Para Substituted Benzaldehydes as Expedient Reagents for the Oxidative Aromatization of Hydroquinoline

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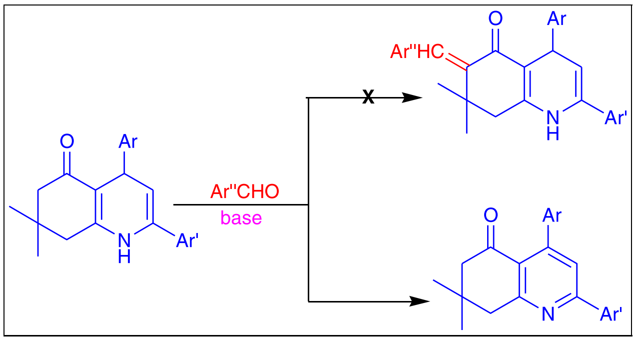

A Cannizzaro-type reaction of tetrahydro-5(1*H*)-quinolinones with para substituted benzaldehydes in the presence of a base formed the corresponding quinoline and aryl methanol rather than arylidene derivatives because of the oxidation of tetrahydroquinoline and reduction of benzaldehydes as a result of unprecedented hydride transfer from tetrahydroquinoline to arylaldehydes. The reaction proceeds best with the participation of substituents with +M effect in substrate molecule.

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INTRODUCTION

Literature survey reveals a plethora of protocols for oxidative aromatization of 1,4-dihydropyridines into the corresponding pyridines. Numerous oxidants were used in the aromatization of 1,4-dihydropyridines such as nitric acid [1,2], nitrous acid *in situ* formed by action of acids to $NaNO_2$ [3], nitrogen oxides [4], metallic nitrates [5], chromium(VI) oxidants [6], CrO_2 [7], manganesse and iron(III) salts [8], mercury(II) and Tl(III) salts [9], $SnCl_4$ [10], $Pb(OAc)_4$ [11], $K_2S_2O_8$ [12], S_8 [13], O_2 [14], I_2 [15], and hypervalent iodine reagents [16], and non-metallic oxidants [17], among others [18]. Some catalytical methods employing stoichiometric amount have been developed such as $RuCl_3/O_2$ [19], $Fe(ClO_4)_3/O_2$ [20], Pd/C [21], activated charcoal/O_2 [22], Co(II)naphthenate/O_2 [23], and $Co(OAc)_2/H_2O_2$ [24–26]. However, many of these systems suffer from disadvantages such as use of expensive transition metal oxidants, strong oxidative conditions, and tedious workup. We reported herein a new protocol for oxidative aromatization of tetrahydro-5(1*H*)-quinolinones **3** from readily available reactants, and this article should also be of practical value because the aromatization process will produce medicinally important quinoline moiety [27–29]. Moreover, they are valuable precursors [30] for the synthesis of medicinally important compounds such as nonsteroidal androgen receptor agonists [31], the antimalarial drug chloroquine [32], and martinellines with antibacterial activity [33].

RESULTS AND DISCUSSION

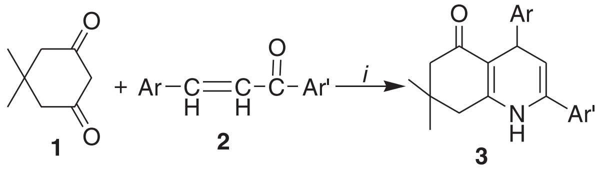
In pursuance of our interest in developing methods for the synthesis of new heterocylic systems having potential biological activities [34], we synthesized tetrahydro-5(1*H*)-quinolinones **3a–t**, by the treatment of dimedone with various chalcones **2** and ammonium acatate in the presence of catalytic amount of acetic acid according to the procedure reported in literature [35] (Scheme 1).

We planned to synthesize the arylidene derivative **4** by the reaction of the hydroquinolinone **3** with para substituted benzaldehydes and sodium acetate in acetic acid (Scheme 2) so as to install different heterocyclic moieties by exploiting the α,β-unsaturated carbonyl unit in the expected product **4**.

During the course of structural elucidation of the product formed in the reaction, we observed that the spectral data of the isolated product did not match with the expected structure **4** for the product. These data led us to assign structure **5** to a product, which is a quinolin-5-one derivative. Thus, according to this criterion, the following survey of results and discusssion is divided into two parts.

The first endeavor started on refluxing equimolar mixture of tetrahydro-5(1*H*)-quinolinones **3a** (Ar═Ar′═Ph), benzaldehyde, and sodium acetate in acetic acid with a view to procure the corresponding benzylidene derivative **4a** (Ar═Ar′═Ar″═Ph). The formation of benzylidene derivative **4a** was primarily ruled out on the basis of its mass and

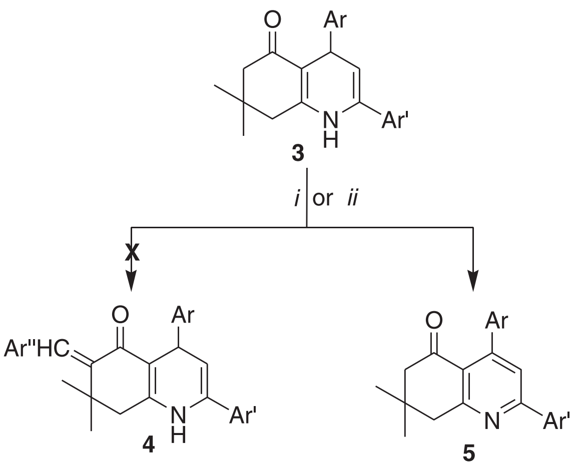
Scheme 1. Synthesis of tetrahydro-5(1*H*)-quinolinones **3a–t**.



i: NH_4OAc / EtOH, AcOH

Ar, Ar' = **a**:Ph, Ph; **b**: Ph, *p*-ClC_6H_4; **c**: Ph, *p*-$OMeC_6H_4$; **d**: Ph, *p*-BrC_6H_4; **e**: *p*-ClC_6H_4, Ph; **f**: *p*-ClC_6H_4, *p*-ClC_6H_4; **g**: *p*-ClC_6H_4, *p*-$OMeC_6H_4$; **h**: *p*-ClC_6H_4, *p*-BrC_6H_4; **i**: *p*-$OMeC_6H_4$, Ph; **j**: *p*-$OMeC_6H_4$, *p*-ClC_6H_4; **k**: *p*-$OMeC_6H_4$, *p*-$OMeC_6H_4$; **l**: *p*-$OMeC_6H_4$, *p*-BrC_6H_4; **m**: *p*-$NO_2C_6H_4$, Ph; **n**: *p*-$NO_2C_6H_4$, *p*-ClC_6H_4; **o**: *p*-$NO_2C_6H_4$, *p*-$OMeC_6H_4$; **p**: *p*-$NO_2C_6H_4$, *p*-BrC_6H_4; **q**: *p*-BrC_6H_4, Ph; **r**: *p*-BrC_6H_4, *p*-ClC_6H_4; **s**: *p*-BrC_6H_4, *p*-$OMeC_6H_4$; **t**: *p*-BrC_6H_4, *p*-BrC_6H_4;

Scheme 2. Synthesis of dihydro-5(6*H*)-quinolinones **5a–t** from **3a–t**.



i: NaOAc/AcOH, Ar''CHO; *ii*: NaOEt/EtOH, Ar''CHO

Ar, Ar' = **a**:Ph, Ph; **b**: Ph, *p*-ClC_6H_4; **c**: Ph, *p*-$OMeC_6H_4$; **d**: Ph, *p*-BrC_6H_4; **e**: *p*-ClC_6H_4, Ph; **f**: *p*-ClC_6H_4, *p*-ClC_6H_4; **g**: *p*-ClC_6H_4, *p*-$OMeC_6H_4$; **h**: *p*-ClC_6H_4, *p*-BrC_6H_4; **i**: *p*-$OMeC_6H_4$, Ph; **j**: *p*-$OMeC_6H_4$, *p*-ClC_6H_4; **k**: *p*-$OMeC_6H_4$, *p*-$OMeC_6H_4$; **l**: *p*-$OMeC_6H_4$, *p*-BrC_6H_4; **m**: *p*-$NO_2C_6H_4$, Ph; **n**: *p*-$NO_2C_6H_4$, *p*-ClC_6H_4; **o**: *p*-$NO_2C_6H_4$, *p*-$OMeC_6H_4$; **p**: *p*-$NO_2C_6H_4$, *p*-BrC_6H_4; **q**: *p*-BrC_6H_4, Ph; **r**: *p*-BrC_6H_4, *p*-ClC_6H_4; **s**: *p*-BrC_6H_4, *p*-$OMeC_6H_4$; **t**: *p*-BrC_6H_4, *p*-BrC_6H_4;
Ar'' = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$, *p*-$N(Me)_2C_6H_4$

elemental analyses. The mass spectra shows a peak at m/z 328, which is compatible with $[M+1]^+$ ion peak of quinolin-5-one **5a** (Ar=Ar′=Ph). Further, the structure **5a** for the product was supported by its IR spectrum with the dissappearence of –NH stretching frequency and a hypsochromic shift of carbonyl stretching frequency from 1656 to 1693 cm^{-1}, which eliminates the formation of exocyclic olefinic bond in conjugation with carbonyl function present in structure **4a**. The shifting of the C=O band to a higher-frequency region is due to the oxidative aromatization of the ring.

