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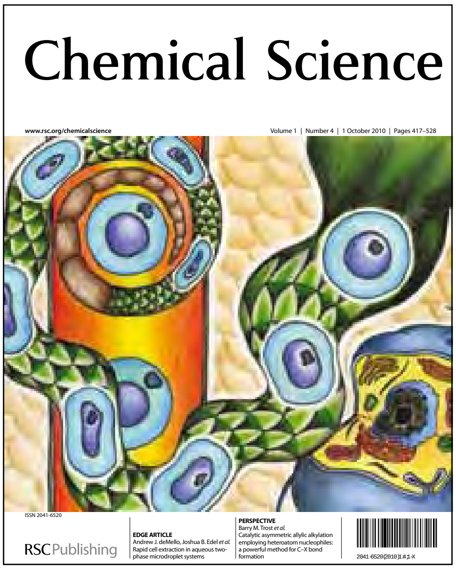

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ARTICLE

Benzenesulfonyl chlorides: New reagents for access to alternative regioisomers in palladium-catalysed direct arylations of thiophenes

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The palladium-catalysed coupling of benzenesulfonyl chlorides with thiophene derivatives allows the regioselective access to *β*-arylated thiophenes. The reaction proceeds with easily accessible catalyst, base and substrates, without oxidant or ligand and tolerates a variety of substituents both on the benzene and thiophene moieties.

Introduction

In recent years, the metal-catalysed functionalization of C-H bonds has emerged as a powerful method for the simpler access to molecules useful to materials or biological applications. If specific C–H bonds of (hetero)arenes can be easily coupled with arenes, it becomes one of the most simple way for access to bi(hetero)arenes.[1] From thiophene derivatives and aryl halides as the coupling partners, the *α*-arylated products were easily obtained using palladium catalysts under various conditions (Fig. 1, left).[1g,2] On the other hand, until recently, relatively little effort has been expended toward developing such metal-catalysed direct arylation reactions for the synthesis of *β*-arylated thiophenes (Fig. 1, right).[3]

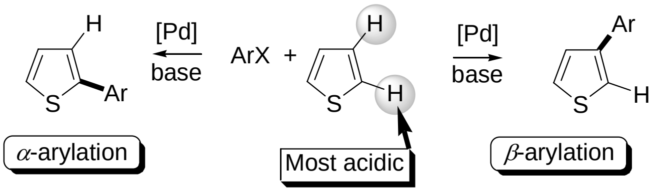

Figure 1.

A few examples of such *β*-arylations[3] have been reported using new catalysts, reactants and/or reaction conditions.[4-9] Some of them employ a directing group on the thiophene derivative such as a 2-pyridyl or a carboxanilide functions to control the regioselectivity of the arylation.[4,5] In 2009, Itami and co-workers have established a catalytic system that promotes the *β*-selective arylation of thiophene derivatives with aryl iodides without directing group on the thiophenes. These *β*-functionalisation were obtained using $PdCl_2$ associated to a phosphite ligand using Ag_2CO_3 as the base (Scheme 1, top).[6] Glorius and co-workers have very recently reported an heterogeneously catalyzed C−H arylation of benzo[*b*]thiophenes.[7] They demonstrated that, using Pd/C catalyst without additional ligands or directing groups on benzothiophene, but in the presence of 10 mol-% $CuCl_2$, the less reactive *β*-position of benzothiophenes was arylated with an excellent selectivity. Studer and Itami have also developed a method for the *β*-arylations of thiophenes with arylboronic acids under Pd/TEMPO catalysis (Scheme 1, middle).[8] The same year, Bach et al. reported that thiophenes substituted at C3 by CH_2COOEt or $CH_2PO(OEt)_2$ undergo a regioselective oxidative coupling reaction at C4 with various arylboronic acids in the presence of silver oxide, cesiumtrifluoroacetate [Cs(tfa)], benzoquinone (BQ), and $Pd(tfa)_2$ catalyst in trifluoroacetic acid.[9] In 2012, Oi et al. described the direct arylation of (benzo)thiophenes with aryltrimethylsilanes. The use of $PdCl_2(MeCN)_2$ catalyst in the presence of $CuCl_2$ as oxidant also gives the *β*-arylated thiophenes (Scheme 1, middle).[10]

