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RAPID COMMUNICATION

Synthesis of Quinolone Substituted Pyrazoles, Isoxazoles and Pyridines as a Potential Blue Luminophors

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Abstract Series of quinolone C_3-substituted pyrazolines, isoxazolines, pyridines and pyrimidines were synthesized in good yields by the cyclocondensation reactions of 1, 2-unsaturated ketones and hydrazines, hydroxylamine hydrochloride and dimedone respectively. The quinolone derivatives (3, 5 and 7) were synthesized and further studied for their photophysical properties. High absorption and quantum yield are found for N_1-phenyl and $C_{3,4}$-dimethoxy substituents on phenyl ring (3h). Energy optimization by PM6 methods showed high stability required for selection of suitable candidates to be use as future blue emitters.

Keywords Dihydropyrazoles · Isoxazoles · Pyridines · Absorption and emission · Quantum yields · Heat of formation · HOMO-LUMO

Introduction

Until the 1950s, fluorescence was merely recognized as an 'odd' physical or physico-chemical phenomenon. However, during the last 50 years, the interest in the application of fluorescent molecules has steadily, sometimes even dramatically, increased and today fluorescent dyes play important role in many aspects of modern life [1]. The oldest use of fluorescent dyes probably represents the coloration of textile goods. More modern applications, to name a few, include optical brightness, which are practically colorless compounds that absorb in the near UV-region and emit in the far blue to violet part of the VIS spectrum, fluorescent pigments used as safety markings on cloth, fluorescent markers and probes, which are extremely important in analytical and medicinal chemistry. Interest in fluorescent dyes has been intensified mainly on analytical applications in biological sciences. Fluorescent compounds are widely used as markers in biochemical and nucleic acid technology is the subject of intensive investigations [2–4]. Recently, pyrazoloquinolines PQ (1*H*-pyrazolo [3,4-*b*] quinolines) are found to be highly fluorescent materials in the blue spectral region [5] as well as promising materials for electroluminescent applications [6, 7]. The substituents effects at different positions on fluorescent were studied on quinoline derivatives [8, 9], except the substituents effect at 3-position. The C_3-heterocyclic moiety explains the long wavelength fluorescing state due to twisted intermolecular charge transfer (TICT) state [10]. Hence, we designed heterocyclic moiety at 3-position on quinolone nucleus.

Recently, we have reported the synthesis of highly fluorescent dipyrazolo [3,4-*b*: 3,4-*d*] pyridines [11], pyrazolo [3,4-*b*]-pyrrolo-[2,3-*d*]-pyridines [12], 2,6-dirayl-4-alkoxy pyridinecarbonitriles [13, 14] and spiro-oxazino-quinolines [15]. These reports and our ongoing interest in this field prompted us to synthesize new carbostyril fluorescent heterocycles. In present communication, we report variety of quinolone C_3-substituted dihydropyrazole, isoxazole and pyridine derivatives and studied their fluorescence properties with the semiempirical study.

Results and discussion

The starting compound chalcones (**1**) are prepared by the known literature methods [16, 17], which on treatment with

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various hydrazines **2a–c** in presence of catalytic amount of acetic acid in alcohol afforded dihydropyrazoles **3** in 60–65% yields. Here, the 1, 3-Micheal addition reactions occurs by attack of NHR on β-enone carbon, followed by SN^2 displacement of hydroxyl group by NH_2 in presence of acid catalyst (Scheme 1). The ambident nucleophile, hydroxylamine hydrochloride **4** in the presence of sodium acetate in glacial acetic acid, more nucleophilic nitrogen attack on β-carbon of the enone **1** and yields isoxazole **5** in 60–65% yields (Scheme 2). The pyridines **7** obtained by the Dimroth rearrangement reaction of chalcones **1** with dimedone **6** in ammonium acetate in presence of catalytic amount of acetic acid. The reaction proceeds via pyrone intermediate followed by the incorporation of nitrogen with ring opening and closing protocol (Scheme 3). The structure of compound **3**, **5** and **7** were confirmed by the spectroscopic analysis. For example, the ^1H NMR spectrum of compound **3a** showed quartet (J=6.3 Hz) at δ 3.45 for one protons of C_3H group in dihydropyrazole, singlet at δ 3.55 for NCH_3, quartet (J=6.3 Hz) at δ 4.02 for C_3H proton and triplet at δ 4.85 for C_2H. The multiplet between 7.22 and 7.80 corresponded to four protons of benzene ring of quinolone in **3a**. The doublet appeared at δ 7.55 and δ 8.10 with coupling constant 8.3 Hz for aromatic proton of p-Cl-substituted aromatic ring. The mass spectrum of **3a** displayed a molecular ion peak m/z at 354, which was constituent with the molecular weight of **3a**. The structure of the other compounds **5** and **7** were established on the basis of spectroscopic and analytical data (experimental section). Spectroscopic data for chalcones **1a–d** were in agreement with the literature data [16, 17]. All the compounds are thermally stable up to 350°C (DSC scanning), hence useful for optoelectronic devices.

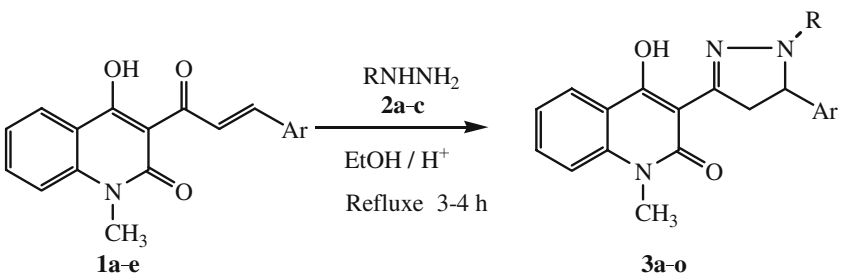
Photophysical study

The photophysical properties of compounds **3**, **5** and **7** were determined with respect to quinine sulphate which was used as a reference standard for the present study. Compounds **3**, **5** and **7** showed absorption and emission in near to visible region (Tables 1, 2 and 3).