In ^1H NMR spectra, the disappearance of the double doublet, doublet, and two singlets at δ 5.30 (dd, 1H, C_3–H), 4.74 (d, 1H, C_4–H), 1.02 (s, 3H, Me), and 1.10 (s, 3H, Me) of **3a** and the appearance of four separate sharp singlets at 1.16 (s, 6H, 2×Me), 2.55 (s, 2H, C_6–H), 3.20 (s, 2H, C_8–H), and 7.51 (s, 1H, C_3–H) (Fig. 1) are agreeable to the structure **5a** as the product. Therefore, the tetrahydroquinolinone **3a**, instead of undergoing condensation with substituted benzaldehydes, undergoes a Cannizaro type of redox reaction with arylaldehydes in the presence of a base to form the corresponding dihydroquinoline and aryl methanol because of the oxidation of tetrahydroquinoline and reduction of arylaldehydes. This transformation is believed to proceed via unprecedented hydride shift from dihydroquinoline to arylaldehydes (Path A) (Scheme 3). The alternative mechanism (Path B) may also be possible for the formation of dihydroquinolinone **5** and aryl methanol. This anomalous result led us to carry out a series of experiments to ascertain the mechanism of the aromatization of the terahydroquinolinone **3**.

In the second criterion, we investigated the aforesaid reaction conditions with 1,4-dihydropyridine **6** and hydroquinoline **7** [35] (Scheme 4) in order to postulate a mechanism for the aromatization of tetrahydro-5(1*H*)-quinolinones **3** and substituent effect on this particular reaction.

In fact, in both cases, the starting materials were regenarated rather than achieving the expected aromatized products **8** and **9**. The possible explanation for this failure of the reaction is the steric effect of the carboethoxy group substituted at β position of the hydropyridine rings and phenyl ring at γ position.

In order to establish the role of benzaldehyde, we refluxed hydroquinoline **3** in acetic acid with stoichometric amount of sodium acatate with the aim of obtaining *in situ* oxidized hydroquinoline derivative **5**. However, this reaction resulted in the same starting hydroquinoline **3**, suggesting the necessity of an arylaldehyde for oxidation. Thus, the oxidative aromatization of **3** was unexpectedly successful as per the reaction condition illustrated in Scheme 2 on the basis of the mechanism demonstrated in Scheme 3.

Under similar reaction conditions, tetrahydropyrido[2,3-*d*]pyrimidin-4(1*H*)-one **11** (Scheme 5) underwent successful oxidative aromatization to afford **12** in good yield. The PMR spectrum of **11** in DMSO solution displayed two separate double doublet at δ 3.78 ($J_{6a,\ 6b}$ = 16.4 Hz, $J_{6a,\ 5}$ = 7.6 Hz) and 3.89 ($J_{6b,\ 6a}$ = 16.4 Hz, $J_{6b,\ 5}$ = 7.6 Hz) for each one proton at C_6 and a triplet at δ 4.74 (J = 7.6 Hz) for C_5–H indicating that pyridopyrimidine derivative **11** is in pyrido [2,3-*d*]pyrimidin-4(1*H*)-one **11′** form in DMSO (Fig. 2), whereas in PMR spectrum of **12**, two double doublets and a triplet disappeared and a singlet for C_3–H appeared at δ 8.03.

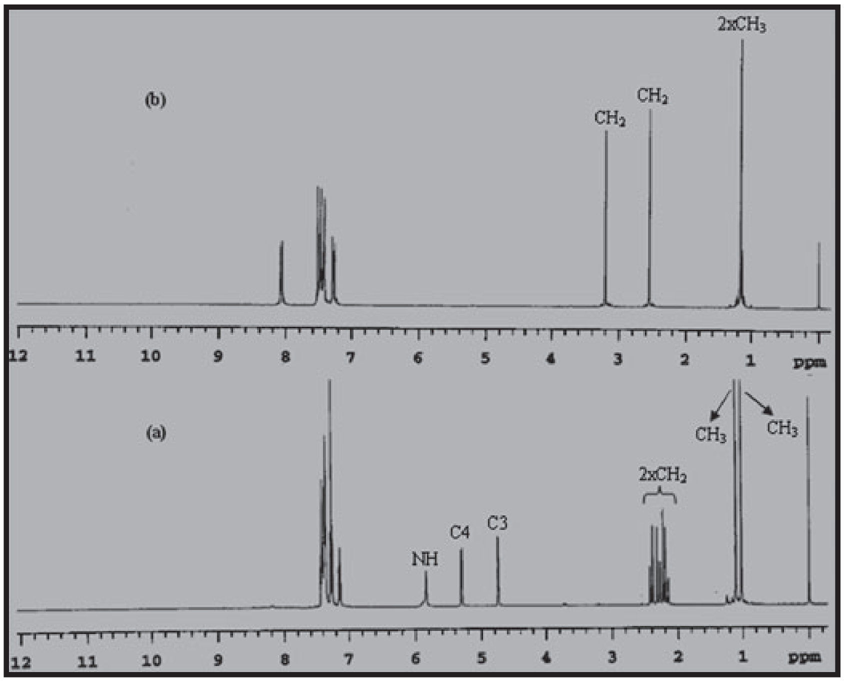
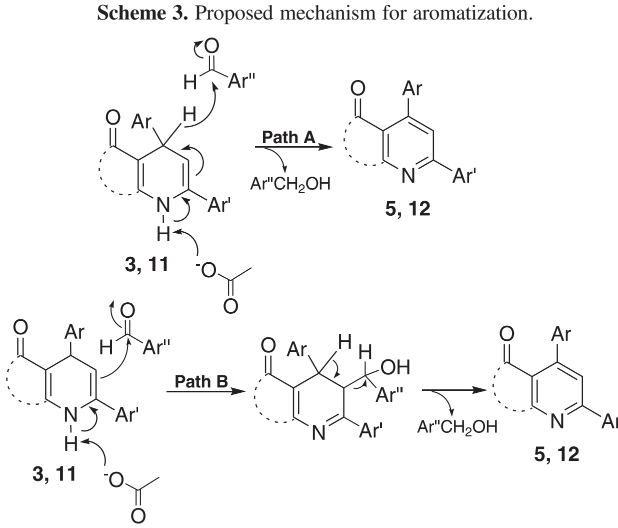
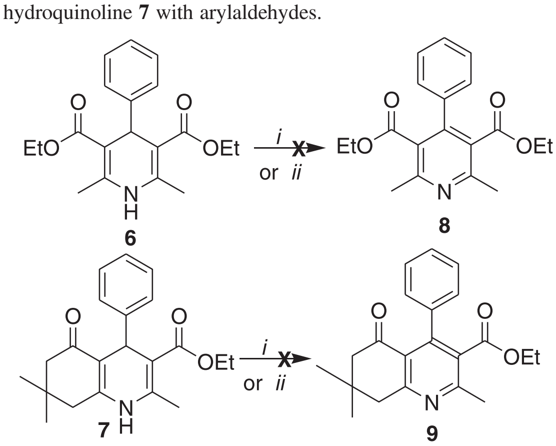


Figure 1. [1]H NMR spectra of (a) tetrahydro-5(1*H*)-quinolinone **3a**. (b) Dihydro-5(6*H*)-quinolinone **5a** in $CDCl_3$.

Scheme 3. Proposed mechanism for aromatization.



Scheme 4. Results for aromatization of 1,4-dihydropyridine **6** and hydroquinoline **7** with arylaldehydes.

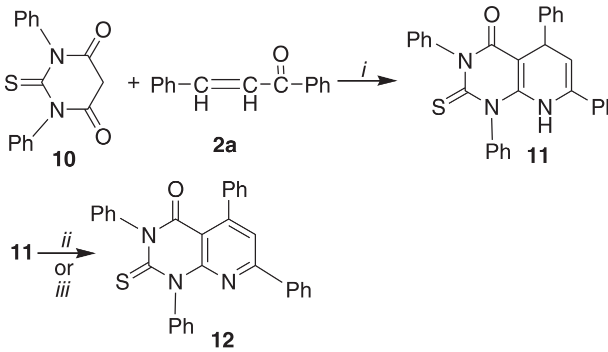


The strategies of this reaction also came out successfully with sodium ethoxide in ethanolic medium.

To investigate the scope of the substituent effect of this reaction, were explored various para substituted aryl groups in **3**. In general, all the reactions with different substituents were very clean, and the aromatized products were obtained in moderate to good yields; however, very low yield of the product was obtained in case of para nitrophenyl substituent (Table 1).

Inspection of Table 1 reveals that *p*-methoxyphenyl, *p*-chlorophenyl, *p*-bromophenyl, and phenyl groups at α position and *p*-chlorophenyl, *p*-bromophenyl, *p*-anisyl, and aryl at γ position of hydroquinolinone **3** bring about the oxidation reaction effectively in the presence of aryl aldehyde as an oxidant. The yield of the product is enhanced by the electron-releasing groups at para position of the benzene rings, whereas the electron withdrawing groups decrease the yield. The effectiveness of the reaction could be explained on the basis of +M effect of the substituents, and the order of the reactivity in para

Scheme 5. Aromatization of tetrahydropyrido[2,3-*d*] pyrimidin-4(1*H*)-one **11** to 2,3-dihydropyrido[2,3-*d*]pyrimidin-4(1*H*)-one **12**.



i: NH4OAc / EtOH, AcOH; *ii*: NaOAc/AcOH, PhCHO; *iii*: NaOEt/EtOH, PhCHO

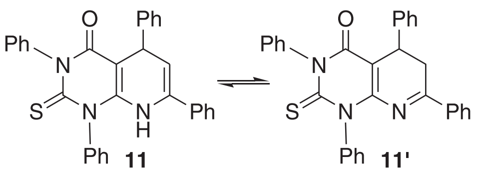


Figure 2. Amino imino tautomerism of pyridopyrimidine derivative **11**.

