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Palladium-Catalyzed Heck Type Regioselective β -Vinylolation of Thiophenes Using a Bromo Substituent as Traceless Directing Group

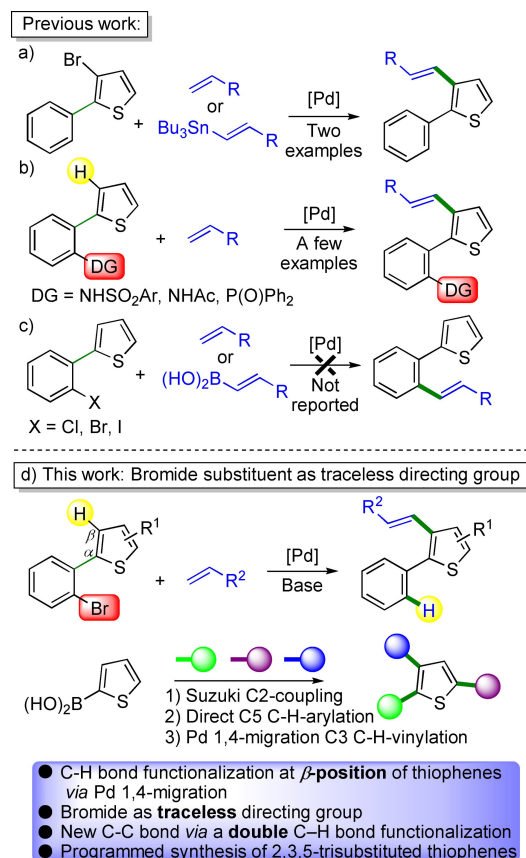
Linhao Liu^[a] and Henri Doucet^{*[a]}

Functionalization of β -C–H bonds of thiophenes such as their vinylation is more challenging than for their α -positions. The use of Pd-catalysis allowed us to vinylate such thienyl β -positions. Oxidative addition of 2-(2-bromoaryl)thiophenes to palladium followed by a Pd 1,4-migration activates these thienyl β -C–H positions, then, classical Pd-catalyzed Heck reaction gives the β -vinyolated 2-arylthiophene derivatives. In the course of this coupling reaction, the bromide substituent on the aryl unit acts as a traceless directing group. It should also be mentioned that

the created C–C bond results from the functionalization of two C–H bonds. This synthesis scheme tolerates a range of substituents on both the aryl ring and the alkene. In addition, this procedure employs an easily available air-stable catalyst and an inexpensive base. This reaction allows the programmed Pd-catalyzed synthesis of 2,3,5-trisubstituted thiophenes using first Suzuki C2-coupling, then Pd-catalyzed direct C5-arylation and finally Pd 1,4-migration Heck C3-vinylation.

Introduction

Thiophene derivatives are widely used in pharmaceutical as well as in material chemistry.^[1] Consequently, the introduction of functional groups onto thiophenes by simple methods remains an important research topic in organic synthesis. The metal-catalyzed direct α -functionalization of thiophenes *via* a C–H bond activation^[2] represents today one of the most efficient methods for the preparation of α -substituted thiophenes.^[3] Some examples of arylations at β -positions of thiophenes – which are generally less reactive than their α -position – have also been reported.^[4] By contrast, their β -C–H vinylation has attracted less attention. On the other hand, C3-vinylation of 2-aryl-3-halothiophenes to access the corresponding β -vinyl-substituted thiophene derivatives *via* a Heck^[5,6] or Stille^[7] reactions has been reported^[8] (Scheme 1, a). However, only a few examples have been described, probably due to the tedious multi-step access to numerous 3-halothiophene derivatives.^[9] The first ones were reported in 2001 using Stille coupling,^[8a,b] then, in 2017 Verma et al. reported the mono-vinylation of a 3,4-dibromothiophene *via* a Heck type reaction.^[8c] A few examples of C3-vinylations of 3-halobenzo-thiophenes, which are easier to prepare than 3-halothiophenes, *via* Heck or Suzuki reactions have also been reported.^[10]



Scheme 1. Pd-catalyzed vinylations at β -position of the thienyl unit of 2-arylthiophenes.

