Arylamino-thieno-oxobutanamides under Lawesson's Conditions: Competition between Thienylpyrrole and Bithiophene Formation

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Received 2 July 2004; revised 20 September 2004

Abstract: 1-Aryl-2-thienyl-substituted pyrroles and/or 5-arylamino-2,2′-bithiophenes were synthesized by treatment of arylamino-thieno-oxobutanamides with Lawesson's reagent. These in turn were prepared by direct amidation of 4-oxo-(2-thienyl)butanoic acid through DCC–BtOH mediated reactions.

Keywords: amides, substituent effects, pyrroles, bicyclic compounds, heterocycles

Thiophene and pyrrole moieties play important roles in natural product chemistry,[1,2] non-linear optics (NLO),[3,4] and supramolecular chemistry.[5] The development of new methods of synthesis of these heterocycles is therefore important. 2-Aryl- and 2-heteroaryl-substituted pyrroles are also of great interest to the pharmaceutical industry, for instance, as precursors in the synthesis of chemotherapeutics.[1,6,7] Some of these molecules, in particular the thienylpyrroles, have served as prospective monomers for non-linear optical materials and organic conductive polymers.[8–18]

The latter combine high electrical conductivity, with thermal and environmental stability. The synthesis of thienylpyrroles containing substituents at the nitrogen atom attracts considerable attention because the substitution makes it possible to modify the properties of polymers, including the synthesis of chiral conducting polymeric materials with better properties for NLO. These new systems are expected to show some advantageous features: i) the aryl group is perpendicular to the π-system such that the coplanarity is affected to a lesser extent and causes a bathochromic shift in its UV-vis absorption spectrum; ii) the perpendicular aryl group prevents the stacking of the π-system and as a result increases its solubility; iii) various aryl groups can be employed in order to modify the physical properties of 1-aryl-2-(2′-thienyl)pyrroles.[8,10,18,19]

A common approach to the synthesis of both thiophene and pyrrole groups involves the use of 1,4-dicarbonyl compounds. In the thiophene case, the 1,4-dicarbonyl compound is reacted with a source of sulfur, usually H_2S and HCl, phosphorus(V) sulfide or Lawesson's reagent (LR).[20–25] Similarly, pyrroles have traditionally been prepared via the condensation of 1,4-dicarbonyl compounds with ammonia or primary amines,[11–16] a reaction known as the Paal–Knorr synthesis.[26]

Due to their numerous potential applications, there is a continuous interest in the development of versatile synthetic routes.

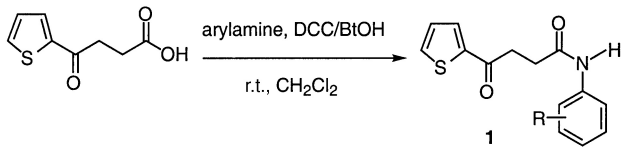
We have previously reported an efficient method for the synthesis of *N,N*-dialkyl-4-(2′-thienyl)-4-oxobutanamides by direct amidation of 4-oxo-(2-thienyl)butanoic acid through a DCC–1-hydroxybenzotriazole (BtOH) mediated reaction.[27] We applied this approach to the synthesis of aryl-4-(2′-thienyl)-4-oxobutanamides, which embody several different substituents [donating substituents (F, Cl, Br, I, CH_3, OH, OMe) or withdrawing substituents (CO_2Me, CN, NO_2)]; thus extending our early work. As part of our continuing interest in non-linear optical materials[27–30] and in order to obtain new compounds as precursors with potential application in NLO in this paper we describe the synthesis and the reactivity studies of aryl-4-(2′-thienyl)-4-oxobutanamides with the Lawesson's reagent. In our study, instead of the expected 5-arylamino-2,2′-bithiophenes, we obtained 1-aryl-2-(2′-thienyl)pyrroles or a mixture of 1-aryl-2-(2′-thienyl)pyrroles and 5-arylamino-2,2′-bithiophenes. The conjugated 1-aryl-2-(2′-thienyl)pyrroles and 5-arylamino-2,2′-bithiophenes, as strong π-electron donor moieties, could be used as precursors in the preparation of compounds with potential application in NLO.[11–15,27]

This method is interesting because the experimental procedures described use mild reaction conditions and simple work-up procedures allow the preparation of these derivatives in moderate to good yields.

Starting from succinic anhydride, we prepared the 3-carbomethoxypropionyl chloride which on Friedel–Crafts reaction with thiophene afforded the methyl 4-(2-thienyl)-4-oxobutanoate. Hydrolysis of the γ-keto ester gave 4-oxo-(2-thienyl)butanoic acid.[27,31,32] Transformation of 4-oxo-(2-thienyl)butanoic acid to the aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v** was carried out by direct amidation of the acid with several commercial arylamines through DCC–BtOH mediated reaction (Scheme 1). No secondary products were detected and the yields were fair to good, depending on the nucleophilicity of the aryl amine (Table 1). A broad correlation could be observed between reaction yields on the synthesis of amides **1** and the chem-

SYNTHESIS 2005, No. 2, pp 0199–0210
Advanced online publication: 03.12.2004
DOI: 10.1055/s-2004-834952; Art ID: T08004SS

ical shift of the nitrogen protons of the starting arylamines; in fact, from the data in Table 1 one may infer that an increase in the chemical shift of the NH_2 protons results in a decrease in the basic character of the aryl amine and lower yields are obtained for the corresponding aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v**. The different effect of substituents in the anilines used is noteworthy (20–73%). As expected the amides **1d–e** and **1j** (Table 1, entries 4, 5 and 10) obtained from the anilines with electron-donating groups in *ortho* or/and in *para* position (δ = 3.99–4.64 ppm) were synthesized in better yields: 62–73%. The amides **1t–v** (Table 1, entries 19–21) obtained from anilines with electron-withdrawing groups in *meta* or *para* position (δ_H = 5.34–5.63 ppm) were synthesized in fair yields: 24–35%. 1-Naphthylamine (δ_H = 5.23 ppm) was even less reactive than the other arylamines giving only 20% of amide **1b** (Table 1, entry 2). Aryl amides **1b**, **1n–o**, **1q–r**, **1t–v**, were obtained in lower yields even after seven days of reaction time. It was possible to detect, by TLC, some unreacted 4-oxo-(2-thienyl)butanoic acid and arylamine starting material.



Scheme 1

We also examined the effect of reaction time on the synthesis of aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v**. As expected a longer reaction time was necessary for the synthesis of aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v** (7 d) compared to the analogous reaction to obtain *N,N*-dialkyl-4-(2′-thienyl)-4-oxobutanamides (1 d).[27] In the case of aryl-4-(2′-thienyl)-4-oxobutanamides **1j** and **1r** the yields improved markedly when the reaction time increased from one day to seven days (**1j**, 14–73%), (**1r**, 8–26%).

The reaction of aryl-4-(2′-thienyl)-4-oxobutanamides **1** with an equimolar amount of LR in toluene at reflux temperature for 15–30 minutes yielded 1-aryl-2-(2′-thienyl)pyrroles **2** and/or 5-arylamino-2,2′-bithiophenes **3** (Scheme 2, Table 2).

Attempts to convert the aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v** into the corresponding 5-arylamino-2,2′-bithiophenes **3** gave only thienylpyrroles **2** (3–55%), (Table 2, entries 2 and 6–8) or a mixture of thienylpyrroles **2** (16–58%) and bithiophene derivatives **3** (Table 2, entries 1, 3–5, 9–11, 14, 16, 17, 19–21) in low yields (7–32%), with pyrroles being the major compounds (Table 2, Scheme 2). Bithiophene derivatives **3m**, **3n**, **3p** and **3s** were obtained as major compounds (21–55%) only in the case of treatment of 2- or 3-haloaryl-4-(2′-thienyl)-4-oxobutanamides **1m**, **1n**, **1p** and **1s** with LR under the same experimental conditions as described above (Table 2, entries 12, 13, 15 and 18).

Table 1 Yields Obtained in the Synthesis of Aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v**

Entry	Compound **1**	R	Yield (%)[a]	δ_H (ppm)[b]
1	**a**	H	42	4.54
2	**b**	1-naphthyl	20	5.23
3	**c**	2-OMe	46	4.36
4	**d**	4-OMe	62[27]	4.21
5	**e**	2,4-diOMe	64[27]	3.99
6	**f**	3,5-diOMe	56	4.64
7	**g**	3,4,5-triOMe	49	4.44
8	**h**	2-OH	54	4.23
9	**i**	2-Me	51	4.35
10	**j**	2-F	73	4.64
11	**l**	4-F	41	4.54
12	**m**	2-Cl	53	4.93
13	**n**	3-Cl	23	5.15
14	**o**	4-Cl	22	4.80
15	**p**	2-Br	53	4.95
16	**q**	4-Br	30	4.83
17	**r**	2,4-diBr	26	5.16
18	**s**	2-I	55	4.89
19	**t**	3-NO_2	24	5.34
20	**u**	4-CO_2Me	35	5.45
21	**v**	4-CN	31	5.63

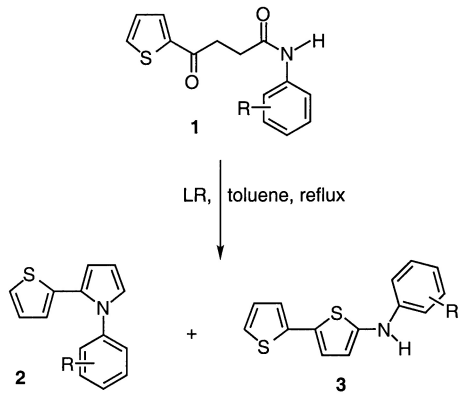
[a] Reaction time: 7 d.
[b] For the NH_2 protons of arylamines (300 MHz, acetone-d_6).

Treatment of 2″-hydroxyphenyl-4-(2′-thienyl)-4-oxobutanamide (**1h**) with LR under the same experimental conditions gave a complex mixture with several products (TLC). After purification by flash chromatography, it was only possible to isolate and identify traces (3%) of pyrrole **2h**. The very low yield of pyrrole **2h** was probably due to the formation of the corresponding phosphorous-containing heterocycle.[22,25]

The moderate total yields obtained for compounds **2** + **3** from the reaction of the corresponding arylamides under Lawesson's conditions may be explained by two factors: decomposition of the aryl amides during the refluxing time and problems in the isolation by flash chromatography of these compounds, particulary for pyrroles **2** and bithiophenes **3** obtained from aryl amides substituted in position 2, due to the similar polarity of the final products.