Table 1

Aromatization of hydroquinoline **3** to hydroquinoline **5**.

Entry	Ar	Ar′	Products	Yields[d] e/f/g/h/i
1.	Ph	Ph	(**5a**)[a]	53/52/59/20/30
2.	Ph	*p*-ClC_6H_4	(**5b**)[a]	59/58/61/13/32
3.	Ph	*p*-$OMeC_6H_4$	(**5c**)[a]	50/50/55/10/28
4.	Ph	*p*-BrC_6H_4	(**5d**)[a]	56/56/59/12/31
5.	*p*-ClC_6H_4	Ph	(**5e**)[a]	56/56/57/10/27
6.	*p*-ClC_6H_4	*p*-ClC_6H_4	(**5f**)[b]	43/42/45/8/22
7.	*p*-ClC_6H_4	*p*-$OMeC_6H_4$	(**5g**)[a]	60/59/61/20/35
8.	*p*-ClC_6H_4	*p*-BrC_6H_4	(**5h**)[b]	51/52/55/11/27
9.	*p*-$OMeC_6H_4$	Ph	(**5i**)[a]	53/51/55/10/25
10.	*p*-$OMeC_6H_4$	*p*-ClC_6H_4	(**5j**)[b]	52/54/56/12/22
11.	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	(**5k**)[a]	50/48/53/10/20
12.	*p*-$OMeC_6H_4$	*p*-BrC_6H_4	(**5l**)[a]	53/54/56/12/21
13.	*p*-$NO_2C_6H_4$	Ph	(**5m**)[a]	—
14.	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	(**5n**)[c]	—
15.	*p*-$NO_2C_6H_4$	*p*-$OMeC_6H_4$	(**5o**)[c]	—
16.	*p*-$NO_2C_6H_4$	*p*-BrC_6H_4	(**5p**)[c]	—
17.	*p*-BrC_6H_4	Ph	(**5q**)[a]	55/56/57/11/25
18.	*p*-BrC_6H_4	*p*-ClC_6H_4	(**5r**)[b]	47/44/50/12/23
19.	*p*-BrC_6H_4	*p*-$OMeC_6H_4$	(**5s**)[b]	56/57/59/18/29
20.	*p*-BrC_6H_4	*p*-BrC_6H_4	(**5t**)[b]	45/47/50/12/23

[a]Reactions were carried out for 8 h.
[b]Reactions were carried out for 10 h.
[c]Reactions were carried out for 13 h.
[d]Isolated yields. Isolated yield e: in the presence of benzaldehyde. f: in the presence of *p*-methoxybenzaldehyde. g: in the presence of *p*-chlorobenzaldehyde. h: in the presence of *p*-nitro benzaldehyde. i: in the presence of *p*-*N*,*N*-dimethyl amino benzaldehyde.

substituted aryl groups at α position of hydroquinoline is *p*-OMe > *p*-Cl > *p*-Br > H.

The efficacy of the oxidant has been further studied by using different *p*-substituted benzaldehydes such as *p*-*N*,*N*-dimethyl amino benzaldehyde, *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, *p*-nitrobenzaldehyde, and benzaldehyde. It has been observed that the substituents attached to para position of the benzene ring with –I effect increases the yield of the oxidized product, and the following order of reactivity of *p*-substituated benzaldehydes is given as *p*-Cl *p*-OMe ≈ H > *p*-N(Me)$_2$ > *p*-NO$_2$.

CONCLUSIONS

In summary, we have for the first time reported a new protocol for oxidative aromatization of tetrahydro-5(1*H*)-quinolinones **3** and tetrahydropyrido[2,3-*d*]pyrimidin-4(1*H*)-one **11** by using *p*-substituated benzaldehydes as oxidants. The yield of product basically depends on the substituents with +M effect attached to para position of benzene rings connected to the α and γ positions of hydroquinolinone moiety and the substituents with –I effect attached to the aryl aldehydes.

EXPERIMENTAL

General information. We took melting points in open capillaries by using sulfuric acid bath and are uncorrected. We checked purity of the products by TLC on silica gel G (BDH) by using toluene–ethyl acetate (4:1) as irrigant. We recorded IR spectra with a Shimadzu FTIR Prestige-21 spectrophotometer in potassium bromide (KBr) by using diffuse reflected spectra (DRS) technique. NMR spectra were recorded on a VARIAN 200 or 400 MHz (^{1}H, 200 or 400 MHz; ^{13}C, 100 MHz) and BRUKER AVANCE III 500 MHz (500 Hz for ^{1}H, 125 MHz for ^{13}C) NMR spectrometer in deuteriochloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6), unless otherwise stated. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The mass spectra were taken on API 2000 LC-MS mass spectrometer. Elemental analyses were performed by Flash 2000 CHN elemental analyzer and were in agreement with the calculated values within ±0.4%. All the reagents and solvents used were of the best grade available and were used without further purification. Literature methods were used for the preparation of chalcones **2** [36], diethyl 2, 6-dimethyl-4-phenyl-1, 4-dihydropyridine-3, 5-dicarboxylate **6** [35], ethyl 2, 7, 7-trimethyl-5-oxo-4-phenyl-1, 4, 5, 6, 7, 8-hexahydroquinoline-3-carboxylate**7** [35], and 1, 3-diphenylthiobarbituric acid **10** [37]. The appropriate time for the preparation and yield of the oxidative aromatized product **5** with the use of different arylaldehydes as oxidant are given in Table 1.

General procedure for 2,4-disubstituted 7,8-dihydroquinoline-5(1*H*)-ones (3a–t). To a solution of dimedone (0.28 g, 2 mmol) **1** and chalcone (2 mmol) **2** in ethanol (10 mL), ammonium acetate (3.06 g) and 3–4 drops of acetic acid were added and refluxed with stirring till solid product **3** occurred. The reaction mixture was allowed to cool, the solid product was filtered, and it was washed thoroughly with water and recrystallized from ethanol. We checked purity of the products by TLC on silica gel G (BDH) by using toluene–ethyl acetate (4:1) as irrigant.

4,6,7,8-Tetrahydro-7,7-dimethyl-2,4-diphenyl-5(1*H*)-quinolinone (3a) [38–41]. The reaction was carried out following the general procedure with chalcone **2a** (0.42 g, 2 mmol). The pale yellow solid product **3a** thus obtained after 10 min was filtered and recrystallized from ethanol. The yield was 65%. mp 213 °C. R_f: 0.38 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{23}NO$: C, 83.89; H, 6.99; N, 4.26. Found: C, 83.75; H, 6.63; N, 3.98.

4,6,7,8-Tetrahydro-2-(4-chlorophenyl)-7,7-dimethyl-4-phenyl-5(1*H*)-quinolinone (3b) [38,39]. The reaction was carried out following the general procedure with chalcone **2b** (0.48 g, 2 mmol). The pale yellow solid product **3b** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 66%. mp 220 °C. R_f: 0.35 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{22}NOCl$: C, 76.03; H, 6.06; N, 3.86. Found: C, 75.89; H, 5.74; N, 3.75.

4,6,7,8-Tetrahydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-phenyl-5(1*H*)-quinolinone (3c) [41]. The reaction was carried out following the general procedure with chalcone **2c** (0.48 g, 2 mmol). The yellow solid product **3c** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 55%. mp 208 °C. R_f: 0.28 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{24}H_{25}NO_2$: C, 80.22; H, 6.96; N, 3.90. Found: C, 79.98; H, 6.67; N, 3.84.

4,6,7,8-Tetrahydro-2-(4-bromophenyl)-7,7-dimethyl-4-phenyl-5(1*H*)-quinolinone (3d) [38–40]. The reaction was carried out following the general procedure with chalcone **2d** (0.57 g, 2 mmol). The yellow solid product **3d** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 62%. mp 266 °C. R_f: 0.26 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{22}NOBr$: C, 67.65; H, 5.39; N, 3.43. Found: C, 67.42; H, 5.14; N, 3.20.

4,6,7,8-Tetrahydro-4-(4-chlorophenyl)-7,7-dimethyl-2-phenyl-5(1*H*)-quinolinone (3e) [38–41]. The reaction was carried out following the general procedure with chalcone **2e** (0.48 g, 2 mmol). The pale yellow solid product **3e** thus obtained after 5 min was filtered and recrystallized from ethanol. The yield was 59%. mp 198 °C. R_f: 0.45 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{22}NOCl$: C, 76.03; H, 6.06; N, 3.86. Found: C, 75.78; H, 5.78; N, 3.72.

