thiophene (8)
From 2-bromofluorene (0.245 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol), **8** was obtained in 61% (0.182 g) yield as a yellow solid (mp: 212-217 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.53)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.86-7.72 (m, 5H), 7.60 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44-7.30 (m, 4H), 3.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 144.0, 143.5, 142.0, 141.1, 140.8, 139.4, 132.8, 127.0, 126.9, 125.4, 125.1, 124.5, 124.2, 123.4, 123.1, 122.2, 120.2, 120.0, 119.2, 36.9. Elemental analysis: calcd (%) for $C_{21}H_{14}S$ (298.40): C 84.53, H 4.73; found: C 84.37, H 4.49.

Methyl 5-(fluoren-2-yl)-2-methylfuran-3-carboxylate (9)
From 2-bromofluorene (0.245 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.210 g, 1.5 mmol), **9** was obtained in 79% (0.240 g) yield as a white solid (mp: 158-163 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.64)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.75 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 3.93 (s, 2H), 3.87 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 159.0, 152.2, 143.7, 143.4, 141.3, 141.2, 128.5, 126.8, 125.0, 122.6, 120.2, 120.1, 119.9, 115.2, 105.1, 51.4, 36.9, 13.9. Elemental analysis: calcd (%) for $C_{20}H_{16}O_3$ (304.34): C 78.93, H 5.30; found: C 79.19, H 5.12.

1-[5-(Fluoren-2-yl)-furan-2-yl]-ethanone (10)
From 2-bromofluorene (0.245 g, 1 mmol) and 1-furan-2-ylethanone (0.165 g, 1.5 mmol), **10** was obtained in 62% (0.170 g) yield as a white solid (mp: 114-119 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.62)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.84-7.77 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 3.5 Hz, 1H), 6.81 (d, *J* = 3.5 Hz, 1H), 3.95 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.2, 158.3, 151.7, 143.8, 143.7, 142.9, 140.9, 127.7, 127.3, 127.0, 125.1, 124.0, 121.5, 120.3, 120.2, 119.8, 107.2, 36.9, 25.9. Elemental analysis: calcd (%) for $C_{19}H_{14}O_2$ (274.31): C 83.19, H 5.14; found: C 83.34, H 5.19.

Acetic acid 5-(fluoren-2-yl)-furan-2-ylmethyl ester (11)
From 2-bromofluorene (0.245 g, 1 mmol) and acetic acid furan-2-ylmethyl ester (0.210 g, 1.5 mmol), **11** was obtained in 65% (0.197 g) yield as a yellow solid (mp: 100-105 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.39)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 5.05 (s, 2H), 3.86 (s, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 154.1, 147.7, 142.7, 142.4, 140.3, 140.2, 128.0, 125.8, 125.7, 124.0, 121.9, 119.5, 119.1, 118.9, 111.9, 104.6, 57.3, 35.9, 20.0. Elemental analysis: calcd (%) for $C_{20}H_{16}O_3$ (304.34): C 78.93, H 5.30; found: C 78.69, H 5.21.

2-Ethyl-3-(fluoren-2-yl)-benzofuran (12)
From 2-bromofluorene (0.245 g, 1 mmol) and 2-ethylbenzofuran (0.219 g, 1.5 mmol), **12** was obtained in 71% (0.220 g) yield as a yellow solid (mp: 110-115 °C). (Column chromatography: EtOAc:pentane 1:9, Rf: 0.35)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53-7.45 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.35-7.20 (m, 3H), 3.99 (s, 2H), 2.94 (q, *J* = 7.6 Hz, 2H), 1.39 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 154.0, 143.8, 143.3, 141.4, 140.7, 131.3, 129.0, 127.8, 126.8, 126.7, 125.6, 125.1, 123.5, 122.5, 120.1, 119.9, 119.5, 116.4, 110.8, 37.0, 20.4, 13.0. Elemental analysis: calcd (%) for $C_{23}H_{18}O$ (310.39): C 89.00, H 5.85; found: C 89.14, H 5.99.

