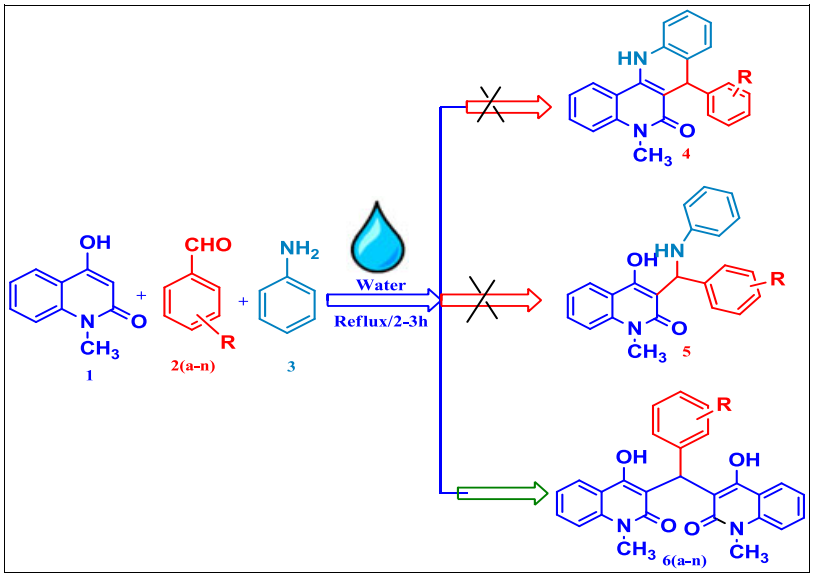
Diversity-oriented Multicomponent Synthesis of Bisquinolones under Green Conditions

Madhu Bandi[a,b]* and Ch.Venkata Ramana Reddy[b]

[a]Jawaharlal Nehru Technological University, Kakinada, AP, India
[b]Department of Chemistry, Jawaharlal Nehru Technological University Hyderabad College of Engineering, Kukatpally, Hyderabad, TS 500 085, India
*E-mail: madhubandi2@gmail.com

Received April 28, 2017
DOI 10.1002/jhet.2994
Published online 00 Month 2017 in Wiley Online Library (wileyonlinelibrary.com).

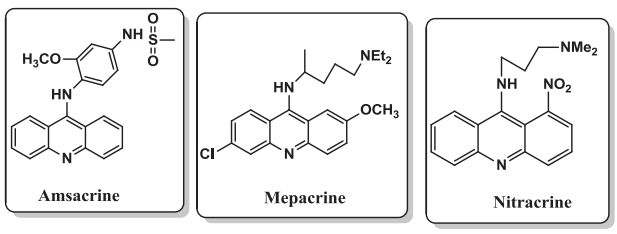


A diversity-oriented green and eco-friendly synthesis of bisquinolones have been developed by simply condensation of *N*-methylquinolone (**1**), with various benzaldehydes **2a**–**n** and aniline (**3**) under catalyst-free conditions. An exciting feature of this communication is the product formation that depends on the intermediate (**II**) generated in the reaction mechanism.

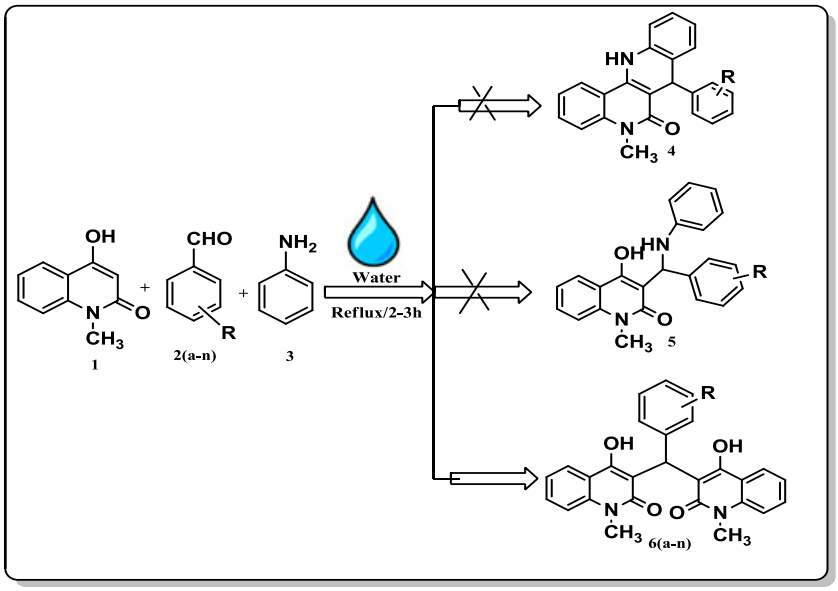
J. Heterocyclic Chem., **00,** 00 (2017).