4,6,7,8-Tetrahydro-2,4-bis(4-chlorophenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3f). The reaction was carried out following the general procedure with chalcone **2f** (0.55 g, 2 mmol). The white solid product **3f** thus obtained after 15 min was filtered and recrystallized from ethanol. The yield was 69%. mp 250 °C. R_f: 0.45 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3336 (–NH), 3066 (–CH, Ar–H), 2949, 2870 (–CH, –CH_3), 1654 (C═O), 1487, 1587 (–C═C–, aromatic ring), 1388 (–C–N), 821 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.03 (s, 3H, Me), 1.12 (s, 3H, Me), 2.21–2.44 (m, 4H, 4H at C6 and C8), 4.72 (d, 1H, $J_{4,3}$ = 5.5 Hz, H-4), 5.23 (dd, 1H, $J_{3,4}$ = 5.5 Hz, $J_{3,NH}$ = 2 Hz, H-3), 5.71 (bs, 1H, NH), 7.22–7.58 (m, 8H, PhH) (H-4), 5.3 (dd, 1H, $J_{3,4}$ = 5.2 Hz, $J_{3,NH}$ = 2 Hz, H-3), 5.84 (bs, 1H, NH), 7.12–7.43 (m, 10H, PhH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.40 (Me), 29.35 (Me), 32.41 (C-7), 37.72 (C-8), 42 (C-6), 50.74 (C-4), 107 (C-3), 108.40 (═C–C═O), 147.65 (C-2), 150.70 (═C–NH), 126.03, 127.94, 128.55, 130.07, 131.05, 132.1, 136.50, 139.02 (eight peaks, Ph–C), 195.45 (C═O); ES-MS *m/z* 398 $[M+1]^+$ (16.05%), 361 (40.36%), 360 (95.68%), 252 (100%). *Anal.* Calcd for $C_{23}H_{21}NOCl_2$: C, 69.52; H, 5.29; N, 3.53. Found: C, 69.22; H, 5.24; N, 3.28.

4,6,7,8-Tetrahydro-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3g) [40]. The reaction was carried out following the general procedure with chalcone **2g** (0.54 g, 2 mmol). The yellow solid product **3g** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 50%. mp 230 °C. R_f: 0.30 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{24}H_{24}NOCl$: C, 76.39; H, 6.37; N, 3.71. Found: C, 76.10; H, 6.14; N, 3.46.

4,6,7,8-Tetrahydro-2-(4-bromophenyl)-4-(4-chlorophenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3h). The reaction was carried out following the general procedure with chalcone **2h** (0.64 g, 2 mmol). The white solid product **3h** thus obtained after 15 min was filtered and recrystallized from ethanol. The yield was 56%. mp 264 °C. R_f: 0.50 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3334 (–NH), 3080, 3032 (–CH, Ar–H), 2949, 2870 (–CH, –CH_3), 1651 (C═O), 1487, 1587 (–C═C–, aromatic ring), 1390 (–C–N), 821 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.03 (s, 3H, Me), 1.10 (s, 3H, Me), 2.21–2.44 (m, 4H, 4H at C6 and C8), 4.74 (d, 1H, $J_{4,3}$ = 5.5 Hz, H-4), 5.23 (dd, 1H, $J_{3,4}$ = 5.5 Hz, $J_{3,NH}$ = 2 Hz, H-3), 5.71 (bs, 1H, NH), 7.22–7.58 (m, 8H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27 (Me), 29.31 (Me), 31.96 (C-7), 37.70 (C-8), 42.01 (C-6), 50.72 (C-4), 107.04 (C-3), 108.42 (═C–C═O), 124.60, 126.35, 127.96, 128.95, 130.12, 131.24, 132.09, 136.57 (eight peaks, Ph–C), 147.60 (C-2), 150.68 (═C–NH), 195.56 (C═O). ES-MS *m/z* 443 $[M+1]^+$ (22.90%), 408 (67%), 328 (56.70%), 252 (100%). *Anal.* Calcd for $C_{23}H_{21}NOClBr$: C, 62.44; H, 4.75; N, 3.17. Found: C, 62.22; H, 4.49; N, 2.92.

4,6,7,8-Tetrahydro-4-(4-methoxyphenyl)-7,7-dimethyl-2-phenyl-5(1*H*)-quinolinone (3i) [39,41]. The reaction was carried out following the general procedure with chalcone **2i** (0.48 g, 2 mmol). The pale yellow solid product **3i** thus obtained after 10 min was filtered and recrystallized from ethanol. The yield was 42%. mp 204 °C. R_f: 0.26 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{24}H_{25}NO_2$: C, 80.22; H, 6.96; N, 3.90. Found: C, 79.98; H, 6.67; N, 3.84.

4,6,7,8-Tetrahydro-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3j). The reaction was carried out following the general procedure with chalcone **2j** (0.54 g, 2 mmol). The yellow solid product **3j** thus obtained after 15 min was filtered and recrystallized from ethanol. The yield was 53%. mp 230 °C. R_f: 0.35 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{24}H_{24}NO_2Cl$: C, 73.28; H, 6.11; N, 3.56. Found: C, 73.05; H, 5.85; N, 3.34.

4,6,7,8-Tetrahydro-2,4-bis(4-methoxyphenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3k) [40]. The reaction was carried out following the general procedure with chalcone **2k** (0.54 g, 2 mmol). The yellow solid product **3k** thus obtained after 10 min was filtered and recrystallized from ethanol. The yield was 42%. mp 204 °C. R_f: 0.23 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{25}H_{27}NO_3$: C, 77.12; H, 6.94; N, 3.60. Found: C, 76.95; H, 6.66; N, 3.55.

4,6,7,8-Tetrahydro-2-(4-bromophenyl)-4-(4-methoxyphenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3l). The reaction was carried out following the general procedure with chalcone **2l** (0.60 g, 2 mmol). The pale yellow solid product **3l** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 50%. mp 233 °C. R_f: 0.40 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3311 (–NH), 3068 (–CH, Ar–H), 2947, 2868 (–CH, –CH_3), 1656 (C═O), 1489, 1585 (–C═C–, aromatic ring), 1392 (–C–N), 825 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.03 (s, 3H, Me), 1.11 (s, 3H, Me), 2.11–2.46 (m, 4H, 4H at C6 and C8), 3.76 (s, 3H, –OMe), 4.85 (d, 1H, $J_{4,3}$ = 5 Hz, H-4), 5.20 (dd, 1H, $J_{3,4}$ = 5.2 Hz, $J_{3,NH}$ = 2 Hz, H-3), 5.79 (bs, 1H, NH), 7.32 (dd, 2H,

$J = 6.5$ Hz, $J = 2$ Hz, Ar–H), 7.36 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH), 7.47 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH), 8.10 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27 (Me), 29.29 (Me), 32.43 (C-7), 37.68 (C-8), 42.21 (C-6), 50.70 (C-4), 55 (OMe), 107.02 (C-3), 108.41 (═C–C═O), 119.09, 125.23, 128.95, 130.46, 131.92, 132.09, 134.53 (seven peaks, Ph–C), 147.63 (C-2), 150.71 (═C–NH), 155.03 (Ph–C), 195.95 (C═O). ES-MS *m/z* 439 $[M+1]^+$ (16.30%), 407 (25.28%), 327 (61.03%), 252 (100%). *Anal.* Calcd for $C_{24}H_{24}NO_2Br$: C, 65.75; H, 5.48; N, 3.20. Found: C, 65.54; H, 5.26; N, 2.94.

4,6,7,8-Tetrahydro-7,7-dimethyl-4-(4-nitrophenyl)-2-phenyl-5(1*H*)-quinolinone (3m) [39,41]. The reaction was carried out following the general procedure with chalcone **2m** (0.51 g, 2 mmol). The golden yellow solid product **3m** thus obtained after 40 min was filtered and recrystallized from acetic acid. The yield was 36%. mp 242 °C. R_f: 0.36 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{22}N_2O_3$: C, 73.80; H, 5.88; N, 7.49. Found: C, 73.57; H, 5.66; N, 7.29.

4,6,7,8-Tetrahydro-2-(4-chlorophenyl)-7,7-dimethyl-4-(4-nitrophenyl)-5(1*H*)-quinolinone (3n). The reaction was carried out following the general procedure with chalcone **2n** (0.57 g, 2 mmol). The golden yellow solid product **3n** thus obtained after 25 min was filtered and recrystallized from ethanol. The yield was 39%. mp 274 °C. R_f: 0.33 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3356 (–NH), 3068 (–CH, Ar–H), 2953, 2875 (–CH, –CH_3), 1654 (C═O), 1485, 1593 (–C═C–, aromatic ring), 1392 (–C–N), 1336 (–NO_2), 831 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.03 (s, 3H, Me), 1.14 (s, 3H, Me), 2.20 (d, 1H, $J_{8e,\ 8a} = 16.5$ Hz), 2.29 (d, 1H, $J_{8a,\ 8e} = 16.5$ Hz), 2.33 (d, 1H, $J_{6e,\ 6a} = 16.4$ Hz), 2.46 (d, 1H, $J_{6a,\ 6e} = 16.5$ Hz) (4H at C-6 and C8), 4.88 (d, 1H, $J_{4,\ 3} = 5$ Hz, H-4), 5.21 (dd, 1H, $J_{3,\ 4} = 5$ Hz, $J_{3,\ NH} = 2$ Hz, H-3), 5.75 (bs, 1H, NH), 7.36–8.15 (m, 8H, PhH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.03 (Me), 28.99 (Me), 32.42 (C-7), 37.62 (C-8), 42.16 (C-6), 50.71 (C-4), 107 (C-3), 108.40 (═C–C═O), 122, 127.49, 128.65, 131.21, 132.57, 134.08 (six peaks, Ph–C), 145 (Ph–C), 146.35 (Ph–C), 147.61 (C-2), 150.99 (═C–NH), 195.06 (C═O). ES-MS *m/z* 407 (5.55%), 406 (19.75%), 405 (41.36%), 404 (100%), 403 (48.15%), 189 (55.56%). *Anal.* Calcd for $C_{23}H_{21}N_2O_3Cl$: C, 67.65; H, 5.15; N, 6.86. Found: C, 67.34; H, 4.90; N, 6.67.