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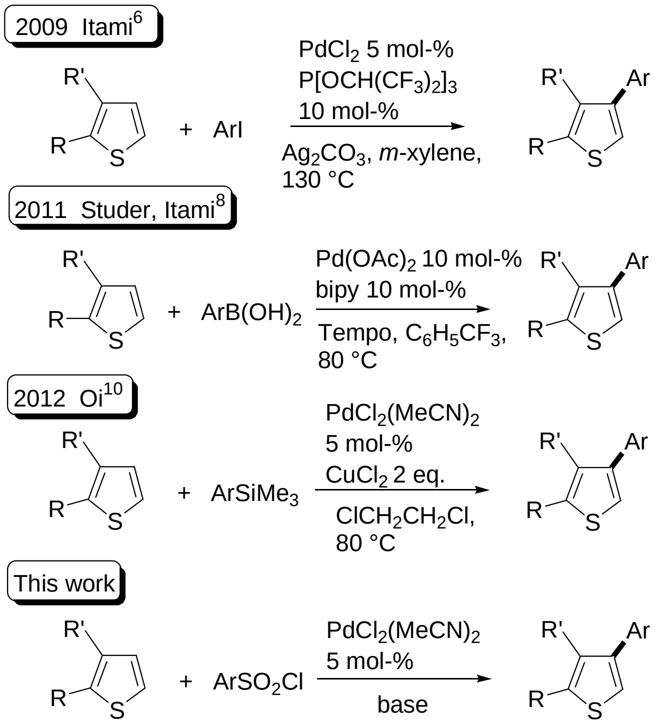

Scheme 1. Procedures for Pd-catalysed *β*-arylations of thiophene derivatives without directing group.

In 2009, Dong and co-workers reported the Pd-catalysed coupling of 2-phenylpyridine with benzenesulfonyl chlorides to prepare sulfones.[11] However, in the course of this study they also observed in one case, a desulfitative[12] direct arylation of a quinoline derivative when using elevated temperature in the presence of Ag_2CO_3 and CuBr. The use of benzenesulfonyl chlorides[13-15] as the coupling partners for the palladium-catalysed desulfitative direct arylation of benzoxazoles derivatives has been recently described by Cheng et al.[16] Using 10 mol-% $Pd(OAc)_2$ catalyst, K_2CO_3 as base and 1 equiv. of CuI as additive, the 2-arylbenzoxazoles were obtained in high yields. On the other hand, to our knowledge, the desulfitative direct arylation of thiophenes with benzenesulfonyl chlorides has not been reported.

Results and discussion

Herein, we describe a novel access to *β*-arylated thiophene derivatives using desulfitative palladium-catalysed C-H functionalisation, from thiophenes and benzenesulfonyl chlorides as the coupling partners (Scheme 1, bottom). The influence of both the benzenesulfonyl chlorides and thiophenes substituents is reported.

We first examined the influence of several reaction conditions on the products formation (Table 1). The reaction of 4-methylbenzenesulfonyl chloride with 2-methylthiophene using $Pd(OAc)_2$ catalyst and K_2CO_3 as the base only gave decomposed benzenesulfonyl chloride (Table 1, entry 1). The use of $PdCl(C_3H_5)(dppb)$ or $PdCl_2$ catalysts led to the desired product **1b** as trace (Table 1, entries 2 and 3). On the other hand, $Pd(PhCN)_2Cl_2$ catalyst in the presence of a mixture of K_2CO_3/LiCl gave product **1b** in 30% yield (Table 1, entry 4). The addition of 1 equiv. of CuI to the reaction mixture or the use of DMSO or toluene as the solvents resulted in very low yields of **1b**. The reaction temperature was found to be a crucial factor for such couplings, as the use of 140°C instead of 120°C allowed to increase the yield in **1b** to 75% (Table 1, entry 8). Moreover, an excellent regioselectivity was observed, as **1b** was produced in 99%. The desired product **1b** was obtained in 43% yield using Li_2CO_3 without additive in the presence of $Pd(PhCN)_2Cl_2$ catalyst; whereas similar conditions using $Pd(MeCN)_2Cl_2$ catalyst gave **1b** in 80% yield (Table 2, entries 9 and 10). Then, we examined the influence of several bases at 140°C using $Pd(MeCN)_2Cl_2$ catalyst. Lower yield in **1b** were obtained using three equiv. of K_3PO_4, KOAc, Na_2CO_3 or K_2CO_3 (Table 1, entries 11-14). A complete decomposition of 4-methylbenzenesulfonyl chloride, without formation of **1b**, was observed in the presence of Cs_2CO_3 (Table 1, entry 15). This difference between carbonated bases might be due to the higher solubility of Cs_2CO_3 than Li_2CO_3, Na_2CO_3 or K_2CO_3 in dioxane. A longer reaction time allowed to increase the yield in **1b** to 84% with complete conversion of 4-methylbenzenesulfonyl chloride (Table 1, entry 17). Finally, the influence of a few other solvents was examined. NMP, DMF and DMSO only gave decomposed benzenesulfonyl chloride (Table 1, entries 18-20); whereas, ethylbenzene and xylene gave **1b** in very low yields (Table 1, entries 21 and 22).

