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Linhao Liu, Henri Doucet. One Pot Access to 2'-Aryl-2,3'-Bithiophenes via Twofold Palladium-Catalyzed C-X/C-H Coupling Associated to a Pd-1,4-Migration. Advanced Synthesis and Catalysis, 2022, 364 (16), pp.2783-2795. 10.1002/adsc.202200563 . hal-03735527

HAL Id: hal-03735527

https://univ-rennes.hal.science/hal-03735527v1

Submitted on 27 Sep 2022

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DOI: 10.1002/adsc.201

One Pot Access to 2'-Aryl-2,3'-bithiophenes via Twofold Palladium-catalyzed C-X/C-H Coupling Associated to a Pd-1,4-migration

Linhao Liu,[a] and Henri Doucet[a]*

[a] Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France
e-mail address: henri.doucet@univ-rennes1.fr

Received:

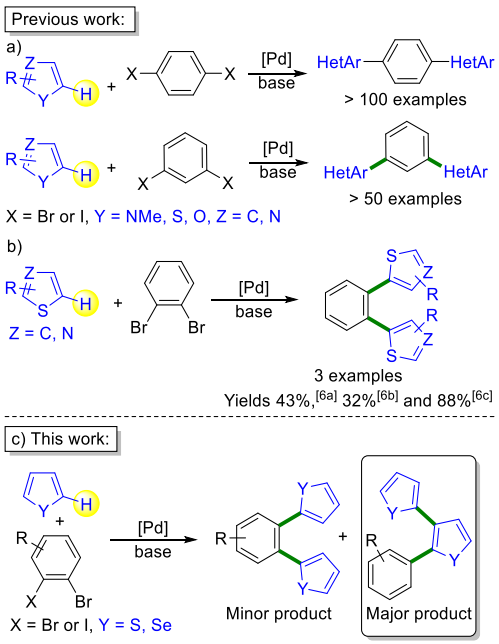
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201#####

Abstract. The reactivity of 1,2-dihalobenzenes in palladium catalyzed polyheteroarylation *via* C-H bond functionalization was investigated. The first catalytic cycle using thiophene as the heteroarene gives the expected 2-(2-bromophenyl)thiophenes. In the course of the second catalytic cycle, in the presence of heteroarenes having a free C3-position, a partial Pd 1,4-migration occurred giving rise to aryl-substituted biheteroarenes such as 2'-aryl-2,3'-bithiophenes as well as the expected 1,2-di(thiophen-2-yl)benzenes. The best selectivities in favor of the formation of 2'-aryl-2,3'-bithiophenes were obtained with electron-rich 1,2-dihalobenzenes. A wide variety of thiophene derivatives bearing useful functions such as formyl, acetyl, cyclopropylmethanone, 2-methyl-1,3-dioxolane, ester, nitrile or chloro was tolerated allowing to prepare poly-functionalized 2'-aryl-2,3'-bithiophenes. Moreover, this one pot preparation of 2'-aryl-2,3'-bithiophenes employs a low loading of an air stable commercially available palladium source associated to an inexpensive base.

Keywords: C-H bond functionalization; Bithiophenes; Heteroarenes; Pd 1,4-migration; Palladium.

Introduction

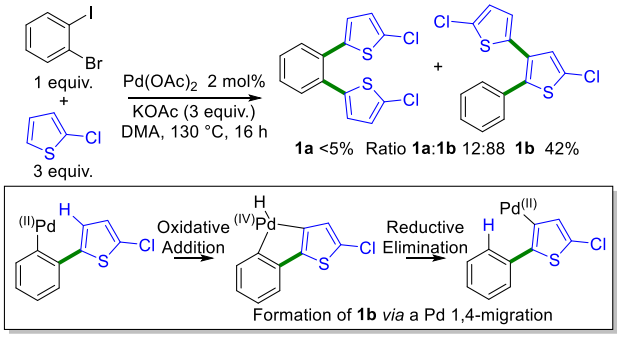
Heteroaryl-substituted benzene derivatives are ubiquitious compounds in both pharmaceutical and oganic material chemistry.[1] In 1990, Ohta et al. described the coupling of several heteroarenes with aryl halides, *via* a C–H bond activation/functionalisation, using palladium catalysis.[2] Since these seminal results, this reaction has been applied to the synthesis of a very wide variety of heteroarylated benzene derivatives.[3,4] Therefore, one of the most direct approach for the access to diheteroarylated arenes is the coupling of dihalobenzenes with heteroaromatics *via* regioselective C-H bond functionalization. This methodology is more attractive than the more classical palladium catalyzed Suzuki, Stille or Negishi cross-coupling reactions, as no previous preparation of an organometallic derivative is required. To the best of our knowledge, concerning the coupling reaction of dihalobenzenes with heteroarenes, several examples using 1,3- or 1,4-dihalobenzenes have been reported (Scheme 1, a).[5] In contrast, the reactivity of 1,2-dihalobenzenes for such couplings has attracted much less attention (only three examples) (Scheme 1, b).[6] For example, Liu, Wen et al. reported in 2018 that the coupling of a thiophene derivative with 1,2-dibromobenzene gave the diheteroarylated benzene in 32% yield.[6b] Furthermore, to the best of our knowledge, no examples of Pd-catalyzed direct diheteroarylations using substituted 2-bromo-1-iodobenzenes have been reported to date (Scheme 1, b). Therefore, the reactivity of such 1,2-dihalobenzenes in direct arylation needed to be explored. We report herein on the reaction outcome of Pd-catalyzed coupling of 1,2-dihalobenzenes with heteroarenes and on the substrate scope for both coupling partners (Scheme 1, c).



Scheme 1. Pd-catalyzed direct heteroarylations of dihalobenzenes.

Results and Discussion

First, we attempted couple 2-chlorothiophene (3 equiv.) with 2-bromo-1-iodobenzene (1 equiv.) (Scheme 2). For this reaction we employed as little as 2 mol% $Pd(OAc)_2$ as the catalyst with KOAc as the base in DMA at 130 °C. We had previously observed that such reaction conditions promote very efficiently the C-H arylation of several heteroaromatics.[4d] In the course of this reaction, a mixture of two coupling products with the same mass was detected by GC/MS analysis of the crude mixture and a partial conversion of 2-bromo-1-iodobenzene was observed. The expected 1,2-diheteroarylation product **1a** was isolated in <5% yield together with 2'-phenyl-2,3'-bithiophene **1b** (Ratio **1a**:**1b** 12:88). The formation of **1b** likely arises from a Pd 1,4-migration after the second oxidative addition to palladium (See scheme 3). Palladium 1,4-migration has already been proposed to explain a few Pd-catalyzed organic transformations.[7-9]



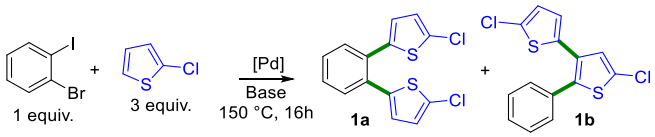
Scheme 2. Reaction outcome of Pd-catalyzed coupling of 2-chlorothiophene with 2-bromo-1-iodobenzene.

It may proceed by oxidative addition of thienyl C3-H bond with the formation of a Pd(IV) intermediate followed by reductive elimination (Scheme 2, bottom).[7] Mechanisms proceeding *via* Pd(II) intermediates for the Pd 1,4-migrations have also been proposed.[7c]

The access to 2'-aryl-2,3'-bithiophenes such as **1b** is quite challenging and requires several steps.[10] For example they can be prepared *via* a double Suzuki coupling with 2,3-dibromothiophene[10a] or *via* a Stille reaction.[10c] Therefore, the scope of this synthetic pathway for the preparation of various 2'-aryl-2,3'-bithiophenes was investigated.