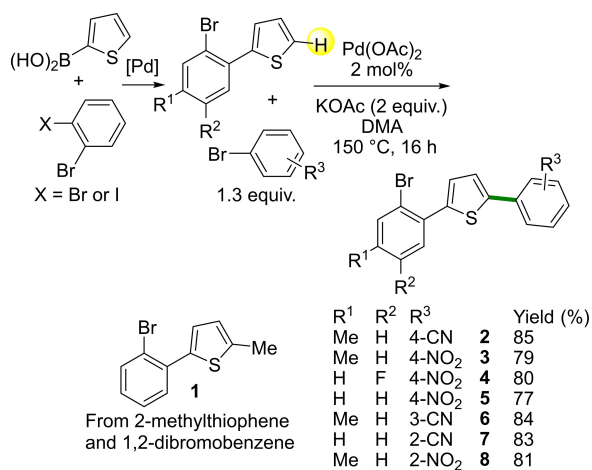
Functionalization of the C–H bond at the C3-position of 2-arylthiophenes *via* oxidative coupling with alkenes has also been described (Scheme 1, b).^[11] This approach, which does not require the pre-activation of thiophene β -position, is very

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attractive. However, for such coupling reactions, the presence of a directing group on the aryl unit of 2-arylthiophene was needed. Youn et al. employed a tosylamide directing group,^[11a] Chuang et al. an acetamide,^[11c] and Yang et al. a biphenylphosphine oxide (Scheme 1, b).^[11b] However, these directing groups have to be introduced onto 2-arylthiophenes and their removal could be challenging. Therefore, the use of a traceless directing group^[12,13] for such C3-vinylations of 2-arylthiophenes would provide a more attractive synthetic route. It's worth mentioning



Scheme 2. Pd-catalyzed Suzuki coupling followed by direct C5-arylation of the thieryl ring of 2-(2-bromoaryl)thiophenes.

that the Heck or Suzuki reactions of 2-(2-haloaryl)thiophenes for the synthesis of 2-(2-vinylphenyl)thiophenes have not been reported to date (Scheme 1, c).

Recently, we reported that in the course of the heteroarylation of 2-(2-bromoaryl)thiophenes by heteroarenes, a partial Pd 1,4-migration occurred,^[14–16] allowing to obtain 2-arylthiophenes heteroarylated at the β -position of the thienyl ring.^[17] This Pd 1,4-migration on 2-arylthiophenes represents an effective tool for functionalizing the C–H bond at β -position of thiophenes.^[4] Consequently, the potential of Pd-catalyzed 1,4-migration associated with Heck vinylation for the traceless directing group access to 2-aryl-3-vinylthiophenes needed to be explored. Here we present *i*) the conditions for the vinylation at β -position of 2-arylthiophenes using Pd 1,4-migration associated with Heck reaction, *ii*) on the scope of the reaction including the programmed Pd-catalyzed synthesis of 2,3,5-trisubstituted thiophenes (Scheme 1, d).

Results and Discussion

First, we synthesized the C₂,C₅-disubstituted 2-(2-bromoaryl)thiophenes 1–8 *via* reported procedures: 1) Suzuki coupling of 2-thienylboronic acid with 1,2-dihalobenzenes, 2) Pd-catalyzed direct C₅-arylation (Scheme 2).^[17b] All the expected products were obtained in very good yields without cleavage of the C–Br bond.

Table 1. Influence of the reaction conditions on the Pd-catalyzed coupling of 2-(2-bromophenyl)-5-methylthiophene 1 with styrene.^[a]

