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Synthesis and Evaluation of Some New 3-methyl-2-substitutedthiophenes as antioxidants and corrosion inhibitors for Egyptian Lubricating Oils.

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ABSTRACT

In an attempt to find a new class of antioxidants and corrosion inhibitors, a series of 5-anilino-4-(4-hydroxyphenylazo)-3-methyl-2-substituted-thiophene derivatives were prepared via the reaction of 2-acetyl-2-(4-hydroxyphenylhydrazono)-thioacetanilide **(3)** with appropriate α-halogenated carbonyl reagents namely, chloroacetone, phenacyl bromide, ethyl bromoacetate and chloroacetonitrile. The antioxidant and corrosion inhibition activities of the synthesized thiophenes were investigated for gasoline lubricating oil and exhibited high antioxidant activity. In addition, the optimum recommended concentration to be used was explored; 0.1 gram with regard to 1 Liter oil from the additive **(4)** had been the greater efficient concentration. An evaluation between the oxidation stability of the examined oil that contains the synthesized thiophene together with lubricating oil containing a commercial additive are already also reported.

Keywords: Thiophenes, chloroacetone, lubricating oil, antioxidant and anticorrosive additives.

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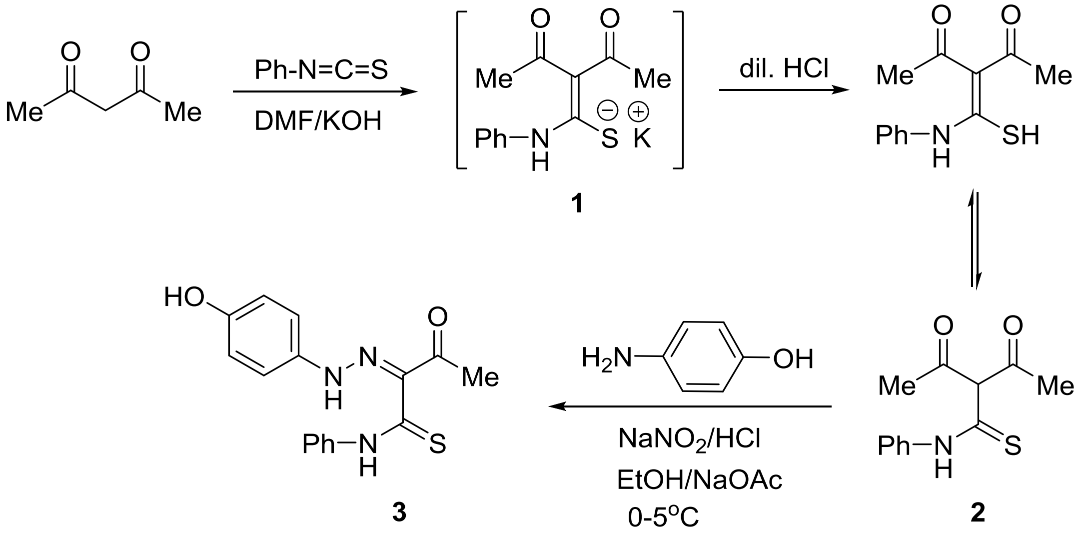
INTRODUCTION

Within the central combustion motors, lubricating oils have problems with autoxidation due to contact with air rate at elevated temperatures for long periods and contact with metals used in the manufacture of the engine such as aluminum, copper and iron. These kind of metals work as a catalyst with regard to oxidation and leading to producing oxygenated soluble as well as insoluble compounds, which often have to apply a bad effect on functionality of lubricating oils. Design properties connected with organic compounds used as antioxidants, attracts the attention of several researchers [1-6]. However, it had been documented that, organosulphur compounds work as powerful antioxidant additives for lubricating oils [7,8]. Prompted by the above mentioned results and in continuation of our previous studies to identify new additives that may be value in designing new potent and selective antioxidants and corrosion inhibitors [9-12], we report in the present investigation on the synthesis of some new 4-(4-hydroxyphenylazo)-2-substituted-thiophene derivatives as well as checking their efficiencies as antioxidant and also corrosion inhibitors for that local lubricating oil.

