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Extension of the Heck reaction to the arylation of activated thiophenes

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Abstract

The direct arylation of activated thiophenes was accomplished in moderate to good yields using a Heck-type reaction with the mixture of $Pd(OAc)_2$ and n-Bu_4NBr as a catalytic system. This new arylation method is applied to different derivatives and has proved to be compatible with sensitive functional groups. Furthermore, the substituent nature and position on the thiophene moiety influence the cross coupling. In particular the substitution is regiospecific when the heterocycle is substituted at position 2 with an electron withdrawing group. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The introduction of functionalized aryl moieties onto heterocyclic compounds is an important task in organic synthesis. We are particularly interested in the preparation of functionalized thiophenes in order to obtain monomers suitable for the synthesis of regioregular polymers with high electrical conductivity [1,2]. As the chemistry of thiophene oligomers offers wide applications in the field of electrically conducting polymers, the search for a new and easier way to prepare them remains a topical issue. Methods to get unsymmetrical aryl–aryl coupling have been developed by Suzuki [3], Kumada [4] and Stille [5]. The Suzuki reaction consists of the cross coupling of an arylboronic acid with an aryl halide catalysed by a palladium phosphine complex in the presence of sodium carbonate. Kumada and co-workers described an efficient method based on a nickel-catalysed coupling between a Grignard reagent and an organo halide. The Stille method implies the reaction of a heteroaryltrialkylstannanes with an aryl halide catalysed by a palladium complex. Although they are all efficient cross-coupling methods, these three methods have several drawbacks. First of all, they are poorly compatible with a number of important functional groups. In addition, these methods require a specific activation of both substrate and reagent, and this increases the overall number of steps in a desired synthesis [6].

Recently, we have reported that activated thiophenes can be successfully arylated by the Heck method [7] using Jeffery conditions [8]. In this paper, the full results about our investigations for this new application of the Heck reaction are described. Our first objective is to underline the various conditions which can affect the selectivity and kinetics of the reactions. These investigations were carried out with a particular example, the reaction of thiophene-3-carboxaldehyde with iodobenzene. In the second part of this article, the reaction is applied to different derivatives bearing various activating groups such as aldehyde, cyano, nitro, methoxy, trifluoromethane, in order to evaluate scope and limitations of this new method.

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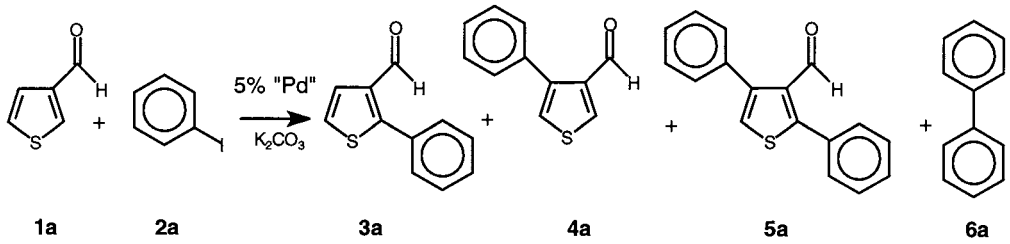


Scheme 1. Arylation of thiophene-3-carboxaldehyde with iodobenzene.

Table 1
Arylation of thiophene-3-carboxaldehyde with iodobenzene catalysed by the mixture $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$ (0.05/0.1/1)

Entry	**1** (mol l^{-1})	**2** (mol l^{-1})	Solvent	Time (h)	Conversion[b] (%)	Selectivity[b] (%) **3a**/**5a**/**6a**
1	1	1	CH_3CN/H_2O	10.5	59	51/4/45
2	2	1	CH_3CN/H_2O	9	100	57/9/34
3	8	4	CH_3CN/H_2O	4	100	57/15/28
4	4	1	CH_3CN/H_2O	2.5	100	66/6/28
5	4	1	H_2O	5	100	56/4/40
6	4	1	CH_3CN[a]	48	93	61/4/40

[a] Base = AcONa.
[b] Determined by GC analysis on an apolar column.

