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Palladium-catalyzed 2,5-diheteroarylation of 2,5-dibromothiophene derivatives

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Full Research Paper

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Abstract

Conditions allowing the one pot 2,5-diheteroarylation of 2,5-dibromothiophene derivatives in the presence of palladium catalysts are reported. Using KOAc as the base, DMA as the solvent and only 0.5–2 mol % palladium catalysts, the target 2,5-diheteroarylated thiophenes were obtained in moderate to good yields and with a wide variety of heteroarenes such as thiazoles, thiophenes, furans, pyrroles, pyrazoles or isoxazoles. Moreover, sequential heteroarylation reactions allow the access to 2,5-diheteroarylated thiophenes bearing two different heteroaryl units.

Introduction

2,2':5',2"-Terthiophene (or 2,5-di(2-thienyl)thiophene) (Figure 1) and many of its derivatives are important structures due to their biological and/or physical properties. For example, 2,2':5',2"-terthiophene itself is a pigment of Tagetes minuta. Some 2,2':5',2"-terthiophene derivatives such as 5,5"-dichloro-α-terthiophene also occur naturally [1]. Moreover, terthiophenes are widely used as building blocks for the synthesis of semiconductors [2]. Due to these multiple uses, the discovery of a simpler access to terthiophene derivatives would be very useful.

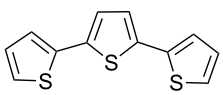


Figure 1: 2,2':5',2"-Terthiophene.

Suzuki, Stille or Negishi Pd-catalyzed cross-coupling reactions represent some of the most efficient methods for the preparation of 2,5-diheteroarylated thiophenes [3-16]. However, an

organometallic derivative must be prepared to perform such reactions. In 1990, Ohta and co-workers reported the Pd-catalyzed direct arylation of heteroaromatics using aryl halides as coupling partners via a C–H bond activation [17,18]. Since then Pd-catalyzed direct arylation of heteroaryls, especially with aryl halides as coupling partners, has been shown to be a very powerful method for an easier and greener access to a very broad range of arylated heterocycles [19-32]. This method is more attractive than other Pd-catalyzed cross-coupling reactions as it avoids the preparation of an organometallic derivative and also as the major byproducts of the reaction are not metallic salts but a base associated to HX.

The metal-catalyzed direct arylation of a wide variety of heteroarenes using aryl halides as coupling partners has been reported in recent years [19-36]. However, to our knowledge, only a few examples of Pd-catalyzed direct arylations at both C2 and C5 carbons of 2,5-dihalothiophene derivatives have been described. In 2006, Borgese et al. reported the Pd-catalyzed coupling of 2,5-dibromothiophene with 3-methoxythiophene to afford the corresponding terthiophene in 29% yield [37]. From 2,5-diiodothiophene and benzoxazole, using 5 mol % $Pd(phen)_2(PF_6)_2$ catalyst, the 2,5-diheteroarylated thiophene was obtained in 89% yield by Murai et al. [38]. A fluorescent π-conjugate thiophene derivative bearing spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan] substituents at C2 and C5 has been prepared in 46% yield by this reaction using $Pd(OAc)_2$ (5 mol %) associated to PPh_3 (10 mol %) as catalytic system [39]. A pyrrole derivative was coupled with 2,5-dibromothiophene in the presence of $Pd(OAc)_2$ (5 mol %) and PCy_3 (10 mol %) catalyst to afford the 2,5-di(pyrrolyl)thiophene in 59% yield [40]. Finally, an indolizine was also successfully coupled with 2,5-dibromothiophene in 47% yield in the presence of $Pd(OAc)_2$ as catalyst [41]. To our knowledge, so far sequential Pd-catalyzed direct couplings using 2,5-dihalothiophene derivatives have not been described. Therefore, the discovery of effective general conditions, for the direct coupling of heteroarenes at both C2 and C5 positions of 2,5-dihalothiophene derivatives, would constitute a considerable advantage allowing a simpler access to terthiophene derivatives.