RESULTS AND DISCUTION

Synthesis of 5-anilino 2-substituted-4-(4-hydroxyphenylazo)-3-methylthiophenes

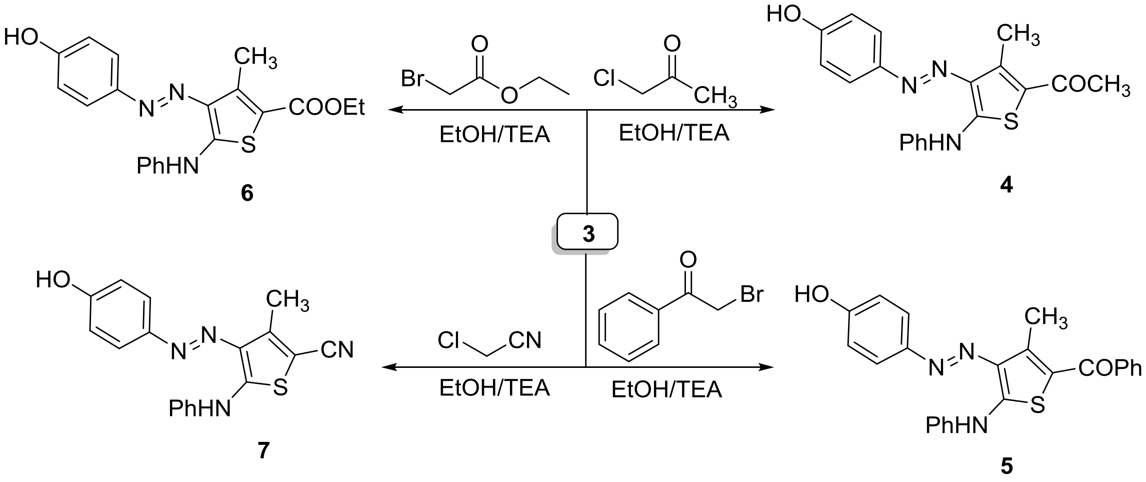
The synthetic strategies adopted to obtain the target compounds are depicted in Schemes **1** and **2**. The base-catalyzed reaction of the acetyl acetone with phenyl isothiocyanate in dry DMF at room temperature yields the non-isolable intermediate **(1)**. Treatment of **(1)** with dilute HCl afforded the corresponding thiocarbamoyl derivative **(2)** [13]. Coupling of **(2)** with diazotized *p*-aminophenol in ethanol and sodium acetate at 0-5ºC gave the hydrazono derivative **(3)** (Scheme 1). The structure of **(3)** has been assigned as a reaction product on the basis of analytical and spectral data. The IR spectrum displayed absorption bands at 3404, 3240 and 1678 cm^{-1} due to OH, NH and C=O functions, respectively. The ^1H NMR spectrum (DMSO–d_6) exhibited three singlet signals at δ 12.10, 11.01 and 9.19 ppm assignable to the protons of imino (NH) and hydroxyl (OH) functions, a multiplet signal in the region δ 8.02–6.74 ppm owing to aromatic protons, and singlet signal at 2.41 ppm for the protons of methyl group. The mass spectrum showed a molecular ion peak at *m/z* = 313 (M^+, 100.00), corresponding to a molecular formula $C_{16}H_{15}N_3O_2S$.



Scheme (1): Synthesis of 2-acetyl-2-(4-hydroxyphenylhydrazono)-thioacetanilide (3)

The hydrazono derivative **3** is versatile reagent and has been extensively used as synthetic starting material for the synthesis of several polysubstituted thiophenes. It was thus of interest to study the reactivity of hydrazono derivative **3** towards a variety of α-halogenated carbonyl reagents. Refluxing of **3** with chloroacetone in ethanol containing a catalytic amount of triethylamine afforded 2-acetyl-5-anilino-4-(4-hydroxyphenylazo)-3-methyl-thiophene **(4)**. The structure of **(4)** was elucidated on the basis of its elemental analysis and spectral data. The IR spectrum showed the presence of absorption bands at 3440, 3352 and 1600

