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Reductive Coupling Reactions of 2-Nitrochalcones and their β-Hydroxy-analogues: New Syntheses of 2-Arylquinoline and 2-Aryl-4-hydroxyquinoline Derivatives

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Summary. A one-pot synthesis of novel 2-arylquinolines and 2-aryl-4-hydroxyquinolines was developed from the intramolecular reductive coupling reactions of 2-nitrochalcones and 3-hydroxy-1-phenyl-3-(2-nitrophenyl)-2-propen-1-ones. Depending on the reduction method and on the presence of electron donating substituents on the A ring of 2-nitrochalcones one can modulate the formation of 2-arylquinolines, their *N*-oxides, and of 2-aminochalcones. The reduction of 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones with stannous chloride in hydrochloric acid gave 2′-aminoflavones and with ammonium formate and Pd/C yielded 2-(2-hydroxyaryl)-4-hydroxyquinolines.

Keywords. 2-Arylquinolines; 2-Aryl-4-hydroxyquinolines; Quinolines-*N*-oxides; 2-Nitrochalcones; Reductive coupling reactions.

Introduction

The quinoline skeleton occurs naturally, especially in alkaloids [1], and is often used synthetically to design compounds with interesting pharmacological properties (*e.g.* anesthetics, anxiolytics, antimalarials and antiseptic agents), or polymers (polyquinolines and polyvinylquinolines), or cyanine dyes (as sensitizers in photographic emulsions), or antioxidants in the rubber industry, or fungicides and also as reagents in organic synthesis (*e.g.* in the synthesis of 2-quinolones and 2-octalones) [2–4]. Other important applications of certain quinoline derivatives involve their chelation with metal ions; some of these chelates present significant fungicide activity. For instance, 8-hydroxyquinoline derivatives have been extensively used as a reagent for qualitative and quantitative determination of several transition metal ions [2]. These important applications and the loss of efficacy of synthetic drugs based on a quinoline structure (the alkaloid quinine has been used as a drug in the treatment of malaria for many centuries), due to the development of resistant strains of plasmodia, led the scientific community to pay attention to the establishment of new methodologies for the synthesis of new quinoline derivatives [2, 4]. The structural core of quinoline has generally been synthesized by various conventional named reactions, such as *Skraup*, *Doebner-von Miller*, *Conrad-Limpach*, and *Combes* syntheses [1]. These classical methods are well-known and frequently used for the preparation of pharmaceutical agents. Due to the interesting and important biological properties of quinoline derivatives, many other synthesis methods are reported in the literature for this type of compounds [5], however the development of new and efficient methods for the preparation of these important molecules still continues to be an important and attractive area of research in synthetic organic chemistry [6, 7].

In the last decade, the cyclisation of 2′-aminochalcones has been extensively studied since it provides 2-aryl-4-quinolone derivatives [5, 8, 9], which

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present important pharmacological activities [9, 10]. More recently, 2′-aminochalcones have been used in the preparation of 2-aryl-4-chloro-*N*-formyl-1,2-dihydroquinolines from their cyclisation under *Vilsmeier* conditions [5]. Recently we reported a one-pot and facile synthesis of 2-(2-hydroxyaryl)quinolines from the intramolecular reductive coupling reaction of 2′-hydroxy-2-nitrochalcones [11], where it was observed that one can modulate the obtained compounds according to the electron donating or withdrawing character of the A ring substituents. So, the reduction of 2′-hydroxy-2-nitrochalcones unsubstituted on the A ring or having 5′-bromo substituents, independently of the used reduction method (ammonium formate and Pd/C or stannous chloride in acidic medium) gave a mixture of 2-(2-hydroxyaryl)quinolines and 2-(2-hydroxyaryl)-quinolines-*N*-oxides while the reduction of 2′-hydroxy-2-nitrochalcones bearing electron donating substituents (4′-OCH_3 or 4′-O*Bn*), gave the corresponding amino-2′-hydroxychalcones by using ammonium formate and Pd/C, and 2-(2-hydroxyaryl)quinolines by using stannous chloride in acidic medium [11].

Aminochalcones and aminoflavones derivatives are also interesting pharmacological molecules. Flavones bearing amino groups on the A or B ring have been reported to be potential antineoplastic agents [12] and proved to be antimutagenic in the *Ames* test using different species of mutagens [13]. On the other hand it was found that a series of aminochalcones, synthesized as candidate of cytotoxic agents, displayed selective toxicity to certain malignant cell and were well tolerated in mice [14].

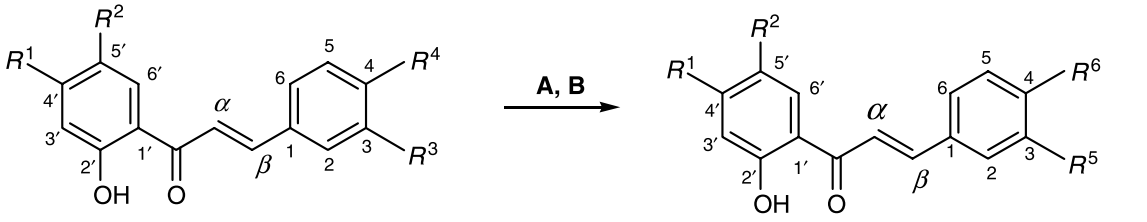
Following our interest in the reactivity of chalcone derivatives, reductive coupling reactions using stannous chloride in acidic medium and ammonium formate and Pd/C were applied to other A-ring substituted 2-nitrochalcones, 2′-hydroxy-3- and -4-nitrochalcones and 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones, in order to compare both methods in terms of the synthesized products and of the obtained yields.

Results and Discussion

Synthesis

2-Nitrochalcones **1a**–**1l** were obtained from an aldol condensation of the appropriate acetophenones and benzaldehydes [15, 16], and 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c** were obtained from adequate 2′-hydroxyacetophenones and benzoyl chloride derivatives by the *Baker-Venkataraman* approach [16]. Taking in account our study on the reductions of 2′-hydroxy-2-nitrochalcones [11] we decided to apply these reduction methods to other nitrochalcones and make a comparative study in order to get information about the method generality in the synthesis of the corresponding aminochalcones and/or 2-hydroxyarylquinolines.

The treatment of 2′-hydroxy-3- or -4-nitrochalcones **1a**–**1d** with ammonium formate and Pd/C, in meth-



