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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 4439–4449

Three-component green synthesis of *N*-arylquinoline derivatives in ionic liquid [Bmim$^+$][BF$_4^-$]: reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and active methylene compounds

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Received 2 November 2006; revised 12 December 2006; accepted 13 March 2007
Available online 16 March 2007

Abstract—Three series of *N*-arylquinoline derivatives were synthesized by the three-component reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and active methylene compounds including malononitrile, meldrum's acid, and 1,3-indenedione in ionic liquid [bmim$^+$][BF$_4^-$] at 90 °C.

1. Introduction

Heteroaromatic rings containing nitrogen atoms often play important roles as the scaffolds of bioactive substances. Quinoline is one of the most popular *N*-heteroaromatic compounds incorporated into the structures of many pharmaceuticals. It is known that many quinoline containing compounds exhibit a wide spectrum of pharmacological activities, such as antiplasmodial,[1] intrinsic,[2] cytotoxic,[3] functional,[4] antibacterial,[5] antiproliferative,[6] antimalarial,[7] and anticancer activities.[8] Therefore, the synthesis of quinolines has attracted much attention in organic synthesis. The classical methods for the synthesis of quinoline derivatives include Skraup, Doebner–Von Miller, Conrad–Limbach, Combes, and Pfitzinger quinoline syntheses.[9] A number of general synthetic methods have also been reported.[10] However, they were either tedious or poor yields, while organic solvents were used during all of the reactions. Furthermore, it should be noted that there was no *N*-substitute in the quinoline derivatives. To our best knowledge, only a few studies[11] concerning *N*-substituted quinolines were reported in the literature, which were also synthesized in traditional organic solvents.

Room temperature ionic liquids (RTILs), especially those based on the 1-*N*-alkyl-3-methyl imidazolium cation, have shown great promise as attractive alternatives to conventional solvents.[12] These materials are also widely used in homogeneous catalysis,[13] electrochemistry,[14] photochemistry,[15] and liquid crystals.[16] The distinctive property of room temperature ionic liquids is that they have essentially no vapor pressure, which makes them optimal replacements for the volatile organic solvents traditionally used as industrial solvents. Another feature of ionic liquids is their ability to be reused many times. Because of this advantage, ionic liquids have made significant contributions to green chemistry and have been used widely as reaction medium in organic chemistry.[17] As a part of a program directed toward the synthesis of new suitably functionalized heterocyclic compounyds of potential biological activity in green solvent,[18] herein we report three series of *N*-arylquinoline derivatives by three-component reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and active methylene compounds including malononitrile, meldrum's acid, and 1,3-indenedione in ionic liquid [bmim$^+$][BF$_4^-$] at 90 °C.

2. Results and discussion

In order to avoid the disadvantages such as volatility and toxicity that many organic solvents inherently have, we employed RTILs into the three-component reaction as a green medium. When the reaction of arylaldehyde **1**, 3-arylamino-5,5-dimethylcyclohex-2-enone **2**, and malononitrile **3** was performed in ionic liquid [bmim$^+$][BF$_4^-$] at 90 °C, high

Keywords: *N*-Arylquinoline; Ionic liquid; Malononitrile; Meldrum's acid; 1,3-Indenedione; Synthesis.
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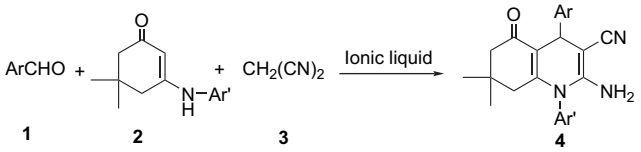
doi:10.1016/j.tet.2007.03.068

yields of 2-amino-1,4-diaryl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles **4** were obtained (Scheme 1).



Scheme 1.

We began our study of the reaction showed in Scheme 1 by optimizing the reaction conditions for the preparation of **4**. A summary of the optimization experiment is provided in Table 1. The results showed that at room temperature, no reaction took place (Table 1, entry 1). To our delight at 90 °C the reaction proceeded smoothly in high yield. To find the optimum reaction time, the reaction was carried out in ionic liquid [bmim$^+$][BF$_4^-$] for 3, 6, or 9 h (Table 1, entries 3–5), leading to **4a** in 82%, 94%, and 94% yield, respectively. Thus, the optimal reaction temperature and reaction time is 90 °C and 6 h, respectively. Moreover, different ionic liquids were further investigated as shown in Table 1, we concluded that the [bmim$^+$][BF$_4^-$] was the best ionic liquid for this reaction. In addition to MeCN, MeOH and EtOH were also tested as the reaction solvents. In these cases, product **4a** was formed in slightly lower yield (Table 1, entries 11–13). We also conducted the reaction under solvent-free conditions; compound **4a** was produced in 90% yield (Table 1, entry 14).

After the reaction was completed (monitored by TLC), the reaction mixtures were cooled to room temperature, the solid was isolated by filtration, and the ionic liquid in filtrate could be recovered easily by evaporation at 80 °C in *vacuum* for several hours. The recovered ionic liquid could be used for the same reactions directly. Alternatively, the ionic liquid was washed with ethyl acetate, followed by evaporation at 80 °C in *vacuum* for several hours, if it was used for the other reaction with different substrates. Investigations by using 4-fluorobenzaldehyde, 3-phenylamino-5,5-dimethylcyclohex-2-enone, and **3** as model substrates proved the successive reuse of the recovered ionic liquid. Even in the fourth cycle the yield (92%) of product **4a** is fairly high.

