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Efficient Synthesis of Nitroflavones by Cyclodehydrogenation of 2′-Hydroxychalcones and by the *Baker-Venkataraman* Method

Ana I. R. N. A. Barros[1] and **Artur M. S. Silva**[2,*]

[1] Chemistry Department, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal
[2] Chemistry Department, University of Aveiro, Aveiro, Portugal

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Summary. Several nitroflavone derivatives were synthesized by cyclodehydrogenation of 2′-hydroxychalcones and by the *Baker-Venkataraman* approach, starting from 2′-hydroxyacetophenones and benzoic acid derivatives. Nitroflavones synthesised by the first synthetic approach were obtained in better global yields than those obtained by the later method. The structures of all new compounds were elucidated by microanalyses, 1D and 2D NMR, IR, and mass spectroscopic measurements.

Keywords. Nitroflavones; Cyclodehydrogenation; 2′-Hydroxychalcones; *Baker-Venkataraman* method; NMR spectroscopy.

Introduction

Flavones (2-phenylchromones) are an important group of heterocyclic polyphenolic compounds widely distributed in the plant kingdom, where they participate in several biological functions [1]. The synthesis of flavone derivatives has attracted considerable attention due to their significant pharmaceutical [2], biocidal [3], and antioxidant [4] activities. For instance, it has been found that several synthetic nitroflavones are selective and competitive ligands for central benzodiazepine receptors (*BDZ*-R) and possess anxiolytic activity *in vivo*, with minor sedative or myorelaxant effects [5]. This led to postulate that these flavonoids represent a new family of *BDZ*-R ligands possessing pharmacological properties distinct from classical *BDZ*s, which bind in every region of the brain with similar affinities [5]. Recently it has also been found that several nitro derivatives are potent antiproliferative agents against human and murine tumor cell lines [6], and others act as chemoprotective agents against colon aberrant crypt foci [7]. A specific nitroflavone derivative, 3′-methoxy-4′-nitroflavone, may act as an aryl hydrocarbon

* Corresponding author. E-mail: arturs@dq.ua.pt

receptor agonist or antagonist of tumor cells depending on its concentration as well as the promoter context of a particular gene [8]. Although it has yet to be established whether any of these nitroflavone derivatives may originate a useful therapeutic drug, it is deemed important to synthesize a wider series of analogous compounds.

The synthesis of flavone derivatives has been extensively studied [9], whereas to our knowledge only a few synthesis methods are available for the preparation of their nitro derivatives, and only a few derivatives are described in literature [5, 10]. Taking into account the potential biological applications of flavones, and especially those having nitro-substituents and the scarce number of those nitroflavone derivatives described in literature, we decided to devote some attention to the synthesis of a number of new nitroflavones. These compounds were obtained by cyclodehydrogenation of 2′-hydroxychalcones or by the *Baker-Venkataraman* approach, starting from appropriate 2′-hydroxyacetophenones and benzoic acid derivatives [9].

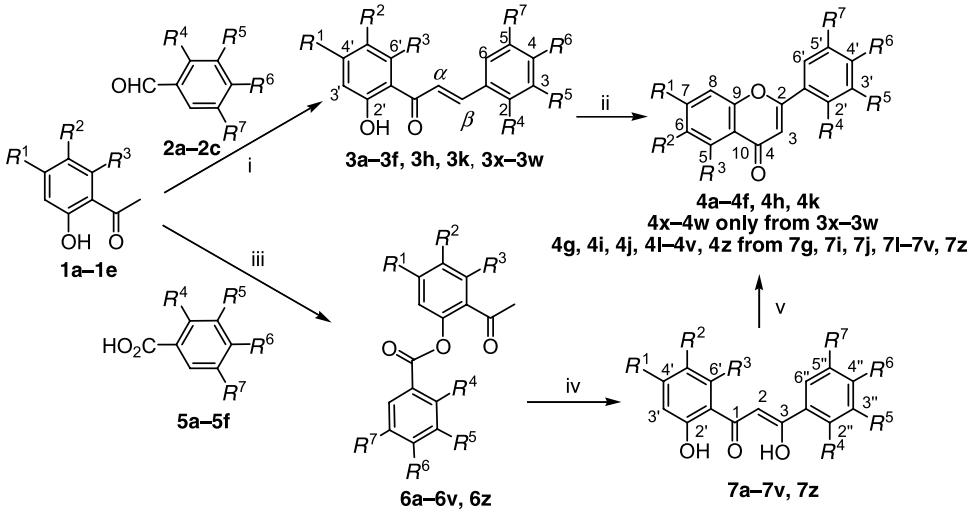
Results and Discussion

Synthesis

Nitroflavones **4** were obtained by cyclodehydrogenation of 2′-hydroxychalcones obtained from an aldol condensation of 2′-hydroxyacetophenones and adequate benzaldehydes [11], and by the *Baker-Venkataraman* approach starting from 2′-hydroxyacetophenones and benzoic acid derivatives (Scheme 1). According to the availability of benzaldehydes and benzoic acids with the same substitution pattern and some difficulties in the synthesis of chalcones [11], nitroflavones **4a**–**4f**, **4h**, and **4k** were synthesized by both referred methods, trying to conclude which one is more adequate to synthesise these compounds in terms of yields and practical execution.

The oxidative cyclisation of 2′-hydroxynitrochalcones **3a**–**3f**, **3h**, **3k**, and **3x**–**3w** into the corresponding nitroflavones **4a**–**4f**, **4h**, **4k**, and **4x**–**4w** was carried out with a catalytic amount of iodine in *DMSO* at reflux, for 0.5 h [12]. These nitroflavones were obtained in good yields (60–86%) with exception of the 2′-nitro derivatives **4a** and **4d** which were obtained in moderate yields (32–36%). The presence of a 2-nitro-substituent on the starting 2′-hydroxynitrochalcones **3a** and **3d** mode their cyclodehydrogenation difficult and led also to great decomposition in the reaction mixture.

In the other synthesis approach, 2′-(nitrobenzoyloxy)acetophenones **6a**–**6v** and **6z** were obtained from the reaction of the 2′-hydroxyacetophenone derivatives **1a**–**1e** with the appropriate benzoyl chlorides, prepared *in situ* from benzoic acids **5a**–**5f** and phosphorous oxychloride. The *Baker-Venkataraman* rearrangement of 2′-(nitrobenzoyloxy)acetophenones **6a**–**6v** and **6z** into the corresponding 1,3-diketones, 1-(2-hydroxyphenyl)-3-(nitrophenyl)propan-1,3-diones **8a**–**8v** and **8z**, was performed upon treatment with sodium hydride in dry *THF* at reflux (Scheme 1 and Fig. 1). In $CDCl_3$ solution these compounds were identified as a mixture of isomers, 1,3-diketones **8a**–**8v** and **8z** and 3-hydroxy-1-(2-hydroxyphenyl)-3-(nitrophenyl)-2-propen-1-ones **7a**–**7v** and **7z** and/or 2-hydroxynitroflavanones **9a**–**9v**



i) NaH, *THF*, room temperature
ii) *DMSO*/I_2, reflux
iii) $POCl_3$, *Py*, 60–70°C
iv) NaH, *THF*, reflux
v) *DMSO*/I_2, 80–90°C, or *DMSO*/*p*-toluenesulfonic acid, 80–90°C, or acetic acid/sulfuric acid (1% *v/v*), 80–90°C

Compounds 1:
a $R^1 = R^2 = R^3 = H$
b $R^1 = OMe$, $R^2 = R^3 = H$
c $R^1 = R^2 = H$, $R^3 = OMe$
d $R^1 = R^3 = OMe$, $R^2 = H$
e $R^1 = R^3 = H$, $R^2 = Br$

Compounds 2:
a $R^4 = NO_2$, $R^5 = R^6 = R^7 = H$
b $R^5 = NO_2$, $R^4 = R^6 = R^7 = H$
c $R^6 = NO_2$, $R^4 = R^5 = R^7 = H$

Compounds 5:
a $R^4 = NO_2$, $R^5 = R^6 = R^7 = H$
b $R^5 = NO_2$, $R^4 = R^6 = R^7 = H$
c $R^6 = NO_2$, $R^4 = R^5 = R^7 = H$
d $R^4 = Me$, $R^5 = NO_2$, $R^6 = R^7 = H$
e $R^6 = Me$, $R^5 = NO_2$, $R^4 = R^7 = H$
f $R^5 = R^7 = NO_2$, $R^4 = R^6 = H$

Compounds 3, 4, 6 and 7:
a $R^1 = R^2 = R^3 = R^5 = R^6 = R^7 = H$, $R^4 = NO_2$
b $R^1 = R^2 = R^3 = R^4 = R^6 = R^7 = H$, $R^5 = NO_2$
c $R^1 = R^2 = R^3 = R^4 = R^5 = R^7 = H$, $R^6 = NO_2$
d $R^1 = OMe$, $R^2 = R^3 = R^5 = R^6 = R^7 = H$, $R^4 = NO_2$
e $R^1 = OMe$, $R^2 = R^3 = R^4 = R^6 = R^7 = H$, $R^5 = NO_2$
f $R^1 = OMe$, $R^2 = R^3 = R^4 = R^5 = R^7 = H$, $R^6 = NO_2$
g $R^1 = R^2 = R^5 = R^6 = R^7 = H$, $R^3 = OMe$, $R^4 = NO_2$
h $R^1 = R^2 = R^4 = R^6 = R^7 = H$, $R^3 = OMe$, $R^5 = NO_2$
i $R^1 = R^2 = R^4 = R^5 = R^7 = H$, $R^3 = OMe$, $R^6 = NO_2$
j $R^1 = R^3 = OMe$, $R^2 = R^5 = R^6 = R^7 = H$, $R^4 = NO_2$
k $R^1 = R^3 = OMe$, $R^2 = R^4 = R^6 = R^7 = H$, $R^5 = NO_2$
l $R^1 = R^3 = OMe$, $R^2 = R^4 = R^5 = R^7 = H$, $R^6 = NO_2$
m $R^1 = R^2 = R^3 = R^6 = R^7 = H$, $R^4 = Me$, $R^5 = NO_2$
n $R^1 = R^2 = R^3 = R^4 = R^7 = H$, $R^5 = NO_2$, $R^6 = Me$
o $R^1 = R^2 = R^3 = R^4 = R^6 = H$, $R^5 = R^7 = NO_2$
p $R^1 = OMe$, $R^2 = R^3 = R^4 = R^7 = H$, $R^5 = NO_2$, $R^6 = Me$
q $R^1 = OMe$, $R^2 = R^3 = R^4 = R^6 = H$, $R^5 = R^7 = NO_2$
r $R^1 = R^2 = R^6 = R^7 = H$, $R^3 = OMe$, $R^4 = Me$, $R^5 = NO_2$
s $R^1 = R^2 = R^4 = R^7 = H$, $R^3 = OMe$, $R^5 = NO_2$, $R^6 = Me$
t $R^1 = R^2 = R^4 = R^4 = H$, $R^3 = OMe$, $R^5 = R^7 = NO_2$
u $R^1 = R^3 = OMe$, $R^2 = R^4 = R^7 = H$, $R^5 = NO_2$, $R^6 = Me$
v $R^1 = R^3 = OMe$, $R^2 = R^4 = R^6 = H$, $R^5 = R^7 = NO_2$
x $R^1 = R^3 = R^5 = R^6 = R^7 = H$, $R^2 = Br$, $R^4 = NO_2$
y $R^1 = R^3 = R^4 = R^6 = R^7 = H$, $R^2 = Br$, $R^5 = NO_2$
w $R^1 = R^3 = R^4 = R^5 = R^7 = H$, $R^2 = Br$, $R^6 = NO_2$
z $R^1 = R^3 = R^4 = R^6 = H$, $R^2 = Br$, $R^5 = R^7 = NO_2$

Scheme 1

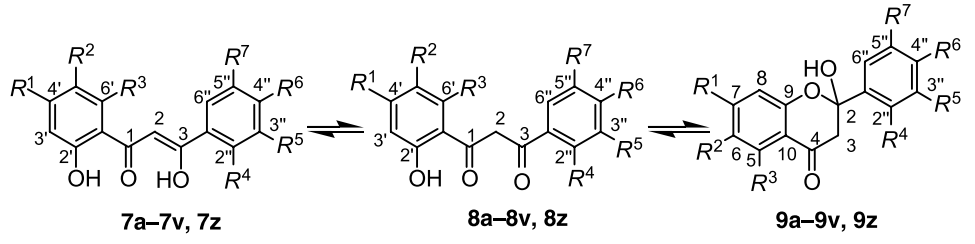


Fig. 1. Equilibrium between isomers **7a**–**7v**, **7z**, **8a**–**8v**, **8z**, and **9a**–**9v**, **9z**

and **9z** (Fig. 1) (*vide* Experimental). In Scheme 1 the structures of the enolic forms **7a**–**7v** and **7z** are shown because they are main isomeric structures of the major part of synthesised compounds.

The treatment of **7a**–**7v** and **7z** (or the correspondent isomers **8a**–**8v** and **8z** or **9a**–**9v** and **9z**) with mixtures of *DMSO*/*p*-toluenesulfonic acid (method A) or *DMSO*/iodine (method B) or acetic/sulfuric acid (1% *v*/*v*) (method C) led to their cyclodehydration yielding the expected nitroflavones **4a**–**4v** and **4z** in moderate to good yields (32–81%). The cyclodehydration of **7a**, **7d**, **7g**, **7j**, **7m**, and **7r** bearing 2″-nitro and 6′-methoxy substituents into the expected flavones **4a**, **4d**, **4g**, **4j**, **4m**, and **4r** did not occur by using methods A and B, even for longer reaction times (more than 60 h). After this long reaction time we could only isolated the corresponding isomers 2-hydroxy-2″-nitroflavanones **9a**, **9d**, **9g**, **9j**, **9m**, and **9r**. The cyclodehydration of these flavone intermediates **7a**, **7d**, **7g**, **7j**, **7m**, and **7r** was obtained upon treating them by method C (mixture of acetic and sulfuric acid). The cyclodehydration of 1,3-diketones **8g** and **8j** bearing 2″-nitro and 6′-methoxy substituents yielded the corresponding flavones **4g** and **4j** only in moderate yields (32–38%), while the others were obtained in better yields (52–81%).

Comparing the two synthesis pathways (cyclodehydrogenation of 2′-hydroxychalcones and *Baker-Venkataraman* approach) to obtain nitroflavones **4a**–**4f**, **4h**, and **4k**, one can conclude that; i) in both methods the *ortho*-nitro derivatives were obtained in lower yields than the other derivatives; ii) the approach involving the cyclodehydrogenation of 2′-hydroxychalcones is generally more favourable, in terms of yields (∼4% better) and practical execution; and iii) the *meta*- and *para*-nitro derivatives were obtained in better global yields by the cyclodehydrogenation of 2′-hydroxychalcones approach (∼50%) than those obtained by the *Baker-Venkataraman* approach (∼40%).

NMR Spectroscopy

The main features of the NMR spectra of 2′-hydroxychalcones **3x**–**3w** are: i) the proton resonances of the vinylic system appearing as doublets at $\delta_{H\beta} = 7.89$–7.91 ppm and $\delta_{H\alpha} = 8.14$–8.16 ppm for **3y** and **3w** and $\delta_{H\alpha} = 7.92$ ppm and $\delta_{H\beta} = 8.03$ ppm for **3x**. The inversion in these chemical shift values of **3x** compared to those of **3y** and **3w** is due to the close proximity of H-β to the 2-NO_2 group in the case of **3x** [11]. The coupling constant of this vinylic system $^3J_{H\alpha-H\beta} = 15.5$–$15.6$ Hz indicates their *trans* configuration; ii) the carbon resonances of the olefinic system appearing at $\delta_{C\alpha} = 125.1$–127.1 ppm and $\delta_{C\beta} = 139.1$–142.5 ppm. The resonances of C-β atoms appear at higher frequency values than those of C-α due to deshielding mesomeric effect of the carbonyl group; iii) the proton resonance of the hydroxyl group ($\delta_{OH} = 11.93$–12.18 ppm). This high resonance frequency is due the intramolecular hydrogen bond formed with the carbonyl group; iv) the carbon resonance of the carbonyl group appearing at $\delta_{C=O} = 191.6$–192.2 ppm.

From the ^{1}H and ^{13}C NMR spectra of 2′-(nitrobenzoyloxy)acetophenones **6a**–**6v** and **6z** it is important to note the proton and carbon resonances of the 2-CH_3 group appearing at $\delta_H = 2.39$–2.59 ppm and $\delta_C = 28.7$–32.1 ppm, and also the carbon resonances of the carbonyl groups appearing at $\delta_{C=O} = 161.3$–165.2 ppm and $\delta_{C\text{-}1} = 195.5$–$200.2$ ppm.