Then, the scope of the substituents on the benzenesulfonyl chloride moiety for reaction with 2-methylthiophene was examined using 5 mol% $Pd(MeCN)_2Cl_2$ catalyst in the presence of Li_2CO_3 (Scheme 2). We initially employed electron-deficient benzenesulfonyl chlorides. Nitro- and cyano-substituents at C4 of benzenesulfonyl chlorides gave regioselectively (>98%) the 4-arylated 2-methylthiophenes **2** and **3** in 78% and 71% yields, respectively. It should be noted that from 4-trifluoromethylbenzenesulfonyl chloride the β-arylation product **3** was only obtained in 92% regioselectivity.

Good yields and high regioselectivities (98%) were also obtained for the coupling of 4-chloro and 4-bromo-benzenesulfonyl chlorides with 2-methylthiophene, as the desired products **5** and **6** were isolated in 67% and 81% yields, respectively. It should be noted that for these two reactions, no cleavage of the C-Cl and C-Br bonds was observed allowing further transformations. A good yield of 88% in **7** was also obtained from the slightly electron-deficient 4-fluorobenzenesulfonyl chloride. On the other hand, poor yields in **9** and **10** were produced from congested naphthalene-1-sulfonyl chloride and from electron-rich 4-methoxybenzenesulfonyl chloride.

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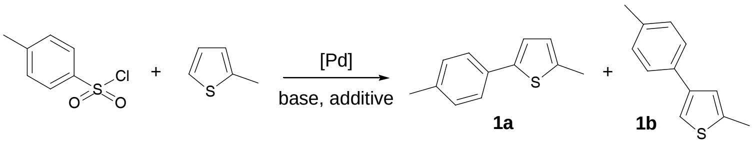
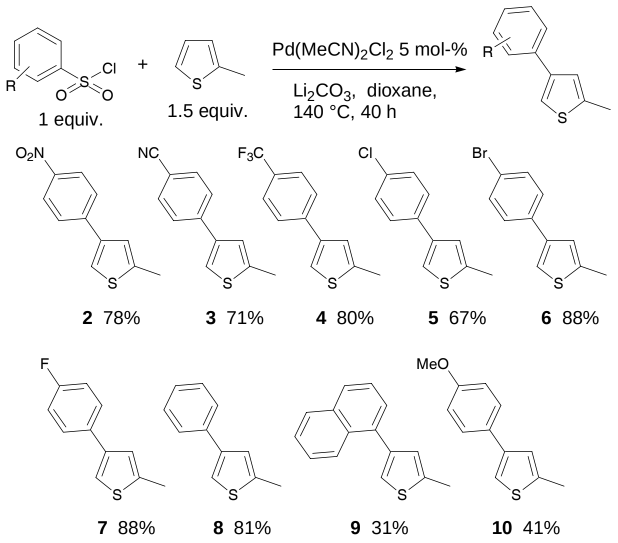
Table 1. Influence of the reaction conditions for the palladium-catalysed desulfitative coupling of 4-methylbenzenesulfonyl chloride with 2-methylthiophene.