Table 2 Yields Obtained in the Synthesis of Pyrroles **2** and Bithiophenes **3** from Aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v**

Entry	R	Reaction time (min)	Compound **2**	Yield (%)	Compound **3**	Yield (%)
1	H	15	**a**	58	**a**	9
2	1-naphthyl	20	**b**	55	**b**	–
3	2-OMe	15	**c**	16	**c**	14[27]
4	4-OMe	15	**d**	33	**d**	14
5	2,4-diOMe	15	**e**	32	**e**	12
6	3,5-diOMe	15	**f**	24	**f**	–
7	3,4,5-triOMe	30	**g**	49	**g**	–
8	2-OH	20	**h**	3	**h**	–
9	2-Me	15	**i**	35	**i**	16
10	2-F	20	**j**	30	**j**	17
11	4-F	15	**l**	58	**l**	8
12	2-Cl	30	**m**	16	**m**	21
13	3-Cl	30	**n**	24	**n**	31
14	4-Cl	15	**o**	22	**o**	15
15	2-Br	15	**p**	6	**p**	46
16	4-Br	30	**q**	34	**q**	7
17	2,4-diBr	25	**r**	24	**r**	15
18	2-I	15	**s**	8	**s**	55
19	3-NO_2	25	**t**	26	**t**	21
20	4-CO_2Me	15	**u**	37	**u**	32
21	4-CN	15	**v**	32	**v**	19



Scheme 2

The yield of 1-(4″-fluorophenyl)-2-(2′-thienyl)pyrrole (**2l**) dropped from 58–26% [and no 5-(4″-fluoroanilino)-2,2′-bithiophene (**3l**) was isolated], when 0.5 equivalents of LR was used in this reaction.

Reflux of 4-methoxyphenyl-4-(2′-thienyl)-4-oxobutanamide (**1d**) in toluene for 9 hours without LR, resulted in recovery of unchanged amide **1d**.

A plausible mechanism for the formation of five-membered heterocycles pyrroles and/or thiophenes from secondary amides has already been proposed.[33]

In summary, the synthesis of 1-aryl-2-(2′-thienyl)pyrroles **2** and 1-arylamino-2,2′-bithiophenes **3** is reported for the first time from aryl-4-(2′-thienyl)-4-oxobutanamides **1a–v** through the combination of Friedel–Crafts and Lawesson reactions. If suitable aryl-4-(2′-thienyl)-4-oxobutanamides were synthesized, the synthesis of a large range of 1-aryl-2-(2′-thienyl)pyrroles **2** and 1-arylamino-2,2′-bithiophenes **3** would be possible.

1-Aryl-2-(2′-thienyl)pyrroles **2** and 1-arylamino-2,2′-bithiophenes **3** have been prepared from aryl-4-(2′-thienyl)-4-oxobutanamides **1**. 1-Aryl-2-(2′-thienyl)pyrroles were the major products, except in the cases of 2 or 3-haloaryl-4-(2′-thienyl)-4-oxobutanamides **1m**,**n**,**p**,**s**.

The thienylpyrroles **2** and the 5-arylamino-2,2′-bithiophenes **3** described above could find application as precursors for non-linear optic materials.

^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Unity Plus Spectrometer at 300 MHz and 75.4 MHz, respectively, using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS). Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. EI mass spectra EI (70 eV) and HRMS were run on a Unicam GC-MS 120. Elemental analysis was carried out on a Leco CHNS-932. Column chromatography was performed on Merck silica gel 60 (Art 9385). Petroleum ether (PE) refers to the fraction with boiling point range of 40–60 °C.

The phenyl amines were purchased from Aldrich and Merck and were used as received. The synthesis of amides **1d**,**e** has been described elsewhere.[27]

Compounds **1**–**3** were completely characterized by elemental analysis and/or HRMS, ^{1}H and ^{13}C spectroscopy and IR spectroscopy.

Synthesis of Amides 1a–c and 1f–v; General procedure

DCC–BtOH–CH_2Cl_2 Method:[27] 1,3-Dicyclohexylcarbodiimide (DCC) (1.50 g, 7.10 mmol) and 1-hydroxybenzotriazole (BtOH) (1.10 g, 7.10 mmol) were added to a stirred solution of 4-oxo-(2-thienyl)butanoic acid (1.00 g, 5.40 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred for 30 min at r.t. after which the amine (5.40 mmol) was added and the mixture was stirred during 7 d. The by-product formed, dicyclohexylurea (DCU), was separated by filtration affording a pale brown solution. This organic solution was extracted with a solution of citric acid (5%) (3 × 25 mL), a solution of $NaHCO_3$ (5%) (3 × 25 mL), dried ($MgSO_4$) and evaporated to give an oily brown residue. Flash chromatography on silica gel with increasing amounts of Et_2O in PE as eluent gave the pure amides **1a**–**c** and **1f**–**v**.

Phenyl-4-(2′-thienyl)-4-oxobutanamide (1a)

Colorless solid (yield: 42%); mp 153.2–155.0 °C. Recrystallization from EtOH–PE (1:1) gave a colorless solid; mp 156.1–157.3 °C.

IR (Nujol): 3352 (NH), 1689 (C=O), 1656 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.82 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.42 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.10 (br t, *J* = 7.5 Hz, 1 H, Ar-H), 7.14–7.18 (m, 1 H, 4′-H), 7.32 (br t, *J* = 7.5 Hz, 2 H, 2 × Ar-H), 7.53 (br d, *J* = 7.5 Hz, 2 H, 2 × Ar-H), 7.67 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.70 (br s, 1 H, NH), 7.81 (dd, *J* = 3.3, 1.2 Hz, 1 H, 3′-H).

^{13}C NMR ($CDCl_3$): δ = 31.4, 34.6, 119.7, 124.2, 128.2, 128.9, 132.4, 134.0, 137.8, 150.0, 170.1, 192.0.

Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.85; H, 5.02; N, 5.40; S, 12.38. Found: C, 65.14; H, 5.26; N, 5.52; S, 12.20.

1-Naphthyl-4-(2′-thienyl)-4-oxobutanamide (1b)

Pale gray solid (yield: 20%); mp 164.9–166.3 °C. Recrystallization from EtOH gave a pale gray solid; mp 168.8–169.8 °C.

IR (Nujol): 3275 (NH), 1660 (C=O, br) cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.05 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.47 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.25–7.31 (m, 1 H, 4′-H), 7.46–7.60 (m, 3 H, 3 × Ar-H), 7.76 (br d, *J* = 8.1 Hz, 1 H, Ar-H), 7.90–8.00 (m, 3 H, 5′-H, 2 × Ar-H), 8.02 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 8.21–8.29 (m, 1 H, Ar-H), 9.34 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 29.9, 33.8, 121.6, 122.9, 125.1, 125.6, 125.8, 126.0, 127.8, 128.1, 128.8, 133.3, 133.7, 134.6, 143.6, 170.9, 192.2.

Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.78; H, 5.08; N, 4.53; S, 10.70. Found: C, 69.89; H, 4.85; N, 4.53; S, 10.37.

2-Methoxyphenyl-4-(2′-thienyl)-4-oxobutanamide (1c)

Beige solid (yield: 46%); mp 106.3–108.0 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 110.4–111.7 °C.

IR (Nujol): 3406 (NH), 1686 (C=O), 1659 (C=O) cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 2.91 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.39 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 6.87–6.95 (m, 1 H, 5″-H), 7.00–7.08 (m, 2 H, 3″-H, 4″-H), 7.24–7.30 (m, 1 H, 4′-H), 7.92 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 8.00 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 8.34 (br d, *J* = 8.1 Hz, 1 H, 6″-H), 8.66 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 31.5, 34.6, 56.1, 111.2, 120.7, 121.2, 124.1, 125.2, 128.0, 129.3, 133.2, 134.4, 145.0, 170.8, 192.3.

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.29; H, 5.19; N, 4.84; S, 11.10. Found: C, 62.08; H, 5.34; N, 4.88; S, 10.92.

3″,5″-Dimethoxyphenyl-4-(2′-thienyl)-4-oxobutanamide (1f)

Beige solid (yield: 56%); mp 142.3–146.7 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 156.8–157.4 °C.

IR (Nujol): 3371 (NH), 1687 (C=O), 1661 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.80 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.41 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.78 (s, 6 H, 2 × OCH_3), 6.23 (t, *J* = 2.1 Hz, 1 H, 4″-H), 6.78 (d, *J* = 2.1 Hz, 2 H, 2″-H, 6″-H), 7.13–7.19 (m, 1 H, 4′-H), 7.65 (br s, 1 H, NH), 7.67 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.80 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H).

^{13}C NMR (DMSO-d_6): δ = 30.3, 33.4, 55.0, 95.0, 97.2, 128.8, 133.2, 134.6, 141.0, 143.5, 160.5, 170.3, 192.0.

Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.18; H, 5.33; N, 4.39; S, 10.05. Found: C, 60.05; H, 5.47; N, 4.42; S, 10.19.

3″,4″,5″-Trimethoxyphenyl-4-(2′-thienyl)-4-oxobutanamide (1g)

Brown solid (yield: 49%); mp 181.5–183.4 °C. Recrystallization from EtOH–PE (1:1) gave a pale brown solid; mp 182.2–183.4 °C.

IR (Nujol): 3336 (NH), 1683 (C=O), 1652 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.80 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.42 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 3.84 (s, 6 H, 2 × OCH_3), 6.84 (br s, 2 H, 2″-H, 6″-H), 7.15–7.18 (m, 1 H, 4′-H), 7.68 (dd, *J* = 4.9, 1.2 Hz, 1 H, 5′-H), 7.75 (br s, 1 H, NH), 7.81 (dd, *J* = 4.0, 1.2 Hz, 1 H, 3′-H).

^{13}C NMR ($CDCl_3$): δ = 31.2, 34.4, 55.9, 60.9, 97.1, 128.3, 132.5, 134.1, 134.3, 143.3, 153.1, 170.2, 192.3.

Anal. Calcd for $C_{17}H_{19}NO_5S$: C, 58.44; H, 5.44; N, 4.01; S, 9.18. Found: C, 58.27; H, 5.70; N, 3.88; S, 9.11.

2″-Hydroxyphenyl-4-(2′-thienyl)-4-oxobutanamide (1h)

Beige solid (yield: 54%); mp 133.2–135.3 °C. Recrystallization from EtOH–PE (1:1) gave a colorless solid; mp 139.0–140.0 °C.

IR (Nujol): 3332 (NH), 3300–3120 (OH), 1659 (C=O), 1634 (C=O) cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 2.97 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.45 (t, *J* = 6.6 Hz, 2 H, CH_2), 6.85 (dt, *J* = 8.1, 1.5 Hz, 1 H, 5″-H), 6.93 (dd, *J* = 8.1, 1.5 Hz, 1 H, 3″-H), 7.05 (dt, *J* = 8.1, 1.5 Hz, 1 H, 4″-H), 7.26–7.31 (m, 1 H, 4′-H), 7.52 (dd, *J* = 8.1, 1.5 Hz, 1 H, 6″-H), 7.93 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 8.02 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 9.30 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 30.1, 33.8, 115.8, 119.1, 122.3, 124.7, 126.5, 128.9, 133.4, 134.7, 143.6, 147.8, 170.9, 192.2.

Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.08; H, 4.73; N, 5.09; S, 11.65. Found: C, 60.96; H, 4.93; N, 5.02; S, 11.44.

2″-Methylphenyl-4-(2′-thienyl)-4-oxobutanamide (1i)
Beige solid (yield: 51%); mp 145.0–145.8 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 151.0–151.8 °C.

IR (Nujol): 3257 (NH), 3087, 1661 (C=O), 1651 (C=O) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.32 (s, 3 H, CH_3), 2.90 (t, *J* = 6.7 Hz, 2 H, CH_2), 3.40 (t, *J* = 6.7 Hz, 2 H, CH_2), 7.06 (br t, *J* = 7.2 Hz, 1 H, 5″-H), 7.13–7.26 (m, 2 H, 3″-H, 4″-H), 7.24–7.29 (m, 1 H, 4′-H), 7.70–7.76 (m, 1 H, 6″-H), 7.92 (dd, *J* = 4.5, 1.2 Hz, 1 H, 5′-H), 8.00 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 8.65 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 18.0, 29.9, 35.9, 125.2, 125.2, 126.0, 129.0, 130.4, 131.9, 133.4, 134.7, 136.5, 143.7, 170.4, 192.3.

