An Amberlyst-15® Mediated Synthesis of New Functionalized Dioxoloquinolinone Derivatives

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Abstract: The commercially available Amberlyst®-15 in the presence of AcOH was conveniently used to catalyze the intramolecular cyclization of a series of 2´-amino[1,3]dioxolochalcones to the corresponding dihydroquinolin-8-ones. This procedure is compatible with different functional groups and may be used as an alternative strategy for the synthesis of this important family of heterocyclic compounds.

Keywords: 2´-Aminochalcones, Michael addition, Dihydroquinolin-8-ones, Amberlyst®-15.

INTRODUCTION

Chalcones have been widely used as versatile starting materials for numerous synthetic reactions including the synthesis of fused heterocyclic rings [1]. As a continuation of our studies directed toward the synthesis and chemical transformation of chalcones [1c,d], we planned to obtain a series of new chalcones **2**, along with their intramolecular cyclization products, i.e. the corresponding 6-aryl-6,7-dihydro-5*H*-[1,3]dioxolo[4,5-*g*]quinolin-8-ones **3**, as target compounds to be tested (**2** and **3**) in further anti-fungal and anti-tumoral assays. Both types of structures have been recognized for their potential medical applications [2]. The presence of the [1,3]dioxolo functionality in compounds **2** and **3** will result interesting because it is known that several synthetic and naturally occurring compounds that contain this functionality in their frameworks have displayed important biological and pharmacological properties [3].

RESULTS AND DISCUSSION

The starting chalcones **2a-o** were readily obtained in 53-95% yield by heating alcoholic solutions of equimolar amounts of 6-amino-3,4-methylenedioxyacetophenone **1** and the corresponding aryl aldehydes **a-o** (see Ar- in Table **1**), in the presence of 20% aq NaOH (entry (i), Scheme **1**) [4]. For the cyclization process to the corresponding quinolinones **3**, the literature procedure using a hot mixture of AcOH and H_3PO_4 was followed [5a]. Unfortunately the reactions proceeded with formation of resinous materials as well as difficult product isolation with subsequent low yields. Other effective procedures have been reported for this cyclization process [5b,c], including microwave irradiation [4d,e] and supported Lewis and Brønsted acids [5f-h]. However, we wished to look for a more suitable procedure according to our purposes and laboratory conditions.

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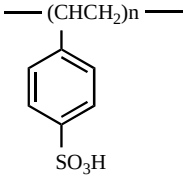
According to our own experience in some heterogeneous catalysts [6] and the literature, is well known that the Amberlyst®-15 is a macro reticular polystyrene-based ion exchange resin with strongly acidic sulfonic groups (Fig. **1**). It have been reported that this material resulted very efficient as acid catalyst for several reactions [7], such as the synthesis of acetals from carbonyls and alcohols [7c], synthesis of esters from alcohols and acids [7d] and hydrolysis of acetals to carbonyls [7e].



Amberlyst-15

Fig. (1). Structure of Amberlyst®-15.

In this sense we decided to try with an Amberlyst®-15/AcOH mixture as an adaptation of the literature procedure [5a], to explore the possible effectiveness of this resin as heterogeneous acid catalyst for our intramolecular Michael-type addition, depicted in the entry (ii), Scheme **1**.

In a first approach, chalcone **2a** (0.2 g) was dissolved in AcOH (5 mL) and stirred at 80 °C in the presence of Amberlyst®-15 (10% w/w) during 4 h (TLC control, entry (ii), Scheme **1**). After filtration of the resin and removal of the solvent, the product crude was purified by column chromatography on silica gel using a mixture of hexanes:AcOEt (5:1) as eluent, yielding the corresponding hydroquinolinone **3a** in 85% isolated yield. Taking into account the success with this approach for chalcone **2a**, this procedure was extended to other chalcones **2b-o** furnishing similar good results. In fact, all chalcones **2a-o** were successfully cyclized to the corresponding quinolinones **3a-o** in 83-98% yield. (see Table **1** and Scheme **1**). Additionally, after solutions were filtered on vacuum for purification of products **3**, the resi-

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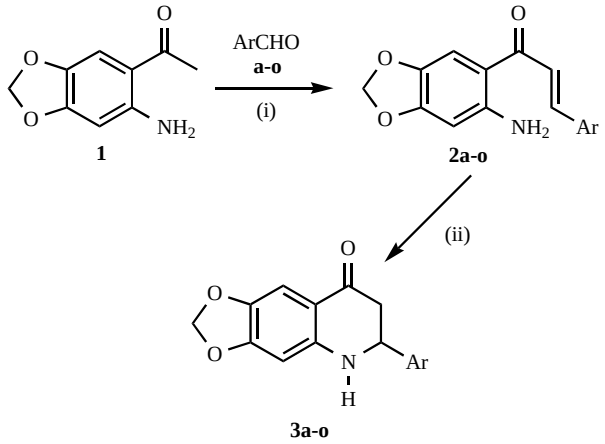
dues of Amberlyst®-15 were recovered by washing with clean AcOH, dried and re-used in further reactions.



[a]Key: (i) Ketone **1** (0.5 g, 2.8 mmol), aldehydes **a-o** (2.8 mmol), NaOH 20% (0.5 mL, 2.5 mmol), EtOH (10 mL) reflux; (ii) chalcones **2a-o** (0.2 g), Amberlyst®-15 (20 mg, 10% w/w), AcOH (5 mL), 80 °C.

Scheme 1. Synthesis of chalcones **2** and hydroquinolinones **3** from the aminoketone **1**.

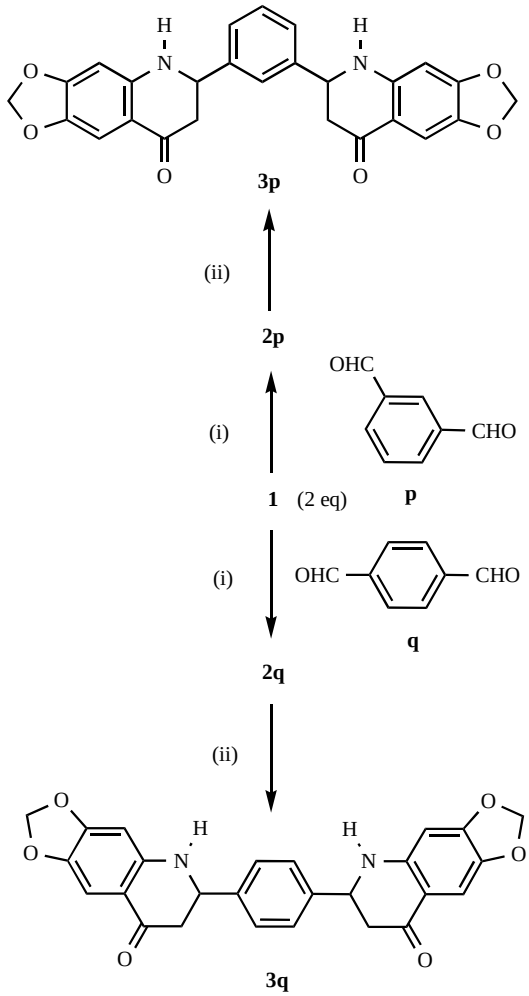
For a more general scope of this approach, *bis*-chalcones **2p** and **2q** were obtained and efficiently cyclized to the corresponding *bis*-quinolones **3p** and **3q** in 92% and 85% yield, respectively, as shown in Scheme **2**.