A) **Photophysical properties of dihydropyrazole derivatives (3a–o)**: Electron acceptor chromophore quinolone and electron donor dihydropyrazole are linked together and showed pseudoaromatacity. Compound **3h** and **3i** having donor chromophores OCH_3 and 3,4-diOCH_3 on C_5-phenyl ring and N_1-phenyl group showed red-shift absorption maximum (**UVλ_{Max}/nm**) equal to 398, 415 nm, emission maximum (**Emλ_{Max}/nm**) equal to 478, 512 nm and quantum yields (Φ_F) 0.22, 0.24 respectively (Fig. 1). While, compound **3j** having acceptor C_4–NO_2 chromophores on phenyl ring showed large decrease in absorption (**UVλ_{Max}/nm**) and emission maximum (**Emλ_{Max}/nm**) to 361 and 431 nm and quantum yield (Φ_F) 0.17 (Table 1). The increasing order of absorption and emission maximum for N_1-substituted is $-CH_2CH_2OH$ < H < Ph, as in compounds **3d**, **3i** and **3n** respectively. This indicates that ethyl group at N_1 in dihydropyrazole (**3k–o**) showed hypsochromic shift, while phenyl groups showed bathochromic shift as compared with N_1H (**3a–e**). Compound with donor substituents showed lowest extension coefficient (e.g. **3i**=ε=8,990 cm^{-1}), showed high fluorescence maximum; while the compound with acceptor substituents (e.g. **3j**=ε=10,220 cm^{-1}), showed lower values of absorption, emission and quantum yields. Figure 2, indicates the fluorescence tubes of the compounds **3h** and **3i** respectively under the fluorescence lamp (Fig. 2).

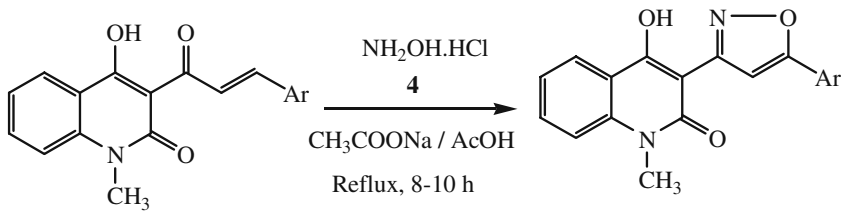
B) **Photophysical properties of isoxazole derivatives (5a–e):** The donor chromophores on C_5-aryl groups showed bathochromic shift in absorption and emission properties. e.g. compound **5c** and **5d** having C_4–OCH_3 and $C_{3,4}$–diOCH_3 chromophores showed absorption maximum (**UVλ_{Max}/nm**) to 375, 380 nm, emission maximum (**Emλ_{Max}/nm**) to 452, 474 nm and quantum yields are 0.21, 0.22 respectively (Table 2). The electron acceptor group on phenyl ring e.g. **5e**, showed lower values of absorption and emission maxima.

Scheme 1 Synthesis of quinolone dihydropyrazole derivatives



1a-e **3a-o**

Scheme 2 Synthesis of quinolone isoxazole derivatives



1a–e **5a–e**

C) **Photophysical properties of pyridine derivatives (7a–e)**: The compound **7d** having C_3, $_4$–diOCH_3 group, showed absorption maximum (**UVλ_{Max}/nm**) to 390 nm, emission maximum (**Emλ_{Max}/nm**) to 478 nm and quantum yield (ϕF) 0.21. While the acceptor chromophores **7e** showed absorption and emission maximum to (361 nm and 415 nm) and quantum yield (ϕF) 0.15 (Table 3).

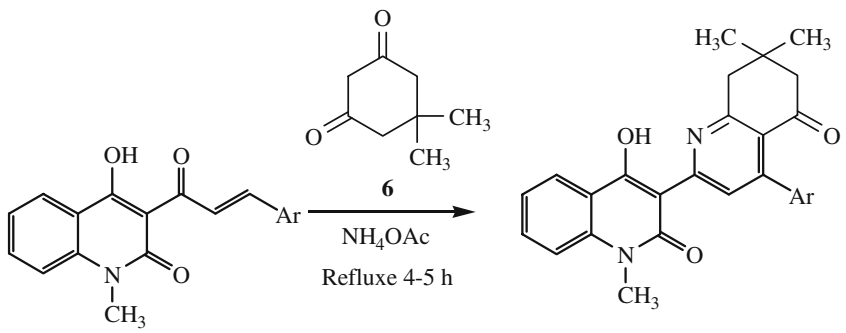
Semiempirical study

The theoretical model obtained by the energy optimization computational programme by PM6 (version 8.331, 2009) [18], showed that fluorescence properties are dependent on the heat of formation and GAP values of the compounds, e.g. compounds **3i** and **3h** showed higher, while **3j** and **3f** showed lower photophysical properties. The compounds **3i** and **3h** showed low GAP values equal to 7.080; 7.083 eV and heat of formation are −51.32 and −15.78 Kcal/mole, hence more thermally stable. While compound **3j** and **3f** showed GAP values about 7.953, 7.156 eV and heat of formation are −15.40, 14.72 Kcal/moles, showed high GAP vales and low heat of formation, hence less thermally stable. Therefore compound **3j** and **3f** has low absorption and emission properties. Similar trends were also observed for compound **5** and **7**. For example, compound **5d** and **5c** showed higher absorption and emission values, while compound **5e** showed lower absorption and emission maximum (Table 4).

Conclusion

In conclusion, we have described a novel and efficient method for the synthesis of quinoline substituted dihydropyrazole, isoxazole and pyridine derivatives. The electron donor chromophores on phenyl ring of the heterocyclic system showed high red shift absorption, while electron withdrawing chromophores showed blue-shift absorption. The semiempirical studied with the help of PM6 method, showed that compound having low GAP values i.e. high HOMO-LUMO energy and high heat of formation showed high fluorescence maximum. While, compound with high GAP values i.e. low HOMO-LUMO energy and low heat of formation showed lower shift to fluorescence maximum. The predicated hypothesis is found true for the observed values. The efficient blue light emission and physical and chemical stability makes these quinolone derivatives as a promising family of materials which may be useful in photophysical applications. The theoretical results obtained are in agreement with the HOMO, LUMO and heat of formation obtained by the semiempirical PM6 methods.