2-(Fluoren-2-yl)-1-methylpyrrole (13)
From 2-bromofluorene (0.245 g, 1 mmol) and 1-methylpyrrole (0.242 g, 3 mmol), **13** was obtained in 62% (0.152 g) yield as a white solid (mp: 116-121 °C). (Column chromatography: pentane, Rf: 0.46)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.75 (m, 3H), 7.58 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.74 (m, 1H), 6.28 (m, 1H), 6.23 (m, 1H), 3.94 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 143.4, 141.5, 140.5, 135.1, 131.9, 127.5, 126.9, 126.8, 125.4, 125.2, 123.7, 120.0, 119.8, 108.8, 107.9, 37.1, 35.3. Elemental analysis: calcd (%) for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16; found: C 88.20, H 6.27.

Methyl 5-(fluoren-2-yl)-1-methylpyrrole-2-carboxylate (14)
From 2-bromofluorene (0.245 g, 1 mmol) and methyl 1-methylpyrrole-2-carboxylate (0.417 g, 3 mmol), **14** was obtained in 65% (0.197 g) yield as a yellow solid (mp: 110-115 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.62)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.25 7.05 (d, *J* = 4.0 Hz, 1H), 3.96 (s, 2H), 3.93 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 143.5, 143.4, 142.1, 141.6, 141.1, 130.4, 128.1, 127.1, 126.9, 125.9, 125.1, 123.4, 120.1, 119.8, 117.7, 109.2, 51.0, 36.9, 34.5. Elemental analysis: calcd (%) for $C_{20}H_{17}NO_2$ (303.35): C 79.19, H 5.65; found: C 79.30, H 5.41.

2-(Fluoren-2-yl)-1-methylindole (15)
From 2-bromofluorene (0.245 g, 1 mmol) and 1-methylindole (0.197 g, 1.5 mmol), **15** was obtained in 53% (0.156 g) yield as a yellow solid (mp: 250-255 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.45) The formation of C3-arylated indole was also observedby GC/MS analysis of the crude mixture. Ratio C2:C3 72:28
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.62 (s, 1H), 3.99 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 143.4, 142.0, 141.5, 141.2, 138.4, 131.2, 128.1, 128.0, 127.0, 126.9, 125.9, 125.1, 121.6, 120.4, 120.0, 119.8, 119.8, 109.6, 101.6, 37.0, 30.9. Elemental analysis: calcd (%) for $C_{22}H_{17}N$ (295.38): C 89.46, H 5.80; found: C 89.41, H 5.67.

5-(Fluoren-2-yl)-1,2-dimethylimidazole (16)
From 2-bromofluorene (0.245 g, 1 mmol) and 1,2-dimethylimidazole (0.144 g, 1.5 mmol), **16** was obtained in 80% (0.208 g) yield as a yellow solid (mp: 190-190 °C). (Column chromatography: MeOH:pentane 1:1, Rf: 0.60)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 3.94 (s, 2H), 3.56 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 143.9, 143.6, 141.5, 141.4, 134.2, 129.2, 127.6, 127.2, 127.1, 126.2, 125.5, 125.3, 120.2, 120.2, 37.2, 31.7, 14.1. Elemental analysis: calcd (%) for $C_{18}H_{16}N_2$ (260.33): C 83.04, H 6.19; found: C 82.87, H 6.28.

3-(Fluoren-2-yl)imidazo[1,2-a]pyridine (17)
From 2-bromofluorene (0.245 g, 1 mmol) and imidazo[1,2-a]pyridine (0.177 g, 1.5 mmol), **17** was obtained in 88% (0.248 g) yield as a yellow solid (mp: 140-145 °C). (Column chromatography: EtOAc:pentane 3:7, Rf: 0.41)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78-7.70 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60-7.55 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 3.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 144.2, 143.3, 141.8, 141.0, 132.6, 127.5, 127.1, 126.9, 126.7, 126.1, 125.1, 124.6, 124.1, 123.4, 120.5, 120.0, 118.3, 112.5, 36.9. Elemental analysis: calcd (%) for $C_{20}H_{14}N_2$ (282.34): C 85.08, H 5.00; found: C 85.18, H 5.12.