All products **2** and **3** were completely characterized by analytical and spectroscopic methods (IR, ^{1}H and ^{13}C NMR and MS). Single crystal X-ray diffraction analysis for some chalcones **2** [8a-c] and quinolinones **3** [8d-e], confirmed their structures. All chalcones **2** were obtained with colors ranging from yellow to dark-red. Quinolinones **3** were pale yellow colored exhibiting strong fluorescence under exposure to long wavelength UV irradiation, in both solid state and solution. This characteristic easily permitted us to follow the reaction progress by TLC and to check the purity of compound **3**. Compound **3k** was the only that did not show fluorescence.

An interesting finding in this research is that related with chalcone **2r**. This product was obtained from aldehyde **r** in 67% overall yield, as a mixture 85:15 of the dark-red product **2r** along with the yellow colored side-product **2s** respectively, Scheme **3**. This latter compound was carefully removed by column chromatography and characterized by spectroscopic and analytical methods. According to the structure of the side-product **2s**, this could be formed by an alcoholysis of the C-Cl bond of **2r,** during the reaction progress. The structure for **2s** was assigned by IR, NMR and MS.

Additionally, we found when individuals chalcones **2r** and **2s** or the mixture of both compounds are subjected to the reaction conditions (ii), a mixture of difficultly separable compounds is obtained, with the pale yellow and sparingly soluble amide **3t** as one of the components, Scheme **4**.

The above behavior observed for (**2r** and **2s**) is in accordance with a Kuethe´s work where recently used the hydrolysis of 2-chloro- and 2-methoxyquinoline-3-carbaldehydes under acidic conditions to obtain some target compound **5** as candidates for KDR kinase inhibition. In that approach Cl- and MeO- were rationalized as masked groups for the CONH functionality, as shown in Scheme **5** [9]. In our case, the AcOH or any moisture of the Amberlyst®-15 used could be the sources of the necessary catalytic amount of water for the hydrolysis process. For that, when we repeated the same reaction of the Scheme **4** but adding 0.3 mL of H_2O, compound **3t** was obtained as the main product, which supports the above assertion.



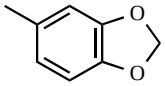
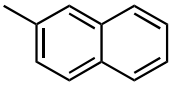
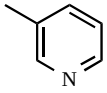
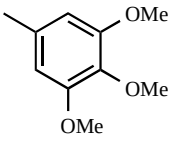
Scheme 2. Synthesis of bis-hydroquinolinones **3p-q** from their dialdehydes **p** and **q** respectively.

Finally, to unambiguously confirm the formation of compound **3t**, this was directly obtained in 82% isolated yield under (ii) conditions from chalcone **2t** (Scheme **6**). In turn, chalcone **2t** was obtained from **1** and the 2-oxoquinolin-3-carbaldehyde **t** [10]. Compound **3t** thus obtained showed the same physicochemical characteristics than that isolated from the reaction depicted in Scheme **4**.

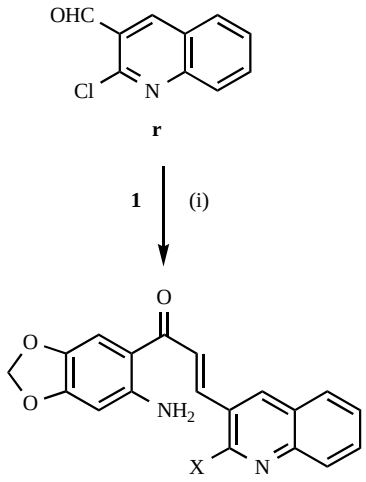
CONCLUSIONS

In summary, we have described here an alternative and general procedure for the synthesis of the new [1,3]dioxoloquinolin-8-ones **3** from their respective 2´-aminochalcones **2** mediated by the sulfonic acid derivative Amberlyst®-15. The use of this heterogeneous catalyst had

Table 1. Hydroquinolin-8-ones 3a-o Obtained from Reactions in Scheme 1

Ar-		Yield (%)	Ar-		Yield (%)
3a	C_6H_5-	85	**3j**	*o*-$F_3CC_6H_4$-	97
3b	*p*-BrC_6H_4-	89	**3k**	*p*-$NO_2C_6H_4$-	85
3c	*p*-ClC_6H_4-	98	**3l**		88
3d	*p*-$MeOC_6H_4$-	95	**3m**		78
3e	*p*-$Me_2NC_6H_4$-	93	**3n**		83
3f	*p*-MeC_6H_4-	96	**3o**		84
3g	*p*-$F_3CC_6H_4$-	83			
3h	*p*-FC_6H_4-	92			
3i	*o*-FC_6H_4-	98			

the additional advantage of facile product isolation with catalyst recovery and reutilization, increasing its practical utility. On the other hand, formation of compound **3t** in a one-step sequence under the reaction conditions was chemically interesting and its feasibility is supported by previous reports. The fact of sharing the same 2-oxoquinline pharmacophore like inhibitors **5** makes compound **3t** interesting for potential KDR activity.



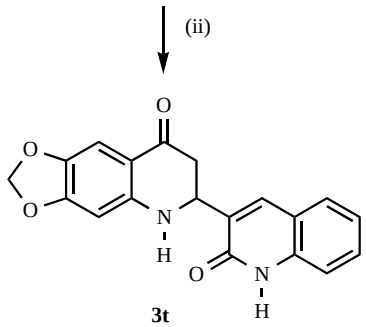
2r: X = Cl (85%) + **2s**: X = OEt (15%)

Scheme 3. Synthesis of chalcone **2r** in mixture with its ethoxy side-product **2s**.

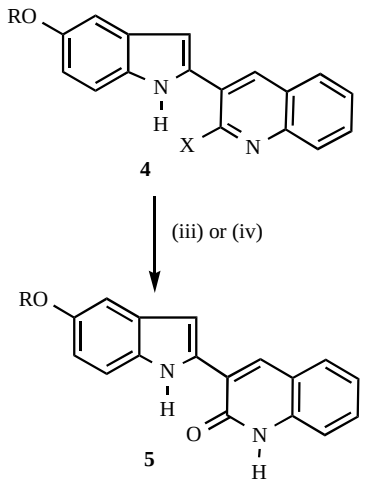
EXPERIMENTAL SECTION

Melting points were determined on a Büchi melting point apparatus and are uncorrected. IR spectra were recorded with a Shimadzu FTIR 8400 on KBr disks. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200, Bruker DPX 300 and Bruker AMX 400 instruments, chemical shifts (δ) are reported in ppm relative to internal tetramethylsilane and

(**2**r or **2s**) or mixture of both compounds

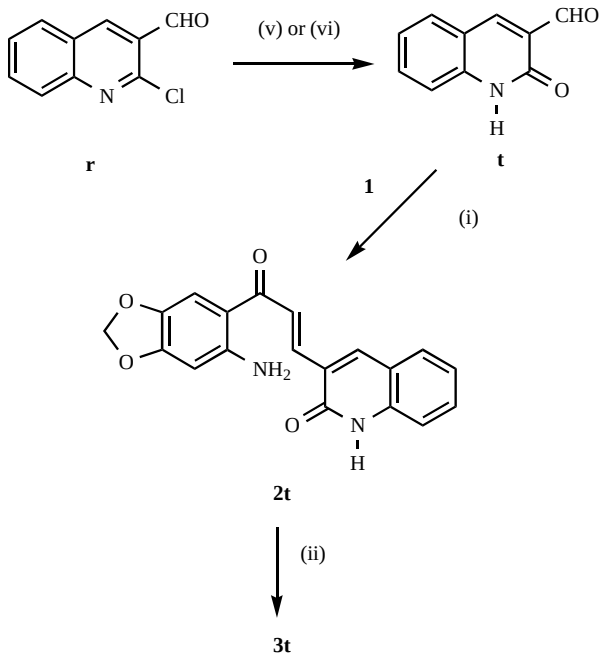


Scheme 4. Cyclization products from chalcones **2r,s**.