Scheme 3 Synthesis of quinolone pyridine derivatives



1a–e **7a–e**

Table 1 The absorbance ($UV\lambda_{Max}$/nm), emission ($Em\lambda_{Max}$/nm) and quantum yield (ϕ_F) of quinolone dihydropyrazole **3** were measured for 0.1 M Conc. in $CHCl_3$

Ar	Pyrazole	R	UV λ_{Max}/nm	Em λ_{Max}/nm	epsilon ε	ϕ_F
p-ClC_6H_4	**3a**	H	360	430	12,200	0.18
p-BrC_6H_4	**3b**	H	363	432	10,440	0.19
p-$OMeC_6H_4$	**3c**	H	372	445	9,940	0.20
3,4-di-$OMeC_6H_3$	**3d**	H	378	460	8,990	0.21
p-$NO_2C_6H_4$	**3e**	H	355	411	10,850	0.15
p-ClC_6H_4	**3f**	Ph	370	455	12,290	0.18
p-BrC_6H_4	**3g**	Ph	378	460	11,110	0.19
p-$OMeC_6H_4$	**3h**	Ph	398	478	**9,950**	**0.22**
3,4-di-$OMeC_6H_3$	**3i**	Ph	415	512	**8,990**	**0.24**
p-$NO_2C_6H_4$	**3j**	Ph	364	431	10,220	0.17
p-ClC_6H_4	**3k**	CH_2CH_2OH	355	422	12,320	0.16
p-BrC_6H_4	**3l**	CH_2CH_2OH	358	424	11,440	0.17
p-$OMeC_6H_4$	**3m**	CH_2CH_2OH	363	435	10,402	0.18
3,4-di-$OMeC_6H_3$	**3n**	CH_2CH_2OH	368	441	9,942	0.19
p-$NO_2C_6H_4$	**3o**	CH_2CH_2OH	342	408	9,960	0.15

Experimental

General

Melting points were determined on a Gallenkamp Melting Point Apparatus in open capillary tubes and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (300 MHz, 75 MHz respectively). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. The solvent for NMR spectra was deuteriochloroform ($CDCl_3$) or DMSO (d_6). Infrared spectra were taken on a Shimadzu IR-408, in potassium bromide pellets. The mass spectra were recorded on QP-2010s. UV spectra were recorded on a Shimadzu UV-1601 UV–VIS Spectrophotometer. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer (150-W Xe lamp), compounds for UV and fluorescence measurements were dissolved in chloroform ($CHCl_3$). UV and fluorescence scan were recorded from 200 to 600 nm. Determination of quantum yields: emission signals were set in relation to known area of the emission signal of quinine sulphate at pH 1. Elemental analyses were performed on a Hosli CH-Analyzer and are within ±0.3 of the theoretical percentages. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F_{254} (Merck) plates using UV light (254 and 366 nm) for detection. Column chromatography was carried out on silica gel (s.d. Fine Chemicals, 60–120 mesh powder). Starting materials were obtained from commercial suppliers and used without further purification. Common reagent-grade chemicals and staring materials are either commercially available and were used without further purification or prepared by standard literature procedures.

General Procedure for the 4, 5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl- quinolin-2-(1H)-one (3a–o) A mixture of chalcone **1** (0.01 mol), hydrazine hydrate *or* phenyl hydrazine *or* 2-hydroxyethylhydrazine **2a–c** (0.01 mol) in catalytic amount of acetic acid (0.5 mL) in ethanol (10 mL) were refluxed for 3–4 h. (TLC Check, toluene: acetone 8:2). The reaction mixture was cooled to room temperature and poured in ice-cold water (30 mL) and further stirred for 30 min. The obtained precipitated solid was filtered, washed with water, dried and recrystallized from ethanol to afford **3** in 50–65% yields.

3-[5-(4-Chlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl quinolin-2-(1H)-one (3a) Yield: 2.60 g, (65%), mp. 147–148°C (ethanol, yellow prism); IR (KBr): 3,484, 3,332, 1,677, 1,614, 1,520 cm^{-1}; ^1H NMR ($CDCl_3$)

Table 2 The absorbance ($UV\lambda_{Max}$/nm), emission ($Em\lambda_{Max}$/nm) and quantum yield (ϕ_F) of quinolone isoxazole **5** were measured for 0.1 M Conc. in $CHCl_3$

Ar	Isoxazole	$UV\lambda_{Max}$/nm	$Em\lambda_{Max}$/nm	epsilon ε	ϕ_F
p-ClC_6H_4	**5a**	365	418	10,440	0.19
p-BrC_6H_4	**5b**	368	422	8,960	0.19
p-$OMeC_6H_4$	**5c**	375	452	8,710	0.21
3,4-di-$OMeC_6H_3$	**5d**	380	474	8,980	**0.22**
p-$NO_2C_6H_4$	**5e**	356	409	10,400	0.16

Table 3 The absorbance ($UV\lambda_{Max}$/nm), emission ($Em\lambda_{Max}$/nm) and quantum yield (ϕ_F) of quinolone pyridines **7** were measured for 0.1 M Conc. in $CHCl_3$

Ar	Pyridine	$UV\lambda_{Max}$/nm	$Em\lambda_{Max}$/nm	epsilon ε	ϕ_F
p-ClC_6H_4	**7a**	371	432	9,520	0.18
p-BrC_6H_4	**7b**	376	436	10,600	0.19
p-$OMeC_6H_4$	**7c**	384	466	9,530	0.20
3,4-di-$OMeC_6H_3$	**7d**	390	478	8,820	**0.21**
p-$NO_2C_6H_4$	**7e**	361	415	12,010	0.15

δ=3.45(q, J=6.3 Hz, 1H, CH), 3.55(s, 3H, NCH_3), 4.02(q, J=6.5 Hz, 1H, CH), 4.85(t, J=6.5 Hz, 1H, CH), 7.22–7.40(m, 4H, ArH), 7.55(d, 2H, J=8.3 Hz, ArH), 8.10(d, 2H, J=8.3 Hz, ArH). MS (70ev): *m/z*=354.0[M+1]. Anal. Calcd for $C_{19}H_{16}ClN_3O_2$ (353.5): C, 64.50; H, 4.56; N, 11.88. Found: C, 64.80; H, 4.70; N, 11.80%.