cm^{-1} attributed to OH, NH and C=O functions, respectively. Its ^1H NMR spectrum (DMSO–d_6) revealed two singlet signals at δ 13.00 and 10.13 ppm characteristic to the protons of NH and OH groups, multiplet signal in the region δ 7.72-6.91 ppm for the aromatic protons, in addition to two singlet signals at δ 2.65 and 2.45 ppm owing to $COCH_3$ and CH_3 protons. The mass spectrum showed a molecular ion peak at *m/z* = 351 corresponding to molecular formula $C_{19}H_{17}N_3O_2S$. In a similar manner, treatment of hydrazono derivative **3** with phenacyl bromide under the same experimental conditions afforded 5-anilino-2-benzoyl-4-(4-hydroxyphenylazo)-3-methyl-thiophene **(5)**. The spectral data of the isolated product was in complete agreement with structure **5**. To investigate the structure-activity relationship with respect to antioxidant properties, the reactivity of **(3)** towards ethyl bromoacetate was also studied. Thus, refluxing the hydrazono derivative **3** with ethyl bromoacetate in ethanol containing a catalytic amount of triethylamine gave a single product, which analyzed correctly for $C_{20}H_{19}N_3O_3S$. The IR spectrum revealed absorption bands at 1744 cm^{-1} corresponding to C=O ester function. The ^1H NMR spectrum displayed a set of signals typical of the ethyl ester group. All other expected signals, too, were observed. In a similar manner to the behavior of ethyl bromoacetate with the hydrazono derivative **3**, chloroacetonitrile reacted with **3** under the same reaction conditions to yield the thiophene **7** in excellent yield. The structure of compound **7** was assigned on the basis of elemental analysis and spectral data of the isolated reaction product. The presence of cyano group in structure **7** was evidenced by the appearance of absorption band at 2207 cm^{-1} in the IR spectrum of the reaction product. The mass spectrum of compound **7** showed a molecular ion peak at *m/z* = 334 (M^+, 100.00), corresponding to molecular formula $C_{18}H_{14}N_4OS$.



Scheme (2): Synthesis of 2-substituted-4-(4-hydroxyphenylazo)-thiophenes 4-7

Antioxidant and anticorrosive additives

Evaluation of the synthesized thiophene derivatives as antioxidants for lubricating oil.

The effectiveness of the synthesized thiophene derivatives **4**, **5**, **6** and **7** as antioxidants was examined by preparation of various solutions with the addition of 0.1 gram of the synthesized thiophene compound to one Liter of the additive free lubricating oil under investigation. The lubricating oil with as well as without additives had been put through sever oxidation at 155°C. Samples had been taken at typical times of three hours and their oxidation stabilities were evaluated in terms of the total acid number (TAN) and compared with the lubricating oil sample free of additives. It is clear that, the oxidation products enhanced with time in the presence of thiophene compounds **4-7** but at rate less than without additives. Therefore, from Table (1) and Figures (1) and (2), we can easily disclose that, the TAN of the oil samples that contains the thiophene additives after 36 hours oxidation exhibited high oxidation resistant properties. The greatest antioxidant activity was attributed to the presence of some antioxidant groups in each of them such as thiophene, OH and NH groups.