[a]Key: (iii) 1:1 AcOH:H_2O under reflux, when X = Cl; (iv) aq HCl under reflux, when X = OMe.

Scheme 5. Products **5** from the acid hydrolysis of 2-chloro- and 2-methoxyquinoline-3-carbaldehyde derivatives **4** according to ref. [9].



[a]Key: (v) aq AcOH (70%), reflux 6h. (vi) aq AcOH (99%), Amberlyst-15®, reflux 2h.

Scheme 6. 2-Oxoquinolin-chalcone **2t** obtained as direct precursor for quinolone **3t**.

coupling constants in Hz, $CDCl_3$ and DMSO-d_6 as solvent. Silica gel aluminum plates (Merck 60 F_{254}) were used for analytical TLC and spots were visualized with short wavelength UV light. Mass spectra were run on Varian Model MAT MS-311 and SHIMADZU-GCMS 2010-DI-2010 spectrometers at 70 eV. Microanalyses were performed with Perkin Elmer Model 240 C and LECO CHNS-932 elemental analyzers and the values are within ± 0.4% of the theoretical values. The Amberlyst®-15, the starting aldehydes **a-r** and the aminoketone **1** were purchased from Aldrich, Fluka and Acros (analytical reagent grades) and were used without further purification.

Chalcones 2a-r and 2t According to Approach (i); General Procedure

Ethanolic solutions (10 mL) of equimolar amounts of aminoketone **1** (2.8 mmol), the corresponding aldehydes **a-r** or **t** and 20% aq NaOH (0.5 mL, 2.5 mmol) were heated to reflux during 10 to 20 min. After cooling the precipitates were filtered off, washed with EtOH, then with water and finally dried on vacuum. Not further purification was required for the most of these products. If necessary, crystallization in EtOH was carried out. In the case of chalcones **2p** and **2q**, 2 eq of ketone **1** were used.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-phenylpropenone 2a

62% yield. Mp 108-110 °C. IR (KBr) ν: 3330, 3277 (NH_2), 1639 (C=O), 1609 (C=C), 1244 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 5.91 (s, 2H, OCH_2O), 6.22 (s, 1H), 6.61 (br s, 2H, NH_2), 7.00-8.00 (m, 8H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 97.0, 101.5 (OCH_2O), 108.2, 111.9, 123.6, 128.2, 129.1, 136.2, 130.0, 139.1, 142.2, 150.9, 153.6, 189.5 (C=O) ppm. EIMS (70 eV): m/z (%): 267 (29, [M^+]), 190 (100, [M-C_6H_5]). Anal. Calcd for $C_{16}H_{13}NO_3$ (267.29): C, 71.90; H, 4.90; N, 5.24. Found: C, 71.84; H, 4.93; N, 5.28.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-bromophenyl)propenone 2b

94% yield. Mp 163-164 °C. IR (KBr) ν: 3449, 3300 (NH_2), 1646 (C=O), 1622 (C=C), 1236 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 5.92 (s, 2H, OCH_2O), 6.18 (s, 1H), 6.62 (br s, 2H, NH_2), 7.21 (s, 1H), 7.44 (d, 1H), 7.46 (d, 2H), 7.52 (d, 2H), 7.60 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 96.9, 101.5 (OCH_2O), 107.8, 111.3, 123.9, 129.5 (contains two signals), 132.1, 134.0, 138.9, 140.7, 150.6, 153.3, 189.0 (C=O) ppm. EIMS (70 eV): m/z (%): 345/347 (32/30, [M^+]), 190 (100, [M-C_6H_4Br]). Anal. Calcd for $C_{16}H_{12}BrNO_3$ (346.18): C, 55.51; H, 3.49; N, 4.05. Found: C, 55.43; H, 3.57; N, 4.16.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-chlorophenyl)propenone 1c

85% yield. Mp 152-153 °C. IR (KBr) ν: 3468, 3294 (NH_2), 1659 (C=O), 1615 (C=C), 1239 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 5.91 (s, 2H, OCH_2O), 6.17 (s, 1H), 6.62 (br s, 2H, NH_2), 7.21 (s, 1H), 7.42 (d, 1H), 7.35 (d, 2H), 7.52 (d, 2H), 7.63 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 96.9, 101.4 (OCH_2O), 107.9, 111.4, 123.8, 129.1 (contains two signals), 134.0, 135.7, 138.9, 140.6, 150.6, 153.3, 188.7 (C=O) ppm. EIMS (70 eV): *m/z* (%): 301/303 (41/14, [M^+]), 190 (100, [M-C_6H_4Cl]). Anal. Calcd for $C_{16}H_{12}ClNO_3$ (301.73): C, 63.69; H, 4.01; N, 4.64. Found: C, 63.80; H, 3.88; N, 4.53.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propenone 2d

60% yield. Mp 108-109 °C. IR (KBr) ν: 3461, 3303 (NH_2), 1644 (C=O), 1603 (C=C), 1223 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.89 (s, 3H, OCH_3), 5.93 (s, 2H, OCH_2O), 6.19 (s, 1H), 6.57 (br s, 2H, NH_2), 6.91 (d, 2H), 7.26 (s, 1H), 7.35 (d, 1H), 7.47 (d, 2H), 7.71 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 55.2 (OCH_3), 96.8, l01.5 (OCH_2O), 108.2, 112.0, 114.5, 121.2, 128.3, 130.0, 138.9, 142.1, 150.0, 153.5, 161.2, 189.0 (C=O) ppm. EIMS (70 eV): *m/z* (%): 297 (27, [M^+]), 190 (100, [M-C_7H_7O]). Anal. Calcd for $C_{17}H_{15}NO_4$ (297.31): C, 68.68; H, 5.09; N, 4.71. Found: C, 68.72; H, 5.11; N, 4.67.

1-(6-aminobenzo[1,3]dioxol-5-yl)-3-[4-(N,N-dimethylamino) phenyl]propenone 2e

54% yield. Mp 162-164 °C. IR (KBr) ν: 3417, 3296 (NH_2), 1647 (C=O), 1596 (C=C), 1228 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.10 (s, 6H, $N(CH_3)_2$), 5.91 (s, 2H, OCH_2O), 6.18 (s, 1H), 6.53 (br s, 2H, NH_2), 6.69 (d, 2H), 7.28 (d, 1H), 7.29 (s, 1H), 7.53 (d, 2H), 7.72 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 41.3 ($N(CH_3)_2$), 97.6, 102.0, 108.9, 112.6, 112.8, 119.1, 124.3, 130.9, 139.7, 143.6, 150.6, 152.6, 153.3, 190.0 (C=O) ppm. EIMS (70 eV): *m/z* (%): 310 (18, [M^+]), 190 (100, [M – $C_8H_{10}N$]). Anal. Calcd for $C_{18}H_{18}N_2O_3$ (310.36): C 69.66, H 5.85, N 9.03. Found: C 69.58, H 5.90, N 9.05.