2. Study of reaction conditions with thiophene-3-carboxaldehyde

Under the classical conditions of Heck, the reaction gives rise to only traces of product. But under the conditions described by Jeffery [9], the coupling of thiophene-3-carboxaldehyde **1a** with iodobenzene **2a** leads selectively to 2-phenylthiophene-3-carboxaldehyde **3a**. The formation of the isomer **4a** resulting from a minor activation of position 4 and consequently the formation of a 2,4-disubstituted product **5a** are also observed. But, only small amounts of **4a** and **5a** are formed and has been identified by GC/MS coupling. Finally, biphenyl **6a** resulting from an Ullmann type coupling type competitive reaction is produced (Scheme 1).

In order to favour thiophene arylation, several conditions have been systematically studied and the influence of various parameters on the kinetics, selectivity and yield has been determined. The parameters studied are: thiophene/iodobenzene ratio and concentrations, solvent conditions and catalytic systems based on Pd(II) precursors, $Pd(OAc)_2$ and $PdCl_2$. Palladium acetate is used with tetra-*n*-butylammonium bromide with or without phosphine. Palladium chloride is used in association with LiCl salt as described by Miura et al.[10].

Results obtained with the mixture $Pd(OAc)_2/n\text{-}Bu_4NBr/PPh_3$, as a catalytic system are compiled in Table 1.

Following conditions described by Jeffery, with a mixture of $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$ in aqueous acetonitrile as catalytic system, the influence of concentrations and thiophene-3-carboxaldehyde/iodobenzene ratio on the selectivity and reaction rate has been evaluated. The use of equimolar ratio of thiophene-3-carboxaldehyde and iodobenzene (Table 1, entry 1) leads to a low reaction rate and a moderate selectivity. When the usual ratio for Heck reaction (**1a**/**2a**: 2/1, Table 1, entry 2) is used, the rate is increased but the selectivity remains modest. Nevertheless, a large excess of **1a** (**1a**/**2a**: 4/1, Table 1, entry 4) provides the most selective and the fastest reaction. However, a large increase of concentrations (thiophene 8 M and iodobenzene 4 M) allows the use of a limited thiophene excess (**1a**/**2a**: 2/1) preserving good rate and selectivity. The reaction appears to be largely influenced by concentration (Table 1, entry 3), but the required amount of potassium carbonate (2.5 equivalents) limits this possibility.

Various solvent conditions, anhydrous or aqueous ones, have also been tested with the catalytic system $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$. In the absence of water (Table 1, entry 6), the selectivity is similar to that obtained with the mixture CH_3CN/H_2O (9/1) (Table 1, entry 4) but the rate is drastically slowed down (48 h to reach 93% conversion). In water (Table 1, entry 5), total conversion is achieved after 5 h as in the mixture CH_3CN/H_2O (9/1), but a loss of selectivity is observed. Under these conditions, the competing formation of biphenyl is favoured. Actually, the best solvent is a CH_3CN/H_2O (9/1) mixture that allows both efficient reaction and good selectivity.

Recently, Miura et al. [10] described the reaction of salicylaldehydes with aryl iodides catalysed by a $PdCl_2/$

Table 2
Arylation of thiophene-3-carboxaldehyde with iodobenzene catalysed by a mixture $PdCl_2$/LiCl (0.05/0.2)

Entry	**1** (mol l^{-1})	**2** (mol l^{-1})	Solvent	Time (h)	Conversion[a] (%)	Selectivity[a] (%) **3a**/**5a**/**6a**
1	4	1	CH_3CN/H_2O	25	96	78/4/18
2	4	1	DMF/H_2O	28	100	50/2/48
3	4	1	DMF	22	59	54/3/43

[a] Determined by GC analysis on an apolar column.

LiCl mixture. In order to evaluate the influence of the nature of the palladium precursor, we tested $PdCl_2$ replacing the $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$ mixture with the $PdCl_2$/LiCl system (Table 2).

$PdCl_2$ in combination with LiCl provides a catalyst which is slightly more selective (Table 2, entry 1) than $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$ (Table 1, entry 4), but the reaction rate appears to be much slower (25 h instead of 2.5 h with catalyst A). This rate decrease is observed whatever the solvent used, but the CH_3CN/H_2O (9/1) mixture leads to the best selectivity.

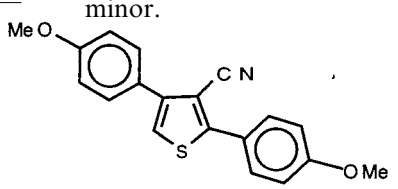
The comparison of Tables 1 and 3 underlines the influence of the phosphine ligand.