3-[5-(4-Bromophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl quinolin-2-(1H)-one (3b) Yield 2.22 g, (62%), mp. 180–182°C (ethanol, yellow prism); IR (KBr): 3,558, 3,230, 1,671, 1,598, 1,515 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.52(q, J=5.8 Hz, 1H, CH), 3.80(s, 3H, NCH_3), 4.22(q, J=5.6 Hz, 1H, CH), 5.20(t, J=5.6 Hz, 1H, CH), 6.80–7.22 (m, 4H, ArH), 7.65(d, 2H, J=8.2 Hz, ArH). 8.08(d, 2H, J=8.2 Hz, ArH). Anal. Calcd. for $C_{19}H_{16}BrN_3O_2$ (398.00): C, 57.30; H, 4.05; N, 10.55. Found: C, 57.50; H, 4.07; N, 10.80.

3-[5-(4-Methoxyphenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl quinolin-2 (1H)-one (3c) Yield 2.10 g, (56%), mp. 174–178°C (ethanol, yellow prism); IR (KBr): 3,480, 3,122, 1,677, 1,590 cm^{-1}; ^1H NMR($CDCl_3$) δ=3.65 (s, 3H, NCH_3), 3.80(q, J=5.9 Hz, 1H, CH), 4.10(s, 3H, OCH_3), 4.30(q, J=6.1 Hz, 1H, CH), 5.20(t, J=6.1 Hz, 1H, CH), 6.80–7.22(m, 4H, ArH), 7.62(d, 2H, J=8.4 Hz, ArH), 8.05(d, 2H, J=8.4 Hz, ArH). Anal. Calcd for $C_{20}H_{19}N_3O_3$ (349.39): C, 68.75; H, 5.48; N, 12.03. Found: C, 68.80; H, 5.70; N, 11.80%.

3-[5-(3,4-Dimethoxyphenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl quinolin-2-(1H)-one (3d) Yield: 2.05 g, (65%), mp. 168–170°C (ethanol, yellow prism); IR (KBr): 3,380, 3,120, 1,667, 1,602, 1,508 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.50(q, J=6.4 Hz, 1H, CH), 3.60(s, 3H, NCH_3), 3.80(s, 6H, 2 × OCH_3), 4.06(q, J=6.2 Hz, 1H, CH), 4.81(t, J=6.4 Hz, 1H, CH), 6.90–7.22(m, 4H, Ar–H), 7.64(d, 2H, J=8.0 Hz, Ar–H), 8.12(d, 2H, J=8.0 Hz, ArH). ^{13}C (75 MHz, $CDCl_3$) δ 28, 44, 56, 60, 62, 108, 110, 112(s), 116, 118, 120, 122, 124, 132, 140, 148, 150, 156, 162, 165. Anal. Calcd for $C_{21}H_{21}N_3O_4$(379.42): C, 66.48; H, 5.58; N, 11.07. Found: C, 66.50; H, 5.70; N, 11.08%.

3-[5-(4-Nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-hydroxy-1-methyl quinolin-2-(1H)-one (3e) Yield: 1.80 g, (45%), mp. 171–172°C (ethanol, yellow prism); IR (KBr): 3,440, 3,315, 1,670, 1,610, 1,510 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.34(q, J=6.3 Hz, 1H, CH), 3.56(s, 3H, NCH_3), 4.08(q, J=6.5 Hz, 1H, CH), 4.66(t, J=6.5 Hz, 1H, CH), 6.85–7.35 (m, 4H, ArH), 7.45(d, 2H, J=8.3 Hz, ArH), 8.16(d, 2H, J=8.3 Hz, ArH). Anal. Calcd for $C_{19}H_{16}N_4O_4$ (364.12): C, 62.63; H, 4.43; N, 15.38. Found: C, 62.80; H, 4.63; N, 15.90%.

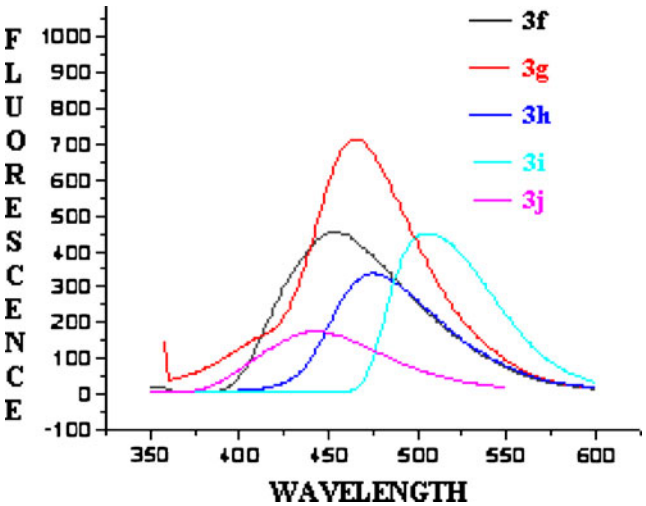


Fig. 1 Fluorescence spectra at room temperature of dihydropyrazole (**3f**–**3j**)

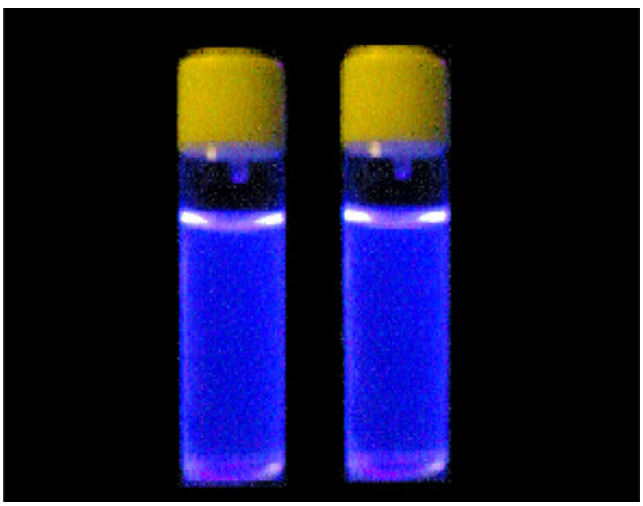


Fig. 2 The Fluorescence compounds **3h** and **3i** respectively under Fluorescence Lamp

Table 4 The molecular electronic properties (HOMO-LUMO energy, GAP) of the dihydropyrazole (**3a–o)** and isoxazole (**5a–e**)