4,6,7,8-Tetrahydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-(4-nitrophenyl)-5(1*H*)-quinolinone (3o). The reaction was carried out following the general procedure with chalcone **2o** (0.56 g, 2 mmol). The golden yellow solid product **3o** thus obtained after 45 min was filtered and recrystallized from ethanol. The yield was 40%. mp 218 °C. R_f: 0.28 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3360, 3288 (–NH), 3074 (–CH, Ar–H), 2954, 2837 (–CH, –CH_3), 1658 (C═O), 1490, 1593 (–C═C–, aromatic ring), 1388 (–C–N), 1338 (–NO_2), 1186, 1033 (–C–O–C–), 829 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.02 (s, 3H, Me), 1.10 (s, 3H, Me), 2.11–2.46 (m, 4H, 4H at C6 and C8), 3.82 (s, 3H, –OMe), 4.87 (d, 1H, $J_{4,\ 3} = 5$ Hz, H-4), 5.20 (dd, 1H, $J_{3,\ 4} = 5$ Hz, $J_{3,\ NH} = 2$ Hz, H-3), 5.80 (bs, 1H, NH), 7.30 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH), 7.36 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH), 7.50 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH), 8.13 (dd, 2H, $J = 6.5$ Hz, $J = 2$ Hz, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.97 (Me), 28.56 (Me), 32.32 (C-7), 37.44 (C-8), 42.10 (C-6), 50.23 (C-4), 55 (OMe), 107 (C-3), 108.42 (═C–C═O), 120.01, 122, 127.53, 128.79, 130.99 (five peaks, Ph–C), 145.01 (Ph–C), 146.56 (Ph–C), 147.56 (C-2), 152.56 (═C–NH), 155.32 (Ph–C), 195.27 (C═O). ES-MS *m/z* 405 $[M+1]^+$ (19.90%), 373 (56.06%), 252 (100%). *Anal.* Calcd for $C_{24}H_{24}N_2O_4$: C, 71.29; H, 5.94; N, 6.93. Found: C, 71.06; H, 5.72; N, 6.68.

4,6,7,8-Tetrahydro-2-(4-bromophenyl)-7,7-dimethyl-4-(4-nitrophenyl)-5(1*H*)-quinolinone (3p) [40]. The reaction was carried out following the general procedure with chalcone **2p** (0.66 g, 2 mmol). The golden yellow solid product **3p** thus obtained after 55 min was filtered and recrystallized from ethanol. The yield was 42%. mp 272 °C. R_f: 0.33 (toluene/ethyl acetate, 4:1). *Anal.* Calcd for $C_{23}H_{21}N_2O_3Br$: C, 60.93; H, 4.64; N, 6.18. Found: C, 60.7; H, 4.41; N, 5.91.

4,6,7,8-Tetrahydro-4-(4-bromophenyl)-7,7-dimethyl-2-phenyl-5(1*H*)-quinolinone (3q). The reaction was carried out following the general procedure with chalcone **2q** (0.57 g, 2 mmol). The pale yellow solid product **3q** thus obtained after 25 min was filtered and recrystallized from ethanol. The yield was 60%. mp 260 °C. R_f: 0.28 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): 3230 (–NH), 3056 (–CH, Ar–H), 2956, 2861 (–CH, –CH_3), 1662 (C═O), 1496, 1583 (–C═C–, aromatic ring), 1383 (–C–N), 825 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (s, 3H, Me), 1.08 (s, 3H, Me), 2.07–2.36 (m, 4H, 4H at C6 and C8), 4.74 (d, 1H, $J_{4,\ 3} = 6.1$ Hz, H-4), 5.35 (dd, 1H, $J_{3,\ 4} = 6.1$ Hz, $J_{3,\ NH} = 2$ Hz, H-3), 5.96 (bs, 1H, NH), 7.10–7.41 (m, 9H, PhH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 28.01 (Me), 29.12 (Me), 34.34 (C-7), 40.99 (C-8), 43.92 (C-6), 53.65 (C-4), 108.15 (C-3), 110.13 (═C–C═O), 119.09, 128.99, 130.02, 131.05, 131.99, 132.44, 136.09, 138.23 (eight peaks, Ph–C), 147.46 (C-2), 153.127 (═C–NH), 196.42 (C═O). ES-MS *m/z* 409 $[M+1]^+$ (22.90%), 328 (46.07%), 253 (100%). *Anal.* Calcd for $C_{23}H_{22}NOBr$: C, 67.65; H, 5.39; N, 3.43. Found: C, 67.4; H, 5.19; N, 3.17.

4,6,7,8-Tetrahydro-4-(4-bromophenyl)-2-(4-chlorophenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3r). The reaction was carried out following the general procedure with chalcone **2r** (0.64 g, 2 mmol). The white solid product **3r** thus obtained after 15 min was filtered and recrystallized from ethanol. The yield was 67%. mp 250 °C. R_f: 0.48 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3339 (–NH), 3082, 3031 (–CH, Ar–H), 2949, 2873 (–CH, –CH_3), 1652 (C═O), 1485, 1587 (–C═C–, aromatic ring), 1391 (–C–N), 824 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.03 (s, 3H, Me), 1.12 (s, 3H, Me), 2.10 (d, 1H, $J_{8e,\ 8a} = 16.2$ Hz), 2.21 (d, 1H, $J_{8a,\ 8e} = 16.2$ Hz), 2.26 (d, 1H, $J_{6e,\ 6a} = 16.2$ Hz), 2.38 (d, 1H, $J_{6a,\ 6e} = 16.2$ Hz) (4H at C-6 and C-8), 4.76 (d, 1H, $J_{4,\ 3} = 5.2$ Hz, H-4), 5.25 (dd, 1H, $J_{3,\ 4} = 5.2$ Hz, $J_{3,\ NH} = 2$ Hz, H-3), 5.78 (bs, 1H, NH), 7.09–7.41 (m, 8H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.99 (Me), 30.04 (Me), 32 (C-7), 37.99 (C-8), 43.55 (C-6), 51.33 (C-4), 107.98 (C-3), 109.56 (═C–C═O), 120.22, 126.21, 127.92, 128.95, 131.22, 132.10, 135.24, 136.97 (eight peaks, Ph–C), 147.56 (C-2), 152.22 (═C–NH), 196.77 (C═O). ES-MS *m/z* 443 $[M+1]^+$ (21.34%), 362 (34.56%), 327 (56.89%), 252 (100%). *Anal.* Calcd for $C_{23}H_{21}NOClBr$: C, 62.44; H, 4.75; N, 3.17. Found: C, 62.21; H, 4.52; N, 2.95.

4,6,7,8-Tetrahydro-4-(4-bromophenyl)-2-(4-methoxyphenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3s). The reaction was carried out following the general procedure with chalcone **2s** (0.60 g, 2 mmol). The pale yellow solid product **3s** thus obtained after 20 min was filtered and recrystallized from ethanol. The yield was 52%. mp 223 °C. R_f: 0.41 (toluene/ethyl acetate, 4:1). IR (KBr, DRS): ν_{max} 3299 (–NH), 3065 (–CH, Ar–H), 2943, 2868 (–CH, –CH_3), 1654 (C═O), 1491, 1585 (–C═C–, aromatic ring), 1180, 1031 (–C–O–C–), 1390 (–C–N), 825 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.96 (s, 3H, Me), 1.08 (s, 3H, Me), 2.9–2.10 (m, 4H, 4H at C6 and C8), 3.70 (s, 3H, –OMe), 4.82 (d, 1H, $J_{4,3}$ = 5.2 Hz, H-4), 5.26 (dd, 1H, $J_{3,4}$ = 5.2 Hz, $J_{3,NH}$ = 2 Hz, H-3), 5.81 (bs, 1H, NH), 7.09–7.40 (m, 8H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.56 (Me), 29 (Me), 31.99 (C-7), 38.13 (C-8), 42.98 (C-6), 52.08 (C-4), 55.02 (OMe), 107.99 (C-3), 110.15 (=C–C=O), 119.21, 126.12, 128.95, 130.43, 131.90, 132.18, 134.55 (seven peaks, Ph–C), 147.56 (C-2), 151.25 (=C–NH), 155.15 (Ph–C), 196.05 (C=O). ES-MS *m/z* 439 $[M+1]^+$ (20.08%), 358 (45.23%), 328 (60.09%), 252 (100%). *Anal.* Calcd for $C_{24}H_{24}NO_2Br$: C, 65.75; H, 5.48; N, 3.20. Found: C, 65.52; H, 5.26; N, 2.95.