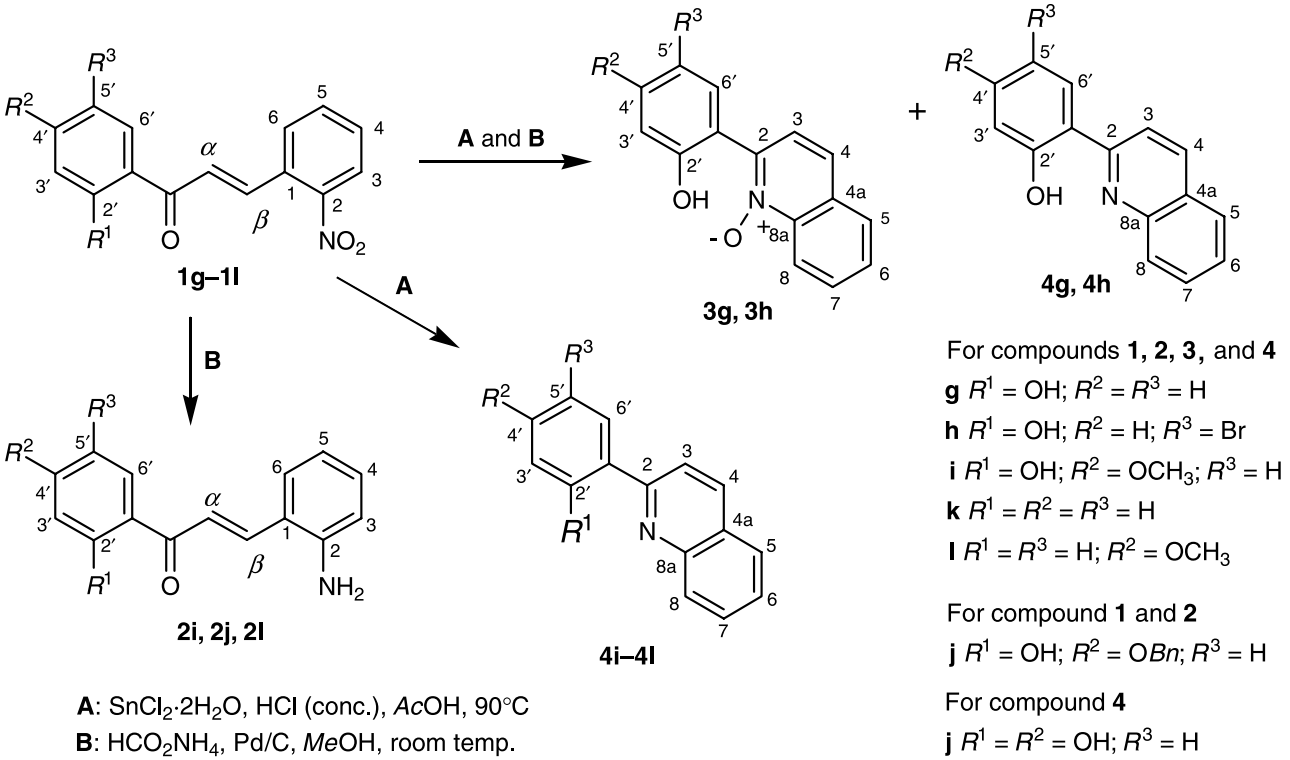
1a $R^1 = R^2 = R^4 = H$; $R^3 = NO_2$
1b $R^1 = R^2 = R^3 = H$; $R^4 = NO_2$
1c $R^1 = OCH_3$; $R^2 = R^4 = H$; $R^3 = NO_2$
1d $R^1 = OCH_3$; $R^2 = R^3 = H$; $R^4 = NO_2$
1e $R^1 = R^4 = H$; $R^2 = Br$; $R^3 = NO_2$
1f $R^1 = R^3 = H$; $R^2 = Br$; $R^4 = NO_2$

2a $R^1 = R^2 = R^4 = H$; $R^3 = NH_2$
2b $R^1 = R^2 = R^3 = H$; $R^4 = NH_2$
2c $R^1 = OCH_3$; $R^2 = R^4 = H$; $R^3 = NH_2$
2d $R^1 = OCH_3$; $R^2 = R^3 = H$; $R^4 = NH_2$
2e $R^1 = R^4 = H$; $R^2 = Br$; $R^3 = NH_2$
2f $R^1 = R^3 = H$; $R^2 = Br$; $R^4 = NH_2$

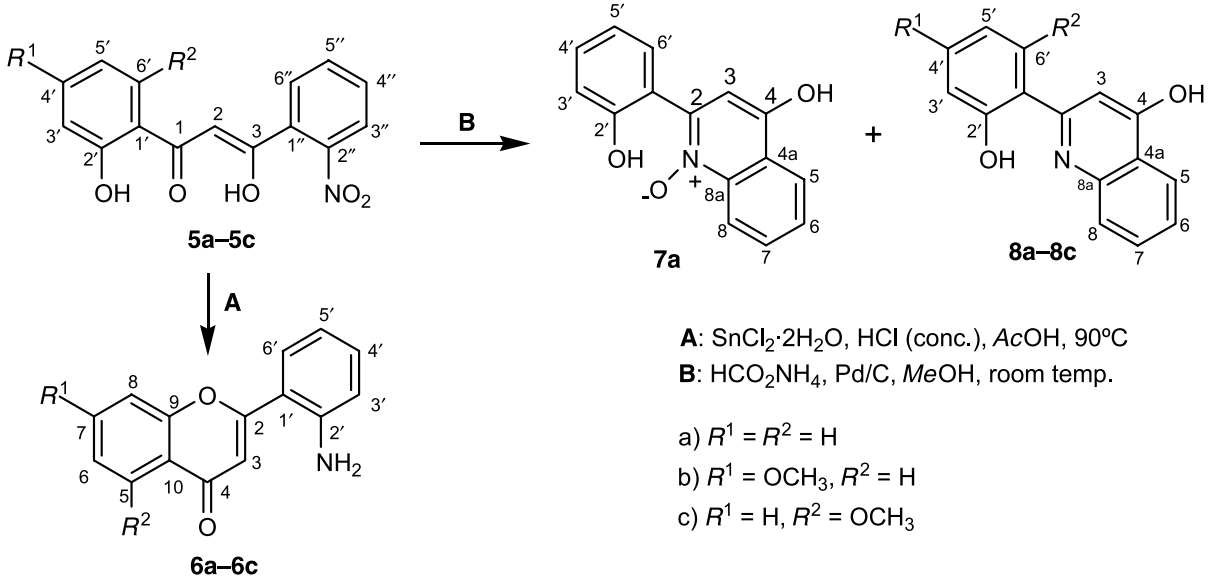
A: $SnCl_2 \cdot 2H_2O$, HCl (conc), *Ac*OH, 90°C
B: HCO_2NH_4, Pd/C, *Me*OH, room temp.

Scheme 1

anol at room temperature for 3 h, gave the corresponding aminochalcones **2a**–**2d** (Scheme 1). Under these conditions only occurs the reduction of the nitro substituents and there was no reduction of the chalcones double bond. In the case of 5′-bromo-3- and -4-nitrochalcones **1e**, **1f** there was the reduction of the nitro group and a debromination process giving the corresponding 3- and 4-amino-2′-hydroxychalcones **2a**, **2b** [17]. Therefore, the aminochalcones **2a**–**2f** were obtained by the reduction of



Scheme 2



Scheme 3

2′-hydroxy-3- and -4-nitrochalcones **1a**–**1f** with an excess of hydrated stannous chloride in hydrochloric acid (Scheme 1). Although in both cases the aminochalcones were obtained in good yields, the reduction with ammonium formate and Pd/C always gave better yields (64–83%) than that using stannous chloride in acidic medium (54–68%) and the work up was also straightforward.

The treatment of 2′-hydroxy-2-nitrochalcones **1g**, **1h** with an excess of hydrated stannous chloride in hydrochloric acid gave 2-(2-hydroxyaryl)quinolines **4g**, **4h** (44–47%) and of 2-(2-hydroxyaryl)quinoline-*N*-oxides **3g**, **3h** (23–27%). However, 2′-hydroxy-2-nitrochalcones **1i**–**1l** gave only the corresponding 2-arylquinolines **4i**–**4l** (49–66%) (Scheme 2). The treatment of 2′-hydroxy-2-nitrochalcones **1g**, **1h** with ammonium formate and Pd/C yielded also 2-(2-hydroxyaryl)quinolines **4g**, **4h** (37–39%) and of 2-(2-hydroxyaryl)quinoline-*N*-oxides **3g**, **3h** (33–36%); in the case of 4′-substituted 2-nitrochalcones **1i**, **1j**, **1l** the corresponding 2-aminochalcones **2i**, **2j**, **2l** (25–68%) were obtained (Scheme 2). These results indicated that the 2′-hydroxy group does not influence the intramolecular reductive coupling/reduction reactions and support the mechanism that we have previously proposed [11]. Thus the presence of a electron donating substituents at C-4′ is important to modulate the obtained products.

The results obtained in the intramolecular reductive coupling reactions of 2-nitrochalcones **1g**–**1l** and the structural similarity with 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c**, which can be seen as β,2′-dihydroxy-2-nitrochalcones, which are being used as intermediates in the synthesis of 2′-nitroflavones by the *Baker-Venkataraman* approach [16], let us to study the behaviour of **5a**–**5c** towards stannous chloride in hydrochloric acid and to ammonium formate-Pd/C in methanol (Scheme 3). The treatment of **5a**–**5c** with stannous chloride in hydrochloric acid led to the formation of 2′-aminoflavones **6a**–**6c**. In a one-pot synthesis we had the nitro group reduction and a cyclodehydration of the corresponding diketones catalysed by the acidic medium [18] leading to the formation of 2′-aminoflavones **6a**–**6c**, which constitutes, to our best knowledge, a new synthesis of 2′-aminoflavones **6a**–**6c**. These compounds **6a**–**6c** were obtained in moderate yields (38–59%).