Cmpd.	Ar	R^2	Heat of Formation (K CAL.)	Ionization Potential (eV)	HOMO (eV)	LUMO (eV)	GAP (eV)
3a	*p*-ClC_6H_4	H	−12.79	8.719	−8.719	−1.075	7.644
3b	*p*-BrC_6H_4	H	−0.869	8.734	−8.734	−1.082	7.652
3c	*p-O*MeC_6H_4	H	−45.57	8.451	−8.451	−0.939	7.600
3d	*3,4-di*OMeC_6H_3	H	−80.70	8.326	−8.326	−0.947	7.379
3e	*p*-$NO_2C_6H_4$	H	−2.592	9.432	−9.433	−1.510	7.923
3f	*p*-ClC_6H_4	Ph	14.72	8.290	−8.290	−1.134	7.156
3g	*p*-BrC_6H_4	Ph	26.71	8.303	−8.303	−1.141	7.162
3h	*p*-$OMeC_6H_4$	Ph	−15.78	8.113	−8.113	−1.030	7.083
3i	*3,4-di*$OMeC_6H_3$	Ph	−51.32	8.167	−8.167	−1.087	7.080
3j	*p*-$NO_2C_6H_4$	Ph	−15.40	9.437	−9.437	−1.484	7.953
3k	*p*-ClC_6H_4	CH_2CH_2OH	−61.12	9.104	−9.104	−1.240	7.864
3l	*p*-BrC_6H_4	CH_2CH_2OH	−41.16	8.863	−8.863	−1.112	7.751
3m	*p*-$OMeC_6H_4$	CH_2CH_2OH	−78.46	8.652	−8.652	−1.131	7.521
3n	*3,4-di*$OMeC_6H_3$	CH_2CH_2OH	−129.22	8.524	−8.524	−1.117	7.407
3o	*p*-$NO_2C_6H_4$	CH_2CH_2OH	−15.60	9.412	−9.412	−1.274	8.138
5a	*p*-ClC_6H_4	–	−40.09	9.005	−9.005	−1.180	7.818
5b	*p*-BrC_6H_4	–	−28.13	9.018	−9.018	−1.187	7.831
5c	*p*-$OMeC_6H_4$	–	−70.75	8.749	−8.749	−1.070	7.679
5d	*3,4-di*$OMeC_6H_3$	–	−105.25	8.343	−8.343	−1.084	7.259
5e	*p*-$NO_2C_6H_4$	–	−59.99	9.128	−9.129	−1.181	7.948

GAP = E_{LUMO}–E_{HOMO}

3-(5-(4-Chlorophenyl)-4,5-dihydro-1-phenyl-1H-pyrazol-3-yl)-4-hydroxy-1-methyl quinolin-2(1H)-one (3f) Yield: 2.15 g, (50%), mp 212–214°C (ethanol, yellow prism); IR (KBr): 3,441, 3,212, 1,665, 1,590, 1,503, 1,473, 1,423, 1,413 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60(s, 3H, NCH_3), 3.70 (q, J=6.3 Hz, 1H, CH), 4.20(q, J=6.1 Hz, 1H, CH), 5.10(t, J=6.3 Hz, 1H, CH), 6.80–7.15(m, 4H, ArH), 7.20–7.30(m, 5H, ArH), 7.70(d, 2H, J=8.20 Hz, ArH), 8.08(d, 2H, J= 8 Hz, ArH). MS (70 eV): *m/z*=352(M^+, 90%), 335(10%), 215(80%), 151(70%), 131(95%), 116(60%), 89(60%), 77 (100%). Anal. Calcd for $C_{25}H_{20}ClN_3O_2$ (429.5): C, 69.85; H, 4.69; N, 9.77. Found: C, 69.70; H, 4.70; N, 9.55%.

3-(5-(4-Bromophenyl)-4,5-dihydro-1-phenyl-1H-pyrazol-3-yl)-4-hydroxy-1-methyl quinolin-2(1H)-one(3g) Yield: 2.30 g (58%), mp. 220–222°C. IR (KBr): 3,464, 3,180, 1,666, 1,604, 1,502, 1,430 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60 (s, 3H, NCH_3), 3.70(q, 1H, J=6.2 Hz, CH), 4.25(q, J= 6.3 Hz, 1H, CH), 5.20(t, J=6.3 Hz, 1H, CH), 6.80–7.01(m, 4H, ArH), 7.20–7.40(m, 5H, ArH), 7.55(d, 2H, J=8.2 Hz, ArH), 8.15(d, 2H, J=8.2 Hz, ArH), 9.10(bs, 1H, OH). Anal. Calcd. for $C_{25}H_{20}BrN_3O_2$ (474.0): C, 63.30; H, 4.25; N, 8.86. Found: C, 63.50; H, 4.02; N, 8.90%.

3-(5-(4-Methoxyphenyl)-4,5-dihydro-1-phenyl-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (3h) Yield: 2.40 g (60%). mp. 226–228°C (ethanol, yellow prism); IR (KBr): 3,502, 3,190, 1,676, 1,605, 1,540 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.52(s, 3H, NCH_3), 3.55(s, 3H. OCH_3), 3.60(q, J=6.1 Hz, 1H, CH), 4.04(q, J=6.2 Hz, 1H, CH), 4.82(t, J= 6.2 Hz, 1H, CH), 6.75–6.90(m, 4H, ArH), 7.20–7.30(m, 5H, ArH), 7.60(d, 2H, J=8.3 Hz, ArH), 8.10(d, 2H, J= 8.3 Hz, ArH). Anal. Calcd for $C_{26}H_{23}N_3O_3$ (425.49): C, 73.40; H, 5.45; N, 9.88. Found: C, 73.45; H, 5.70; N, 9.38%.

