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AN EFFECTIVE ACTIVATION OF PALLADIUM PHOSPHINE COMPLEXES IN AQUEOUS PHASE REACTIONS OF HETERO-AROMATIC BORONIC ACIDS WITH ARYL HALIDES

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We have developed a simple and effective method for the activation of palladium phosphine complexes in the Suzuki reaction (TON up to 9800, TOF up to 58800 h^{-1}) by selecting an aqueous reaction medium instead of organic solvents. This method was elaborated for a high yield synthesis of heteroaromatic biaryls with furyl and thienyl groups.

Keywords: heteroaromatic boronic acids, palladium phosphine complexes, water, activation, Suzuki reaction.

Palladium-catalyzed cross coupling of arylboronic acids with aryl halides (the Suzuki reaction) is a convenient and universal method used in the modern organic synthesis for the preparation of biaryls, including ones with heteroaromatic groups [1, 2]. Heterocyclic biaryls with furyl and thienyl rings are of great practical interest as structural motifs of new medications [3-6]. Besides that, polythiophene structures are frequently incorporated in electroconductive polymers [7]. However, the 2-furyl and 2-thienylboronic acids that might be selected for the synthesis of such compounds are prone to protodeboration, and therefore are not convenient reagents for Suzuki reactions. Solutions to this problem have been proposed by substituting heteroaromatic boronic acids with their methyliminodiacetic acid derivatives (MIDA boronates) [8], cyclic triol borates [9], and trifluoroborate salts [10], which offer a better stability against protodeboration in basic media. Another approach involves the improvement of palladium catalyst activity to enable cross-coupling reactions at temperatures that do not exceed 40°C, that is, under conditions where heteroaromatic boronic acids are resistant to protolysis [2]. However, a large scale use of these methods is problematic due to the high consumption (up to 10 mol%) of Pd catalysts with expensive *ortho*-biphenyl phosphine ligands (Buchwald ligands), the requirement for an inert atmosphere, the lengthy preparation of boronic acid derivatives, the lengthy reaction times, and the use of toxic and flammable solvents.

This problem could be best solved by selecting the simplest and most accessible catalysts or minimum quantities of palladium complexes, and using aqueous reaction media. The many unique properties of water offer great advantages for performing catalytic processes, and for the development of environmentally friendly

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synthetic technologies. Since water is nontoxic, non-flammable, and cheap even in distilled form, it also offers advantages in the terms of cost. The highly polar nature and the very high dielectric constant of water facilitate reactions involving ions. Its high thermal conductivity, heat capacity, and heat of vaporization ensure process safety even during rapid carbon–carbon bond formation reactions, which are known to be quite exothermic. The density of water (1 g/cm^3) is sufficiently different from most organic solvents to ensure effective separation of liquid phases. However, the low aqueous solubility of most organic compounds must be overcome before the full potential of catalysis in aqueous media can be exploited.