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.92; H, 5.49; N, 5.13; S, 11.74. Found: C, 65.67; H, 5.59; N, 5.14; S, 11.91.

2″-Fluorophenyl-4-(2′-thienyl)-4-oxobutanamide (1j)
Beige solid (yield: 73%); mp 127.4–128.6 °C. Recrystallization from EtOH–PE (1:1) gave a colorless solid; mp 126.0–127.6 °C.

IR (Nujol): 3376 (NH), 1694 (C=O), 1652 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.85 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.45 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.00–7.12 (m, 3 H, 3 × Ar-H), 7.12–7.17 (m, 1 H, 4′-H), 7.14–7.18 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.69 (br s, 1 H, NH), 7.81 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 8.29 (m, 1 H, Ar-H).

Anal. Calcd for $C_{14}H_{12}FNO_2S$: C, 60.65; H, 4.33; N, 5.05; S, 11.55. Found: C, 60.50; H, 4.45; N, 5.06; S, 11.41.

4″-Fluorophenyl-4-(2′-thienyl)-4-oxobutanamide (1l)
Colorless solid (yield: 41%); mp 144.0–145.3 °C. Recrystallization from Et_2O gave a colorless solid; mp 153.7–155.2 °C.

IR (Nujol): 3357 (NH), 1694 (C=O), 1658 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.81 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.42 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.01 (t, *J* = 8.7 Hz, 2 H, 3″-H, 5″-H), 7.14–7.18 (m, 1 H, 4′-H), 7.48 (dd, *J* = 8.6, 4.8 Hz, 2 H, 2″-H, 6″-H), 7.68 (dd, *J* = 4.7, 1.2 Hz, 1 H, 5′-H), 7.78 (br s, 1 H, NH), 7.81 (dd, *J* = 3.4, 1.2 Hz, 1 H, 3′-H).

^{13}C NMR (acetone-d_6): δ = 31.1, 34.4, 115.6, 115.9 (d, *J* = 22 Hz, C3″, C5″), 121.6, 121.6 (d, *J* = 8 Hz, C2″, C6″), 129.2, 133.3, 134.5, 136.7, 137.2, 144.8, 145.5, 157.7, 160.9 (d, *J* = 238 Hz, C4″), 171.0, 192.4.

Anal. Calcd for $C_{14}H_{12}FNO_2S$: C, 60.49; H, 4.48; N, 5.07; S, 11.59. Found: 60.64; H, 4.33; N, 5.05; S, 11.57.

2″-Chlorophenyl-4-(2′-thienyl)-4-oxobutanamide (1m)
Brown solid (yield: 53%); mp 117.0–118.3 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 123.9–125.0 °C.

IR (Nujol): 3313 (NH), 1667 (C=O, br) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.97 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.42 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.14 (dt, *J* = 8.1, 1.5 Hz, 1 H, 4″-H), 7.25–7.29 (m, 1 H, 4′-H), 7.33 (dt, *J* = 8.1, 1.5 Hz, 1 H, 5″-H), 7.47 (dd, *J* = 8.1, 1.5 Hz, 1 H, 3″-H), 7.93 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 8.01 (dd, *J* = 3.8, 1.2 Hz, 1 H, 3′-H), 8.22 (dd, *J* = 8.1, 1.2 Hz, 1 H, 6″-H), 8.78 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 29.7, 33.6, 126.0, 126.2, 127.3, 128.7, 129.4, 133.2, 134.6, 135.0, 139.4, 143.5, 170.6, 191.9.

Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.09; N, 4.77; S, 10.92. Found: C, 57.07; H, 4.33; N, 4.78; S, 10.84.

3″-Chlorophenyl-4-(2′-thienyl)-4-oxobutanamide (1n)
Beige solid (yield: 23%); mp 126.0–129.0 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 166.6–169.4 °C.

IR (Nujol): 3353 (NH), 1703 (C=O), 1661 (C=O) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.86 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.39 (t, *J* = 6.6 Hz, 2 H, CH_2), 6.96–7.11 (m, 1 H, 4″-H), 7.25–7.30 (m, 1 H, 4′-H), 7.33 (t, *J* = 7.8 Hz, 1 H, 5″-H), 7.48–7.54 (m, 1 H, 6″-H), 7.92 (dd, *J* = 5.0, 1.2 Hz, 1 H, 5′-H), 7.94 (t, *J* = 2.1 Hz, 1 H, 2″-H), 8.00 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 9.50 (br s, 1 H, NH).

Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.09; N, 4.77; S, 10.92. Found: C, 57.51; H, 4.25; N, 4.80; S, 10.85.

4″-Chlorophenyl-4-(2′-thienyl)-4-oxobutanamide (1o)
Beige solid (yield: 22%); mp 169.2–171.0 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 152.4–153.5 °C.

IR (Nujol): 3357 (NH), 1698 (C=O), 1652 (C=O) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.85 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.38 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.24–7.28 (m, 1 H, 4′-H), 7.33 (d, *J* = 9.0 Hz, 2 H, 2″-H, 6″-H), 7.72 (d, *J* = 9.0 Hz, 2 H, 3″-H, 5″-H), 7.91 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.99 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 9.40 (br s, 1 H, NH).

Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.09; N, 4.77; S, 10.92. Found: C, 57.12; H, 4.33; N, 4.69; S, 10.63.

2″-Bromophenyl-4-(2′-thienyl)-4-oxobutanamide (1p)
Brown solid (yield: 53%); mp 114.0–115.7 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 121.6–123.5 °C.

IR (Nujol): 3281 (NH), 1665 (C=O, broad) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.90 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.42 (t, *J* = 7.0 Hz, 2 H, CH_2), 6.98 (dt, *J* = 7.8, 1.5 Hz, 1 H, 5″-H), 7.13–7.18 (m, 1 H, 4′-H), 7.30 (dt, *J* = 7.8, 1.5 Hz, 1 H, 4″-H), 7.54 (dd, *J* = 7.8, 1.5 Hz, 1 H, 6″-H), 7.67 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.82 (dd, *J* = 3.3, 1.2 Hz, 1 H, 3′-H), 7.93 (br s, 1 H, NH), 8.32 (br d, *J* = 7.8 Hz, 1 H, 3″-H).

^{13}C NMR ($CDCl_3$): δ = 31.4, 34.3, 113.3, 121.9, 125.1, 128.2, 128.3, 132.2, 132.3, 133.9, 135.6, 143.4, 170.1, 191.4.

Anal. Calcd for $C_{14}H_{12}BrNO_2S$: C, 49.71; H, 3.55; N, 4.14; S, 9.49. Found: C, 49.61; H, 3.45; N, 4.18; S, 9.17.

4″-Bromophenyl-4-(2′-thienyl)-4-oxobutanamide (1q)
Beige solid (yield: 30%); mp 168.0–170.0 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 176.0–178.0 °C.

IR (Nujol): 3359 (NH), 1698 (C=O), 1654 (C=O) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.81 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.37 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.24–7.28 (m, 1 H, 4′-H), 7.46 (d, *J* = 9.0 Hz, 2 H, 2″-H, 6″-H), 7.65 (d, *J* = 9.0 Hz, 2 H, 3″-H, 5″-H), 7.91 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.98 (dd, *J* = 3.8 Hz, 1.2 Hz, 1 H, 3′-H), 9.43 (br s, 1 H, NH).

Anal. Calcd for $C_{14}H_{12}BrNO_2S$: C, 49.71; H, 3.55; N, 4.14; S, 9.49. Found: C, 49.56; H, 3.71; N, 4.17; S, 9.59.

2″,4″-Dibromophenyl-4-(2′-thienyl)-4-oxobutanamide (1r)
Pale brown solid (yield: 26%); mp 146.4–149.0 °C. Recrystallization from EtOH gave a beige solid; mp 156.2–156.6 °C.

IR (Nujol): 3382 (NH), 1701 (C=O), 1659 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.89 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.42 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.15–7.18 (m, 1 H, 4′-H), 7.42 (dd, *J* = 8.7, 2.4 Hz, 1 H, 5″-H), 7.66–7.71 (m, 2 H, 5′-H, 3″-H), 7.82 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 7.93 (br s, 1 H, NH), 8.25 (d, *J* = 9 Hz, 1 H, 6″-H).

^{13}C NMR ($CDCl_3$): δ = 31.4, 34.3, 113.7, 116.6, 122.8, 128.2, 131.3, 132.3, 134.0, 134.4, 134.9, 143.3, 170.2, 191.3.

Anal. Calcd for $C_{14}H_{11}Br_2NO_2S$: C, 40.30; H, 2.64; N, 3.36; S, 7.68. Found: C, 40.60; H, 2.71; N, 3.38; S, 7.55.

2″-Iodophenyl-4-(2′-thienyl)-4-oxobutanamide (1s)
Beige solid (yield: 55%); mp 124.0–125.2 °C. Recrystallization from EtOH gave a beige solid; mp 129.2–131.0 °C.

IR (Nujol): 3282 (NH), 1660 (C=O), 1652 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.90 (t, *J* = 6.7 Hz, 2 H, CH_2), 3.41 (t, *J* = 6.6 Hz, 2 H, CH_2), 6.85 (dt, *J* = 7.8, 1.5 Hz, 1 H, 4″-H), 7.15–7.18 (m, 1 H, 4′-H), 7.33 (dt, *J* = 7.8, 1.5 Hz, 1 H, 5″-H), 7.67 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.71 (br s, 1 H, NH), 7.78 (dt, *J* = 7.8 1.5 Hz, 1 H, 3″-H), 7.82 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 8.20 (br d, *J* = 7.8 Hz, 1 H, 6″-H).

Anal. Calcd for $C_{14}H_{12}INO_2S$: 43.64; H, 3.12; N, 3.64; S, 8.33. Found: C, 43.91; H, 3.43; N, 3.69; S, 8.10.

3″-Nitrophenyl-4-(2′-thienyl)-4-oxobutanamide (1t)
The pure amide precipitated as a brown solid after addition of acetone to the crude mixture. Evaporation of the filtrate under reduce pressure gave more crude amide which was submitted to flash chromathography [Et_2O–PE, 2:8 → 5:5] to give another crop of pure amide as a colorless solid; global yield: 24%; mp 143.7–145.5 °C. Recrystallization from EtOH–PE (1:1) gave a colorless solid; mp 159.2–160.1 °C.

IR (Nujol): 3333 (NH), 1698 (C=O), 1646 (C=O) cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.76 (t, *J* = 6.7 Hz, 2 H, CH_2), 3.43 (t, *J* = 6.7 Hz, 2 H, CH_2), 7.27–7.30 (m, 1 H, 4′-H), 7.63 (t, *J* = 8.1 Hz, 1 H, 5″-H), 7.92–8.04 (m, 4 H, 4″-H, 6″-H, 3′-H, 5′-H), 8.76 (t, *J* = 2.1 Hz, 1 H, 2″-H), 9.75 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 30.3, 33.3, 112.9, 117.5, 124.8, 128.8, 130.2, 133.3, 134.7, 140.4, 143.4, 148.1, 171.1, 191.9.