INTRODUCTION

Among the all nitrogen-containing and oxygen-containing heterocycles, quinolines and quinolones are the common core skeletons of some potent pharmaceutical drugs [1] and biologically active alkaloids [2]. These derivatives are important class of organic and biomolecules that attract the interest of both synthetic and medicinal researchers. Some of the functionalized quinolines [3] have found applications as pharmaceuticals and agrochemicals [4] as well as useful synthetic blocks in the preparation of several natural products [5]. Especially quinoline-containing drugs are found in a verity of biologically active compounds and are widely used in the treatment of malaria [6], and some of the quinoline-based drugs act as antibacterial [7], antiviral [8], antifungal [9], anti-malarial [10], and anti-inflammatory [11] agents. In addition, because of their medicinal applications, quinolines and quinolone derivatives have been employed in the study of bioorganic and bioorgano-metallic process [12]. Several methods have been developed for the preparation of 3 and 4-substituted quinoline derivatives [13], and because of their biological importance as substructures in a broad range of designed and natural products [14], significant efforts continue to be directed into the development of new quinoline-based structures and new methods for their construction. Many of the biologically important quinolines and its derivatives can easily be synthesized from readily available chemicals with the help of multi-component reactions [15]. These reactions are allowed for rapid synthesis of biologically active compound libraries by combining three or more reagents into a single product in one step.



Scheme 1. Multi-component reaction of **1** with **2a**–**n** and **3** in water. [Color figure can be viewed at wileyonlinelibrary.com]



The naphthyridine [16] and acridine [17] derivatives are an important class of nitrogen heterocycles that can be converted into biologically active compounds exhibiting variety of biological and pharmaceutical properties, such as anti-tumor [18], anti-cancer [19], anti-malarial [20], anti-multidrug-resistant [21], fungicidal [22], and cytotoxic [23] properties, and are widely prescribed as calcium bêta-blockers. In addition to their important pharmacological properties, these derivatives are used as dyes, fluorescent materials for visualization of bioactive molecules, and in laser technology because of their useful spectroscopic properties. The synthesis of naphthyridine analogues related to the anti-malarial natural product dependents would allow for an interesting analysis of the relationship between the two heterocyclic systems and their biological effects. In view of the broad utility of naphthyridine and acridine derivatives, the synthesis of this class of compounds under green conditions is of paramount importance in synthetic organic chemistry [24]. The multi-component condensation of 1,3-dione-like compounds, aromatic aldehydes, and anilines by heating in organic solvent or under microwave irradiation has recently emerged as a potential route for the synthesis of structurally divers naphthyridine and acridine molecules. Few catalytic methods are available in literature, which deals with the synthesis of these molecules via multi-component route. Recently, Hivani et al. [25] reported one-pot three-component synthesis of novel acridine-5,6-diones from naphthoquinone under PTSA condition. Li et al. [26] reported ionic liquid-mediated one-pot synthesis of acridine-1,6-diones from 2-hydroxy naphthoquinone at room temperature. Javad et al. [27] reported ZnO nanoparticle-catalyzed synthesis of acridine derivatives from 1,3-dione under solvent-free condition.

According to the literature mentioned previously, the multi-component reaction of 1,3-diones or active hydroxyl compounds with aromatic aldehydes and anilines gave either naphthyridine or acridine derivatives are the desired products. In this paper, our study began with the multi-component reaction of 4-hydroxy-1-methylquinolin-2(1*H*)-one [28] with aniline and different aromatic aldehydes under green conditions.