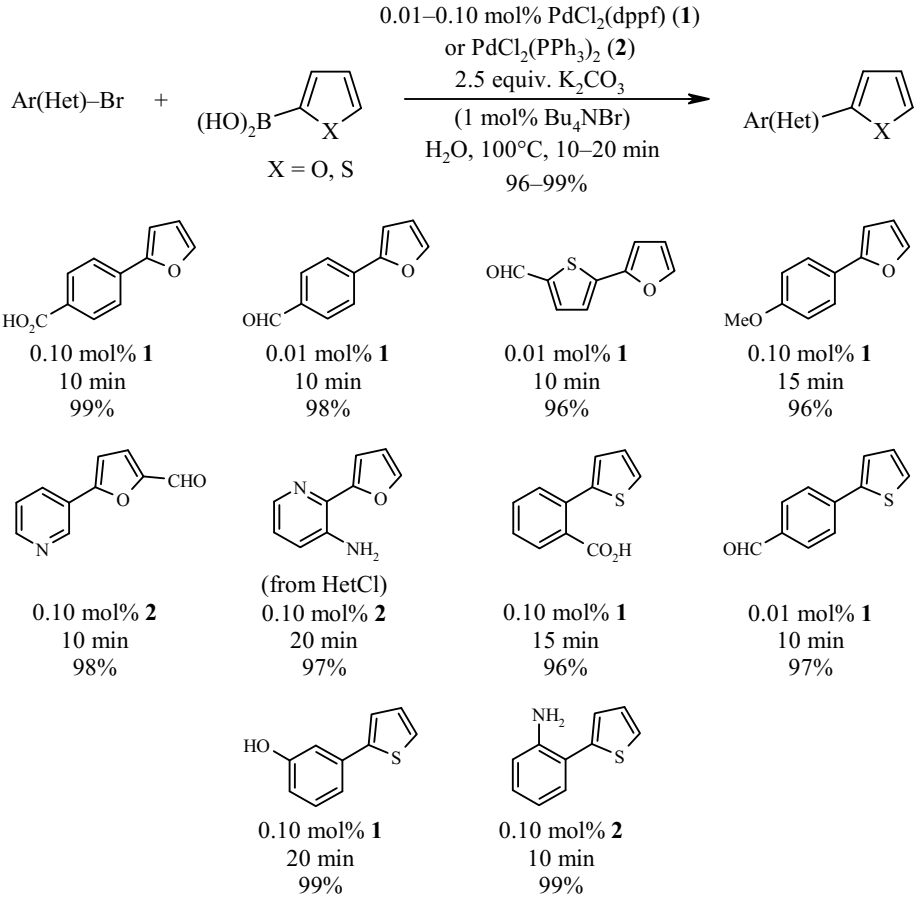
The first investigations of cross-coupling reactions in aqueous media were performed in 1980-1990s with ligand-free palladium [11-17], water-soluble palladium phosphine complexes [18-20], or in the presence of phase transfer catalysts [21-24]. Various aspects of homogeneous or heterogeneous catalysis in water or water-containing media have been reviewed in detail [25-27], including a critical consideration of environmental safety in such reactions. Of particular interest are aqueous catalytic processes promoted by microwave irradiation [28]. The use of microwave irradiation in the presence of water had a very strong activating effect on the catalytic system [29, 30], enabling an effective Suzuki reaction even with trace amounts of palladium (H_2O, MW, 150 W, 0.05-2.50 ppm Pd, Na_2CO_3, 1 equiv. Bu_4NBr, 150°C, 5 min, yields up to 99%). This methodology, however, requires arylboronic acids of high purity [30]. A recent study accomplished the Suzuki reactions of various aromatic and heteroaromatic halides with MIDA derivatives of boronic acids at room temperature in aqueous medium without organic solvents, but in the presence of non-ionic amphiphilic additive TPGS-750-M (a PEG derivative of α-tocopherol) (2 mol% $PdCl_2$(dtbpf) (dtbpf – 1,1'-bis(di-*tert*-butyl-phosphino)ferrocene), 3 equiv. Et_3N, TPGS-750-M/H_2O (2% by mass), 1 mol/l, 20°C, 16-24 h, yields up to 99%) [31].

This work continues our studies aimed at the development of novel catalytic systems [32, 33] by showing that the efficiency of palladium phosphine complexes can be increased by tens and hundreds of times if the catalytic cross-coupling reactions are performed in aqueous medium without organic solvents. We used the example of the reaction of 2-furylboronic acid and 4-bromobenzoic acid to show for the first time the extremely high activity of a palladium phosphine cross-coupling catalyst in an aqueous medium (Scheme 1). The reaction was accomplished in 10 min in boiling water with catalysis by 0.1 mol% of the $PdCl_2$(dppf) complex (**1**) (dppf – 1,1'-bis(diphenylphosphino)ferrocene) in the presence of K_2CO_3 and without inert atmosphere, giving the 4-(2-furyl)benzoic acid in a quantitative yield. It should be noted that 4-bromobenzoic acid was quickly converted to its salt under these conditions, and the species undergoing cross coupling was actually potassium 4-bromobenzoate. Even more surprising was the reaction of 2-thienylboronic acid with the water-insoluble and relatively inert 2-bromoaniline upon catalysis by the palladium triphenylphosphine complex $PdCl_2(PPh_3)_2$ (**2**). A quantitative yield of 2-(2-thienyl)aniline was obtained over 10 min at 100°C in the presence of the complex **2** (0.1 mol%) and the phase transfer agent Bu_4NBr (1 mol%). No traces of the cross-coupling products were observed in the absence of palladium complexes (100°C, 60 min).