Anal. Calcd for $C_{14}H_{12}N_2O_4S$: C, 55.29; H, 4.23; N, 9.00; S, 10.42. Found: C, 55.15; H, 3.95; N, 9.21; S, 10.54.

4″-Methyloxycarbonylphenyl-4-(2′-thienyl)-4-oxobutanamide (1u)
Beige solid (yield: 35%); mp 128.6–130.5 °C. Recrystallization from EtOH–PE (1:1) gave a beige solid; mp 138.4–139.7 °C.

IR (Nujol): 3356 (NH), 1716 (C=O), 1697 (C=O), 1652 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.84 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.42 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 7.14–7.19 (m, 1 H, 4′-H), 7.62 (d, *J* = 8.7 Hz, 2 H, 2 × Ar-H), 7.69 (dd, *J* = 5.3, 1.2 Hz, 1 H, 5′-H), 7.82 (dd, *J* = 3.5, 1.2 Hz, 1 H, 3′-H), 8.00 (m, 3 H, NH, 2 × Ar-H).

^{13}C NMR (DMSO-d_6): δ = 30.5, 33.5, 52.0, 118.4, 123.8, 129.1, 130.5, 133.4, 134.8, 143.6, 143.8, 166.0, 171.1, 192.1.

Anal. Calcd for $C_{16}H_{15}NO_4S$: C, 60.56; H, 4.73; N, 4.42; S, 10.11. Found: 60.66; H, 4.99; N, 4.44; S, 10.14.

4″-Cyanophenyl-4-(2′-thienyl)-4-oxobutanamide (1v)
The pure amide precipitated as a brown solid after addition of acetone to the crude mixture. Evaporation of the filtrate under reduce pressure gave the crude amide which was submitted to flash chromathography [Et_2O–PE (3:7 → 1:0) and EtOAc–PE (5:5)] to give more pure amide as a colorless solid; global yield: 31%; mp 206.9–208.1 °C. Recrystallization from EtOH gave a colorless solid; mp 206.7–207.8 °C.

IR (Nujol): 3341 (NH), 2224 (CN), 1704 (C=O), 1644 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.83 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.43 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.16–7.19 (m, 1 H, 4′-H), 7.60 (d, *J* = 8.7 Hz, 2 H, 2 × Ar-H), 7.67 (d, *J* = 8.7 Hz, 2 H, 2 × Ar-*H*), 7.70 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.81 (dd, *J* = 3.5, 1.2 Hz, 1 H, 3′-H), 8.14 (br s, 1 H, NH).

^{13}C NMR (acetone-d_6): δ = 31.3, 34.2, 106.6, 119.5, 119.9, 129.2, 133.3, 133.9, 134.5, 144.4, 144.8, 171.7, 192.1.

Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.54; H, 4.44; N, 9.78; S, 11.51. Found: C, 63.35; H, 4.22; N, 9.85; S, 11.26.

Reaction of Amides 1a–v with Lawesson's Reagent (LR); General Procedure
A mixture of the Lawesson reagent (0.93 g, 2.30 mmol) and the amides **1a–v** (2.30 mmol) was heated at reflux in toluene (12 mL) for the time indicated in Table 2. The mixture was cooled and the solvent was evaporated under reduced pressure to give the crude mixture of aryl pyrroles **2** and/or bithiophenes **3**, which was purified by flash chromatography on silica gel with increasing amounts of Et_2O in PE as eluent.

1-Phenyl-2-(2′-thienyl)pyrrole (2a) and 5-Anilino-2,2′-bithiophene (3a)
Treatment of amide **1a** with Lawesson's reagent gave a mixture of 1-phenyl-2-(2′-thienyl)pyrrole (**2a**) and 5-anilino-2,2′-bithiophene (**3a**). The first component eluted was 1-phenyl-2-(2′-thienyl)pyrrole (**2a**) as a beige solid (yield: 58%); mp 96.4–97.6 °C [Et_2O–PE (1:2)].

IR (Nujol): 1593, 1560, 1496, 1428, 1403, 1353, 1325, 1316, 1303, 1227, 1161, 1093, 1081, 1072, 1034, 976, 917, 841, 792, 776, 727, 705, 697 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.32–6.36 (m, 1 H, 4-H), 6.50 (dd, *J* = 4.2, 1.8 Hz, 1 H, 3-H), 6.57 (dd, *J* = 3.8, 1.2 Hz, 1 H, 3′-H), 6.84–6.88 (m, 1 H, 4′-H), 6.89–6.92 (m, 1 H, 5-H), 7.12 (dd, *J* = 5.4, 1.2 Hz, 1 H, 5′-H), 7.25–7.30 (m, 2 H, 2 × Ar-H), 7.34–7.42 (m, 3 H, 3 × Ar-H).

^{13}C NMR ($CHCl_3$): δ = 110.9, 109.1, 124.1, 124.4, 124.8, 126.5, 126.9, 127.4, 128.9, 134.9, 140.0.

MS (EI): *m*/*z* (%) = 225 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{11}NS$: 225.0612; found: 225.0611.

The second component eluted was 5-anilino-2,2′-bithiophene (**3a**) as a pale green solid (yield: 9%); mp 81.0–83.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 3367 (NH), 2925, 1598, 1556, 1515, 1498, 1434, 1305, 1258, 1233, 1173, 1150, 1077, 1049, 886, 834, 791, 747, 690, 685 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.64 (d, *J* = 3.9 Hz, 1 H, 4-H), 6.89 (br t, *J* = 6.6 Hz, 1 H, 4″-H), 6.93–6.97 (m, 3 H, 3-H, 2 × Ar-H), 6.98–7.00 (m, 1 H, 4′-H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.18 (dd, *J* = 4.5, 1.2 Hz, 1 H, 5′-H), 7.22–7.32 (m, 2 H, 2 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 115.7, 115.7, 116.3, 116.4, 120.6, 123.2, 123.3, 124.4, 128.7, 130.1.

MS (EI): *m*/*z* (%) = 257 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{11}NS_2$: 257.0333; found: 257.0336.

1-Naphthyl-2-(2′-thienyl)pyrrole (2b)
Treatment of amide **1b** with Lawesson's reagent gave the crude 1-naphthyl-2-(2′-thienyl)pyrrole (**2b**) which was purified by flash chromatography; green solid (yield: 55%); mp 111.8–112.7 °C [Et_2O–PE (1:2)].

IR (Nujol): 2921, 1594, 1463, 1375, 1300, 1200, 1169, 1143, 1075, 1001, 843, 780, 711 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.40–6.45 (m, 1 H, 4-H), 6.46 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 6.65 (dd, *J* = 3.8, 1.8 Hz, 1 H, 3-H), 6.70–6.75 (m, 1 H, 4′-H), 6.98–7.02 (m, 1 H, 5-H), 7.07 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.27 (br d, *J* = 8.1 Hz, 1 H, Ar-H), 7.46–7.70 (m, 4 H, 4 × Ar-H), 8.05 (br d, *J* = 8.1 Hz, 1 H, Ar-H), 8.12 (br d, 1 H, Ar-H).

^{13}C NMR (acetone-d_6): δ = 110.0, 109.9, 123.6, 124.1, 124.4, 126.3, 126.4, 127.1, 127.5, 127.6, 128.1, 129.0, 130.0, 130.2, 132.6, 135.0, 135.7, 137.7.

MS (EI): *m*/*z* (%) = 275 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{18}H_{13}NS$: 275.0769; found: 275.0772.

1-(2″-Methoxyphenyl)-2-(2′-thienyl)pyrrole (2c) and 5-(2″-Methoxyanilino)-2,2′-bithiophene (3c)

Treatment of amide **1c** with Lawesson's reagent gave a mixture of 1-(2″-methoxyphenyl)-2-(2′-thienyl)pyrrole (**2c**) and 5-(2″-methoxyanilino)-2,2′-bithiophene (**3c**). The first component eluted was 1-(2″-methoxyphenyl)-2-(2′-thienyl)pyrrole (**2c**) as a pale yellow solid (yield: 16%); mp 113.6–116.2 °C [Et_2O–PE (1:2)].

IR (Nujol): 3098, 2925, 1599, 1565, 1504, 1428, 1404, 1349, 1328, 1310, 1279, 1249, 1235, 1208, 1188, 1179, 1161, 1084, 1021, 981, 943 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.68 (s, 3 H, OCH_3), 6.24–6.29 (m, 1 H, 4-H), 6.46 (dd, *J* = 3.8, 1.8 Hz, 1 H, 3-H), 6.59 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.84–6.88 (m, 1 H, 4′-H), 7.04–7.10 (m, 2 H, 5-H, 5′-H), 7.15–7.22 (m, 2 H, 2 × Ar-H), 7.26 (dd, *J* = 7.5, 1.5 Hz, 1 H, Ar-H), 7.47 (dt, *J* = 7.5, 1.5 Hz, 1 H, Ar-H).

^{13}C NMR (acetone-d_6): δ = 55.9, 109.4, 109.8, 113.4, 121.4, 123.8, 124.2, 125.5, 127.6, 129.2, 130.1, 130.7, 136.4, 156.5.

MS (EI): *m*/*z* (%) = 255 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}NOS$: 255.0718; found: 255.0719.

The second component eluted was 5-(2″-methoxyanilino)-2,2′-bithiophene (**3c**) as a green oil (yield: 14%).

IR (liquid film): 3397 (NH), 1500, 1525, 1504, 1462, 1243, 1113, 1021, 740, 692 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.91 (s, 3 H, OCH_3), 6.70 (d, *J* = 3.9 Hz, 1 H, 4-H), 6.84–6.92 (m, 2 H, 2 × Ar-H), 6.99 (dd, *J* = 9.0, 1.8 Hz, 1 H, Ar-H), 7.05 (m, 2 H, 3-H, 4′-H), 7.17 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3-H), 7.24 (dd, *J* = 9.0, 1.8 Hz, 1 H, Ar-H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H).

^{13}C NMR (acetone-d_6): δ = 56.0, 111.4, 113.8, 117.2, 117.4, 120.5, 121.7, 123.2, 124.4, 128.7, 130.7, 137.8, 138.7, 146.8, 154.0.

MS (EI): *m*/*z* (%) = 287 (100) [M$^+$].

HRMS (EI): *m*/*z* for $C_{15}H_{13}NOS_2$: 287.0438; found: 287.0447.

1-(4″-Methoxyphenyl)-2-(2′-thienyl)pyrrole (2d) and 5-(4″-Methoxyanilino)-2,2′-bithiophene (3d)

Treatment of amide **1d** with Lawesson's reagent gave a mixture of 1-(4″-methoxyphenyl)-2-(2′-thienyl)pyrrole (**2d**) and 5-(4″-methoxyanilino)-2,2′-bithiophene (**3d**). The first component eluted was 1-(4′-methoxyphenyl)-2-(2′-thienyl)pyrrole (**2d**) as a yellow solid (yield: 33%); mp 83.0–85.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 1508, 1480, 1465, 1436, 1412, 1240, 1180, 1122, 1034, 819, 796, 763, 690, 628, 618 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 6.28–6.32 (m, 1 H, 4-H), 6.46 (dd, *J* = 3.6, 1.5 Hz, 1 H, 3-H), 6.59 (dd, *J* = 3.3, 1.2 Hz, 1 H, 3′-H), 6.82–6.87 (m, 2 H, 5-H, 4′-H), 6.90 (d, *J* = 8.9 Hz, 2 H, 2 × Ar-H), 7.09 (dd, *J* = 5.2, 1.2 Hz, 1 H, 5′-H), 7.20 (d, 2 H, 8.9 Hz, 2 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 55.8, 109.6, 110.8, 115.0, 124.9, 125.1, 125.5, 127.8, 128.4, 128.8, 133.8, 135.9, 160.1.