The mixture $Pd(OAc)_2/n\text{-}Bu_4NBr$ (0.05/1) exhibits a similar behaviour with or without phosphine addition. The use of $Pd(OAc)_2/n\text{-}Bu_4NBr$ without added phosphine ligand as a catalytic system (Table 3, entry 1) slightly decreases the reaction rate but leads to a better selectivity than the usual catalyst $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$ (Table 1, entry 4). The comparison of Tables 2 and 3 reveals that the $Pd(OAc)_2/n\text{-}Bu_4NBr$ (0.05/1) catalyst is as selective as the $PdCl_2$/LiCl catalytic system with a rate comparable to that with $Pd(OAc)_2/PPh_3/n\text{-}Bu_4NBr$.

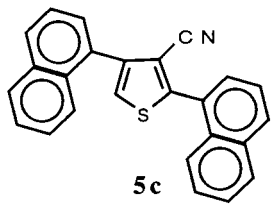
3. Scope and limitations

Attempts to achieve a Heck coupling of benzaldehyde or benzonitrile were unsuccessful. The arylation of substituted thiophenes has shown that the nature and position of the substituent influence the cross-coupling. Reactions of thiophene-3-carboxaldehyde or 3-cyanothiophene, is regioselective at position 2 (Scheme 3 and Table 4).

A cyano moiety also activates thiophene for the coupling reaction (entries 1 and 2). Although the coupling is regioselective at position 2, traces of a regioisomer resulting from a minor activation are always observed. However, these two regioisomers could not be isolated. Actually, we attribute the minor activation at position 4 in comparison with the disubstitution product also formed and which could be isolated in the case of **5b** and **5c**. Indeed, the ^{13}C-NMR analysis of disubstitution product **5b** indicates that the arylation of thiophene occurs at positions 2 and 4. So, the substitution appears to be related to the activation by the cyano group predominantly and the sulfur effect appears to be minor.



5b



5c

The reaction between 3-cyanothiophene and iodonaphthalene (entry 2) leads to a drastic loss of selectivity and 2,4-dinaphthyl-3-cyanothiophene **5c** is formed in up to 47% yield. In this case, the selectivity seems to be related to steric hindrance of the iodoaryl moiety, so the activation at position 4 is not yet negligible.

On the other hand, 2-substituted thiophenes **7** are subject to a regiospecific arylation at the 5-position, a single regioisomer **8** is obtained, no traces of substitution at the 3-position are observed. The competitive formation of biaryl **6** depends on the nature of the activating group *Z* (Scheme 2, Table 5).

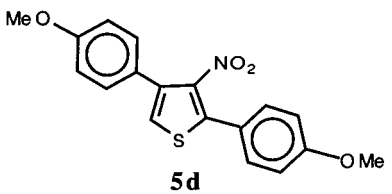
In spite of regiospecificity, thiophene-2-carboxaldehyde **7a** (Table 5, entry 1) is less reactive than thiophene-3-carboxaldehyde **1a** (Table 4, entry 1). This lack of reactivity leads to the formation of biaryl **6** as the major product. Furthermore, 2-nitrothiophene (entry 2) gives lower yields due to lack of stability of the substrate and its derivatives which are very light sensitive. Therefore, 2-nitrothiophene has to be purified before use and the reaction has to be performed in darkness. However, an isomerisation of 2-nitrothiophene can occur and lead to a loss of regiospecificity. Actually, traces of a regioisomer are detected and the formation of two monosubstituted isomers is confirmed by GC/MS coupling. A 2,4-diarylated product **5d** has been

Table 3
Arylation of thiophene-3-carboxaldehyde with iodobenzene catalysed by $Pd(OAc)_2/n\text{-}Bu_4NBr$ (0.05/1) without a phosphine ligand

Entry	**1** (mol l^{-1})	**2** (mol l^{-1})	Solvent	Time (h)	Conversion[a] (%)	Selectivity[a] (%) **3a**/**5a**/**6a**
1	4	1	CH_3CN/H_2O	5	100	74/8/16
2	8	4	CH_3CN/H_2O	3.5	100	70/15/15
3	2	1	CH_3CN/H_2O	8	100	69/4/27
4	4	4	CH_3CN/H_2O	4	98	52/24/24
5	4	1	H_2O	6	97	61/4/35

[a] Determined by GC analysis on an apolar column.

isolated and characterized by NMR spectroscopy. Both by-products could arise after the isomerization of 2-nitrothiophene into 3-nitrothiophene.



