Graphical Abstract

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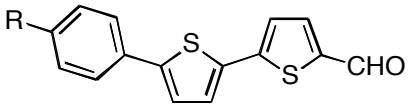
Cyril Herbivo, Alain Comel, G. Kirsch and M. Manuela M. Raposo*



R = H, alkoxy, *N,N*-dialkylamino

5a-f

Synthesis of 5-aryl-5´-formyl-2,2´-bithiophenes as new precursors for nonlinear optical (NLO) materials

Cyril Herbivo,[a] Alain Comel,[a] G. Kirsch[a] and M. Manuela M. Raposo[b]*

[a] *Laboratoire d´Ingénierie Moléculaire et Biochimie Pharmacologique, UFR SciFA, Université de Metz, 1, Boulevard Arago, Metz Technopôle, 57078 Metz Cedex 3, France*

[b] *Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*

*Corresponding author. Tel: + 351 253 604381; Fax: +351 253 604382; *e-mail:* mfox@quimica.uminho.pt

Abstract – A series of formyl-substituted 5-aryl-2,2´-bithiophenes **5** were synthesized using two different methods: Vilsmeier-Haack-Arnold reaction (VHA) or through Suzuki coupling. The synthesis of compounds **5** through the Vilsmeier-Haack-Arnold reaction, starting from inexpensive and easily available precursors such as acetophenones, gave the title compounds in low yields after four reaction steps. On the other hand Suzuki coupling of functionalized aryl boronic acids **7** and the 5-bromo-5´-formyl-2,2´-bithiophene **6** gave compounds **5** in good yields in only one step.

Keywords: Vilsmeier-Haack-Arnold (VHA) formylation, Chloroformylation, Suzuki coupling, Aldehydes, Formyl-substituted aryl-bithiophenes, π-conjugated systems, UV-visible spectroscopy, Nonlinear optical (NLO) precursors

1. Introduction

Formyl (oligo)thiophene derivatives are versatile "crossroads" intermediates. Not surprisingly, a large number of methods have been developed in order to obtain these functionalized heterocycles. Vilsmeier formylation[1] and metalation followed by quenching with DMF constitute the most important routes for the preparation of formyl-substituted (oligo)thiophenes.[1e,2]

The obtained formyl- derivatives can further react to yield more complex molecules which have made of formyl-(oligo)thiophenes some of the most important molecules to be used as building blocks in biological active compounds, supramolecular chemistry, and molecular electronics.[3]

Having in mind our recent work in which we have used formyl heterocyclic systems (oligothiophenes,[4] arylthiophenes[5] and thienylpyrroles[6]) as precursors for the synthesis of more complex molecules (dicyanovinyl-derivatives,[4a-b,7] organometallic compounds,[8] benzothiazoles,[5,9] benzimidazoles,[10] benzoxazoles,[11] imidazo-anthraquinones,[12] imidazo-phenanthrolines,[13] *bis*-indolylmethanes,[14] Schiff-bases and tertiary amines bearing crown ether moieties[15] for several optical and sensors applications, we decided to synthesize the new functionalized 5-aryl-5′-formyl-2,2′-bithiophenes which will be used in the future as versatile synthons in the preparation of a large variety of heterocyclic donor-acceptor π- conjugated systems.

As part of our continuing interest in heterocyclic derivatives for optical applications, we report in this paper the synthesis and the UV-visible study of the new 5-formyl-5′-aryl-2,2′-bithiophenes, **5** which have the conjugated 5-alkoxyaryl- or 5-*N,N*-dialkylaminoaryl-2,2′-bithiophene, as strong π-electron donor moieties.

2. Results and discussion

2.1. Synthesis

Recently we have reported the synthesis and the characterization of 5-alkoxy- and 5-*N,N*-dialkylamino-5′-formyl-2,2′-bithiophenes **8**[4a] (Figure 1). Formyl derivatives **8** were prepared by functionalization of 5-alkoxy- or 5-*N,N*-dialkylamino-2,2′-bithiophenes[16] through the Vilsmeier-Haack reaction or through lithiation followed by quenching with DMF. Formyl-terthiophenes **9**[4b] were also reported by us through Stille coupling reaction. The stannylated derivatives, readily prepared from 5-*N,N*-dialkylamino-2,2′-bithiophenes were coupled with 2-bromo-5-formylthiophene to give the expected products. More recently we also reported the synthesis of 2-formyl-5-arylthiophenes **10**[5] (Figure 1) through Suzuki coupling. Formyl derivatives **8** and **10** were used as precursors for the synthesis of several heterocyclic derivatives with interesting optical applications (e.g. solvatochromic probes, fluorescent markers, nonlinear optical materials and colorimetric and fluorimetric sensors).[4a,5,8,9a,c,12a,13]

On the basis of our recent results we decided to synthesize the new 5-alkoxy- or 5-*N,N*-dialkylaminoaryl-5′-formyl-2,2′-bithiophenes **5** in order to study the influence of the structure modification (*i.e.* the lenght and the electronic nature of the π-conjugated

bridge) on the optical properties (UV-visible) of compounds **5** and also to compare them with our recently reported systems containing the bithiophene **(8)**, terthiophene **(9)** or arylthiophene (**10**) entities.[4a-b,5]

In order to choose the most efficient method for the synthesis of the mentioned formyl derivatives, compounds **5** with aryl and bithiophene units acting as linking π-conjugated bridges between the donor groups (alkoxy, *N,N*-dialkylamino) and the formyl functionality were synthesized using two different methods: a simple multi-step procedure: Vilsmeier-Haack-Arnold reaction (VHA)[17], or through Suzuki coupling.[5]