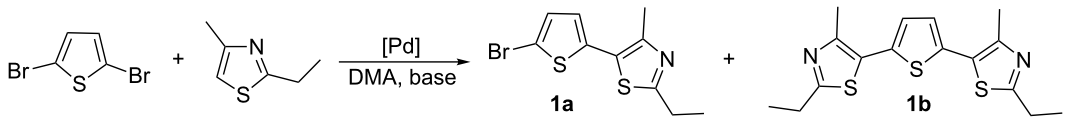
Here, we wish to report (i) that only 0.5–2 mol % of air-stable palladium catalysts associated to KOAc promote the direct access to 2,5-diheteroarylated thiophenes in one pot, (ii) on the reaction scope using a large set of heteroarenes, and (iii) conditions allowing the sequential diheteroarylation of 2,5-dibromothiophene.

Results and Discussion

Based on our previous results, DMA was initially chosen as the solvent and KOAc as the base for this study [42,43]. The reactions were conducted at 140 °C under inert conditions using $PdCl(C_3H_5)(dppb)$ or $Pd(OAc)_2$ catalysts. Using only 0.5 mol % $Pd(OAc)_2$, the reaction of 1 equiv of 2,5-dibromothiophene with 2 equiv 2-ethyl-4-methylthiazole as coupling partners affords the mono- and diarylation products **1a** and **1b** in a 2:98 ratio and the desired product **1b** was isolated in 79% yield (Scheme 1, Table 1, entry 1). The use of 3 equiv of 2-ethyl-4-methylthiazole afforded **1b** in similar yield (Table 1, entry 2). Then, we examined the influence of the amount of catalyst and other parameters on the reaction. The use of 1 or 2 mol % $PdCl(C_3H_5)(dppb)$ catalyst, which had been previously found to be very effective to promote the direct arylation of several hereroaromatics [42-44], also afforded **1b** in high yields (Table 1, entries 3–5). Even at 100 °C, the desired product **1b** was obtained in 78% yield (Table 1, entry 6). When CsOAc was employed as the base instead of KOAc, in the presence of 2 mol % $PdCl(C_3H_5)(dppb)$ catalyst, **1b** was isolated in 80% yield, whereas NaOAc led to target product **1b** in only 68% yield and Cs_2CO_3 was ineffective (Table 1, entries 7–9). It should be noted that in the presence of an excess of 2,5-dibromothiophene (4 equiv) with 1 equiv of 2-ethyl-4-methylthiazole the products **1a** and **1b** were produced in a 72:28 ratio and **1a** was isolated in 52% yield, without cleavage of the second C–Br bond on the thiophene ring allowing sequential arylations (Table 1, entry 10).

Then, with the most effective reaction conditions in hand for diheteroarylation (DMA, KOAc, $Pd(OAc)_2$ or $PdCl(C_3H_5)(dppb)$, 100 or 140 °C, 20 h), we explored the scope of this reaction using a variety of heteroarenes as the coupling partner (Scheme 2).

First, we investigated the reaction of 2,5-dibromothiophene with 4-methylthiazole (Scheme 2). The reaction proceeded very smoothly to afford the product **2** in 82% yield. It should be noted that no arylation at C2 of this thiazole derivative was observed. Then, a set of thiophene derivatives was employed.