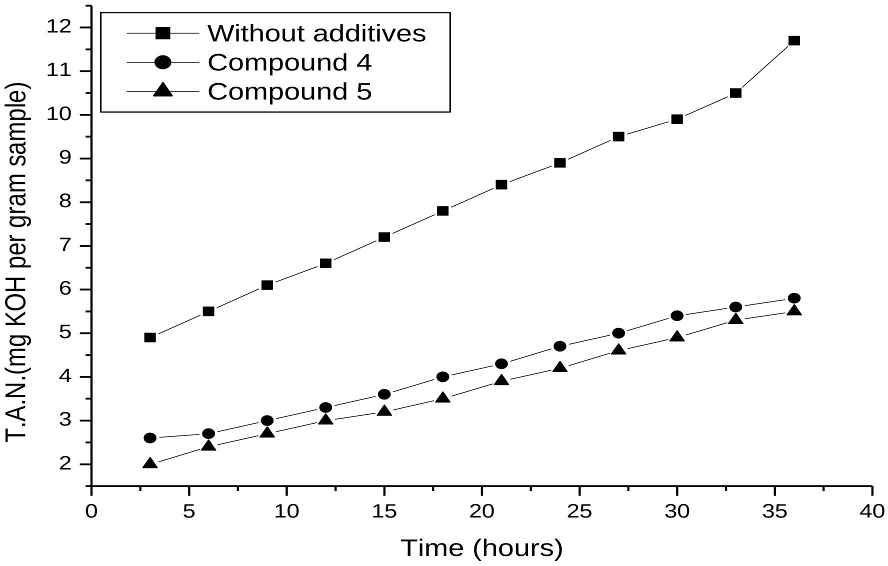


Figure 1: Variant of the T.A.N. with oxidation time of tested lubricating oil without and with compounds 4 and 5 at 0.1 g/Liter concentration at 155ºC.

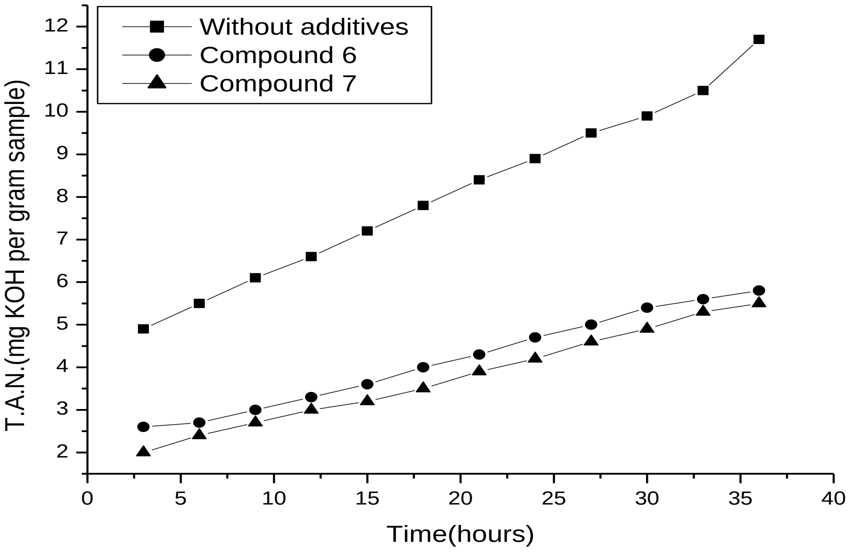


Figure 2: Variant of the T.A.N. with oxidation time of the tested lubricating oil without and with compounds 6 and 7 at 0.1 g/Liter concentration at 155ºC.

Effect of concentration.

It was exciting to examine the concentration effect of the most extremely antioxidant character in order to obtain the perfect concentration encouraged to be utilized. Therefore, three diverse concentrations of compound **4** specifically; 0.1, 0.05 and 0.01 g/L had been applied, and the TAN of the oil had been determined. The attained data showed that, growing the concentration results in a decrease of the oxidative products and also the 0.1 g/L will be the better efficient concentration to be applied (Figure 3).