The *Baker-Venkataraman* rearrangement of 2′-(nitrobenzoyloxy)acetophenones **6a**–**6v** and **6z** gave 1,3-diketones **8a**–**8v** and **8z** which are in equilibrium with their isomeric structures 3-hydroxy-1-(2-hydroxyphenyl)-3-(nitrophenyl)-2-propen-1-ones **7a**–**7v** and **7z** and 2-hydroxynitroflavanones **9a**–**9v** and **9z** in $CDCl_3$ solutions (Fig. 1). The proportion of these structures in equilibrium was determined from the integral of H-2 in the case of diketones **8** and enolic forms **7** and of H-3 in the case of flavanones **9**. The main NMR features of diketones **8b**–**8d**, **8g**–**8l**, **8n**, **8p**, **8r**, and **8t**–**8v** are the proton resonances of H-2 (singlet at $\delta = 4.22$–4.92 ppm) and 2-hydroxyl group (singlet at $\delta = 11.20$–13.65 ppm), while in the case of their enolic forms **7a**, **7b**, **7c**–**7n**, and **7p**–**7v** one can observe the typical proton resonances of H-2 (singlet at $\delta = 6.31$–7.92 ppm), 2′-OH (singlet at $\delta = 10.36$–13.35 ppm), and 3-OH (singlet at $\delta = 13.80$–16.38 ppm). From the ^{13}C NMR spectra of the latter it is possible to assign the resonances of C-2 ($\delta = 93.0$–105.3 ppm), C-3 ($\delta = 168.9$–182.7 ppm), and C-1 ($\delta = 189.0$–195.9 ppm). The presence of flavanones **7a**–**7c**, **7i**, **7n**–**7p**, and **7z** was concluded from their characteristic resonances of H-3 protons, which appear as doublets ($^2J \sim 16$ Hz) at $\delta = 2.77$–3.03 and 3.24–3.60 ppm, and C-2, C-3, and C-4 carbons, appearing at $\delta = 96.0$–101.6, 47.6–50.4, and 188.5–191.6 ppm. The assignments of all possible carbon resonances of the tautomeric structures **7**, **8**, and **9** were based on the analysis of the HSQC and HMBC spectra. Figure 2A shows some of the main connectivities found in the HMBC spectra of **7a**–**7c**, **7i**, **7n**–**7p**, and **7z**.

From the NMR spectra of flavones **4a**–**4z** one can find some typical proton and carbon resonances, namely those of H-3 (singlet at $\delta = 6.43$–7.69 ppm), C-3 ($\delta = 107.5$–114.1 ppm), and C-4 ($\delta = 174.8$–177.8 ppm). C-4 assignment was based on high frequency value, since it is the most deshielded carbon atom of the flavones **4a**–**4z**, while that of C-3 was based on the correlation with H-3 in the HSQC of **4a**–**4z**. The assignments of all carbon resonances of flavones **4a**–**4z** were based on the analysis of the HSQC and HMBC spectra. Figure 2B shows some of the typical connectivities found in their HMBC spectra.

Experimental

Melting points were measured in a Buchi 535 apparatus. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. The internal standard was *TMS*. Unequivocal ^{13}C assignments were made by means of 2D *g*HSQC and *g*HMBC (delays for one bond and long-range

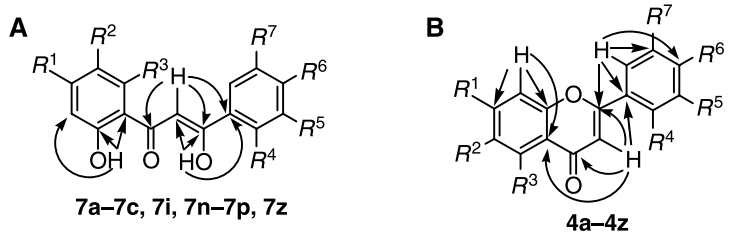


Fig. 2. Main connectivities found in the HMBC spectra of compounds **7a**–**7c**, **7i**, **7n**–**7p**, **7z** and **4a**–**4z**

C/H couplings were optimised for $J = 145$ and 7 Hz, respectively) experiments. Electron impact (EI, 70 eV) MS were recorded on VG Autospec Q and M spectrometers. Elemental analyses (CHN) were obtained with a Carlo Erba 1108 CHNS analyzer and were in good agreement ($\pm 0.4\%$) 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′-Hydroxychalcones **3a–3f**, **3h**, and **3k** have been prepared according to Ref. [11].

*General Method for the Synthesis of 2′-Hydroxychalcones **3x–3w***

NaH (0.88 g, 36.5 mmol) was slowly added to a solution of **1e** (16.6 mmol) in 10 cm^3 *THF* and the reaction mixture was stirred at room temperature for 20 min. After this period the appropriate **2a–2c** (18.3 mmol) dissolved 10 cm^3 *THF* was added. The solution was stirred, under N_2, at room temperature until the starting materials disappeared. The solution was poured into 50 g ice and 100 cm^3 H_2O, and the *pH* was adjusted to 3 with HCl. The obtained solid was removed by filtration, taken in 30 cm^3 $CHCl_3$, and washed with H_2O (2×20 cm^3). The organic layer was dried (Na_2SO_4) and evaporated to dryness, and the residue obtained was purified by column chromatography using mixtures of chloroform: *n*-hexane as the eluent. The residue was recrystallised from ethanol, giving **3x–3w**.

5′-Bromo-2′-hydroxy-2-nitrochalcone (**3x**, $C_{15}H_{11}NO_4Br$)

Yield 64%; mp 124–125°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.00$ (d, $J = 8.8$ Hz, H-3′), 7.67–7.74 (m, H-4 and H-4′), 7.84 (t, $J = 7.8$ Hz, H-5), 7.92 (d, $J = 15.5$ Hz, H-α), 8.03 (d, $J = 15.5$ Hz, H-β), 8.10 (d, $J = 7.8$ Hz, H-3), 8.17 (d, $J = 7.8$ Hz, H-6), 8.24 (d, $J = 2.0$ Hz, H-6′), 11.93 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 110.5$ (C-5′), 120.1 (C-3′), 123.6 (C-1′), 124.8 (C-3), 127.1 (C-α), 129.5 (C-1), 129.6 (C-6), 131.4 (C-4), 132.7 (C-6′), 133.8 (C-5), 138.3 (C-4′), 139.1 (C-β), 148.8 (C-2), 159.8 (C-2′), 191.6 (C=O) ppm; IR (KBr): $\bar{\nu} = 1641$, 1585, 1569, 1517, 1469, 1344, 1284, 1193 cm^{-1}; MS (EI, 70 eV): m/z (%) = 349 ($M^{+\bullet}$, ^{81}Br, 18), 347 ($M^{+\bullet}$, ^{79}Br, 18), 330 (100), 300 (57), 225 (6), 201 (95), 171 (17), 149 (18), 120 (15), 102 (23), 77 (20), 65 (38).

5′-Bromo-2′-hydroxy-3-nitrochalcone (**3y**, $C_{15}H_{11}NO_4Br$)

Yield 85%; mp 217–218°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.00$ (d, $J = 8.8$ Hz, H-3′), 7.70 (dd, $J = 2.3$, 8.8 Hz, H-4′), 7.76 (t, $J = 8.1$ Hz, H-5), 7.91 (d, $J = 15.6$ Hz, H-β), 8.16 (d, $J = 15.6$ Hz, H-α), 8.29 (dd, $J = 2.0$, 8.1 Hz, H-4), 8.35 (d, $J = 2.3$ Hz, H-6′), 8.36 (d, $J = 8.1$ Hz, H-6), 8.76 (d, $J = 2.0$ Hz, H-2), 12.18 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 110.5$ (C-5′), 120.2 (C-3′), 123.2 (C-1′), 123.4 (C-2), 125.1 (C-α and C-4), 130.5 (C-5), 132.7 (C-6′), 135.6 (C-6), 136.3 (C-1), 138.5 (C-4′), 142.5 (C-β), 148.4 (C-3), 160.2 (C-2′), 192.2 (C=O) ppm; IR (KBr): $\bar{\nu} = 1644$, 1587, 1571, 1519, 1475, 1359, 1286, 1195 cm^{-1}; MS (EI, 70 eV): m/z (%) = 349 ($M^{+\bullet}$, ^{81}Br, 79), 347 ($M^{+\bullet}$, ^{79}Br, 80), 330 (12), 300 (11), 225 (100), 200 (77), 176 (28), 165 (38), 142 (24), 129 (19), 100 (75), 77 (35), 64 (60).

5′-Bromo-2′-hydroxy-4-nitrochalcone (**3w**, $C_{15}H_{11}NO_4Br$)

Yield 64%; mp 209–211°C; ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.02$ (d, $J = 8.8$ Hz, H-3′), 7.72 (dd, $J = 2.3$, 8.8 Hz, H-4′), 7.89 (d, $J = 15.6$ Hz, H-β), 8.14 (d, $J = 15.6$ Hz, H-α), 8.19 (d, $J = 8.6$ Hz, H-2,6), 8.31 (d, $J = 8.6$ Hz, H-3,5), 8,33 (d, $J = 2.3$ Hz, H-6′), 12.11 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, *DMSO*-d_6): $\delta = 110.5$ (C-5′), 120.1 (C-3′), 123.5 (C-1′), 124.0 (C-3,5), 126.6 (C-α), 130.2 (C-2,6), 132.7 (C-6′), 138.5 (C-4′), 140.9 (C-1), 141.9 (C-β), 148.3 (C-4), 160.0 (C-2′), 192.0 (C=O) ppm; IR (KBr): $\bar{\nu} = 1639$, 1585, 1511, 1463, 1336, 1184 cm^{-1}; MS (EI, 70 eV): m/z (%) = 349 ($M^{+\bullet}$, ^{81}Br, 100), 347 ($M^{+\bullet}$, ^{79}Br, 100), 330 (9), 302 (10), 225 (85), 200 (66), 176 (20), 165 (27), 142 (16), 129 (13), 100 (51), 75 (21), 65 (35).

*General Method for the Synthesis of 2′-(Nitrobenzoyloxy)acetophenones **6a–6v** and **6z***

The appropriate **5a–5f** (14.5 mmol) and 1.40 cm^3 $POCl_3$ (14.5 mmol) were added to a solution of the appropriate **1a–1e** (12 mmoles) in 15 cm^3 dry pyridine. The solution was stirred at 60–70°C for 3 h; then poured into 80 g ice, 100 cm^3 H_2O, and HCl (*pH* adjusted to 5). The obtained solid was removed by filtration, taken in 100 cm^3 $CHCl_3$ and purified by silica gel column chromatography, using a 7:3 mixture of chloroform:*n*-hexane as the eluent. The solvent was evaporated to dryness and the residue recrystallized from ethanol, giving the expected compound.

2′-(2-Nitrobenzoyloxy)acetophenone (**6a**, $C_{15}H_{11}NO_5$)

Yield 43%; mp 93–94°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.54$ (s, H-2), 7.34 (dd, $J = 1.1$, 8.0 Hz, H-3′), 7.51 (dt, $J = 1.1$, 8.0 Hz, H-5′), 7.74 (dt, $J = 1.5$, 8.0 Hz, H-4′), 7.88–7.98 (m, H-4″,5″,6″), 8.04 (dd, $J = 1.5$, 8.0 Hz, H-6′), 8.17 (dd, $J = 1.1$, 8.0 Hz, H-3″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.2$ (C-2), 123.3 (C-3′), 124.1 (C-3″), 125.4 (C-1″), 127.1 (C-5′), 130.2 (C-1′), 130.3 (C-6″), 131.1 (C-6′), 133.5 (C-4″), 134.0 (C-5″), 134.1 (C-4′), 147.9 (C-2′), 147.7 (C-2″), 163.1 (C=O), 197.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1755$, 1679, 1604, 1529, 1444, 1346, 1278, 1253, 1187, 1058, 761 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 21), 150 (100), 134 (5), 121 (4), 104 (37), 92 (13), 76 (34), 64 (6).

2′-(3-Nitrobenzoyloxy)acetophenone (**6b**, $C_{15}H_{11}NO_5$)

Yield 64%; mp 124–125°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.54$ (s, H-2), 7.43 (dd, $J = 1.2$, 8.1 Hz, H-3′), 7.51 (dt, $J = 1.2$, 7.7 Hz, H-5′), 7.72 (ddd, $J = 1.7$, 7.7, 8.1 Hz, H-4′), 7.92 (t, $J = 7.9$ Hz, H-5″), 8.05 (dd, $J = 1.7$, 7.7 Hz, H-6′), 8.52 (ddd, $J = 1.3$, 2.2, 7.9 Hz, H-6″), 8.58 (ddd, $J = 1.3$, 2.2, 7.9 Hz, H-4″), 8.77 (t, $J = 2.2$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.3$ (C-2), 124.1 (C-3′), 124.2 (C-2″), 126.9 (C-5′), 128.4 (C-4″), 130.6 (C-1′, C-1″), 131.0 (C-6′, C-5″), 134.0 (C-4′), 136.0 (C-6″), 148.0 (C-3″), 148.3 (C-2′), 163.1 (C=O), 197.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1739$, 1685, 1600, 1525, 1442, 1347, 1265, 1245, 1191, 1124, 1076, 840, 765 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 45), 270 (11), 223 (10), 197 (26), 168 (23), 150 (100), 104 (13), 92 (11), 76 (27).

2′-(4-Nitrobenzoyloxy)acetophenone (**6c**, $C_{15}H_{11}NO_5$)

Yield 62%; mp 93–95°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.56$ (s, H-2), 7.26 (dd, $J = 1.3$, 8.1 Hz, H-3′), 7.42 (dt, $J = 1.3$, 7.6 Hz, H-5′), 7.63 (ddd, $J = 1.8$, 7.6, 8.1 Hz, H-4′), 7.91 (dd, $J = 1.8$, 7.6 Hz, H-6′), 8.34 (d, $J = 9.3$ Hz, H-2″,6″), 8.38 (d, $J = 9.3$ Hz, H-3″,5″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.6$ (C-2), 123.6 (C-3″,5″), 123.7 (C-3′), 126.5 (C-5′), 130.0 (C-1′, C-6′), 131.3 (C-2″,6″), 133.7 (C-4′), 134.8 (C-1″), 148.7 (C-2′), 150.7 (C-4″), 163.4 (C=O), 197.1 (C-1) ppm; IR (KBr): $\bar{\nu} = 1743$, 1687, 1600, 1446, 1349, 1267, 1193, 1079, 767, 709 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 31), 150 (100), 134 (4), 120 (12), 104 (33), 92 (24), 76 (23), 64 (7).

4′-Methoxy-2′-(2-nitrobenzoyloxy)acetophenone (**6d**, $C_{16}H_{13}NO_6$)

Yield 44%; mp 138–139°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (s, H-2), 3.89 (s, OCH_3), 6.85 (d, $J = 2.5$ Hz, H-3′), 7.06 (dd, $J = 2.5$, 8.8 Hz, H-5′), 7.89–8.00 (m, H-4″ and H-5″), 8.05 (d, $J = 8.8$ Hz, H-6′), 8.16 (dd, $J = 1.2$, 7.7 Hz, H-3″), 8.20 (dd, $J = 1.6$, 7.7 Hz, H-6″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.9$ (C-2), 56.1 (OCH_3), 109.0 (C-3′), 112.1 (C-5′), 122.4 (C-1′), 124.3 (C-3″), 125.1 (C-1″), 133.4 (C-6′ and C-6″), 133.6 (C-4″), 136.8 (C-5″), 148.1 (C-2″), 150.0 (C-2′), 162.7 (C=O), 163.5 (C-4′), 195.7 (C-1) ppm; IR (KBr): $\bar{\nu} = 1760$, 1675, 1610, 1565, 1527, 1498, 1347, 1288, 1253, 1128, 1062, 800 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 5), 150 (45), 104 (3), 83 (100), 76 (6).

4′-Methoxy-2′-(3-nitrobenzoyloxy)acetophenone (**6e**, $C_{16}H_{13}NO_6$)

Yield 58%; mp 96–98°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (s, H-2), 3.89 (s, OCH_3), 6.76 (d, $J = 2.5$ Hz, H-3′), 6.91 (dd, $J = 2.5$, 8.8 Hz, H-5′), 7.74 (t, $J = 8.0$ Hz, H-5″), 7.92 (d, $J = 8.8$ Hz, H-6′), 8.48–8.55 (m, H-4″ and H-6″), 9.03 (t, $J = 1.7$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.6$ (C-2), 55.8 (OCH_3), 109.5 (C-3′), 111.9 (C-5′), 122.2 (C-1′), 125.2 (C-2″), 127.8 (C-4″), 129.8 (C-5″),

131.3 (C-1″), 132.9 (C-6′), 133.9 (C-6″), 148.2 (C-3″), 151.0 (C-2′), 163.2 (C=O), 163.9 (C-4′), 195.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1731$, 1675, 1608, 1548, 1494, 1434, 1351, 1284, 1261, 1143, 1066, 878, 815, 711 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 29), 300 (15), 150 (100), 104 (30), 76 (24).