2.1.1. Synthesis of compounds 5 through Vilsmeier-Haack-Arnold (VHA) reaction

Compounds **5** were first synthesized through a sequence in which the first step was VHA[17] reaction starting from inexpensive and easily available precursors (Scheme 1). The starting acetophenones **1a-b** were commercially available while compounds **1c-f** were prepared according previously published procedures[18-21] Therefore, compounds **2** were prepared from acetophenones **1a-f** through Vilsmeier-Haack-Arnold (VHA) reaction to give β-chloro-β-arylacroleins **2a-f** in moderate to excellent yields (40-99%) (Table 1). Compounds **2a-b**,[17c] **2c**[22] and **2d**[17c] were described previously using the same experimental procedure. Compounds **2a-f** were converted to the arylthienyl-ethanones **3a-f** in fair to excellent yields, 23-95%, through condensation with sodium sulfide, monohydrate or $Na_2S.9H_2O$, in DMF in the presence of chloroacetone and base (K_2CO_3) at 60 ^oC. Compounds **3a**[23] and 3**b**[24] have been previously reported. Although thiophene **3a**[23] is largely described by palladium catalyzed coupling reaction in the literature, preparation of **3b**[24] is only reported by building of the thiophene ring and derivatives **3c-f** remain surprisingly undescribed. The new compounds **3c-f** were prepared by us, in moderate to excellent yields (50-95%). The second VHA reaction on arylthienyl-ethanones **3** gave compounds **4** in fair to excellent yields (10-99%). Finally, the second condensation of sodium sulfide, with compounds **4**, using the same experimental conditions described above gave the 5-formyl-5'-(4-substituted-phenyl)-2,2'-bithiophenes **5** in fair to moderate yields.

Although the very low global yields for the synthesis of aldehydes **5** using the VHA reaction this synthetic route seems to have some interest due to its originality which lies

on the double use of the classical combination of VHA reaction and condensation with sodium sulfide to obtain functionalized aryl-bithiophenes. Even in our case the Vilsmeier-Haack-Arnold reaction were not very successful due to the lower yields, there are several reported examples in which the VHA formylation works very well demonstrating the synthetic potential of this reaction.[17]

<Scheme 1>

<Table 1>

2.1.2. Synthesis of compounds 5 through Suzuki coupling

Secondly, formyl compounds **5** were synthesized through a Suzuki cross-coupling reaction of commercially available arylboronic acids **6a-d** with 5'-bromo-5-formyl-2,2'-bithiophene **7**. Precursor **7** was obtained from commercial 5-formyl-2,2'-bithiophene by bromination with NBS in DMF in 98 % yield.[11c] The Suzuki coupling reactions were performed in 1,2-dimethoxyethane (DME) and aqueous 2 M Na_2CO_3 (2 equiv.) under an argon atmosphere and $Pd(PPh_3)_4$ (6 mol%) was used as palladium catalyst at 80 °C[5] for 2–24 h (Scheme 2). Formyl derivatives **5** were obtained in good yields 53-80% (Table 2).

<Scheme 2>

<Table 2>

Bithiophenes **5** are rarely described in the literature. The preparation of compound **5a** by building of the thiophene ring using a three steps synthetic way is reported in a patent[25a] but only elemental analyses are given. More recently the synthesis of the same compound has been described through Suzuki coupling of phenyl boronic acid and 5-formyl-5´-iodo-2,2'-bithiophene using different coupling conditions and again no experimental data are reported.[25b] The synthesis of 5-formyl-5'-(4-*N,N*-dimethylaminophenyl)-2,2'-bithiophene **5d** have been reported by Mignani,[2a] et al (overall yield 20 % yield) through Negishi coupling between 2,2´-bithiophen-5-yl zinc chloride with 1-bromo-4-*N,N*-dimethylaminobenzene followed by lithiation and reaction with DMF in THF. No experimental details or analytical data about the derivative were given. More recently the same formyl derivative **5d** was prepared by Clays *et al*[26] in 97 % yield, through Suzuki coupling using the same coupling

components described by us but sligtly different reaction conditions (1 eq. of aldehyde **7**, 1.2 eq. of boronic acid **6d**, (10 mol%) of $Pd(PPh_3)_4$ and 10 eq. of K_2CO_3, toluene, reflux). In comparison to the method described earlier, compound **5d**, was obtained by us, through our experimental conditions, in a similar yield (64%). Attempts to synthesize compound **5d** using the same experimental procedure described by Clays *et al*, gave, in our hands, the expected compound but only in 65% yield after 24 h of reflux (Table 2). More recently the synthesis of compound **5e** has been described in a Japanese patent[27] through Suzuki coupling using 5-formyl-5'-bromo-2,2'-bithiophene and 4-(*N,N*-diethylamino)phenyl boronic acid as coupling components. Unfortunately, the details concerning the practical procedure are given in Japanese. The formyl derivative **5e** was used as precursor in the preparation of organic electroluminescent materials.

The synthesis of compounds **5** through Vilsmeier-Haack-Arnold reactions gave the title compounds in low yields after four reaction steps. In comparison to the first method described earlier, compounds **5a-d** were prepared by Suzuki coupling in higher yields using only one step, from commercially available reagents, using simple work-up procedures, resulting in good yielding preparation and ease of isolation of these derivatives. Moreover, compound **5c** which was not possible to obtain using the VHA reaction was prepared through Suzuki coupling in a good yield (80%).

The structures of compounds **5** were unambiguously confirmed by their analytical and spectral data.

2.2. UV-visible study of formyl-aryl-2,2´bithiophenes 5

The electronic spectra of formyl-aryl-2,2´bithiophenes **5**, recorded in ethanol solutions (10^{-4} M) showed an intense lowest energy charge-transfer absorption band in the UV-visible region. The position of this band depended on the electronic nature of the substitutent (H, alkoxy, or *N,N*-dialkylamino) at position 4 of the aryl moiety (Table 3). The reason for the substantial red shift in the investigated compounds **5b-f**, functionalized with donor groups, λ_{max}= 397.0-442.0 nm, relative to that of unsubstituted formyl-aryl-2,2´bithiophene **5a** (λ_{max}= 382.5 nm) was the strong inductive and conjugative effect of the alkoxy and *N,N*-dialkylamino substituents at the *para* position of the phenyl ring.