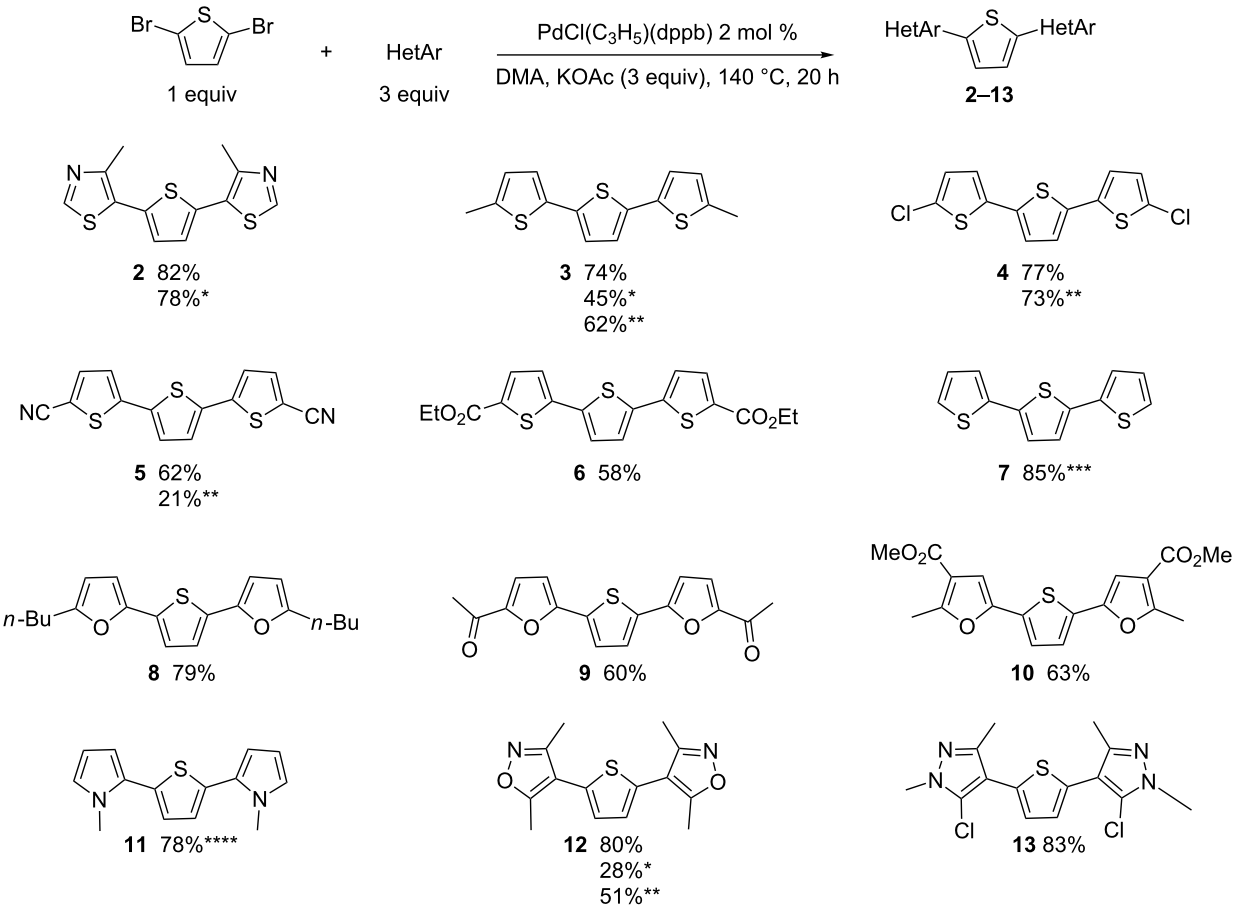


Scheme 1: Palladium-catalyzed direct arylation using 2,5-dibromothiophene and 2-ethyl-4-methylthiazole as coupling partners.

Table 1: Influence of the reaction conditions for palladium-catalyzed direct arylation using 2,5-dibromothiophene and 2-ethyl-4-methylthiazole as coupling partners (Scheme 1).[a]

Entry	Catalyst (mol %)	Base	2-Ethyl-4-methylthiazole (equiv)	Temperature (°C)	Ratio **1a**:**1b**	Yield in **1b** (%)
1	$Pd(OAc)_2$ (0.5)	KOAc	2	140	2:98	79
2	$Pd(OAc)_2$ (0.5)	KOAc	3	140	1:99	80
3	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	3	140	0:100	81
4	$PdCl(C_3H_5)(dppb)$ (1)	KOAc	3	140	0:100	80
5	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	2.2	140	1:99	78
6	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	3	100	0:100	78
7	$PdCl(C_3H_5)(dppb)$ (2)	NaOAc	3	140	7:93	68
8	$PdCl(C_3H_5)(dppb)$ (2)	CsOAc	3	140	0:100	80
9	$PdCl(C_3H_5)(dppb)$ (2)	Cs_2CO_3	3	140	nd	<5
10	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	3	140	72:28	52[b]

[a]Conditions: 2,5-dibromothiophene (1 equiv), base (3 equiv), DMA, 20 h, isolated yields. [b]2,5-Dibromothiophene (4 equiv), 2-ethyl-4-methylthiazole (1 equiv), yield in **1a**.



