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A facile and expeditious microwave-assisted synthesis of 4-aryl-2-ferrocenyl-quinoline derivatives via multi-component reaction

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ABSTRACT

An efficient and rapid route for the synthesis of 4-aryl-2-ferrocenyl-quinoline derivatives through microwave-assisted multi-component reaction of acetylferrocene with aromatic aldehyde and dimedone in the presence of ammonium acetate using DMF as reaction media at 100 °C is described. This novel procedure lends itself well to combinatorial methods, providing the target heteropolymetallic compounds in excellent yield without further purification.

1. Introduction

Since the report of ferrocene by Kealy and Pauson [1], an important area of organometallic chemistry is focused on ferrocene and its derivatives. Ferrocene derivatives containing heterocyclic systems have attracted special attention in recent years [2–7] because of their organic and inorganic properties, as well as for their applications in various areas including components of molecular wires [8], anion sensors [9] and potential organic ferromagnets [10]. Compared with the classical heterocyclic compounds, incorporation of a ferrocene fragment into heterocycles often obtained unexpected biological activity [11]. Furthermore, ferrocene has been studied extensively as it is thought to be responsible for a variety of biological stability and non-toxicity rendering such drugs compatible with other treatment [12–14]. In the light of current studies, the combination of ferrocene units with heterocyclic molecules offers a desired way to endow novel functional molecules [15–17].

The quinoline moiety is one of the significant core structures among the most extensively natural and unnatural heterocyclic compounds [18–21] with remarkable medicinal activities [22]. In particular, quinolines have played a unique role in the design and synthesis of novel biologically active compounds serving as antiinflammatory, antiasthmatic, antituberculosis, antibacterial, antihypertensive, antitumor, and, most notably, antimalarial agents [18,23–26]. Moreover, ferrocenyl substitutes are biologically active and exist in the structures of various antimalarial and antitumor agents [27–29]. Consequently, integration of a ferrocenyl moiety into quinoline derivatives may increase their biological activities or create new medicinal properties [30–33]. Although much work has been directed toward the synthetic manipulation of quinoline derivatives, the synthesis of ferrocenyl-substituted quinolines [34–37], especially 2-ferrocenylquinolin-5(1*H*,4*H*,6*H*)-ones, has seldom been reported. As a result, the synthesis of ferrocenyl heterocycles is a key desiderated issue in organometallic chemistry.

With the aim to develop efficient synthetic processes, reduce laborious multi-steps and minimize byproducts, as well as in continuation of recent interest in the organoferrocene chemistry [38–41], here we describe a practical, inexpensive, and rapid microwave-promoted (MW) method for the preparation of 2-ferrocenyl-quinoline derivatives **5** via multi-component reactions of acetylferrocene **1**, aromatic aldehyde **2,** dimedone **3** and ammonium acetate **4** in DMF (Scheme 1).

2. Results and discussion

To choose the most appropriate solvent, the MW-assisted reaction (Scheme 2) of acetylferrocene (**1**, 1.0 mmol), 4-chlorobenzaldehyde (**2a**, 1.0 mmol), dimedone (**3**, 1.0 mmol) and ammonium acetate (**4**, 2.5 mmol) was examined using glacial acetic acid (HOAc), glycol, *N*,*N*-dimethylformamide (DMF), water as the solvent (2.0 mL) and solvent-free at 80 °C, respectively. All the reactions were carried out at the maximum power of 200 W. As

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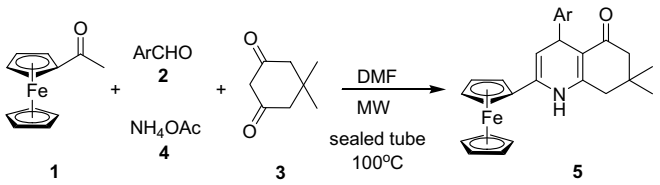
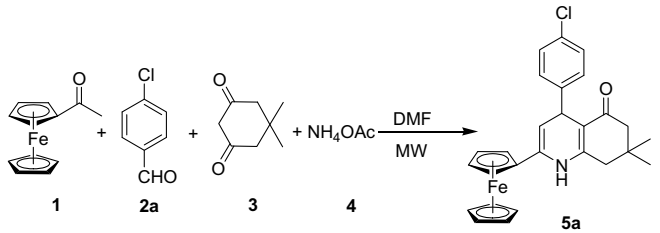


Scheme 1.



Scheme 2.

Table 1
Solvent optimization for the synthesis of **5a** under microwave irradiation.

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	HOAc	80	15	Trace
2	Glycol	80	10	36
3	DMF	80	15	82
4	Water	80	8	49
5	None	80	7	27

Table 2
Temperature optimization for the synthesis of **5a** under microwave irradiation.

Entry	Temperature (°C)	Time (min)	Yield (%)
1	70	20	41
2	80	15	82
3	90	12	83
4	100	10	92
5	110	8	78
6	120	7	66
7	130	5	60

Table 3
Synthesis of compound **5** under microwave irradiation.