5-(Fluoren-2-yl)-1-methylpyrazole (18)
From 2-bromofluorene (0.245 g, 1 mmol) and 1-methylpyrazole (0.123 g, 1.5 mmol), **18** was obtained in 58% (0.143 g) yield as a yellow solid (mp: 84-89 °C). (Column chromatography: EtOAc:pentane 1:9, Rf: 0.43)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 143.4, 142.1, 140.9, 138.3, 128.8, 127.5, 127.2, 126.9, 125.4, 125.1, 120.2, 119.9, 106.1, 37.5, 36.9. Elemental analysis: calcd (%) for $C_{17}H_{14}N_2$ (246.31): C 82.90, H 5.73; found: C 82.98, H 5.59.

4-(Fluoren-2-yl)-3,5-dimethylisoxazole (19)
From 2-bromofluorene (0.245 g, 1 mmol) and 3,5-dimethyl-isoxazole (0.146 g, 1.5 mmol), **19** was obtained in 82% (0.214 g) yield as a yellow solid (mp: 156-161 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.48)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.20-7.17 (m, 1H), 3.87 (s, 2H), 2.36 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 159.1, 144.1, 143.5, 141.5, 141.4, 129.0, 128.1, 127.3, 127.2, 126.0, 125.4, 120.4, 120.3, 117.3, 37.1, 11.9, 11.2. Elemental analysis: calcd (%) for $C_{18}H_{15}NO$ (261.32): C 82.73, H 5.79; found: C 82.89, H 5.69.

2-(Fluoren-2-yl)-benzoxazole (20)
From 2-bromofluorene (0.245 g, 1 mmol) and benzoxazole (0.178 g, 1.5 mmol), **20** was obtained in 17% (0.048 g) yield as a yellow solid (mp: 160-165 °C). (Column chromatography: EtOAc:pentane 1:9, Rf: 0.46)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80-7.75 (m, 1H), 7.63-7.58 (m, 2H), 7.45-7.30 (m, 4H), 4.02 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 150.8, 145.1, 144.1, 143.7, 142.3, 140.7, 127.8, 127.1, 126.7, 125.3, 125.2, 124.9, 124.5, 124.2, 120.6, 120.2, 119.8, 110.5, 36.9. Elemental analysis: calcd (%) for $C_{20}H_{13}NO$ (283.32): C 84.78, H 4.62; found: C 84.50, H 4.60.

5-(9,9-Dioctylfluoren-2-yl)-2-ethyl-4-methylthiazole (21)
From 2-bromo-9,9-dioctylfluorene (0.470 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **21** was obtained in 82% (0.422 g) yield as a yellow oil. (Column chromatography: EtOAc:pentane 1:9, Rf: 0.67)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.01 (q, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 2.15-2.05 (m, 2H), 1.45-1.35 (m, 5H), 1.25-0.75 (m, 28H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 147.1, 146.9, 146.7, 140.0, 131.6, 131.3, 129.6, 128.7, 127.8, 124.4, 124.0, 119.9, 119.8, 87.7, 63.6, 40.2, 31.8, 31.7, 30.2, 29.8, 29.4, 29.3, 29.2, 29.1, 26.9, 26.1, 23.4, 22.6, 22.5, 16.3, 14.3, 14.1. Elemental analysis: calcd (%) for $C_{35}H_{49}NS$ (515.84): C 81.49, H 9.57; found: C 81.60, H 9.47.