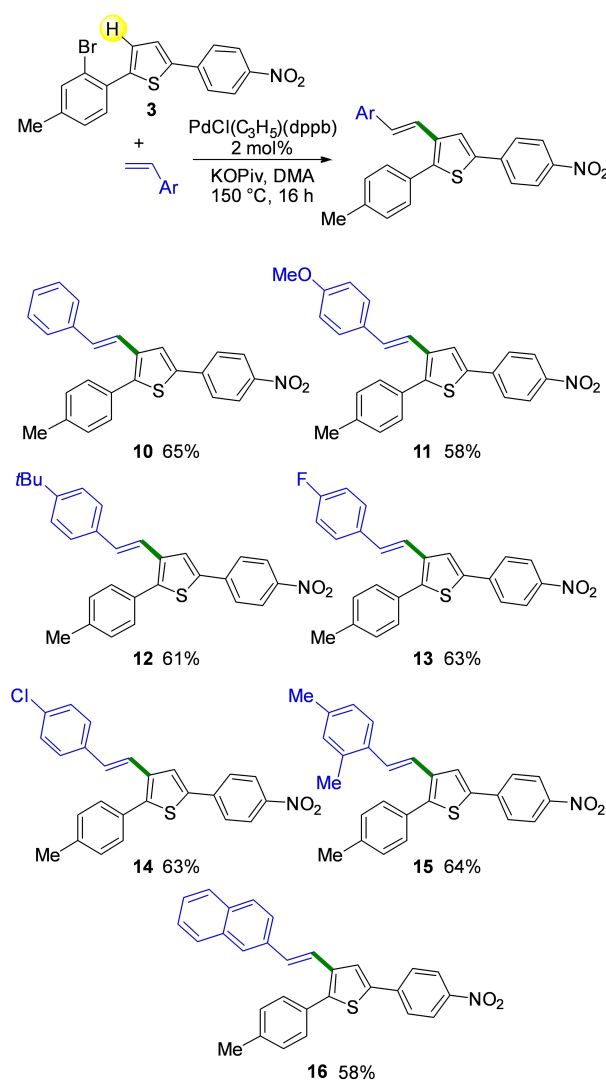
Entry	Catalyst	Solvent	Base	Conv. (%)	Ratio 9a:9b	Yield in 9b (%)
1	Pd(OAc) ₂	DMA	KOAc	30	34:66	16
2	PdCl(C ₃ H ₅)(dppb)	DMA	KOAc	100	33:67	41
3	PdCl(C ₃ H ₅)(dppb)	DMA	Cs ₂ CO ₃	56	71:29	–
4	PdCl(C ₃ H ₅)(dppb)	DMA	NaOAc	100	51:49	–
5	PdCl(C ₃ H ₅)(dppb)	DMA	CsOAc	94	22:78	51
6	PdCl(C ₃ H ₅)(dppb)	DMA	KOPiv	100	22:78	57
7	PdCl(C ₃ H ₅)(dppb)	DMA	K ₂ CO ₃	92	90:10	61 of 9a
8	Pd(OAc) ₂ /dppb	DMF	KOPiv	100	28:72	53
9	Pd(OAc) ₂ /2 PPh ₃	DMF	KOPiv	100	30:70	51
10	Pd(OAc) ₂ /dppe	DMF	KOPiv	100	27:73	50
11	Pd(OAc) ₂ /dppf	DMF	KOPiv	100	29:71	51
12	PdCl(C ₃ H ₅)(dppb)	DMF	KOPiv	100	27:73	–
13	PdCl(C ₃ H ₅)(dppb)	NMP	KOPiv	100	–	–
14	PdCl(C ₃ H ₅)(dppb)	Xylene	KOPiv	95	95:5	66 of 9a
15	PdCl(C ₃ H ₅)(dppb)	DEC	KOPiv	96	85:15	–
16	PdCl(C ₃ H ₅)(dppb)	DMA	KOPiv	94	20:80	53 ^[b]

[a] Pd] (0.02 equiv.), 2-(2-bromophenyl)-5-methylthiophene 1 (1 equiv.), styrene (2 equiv.), base (3 equiv.), 150 °C, 16 h, conversion of 1, 9a:9b ratios determined by ¹H NMR and GC/MS analysis of the crude mixtures, isolated yields. [b] 130 °C.