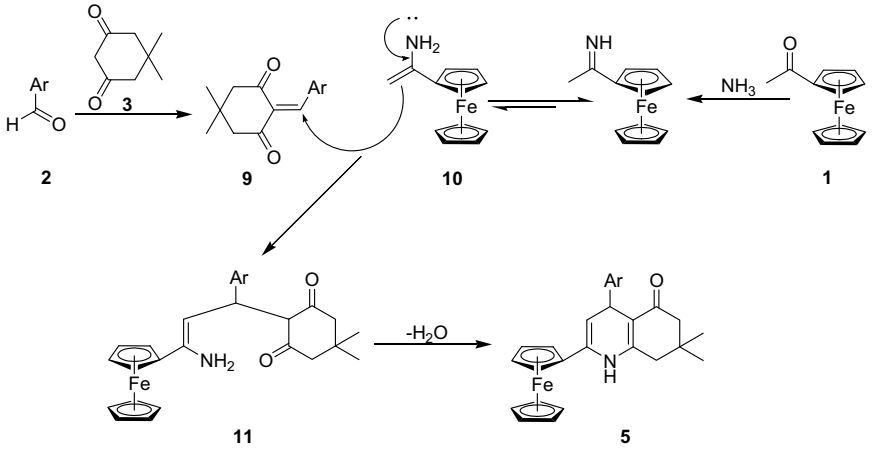
Entry	Product	Ar	Time (min)	Yield (%)	Mp (°C)
1	**5a**	4-ClC_6H_4	10	92	238–240
2	**5b**	4-BrC_6H_4	9	93	241–244
3	**5c**	4-MeC_6H_4	11	90	221–223
4	**5d**	4-$MeOC_6H_4$	12	91	213–215
5	**5e**	3,4-$(MeO)_2C_6H_3$	13	78	192–195
6	**5f**	3,4,5-$(MeO)_3C_6H_2$	15	79	197–199
7	**5g**	4-$Me_2NC_6H_4$	12	75	198–201
8	**5h**	Thiophen-2-yl	10	86	206–208
9	**5i**	3,4-$(OCH_2O)C_6H_3$	12	82	228–231

shown in Table 1, we could see the reaction in DMF gave the best results (Table 1, entry 3). So DMF was chosen as the reaction solvent.

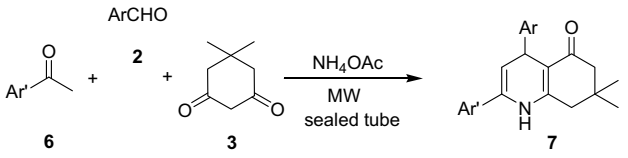
To further optimize reaction conditions, the same reaction was performed in DMF and 200 W at temperatures ranging from 70 to 130 °C, with an increment of 10 °C each time. The yield of product **5a** was increased and the reaction time was shortened as the temperature was raised from 70 °C to 100 °C (Table 2, entries 1–4). However, no significant increase in the yield of product **5a** was observed as the reaction temperature was raised from 110 °C to 130 °C (Table 2, entries 5–7). Therefore, 100 °C was chosen as the reaction temperature for all further reactions.

Under the optimal conditions [DMF, 100 °C, 200 W (maximum power)], reactions of different aromatic aldehydes were performed and afforded 2-ferrocenylquinolin-5(1*H*,4*H*,6*H*)-ones with good yields. As shown in Table 3, at the beginning, we made a search for the aldehyde substrate scope, acetylferrocene and dimedone were used as model substrates (Table 3, entries 1–9), and the results indicated that aromatic aldehydes bearing either electron-donating or electron-withdrawing functional groups such as chloro, bromo, methyl, or methoxy were able to affect the synthesis of compounds **5**. We have also observed delicate electronic effects: that is, aryl aldehydes with electron-withdrawing groups (Table 3, entries 1 and 2) reacted rapidly, while the substitution of electron-rich groups (Table 3, entries 3–7 and 9) on the benzene ring decreased the reactivity, requiring longer reaction times. Moreover, the heterocyclic aldehydes such as thiophene-2-carbaldehyde (Table 3, entry 8) still displayed a high reactivity under this standard condition. It is worth noting that this conclusion is significant since there is no literature precedent for the synthesis of 2-ferrocenylquinolin-5(1*H*,4*H*,6*H*)-ones.

The formation of **5** is expected to proceed via initial condensation of aldehydes with dimedone to afford 2-arylidene-5,5-dimeth-



Scheme 3.



Scheme 4.

ylcyclohexane-1,3-dione **9**, which further undergoes in situ Michael addition with 1-ferrocenylethenamine **10**, obtained by treating acetylferrocene with ammonia from ammonium acetate, to yield intermediate **11**, which is then cyclized to afford the products **5** (Scheme 3).

In order to further expand the scope of the present method, the replacement of acetylferrocene with various arones including **6a–e** was examined (Scheme 4). In all these cases, the reactions proceeded smoothly to give the corresponding 2,4-diarylpolyhydroquinolines **7** in good yields (Table 4).

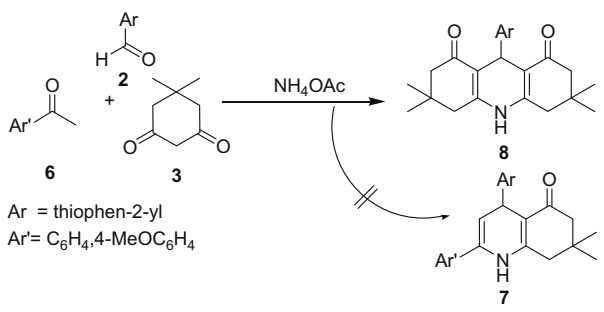
Although a good many of methods for the synthesis of the 2,4-diarylpolyhydroquinolines have been reported [42–46], all of the present methods still have limitations of inaccessibility of precursors, multi-step processes, narrow substrate scope and operational complexity. Central to our approach was to develop a simple method, using readily available starting materials and simple experimental procedures, for the rapid synthesis of diverse polyhydroquinoline derivatives.

In a further study, thiophene-2-carbaldehyde was employed in the synthesis of **7** (Scheme 5). The reactions proceeded to unexpected products **8** [47] when arones with electron-rich groups (Table 4, entry 18) were as precursors whereas the substitution of electron-withdrawing groups (Table 4, entries 12 and 17) on the arone ring generated desired products **7** in high yields (Scheme 5). The results are summarized in Table 4.