3-(5-(4-Dimethoxyphenyl)-4,5-dihydro-1-phenyl-1H-pyrazol-3-yl)-4-hydroxy-1-methyl- quinolin-2(1H)-one (3i) Yield 2.25 g (56%); mp. 248–250°C (ethanol, yellow prism). IR (KBr): 3,488, 3,192, 1,644, 1,607 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.58(s, 3H, NCH_3), 3.62(q, J=5.6 Hz, 1H, CH), 3.80–3.88(s, 6H, 2 × OCH_3), 4.28(q, J=5.9 Hz, 1H, CH), 5.15(d, J=5.91 Hz, 1H, CH), 6.95–7.28(m, 4H, ArH), 7.20–7.35 (m, 5H, ArH), 7.55(d, 2H, J=8.1 Hz, ArH). 8.15(d, 2H, J= 8.1 Hz, ArH), 9.15(bs, 1H, OH). ^{13}C (75 MHz, $CDCl_3$) δ= 30, 46, 56 (s), 64 (s), 104, 108, 112(s), 114(s), 118, 119, 120, 122, 125, 130, 132, 136, 140, 144, 148, 149, 151, 160, 162. MS (70 eV): *m/z*=455(M^+, 90%), 424(10%), 396 (10%), 364(15%), 318(98%), 304(20%), 228(40%), 134 (50%), 104(60%), 91(95%), 77(100%). Anal. Calcd. for $C_{27}H_{25}N_3O_4$ (455.52): C, 71.19; H, 5.53; N, 9.22. Found: C, 71.32; H, 5.44; N, 9.40%.

3-(5-(4-Nitrophenyl)-4,5-dihydro-1-phenyl-1H-pyrazol-3-yl)-4-hydroxy-1-methyl quinolin-2(1H)-one(3j) Yield: 1.70 g (40%), mp. 212–213°C. IR (KBr): 3,460, 3,182, 1,660, 1,588, 1,510, 1,415 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.40 (s, 3H, NCH_3), 3.70(q, 1H, J=6.2 Hz, CH), 4.12(q, J= 6.3 Hz, 1H, CH), 5.02(t, J=6.3 Hz, 1H, CH), 6.80–7.10(m, 4H, ArH), 7.25–7.45(m, 5H, ArH), 7.60(d, 2H, J=8.2 Hz, ArH), 8.22(d, 2H, J=8.2 Hz, ArH), 9.10(bs, 1H, OH). Anal. Calcd. for $C_{25}H_{20}N_4O_4$ (440.15): C, 68.17; H, 4.58; N, 12.72. Found: C, 68.40; H, 4.32; N, 12.90%.

3-(5-(4-Chlorophenyl)-4,5-dihydro-1-(2-hydroxyethyl)-1H-pyrazol-3-yl)-4-hydroxy -1-methylquinolin-2(1H)-one (3k) Yield 2.15 g (60%); mp. 190–192°C (ethanol, yellow prism); IR (KBr): 3,522, 3,125, 1,674, 1,610, and 1,501 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.81(t, J=7.1 Hz, 2H, CH_2), 3.5(s, 3H, NCH_3), 3.86(t, J=6.7 Hz, 2H, CH_2), 4.01 (dd, J=7.6 & 6.5 Hz, 1H, CH), 4.32(dd, J=7.6 Hz & 6.5 Hz, 1H, $CH_{pyrazole}$), 4.80(dd, J=7.8 & 6.5 Hz, 1H, $CH_{pyrazole}$), 6.98–7.22(m, 4H, ArH), 7.62(d, 2H, J=7.8 Hz, ArH). 8.12(d, 2H, J=7.8 Hz, ArH). Anal. Calcd. for $C_{21}H_{20}ClN_3O_3$(397.86): C, 63.40; H, 5.07; N, 10.56. Found: C, 63.50; H, 5.10; N, 10.70%.

3-(5-(4-Bromophenyl)-4,5-dihydro-1-(2-hydroxyethyl)-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (3l) Yield: 2.40 g (64%), mp. 186–188°C (ethanol, yellow prism); IR (KBr): 3,512, 3,195, 1,678, 1,605, 1,530 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77(t, J=6.4 Hz, 2H, CH_2), 3.45(s, 3H, NCH_3), 3.66(t, J=6.4 Hz, 2H, CH_2), 3.92(dd, J=7.6 & 6.5 Hz, 1H, CH), 4.22(dd, J=7.6 Hz & 6.5 Hz, 1H, $CH_{pyrazole}$), 4.62(dd, J=7.8 & 6.5 Hz, 1H, $CH_{pyrazole}$), 7.02–7.30(m, 4H, ArH), 7.55(d, 2H, J=7.8 Hz, ArH). 8.44(d, 2H, J=7.8 Hz, ArH). Anal. Calcd. for $C_{21}H_{20}BrN_3O_3$ (442.32): C, 57.03; H, 4.56; N, 9.50. Found: C, 57.16; H, 4.72; N, 9.62%.

3-(5-(4-Methoxyphenyl)-4,5-dihydro-1-(2-hydroxyethyl)-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (3m) Yield 2.02 g (55%), mp. 202–204°C (ethanol, yellow prism); IR (KBr): 3,502, 3,108, 1,675, 1,606, 1,515 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.80(t, J=6.4 Hz, 2H, CH_2), 3.40(s, 3H, NCH_3), 3.52(s, 3H, OCH_3), 3.60(t, J=6.4 Hz, 2H, CH_2), 3.97(q, J=7.6 & 6.5 Hz, 1H, CH), 4.30(q, J=7.6 Hz & 6.5 Hz, 1H, $CH_{pyrazole}$), 4.75(t, J=7.8 & 6.5 Hz, 1H, $CH_{pyrazole}$), 6.90–7.20(m, 4H, ArH), 7.55(d, 2H, J=7.8 Hz, ArH). 8.01(d, 2H, J=7.8 Hz, ArH). Anal. Calcd. for $C_{22}H_{23}N_3O_4$ (393.45): C, 67.16; H, 5.89; N, 10.68. Found: C, 67.22; H, 6.05; N, 10.72%.