4′-Methoxy-2′-(4-nitrobenzoyloxy)acetophenone (**6f**, $C_{16}H_{13}NO_6$)
Yield 63%; mp 95–97°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (s, H-2), 3.86 (s, OC*H*$_3$), 7.02 (d, $J = 2.5$ Hz, H-3′), 7.03 (dd, $J = 2.5$, 7.5 Hz, H-5′), 8.04 (d, $J = 7.5$ Hz, H-6′), 8.33 (d, $J = 8.8$ Hz, H-2″,6″), 8.42 (d, $J = 8.8$ Hz, H-3″,5″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28$, 9 (C-2), 56.1 (O*C*H$_3$), 109.6 (C-3′), 112.2 (C-5′), 122.1 (C-1′), 124.0 (C-3″,5″), 131.4 (C-2″,6″), 132.2 (C-6′), 134.6 (C-1″), 150.5 (C-2′), 150.7 (C-4″), 163.1 (C=O), 163.5 (C-4′), 195.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1743$, 1671, 1608, 1565, 1527, 1347, 1267, 1240, 1137, 1074, 1014, 709 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 15), 150 (100), 104 (9), 76 (17).

6′-Methoxy-2′-(2-nitrobenzoyloxy)acetophenone (**6g**, $C_{16}H_{13}NO_6$)
Yield 36%; mp 108–109°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.46$ (s, H-2), 3.91 (s, OC*H*$_3$), 6.95 (d, $J = 8.3$ Hz, H-3′), 7.06 (d, $J = 8.3$ Hz, H-5′), 7.58 (t, $J = 8.3$ Hz, H-4′), 7.91–7.98 (m, H-4″,5″,6″), 8.19 (dd, $J = 1.0$, 7.5 Hz, H-3″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.6$ (C-2), 56.4 (O*C*H$_3$), 110.3 (C-5′), 114.4 (C-3′), 123.6 (C-1′), 124.5 (C-3″), 125.1 (C-1″), 130.0 (C-6″), 131.8 (C-4′), 133.6 (C-4″), 134.1 (C-5″), 146.3 (C-6′), 147.6 (C-2″), 157.3 (C-2′), 163.0 (C=O), 199.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1639$, 1581, 1525, 1427, 1342, 1222, 1160, 1112, 971, 804, 732 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 92), 300 (100), 298 (40), 284 (23), 277 (77), 104 (33), 76 (21).

6′-Methoxy-2′-(3-nitrobenzoyloxy)acetophenone (**6h**, $C_{16}H_{13}NO_6$)
Yield 59%; mp 151–153°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.46$ (s, H-2), 3.91 (s, OC*H*$_3$), 7.03 (d, $J = 8.3$ Hz, H-3′), 7.16 (d, $J = 8.3$ Hz, H-5′), 7.56 (dt, $J = 8.3$, 8.3 Hz, H-4′), 7.92 (t, $J = 8.0$ Hz, H-5″), 8.47 (dd, $J = 0.9$, 8.0 Hz, H-6″), 8.59 (dt, $J = 0.9$, 8.0 Hz, H-4″), 8.70 (br s, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.7$ (C-2), 56.4 (O*C*H$_3$), 110.1 (C-5′), 115.2 (C-3′), 123.5 (C-1′), 124.1 (C-2″), 128.6 (C-4″), 130.1 (C-1″), 131.0 (C-5″), 131.7 (C-4′), 135.8 (C-6″), 146.9 (C-2′), 148.0 (C-3″), 157.3 (C-6′), 162.7 (C=O), 199.7 (C-1) ppm; IR (KBr): $\bar{\nu} = 1741$, 1685, 1604, 1525, 1469, 1347, 1267, 1222, 1097, 846, 715 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 26), 300 (20), 165 (4), 150 (100), 104 (34), 83 (23), 76 (28); 1741, 1685, 1604, 1525, 1469, 1347, 1267, 1222, 1097, 846, 715 cm^{-1}.

6′-Methoxy-2′-(4-nitrobenzoyloxy)acetophenone (**6i**, $C_{16}H_{13}NO_6$)
Yield 68%; mp 150–151°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.44$ (s, H-2), 3.90 (s, OC*H*$_3$), 7.01 (dd, $J = 0.6$, 8.2 Hz, H-3′), 7.14 (d, $J = 8.2$ Hz, H-5′), 7.54 (t, $J = 8.2$ Hz, H-4′), 8.27 (d, $J = 9.0$ Hz, H-2″,6″), 8.40 (d, $J = 9.0$ Hz, H-3″,5″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.7$ (H-2), 56.4 (O*C*H$_3$), 110.1 (C-5′), 115.2 (C-3′), 123.4 (C-1′), 124.1 (C-3″,5″), 131.3 (C-2″,6″), 131.6 (C-4′), 133.9 (C-1″), 146.9 (C-4″), 150.7 (C-6′), 157.2 (C-2′), 162.9 (C=O), 199.6 (C-1) ppm; IR (KBr): $\bar{\nu} = 1741$, 1685, 1602, 1525, 1467, 1440, 1347, 1265, 1218, 1095, 844, 782, 713 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 38), 300 (25), 284 (4), 150 (100), 104 (34), 83 (23), 76 (28).

4′,6′-Dimethoxy-2′-(2-nitrobenzoyloxy)acetophenone (**6j**, $C_{17}H_{15}NO_7$)
Yield 33%; mp 114–115°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (s, H-2), 3.88 (s, 2×OC*H*$_3$), 6.43 (d, $J = 2.2$ Hz, H-3′), 6.48 (d, $J = 2.2$ Hz, H-5′), 7.68 (dt, $J = 1.4$, 7.7 Hz, H-4″), 7.79 (dt, $J = 1.0$, 7.7 Hz, H-5″), 8.00 (dd, $J = 1.4$, 7.7 Hz, H-6″), 8.08 (dd, $J = 1.0$, 7.7 Hz, H-3″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.1$ (H-2), 55.8 (O*C*H$_3$), 55.9 (O*C*H$_3$), 97.3 (C-5′), 99.5 (C-3′), 116.5 (C-1′), 124.0 (C-3″), 127.9 (C-1″), 130.0 (C-6″), 131.6 (C-4″), 133.8 (C-5″), 146.9 (C-2″), 157.3 (C-2′), 159.7 (C-6′), 162.7 (C-4′), 164.1 (C=O), 199.0 (C-1) ppm; IR (KBr): $\bar{\nu} = 1749$, 1671, 1614, 1575, 1531, 1342, 1282, 1259, 1226, 1151, 1122, 1078, 827, 792, 736 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 23), 330 (12), 181 (8), 167 (6), 150 (100), 104 (9), 76 (19), 69 (4).

4′,6′-Dimethoxy-2′-(3-nitrobenzoyloxy)acetophenone (**6k**, $C_{17}H_{15}NO_7$)
Yield 56%; mp 143–145°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (s, H-2), 3.85 (s, OCH_3), 3.90 (s, OCH_3), 6.37 (d, $J = 2.2$ Hz, H-3′), 6.45 (d, $J = 2.2$ Hz, H-5′), 7.71 (t, $J = 8.0$ Hz, H-5″), 8.46–8.50 (m, H-4″ and H-6″), 8.96 (t, $J = 2.0$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.1$ (C-2), 55.7 (O*C*H$_3$), 56.0 (O*C*H$_3$), 96.9 (C-5′), 100.2 (C-3′), 116.5 (C-1′), 125.2 (C-2″), 127.9 (C-4″), 129.8 (C-5″), 131.1 (C-1″), 135.9 (C-6″), 148.3 (C-3″), 149.8 (C-2′), 159.8 (C-6′), 162.6 (C-4′), 163.2 (C=O), 198.8 (C-1) ppm; IR (KBr): $\bar{\nu} = 1745$, 1660, 1610, 1569, 1344, 1251, 1116, 1066, 825, 748, 707 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 39), 330 (80), 195 (2), 178 (10), 150 (100), 137 (6), 104 (41), 76 (32).

4′,6′-Dimethoxy-2′-(4-nitrobenzoyloxy)acetophenone (**6l**, $C_{17}H_{15}NO_7$)
Yield 62%; mp 155–156°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.39$ (s, H-2), 3.83 (s, OCH_3), 3.90 (s, OCH_3), 6.64 (d, $J = 2.2$ Hz, H-3′), 6.67 (d, $J = 2.2$ Hz, H-5′), 8.26 (d, $J = 9.0$ Hz, H-2″,6″), 8.41 (d, $J = 9.0$ Hz, H-3″,5″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.9$ (C-2), 56.0 (O*C*H$_3$), 56.4 (O*C*H$_3$), 97.1 (C-5′), 101.0 (C-3′), 115.9 (C-1′), 124.1 (C-3″,5″), 131.3 (C-2″,6″), 134.2 (C-1″), 149.1 (C-2′), 150.6 (C-4″), 159.3 (C-6′), 162.3 (C-4′), 162.9 (C=O), 198.1 (C-1) ppm; IR (KBr): $\bar{\nu} = 1731$, 1691, 1616, 1527, 1347, 1218, 1159, 1130, 852, 823, 711 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 57), 330 (71), 178 (13), 150 (100), 120 (10), 104 (40), 92 (14), 76 (19).

2′-(2-Methyl-3-nitrobenzoyloxy)acetophenone (**6m**, $C_{16}H_{13}NO_5$)
Yield 59%; mp 103–104°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.58$ (s, H-2), 2.65 (s, 2″-CH_3), 7.40 (dd, $J = 1.1$, 7.9 Hz, H-3′), 7.49 (dt, $J = 1.1$, 7.9 Hz, H-5′), 7.65 (t, $J = 8.0$ Hz, H-5″), 7.68–7.73 (m, H-4′), 8.04–8.08 (m, H-4″ and H-6′), 8.40 (dd, $J = 1.1$, 8.0 Hz, H-6″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.9$ (2″-*C*H$_3$), 29.0 (C-2), 124.8 (C-3′), 127.4 (C-5′), 128.0 (C-4″ and C-5″), 129.0 (C-2″), 131.5 (C-1′), 131.6 (C-6′), 133.4 (C-1″), 135.0 (C-4′ and C-6″), 149.5 (C-2′), 153.0 (C-3″), 165.2 (C=O), 198.0 (C-1) ppm; IR (KBr): $\bar{\nu} = 1743$, 1677, 1602, 1573, 1529, 1444, 1357, 1255, 1193, 1085, 1018, 954, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 299 ($M^{+\bullet}$, 4), 164 (100), 147 (6), 118 (23), 105 (3), 90 (22).

2′-(4-Methyl-3-nitrobenzoyloxy)acetophenone (**6n**, $C_{16}H_{13}NO_5$)
Yield 77%; mp 91–92°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (s, H-2), 2.64 (s, 4″-CH_3), 7.21 (d, $J = 7.6$ Hz, H-3′), 7.36 (t, $J = 7.6$ Hz, H-5′), 7.48 (d, $J = 7.9$ Hz, H-5″), 7.56 (dt, $J = 1.0$, 7.6 Hz, H-4′), 7.85 (dd, $J = 1.0$, 7.6 Hz, H-6′), 8.26 (dd, $J = 0.9$, 7.9 Hz, H-6″), 8.72 (d, $J = 0.9$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.5$ (4″-*C*H$_3$), 28.9 (C-2), 123.6 (C-3′), 126.2 (C-2″), 126.3 (C-5′), 128.5 (C-1′), 130.0 (C-1″), 130.5 (C-6′), 130.7 (C-5″), 133.5 (C-4′), 133.8 (C-6″), 139.1 (C-4″), 148.6 (C-3″), 148.9 (C-2′) 163.1 (C=O), 197.0 (C-1) ppm; IR (KBr): $\bar{\nu} = 1745$, 1687, 1600, 1527, 1446, 1355, 1294, 1249, 1213, 1106, 848, 765, 738 cm^{-1}; MS (EI, 70 eV): m/z (%) = 299 ($M^{+\bullet}$, 20), 279 (5), 164 (100), 149 (16), 118 (28), 106 (3), 90 (22), 77 (4), 63 (9).

2′-(3,5-Dinitrobenzoyloxy)acetophenone (**6o**, $C_{15}H_{10}N_2O_7$)
Yield 75%; mp 130–131°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.59$ (s, H-2), 7.29 (dd, $J = 1.1$, 7.8 Hz, H-3′), 7.49 (dt, $J = 1.1$, 7.8 Hz, H-5′), 7.69 (dt, $J = 1.6$, 7.8 Hz, H-4′), 7.98 (dd, $J = 1.6$, 7.8 Hz, H-6′), 9.29–9.33 (m, H-2″,6″ and H-4″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.7$ (C-2), 122.8 (C-4″), 123.9 (C-3′), 127.1 (C-5′), 129.0 (C-1′), 130.1 (C-2″,6″), 131.2 (C-6′), 133.4 (C-1″), 134.3 (C-4′), 148.5 (C-2′), 148.7 (C-3″,5″), 161.6 (C=O), 197.1 (C-1) ppm; IR (KBr): $\bar{\nu} = 1745$, 1689, 1631, 1604, 1548, 1448, 1346, 1270, 1193, 1147, 1076, 717 cm^{-1}; MS (EI, 70 eV): m/z (%) = 330 ($M^{+\bullet}$, 40), 315 (42), 195 (100), 179 (6), 163 (4), 149 (41), 121 (12), 103 (16), 92 (7), 75 (37), 63 (7).

4′-Methoxy-2′-(4-methyl-3-nitrobenzoyloxy)acetophenone (**6p**, $C_{17}H_{15}NO_6$)
Yield 82%; mp 131–132°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.46$ (s, H-2), 2.64 (s, 4″-CH_3), 3.86 (s, OCH_3), 7.02 (d, $J = 2.4$ Hz, H-3′), 7.03 (dd, $J = 2.4$, 7.2 Hz, H-5′), 7.75 (d, $J = 8.1$ Hz, H-5″), 8.03 (dd, $J = 2.4$, 7.2 Hz, H-6′), 8.29 (dd, $J = 1.8$, 8.1 Hz, H-6″), 8.58 (d, $J = 1.8$ Hz, H-2″) ppm; ^{13}C NMR

(75 MHz, $CDCl_3$): $\delta = 19.9$ (4″-CH_3), 29.0 (C-2), 56.1 (OCH_3), 109.6 (C-3′), 112.2 (C-5′), 122.3 (C-1′), 125.5 (C-2″), 128.4 (C-1″), 133.1 (C-6′), 133.8 (C-5″), 133.9 (C-6″), 138.9 (C-4″), 149.0 (C-3″), 150.7 (C-2′), 162.8 (C=O), 163.5 (C-4′), 195.5 (C-1) ppm; IR (KBr): $\bar{\nu} = 1733$, 1675, 1614, 1567, 1535, 1353, 1282, 1241, 1143, 1066, 875, 815 cm^{-1}; MS (EI, 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 33), 314 (7), 164 (100), 147 (13), 118 (33), 106 (5), 90 (25), 63 (8).

4′-Methoxy-2′-(3,5-dinitrobenzoyloxy)acetophenone (**6q**, $C_{16}H_{12}N_2O_8$)
Yield 76%; mp 103–104°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (s, H-2), 3.89 (s, OCH_3), 7.06 (d, $J = 2.5$ Hz, H-3′), 7.07 (dd, $J = 2.5$, 9.4 Hz, H-5′), 8.09 (d, $J = 9.4$ Hz, H-6′), 9.06 (d, $J = 2.1$ Hz, H-2″,6″), 9.13 (t, $J = 2.1$ Hz, H-4″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.8$ (C-2), 56.1 (OCH_3), 109.6 (C-3′), 112.3 (C-5′), 121.7 (C-1′), 123.1 (C-4″), 129.3 (C-2″,6″), 132.2 (C-1″), 133.5 (C-6′), 148.5 (C-3″,5″), 150.3 (C-2′), 161.5 (C=O), 163.6 (C-4′), 195.7 (C-1) ppm; IR (KBr): $\bar{\nu} = 1756$, 1671, 1610, 1548, 1461, 1347, 1272, 1159, 1070, 711 cm^{-1}; MS (EI, 70 eV): m/z (%) = 360 ($M^{+\bullet}$, 53), 345 (100), 195 (87), 149 (45), 103 (12), 75 (47).

6′-Methoxy-2′-(2-methyl-3-nitrobenzoyloxy)acetophenone (**6r**, $C_{17}H_{15}NO_6$)
Yield 78%; mp 137–138°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.45$ (s, H-2), 2.52 (s, 4″-CH_3), 3.90 (s, OCH_3), 7.02 (d, $J = 8.3$ Hz, H-3′), 7.14 (d, $J = 8.3$ Hz, H-5′), 7.54 (t, $J = 8.3$ Hz, H-4′), 7.65 (t, $J = 7.9$ Hz, H-5″), 8.12–8.15 (m, H-4″ and H-6″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.5$ (4″-CH_3), 31.7 (C-2), 56.4 (OCH_3), 110.1 (C-5′), 115.3 (C-3′), 123.5 (C-1′), 127.6 (C-5″), 130.0 (C-4″), 131.6 (C-1″), 131.8 (C-4′), 132.1 (C-2″), 133.6 (C-6″), 146.8 (C-2′), 151.7 (C-3″), 157.4 (C-6′), 164.1 (C=O), 200.0 (C-1) ppm; IR (KBr): $\bar{\nu} = 1749$, 1687, 1602, 1573, 1525, 1469, 1438, 1344, 1276, 1213, 1101, 1022, 734 cm^{-1}; MS (EI, 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 12), 164 (100), 147 (6), 118 (24), 107 (8), 90 (27), 63 (11).