The treatment of **5b** and **5c** with ammonium formate and Pd/C in methanol at room temperature for 3 h led to the formation of 2-(2-hydroxyaryl)-4-hydroxyquinolines **8b**, **8c** (Scheme 3). However, the treatment of **5a** with ammonium formate and Pd/C in the same conditions, yielded a mixture of 2-(2-hydroxyphenyl)-4-hydroxyquinoline **8a** (34%) and 2-(2-hydroxyphenyl)-4-hydroxyquinoline-*N*-oxide **7a** (52%). These results confirm and support our hypothesis that in the absence of electron donating groups in the A ring, the reduction of hydroxylamine derivatives is very slow, allowing the formation of quinoline-*N*-oxides [11].

NMR Spectroscopy

The main ^{1}H NMR characteristics of the 3- and 4-amino-2′-hydroxychalcones **2a**–**2f** are the resonances of the amino group appearing in almost all cases as a broad singlet at δ 4.05–5.24 ppm and of the hydroxyl group, which appears as a narrow singlet at high frequency values (δ 12.50–13.71 ppm) due to the existence of an intramolecular hydrogen bond with the carbonyl oxygen atom. The vinylic protons of these compounds appear as two doublets (at δ 7.36–7.84 ppm for H-α and δ 7.68–7.90 ppm for H-β) with a coupling constant typical of a (*E*)-configuration ($^3J_{H\alpha\text{-}H\beta}$ 15–16 Hz). From the ^{13}C NMR spectra of **2a**–**2f** one can notice the resonances of C-α (δ 114.6–120.8 ppm) and C-β (δ 144.7–147.0 ppm); being the latter deshielded relatively to the former due to the mesomeric deshielding effect of the carbonyl group. It is also important to refer the shielding effect of the 4-amino group on the C-α carbon resonance (δ 114.6–115.6 ppm) of 4-aminochalcones **2a**, **2c**, **2e** relatively to those of 3-aminochalcones (δ 119.2–120.8 ppm) due to the conjugation with the α,β-unsaturated system which increase the electronic density on C-α. In the ^{13}C NMR spectra of **2a**–**2f** one can also observe other two typical carbon resonances, those of C-2′ and C=O appearing at δ 161.8–166.6 and 191.9–193.6 ppm.

The NMR data of 2-amino-2′-hydroxychalcones **2i**, **2j**, **2l** are similar to that of **2a**–**2f** except for the proton and carbon resonances of the vinylic system, due to the already reported steric interactions between H-β and the 2′-substituent, which are responsible for the deshielding effect of the H-β (appearing at δ 7.97–8.05 ppm) and shielding of the corresponding carbon C-β (appearing at δ 139.6–139.8 ppm) [19].

The characteristics of the NMR data of 2-(2-hydroxyaryl)quinolines **4g**–**4j** which support their struc-

ture are the: i) presence of a hydroxyl group involved in a strong hydrogen bond (δ_{OH} 14.93–15.34 ppm in the ^{1}H NMR spectra); ii) absence of double bonds in a (*E*)-configuration, well established in the ^{1}H NMR spectra of chalcones; iii) absence of carbonyl groups in the ^{13}C NMR spectra; and iv) molecular ions ($M^{+\bullet}$ in the EIMS) corresponding to the reduction of the nitro substituent into the amino group and the loss of one water molecule. From their ^{1}H NMR spectra one can also notice the typical resonances of H-3 (doublet, $^3J_{H3\text{-}H4} \sim 9$ Hz), H-4 (doublet), and H-8 appearing at δ 8.21–8.46, 8.47–8.61, and 7.96–8.09 ppm, while from the ^{13}C NMR spectra one can refer the carbon resonances of C-2 (δ 156.3–158.0 ppm), C-3 (δ 117.5–118.4 ppm), C-4 (δ 138.0–138.6 ppm), and C-8 (δ 126.5–128.0 ppm). 2-(2-Hydroxyaryl)quinoline-*N*-oxides **3g**, **3h** present similar spectroscopic features to those of **4g**, **4h**, but the hydroxyl group involved in a hydrogen bond appears at lower frequency values (δ_{OH} 11.30–11.37 ppm in the ^{1}H NMR spectra) and the molecular ion ($M^{+\bullet}$ in the EIMS) presents 16 a.m.u. more. One can also notice the important shielding effect on carbons C-2 ($\Delta\delta \sim 10$ ppm) and C-4 and C-8 ($\Delta\delta \sim 8$ ppm) and deshielding effect on carbon C-3 ($\Delta\delta \sim 6$ ppm) of **3g**, **3h** relatively to those of **4g**, **4h**. The NMR data of 2-arylquinolines **4k**, **4l** are similar to that of **4a**, **4j** except the absence of the 2-hydroxyl group.

As the main ^{1}H NMR characteristics of 2-(2-hydroxyphenyl)-4-hydroxyquinolines **8a**–**8c** one can notice the proton resonances of the 2′-OH and H-3, appearing as broad singlets at δ_H 11.24–12.35 and 6.40–6.57 ppm, and also those of H-5 and H-8 which appear at relatively high frequency values (δ_H 8.20–8.44 and 8.20–8.26 ppm). From the ^{13}C NMR of **8a**–**8c** one can observe the typical resonances of C-2 (δ_C 146.4–150.1 ppm), C-3 (δ_C 102.1–106.5 ppm), C-4 (δ_C 157.8–164.8 ppm), C-8 (δ_C 123.2–124.4 ppm), and also C-2′ (δ_C 157.4–160.3 ppm). 2-(2-Hydroxyaryl)-4-hydroxyquinoline-*N*-oxide **7a** presents similar spectroscopic features to those of **8a**, but the hydroxyl group involved in a hydrogen bond appears at lower frequency values (δ_{OH} 12.00 ppm in the ^{1}H NMR spectra) and the molecular ion ($M^{+\bullet}$ in the EIMS) presents 16 a.m.u. more.

The main features of the NMR data of 2′-aminoflavones **6a**–**6c** are the resonances of: i) H-3 appearing as a singlet at δ 6.36–6.70 ppm; ii) NH_2 appearing as a broad singlet at δ 5.61–5.71 ppm; iii) C-3 at δ 107.4–111.1 ppm; iv) C-2′ at δ 146.9–147.2 ppm; v) C-2 at δ 162.2–165.0 ppm; and vi) the carbonyl group appearing at δ 176.4–177.9 ppm [20].

The confirmation of all proton and carbon resonances and the assignments of those of the quaternary carbons were based on the connectivities found in the HMBC spectra of all compounds reported in this report.

Experimental

Melting points were measured in a Büchi 535 apparatus. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300.13 for ^{1}H and 75.47 MHz for ^{13}C), with *DMSO*-d_6 as the solvent. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. The internal standard was *TMS*. Unequivocal ^{13}C assignments were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one bond and long-range *J* C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. Electron impact (EI, 70 eV) MS were recorded on VG Autospec Q and M spectrometers [high resolution mass spectra were in good agreement (±5 ppm) with the calculated values]. Elemental Analyses (CHN) were obtained with a Carlo Erba 1108 CHNS analyzer and were in good agreement (±0.4%) with the calculated values. Preparative thin-layer chromatography was performed with Merck silica gel 60 DGF_{254}. Column chromatography was performed with Merck silica gel 60, 70–230 mesh. All other chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

2′-Hydroxy-2-nitrochalcones **1a**–**1j** and 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c** have been prepared according to Refs. [15, 16].

*Synthesis of 2-Nitrochalcones **1k** and **1l***

Sodium hydride (0.88 g, 36.5 mmol) was slowly added to a solution of the appropriate acetophenone (16.6 mmol) in 10 cm^3 *THF* and the reaction mixture stirred at room temperature for 20 minutes. After this period a solution of 2.76 g 2-nitrobenzaldehyde (18.3 mmol) in 10 cm^3 *THF* was added to the reaction mixture. The solution was stirred under N_2 at room temperature for 2 h. The disappearance of the starting materials was monitored by tlc. The reaction mixture was poured into 50 g ice and 50 cm^3 H_2O, and the *pH* adjusted to 3 with HCl. The obtained solid was removed by filtration, taken up in 2×30 cm^3 $CHCl_3$ and washed with 2×20 cm^3 H_2O. The organic layer was dried (Na_2SO_4) and evaporated to dryness; the obtained crude material was chromatographed over a silica gel column (eluent: several mixtures of light petroleum:chloroform to eliminate undesired compounds and, lastly $CHCl_3$) to provide **1k** and **1l**. Both compounds were recrystallised from ethanol.