2-(9,9-Dioctylfluoren-2-yl)-thiophene (22)
From 2-bromo-9,9-dioctylfluorene (0.470 g, 1 mmol) and thiophene (0.252 g, 3 mmol), **22** was obtained in 60% (0.283 g) yield as a yellow oil. (Column chromatography: EtOAc:pentane 1:9, Rf: 0.70)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.33-7.25 (m, 4H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 1.96 (t, *J* = 7.5 Hz, 4H), 1.20-0.95 (m, 20H), 0.77 (t, *J* = 7.5 Hz, 6H), 0.70-0.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 150.5, 144.9, 140.4, 140.3, 132.8, 127.7, 126.7, 126.4, 124.5, 124.1, 122.5, 122.4, 119.8, 119.7, 119.3, 54.8, 40.0, 31.4, 29.7, 28.8, 23.4, 22.2, 13.7. Elemental analysis: calcd (%) for $C_{33}H_{44}S$ (472.77): C 83.84, H 9.38; found: C 83.74, H 9.48.

2,7-Di(2-ethyl-4-methylthiazol-5-yl)-fluorene (23)
From 2,7-dibromofluorene (0.324 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.382 g, 3 mmol), **23** was obtained in 81% (0.337 g) yield as a white solid (mp: 164-169 °C). (Column chromatography: EtOAc:pentane 1:9, Rf: 0.35)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 2H), 3.02 (q, *J* = 7.5 Hz, 4H), 2.52 (s, 6H), 1.42 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 146.7, 143.8, 140.5, 131.2, 130.9, 128.0, 125.7, 120.0, 36.8, 26.8, 14.6, 14.2. Elemental analysis: calcd (%) for $C_{25}H_{24}N_2S_2$ (416.60): C 72.08, H 5.81; found: C 72.01, H 5.68.

2,7-Di(5-methylthiophen-2-yl)-fluorene (24)
From 2,7-dibromofluorene (0.324 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol), **24** was obtained in 71% (0.254 g) yield as a white solid (mp: 210-215 °C). (Column chromatography: pentane, Rf: 0.32)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 3.5 Hz,

2H), 6.75 (d, *J* = 3.5 Hz, 2H), 3.95 (s, 2H), 2.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 142.3, 140.3, 139.2, 133.1, 126.1, 124.3, 122.6, 121.9, 119.9, 36.7, 15.4. Elemental analysis: calcd (%) for $C_{23}H_{18}S_2$ (358.52): C 77.05, H 5.06; found: C 77.18, H 5.00.

2,7-Di(thiophen-2-yl)-fluorene (25)[15]
From 2,7-dibromofluorene (0.324 g, 1 mmol) and thiophene (0.504 g, 6 mmol), **25** was obtained in 66% (0.218 g) yield as a yellow solid (mp: 240-245 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.32)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 3.6 Hz, 2H), 7.29 (d, *J* = 5.1 Hz, 2H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 2H), 3.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 143.8, 140.4, 132.7, 127.7, 124.6, 124.3, 122.6, 122.2, 119.9, 36.6.

2,7-Di[5-(2-methyl-[1,3]dioxolan-2-yl)-thiophen-2-yl]-fluorene (26)
From 2,7-dibromofluorene (0.324 g, 1 mmol) and 2-methyl-2-thiophen-2-yl-[1,3]dioxolane (0.510 g, 3 mmol), **26** was obtained in 77% (0.386 g) yield as a white solid (mp: 240-245 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.40)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 3.5 Hz, 2H), 6.95 (d, *J* = 3.5 Hz, 2H), 4.05-3.90 (m, 8H), 3.88 (s, 2H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 144.3, 144.1, 140.7, 133.0, 125.1, 124.7, 122.5, 122.2, 120.2, 107.2, 65.0, 36.9, 27.5. Elemental analysis: calcd (%) for $C_{29}H_{26}O_4S_2$ (502.64): C 69.30, H 5.21; found: C 69.04, H 5.08.