The influence of the strength of the donor group was demonstrated by comparison of the absorption maxima of compounds **5b** and **5e** as the longest wavelength transition was shifted from 397.0 nm in 5-formyl-5'-(4-methoxyphenyl)-2,2'-bithiophene **5b** to 442.0 nm in 5-formyl-5'-(4-*N,N*-diethylaminopheny)-2,2'-bithiophene **5e** (Table 3, entries 2 and 5 respectively).
The shifts of the absorption maxima were proportional to the intramolecular charge-transfer (ICT) between the electron-releasing and withdrawing group. In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption.[28]

At this stage, a comparison could also be made between the UV-visible study of the new 5-formyl-5'-aryl-2,2'-bithiophenes **5** with 5-formyl-5'-alkoxy- and 5-*N,N*-dialkylamino-2,2'-bithiophenes **8**,[4a] formyl- *N,N*-dialkylamino-terthiophenes **9**[4b] and 5-formyl-2-arylthiophenes **10**[5], recently reported by us (Figure 1). The nature of the thiophenic bridge had a clear influence on the absorption bands of compounds **5**, **8**, **9** and **10**. The obtained results showed that, the substitution of a benzene ring by a thiophene on the π-conjugated bridge, while maintaining the same donor group produced a bathochromic shift on the absorption wavelength maxima (see, for example, the comparison between **10d**, R = NMe_2, λ_{max}= 410.0 nm, with **8d**, R = NMe_2, λ_{max}= 451.0) (Table 3, entry 4) or comparison between **8d** with **9d**, R = NMe_2, λ_{max}= 465.5.[4b] This observation clearly indicates that the incorporation of thiophene units in push-pull compounds enhances their charge-transfer properties. The optical data obtained are not surprising and could be explained having in mind the bathochromic effect of sulphur, the partial decrease of aromatic character of the thiophene heterocycle compared to benzene and also the increase of the π-overlap between the thiophene units.[4b,29]

The wavelength of maximum absorption for compounds **5** compared to compounds **10** was shifted to longer wavelengths (20.5-95.5 nm) as the number of thiophene units increased, as expected from the increase in conjugation. The same trend was observed also for the formyl-terthiophene derivative **9d** (λ_{max}= 465.5 nm) compared to the formyl-bithiophene **8d** (λ_{max}= 451.0 nm). In the case of alkoxyphenyl-2,2´-bithiophene derivatives **5a**-**b** a bathochromic shift of 12-15 nm was also observed in comparison to the alkoxy-2,2´-bithiophenes **8a**-**b** due to the introduction of a benzene ring on the

bithienyl conjugated bridge. On the contrary, comparison of the wavelength of maximum absorption of the *N,N*-dialkylaminophenyl-2,2´-bithiophenes **5d** and **5e** with *N,N*-dialkylamino-2,2´-bithiophenes **8d** and **8e** functionalized with the same donor groups, showed that although compounds **8d-e** contain a smaller π-conjugating system constituted by the bithienyl moiety, the wavelength of their maximum absorption exhibits batochromic shifts of 21 nm. This experimental result could perhaps be explained by evoking the auxiliary donor effect of the electron-rich thiophene heterocycle[7,9b,10,30] directly linked to the stronger *N,N*-dialkylamino donor groups, in compounds **8d-e**, and also some lost of planarity of molecules **5d-e** in which the *N,N*-dialkylamino donor groups are linked on 4-position on the benzene ring.

<Figure 1>

<Table 3>

3. Conclusions

In summary, we have achieved the first synthesis of a series of 5-formyl-5´-(aryl-2,2´-bithiophenes **5** through two different synthetic strategies: a sequence using Vilsmeier-Haack-Arnold reaction and Suzuki coupling. As far as we know this is the first time that the double use of the classical combination between VHA reaction and condensation with sodium sulfide was used to synthesize functionalized aryl-bithiophenes. Commercial reagents and simple and convenient procedures were used in the preparation of the mentioned compounds in both synthetic routes.

The formyl- derivatives **5** studied exhibit an absorption band in the UV-visible range influenced by electronic nature of the substituent on the 4-position of the aryl-bithienyl π-conjugated bridge. Compounds **5** revealed also good optical properties compared to similar formyl derivatives **8-10**.

In agreement with previous findings[4a-b,5,7,9] the new compounds have potential importance in the manufacture of new materials for several optical applications. Therefore, the conjugated formyl derivatives of 5-arylbithiophenes **5** will be used in the future, as precursors in the preparation of compounds with stronger electron withdrawing groups which should exhibit strong NLO properties.[4a-b,7]

4. Experimental

4.1. General

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh). IR spectra were determined on a BOMEM MB 104 spectrophotometer using KBr discs or nujol. UV-visible absorption spectra (200 – 800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. ^{1}H NMR spectra were recorded on a Varian 300 spectrometer in $CDCl_3$ at 300 MHz at 25 ºC. All chemical shifts are given in ppm using δ_H Me_4Si = 0 ppm as reference and *J* values are given in Hz. ^{13}C NMR spectra were run in the same instrument at 75.4 MHz using the solvent peak as internal reference (Braga, Portugal). ^{1}H NMR spectra were also recorded on a AC Bruker 250 MHz spectrometer. ^{13}C NMR spectra were run in the same instrument at 62.9 MHz using the solvent peak as internal reference (Metz, France). Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. Mass spectrometry analyses were performed at the "C.A.C.T.I. -Unidad de Espectrometria de Masas" at the University of Vigo, Spain. Elemental analyses were carried out on a Leco CHNS 932 instrument.

Acetophenone **1a** and 4-methoxyacetophenone **1b** used as precursors for the synthesis of compounds **5** were purchased from Aldrich and Acros and used as received.

The synthesis of arylacrylaldehydes **2a-b**[17c], **2 d**[17c] and 5-bromo-5'-formyl-2,2'-bithiophene **7**[11c] was described elsewhere.