Entry	Catalyst	Base (equiv.)	Additive (equiv.)	solvent	Temp. (°C)	Yield in **1b** (%)
1	$Pd(OAc)_2$	K_2CO_3 (2)	-	dioxane	120	0
2	$PdCl(C_3H_5)$(dppb)	K_2CO_3 (2)	-	dioxane	120	<5
3	$PdCl_2$	K_2CO_3 (2)	LiCl (4)	dioxane	120	<5
4	$Pd(PhCN)_2Cl_2$	K_2CO_3 (2)	LiCl (4)	dioxane	120	30 (25)
5	$Pd(MeCN)_2Cl_2$	K_2CO_3 (2)	LiCl (1) / CuI (1)	dioxane	120	<5
6	$Pd(PhCN)_2Cl_2$	K_2CO_3 (2)	LiCl (1)	DMSO	120	0
7	$Pd(PhCN)_2Cl_2$	K_2CO_3 (2)	LiCl (1)	toluene	120	<5
8	$Pd(PhCN)_2Cl_2$	K_2CO_3 (3)	LiCl (2)	dioxane	140	75 (71)
9	$Pd(PhCN)_2Cl_2$	Li_2CO_3 (2)	-	dioxane	140	43 (40)
10	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)	-	dioxane	140	80 (62)
11	$Pd(MeCN)_2Cl_2$	K_3PO_4 (3)	-	dioxane	140	48
12	$Pd(MeCN)_2Cl_2$	KOAc (3)	-	dioxane	140	56
13	$Pd(MeCN)_2Cl_2$	Na_2CO_3 (3)	-	dioxane	140	41
14	$Pd(MeCN)_2Cl_2$	K_2CO_3 (3)	-	dioxane	140	31
15	$Pd(MeCN)_2Cl_2$	Cs_2CO_3 (3)	-	dioxane	140	0
16	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (6)	-	dioxane	140	62 (60)[a]
17	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)	-	dioxane	140	84 (75)[a]
18	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)		NMP	140	0
19	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)		DMF	140	0
20	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)		DMSO	140	0
21	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)		Ethylbenzene	140	< 5%
22	$Pd(MeCN)_2Cl_2$	Li_2CO_3 (3)	-	*p*-xylene	140	< 5%

Conditions: [Pd] 5 mol-%, 4-methylbenzenesulfonyl chloride (1 equiv.), 2-methylthiophene (1.5 equiv.), yield determined by GC and crude ^{1}H NMR, 20 h, yields in parenthesis are isolated **1b**. [a] 40 h.



Scheme 2. Structural variation of the benzenesulfonyl chloride partner.

The influence of the substituents at C2 on the thiophene moiety was also evaluated (Scheme 3). Three benzenesulfonyl chlorides were coupled with 2-*n*-butylthiophene. Again, satisfactory yields in **11** and **12** were obtained in the presence of 4-chloro or 4-methyl substituents on the benzene ring; whereas, a 4-methoxy substituent led to a poor yield of **13**. The arylation of unsubstituted thiophene was also found to proceed at *β*-position. However, moderate yields in **14** and **15** were obtained due to some formation of 3,4-diarylated thiophenes. Both chloro- or bromo-substituent at C2 of thiophene were also tolerated, and the 4-arylated 2-halothiophenes **16**-**22** were obtained in moderate to high yields. Even the use of protected 2-acetylthiophene led to the desired products **23** and **24** with high regioselectivity and moderate to good yields. The reaction of 4-trifluoromethyl- or 4-bromo-benzenesulfonyl chlorides with [2,2']bithiophenyl also afforded the desired *β*-arylated compounds **25** and **26** in 78% and 60% yields, respectively.