These key results of aqueous Suzuki reactions with effective catalysis by palladium phosphine complexes served as the starting point for biaryl synthesis with furyl and thienyl groups. 2-Furyl- and 2-thienyl-boronic acids reacted with various electron-rich and electron-poor aryl bromides in our developed conditions (0.01-0.10 mol% of Pd complex **1** or **2**, 2.5 equiv. K_2CO_3, for water-insoluble aryl halides 1 mol% of Bu_4NBr was added, aqueous medium, 100°C), forming the corresponding heterocyclic biaryls in high yields (Scheme 1).

The catalytic system was so effective in aqueous medium that the palladium concentration could be as low as 0.01 mol% in the case of activated aryl bromides with electron-withdrawing substituents, without impacting the product yield and the reaction time. 4-Bromobenzaldehyde and 5-bromothiophene-2-carb-aldehyde smoothly reacted under these conditions with 2-furyl- and 2-thienylboronic acids, giving the corresponding cross-coupling products in 96-98% yields. For comparison, analogous reactions in ethanol with 1 mol% of the phosphine complex catalyst $Pd(OAc)_2$+2RuPhos occurred at 85°C under a strictly inert atmosphere, and were complete in 2-24 h (RuPhos–dicyclohexyl(2',6'-diisopropylbiphenyl-2-yl)phosphine) [10].

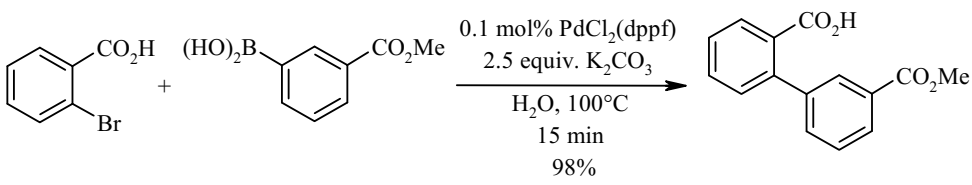
Scheme 1



The example of 3-amino-2-(2-furyl)pyridine synthesis showed that in our developed reaction conditions the heterocyclic aryl bromides in many cases could be substituted with the cheaper chlorides (Scheme 1). The reaction of 3-amino-2-chloropyridine with 2-furylboronic acid in the presence of 0.1 mol% of the complex **2** was complete in 20 min, giving the target compound in a practically quantitative yield. The completion of the same reaction in anhydrous dioxane with 3 mol% of Pd[P(*t*-Bu)$_3$]$_2$ catalyst required refluxing for 18 h with a twofold excess of 2-furylboronic acid, and the yield was 88% [34].

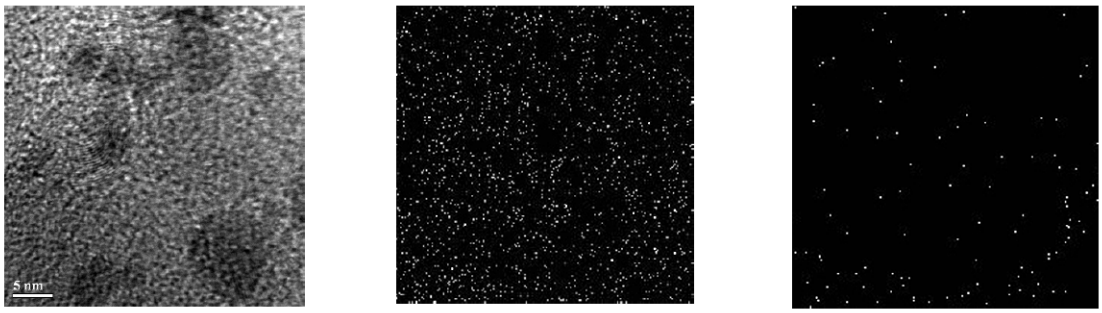
The potential capabilities of our developed catalytic system for the synthesis of polyfunctional compounds were demonstrated with the high yield synthesis of 3'-(methoxycarbonyl)biphenyl-2-carboxylic acid, the structure of which contains both carboxyl and ester groups (Scheme 2).