2-(7-Bromofluoren-2-yl)-5-methylthiophene (27)
From 2,7-dibromofluorene (0.972 g, 3 mmol) and 2-methylthiophene (0.098 g, 3 mmol), **27** was obtained in 64% (0.218 g) yield as a yellow solid (mp: 178-183 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.65)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.45 (m, 6H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 3.91 (s, 2H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3, 143.6, 142.2, 140.4, 139.6, 139.5, 133.8, 130.0, 128.2, 126.3, 124.5, 122.9, 122.0, 121.0, 120.4, 120.2, 36.7, 15.5. Elemental analysis: calcd (%) for $C_{18}H_{13}BrS$ (341.26): C 63.35, H 3.84; found: C 63.47, H 3.99.

5-(7-Bromofluoren-2-yl)-2-ethyl-4-methylthiazole (28)
From 2,7-dibromofluorene (0.972 g, 3 mmol) and 2-ethyl-4-methylthiazole (0.128g, 1 mmol), **28** was obtained in 72% (0.266 g) yield as a white solid (mp: 72-76 °C). (Column chromatography: EtOAc:pentane 1:19, Rf: 0.50)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 2H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.50 (s, 3H), 1.41 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 146.1, 144.4, 142.4, 139.2, 130.4, 130.2, 129.2, 127.4, 127.2, 124.8, 120.3, 119.9, 119.1, 35.8, 26.1, 15.4, 13.5. Elemental analysis: calcd (%) for $C_{19}H_{16}BrNS$ (370.31): C 61.63, H 4.36; found: C 61.40, H 4.47.

2-Ethyl-5-(7-(imidazo[1,2-a]pyridin-3-yl)-fluoren-2-yl)-4-methylthiazole (29)
From 5-(7-bromofluoren-2-yl)-2-ethyl-4-methylthiazole **28** (0.370 g, 1 mmol) and imidazo[1,2-a]pyridine (0.177 g, 1.5 mmol), **29** was obtained in 82% (0.334 g) yield as a yellow solid (mp: 118-121 °C). (Column chromatography: EtOAc:pentane 1:4, Rf: 0.45)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78-7.70 (m, 3H), 7.63 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 4.04 (s, 2H), 3.02 (q, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H). Elemental analysis: calcd (%) for $C_{26}H_{21}N_3S$ (407.53): C 76.63, H 5.19; found: C 76.67, H 5.00.

2,7-Bis-(2-ethyl-4-methylthiazol-5-yl)-fluoren-9-one (30)
From 2,7-dibromofluoren-9-one (0.338 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.382 g, 3 mmol), **30** was obtained in 88% (0.378 g) yield as a yellow solid (mp: 176-181 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.52)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 3.01 (q, *J* = 7.5 Hz, 4H), 2.50 (s, 6H), 1.41 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 170.8, 147.8, 142.8, 135.2, 134.7, 133.7, 129.7, 124.8, 120.6, 26.9, 16.3, 14.2. Elemental analysis: calcd (%) for $C_{25}H_{22}N_2OS_2$ (430.58): C 69.73, H 5.15; found: C 69.80, H 5.24.

2,7-Bis-(5-methylthiophen-2-yl)-fluoren-9-one (31)
From 2,7-dibromofluoren-9-one (0.338 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol), **31** was obtained in 67% (0.249 g) yield as a yellow solid (mp: 146-151 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.73)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 3.4 Hz, 2H), 6.68 (d, *J* = 3.4 Hz, 2H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 142.7, 141.0, 140.7, 135.9, 135.4, 131.5, 126.8, 123.9, 121.4, 120.9, 15.8. Elemental analysis: calcd (%) for $C_{23}H_{16}OS_2$ (372.50): C 74.16, H 4.33; found: C 74.27, H 4.10.

2,7-Dithiophen-2-ylfluoren-9-one (32)[16]
From 2,7-dibromofluoren-9-one (0.338 g, 1 mmol) and thiophene (0.504 g, 6 mmol), **32** was obtained in 61% (0.210 g) yield as a red solid (mp: 252-257 °C). (Column chromatography: EtOAc:pentane 3:9, Rf: 0.38)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 3.5 Hz, 2H), 7.25 (d, *J* = 5.1 Hz, 2H), 7.04 (dd, *J* = 5.1, 3.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 143.1, 142.8, 135.4, 135.1, 131.8, 128.3, 125.5, 123.8, 121.7, 120.8.