4.2. Synthesis of acetophenones 1c-f

4.2.1. 4-Ethoxyacetophenone (1c). To a solution of 4-hydroxyacetophenone (68 g, 0.5 mol) in 250 ml of DMF was added bromoethane (65.4 g, 0.6 mol) and K_2CO_3 (83 g, 0.6 mol). The mixture was stirred at 60°C during one day, cooled at room temperature and quenched in a mixture of ice and water. The product was filtered and washed with water to afford the 4-ethoxyacetophenone 77g (94%) as a pale brown solid. Mp 38-39°C (lit.[18]

34-38°C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.42 (t, 3H, *J*=5.1Hz), 2.52 (s, 3H), 4.07 (q, 2H, *J*=5.1Hz), 6.95 (d, 2H, 7.5Hz), 7.90 (d, 2H, *J*=7.5Hz).

4.2.2. 4-*N,N*-Dimethylaminoacetophenone (1d). To a solution of 4-aminoacetophenone (27 g, 0.2 mol) in 200 ml of DMF was added iodomethane (62 g, 0.44 mol) and K_2CO_3 (61 g, 0.44 mol). The mixture was stirred at 60°C during one day, cooled at room temperature and quenched with a mixture of ice and water. The product was filtered and washed with water to afford the 4-*N,N*-dimethylaminoacetophenone (31 g, 95%) as a white solid. Mp 108-109°C (lit.[19] 105°C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.05 (s, 6H), 6.64 (d, 2H, *J*=7.5Hz), 7.86 (d, 2H, *J*=7.5Hz).

4.2.3. 4-*N,N*-Diethylaminoacetophenone (1e). To a solution of 4-aminoacetophenone (20 g, 148 mmol) in 150 ml of DMF was added bromoethane (35.5 g, 326 mmol), K_2CO_3 (50 g, 355 mmol) and KI (27 g, 326 mmol). The mixture was stirred at 60°C during one day, cooled at room temperature and quenched with a mixture of ice and water. The product was filtered and washed with water to afford (32 g, 99%) of 4-*N,N*-diethylaminoacetophenone as a pale yellow solid. Mp 44-45°C (lit.[20] 47-48°C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.18 (t, 6H, *J*=7.0Hz), 2.49 (s, 3H), 3.39 (q, 4H, *J*=7.0Hz), 6.60 (d, 2H, 7.2Hz), 7.82 (d, 2H, *J*=7.2Hz).

4.2.4. 4-Pyrrolidinoacetophenone (1f). To a solution of 4-aminoacetophenone (20 g, 148 mmol) in 300 ml of DMF was added 1,4-dichlorobutane (20.7 g, 163 mmol), K_2CO_3 (52 g, 370 mmol) and KI (55 g, 326 mmol). The mixture was stirred at 60°C during two days, cooled at room temperature and quenched with a mixture of ice and water. The product was filtered and washed with water to afford (24g, 84%) of 4-pyrrolinoacetophenone as a pale orange solid. Mp. 127-128°C (lit.[21] 134-135°C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.18 (q, 4H, *J*=6.7Hz), 2.49 (s, 3H), 3.33 (q, 4H, *J*=6.7Hz), 6.48 (d, 2H, 7.0Hz), 7.84 (d, 2H, *J*=7.0Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 25.4, 25.7, 47.8, 111.8, 126.6, 130.2, 151.0, 196.2.

4.3. General procedure for the Vilsmeier-Haack-Arnold reaction of acetophenones 1 to give β-chloro β-aryl propenal **2**

$POCl_3$ (17 ml, 182 mmol) was slowly added to DMF (20 ml, 255 mmol) at 0 °C and the mixture was stirred for 10 min. at 0° C. After this time a solution of acetophenones **1** (148 mmol) in DMF (150 ml) was added dropwise with stirring. The reaction mixture was then heated 3 h at 60 °C. The solution cooled at room temperature was then poured slowly into a sodium acetate aqueous solution (10%). The pH was adjusted at 4 with sodium acetate. The solid obtained was filtered and washed with water to afford compounds **2a-f** wish were used in the next reaction step without further purification.

4.3.1. β-Chloro-β-(4-ethoxyphenyl)-propenal (2c). Orange solid (85%). Mp 40-41°C (lit.[22] 44 °C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.44 (t, 3H, *J*=7.0Hz), 4.1 (q, 2H, *J*=7.0Hz), 6.65 (d, 1H, *J*=7.0Hz), 6.8 (d, 2H, *J*=9.0Hz), 7.3 (d, 2H, *J*=9.0Hz), 10.1 (d, 1H, *J*=7.0Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.6, 63.7, 114.4, 122.3, 130.5, 152.2, 162.1, 191.5.

4.3.2. β-Chloro-β-(4-*N*,*N*-diethylaminophenyl)-propenal (2e). Orange solid (52%). Mp 80-81°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.16 (t, 6H, *J*=7.1Hz), 3.43 (q, 4H, *J*=7.1Hz), 6.54 (d, 1H, *J*=7.5Hz), 6.63 (d, 2H, *J*=9.0Hz), 7.65 (d, 2H, *J*=9.0Hz), 10.12 (d, 1H, *J*=7.5Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 12.2, 45.3, 111.6, 119.7, 129.2, 132.0, 149.7, 152.7, 191.6.

4.3.3. β-Chloro-β-(4-pyrrolidinophenyl)-propenal (2f). Green solid (99%). Mp 120-121°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.03 (q, 4H, *J*=3.4Hz), 3.36 (t, 4H, *J*=3.4Hz), 6.55 (d, 2H, *J*=8.9Hz), 6. 60 (d, 1H, *J*=7.0Hz), 7.66 (d, 2H, *J*=8.9Hz),10.13 (d, 1H, *J*=7.0Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 25.4, 47.6, 111.9, 119.0, 121.0, 113.9, 150.3, 153.4, 191.6.

4.4. General procedure for the synthesis of arylthenyl-ethanones 3a-f

To a solution of $Na_2S.9H_2O$ (30.5 g, 127 mmol) and DMF (200 ml) was added β-chloroacroleine (127 mmol). The mixture was stirred at 60°C during 2 hours. Chloroacetone (11.7 g, 127 mmol) was added rapidly and the reaction was stirred during 3 hours at 60°C. K_2CO_3 (17.6 g, 127 mmol) was dissolved in water (1 ml) and added to the reaction. The mixture was stirred during 10 minutes at 60°C, cooled at

room temperature and quenched in water. The solid obtained was filtered and the crude product was washed with water and recristalysed from ethanol.