*: heteroarenes (2.2 equiv), $Pd(OAc)_2$ 0.5 mol %, 100 °C
**: heteroarenes (2.2 equiv), $Pd(OAc)_2$ 0.5 mol %
***: thiophene (6 equiv)
****: 1-methylpyrrole (5 equiv)

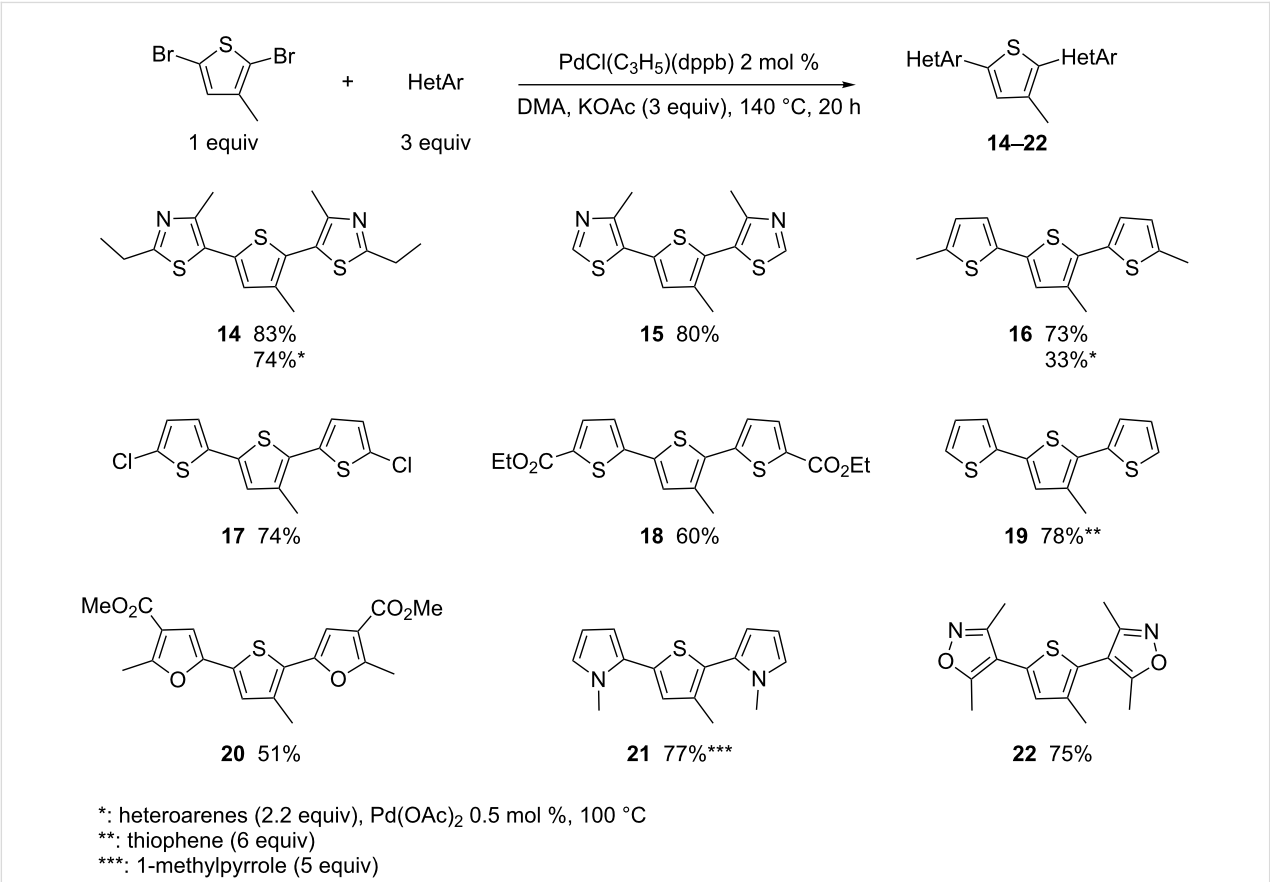
Scheme 2: Reactivity of 2,5-dibromothiophene with different heteroarenes.