6′-Methoxy-2′-(4-methyl-3-nitrobenzoyloxy)acetophenone (**6s**, $C_{17}H_{15}NO_6$)
Yield 87%; mp 117–118°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (s, H-2), 270 (s, 4″-CH_3), 3.90 (s, OCH_3), 6.85 (dd, $J = 0.6$, 8.3 Hz, H-3′), 6.91 (dd, $J = 0.6$, 8.3 Hz, H-5′), 7.43 (t, $J = 8.3$ Hz, H-4′), 7.50 (d, $J = 8.0$ Hz, H-5″), 8.23 (dd, $J = 1.8$, 8.0 Hz, H-6″), 8.70 (d, $J = 1.8$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$ (4″-CH_3), 31.7 (C-2), 56.0 (OCH_3), 109.2 (C-5′), 115.0 (C-3′), 123.9 (C-1′), 126.4 (C-2″), 128.4 (C-1″), 131.3 (C-4′), 133.3 (C-5″), 133.9 (C-6″), 139.3 (C-4″), 147.6 (C-3″), 149.2 (C-2′), 157.7 (C-6′), 163.0 (C=O), 200.2 (C-1) ppm; IR (KBr): $\bar{\nu} = 1745$, 1698, 1604, 1521, 1473, 1346, 1292, 1234, 1124, 1068, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 32), 314 (14), 298 (5), 164 (100), 148 (21), 118 (36), 107 (13), 90 (29), 63 (11).

6′-Methoxy-2′-(3,5-dinitrobenzoyloxy)acetophenone (**6t**, $C_{16}H_{12}N_2O_8$)
Yield 54%; mp 180–182°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.56$ (s, H-2), 3.94 (s, OCH_3), 6.87 (dd, $J = 0.6$, 8.3 Hz, H-3′), 6.97 (dd, $J = 0.6$, 8.3 Hz, H-5′), 7.49 (t, $J = 8.3$ Hz, H-4′), 9.25 (d, $J = 2.1$ Hz, H-2″,6″), 9.28 (t, $J = 2.1$ Hz, H-4″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.0$ (C-2), 56.1 (OCH_3), 109.9 (C-5′), 114.9 (C-3′), 122.9 (C-4″), 123.0 (C-1′), 130.0 (C-2″,6″), 132.0 (C-4′), 133.0 (C-1″), 147.6 (C-2′), 148.7 (C-3″,5″), 158.4 (C-6′), 161.3 (C=O), 199.9 (C-1) ppm; IR (KBr): $\bar{\nu} = 1754$, 1691, 1600, 1550, 1469, 1344, 1272, 1226, 1155, 1068, 921, 800 cm^{-1}; MS (EI, 70 eV): m/z (%) = 360 ($M^{+\bullet}$, 51), 345 (100), 195 (91), 179 (7), 149 (56), 103 (20), 91 (9), 75 (52).

4′,6′-Dimethoxy-2′-(4-methyl-3-nitrobenzoyloxy)acetophenone (**6u**, $C_{18}H_{17}NO_7$)
Yield 87%; mp 135–136°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.48$ (s, H-2), 2.69 (s, 4″-CH_3), 3.84 (s, OCH_3), 3.88 (s, OCH_3), 6.36 (d, $J = 2.2$ Hz, H-3′), 6.43 (d, $J = 2.2$ Hz, H-5′), 7.49 (d, $J = 8.0$ Hz, H-5″), 8.24 (dd, $J = 1.8$, 8.0 Hz, H-6″), 8.70 (d, $J = 1.8$ Hz, H-2″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$ (4″-CH_3), 32.0 (C-2), 55.4 (OCH_3), 56.6 (OCH_3), 96.8 (C-5′), 100.1 (C-3′), 116.5 (C-1′), 126.4 (C-2″), 128.6 (C-1″), 133.2 (C-5″), 134.0 (C-6″), 139.1 (C-4″), 149.2 (C-3″), 149.7 (C-2′), 159.7 (C-6′), 162.5 (C-4′), 163.1 (C=O), 198.8 (C-1) ppm; IR (KBr): $\bar{\nu} = 1743$, 1670, 1612, 1577, 1533,

1353, 1335, 1284, 1249, 1228, 1149, 1118, 1068, 836, 738 cm^{-1}; MS (EI, 70 eV): m/z (%) = 359 ($M^{+\bullet}$, 48), 344 (53), 181 (14), 164 (100), 147 (13), 137 (6), 118 (36), 90 (25), 63 (7).

4′,6′-Dimethoxy-2′-(3,5-dinitrobenzoyloxy)acetophenone (**6v**, $C_{17}H_{14}N_2O_9$)
Yield 45%; mp 201–202°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, H-2), 3.85 (s, OCH_3), 3.92 (s, OCH_3), 6.68 (d, J = 2.0 Hz, H-3′), 6.70 (d, J = 2.0 Hz, H-5′), 8.98 (t, J = 2.1 Hz, H-2″,6″), 9.10 (t, J = 2.1 Hz, H-4″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.0 (C-2), 56.0 (OCH_3), 56.5 (OCH_3), 97.3 (C-5′), 101.0 (C-3′), 115.5 (C-1′), 123.2 (C-4″), 129.2 (C-2″,6″), 131.8 (C-1″), 148.5 (C-3″,5″), 149.0 (C-2′), 159.6 (C-6′), 161.3 (C-4′), 164.2 (C=O), 198.0 (C-1) ppm; IR (KBr): $\bar{\nu}$ = 1762, 1683, 1608, 1546, 1455, 1344, 1280, 1157, 1068, 919, 831, 715 cm^{-1}; MS (EI, 70 eV): m/z (%) = 390 ($M^{+\bullet}$, 41), 375 (100), 195 (56), 181 (14), 149 (39), 137 (7), 103 (13), 75 (27).

5′-Bromo-2′-(3,5-dinitrobenzoyloxy)acetophenone (**6z**, $C_{15}H_9N_2O_7Br$)
Yield 89%; mp 131–132°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, H-2), 7.49 (d, J = 8.6 Hz, H-3′), 7.97 (dd, J = 2.4, 8.6 Hz, H-4′), 8.25 (d, J = 2.4 Hz, H-6′), 9,07 (d, J = 2.0 Hz, H-2″,6″), 9.13 (t, J = 2.0 Hz, H-4″) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3 (C-2), 97.3 (C-5′), 101.0 (C-3′), 119.4 (C-5′), 123.3 (C-4″), 126.3 (C-3′), 129.4 (C-2″,6″), 131.5 and 131.8 (C-1′ and C-1″), 133.5 (C-6′), 136.7 (C-4′), 147.1 (C-2′), 148.6 (C-3″,5″), 161.4 (C=O), 196.7 (C-1) ppm; IR (KBr): $\bar{\nu}$ = 1739, 1687, 1627, 1548, 1457, 1343, 1274, 1236, 1191, 1147, 1070, 713 cm^{-1}; MS (EI, 70 eV): m/z (%) = 410 ($M^{+\bullet}$, ^{81}Br, 26), 408 ($M^{+\bullet}$, ^{79}Br, 26), 393 (4), 195 (100), 187 (3), 179 (6), 149 (36), 103 (14), 75 (39), 63 (19).

*General Method for the Baker-Venkataraman Rearrangement of 2′-(Nitrobenzoyloxy) acetophenones **6a–6v** and **6z***
NaH (0.270 g, 11.2 mmol) was added to a solution of the appropriate **6a**–**6v** and **6z** (7 mmol) in 15 cm^3 dry *THF*. The mixture was refluxed until complete disappearance of the starting material, which was monitored by tlc (2 h for *ortho*-nitro derivatives **6a**, **6d**, **6g**, **6j**; 3 h for *meta*- and *para*-nitro derivatives **6b**, **6c**, **6e**, **6f**, **6h**, **6i**, **6k**, **6l**; 3.5 h for dinitro derivatives **6o**, **6q**, **6t**, **6v**, **6z**; 2.5 h for 4′-methyl-3′-nitro derivatives **6n**, **6p**, **6s**, **6u**; 5 h for 2′-methyl-3′-nitro derivatives **6m**, **6r**). After that period, the solution was poured into 50 g ice and 50 cm^3 water, and *pH* was adjusted to 3 with HCl. The obtained solid was removed by filtration, taken in 40 cm^3 $CHCl_3$, and purified by silica gel column chromatography, using $CDCl_3$ as the eluent. The solvent was evaporated in each case to dryness and the residue was crystallized from ethanol to give the expected products. From the NMR data one can find these compounds as a mixture of two or three isomeric structures – 3-hydroxy-1-(2-hydroxyphenyl)-3-(nitrophenyl)-2-propen-1-ones **7a**–**7v** and **7z**, or 1-(2-hydroxyphenyl)-3-(nitrophenyl)propan-1,3-diones **8a**–**8v**, **8z**, or 2-hydroxyflavanones **9a**–**9v** and **9z**. The reaction yields were calculated thinking to have the presence of 3-hydroxy-1-(2-hydroxyphenyl)-3-(nitrophenyl)-2-propen-1-ones **7a**–**7v**, **7z**: **7a**, 53%; **7b**, 64%; **7c**, 75%; **7d**, 45%; **7e**, 65%; **7f**, 62%; **7g**, 52%; **7h**, 72%; **7i**, 70%; **7j**, 21%; **7k**, 61%; **7l**, 58%; **7m**, 73%; **7n**, 80%; **7o**, 65%; **7p**, 68%; **7q**, 48%; **7r**, 77%; **7s**, 80%; **7t**, 60%; **7u**, 63%; **7v**, 47%; **7z**, 64%. We will present data of the main isomeric structure present in the NMR spectra, together with the main NMR features of the minor one(s).

*Isomers **7a**:**9a** in the Proportion of 8:92*

3-Hydroxy-1-(2-hydroxyphenyl)-3-(2-nitrophenyl)-2-propen-1-one (**7a**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, H-2), 11.18 (s, 2′-O*H*), 14.96 (s, 3-O*H*) ppm.

2-Hydroxy-2′-nitroflavanone (**9a**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.92 (d, J = 16.3 Hz, H-3), 3.43 (d, J = 16.3 Hz, H-3), 7.12–7.18 (m, H-6 and H-8), 7.65 (t, J = 7.7 Hz, H-7), 7.89 (d, J = 8.1 Hz, H-5), 8.17 (d, J = 8.2 Hz, H-5′), 8.28 (d, J = 8.2 Hz, H-4′), 8.36 (d, J = 8.2 Hz, H-6′), 8.46 (d, J = 8.2 Hz, H-3′) ppm; ^{13}C NMR (75 MHz,

$CDCl_3$): $\delta = 49.6$ (C-3), 96.7 (C-2), 118.5 (C-8), 120.5 (C-10), 122.0 (C-6), 123.6 (C-3′), 125.6 (C-5), 126.6 (C-1′), 131.6 (C-6′), 133.9 (C-4′), 135.0 (C-5′), 135.9 (C-7), 148.0 (C-2′), 157.5 (C-9), 190.6 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1635$, 1575, 1513, 1486, 1430, 1295, 1178, 956, 813, 748 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 75), 268 (25), 163 (22), 150 (100), 134 (10), 121 (85), 104 (24), 92 (18), 76 (19), 65 (20).

*Isomers **7b**:**8b**:**9b** in the Proportion of 5:30:65*

3-Hydroxy-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)-2-propen-1-one (**7b**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (s, H-2), 11.19 (s, 2′-O*H*), 16.38 (s, 3-O*H*) ppm.

1-(2-Hydroxyphenyl)-3-(3-nitrophenyl)propan-1,3-dione (**8b**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.92$ (s, H-2), 11.19 (s, 2′-O*H*) ppm.

2-Hydroxy-3′-nitroflavanone (**9b**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.92$ (d, $J = 16.2$ Hz, H-3), 3.43 (d, $J = 16.2$ Hz, H-3), 7.12–7.19 (m, H-6 and H-8), 7.65 (t, $J = 7.7$ Hz, H-7), 7.80 (d, $J = 7.0$ Hz, H-5), 8.14 (d, $J = 7.9$ Hz, H-5′), 8.30 (d, $J = 7.9$ Hz, H-4′), 8.46 (d, $J = 7.9$ Hz, H-6′), 8.51 (br s, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 48.9$ (C-3), 96.7 (C-2), 118.6 (C-8), 120.5 (C-2′), 121.4 (C-10), 121.7 (C-6), 123.6 (C-4′), 125.7 (C-5), 127.0 (C-1′), 130.1 (C-6′), 132.6 (C-5′), 136.3 (C-7), 147.6 (C-3′), 157.8 (C-9), 190.6 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1600$, 1577, 1529, 1486, 1432, 1346, 1295, 1201, 750 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 73), 268 (24), 163 (18), 150 (100), 134 (9), 121 (83), 104 (22), 92 (16), 76 (19), 65 (18).

*Isomers **8c**:**9c** in the Proportion of 13:87*

1-(2-Hydroxyphenyl)-3-(4-nitrophenyl)propan-1,3-dione (**8c**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.87$ (s, H-2), 11.16 (s, 2′-O*H*) ppm.

2-Hydroxy-4′-nitroflavanone (**9c**, $C_{15}H_{11}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.89$ (d, $J = 16.3$ Hz, H-3), 3.35 (d, $J = 16.3$ Hz, H-3), 7.14 (d, $J = 7.8$ Hz, H-6 and H-8), 7.64 (ddd, $J = 1.5$, 7.2, 7.8 Hz, H-7), 7.79 (dd, $J = 1.5$, 7.2 Hz, H-5), 7.95 (d, $J = 8.9$ Hz, H-2′,6′), 8.31 (d, $J = 8.9$ Hz, H-3′,5′), 11.27 (br s, 2-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 49.8$ (C-3), 101.6 (C-2), 117.7 (C-10), 118.5 (C-8), 121.7 (C-6), 123.5 (C-3′,5′), 125.7 (C-5), 127.2 (C-2′,6′), 136.3 (C-7), 139.8 (C-1′), 147.6 (C-9), 149.2 (C-4′), 157.8 (C-9), 190.5 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1614$, 1575, 1517, 1484, 1434, 1338, 1295, 1197, 1160, 1029, 757 cm^{-1}; MS (EI, 70 eV): m/z (%) = 285 ($M^{+\bullet}$, 79), 268 (24), 163 (13), 150 (100), 134 (3), 121 (62), 104 (23), 92 (21), 76 (14), 65 (19).

*Isomers **7d**:**8d** in the Proportion of 75:25*

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-3-(2-nitrophenyl)-2-propen-1-one (**7d**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, OCH_3), 6.41 (s, H-2), 6.46 (d, $J = 2.3$ Hz, H-3′), 6.49 (dd, $J = 2.3$, 8.8 Hz, H-5′), 7.56–7.65 (m, H-4″ and H-5″), 7.68 (d, $J = 8.8$ Hz, H-6′), 7.70 (d, $J = 8.0$ Hz, H-3″), 7.93 (d, $J = 7.6$ Hz, H-6″), 12.38 (s, 2′-O*H*), 14.94 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$ (OCH_3), 96.0 (C-2), 100.8 (C-3′), 108.4 (C-5′), 112.6 (C-1′), 124.3 (C-6″), 130.2 (C-3″), 130.9 (C-6′), 132.6 (C-5″), 132.8 (C-4″), 134.7 (C-1″), 148.4 (C-2″), 165.2 (C-2′), 166.4 (C-4′), 174.2 (C-3), 194.7 (C-1) ppm.

1-(2-Hydroxy-4-methoxyphenyl)-3-(2-nitrophenyl)propan-1,3-dione (**8d**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.49$ (s, H-2), 12.26 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1621$, 1569, 1527, 1471, 1347, 1253, 1155, 1018, 788 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 59), 298 (22), 193 (16), 151 (100), 134 (5), 124 (15), 95 (5), 76 (10).

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-3-(3-nitrophenyl)-2-propen-1-one (**7e**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, OC*H*$_3$), 6.46 (d, $J = 2.4$ Hz, H-3′), 6.51 (dd, $J = 2.4$, 8.9 Hz, H-5′), 6.77 (s, H-2), 7.66–7.71 (m, H-5″), 7.72 (d, $J = 8.9$ Hz, H-6′), 8.24 (d, $J = 7.8$ Hz, H-6″), 8.37 (dd, $J = 1.2$, 8.1 Hz, H-4″), 8.72 (br s, H-2″), 12.41 (s, 2′-O*H*), 15.31 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.6$ (O*C*H$_3$), 93.0 (C-2), 101.3 (C-3′), 108.3 (C-5′), 112.3 (C-1′), 121.4 (C-2″), 126.1 (C-4″), 129.9 (C-5″), 130.3 (C-6′), 132.2 (C-6″), 135.6 (C-1″), 148.4 (C-3″), 165.6 (C-2′), 166.4 (C-4′), 172.2 (C-3), 194.7 (C-1) ppm; IR (KBr): $\bar{\nu} = 1616$, 1585, 1519, 1444, 1342, 1257, 1199, 1016, 786 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 53), 298 (23), 193 (18), 151 (100), 124 (17), 104 (20), 76 (20).