5d

Nevertheless, the arylation of 2-cyanothiophene (Table 5, entries 3–7) proceeds regiospecifically with good isolated yields and limited formation of biaryl **6**. It is noteworthy that the substitution rate and kinetic data are not really sensitive to electronic effects on the aryl iodide and to steric hindrance. Indeed, yields and reaction times are similar with electron donating as well as withdrawing substituents on the iodoaryl moiety (Table 5, entries 3–5) and with more or less sterically crowded substrates (Table 5, entries 6–7). On the contrary, sterically demanding iodoaryl reagents appear to yield less of the Ullmann type product **6** and more of the selectively Heck type product **8**.

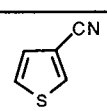
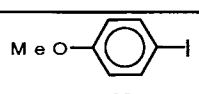
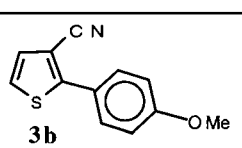
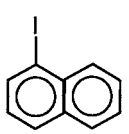
Thiophenes **1** bearing an electron withdrawing group react regioselectively at position 2 due to the balance between the sulfur and substituent effect. Substitution at position 4 can also occur but less than at position 2. On the other hand, 2-activated thiophenes are subject to a regiospecific reaction at position 5. Indeed, this position is favored by both the sulfur and the activating group effect (with conjugation). Bromoaryls may be used instead of iodoaryls. Thus, the reaction of 2-cyanothiophene **7b** with bromobenzene **2g** yields 5-phenyl-2-cyanothiophene (Scheme 3).

Although bromoaryls are less reactives than iodo ones, their use offers a larger range for synthetic applications. On the other hand, the chlorobenzene did not react with 2-cyanothiophene.

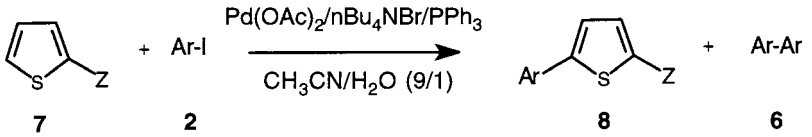
4. Conclusion

In this paper, we have shown that a one step arylation of thiophene derivatives can be performed with $Pd(OAc)_2/n\text{-}Bu_4NBr$ as catalytic system. The reaction proceeds with moderate yields with thiophene-2-carboxaldehyde and best results were obtained with 2-cyanothiophene because of a fast and regiospecific substitution. Compared to usual reactions, the large chemocompatibility of our method allows the synthesis of biaryls bearing various functional groups such as sensitive carboxaldehyde, cyano or nitro. So, this new reaction seems to be powerful for the synthesis of unsymmetrical and functionalized biaryls which are

Table 4
Arylation of 3-substituted thiophenes with various aryl iodides

Entry		Ar-I **2**	Time (hours)	Product **3**	Yield (%) GC[a]	Yield (%) isolated
1	 **1b**	 **2b**	2	 **3b**	65	30
2	"	 **2c**	7	 **3c**	44	27

[a] Determined on an apolar column.



Scheme 2. Arylation of thiophenes activated at position 2.

useful intermediates for the preparation of condensed ring systems. Research about the real nature of the catalyst to extend this reaction to other heterocycles is currently underway.

5. Experimental part

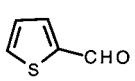
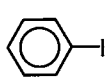
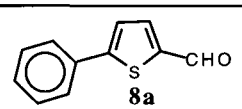
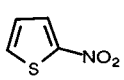
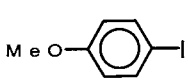
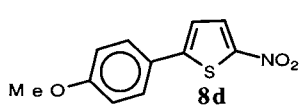
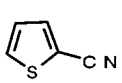
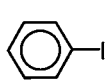
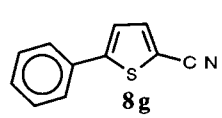
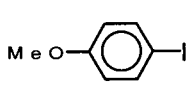
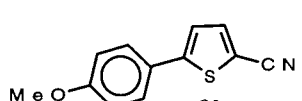
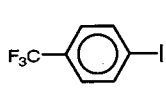
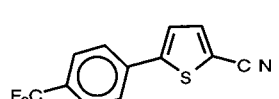
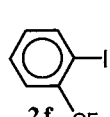
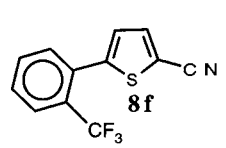
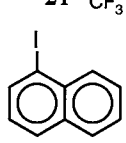
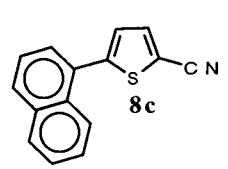
5.1. Apparatus