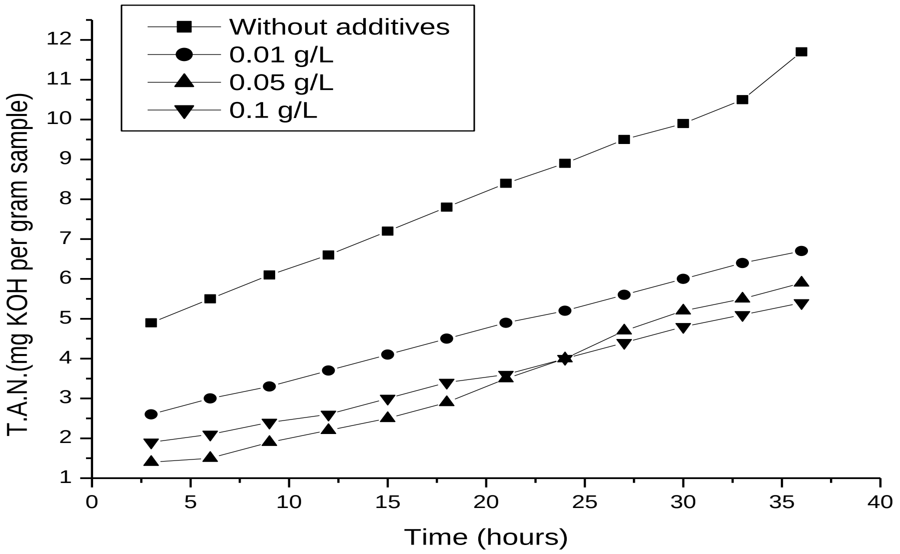


Figure 3: Variant of the T.A.N. values with oxidation time of the tested lubricating oil without and with diverse concentrations for compound 4 at 155ºC.

An evaluation of the oxidation stability of the examined oil that contains the additives together with lubricating oil that contains the commercial additive.

It had been also exciting to be able to evaluate the oxidation stability of the examined lubricating oil that contains the remarkably efficient synthesized thiophene additives (0.1 g/L) with a lubricating oil that contains a commercial antioxidant additive obtained from the marketplace (CO-OP Cosf/cc 21 w 151 oil). After 36 hours oxidation at 155°C, the results showed that, the lubricating oil that contains the thiophene additives **4-7** exhibited greater oxidation stability compared to the employed commercial lubricating oil Figure (4).

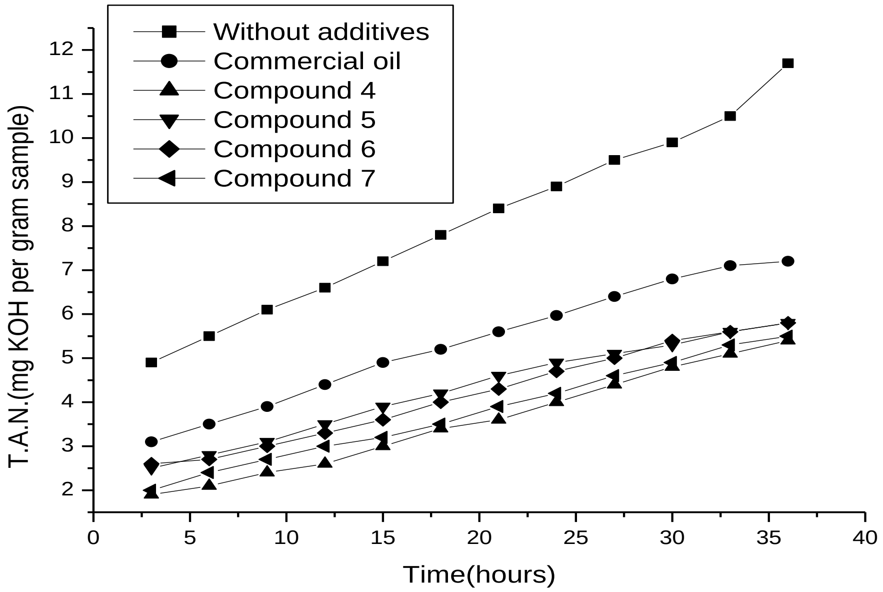


Figure 4: A comparison between the T.A.N. of the tested lubricating oil samples containing 0.1 g/L of compounds 4-7, 10 with that of the commercial lubricating oil sample at 155 ºC up to 36 hours oxidation.

Examination of the synthesized thiophene additives as corrosion inhibitors for the tested lubricating oil.

Again, the thiophene additives had been examined as corrosion inhibitors for the tested lubricating oil utilizing two diverse strips of cupper as well as iron having area 1 cm^2. The metal was purified from its oxide, weighed, in addition to immerse inside the oxidation system for 36 hours under the earlier conditions. The metal was purified and its weight had been once again established. The variation in weight was determined and the performance of additives was evaluated as corrosion inhibitors utilizing weight loss technique Table (2). The data exposed a decrease in corrosion within existence of oil without additives and a greater corrosion inhibition was discovered in the existence of compounds **4-7**.