RESULTS AND DISCUSSION

As illustrated in Scheme 1, the first experiment was carried out in water at a room temperature, and

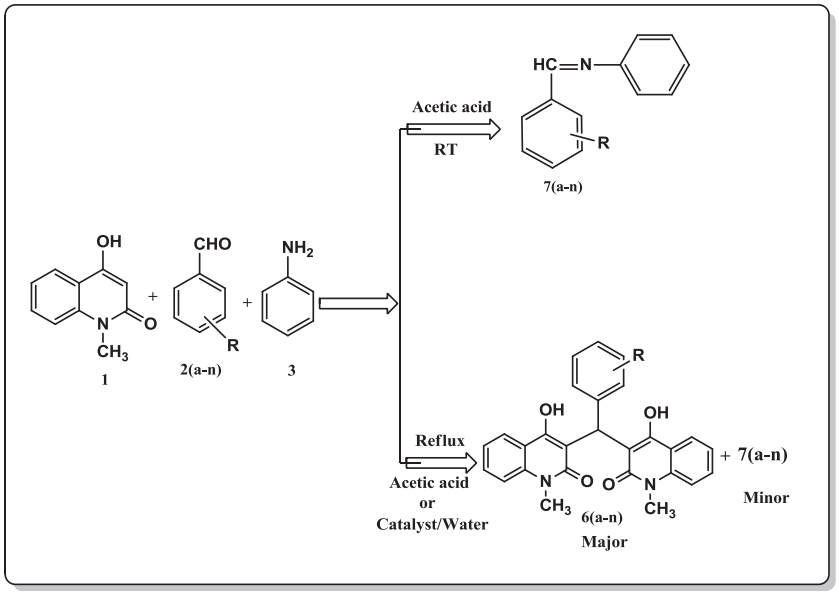
Table 1

Effect of solvent and temperature on formation of **6a**.

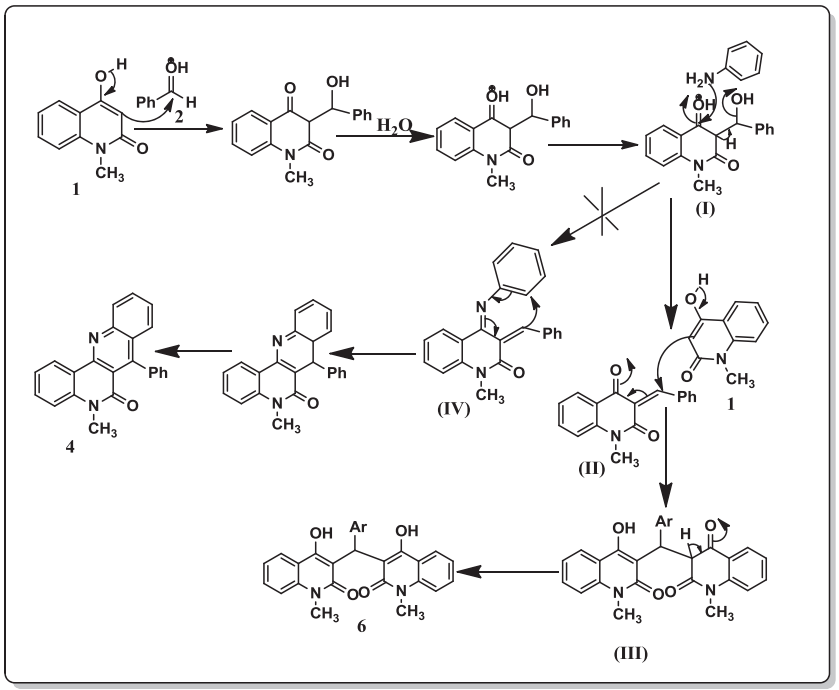
Entry	Solvent	Temp (°C)	Time (min)	Yield (**6a**)	Yield (**7a**)
1	Water	RT	120	—	—
2	Water	Reflux	60	91	—
3	Acetic acid	RT	120	—	90
4	Acetic acid	Reflux	60	80	15
5	Ethylene glycol	Reflux	60	86	Trace
6	Glycerol	Reflux	60	82	Trace
7	PEG-600	Reflux	60	85	Trace
8	DMF	Reflux	60	70	Trace
9	Acetonitrile	Reflux	60	68	Trace
10	THF	Reflux	60	68	Trace
11	Methanol	Reflux	60	74	Trace
12	Solvent-free	100	15	30	Trace

4-hydroxy-1-methylquinolin-2(1*H*)-one (**1**), benzaldehyde (**2a**), and aniline (**3**) were chosen as model reaction; there is no product formation obtained, but the reaction mixture was refluxed for 2–3 h till the reaction was complete (checked by TLC) and once the main product was purified, and the structural elucidation of the isolated substance revealed surprisingly that instead of the desired molecules 5-methyl-7-phenyl-7,12-dihydrodibenzo[*b*,*h*][1,6]naphthyridin-6(5*H*)-one (**4a**) and 4-hydroxy-1-methyl-3-(phenyl(phenylamino) methyl)quinolin-2(1*H*)-one (**5a**), a new compound **6a** with the 3,3′-(phenylmethylene)bis(4-hydroxy-1-methylquinolin-2(1*H*)-one) was obtained as a single product and in good yield. The structure of the **6a** was

Scheme 2. Effect of solvent and catalyst on formation of **6a**–**n** and **7a**–**n**.