Both, 2-methyl- and 2-chlorothiophenes afforded the desired products **3** and **4** in good yields in the presence of $PdCl(C_3H_5)(dppb)$ as the catalyst. Yields of 62% and 73% of these two products were obtained using 0.5 mol % $Pd(OAc)_2$ catalyst at 140 °C, whereas a reaction performed at 100 °C led to only a partial conversion of 2,5-dibromothiophene to afford **3** in 45% yield. This slightly lower reactivity of thiophene derivatives under these conditions was expected, as they are known to be less reactive than thiazole derivatives [44]. Moderate yields for **5** and **6** were obtained starting form thiophene-2-carbonitrile and ethyl thiophene-2-carboxylate, respectively in the presence of 2 mol % $PdCl(C_3H_5)(dppb)$ catalyst due to the formation of unidentified degradation products. The use of 6 equiv of thiophene allowed the formation of 2,2':5',2''-terthiophene (**7**) in 85% yield. The reactivity of three furan derivatives was also studied using $PdCl(C_3H_5)(dppb)$ as the catalyst. From 2-*n*-butylfuran, **8** was obtained in 79% yield, whereas 2-acetylfuran and methyl 2-methylfuran-3-carboxylate afforded **9** and **10** in 60% and 63% yield, respectively. The reaction of 1 equiv of 2,5-dibromothiophene with 5 equiv of 1-methylpyrrole gave **11** in 78% yield. No significant formation of other polyheterocycles was observed by GC–MS analysis of the crude mixture.

Arylation at C4 of 3,5-dimethylisoxazole and 5-chloro-1,3-dimethylpyrazole afforded **12** and **13** in 80% and 83% yields, respectively. With 3,5-dimethylisoxazole, a reaction performed using only 0.5 mol% $Pd(OAc)_2$ catalyst at 100 °C led to a partial conversion of 2,5-dibromothiophene.

As several terthiophene derivatives bearing alkyl substituents at C3 in their central unit have been employed in material chemistry [2], the reactivity of 2,5-dibromo-3-methylthiophene was also examined (Scheme 3). Similar results to those of 2,5-dibromothiophene were obtained. Both, 2-ethyl-4-methylthiazole and 4-methylthiazole reacted nicely to afford **14** and **15** in 83% and 80% yields, respectively. The four terthiophenes **16**–**19** were also obtained in satisfactory yields. Again a moderate yield in **20** was obtained in the presence of methyl 2-methylfuran-3-carboxylate due to the formation of degradation products, whereas the reaction with 1-methylpyrrole and 3,5-dimethylisoxazole resulted in good yields of **21** and **22**, respectively.