We examined the influence of several reaction conditions in order to improve the reaction selectivity and yield (Table 1). The use of a more elevated temperature (150 °C instead of 130 °C) allowed to obtain a complete conversion of 2-bromo-1-iodobenzene with the same **1a**:**1b** ratio (12:88) affording **1b** in 64% yield (Table 1, entries 1 and 2). In the presence of carbonate bases instead of KOAc, a lower selectivity of the reaction was observed. In addition, poor yields in **1b** were obtained (Table 1, entries 3 and 4). Better results were obtained using CsOAc or KOPiv resulting in the formation of **1b** in 56 and 58% yield, respectively with similar selectivities in favor of **1b** compared to the reaction with KOAc (Table 1, entries 6 and 7). In all cases, the presence of carboxylate bases led to much higher selectivities in product **1b** compared to the reactions performed with carbonate bases, indicating that palladium carboxylate ligands may favor the Pd 1,4-migration. The use of a palladium catalyst bearing PPh_3 or diphosphine ligands had almost no influence on the reaction (Table 1, entry 8-12). The influence of a few solvent was also examined. Both polar solvents DMF and NMP led to very similar **1a**:**1b** ratios and afforded **1b** in slightly lower yields that with DMA (Table 1, entries 13 and 14). Conversely, diethylcarbonate (DEC) and xylene solvents were completely ineffective (Table 1, entries 15 and 16). Using 1,2-dibromobenzene instead of 2-bromo-1-iodobenzene, the **1a**:**1b** selectivity was similar, but the **1b** yield dropped to 45% (Table 1, entry 17).

Table 1. Influence of the reaction conditions on the Pd-catalyzed reaction of 2-chlorothiophene with 2-bromo-1-iodobenzene.[a]



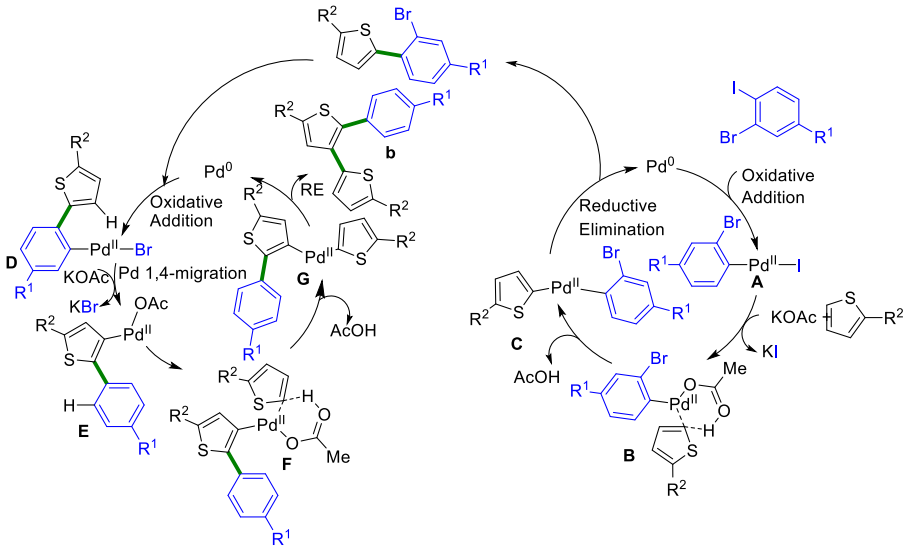
Entry	Catalyst	Solvent	Base	Ratio **1a**:**1b**	Yield in **1b** (%)
1	$Pd(OAc)_2$	DMA	KOAc	12:88	42[b]
2	$Pd(OAc)_2$	DMA	KOAc	12:88	64
3	$Pd(OAc)_2$	DMA	Cs_2CO_3	70:30	<10
4	$Pd(OAc)_2$	DMA	K_2CO_3	41:59	<10
5	$Pd(OAc)_2$	DMA	NaOAc	12:88	28
6	$Pd(OAc)_2$	DMA	CsOAc	13:87	56
7	$Pd(OAc)_2$	DMA	KOPiv	14:86	58
8	$PdCl(C_3H_5)$(dppb)	DMA	KOAc	12:88	62
9	$Pd(OAc)_2$ / dppe	DMA	KOAc	12:88	60
10	$Pd(OAc)_2$ / dppb	DMA	KOAc	12:88	55
11	$Pd(OAc)_2$ / dppf	DMA	KOAc	13:87	56
12	$Pd(OAc)_2$ / 2 PPh_3	DMA	KOAc	12:88	57
13	$Pd(OAc)_2$	DMF	KOAc	13:87	51
14	$Pd(OAc)_2$	NMP	KOAc	12:88	58
15	$Pd(OAc)_2$	Xylene	KOAc	-	0
16	$Pd(OAc)_2$	DEC	KOAc	-	0
17	$Pd(OAc)_2$	DMA	KOAc	13:87	45[c]

[a)] [Pd] (0.02 equiv.), 2-chlorothiophene (3 equiv.), 2-bromo-1-iodobenzene (1 equiv.), base (3 equiv.), 150 °C, 16h, **1a**:**1b** ratios determined by ^{1}H NMR and GC/MS analysis of the crude mixtures, isolated yields. [b)] 130 °C. [c)] Using 1,2-dibromobenzene.

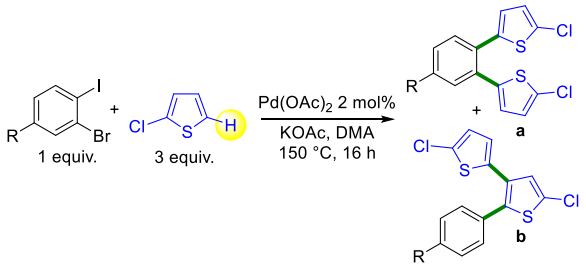
Plausible mechanisms for the access either to 1,2-bis(5-chlorothiophen-2-yl)benzenes **a** or to 5,5'-dichloro-2'-phenyl-2,3'-bithiophenes **b** are described in the scheme 3. In both cases, first step of the catalytic cycle involves the oxidative addition of the 1-bromo-2-iodobenzenes to give intermediate **A**. Then, after a concerted metallation deprotonation[11] (CMD), the intermediate **C** is obtained. A reductive elimination provides the 2-(2-bromophenyl)thiophene intermediate. Access to 1,2-bis(5-chlorothiophen-2-yl)benzene **a** probably occurs *via* a second identical classical "direct arylation" catalytic cycle such as the one described on the right of scheme 3. Conversely, the access to 5,5'-dichloro-2'-phenyl-2,3'-bithiophene **b** would proceed *via* a Pd-1,4-migration of the intermediate **D** to give **E**. Finally, after CMD and reductive elimination steps, the product **b** is obtained with regeneration of Pd(0). The use of substituted 1-bromo-2-iodobenzenes allows to regioselectively introduce substituents at the desired positions on the aryl ring, due to the faster oxidative addition to palladium of the C–I bond than for the C–Br bond.