4,6,7,8-Tetrahydro-2,4-bis(4-bromophenyl)-7,7-dimethyl-5(1*H*)-quinolinone (3t) [40]. The reaction was carried for out following the general procedure with chalcone **2t** (0.73 g, 2 mmol). The pale yellow solid product **3t** thus obtained after 10 min was filtered and recrystallized from ethanol. The yield was 59%. *Anal.* Calcd for $C_{23}H_{21}NOBr_2$: C, 56.67; H, 4.31; N, 2.87. Found: C, 56.46; H, 4.08; N, 2.62.

General procedure for 7,7-dimethyl-2,4-diaryl-7,8-dihydroquinolin-5(6*H*)-one (5). To a solution of 2,4-disubstituted hydroquinolin-5(1*H*,4*H*,6*H*)-one (2 mmol) **3** in acetic acid (3 mL), anhydrous sodium acetate (2 mmol) and benzaldehyde (2 mmol) were added and refluxed on hot plate at 140 °C for appropriate time. The reaction mixture was allowed to cool at room temperature. The suspension was poured into ice-cold water and neutralized with sodium bicarbonate. We purified the gummy solid thus obtained by silica chromatography using toluene as eluent to give **5**.

7,8-Dihydro-7,7-dimethyl-2,4-diphenyl-5(6*H*)-quinolinone (5a) [42]. The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3a** (0.33 g, 1 mmol). We obtained the pale yellow solid product **5a** after purification by silica chromatography using toluene as eluent. mp 118 °C. R_f: 0.49. *Anal.* Calcd for $C_{23}H_{21}NO$: C, 84.40; H, 6.42; N, 4.28. Found: C, 84.17; H, 6.17; N, 4.07.

7,8-Dihydro-2-(4-chlorophenyl)-7,7-dimethyl-4-phenyl-5(6*H*)-quinolinone (5b). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3b** (0.36 g, 1 mmol). We obtained the pale yellow solid product **5b** after purification by silica chromatography using toluene as eluent. mp 154 °C. R_f: 0.42. IR (KBr, DRS): ν_{max} 3057, 2988 (Ar–H), 2872 (–CH, $-CH_3$ and $-CH_2$), 1697 (C=O), 1583 (–C=N), 1531, 1490 (–C=C–, aromatic ring), 837 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.65 (s, 6H, 2× Me), 2.49 (s, 2H, H-6), 3.20 (s, 2H, H-8), 7.30–7.50 (m, 9H, PhH), 7.57 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.90 (Me), 32.70 (C-7), 47.80 (C-8), 53.83 (C-6), 121.89 (C-3), 123.85 (=C–C=O), 127.23, 127.79, 128.11, 128.87, 130.15, 131.16, 136.10, 140.45 (eight peaks, Ph–C), 153.22 (C-4), 159.45 (=C–N=), 163.67 (C=N), 198.85 (C=O). ES-MS *m/z* 362 $[M+1]^+$ (54.07%), 326 (45.09%), 206 (100%). *Anal.* Calcd for $C_{23}H_{20}NOCl$: C, 76.45; H, 5.54; N, 3.88. Found: C, 76.20; H, 5.31; N, 3.64.

7,8-Dihydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-phenyl-5(6*H*)-quinolinone (5c). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3c** (0.36 g, 1 mmol). We obtained the pale yellow solid product **5c** after purification by silica chromatography using toluene as eluent. mp 165 °C. R_f: 0.49. IR (KBr, DRS): ν_{max} 3059, 2951 (–CH, Ar–H), 2864 (–CH, $-CH_3$ and $-CH_2$), 1681 (C=O), 1602, 1573 (–C=N), 1529, 1492 (–C=C–, aromatic ring), 1147, 1022 (–C–O–C–), 842 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.60 (s, 6H, 2× Me), 2.48 (s, 2H, H-6), 3.17 (s, 2H, H-8), 3.74 (s, 3H, –OMe), 7.20–7.44 (m, 9H, PhH), 7.52 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.56 (Me), 32.72 (C-7), 47.81 (C-8), 53.83 (C-6), 55.14 (OMe), 119.05 (Ph–C), 121.90 (C-3), 123.57 (=C–C=O), 127.27, 128.03, 128.11, 129.12, 131.16, 137.15 (six peaks, Ph–C), 157.56 (=C–N=), 158.43 (Ph–C), 163.52 (C=N), 198.80 (C=O). ES-MS *m/z* 358 $[M+1]^+$ (59.16%), 326 (43.09%), 250 (63.90%), 205 (100%). *Anal.* Calcd for $C_{24}H_{23}NO_2$: C, 80.67; H, 6.44; N, 3.92. Found: C, 80.44; H, 6.19; N, 3.69.

7,8-Dihydro-2-(4-bromophenyl)-7,7-dimethyl-4-phenyl-5(6*H*)-quinolinone (5d). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3d** (0.41 g, 1 mmol). We obtained the pale yellow solid product **5d** after purification by silica chromatography using toluene as eluent. mp 170 °C. R_f: 0.43. IR (KBr, DRS): ν_{max} 3064, 2976 (–CH, Ar–H), 2865 (–CH, $-CH_3$ and $-CH_2$), 1692 (C=O), 1571 (–C=N), 1531, 1492 (–C=C–, aromatic ring), 835 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.64 (s, 6H, 2× Me), 2.59 (s, 2H, H-6), 3.26 (s, 2H, H-8), 7.27–7.54 (m, 9H, PhH), 7.56 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.85 (Me), 32.76 (C-7), 47.85 (C-8), 52.99 (C-6), 121.89 (C-3), 122 (Ph–C), 123.87 (=C–C=O), 127.25, 128.11, 128.87, 129.02, 131.16, 134.13, 138.32 (seven peaks, Ph–C), 152.13 (C-4), 159.48 (=C–N=), 163.60 (C=N), 198.79 (C=O). ES-MS *m/z* 407 $[M+1]^+$ (58.09%), 206 (100%). *Anal.* Calcd for $C_{23}H_{20}NOBr$: C, 67.98; H, 4.93; N, 3.45. Found: C, 67.76; H, 4.68; N, 3.21.

7,8-Dihydro-4-(4-chlorophenyl)-7,7-dimethyl-2-phenyl-5(6*H*)-quinolinone (5e) [41]. The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3e** (0.36 g, 1 mmol). We obtained the pale yellow solid product **5e** after purification by silica chromatography using toluene as eluent. mp 156 °C. R_f: 0.40. *Anal.* Calcd for $C_{23}H_{20}NOCl$: C, 76.45; H, 5.54; N, 3.88. Found: C, 76.22; H, 5.29; N, 3.63.

7,8-Dihydro-2,4-bis(4-chlorophenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5f). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3f** (0.40 g, 1 mmol). We obtained the pale yellow solid product **5f** after purification by silica chromatography using toluene as eluent. mp 140 °C. R_f: 0.42. IR (KBr, DRS): ν_{max} 3064, 2956 (–CH, Ar–H), 2870 (–CH, $-CH_3$ and $-CH_2$), 1683 (C=O), 1581 (–C=N), 1531, 1489 (–C=C–, aromatic ring), 834 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.62 (s, 6H, 2× Me), 2.58 (s, 2H, H-6), 3.19 (s, 2H, H-8), 7.34–7.51 (m, 8H, PhH), 7.65 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.92 (Me), 32.71 (C-7), 47.81 (C-8), 53.69 (C-6), 121.21 (Ph–C), 121.65 (C-3), 123.78 (=C–C=O), 128.54, 128.99, 129.21, 130.23, 132.12, 135.32, 136.10 (seven peaks, Ph–C), 153.43 (C-4), 159.41 (=C–N=), 163.90 (C=N), 198.89 (C=O). ES-MS *m/z* 396 $[M+1]^+$ (30.6%), 325 (45.09%), 205 (100%). *Anal.* Calcd for $C_{23}H_{19}NOCl_2$: C, 69.87; H, 4.81; N, 3.54. Found: C, 69.64; H, 4.56; N, 3.33.

7,8-Dihydro-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5g). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3g** (0.38 g, 1 mmol). We obtained the pale yellow solid product **5g** after purification by silica chromatography using toluene as eluent. mp 145 °C. R_f: 0.48. IR (KBr, DRS): ν_{max} 3061, 2954 (–CH, Ar–H), 2868 (–CH, $-CH_3$, and $-CH_2$), 1685 (C=O), 1581 (–C=N), 1529, 1490 (–C=C–, aromatic ring), 1174, 1024 (–C–O–C–), 831 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55 (s, 6H, 2× Me), 2.47 (s, 2H, H-6), 3.18 (s, 2H, H-8), 3.82 (s, 3H, –OMe), 7.30–7.5 (m, 8H, PhH), 7.58 (s, 1H, H-3); ^{13}C NMR

($CDCl_3$, 100 MHz): δ 28.92 (Me), 32.56 (C-7), 47.82 (C-8), 51.99 (C-6), 55.6 (OMe), 119 (Ph–C), 122.01 (C-3), 123.53 (=C–C=O), 128.23, 128.69, 129.53, 129.67, 133.14, 136.27 (six peaks, Ph–C), 153.22 (C-4), 155.32 (Ph–C), 159.40 (=C–N=), 163.68 (C=N), 198.89 (C=O). ES-MS *m/z* 392 $[M+1]^+$ (53.05%), 206 (100%). *Anal.* Calcd for $C_{24}H_{22}NO_2Cl$: C, 73.66; H, 5.63; N, 3.58. Found: C, 73.43; H, 5.38; N, 3.33.