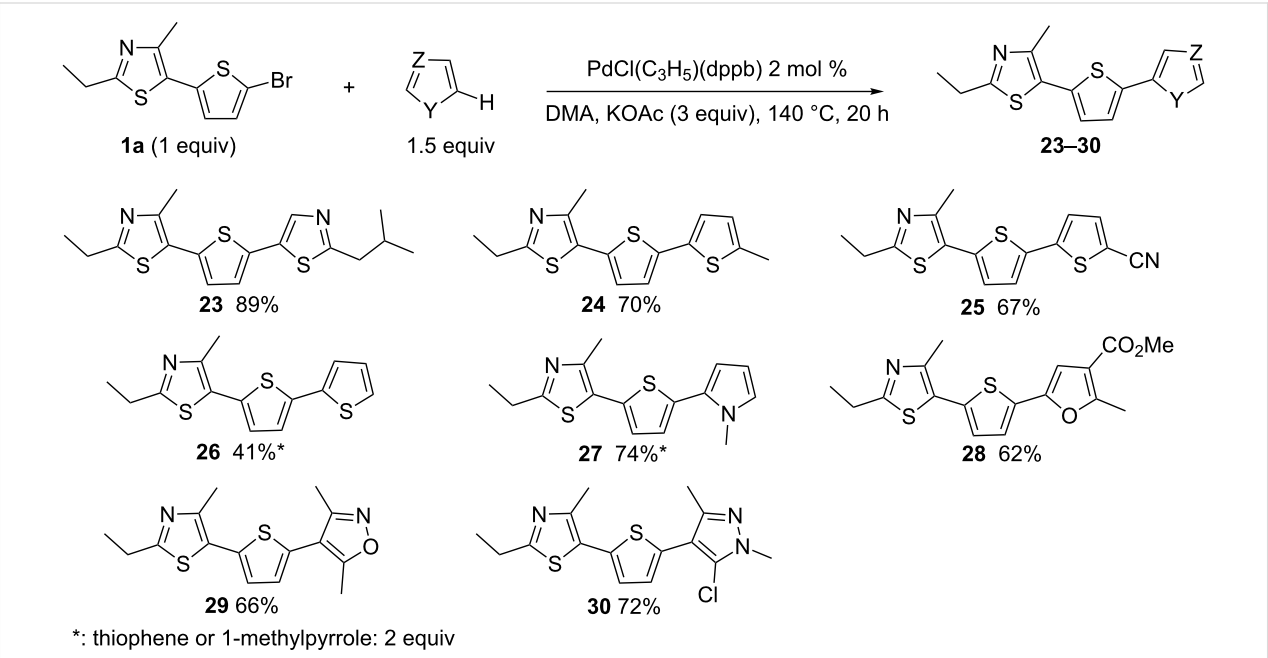
To our knowledge, the sequential Pd-catalyzed direct diheteroarylation of 2,5-dibromothiophene has not yet been reported. A



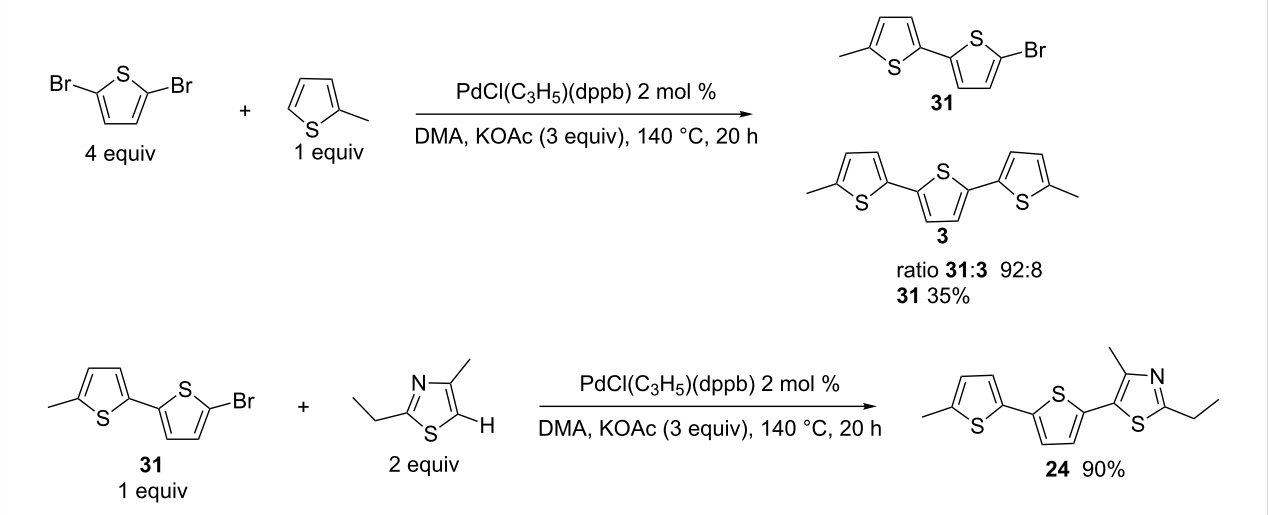
Scheme 3: Reactivity of 2,5-dibromo-3-methylthiophene with different heteroarenes.