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-3-(4-nitrophenyl)-2-propen-1-one (**7f**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.87$ (s, OC*H*$_3$), 6.49 (d, $J = 2.5$ Hz, H-3′), 6.51 (dd, $J = 2.5$, 8.8 Hz, H-5′), 6.76 (s, H-2), 7.68 (d, $J = 8.8$ Hz, H-6′), 8.06 (d, $J = 8.8$ Hz, H-2″,6″), 8.31 (d, $J = 8.8$ Hz, H-3″,5″), 12.28 (s, 2′-O*H*), 15.15 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.6$ (O*C*H$_3$), 94.1 (C-2), 101.7 (C-3′), 108.4 (C-5′), 112.7 (C-1′), 123.9 (C-3″,5″), 127.5 (C-2″,6″), 130.3 (C-1″), 133.6 (C-6′), 149.9 (C-4″), 165.9 (C-2′), 166.7 (C-4′), 172.4 (C-3), 194.9 (C-1) ppm; IR (KBr): $\bar{\nu} = 1616$, 1585, 1519, 1342, 1275, 1199, 1133, 1016, 786 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 58), 298 (20), 193 (12), 151 (100), 124 (18), 104 (22), 91 (24), 76 (21), 65 (19).

*Isomers **7g**:**8g** in the Proportion of 50:50*

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(2-nitrophenyl)-2-propen-1-one (**7g**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.79$ (s, OC*H*$_3$), 6.48–6.59 (m, H-3′ and H-5′), 6.42 (s, H-2), 7.39 (t, $J = 8.3$ Hz, H-4′), 7.74–7.91 (m, H-4″,5″,6″), 8.03 (dd, $J = 2.0$, 8.7 Hz, H-3″), 10.36 (s, 2′-O*H*), 14.81 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.9$ (O*C*H$_3$), 102.4 (C-5′), 105.1 (C-2), 109.7 (C-3′), 112.9 (C-1′), 124.5 (C-6″), 129.8 (C-3″), 131.9 (C-5″), 133.3 (C-4″), 134.2 (C-1″), 135.5 (C-4′), 148.2 (C-2″), 158.4 (C-6′), 160.7 (C-2′), 173.6 (C-3), 191.7 (C-1) ppm.

1-(2-Hydroxy-6-methoxyphenyl)-3-(2-nitrophenyl)propan-1,3-dione (**8g**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.79$ (s, OC*H*$_3$), 4.63 (s, H-2), 6.48–6.59 (m, H-3′ and H-5′), 7.28 (t, $J = 8.3$ Hz, H-4′), 7.74–7.91 (m, H-4″,5″,6″), 8.03 (dd, $J = 2.0$, 8.7 Hz, H-3″), 10.36 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 50.0$ (C-2), 57.0 (O*C*H$_3$), 102.3 (C-5′), 109.2 (C-3′), 112.5 (C-1′), 124.2 (C-3″), 129.5 (C-6″), 130.6 (C-1″), 132.7 (C-4″), 132.8 (C-4′), 133.6 (C-5″), 148.2 (C-2″), 158.3 (C-6′), 160.7 (C-2′), 192.4 (C-3), 198.9 (C-1) ppm.

IR (KBr): $\bar{\nu} = 1758$, 1688, 1608, 1543, 1470, 1352, 1282, 1227, 1111, 1083, 783, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 11), 284 (4), 181 (15), 164 (19), 151 (100), 136 (14), 125 (19), 107 (23), 92 (11), 76 (24), 65 (19).

*Isomers **7h**:**8h** in the Proportion of 84:16*

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(3-nitrophenyl)-2-propen-1-one (**7h**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.00$ (s, OC*H*$_3$), 6.47 (d, $J = 8.3$, H-3′), 6.63 (dd, $J = 0.8$, 8.3 Hz, H-5′), 7.38 (t, $J = 8.3$ Hz, H-4′), 7.47 (s, H-2), 7.69 (t, $J = 8.0$ Hz, H-5″), 8.23 (dd, $J = 1.1$, 8.0 Hz, H-6″), 8.37 (ddd, $J = 1.1$, 2.0, 8,0 Hz, H-4″), 8.74 (t, $J = 2.0$ Hz, H-2″), 12.43 (s, 2′-O*H*), 15.50 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.1$ (O*C*H$_3$), 99.8 (C-2), 101.9 (C-3′), 110.4 (C-5′), 111.3 (C-1′), 121.7 (C-2″), 127.7 (C-4″), 129.9 (C-5″), 132.3 (C-6″), 136.0 (C-4′), 137.1 (C-1″), 148.5 (C-3″), 160.5 (C-6′), 164.1 (C-2′), 173.2 (C-3), 195.5 (C-1) ppm.

1-(2-Hydroxy-6-methoxyphenyl)-3-(3-nitrophenyl)propan-1,3-dione (**8h**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.68$ (s, H-2), 12.89 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1631$, 1579, 1527, 1355, 1241, 1089, 821 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 55), 298 (33), 284 (64), 193 (18), 150 (100), 136 (15), 122 (25), 104 (29), 92 (8), 76 (22), 65 (11).

*Isomers **7i:8i:9i** in the Proportion of 46:15:39*

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(4-nitrophenyl)-2-propen-1-one (**7i**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, OC*H*$_3$), 6.58 (d, $J = 8.3$ Hz, H-3′), 6.59 (d, $J = 8.3$ Hz, H-5′), 6.89 (s, H-2), 7.52 (t, $J = 8.3$ Hz, H-4′), 8.18 (d, $J = 8.7$ Hz, H-2″,6″), 8.40 (d, $J = 8.7$ Hz, H-3″,5″), 10.38 (s, 2′-O*H*), 15.93 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.7$ (O*C*H$_3$), 101.3 (C-2), 102.2 (C-3′), 109.5 (C-5′), 110.4 (C-1′), 124.4 (C-3″,5″), 128.6 (C-2″,6″), 130.0 (C-1″), 136.4 (C-4′), 149.7 (C-4″), 158.5 (C-6′), 160.1 (C-2′), 176.6 (C-3), 192.8 (C-1) ppm.

1-(2-Hydroxy-6-methoxyphenyl)-3-(4-nitrophenyl)propan-1,3-dione (**8i**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.74$ (s, H-2), 12.24 (s, 2′-O*H*) ppm.

2-Hydroxy-5-methoxy-4′-nitroflavanone (**9i**, $C_{16}H_{13}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.77$ (d, $J = 15.6$ Hz, H-3), 3.24 (d, $J = 15.6$ Hz, H-3), 3.88 (s, OC*H*$_3$), 6.70 (d, $J = 8.4$ Hz, H-6), 6.73 (d, $J = 8.4$ Hz, H-6), 7.29 (t, $J = 8.4$ Hz, H-7), 7.93 (d, $J = 8.7$ Hz, H-2′,6′), 8.30 (d, $J = 8.7$ Hz, H-3′,5′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 50.4$ (C-3), 56.3 (O*C*H$_3$), 96.0 (C-2), 105.3 (C-8), 110.6 (C-6), 120.6 (C-10), 123.9 (C-3′,5′), 127.5 (C-2′,6′), 130.4 (C-1′), 133.0 (C-7), 147.9 (C-4′), 157.5 (C-9), 159.7 (C-5), 188.5 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1725$, 1621, 1594, 1457, 1344, 1236, 1182, 1093, 788, 727 cm^{-1}; MS (EI, 70 eV): m/z (%) = 315 ($M^{+\bullet}$, 37), 298 (41), 284 (65), 193 (11), 149 (100), 136 (10), 122 (18), 102 (27), 90 (11), 75 (18), 65 (10).

*Isomers **7j:8j** in the Proportion of 35:65*

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(2-nitrophenyl)-2-propen-1-one (**7j**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.79$ (s, H-2), 12.03 (s, 2′-O*H*), 13.80 (s, 3-O*H*) ppm.

1-(2-Hydroxy-4,6-methoxyphenyl)-3-(2-nitrophenyl)propan-1,3-dione (**8j**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, OC*H*$_3$), 3.83 (s, OC*H*$_3$), 4.65 (s, H-2), 6.10 (d, $J = 2.4$ Hz, H-5′), 6.13 (d, $J = 2.4$ Hz, H-3′), 7.81–7.84 (m, H-4″), 7.89 (dt, $J = 1.5$, 7.5 Hz, H-5″), 7.98 (dd, $J = 1.5$, 7.5 Hz, H-6″), 8.04 (dd, $J = 1.5$, 8.5 Hz, H-3″), 13.41 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$ (O*C*H$_3$), 55.9 (O*C*H$_3$), 56.3 (C-2), 91.0 (C-5′), 93.9 (C-3′), 105.4 (C-1′), 124.1 (C-3″), 129.6 (C-6″), 130.0 (C-1″), 132.3 (C-4″), 133.4 (C-5″), 147.3 (C-2″), 161.4 (C-6′), 166.4 (C-4′), 166.7 (C-2′), 194.8 (C-3), 197.8 (C-1) ppm.

IR (KBr): $\bar{\nu} = 1617$, 1594, 1565, 1525, 1434, 1353, 1255, 1214, 1157, 1108, 821 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 10), 211 (11), 194 (8), 181 (100), 150 (11), 137 (14), 109 (12), 95 (18), 76 (25), 69 (22), 63 (13).

*Isomers **7k:8k** in the Proportion of 66:34*

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(3-nitrophenyl)-2-propen-1-one (**7k**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.89$ (s, OC*H*$_3$), 3.96 (s, OC*H*$_3$), 6.01 (d, $J = 2.4$ Hz, H-5′), 6.06 (d, $J = 2.4$ Hz, H-3′), 7.43 (s, H-2), 7.67 (t, $J = 8.1$ Hz, H-5″), 8.20 (dt, $J = 2.0$, 8.1 Hz, H-6″), 8.35 (dt, $J = 2.0$, 8.1 Hz, H-4″), 8.71 (t, $J = 2.0$ Hz, H-2″), 13.33 (s, 2′-O*H*), 15.35 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$ (O*C*H$_3$), 56.0 (O*C*H$_3$), 91.6 (C-5′), 93.9 (C-3′), 99.1 (C-2), 104.5 (C-1′), 121.5 (C-2″), 125.8 (C-4″), 129.9 (C-5″), 132.1 (C-6″), 136.2 (C-1″), 148.4 (C-3″), 162.0 (C-6′), 166.0 (C-4′), 167.4 (C-2′), 171.8 (C-3), 194.1 (C-1) ppm.

1-(2-Hydroxy-4,6-dimethoxyphenyl)-3-(3-nitrophenyl)propan-1,3-dione (**8k**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.61$ (s, H-2), 13.56 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1612$, 1569, 1531, 1351, 1292, 1261, 1220, 1164, 1116, 811 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 36), 328 (23) 314 (24), 223 (8), 181 (100), 154 (22), 137 (6), 104 (9), 76 (10).

*Isomers **7l**:**8l** in the Proportion of 42:58*

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(4-nitrophenyl)-2-propen-1-one (**7l**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, OC*H*$_3$), 3.91 (s, OC*H*$_3$), 6.15 (d, $J = 2.4$ Hz, H-5′), 6.19 (d, $J = 2.4$ Hz, H-3′), 7.25 (s, H-2), 7.90 (d, $J = 8.9$ Hz, H-3″,5″), 8.14 (d, $J = 8.9$ Hz, H-2″,6″), 12.14 (s, 2′-O*H*), 15.30 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.7$ (O*C*H$_3$), 55.9 (O*C*H$_3$), 91.2 (C-5′), 100.7 (C-3′), 103.9 (C-1′), 105.0 (C-2), 126.9 (C-3″,5″), 128.0 (C-2″,6″), 130.4 (C-1″), 149.2 (C-4″), 166.3 (C-6′), 166.4 (C-4′), 167.0 (C-2′), 171.6 (C-3), 191.6 (C-1) ppm.

1-(2-Hydroxy-4,6-dimethoxyphenyl)-3-(4-nitrophenyl)propan-1,3-dione (**8l**, $C_{17}H_{15}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.88$ (s, OC*H*$_3$), 3.94 (s, OC*H*$_3$), 4.70 (s, H-2), 6.05 (d, $J = 2.1$ Hz, H-5′), 6.15 (d, $J = 2.1$ Hz, H-3′), 8.21 (d, $J = 8.7$ Hz, H-3″,5″), 8.38 (d, $J = 8.7$ Hz, H-2″,6″), 13.43 (s, 2′-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 50.1$ (C-2), 55.6 (O*C*H$_3$), 56.0 (O*C*H$_3$), 90.9 (C-5′), 100.3 (C-3′), 107.0 (C-1′), 123.9 (C-3″,5″), 130.1 (C-2″,6″), 136.6 (C-1″), 149.1 (C-4″), 162.2 (C-6′), 166.2 (C-4′), 166.7 (C-2′), 194.0 (C-3), 198.4 (C-1) ppm.

IR (KBr): $\bar{\nu} = 1617$, 1567, 1535, 1347, 1251, 1164, 1027, 790, 728 cm^{-1}; MS (EI, 70 eV): m/z (%) = 345 ($M^{+\bullet}$, 50), 328 (35), 314 (34), 223 (9), 181 (100), 154 (34), 137 (7), 104 (13), 76 (6).

3-Hydroxy-1-(2-hydroxyphenyl)-3-(2-methyl-3-nitrophenyl)-2-propen-1-one (**7m**, $C_{16}H_{13}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.60$ (s, C*H*$_3$), 6.40–6.44 (m, H-3′ and H-5′), 6.90 (s, H-2), 7.48 (d, $J = 9.2$ Hz, H-4′), 7.52 (t, $J = 8.0$ Hz, H-5″), 7.70 (dd, $J = 1.0$, 8.0 Hz, H-6″), 7.84 (dd, $J = 1.0$, 8.0 Hz, H-4″), 8.06 (d, $J = 7.8$ Hz, H-6′), 12.43 (s, 2′-O*H*), 15.40 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.5$ (*C*H$_3$), 99.6 (C-2), 119.4 (C-1′), 117.4 (C-3′), 119.4 (C-1′), 119.6 (C-5′), 127.4 (C-6′), 127.6 (C-4″), 127.9 (C-5″), 131.4 (C-4″), 135.6 (C-4′), 137.6 (C-1″), 141.9 (C-3″), 150.9 (C-2″), 178.6 (C-3), 190.0 (C-1) ppm; IR (KBr): $\bar{\nu} = 1624$, 1586, 1520, 1464, 1359, 1239, 1089, 717 cm^{-1}; MS (EI 70 eV): m/z (%) = 299 ($M^{+\bullet}$, 60), 298 (50), 282 (47), 164 (100), 144 (70), 120 (27), 77 (12), 65 (28).

*Isomers **7n**:**8n**:**9n** in the Proportion of 43:7:50*

3-Hydroxy-1-(2-hydroxyphenyl)-3-(4-methyl-3-nitrophenyl)-2-propen-1-one (**7n**, $C_{16}H_{13}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.59$ (s, C*H*$_3$), 6.93–7.03 (m, H-3′ and H-5′), 7.49 (s, H-2), 7.50 (d, $J = 9.6$ Hz, H-4′), 7.70 (d, $J = 8.0$ Hz, H-5″), 7.91 (dd, $J = 1.6$, 8.0 Hz, H-6″), 8.06 (d, $J = 6.8$ Hz, H-6′), 8.55 (d, $J = 1.2$ Hz, H-2″), 11.32 (s, 2′-O*H*), 14.97 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.7$ (*C*H$_3$), 96.1 (C-2), 117.6 (C-3′), 119.4 (C-5′), 119.8 (C-1′), 122.7 (C-2″), 129.8 (C-6′), 130.6 (C-6″), 133.5 (C-1″), 133.6 (C-5″), 135.3 (C-4′), 137.3 (C-4″), 149.3 (C-3″), 159.5 (C-2′), 179.2 (C-3), 189.0 (C-1) ppm.

1-(2-Hydroxyphenyl)-3-(4-methyl-3-nitrophenyl)propan-1,3-dione (**8n**, $C_{16}H_{13}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.86$ (s, H-2), 11.20 (s, 2′-O*H*) ppm.

2-Hydroxy-4′-methyl-3′-nitroflavanone (**9n**, $C_{16}H_{13}NO_5$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.56$ (s, C*H*$_3$), 2.89 (d, $J = 16.1$ Hz, H-3), 3.39 (d, $J = 16.1$ Hz, H-3), 7.12 (d, $J = 7.7$ Hz, H-6), 7.14 (d, $J = 7.7$ Hz, H-8), 7.60 (t, $J = 7.7$ Hz, H-7), 7.62 (d, $J = 7.6$ Hz, H-5′), 7.79 (dd, $J = 1.1$, 7.7 Hz, H-5), 8.22 (d, $J = 7.6$ Hz, H-6′), 8.24 (d, $J = 1.6$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.6$ (*C*H$_3$), 49.6 (C-3), 101.3 (C-2), 118.6 (C-8), 120.6 (C-10), 121.6 (C-6), 125.6 (C-5), 131.1 (C-6′), 133.2 (C-5′), 133.4 (C-1′), 136.2 (C-7), 142.1 (C-4′), 148.6 (C-3′), 157.5 (C-9), 190.7 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1614$, 1577, 1529, 1488, 1432, 1340, 1305, 1207, 1047, 771 cm^{-1}; MS (EI, 70 eV): m/z (%) = 299 ($M^{+\bullet}$, 64), 282 (15), 164 (100), 148 (9), 121 (68), 90 (12), 77 (7), 65 (14).