7,8-Dihydro-2-(4-bromophenyl)-4-(4-chlorophenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5h). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3h** (0.44 g, 1 mmol). We obtained the pale yellow solid product **5h** after purification by silica chromatography using toluene as eluent. mp 215 °C. R_f: 0.38. IR (KBr, DRS): ν_{max} 3068, 2954 (–CH str, Ar–H), 2868 (–CH, –CH_3, and –CH_2), 1683 (C=O), 1589 (–C=N), 1533, 1487 (–C=C–, aromatic ring), 826 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.48 (s, 6H, 2× Me), 2.48 (s, 2H, H-6), 3.18 (s, 2H, H-8), 7.28–7.55 (m, 9H, PhH, and H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.04 (Me), 32.55 (C-7), 47.65 (C-8), 53.76 (C-6), 121.02 (Ph–C), 21.71 (C-3), 123.65 (=C–C=O), 128.11, 129.81, 130.15, 132.21, 133.09, 135.32, 136.19 (seven peaks, Ph–C), 153.54 (C-4), 159.54 (=C–N=), 163.78 (C=N), 199 (C=O). ES-MS *m/z* 441 $[M+1]^+$ (54.86%), 326 (25.76%), 205 (100%). *Anal.* Calcd for $C_{23}H_{19}NOClBr$: C, 62.73; H, 4.32; N, 3.18. Found: C, 62.50; H, 4.07; N, 2.96.

7,8-Dihydro-4-(4-methoxyphenyl)-7,7-dimethyl-2-phenyl-5(6*H*)-quinolinone (5i). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3i** (0.36 g, 1 mmol). We obtained the pale yellow solid product **5i** after purification by silica chromatography using toluene as eluent. mp 148 °C. R_f: 0.49. IR (KBr, DRS): ν_{max} 3070, 2954 (–CH, Ar–H), 2868 (–CH, –CH_3, and –CH_2), 1691 (C=O), 1606, 1577 (–C=N), 1529, 1512 (–C=C–, aromatic ring), 1111, 1029 (–C–O–C–), 825 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.52 (s, 6H, 2× Me), 2.49 (s, 2H, H-6), 3.15 (s, 2H, H-8), 3.76 (s, 3H, –OMe), 7.11–7.43 (m, 10H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.95 (Me), 32.54 (C-7), 47.81 (C-8), 52.69 (C-6), 55.23 (OMe), 118 (Ph–C), 122.01 (C-3), 124.03 (=C–C=O), 127.41, 127.87, 128.21, 128.87, 131.32, 135.15 (six peaks, Ph–C), 154 (C-4), 159.32 (=C–N=), 160.45 (Ph–C), 163.88 (C=N), 198.96 (C=O). ES-MS *m/z* 358 $[M+1]^+$ (56.87%), 206 (100%). *Anal.* Calcd for $C_{24}H_{23}NO_2$: C, 80.67; H, 6.44; N, 3.92. Found: C, 80.47; H, 6.25; N, 3.69.

7,8-Dihydro-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5j). The reaction was carried out following the general procedure tetrahydro-5(1*H*)-quinolinone **3j** (0.39 g, 1 mmol). We obtained the pale yellow solid product **5j** after purification by silica chromatography using toluene as eluent. mp 136 °C. R_f: 0.51. IR (KBr, DRS): ν_{max} 3037 (–CH, Ar–H), 2870 (–CH, –CH_3, and –CH_2), 1683 (C=O), 1610, 1579 (–C=N), 1529, 1490 (–C=C–, aromatic ring), 1124, 1035 (–C–O–C–), 819 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.69 (s, 6H, 2× Me), 2.84 (s, 2H, H-6), 3.26 (s, 2H, H-8), 3.85 (s, 3H, –OMe), 7.31–7.51 (m, 9H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29 (Me), 32.65 (C-7), 48.03 (C-8), 53.89 (C-6), 55.6 (OMe), 119.05 (Ph–C), 121.98 (C-3), 123.76 (=C–C=O), 127.80, 128.23, 128.88, 130.15, 130.22, 134.15 (six peaks, Ph–C), 153.237 (C-4), 159.66 (=C–N=), 161.04 (Ph–C), 163.80 (C=N), 198.90 (C=O). ES-MS *m/z* 392 $[M+1]^+$ (40.09%), 325 (41.08%), 205 (100%). *Anal.* Calcd for $C_{24}H_{22}NO_2Cl$: C, 73.66; H, 5.63; N, 3.58. Found: C, 73.4; H, 5.42; N, 3.37.

7,8-Dihydro-2,4-bis(4-methoxyphenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5k). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3k** (0.39 g, 1 mmol). We obtained the pale yellow solid product **5k** after purification by silica chromatography using toluene as eluent. mp 206 °C. R_f: 0.49. IR (KBr, DRS): ν_{max} 3083, 2960 (–CH, Ar–H), 2968 (–CH, –CH_3, and –CH_2), 1685 (C=O), 1604, 1577 (–C=N), 1531, 1490 (–C=C–, aromatic ring), 1186, 1022 (–C–O–C–), 833 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.56 (s, 6H, 2× Me), 2.50 (s, 2H, H-6), 3.19 (s, 2H, H-8), 3.80 (s, 6H, –OMe), 7.19–7.46 (m, 9H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.87 (Me), 32.77 (C-7), 47.81 (C-8), 53.87 (C-6), 55.65 (OMe), 119.06 (Ph–C), 120.90 (Ph–C), 122 (C-3), 123.94 (=C–C=O), 128.37, 128.78, 129.10, 131.22 (four peaks, Ph–C), 153.27 (C-4), 159.40 (=C–N=), 159.99 (Ph–C), 161.02 (Ph–C), 163.59 (C=N), 199 (C=O). ES-MS *m/z* 388 $[M+1]^+$ (41.77%), 326 (56.65%), 205 (100%). *Anal.* Calcd for $C_{25}H_{25}NO_3$: C, 77.52; H, 6.46; N, 3.62. Found: C, 77.29; H, 6.24; N, 3.40.

7,8-Dihydro-2-(4-bromophenyl)-4-(4-methoxyphenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5l). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3l** (0.44 g, 1 mmol). We obtained the pale yellow solid product **5l** after purification by silica chromatography using toluene as eluent. mp 154 °C. R_f: 0.51. IR (KBr, DRS): ν_{max} 3077 (–CH, Ar–H), 2870 (–CH, –CH_3, and –CH_2), 1690 (C=O), 1573 (–C=N), 1529, 1492 (–C=C–, aromatic ring), 1175, 1019 (–C–O–C–), 823 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.63 (s, 6H, 2× Me), 2.50 (s, 2H, H-6), 3.20 (s, 2H, H-8), 3.77 (s, 3H, –OMe), 7.24–7.46 (m, 8H, PhH), 7.53 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.07 (Me), 32.88 (C-7), 48 (C-8), 53.89 (C-6), 55.09 (OMe), 120.04 (Ph–C), 121.78 (C-3), 123.86 (=C–C=O), 127.80, 128.09, 129.65, 130.15, 131.98, 135 (six peaks, Ph–C), 154 (C-4), 159.96 (=C–N=), 161.03 (Ph–C), 163.67 (C=N), 199.02 (C=O). ES-MS *m/z* 437 $[M+1]^+$ (43.09%), 206 (100%). *Anal.* Calcd for $C_{24}H_{22}NO_2Br$: C, 66.06; H, 5.05; N, 3.21. Found: C, 65.84; H, 4.86; N, 2.99.

7,8-Dihydro-7,7-dimethyl-4-(4-nitrophenyl)-2-phenyl-5(6*H*)-quinolinone (5m). The reaction was carried out following the general procedure with hydroquinolin-5(1*H*,4*H*,6*H*)-one **3m** (0.37 g, 1 mmol). The same starting compound **3m** was obtained instead of oxidized product **5m**.

7,8-Dihydro-2-(4-chlorophenyl)-7,7-dimethyl-4-(4-nitro phenyl)-5(6*H*)-quinolinone (5n). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3n** (0.40 g, 1 mmol). The same starting compound **3n** was obtained instead of oxidized product **5n**.

7,8-Dihydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-(4-nitro phenyl)-5(6*H*)-quinolinone (5o). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3o** (0.39 g, 1 mmol). The same starting compound **3o** was obtained instead of oxidized product **5o**.

7,8-Dihydro-2-(4-bromophenyl)-7,7-dimethyl-4-(4-nitro phenyl)-5(6*H*)-quinolinone (5p). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3p** (0.44 g, 1 mmol). The same starting compound **3p** was obtained instead of oxidized product **5p**.