The **a**:**b** ratio of this reaction depends on the crucial Pd 1,4-migration step to obtain intermediate **E** after the formation of **D** in the scheme 3. Therefore, the electronic properties of the substituents on the 1,2-dihalobenzene was expected to exhibit an influence in this **a**:**b** ratio. First, the **a**:**b** selectivity of this reaction using a variety of 4-substituted 2-bromo-1-iodobenzenes was examined (Scheme 4). For these substrates, the C-Br bond is in *meta*-position of the substituent. A 4-methoxy-substituted 2-bromo-1-iodobenzene gave the products **2a** and **2b** in 19:81 ratio. A quite similar **3a**:**3b** ratio (12:88) was obtained using 2-bromo-1-iodo-4-methylbenzene. With 4-fluoro and 4-chloro-substituted 2-bromo-1-iodobenzene the **a**:**b** ratios were 34:66 and 36:64, respectively. From the more electron-deficient 1-bromo-2-iodobenzenes bearing trifluoromethyl- or cyano-substituents, the **7b** and **8b** products were obtained in 66% and 60% selectivity, respectively. Therefore, the selectivity of the reaction seems to be linked to the Hammett σ_m constants (aryl-substituent is at *meta*-position of the C-Br bond), and the Pd 1,4-migration appears to be favored by the presence of electron-donating groups on the 2-bromo-1-iodobenzene (See Hammett σ_m constant *vs* **b** selectivity correlation in the scheme 5).[12]

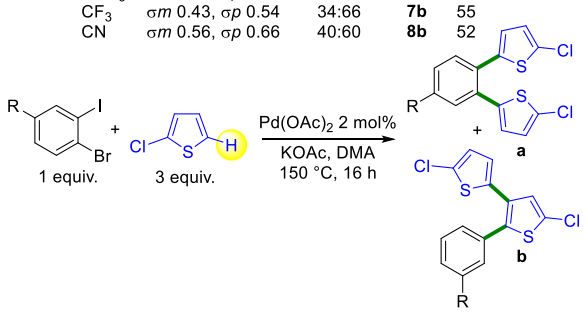
In order to confirm this trend, we employed two 5-substituted 2-bromo-1-iodobenzenes (Scheme 4). With 5-fluoro-2-bromo-1-iodobenzene the product **9b** was obtained in a high 89% selectivity (Hammett σ_p constant = 0.06, as F-substituent is at *para*-position of the C-Br bond); and with 5-chloro-2-bromo-1-iodobenzene the product **10b** was obtained in a high 87% selectivity (Hammett σ_p constant = 0.23 Cl-substituent). Finally, 1-bromo-3-fluoro-2-iodobenzene gave **12b** in 78% selectivity for a Hammett σ_m constant of 0.34.



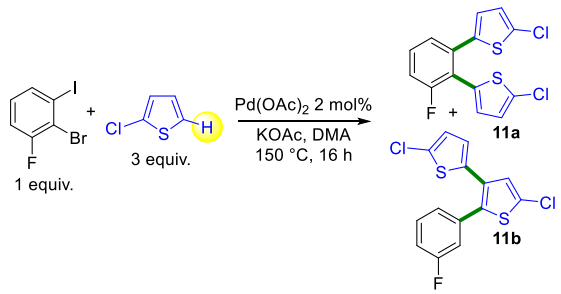
Scheme 3. Proposed reaction mechanism.



R	Hammett constants	Ratio **a**:**b**		Yield (%)
H	σm 0, σp 0	12:88	**1b**	64
OMe	σm 0.12, σp -0.27	19:81	**2b**	52
Me	σm -0.07, σp -0.17	12:88	**3b**	62
F	σm 0.34, σp 0.06	34:66	**4b**	51
Cl	σm 0.37, σp 0.23	36:64	**5b**	54
OCF_3	σm 0.38, σp 0.35	42:58	**6b**	50
CF_3	σm 0.43, σp 0.54	34:66	**7b**	55
CN	σm 0.56, σp 0.66	40:60	**8b**	52

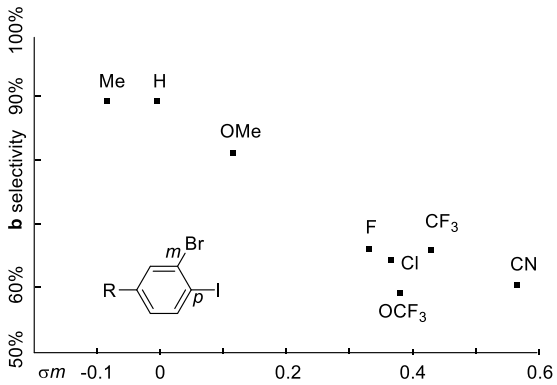


R	Hammett constants	Ratio **a**:**b**		Yield (%)
F	σm 0.34, σp 0.06	11:89	**9b**	58
Cl	σm 0.37, σp 0.23	13:87	**10b**	61



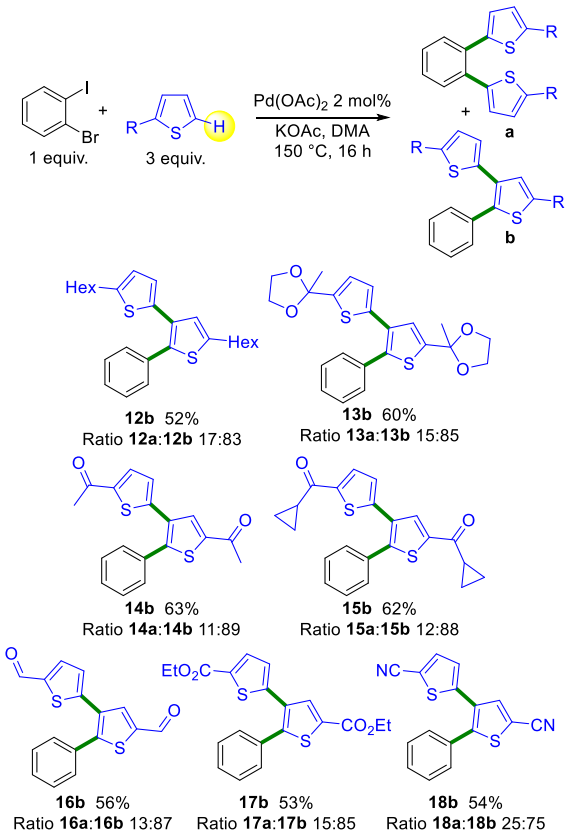
σm 0.34, σp 0.06 Ratio **11a**:**11b** 22:78 **11b** 56%

Scheme 4. Influence of the 1-bromo-2-iodobenzene substituent on the **a**:**b** selectivity of the reaction *vs* Hammett constants.



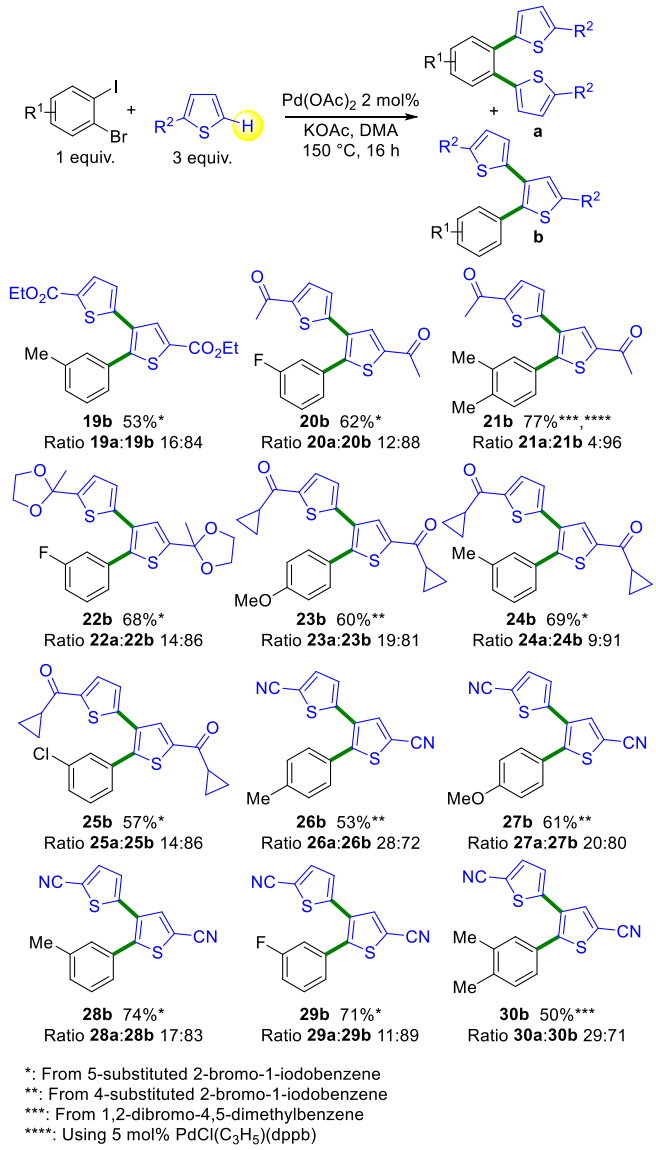
Scheme 5. Influence of the 4-substituent of 2-bromo-1-iodobenzenes: correlation of the **a**:**b** selectivity with *meta* Hammett constants.