3-(5-(4-Dimethoxyphenyl)-4,5-dihydro-1-(2-hydroxyethyl)-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (3n) Yield 2.12 g (65%). mp. 221–223°C (ethanol, yellow prism); IR (KBr): 3,558, 3,180, 1,680, 1,615, 1,540 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.74(t, J=6.71 Hz, 2H, CH_2), 3.45(s, 3H, NCH_3), 3.50–3.58(s, 6H, 2 × OCH_3), 3.86(t, J= 6.74 Hz, 2H, CH_2), 4.0(q, J=7.6 & 6.5 Hz, 1H, CH), 4.32(q, J=7.6 Hz & 6.5 Hz, 1H, $CH_{pyrazole}$), 4.81(t, J=7.8 & 6.5 Hz, 1H, $CH_{pyrazole}$), 6.98–7.22(m, 4H, ArH), 7.62(d, 2H, J=7.8 Hz, ArH), 8.12(d, 2H, J=7.8 Hz, ArH). MS (70e/v): m/z=424.00 [M+1, 100%], 395(50%), 383(80%), 361(55%), 345(50%), 317(60%), 272(40%), 178(72%), 128 (98%). Anal. Calcd. for $C_{23}H_{25}N_3O_5$ (423.47): C, 65.24; H, 5.95; N, 9.92. Found: C, 65.30; H, 5.82; N, 10.05%.

3-(5-(4-Nitrophenyl)-4,5-dihydro-1-(2-hydroxyethyl)-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (3o) Yield 2.01 g (52%); mp. 194–195°C (ethanol, yellow prism); IR (KBr): 3,512, 3,180, 1,671, 1,608, and 1,512 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.78(t, J=7.1 Hz, 2H, CH_2), 3.54(s, 3H, NCH_3), 3.91(t, J=6.7 Hz, 2H, CH_2), 4.12 (dd, J=7.6 & 6.5 Hz, 1H, CH), 4.38(dd, J=7.6 Hz & 6.5 Hz, 1H, $CH_{pyrazole}$), 4.60(dd, J=7.8 & 6.5 Hz, 1H, $CH_{pyrazole}$), 6.90–7.15(m, 4H, ArH), 7.55(d, 2H, J=7.8 Hz, ArH). 8.16(d, 2H, J=7.8 Hz, ArH). Anal. Calcd. for $C_{21}H_{20}N_4O_5$(408.14): C, 61.76; H, 4.94; N, 13.72. Found: C, 61.50; H, 5.11; N, 13.70%.

General Procedure for the isoxazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one-(5a–e) To a mixture of chalcone **1** (0.01 mol), hydroxylamine hydrochloride **4** (0.69 g, 0.01 mol), sodium acetate (0.73 g, 0.01mole) and catalytic amount of acetic acid (1 mL) in ethanol (15 mL) were refluxed for 8–10 h (TLC Check, toluene: acetone 8:2). The reaction mixture was cooled, concentrated and neutralized with NaOH. The product was isolated and crystallized from ethanol to afford **5** 50–65% yields.

3-(5-(4-Chlorophenyl)-isoxazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one-(5a) Yield 1.85 g (60%). mp. 225–226°C (ethanol, colorless flakes); IR (KBr): 3,431, 3,112, 1,685, 1,612, 1,515 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.64 (s, 3H, NCH_3), 7.32–7.50(m, 4H, ArH), 7.63(s, 1H, ArH), 7.96(d, 2H, J=8.1 Hz, ArH), 8.15(d, 2H, J=8.1ArH), 11.46 (bs, 1H, OH). MS (70 eV): *m/z*=353(M+1, 90%), 335 (10%), 309(10%), 280(10%), 241(20%), 228(15%), 215 (95%), 176(100%), 151(90%), 131(90%), 116(50%), 77 (98%), 63(60%), 51(40%). Anal. Calcd for $C_{19}H_{13}ClN_2O_3$ (352.5): C, 64.69; H, 3.71; N, 7.94. Found: C, 64.80; H, 3.85; N, 7.80%.

3-[5-(4-Bromophenyl)-isoxazol-3-yl]-4-hydroxy-1-methylquinolin-2-(1H)-one(5b) Yield: 1.90 g (65%), mp. 196–197°C (ethanol, colorless flakes); IR (KBr): 3,512, 3,234, 1,674, 1,611, 1,524 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.72 (s, 3H, NCH_3), 7.15–7.40(m, 4H, ArH), 7.66(s, 1H, ArH),

7.84(d, 2H, J=8.20 Hz, ArH), 8.22(d, 2H, J=8.20 Hz, ArH), 11.50(bs, 1H, OH). Anal. Calcd. for $C_{19}H_{13}BrN_2O_3$ (397.22): C, 57.45; H, 3.30; N, 7.05. Found: C, 57.62; H, 3.22; N, 7.15%.

3-[5-(4-Methoxyphenyl)-isoxazol-3-yl]-4-hydroxy-1-methylquinolin-2(1H)-one (5c) Yield 1.75 g (50%), mp. 208–209°C (ethanol, colorless flakes); IR (KBr): 3,512, 3,235, 1,672, 1,602, 1,520 cm^{-1}; ^1H NMR (DMSO-d_6) δ= 3.77(s, 3H, NCH_3), 4.02(s, 3H, OCH_3), 7.20–7.40(m, 4H, ArH), 7.60(s, 1H, ArH), 8.08(d, 2H, J=8.4 Hz, ArH), 8.22 (d, 2H, J=8.4 Hz, ArH), 11.50(bs, 1H, OH). Anal. Calcd for $C_{20}H_{16}N_2O_4$ (348.35): C, 68.96; H, 4.63; N, 8.04. Found: C, 68.80; H, 4.70; N, 7.80%.

3-[5-(3,4-Dimethoxyphenyl)-isoxazol-3-yl]-4-hydroxy-1-methylquinolin-2(1H)-one (5d) Yield 1.80 g (55%), mp. 215–216°C (ethanol, colorless flakes); IR (KBr): 3,492, 3,231, 1,666, 1,612, 1,521 cm^{-1}; ^1H NMR (DMSO-d_6) δ= 3.52(s, 3H, NCH_3), 3.60–3.69(s, 6H, 2 × OCH_3), 6.25(s, 1H, ArH), 6.61–6.84(m, 4H, ArH), 7.40(d, 6.9 Hz, 1H, ArH), 7.73(d, J=6.3 Hz, 1H, ArH), 8.09(dd, J=6.9 & 6.3 Hz, 1H, ArH), 12.68(bs, 1H, OH). MS (70 eV): *m/z*= 380(M+1, 80%), 319(20%), 304(30%), 288(10%), 243 (30%), 227(10%), 215(80%), 201(50%), 180(80%), 165 (80%), 116(70%), 77(90%). Anal. Calcd for $C_{21}H_{18}N_2O_5$ (378.38): C, 66.66; H, 4.79; N, 7.40. Found: C, 66.80; H, 4.65; N, 7.35%.