Scheme 3. Plausible mechanism for synthesis of **6**.



established based on its spectral properties (IR, ^{1}H-NMR, mass). Thus, its IR (KBr) spectrum showed a very broad absorption at 2970 cm^{-1} due to the presence of the hydroxyl groups and a strong, sharp absorption at 1627 cm^{-1} due to the amide carbonyl groups. Its ^{1}H-NMR, in DMSO-d_6, showed peaks at δ 3.72 (s, 6H, 2X–C**H**$_3$, 6.28 (s, 1H, −C**H**–**Ar**), 7.06–8.07 (m, 13H, eight aryl protons of quinoline rings plus five protons of the phenyl ring), 12.60 (s, 2H, −O**H**, D_2O exchangeable). Its LC-MS spectrum, when recorded in the Q + 1 mode, showed the molecular ion peak at *m*/*z* 439 corresponding to a molecular mass of 438.

The reaction conditions were varied (Table 1), in order to improve the yield and to establish a green method for the selective preparation of product **6a**, and all the experiments gave good-to-excellent yield in green solvents and moderate yield in organic solvents. But when the reaction was carried out in acetic acid at room temperature, Schiff's base (**7a**) was found as single product instead of **6a** (Scheme 2). But the same reaction

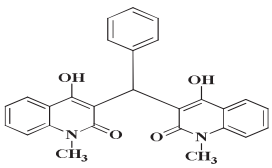
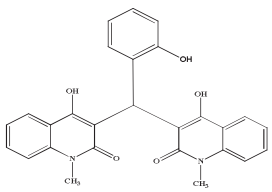
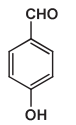
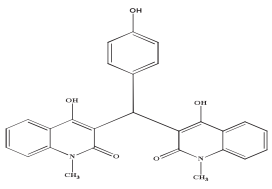
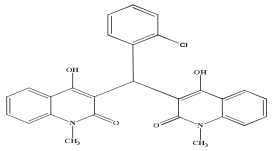
Table 2

Effect of Lewis acid catalysts on formation of **6a**.

Entry	Catalyst	Solvent	Temp (°C)	Yield (%) (**6a**)	Yield (%) (**7a**)
1	No catalyst	Water	Reflux	91	—
2	$InCl_3$	Water	Reflux	80	15
3	$ZnCl_2$	Water	Reflux	80	15
4	$FeCl_3$	Water	Reflux	75	20
5	$SnCl_2$	Water	Reflux	78	16
6	L-Proline	Water	Reflux	82	14
7	PTSA	Water	Reflux	80	16

Table 3

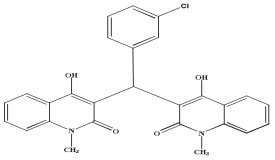
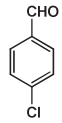
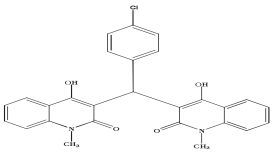
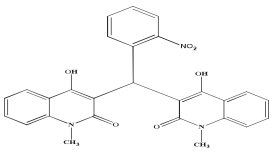
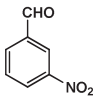
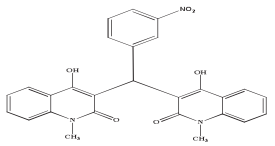
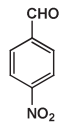
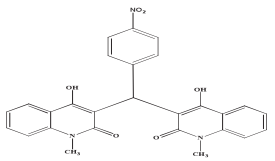
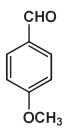
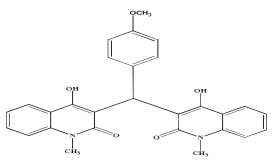
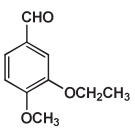
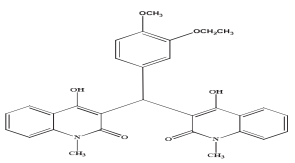
Synthesis of **6a**–**n** under green condition.