The influence of the thienyl 2-substituents on the selectivity and yield was also investigated (Scheme 6). 2-Hexylthiophene afforded the products **12a** and **12b** in 17:83 ratio. Slightly higher selectivities in favor of the formation the 2'-phenyl-2,3'-bithiophenes **13b** and **14b** were obtained from and 2-acetylthiophene protected as an acetal or unprotected. Cyclopropyl(thiophen-2-yl)methanone also provided the product **15b** with high selectivity (88%) and good yield. Both 2-formyl- and 2-ester-substituted thiophene also led to the 1,4-migration products **16b** and **17b** with similar selectivities (87% and 85%) and moderate yields. Conversely, the use of thiophene-2-carbonitrile gave a lower **a**:**b** selectivity of 25:75, and **18b** was isolated in 54% yield. In summary, the thienyl 2-substituents appear to have less influence on the **a**:**b** selectivity than the substituents carried by 1,2-dihalobenzenes.



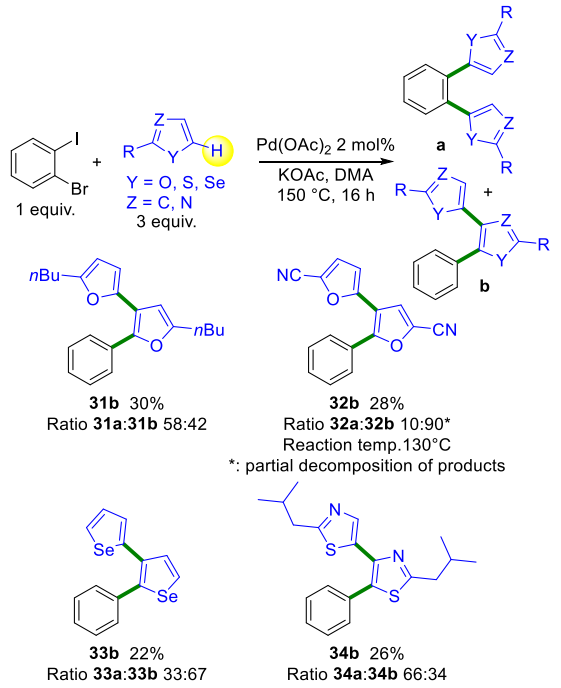
Scheme 6. Influence of the thienyl substituent on the **a**:**b** selectivity of the reaction.

By using the appropriate substrates, this methodology allows to introduce functional groups at desired positions of 2'-aryl-2,3'-bithiophenes (Scheme 7). From 1-bromo-2-iodo-4-methylbenzene or 1-bromo-2-iodo-4-fluorobenzene and ethyl thiophene-2-carboxylate or 2-acetylthiophene, the *meta*-substituted 2'-aryl-2,3'-bithiophenes **19b** and **20b** were obtained in high selectivity and good yields. From 1,2-dibromo-4,5-dimethylbenzene and 2-acetylthiophene, the 2'-xylyl-2,3'-bithiophene **21b** was formed in 96% selectivity and 77% yield. Several other 2'-aryl-2,3'-bithiophenes **22b**-**30b** containing useful functional groups on the thienyl moiety such as protected acetyl, cyclopropyl(thiophen-2-yl)methanone or nitrile and also fluoro, chloro, methyl or methoxy on the benzene ring were also obtained in high selectivities and good yields demonstrating the potential of this methodology for the preparation of poly-functionalized 2'-aryl-2,3'-bithiophenes.



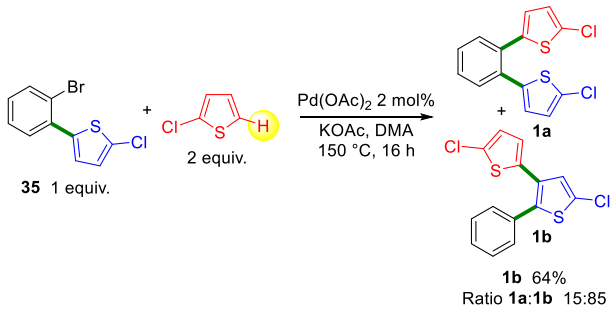
Scheme 7. Access to polyfunctionalized 2'-aryl-2,3'-bithiophenes.

The selectivity of the reaction using a few other heteroarenes was then studied (Scheme 8). The use of 2-butylfuran led to a 58:42 mixture of products **31a** and **31b**, and **31b** was isolated in 30% yield. The analysis of the crude mixture of the reaction using 2-furonitrile indicated a high ratio in favor of the formation of **32b** product. However, an important decomposition was observed in the course of this reaction and **32b** was isolated in low yield (28%). The high selectivity in **32b** may be due to partial decomposition of **32a**. From selenophene and 2-bromo-1-iodobenzene, the Pd 1,4-migration product 2'-phenyl-2,3'-biselenophene **33b** was obtained 67% selectivity but in quite low yield (22%). It should be mentioned that, to our knowledge, this is the first method allowing to prepare a 2'-aryl-2,3'-biselenophene. The Pd 1,4-migration appeared to be less favored in the presence of 2-isobutylthiazole with the formation of products **34a** and **34b** in 66:34 ratio.



Scheme 8. Influence of the heteroarene on the **a**:**b** selectivity of the reaction.

In order to control that the reaction proceeds *via* the formation of a 2-(2-bromophenyl)-5-chlorothiophene, this substrate was reacted with 2-chlorothiophene under the same direct arylation conditions (Scheme 9). As expected a mixture of products **1a** and **1b** was obtained in 15:85 ratio.



Scheme 9. Mechanism control experiment, **1a**:**1b** selectivity for the reaction with 2-(2-bromophenyl)-5-chlorothiophene.

Conclusion

In summary, the reactivity of 1,2-dihalobenzenes in Pd-catalyzed direct arylation is less predictable than with 1,3- and 1,4-dihalobenzenes. In the presence of heteroarenes with a substituent-free C3-position, a Pd 1,4-migration occurred at that position in several cases. With thiophenes, a double C-H bond activation associated to this Pd 1,4-migration allowed to obtain the 2'-aryl-2,3'-bithiophenes **b** in moderate to high selectivities. A good correlation between Hammett constants and the selectivity was observed, and the best selectivities in products **b** were obtained with electron-donating substituents at *meta*-position *vs* aryl C-Br bond of the 2-bromo-1-iodobenzenes. It should be mentioned that a wide variety of thiophene derivatives bearing useful functions such as formyl, acetyl, cyclopropylmethanone, 2-methyl-1,3-dioxolane, ester, nitrile or chloro was tolerated. Moreover, this one pot reaction employs a low loading of an air stable commercially available palladium source associated to an inexpensive base. Therefore, it provides a very convenient access to a wide variety of functionalized 2'-aryl-2,3'-bithiophenes compared to reported procedures.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High-resolution mass spectra were measured on an Agilent 6510 spectrometer. Low-resolution mass spectra were measured on a Shimadzu QP2010 SE. DMA (99%) was purchased from Acros. $Pd(OAc)_2$ (98 %) was purchased from Aldrich. KOAc (99%) was purchased from Fischer. These compounds were not purified before use.