1-(6-aminobenzo[1,3]dioxol-5-yl)-3-p-tolylpropenone 2f

91% yield. Mp 128-129 °C. IR (KBr) ν: 3454, 3278 (NH_2), 1646 (C=O), 1606 (C=C), 1224 (OCH_2O) cm^{-1}. ^1H

NMR (400 MHz, DMSO) δ: 2.33 (s, 3H, CH_3), 5.96 (s, 2H, OCH_2O), 6.35 (s, 1H), 7.23 (d, 2H), 7.53 (d, 1H), 7.65 (s, 1H), 7.67 (br s, 2H, NH_2), 7.73 (d, 2H), 7.81 (d, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 21.1 (CH_3), 95.9, 101.2 (OCH_2O), 108.3, 110.1, 122.8, 128.7, 129.5, 132.7, 137.9, 139.8, 141.2, 151.7, 152.8, 187.9 (C=O) ppm. EIMS (70 eV): *m/z* (%): 281 (41, [M^+]), 190 (100, [M-C_7H_7]). Anal. Calcd for $C_{17}H_{15}NO_3$ (281.31): C 72.58, H 5.37, N 4.98. Found: C 72.59, H 5.49, N 5.05.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-trifluoromethylphenyl)propenone 2g

75% yield. Mp 144-145 °C. IR (KBr) ν: 3468, 3305 (NH_2), 1649 (C=O), 1612 (C=C), 1228 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.97 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.60 (d, 1H), 7.69 (s, 1H), 7.76 (d, 2H), 7.76 (br s, 2H, NH_2), 8.00 (d, 1H), 8.02 (d, 2H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 24.5 (CF_3), 95.8, 101.3 (OCH_2O), 108.1, 109.4 (C-CF_3), 125.6, 126.1, 126.7, 129.2, 138.0, 139.1, 139.5, 152.2, 153.2, 187.3 (C=O) ppm. EIMS (70 eV): *m/z* (%): 335.5 (100, [M^+]), 190 (58, [M-$C_6H_4CF_3$]). Anal. Calcd for $C_{17}H_{12}F_3NO_3$ (335.29): C 60.90, H 3.61, N 4.18. Found: C 70.00, H 3.69, N 4.12.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-fluorophenyl)propenone 2h

62% yield. Mp 125-127 °C. IR (KBr) ν: 3436, 3320 (NH_2), 1647 (C=O), 1601 (C=C), 1232 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.96 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.25 (t, 2H), 7.55 (s, 1H), 7.67 (s, 1H), 7.70 (br s, 2H), 7.83 (d, 1H), 7.90 (t, 2H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 95.9, 101.1, 109.3, 115.9, 123.8, 130.9, 132.1, 137.5, 137.9, 139.8, 150.3, 152.6, 152.9, 187.7 (C=O) ppm. EIMS (70 eV): *m/z* (%): 285 (100, [M^+]), 190 (45, [M-C_6H_4F]). Anal. Calcd for $C_{16}H_{12}FNO_3$ (285.28): C 67.37, H 4.24, N 4.91. Found: C 67.48, H 4.30, N 5.01.

1-(6-Amino-benzo[1,3]dioxol-5-yl)-3-(2-fluorophenyl)propenone 2i

53% yield. Mp 132-133 °C. IR (KBr) ν: 3360, 3264 (NH_2), 1658 (C=O), 1622 (C=C), 1224 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.97 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.27 (m, 2H), 7.43 (m, 1H), 7.62 (s, 1H), 7.69 (d, 1H), 7.73 (br s, 2H, NH_2), 7.91 (d, 1H), 8.14 (t, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 95.9, 101.3, 107.9, 109.8, 116.0, 123.0, 124.8, 126.0, 128.7, 131.9, 138.0, 152.0, 153.1, 159.0, 162.4, 187.2 (C=O) ppm. EIMS (70 eV): *m/z* (%): 285 (100, [M^+]), 190 (48, [M-C_6H_4F]). Anal. Calcd for $C_{16}H_{12}FNO_3$ (285.28): C 67.37, H 4.24, N 4.91. Found: C 67.29, H 4.33, N 4.85.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(2-trifluoromethylphenyl)propenone 2j

65% yield. Mp 165-167 °C. IR (KBr) ν: 3456, 3295 (NH_2), 1643(C=O), 1615(C=C), 1225 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.99 (s, 2H, OCH_2O), 6.39 (s, 1H), 7.61 (t, 1H), 7.69 (s, 1H), 7.73-7.81 (m, 4H), 7.86 (dd, 1H), 7.97 (d, 1H), 8.33 (d, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 26.8 (CF_3), 95.7, 101.2 (OCH_2O), 107.9, 109.6, 125.6 (C-CF_3), 127.0, 127.9, 128.7, 129.6, 132.7, 133.5, 134.9, 137.9, 152.2,153.1, 186.7 (C=O) ppm. EIMS (70 eV): *m/z* (%): 335.5 (32, [M^+]), 190 (62, [M-$C_6H_4CF_3$]). Anal. Calcd for $C_{17}H_{12}F_3NO_3$ (335.29): C 60.90, H 3.61, N 4.18. Found: C 60.79, H 3.72, N 4.10.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(4-nitrophenyl)propenone 2k

80% yield. Mp 236-237 °C. IR (KBr) ν: 3456 (NH_2) 1649 (C=O), 1611 (C=C), 1508 and 1338 (NO_2), 1230 (O-CH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.97 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.62 (d, 1H), 7.68 (s, 1H), 7.80 (br s, 2H, NH_2), 8.06 (d, 1H), 8.10 (d, 2H), 8.23 (d, 2H). ^{13}C NMR (100.6 MHz, DMSO) δ: 95.9, 101.4 (OCH_2O), 108.0, 109.9, 123.3, 123.9, 127.4, 129.5, 138.0, 138.3, 152.2, 152.3, 153.3, 186.9 (C=O) ppm. EIMS (70 eV): *m/z* (%): 312 (100, [M^+]), 190 (36, [M-$C_6H_4NO_2$]). Anal. Calcd for $C_{16}H_{12}N_2O_5$ (312.28): C, 61.54; H, 3.87; N, 8.97. Found: C, 61.60; H, 3.75; N, 9.09.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-benzo[1,3]dioxol-5-ylpropenone 2l

61% yield. Mp 168-169 °C. IR (KBr) ν: 3461, 3270 (NH_2) 1641 (C=O), 1604 (C=C), 1257, 1220 (OCH_2O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.94 (s, 2H, OCH_2O), 6.03 (s, 2H, OCH_2O), 6.19 (s, 1H), 6.6 (br s, 2H, NH_2), 6.84 (d, 1H), 7.10 (dd, 1H), 7.15 (s, 1H), 7.26 (s, 1H), 7.33 (d, 1H), 7.64 (d, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 96.9, 101.3 (OCH_2O), 101.5 (OCH_2O), 106.6, 107.9, 108.6, 111.6, 121.4, 124.4, 129.9, 138.9, 142.0, 148.3, 149.3, 150.3, 153.0, 189.1 (C=O) ppm. EIMS (70 eV): *m/z* (%): 311 (54, [M^+]), 190 (100, [M-$C_7H_5O_2$]). Anal. Calcd for $C_{17}H_{13}NO_5$ (311.30): C 65.59, H 4.21, N 4.50. Found: C 65.48, H 4.30, N 4.43.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-naphthalen-2-ylpropenone 2m