Entry	Starting material used **2a**–**n**	Product obtained **6a**–**n**	Time (min)	Yield	mp (°C)
1	 **(2a)**	 **(6a)**	60	91	287–289
2	 **(2b)**	 **(6b)**	120	72	220–222
3	 **(2c)**	 **(6c)**	120	76	209–211
4	 **(2d)**	 **(6d)**	90	80	202–204

(*Continues*)

Table 3

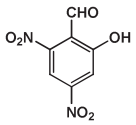
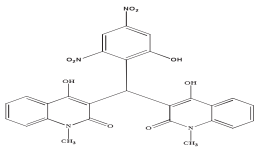
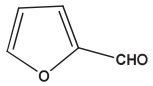
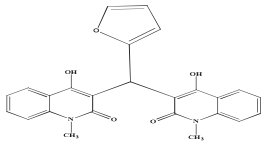
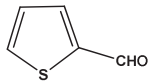
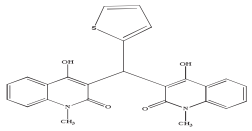
(*Continued*)

Entry	Starting material used **2a**–**n**	Product obtained **6a**–**n**	Time (min)	Yield	mp (°C)
5	 **(2e)**	 **(6e)**	90	84	190–192
6	 **(2f)**	 **(6f)**	90	83	174–175
7	 **(2g)**	 **(6g)**	60	88	Above 300
8	 **(2h)**	 **(6h)**	60	85	296–298
9	 **(2i)**	 **(6i)**	60	85	293–294
10	 **(2j)**	 **(6j)**	120	75	237–238
11	 **(2k)**	 **(6k)**	120	71	240–242

(*Continues*)

Table 3

(*Continued*)

Entry	Starting material used **2a**–**n**	Product obtained **6a**–**n**	Time (min)	Yield	mp (°C)
12	 **(2l)**	 **(6l)**	60	89	290–292
13	 **(2m)**	 **(6m)**	90	82	242–243
14	 **(2n)**	 **(6n)**	90	84	265–266

was carried out under refluxing conditions **6a** was found as a major product. However, reaction in water under refluxing conditions for 2–3 h gave, reasonably, high yield (91%) of the product **6a** (Table 1, **entry 2**). All these results were summarized in Table 1.

Next, the reaction conditions were optimized for the aforementioned reaction in order to know the best catalyst. Thus, the aforementioned reaction was carried out in water by using different types of Lewis acid catalysts like $SnCl_2$, $InCl_3$, $ZnCl_2$, $FeCl_3$, L-Proline, and PTSA. But in presence of catalyst, the reaction was proceeded via formation of **7a** along with **6a** (Scheme 3). However, reaction in water without catalyst under refluxing conditions for 2–3 h gave, reasonably, high yield (91%) of the product **6a** (Table 2, entry 1).

A plausible mechanism has been proposed for the formation of **6**. Initially, one equivalent of *N*-methylquinolone (**1**) undergoes simple Knoevenagel condensation with the activated aldehyde (**2**) to yield an intermediate (**I**). If **I** undergoes nucleophilic addition with aniline (**3**), it leads to formation of intermediate (**IV**). And finally, **IV** was cyclized followed by aerial oxidation to afford expected product **4**. But original reaction pathway is completely different from the expected pathway. In this mechanism, dehydration of intermediate (**I**) leads to **II**, which acts as a strong Michael acceptor. The latter undergoes Michael addition with another equivalent of **1** to yield the keto–enol intermediate **III** followed by isomerisation of the latter intermediate yielding the final product **6**.

With the optimized conditions in hand, to delineate this approach, the scope and generality of this protocol were next accessed by employing various aromatic aldehydes **2a**–**n** to synthesize the corresponding divers 3,3′-(phenylmethylene)bis(4-hydroxy-1-methylquinolin-2(1*H*)-one). An assembly of 14 compounds was synthesized by using this protocol. The reaction could tolerate various substitutions on aromatic aldehydes. Notably, aromatic aldehydes bearing electron-withdrawing groups (Cl, F, NO_2, etc.) at the aryl ring afforded the desired products with excellent efficiency (Table 3).