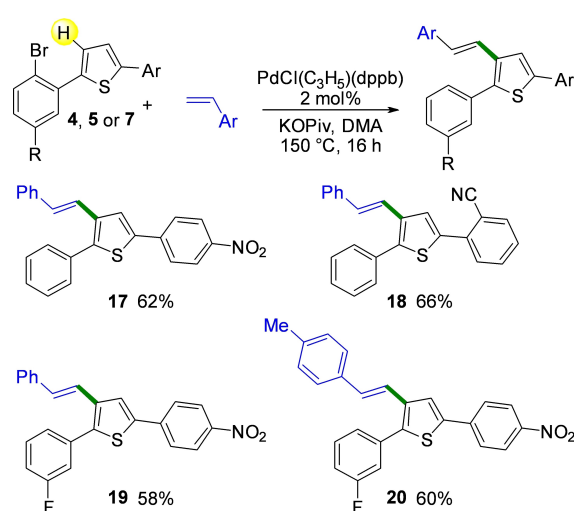
We first studied the outcome of the Pd-catalyzed coupling of 2-(2-bromophenyl)-5-methylthiophene **1** with styrene (Table 1). Using 2 mol% Pd(OAc)₂ catalyst associated to KOAc base in DMA at 150 °C, the formation of a mixture of Heck type product **9a** and Pd 1,4-migration product **9b** was obtained in 34:66 ratio, but **9b** was isolated in only 16% yield due to a low conversion of the thiophene derivative **1** (Table 1, entry 1). By contrast, in the presence of PdCl(C₃H₅)(dppb)^[18] catalyst a complete conversion of **1** was observed with the formation **9a** and **9b** in 33:67 ratio, and **9b** was isolated in 41% yield (Table 1, entry 2). The use of Cs₂CO₃ and NaOAc bases led to mixtures of **9a** and **9b** (Table 1, entries 3 and 4); whereas a higher selectivity in favor of the formation of **9b** (78%) was obtained using CsOAc or KOiPr as bases (Table 1, entries 5 and 6). Conversely the use of K₂CO₃ base led to a reversed selectivity with the formation of **9a** in 90% selectivity and in 61% yield (Table 1, entry 7). The use of Pd(OAc)₂ catalyst in the presence of PPh₃, dppb, dppe or dppf ligands instead of PdCl(C₃H₅)(dppb) catalyst had almost no influence on the selectivity of the reaction (Table 1, entries 8–11). The influence of a few solvents was also studied, but DMF led to a lower selectivity in **9b**; whereas xylene and diethyl carbonate (DEC) led to 95% and 85% selectivity in favor of Heck type product **9a**, and NMP was ineffective to promote this reaction (Table 1, entries 12–15). A lower reaction temperature of 130 °C instead of 150 °C with KOiPr base in DMA gave **9b** in 80% selectivity and in 53% yield due to partial conversion of 2-(2-bromophenyl)-5-methylthiophene **1** (Table 1, entry 16).

The scope of the thienyl ring β-vinylation reaction, which is more challenging than the vinylation of the benzene ring, using several styrene derivatives with the 2,5-diarylthiophene **3** was investigated (Scheme 3). Using styrene, 2 mol% PdCl(C₃H₅)(dppb) catalyst, KOiPr base in DMA at 150 °C, a complete selectivity in favor of the formation of the Pd 1,4-migration product **10** was observed which was isolated in 65% yield. The reaction also tolerated styrene derivatives bearing the electron donating *para*-substituents methoxy and *tert*-butyl affording the products **11** and **12** with complete selectivity and good yields. 4-Fluoro- and 4-chloro-styrenes were also found to be suitable substrates giving rise to products **13** and **14** in 63% yield. Finally, more hindered 2,4-dimethylstyrene and also 2-vinylnaphthalene gave the target products **15** and **16** in 64% and 58% yield, respectively. For all the reactions with the 2,5-diarylthiophene **3**, only the Pd 1,4-migration/direct vinylation products were detected, indicating that the presence of two aryl substituents at positions 2 and 5 on the thienyl unit favors such Pd migration. The moderate yields obtained in some cases are probably due to partial degradation of the products formed, as well as to the formation of secondary products, since a complete conversion of **3** was observed in all cases.

We also investigated the influence of a few other aryl units on the 2,5-diarylthiophenes on the selectivity of the reaction (Scheme 4). The use of a 2-bromophenyl instead of a 2-bromo-4-methylphenyl substituent has almost no influence, with the formation of product **17** in 62% yield. The 2-(thiophen-2-yl)benzotrile derivative **7** also reacted nicely to give **18** in 66% yield. A fluoro-substituent on the 2-bromobenzene unit



Scheme 3. β-Vinylations of the thienyl ring of **3** with a set of styrenes via Pd 1,4-migration.

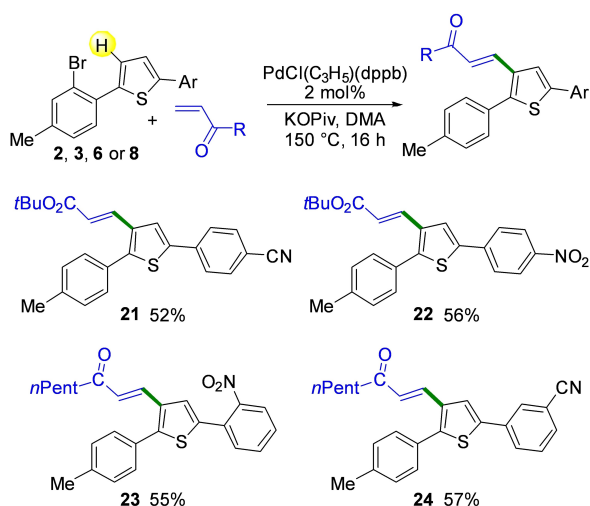


Scheme 4. β-Vinylations of the thienyl ring of a set of 2,5-diarylthiophenes via Pd 1,4-migration.