4.4.1. 1-(5-Phenylthiophen-2-yl)ethanone (3a). Dark brown solid (23%). Mp 101-102°C (lit.[23] 109-110°C). IR (nujol) ν 1650 (C=O), 1531, 1274, 1087, 1074, 999, 966, 926, 909, 843, 808, 757, 720, 688, 661, 641, 611, 590 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 2.54 (s, 3H), 7.32 (d, 1H, *J*=4.0Hz), 7.41 (m, 3H), 7.64 (m, 2H), 7.66 (d, 1H, *J*=4.0Hz). ^{13}C NMR (62.9MHz, $CDCl_3$) δ 26.0, 123.3, 125.7, 128.5, 128.6, 132.8, 132.9, 142.5, 152.3, 190.1.

4.4.2. 1-(5-(4-Methoxyphenyl)thiophen-2-yl)ethanone (3b). Dark brown solid (77%). Mp 156-157°C (lit.[24] 150-152°C). ^1H NMR (250 MHz, $CDCl_3$) δ 2.55 (s, 3H), 3.85 (s, 3H), 6.95 (d, 2H, *J*=8.8Hz), 7.21 (d, 1H, *J*=3.9Hz), 7.59 (d, 2H, *J*=8.8Hz), 7.63 (d, 1H, *J*=3.9). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 44.2, 56.5, 111.2, 120.2, 121.0, 127.3, 133.8, 140.6, 147.3, 155.7, 190.2.

4.4.3. 1-(5-(4-Ethoxyphenyl)thiophen-2-yl)ethanone (3c). Dark brown solid (95%). Mp 117-118°C. IR (nujol) ν 1651 (C=O), 1603, 1571, 1533, 1509, 1311, 1083, 1034, 962, 921, 893, 838, 797, 748, 723, 695, 642, 628, 610, 591, 535 cm^{-1}. ^1H NMR (250MHz, $CDCl_3$) δ 1.42 (t, 3H, *J*=3.1Hz), 2.59 (s, 3H), 4.07 (q, 2H, *J*=3.1Hz), 6.91 (d, 2H, *J*=8.85Hz), 7.20 (d, 1H, *J*=3.95), 7.56 (d, 2H, *J*=8.85Hz), 7.62 (d, 1H, *J*=3.95Hz). ^{13}C NMR (62.9MHz, $CDCl_3$) δ 12.5, 26.3, 44.4, 111.4, 120.2, 121.0, 127.5, 133.9, 140.3, 148.3, 154.6, 190.3. MS (EI) *m/z* (%): 246 (M^+, 75), 231 (30), 218 (20), 203.0 (100), 189 (10), 175 (11), 147 (11), 131 (12), 121 (5), 102 (7). HRMS: m/z (EI) for $C_{14}H_{14}O_2S$; calcd 246.0715; found: 246.0712.

4.4.4. 1-(5-(4-*N*,*N*-Dimethylaminophenyl)thiophen-2-yl)ethanone (3d). Dark brown solid (59%). Mp 124-125°C. IR (nujol) ν 1699 (C=O), 1650, 1601, 1515, 1354, 1270, 1194, 1155, 1093, 1077, 1033, 1014, 961, 922, 899, 813, 769, 747, 735, 724, 685, 633, 609 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.02 (s, 6H), 6.70 (d, 2H, *J*=8.8Hz), 7.15 (d, 1H, *J*=4.0Hz), 7.53 (d, 2H, *J*=8.8Hz), 7.60 (d, 1H, *J*=4.0Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 47.6, 55.2, 112.0, 120.5, 121.0, 127.6, 134.2, 140.0, 148.3,

154.8, 190.2. MS (EI) *m/z* (%): 245 (M^+, 100), 230 (60), 202 (40), 158 (55). HRMS: m/z (EI) for $C_{14}H_{15}NOS$; calcd 245.0874; found: 245.0871.

4.4.5. 1-(5-(4-*N*,*N*-Diethylaminophenyl)thiophen-2-yl)ethanone (3e). Dark brown solid (64%). Mp 90-91°C. IR (nujol) ν 1651 (C=O), 1608, 1517, 1290, 1231, 1193, 1168, 1090, 1064, 1035, 1008, 963, 945, 922, 869, 813, 798, 722, 614, 514 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.20 (t, 6H, *J*=5.47Hz), 2.52 (s, 3H), 3.38 (q, 4H, *J*=5.47Hz), 6.65 (d, 2H, *J*=9Hz), 7.12 (d, 1H, *J*=4Hz), 7.50 (d, 2H, *J*=9Hz), 7.59 (d, 1H, *J*=4Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 25.4, 26.3, 47.5, 112.0, 120.4, 120.9, 127.5, 133.5, 140.3, 149.4, 153.8, 190.4. MS (EI) *m/z* (%): 273 (M^+, 39), 258 (100), 230 (30). HRMS: m/z (EI) for $C_{16}H_{19}NOS_2$; calcd 273.1187; found: 273.1192.

4.4.6. 1-(5-(4-(Pyrrolidinophenyl)thiophen-2-yl)ethanone (3f). Dark brown solid (50%). Mp 198-199°C. IR (nujol) ν 1643 (C=O), 1605, 1536, 1519, 1483, 1316, 1288, 1249, 1229, 1214, 1183, 1119, 1087, 1030, 1006, 969, 955, 921, 894, 862, 815, 809, 862, 697, 666, 609, 596, 521 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 2.03 (qu, 4H, *J*=2.5Hz), 2.53 (s, 3H), 3.33 (t, 4H, *J*=2.5Hz), 6.55 (d, 2H, *J*=7.5Hz), 7.14 (d, 1H, *J*=5Hz), 7.52 (d, 2H, *J*=7.5Hz), 7.61 (d, 1H, *J*=5Hz). ^{13}C NMR (62.9MHz, $CDCl_3$) δ 25.4, 26.3, 47.5, 111.7, 120.4, 120.9, 127.3, 133.9, 140.3, 148.4, 154.8, 190.2. MS (EI) *m/z* (%): 271 (M^+, 100), 270 (80), 228 (25), 215 (25), 184 (11). HRMS: m/z (EI) for $C_{16}H_{17}NOS$; calcd 271.1031; found: 271.1032.