sequential heteroarylation would allow the synthesis of non-symmetrically 2,5-disubstituted thiophene derivatives. Our attempts to prepare these compounds are shown in Scheme 4. Eight heteroarenes were reacted with **1a** to afford the 2,5-di-heteroarylated thiophenes **23**–**30** in 41–89% yield. A high yield of 89% for **23** was obtained from **1a** and 2-isobutylthiazole as the coupling partners. The reactions with 2-methylthiophene and thiophene-2-carbonitrile also afforded the desired products **24** and **25** in good yields. A decreased yield of 41% for **26** was obtained with thiophene as coupling partner, whereas, 1-methylpyrrole gave **27** in 74%. Coupling of **1a** with methyl 2-methylfuran-3-carboxylate afforded **28** in 62% yield. The arylation at C4 of 3,5-dimethylisoxazole and 5-chloro-1,3-dimethylpyrazole also proceeded nicely to give **29** and **30** in 66% and 72% yield, respectively.

It should be noted that, for the synthesis of **24**, the introduction of the thiazole unit in the first step (Scheme 1 and Scheme 4, 36% over 2 steps) led to a slightly higher yield than the introduction of 2-methylthiophene followed by the coupling with 2-ethyl-4-methylthiazole (Scheme 5, 32% yield over 2 steps).



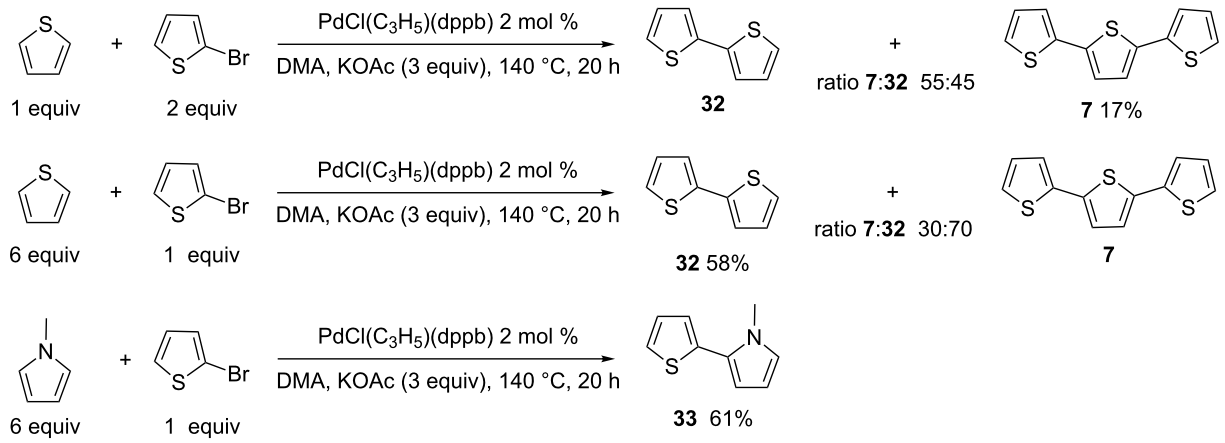
Scheme 4: Sequential diheteroarylation of 2,5-dibromothiophene.