Table 4
Synthesis of compound **7** under microwave irradiation[a].

Entry	Product[b]	Ar	6	Ar′	Time (min)	Yield[c] (%)	Mp (°C)
1	**7a**	4-ClC_6H_4	**6a**	Ph	10	87	221–223
2	**7b**	Ph	**6a**	Ph	13	83	223–224
3	**7c**	4-MeC_6H_4	**6a**	Ph	11	85	227–229
4	**7d**	4-OH-3-$O_2NC_6H_3$	**6a**	Ph	12	90	231–232
5	**7e**	4-ClC_6H_4	**6b**	4-$MeOC_6H_4$	11	80	237–239
6	**7f**	4-$MeOC_6H_4$	**6b**	4-$MeOC_6H_4$	13	91	218–221
7	**7g**	4-ClC_6H_4	**6c**	4-$O_2NC_6H_4$	8	92	270–271
8	**7h**	Ph	**6c**	4-$O_2NC_6H_4$	11	90	248–251
9	**7i**	4-MeC_6H_4	**6c**	4-$O_2NC_6H_4$	9	93	259–261
10	**7j**	4-$O_2NC_6H_4$	**6c**	4-$O_2NC_6H_4$	10	81	274–276
11	**7k**	4-OH-3-$O_2NC_6H_3$	**6c**	4-$O_2NC_6H_4$	9	95	280–281
12	**7l**	Thiophen-2-yl	**6c**	4-$O_2NC_6H_4$	8	90	241–244
13	**7m**	4-BrC_6H_4	**6d**	4-BrC_6H_4	12	82	265–266
14	**7n**	Ph	**6d**	4-BrC_6H_4	13	80	270–272
15	**7o**	4-MeC_6H_4	**6d**	4-BrC_6H_4	14	90	256–257
16	**7p**	4-$O_2NC_6H_4$	**6d**	4-BrC_6H_4	9	75	279–281
17	**7q**	Thiophen-2-yl	**6d**	4-BrC_6H_4	9	83	235–237
18	**8**	Thiophen-2-yl	**6a**	Ph	8	70	>300
			6b	4-$MeOC_6H_4$			

[a] The power of MWI was 200 W at 100 °C.
[b] All the reactions are carried out with NH_4OA_C in the sealed tube.
[c] Isolated yields.



Scheme 5.

3. Conclusion

In summary, we demonstrated a rapid and direct method that offered a simple and efficient route for the one-pot, four-component synthesis of poly-substituted quinolines (4-aryl-2-ferrocenyl-quinolines and 2,4-diarylpolyhydroquinolines) in good to excellent yields. Particularly valuable features of this method included operational simplicity, increased safety for small-scale high-speed synthesis, and broader substrate scope.

4. Experimental

4.1. General information and the microwave reactor

All reactions were performed in a monomodal Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a FT-IR-tensor 27 spectrometer in KBr. ^{1}H NMR spectra were measured on a DPX 400 MHz spectrometer using TMS as an internal standard and DMSO-d_6 as solvent. Elemental analysis was determined by using a Perkin–Elmer 240c elemental analysis instrument.

4.2. General procedure for the synthesis of 4-aryl-2-ferrocenyl-quinoline derivatives *5* under microwave irradiation

All microwave-assisted reactions were performed in a monomodal Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Typically, in a 10 mL Emrys™ reaction vial, acetylferrocenyl (1 mmol), aromatic aldehyde (1 mmol), dimedone (1 mmol) and ammonium acetate (2.5 mmol) in DMF (2 mL) were mixed and then capped. The mixture was irradiated by microwave at 200 W and 100 °C for a given time. The automatic mode stirring helped the mixing and uniform heating of the reactants. Upon completion, monitored by TLC, the reaction mixture was cooled to room temperature and washed with 2 mL 95% EtOH, filtered to give the crude products, which were further purified by recrystallization from 95% EtOH. The reaction time and the yields are listed in Table 3. The analytical data of new products are as following:

4-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5a**): yellow solid; IR (KBr): ν 3300 (NH), 3098, 2958, 2865, 1668 (C=O), 1587, 1491, 1307, 1251, 1131, 1085, 819, 596 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.99 (s, 1H, NH), 7.29 (s, 2H, ArH), 7.24 (s, 2H, ArH), 5.13 (s, 1H, CH), 4.66 (d, J = 12.8 Hz, 2H, ferroceneyl), 4.40 (s, 1H, CH), 4.26 (s, 2H, ferroceneyl), 4.12 (s, 5H, ferroceneyl), 2.17 (d, J = 16.4 Hz, 1H, CH), 1.99 (d, J = 16.8 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.7, 152.2, 147.5, 132.8, 130.0, 129.1, 127.8, 105.8, 101.6, 80.0, 69.1, 68.6, 68.4, 65.2, 65.0, 50.2, 36.4, 32.0, 28.9, 26.9. Anal. Calc. for $C_{27}H_{26}ClFeNO$: C, 68.73; H, 5.55; N, 2.97. Found: C, 68.86; H, 5.45; N, 2.93%.