2-Hydroxy-3′,5′-dinitroflavanone (**9o**, $C_{15}H_{10}N_2O_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.99$ (d, $J = 16.3$ Hz, H-3), 3.56 (d, $J = 16.3$ Hz, H-3), 7.01–7.21 (m, H-6 and H-8), 7.67 (t, $J = 7.4$ Hz, H-7), 7.83 (d, $J = 7.4$ Hz, H-5), 8.87–8.90 (m, H-2′,4′,6′) ppm; ^{13}C

NMR (75 MHz, $CDCl_3$): $\delta = 50.1$ (C-3), 100.9 (C-2), 118.6 (C-8), 119.0 (C-4′), 120.6 (C-10), 122.0 (C-6), 125.7 (C-5), 126.5 (C-2′,6′), 126.8 (C-1′), 136.4 (C-7), 148.1 (C-3′,5′), 157.5 (C-9), 190.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 1613$, 1570, 1542, 1486, 1345, 1297, 1194, 1160, 917, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 330 ($M^{+\bullet}$, 68), 313 (31), 195 (29), 183 (46), 163 (31), 157 (8), 149 (19), 121 (100), 92 (23), 65 (17).

*Isomers **7p**:**8p**:**9p** in the Proportion of 40:13:47*

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-3-(4-methyl-3-nitrophenyl)-2-propen-1-one (**7p**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.59$ (s, CH_3), 3.83 (s, OCH_3), 6.52 (d, $J = 2.4$ Hz, H-3′), 6.57 (dd, $J = 2.4$, 9.0 Hz, H-5′), 7.38 (s, H-2), 7.60 (d, $J = 8.2$ Hz, H-6″), 7.84 (d, $J = 8.2$ Hz, H-5″), 8.14 (d, $J = 9.0$ Hz, H-6′), 8.25 (d, $J = 1.7$ Hz, H-2″), 11.95 (s, 2′-O*H*), 15.93 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.6$ (*C*H_3), 55.7 (O*C*H_3), 94.5 (C-2), 100.9 (C-3′), 107.5 (C-5′), 112.7 (C-1′), 121.5 (C-2″), 130.3 (C-1″), 130.6 (C-5″), 131.9 (C-6′), 133.1 (C-6″), 136.5 (C-4″), 149.4 (C-3″), 164.7 (C-2′), 165.8 (C-4′), 175.0 (C-3), 191.1 (C-1) ppm.

1-(2-Hydroxy-4-methoxyphenyl)-3-(4-methyl-3-nitrophenyl)propan-1,3-dione (**8p**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.86$ (s, H-2), 11.90 (s, 2′-O*H*) ppm.

2-Hydroxy-4′-methyl-7-methoxy-3′-nitroflavanone (**9p**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.60$ (s, CH_3), 2.90 (d, $J = 16.0$ Hz, H-3), 3.56 (d, $J = 16.0$ Hz, H-3), 3.88 (s, OCH_3), 6.70 (dd, $J = 2.4$, 8.5 Hz, H-6), 6.71 (d, $J = 2.4$ Hz, H-8), 7.68 (d, $J = 8.0$ Hz, H-5′), 7.73 (d, $J = 8.5$ Hz, H-5), 8.27 (d, $J = 8.0$ Hz, H-6′), 8.56 (d, $J = 1.6$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.6$ (*C*H_3), 47.6 (C-3), 55.7 (O*C*H_3), 100.7 (C-1′), 101.5 (C-2), 101.9 (C-6), 109.6 (C-8), 114.3 (C-10), 122.4 (C-2′), 124.6 (C-6′), 126.5 (C-5), 133.5 (C-5′), 136.9 (C-4′), 148.6 (C-3′), 157.8 (C-9), 162.6 (C-7), 191.6 (C-4) ppm.

IR (KBr): $\bar{\nu} = 1600$, 1527, 1498, 1349, 1255, 1135, 1018, 806 cm^{-1}; MS (EI, 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 70), 312 (27), 193 (15), 164 (54), 151 (100), 124 (20), 108 (12), 90 (15), 77 (10).

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-3-(3,5-dinitrophenyl)-2-propen-1-one (**7q**, $C_{16}H_{12}N_2O_8$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.89$ (s, OCH_3), 6.49 (d, $J = 2.5$ Hz, H-3′), 6.57 (dd, $J = 2.5$, 8.9 Hz, H-5′), 6.87 (s, H-2), 7.76 (d, $J = 8.9$ Hz, H-6′), 9.05 (d, $J = 2.0$ Hz, H-2″,6″), 9.17 (t, $J = 2.0$ Hz, H-4″), 12.30 (s, 2′-O*H*), 15.34 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$ (O*C*H_3), 94.1 (C-2), 101.4 (C-3′), 108.8 (C-5′), 112.2 (C-1′), 120.8 (C-4″), 126.6 (C-2″,6″), 130.6 (C-6′), 137.8 (C-1″), 148.9 (C-3″,5″), 166.0 (C-2′), 167.0 (C-4′), 168.9 (C-3), 194.7 (C-1) ppm; IR (KBr): $\bar{\nu} = 1612$, 1585, 1515, 1340, 1261, 1216, 1159, 1112, 750 cm^{-1}; MS (EI, 70 eV): m/z (%) = 360 ($M^{+\bullet}$, 42), 343 (14), 193 (13), 151 (100), 137 (3), 124 (8), 95 (5), 75 (10), 69 (7).

*Isomers **7r**:**8r** in the Proportion of 86:14*

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(2-methyl-3-nitrophenyl)-2-propen-1-one (**7r**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.62$ (s, CH_3), 3.88 (s, OCH_3), 6.42 (dd, $J = 0.8$, 8.4 Hz, H-3′), 6.62 (dd, $J = 0.8$, 8.4 Hz, H-5′), 6.92 (s, H-2), 7.36 (t, $J = 8.4$ Hz, H-4′), 7.43 (t, $J = 8.0$ Hz, H-5″), 7.72 (dd, $J = 1.2$, 8.0 Hz, H-6″), 7.89 (dd, $J = 1.2$, 8.0 Hz, H-4″), 12.39 (s, 2′-O*H*), 15.37 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.7$ (*C*H_3), 56.0 (O*C*H_3), 101.8 (C-3′), 104.5 (C-2), 110.2 (C-1′), 111.2 (C-5′), 125.6 (C-4″), 126.7 (C-5″), 131.1 (C-2″), 132.5 (C-6″), 135.9 (C-4′), 138.4 (C-1″), 151.4 (C-3″), 160.4 (C-6′), 164.1 (C-2′), 177.3 (C-3), 195.4 (C-1) ppm.

1-(2-Hydroxy-6-methoxyphenyl)-3-(2-methyl-3-nitrophenyl)propan-1,3-dione (**8r**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.60$ (s, H-2), 12.88 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1619$, 1583, 1523, 1454, 1359, 1238, 1089, 717 cm^{-1}; MS (EI, 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 60), 312 (25), 298 (53), 280 (8), 193 (14), 164 (85), 151 (100), 136 (20), 124 (17), 118 (26), 108 (23), 90 (27), 77 (16), 65 (18).

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(4-methyl-3-nitrophenyl)-2-propen-1-one (**7s**, $C_{17}H_{15}NO_6$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.37$ (s, CH_3), 3.78 (s, OCH_3), 6.31 (s, H-2), 6.52–6.58 (m, H-3′ and H-5′), 7.28 (t, $J = 8.3$ Hz, H-4′), 7.58 (d, $J = 7.6$ Hz, H-5″), 7.81 (d, $J = 7.6$ Hz, H-6″), 8.03 (d, $J = 1.9$ Hz, H-2″), 10.39 (s, 2′-O*H*), 15.38 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.30$ (*C*H$_3$), 55.9 (O*C*H$_3$), 101.5 (C-3′), 105.3 (C-2), 109.2 (C-5′), 110.1 (C-1′), 125.9 (C-2″), 127.6 (C-5″), 132.4 (C-6″), 135.5 (C-4′), 136.0 (C-1″), 138.5 (C-4″), 151.2 (C-3″), 158.3 (C-6′), 160.0 (C-2′), 182.7 (C-3), 189.2 (C-1) ppm; IR (KBr): $\bar{\nu} = 1619$, 1583, 1525, 1455, 1361, 1240, 1091, 719 cm^{-1}; MS (EI 70 eV): m/z (%) = 329 ($M^{+\bullet}$, 69), 312 (41), 298 (83), 193 (17), 164 (56), 151 (100), 136 (19), 118 (32), 107 (29), 90 (27), 77 (16), 65 (18).

*Isomers **7t:8t** in the Proportion of 88:12*

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-3-(3,5-dinitrophenyl)-2-propen-1-one (**7t**, $C_{16}H_{12}N_2O_8$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.02$ (s, OCH_3), 6.49 (d, $J = 8.2$ Hz, H-3′), 6.62 (d, $J = 8.2$ Hz, H-5′), 7.41 (t, $J = 8.2$ Hz, H-4′), 7.57 (s, H-2), 9.03 (d, $J = 2.1$ Hz, H-2″,6″), 9.16 (t, $J = 2.1$ Hz, H-4″), 12.34 (s, 2′-O*H*), 15.33 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.2$ (O*C*H$_3$), 100.8 (C-3′), 101.9 (C-2), 110.2 (C-5′), 111.5 (C-1′), 120.7 (C-4″), 126.3 (C-2″,6″), 136.6 (C-4′), 138.1 (C-1″), 148.9 (C-3″,5″), 160.6 (C-6′), 164.5 (C-2′), 169.5 (C-3), 195.9 (C-1) ppm.

1-(2-Hydroxy-6-methoxyphenyl)-3-(3,5-dinitrophenyl)propan-1,3-dione (**8t**, $C_{16}H_{12}N_2O_8$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.74$ (s, H-2), 12.66 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1610$, 1573, 1542, 1448, 1342, 1220, 1180, 1083, 819, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 360 ($M^{+\bullet}$, 56), 343 (35), 329 (68), 193 (21), 151 (100), 136 (15), 122 (21), 93 (6), 75 (24), 65 (10).

*Isomers **7u:8u** in the Proportion of 87:13*

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(4-methyl-3-nitrophenyl)-2-propen-1-one (**7u**, $C_{18}H_{17}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.67$ (s, CH_3), 3.86 (s, OCH_3), 3.94 (s, OCH_3), 5.99 (d, $J = 2.3$ Hz, H-5′), 6.10 (d, $J = 2.3$ Hz, H-3′), 7.36 (s, H-2), 7.40–7.49 (m, H-5″), 7.98 (dd, $J = 1.4$, 8.1 Hz, H-6″), 8.46 (d, $J = 1.4$ Hz, H-2″), 13.35 (s, 2′O*H*), 15.37 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$ (*C*H$_3$), 55.8 (O*C*H$_3$), 56.0 (O*C*H$_3$), 91.6 (C-5′), 94.1 (C-3′), 98.5 (C-2), 104.4 (C-1′), 124.3 (C-2″), 130.7 (C-5″), 133.3 (C-6″), 136.8 (C-1″), 149.3 (C-4″), 150.7 (C-3″), 161.9 (C-6′), 166.0 (C-4′), 167.3 (C-2′), 172.1 (C-3), 193.9 (C-1) ppm.

1-(2-Hydroxy-4,6-dimethoxyphenyl)-3-(4-methyl-3-nitrophenyl)propan-1,3-dione (**8u**, $C_{18}H_{17}NO_7$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.56$ (s, H-2), 13.59 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1731$, 1612, 1558, 1529, 1442, 1347, 1261, 1220, 1110, 821 cm^{-1}; MS (EI, 70 eV): m/z (%) = 359 ($M^{+\bullet}$, 47), 342 (27), 328 (29), 223 (8), 181 (100), 164 (18), 154 (38), 118 (13), 90 (10), 69 (5).

*Isomers **7v:8v** in the Proportion of 86:14*

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(3,5-dinitrophenyl)-2-propen-1-one (**7v**, $C_{17}H_{14}N_2O_9$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.85$ (s, OCH_3), 3.88 (s, OCH_3), 6.28 (d, $J = 2.2$ Hz, H-5′), 6.30 (d, $J = 2.2$ Hz, H-3′), 7.06 (s, H-2), 8.79 (d, $J = 2.0$ Hz, H-2″,6″), 9.00 (t, $J = 2.0$ Hz, H-4″), 13.23 (s, 2′-O*H*), 15.25 (s, 3-O*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.4$ (O*C*H$_3$), 55.6 (O*C*H$_3$), 93.2 (C-5′), 94.7 (C-3′), 99.9 (C-2), 106.6 (C-1′), 122.1 (C-4″), 126.0 (C-2″,6″), 136.8 (C-1″), 148.0 (C-3″,5″), 161.3 (C-6′), 162.7 (C-4′), 166.0 (C-2′), 170.8 (C-3), 195.9 (C-1) ppm.

1-(2-Hydroxy-4,6-dimethoxyphenyl)-3-(3,5-dinitrophenyl)propan-1,3-dione (**8v**, $C_{17}H_{14}N_2O_9$)
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.22$ (s, H-2), 13.65 (s, 2′-O*H*) ppm.

IR (KBr): $\bar{\nu} = 1616$, 1571, 1535, 1346, 1286, 1218, 1159, 1110, 833 cm^{-1}; MS (EI 70 eV): m/z (%) = 390 ($M^{+\bullet}$, 40), 374 (6), 359 (28), 223 (16), 181 (100), 166 (8), 154 (22), 137 (10), 95 (9), 75 (16).

6-Bromo-2-hydroxy-3′,5″-dinitroflavanone (**9z**, $C_{15}H_9N_2O_7Br$)
^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.03$ (d, $J = 16.2$ Hz, H-3), 3.60 (d, $J = 16.2$ Hz, H-3), 7.21 (d, $J = 8.7$ Hz, H-8), 7.83 (dd, $J = 2.4$, 8.7 Hz, H-7), 7.89 (d, $J = 2.4$ Hz, H-5), 8.86 (d, $J = 1.8$ Hz, H-2′,6′), 8.91 (t, $J = 1.8$ Hz, H-4′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 48.3$ (C-3), 100.4 (C-2), 48.3 (C-2), 101.3 (C-1′), 113.7 (C-6), 119.2 (C-3′,5′), 121.3 (C-8), 122.1 (C-10), 126.5 (C-2′,6′ and C-4′), 127.8 (C-5), 138.7 (C-7), 156.7 (C-9), 189.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 1621$, 1567, 1542, 1529, 1471, 1344, 1272, 1197, 829, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 410 ($M^{+\bullet}$ ^{81}Br, 75), 408 ($M^{+\bullet}$ ^{79}Br, 75), 393 (14), 241 (19), 200 (100), 179 (15), 172 (27), 149 (46), 120 (11), 89 (16), 75 (79), 63 (52).

*General Method for the Preparation of Flavones **4a–4f**, **4h**, **4k**, and **4x–4w** from 2′-Hydroxychalcones **3a–3f**, **3h**, **3k**, and **3x–3w***
Iodine (0.39 mmol) was added to a solution of **3a–3f**, **3h**, **3k**, and **3x–3w** (10 mmol) in 15 cm^3 *DMSO*. The mixture was heated at reflux for 30 min, and then was poured into 150 g ice and 150 cm^3 water with a few crystals of sodium thiosulfate. The obtained solid was removed by filtration, taken in 150 cm^3 $CHCl_3$, and washed with a 20% aqueous solution of sodium thiosulfate (2×150 cm^3). The organic layer was dried (Na_2SO_4) and the solvent evaporated to dryness. The residue was purified by column chromatography, using $CHCl_3$ as the eluent. Finally the compound, in each case, was recrystallized from ethanol. The obtained yields were as follows: **4a**, 32%; **4b**, 86%; **4c**, 79%; **4d**, 36%; **4e**, 69%; **4f**, 74%; **4h**, 74%; **4k**, 62%; **4x**, 60%; **4y**, 81%; **4w**, 64%.

*General Method for the Preparation of Flavones **4a–4v** and **4z** from 3-Hydroxy-1-(2-hydroxyphenyl)-3-(nitrophenyl)-2-propen-1-ones **7a–7v** and **7z***

Method A
p-Toluenesulfonic acid (0.85 g, 4.4 mmol) was added to a solution of the appropriate **7b**, **7e**, **7h**, **7k**, **7o**, **7q**, **7t**, **7v**, and **7z** (8.8 mmol) in 20 cm^3 *DMSO*. The solution was heated at 80–90°C until the disappearance of the starting material (tlc). The solution was poured into 50 g ice and 50 cm^3 H_2O and the obtained solid was removed by filtration, taken in 20 cm^3 $CHCl_3$, and purified by silica gel column chromatography, using $CHCl_3$ as the eluent. The solvent was evaporated to dryness and the residue was recrystallized from ethanol:acetone to give the expected products: **4b**, 68%, **4e**, 58%; **4h**, 65%; **4k**, 53%; **4o**, 59%; **4q**, 57%; **4t**, 82%; **4v**, 63%; **4z**, 63%.