2-Nitrochalcone (**1k**, $C_{15}H_{11}NO_3$)

Yield 42%, mp: 97–98°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.33$ (d, $J = 15.7$ Hz, H-α), 7.45–7.52 (m, H-4), 7.53 (d, $J = 7.8$ Hz, H-3′,5′), 7.58–7.61 (m, H-4′), 7.71 (dt, $J = 1.1$, 7.1 Hz, H-5), 7.75 (dd, $J = 1.7$, 7.1 Hz, H-6), 8.02 (d,

$J = 7.8$ Hz, H-2′,6′), 8.08 (dd, $J = 1.1$, 8.1 Hz, H-3), 8.14 (d, $J = 15.7$ Hz, H-β) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 125.0$ (C-3), 127.3 (C-α), 128.7 (C-3′,5′), 128.8 (C-2′,6′), 129.2 (C-6), 130.3 (C-4), 131.3 (C-1), 133.2 (C-4′), 133.8 (C-5), 137.3 (C-1′), 140.2 (C-β), 148.9 (C-2), 190.5 (C=O) ppm; IR (KBr): $\bar{\nu} = 1681$, 1670, 1569, 1513, 1340, 1214, 1012, 858, 740, 684 cm^{-1}; MS (EI, 70 eV): m/z (%) = 253 ($M^{+\bullet}$, 100), 220 (59), 193 (25), 180 (15), 167 (30), 154 (7).

4′-Methoxy-2-nitrochalcone (**1l**, $C_{16}H_{13}NO_3$)
Yield 32%, mp: 93–94°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 3.90$ (s, OC*H*$_3$), 6.99 (d, $J = 9.0$ Hz, H-3′,5′), 7.33 (d, $J =$ 15.6 Hz, H-α), 7.56 (dt, $J = 1.7$, 7.4 Hz, H-4), 7.68 (dt, $J = 1.4$, 7.4 Hz, H-5), 7.74 (dd, $J = 1.7$, 7.4 Hz, H-6), 8.04 (d, $J = 9.0$ Hz, H-2′,6′), 8.06 (dd, $J = 1.4$, 7.4 Hz, H-3), 8.11 (d, $J = 15.6$ Hz, H-β) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 55.6$ (O*C*H$_3$), 114.0 (C-3′,5′), 125.0 (C-3), 127.3 (C-α), 129.3 (C-6), 130.2 (C-4), 130.3 (C-1′), 131.2 (C-2′,6′), 131.5 (C-1), 133.5 (C-5), 139.2 (C-β), 148.6 (C-2), 163.7 (C-4′), 188.7 (C=O) ppm; IR (KBr): $\bar{\nu} = 1652$, 1602, 1569, 1517, 1421, 1351, 1297, 1259, 1220, 1016, 977, 835, 755 cm^{-1}.

General Procedure for the Reduction/Reductive Coupling With $SnCl_2 \cdot 2H_2O$ in HCl/AcOH
A solution of 5.2 g $SnCl_2 \cdot 2H_2O$ (23 mmol) in 20 cm^3 concentrated HCl was added to a suspension of the appropriate 2-nitrochalcones **1a**–**1l** or 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c** (5.7 mmol), in 60 cm^3 acetic acid. The obtained mixture was heated at 90°C for 4 h. After that period, the reaction mixture was cooled and treated with a 25% aqueous NaOH solution to adjust *pH* to 9. The obtained residue was extracted with 2×50 cm^3 $CHCl_3$, dried (Na_2SO_4), and evaporated to dryness.

In the case of 2′-hydroxy-3- and 4-nitrochalcones **1a**–**1f**, the obtained residue was recrystallized from ethanol giving the corresponding 3- and 4-amino-2′-hydroxychalcones **2a**–**2f** (**2a**, 61%; **2b**, 64%; **2c,** 54%; **2d**, 58%; **2e**, 68%; **2f**, 54%). For 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)2-propen-1-ones **5a**–**5c**, the obtained residue was recrystallized from ethanol giving the corresponding 2′-aminoflavones **6a**–**6c** (**6a**, 38%; **6b**, 54%; **6c**, 59%).

In the case of 2-nitrochalcones **1i**–**1l** the residue was purified by silica gel column chromatography, using chloroform as eluent. After solvent evaporation, the obtained residue was recrystallized from ethanol to give 2-(2-hydroxyaryl)quinolines **4i**–**4l** (**4i**, 66%; **4j**, 58%; **4k**, 54%; **4l**, 49%). For 2′-hydroxy-2-nitrochalcones **1g**, **1h** the obtained crude material was chromatographed over a silica gel column (eluent: 1:1 mixture of light petroleum:chloroform and then chloroform) to provide 2-(2-hydroxyaryl)quinolines **4g**, **4h** and the corresponding 2-(2-hydroxyaryl)quinoline-*N*-oxides **3g**, **3h** (**4g**, 47%; **4h**, 44%; **3g**, 23%; **3h**, 27%).

General Procedure for the Reduction/Reductive Coupling With Ammonium Formate and Pd/C
To a stirred suspension of the appropriate 2-nitrochalcones **1a**–**1l** or 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c** (5 mmol) and 0.25 g 10% palladium on charcoal in 10 cm^3 dry methanol at room temperature, was added anhydrous ammonium formate (23 mmol), in a single portion under N_2. The resulting mixture was stirred at room temperature for 3 h. The catalyst was removed by filtration through celite and washed with 2×10 cm^3 methanol. The filtrate was evaporated under reduced pressure and the residue was taken up in $CHCl_3$ and washed with 3×25 cm^3 H_2O. The organic layer was dried (Na_2SO_4) and evaporated to dryness.

In the case of 2′-hydroxy-3- and 4-nitrochalcones **1a**–**1d**, the obtained residue was recrystallized from ethanol, giving the corresponding 3- and 4-amino-2′-hydroxychalcones **2a**–**2d** (**2a**, 77%; **2b**, 83%; **2c**, 72%; **2d**, 68%). For 5′-bromo-3- and -4-nitrochalcones **1e**, **1f**, there was the formation of 3- and 4-amino-2′-hydroxychalcone **2a**, **2b** (**2a**, 64%; **2b**, 68%). For 4′-substituted-2′-hydroxy-2-nitrochalcones **1i**, **1j**, the obtained residue was recrystallized from ethanol, giving also the correspondent amino derivatives, 2-amino-2′-hydroxychalcones **2i**, **2j** (**2i**, 68%; **2j**, 50%). For 4′-methoxy-2-nitrochalcone **1l** the obtained crude material was chromatographed over a silica gel column (eluent, chloroform) to provide 2-amino-4′-methoxychalcone **2l** (25%).

In the case of 2′-hydroxy-2-nitrochalcones **1g**, **1h** and 3-hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-ones **5a**–**5c**, the obtained crude material was chromatographed over a silica gel column (eluent: 1:1 mixture of light petroleum:chloroform and then chloroform) to provide 2-(2-hydroxyaryl)quinolines **4g**, **4h** and also 2-(2-hydroxyaryl)quinoline-*N*-oxides **3g**, **3h** (**3g**, 36%; **4g**, 39%; **3h**, 33%; **4h**, 37%) in the first case, and of 2-(2-hydroxyphenyl)-4-hydroxyquinoline **8a**–**8c** and the corresponding 2-(2-hydroxyphenyl)-4-hydroxyquinoline-*N*-oxide **7a** (**8a**, 52%; **7a**, 34%; **8b**, 36%; **8c**, 63%) for the last one.