CONCLUSIONS

In summary, we have described an unexpected and interesting reaction between *N*-methylquinolone, various benzaldehydes, and aniline in which different bisquinolone derivatives are formed. The products were produced under classic reaction conditions in presence of water as an available green solvent. The syntheses are eco-friendly involving easy workup; moreover, they gave high yields without the need of costly catalyst and column chromatography.

EXPERIMENTAL

General information. Melting points are uncorrected and were determined in open capillary tubes in sulphuric acid bath. TLC was run on silica gel – G and visualization was done using iodine or UV light. IR spectra were recorded using PerkinElmer 1000 instrument in KBr pellets. ^{1}H-NMR spectra were recorded in DMSO-d_6 using TMS as internal standard on a 400-MHz spectrometer. Mass spectra were recorded on Agilent LC-MS instrument under CI conditions and given by Q + 1 value only. Starting material **1** was prepared by using previously reported procedure [24]. Compounds **2** and **3** were obtained from commercial suppliers and used as such.

Typical procedure for the preparation of 6 from **1**, **2, and 3** by multi-component method. A mixture of **1**(10 mmol), **2** (10 mmol), **3** (10 mmol), and water (5 mL) was refluxed for 2–3 h. The latter was filtered to collect the insoluble solid by filtration, and the insoluble solid was washed with methanol (10 mL × 3) and dried. It was recrystallized from methanol to obtain pure **6**.

Typical procedure for the preparation of 6 from 1 and 2. A mixture of **1** (10 m*M*), **2** (5 m*M*), and water (20 mL) was refluxed at 100°C for 1 h. The reaction was monitored by checking TLC for the disappearance of the starting material, that is, **2**. At the end of this period, a colorless solid separated out from the reaction mixture, which was collected by filtration. The crude product was then washed with methanol (10 mL) and dried. It was recrystallized from methanol to obtain pure **6**.

3,3′-(Phenylmethylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5a). IR (KBr): 2970 (−OH group, broad), 1627 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.72 (s, 6H, −$(CH_3)_2$), 6.28 (s, 1H, −CH), 7.06–8.07 (m, 13H, Ar–H), 12.60 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.88, 55.36, 115.71, 117.26, 123.12, 123.99, 126.02, 126.57, 128.43, 131.97, 137.99, 138.51, 160.87. *m*/*z* (M^+ + 1): 439. *Anal* Calcd for $C_{27}H_{22}N_2O_4$ (438.47): C, 73.96; H, 5.06; N, 6.39; found: C, 73.84; H, 5.03; N, 6.28.

3,3′-((2-Hydroxyphenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5b). IR (KBr): 2972 (−OH group, broad), 2968 (−OH group, broad), 1638, cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.79 (s, 6H, −$(CH_3)_2$), 6.35 (s, 1H, −CH), 7.12–8.32 (m, 12H, Ar–H), 12.16 (s, 1H, −OH, D_2O exchangeable); 12.38 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.71, 55.24, 115.62, 117.51, 123.24, 123.83, 126.11, 126.72, 128.24, 131.95, 137.14, 138.63, 160.69. *m*/*z* (M^+ + 1): 455. *Anal*. Calcd for $C_{27}H_{22}N_2O_5$ (454.47): C, 71.35; H, 4.88; N, 6.16; found: C, 71.28; H, 4.91; N, 6.18.

3,3′-((4-Hydroxyphenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5c). IR (KBr): 2985 (−OH group, broad), 2925 (−OH group, broad), 1664, cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.68 (s, 6H, −$(CH_3)_2$), 6.29 (s, 1H, −CH), 7.20–8.44 (m, 12H, Ar–H), 12.23 (s, 1H, −OH, D_2O exchangeable); 12.40 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.71, 55.42, 115.62, 117.47, 123.11, 123.92, 126.24, 126.39, 128.82, 131.73, 137.61, 138.83, 160.75. *m*/*z* (M^++1): 455. *Anal*. Calcd for $C_{27}H_{22}N_2O_5$ (454.47): C, 71.31; H, 4.83; N, 6.13; found: C, 71.22; H, 4.94; N, 6.16.