7,8-Dihydro-4-(4-bromophenyl)-7,7-dimethyl-2-phenyl-5(6*H*)-quinolinone (5q). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3q** (0.45 g, 1 mmol). We obtained the pale yellow solid product

5q after purification by silica chromatography using toluene as eluent. mp 155 °C. R_f: 0.44. IR (KBr, DRS): ν_{max} 3066, 2961 (–CH, Ar–H), 2870 (–CH, $-CH_3$, and $-CH_2$), 1684 (C=O), 1573 (–C=N), 1521, 1489 (–C=C–, aromatic ring), 833 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55 (s, 6H, 2× Me), 2.43 (s, 2H, H-6), 3.20 (s, 2H, H-8), 7.15–7.46 (m, 9H, PhH), 7.50 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.91 (Me), 32.67 (C-7), 47.82 (C-8), 53.85 (C-6), 121.91 (C-3), 123.76 (=C–C=O), 127.20, 127.81, 128.21, 129.54, 130.06, 132.04, 135.43, 136.78 (eight peaks, Ph–C), 153.30 (C-4), 159.56 (=C–N=), 163.70 (C=N), 199 (C=O). ES-MS *m/z* 407 $[M+1]^+$ (52.33%), 206 (100%). *Anal.* Calcd for $C_{23}H_{20}NOBr$: C, 67.98; H, 4.93; N, 3.45. Found: C, 67.77; H, 4.71; N, 3.22.

7,8-Dihydro-4-(4-bromophenyl)-2-(4-chlorophenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5r). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3r** (0.44 g, 1 mmol). We obtained the pale yellow solid product **5r** after purification by silica chromatography using toluene as eluent. mp 193 °C. R_f: 0.41. IR (KBr, DRS): ν_{max} 3069 (–CH, Ar–H), 2873 (–CH, $-CH_3$, and $-CH_2$), 1683 (C=O), 1574 (–C=N), 1511, 1490 (–C=C–, aromatic ring), 830 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.59 (s, 6H, 2× Me), 2.50 (s, 2H, H-6), 3.18 (s, 2H, H-8), 7.22–7.50 (m, 9H, PhH, and H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.99 (Me), 32.75 (C-7), 47.81 (C-8), 53.83 (C-6), 121.91 (C-3), 123.86 (=C–C=O), 124.01, 128.21, 129.20, 129.65, 130.15, 131.96, 134.14, 137 (eight peaks, Ph–C), 153.31 (C-4), 159.64 (=C–N=), 164 (C=N), 198.96 (C=O). ES-MS *m/z* 441 $[M+1]^+$ (55.01%), 325 (45.09%), 205 (100%). *Anal.* Calcd for $C_{23}H_{19}NOClBr$: C, 62.73; H, 4.32; N, 3.18. Found: C, 62.50; H, 4.07; N, 2.95.

7,8-Dihydro-4-(4-bromophenyl)-2-(4-methoxyphenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5s). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3s** (0.44 g, 1 mmol). We obtained the pale yellow solid product **3s** after purification by silica chromatography using toluene as eluent. mp 139 °C. R_f: 0.48. IR (KBr, DRS): ν_{max} 3059, 2962 (–CH, Ar–H), 2870 (–CH, $-CH_3$, and $-CH_2$), 1685 (C=O), 1571 (–C=N), 1511, 1485 (–C=C–, aromatic ring), 1156, 1024 (–C–O–C–), 839 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.61 (s, 6H, 2× Me), 2.57 (s, 2H, H-6), 3.22 (s, 2H, H-8), 3.82 (s, 3H, –OMe), 7.19–7.50 (m, 8H, PhH), 7.54 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.05 (Me), 32.95 (C-7), 48 (C-8), 53.89 (C-6), 55.21 (OMe), 120 (Ph–C), 122.01 (C-3), 123.99 (=C–C=O), 124.29 (Ph–C), 128.10, 128.88, 129.25, 130.15, 131.99, 136.22 (six peaks, Ph–C), 153.24 (C-4), 158.23 (Ph–C), 160.12 (=C–N=), 163.65 (C=N), 199.06 (C=O). ES-MS *m/z* 437 $[M+1]^+$ (55.87%), 205 (100%). *Anal.* Calcd for $C_{24}H_{22}NO_2Br$: C, 66.06; H, 5.05; N, 3.21. Found: C, 65.81; H, 4.83; N, 2.98.

7,8-Dihydro-2,4-bis(4-bromophenyl)-7,7-dimethyl-5(6*H*)-quinolinone (5t). The reaction was carried out following the general procedure with tetrahydro-5(1*H*)-quinolinone **3t** (0.49 g, 1 mmol). We obtained the pale yellow solid product **5t** after purification by silica chromatography using toluene as eluent. mp 185 °C. R_f: 0.38. IR (KBr, DRS): ν_{max} 3076 (–CH, Ar–H), 2961 (–CH, $-CH_3$, and $-CH_2$), 1686 (C=O), 1570 (–C=N), 1519, 1492 (–C=C–, aromatic ring), 835 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.60 (s, 6H, 2× Me), 2.49 (s, 2H, H-6), 3.19 (s, 2H, H-8), 7.29–7.54 (m, 9H, PhH, and H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.97 (Me), 32.81 (C-7), 47.84 (C-8), 53.94 (C-6), 121.92 (C-3), 122 (Ph–C), 123.85 (=C–C=O), 124.21, 128.23, 129.21, 129.88, 132.04, 134.90, 136.64 (seven peaks, Ph–C), 153.52 (C-4), 159.65 (=C–N=), 164.06 (C=N), 198.98 (C=O). ES-MS *m/z* 486 $[M+1]^+$ (59.08%), 325 (44.67%), 206 (100%). *Anal.* Calcd for $C_{23}H_{19}NOBr_2$: C, 56.91; H, 3.92; N, 2.89. Found: C, 56.69; H, 3.71; N, 2.64.

2,3,5,8-Tetrahydro-1,3,5,7-tetraphenyl-2-thioxopyrido[2,3-*d*]pyrimidin-4(1*H*)-one (11). To a solution of 1, 3-diphenylthiobarbituric acid (0.60 g, 2 mmol) **10** and chalcone (0.42 g, 2 mmol) **2a** in ethanol (20 mL), ammonium acetate (3.08 g) and two drops of acetic acid was added. The reaction mixture was stirred under reflux for 4 h. The reaction mixture was cooled and poured into ice-cold water. The pale yellow solid **11** thus obtained was filtered, washed, dried, and recrystallized from ethanol. The yield was 65%. mp 175 °C. R_f: 0.33. IR (KBr, DRS): ν_{max} 3147 (N-H), 1662 (C=O), 1593, 1568 (–C=C–, aromatic ring), 1298 (C=S) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.78 (dd, 1H, $J_{6a,\ 6b}=16.4$ Hz, $J_{6a,\ 5}=7.6$ Hz, H-6), 3.89 (dd, 1H, $J_{6b,\ 6a}=16.4$ Hz, $J_{6b,\ 5}=7.6$ Hz, H-6), 4.74 (t, 1H, $J=7.6$ Hz, H-5), 6.94–8.35 (m, 20H, PhH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 49 (C-5), 84 (=C–C=O), 100.01 (C-6), 121 (Ph–C), 123.10 (Ph–C), 124.21 (Ph–C), 125.6 (Ph–C), 126.09 (Ph–C), 127.21 (Ph–C), 128.62–129.02 (closely spaced six peaks), 131.99 (Ph–C), 134.03 (Ph–C), 134.65 (Ph–C), 142.43 (Ph–C), 146.23 (C-7), 152 (=C–NH), 171 (C=O), 193 (C=S). ES-MS *m/z* 486 $[M+1]^+$ (59.08%). *Anal.* Calcd for $C_{31}H_{23}N_3OS$: C, 76.70; H, 4.74; N, 8.66. Found: C, 76.33; H, 4.56; N, 8.34.

2,3-Dihydro-1,3,5,7-tetraphenyl-2-thioxopyrido[2,3-*d*]pyrimidin-4(1*H*)-one (12). To a solution of 2-thioxopyrido[2,3-*d*]pyrimidin-4(1*H*)-one (0.98 g, 2 mmol) **11** in acetic acid (2 mL), anhydrous sodium acetate (2 mmol) and arylaldehyde (2 mmol) were added and refluxed on hot plate at 140 °C for 5 h. The reaction mixture was cooled and poured into ice-cold water. The solid thus obtained was filtered, washed, and dried. We obtained The pale yellow solid product **12** after purification by silica chromatography using toluene as eluent. The yield was 57%. mp 213 °C. R_f: 0.38. IR (KBr, DRS): ν_{max} 3059, 3028 (–CH, Ar–H), 1689 (C=O), 1597 (–C=N), 1543, 1490 (–C=C–, aromatic ring). ^{1}H NMR (500 MHz, $CDCl_3$): (δ) 7.06–7.91 (m, 20H, PhH), 8.03 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 105 (=C–C=O), 110.21 (C-6), 122.02 (Ph–C), 123.22 (Ph–C), 124.4 (Ph–C), 125.71 (Ph–C), 126.67 (Ph–C), 127.18 (Ph–C), 128.64–129.02 (closely spaced six peaks), 131.94 (Ph–C), 134 (Ph–C), 134.54 (Ph–C), 142.03 (Ph–C), 149.13 (C-7), 152.10 (C-5), 164.23 (=C–NH), 172.12 (C=O), 193.13 (C=S). ES-MS *m/z* 484 $[M+1]^+$ (56.98%). *Anal.* Calcd for $C_{31}H_{21}N_3OS$: C, 77.02; H, 4.35; N, 8.70. Found: C, 76.78; H, 4.10; N, 8.47.

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