3-Amino-2′-hydroxychalcone (**2a**, $C_{15}H_{13}NO_2$)
Mp: 120–121°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 5.24$ (s br, N*H*$_2$), 6.70 (d, $J = 8.1$ Hz, H-3′), 6.98 (t, $J = 7.4$ Hz, H-5′), 7.00 (d, $J = 7.5$ Hz, H-4), 7.01 (s br, H-2), 7.06 (d, $J = 7.5$ Hz, H-6), 7.13 (t, $J = 7.5$ Hz, H-5), 7.54 (ddd, $J = 1.2$, 7.4, 8.1 Hz, H-4′), 7.68 (d, $J = 15.5$ Hz, H-β), 7.84 (d, $J = 15.5$ Hz, H-α) 8.16 (dd, $J = 1.2$, 7.4 Hz, H-6′), 12.50 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 114.0$ (C-2), 117.0 (C-3′ and C-6), 117.8 (C-4), 119.2 (C-5′), 120.8 (C-α), 121.0 (C-1′), 129.5 (C-5), 130.7 (C-6′), 134.9 (C-1), 136.2 (C-4′), 146.0 (C-β), 149.2 (C-3), 161.8 (C-2′), 193.6 (C=O) ppm; IR (KBr): $\bar{\nu} = 1641$, 1579, 1486, 1440, 1342, 1295, 1203, 1025, 846 cm^{-1}; MS (EI, 70 eV): m/z (%) = 239 ($M^{+\bullet}$, 100), 221 (23), 210 (15), 194 (11), 165 (8), 147 (38), 119 (43), 106 (9), 93 (22), 65 (27).

4-Amino-2′-hydroxychalcone (**2b**, $C_{15}H_{13}NO_2$)
Mp: 155–157°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 4.07$ (s br, N*H*$_2$), 6.70 (d, $J = 8.6$ Hz, H-3,5), 6.93 (dt, $J = 1.1$, 8.3 Hz, H-3′), 7.02 (dt, $J = 1.1$, 8.3 Hz, H-5′), 7.47 (dt, $J = 1.7$, 8.3 Hz, H-4′), 7.49 (d, $J = 15.4$ Hz, H-α), 7.52 (d, $J = 8.6$ Hz, H-2,6), 7.89 (d, $J = 15.4$ Hz, H-β), 7.94 (dd, $J = 1.7$, 8.3 Hz, H-6′), 13.09 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 114.8$ (C-3,5), 115.5 (C-α), 118.5 (C-3′), 118.6 (C-5′), 120.2 (C-1′), 124.8 (C-1), 129.4 (C-6′),

130.9 (C-2,6), 135.9 (C-4′), 146.1 (C-β), 152.7 (C-4), 163.5 (C-2′), 193.6 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1627, 1546, 1486, 1442, 1302, 1201, 1027, 765 cm^{-1}; MS (EI, 70 eV): m/z (%) = 239 ($M^{+\bullet}$, 64), 238 (34), 222 (9), 165 (5), 146 (16), 119 (100), 106 (47), 93 (27), 65 (26).

3-Amino-2′-hydroxy-4′-methoxychalcone (**2c**, $C_{16}H_{15}NO_3$)
Mp: 114–115°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 3.85 (s, OC*H*$_3$), 6.47 (s br, H-3′), 6.50 (dd, *J* = 2.5, 8.2 Hz, H-5′), 6.74 (dt, *J* = 2.0, 7.8 Hz, H-4), 6.93 (t, *J* = 2.0 Hz, H-2), 7.05 (d, *J* = 7.8 Hz H-6), 7.21 (t, *J* = 7.8 Hz, H-5), 7.51 (d, *J* = 15.4 Hz, H-α), 7.79 (d, *J* = 15.4 Hz, H-β), 7.82 (d, *J* = 8.2 Hz, H-6′), 13.48 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 55.6 (O*C*H$_3$), 101.0 (C-3′), 107.7 (C-5′), 114.0 (C-1′), 114.5 (C-2), 117.5 (C-4), 119.0 (C-6), 120.0 (C-α), 129.8 (C-5), 131.2 (C-6′), 135.7 (C-1), 144.7 (C-β), 146.8 (C-3), 166.1 (C-4′), 166.6 (C-2′), 193.6 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1637, 1579, 1506, 1359, 1267, 1214, 1128, 1018, 825 cm^{-1}; MS (EI, 70 eV): m/z (%) = 269 ($M^{+\bullet}$, 100), 268 (48), 252 (15), 252 (15), 240 (6), 177 (47), 151 (48), 146 (6), 119 (35), 108 (12), 91 (15).

4-Amino-2′-hydroxy-4′-methoxychalcone (**2d**, $C_{16}H_{15}NO_3$)
Mp: 130–131°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 3.84 (s, OC*H*$_3$), 4.05 (s br, N*H*$_2$), 6.46 (d, *J* = 2.5 Hz, H-3′), 6.47 (dd, *J* = 2.5, 6.9 Hz, H-5′), 6.68 (d, *J* = 8.5 Hz, H-3,5), 7.39 (d, *J* = 15.5 Hz, H-α), 7.48 (d, *J* = 8.5 Hz, H-2,6), 7.83 (d, *J* = 15.5 Hz, H-β), 7.85 (d, *J* = 6.9 Hz, H-6′), 13.71 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 55.5 (O*C*H$_3$), 101.0 (C-3′), 107.4 (C-5′), 114.2 (C-1′), 114.8 (C-3,5), 115.6 (C-α), 124.9 (C-1), 130.7 (C-2,6), 131.0 (C-6′), 145.0 (C-β), 149.3 (C-4), 165.8 (C-4′), 166.5 (C-2′), 191.9 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1629, 1563, 1508, 1367, 1290, 1226, 1020, 831 cm^{-1}; MS (EI, 70 eV): m/z (%) = 269 ($M^{+\bullet}$, 67), 268 (22), 252 (4), 177 (7), 151 (20), 146 (9), 119 (100), 106 (70), 93 (13), 65 (9).

3-Amino-5′-bromo-2′-hydroxychalcone (**2e**, $C_{15}H_{12}NO_2Br$)
Mp: 1120–121°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 6.78 (dt, *J* = 1.8, 7.8 Hz, H-4), 6.94 (d, *J* = 8.9 Hz, H-3′), 6.98 (t, *J* = 1.8 Hz, H-2), 7.09 (d, *J* = 7.8 Hz, H-6), 7.23 (t, *J* = 7.8 Hz, H-5), 7.51 (d, *J* = 15.4 Hz, H-α), 7.57 (dd, *J* = 2.4, 8.9 Hz, H-4′), 7.86 (d, *J* = 15.4 Hz, H-β), 8.00 (d, *J* = 2.4 Hz, H-6′), 12.78 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 110.4 (C-5′), 114.5 (C-2), 118.1 (C-4), 119.2 (C-α), 119.6 (C-6), 120.6 (C-3′), 121.3 (C-1′), 130.0 (C-5), 130.9 (C-1), 131.8 (C-6′), 135.3 (C-3), 138.9 (C-4′), 147.0 (C-β), 162.5 (C-2′), 192.8 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1643, 1619, 1571, 1463, 1400, 1357, 1332, 1284, 1251, 1176, 844 cm^{-1}; MS (EI, 70 eV): m/z (%) = 319 ($M^{+\bullet}$ ^{81}Br, 100), 317 ($M^{+\bullet}$ ^{79}Br, 100), 301 (73), 290 (4), 284 (7), 179 (18), 238 (12), 225 (28), 209 (17), 193 (16), 180 (10), 167 (25), 149 (46).

4-Amino-5′-bromo-2′-hydroxychalcone (**2f**, $C_{15}H_{12}NO_2Br$)
Mp: 156–158°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 6.70 (d, *J* = 8.5 Hz, H-3,5), 6.92 (d, *J* = 8.7 Hz, H-3′), 7.36 (d, *J* = 15.2 Hz, H-α), 7.52 (d, *J* = 8.5 Hz, H-2,6), 7.53 (dd, *J* = 2.4, 8.7 Hz, H-4′), 7.90 (d, *J* = 15.2 Hz, H-β), 7.99 (d, *J* = 2.4 Hz, H-6′), 13.04 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 110.2 (C-5′), 114.6 (C-α), 114.8 (C-3,5), 120.5 (C-3′), 124.5 (C-1′), 129.4 (C-1), 131.2 (C-2,6), 131.6 (C-6′), 138.3 (C-4′), 147.3 (C-β), 149.9 (C-4), 162.4 (C-2′), 192.5 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 16313, 1600, 1556, 1515, 1467, 1422, 1336, 1271, 1172, 1027, 823 cm^{-1}; MS (EI, 70 eV): m/z (%) = 319 ($M^{+\bullet}$ ^{81}Br, 97), 317 ($M^{+\bullet}$ ^{79}Br, 100), 300 (7), 238 (16), 209 (9), 180 (7), 165 (8), 146 (34).