4-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5b**): yellow solid; IR (KBr): ν 3301 (NH), 3090,

2957, 2864, 1668 (C=O), 1588, 1492, 1307, 1252, 1130, 1082, 817, 592 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.00 (s, 1H, NH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.18 (d, J = 8.4 Hz, 2H, ArH), 5.13 (d, J = 4.8 Hz, 1H, CH), 4.66 (d, J = 13.2 Hz, 2H, ferroceneyl), 4.39 (d, J = 5.2 Hz, 1H, CH), 4.26 (s, 2H, ferroceneyl), 4.13 (s, 5H, ferroceneyl), 2.52 (s, 2H, CH_2), 2.17 (d, J = 16.4 Hz, 1H, CH), 1.99 (d, J = 16.8 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.7, 152.2, 147.9, 132.8, 130.8, 129.5, 118.4, 105.7, 101.6, 80.0, 69.1, 68.6, 68.4, 65.2, 65.0, 50.3, 36.5, 32.0, 28.9, 27.0. Anal. Calc. for $C_{27}H_{26}BrFeNO$: C, 62.82; H, 5.08; N, 2.71. Found: C, 62.97; H, 5.12; N, 2.69%.

7,8-Dihydro-7,7-dimethyl-2-ferrocenyl-4-p-tolylquinolin-5(1H,4H,6H)-one (**5c**): yellow solid; IR (KBr): ν 3300 (NH), 3081, 2958, 2866, 1669 (C=O), 1581, 1491, 1358, 1252, 1105, 999, 819, 591 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.92 (s, 1H, NH), 7.11 (s, 2H, ArH), 7.04 (s, 2H, ArH), 5.13 (s, 1H, CH), 4.68 (s, 1H, ferroceneyl), 4.63 (s, 1H, ferroceneyl), 4.34 (s, 1H, CH), 4.25 (s, 2H, ferroceneyl), 4.13 (s, 5H, ferroceneyl), 2.22 (s, 3H, CH_3), 2.16 (d, J = 16.0 Hz, 1H, CH), 1.98 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.6, 151.8, 145.7, 134.3, 132.2, 128.4, 127.2, 106.3, 102.4, 80.3, 69.1, 68.5, 68.4, 65.1, 65.0, 50.3, 36.5, 31.9, 29.0, 26.9, 20.5. Anal. Calc. for $C_{28}H_{29}FeNO$: C, 74.50; H, 6.48; N, 3.10. Found: C, 74.38; H, 6.51; N, 2.98%.

7,8-Dihydro-4-(4-methoxyphenyl)-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5d**): yellow solid; IR (KBr): ν 3302 (NH), 3095, 2958, 2865, 1666 (C=O), 1583, 1491, 1379, 1253, 1105, 1034, 821, 591 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.91 (s, 1H, NH), 7.13 (d, J = 7.2 Hz, 2H, ArH), 6.79 (d, J = 7.6 Hz, 2H, ArH), 5.12 (s, 1H, CH), 4.67 (s, 1H, ferroceneyl), 4.63 (s, 1H, ferroceneyl), 4.33 (d, J = 4.0 Hz, 2H, CH), 4.25 (s, 2H, ferroceneyl), 4.13 (s, 5H, ferroceneyl), 2.15 (d, J = 15.6 Hz, 1H, CH), 1.97 (d, J = 16.0 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.6, 157.2, 151.7, 140.8, 132.1, 128.2, 113.3, 106.4, 102.4, 80.4, 69.1, 68.5, 68.3, 65.1, 64.9, 54.9, 50.4, 35.9, 32.0, 29.0, 26.9. Anal. Calc. for $C_{28}H_{29}FeNO_2$: C, 71.95; H, 6.25; N, 3.00. Found: C, 72.07; H, 6.31; N, 2.95%.

7,8-Dihydro-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5e**): yellow solid; IR (KBr): ν 3297 (NH), 3094, 2953, 2833, 1625 (C=O), 1587, 1492, 1378, 1260, 1126, 1030, 806, 592 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.91 (s, 1H, NH), 6.82–6.80 (m, 2H, ArH), 6.73–6.69 (m, 1H, ArH), 5.13 (d, J = 5.2 Hz, 1H, CH), 4.67 (s, 1H, ferroceneyl), 4.61 (s, 1H, ferroceneyl), 4.32 (d, J = 5.2 Hz, 1H, CH), 4.25 (s, 2H, ferroceneyl), 4.12 (s, 5H, ferroceneyl), 3.69–3.62 (m, 6H, $2OCH_3$), 2.52 (s, 1H, CH), 2.17 (d, J = 16.4 Hz, 1H, CH), 2.08 (s, 1H, CH), 1.98 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.8, 151.9, 148.4, 146.9, 141.5, 132.0, 119.2, 111.6, 111.5, 106.2, 102.5, 80.3, 69.1, 68.5, 68.4, 65.1, 65.0, 55.5, 55.3, 50.3, 36.4, 31.9, 29.2, 26.7. Anal. Calc. for $C_{29}H_{31}FeNO_3$: C, 70.03; H, 6.28; N, 2.82. Found: C, 70.14; H, 6.23; N, 2.80%.

7,8-Dihydro-4-(3,4,5-trimethoxyphenyl)-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5f**): yellow solid; IR (KBr): ν 3308 (NH), 3094, 2956, 2833, 1682 (C=O), 1586, 1496, 1379, 1305, 1247, 1127, 1033, 1006, 815, 669, 591 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.93 (s, 1H, NH), 6.50 (s, 2H, ArH), 5.14 (d, J = 4.4 Hz, 1H, CH), 4.67 (s, 1H, ferroceneyl), 4.62 (s, 1H, ferroceneyl), 4.34 (d, J = 5.2 Hz, 1H, CH), 4.25 (s, 2H, ferroceneyl), 4.11 (s, 5H, ferroceneyl), 3.71 (s, 6H, $2OCH_3$), 3.59 (s, 3H, OCH_3), 2.55 (s, 2H, CH_2), 2.20 (d, J = 16.0 Hz, 1H, CH), 2.01 (d, J = 16.0 Hz, 1H, CH), 1.07 (s, 3H, CH_3), 1.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.8, 152.5, 152.2, 144.6, 135.5, 132.0, 105.7, 104.5, 102.5, 80.2, 69.1, 68.6, 68.4, 65.2, 65.0, 59.9, 55.6, 50.3, 37.3, 31.9, 29.3, 26.6. Anal. Calc. for $C_{30}H_{33}FeNO_4$: C, 68.32; H, 6.31; N, 2.66. Found: C, 68.43; H, 6.38; N, 2.68%.