4.5. General procedure for the Vilsmeier-Haach-Arnold reaction of ethanones 3a-f to give β-chloro-β-arylthienyl-propenal 4a-f

$POCl_3$ (17 ml, 182 mmol) was slowly added to DMF (20 ml, 255 mmol) at 0 °C and the mixture was stirred for 10 min. at 0° C. After this time a solution of acetophenones **1** (148 mmol) in DMF (150 ml) was added dropwise with stirring. The reaction mixture was then heated 3 h at 60 °C. The solution cooled at room temperature was then poured slowly into a sodium acetate aqueous solution (10%). The pH was adjusted at 4 with sodium acetate. The solid obtained was filtered and washed with water to afford compounds **4** which were used in the next reaction step without further purification.

4.5.1. β-Chloro-β-(5-phenylthiophen-2-yl)-propenal (4a). Dark brown solid (10%). Mp 105-106°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.59 (d, 1H, *J*=6.9Hz), 7.33 (d, 1H, *J*=4.0Hz), 7.41 (m, 3H), 7.64 (m, 3H), 10.16 (d, 1H, *J*=6.9Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 115.5, 122.2, 123.1, 126.4, 127.5, 132.6, 137.4, 145.2, 151.3, 161.3, 190.3.

4.5.2. β-Chloro-β-(5-(4-methoxyphenyl)thiophen-2-yl)-propenal (4b). Dark brown solid (25%). Mp 126-127°C. ^{1}H NMR (250MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.55 (d, 1H, *J*=6.9Hz), 6.96 (d, 2H, *J*=8.8Hz), 7.20 (d, 1H, *J*=4.0Hz), 7.52 (d, 2H, *J*=8.8Hz), 7.61 (d, 1H, *J*=4.0Hz), 10.12 (d, 1H, *J*=6.9Hz). ^{13}C NMR (62.9MHz, $CDCl_3$) δ 57.5, 115.6, 121.2, 123.1, 126.2, 127.5, 132.5, 137.5, 145.0, 151.2, 160.0, 191.2.

4.5.3. β-Chloro-β-(5-(4-ethoxyphenyl)thiophen-2-yl)-propenal (4c). Dark brown solid (50%). Mp 120-121°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.27 (t, 3H, *J*=2.4Hz), 3.84 (q, 2H, *J*=2.4Hz), 6.36 (d, 1H, *J*=6.9Hz), 6.73 (d, 2H, *J*=8.8Hz), 7.01 (d, 1H, *J*=4.0Hz), 7.34 (d, 2H, *J*=8.8Hz), 7.42 (d, 1H, *J*=4.0Hz), 9.93 (d, 1H, *J*=6.9Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ14.6, 63.3, 115.3, 121.0, 123.8, 126.4, 127.2, 132.3, 137.8, 145.0, 151.2, 160.0, 191.3.

4.5.4. β-Chloro-β-(5-(4-*N*,*N*-dimethylaminophenyl)thiophen-2-yl)-propenal (4d). Dark brown solid (99%). Mp 74-75°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.00 (s, 6H), 6.04 (d, 1H, *J*=7.5Hz), 6.65 (d, 2H, *J*=8.8Hz), 7.03 (d, 1H, *J*=4.0Hz), 7.49 (d, 2H, *J*=8.8Hz), 7.62 (d, 1H, *J*=4.0Hz), 10.12 (d, 1H, *J*=7.5Hz).^{13}C NMR (62.9 MHz, $CDCl_3$) δ 55.4, 114.6, 120.6, 122.7, 125.6, 127.0, 132.1, 137.0, 144.5, 150.6, 160.4, 190.7.

4.5.5. β-Chloro-β-(5-(4-*N*,*N*-Diethylaminophenyl)thiophen-2-yl)-propenal (4e). Dark brown solid (70%). Mp 74-75°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.21 (t, 6H, *J*=6.75Hz), 3.83 (q, 4H, *J*=6.75Hz), 6.32 (d, 1H, *J*=6.92Hz), 6.69 (d, 2H, *J*=8.82Hz), 6.98 (d, 1H, *J*=4.05Hz), 7.29 (d, 2H, *J*=8.82Hz), 7.38 (d, 1H, *J*=4.05Hz), 9.88 (d, 1H, *J*=6.92Hz). ^{13}C NMR (62.9MHz, $CDCl_3$) δ 25.5, 43.6, 111.5, 119.3, 120.4, 127.2, 132.6, 134.9, 144.7, 148.4, 152.5, 160.3, 190.7.

4.5.6. β-Chloro-β-(5-(4-(pyrrolidino)phenyl)thiophen-2-yl)-propenal (4f). Dark brown solid (99%). Mp 115-116°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.00 (q, 4H, *J*=3.6Hz), 3.30 (t, 4H, *J*=3.6Hz), 6.51 (d, 1H, *J*=7.0Hz), 6.55 (d, 2H, *J*=8.8Hz), 7.14 (d, 1H, *J*=4.1Hz), 7.48 (d, 2H, *J*=8.8Hz), 7.60 (d, 1H, *J*=4.1Hz), 10.10 (d, 1H, *J*=7.0Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 25.3, 44.3, 111.6, 120.5, 122.6, 127.0, 127.5, 128.1, 133.8, 136.9, 146.8, 147.6, 191.5.

4.6. General procedure for the synthesis of 5-formyl-5'-aryl-2,2'-bithiophenes 5a-f

To a solution of $Na_2S.9H_2O$ (30.5 g, 127 mmol) and DMF (200 ml) was added β-chloroacroleine (127 mmol). The mixture was stirred at 60°C during 2 hours. Chloroacetaldehyde (11.7 g, 127 mmol) was added rapidly and the reaction was stirred during 3 hours at 60°C. K_2CO_3 (17.6 g, 127 mmol) was dissolved in water (1 l) and added to the reaction. The mixture was stirred during 10 minutes at 60°C, cooled at room temperature and quenched in water. The mixture was filtered and the crude was washed with water. The solid was recristalyzed from ethanol and purified through column chromatography on silica with increasing amounts of dichloromethane in light petroleum as eluent.