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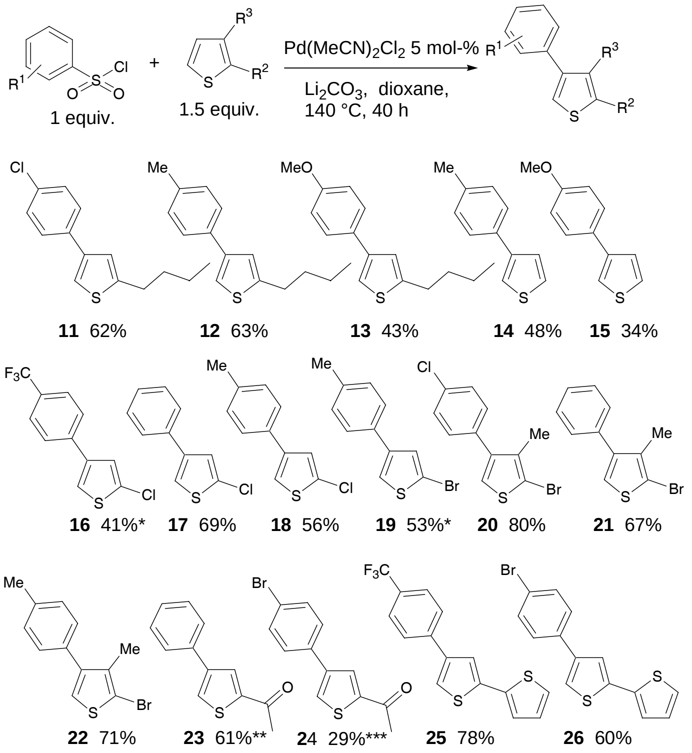
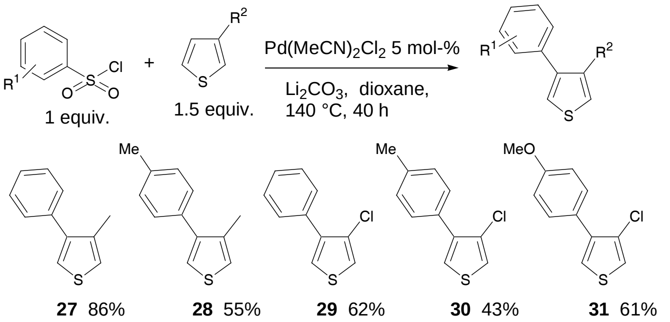


* From 2-halothiophene (1 equiv) and ArSO$_2$Cl (2 equiv.)
** From 2-methyl-2-thiophen-2-yl-[1,3]dioxolane (1 equiv.) and PhSO$_2$Cl (2 equiv.)
*** From 2-methyl-2-thiophen-2-yl-[1,3]dioxolane

Scheme 3. Variation of C2-substituents on the thiophene partner.

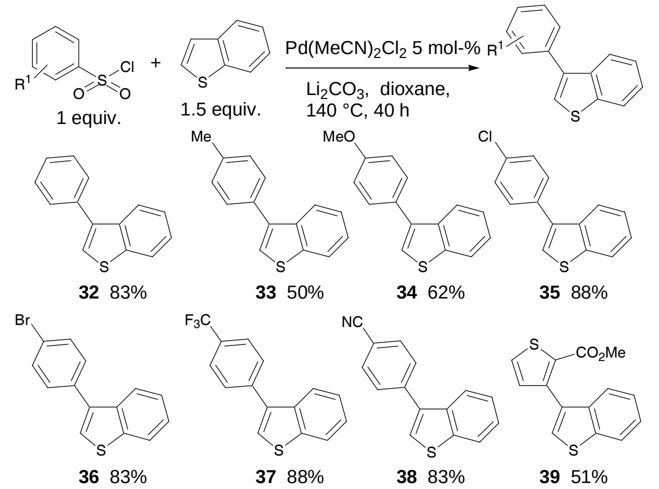
The 4-arylation of 3-substituted thiophenes was also found to proceed under these reaction conditions (Scheme 4). We first examined the reactivity of 3-methylthiophene in the presence of two benzenesulfonyl chlorides. A high yield of 86% in **27** was obtained using benzenesulfonyl chloride; whereas from 4-methylbenzenesulfonyl chloride, **28** was isolated in only 55% yield. The coupling of benzenesulfonyl chlorides with 3-chlorothiophene also produced the desired 4-arylated 3-chlorothiophenes **29**-**31**. It should be noted that no cleavage of the C-Cl thiophene bond was observed.



Scheme 4. Variation of C3-substituents on the thiophene partner.