General procedure for the preparation of 2'-aryl-2,3'-bithiophenes:

As a typical experiment, the reaction of the aryl dihalide (3 mmol), heteroarene (1 mmol) and KOAc (3 mmol) at 150 °C during 16 h in DMA (4 mL) in the presence of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) under argon affords the coupling product after evaporation of the solvent and purification on silica gel. The **a**:**b** ratios were determined by ^{1}H NMR and GC/MS analysis of the crude mixtures.

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 were 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 (162 MHz, $CDCl_3$) δ = 19.3 (s).

5,5'-Dichloro-2'-phenyl-2,3'-bithiophene (1b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **1a** and **1b** was obtained in 12:88 ratio and **1b** was isolated in 64% (0.199 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 5H), 6.99 (s, 1H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 132.7, 130.0, 129.6, 129.3, 129.1, 128.9, 128.8, 127.8, 126.3, 125.7, 125.4.

HRMS calcd for $[M+H]^+$ $C_{14}H_9Cl_2S_2$ 310.9517, found: 310.9519.

1a was also isolated in 8% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.41 (m, 2H), 7.40-7.35 (m, 2H), 6.80 (d, *J* = 3.8 Hz, 2H), 6.70 (d, *J* = 3.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 133.1, 131.1, 130.7, 128.6, 126.7, 126.3.

5,5'-dichloro-2'-(4-methoxyphenyl)-2,3'-bithiophene (2b)

From 2-bromo-1-iodo-4-methoxybenzene (0.313 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **2a** and **2b** was obtained in 19:81 ratio and **2b** was isolated in 52% (0.177 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.67 (d, *J* = 3.8 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 137.3, 136.2, 131.4, 129.5, 129.4, 128.7, 127.5, 126.2, 125.2, 124.8, 114.4, 55.5.

LRMS calcd for $[M]^+$ $C_{15}H_{10}Cl_2OS_2$ 340, found: 340.

5,5'-Dichloro-2'-(*p*-tolyl)-2,3'-bithiophene (3b)

From 2-bromo-1-iodo-4-methylbenzene (0.296 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **3a** and **3b** was obtained in 12:88 ratio and **3b** was isolated in 62% (0.201 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.97 (s, 1H), 6.73 (d, *J* = 3.8 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 137.6, 136.1, 129.8, 129.7, 129.4, 129.0,4. 127.8, 127.1, 126.2, 125.6, 125.3, 21.5.

HRMS calcd for $[M+H]^+$ $C_{15}H_{11}Cl_2S_2$ 324.9674, found: 324.9673.

5,5'-Dichloro-2'-(4-fluorophenyl)-2,3'-bithiophene (4b)

From 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **4a** and **4b** was obtained in 34:66 ratio and **4b** was isolated in 51% (0.168 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.99 (s, 1H), 6.73 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 (d, *J* = 249.4 Hz), 136.0, 135.7, 131.9 (d, *J* = 8.2 H), 130.0, 129.8, 129.4, 128.6, 127.8, 126.3, 125.5, 116.1 (d, *J* = 21.9 Hz).

HRMS calcd for $[M+H]^+$ $C_{14}H_8Cl_2FS_2$ 328.9423, found: 328.9426.

5,5'-Dichloro-2'-(4-chlorophenyl)-2,3'-bithiophene (5b)

From 2-bromo-4-chloro-1-iodobenzene (0.317 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **5a** and **5b** was obtained in 36:64 ratio and **5b** was isolated in 54% (0.186 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.98 (s, 1H), 6.74 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 135.5, 135.0, 131.2, 131.1, 130.0, 129.9, 129.7, 129.2, 128.1, 126.4, 125.7.

HRMS calcd for $[M+H]^+$ $C_{14}H_8Cl_3S_2$ 344.9127, found: 344.9124.

5,5'-Dichloro-2'-(4-(trifluoromethoxy)phenyl)-2,3'-bithiophene (6b)

From 2-bromo-1-iodo-4-(trifluoromethoxy)benzene (0.367 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **6a** and **6b** was obtained in 42:58 ratio and **6b** was isolated in 50% (0.197 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.99 (s, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6 (q, *J* = 1.9 Hz), 135.6, 135.5, 131.4, 131.3, 130.2, 130.1, 129.9, 128.1, 126.5, 125.7, 121.2, 120.6 (q, *J* = 258.4 Hz).

HRMS calcd for $[M]^+$ $C_{15}H_7Cl_2F_3OS_2$ 393.9262, found: 393.9259.

6a was also isolated in low yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.5 Hz, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 3.8 Hz, 2H), 6.75 (d, *J* = 3.8 Hz, 1H), 6.71 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0 (q, *J* = 1.9 Hz), 139.3, 139.2, 134.9, 132.7, 131.8, 131.6, 131.3, 127.3, 127.2, 126.5, 123.1, 120.6, 120.5 (q, *J* = 258.4 Hz).

5,5'-Dichloro-2'-(4-(trifluoromethyl)phenyl)-2,3'-bithiophene (7b)

From 2-bromo-1-iodo-4-(trifluoromethyl)benzene (0.315 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **7a** and **7b** was obtained in 34:66 ratio and **7b** was colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.00 (s, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 6.64 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 135.6, 135.2, 130.5, 130.4 (q, *J* = 31.5 Hz), 130.1, 128.5, 127.1, 126.6, 126.0, 125.9 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 272.1 Hz), 123.2.

HRMS calcd for $[M]^+$ $C_{15}H_7F_3Cl_2S_2$ 377.9313, found: 377.9319.

4-(5,5'-Dichloro-[2,3'-bithiophen]-2'-yl)benzonitrile (8b)

From 3-bromo-4-iodobenzonitrile (0.308 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **8a** and **8b** was obtained in 40:60 ratio and **9b** was isolated in 52% (0.175 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.99 (s, 1H), 6.77 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 135.1, 134.9, 132.7, 131.2, 130.9, 130.6, 130.2, 128.9, 126.6, 126.2, 118.5, 112.2.

HRMS calcd for $[M+H]^+$ $C_{15}H_8NCl_2S_2$ 335.9470, found: 335.9473.

5,5'-Dichloro-2'-(3-fluorophenyl)-2,3'-bithiophene (9b)

From 1-bromo-4-fluoro-2-iodobenzene (0.301 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **9a** and **9b** was obtained in 11:89 ratio and **9b** was isolated in 58% (0.190 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.28 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.10-7.03 (m, 2H), 6.98 (s, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 247.6 Hz), 135.7, 135.4, 134.7 (d, *J* = 8.3 Hz), 130.6 (d, *J* = 8.6 Hz), 130.1, 130.0, 129.9, 128.1, 126.4, 125.8, 125.7, 116.9 (d, *J* = 22.3 Hz), 115.9 (d, *J* = 21.1 Hz).

LRMS calcd for $[M]^+$ $C_{14}H_7Cl_2FS_2$ 328, found: 328.

5,5'-Dichloro-2'-(3-chlorophenyl)-2,3'-bithiophene (10b)

From 1-bromo-4-chloro-2-iodobenzene (0.317 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **10a** and **10b** was obtained in 13:87 ratio and **10b** was isolated in 61% (0.211 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 4H), 6.99 (s, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 135.4, 130.2, 130.1, 130.0, 129.9, 129.0, 128.2, 128.0, 126.4, 125.7.

LRMS calcd for $[M]^+$ $C_{14}H_7Cl_3S_2$ 346, found: 346.