MS (EI): *m*/*z* (%) = 255 (100) [M$^+$].

Anal. Calcd for $C_{15}H_{13}NOS$: C, 70.57; H, 5.10; N, 5.49; S, 12.57. Found: C, 70.35; H, 5.22; N, 5.57; S, 12.83.

The second component eluted was 5-(4″-methoxyanilino)-2,2′-bithiophene (**3d**) as a green solid (yield: 14%); mp 113.0–115.0 °C [Et_2O–PE (1:2)] [lit.[27] 113.0–115.0 °C].

1-(2″,4″-Dimethoxyphenyl-2-(2′-thienyl)pyrrole (2e) and 5-(2″,4″-Dimethoxyanilino)-2,2′-bithiophene (3e)

Treatment of amide **1e** with Lawesson's reagent gave a mixture of 1-(2″,4″-dimethoxyphenyl-2-(2′-thienyl)pyrrole (**2e**) and 5-(2″,4″-dimethoxyanilino)-2,2′-bithiophene (**3e**). The first component eluted was 1-(2″,4″-dimethoxyphenyl-2-(2′-thienyl)pyrrole (**2e**) as a pale green solid (yield: 32%); mp 107.0–109.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 1611, 1587, 1515, 1464, 1439, 1419, 1302, 1285, 1208, 1159, 1135, 1091, 1044, 1029, 927, 841, 710, 690 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.70 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 6.20–6.25 (m, 1 H, 4-H), 6.45 (dd, *J* = 4.2, 1.5 Hz, 1 H, 3-H), 6.62 (dd, *J* = 9.0, 2.7 Hz, 1 H, 5″-H), 6.66 (dd, *J* = 3.5, 1.2 Hz, 1 H, 3′-H), 6.72 (d, *J* = 2.7 Hz, 1 H, 3″-H), 6.74–6.77 (m, 1 H, 5-H), 6.86–6.90 (m, 1 H, 4′-H), 7.16 (d, *J* = 9.0 Hz, 1 H, 6″-H), 7.19 (dd, *J* = 4.9, 1.2 Hz, 1 H, 5′-H).

^{13}C NMR ($CDCl_3$): δ = 55.5, 55.7, 99.6, 104.1, 108.6, 108.7, 122.2, 123.1, 123.2, 124.8, 126.7, 128.8, 129.9, 135.4, 156.5, 160.8.

MS (EI): *m*/*z* (%) = 285 (100) [M$^+$].

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.26; N, 4.91; S, 11.25. Found: C, 67.36; H, 5.42; N, 4.98; S, 11.25.

The second component eluted was 5-(2″,4″-dimethoxyanilino)-2,2′-bithiophene (**3e**) as a green oil (yield: 8%).

IR (liquid film): 3372 (NH), 3104, 3071, 2926, 2246, 2067, 1614, 1600, 1565, 1556, 1538, 1505, 1456, 1417, 1283, 1258, 1208, 1158, 1125, 1029, 931, 909, 834, 726, 694, 630 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 6.44 (dd, *J* = 8.7, 2.7 Hz, 1 H, 5″-H), 6.52 (d, *J* = 2.7 Hz, 1 H, 3″-H), 6.55 (br d, *J* = 3.6 Hz, 1 H, 4-H), 6.93 (br d, *J* = 3.6 Hz, 1 H, 3-H), 6.96–7.01 (m, 1 H, 4′-H), 7.04 (br d, *J* = 3.6 Hz, 1 H, 3′-H), 7.13 (m, 2 H, 5′-H, 6″-H).

^{13}C NMR ($CDCl_3$): δ = 55.7, 55.7, 99.2, 103.8, 114.3, 115.4, 122.3, 123.2, 127.6, 128.3, 130.0, 138.1, 146.8, 148.4, 154.0.

MS (EI): *m*/*z* (%) = 317 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{16}H_{15}NO_2S_2$: 317.0544; found: 317.0544.

1-(3″,5″-Dimethoxyphenyl)-2-(2′-thienyl)pyrrole (2f)

Treatment of amide **1f** with Lawesson's reagent gave the crude 1-(3″,5″-dimethoxiphenyl)-2-(2′-thienyl)pyrrole (**2f**) which was purified by flash chromatography; yellow oil (yield: 24%).

IR (liquid film): 3104, 2958, 2935, 1508, 1476, 1463, 1428, 1322, 1265, 1231, 1205, 1156, 1098, 1064, 1035, 928, 846, 814, 790, 716, 691, 623 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.72 (s, 6 H, 2 × OCH_3), 6.28–6.31 (m, 1 H, 4-H), 6.41–6.46 (m, 3 H, 2″-H, 4″-H, 6″-H), 6.48 (dd, *J* = 3.4, 2.1 Hz, 1 H, 3-H), 6.67 (dd, *J* = 3.4, 1.2 Hz, 1 H, 3′-H), 6.87–6.89 (m, 1 H, 4′-H), 6.91 (dd, *J* = 3.2, 1.8 Hz, 1 H, 5-H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H).

^{13}C NMR (acetone-d_6): δ = 55.8, 100.2, 105.4, 109.8, 111.8, 125.2, 125.4, 125.9, 127.7, 127.8, 135.7, 142.5, 161.9.

MS (EI): *m*/*z* (%) = 285 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{16}H_{15}NO_2S$: 285.0823; found: 285.0824.

1-(3″,4″,5″-Trimethoxyphenyl)-2-(2′-thienyl)pyrrole (2g)
Treatment of amide **1g** with Lawesson's reagent gave the crude 1-(3″,4″,5″-trimethoxiphenyl)-2-(2′-thienyl)pyrrole (**2g**) which was purified by flash chromatography; pale green solid (yield: 49%); mp 103.7–104.7 °C [Et_2O–PE (1:2)].

IR (Nujol): 3104, 3072, 2999, 2937, 1506, 1417, 1365, 1340, 1297, 1266, 1243, 1230, 1180, 1164, 1127, 1063, 1006, 953, 944, 852, 836, 769, 715, 666, 631, 611 cm^{-1}.

^1H NMR (acetone-d_6): δ = 3.79 (s, 9 H, 3 × OCH_3), 6.27 (m, 1 H, 4-H), 6.46 (dd, *J* = 3.6, 1.7 Hz, 1 H, 3-H), 6.59 (s, 2 H, 2″-H, 6″-H), 6.73 (dd, *J* = 3.3, 1.2 Hz, 1 H, 3′-H), 6.94–7.00 (m, 1 H, 4′-H), 7.00–7.03 (m, 1 H, 5-H), 7.33 (dd, *J* = 4.7, 1.2 Hz, 1 H, 5′-H).

^{13}C NMR (acetone-d_6): δ = 56.4, 60.6, 105.0, 109.6, 111.3, 125.3, 125.8, 127.8, 127.9, 135.7, 136.4, 138.4, 154.28.

Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.75; H, 5.40; N, 4.44; S, 10.17. Found: C, 64.58; H, 5.54; N, 4.54; S, 10.47.

1-(2″-Hydroxyphenyl)-2-(2′-thienyl)pyrrole (2h)
Treatment of amide **1h** with Lawesson's reagent gave a complex mixture with several products (TLC). After purification by flash chromatography it was possible to purify and identify only 1-(2″-hydroxyphenyl)-2-(2′-thienyl)pyrrole (**2h**); pale green solid (yield: 3%); mp 135.8–136.9 °C [Et_2O–PE (1:2)].

IR (Nujol): 3510–3290 (OH), 2923, 1585, 1501, 1323, 1306, 1195, 1144, 1080, 1050, 1033, 949, 919, 844, 832, 793, 767, 723, 704, 616 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.25–6.28 (m, 1 H, 4-H), 6.46–6.48 (m, 1 H, 3-H), 6.66 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.82–6.83 (m, 1 H, 4′-H), 6.85–6.88 (m, 1 H, 5-H), 6.94 (dt, *J* = 7.8, 1.5 Hz, 1 H, 5″-H), 7.07 (dd, *J* = 8.1, 1.2 Hz, 1 H, 6″-H), 7.15–7.19 (m, 2 H, 5′-H, 3″-H), 7.34 (dt, *J* = 7.8, 1.5 Hz, 1 H, 4″-H).

^{13}C NMR (acetone-d_6): δ = 109.8, 109.6, 117.6, 120.6, 123.8, 124.1, 125.6, 127.7, 130.5, 130.6, 130.6, 136.3, 154.6, 157.4.

MS (EI): *m*/*z* (%) = 241 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{11}NOS$: 241.0561; found: 241.0560.

1-(2″-Methylphenyl)-2-(2′-thienyl)pyrrole (2i) and 5-(2″-Methylanilino)-2,2′-bithiophene (3i)
Treatment of amide **1i** with Lawesson's reagent gave a mixture of 1-(2″-methylphenyl)-2-(2′-thienyl)pyrrole (**2i**) and 5-(2″-methylanilino)-2,2′-bithiophene (**3i**). The first component eluted was 1-(2″-methylphenyl)-2-(2′-thienyl)pyrrole (**2i**) as a pale yellow oil (yield: 35%).

IR (liquid film): 3104, 3071, 2957, 2925, 2858, 1605, 1583, 1497, 1463, 1430, 1405, 1382, 1348, 1326, 1309, 1279, 1227, 1212, 1200, 1168, 1091, 1081, 1014, 917, 844, 823, 766, 715, 692, 616 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.96 (s, 3 H, CH_3), 6.33–6.35 (m, 1 H, 4-H), 6.49 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.72–6.73 (m, 1 H, 5-H), 6.78–6.81 (m, 1 H, 4′-H), 7.01 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.25–7.33 (m, 4 H, 4 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 17.3, 109.6, 109.9, 123.6, 124.2, 124.7, 127.5, 127.8, 129.0, 129.3, 129.7, 131.5, 136.0, 137.4, 140.2.

MS (EI): *m*/*z* (%) = 239 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}NS$: 239.0769; found: 239.0772.

The second component eluted was 5-(2″-methylanilino)-2,2′-bithiophene (**3i**) as a green oil (yield: 16%).

IR (liquid film): 3399 (NH), 3105, 3069, 2958, 2924, 2854, 1606, 1586, 1521, 1498, 1467, 1446, 1382, 1294, 1260, 1241, 1199, 1159, 1109, 1079, 1048, 836, 778, 747, 693 cm^{-1}.