83% yield. Mp 144-146 °C. IR (KBr) ν: 3394, 3294 (NH_2), 1646 (C=O), 1615 (C=C), 1228 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 5.92 (s, 2H, OCH_2O), 6.20 (s, 1H), 6.63 (br s, 2H, NH_2), 7.31 (s, 1H), 7.47 - 7.52 (m, 2H), 7.58 (d, 1H), 7.73 – 7.86 (m, 5H), 7.93 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 96.9, 101.4 (OCH_2O), 108.0, 111.6, 123.5, 123.8, 126.6, 127.0, 127.8, 128.5, 128.6, 129.9, 133.0, 133.5, 134.0, 138.8, 142.1, 150.5, 153.2, 189.1 (C=O) ppm. EIMS (70 eV): *m/z* (%): 317 (100, [M^+]), 190 (43, $C_{10}H_7$). Anal. Calcd for $C_{20}H_{15}NO_3$ (317.35): C, 75.70; H, 4.76; N, 4.41. Found: C, 75.66; H, 4.75; N, 4.45.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-pyridin-3-ylpropenone 2n

87% yield. Mp 164-166 °C. IR (KBr) ν: 3386, 3298 (NH_2), 1653 (C=O), 1621 (C=C), 1230 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 5.97 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.44 (dd, 1H), 7.57 (d, 1H), 7.68 (s, 1H), 7.74 (br s, 2H, NH_2), 7.99 (d, 1H), 8.31 (d, 1H), 8.54 (dd, 1H), 8.95 (d, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 95.9, 101.3 (O-CH_2O), 108.2, 109.8, 123.9, 125.8, 131.2, 134.9, 137.6, 138.0, 150.1, 150.4, 152.1, 153.1, 187.3 (C=O) ppm. EIMS (70 eV): *m/z* (%): 268 (100 [M^+]), 190 (14, [M – C_5H_4N]. Anal. Calcd for $C_{15}H_{12}N_2O_3$ (268.27): C 67.16, H 4.51, N 10.44. Found C 67.18, H 4.57, N 10.53.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(3,4,5-trimethoxyphenyl)propenone 2o

95% yield. Mp 191-192 °C. IR (KBr) ν: 3424, 3302 (NH_2) 1645 (C=O), 1608 (C=C), 1222 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.91 (s, 3H, OCH_3), 3.95 (s, 6H,

OCH_3 x 2), 5.96 (s, 2H, OCH_2O), 6.21 (s, 1H), 6.61 (br s, 2H, NH_2), 6.83 (s, 2H), 7.22 (s, 1H), 7.40 (d, 1H), 7.66 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 57.6 (OCH_3 x 2), 62.9 (OCH_3), 98.3, 102.8 (OCH_2O), 107.1, 112.6, 124.1, 109.1, 154.9, 132.5, 141.3, 140.2, 143.5, 151.3, 154.3, 190.0 (C=O) ppm. EIMS (70 eV): *m/z* (%): 357 (25, [M^+]), 190 (100, [M-$C_9H_{11}O_3$]). Anal. Calcd for $C_{19}H_{19}NO_6$ (357.37): C 63.86, H 5.36, N 3.92. Found: C 63.94, H 5.28, N 4.01.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-{3-[3-(6-aminobenzo [1,3]dioxol-5-yl)-3-oxopropenyl]phenyl}propenone 2p

53% yield. Mp 239-241 °C. IR (KBr) ν: 3425, 3295 (NH_2), 1642 (C=O), 1615 (C=C), 1220 (OCH_2O) cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ: 6.00 (s, 4H, OCH_2O), 6.40 (s, 2H), 7.49 (t, 1H), 7.65 (d, 2H), 7.72 (s, 2H), 7.75 (br s, 4H, NH_2), 7.87 (dd, 2H), 7.99 (d, 2H), 8.37 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 95.8, 101.1 (OCH_2O), 108.0, 110.0, 124.3, 128.1, 129.2, 129.9, 135.9, 137.8, 140.5, 151.9, 152.8, 187.3 (C=O). EIMS (70 eV): *m/z* (%): 456 (100, [M^+]), 295 (10). Anal. Calcd for $C_{26}H_{20}N_2O_6$ (456.46): C 68.42, H 4.42, N 6.14. Found C 68.25, H 4.38, N 6.21.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-{4[3-(6-aminobenzo [1,3]dioxol-5-yl)-3-oxopropenyl]phenyl}propenone 2q

64% yield. Mp 249-250 °C. IR (KBr) ν: 3468, 3300 (NH_2), 1653 (C=O), 1609 (C=C), 1230 (OCH_2O) cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ: 5.97 (s, 2H, OCH_2O), 6.36 (s, 1H), 7.59 (d, 1H), 7.71 (s, 1H), 7.75 (br s, 2H, NH_2), 7.91 (br s, 2H), 7.96 (d, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 95.8, 101.1 (OCH_2O), 107.9, 110.0, 124.3, 129.0, 136.6, 137.8, 140.1, 151.9, 152.8, 187.5 (C=O). EIMS (70 eV): *m/z* (%): 456 (100, [M^+]), 295 (4), 228 (2). Anal. Calcd for $C_{26}H_{20}N_2O_6$ (456.46): C 68.42, H 4.42, N 6.14. Found C 68.34, H 4.47, N 6.09.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(2-chloroquinolin-3-yl) propenone 2r

57% yield. Mp 111-113 °C. IR (KBr) ν: 3422, 3280 (NH_2), 1649 (C=O), 1609 (C=C), 1223 (OCH_2O) cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ: 5.99 (s, 2H, OCH_2O), 6.38 (s, 1H), 7.69 (br s, 2H), 7.80-7.87 (m, 3H, contains NH_2), 7.93 (d, 2H), 7.96-8.11 (m, 2H), 9.21 (s, 1H) ppm. ^{13}C NMR (100.6 MHz DMSO) δ: 95.9, 101.4 (OCH_2O), 107.9, 109.8, 127.2, 127.7, 127.8, 127.9, 128.3, 128.5, 131.7, 134.7, 137.1, 138.0, 147.0, 149.8, 152.4, 153.3, 186.5 (C=O) ppm. EIMS (70 eV): *m/z* (%): 352/354 (100/34, [M^+]), 190 (28). Anal. Calcd for $C_{19}H_{13}ClN_2O_3$ (352.78): C, 64.69; H, 3.71; N, 7.94. Found: C, 64.50; H, 3.58; N, 8.05.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(2-ethoxyquinolin-3-yl) propenone 2s

10% yield. Mp 179-182 °C. IR (KBr) ν: 3447 (br, NH_2), 1640 (C=O), 1608 (C=C), 1216 (br, OCH_2O) cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ: 1.46 (t, 3H), 4.56 (q, 2H), 6.00 (s, 2H, OCH_2O), 6.40 (s, 1H), 7.47 (t, 1H), 7.62 (s, 1H), 7.69-7.71 (m, 1H), 7.76 (br d, 2H, NH_2), 7.85-7.90 (m, 3H), 8.08 (d, 1H), 8.92 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 14.4, 61.9, 95.8, 101.2 (OCH_2O), 107.6, 109.8, 119.9, 124.6, 124.9, 126.2, 126.5, 128.1, 130.5, 134.0, 137.1, 137.8, 146.0, 152.0, 152.9, 159.2, 187.1 (C=O) ppm. EIMS (70 eV): *m/z* (%): 362 (45, [M^+]), 333 (26), 190 (100). Anal. Calcd for $C_{21}H_{18}N_2O_4$ (362.39): C, 69.60; H, 5.01; N, 7.73. Found: C, 69.43; H, 4.88; N, 7.87.