3,3′-((2-Chlorophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5d). IR (KBr): 2985 (−OH group, broad), 1664 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.71 (s, 6H, −$(CH_3)_2$), 6.31 (s, 1H, −CH), 7.29–8.38 (m, 12H, Ar–H), 12.48 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.16, 55.32, 115.71, 117.16, 123.72, 123.89, 126.21, 126.62, 128.34, 131.91, 137.26, 137.51, 138.29, 138.53, 160.34. *m*/*z* (M^+ + 1): 473. *Anal*. Calcd for $C_{27}H_{21}ClN_2O_4$ (472.92): C, 68.57; H, 4.48; N, 5.92; found: C, 68.53; H, 4.45; N, 5.98.

3,3′-((3-Chlorophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5e). IR (KBr): 2975 (−OH group, broad), 1673 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.83 (s, 6H, −$(CH_3)_2$), 6.46 (s, 1H, −CH), 7.41–8.72 (m, 12H, Ar–H), 12.13 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.19, 55.28, 115.63, 117.26, 123.28, 123.72, 126.38, 126.75, 128.18, 131.82, 137.37, 137.81, 138.01, 138.28, 160.46. *m*/*z* (M^+ + 1): 473. *Anal*. Calcd for $C_{27}H_{21}ClN_2O_4$ (472.95): C, 68.54; H, 4.49; N, 5.96; found: C, 68.52; H, 4.48; N, 5.94.

3,3′-((4-Chlorophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5f). IR (KBr): 2979 (−OH group, broad), 1683 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.48 (s, 6H, −$(CH_3)_2$), 6.96 (s, 1H, −CH), 7.23–8.61 (m, 12H, Ar–H), 12.36 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.62, 55.31, 115.81, 117.26, 123.62, 123.83, 126.36, 126.71, 128.76, 131.28, 137.51, 138.76, 160.69. *m*/*z* (M^++1): 473. *Anal*. Calcd for $C_{27}H_{21}ClN_2O_4$ (472.92): C, 68.57; H, 4.48; N, 5.92; found: C, 68.53; H, 4.45; N, 5.98.

3,3′-((2-Nitrophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5g). IR (KBr): 2981 (−OH group, broad), 1698 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.61 (s, 6H, −$(CH_3)_2$), 6.72 (s, 1H, −CH), 7.81–8.43 (m, 12H, Ar–H), 12.51 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.27, 55.46, 115.71, 117.34, 123.51, 123.82, 126.41, 126.85, 128.23, 131.72, 137.29, 137.76, 138.13, 138.42, 160.72. *m*/*z* (M^++1): 484. *Anal*. Calcd for $C_{27}H_{21}N_3O_6$

(483.47): C, 67.07; H, 4.38; N, 8.69; found: C, 67.08; H, 4.34; N, 8.65.

3,3′-((3-Nitrophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5h). IR (KBr): 2986 (−OH group, broad), 1679 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400MHZ): δ 3.82 (s, 6H, $-(CH_3)_2$), 6.46 (s, 1H, −CH), 7.82–8.49 (m, 12H, Aromatic hydrogens), 12.62 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.31, 55.36, 115.52, 117.29, 123.38, 123.91, 126.71, 126.79, 128.38, 131.57, 137.35, 137.62, 138.29, 138.58, 160.59. *m*/*z* (M^++1): 484. *Anal*. Calcd for $C_{27}H_{21}N_3O_6$ (483.43): C, 67.02; H, 4.31; N, 8.69; found: C, 67.03; H, 4.32; N, 8.61.

3,3′-((4-Nitrophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5i). IR (KBr): 2991 (−OH group, broad), 1685 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.87 (s, 6H, $-(CH_3)_2$), 6.63 (s, 1H, −CH), 7.92–8.41 (m, 12H, Ar–H), 12.83 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR δ_C (100 MHz; DMSO-d_6): 18.27, 55.31, 115.46, 117.69, 123.26, 123.71, 126.53, 126.77, 128.81, 131.68, 137.19, 138.81, 160.93. *m*/*z* (M^++1): 484. *Anal*. Calcd for $C_{27}H_{21}N_3O_6$ (483.49): C, 67.02; H, 4.36; N, 8.64; found: C, 67.01; H, 4.32; N, 8.63.