2-Amino-2′-hydroxy-4′-methoxychalcone (**2i**, $C_{16}H_{15}NO_3$)
Mp: 157–158°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 3.86 (s, OC*H*$_3$), 4.09 (s br, N*H*$_2$), 6.47 (s br, H-3′), 6.50 (dd, *J* = 2.5, 9.6 Hz, H-5′), 6.74 (d, *J* = 7.6 Hz, H-3), 6.81 (t, *J* = 7.6 Hz, H-5), 7.22 (dt, *J* = 1.2, 7.6 Hz, H-4), 7.50 (d, *J* = 7.6 Hz, H-6), 7.51 (d, *J* = 15.2 Hz, H-α), 7.82 (d, *J* = 9.6 Hz, H-6′), 8.05 (d, *J* = 15.2 Hz, H-β), 13.52 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 55.6 (O*C*H$_3$), 101.0 (C-3′), 107.7 (C-5′), 114.1 (C-1′), 116.9 (C-3), 118.9 (C-5), 120.1 (C-α), 120.2 (C-1), 128.2 (C-6), 131.2 (C-6′), 131.8 (C-4), 139.7 (C-β), 146.3 (C-2), 166.1 (C-4′), 166.7 (C-2′), 191.8 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1629, 1577, 1367, 1288 cm^{-1}; MS (EI, 70 eV): m/z (%) = 269 ($M^{+\bullet}$, 27), 252 (62), 251 (100), 250 (38), 222 (8), 208 (11), 180 (10), 151 (33), 146 (16), 128 (15), 118 (34), 108 (12), 91 (17).

2-Amino-4′-benzyloxy-2′-hydroxychalcone (**2j**, $C_{22}H_{19}NO_3$)
Mp: 150–151°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 4.09 (s br, N*H*$_2$), 5.11 (s, C*H*$_2$), 6.53–6.57 (m, H-3′ and H-5′), 6.73 (dd, *J* = 0.9, 7.9 Hz, H-3), 6.80 (t, *J* = 7.9 Hz, H-5), 7.21 (dt, *J* = 1.4, 7.9 Hz, H-4), 7.34–7.44 (m, H-2″,3″,4″,5″,6″), 7.49 (d, *J* = 7.9 Hz, H-6), 7.50 (d, *J* = 15.2 Hz, H-α), 7.82 (d, *J* = 9.7 Hz, H-6′), 8.04 (d, *J* = 15.2 Hz, H-β), 13.49 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 70.2 (*C*H$_2$), 102.1 (C-3′), 108.2 (C-5′), 114.2 (C-1′), 116.8 (C-3), 118.9 (C-5), 120.1 (C-α), 120.2 (C-1), 127.6 (C-2″,6″), 128.2 (C-4″), 128.3 (C-6), 128.7 (C-3″,5″), 131.2 (C-6′), 131.8 (C-4), 135.8 (C-1″), 139.8 (C-β), 146.3 (C-2), 165.2 (C-4′), 166.6 (C-2′), 191.8 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1625, 1571, 1359, 1282 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 15), 327 (52), 299 (3), 237 (8), 208 (13), 180 (7), 146 (5), 118 (12), 91 (100), 65 (14).

2-Amino-4′-methoxychalcone (**2l**, $C_{16}H_{15}NO_2$)
Mp: 93–94°C; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): δ = 3.86 (s, OC*H*$_3$), 5.70 (s br, N*H*$_2$), 6.58 (t, *J* = 7.8 Hz, H-5), 6.71 (d, *J* = 7.8 Hz, H-3), 7.08 (d, *J* = 8.8 Hz, H-3′,5′), 7.09–7.13 (m, H-4), 7.81 (d, *J* = 15.1 Hz, H-α), 7.71 (d, *J* = 7.8 Hz, H-6), 7.97 (d, *J* = 15.1 Hz, H-β), 8.14 (d, *J* = 8.8 Hz, H-H-2′,6′) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): δ = 55.6 (O*C*H$_3$), 114.0 (C-3′,5′), 114.3 (C-1′), 116.3 (C-3), 116.5 (C-5), 118.3 (C-1), 119.4 (C-α), 127.8 (C-6), 130.7 (C-2′,6′), 131.5 (C-4), 139.6 (C-β), 149.0 (C-2), 162.9 (C-4′), 187.4 (C=O) ppm; IR (KBr): $\bar{\nu}$ = 1652, 1604, 1583, 1459, 1336, 1259, 1216, 1110, 1018, 590 cm^{-1}; MS (EI, 70 eV): m/z (%) = 253 ($M^{+\bullet}$, 23), 236 (100), 220 (6), 165 (3), 146 (38), 118 (51), 92 (28), 77 (32), 64 (15).

2-(2-Hydroxyphenyl)quinoline-N-oxide (**3g**, $C_{15}H_{11}NO_2$)
Mp: 180–181°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.05$ (dd, $J = 1.0$, 7.7 Hz, H-3′), 7.10 (dt, $J = 1.0$, 7.7 Hz, H-5′), 7.53 (dt, $J = 1.6$, 7.7 Hz, H-4′), 7.69 (dd, $J = 1.6$, 7.7 Hz, H-6′), 7.87 (dt, $J = 1.0$, 7.8 Hz, H-6), 7.96 (d, $J = 8.9$ Hz, H-3), 8.01–8.04 (m, H-7), 8.25 (d, $J = 7.8$ Hz, H-5), 8.35 (d, $J = 8.9$ Hz, H-4), 8.75 (d, $J = 8.7$ Hz, H-8), 11.30 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 119.0$ (C-8), 119.6 (C-3′), 120.0 (C-5′), 121.4 (C-1′), 124.7 (C-3), 128.7 (C-5), 128.8 (C-4a), 129.2 (C-6), 130.2 (C-4), 132.1 (C-6′), 132.2 (C-7), 132.4 (C-4′), 139.9 (C-8a), 147.6 (C-2), 159.1 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1562$, 1506, 1481, 1334 cm^{-1}; MS (EI, 70 eV): m/z (%) = 237 ($M^{+\bullet}$, 48), 221 (32), 220 (100), 208 (7), 191 (20), 180 (15), 165 (14), 140 (5), 128 (9), 102 (3), 95 (6), 77 (5), 63 (4).

2-(5-Bromo-2-hydroxyphenyl)quinoline-N-oxide (**3h**, $C_{15}H_{10}NO_2Br$)
Mp: 167–168°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.00$ (d, $J = 8.8$ Hz, H-3′), 7.65 (dd, $J = 2.5$, 8.8 Hz, H-4′), 7.84 (d, $J = 2.5$ Hz, H-6′), 7.88 (dt, $J = 0.9$, 8.0 Hz, H-6), 7.98 (d, $J = 8.8$ Hz, H-3), 7.97–8.03 (m, H-7), 8.24 (dd, $J = 0.9$, 8.0 Hz, H-5), 8.33 (d, $J = 8.8$ Hz, H-4), 8.72 (d, $J = 8.8$ Hz, H-8), 11.37 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 110.7$ (C-5′), 119.0 (C-8), 121.4 (C-3′), 123.3 (C-1′), 124.7 (C-3), 128.7 (C-5), 129.1 (C-4a), 129.3 (C-6), 129.9 (C-4), 131.6 (C-7), 133.8 (C-6′), 134.7 (C-4′), 139.9 (C-8a), 145.8 (C-2), 158.2 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1560$, 1506, 1473, 1330 cm^{-1}; MS (EI, 70 eV): m/z (%) = 317 ($M^{+\bullet}$, 62), 315 (62), 300 (100), 286 (7), 219 (66), 208 (8), 191 (43), 180 (23), 164 (13), 140 (7), 128 (27), 96 (22), 77 (12), 63 (14).