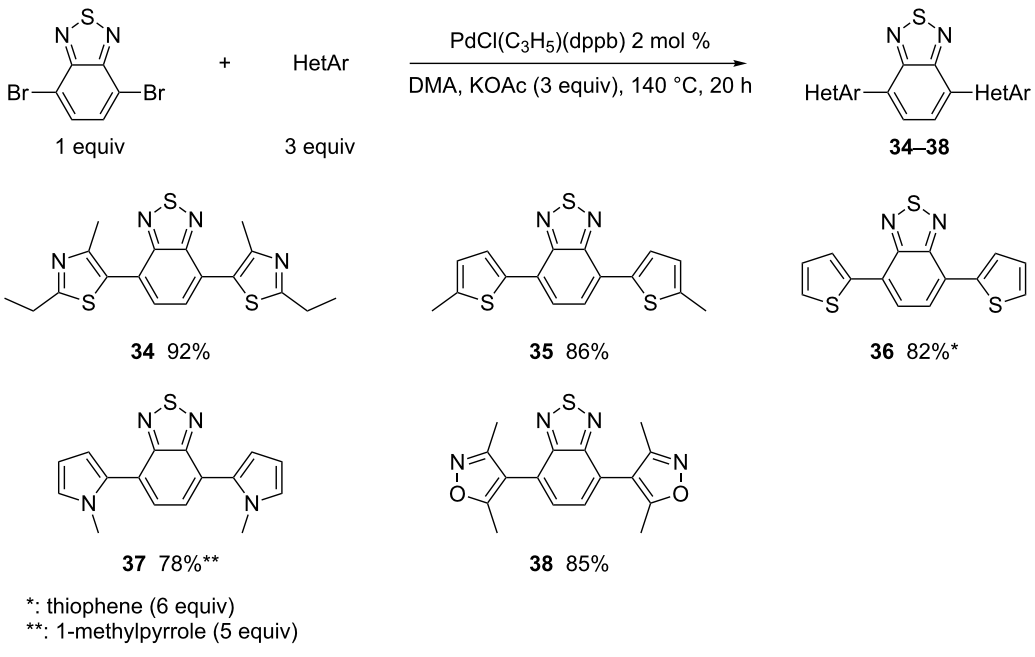
Scheme 5: Sequential diheteroarylation of 2,5-dibromothiophene.

We also compared the preparation of 2,2':5',2''-terthiophene (**7**) starting from either 2,5-dibromothiophene (Scheme 2) or from 2-bromothiophene (Scheme 6). The reaction of 1 equiv thiophene with 2 equiv of 2-bromothiophene resulted in a poor yield for **7** due to the formation of a mixture of bithiophene **32**, terthiophene **7** and also a quaterthiophene (as was observed by GC–MS analysis of the crude mixture). On the other hand, the use of 6 equiv of thiophene in the presence of 1 equiv of 2-bromothiophene afforded **7** and **32** in a 30:70 ratio and only low amounts of a quaterthiophene were observed; compound **32** was isolated in 58% yield (Scheme 6, middle). The same reaction conditions allowed to prepare 1-methyl-2-(thiophen-2-yl)pyrrole (**33**) in 61% yield (Scheme 6, bottom).

Finally, as 4,7-diarylbenzothiadiazoles also display important physical properties [45], we applied our procedure to 4,7-dibromobenzothiadiazole which is commercially available (Scheme 7). In all cases, the desired 4,7-diarylbenzothiadiazoles **34**–**38** were obtained in high yields.



Scheme 6: Heteroarylation of 2-bromothiophene.



Scheme 7: Reactivity of 4,7-dibromobenzothiadiazole.

Conclusion

In summary we report here a simple one-pot catalytic method leading to 2,5-diheteroarylated thiophenes in good yields. We established that 2 mol % of air-stable $PdCl(C_3H_5)$(dppb) catalyst (and in some cases 0.5 mol % $Pd(OAc)_2$ catalyst) in the presence of KOAc as the base promotes the 2,5-diheteroarylation of 2,5-dibromothiophene in the presence of a variety of heteroarenes such as thiophenes, furans, pyrroles, pyrazoles or isoxazoles as the coupling partners. The sequential diheteroarylation of 2,5-dibromothiophene was also found to be possible to afford 2,5-diheteroarylated thiophenes bearing two different heteroarene units. As both, 2,5-dibromothiophene and a wide variety of heteroarenes are commercially available, this method gives a convenient access to a large number of terthiophene derivatives.

Supporting Information

Supporting Information File 1

Experimental procedures and characterization data.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-309-S1.pdf]

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