4-(4-(Dimethylamino)phenyl)-7,8-dihydro-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5g**): yellow solid; IR (KBr): ν 3300 (NH), 3089, 2949, 2886, 1664 (C=O), 1580, 1494, 1380, 1306, 1253, 1133, 1080, 951, 815, 654, 594 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.85 (s, 1H, NH), 7.03 (d, J = 8.4 Hz, 2H, ArH), 6.60 (d, J = 8.8 Hz, 2H, ArH), 5.10 (d, J = 4.8 Hz, 1H, CH), 4.67 (s 1H, ferroceneyl), 4.62 (s, 1H, ferroceneyl), 4.26 (s, 1H, CH), 4.24 (s, 2H, ferroceneyl), 4.13 (s, 5H, ferroceneyl), 2.80 (s, 6H, $2CH_3$), 2.15 (d, J = 16.0 Hz, 1H, CH), 1.96 (d, J = 16.0 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.6, 151.4, 148.7, 136.9, 131.7, 127.9, 112.3, 106.7, 102.7, 80.5, 69.1, 68.4, 68.3, 65.1, 64.9, 50.4, 40.4, 35.7, 31.9, 29.1, 26.9. Anal. Calc. for $C_{29}H_{32}FeN_2O$: C, 72.50; H, 6.71; N, 5.83. Found: C, 72.41; H, 6.68; N, 5.80%.

7,8-Dihydro-7,7-dimethyl-2-ferrocenyl-4-(thiophen-2-yl)quinolin-5(1H,4H,6H)-one (**5h**): yellow solid; IR (KBr): ν 3324 (NH), 3093, 2959, 2868, 1661 (C=O), 1590, 1486, 1379, 1256, 1134, 1082, 816, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.08 (s, 1H, NH), 7.23 (d, J = 4.8 Hz, 1H, thienyl-H), 6.86 (t, J = 4.0 Hz, 1H, thienyl-H), 6.80 (s, 1H, thienyl-H), 5.24 (d, J = 5.2 Hz, 1H, CH), 4.73 (d, J = 6.8 Hz, 1H, CH), 4.68 (d, J = 13.6 Hz, 2H, ferroceneyl), 4.27 (s, 2H, ferroceneyl), 4.16 (s, 5H, ferroceneyl), 2.20 (d, J = 16.0 Hz, 1H, CH), 2.03 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 193.6, 153.0, 151.7, 133.3, 126.3, 123.5, 122.3, 106.1, 100.8, 80.0, 69.1, 68.6, 68.5, 65.3, 65.1, 50.3, 31.9, 31.4, 29.1, 26.7. Anal. Calc. for $C_{25}H_{25}FeNOS$: C, 67.72; H, 5.68; N, 3.16; S, 7.23. Found: C, 67.85; H, 5.72; N, 3.13; S, 7.20%.

4-(Benzo[d][1,3]dioxol-6-yl)-7,8-dihydro-7,7-dimethyl-2-ferrocenylquinolin-5(1H,4H,6H)-one (**5i**): yellow solid; IR (KBr): ν 3358 (NH), 3079, 2952, 2889, 1665 (C=O), 1599, 1483, 1387, 1294, 1138, 1038, 925, 809, 592 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.97 (s, 1H, NH), 6.80–6.72 (m, 3H, ArH), 5.92 (s 2H, CH_2), 5.15 (s 1H, CH), 4.68 (s, 2H, ferroceneyl), 4.67 (s, 1H, CH), 4.27 (s, 2H, ferroceneyl), 4.14 (s, 5H, ferroceneyl), 2.20–1.98 (m, 2H, CH_2), 1.08–0.98 (m, 6H, $2CH_3$). Anal. Calc. for $C_{28}H_{27}FeNO_3$: C, 69.86; H, 5.65; N, 2.91. Found: C, 70.01; H, 5.70; N, 2.88%.

4.3. General procedure for the synthesis of 2,4-diarylpolyhydroquinolines **7** under microwave irradiation

In a 10-mL reaction vial, arones (1 mmol), aromatic aldehyde (1 mmol), dimedone (1 mmol) were mixed in the present of ammonium acetate (2.5 mmol) and then the vial was capped. The mixture was irradiated for a given time at maximum power of 200 W and 100 °C. When the reaction was completed (monitored by TLC), the subsequent workup was the performed as for the preparation of **5** under microwave irradiation.

4-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-2-phenylquinolin-5(1H,4H,6H)-one (**7a**): yellow crystal; IR (KBr): ν 3231 (NH), 3057, 2952, 2865, 1661 (C=O), 1583, 1494, 1393, 1278, 1122, 1087, 822, 767, 697, 594 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.64 (s, 1H, NH), 7.50–7.47 (m, 2H, ArH), 7.41–7.35 (m, 3H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 7.23 (d, J = 8.4 Hz, 2H, ArH), 5.18 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.57 (d, J = 5.6 Hz, 1H, CH), 2.46 (d, J = 5.2 Hz, 2H, CH_2), 2.17 (d, J = 16.0 Hz, 1H, CH), 2.00 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{22}ClNO$: C, 75.92; H, 6.09; N, 3.85. Found: C, 76.02; H, 6.05; N, 3.83%.