1-(6-Aminobenzo[1,3]dioxol-5-yl)-3-(2-oxoquinolin-3-yl) propenone 2t

55% yield. Mp 250-251 °C. IR (KBr) ν: 3455, 3294 (NH_2), 3400 (NHCO overlaped with the band at 3455 in form as a shoulder), 1656 (-NH-C=O), 1602 (C=O), 1231 (br, OCH_2O) cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ: 5.93 (s, 2H), 6.35 (s, 1H), 6.89 (t, 1H), 7.20 (d, 1H), 7.28 (t, 1H), 7.46 (s, 1H), 7.48 (d, 1H), 7.56 (br s, 2H, NH_2), 7.78 (d, 1H), 8.14 (s, 1H), 8.23 (d, 1H) ppm, NH is missing. ^{13}C NMR (100.6 MHz, DMSO) δ: 96.9, 100.1, 101.5 (OCH_2O), 108.4, 111.6, 113.9, 118.9, 121.5, 121.6, 122.5, 124.4, 125.3, 127.9, 129.3, 137.9, 138.4, 141.1, 152.8 (NH-**C**=O), 168.8 (C=O) ppm. EIMS (70 eV): *m/z* (%): 334 (12 [M^+]), 333 (62 [M – 1]), 190 (23, [M – C_9H_6N]. Anal. Calcd. for $C_{19}H_{14}N_2O_4$ (334.33): C, 68.26; H, 4.22; N, 8.38. Found: C, 68.34; 4.11; 8.25.

Synthesis of Hydroquinolinones 3a-q and 3t According to Approach (ii), General Procedure

Amberlyst®-15 (10% w/w) was added to a solution of each chalcone **2** (0.75 mmol) in AcOH (3-5 mL). The mixtures were heated at 80 °C during 3-5 h until not starting material was detected by TLC. The still hot solutions were decanted and the Amberlyst®-15 was washed with fresh AcOH (3 mL). The combined fractions were evaporated under vacuum and the residues were crystallized from EtOH. No further purification was necessary in most cases, but if it was needed, column chromatographies were run on silica gel using mixtures of hexanes-AcOEt (5:1) as eluents. In all cases, Amberlyst®-15 was recovered by washing with clean AcOH, dried on vacuum and re-used for two more times with similar efficiency.

6-Phenyl-6,7-dihydro-5H-[1,3]dioxolo[4,5-g]quinolin-8-one 3a

Mp 211-213 ºC. IR (KBr) ν: 3271 (NH), 1605 (C=O), 1241 (OCH_2O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.72 (dd, 1H,), 2.90 (dd, 1H), 4.42 (br s, 1H, NH), 4.70 (dd, 1H), 5.94 (s, 2H, OCH_2O), 6.20 (s, 1H), 7.26 (s, 1H), 7.45 (br s, 5H, phenyl-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 44.7, 59.1, 95.9, 101.3 (OCH_2O), 105.2, 113.2, 126.7, 128.5, 129.2, 141.1, 141.8, 150.0, 154.4, 191.2 (C=O) ppm. EIMS (70 eV): *m/z* (%): 267 (78, [M^+]), 190 (100, [M-C_6H_5]), 163 (71). Anal. Calcd for $C_{16}H_{13}NO_3$ (267.29): C, 71.90; H, 4.90; N, 5.24. Found: C, 71.92; H, 4.97; N, 5.30.

6-(4-Bromophenyl)-6-7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3b

Mp 217-218 ºC. IR (KBr) ν: 3301 (NH), 1634 (C=O), 1249 (OCH_2O) cm^{-1}. ^{1}H NMR (200 MHz, DMSO) δ: 2.58 (dd, 1H), 2.68 (dd, 1H), 4.65 (dd, 1H), 5.95 (s, 2H, OCH_2O), 6.42 (s, 1H), 6.98 (s, 1H), 7.02 (br s, 1H, NH), 7.42 (d, 2H), 7.57 (d, 2H) ppm. ^{13}C NMR (50 MHz, DMSO) δ: 44.5, 56.0, 95.6, 101.2 (OCH_2O), 103.1, 110.9, 120.6, 129.0, 131.3, 140.2, 141.0, 150.7, 153.6, 189.8 (C=O) ppm. EIMS (70 eV): m/z (%): 345/347 (90/87, [M^+]), 190 (100, [M-C_6H_4Br]), 163 (61, [M-CH_2=CHC_6H_4Br]). Anal. Calcd for $C_{16}H_{12}BrNO_3$ (346.18): C, 55.51; H, 3.49; N, 4.05. Found: C, 55.61; H, 3.38; N, 3.94.

6-(4-Chlorophenyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3c

Mp 215-217 ºC. IR (KBr) ν: 3344 (NH), 1631 (C=O), 1249 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.62 (dd, 1H), 2.72 (dd, 1H), 4.41 (br s, 1H, NH), 4.63 (dd, 1H), 5.91 (d, 2H, OCH_2O), 6.19 (s, 1H), 7.25 (s, 1H), 7.35 (br s, 4H, aryl-H) ppm. $_{13}C$ NMR (50 MHz, $CDCl_3$) δ: 44.6, 56.0, 95.6, 101.2 (OCH_2O), 103.1, 110.9, 128.4, 128.7, 132.1, 140.2, 140.6, 150.7, 153.6, 189.7 (C=O) ppm. EIMS (70 eV): m/z (%): 301/303 (100, [M^+]), 190 (69, [M-C_6H_4Cl]), 163 (32). Anal. Calcd for $C_{16}H_{12}ClNO_3$ (301.73): C, 63.69; H, 4.01; N, 4.64. Found: C, 63.74; H, 4.03; N, 4.66.

6-(4-Methoxyphenyl)-6,7-dihydro-5H-[1,3]dioxolo[4.5-g] quinolin-8-one 3d

Mp 212-214 ºC. IR (KBr) ν: 3278 (NH), 1607 (C=O), 1243 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.67 (dd, 1H), 2.80 (dd, 1H), 3.82 (s, 3H, OCH_3), 4.32 (s, 1H), 4.63 (dd, 1H), 5.92 (d, 2H, OCH_2O), 6.16 (s, 1H), 6.91 (d, 2H), 7.29 (s, 1H), 7.36 (d, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 45.4, 55.5 (OCH_3), 56.4, 95.5, 101.4 (OCH_2O), 103.2, 111.0, 114.2, 128.8, 133.4, 140.1, 150.8, 153.5, 158.9, 189.9 (C=O) ppm. EIMS (70 eV): m/z (%): 297 (50, [M^+]), 190 (100, [M-C_6H_4OMe]), 163(78). Anal. Calcd for $C_{17}H_{15}NO_4$ (297.31): C, 68.68; H, 5.09; N, 4.71. Found: C, 68.65; H, 5.13; N, 4.80.

6-(4-N,N-Dimethylaminophenyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g]quinolin-8-one 3e

Mp 186-187 ºC. IR (KBr) ν: 3282 (NH), 1610 (C=O), 1239 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.71 (dd, 1H), 2.90 (dd, 1H), 2.98 (s, 6H, NMe_2), 4.35 (br s, 1H, NH), 4.60 (dd, 1H), 5.92 (s, 2H, OCH_2O), 6.18 (s, 1H), 6.74 (d, 2H), 7.27 (s, 1H), 7.29 (d, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 42.1 (NMe_2), 47.3, 60.1, 97.4, 102.9 (OCH_2O), 107.7, 113.9, 128.0, 129.3, 130.6, 131.5, 151.6, 152.0, 155.2, 193.5 (C=O) ppm. EIMS (70 eV): m/z (%): 310 (35, [M^+]), 190 (100, [M-$C_6H_4NMe_2$]), 163 (85). Anal. Calcd for $C_{18}H_{18}N_2O_3$ (310.36): C, 71.90; H, 5.85; N, 9.03. Found: C, 69.58; H, 5.90; N, 9.05.