5,5'-Dichloro-2'-(2-fluorophenyl)-2,3'-bithiophene (11b)

From 1-bromo-3-fluoro-2-iodobenzene (0.301 g, 1 mmol), 2-chlorothiophene (0.356 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **11a** and **11b** was obtained in 22:78 ratio and **11b** was isolated in 56% (0.184 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.37 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, *J* = 249.9 Hz), 135.9, 132.9 (d, *J* = 2.0 Hz), 132.0, 131.3 (d, *J* = 8.0 Hz), 130.7, 129.8, 129.1, 127.0, 126.3, 124.9, 124.6 (d, *J* = 3.8 Hz), 120.4 (d, *J* = 15.6 Hz), 116.5 (d, *J* = 21.5 Hz).

LRMS calcd for $[M]^+$ $C_{14}H_7Cl_2FS_2$ 328, found: 328.

1,1'-(2'-Phenyl-[2,3'-bithiophene]-5,5'-diyl)bis(hexan-1-one) (12b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-hexylthiophene (0.504 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **12a** and **12b** was obtained in 17:83 ratio and **12b** was isolated in 52% (0.214 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.35-7.27 (m, 3H), 6.86 (s, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 6.55 (d, *J* = 3.8 Hz, 1H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.70 (quint., *J* = 7.5 Hz, 2H), 1.61 (quint., *J* = 7.5 Hz, 2H), 1.47-1.38 (m, 2H), 1.38-1.18 (m, 10H), 0.95-0.80 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 144.6, 136.2, 135.3, 134.7, 130.7, 129.8, 128.5, 127.7, 126.8, 125.2, 124.1, 31.7 (3C), 31.6, 30.2, 30.1, 29.0, 28.9, 22.7, 14.3, 14.2.

LRMS calcd for $[M]^+$ $C_{26}H_{34}S_2$ 410, found: 410.

2,2'-(2'-Phenyl-[2,3'-bithiophene]-5,5'-diyl)bis(2-methyl-1,3-dioxolane) (13b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.510 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **13a** and **13b** was obtained in 15:85 ratio and **13b** was isolated in 60% (0.248 g) yield as a white solid: mp 118-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.37 (m, 2H), 7.35-7.30 (m, 3H), 7.13 (s, 1H), 6.82 (d, *J* = 3.8 Hz, 1H), 6.68 (d, *J* = 3.8 Hz, 1H), 4.10-3.90 (m, 8H), 1.82 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 146.0, 138.2, 138.1, 134.0, 130.4, 129.8, 128.6, 128.2, 126.6, 125.5, 124.4, 107.3, 107.2, 65.2, 65.1, 27.6, 27.5.

HRMS calcd for $[M+H]^+$ $C_{22}H_{23}O_4S_2$ 415.1032, found: 415.1032.

1,1'-(2'-Phenyl-[2,3'-bithiophene]-5,5'-diyl)bis(ethan-1-one) (14b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 1-(thiophen-2-yl)ethan-1-one (0.378 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **14a** and **14b** was obtained in 11:89 ratio and **14b** was isolated in 63% (0.205 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.50 (d, *J* = 3.8 Hz, 1H), 7.45-7.37 (m, 5H), 6.85 (d, *J* = 3.8 Hz, 1H), 2.60 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 190.5, 148.8, 145.5, 143.7, 142.9, 133.9, 132.8, 132.6, 131.1, 129.6, 129.5, 129.1, 127.3, 26.8, 26.7.

HRMS calcd for $[M+H]^+$ $C_{18}H_{15}O_2S_2$ 327.0508, found: 327.0507.

(2'-Phenyl-[2,3'-bithiophene]-5,5'-diyl)bis(cyclopropylmethanone) (15b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), cyclopropyl(thiophen-2-yl)methanone (0.456 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **15a** and **15b** was obtained in 12:88 ratio and **15b** was isolated in 62% (0.234 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.62 (d, *J* = 3.8 Hz, 1H), 7.45-7.35 (m, 5H), 6.89 (d, *J* = 3.8 Hz, 1H), 2.60-2.50 (m, 1H), 2.50-2.40 (m, 1H), 1.31-1.25 (m, 2H), 1.25-1.19 (m, 2H), 1.11-1.04 (m, 2H), 1.04-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 192.7, 148.1, 145.1, 144.1, 143.3, 133.0, 132.7, 131.8, 131.2, 129.6, 129.5, 129.0, 127.3, 18.0, 17.9, 11.8, 11.5.

HRMS calcd for $[M+H]^+$ $C_{22}H_{19}O_2S_2$ 379.0821, found: 379.0822.

2'-Phenyl-[2,3'-bithiophene]-5,5'-dicarbaldehyde (16b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), thiophene-2-carboxaldehyde (0.336 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **16a** and **16b** was obtained in 13:87 ratio and **16b** was isolated in 56% (0.167 g) yield as a yellow solid: mp 150-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 9.84 (s, 1H), 7.89 (s, 1H), 7.60 (d, *J* = 3.8 Hz, 1H), 7.48-7.39 (m, 5H), 6.97 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 182.6, 150.5, 146.4, 143.2, 142.3, 137.4, 136.7, 132.2, 131.2, 130.0, 129.6, 129.2, 127.6.

HRMS calcd for $[M+H]^+$ $C_{16}H_{11}O_2S_2$ 299.0195, found: 299.0195.

Diethyl 2'-phenyl-[2,3'-bithiophene]-5,5'-dicarboxylate (17b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), ethyl thiophene-2-carboxylate (0.468 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **17a** and **17b** was obtained in 15:85 ratio and **17b** was isolated in 53% (0.204 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.60 (d, *J* = 3.9 Hz, 1H), 7.43-7.35 (m, 5H), 6.83 (d, *J* = 3.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 161.9, 146.8, 144.0, 134.9, 133.6, 133.2, 132.7, 130.8, 129.7, 129.4, 129.0, 126.9, 61.6, 61.3, 14.5, 14.4.

HRMS calcd for $[M+H]^+$ $C_{20}H_{19}O_4S_2$ 387.0719, found: 387.0724.

2'-Phenyl-[2,3'-bithiophene]-5,5'-dicarbonitrile (18b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **18a** and **18b** was obtained in 25:75 ratio and **18b** was isolated in 54% (0.158 g) yield as a yellow solid: mp 122-124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.52-7.42 (m, 5H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 142.9, 138.2, 137.6, 130.7, 130.5, 129.9, 129.7, 129.5, 126.9, 113.9, 113.4, 109.9, 109.6.

HRMS calcd for $[M+H]^+$ $C_{16}H_9N_2S_2$ 293.0202, found: 293.0205.

Diethyl 2'-(m-tolyl)-[2,3'-bithiophene]-5,5'-dicarboxylate (19b)

From 1-bromo-2-iodo-4-methylbenzene (0.297 g, 1 mmol), ethyl thiophene-2-carboxylate (0.468 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **19a** and **19b** was obtained in 16:84 ratio and **19b** was isolated in 53% (0.212 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.60 (d, *J* = 3.9 Hz, 1H), 7.29-7.15 (m, 4H), 6.83 (d, *J* = 3.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 162.0, 147.1, 144.1, 138.8, 134.8, 133.6, 133.1, 132.6, 132.5, 130.7, 130.3, 130.2, 128.9, 126.8, 126.7, 61.6, 61.3, 21.9, 14.5.

LRMS calcd for $[M]^+$ $C_{21}H_{20}O_4S_2$ 400, found: 400.