4.6.1. 5-Formyl-5'-phenyl-2,2'-bithiophene (5a).[25] Brown solid (22%). Mp 119-120°C. UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 382.5 (26,609). IR (nujol) ν 1654 (C=O), 1546, 1516, 1300, 1229, 1152, 1100, 1077, 1052, 1027, 998, 955, 906, 813, 798, 755, 723, 699, 687, 668, 627, 598, 580, 546 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.38 (m, 1H, 4"-H), 7.44 (m, 2H, 3"-H and 5"-H), 7.55 (d, 1H, 3.9Hz, 4-H), 7.59 (d, 1H, 3.9Hz, 3'-H), 7.62 (d, 1H, 3.9Hz, 3-H), 7.72 (m, 2H, 2"-H and 6"-H), 8.00 (d, 1H, 3.9Hz, 4'-H), 9.88 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 125.2, 125.3, 125.4, 128.2, 128.4, 129.2, 132.7, 134.2, 139.2, 141.2, 145.0, 145.3, 183.8. MS (EI) *m/z* (%): 270 (M^+, 45), 241 (6), 213 (12), 197 (16), 185 (16), 129 (26), 97 (35), 95 (29), 83 (38), 81 (64), 69 (100). HRMS: m/z (EI) for $C_{15}H_{10}OS_2$; calcd 270.0173; found: 270.0170.

4.6.2. 5-Formyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (5b). Orange solid (44%). Mp 134-135°C. UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 394.5 (27,936) inf. 323.5 (4,816). IR (nujol) ν 1665 (C=O), 1606, 1571, 1548, 1522, 1504, 1417, 1309, 1287, 1255, 1226, 1213, 1179, 1113, 1051, 1027, 958, 830, 795, 753, 722, 697, 669, 629, 594 cm^{-1}. ^{1}H

NMR (300MHz, DMSO-d_6) δ 3.79 (s, 3H, OCH_3), 7.00 (d, 2H, *J*=9.0Hz, 3”-H and 5”-H), 7.45 (d, 1H, *J*=3.9Hz, 4-H), 7.51 (d, 1H, *J*=3.9Hz, 3’-H), 7.57 (d, 1H, *J*=3.9Hz, 3-H), 7.63 (d, 2H, *J*=9.0Hz, 2”-H and 6”-H), 7.98 (d, 1H, *J*=3.9Hz, 4’-H), 9.87 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 55.3, 79.2, 114.7, 124.1, 124.8, 125.5, 126.9, 128.3, 133.1, 139.3, 145.2, 145.6, 159.5, 183.8. MS (EI) *m/z* (%): 301 (M+, 100), 288 (33), 239 (30), 197 (60). HRMS: *m/z* (EI) for $C_{16}H_{12}O_2S_2$; calcd 301.03515; found: 301.03501. Anal. Calcd. for $C_{16}H_{12}O_2S_2$: C, 63.97; H, 4.03; S, 21.35. Found: C, 63.64; H, 3.99; N, 11.47; S, 20.57.

4.6.3. 5-Formyl-5'-(4-*N,N*-dimethylaminophenyl)-2,2'-bithiophene (5d).[2a,26] Orange solid (44%). Mp 228-230°C (lit[26] 228-230°C). UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 424.0 (24,538), 322.0 (10,448) inf. 352.0 (6,375). IR (nujol) ν 1657 (C=O), 1644, 1606, 1553, 1546, 1526, 1507, 1326, 1293, 1230, 1171, 1139, 1071, 1051, 1005 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.94 (s, 6H, (CH_3)$_2$N), 6.74 (d, 2H, *J*=9.0Hz, 3”-H and 5”-H), 7.34 (d, 1H, *J*=3.9Hz, 4-H), 7.47 (d, 1H, *J*=3.9Hz, 3’-H), 7.51 (d, 2H, *J*=9.0Hz, 2”-H and 6”-H), 7.54 (d, 1H, *J*=3.9Hz, 3-H), 7.97(d, 1H, *J*=3.9Hz, 4’-H), 9.84 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 39.8, 112.3, 120.4, 122.3, 124.2, 126.4, 128.2, 131.5, 139.3, 140.4, 146.0, 146.6, 150.3, 183.5. MS (EI) *m/z* (%): 313 (M^+, 39), 236 (29), 155 (22), 129 (22), 127 (35), 111 (60), 98 (47), 97 (99), 95 (78), 83 (100), 81 (84), 71 (80). HRMS: *m/z* (EI) for $C_{19}H_{19}NOS_2$; calcd 313.0595; found: 313.0582. Anal. Calcd. for $C_{17}H_{15}NOS_2$: C, 65.14; H, 4.82; N, 4.47; S, 20.46. Found: C, 65.32; H, 4.72; N, 4.54; S, 20.14.

4.6.4. 5-Formyl-5'-(4-*N,N*-diethylaminophenyl)-2,2'-bithiophene (5e).[27] Red solid (13%). Mp 158-160°C. UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 435.5 (26,966), 325.5 (11,803) inf. 357.5 (6,391). IR (nujol) ν 1652 (C=O), 1601, 1555, 1524, 1505, 1269, 1227, 1196, 1156, 1096, 1072, 1049, 1003, 877, 815, 796, 750, 738, 733, 693, 661, 631 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.1 (t, 6H, *J*=6.9Hz, CH_3-CH_2-N), 3.35 (q, 2H, *J*=6.9Hz, CH_3-CH_2-N), 6.68 (d, 2H, *J*=8.7Hz, 3”-H and 5”-H), 7.30 (d, 1H, *J*=3.9Hz, 4-H), 7.47 (m, 3H, 2”-H, 6”-H and 3’-H), 7.53 (d, 1H, *J*=3.9Hz, 3-H), 7.97 (d, 1H, *J*=3.9Hz, 4’-H), 9.85 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 12.4, 43.6, 111.5, 119.4, 121.9, 124.1, 126.7, 128.3, 131.1, 139.3, 140.3, 146.1, 146.8, 147.5, 183.5. MS (EI) *m/z* (%): 341 (M^+, 60), 326 (100), 312 (4), 297 (54), 224.0 (13), 155.1

(12), 127.1 (34). HRMS: *m/z* (EI) for $C_{19}H_{19}NOS_2$; calcd 341.0908; found: 341.0907. Anal. Calcd. for $C_{19}H_{19}NOS_2$: C, 66.83; H, 5.61; N, 4.10; S, 18.78. Found: C, 66.92; H, 5.45; N, 4.19; S, 18.72.