GC and GC-mass analysis were carried out on an apolar type column (JW DB-5, 95% dimethyl-(5%)-diphenylpolysiloxane, $L = 15$ m, $\varnothing = 0.25$ mm), GC-mass spectra were obtained on a FISONS MD 800 spectrometer. NMR spectra were recorded on a BRUKER AC 200 spectrometer.

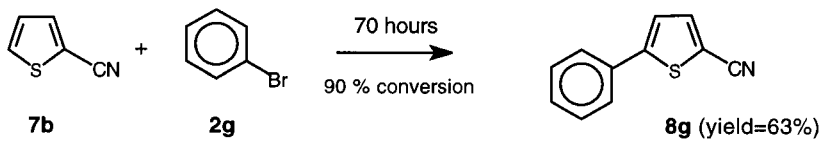
5.2. General procedure for the reactivity studies

A suspension of potassium carbonate (2.5 equivalents) and various catalytic systems in an acetonitrile/

Table 5
Arylation of thiophenes activated at position 2

Entry		Ar-I 2	Time (hours)	Product 8	Yield (%) GC[a]	isolated
1	 7a	 2a	7	 8a	41	30
2	 7d	 2b	54	 8d	61	37
3	 7b	 2a	5	 8g	89	63
4	"	 2b	4	 8b	89	77
5	"	 2e	3,25	 8e	85	79
6	"	 2f	3	 8f	96	81
7	"	 2c	4	 8c	94	77

[a] Determined on an apolar column.



Scheme 3. Phenylation of 2-cyanothiophene with bromobenzene.

water mixture (9/1) was stirred under nitrogen for 5 min. As a catalytic system either a mixture of tetra-*n*-butylammonium bromide (one equivalent) and triphenylphosphine (0.1 equivalent) and palladium acetate (0.05 equivalent) (Table 1) or a mixture of lithium chloride (0.2 equivalent) and palladium chloride (0.05 equivalent) (Table 2) or a mixture of tetra-*n*-butylammonium bromide (one equivalent) and palladium acetate (0.05 equivalent) (Tables 3–5) were used. Substituted thiophene and iodoaryl were successively added. The mixture was heated at 80°C for the time indicated. After cooling to room temperature, water and ether were added. The organic phase was washed with water and dried over $MgSO_4$. After removal of the solvent under vacuum, the substitution product was purified by column chromatography.

5.3. Typical procedure for study of the scope and limitations

A suspension of potassium carbonate (40 mmol) tetra-*n*-butylammonium bromide (16 mmol) and palladium acetate (0.8 mmol) in an acetonitrile/water mixture (3.7/0.4 ml) was stirred under nitrogen for 5 min. Substituted thiophene **1** or **7** (32 mmol) and iodoaryl **2** (16 mmol) were successively added. The mixture was heated at 80°C for the time indicated. After cooling to room temperature, water and ether were added. The organic phase was washed with water and dried over $MgSO_4$. After removal of the solvent under vacuum, the substitution product was purified by column chromatography or recrystallization.

5.4. Characterization of 2,3-disubstituted thiophenes *3*

3a. Isolated yield: 35%; colorless oil; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.26 (1H, d, $J = 5.4$ Hz), 7.48 (5H, m), 7.56 (1H, d, $J = 5.4$ Hz), 9.87 (1H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 125.1 (CH), 126.6 (CH), 128.9 (CHarom), 129.4 (Carom), 130.1 (CHarom), 131.4 (Carom), 137.1 (C), 156.1 (C), 185.8 (CHO); HRMS calc. for $C_{11}H_8OS$ (M^+): 188.0295868, found: 188.0293000. Compound **3a** is known see Ref. [11].