Scheme 2



It should be noted that we performed all of the above described reactions in air, without using an inert atmosphere. We did not observe the formation of palladium black during any of the experiments with catalyst quantities in the range from 0.01 to 0.10 mol%, and the mixtures remained practically colorless throughout the entire reactions. Samples of the reaction mixtures were observed with an optical microscope equipped with a

video camera, at 2000× magnification. The TLC data indicated a complete absence of aryl(heteraryl) halide in the reaction mixture at the moment when particles of palladium black (0.8-2.0 μm) precipitated.



a) *b*) *c*)

Fig. 1. (*a*) Transmission electron microscopy image of a sample from the reaction of 2-furylboronic acid with 4-bromobenzoic acid (80% conversion) with element distribution maps for: (*b*) carbon and (*c*) palladium.

The high-resolution transmission electron microscopy analysis of reaction mixture samples collected at 40-80% conversion degree indicated the absence of palladium nanoparticles larger than 1 nm (Fig. 1, *a*). At the same time, the energy-dispersive X-ray spectroscopy (Fig. 1, *b,c*), showed a uniform distribution of palladium particles among carbon-containing compounds (ArBr, $Ar^1B(OH)_2$, $ArAr^1$, K_2CO_3). The microscopy data indicated that palladium black or nanophase palladium did not significantly contribute to the catalysis under these conditions. The catalytic cycle may include palladium subnanoclusters or molecular complexes with weakly coordinated phosphine oxide ligands that may form under the reaction conditions in a aqueous basic medium [35]. This suggestion agrees with an example from the literature [36], where three- and four-atom palladium subnanoclusters were identified as the most likely cross coupling intermediates in reactions that were performed under identical conditions (0.3-300 ppm Pd, *N*-methylpyrrolidone, 135°C, KOAc, 1 vol% H_2O, 8-24 h), regardless of the palladium source (nanoparticles, salts, palladacycles, phosphine complexes, Pd black). The addition of small amounts of water or amines under the reaction conditions caused a rapid formation of catalytically active (TOF up to $2 \cdot 10^5$ h^{-1}) and stable palladium clusters. The palladium nanoparticles were only slowly dissociated into atoms by aryl halides in the absence of water, and all the reactions had an induction period of approximately two hours.

Thus, we have used heterocyclic arylboronic acids that are difficult substrates for cross coupling, and demonstrated a high efficiency of palladium complex activation in aqueous medium (TON up to 9800, TOF up to 58800 h^{-1}). The developed reaction conditions gave nearly quantitative yields, which allowed simple isolation of the target compounds.

EXPERIMENTAL

IR spectra were recorded for thin film samples on a Nicolet Protege-460 FTIR instrument. ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance II NMR 400 spectrometer (400 and 100 MHz, respectively). Mass spectra were recorded on a Hewlett Packard 5890/5972 instrument with EI ionization (70 eV). Elemental analyses were performed on a vario Micro cube instrument. Melting points were determined on a Kofler hot stage apparatus. Samples of the reaction mixtures were examined by transmission electron microscopy using a JEM-100CX II instrument. The reagents and solvents were purchased from Sigma-Aldrich, Acros Organics, and Merck and were used without additional purification.

The Suzuki Reaction Catalyzed by the Palladium Phosphine Complexes 1 and 2 (General Method). The palladium complex **1** or **2** (as 0.1 ml of 0.001-0.010 mol/l solution in $CHCl_3$, for a total Pd quantity of 0.01-0.10 mol%) was added to a hot (80°C) mixture of heterocyclic arylboronic acid (1.20 mmol),

aryl(hetaryl) bromide (1.00 mmol), Bu_4NBr (3.22 g, 0.01 mmol, for the water-insoluble ArX), and K_2CO_3 (0.35 g, 2.50 mmol) in water (5 ml). The reactor with a reflux condenser was placed in a hot (150°C) silicone oil bath, and the reaction mixture was vigorously stirred at reflux until full conversion (the catalyst load, reaction duration, and target compound yields are indicated in the Schemes 1 and 2). The reaction progress was controlled by TLC (eluent hexane–Et_2O, 3:1). The reaction was very exothermic in the case of the activated aryl bromides, thus an effective reflux condenser was necessary for scaling up this synthesis.