1,1'-(2'-(3-Fluorophenyl)-[2,3'-bithiophene]-5,5'-diyl)bis(ethan-1-one) (20b)

From 1-bromo-4-fluoro-2-iodobenzene (0.301 g, 1 mmol), 1-(thiophen-2-yl)ethan-1-one (0.378 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **20a** and **20b** was obtained in 12:88 ratio and **20b** was isolated in 62% (0.213 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.52 (d, *J* = 3.8 Hz, 1H), 7.40-7.33 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.15-7.06 (m, 2H), 6.87 (d, *J* = 3.8 Hz, 1H), 2.60 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 190.4, 162.9 (d, *J* = 248.2 Hz), 146.8, 144.9, 144.1, 143.4, 134.5 (d, *J* = 8.1 Hz), 133.9, 132.8, 131.6, 130.8 (d, *J* = 8.5 Hz), 127.5, 125.4 (d, *J* = 3.1 Hz), 116.6 (d, *J* = 20.6 Hz), 116.5, 26.8, 26.7.

LRMS calcd for $[M]^+$ $C_{18}H_{13}FO_2S_2$ 344, found: 344.

1,1'-(2'-(3,4-dimethylphenyl)-[2,3'-bithiophene]-5,5'-diyl)bis(ethan-1-one) (21b)

From 1,2-dibromo-4,5-dimethylbenzene 1-bromo-2-iodo-4,5-dimethylbenzene (0.264 g, 1 mmol), 1-(thiophen-2-yl)ethan-1-one (0.378 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **21a** and **21b** was obtained in 4:96 ratio and **21b** was isolated in 77% (0.272 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.50 (d, *J* = 3.8 Hz, 1H), 7.18 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 2.58 (s, 3H), 2.52 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 190.5, 149.4, 145.8, 143.5, 142.4, 138.5, 137.5, 133.9, 132.8, 130.7, 130.5, 130.3, 130.0, 127.2, 126.9, 26.8, 26.7, 19.9, 19.8.

LRMS calcd for $[M]^+$ $C_{20}H_{18}O_2S_2$ 354, found: 354.

2,2'-(2'-(3-Fluorophenyl)-[2,3'-bithiophene]-5,5'-diyl)bis(2-methyl-1,3-dioxolane) (22b)

From 1-bromo-4-fluoro-2-iodobenzene (0.301 g, 1 mmol), 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.510 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **22a** and **22b** was obtained in 14:86 ratio and **22b** was isolated in 68% (0.294 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 7.11-7.07 (m, 1H), 7.05-6.68 (m, 1H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.70 (d, *J* = 3.8 Hz, 1H), 4.11-3.94 (m, 8H), 1.81 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 247.6 Hz), 146.8, 146.6, 137.5, 136.5 (d, *J* = 2.4 Hz), 136.0 (d, *J* = 8.4 Hz), 131.0, 130.1 (d, *J* = 8.4 Hz), 126.8, 125.7, 125.5 (d, *J* = 3.0 Hz), 124.4, 116.6 (d, *J* = 22.3 Hz), 115.0 (d, *J* = 21.2 Hz), 107.2, 107.1, 65.2, 65.0, 27.6, 27.5.

LRMS calcd for $[M]^+$ $C_{22}H_{21}FO_4S_2$ 432, found: 432.

(2'-(4-Methoxyphenyl)-[2,3'-bithiophene]-5,5'-diyl)bis(cyclopropylmethanone) (23b)

From 2-bromo-1-iodo-4-methoxybenzene (0.313 g, 1 mmol), cyclopropyl(thiophen-2-yl)methanone (0.456 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **23a** and **23b** was obtained in 19:81 ratio and **23b** was isolated in 60% (0.245 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.64 (d, *J* = 3.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 2.60-2.50 (m, 1H), 3.84 (s,

3H), 2.50-2.42 (m, 1H), 1.30-1.21 (m, 4H), 1.11-1.04 (m, 2H), 1.04-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 192.7, 160.7, 148.4, 145.3, 144.0, 142.7, 133.1, 131.9, 130.9, 130.8, 127.2, 124.9, 114.5, 55.5, 18.0, 11.7, 11.5.

LRMS calcd for $[M]^+$ $C_{23}H_{20}O_3S_2$ 408, found: 408.

(2'-(*m*-Tolyl)-[2,3'-bithiophene]-5,5'-diyl)bis(cyclopropylmethanone) (24b)

From 1-bromo-2-iodo-4-methylbenzene (0.297 g, 1 mmol), cyclopropyl(thiophen-2-yl)methanone (0.456 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **24a** and **24b** was obtained in 9:91 ratio and **24b** was isolated in 69% (0.270 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.62 (d, *J* = 3.8 Hz, 1H), 7.30-7.16 (m, 4H), 6.89 (d, *J* = 3.8 Hz, 1H), 2.60-2.50 (m, 1H), 2.50-2.40 (m, 1H), 2.35 (s, 3H), 1.31-1.25 (m, 2H), 1.25-1.19 (m, 2H), 1.11-1.04 (m, 2H), 1.04-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 192.7, 148.3, 145.2, 143.9, 143.1, 138.8, 132.9, 132.6, 131.8, 131.1, 130.2, 130.1, 128.9, 127.2, 126.7, 21.5, 18.0, 17.9, 11.7, 11.5.

HRMS calcd for $[M+H]^+$ $C_{23}H_{21}O_2S_2$ 393.0977, found: 393.0975.

(2'-(3-Chlorophenyl)-[2,3'-bithiophene]-5,5'-diyl)bis(cyclopropylmethanone) (25b)

From 1-bromo-4-chloro-2-iodobenzene (0.317 g, 1 mmol), cyclopropyl(thiophen-2-yl)methanone (0.456 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **25a** and **25b** was obtained in 14:86 ratio and **25b** was isolated in 57% (0.235 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.65 (d, *J* = 3.8 Hz, 1H), 7.42 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 2.60-2.51 (m, 1H), 2.51-2.43 (m, 1H), 1.32-1.24 (m, 4H), 1.12-1.05 (m, 2H), 1.05-0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 192.7, 145.8, 144.5, 143.8, 135.0, 134.5, 133.0, 132.0, 131.8, 130.3, 129.6, 129.5, 127.9, 127.5, 18.1, 18.0, 11.9, 11.6.

LRMS calcd for $[M]^+$ $C_{22}H_{17}ClO_2S_2$ 412, found: 412.

2'-(*p*-Tolyl)-[2,3'-bithiophene]-5,5'-dicarbonitrile (26b)

From 2-bromo-1-iodo-4-methylbenzene (0.296 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **26a** and **26b** was obtained in 28:72 ratio and **26b** was isolated in 53% (0.162 g) yield as a yellow solid: mp 106-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.47 (d, *J* = 3.9 Hz, 1H), 7.25-7.22 (m, 4H), 6.95 (d, *J* = 3.9 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 143.0, 140.9, 138.2, 137.6, 130.2, 129.7, 129.4, 127.6, 126.8, 114.0, 113.5, 109.7, 109.2, 21.6.

LRMS calcd for $[M]^+$ $C_{17}H_{10}N_2S_2$ 306, found: 306.

2'-(4-Methoxyphenyl)-[2,3'-bithiophene]-5,5'-dicarbonitrile (27b)

From 2-bromo-1-iodo-4-methoxybenzene (0.313 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **27a** and **27b** was obtained in 20:80 ratio and **27b** was isolated in 61% (0.196 g) yield as a yellow solid: mp 105-107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.47 (d, *J* = 3.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.98-6.91 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 148.0, 143.1, 138.2, 137.6, 131.3, 129.3, 126.7, 122.6, 114.9, 114.0, 113.5, 109.7, 109.0, 55.6.

LRMS calcd for $[M]^+$ $C_{17}H_{10}N_2OS_2$ 322, found: 322.

2'-(*m*-Tolyl)-[2,3'-bithiophene]-5,5'-dicarbonitrile (28b)

From 1-bromo-2-iodo-4-methylbenzene (0.297 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **28a** and **28b** was obtained in 17:83 ratio and **28b** was isolated in 74% (0.226 g) yield as a yellow solid: mp 86-88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.46 (d, *J* = 3.9 Hz, 1H), 7.34-7.29 (m, 2H), 7.18 (s, 1H), 7.17-7.12 (m, 1H), 6.95 (d, *J* = 3.9 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 143.0, 139.4, 138.1, 137.6, 131.2, 130.5, 130.4, 129.6, 129.3, 127.0, 126.8, 114.0, 113.5, 109.8, 109.4, 21.5.