3b. Isolated yield: 30%; white solid; m.p. = 45.5°C; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.5 (CH_3), 105.1 (C), 114.7 (CHarom), 116.2 (CN), 123.9 (Carom), 124.5 (CH), 129.2 (CHarom), 130.2 (CH), 154.1 (C), 160.9 (Carom); HRMS calc. for $C_{12}H_9NOS$ (M^+): 215.0404858, found: 215.0412000.

3c. Isolated yield: 27%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.39 (1H, d, $J = 5.3$ Hz); 7.50 (1H, d, $J = 5.3$ Hz); 7.52–7.62 (4Hnaphtyl, M); 7.85–8.00 (3Hnaphtyl, M); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 110.5 (C); 115.0 (CN); 125.1 (CHnaphtyl); 125.2 (CHnaphtyl); 126.6 (CHnaphtyl); 126.9 (CHnaphtyl); 127.2 (CH); 128.3 (Cnaphtyl); 128.6 (CHnaphtyl); 129.2 (CHnaphtyl); 129.3 (CHnaphtyl); 130.5 (CH); 131.7 (Cnaphtyl); 133.8 (Cnaphtyl); 152.2 (C).

5.5. Characterization of 2,3,4-trisubstituted thiophenes *5*

5b. Isolated yield: 5%, yellow solid; m.p. = 137.5°C, ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.84 (3H, s); 3.86 (3H, s); 6.94 (2H, d, $J = 9.2$ Hz); 6.99 (2H, d, $J = 9.2$ Hz); 7.27 (1H, s); 7.50 (2H, d, $J = 8.7$ Hz); 7.73 (2H, d, $J = 8.7$ Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.5 ($2 \times CH_3$); 105.5 (C); 114.7 ($4 \times$ CHarom); 116.3 (CN); 124.2 ($2 \times$ Carom); 125.3 (CH); 127.3 ($2 \times$ CHarom); 128.9 ($2 \times$ CHarom); 143.2 (C); 151.8 (C); 160.2 (Carom); 160.8 (Carom); HRMS calc. for $C_{19}H_{15}NO_2S$ (M^+): 321.0823507, found: 321.0830000.

5c. Isolated yield: 12%, yellow solid; m.p. = 85°C, ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.49 (1H, s), 7.53–7.63 (8Hnaphtyl, M); 7.92–8.01 (6Hnaphtyl, M); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 11.4 (C); 115.2 (CN); 125.1 (CHnaphtyl);125.2 (CHnaphtyl); 125.3 (CHnaphtyl); 125.4 (CHnaphtyl); 126.5 (CHnaphtyl); 126.6 (CHnaphtyl); 127.2 (CHnaphtyl); 127.3 (CHnaphtyl); 128.4 (Cnaphtyl); 128.6 ($2 \times$ CHnaphtyl); 128.7 ($2 \times$ CHnaphtyl); 129.3 (CHnaphtyl); 129.7 (CHnaphtyl); 130.1 (Cnaphtyl); 130.6 (CH); 131.5 (Cnaphtyl); 131.6 (Cnaphtyl); 133.9 (Cnaphtyl); 134.0 (Cnaphtyl); 143.5 (C); 152.0 (C); HRMS calc. for $C_{25}H_{15}NS$ (M^+): 361.0925214, found: 361.0934000.

5d. Isolated yield: 4%, orange solid; m.p. = 136°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.85 (3H, s), 3.87 (3H, s), 6.96 (2H, d, $J = 8.8$ Hz), 6.97 (2H, d, $J = 8.8$ Hz), 7.50 (4H, 2d, $J = 8.8$ Hz), 7.70 (1H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.4 (CH_3), 55.5 (CH_3), 114.0 (CHarom), 114.7 (CHarom), 118.8 (CH), 122.8 (Carom), 125.0 (Carom), 127.0 (CHarom), 131.1 (CHarom), 142.5 (C), 143.5 (C), 159.6 (C), 160.3 (Carom), 160.7 (Carom).

5.6. Characterization of 2,5-disubstituted thiophenes *8*

8a. Isolated yield: 30%; yellow solid; m.p. = 89°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.39 (1H, d, $J = 4$ Hz),

7.40 (2H, dd, $J = 7.1$ Hz and $J = 8.1$ Hz), 7.42 (1H, dd, $J = 1$ Hz and $J = 8.1$ Hz), 7.66 (2H, dd, $J = 7.1$ Hz and $J = 1$ Hz), 7.72 (1H, d, $J = 4$ Hz), 9.88 (1H, 1s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 124.1 (CH), 126.4 (CHarom), 129.2 (CHarom), 129.4 (Carom), 133.0 (Carom), 137.4 (CH), 142.5 (C), 154.3 (C), 182.8 (CHO); HRMS calc. for $C_{11}H_8OS$ (M^+): 188.0295868, found: 188.0296000. Compound **8a** is known see Ref. [12].