3,3′-((4-Methoxyphenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5j). IR (KBr): 2976 (−OH group, broad), 1672 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.51 (s, 6H, $-(CH_3)_2$), 3.83 (s, 3H, $-OCH_3$), 6.84 (s, 1H, −CH), 7.58–8.72 (m, 12H, Ar–H), 12.91 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.11, 42.26, 55.42, 115.61, 117.72, 123.51, 123.85, 126.53, 126.79, 128.67, 131.73, 137.27, 138.66, 160.58. *m*/*z* (M^++1): 469. *Anal*. Calcd for $C_{28}H_{24}N_2O_5$ (468.50): C, 71.78; H, 5.16; N, 5.98; found: C, 71.76; H, 5.19; N, 5.95.

3,3′-((3-Ethoxy-4-methoxyphenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5k). IR (KBr): 2982 (−OH group, broad), 1678 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.43 (s, 6H, $-(CH_3)_2$), 3.74 (s, 3H, $-CH_3$), 3.61 (q, 2H, $-OCH_2$), 2.81 (t, 3H, $-CH_2$–CH_3), 6.74 (s, 1H, −CH), 7.31–8.62 (m, 11H, Ar–H), 12.91 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.23, 33.61, 42.32, 45.63, 55.34, 115.57, 117.78, 123.36, 123.75, 126.44, 126.82, 128.53, 131.39, 137.31, 138.48, 160.48. *m*/*z* (M^++1): 513 *Anal*. Calcd for $C_{30}H_{28}N_2O_6$ (512.55): C, 70.30; H, 5.51; N, 5.47; found: C, 70.34; H, 5.56; N, 5.44.

3,3′-((2-Hydroxy-4,6-dinitrophenyl)methylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5l). IR (KBr): 2968 (−OH group, broad), 2982 (−OH group, broad), 1641 cm^{-1} (−CO– group, broad);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.43 (s, 6H, $-(CH_3)_2$), 6.94 (s, 1H, −CH), 7.25–8.41 (m, 10H, Ar–H), 9.31(s, 1H, −OH, D_2O exchangeable); 12.72 (s, 2H, −OH, D_2O exchangeable); ^{13}C NMR (100 MHz; DMSO-d_6): δ_C 18.27, 55.41, 115.61, 117.37, 123.42, 123.83, 126.35, 126.81, 128.38, 131.29, 137.58, 137.91, 138.36, 138.67, 160.74. *m*/*z* (M^++1): 545. *Anal*. Calcd for $C_{27}H_{20}N_4O_7$ (544.47): C, 59.56; H, 3.70; N, 10.29; found: C, 59.54; H, 3.73; N, 10.25.

3,3′-(Furan-2-ylmethylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5m). IR (KBr): 2973 (−OH group, broad), 1689 cm^{-1} (−CO– group, sharp); ^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.52 (s, 6H, $-(CH_3)_2$), 6.83 (s, 1H, −CH), 7.63–8.89 (m, 11H, Ar–H), 12.13 (s, 2H, −OH, D_2O exchangeable); ^{13}C-NMR (100 MHz; DMSO-d_6): δ_C 20.89, 56.45, 119.64, 121.17, 124.33, 125.24, 128.62, 129.51, 132.84, 137.93, 139.73, 160.72. *m*/*z* (M^++1): 429. *Anal*. Calcd for $C_{25}H_{20}N_2O_5$ (428.44): C, 70.08; H, 4.71; N, 6.54; found: C, 70.04; H, 4.76; N, 6.58.

3,3′-(Thiophen-2-ylmethylene)bis(4-hydroxy-1-methylquinolin-2(1H)-one) (5n). IR (KBr): 2914 (−OH group, broad), 1685 cm^{-1} (−CO– group, sharp);^{1}H-NMR (DMSO-d_6/TMS, 400 MHZ): δ 3.73 (s, 6H, $-(CH_3)_2$), 6.81 (s, 1H, −CH), 7.55–8.61 (m, 11H, Ar–H), 12.92 (s, 2H, −OH, D_2O exchangeable); ^{13}C-NMR (100 MHz; DMSO-d_6,): δ_C 19.62, 57.47, 120.82, 122.77, 123.18, 127.55, 128.57, 130.76, 133.88, 138.73, 140.26, 160.91. *m*/*z* (M^++1): 445. *Anal*. Calcd for $C_{25}H_{20}N_2O_4S$ (444.50): C, 67.55; H, 4.54; N, 6.30; found: C, 67.52; H, 4.58; N, 6.34.

Acknowledgments. Authors are thankful to the authorities of Jawaharlal Nehru Technological University Hyderabad for providing laboratory facilities.

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