4.6.5. 5-Formyl-5'-(4-pyrrolidino)phenyl)-2,2'-bithiophene (5f). Dark brown solid (10%). Mp 228-229°C. UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 433.0 (32,976), 326.5 (12,716) inf. 355.0 (8,647). IR (nujol) ν 1645 (C=O), 1605, 1553, 1541, 1525, 1318, 1280, 1248, 1225, 1184, 1163, 969, 951, 925, 877, 809, 792, 750, 723, 699, 682, 663, 637, 629 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.96 (m, 4H, CH_2-CH_2-N), 3.26 (m, 4H, CH_2-CH_2-N), 6.59 (d, 2H, *J*=9.0Hz, 3"-H and 5"-H), 7.32 (d, 1H, *J*=3.9Hz, 4-H), 7.46 (d, 1H, *J*=3.9Hz, 3'-H), 7.51 (d, 2H, *J*=9.0Hz, 2"-H and 6"-H), 7.53 (d, 1H, *J*=3.9Hz, 3-H), 7.97(d, 1H, *J*=3.9Hz, 4'-H), 9.85 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 24.9, 47.2, 111.9, 119.7, 121.9, 124.1, 126.5, 128.3, 131.1, 139.3, 140.3, 146.1, 147.0, 147.6, 183.5. MS (EI) *m/z* (%): 339 (M^+, 21), 338 (10), 311 (7), 257 (17), 236 (26), 155 (26), 137 (23), 127 (34), 111 (48), 98 (42), 97 (91), 83 (100), 69 (91). HRMS: *m/z* (EI) for $C_{19}H_{17}NOS_2$; calcd 339.0752; found: 339.0752.

4.7. General procedure for the synthesis of aldehydes 5 through Suzuki coupling

5-Bromo-5'-formyl-2,2'-bithiophene **7** (0.25 mmol, 67 mg) was coupled to boronic acids **6a-d** (0.33 mmol) in a mixture of DME (4 mL), aqueous 2 M Na_2CO_3 (0.2 mL) and $Pd(PPh_3)_4$ (6 mol%) at 80°C under nitrogen. The reactions were monitored by TLC which determined the different reaction times (2-24 h). After cooling, the mixture was filtered. Ethyl acetate and a saturated solution of NaCl were added and the phases were separated. The organic phase was washed with water (3 x 10 mL) and with a solution of NaOH (10%) (1 x 10 mL). The organic phase obtained was dried ($MgSO_4$), filtered and solvent removed to give a crude mixture which was submitted to column chromatography on silica with increasing amounts of ether in light petroleum as eluent to afford the coupled products **5**.

4.7.1. 5-Formyl-5'-phenyl-2,2'-bithiophene (5a). Yellow solid (78%). Mp 116-117°C. Other analytical data were identical to those described above for the same compound.

4.7.2. 5-Formyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (5b). Yellow solid (53%). Mp 156-157°C. Other analytical data were identical to those described above for the same compound.

4.7.3. 5-Formyl-5'-(4-ethoxyphenyl)-2,2'-bithiophene (5c). Yellow solid (80%). Mp 140-141°C. UV (dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 395.5 (18,965), 323.5 (6220). IR (nujol) ν 1672 (C=O), 1604, 1570, 1549, 1522, 1504, 1400, 1310, 1284, 1254, 1224, 1212, 1181, 1118, 1048, 958, 921, 881, 835, 830, 795, 753, 670 cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6) δ 1.32 (t, 3H, *J*=7.0Hz), 4.06 (q, 2H, *J*=7.0Hz), 7.00 (d, 2H, *J*=8.8Hz), 7.45 (d, 1H, *J*=3.9Hz), 7.52 (d, 1H, *J*=3.9Hz), 7.58 (d, 1H, *J*=3.9Hz), 7.62 (d, 2H, *J*=8.8Hz), 7.99 (d, 1H, *J*=3.9Hz), 9.86 (s, 1H, CHO). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.5, 63.2, 115.1, 123.9, 124.7, 125.3, 126.9, 128.1, 133.0, 139.2, 140.8, 145.3, 145.6, 158.8, 183.7. HRMS: *m/z* (EI) for $C_{17}H_{14}O_2S_2$; calcd 314.0435; found: 314.0440.

4.7.4. 5-Formyl-5'-(4-*N*,*N*-dimethylaminophenyl)-2,2'-bithiophene (5d). Orange solid (64%). Mp 226-227. Other analytical data were identical to those described above for the same compound.

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Captions

Scheme 1. Synthesis of compounds **2-5** through Vilsmeier-Haack-Arnold reactions.

Scheme 2. Synthesis of formyl-arylbithiophenes **5** through Suzuki coupling.

Table 1. Yields of compounds **2-5**.

Table 2. Yields of compounds **5** through Suzuki coupling and ^{1}H NMR, IR and UV-vis absorption data.

[a] For the C*H*O proton for formyl-arylbithiophenes **5** (300 MHz, DMSO-d_6).

[b] For the C=O stretching band (recorded in nujol).

[c] All the UV-vis spectra were recorded in dioxane.

[d] Using the experimental procedure reported by Clays[26] *et al*..

Table 3. UV-vis absorption data for formyl derivatives **5**, **8**[4a] and **10**[5] in ethanol.

Figure 1. Structure of compounds **8**,[4a] **9**[4b] and **10**.[5]