2-(2-Hydroxyphenyl)quinoline (**4g**, $C_{15}H_{11}NO$)
Mp: 110–111°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 6.97$–7.03 (m, H-3′ and H-5′), 7.41 (dt, $J = 1.2$, 7.7 Hz, H-4′), 7.67 (dt, $J = 0.7$, 7.5 Hz, H-6), 7.85 (dt, $J = 1.1$, 7.5 Hz, H-7), 8.05–8.10 (m, H-5 and H-8), 8.22 (dd, $J = 1.2$, 7.7 Hz, H-6′), 8.39 (d, $J = 8.9$ Hz, H-3), 8.59 (d, $J = 8.9$ Hz, H-4), 14.93 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 118.0$ (C-3 and C-3′), 118.8 (C-1′), 118.9 (C-5′), 126.4 (C-4a), 127.0 (C-6 and C-8), 127.9 (C-6′), 128.0 (C-5), 130.9 (C-7), 132.2 (C-4′), 138.4 (C-4), 144.1 (C-8a), 157.7 (C-2), 160.2 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1606$, 1585, 1550, 1506 cm^{-1}; MS (EI, 70 eV): m/z (%) = 221 ($M^{+\bullet}$, 100), 220 (59), 193 (25), 180 (15), 167 (30), 154 (7), 128 (16), 111 (8), 96 (10), 89 (4), 84 (15), 77 (9), 63 (7).

2-(5-Bromo-2-hydroxyphenyl)quinoline (**4h**, $C_{15}H_{10}NOBr$)
Mp: 165–166°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 6.99$ (d, $J = 8.7$ Hz, H-3′), 7.54 (dd, $J = 2.2$, 8.7 Hz, H-4′), 7.69 (t, $J = 7.4$ Hz, H-6), 7.86 (t, $J = 7.4$ Hz, H-7), 8.07–8.11 (m, H-5 and H-8), 8.39 (d, $J = 2.2$ Hz, H-6′), 8.46 (d, $J = 8.9$ Hz, H-3), 8.61 (d, $J = 8.9$ Hz, H-4), 14.94 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 110.1$ (C-5′), 118.4 (C-3), 120.3 (C-3′), 120.9 (C-1′), 126.7 (C-4a), 127.2 (C-8), 127.4 (C-6), 128.0 (C-5), 130.1 (C-6′), 131.1 (C-7), 134.5 (C-4′), 138.6 (C-4), 144.0 (C-8a), 156.3 (C-2), 159.2 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1604$, 1579, 1550, 1509 cm^{-1}; MS (EI, 70 eV): m/z (%) = 301 ($M^{+\bullet}$, 100), 300 (55), 299 (100), 298 (39), 271 (4), 219 (6), 191 (48), 165 (13), 128 (15), 110 (8), 96 (27), 77 (7), 63 (8), 57 (5).

2-(2-Hydroxy-4-methoxyphenyl)quinoline (**4i**, $C_{16}H_{13}NO_2$)
Mp: 123–124°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 3.81$ (s, OC*H*$_3$), 6.52 (d, $J = 2.5$ Hz, H-3′), 6.56 (dd, $J = 2.5$, 8.8 Hz, H-5′), 7.60 (dt, $J = 1.0$, 7.6 Hz, H-6), 7.80 (dt, $J = 1.4$, 7.6 Hz, H-7), 7.98–8.01 (m, H-5 and H-8), 8.12 (d, $J = 8.8$ Hz, H-6′), 8.27 (d, $J = 9.0$ Hz, H-3), 8.50 (d, $J = 9.0$ Hz, H-4), 15.34 (s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 55.5$ (O*C*H$_3$), 101.9 (C-3′), 106.4 (C-5′), 111.9 (C-1′), 117.7 (C-3), 126.0 (C-4a), 126.5 (C-6), 128.0 (C-5 and C-8), 129.1 (C-6′), 130.9 (C-7), 138.2 (C-4), 148.9 (C-8a), 157.7 (C-2), 162.4 (C-4′), 162.6 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1606$, 1587, 1548, 1506 cm^{-1}; MS (EI, 70 eV): m/z (%) = 251 ($M^{+\bullet}$, 100), 250 (42), 222 (19), 208 (34), 180 (32), 167 (7), 154 (13), 128 (22), 112 (8), 77 (12), 63 (6).

2-(2,4-Dihydroxyphenyl)quinoline (**4j**, $C_{15}H_{11}NO_2$)
Mp: 175–176°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 6.36$ (d, $J = 2.4$ Hz, H-3′), 6.43 (dd, $J = 2.4$, 8.7 Hz, H-5′), 7.59 (dt, $J = 0.9$, 8.0 Hz, H-6), 7.76–7.82 (m, H-7), 7.96 (d, $J = 8.0$ Hz, H-8), 7.99 (d, $J = 8.0$ Hz, H-5), 8.02 (d, $J = 8.7$ Hz, H-6′), 8.21 (d, $J = 9.0$ Hz, H-3), 8.47 (d, $J = 9.0$ Hz, H-4), 10.03 (s, 4′-O*H*), 15.23 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 103.5$ (C-3′), 107.5 (C-5′), 110.8 (C-1′), 117.5 (C-3), 125.8 (C-4a), 126.3 (C-6), 126.5 (C-8), 128.0 (C-5), 129.2 (C-6′), 130.8 (C-7), 138.0 (C-4), 144.0 (C-8a), 158.0 (C-2), 161.2 (C-4′), 162.4 (C-2′) ppm; IR (KBr): $\bar{\nu} = 1612$, 1582, 1552, 1509 cm^{-1}; MS (EI, 70 eV): m/z (%) = 237 ($M^{+\bullet}$, 92), 236 (64), 207 (33), 191 (3), 180 (36), 167 (9), 128 (12), 105 (100), 89 (11), 77 (67), 63 (15).

2-Phenylquinoline (**4k**, $C_{15}H_{11}NO_2$)
Mp: 66–68°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.48$ (d, $J = 7.0$ Hz, H-4′), 7.52 (d, $J = 7.0$ Hz, H-2′,6′), 7.53–7.56 (m, H-6), 7.73 (dt, $J = 1.4$, 7.7 Hz, H-7), 7.84 (dd, $J = 1.4$, 8.7 Hz, H-5), 7.88 (d, $J = 8.7$ Hz, H-3), 8.16 (d, $J = 7.0$ Hz, H-3′,5′), 8.18 (d, $J = 7.7$ Hz, H-8), 8.23 (d, $J = 8.7$ Hz, H-4) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 119.0$ (C-3), 126.3 (C-6), 127.2 (C-4a), 127.4 (C-5), 127.6 (C-2′,6′), 128.8 (C-3′,5′), 129.3 (C-4′), 129.6 (C-8), 129.7 (C-7), 136.8 (C-4), 139.6 (C-1′), 148.2 (C-8a), 157.3 (C-2) ppm; IR (KBr): $\bar{\nu} = 1727$, 1596, 1490, 1282, 1126, 1072, 829, 771, 690 cm^{-1}; MS (EI, 70 eV): m/z (%) = 205 ($M^{+\bullet}$, 100), 204 (72), 176 (6), 167 (14), 149 (35), 102 (16), 71 (12), 57 (19).

2-(4-Methoxyphenyl)quinoline (**4l**, $C_{16}H_{13}NO$)
Mp: 87–89°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 3.85$ (s, OC*H*$_3$), 7.11 (d, $J = 8.6$H, H-3′,5′), 7.67 (t, $J = 7.7$ Hz, H-6), 7.77 (t, $J = 7.7$ Hz, H-7), 7.87 (d, $J = 7.7$ Hz, H-5), 8.04 (d, $J = 7.7$ Hz, H-8), 8.10 (d, $J = 8.6$ Hz, H-3), 8.26 (d, $J = 8.6$ Hz, H-2′,6′), 8.41 (d, H-4, $J = 8.6$ Hz) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 55.4$ (O*C*H$_3$), 114.3 (C-3′,5′), 118.4 (C-3), 126.1 (C-6), 127.5 (C-4a), 127.8 (C-5), 128.7 (C-2′,6′), 129.0 (C-8), 129.9 (C-7), 136.4 (C-1′), 137.1 (C-4), 147.6 (C-8a), 155.8 (C-2), 160.7 (C-4′) ppm; IR (KBr): $\bar{\nu} = 1743$,

1576, 1493, 1280, 1136, 834, 779, 699 cm^{-1}; MS (EI, 70 eV): m/z (%) = 235 ($M^{+\bullet}$, 100), 234 (78), 226 (9), 167 (44), 133 (39), 100 (26), 77 (12).