After the formation of the desired heterocyclic arylbenzoic acids, analytically pure samples were prepared by diluting the reaction mixture with water, heating, and filtering while hot to remove the small amount (~0.01-0.10 mol%) of palladium black, adding 10-15% aqueous solution of alcohol, heating to ~50°C, and finally by slowly adding 5% HCl with stirring until pH 2-3. The resulting precipitate could be easily collected by filtration, and analytically pure samples were thus obtained without resorting to chromatography. In the cases of the heterocyclic biaryls that were insoluble in water, the reaction mixture was diluted with a saturated solution of NaCl, extracted with Et_2O or EtOAc, the extract was dried over Na_2SO_4 and filtered through a thin layer of silica gel. The solvent was evaporated at reduced pressure, giving a residue that was at least 99% pure as a rule in all cases. Analytically pure samples were obtained by recrystallization of the heterocyclic biaryls from a minimum amount of alcohol containing 10-20% H_2O, or by converting the free amines into hydrochlorides.

Several of the synthesized compounds are characterized below.

4-(2-Furyl)benzoic Acid. White crystalline powder, mp 231-232°C (mp 230-232°C [37]). ^{1}H NMR spectrum (DMSO-d_6–$CDCl_3$, 1:3), δ, ppm (*J*, Hz): 6.65 (1H, dd, *J* = 3.4, *J* = 1.8, H-4 Fur); 7.15 (1H, d, *J* = 3.4, H-3 Fur); 7.78-7.83 (3H, m, H-3,5, H-5 Fur); 7.98 (2H, d, *J* = 8.5, H-2,6); 12.90 (1H, br. s, COOH). ^{13}C NMR spectrum (DMSO-d_6–$CDCl_3$, 1:3), δ, ppm: 104.8 (C-3 Fur); 108.9 (C-4 Fur); 125.3 (C-1); 128.4 (C-3,5); 130.2 (C-2,6); 133.3 (C-4); 141.8 (C-5 Fur); 154.6 (C-2 Fur); 171.1 (COOH). Found, %: C 70.12; H 4.35. $C_{11}H_8O_3$. Calculated, %: C 70.21; H 4.29.

2-(2-Thienyl)benzoic Acid. Flesh-colored crystalline powder, mp 97-98°C (mp 95-97°C [38]). ^{1}H NMR spectrum (DMSO-d_6–$CDCl_3$, 1:3), δ, ppm (*J*, Hz): 7.04-7.12 (2H, m, H-3,4 Th); 7.36 (1H, dd, *J* = 4.9, *J* = 1.3, H-5 Th); 7.60-7.80 (3H, m, H-4,5,6); 7.89 (1H, d, *J* = 7.6, H-3). ^{13}C NMR spectrum (DMSO-d_6–$CDCl_3$, 1:3), δ, ppm: 126.1. (C-5 Th); 126.9 (C-3 Th); 127.3 (C-4, Th); 127.9 (C-4); 130.2 (C-2); 130.6 (C-3); 131.8 (C-6); 132.0 (C-5); 135.3 (C-1); 141.7 (C-2 Th); 171.1 (COOH). Mass spectrum, *m*/*z* (I_{rel}, %): 204 $[M]^+$ (100), 187 (23), 171 (35), 115 (27). Found, %: C 64.60; H 4.02; S 15.61. $C_{11}H_8O_2S$. Calculated, %: C 64.69; H 3.95; S 15.70.

2-(2-Thienyl)aniline. Light-brown powder, mp 36-37°C (mp 35-37°C [39]). IR spectrum, ν, cm^{-1}: 3451, 3373, 3069, 2992, 2924, 1615, 1488, 1452, 1304, 1204, 1158, 955, 848, 751, 703. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.96 (2H, br. s, NH_2); 6.76-6.82 (2H, m, H-3,5); 7.10-7.17 (2H, m, H-4, H-4 Th); 7.19 (1H, d, *J* = 3.1, H-3 Th); 7.28 (1H, d, *J* = 7.6, H-6); 7.32 (1H, *J* = 5.3, H-5 Th). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 115.9 (C-3); 118.5 (C-5); 120.0 (C-1); 125.2 (C-5 Th); 125.8 (C-3 Th); 127.5 (C-4 Th); 129.1 (C-4); 131.0 (C-6); 141.5 (C-2 Th); 144.0 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 175 $[M]^+$ (91), 147 (10), 130 (100), 115 (22), 103 (25). Found, %: C 68.48; H 5.26; N 7.90; S 18.36. $C_{10}H_9NS$. Calculated, %: C 68.54; H 5.18; N 7.99; S 18.30.