2,7-Bis-[5-(2-methyl-[1,3]dioxolan-2-yl)-thiophen-2-yl]-fluoren-9-one (33)
From 2,7-dibromofluoren-9-one (0.338 g, 1 mmol) and 2-methyl-2-thiophen-2-yl-[1,3]dioxolane (0.510 g, 3 mmol), **33** was obtained in 90% (0.464 g) yield as a red solid (mp: 214-219 °C). (Column chromatography: EtOAc:pentane 3:17, Rf: 0.46)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 3.6 Hz, 2H), 7.03 (d, *J* = 3.6 Hz, 2H), 4.12-4.00 (m, 8H), 1.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 147.5, 142.8, 142.5, 135.3, 135.1, 131.5, 125.2, 123.4, 121.3, 120.8, 107.0, 65.0, 27.4. Elemental analysis: calcd (%) for $C_{29}H_{24}O_5S_2$ (516.63): C 67.42, H 4.68; found: C 67.30, H 4.74.

Notes and references

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1 (a) Peng, Z.; Tao, S.; Zhang, X.; Tang, J.; Lee, C. S.; Lee, S. T. *J. Phys. Chem. C* **2008**, *112*, 2165; (b) Jiang, Z.; Liu, Z.; Yang, C.; Zhong, C.; Qin, J.; Yu, G.; Liu, Y. *Adv. Funct. Mater.* **2009**, *19*, 3987; (c) Zhu, M.; Ye, T.; Li, C. G.; Cao, X.; Zhong, C.; Ma, D.; Qin, J.; Yang, C. *J. Phys. Chem. C* **2011**, *115*, 17965; (d) Kumar, D.; Thomas, K. R. J.; Lee, C.-P.; Ho K.-C. *J. Org. Chem.* **2014**, *79*, 3159.

2 (a) Akita, Y.; Inoue, A.; Yamamoto, K.; Ohta, A.; Kurihara, T.; Shimizu, M. *Heterocycles* **1985**, *23*, 2327; (b) Ohta, A.; Akita, Y.; Ohkuwa, T.; Chiba, M.; Fukunaga, R.; Miyafuji, A.; Nakata, T.; Tani, N.; Aoyagi, Y. *Heterocycles* **1990**, *31*, 1951; (c) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174; (d) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200; (e) Campeau, L.-C.; Stuart, D. R.; Fagnou, K. *Aldrichimica Acta* **2007**, *40*, 35; (f) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173; (g) Li, B.-J.; Yang, S.-D.; Shi, Z.-J. *Synlett* **2008**, 949; (h) Ackermann, L.; Vicente, R.; Kapdi, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; (i) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269; (j) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447; (k) Roger, J.; Gottumukkala, A. L.; Doucet, H. *ChemCatChem* **2010**, *2*, 20; (l) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677; (m) Fischmeister, C.; Doucet, H. *Green Chem.* **2011**, *13*, 741; (n) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236; (o) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960; (p) Wencel-Delord, J.; Glorius, F. *Nature Chem.* **2013**, *5*, 369; (q) Kuzhushkov, S. I.; Potukuchi, H. K.; Ackermann, L. *Catal. Sci. Technol.* **2013**, *3*, 562; (r) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17.