6-(p-Tolyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g]quinolin-8-one 3f

Mp 204-205 ºC. IR (KBr) ν: 3271 (NH), 1607 (C=O), 1241 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.36 (s, 3H, Me), 2.69 (dd, 1H), 2.79 (dd, 1H), 4.37 (br s, 1H, NH), 4.64 (dd, 1H), 5.91 (d, 2H, OCH_2O), 6.16 (s, 1H), 7.18 (d, 2H), 7.28 (s, 1H), 7.32 (d, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 21.0 (Me), 45.8, 58.6, 95.6, 101.3 (OCH_2O), 104.9, 112.6, 126.4, 129.5, 137.9, 138.1, 141.4, 149.9, 154.1, 191.3 (C=O) ppm. EIMS (70 eV): m/z (%): 281 (100, [M^+]), 190 (56, [M-C_6H_4Me]), 163 (19). Anal. Calcd for $C_{17}H_{15}NO_3$ (281.31): C, 72.58; H, 5.37; N, 4.98. Found: C, 72.46; H, 5.46; N, 5.00.

6-(4-Trifluoromethylphenyl)-6,7-dihydro-5H-[1,3]dioxolo [4,5-g]quinolin-8-one 3g

Mp 182-183 ºC. IR (KBr) ν: 3343 (NH), 1630 (C=O), 1246 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 2.64 - 2.72 (m, 2H), 4.80 (dd, 1H), 5.97 (d, 2H, OCH_2O), 6.42 (s, 1H), 6.98 (s, 1H), 7.10 (br s, 1H, NH), 7.68 (d, 2H), 7.74 (d, 2H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 44.53, 56.33, 95.81, 101.46 (OCH_2O), 103.00, 125.5, 127.8 (C x 4), 140.0, 145.8, 153.8, 162.9, 189.70 (C=O) ppm, CF_3 and C-CF_3 are not observed for multiplicity with the fluorine. EIMS (70 eV): m/z (%): 335.5 (78, [M^+]), 190 (100, [M-$C_6H_4CF_3$]). Anal. Calcd for $C_{17}H_{12}F_3NO_3$ (335.29): C 60.90, H 3.61, N 4.18. Found: C 60.98, H 3.54, N 4.26.

6-(4-Fluorophenyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3h

Mp 188-189 ºC. IR (KBr) ν: 3275 (NH), 1606 (C=O), 1239 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.72 (dd, 1H), 2.80 (dd, 1H), 4.69 (dd, 1H), 5.94 (d, 2H, OCH_2O), 6.21 (s, 1H), 7.08 (dd, 2H), 7.29 (s, 1H), 7.43 (dd, 2H) ppm, NH is missing. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 45.8, 58.3, 95.8, 101.4 (OCH_2O), 104.9, 112.8, 115.8 (d, J = 21.5 Hz), 128.3 (d, J = 8.1 Hz), 136.6, 141.7, 149.5, 154.2, 163.2 (d, J = 245 Hz, C-F), 190.8 (C=O) ppm. EIMS (70 eV): m/z (%): 285 (100, [M^+]), 190 (40, [M-C_6H_4F]), 163 (17). Anal. Calcd for $C_{16}H_{12}FNO_3$ (285.28): C 67.37, H 4.24, N 4.91. Found: C 67.28, H 4.31, N 5.00.

6-(2-Fluorophenyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3i

Mp 226-268 ºC. IR (KBr) ν: 3335 (NH), 1632 (C=O), 1242 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.83 (br d, 2H), 4.37 (br s, 1H, NH), 5.08 (dd, 1H), 5.94 (s, 2H, O-CH_2O), 6.19 (s, 1H), 7.04 – 7.17 (m, 2H), 7.26 – 7.34 (m, 2H), 7.50 – 7.59 (m, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 43.6, 51.4, 95.8, 101.4 (OCH_2O), 104.9, 112.7, 115.7 (d, J = 21.2 Hz), 124.5, 127.5 (d, J = 9.3 Hz), 127.9, 129.7, 141.6, 149.6, 154.1, 164.2 (d, J = 242 Hz, C-F), 190.7 (C=O) ppm. EIMS (70 eV): m/z (%): 285 (100, [M^+]), 190 (37, [M-C_6H_4F]), 163 (17). Anal. Calcd for $C_{16}H_{12}FNO_3$ (285.28): C 67.37, H 4.24, N 4.91. Found: C 69.45, H 4.17, N 5.02.

6-(2-Trifluoromethylphenyl)-6,7-dihydro-5H-[1,3]dioxolo [4,5-g]quinolin-8-one 3j

Mp 201-203 ºC. IR (KBr) ν: 3335 (NH), 1632 (C=O), 1243 (OCH_2O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.78 (br d, 2H), 4.31 (br s, 1H, NH), 5.16 (dd, 1H), 5.96 (d, 2H, OCH_2O), 6.21 (s, 1H), 7.33 (s, 1H), 7.48 (t, 1H), 7.65 (t, 1H), 7.70 (d, 1H), 8.01 (d, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.7 (CF_3), 45.6, 54.4, 77.4, 95.9, 101.5 (OCH_2O), 105.1, 112.7, 126.1, 128.4, 132.6, 139.9, 141.9, 149.8, 154.3, 190.3 (C=O) ppm, C-CF_3 is missing for coupling with CF_3. EIMS (70 eV): *m/z* (%): 335.5 (53, [M^+]), 190 (100, [M-$C_6H_4CF_3$]). Anal. Calcd for $C_{17}H_{12}F_3NO_3$ (335.29): C 60.90, H 3.61, N 4.18. Found: C 60.83, H 3.53, N 4.25.

6-(4-Nitrophenyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3k

Mp 289-291 ºC. IR (KBr) ν: 3336 (NH), 1647 (C=O), 1247 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 2.65 – 2.77 (m, 2H), 4.88 (dd, 1H), 5.99 (d, 2H, OCH_2O), 6.45 (s, 1H), 7.00 (s, 1H), 7.14 (s, 1H, NH), 7.75 (d, 2H), 8.28 (d, 2H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 44.2, 56.0, 95.7, 101.3, 103.2 (OCH_2O), 111.1, 123.6, 128.1, 140.4, 146.9, 149.4, 150.5, 153.7, 189.3 (C=O) ppm. EIMS (70 eV): *m/z* (%): 312 (100, [M^+]), 190 (56, [M-$C_6H_4NO_2$]), 163 (19). Anal. Calcd for $C_{16}H_{12}N_2O_5$ (312.28): C, 61.54; H, 3.87; N, 8.97. Found: C, 61.42; H, 3.95; N, 8.88.

6-Benzo[1,3]dioxol-5-yl-6,7-dihydro-5H-[1,3]dioxolo[4,5-g]quinolin-8-one 3l

Mp 197-198 ºC. IR (KBr) ν: 3326 (NH), 1633 (C=O), 1250 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 2.48 (dd, 1H), 2.70 (dd, 1H), 4.58 (dd, 1H), 5.95 (d, 2H, OCH_2O), 6.00 (s, 2H, OCH_2O), 6.41 (s, 1H), 6.87 – 6.94 (m, 3H, including NH), 6.97 (s, 1H), 7.06 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 45.0, 56.6, 95.6, 101.0 (OCH_2O), 101.2 (OCH_2O), 103.2, 107.3, 108.1, 110.9, 120.2, 135.5, 140.1, 145.7, 147.3, 150.9, 153.6, 190.2 (C=O) ppm. EIMS (70 eV): *m/z* (%) = 311 (100, [M^+]), 190 [85, M-$C_7H_5O_2$]. Anal. Calcd for $C_{17}H_{13}NO_5$ (311.30): C 65.59, H 4.21, N 4.50. Found: C 65.66, H 4.14, N 4.46.