Table 1: Comparison of oxidation products obtained using additives 4-7

Compound No.	**Time (hours)**											
	3	6	9	12	15	18	21	24	27	30	33	36
Without additives	4.9	5.5	6.1	6.6	7.2	7.8	8.4	8.9	9.5	9.9	10.5	11.7
4	1.9	2.1	2.4	2.6	3.0	3.4	3.6	4.0	4.4	4.8	5.1	5.4
5	2.5	2.8	3.1	3.5	3.9	4.2	4.6	4.9	5.1	5.3	5.6	5.8
6	2.6	2.7	3.0	3.3	3.6	4.0	4.3	4.7	5.0	5.4	5.6	5.8
7	2.0	2.4	2.7	3.0	3.2	3.5	3.9	4.2	4.6	4.9	5.3	5.5

Table 2: Effect of additive types at 0.1 g/L concentration in the oil on the weight loss of metals (copper and iron) after 36 h oxidation at 155ºC with air rate 5 L/h.

Compound No.	**Weight loss** (10^{-3} g)	
	Cu	**Fe**
Oil without additive	9.8	10.1
4	2.7	1.7
5	2.6	2.1
6	2.5	1.8
7	2.9	1.6

EXPERMINTAL

All melting points were determined on an electrothermal Gallenkamp apparatus (Germany). The IR spectra were measured on a Mattson 5000 FTIR Spectrometer (USA) in potassium bromide discs. The ^{1}H NMR spectra were recorded in DMSO-d_6 on a Bruker WP spectrometer (USA) (300 MHz) and the chemical shifts δ downfield from TMS as an internal standard. The mass spectra were recorded on Finnegan MAT 212 instrument (USA), and the ionizing voltage was 70 ev, at Faculty of Science, Cairo University. Elemental analyses were carried out by the Micro-analytical unit of Faculty of Science, Cairo University, Giza, Egypt. All reactions were followed by TLC (Silica gel, aluminum sheets 60 F254, Merck). 2-Acetyl-3-oxo-N-phenylbutanethioamide **(2)** was prepared according to literature procedure [13].

Synthesis of 2-acetyl-2-(4-hydroxyphenylhydrazono)-thioacetanilide (3):

To a cold solution of compound 2 (4.70 g, 0.02 mol) in ethanol (30 mL) and sodium acetate (6 g), was added the diazonium salt of *p*-aminophenol [prepared by dissolving sodium nitrite (1.37 g, 0.02 mol) in water (3 mL) and adding to a cold solution of *p*-aminophenol (2.18 g, 0.02 mol) containing the appropriate amount of hydrochloric acid with continuous stirring] portion wise over a period of 30 min. The reaction mixture was kept in an ice bath for 24 h and then diluted with water, filtered off, dried, and recrystallized from ethanol. Red crystals; yield 85%; mp 220-222^{o}C; IR (KBr) ν_{max}/cm^{-1}: 3404 (OH), 3240 (NH), 3194 (NH), 1678 (C=O), 1630 (C=N), 1584 (N=N); ^{1}H NMR (DMSO-d_6) δ_{ppm}: 12.10 (s, 1H, NH), 11.01 (s, 1H, NH), 9.19 (s, 1H, OH), 8.02-6.74 (m, 9H, Ar-H), 2.41 (s, 3H, CH$_3$); MS: *m/z* (%) 313 (M$^+$, 100.00), 205 (50.15), 173 (38.69), 122 (48.35), 108 (58.06), 93 (22.31), 77 (16.76), 65 (6.58). Anal. calcd. for $C_{16}H_{15}N_3O_2S$ (313.38): C, 61.32; H, 4.82; N, 13.41%. Found: C, 61.20; H, 4.85; N, 13.36%.

General procedure for the synthesis of thiophene derivatives (4-7):

To a solution of compound **3** (0.62 g, 0.002 mol) in absolute ethanol (20 mL), an equimolar amount of the appropriate reagents namely; chloroacetone, phenacyl bromide, ethyl bromoacetate and 2-chloroacetonitrile (0.002 mol), and three drops of triethylamine was added. The reaction mixture was heated under reflux for 4 h, then left to cool. The solid products that obtained was collected by filtration, washed with ethanol, dried well and recrystallized from ethanol.