LRMS calcd for $[M]^+$ $C_{17}H_{10}N_2S_2$ 306, found: 306.

2'-(3-Fluorophenyl)-[2,3'-bithiophene]-5,5'-dicarbonitrile (29b)

From 1-bromo-4-fluoro-2-iodobenzene (0.301 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **29a** and **29b** was obtained in 11:89 ratio and **29b** was isolated in 71% (0.220 g) yield as a yellow solid: mp 120-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.48 (d, *J* = 3.8 Hz, 1H), 7.47-7.39 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 248.2 Hz), 145.8, 142.3, 138.4, 137.7, 132.5 (d, *J* = 8.4 Hz), 131.2 (d, *J* = 8.5 Hz), 130.1, 127.2, 125.7 (d, *J* = 3.3 Hz), 117.5 (d, *J* = 20.9 Hz), 116.9 (d, *J* = 23.0 Hz), 113.7, 113.2, 110.3, 110.1.

LRMS calcd for $[M]^+$ $C_{16}H_7FN_2S_2$ 310, found: 310.

2'-(3,4-Dimethylphenyl)-[2,3'-bithiophene]-5,5'-dicarbonitrile (30b)

From 1,2-dibromo-4,5-dimethylbenzene (0.264 g, 1 mmol), thiophene-2-carbonitrile (0.327 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **30a** and **30b** was obtained in 29:71 ratio and **30b** was isolated in 50% (0.160 g) yield as a yellow solid: mp 140-142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.46 (d, *J* = 3.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 3.8 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.2, 139.6, 138.1, 138.0, 137.6, 130.8, 130.7, 129.3, 128.0, 127.3, 126.7, 114.1, 113.6, 109.7, 109.1, 19.9 (2C).

LRMS calcd for $[M]^+$ $C_{18}H_{12}N_2S_2$ 320, found: 320.

5,5'-Dibutyl-2'-phenyl-2,3'-bifuran (31b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-butylfuran (0.372 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **31a** and **31b** was obtained in 58:42 ratio and **31b** was isolated in 30% (0.097 g) yield as a yellow oil.

31b ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.39-7.32 (m, 3H), 6.32 (d, *J* = 3.1 Hz, 1H), 6.24 (s, 1H), 6.01 (d, *J* = 3.1 Hz, 1H), 2.71-2.58 (m, 4H), 1.77-1.58 (m, 4H), 1.49-1.32 (m, 4H), 1.00-0.90 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 155.7, 146.7, 146.6, 131.7, 128.3, 127.4, 126.5, 113.8, 107.4, 107.2, 106.5, 30.5, 30.2, 27.9, 27.8, 22.5, 22.4, 14.0.

HRMS calcd for $[M+H]^+$ $C_{22}H_{27}O_2$ 323.2006, found: 323.2005.

31a was also isolated: 7.60-7.55 (m, 2H), 7.33-7.28 (m, 2H), 6.00 (d, *J* = 3.2 Hz, 2H), 5.95 (d, *J* = 3.2 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 4H), 1.62 (quint., *J* = 7.6 Hz, 4H), 1.38 (sext., *J* = 7.6 Hz, 4H), 0.93 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 151.3, 129.4, 128.8, 127.6, 108.9, 106.7, 30.5, 28.0, 22.4, 14.0.

2'-Phenyl-[2,3'-bifuran]-5,5'-dicarbonitrile (32b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-furonitrile (0.279 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **32a** and **32b** was obtained in 10:90 ratio and **32b** was isolated in 28% (0.073 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.52-7.46 (m, 3H), 7.41 (s, 1H), 7.13 (d, *J* = 3.7 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 150.5, 131.0, 129.2, 128.2, 127.8, 126.1, 125.8, 123.7, 122.6, 112.5, 111.3, 111.0, 109.2.

HRMS calcd for $[M+H]^+$ $C_{16}H_9N_2O_2$ 261.0659, found: 261.0659.

2'-Phenyl-2,3'-biselenophene (33b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), selenophene (0.393 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **33a** and **33b** was obtained in 33:67 ratio and **34b** was isolated in 22% (0.074 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 5.7 Hz, 1H), 7.83 (dd, *J* = 5.5, 1.2 Hz, 1H), 7.53 (d, *J* = 5.7 Hz, 1H), 7.44-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.14 (dd, *J* = 5.5, 3.7 Hz, 1H), 7.11 (dd, *J* = 3.7, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.5, 136.1, 135.2, 132.9, 130.4, 130.2, 129.6, 129.0, 128.6, 128.3, 128.2.

HRMS calcd for $[M+H]^+$ $C_{14}H_{11}Se_2$ 338.9186, found: 338.9189.

2,2'-Diisobutyl-5-phenyl-4,5'-bithiazole (34b)

From 1-bromo-2-iodobenzene (0.283 g, 1 mmol), 2-isobutylthiazole (0.423 g, 3 mmol) and KOAc (0.294 g, 3 mmol) in DMA (4 mL), a mixture of **34a** and **34b** was obtained in 66:34 ratio and **34b** was isolated in 26% (0.093 g) yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.46-7.37 (m, 5H), 2.87 (d, *J* = 7.2 Hz, 2H), 2.79 (d, *J* = 7.2 Hz, 2H), 2.21-2.00 (m, 2H), 1.04 (d, *J* = 7.2 Hz, 6H), 0.95 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.0, 141.4, 140.4, 132.2, 131.8, 131.4, 130.1, 129.1, 129.0, 42.4, 42.3, 29.9, 29.8, 22.5, 22.4.

HRMS calcd for $[M+H]^+$ $C_{20}H_{25}N_2S_2$ 357.1454, found: 357.1452.

2-(2-Bromophenyl)-5-chlorothiophene (35)[14]

To a solution of 2-chlorothiophene (1.42 g, 12.0 mmol) in THF (25 mL) was added dropwise *n*BuLi (1.55 M in hexane, 7.70 mL, 12.0 mmol) at 0 °C. After being stirred for 1 h, 1,2-dibromobenzene (2.36 g, 10.0 mmol) was added to the solution at the same temperature. Then, the mixture was warmed to room temperature and stirred for 2 h. The residue was purified by column chromatography on silica gel (100% heptane) to afford **35** in 53% (1.45 g) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.33 (td, *J* = 7.8, 1.3 Hz, 1H), 7.19 (td, *J* = 7.8, 1.7 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 6.92 (d, *J* = 3.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 134.6, 133.9, 131.8, 130.7, 129.5, 127.7, 127.2, 126.2, 122.8.

LRMS calcd for $[M]^+$ $C_{10}H_6BrClS$ 274, found: 274.

Acknowledgements

We are grateful to the CSC for a grant to L. L. We thank CNRS and "Rennes Metropole" for providing financial support.

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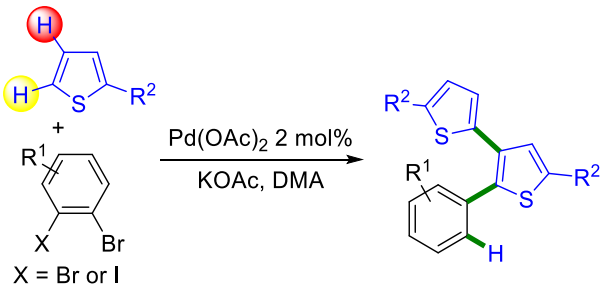
Linhao Liu,[a] and Henri Doucet[a]*