Method B
Iodine (1.76 mmol) was added to a solution of the appropriate **7b**, **7c**, **7e**, **7f**, **7h**, **7i**, **7k**, **7l**, **7n**, **7p**, **7s**, and **7u** (8.8 mmol). The solution was heated, under N_2, at 80–90°C for 3 h. After that period it was poured into 50 g ice and 50 cm^3 H_2O with a few crystals of sodium thiosulfate. The solid obtained was removed by filtration, taken in 50 cm^3 $CHCl_3$, and purified by silica gel column chromatography, using $CHCl_3$ as the eluent. The solvent was evaporated to dryness and the residue was recrystallized from ethanol or ethyl acetate to give the expected products: **4b**, 72%; **4c**, 71%; **4e**, 64%; **4f**, 80%; **4h**, 71%; **4i**, 78%; **4k**, 65%; **4l**, 52%; **4n**, 70%; **4p**, 81%; **4s**, 72%; **4u**, 54%.

Method C
A 1% (*v*/*v*) mixture of acetic acid/sulfuric acid (10 cm^3) was added to a solution of the appropriate **7a**, **7d**, **7g**, **7j**, **7m**, and **7r** (8.8 mmol). The reaction mixture was heated at 80–90°C, under N_2, for 6 h. After that period it was poured into 50 g ice and 50 cm^3 H_2O; the obtained solid was removed by filtration, taken in 30 cm^3 chloroform, and purified by silica gel column chromatography, using a 2:3

mixture of *n*-hexane:$CHCl_3$ as the eluent. The solvent was evaporated to dryness and the residue was recrystallized from ethyl acetate to give the expected products: **4a**, 64%; **4d**, 47%; **4g**, 32%; **4j**, 38%; **4m**, 63%; **4r**, 60%.

2′-Nitroflavone (**4a**, $C_{15}H_9NO_4$)
Mp 181–183°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.77$ (s, H-3), 7.52 (t, $J = 7.8$ Hz, H-6), 7.57 (d, $J = 7.8$ Hz, H-8), 7.78–7.96 (m, H-4′,5′,6′, H-7), 8.07 (dd, $J = 1.3$, 7.8 Hz, H-5), 8.18 (dd, $J = 1.1$, 7.9 Hz, H-3′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 111.1$ (C-3), 118.4 (C-8), 123.3 (C-10), 125.2 (C-3′, C-5), 126.2 (C-6), 126.6 (C-1′), 131.8 (C-6′), 132.9 (C-4′), 134.3 (C-5′), 135.1 (C-7), 147.7 (C-2′), 155.9 (C-9), 162.1 (C-2), 177.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 1646$, 1610, 1533, 1477, 1380, 1347, 781 cm^{-1}; MS (EI, 70 eV): m/z (%) = 267 ($M^{+\bullet}$, 12), 246 (4), 239 (20), 211 (18), 195 (11), 181 (12), 165 (25), 152 (14), 139 (13), 120 (100), 104 (26), 92 (80), 83 (5), 76 (29), 63 (31).

3′-Nitroflavone (**4b**)
Mp 196–197°C (Ref. [10c] 197°C, [10e] 200–201°C, [10d] 194–195°C).

4′-Nitroflavone (**4c**)
Mp 242–244°C (Ref. [10c] 242°C, [10e] 246–247°C, [10d] 244–245°C).

7-Methoxy-2′-nitroflavone (**4d**, $C_{16}H_{11}NO_5$)
Mp 181–182°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.90$ (s, OCH_3), 6.64 (s, H-3), 7.00 (d, $J = 1.8$ Hz, H-8), 7.11 (dd, $J = 1.8$, 8.4 Hz, H-6), 7.84–7.94 (m, H-4′, H-5′, H-6′), 8.00 (d, $J = 8.4$ Hz, H-5), 8.20 (d, $J = 7.7$ Hz, H-3′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.0$ (OCH_3), 100.5 (C-8), 110.7 (C-3), 114.9 (C-6), 116.9 (C-10), 124.7 (C-3′), 126.3 (C-5), 126.1 (C-1′), 131.4 (C-6′), 132.3 (C-4′), 133.9 (C-5′), 147.3 (C-2′), 157.5 (C-9), 161.2 (C-2), 164.1 (C-7), 175.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1643$, 1612, 1519, 1442, 1376, 1347, 1247, 858 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 24), 276 (3), 254 (4), 240 (5), 227 (8), 196 (3), 180 (4), 168 (5), 150 (100), 134 (6), 122 (57), 107 (30), 92 (13), 79 (18), 63 (16).

7-Methoxy-3′-nitroflavone (**4e**, $C_{16}H_{11}NO_5$)
Mp 213–214°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.95$ (s, OCH_3), 7.09 (dd, $J = 2.4$, 8.8 Hz, H-6), 7.12 (s, H-3), 7.37 (d, $J = 2.4$ Hz, H-8), 7.86 (t, $J = 8.0$ Hz, H-5′), 7.96 (d, $J = 8.8$ Hz, H-5), 8.50 (ddd, $J = 1.0$, 2.0, 8.0 Hz, H-4′), 8.51 (t, $J = 1.0$, 2.0, 8.0 Hz, H-6′), 8.80 (t, $J = 2.0$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.0$ (OCH_3), 101.0 (C-8), 108.2 (C-3), 114.9 (C-6), 117.0 (C-10), 120.5 (C-2′), 125.7 (C-4′), 126.1 (C-5), 130.6 (C-5′), 132.6 (C-6′), 132.9 (C-1′), 148.3 (C-3′), 157.4 (C-9), 159.6 (C-2), 164.0 (C-7), 175.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1641$, 1531, 1440, 1382, 1346, 1280, 1166, 862 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 100), 269 (43), 254 (23), 223 (11), 208 (9), 196 (3), 180 (3), 150 (18), 122 (14), 107 (9), 79 (7).

7-Methoxy-4′-nitroflavone (**4f**, $C_{16}H_{11}NO_5$)
Mp 213–214°C (Ref. [10a] 216–217°C); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.95$ (s, OCH_3), 7.10 (dd, $J = 2.2$, 8.9 Hz, H-6), 7.13 (s, H-3), 7.34 (d, $J = 2.2$ Hz, H-8), 7.98 (d, $J = 8.9$ Hz, H-5), 8.38 (br s, H-2′,6′ and H-3′,5′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.0$ (OCH_3), 100.9 (C-8), 109.0 (C-3), 114.8 (C-6), 117.0 (C-10), 123.8 (C-3′,5′), 126.2 (C-5), 127.4 (C-2′,6′), 137.1 (C-1′), 148.9 (C-4′), 157.4 (C-9), 159.7 (C-2), 164.1 (C-7), 176.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 1650$, 1612, 1517, 1442, 1347, 1089, 852 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 100), 269 (43), 254 (20), 239 (9), 223 (14), 208 (10), 196 (4), 180 (3), 150 (24), 122 (23), 107 (19), 85 (8), 79 (13), 63 (14).

5-Methoxy-2′-nitroflavone (**4g**, $C_{16}H_{11}NO_5$)
Mp 144–145°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.01$ (s, OCH_3), 6.51 (s, H-3), 6.85 (dd, $J = 0.8$, 8.4 Hz, H-6), 6.93 (dd, $J = 0.8$, 8.4 Hz, H-8), 7.56 (t, $J = 8.4$ Hz, H-7), 7.67–7.79 (m, H-4′, H-5′ and

H-6′), 8.05 (dd, $J = 1.4$, 8.1 Hz, H-3′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.5$ (O*C*H$_3$), 106.8 (C-6), 109.9 (C-8), 112.7 (C-3), 114.4 (C-10), 124.9 (C-3′), 127.3 (C-1′), 131.0 (C-4′), 131.7 (C-6′), 133.3 (C-5′), 134.2 (C-7), 148.1 (C-2′), 158.3 (C-9), 159.7 (C-2), 159.9 (C-5), 177.7 (C-4) ppm; IR (KBr): $\bar{\nu} = 1644$, 1606, 1529, 1475, 1440, 1384, 1353, 1259, 1110, 1078, 860, 754 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 100), 296 (17), 279 (13), 268 (18), 250 (9), 239 (16), 221 (11), 165 (19), 149 (50), 132 (20), 120 (30), 107 (32), 92 (33), 76 (26), 63 (17).

5-Methoxy-3′-nitroflavone (**4h**, $C_{16}H_{11}NO_5$)
Mp 162–166°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.02$ (s, OC*H*$_3$), 6.82 (s, H-3), 6.88 (d, $J = 8.4$ Hz, H-6), 7.20 (d, $J = 8.4$ Hz, H-8), 7.63 (t, $J = 8.4$ Hz, H-7), 7.73 (t, $J = 8.0$ Hz, H-5′), 8.19 (d, $J = 8.0$ Hz, H-6′), 8.38 (d, $J = 8.0$ Hz, H-4′), 8.77 (s, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.5$ (O*C*H$_3$), 106.8 (C-6), 110.1 (C-8), 110.2 (C-3), 114.4 (C-10), 121.0 (C-2′), 125.7 (C-4′), 130.2 (C-5′), 131.5 (C-6′), 133.3 (C-1′), 134.3 (C-7), 148.7 (C-3′), 158.0 (C-2), 158.2 (C-9), 159.8 (C-5), 177.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1648$, 1602, 1527, 1475, 1344, 1267, 1108, 1035, 836 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 100), 296 (41), 279 (13), 268 (38), 251 (50), 239 (16), 222 (23), 205 (28), 193 (12), 176 (6), 165 (22), 152 (10), 120 (31), 107 (24), 101 (7), 92 (27), 75 (19), 63 (15).

5-Methoxy-4′-nitroflavone (**4i**, $C_{16}H_{11}NO_5$)
Mp 264–265°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.02$ (s, OC*H*$_3$), 6.83 (s, H-3), 6.88 (d, $J = 8.5$ Hz, H-6), 7.17 (dd, $J = 0.9$, 8.5 Hz, H-8), 7.63 (t, $J = 8.5$ Hz, H-7), 8.08 (d, $J = 9.0$ Hz, H-2′,6′), 8.37 (d, $J = 9.0$ Hz, H-3′,5′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.6$ (O*C*H$_3$), 106.9 (C-6), 110.0 (C-8), 111.1 (C-3), 114.5 (C-10), 124.2 (C-3′,5′), 127.0 (C-2′,6′), 134.4 (C-7), 137.4 (C-1′), 149.2 (C-4′), 158.1 (C-2), 158.4 (C-9), 159.8 (C-5), 177.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1639$, 1606, 1515, 1475, 1342, 1267, 1097, 1029, 848, 752 cm^{-1}; MS (EI, 70 eV): m/z (%) = 297 ($M^{+\bullet}$, 100), 296 (43), 279 (10), 268 (36), 251 (51), 239 (15), 222 (26), 205 (34), 181 (6), 165 (21), 149 (23), 120 (41), 105 (27), 90 (30), 64 (13).

5,7-Dimethoxy-2′-nitroflavone (**4j**, $C_{17}H_{13}NO_6$)
Mp 215–216°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, OC*H*$_3$), 3.96 (s, OC*H*$_3$), 6.35 (d, $J = 2.2$ Hz, H-6), 6.39 (d, $J = 2.2$ Hz, H-8), 6.46 (s, H-3), 7.66–7.76 (m, H-4′, H-5′, and H-6′), 8.05 (dd, $J = 1.5$, 7.4 Hz, H-3′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.7$ (O*C*H$_3$), 56.4 (O*C*H$_3$), 92.5 (C-6), 96.5 (C-8), 109.1 (C-10), 112.8 (C-3), 124.8 (C-3′), 127.4 (C-1′), 131.0 (C-4′), 131.6 (C-6′), 133.3 (C-5′), 148.0 (C-2′), 159.3 (C-2), 160.0 (C-9), 160.9 (C-5), 164.3 (C-7), 176.9 (C-4) ppm; IR (KBr): $\bar{\nu} = 1654$, 1616, 1571, 1527, 1457, 1349, 1164, 1120, 1083, 829 cm^{-1}; MS (EI, 70 eV): m/z (%) = 327 ($M^{+\bullet}$, 100), 326 (27), 313 (9), 298 (21), 281 (8), 179 (42), 150 (26), 137 (13), 122 (22), 76 (8), 63 (10).

5,7-Dimethoxy-3′-nitroflavone (**4k**, $C_{17}H_{13}NO_6$)
Mp 206–207°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.84$ (s, OC*H*$_3$), 3.92 (s, OC*H*$_3$), 6.52 (d, $J = 2.1$ Hz, H-6), 6.95 (d, $J = 2.1$ Hz, H-8), 7.00 (s, H-3), 7.83 (t, $J = 8$,0 Hz, H-5′), 8.39 (dd, $J = 1.5$, 8.0 Hz, H-4′), 8.49 (d, $J = 8.0$ Hz, H-6′), 8.76 (br s, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.0$ (O*C*H$_3$), 56.1 (O*C*H$_3$), 91.9 (C-6), 96.9 (C-8), 108.4 (C-10), 109.8 (C-3), 120.4 (C-2′), 125.8 (C-4′), 130.7 (C-5′), 132.3 (C-6′), 132.7 (C-1′), 148.4 (C-3′), 157.2 (C-2), 159.1 (C-5), 164.0 (C-7), 160.3 (C-9), 164.0 (C-2), 175.5 (C-4) ppm; IR (KBr): $\bar{\nu} = 1660$, 1610, 1527, 1463, 1342, 1272, 1124, 1056, 747 cm^{-1}; MS (EI, 70 eV): m/z (%) = 327 ($M^{+\bullet}$, 100), 326 (37), 310 (4), 298 (28), 281 (30), 269 (10), 254 (15), 235 (9), 223 (11), 208 (7), 150 (20), 137 (8), 122 (7), 107 (6), 75 (11), 63 (7).

5,7-Dimethoxy-4′-nitroflavone (**4l**, $C_{17}H_{13}NO_6$)
Mp 235–236°C (Ref. [10a] 235°C); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.96$ (s, OC*H*$_3$), 4.00 (s, OC*H*$_3$), 6.44 (d, $J = 2.2$ Hz, H-6), 6.62 (d, $J = 2.2$ Hz, H-8), 7.69 (s, H-3), 8.07 (d, $J = 8.8$ Hz, H-2′,6′), 8.38 (d, $J = 8.8$ Hz, H-3′,5′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.9$ (O*C*H$_3$), 56.3 (O*C*H$_3$), 92.8 (C-6), 96.5 (C-8), 109.3 (C-10), 111.2 (C-3), 124.2 (C-3′,5′), 126.8 (C-2′,6′), 137.5 (C-1′), 149.1 (C-4′), 157.9

(C-2), 159.8 (C-9), 161.1 (C-5), 164.5 (C-7), 177.0 (C-4) ppm; IR (KBr): $\bar{\nu} = 1650$, 1610, 1511, 1467, 1342, 1220, 1159, 1025, 850 cm^{-1}; MS (EI, 70 eV): m/z (%) = 327 ($M^{+\bullet}$, 100), 326 (35), 298 (27), 281 (33), 269 (19), 252 (15), 235 (11), 180 (3), 150 (12), 137 (7), 107 (6), 75 (11), 69 (8).

2′-Methyl-3′-nitroflavone (**4m**, $C_{16}H_{11}NO_4$)
Mp 183–184°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.49$ (s, CH_3), 6.61 (s, H-3), 7.53 (dt, $J = 0.8$, 7.7 Hz, H-6), 7.63 (t, $J = 8.0$ Hz, H-5′), 7.70 (d, $J = 8.2$ Hz, H-8), 7.84 (ddd, $J = 1.7$, 7.7, 8.2 Hz, H-7), 7.94 (dd, $J = 1.0$, 8.0 Hz, H-6′), 8.08 (dd, $J = 1.0$, 8.0 Hz H-4′), 8.12 (dd, $J = 1.7$, 7.7 Hz, H-5) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.7$ (*C*H_3), 112.5 (C-3), 118.3 (C-8), 123.1 (C-10), 124.7 (C-5), 125.4 (C-5′), 125.6 (C-4′), 125.7 (C-6), 130.1 (C-2′), 133.5 (C-6′), 134.3 (C-7), 135.0 (C-1′), 150.9 (C-3′), 155.8 (C-9), 163.0 (C-2), 176.6 (C-4) ppm; IR (KBr): $\bar{\nu} = 1639$, 1606, 1523, 1467, 1374, 1340, 827, 779 cm^{-1}; MS (EI, 70 eV): m/z (%) = 281 ($M^{+\bullet}$, 100), 264 (25), 234 (49), 221 (5), 205 (10), 178 (16), 152 (6), 146 (44), 121 (74), 115 (11), 92 (56), 76 (11), 63 (21).