2-Acetyl-5-anilino-4-(4-hydroxyphenylazo)-3-methyl-thiophene (4).

This compound was prepared from chloroacetone (0.16 mL). Red crystals; yield 87%; mp 265-267^{o}C; IR (KBr) ν_{max}/cm^{-1}: 3440 (OH), 3352 (NH), 1600 (C=O), 1586 (C=C), 1549 (N=N); ^{1}H NMR (DMSO-d_6) δ_{ppm}: 13.00 (s, 1H, NH), 10.13 (s, 1H, OH), 7.72-6.91 (m, 9H, Ar-H), 2.65 (s, 3H, CH_3CO), 2.45 (s, 3H, CH_3); MS: *m/z* (%) 351 (M$^+$, 100.00), 308 (15.41), 243 (31.48), 186 (11.85), 108 (17.46), 65 (2.92). Anal. calcd. for $C_{19}H_{17}N_3O_2S$ (351.42): C, 64.94; H, 4.88; N, 11.96%. Found: C, 64.98; H, 4.83; N, 11.88%.

5-Anilino-2-benzoyl-4-(4-hydroxyphenylazo)-3-methyl-thiophene (5).

This compound was prepared from phenacyl bromide (0.4 mL). Grey crystals; yield 65%; mp 230-232^{o}C; IR (KBr) ν_{max}/cm^{-1}: 3437 (OH), 3352 (NH), 1620 (C=O), 1597 (C=C), 1556 (N=N); MS: *m/z* (%) 413 (M$^+$, 100.00), 385 (13.32), 305 (36.24), 249 (1.29), 203 (5.71), 168 (2.53), 105 (42.38), 77 (28.83), 66 (2.84). Anal. calcd. for $C_{24}H_{19}N_3O_2S$ (413.50): C, 69.71; H, 4.63; N, 10.16%. Found: C, 69.69; H, 4.60; N, 10.11%.

5-Anilino-2-ethoxycarbonyl-4-(4-hydroxyphenylazo)-3-methyl-thiophene (6).

This compound was prepared from ethyl bromoacetate (0.3 mL). Red crystals; yield 60%; mp 210-212^{o}C; IR (KBr) ν_{max}/cm^{-1}: 3449 (OH), 3356 (NH), 1744 (C=O ester), 1653 (C=C), 1594 (N=N), 2926 (CH aliphatic); ^{1}H NMR (DMSO-d_6) δ_{ppm}: 12.98 (s, 1H, NH), 9.93 (s, 1H, OH), 7.71-6.88 (m, 9H, Ar-H), 4.26-4.19 (q, 2H, CH_2), 2.48 (s, 3H, CH_3), 1.29-1.25 (t, 3H, CH_3); MS: *m/z* (%) 381 (M$^+$, 100.00), 352 (34.35), 279 (12.92), 245 (10.56), 187 (20.48), 93 (14.75), 53 (2.40). Anal. calcd. for $C_{20}H_{19}N_3O_3S$ (381.45): C, 62.98; H, 5.02; N, 11.02%. Found: C, 62.90; H, 5.08; N, 11.11%.

5-Anilino-2-cyano-4-(4-hydroxyphenylazo)-3-methyl-thiophene (7).

This compound was prepared from 2-chloroacetonitrile (0.14 mL). Grey crystals; yield 73%; mp 240-242^{o}C; IR (KBr) ν_{max}/cm^{-1}: 3445 (OH), 3352 (NH), 2207 (CN), 1641 (C=C), 1543 (N=N); MS: *m/z* (%) 334 (M$^+$, 100.00), 272 (1.88), 226 (18.79), 186 (5.08), 109 (11.23), 77 (19.79), 65 (7.57). Anal. calcd. for $C_{18}H_{14}N_4OS$ (334.40): C, 64.65; H, 4.22; N, 16.75%. Found: C, 64.53; H, 4.25; N, 16.79%.

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