^1H NMR (acetone-d_6): δ = 2.29 (s, 3 H, CH_3), 5.41 (br s, 1 H, NH), 6.62 (d, *J* = 3.6 Hz, 1 H, 4-H), 6.85 (dt, *J* = 7.2, 1.8 Hz, 1 H, Ar-H), 7.01 (d, *J* = 3.6 Hz, 1 H, 3-H), 6.99–7.02 (m, 1 H, 4′-H), 7.07–7.20 (m, 5 H, 3′-H, 5′-H, 3 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 17.9, 116.0, 116.9, 121.4, 123.2, 123.2, 124.3, 124.9, 126.2, 127.6, 128.4, 128.7, 128.7, 131.5, 138.8.

MS (EI): *m*/*z* (%) = 271 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}NS_2$: 271.0489; found: 271.0494.

1-(2″-Fluorophenyl)-2-(2′-thienyl)pyrrole (2j) and 5-(2″-Fluoroanilino)-2,2′-bithiophene (3j)
Treatment of amide **1j** with Lawesson's reagent gave a mixture of 1-(2″-fluorophenyl)-2-(2′-thienyl)pyrrole (**2j**) and 5-(2″-fluoroanilino)-2,2′-bithiophene (**3j**). The first component eluted was 1-(2″-fluorophenyl)-2-(2′-thienyl)pyrrole (**2j**) as a green solid (yield: 30%); mp 64.4–66.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 2924, 1610, 1588, 1455, 1401, 1352, 1328, 1308, 1266, 1227, 1162, 1152, 1114, 1085, 1033, 987, 950, 919, 842, 817, 792, 769, 722, 700, 639 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.38–6.34 (m, 1 H, 4-H), 6.50–6.54 (dd, *J* = 3.6, 1.5 Hz, 1 H, 3-H), 6.65 (dd, *J* = 3.8, 1.2 Hz, 1 H, 3′-H), 6.89–6.93 (m, 1 H, 4′-H), 6.94–6.97 (m, 1 H, 5-H), 7.27 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.30–7.38 (m, 2 H, 2 × Ar-H), 7.45 (dt, *J* = 8.1, 1.8 Hz, 1 H, Ar-H), 7.52–7.60 (m, 1 H, Ar-H).

MS (EI): *m*/*z* (%) = 243 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}FNS$: 243.0518; found: 243.0510.

The second component eluted was 5-(2″-fluoroanilino)-2,2′-bithiophene (**3j**) as a green oil (yield: 17%).

IR (liquid film): 3365 (NH), 3070, 2925, 2853, 1619, 1592, 1562, 1575, 1505, 1478, 1463, 1428, 1325, 1292, 1258, 1242, 1185, 1096, 1035, 920, 836, 805, 745, 694, 693 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.75 (d, *J* = 3.6 Hz, 1 H, 4-H), 6.84–6.92 (m, 1 H, Ar-H), 7.07 (d, *J* = 3.6 Hz, 1 H, 3-H), 7.10–7.17 (m, 3 H, 4′-H, 2 × Ar-H), 7.20 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.29 (dt, *J* = 8.1, 1.8 Hz, 1 H, Ar-H), 7.39 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.67 (br s, 1 H, NH).

MS (EI): *m*/*z* (%) = 275 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}FNS_2$: 275.0239; found: 275.0236.

1-(4″-Fluorophenyl)-2-(2′-thienyl)pyrrole (2l) and 1-(4″-Fluorophenyl)-2-(2′-thienyl)pyrrole (3l)
Treatment of amide **1l** with Lawesson's reagent gave a mixture of 1-(4″-fluorophenyl)-2-(2′-thienyl)pyrrole (**2l**) and 5-(4″-fluoroanilino)-2,2′-bithiophene (**3l**).

The first component eluted was 1-(4″-fluorophenyl)-2-(2′-thienyl)pyrrole (**2l**); pale yellow solid (yield: 58%); mp 77.7–78.7 °C [Et_2O–PE (1:2)].

IR (Nujol): 1593, 1560, 1519, 1496, 1428, 1403, 1353, 1325, 1316, 1303, 1227, 1161, 1093, 1081, 1072, 1034, 976, 917, 841, 792, 776, 727, 705, 697 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.29–6.33 (m, 1 H, 4-H), 6.48 (dd, *J* = 3.8, 1.8 Hz, 1 H, 3-H), 6.65 (dd, *J* = 3.8, 1.2 Hz, 1 H, 3′-H), 6.92–6.96 (m, 1 H, 4′-H), 6.98–7.01 (m, 1 H, 5-H), 7.26 (t, *J* = 8.7 Hz, 2 H, 2 × Ar-H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.36 (dd, *J* = 9.3, 4.8 Hz, 2 H, 2 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 110.0, 110.0, 111.5, 116.5, 116.8 (d, *J* = 9 Hz, C2″, C6″), 135.5, 161.0, 164.2 (d, *J* = 245 Hz, C4″), 125.3, 125.5, 125.6, 127.9, 128.2, 129.4, 129.5 (d, *J* = 23 Hz, C3″, C5″).

MS (EI): *m*/*z* (%) = 243 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}FNS$: 243.0518; found: 243.0516.

The second component eluted was 1-(4″-fluorophenyl)-2-(2′-thienyl)pyrrole (**3l**) as a green oil (yield: 8%).

IR (liquid film): 3377 (NH), 2924, 2728, 1563, 1509, 1407, 1304, 1260, 1226, 1154, 1045, 1019, 819, 769, 722, 689, 615 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.62 (d, *J* = 3.9 Hz, 1 H, 4-H), 7.02–7.14 (m, 6 H, 3′-H, 4′-H, 4 × Ar-H), 7.30 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.84 (br s, 1 H, NH).

MS (EI): *m*/*z* (%) = 275 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}FNS_2$: 275.0239; found: 275.0243.

1-(2′-Chlorophenyl)-2-(2′-thienyl)pyrrole (2m) and 5-(2″-Chloroanilino)-2,2′-bithiophene (3m)

Treatment of amide **1m** with Lawesson's reagent gave a mixture of 1-(2′-chlorophenyl)-2-(2′-thienyl)pyrrole (**2m**) and 5-(2″-chloroanilino)-2,2′-bithiophene (**3m**).

The first component eluted was 1-(2′-chlorophenyl)-2-(2′-thienyl)pyrrole (**2m**); green solid (yield: 16%); mp 72.8–74.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 2922, 2840, 1587, 1510, 1441, 1426, 1328, 1222, 1187, 1160, 1104, 1083, 1067, 1030, 917, 843, 827, 790, 770, 700 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.32–6.36 (m, 1 H, 4-H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.60 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.85–6.90 (m, 2 H, 4′-H, 5-H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.47–7.65 (m, 4 H, 3″-H, 4″-H, 5″-H, 6″-H).

^{13}C NMR (acetone-d_6): δ = 110.1, 110.2, 110.6, 124.2, 124.7, 125.1, 127.8, 128.8, 131.0, 131.2, 131.4, 133.7, 135.6, 138.7.

MS (EI): *m*/*z* (%) = 261 (35) [M^+, ^{37}Cl], 259 (100) [M^+, ^{35}Cl].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{35}ClNS$: 259.0222; found: 259.0222.

The second component eluted was 5-(2″-chloroanilino)-2,2′-bithiophene (**3m**) as a green oil (yield: 21%).

IR (liquid film): 3377 (NH), 1624, 1587, 1488, 1441, 1426, 1403, 1348, 1328, 1258, 1222, 1208, 1187, 1164, 1082, 1067, 1031, 917, 827, 769, 699, 612 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.81 (d, *J* = 3.8 Hz, 1 H, 4-H), 6.87 (dt, *J* = 7.5, 1.8 Hz, 1 H, 4″-H), 7.06–7.10 (m, 1 H, 4′-H), 7.13 (d, *J* = 3.8 Hz, 1 H, 3-H), 7.16–7.27 (m, 3 H, 3′-H, 5″-H, 6″-H), 7.36 (br s, 1 H, NH), 7.38 (m, 2 H, 5′-H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.3, 115.2, 120.7, 121.4, 122.8, 123.6, 124.8, 128.4, 128.5, 130.1, 131.5, 138.0, 143.0, 144.4.

MS (EI): *m*/*z* (%) = 293 (40) [M^+, ^{37}Cl], 291 (100) [M^+, ^{35}Cl].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{35}ClNS_2$: 290.9943; found: 290.9944.

1-(3″-Chlorophenyl)-2-(2′-thienyl)pyrrole (2n) and 5-(3″-Chloroanilino)-2,2′-bithiophene (3n)

Treatment of amide **1n** with Lawesson's reagent gave a mixture of 1-(3″-chlorophenyl-2-(2′-thienyl)pyrrole (**2n**) and 5-(3″-chloroanilino)-2,2′-bithiophene (**3n**).

The first component eluted was 1-(3″-chlorophenyl-2-(2′-thienyl)pyrrole (**2n**); green oil (yield: 24%).

IR (Nujol): 1594, 1483, 1436, 1348, 1325, 1187, 1167, 1108, 1077, 1037, 924, 876, 844, 786, 767, 689, 610 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.32–6.36 (m, 1 H, 4-H), 6.49 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.62 (dd, *J* = 3.9, 1.2 Hz, 1 H, 3′-H), 6.86–6.92 (m, 2 H, 4′-H, 5-H), 7.10–7.18 (m, 2 H, 5′-H, Ar-H), 7.28–7.34 (m, 3 H, 3 × Ar-H).

^{13}C NMR (acetone-d_6): δ = 110.1, 110.2, 110.6, 124.2, 124.7, 125.1, 127.8, 128.8, 131.0, 131.2, 131.4, 133.7, 135.6, 138.7.

MS (EI): *m*/*z* (%) = 261 (36) [M^+, ^{37}Cl], 259 (100) [M^+, ^{35}Cl].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{35}ClNS$: 259.0222; found: 259.0226.

The second component eluted was 5-(3″-chloroanilino)-2,2′-bithiophene (**3n**) as a green solid (yield: 31%); mp 74.7–75.6 °C [Et_2O–PE (1:2)].

IR (liquid film): 3372 (NH), 1595, 1519, 1479, 1301, 1226, 1075, 1049, 990, 836, 790, 769 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 5.63 (br s, 1 H, NH), 6.69 (d, *J* = 3.9 Hz, 1 H, 4-H), 6.76–6.80 (m, 1 H, Ar-H), 6.81–6.86 (m, 1 H, Ar-H), 6.90–6.92 (m, 1 H, Ar-H), 6.99 (d, *J* = 3.9 Hz, 1 H, 3-H), 7.00–7.04 (m, 1 H, 4′-H), 7.10–7.15 (m, 2 H, 3′-H, 5′-H), 7.17–7.22 (m, 1 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 113.7, 119.1, 119.9, 123.3, 123.7, 124.9, 128.7, 130.0, 131.5, 135.5, 135.3, 138.3, 145.2, 148.1.

MS (EI): *m*/*z* (%) = 293 (42) [M^+, ^{37}Cl], 291 (100) [M^+, ^{35}Cl].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{37}ClNS_2$: 292.9914; found: 292.9915.

1-(4″-Chlorophenyl-2-(2′-thienyl)pyrrole (2o) and 5-(4″-Chloroanilino)-2,2′-bithiophene (3o)

Treatment of amide **1o** with Lawesson's reagent gave a mixture of 1-(4″-chlorophenyl-2-(2′-thienyl)pyrrole (**2o**) and 5-(4″-chloroanilino)-2,2′-bithiophene (**3o**). The first component eluted was 1-(4″-chlorophenyl)-2-(2′-thienyl)pyrrole (**2o**) as a green solid (yield: 22%); mp 51.7–53.0 °C [Et_2O–PE (1:2)].