7,8-Dihydro-7,7-dimethyl-2,4-diphenylquinolin-5(1H,4H,6H)-one (**7b**): yellow crystal; IR (KBr): ν 3284 (NH), 3075, 2957, 2867, 1656 (C=O), 1590, 1491, 1328, 1240, 1153, 1055, 846, 766, 698, 577 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.58 (s, 1H, NH), 7.49–7.47 (m, 2H, ArH), 7.40–7.34 (m, 3H, ArH), 7.26–7.21 (m, 4H, ArH), 7.12–7.07 (m, 1H, ArH), 5.21 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H, CH), 4.56 (d, J = 5.2 Hz, 1H, CH), 2.47 (d, J = 3.6 Hz, 2H, CH_2),

2.17 (d, J = 16.0 Hz, 1H, CH), 1.99 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.95; H, 6.99; N, 4.23%.

7,8-Dihydro-7,7-dimethyl-2-phenyl-4-p-tolylquinolin-5(1H,4H,6H)-one (**7c**): yellow crystal; IR (KBr): ν 3232 (NH), 3053, 2951, 2865, 1661 (C=O), 1583, 1491, 1385, 1278, 1121, 1060, 810, 769, 697, 594 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.58 (s, 1H, NH), 7.48–7.46 (m, 2H, ArH), 7.40–7.34 (m, 3H, ArH), 7.10 (d, J = 8.0 Hz, 2H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 5.18 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.51 (d, J = 5.2 Hz, 1H, CH), 2.46 (d, J = 6.4 Hz, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.16 (d, J = 16.0 Hz, 1H, CH), 1.98 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). Anal. Calc. for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 84.04; H, 7.37; N, 4.06%.

7,8-Dihydro-4-(4-hydroxy-3-nitrophenyl)-7,7-dimethyl-2-phenylquinolin-5(1H,4H,6H)-one (**7d**): yellow solid; IR (KBr): ν 3369 (NH), 2948, 2886, 1659 (C=O), 1590, 1483, 1327, 1232, 1056, 828, 759, 685, 571 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 10.67 (s, 1H, OH), 8.71 (s, 1H, NH), 7.68 (s, 1H, ArH), 7.51–7.36 (m, 6H, ArH), 7.05 (d, J = 8.4 Hz, 2H, ArH), 5.22 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.59 (d, J = 5.2 Hz, 1H, CH), 2.47 (d, J = 8.0 Hz, 2H, CH_2), 2.19 (d, J = 16.0 Hz, 1H, CH), 2.00 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.17. Found: C, 70.88; H, 5.71; N, 7.15%.

4-(4-Chlorophenyl)-7,8-dihydro-2-(4-methoxyphenyl)-7,7-dimethylquinolin-5(1H,4H,6H)-one (**7e**): yellow crystal; IR (KBr): ν 3237 (NH), 3199, 3073, 2997, 2866, 1662 (C=O), 1609, 1588, 1499, 1389, 1237, 1185, 1057, 822, 625, 551 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6, 25 °C): δ = 8.57 (s, 1H, NH), 7.41 (d, J = 8.8 Hz, 2H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 6.94 (d, J = 8.8 Hz, 2H, ArH), 5.08 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.55 (d, J = 5.6 Hz, 1H, CH), 3.76 (s, 3H, OCH_3), 2.46 (d, J = 5.2 Hz, 2H, CH_2), 2.16 (d, J = 16.0 Hz, 1H, CH), 1.99 (d, J = 16.0 Hz, 1H, CH), 1.02 (s, 3H, CH_3), 0.93 (s, 3H, CH_3). Anal. Calc. for $C_{24}H_{24}ClNO_2$: C, 73.18; H, 6.14; N, 3.56. Found: C, 73.03; H, 6.17; N, 3.52%.

7,8-Dihydro-2,4-bis(4-methoxyphenyl)-7,7-dimethylquinolin-5(1H,4H,6H)-one (**7f**): yellow crystal; IR (KBr): ν 3239 (NH), 3267, 3071, 2951, 2866, 1660 (C=O), 1586, 1491, 1391, 1237, 1184, 1033, 830, 762, 623, 534 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.47 (s, 1H, NH), 7.41 (d, J = 8.8 Hz, 2H, ArH), 7.11 (d, J = 8.4 Hz, 2H, ArH), 6.93 (d, J = 9.2 Hz, 2H, ArH), 6.79 (d, J = 8.4 Hz, 2H, ArH), 5.08 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.47 (d, J = 5.2 Hz, 1H, CH), 3.76 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.44 (d, J = 6.0 Hz, 2H, CH_2), 2.15 (d, J = 16.0 Hz, 1H, CH), 1.97 (d, J = 16.0 Hz, 1H, CH), 1.02 (s, 3H, CH_3), 0.93 (s, 3H, CH_3). Anal. Calc. for $C_{25}H_{27}NO_3$: C, 77.09; H, 6.99; N, 3.60. Found: C, 77.17; H, 7.04; N, 3.57%.

4-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-2-(4-nitrophenyl)-quinolin-5(1H,4H,6H)-one (**7g**): yellow solid; IR (KBr): ν 3330 (NH), 3110, 3077, 2948, 2866, 1659 (C=O), 1588, 1488, 1347, 1247, 1123, 1013, 850, 752, 696, 560 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.82 (s, 1H, NH), 8.24 (d, J = 8.8 Hz, 2H, ArH), 7.78 (d, J = 9.2 Hz, 2H, ArH), 7.31 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8.4 Hz, 2H, ArH), 5.47 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.62 (d, J = 5.6 Hz, 1H, CH), 2.49 (d, J = 2.8 Hz, 2H, CH_2), 2.18 (d, J = 16.0 Hz, 1H, CH), 2.02 (d, J = 16.0 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{21}ClN_2O_3$: C, 67.56; H, 5.18; N, 6.85. Found: C, 67.64; H, 5.21; N, 6.86%.