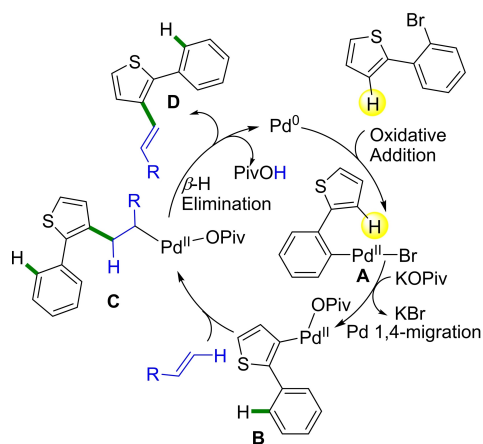
was also well tolerated giving rise to the 3-vinylthiophenes **19** and **20** in good yields. For all these reactions, again only the Pd 1,4-migration/direct vinylation products were detected.

The influence of two other substituents on the vinyl derivative was also examined (Scheme 5). Both *t*-butylacrylate and oct-1-en-3-one gave the Pd 1,4-migration/direct vinylation products **21–24** in 52–57% yields. Again, the Heck type products without Pd 1,4-migration were not detected.

Mechanism for the access to 2-aryl-3-vinylthiophenes **D** likely proceed *via* a Pd-1,4-migration followed by a Heck vinylation^[6] as described in the scheme 6. The first step of the catalytic cycle involves the oxidative addition of the 2-(2-bromoaryl)thiophene affording **A**. Then, a Pd-1,4-migration^[14] occurs to give the intermediate **B**. Insertion of the alkene in the thienyl–Pd bond gives **C**. Finally, a β -H elimination provides the 2-aryl-3-vinylthiophene with regeneration of the catalyst.



Scheme 5. β -Vinylation of the thienyl ring of a 2,5-diarylthiophenes with an acrylate and an alk-1-en-3-one *via* Pd 1,4-migration.



Scheme 6. Proposed catalytic cycle for the access of β -vinylation thienyl derivatives from 2-(2-bromoaryl)thiophenes.

Conclusions

In summary, bromide as traceless directing group was successfully employed in the Pd 1,4-migration/Heck vinylation of 2-arylthiophenes. The reaction led to the 2-aryl-3-vinylthiophenes using a variety of alkenes and substituted thiophenes. In this coupling reaction, the new C–C bond results from the functionalization of two C–H bonds. In addition, this method enables the functionalization of C–H bonds at β -position of thiophenes which is very attractive from a synthetic point of view as very few β -bromothiophenes, which could give access to the same products by a classical Heck reaction, are commercially available at an affordable cost. Moreover, this procedure requires a low loading of an air stable palladium catalyst associated to an inexpensive base. We have successfully applied this reaction to the programmed synthesis of 2,3,5-trisubstituted thiophenes using first Suzuki C2-coupling, then Pd-catalyzed direct C5-arylation and finally Pd 1,4-migration Heck C3-vinylation. Thus, we believe that the use of bromide as a traceless directing group associated with Pd 1,4 migration will lead in the near future to a powerful tool for the polyfunctionalization of (hetero)arenes including those having weakly reactive C–H bonds.

Experimental Section

General procedure for the preparation of products **9b** and **10–24**: As a typical experiment, the reaction of the 2-(2-bromoaryl)thiophene derivative **1–8** (1 mmol), alkene (2 mmol) and KOAc (0.294 g, 3 mmol) at 150 °C during 16 h in DMA (4 mL) in the presence of PdCl(C₃H₅)(dppb) (12.2 mg, 0.02 mmol) under argon affords the coupling product after evaporation of the solvent and purification on silica gel.

Supporting Information

Experimental procedures and characterization data are available in Supporting Information. Additional reference cited within the Supporting Information.^[19]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Heck reaction · homogeneous catalysis · migration · palladium · thiophenes

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