IR (liquid film): 3104, 1596, 1496, 1463, 1430, 1408, 1348, 1328, 1313, 1211, 1187, 1165, 1091, 1034, 1017, 915, 878, 844, 832, 790, 739, 711, 696 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.30–6.34 (m, 1 H, 4-H), 6.48 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.67 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.92–6.97 (m, 1 H, 4′-H), 7.00–7.02 (m, 1 H, 5-H), 7.29–7.35 (m, 3 H, 5-H, 2″-H, 6″-H), 7.50 (d, *J* = 9.0 Hz, 2 H, 3″-H, 5″-H).

^{13}C NMR (acetone-d_6): δ = 110.3, 110.5, 112.1, 125.3, 125.5, 126.0, 128.0, 128.8, 130.0, 133.5, 135.3, 139.7.

MS (EI): *m*/*z* (%) = 261 (34) [M^+, ^{37}Cl], 259 (100) [M^+, ^{35}Cl], 224 (14).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{37}ClNS$: 261.0193; found: 261.0195.

The second component eluted was 5-(4″-chloroanilino)-2,2′-bithiophene (**3o**) as a green solid (yield: 15%); mp 123.0–125.0 °C [Et_2O–PE (1:2)].

IR (liquid film): 3393 (NH), 2256, 1248, 1169, 1086, 1033, 963, 889, 671 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.68 (d, *J* = 3.8 Hz, 1 H, 4-H), 7.05–7.12 (m, 4 H, 3′-H, 4′-H, 2″-H, 6″-H), 7.18, (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.27 (d, *J* = 9.0 Hz, 2 H, 3″-H, 5′-H), 7.38 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.95 (br s, 1 H, NH).

^{13}C NMR (acetone-d_6): δ = 116.8, 117.7, 123.3, 123.5, 124.4, 124.7, 128.7, 129.1, 129.9, 138.0, 145.2, 146.1.

MS (EI): *m*/*z* (%) = 293 (24) [M^+, ^{37}Cl], 291 (81) [M^+, ^{35}Cl], 207 (100).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{37}ClNS_2$: 292.9914; found: 292.9917.

1-(2″-Bromophenyl-2-(2′-thienyl)pyrrole (2p) and 5-(2″-Bromoanilino)-2,2′-bithiophene (3p)

Treatment of amide **1p** with Lawesson's reagent gave a mixture of 1-(2″-bromophenyl-2-(2′-thienyl)pyrrole (**2p**) and 5-(2″-bromoanilino)-2,2′-bithiophene (**3p**). The first component eluted was 1-(2″-bromophenyl-2-(2′-thienyl)pyrrole (**2p**; yield: 6%) as a green solid; mp 94.5–96.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 2925, 1582, 1504, 1482, 1328, 1308, 1221, 1208, 1187, 1161, 1083, 1056, 1028, 955, 918, 843, 828, 771, 724, 701 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.32–6.34 (m, 1 H, 4-H), 6.52–6.54 (m, 1 H, 3-H), 6.59 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.84–6.89 (m, 2 H, 4′-H, 5-H), 7.22 (dd, *J* = 5.4, 1.2 Hz, 1 H, 5′-H), 7.46–7.56 (m, 3 H, 4″-H, 5″-H, 6″-H), 7.80 (dd, *J* = 8.0, 1.8 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.0, 110.1, 124.0, 124.2, 124.7, 125.0, 127.8, 129.1, 129.4, 131.4, 131.5, 134.2, 135.6, 140.4.

MS (EI): *m*/*z* (%) = 305 (70) [M^+, ^{81}Br], 303 (67) [M^+, ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{81}BrNS$: 304.9697; found: 304.9696.

The second component eluted was 5-(2″-bromoanilino)-2,2′-bithiophene (**3p**) as a yellow oil (yield: 46%).

IR (liquid film): 3375 (NH), 3105, 3022, 2926, 2853, 2589, 1592, 1561, 1488, 1451, 1427, 1353, 1320, 1298, 1254, 1223, 1164, 1118, 1046, 1022, 931, 916, 888, 836, 800, 745, 694, 666, 629, 611 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.78–6.84 (m, 2 H, 4-H, 4″-H), 7.07–7.12 (m, 2 H, 3-H, 4′-H), 7.14 (dd, *J* = 8.3, 1.8 Hz, 1 H, 6″-H), 7.18 (br s, 1 H, NH), 7.23 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.28 (dt, *J* = 8.0, 1.5 Hz, 1 H, 5″-H), 7.41 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.56 (dd, *J* = 7.8, 1.5 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.6, 115.8, 121.6, 122.1, 123.1, 123.9, 125.1, 128.8, 129.4, 132.0, 133.6, 138.3, 144.4, 144.8.

MS (EI): *m*/*z* (%) = 337 (100) [M^+, ^{81}Br], 335 (93) [M^+, ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{81}BrNS_2$: 336.9417; found: 336.9418.

1-(4″-Bromophenyl-2-(2′-thienyl)pyrrole (2q) and 5-(4″-Bromoanilino)-2,2′-bithiophene (3q)

Treatment of amide **1q** with Lawesson's reagent gave a mixture of 1-(4″-bromophenyl-2-(2′-thienyl)pyrrole (**2q**) and 5-(4″-bromoanilino)-2,2′-bithiophene (**3q**). The first component eluted was 1-(4″-bromophenyl)-2-(2′-thienyl)pyrrole (**2q**; yield: 34%) as a pale yellow oil.

IR (Nujol): 1632, 1491, 1428, 1347, 1097, 1069, 913, 828, 712, 674 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.28–6.32 (m, 1 H, 4-H), 6.48 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H) 6.60 (dd, *J* = 3.6, 1.0 Hz, 1 H, 3′-H), 6.85–6.92 (m, 2 H, 5-H, 4′-H), 7.13 (d, *J* = 8.9 Hz, 2 H, 2 × Ar-H), 7.16 (dd, *J* = 5.2, 1.2 Hz, 1 H, 5′-H), 7.50 (d, *J* = 8.9 Hz, 2 H, 2 × Ar-H).

MS (EI): *m*/*z* (%) = 305 (100) [M^+, ^{81}Br], 303 (97) [M^+, ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{79}BrNS$: 302.9917; found: 302.9713.

The second component eluted was 5-(4″-bromoanilino)-2,2′-bithiophene (**3q**) as a green metallic solid (yield: 7%); mp 129–131 °C [Et_2O–PE (1:2)].

IR (liquid film): 3428 (NH), 1592, 1519, 1488, 1426, 1175, 1072, 814, 693, 629 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 5.63 (br s, 1 H, NH), 6.65 (d, *J* = 3.6 Hz, 1 H, 4-H), 6.82 (d, *J* = 8.7, 2 H, 2″-H, 6″-H), 6.97 (d, *J* = 3.6 Hz, 1 H, 3-H), 6.98–7.02 (m, 1 H, 4′-H), 7.09 (br d, *J* = 2.4 Hz, 1 H, 3′-H), 7.19 (br d, *J* = 5.4 Hz, 1 H, 5′-H), 7.33 (d, *J* = 8.7, 2 H, 3″-H, 5″-H).

MS (EI): *m*/*z* (%) = 337 (100) [M^+, ^{81}Br], 335 (93) [M^+, ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}{}^{79}BrNS_2$: 334.9438; found: 334.9429.

1-(2″,4″-Dibromophenyl)-2-(2′-thienyl)pyrrole (2r) and 5-(2″,4″-Dibromoanilino)-2,2′-bithiophene (3r)

Treatment of amide **1r** with Lawesson's reagent gave a mixture of 1-(2″,4″-dibromophenyl)-2-(2′-thienyl)pyrrole (**2r**) and 5-(2″,4″-dibromoanilino)-2,2′-bithiophene (**3r**). The first component eluted was 1-(2″,4″-dibromophenyl)-2-(2′-thienyl)pyrrole (**2r**; yield: 24%) as a pale yellow oil.

IR (Nujol): 3104, 3081, 2924, 2855, 1576, 1554, 1508, 1481, 1428, 1407, 1378, 1347, 1327, 1245, 1209, 1187, 1167, 1102, 1079, 1057, 1009, 915, 869, 844, 823, 788, 759, 696, 610, 566 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.32–6.38 (m, 1 H, 4-H), 6.53 (dd, *J* = 3.6, 1.5 Hz, 1 H, 3-H), 6.66 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.86–6.88 (m, 1 H, 5-H), 6.90–6.94 (m, 1 H, 4′-H), 7.26 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.45 (d, *J* = 8.4 Hz, 1 H, 6″-H), 7.74 (dd, *J* = 8.4, 2.1 Hz, 1 H, 5″-H), 8.0 (d, *J* = 2.1 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.4, 110.5, 123.5, 124.6, 124.9, 125.0, 125.2, 127.9, 129.0, 132.5, 132.9, 135.3, 136.3, 139.8.

MS (EI): *m*/*z* (%) = 385 (53) [M^+, 2 × ^{81}Br], 383 (100) [M^+, $^{79}Br^{81}Br$], 381 (51) [M^+, 2 × ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_9{}^{81}Br_2NS$: 384.8782; found: 384.8782.

The second component eluted was 5-(2″,4″-dibromoanilino)-2,2′-bithiophene (**3r**) as a green oil (yield: 15%).

IR (Nujol): 3375 (NH), 1585, 1563, 1486, 1427, 1383, 1293, 1264, 1247, 1176, 1031, 867, 838, 800, 694, 529 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.84 (d, *J* = 3.9 Hz, 1 H, 4-H), 7.05 (d, *J* = 8.7 Hz, 1 H, 6″-H), 7.08–7.12 (m, 1 H, 4′-H), 7.14 (d, *J* = 3.9 Hz, 1 H, 3-H), 7.24 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.31 (br s, 1 H, NH), 7.40–7.46 (m, 2 H, 5′-H, 5″-H), 7.72 (d, *J* = 2.4 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.8, 111.3, 116.9, 123.1, 123.2, 124.2, 125.3, 128.8, 132.2, 132.9, 135.4, 138.1, 143.9, 144.3.

MS (EI): *m*/*z* (%) = 417 (56) [M^+, 2 × ^{81}Br], 415 (100) [M^+, $^{79}Br^{81}Br$], 413 (49) [M^+, 2 × ^{79}Br].

HRMS (EI): *m*/*z* calcd for $C_{14}H_9{}^{81}Br_2NS_2$: 416.8502; found: 416.8495.

1-(2″-Iodophenyl)-2-(2′-thienyl)pyrrole (2s) and 5-(2″-Iodoanilino)-2,2′-bithiophene (3s)

Treatment of amide **1s** with Lawesson's reagent gave a mixture of 1-(2″-iodophenyl)-2-(2′-thienyl)pyrrole (**2s**) and 5-(2″-iodoanilino)-2,2′-bithiophene (**3s**). The first component eluted was 1-(2″′-iodophenyl)-2-(2′-thienyl)pyrrole (**2s**) as a green solid (yield: 8%); mp 97.6–99.0 °C [Et_2O–PE (1:2)].