3 For selected examples of palladium-catalysed direct arylations of furans: (a) Parisien, M.; Valette, D.; Fagnou, K. *J. Org. Chem.* **2005**, *70*, 7578; (b) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.*, **2006**, *128*, 581; (c) Dong, J. J.; Roger, J.; Pozgan, F.; H. Doucet, *Green Chem.* **2009**, *11*, 1832; (d) Ionita, M.; Roger, J.; Doucet, H. *ChemSusChem* **2010**, *3*, 367; (e) Roger, J.; Pozgan, F.; Doucet, H. *Adv. Synth. Catal.* **2010**, *352*, 696; (f) Liegault, B.; Petrov, I.; Gorelsky, S. I.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 1047; (g) Lapointe, D.; Markiewicz, T.; Whipp, C. J.; Toderian, A.; Fagnou, K. *J. Org. Chem.* **2011**, *76*, 749; (h) Loukotova, L.; Yuan, K. Doucet, H. *ChemCatChem* **2014**, *6*, 1303.

4 For selected examples of palladium-catalysed direct arylations of thiophenes: (a) Okazawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 5286; (b) Hassan, J.; Gozzi, C.; Schulz, E.; Lemaire, M. *J. Organomet. Chem.* **2003**, *687*, 280; (c) Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, *126*, 5074; (d) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851; (e) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826; (f) Beydoun, K.; Doucet, H. *ChemSusChem* **2011**, *4*, 526; (g) Schipper, D. J.; Fagnou, K. *Chem. Mater.* **2011**, *23*, 1594.

5 For selected examples of palladium-catalysed direct arylations of thiazoles: (a) Yokooji, A.; Okazawa, T.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2003**, *59*, 5685; (b) Kobayashi, K.; Mohamed, A.; Mohamed, S.; Mori, A. *Tetrahedron* **2006**, *62*, 9548; (c) Campeau, L.-C.; Bertrand-Laperle, M.; Leclerc, J.-P.; Villemure, E.; Gorelsky, S.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 3276.

6 For selected examples of palladium-catalysed direct arylations of oxazoles or isoxazoles: (a) Hoarau, C.; Du Fou de Kerdaniel, A.; Bracq, N.; Grandclaudon, P.; Couture, A.; Marsais, F. *Tetrahedron Lett.* **2005**, *46*, 8573; (b) Turner, G. L.; Morris, J. A.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 7996; (c) Dong, J. J.; Roger, J.; Verrier, C.; Martin, T.; Le Goff, R.; Hoarau, C.; Doucet, H. *Green Chem.* **2010**, *12*, 2053.

7 For selected examples of palladium-catalysed direct arylations of pyrroles or pyrazoles: (a) Olsen, C. A.; Parera, N.; Albericio, F.; Alvarez, M. *Tetrahedron Lett.* **2005**, *46*, 2041; (b) Pla, D.; Marchal, A.; Olsen, C. O.; Albericio, F.; Alvarez, M. *J. Org. Chem.* **2005**, *70*, 8231; (c) Arai, N.; Takahashi, M.; Mitani, M.; Mori, A. *Synlett* **2006**, 3170; (d) Joucla, L.; Popowycz, F.; Lozach, O.; Meijer, L.; Joseph, B. *Helv. Chim. Acta* **2007**, *90*, 753; (e) Fall, Y.; Doucet, H.; Santelli, M. *ChemSusChem* **2009**, *2*, 153; (f) Nadres, E. T.; Lazareva, A.; Daugulis, O. *J. Org.Chem.* **2011**, *76*, 471; (g) Bellina, F.; Lessi, M.; Manzini C. *Eur. J. Org. Chem.* **2013**, 5621; (h) Beladhria, A.; Beydoun, K.; Ben Ammar, H.; Ben Salem, R.; Doucet H. *Synthesis* **2011**, 2553.