4-(2-Furyl)benzaldehyde. Light-yellow powder, mp 43-44°C (mp 42-44°C [40]). IR spectrum, ν, cm^{-1}: 3018, 2917, 2849, 1696, 1608, 1565, 1476, 1215, 1169, 1012. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.52 (1H, dd, *J* = 3.3, *J* = 2.0, H-4 Fur); 6.83 (1H, d, *J* = 3.3, H-3 Fur); 7.54 (1H, d, *J* = 2.0, H-5 Fur); 7.79 (2H, dd, *J* = 8.0, *J* = 2.5, H-3,5); 7.88 (2H, dd, *J* = 8.0, *J* = 2.0, H-2,6); 9.99 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 108.1 (C-3 Fur); 112.2 (C-4 Fur); 123.8 (C-3,5); 130.3 (C-2,6); 134.8 (C-4); 136.0 (C-1); 143.6 (C-5 Fur); 152.5 (C-2 Fur); 191.5 (CHO). Found, %: C 76.66; H 4.77. $C_{11}H_8O_2$. Calculated, %: C 76.73; H 4.68.

3-Amino-2-(2-furyl)pyridine [34]. Light-yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.52 (2H, br. s, NH_2); 6.56 (1H, dd, *J* = 3.4, *J* = 1.8, H-4 Fur); 6.97 (1H, d, *J* = 3.3, H-3 Fur); 7.02 (1H, dd, *J* = 9.4, *J* = 1.9, H-4); 7.17 (1H, dd, *J* = 9.4, *J* = 4.2, H-5); 7.40 (1H, d, *J* = 1.8, H-5 Fur); 7.91 (1H, dd, *J* = 4.2, *J* = 1.9,

H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 107.8 (C-3 Fur); 110.5 (C-4 Fur); 122.3 (C-4); 123.6 (C-5); 138.5 (C-2); 139.7 (C-3); 141.9 (C-5 Fur); 142.7 (C-6); 151.2 (C-2 Fur). Mass spectrum, *m*/*z* (I_{rel}, %): 160 $[M]^+$ (100), 131 (62), 104 (17). Found, %: C 67.41; H 5.10; N 17.43. $C_9H_8N_2O$. Calculated, %: C 67.49; H 5.03; N 17.49.

5-(2-Furyl)thiophene-2-carbaldehyde. Light-orange powder, mp 39-40°C (mp 38°C [41]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.49 (1H, dd, *J* = 3.4, *J* = 1.9, H-4 Fur); 6.77 (1H, d, *J* = 3.4, H-3 Fur); 7.32 (1H, d, *J* = 4.0, H-4 Th); 7.50 (1H, d, *J* = 1.9, H-5 Fur); 7.70 (1H, d, *J* = 4.0, H-3 Th); 9.91 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 108.8 (C-3 Fur); 112.4 (C-4 Fur); 123.0 (C-3 Th); 137.3 (C-4 Th); 141.6 (C-2 Th); 142.4 (C-5 Th); 143.6 (C-5 Fur); 148.3 (C-2 Fur); 182.7 (CHO). Found, %: C 60.59; H 3.46; S 17.92. $C_9H_6O_2S$. Calculated, %: C 60.66; H 3.39; S 17.99.

2-(4-Methoxyphenyl)furan [42], **4-(2-thienyl)benzaldehyde** [43], **3-(2-thienyl)phenol** [44], **5-(3-pyridyl)furan-2-carbaldehyde** [45] and **2-(3'-methoxycarbonyl)biphenyl-2-carboxylic acid** [46] have been described in the literature, with physicochemical characteristics matching those of the samples prepared as described above.

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