3-(5-(4-Nitrophenyl)-isoxazol-3-yl)-4-hydroxy-1-methylquinolin-2(1H)-one-(5e) Yield 1.55 g (45%). mp. 210–211°C (ethanol, colorless flakes); IR (KBr): 3,413, 3,110, 1,674, 1,602, 1,514 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.52(s, 3H, NCH_3), 7.22–7.44(m, 4H, ArH), 7.60(s, 1H, ArH), 7.80(d, 2H, J=8.1 Hz, ArH), 8.17(d, 2H, J=8.1ArH), 11.50(bs, 1H, OH). Anal. Calcd for $C_{19}H_{13}N_3O_5$ (363.09): C, 62.81; H, 3.61; N, 11.57. Found: C, 62.70; H, 3.65; N, 11.80%.

General Procedure for the 5, 6, 7, 8-tetrahydro-7, 7-dimethyl-5-oxoquinolin-2-yl)-4 -hydroxy-1-methylquinolin-2(1H)-one (7a–e) A mixture of chalcone **1** (0.01 mol) and dimedone **6** (0.01 mol) in presence of ammonium acetate (0.01 mol) and ethanol (15 mL) was refluxed for 20–24 h. (TLC, toluene: acetone 8:2). Reaction mixture was cooled at room temperature; the colorless solid precipitated was filtered, washed with cold ethanol, dried and recrystallized from ethanol to afford **9a** in 60–70% yields.

3-(4-(4-Chlorophenyl)-5, 6, 7, 8-tetrahydro-7, 7-dimethyl-5-oxoquinolin-2-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (7a) Yield 2.55 g (68%), mp. 252–253°C (ethanol colorless flakes); IR (KBr): 3,544, 3,234, 1,671, 1,641, 1,508 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ: 2.50(s, 6H, 2 × CH_3), 3.20 (s, 4H, 2 × CH_2), 3.44(s, 3H, NCH_3), 7.12–7.40(m, 4H, ArH), 7.81(d, 2H, J=7.8 Hz, ArH), 8.15(d, 2H, J=7.8 Hz, ArH), 9.54(s, 1H, ArH), 12.33(bs, 1H, OH). Anal. Calcd for $C_{27}H_{23}ClN_2O_3$ (458.0): C, 70.66; H, 5.05; N, 6.10. Found: C, 70.80; H, 5.12; N, 6.17%.

3-(4-(4-Bromophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxoquinolin-2-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (7b) Yield 3.10 g (70%), mp. 256–258°C (ethanol, colorless flakes); IR (KBr): 3,488 (OH), 3,084 (CH), 1,646 (CO), 1,605 (CO), 1,505 (C=N); ^1H NMR ($CDCl_3$) δ=2.42 (s, 6H, 2 × CH_3), 3.12(s, 4H, 2 × CH_2), 3.34(s, 3H, NCH_3), 7.25–7.60(m, 4H, ArH), 7.91(d, 2H, J=8.1 Hz, ArH), 8.20 (d, 2H, J=8.1 Hz, ArH), 9.25(s, 1H, ArH), 12.80(bs, 1H, OH). Anal. Calcd for $C_{27}H_{23}BrN_2O_3$ (502.0): C, 64.42; H, 4.61; N, 5.56. Found: C, 64.66; H, 4.71; N, 5.83%.

3-(4-(4-Methoxyphenyl)-5, 6, 7, 8-tetrahydro-7,7-dimethyl-5-oxoquinolin-2-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (7c) Yield 2.15 g (65%); mp. 268–270°C (ethanol, colorless flakes); IR (KBr): 3,512, 3,221, 1,678, 1,612, 1,544 cm^{-1}; ^1H NMR ($CDCl_3$) δ : 1.60(s, 6H, 2 × CH_3), 2.10(s, 4H, 2 × CH_2), 3.55(s, 3H, NCH_3), 3.80(s, 3H, OCH_3), 7.20–7.80(m, 4H, ArH), 8.10(d, 2H, J=8.3 Hz, ArH). 8.25(d, 2H, J=8.3 Hz, ArH), 9.02(s, 1H, ArH). Anal. Calcd for $C_{28}H_{26}N_2O_4$ (454.0): C, 73.99; H, 5.77; N, 6.16; Found: C, 73.80; H, 5.70; N, 6.36%.

3-(4-(3,4-Dimethoxyphenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxoquinolin-2-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (7d) Yield 2.80 g (65%),; mp 241–243°C (ethanol, colorless flakes): IR (KBr): 3,466, 3,031, 1,678, 1,656 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3–1.33(s, 6H, 2 × CH_3), 2.19–2.33(s, 4H, 2 × CH_2), 3.25(s, 3H, NCH_3), 3.34–3.42(s, 6H, 2 × OCH_3), 7.07–7.73(m, 4H, ArH), 7.98(d, 2H, J=8.6 Hz, ArH), 8.14 (d, 2H, J=8.6 Hz, ArH), 9.20(s, 1H, ArH), 11.40(bs, 1H, OH). Anal. Calcd for $C_{29}H_{28}N_2O_5$ (484.0): C, 71.88; H, 5.82; N, 5.78. Found: C, 72.02; H, 5.91; N, 5.86%.

3-(4-(4-Nitrophenyl)-5, 6, 7, 8-tetrahydro-7, 7-dimethyl-5-oxoquinolin-2-yl)-4-hydroxy-1-methylquinolin-2(1H)-one (7e) Yield 1.90 g (48%), mp. 252–253°C (ethanol colorless flakes); IR (KBr): 3,520, 3,230, 1,660, 1,635, 1,510 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ : 2.402.45(s, 6H, 2 × CH_3), 3.15–3.20(s, 4H, 2 × CH_2), 3.52(s, 3H, NCH_3), 7.10–7.35 (m, 4H, ArH), 7.77(d, 2H, J=7.8 Hz, ArH), 8.12(d, 2H, J= 7.8 Hz, ArH), 9.86(s, 1H, ArH), 12.60(bs, 1H, OH). Anal. Calcd for $C_{27}H_{23}N_3O_5$ (469.16): C, 69.07; H, 4.94; N, 8.95. Found: C, 69.12; H, 5.13; N, 8.72%.

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