8 For examples of palladium-catalysed direct arylations using halofluorenes and heteroarenes: (a) Amaladass, P.; Clement, J. A.; Mohanakrishnan, A. K. *Tetrahedron* **2007**, *63*, 10363; (b) Kowada, T.; Ohe, K. *Bull. Korean Chem. Soc.* **2010**, *31*, 577; (c) Chen, L.; Roger, J.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Chem. Commun.* **2011**, *47*, 1872; (d) Baloch, M.; Roy, R. J.; Roy, D.; Beydoun, K.; Doucet, H. *RSC Advances* **2011**, 1, 1527; (e) Yamaguchi, E.; Shibahara, F.; Murai, T. *Chem. Lett.* **2011**, *40*, 939; (f) Das, S. K.; Lim, C. S.; Yang, S. Y.; Han, J. H.; Cho, B. R. *Chem. Commun.* **2012**, *48*, 8395; (g) Vamvounis, G.; Gendron, D. *Tetrahedron Lett.* **2013**, *54*, 3785; (h) Koszarna, B.; Matczak, R.; Krzeszewski, M.; Vakuliuk, O.; Klajn, J.; Tasior, M.; Nowicki, J. T.; Gryko, D. T. *Tetrahedron* **2014**, *70*, 225.

9 For selected recent examples of palladium-catalysed direct arylations using halofluorenes and thiophene derivatives for access to polymers: (a) Fujinami, Y.; Kuwabara, J.; Lu, W.; Hayashi, H.; Kanbara, T. *ACS Macro Lett.* **2012**, *1*, 67; (b) Yamazaki, K.; Kuwabara, J.; Kanbara, T. *Macromol. Rapid Commun.* **2013**, *34*, 69; (c) Guo, Q.; Dong, J.; Wan, D.; Wu, D.; You, J. *Macromol. Rapid Commun.* **2013**, *34*, 522.

10 For examples of palladium-catalysed direct arylations using halofluorenes and polyfluorobenzenes: Wakioka, M.; Kitano, Y.; Ozawa, F. *Macromolecules* **2013**, *46*, 370.

11 For synthesis of heteroarylated fluorenes via Suzuki, Stille or Negishi couplings: (a) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924; (b) Thomas, K. R. J.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Chem. Commun.* **2005**, 4098; (c) Zeng, L.; Blanton, T. N.; Chen, S. H. *Langmuir* **2010**, *26*, 12877; (d) Porzio, W.; Destri, S.; Pasini, M.; Giovanella, U.; Ragazzi, M.; Scavia, G.; Kotowski, D.; Zotti, G.; Vercelli, B. *New J. Chem.* **2010**, *34*, 1961; (e) Cheng, Y.-J.; Hung, L.-C.; Cao, F.-Y.; Kao, W.-S.; Chang, C.-Y.; Hsu, C.-S. *J. Polym. Sci.*,

Part A: Polym. Chem. **2011**, *49*, 1791; (f) Nie, G.; Yang, H.; Chen, J.; Bai, Z. *Org. Electron.* **2012**, *13*, 2167; (g) Macor, L.; Gervaldo, M.; Fungo, F.; Otero, L.; Dittrich, T.; Lin, C.-Y.; Chi, L.-C.; Fang, F.-C.; Lii, S.-W.; Wong, K.-T., Tsai, C.-H., Wu, C. C. *RSC Advances* **2012**, *2*, 4869.

12 (a) de Vries, A. H. M.; Mulders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285; (b) Fu, H. Y.; Chen, L.; Doucet, H. *J. Org. Chem.* **2012**, *77*, 4473.

13 Cantat, T.; Génin, E.; Giroud, C.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *687*, 365.

14 Poolmee, P.; Ehara, M.; Hannongbua, S.; Nakatsuji, H. *Polymer* **2005**, *46*, 6474.

15 Tirapattur, S.; Belletete, M.; Drolet, N.; Bouchard, J.; Ranger, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem. B* **2002**, *106*, 8959.

16 Pasini, M.; Giovanella, U.; Betti, P.; Bolognesi, A.; Botta, C.; Destri, S.; Porzio, W.; Vercelli, B.; Zotti, G. *ChemPhysChem* **2009**, *10*, 2143.

The palladium-catalysed direct arylation using 2-bromofluorene of 2,7-dibromofluorene and heteroaromatics as the coupling partners proceed using only 0.1-0.5 mol% catalysts.

ABSTRACT