4′-Methyl-3′-nitroflavone (**4n**, $C_{16}H_{11}NO_4$)
Mp 198–199°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (s, CH_3), 7.10 (s, H-3), 7.50 (t, $J = 7.3$ Hz, H-6), 7.68 (d, $J = 7.9$ Hz, H-5′), 7.77–7.86 (m, H-7 and H-8), 8.05 (d, $J = 7.3$ Hz, H-5), 8.29 (d, $J = 7.9$ Hz, H-6′), 8.58 (br s, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.9$ (*C*H_3), 107.6 (C-3), 118.3 (C-8), 121.5 (C-2′), 123.1 (C-10), 124.5 (C-5), 125.4 (C-6), 130.1 (C-6′), 130.3 (C-1′), 133.3 (C-5′), 134.1 (C-7), 135.6 (C-4′), 149.5 (C-3′), 155.4 (C-9), 160.1 (C-2), 176.7 (C-4) ppm; IR (KBr): $\bar{\nu} = 1643$, 1533, 1461, 1376, 1338, 1139, 728 cm^{-1}; MS (EI, 70 eV): m/z (%) = 281 ($M^{+\bullet}$, 100), 264 (50), 236 (27), 208 (18), 178 (14), 120 (34), 115 (9), 92 (37), 63 (13).

3′,5′-Dinitroflavone (**4o**, $C_{15}H_8N_2O_6$)
Mp 272–273°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.53$ (s, H-3), 7.57 (dd, $J = 1.2$, 7.7 Hz, H-6), 7.89–7.92 (m, H-7), 7.96 (d, $J = 7.7$ Hz, H-8), 8.08 (dd, $J = 1.2$, 7.7 Hz, H-5), 8.99 (t, $J = 2.0$ Hz, H-4′), 9.23 (d, $J = 2.0$ Hz, H-2′,6′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 109.8$ (C-3), 119.0 (C-8), 120.9 (C-4′), 123.3 (C-6), 124.9 (C-5), 126.1 (C-10), 126.6 (C-2′,6′), 134.6 (C-1′), 134.9 (C-7), 148.8 (C-3′,5′), 155.7 (C-9), 158.4 (C-2), 177.2 (C-4) ppm; IR (KBr): $\bar{\nu} = 1639$, 1604, 1521, 1465, 1374, 1338, 1132, 777 cm^{-1}; MS (EI, 70 eV): m/z (%) = 312 ($M^{+\bullet}$, 100), 284 (23), 219 (10), 192 (8), 163 (11), 145 (8), 120 (33), 92 (29); HRMS (EI): Calcd for $C_{15}H_8N_2O_6$ 312.0382, found: 312.0388.

4′-Methyl-7-methoxy-3′-nitroflavone (**4p**, $C_{17}H_{13}NO_5$)
Mp 233–234°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.57$ (s, CH_3), 3.93 (s, OCH_3), 6.99 (s, H-3), 7.04 (dd, $J = 2.3$, 8.8 Hz, H-6), 7.28 (d, $J = 2.3$ Hz, H-8), 7.65 (d, $J = 8.0$ Hz, H-5′), 7.92 (d, $J = 8.8$ Hz, H-5), 8.24 (dd, $J = 1.6$, 8.0 Hz, H-6′), 8.54 (d, $J = 1.6$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.8$ (*C*H_3), 55.9 (O*C*H_3), 100.8 (C-8), 107.5 (C-3), 114.5 (C-6), 117.0 (C-10), 121.2 (C-2′), 125.9 (C-5), 129.9 (C-6′), 130.3 (C-1′), 133.3 (C-5′), 135.3 (C-4′), 149.4 (C-3′), 157.2 (C-9), 159.5 (C-2), 163.0 (C-7), 175.9 (C-4) ppm; IR (KBr): $\bar{\nu} = 1631$, 1600, 1525, 1438, 1247, 1085 cm^{-1}; MS (EI, 70 eV): m/z (%) = 311 ($M^{+\bullet}$, 100), 294 (20), 283 (14), 266 (9), 238 (29), 222 (18), 165 (17), 150 (21), 122 (25), 107 (20), 89 (9), 63 (19).

7-Methoxy-3′,5′-dinitroflavone (**4q**, $C_{16}H_{10}N_2O_7$)
Mp 300–302°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.97$ (s, OCH_3), 7.10–7.14 (m, H-6), 7.35 (s, H-3), 7.45 (d, $J = 1.4$ Hz, H-8), 7.99 (d, $J = 9.0$ Hz, H-5), 8.98 (br s, H-4′), 9.18 (br s, H-2′,6′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.1$ (O*C*H_3), 101.1 (C-8), 109.6 (C-3), 115.1 (C-6), 117.0 (C-10), 120.3 (C-4′), 126.1 (C-2′,6′ and C-5), 134.5 (C-1′), 148.7 (C-3′,5′), 157.4 (C-9), 157.8 (C-2), 164.2 (C-7), 176.0 (C-4) ppm; IR (KBr): $\bar{\nu} = 1643$, 1606, 1536, 1440, 1382, 1340, 1282, 1093, 865 cm^{-1}; MS (EI, 70 eV): m/z (%) = 342 ($M^{+\bullet}$, 46), 314 (12), 299 (5), 242 (23), 222 (6), 150 (8), 107 (7), 91 (100), 79 (6), 65 (14); HRMS (EI): Calcd for $C_{16}H_{10}N_2O_7$ 342.0488, found 342.0480.

2-Methyl-5-methoxy-3′-nitroflavone (**4r**, $C_{17}H_{13}NO_5$)
Mp 189–190°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (s, CH_3), 3.88 (s, OCH_3), 6.43 (s, H-3), 7.02 (d, $J = 8.3$ Hz, H-6), 7.18 (d, $J = 8.3$ Hz, H-8), 7.61 (t, $J = 7.9$ Hz, H-5′), 7.70 (t, $J = 8.3$ Hz, H-7), 7.91 (d, $J = 7.9$ Hz, H-6′), 8.07 (d, $J = 7.9$ Hz, H-4′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.2$ (*C*H_3), 56.3 (O*C*H_3), 107.5 (C-6), 110.0 (C-8), 113.7 (C-10), 114.1 (C-3), 126.0 (C-4′), 127.6 (C-5′), 130.4 (C-2′), 133.8 (C-6′), 134.7 (C-7), 134.8 (C-1′), 151.0 (C-3′), 157.9 (C-9), 159.2 (C-5), 160.7 (C-2), 176.2 (C-4) ppm; IR (KBr): $\bar{\nu} = 1641$, 1602, 1475, 1374, 1320, 1267, 1081, 800 cm^{-1}; MS (EI, 70 eV): m/z (%) = 311 ($M^{+\bullet}$, 100), 310 (32), 293 (9), 282 (27), 265 (34), 247 (11), 219 (12), 178 (7), 151 (6), 121 (17), 107 (25), 92 (16), 63 (16).

4′-Methyl-5-methoxy-3′-nitroflavone (**4s**, $C_{17}H_{13}NO_5$)
Mp 201–203°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.59$ (s, CH_3), 3.88 (s, OCH_3), 6.91 (s, H-3), 7.02 (d, $J = 8.3$ Hz, H-6), 7.30 (d, $J = 8.3$ Hz, H-8), 7.67–7.74 (m, H-5′ and H-7), 8.24 (dd, $J = 1.8$, 8.1 Hz, H-6′), 8.53 (d, $J = 1.8$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.7$ (*C*H_3), 56.0 (O*C*H_3), 107.5 (C-6), 109.0 (C-3), 109.8 (C-8), 113.8 (C-10), 121.1 (C-2′), 129.7 (C-6′), 130.0 (C-1′), 133.2 (C-5′), 134.0 (C-7), 135.1 (C-4′), 149.5 (C-3′), 157.2 (C-9), 157.6 (C-2), 159.0 (C-5), 175.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1652$, 1602, 1525, 1469, 1376, 1261, 1103, 1031, 840, 754 cm^{-1}; MS (EI, 70 eV): m/z (%) = 311 ($M^{+\bullet}$, 100), 310 (23), 293 (7), 282 (22), 265 (44), 236 (28), 219 (25), 208 (14), 178 (21), 165 (23), 152 (11), 115 (29), 107 (58), 92 (56), 76 (20), 63 (29).

5-Methoxy-3′,5′-dinitroflavone (**4t**, $C_{16}H_{10}N_2O_7$)
Mp 286–287°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3{,}90$ (s, OCH_3), 7.04 (d, $J = 8.4$ Hz, H-6), 7.21 (s, H-3), 7.37 (d, $J = 8.4$ Hz, H-8), 7.73 (t, $J = 8.4$ Hz, H-7), 8.95 (s, H-4′), 9.11 (s, H-2′,6′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.1$ (O*C*H_3), 107.7 (C-6), 109.9 (C-8), 111.0 (C-3), 113.7 (C-10), 120.1 (C-4′), 125.8 (C-2′,6′), 134.2 (C-1′), 134.4 (C-7), 148.6 (C-3′,5′), 155.7 (C-2), 157.2 (C-9), 159.0 (C-5), 175.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1644$, 1602, 1536, 1473, 1363, 1342, 1041, 952, 730 cm^{-1}; MS (EI, 70 eV): m/z (%) = 342 ($M^{+\bullet}$, 100), 341 (23), 324 (8), 313 (24), 296 (26), 284 (8), 250 (17), 232 (10), 221 (15), 192 (10), 163 (17), 150 (10), 120 (24), 107 (25), 69 (25); HRMS (EI): Calcd for $C_{16}H_{10}N_2O_7$ 342.0488, found 342.0480.

4′-Methyl-5,7-dimethoxy-3′-nitroflavone (**4u**, $C_{18}H_{15}NO_6$)
Mp 246–247°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.69$ (s, CH_3), 3.94 (s, OCH_3), 3.97 (s, OCH_3), 6.41 (d, $J = 2.3$ Hz, H-6), 6.62 (d, $J = 2.3$ Hz, H-8), 6.71 (s, H-3), 7.50 (d, $J = 8.1$ Hz, H-5′), 7.94 (dd, $J = 1.8$, 8.1 Hz, H-6′), 8.52 (d, $J = 1.8$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$ (*C*H_3), 55.9 (O*C*H_3), 56.5 (O*C*H_3), 92.8 (C-6), 96.5 (C-8), 109.2 (C-10), 109.7 (C-3), 122.0 (C-2′), 129.6 (C-6′), 130.8 (C-1′), 133.6 (C-5′), 136.5 (C-4′), 149.6 (C-3′), 157.9 (C-2), 159.7 (C-5), 160.9 (C-7), 164.3 (C-9), 177.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 1654$, 1612, 1571, 1527, 1347, 1276, 1122, 825 cm^{-1}; MS (EI, 70 eV): m/z (%) = 341 ($M^{+\bullet}$, 100), 340 (33), 330 (5), 312 (19), 295 (26), 266 (11), 249 (7), 222 (6), 181 (4), 150 (15), 122 (8), 69 (6).

5,7-Dimethoxy-3′,5′-dinitroflavone (**4v**, $C_{17}H_{12}N_2O_8$)
Mp 244–245°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.85$ (s, OCH_3), 3.93 (s, OCH_3), 6.51 (d, $J = 1.7$ Hz, H-6), 6.91 (d, $J = 1.7$ Hz, H-8), 7.11 (s, H-3), 8.92 (s, H-4′), 9.07 (s, H-2′,6′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.9$ (O*C*H_3), 56.0 (O*C*H_3), 93.5 (C-6), 96.6 (C-8), 110.9 (C-3 and C-10), 119.9 (C-4′), 125.6 (C-2′,6′), 134.3 (C-1′), 148.5 (C-3′,5′), 155.1 (C-2), 158.8 (C-5), 160.2 (C-9), 164.0 (C-7), 174.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 1643$, 1600, 1536, 1471, 1340, 1263, 1041, 728 cm^{-1}; MS (EI, 70 eV): m/z (%) = 372 ($M^{+\bullet}$, 100), 371 (39), 354 (8), 343 (31), 326 (35), 314 (14), 299 (7), 279 (22), 251 (18), 234 (13), 207 (14), 172 (10), 150 (13), 137 (10), 107 (7), 79 (4); HRMS (EI): Calcd for $C_{17}H_{12}N_2O_8$ 372.0594, found 372.0581.

6-Bromo-2′-nitroflavone (**4x**, $C_{15}H_8NO_4Br$)
Mp 208–210°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.86$ (s, H-3), 7.55 (d, $J = 8.9$ Hz, H-8), 7.88 (ddd, $J = 1.8$, 7.2, 8.0 Hz, H-4′), 7.92–7.96 (m, H-5′ and H-6′), 7.98 (dd, $J = 2.3$, 8.9 Hz, H-7), 8.14 (d, $J = 2.3$ Hz, H-5), 8.21 (d, $J = 8.0$ Hz, H-3′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 111.0$ (C-3), 118.4 (C-6), 120.9 (C-8), 124.6 (C-10), 125.1 (C-3′), 126.3 (C-1′), 127.1 (C-5), 131.7 (C-6′), 132.8 (C-4′), 134.2 (C-5′), 137.4 (C-7), 147.4 (C-2′), 154.7 (C-9), 162.2 (C-2), 175.6 (C-4) ppm; IR (KBr): $\bar{\nu} = 1658$, 1604, 1523, 1469, 1361, 1282, 1133, 813, 709 cm^{-1}; MS (EI, 70 eV): m/z (%) = 347 ($M^{+\bullet}$ ^{81}Br, 98), 345 ($M^{+\bullet}$ ^{79}Br, 100), 300 (3), 289 (13), 238 (20), 220 (10), 210 (25), 198 (75), 163 (47), 146 (15), 119 (100), 104 (43), 90 (35), 75 (46), 63 (70).

6-Bromo-3′-nitroflavone (**4y**, $C_{15}H_8NO_4Br$)
Mp 243–244°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$ (s, H-3), 7.85–7.90 (m, H-8 and H-5′), 8.01 (dd, $J = 2.4$, 8.9 Hz, H-7), 8.13 (d, $J = 2.4$ Hz, H-5), 8.43 (ddd, $J = 0.8$, 1.5, 8.0 Hz, H-4′), 8.53 (dd, $J = 0.8$, 8.0 Hz, H-6′), 8.82 (t, $J = 1.5$ Hz, H-2′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 108.3$ (C-3), 118.0 (C-6), 120.8 (C-2′), 121.2 (C-8), 124.7 (C-10), 126.0 (C-4′), 126.7 (C-5), 130.6 (C-5′), 132.5 (C-6′), 132.5 (C-1′), 136.9 (C-7), 148.3 (C-3′), 154.5 (C-9), 160.4 (C-2), 175.6 (C-4) ppm; IR (KBr): $\bar{\nu} = 1641$, 1598, 1527, 1436, 1344, 1137, 937, 777 cm^{-1}; MS (EI, 70 eV): m/z (%) = 347 ($M^{+\bullet}$, ^{81}Br, 100), 345 ($M^{+\bullet}$, ^{79}Br, 100), 317 (16), 271 (5), 220 (12), 198 (55), 163 (24), 81 (15), 74 (23), 64 (38).

6-Bromo-4′-nitroflavone (**4w**, $C_{15}H_8NO_4Br$)
Mp 237–238°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.24$ (s, H-3), 7.82 (d, $J = 8.9$ Hz, H-8), 8.02 (dd, $J = 2.5$, 8.9 Hz, H-7), 8.16 (d, $J = 2.5$ Hz, H-5), 8.38 (br s, H-2′,6′ and H-3′,5′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 109.0$ (C-3), 117.9 (C-6), 121.1 (C-8), 123.7 (C-3′,5′), 124.6 (C-10), 126.7 (C-5), 127.7 (C-2′,6′), 136.6 (C-1′), 137.0 (C-7), 149.1 (C-4′), 154.5 (C-9), 160.4 (C-2), 175.5 (C-4) ppm; IR (KBr): $\bar{\nu} = 1641$, 1598, 1527, 1436, 1344, 1237, 937, 777 cm^{-1}; MS (EI, 70 eV): m/z (%) = 347 ($M^{+\bullet}$, ^{81}Br, 100), 345 ($M^{+\bullet}$, ^{79}Br, 100), 317 (13), 299 (7), 220 (10), 198 (60), 170 (27), 163 (20), 117 (9), 74 (20), 64 (35).

6-Bromo-3′,5′-dinitroflavone (**4z**, $C_{15}H_7N_2O_6Br$)
Mp 300–302°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (s, H-3), 7.92 (d, $J = 8.9$ Hz, H-8), 8.04 (dd, $J = 2.4$, 8.9 Hz, H-7), 8.17 (d, $J = 2.4$ Hz, H-5), 9.00 (t, $J = 2.0$ Hz, H-4′), 9.20 (d, $J = 2.0$ Hz, H-2′,6′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 109.6$ (C-3), 118.0 (C-6), 120.5 (C-4′), 121.2 (C-8), 124.6 (C-10), 126.3 (C-2′,6′), 126.7 (C-5), 134.2 (C-1′), 137.0 (C-7), 148.6 (C-3′,5′), 154.4 (C-9), 158.5 (C-2), 175.5 (C-4) ppm; IR (KBr): $\bar{\nu} = 1658$, 1531, 1459, 1436, 1342, 1274, 948, 7819 cm^{-1}; MS (EI, 70 eV): m/z (%) = 392 ($M^{+\bullet}$, ^{81}Br, 100), 390 ($M^{+\bullet}$, ^{79}Br, 100), 362 (7), 299 (8), 270 (2), 198 (37), 170 (20), 163 (14), 100 (4), 74 (12), 63 (24); HRMS (EI): Calcd for $C_{15}H_7N_2O_6Br$ 391.9467, found 391.9486.

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