7,8-Dihydro-7,7-dimethyl-2-(4-nitrophenyl)-4-phenylquinolin-5(1H,4H,6H)-one (**7h**): yellow crystal; IR (KBr): ν 3250 (NH), 3073, 2941, 2887, 1644 (C=O), 1590, 1503, 1392, 1241, 1126, 1056, 850, 752, 699, 585 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.76 (s, 1H, NH), 8.23 (d, J = 9.2 Hz, 2H, ArH), 7.77 (d, J = 9.2 Hz, 2H, ArH), 7.27–7.22 (m, 4H, ArH), 7.13–7.09 (m, 1H, ArH), 5.49 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.60 (d, J = 5.6 Hz, 1H, CH), 2.49 (s, 2H, CH_2), 2.18 (d, J = 16.0 Hz, 1H, CH), 2.02 (d, J = 16.4 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C, 73.65; H, 5.96; N, 7.51%.

7,8-Dihydro-7,7-dimethyl-2-(4-nitrophenyl)-4-p-tolylquinolin-5(1H,4H,6H)-one (**7i**): yellow crystal; IR (KBr): ν 3260 (NH), 3074, 2964, 2886, 1635 (C=O), 1593, 1489, 1338, 1242, 1125, 1056, 850, 752, 690, 580 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.74 (s, 1H, NH), 8.23 (d, J = 9.2 Hz, 2H, ArH), 7.76 (d, J = 8.8 Hz, 2H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 5.46 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.55 (d, J = 5.6 Hz, 1H, CH), 2.47 (s, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.18 (d, J = 16.0 Hz, 1H, CH), 2.00 (d, J = 16.0 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). Anal. Calc. for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21. Found: C, 74.30; H, 6.27; N, 7.18%.

7,8-Dihydro-7,7-dimethyl-2,4-bis(4-nitrophenyl)quinolin-5(1H,4H,6H)-one (**7j**): yellow solid; IR (KBr): ν 3345 (NH), 3077, 2951, 2867, 1657 (C=O), 1592, 1487, 1339, 1244, 1108, 1057, 852, 752, 695, 586 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.93 (s, 1H, NH), 8.24 (d, J = 8.8 Hz, 2H, ArH), 8.15 (d, J = 8.0 Hz, 2H, ArH), 7.78 (d, J = 9.2 Hz, 2H, ArH), 7.50 (d, J = 8.4 Hz, 2H, ArH), 5.47 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.78 (d, J = 5.2 Hz, 1H, CH), 2.49 (s, 2H, CH_2), 2.20 (d, J = 16.0 Hz, 1H, CH), 2.03 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{21}N_3O_5$: C, 65.86; H, 5.05; N, 10.02. Found: C, 65.74; H, 5.03; N, 9.99%.

7,8-Dihydro-4-(4-hydroxy-3-nitrophenyl)-7,7-dimethyl-2-(4-nitrophenyl)quinolin-5(1H,4H,6H)-one (**7k**): yellow solid; IR (KBr): ν 3287 (NH), 3063, 2965, 2868, 1625 (C=O), 1589, 1499, 1337, 1244, 1155, 1060, 851, 755, 691, 590 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6, 25 °C): δ = 10.72 (s, 1H, OH), 8.89 (s, 1H, NH), 8.25 (d, J = 9.2 Hz, 2H, ArH), 7.79 (d, J = 9.2 Hz, 2H, ArH), 7.69 (s, 1H, ArH), 7.45 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.06 (d, J = 8.4 Hz, 1H, ArH), 5.49 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.63 (d, J = 5.6 Hz, 1H, CH), 2.49 (s, 2H, CH_2), 2.20 (d, J = 16.0 Hz, 1H, CH), 2.03 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{21}N_3O_6$: C, 63.44; H, 4.86; N, 9.65. Found: C, 63.36; H, 4.89; N, 9.70%.

7,8-Dihydro-7,7-dimethyl-2-(4-nitrophenyl)-4-(thiophen-2-yl)quinolin-5(1H,4H,6H)-one (**7l**): yellow crystal; IR (KBr): ν 3280 (NH), 3077, 2955, 2883, 1650 (C=O), 1594, 1490, 1339, 1242, 1123, 1057, 851, 696, 592 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.93 (s, 1H, NH), 8.26 (d, J = 8.8 Hz, 2H, ArH), 7.80 (d, J = 8.8 Hz, 2H, ArH), 7.25 (d, J = 5.2 Hz, 1H, thienyl-H), 6.88 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H, thienyl-H), 6.82 (d, J = 3.2 Hz, 1H, thienyl-H), 5.57 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.92 (d, J = 5.6 Hz, 1H, CH), 2.49 (s, 1H, CH), 2.42 (d, J = 16.8 Hz, 1H, CH), 2.22 (d, J = 16.0 Hz, 1H, CH), 2.06 (d, J = 16.0 Hz, 1H, CH), 1.05 (s, 3H, CH_3), 0.98 (s, 3H, CH_3). Anal. Calc. for $C_{21}H_{20}N_2O_3S$: C, 66.29; H, 5.30; N, 7.36; S, 8.43. Found: C, 66.35; H, 5.28; N, 7.41; S, 8.39%.