2′-Aminoflavone (**6a**)
Mp: 311–312°C; ^1H and ^{13}C NMR data see Ref. [20]; IR (KBr): $\bar{\nu}$ = 1644, 1602, 1565, 1459, 1373, 1128, 752 cm^{-1}; MS (EI, 70 eV): m/z (%) = 237 ($M^{+\bullet}$, 100), 236 (17), 221 (6), 209 (16), 180 (3), 121 (5), 117 (56), 105 (5), 92 (10), 63 (7).

2′-Amino-7-methoxyflavone (**6b**)
Mp: 172–174°C; ^1H and ^{13}C NMR data see Ref. [20]; MS (EI, 70eV): m/z (%) = 267 ($M^{+\bullet}$, 100), 266 (18), 251 (5), 239 (15), 224 (32), 167 (5), 151 (20), 117 (45), 107 (9), 79 (9), 63 (11).

2′-Amino-5-methoxyflavone (**6c**)
Mp: 161–162°C; ^1H and ^{13}C NMR data see Ref. [20]; IR (KBr): $\bar{\nu}$ = 1727, 1629, 1567, 1475, 1434, 1382, 1307, 1268, 1238, 1101, 750 cm^{-1}; MS (EI, 70 eV): m/z (%) = 267 ($M^{+\bullet}$, 100), 266 (39), 248 (15), 238 (22), 221 (36), 167 (13), 149 (23), 122 (8), 117 (66), 107 (17), 90 (25), 77 (5).

2-(2-Hydroxyphenyl)-4-hydroxyquinoline-N-oxide
(**7a**, $C_{15}H_{11}NO_3$)
Mp: 189–190°C; ^1H NMR (300 MHz, *DMSO*-d_6): δ = 6.91 (s br, H-3), 6.98–7.06 (m, H-3′ and H-5′), 7.48 (dt, J = 1.3, 7.7 Hz, H-4′), 7.55 (d, J = 7.7 Hz, H-6′), 7.74 (t, J = 7.7 Hz, H-6), 7.95 (ddd, J = 0.7, 7.7, 8.6 Hz, H-7), 8.28 (d, J = 7.7 Hz, H-5), 8.55 (d, J = 8.6 Hz, H-8), 12.00 (br s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): δ = 106.3 (C-3), 118.4 (C-8), 119.2 and 119.3 (C-3′ and C-5′), 121.6 (C-4a), 121.8 (C-1′), 123.4 (C-5), 127.1 (C-6), 131.2 (C-6′), 132.2 (C-4′), 132.5 (C-7), 140.2 (C-8a), 149.5 (C-2), 159.1 (C-2′ and C-4) ppm; IR (KBr): $\bar{\nu}$ = 1598, 1546, 1455, 1409, 1201, 1091, 806, 757 cm^{-1}; MS (EI, 70eV): m/z (%) = 253 ($M^{+\bullet}$, 35), 237 (100), 236 (96), 224 (7), 209 (25), 180 (18), 152 (11), 116 (5), 89 (15), 77 (14), 63 (6).

2-(2-Hydroxyphenyl)-4-hydroxyquinoline (**8a**, $C_{15}H_{11}NO_2$)
Mp: 105–106°C; ^1H NMR (300 MHz, *DMSO*-d_6): δ = 6.57 (s br, H-3), 6.87–6.90 (m, H-3′ and H-5′), 7.38 (dt, J = 1.5, 7.2 Hz, H-4′), 7.46 (dd, J = 1.5, 8.0 Hz, H-6′), 7.57 (t, J = 8.6 Hz, H-6), 7.83–7.87 (m, H-7), 8.26 (dd, J = 0.9, 8.6 Hz, H-8), 8.44 (d, J = 8.6 Hz, H-5), 12.35 (br s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): δ = 106.5 (C-3), 116.8 (C-1′), 118.0 (C-5), 118.3 (C-5′), 119.4 (C-3′), 122.5 (C-4a), 124.0 (C-8), 125.3 (C-6), 130.9 (C-6′), 131.6 (C-7), 131.7 (C-4′), 140.2 (C-8a), 150.1 (C-2), 160.3 (C-2′), 164.8 (C-4) ppm; IR (KBr): $\bar{\nu}$ = 1596, 1546, 1455, 1407, 1201, 1089, 804, 755 cm^{-1}; MS (EI, 70 eV): m/z (%) = 237 ($M^{+\bullet}$, 100), 236 (44), 220 (5), 209 (19), 183 (11), 149 (12), 121 (7), 89 (9), 83 (47), 77 (10).

2-(2-Hydroxy-4-methoxyphenyl)-4-hydroxyquinoline
(**8b**, $C_{15}H_{11}NO_2$)
Mp: 110–111°C; ^1H NMR (300 MHz, *DMSO*-d_6): δ = 6.40 (s br, H-3), 6.50 (d, J = 1.2 Hz, H-3′), 6.52 (dd, J = 1.2, 8.0 Hz, H-5′), 7.57 (t, J = 8.0 Hz, H-6), 7.77 (d, J = 8.0 Hz, H-6′), 7.80 (t, J = 8.0 Hz, H-7), 8.24 (d, J = 8.0 Hz, H-8), 8.27 (d, J = 8.0 Hz, H-5), 12.29 (br s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): δ = 104.3 (C-3), 115.4 (C-1′), 105.9 (C-5′), 110.3 (C-3′), 115.4 (C-1′), 120.0 (C-5), 123.6 (C-4a), 123.9 (C-8), 129.7 (C-6), 131.8 (C-7), 132.4 (C-6′), 131.7 (C-4′), 140.4 (C-8a), 148.0 (C-2), 157.4 (C-2′), 160.0 (C-4) ppm; IR (KBr): $\bar{\nu}$ = 1594, 1566, 1478, 1438, 1221, 1090, 824, 757 cm^{-1}; MS (EI, 70 eV): m/z (%) = 267 ($M^{+\bullet}$, 100), 266 (48), 237 (16), 209 (25), 183 (10), 141 (12), 136 (15), 97 (39), 83 (47), 77 (10).

2-(2-Hydroxy-6-methoxyphenyl)-4-hydroxyquinoline
(**8c**, $C_{16}H_{13}NO_3$)
Mp: 120–121°C; ^1H NMR (300 MHz, *DMSO*-d_6): δ = 3.75 (s, OCH_3), 6.43 (br s, H-3), 6.60 (d, J = 8.1 Hz, H-3′), 6.63 (d, J = 8.1 Hz, H-5′), 7.30 (t, J = 8.1 Hz, H-4′), 7.56 (t, J = 7.7 Hz, H-6), 7.83 (t, J = 7.7 Hz, H-7), 8.20 (d, J = 7.7 Hz, H-5, H-8), 11.24 (br s, O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): δ = 55.7 (OCH_3), 102.1 (C-3 and C-5′), 109.0 (C-3′), 110.2 (C-1′), 116.7 (C-5), 123.2 (C-8), 123.8 (C-4a), 131.1 (C-4′), 131.6 (C-6 and C-7), 140.1 (C-8a), 146.4 (C-2 and C-6′), 157.8 (C-4 and C-2′) ppm; IR (KBr): $\bar{\nu}$ = 1602, 1562, 1479, 1392, 1334, 1301, 1178, 823, 755 cm^{-1}; MS (EI 70 eV): m/z (%) = 267 ($M^{+\bullet}$, 100), 266 (50), 252 (24), 237 (21), 224 (49), 209 (15), 196 (13), 183 (11), 167 (16), 141 (8), 131 (20), 120 (30), 111 (10), 97 (9).

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