IR (Nujol): 1580, 1504, 1479, 1423, 1402, 1348, 1326, 1309, 1260, 1220, 1187, 1167, 1096, 1021, 917, 794, 764, 709 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.31–6.34 (m, 1 H, 4-H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.58 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.78–6.82 (m, 1 H, 5-H), 6.85 (m, 1 H, 4′-H), 7.22 (dd, *J* = 5.2, 1.2 Hz, 1 H, 5′-H), 7.31 (dt, *J* = 8.1, 1.5 Hz, 1 H, 4″-H), 7.46 (dd, *J* = 8.1, 1.5 Hz, 1 H, 6″-H), 7.58 (dt, *J* = 8.1, 1.5 Hz, 1 H, 5″-H), 8.04 (dd, *J* = 8.1, 1.5 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.1, 110.2, 124.2, 124.6, 124.7, 127.8, 130.1, 130.8, 131.4, 135.8, 138.5, 140.5, 143.3, 144.0.

MS (EI): *m*/*z* (%) = 351 (100) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}INS$: 350.9579; found: 350.9582.

The second component eluted was 5-(2″-iodoanilino)-2,2′-bithiophene (**3s**) as a green solid (yield: 55%); mp 91.5–92.5 °C [Et_2O–PE (1:1)].

IR (liquid film): 3342 (NH), 1582, 1558, 1523, 1480, 1443, 1426, 1292, 1279, 1171, 1079, 1048, 1008, 836, 807, 746, 693 cm^{-1}.

^1H NMR (acetone-d_6): δ = 6.69 (dt, *J* = 8.0, 1.5 Hz, 1 H, 4″-H), 6.78 (d, *J* = 3.6 Hz, 1 H, 4-H), 6.90 (br s, 1 H, NH), 7.06–7.10 (m, 2 H, 4′-H, 6″-H), 7.12 (d, *J* = 3.6 Hz, 1 H, 3-H), 7.23 (dd, *J* = 3.6, 1.2 Hz,

1 H, 3′-H), 7.31 (dt, *J* = 8.0, 1.5 Hz, 1 H, 5″-H), 7.41 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1 H, 3″-H).

^{13}C NMR (acetone-d_6): δ = 110.6, 115.8, 121.6, 122.6, 123.2, 123.9, 125.1, 128.8, 130.2, 131.8, 138.3, 140.4, 145.5, 147.1.

MS (EI): *m*/*z* (%) = 383 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}INS_2$: 382.9299; found: 382.9298.

1-(3″-Nitrophenyl)-2-(2′-thienyl)pyrrole (2t) and 5-(3″-Nitroanilino)-2,2′-bithiophene (3t)

Treatment of amide **1t** with Lawesson's reagent gave a mixture of 1-(3″-nitrophenyl)-2-(2′-thienyl)pyrrole (**2t**) and 5-(3″-nitroanilino)-2,2′-bithiophene (**3t**). The first component eluted was 1-(3″-nitrophenyl)-2-(2′-thienyl)pyrrole (**2t**) as a green oil (yield: 26%).

IR (Nujol): 3105, 2957, 2926, 2870, 1617, 1587, 1531, 1487, 1463, 1426, 1351, 1328, 1273, 1187, 1167, 1113, 1087, 1038, 928, 896, 865, 844, 804, 738, 710, 683 cm^{-1}.

^{1}H NMR (acetone-d_6): 6.38–6.42 (m, 1 H, 4-H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.74 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.95–7.00 (m, 1 H, 4′-H), 7.18–7.22 (m, 1 H, 5-H), 7.38 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.74–7.82 (m, 2 H, 2 × Ar-H), 8.12–8.16 (m, 1 H, Ar-H), 8.26–8.32 (m, 1 H, Ar-H).

^{13}C NMR (acetone-d_6): δ = 111.0, 113.0, 121.6, 122.7, 125.4, 126.2, 126.8, 127.8, 128.2, 131.2, 133.1, 134.5, 134.8, 141.7.

MS (EI): *m*/*z* (%) = 270 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}N_2OS_2$: 270.0463; found: 270.0463.

The second component eluted was 5-(3″-nitroanilino)-2,2′-bithiophene (**3t**) as a green solid (yield: 21%); mp 134.1–136.2 °C [Et$_2$O–PE (1:2)].

IR (Nujol): 3351 (NH), 1615, 1563, 1539, 1520, 1344, 1271, 1260, 1169, 993, 864, 838, 818, 799, 792, 730 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 6.85 (d, *J* = 3.9 Hz, 1 H, 4-H), 7.07–7.12 (m, 1 H, 4′-H), 7.16 (d, *J* = 3.9 Hz, 1 H, 3-H), 7.25 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.41–7.46 (m, 2 H, 5′-H, 6″-H), 7.54 (t, *J* = 8.1 Hz, 1 H, 5″-H), 7.69 (m, 1 H, 4″-H), 7.86 (d, *J* = 2.4 Hz, 1 H, 2″-H), 8.24 (br s, 1 H, NH).

^{13}C NMR (acetone-d_6): δ = 108.8, 114.4, 120.5, 122.0, 123.4, 124.0, 125.2, 128.8, 131.2, 137.1, 138.1, 144.3, 148.1, 150.2.

MS (EI): *m*/z (%) = 302 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}N_2O_2S_2$: 302.0184; found: 302.0186.

1-(4″-Methyloxycarbonylphenyl)-2-(2′-thienyl)pyrrole (2u) and 5-(4″-Methyloxycarbonylanilino)-2,2′-bithiophene (3u)

Treatment of amide **1u** with Lawesson's reagent gave a mixture of 1-(4″-methyloxycarbonylphenyl)-2-(2′-thienyl)pyrrole (**2u**) and 5-(4″-methyloxycarbonylanilino)-2,2′-bithiophene (**3u**). The first component eluted was 1-(4″-methyloxycarbonylphenyl)-2-(2′-thienyl)pyrrole (**2u**) as a greenish yellow solid (yield: 37%); mp 76.7–77.8 °C [Et$_2$O–PE (1:2)].

IR (liquid film): 3132, 3103, 3084, 3063, 3017, 2950, 2842, 1727 (C=O), 1512, 1505, 1462, 1455, 1436, 1413, 1348, 1328, 1319, 1305, 1288, 1253, 1213, 1190, 1170, 1099, 1053, 1036, 1021, 1013, 966, 915 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.94 (s, 3 H, CO_2CH_3), 6.35 (m, 1 H, 4-H), 6.50 (dd, *J* = 3.6, 1.8 Hz, 1 H, 3-H), 6.68 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.94–6.98 (m, 1 H, 4′-H), 7.10–7.13 (m, 1 H, 5-H), 7.36 (dd, *J* = 5.2, 1.2 Hz, 1 H, 5′-H), 7.43 (d, *J* = 8.7 Hz, 2 H, 2″-H, 6″-H), 8.08 (d, *J* = 8.7 Hz, 2 H, 3″-H, 5″-H).

^{13}C NMR (acetone-d_6): δ = 110.7, 112.9, 125.2, 125.8, 126.4, 126.8, 127.7, 128.0, 129.6, 131.1, 135.2, 144.7, 166.5.

MS (EI): *m*/*z* (%) = 283 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{16}H_{13}NO_2S$: 283.0667; found: 283.0666.

The second component eluted was 5-(4″-methyloxycarbonylanilino)-2,2′-bithiophene (**3u**) as a yellow solid (yield: 32%); mp 146.4–148.3 °C [Et$_2$O–PE (1:2)].

IR (Nujol): 3314 (NH), 2922, 1679 (C=O), 1601, 1583, 1558, 1530, 1515, 1417, 1266, 1243, 1197, 1173, 1122, 1051, 971, 886, 838, 814, 790, 763, 689 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 3.85 (s, 3 H, CO_2CH_3), 6.80 (d, *J* = 3.8 Hz, 1 H, 4-H), 7.07–7.15 (m, 4 H, 3-H, 4′-H, 2″-H, 6″-H), 7.23 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.41 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.92 (d, *J* = 8.4 Hz, 2 H, 3″-H, 5″-H), 8.30 (br s, 1 H, NH).

^{13}C NMR (acetone-d_6): δ = 51.8, 114.2, 119.9, 121.4, 123.25, 123.9, 125.0, 128.8, 130.6, 132.0, 138.2, 144.3, 150.6, 166.9.

MS (EI): *m*/*z* (%) = 315 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{16}H_{13}NO_2S_2$: 315.0388; found: 315.0386.

1-(4″-Cyanophenyl)-2-(2′-thienyl)pyrrole (2v) and 5-(4″-Cyanoanilino)-2,2′-bithiophene (3v)

Treatment of amide **1v** with Lawesson's reagent gave a mixture of 1-(4″-cyanophenyl)-2-(2′-thienyl)pyrrole (**2v**) and 5-(4″-cyanoanilino)-2,2′-bithiophene (**3v**). The first component eluted was 1-(4″-cyanophenyl)-2-(2′-thienyl)pyrrole (**2v**) as a beige solid (yield: 32%); mp 114.2–115.5 °C (Et$_2$O).

IR (Nujol): 2227 (CN), 1576, 1559, 1569, 1540, 1521, 1507, 1457, 1436, 1390, 1318, 1209, 1188, 914, 844, 794, 719, 697, 668 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 6.38–6.42 (m, 1 H, 4-H), 6.52 (dd, *J* = 3.5, 1.8 Hz, 1 H, 3-H), 6.72 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 6.97–7.02 (m, 1 H, 4′-H), 7.14–7.18 (m, 1 H, 5-H), 7.40 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.50 (d, *J* = 8.7 Hz, 2 H, 2″-H, 6″-H), 7.88 (d, *J* = 8.7 Hz, 2 H, 3″-H, 5″-H).

^{13}C NMR (acetone-d_6): δ = 111.1, 111.4, 113.4, 118.8, 125.3, 126.2, 126.8, 127.5, 127.6, 128.2, 134.0, 134.9, 144.5.

MS (EI): *m*/*z* (%) = 250 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{10}NO_2S$: 250.0565; found: 250.0566.

The second component eluted was 5-(4″-cyanoanilino)-2,2′-bithiophene (**3v**) as a yellow solid (yield: 19%); mp 139.6–141.1 °C.

IR (Nujol): 3272 (NH), 2213 (CN), 1604, 1562, 1517, 1322, 1266, 1172, 1116, 1047, 1021, 830, 789, 722, 693, 612 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 6.83 (d, *J* = 3.6 Hz, 1 H, 4-H), 7.08–7.12 (m, 1 H, 4′-H), 7.13 (m, 3 H, 3-H, 2″-H, 6″-H), 7.24 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′-H), 7.43 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′-H), 7.63 (d, *J* = 9.0 Hz, 2 H, 3″-H, 5″-H), 8.39 (br s, 1 H, NH).

^{13}C NMR (acetone-d_6): δ = 102.0, 115.0, 120.1, 121.0, 123.3, 124.1, 125.2, 128.8, 131.6, 134.4, 138.0, 143.4, 150.5.

MS (EI): *m*/*z* (%) = 282 (100) [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{10}N_2S_2$: 282.2854; found: 282.2885.

Acknowledgment

Thanks are due to Foundation for Science and Technology (Portugal) for financial support through IBQF (UM) and through FEDER, POCTI (ref. POCTI/QUI/37816/2001).

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