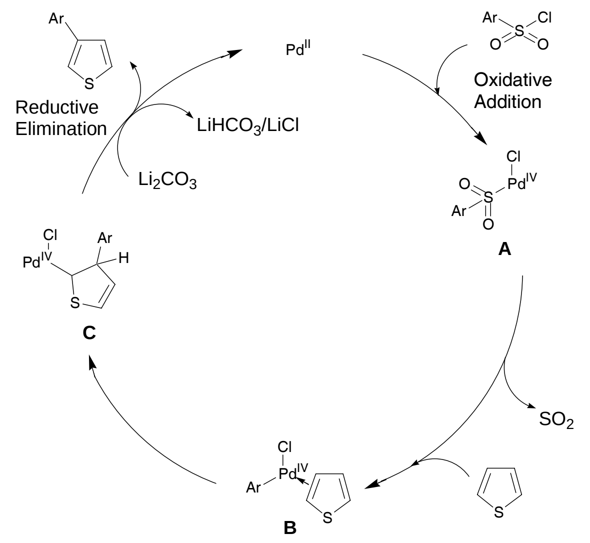
Finally, we examined the regioselectivity of the arylation of benzothiophene (Scheme 5). Glorius et al. have recently reported that benzothiophenes can be arylated at β-position with aryl chlorides using an heterogeneous palladium catalyst associated to copper.[7]

Using our reaction conditions, in all cases the β-aryl-benzothiophenes were regioselectively produced. Again the best yields were obtained in the presence of electron-deficient benzenesulfonyl chlorides. For example, the use of 4-chloro- of 4-trifluoromethyl-benzenesulfonyl chlorides led to **35** and **37** in 88% yields, respectively. Again, from 4-trifluoromethylbenzenesulfonyl chloride the α-arylation product was also detected in 8% selectivity by GC/MS analysis. Benzenesulfonyl chloride also reacts nicely with benzothiophene to give **32** in 83% yield. It is worth noting that 4-bromobenzenesulfonyl chloride allows the formation of **36** in 83% yield. A reaction of benzothiophene with methyl 3-chlorosulfonylthiophene-2-carboxylate gave **39** in 51% yield, due to an α:β arylation ratio of 11:89; but without formation of bithiophene from self-coupling. This lower regioselectivity might come from the steric hindrance of this chlorosulfonyl derivative.



Scheme 5. β-Arylations of benzo[b]thiophene.

Although the mechanism cannot yet be elucidated, a catalytic cycle shown on scheme 6 can be proposed. The first step of the catalytic cycle is probably the oxidative addition of the benzenesulfonyl chloride to Pd(II) to afford the Pd(IV) intermediate A as for Dong reaction.[11] Such oxidative addition on Pd(II) have been found to proceed even at room temperature.[11b] Then, after elimination of SO$_2$, the coordination of thiophene gives B. The migration of the aryl group to the β-carbon atom of thiophene gives C. Finally, base-assisted proton abstraction gives the β-arylated thiophene and regenerates the Pd(II) species.



Scheme 6. Proposed catalytic cycle

Experimental

General procedure for synthesis of arylated (benzo)thiophenes:

To a 25 mL oven dried Schlenk tube, arylsulfonyl chloride (1 mmol), thiophene derivative (1.5 mmol), Li_2CO_3 (6 mmol, 0.444 g), 1,4–dioxane (2 mL) and bis(acetonitrile)dichloropalladium(II) (0.05 mmol, 12.9 mg) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 140 °C (oil bath temperature) for 40 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (Et_2O/PE) to afford the C3 or C4 arylated products.

Conclusions

In summary, we report here the first palladium-catalysed desulfitative arylation of thiophene derivatives. The reaction was found to provide, in most cases, very regioselectively (≥98%) the β-arylated thiophenes. The reaction proceeds with easily accessible ligand-free $Pd(MeCN)_2Cl_2$ catalyst and Li_2CO_3 as base and tolerates a wide variety of substituents both on the benzenesulfonyl chloride and thiophene moieties. Due to the wide availability of diversely functionalised benzenesulfonyl chlorides, such simple reaction conditions (no expensive base and ligand) should be very attractive to synthetic or material chemists for access to β-arylthiophenes.

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Notes and references

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Electronic Supplementary Information (ESI) available: Procedures and ^1H and ^{13}C NMR. See DOI: 10.1039/b000000x/

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