8b. Isolated yield: 77%; brown solid; m.p. = 105.5°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.83 (3H, s), 6.93 (2H, d, $J = 8.1$ Hz), 7.14 (1H, d, $J = 3.9$ Hz), 7.50 (2H, d, $J = 8.1$ Hz), 7.62 (1H, d, $J = 3.9$ Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.5 (CH_3), 106.9 (C), 109.9 (CN), 114.7 (CHarom), 122.2 (CH), 125.0 (Carom), 127.8 (CHarom), 138.5 (CH), 151.9 (C), 160.7 (Carom); HRMS calc. for $C_{12}H_9NOS$ (M^+): 215.0404858, found: 215.0409000.

8c. Isolated yield: 77%; yellow solid; m.p. = 76°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.24 (1H, d, $J = 3.8$ Hz), 7.54 (4H, m), 7.70 (1H, d, $J = 3.8$ Hz), 7.93 (2H, m), 8.07 (1H, m); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 109.4 (CN), 114.2 (C), 124.8 (Carom), 125.2 (Carom), 125.6 (CH), 126.5 (Carom), 127.2 (Carom), 127.6 (Carom), 128.6 (Carom), 129.7 (Carom), 129.9 (Carom), 131.3 (Carom), 133.8 (Carom), 137.6 (CH), 149.6 (C); HRMS calc. for $C_{15}H_9NS$ (M^+): 235.0455712, found: 235.046600.

8d. Isolated yield: 37%; orange solid; m.p. = 135°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.96 (2H, d, $J = 8.9$ Hz), 7.13 (1H, d, $J = 4.3$ Hz), 7.57 (2H, d, $J = 8.9$ Hz), 7.88 (1H, d, $J = 4.3$ Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.5 (CH_3), 114.2 (C), 114.9 (CHarom), 121.2 (CH), 124.8 (Carom), 127.8 (CHarom), 130.0 (CH), 152.5 (C), 161.3 (Carom); HRMS calc. for $C_{11}H_9NO_3S$ (M^+): 235.0303151, found: 235.0319000.

8e. Isolated yield: 79%; yellow solid; m.p. = 108°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.36 (1H, d, $J = 4.0$ Hz), 7.63 (1H, d, $J = 4.0$ Hz), 7.71 (4H, s); HRMS calc. for $C_{12}H_6F_3NS$ (M^+): 253.0173058, found: 253.0151000.

8f. Isolated yield: 81%; yellow solid; m.p. = 48°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.12 (1H, d, $J = 3.9$ Hz), 7.48 (1H, m), 7.60 (3H, m), 7.80 (1H, m); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 110.4 (C), 113.9 (CN), 123.6 (CF_3, q, $^1J_{CF} = 272$ Hz), 126.8 (CHarom, q, $^3J_{CF} = 5.4$ Hz), 128.3 (CHarom, q, $^4J_{CF} = 2.5$ Hz), 129.4 (Carom, q, $^2J_{CF} = 30$ Hz), 129.6 (CH), 130.9 (Carom, q, $^3J_{CF} = 1.9$ Hz), 131.8 (CHarom), 133.0 (CHarom), 137.2(CH), 147.1(C); HRMS calc. for $C_{12}H_6F_3NS$ (M^+): 253.0173057, found: 253.0182000.

8g. Isolated yield: 63%; yellow solid; m.p. = 88°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.27 (1H, d, $J = 4$ Hz), 7.42 (2H, dd, $J = 5.4$ Hz and $J = 4.5$ Hz), 7.47 (1H, dd, $J = 4.5$ Hz and $J = 2.7$ Hz), 7.58 (1H, d, $J = 4$ Hz), 7.59 (2H, dd, $J = 5.4$ Hz and $J = 2.7$ Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 108.3 (C), 114.4 (CN), 123.4 (CH), 126.5 (CHarom), 129.4 (CHarom), 129.5 (Carom), 132.3 (Carom), 138.5 (CH), 151.9 (C).

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