6-Naphthalen-2-yl-6,7-dihydro-5H-[1,3]dioxolo[4,5-g] quinolin-8-one 3m

Mp 287-288 ºC. IR (KBr) ν: 3264 (NH), 1639 (C=O), 1603 (C=C), 1240 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.82 (dd, 1H), 2.92 (dd, 1H), 4.47 (br s, 1H, NH), 4.86 (dd, 1H), 5.94 (d, 2H, OCH_2O), 6.22 (s, 1H), 7.32 (s, 1H), 7.49 - 7.59 (m, 3H), 7.83 - 7.88 (m, 4H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 44.8, 56.9, 95.4, 101.0 (OCH_2O), 103.2, 110.9, 125.0, 125.3, 125.9, 126.4, 127.2, 127.5, 128, 132.6, 132.9, 139.0, 140.1, 150.9, 153.7, 190.0 (C=O) ppm. EIMS (70 eV): *m/z* (%): 317 (100, [M^+]), 190 (37, [M-$C_{10}H_7$]), 163(13). Anal. Calcd for $C_{20}H_{15}NO_3$ (317.35): C, 75.70; H, 4.76; N, 4.41. Found: C, 75.76; H, 4.80; N, 4.35.

6-(3-pyridinyl)-6,7-dihydro-5H-[1,3]dioxolo[4,5g]quinolin-8-one 3n

Mp 234-235 ºC. IR (KBr) ν: 3284 (NH), 1648 (C=O), 1613 (C=C), 1244 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 2.61 – 2.83 (m, 2H), 4.75 (dd, 1H), 5.98 (d, 2H, OCH_2O), 6.43 (s, 1H), 7.01 (s, 1H), 7.04 (br s 1H, NH), 7.42 (dd, 1H), 7.90 (dd, 1H), 8.53 (t, 1H), 8.68 (d, 1H) ppm. ^{13}C NMR (100.6 MHz, DMSO) δ: 43.1, 53.4, 94.6, 100.2 (OCH_2O), 102.2, 109.9, 122.4, 133.4, 135.8, 139.2, 147.4, 147.9, 149.6, 152.5, 188.6 (C=O) ppm. EIMS (70 eV): *m/z* (%): 268 (100, [M^+]), 190 (21, [M – C_5H_4N]), 163 (10). Anal. Calcd for $C_{15}H_{12}N_2O_3$ (268.27): Calcd. C 67.16, H 4.51, N 10.44. Found C 77.10, H 4.48, N 11.52.

6-(3,4,5-trimethoxyphenyl)-6,7-dihydro-5H-[1,3]dioxolo [4,5-g]quinolin-8-one 3o

Mp 198-200 ºC. IR (KBr) ν: 3325 (NH), 1650(C=O), 1241 (OCH_2O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.72 (dd, 1H), 2.85 (dd, 1H), 3.85 (s, 3H, p-OCH_3), 3.90 (s, 6H, m-OCH_3 x 2), 4.41 (s, 1H, NH), 4.62 (dd, 1H), 5.98 (s, 2H, OCH_2O), 6.21 (s, 1H), 6.68 (s, 2H), 7.29 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 46.5, 56.4 (p-OCH_3), 59.3 (m-OCH_3 x 2), 61.0, 96.0, 101.6 (OCH_2O), 103.5, 105.2, 112.9, 130.7, 136.9, 141.9, 149.8, 154.0, 154.8, 191.5 (C=O) ppm. EIMS (70 eV): m/z (%): 357 (42, [M^+]), 190 (100, [M-$C_9H_{11}O_3$]), 163 (81). Anal. Calcd for $C_{19}H_{19}NO_6$ (357.37): C, 63.86; H, 5.36; N, 3.92. Found: C, 63.92; H, 5.30; N, 3.87.

1,3-bis-(6,7-Dihydro-5H-[1,3]dioxolo[4,5-g]-8-oxoquinolin-6-yl)benzene 3p

Mp > 350 ºC. IR (KBr) ν: 3348 (NH), 1630 (C=O), 1242 (OCH_2O) cm^{-1}. ^1H NMR (300 MHz, DMSO) δ: 2.57 (dd, 2H), 2.70 (dd, 2H), 4.67 (dd, 2H), 5.95 (br d, 4H, OCH_2O x 2), 6.44 (s, 2H), 6.99 (s, 2H), 7.41 (br s, 3H, aryl-H), 7.63 (s, 1H, aryl-H), ppm. NH are missing. ^{13}C NMR (75 MHz, DMSO) δ: 45.22, 56.5, 96.2, 101.7 (OCH_2O), 103.6, 111.3, 126.6, 129.2, 140.7, 142.3, 151.5, 154.2, 163.0, 190.7 (C=O) ppm. EIMS (70 eV): *m/z* (%) = 456 (54, [M^+]), 190 (100). Anal. Calcd for $C_{26}H_{20}N_2O_6$ (456.46): C 68.42, H 4.42, N 6.14. Found C 68.32, H 4.30, N 6.31.

1,4-bis-(6,7-Dihydro-5H-[1,3]dioxolo[4,5-g]-8-oxoquinolin-6-yl)benzene 3q

Mp > 350 ºC. IR (KBr) ν: 3269 (NH), 1612 br (C=O), 1241 (OCH_2O) cm^{-1}. ^1H NMR (400 MHz, DMSO) δ: 2.64 (dd, 1H), 2.69 (dd, 1H), 4.68 (dd, 1H), 5.91 (s, 2H, OCH_2O), 6.43 (s, 1H), 7.00 (s, 1H), 7.48 (s, 2H) ppm. NH is missing. ^{13}C NMR (100.6 MHz, DMSO) δ: 44.0, 55.8, 95.6, 101.4 (OCH_2O), 102.7, 110.0, 126.1, 139.7, 140.6, 149.9, 153.0, 189.0 (C=O) ppm. EIMS (70 eV): *m/z* (%) = 456 (92, [M^+]), 190 (100), 163 (43). Anal. Calcd for $C_{26}H_{20}N_2O_6$: (456.46) C, 68.42; H, 4.42; N, 6.14. Found: C, 68.36; H, 4.48; N, 6.10.

6,7-Dihydro-6-(1,2-dihydro-2-oxoquinolin-3-yl)-[1,3]dioxolo[4,5-g]quinolin-8(5H)-one 3t

82% yield by approach (iii). Mp > 300 ºC. IR (KBr) ν: 3337 br (NH and NHCO overlapped), 1654 (C=O), 1608 (C=O), 1243 (OCH_2O) cm^{-1}. Adequate NMR spectra were not possible to obtain owing to its scarce solubility even in heated DMSO. EIMS (70 eV): *m/z* (%): 334 (46 [M^+]), 333 (100 [M – 1]), 190 (16, [M – C_9H_6NO]). Anal. Calcd. for $C_{19}H_{14}N_2O_4$ (334.33): C, 68.26; H, 4.22; N, 8.38. Found: C, 68.18; H, 4.31; 8.43.

ACKNOWLEDGEMENTS

RA thanks the "Fundación para la Promoción de la Investigación y la Tecnología (Banco de la República)" and the Universidad del Valle for financial support. PC thanks COLCIENCIAS for a doctoral fellowship. MN and JC thanks the Spanish "Consejería de Innovación, Ciencia y Empresa, Junta de Andalucía" and Servicios Técnicos de la Universidad de Jaén for financial support.

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Received: January 02, 2008 Revised: April 02, 2008 Accepted: April 03, 2008