2,4-Bis(4-bromophenyl)-7,8-dihydro-7,7-dimethylquinolin-5(1H,4H,6H)-one (**7m**): white solid; IR (KBr): ν 3331 (NH), 3072, 2952, 2866, 1652 (C=O), 1609, 1586, 1485, 1385, 1238, 1126, 1069, 1008, 818, 586 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.68 (s, 1H, NH), 7.58 (d, J = 8.4 Hz, 2H, ArH), 7.45–7.42 (m, 4H, ArH), 7.17 (d, J = 8.4 Hz, 2H, ArH), 5.23 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.55 (d, J = 5.2 Hz, 1H, CH), 2.46 (d, J = 7.6 Hz, 2H, CH_2), 2.17 (d, J = 16.0 Hz, 1H, CH), 1.99 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{21}Br_2NO$: C, 56.70; H, 4.34; N, 2.87. Found: C, 56.83; H, 4.36; N, 2.90%.

2-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-4-phenylquinolin-5(1H,4H,6H)-one (**7n**): white solid; IR (KBr): ν 3228 (NH), 3065, 2959, 2866, 1665 (C=O), 1586, 1497, 1326, 1239, 1122, 886, 769, 695, 592 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.62 (s, 1H, NH), 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.44 (d, J = 8.8 Hz, 2H, ArH), 7.26–7.20 (m, 4H, ArH), 7.12–7.08 (m, 1H, ArH), 5.26 (dd, J_1 = 5.6

Hz, J_2 = 1.6 Hz, 1H, CH), 4.55 (d, J = 5.2 Hz, 1H, CH), 2.47 (d, J = 5.6 Hz, 2H, CH_2), 2.17 (d, J = 16.0 Hz, 1H, CH), 2.00 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{22}BrNO$: C, 67.65; H, 5.43; N, 3.43. Found: C, 67.72; H, 5.41; N, 3.46%.

2-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-4-p-tolylquinolin-5(1H,4H,6H)-one (**7o**): white solid; IR (KBr): ν 3320 (NH), 3080, 2969, 2865, 1650 (C=O), 1602, 1579, 1486, 1387, 1238, 1127, 1008, 803, 640, 560 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.59 (s, 1H, NH), 7.57 (d, J = 8.8 Hz, 2H, ArH), 7.43 (d, J = 8.4 Hz, 2H, ArH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 5.23 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.50 (d, J = 5.2 Hz, 1H, CH), 2.45 (d, J = 7.6 Hz, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.16 (d, J = 16.0 Hz, 1H, CH), 1.98 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). Anal. Calc. for $C_{24}H_{24}BrNO$: C, 67.65; H, 5.43; N, 3.43. Found: C, 67.78; H, 5.48; N, 3.45%.

2-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-4-(4-nitrophenyl)-quinolin-5(1H,4H,6H)-one (**7p**): yellow solid; IR (KBr): ν 3354 (NH), 3078, 2953, 2869, 1654 (C=O), 1591, 1485, 1340, 1239, 1127, 1006, 829, 756, 543 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.79 (s, 1H, NH), 8.15 (d, J = 8.8 Hz, 2H, ArH), 7.59 (d, J = 8.4 Hz, 2H, ArH), 7.49–7.44 (m, 4H, ArH), 5.24 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H, CH), 4.73 (d, J = 5.2 Hz, 1H, CH), 2.48 (s, 1H, CH), 2.19 (d, J = 16.0 Hz, 1H, CH), 2.08 (s, 1H, CH), 2.01 (d, J = 16.0 Hz, 1H, CH), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{21}BrN_2O_3$: C, 60.94; H, 4.67; N, 6.18. Found: C, 61.04; H, 4.71; N, 6.21%.

2-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-4-(thiophen-2-yl)-quinolin-5(1H,4H,6H)-one (**7q**): white solid; IR (KBr): ν 3275 (NH), 3076, 2959, 2870, 1653 (C=O), 1594, 1488, 1386, 1239, 1008, 807, 699, 516 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.79 (s, 1H, NH), 7.61 (d, J = 8.8 Hz, 2H, ArH), 7.47 (d, J = 8.4 Hz, 2H, ArH), 7.23 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz,, 1H, thienyl-H), 6.87 (dd, J_1 = 4.8 Hz, J_2 = 3.2 Hz, 1H, thienyl-H), 6.80 (d, J = 3.6 Hz, 1H, thienyl-H), 5.35 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H, CH), 4.87 (d, J = 5.6 Hz, 1H, CH), 2.46 (s, 1H, CH), 2.38 (d, J = 17.2 Hz, 1H, CH), 2.21 (d, J = 16.0 Hz, 1H, CH), 2.04 (d, J = 16.0 Hz, 1H, CH), 1.03 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). Anal. Calc. for $C_{21}H_{20}BrNOS$: C, 60.87; H, 4.87; N, 3.38; S, 7.74. Found: C, 60.79; H, 4.91; N, 3.42; S, 7.78%.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(thiophen-2-yl)acridine-1,8(2H,5H,9H,10H)-dione (**8a**): yellow crystal; IR (KBr): ν 3276 (NH), 3065, 2956, 2931, 2872, 1638 (C=O), 1633 (C=O), 1609, 1482, 1371, 1219, 1141, 1003, 980, 850, 716, 691, 558 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.43 (s, 1H, NH), 7.13 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, thienyl-H), 6.80–6.77 (m, 1H, thienyl-H), 6.65 (d, J = 3.2 Hz, 1H, thienyl-H), 5.14 (s, 1H, CH), 2.44 (d, J = 17.2 Hz, 2H, CH_2), 2.31 (d, J = 17.2 Hz, 2H, CH_2), 2.21 (d, J = 16.0 Hz, 2H, CH_2), 2.07 (d, J = 16.0 Hz, 2H, CH_2), 1.02 (s, 6H, $2CH_3$), 0.93 (s, 6H, $2CH_3$).

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