Table 1. Synthesis of **4a** in ionic liquid at different reaction conditions[a]

Entry	T (°C)	Ionic liquid[b]	Time (h)	Yield[c] (%)
1	rt	[bmim$^+$][BF$_4^-$]	6	0
2	50	[bmim$^+$][BF$_4^-$]	6	78
3	90	[bmim$^+$][BF$_4^-$]	3	82
4	**90**	**[bmim$^+$][BF$_4^-$]**	**6**	**94**
5	90	[bmim$^+$][BF$_4^-$]	9	94
6	90	[emim$^+$]Br$^-$	6	86
7	90	[pmim$^+$]Br$^-$	6	87
8	90	[bmim$^+$] Br$^-$	6	90
9	90	[emim$^+$][BF$_4^-$]	6	90
10	90	[pmim$^+$][BF$_4^-$]	6	91
11	Reflux	CH_3CN	10	90
12	Reflux	CH_3OH	11	87
13	Reflux	EtOH	8	89
14	90	Solvent free	8	90

[a] Reaction condition: 10 mL ionic liquid, 1 mmol 4-fluorobenzaldehyde, 1 mmol 3-phenylamino-5,5-dimethylcyclohex-2-enone, and 1 mmol **3**.
[b] bmim=1-butyl-3-methylimidazolium; emim=1-ethyl-3-methylimidazolium; pmim=1-methyl-3-propylimidazolium.
[c] Isolated yields.

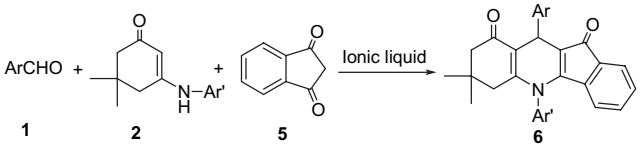
Table 2. The reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and malononitrile in ionic liquid[a]

Entry	Ar	Ar′	Products	Time (h)	Yields[b] (%)
1	4-FC_6H_4	C_6H_5	**4a**	6	94
2	4-BrC_6H_4	C_6H_5	**4b**	7	95
3	3-$NO_2C_6H_4$	C_6H_5	**4c**	5	96
4	3-$NO_2C_6H_4$	4-BrC_6H_4	**4d**	5	93
5	4-FC_6H_4	4-BrC_6H_4	**4e**	6	94
6	4-BrC_6H_4	4-BrC_6H_4	**4f**	7	95
7	3,4-$Cl_2C_6H_3$	4-BrC_6H_4	**4g**	6	94
8	3,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	**4h**	5	98
9	3-$NO_2C_6H_4$	4-$CH_3C_6H_4$	**4i**	5	99
10	4-ClC_6H_4	4-$CH_3C_6H_4$	**4j**	6	96
11	2,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	**4k**	5	96
12	4-Cl-2-$NO_2C_6H_3$	4-$CH_3C_6H_4$	**4l**	4	98
13	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**4m**	6	94
14	4-BrC_6H_4	4-$CH_3C_6H_4$	**4n**	6	96

[a] Reaction condition: 10 mL [bmim$^+$][BF$_4^-$], 1 mmol **1**, 1 mmol **2**, and 1 mmol **3**.
[b] Isolated yields.

In order to demonstrate the efficiency and the applicability of the present method, we performed the reaction of a variety of arylaldehydes **1** and 3-arylamino-5,5-dimethylcyclohex-2-enones **2** with **3** at 90 °C in ionic liquid medium of [bmim$^+$][BF$_4^-$]. As shown in Table 2, for series of **1** and **2**, either the aromatic ring containing electron-withdrawing groups (such as halide, nitro) or electron-donating groups (such as alkyl group), reacted well with **3** to give the corresponding products **4** in high yields under the same reaction conditions. So we concluded that no obvious effects from the electronic or nature of the aromatic ring substituents were observed in the above reactions.

As expected, when the methylene compound of malononitrile was replaced by 1,3-indenedione **5**, another series of 5,10-diaryl-7,8-dihydro-7,7-dimethyl-5*H*-indeno[1,2-*b*]-quinolin-9,11(6*H*,10*H*)-dione derivatives **6** were obtained under the same reaction conditions (Scheme 2). The results are summarized in Table 3. The product of **6a** was further confirmed by X-ray diffraction analysis,[19] and the crystal structure is shown in Figure 1.



Scheme 2.

When the meldrum's acid was selected as methylene compound (Scheme 3), it was interesting that the desired products **9** were not detected at all, while 4-aryl-7,7-dimethyl-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione derivatives **8** were obtained in good yields via an

Table 3. The reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and 1,3-indenedione in ionic liquid[a]

Entry	Ar	Ar′	Products	Time (h)	Yields[b] (%)
1	4-BrC_6H_4	C_6H_5	**6a**	6	95
2	4-BrC_6H_4	4-BrC_6H_4	**6b**	7	95
3	2-ClC_6H_4	4-$CH_3C_6H_4$	**6c**	5	96
4	4-ClC_6H_4	1-Napthylphenyl	**6d**	6	91
5	3,4-$Cl_2C_6H_3$	1-Napthylphenyl	**6e**	6	92
6	4-BrC_6H_4	1-Napthylphenyl	**6f**	6	90
7	2,4-$Cl_2C_6H_3$	1-Napthylphenyl	**6g**	6	93
8	4-$NO_2C_6H_4$	1-Napthylphenyl	**6h**	5	93
9	4-$CH_3C_6H_4$	2-Napthylphenyl	**6i**	7	90
10	4-BrC_6H_4	2-Napthylphenyl	**6j**	6	93
11	4-$NO_2C_6H_4$	2-Napthylphenyl	**6k**	5	92
12	2,4-$Cl_2C_6H_3$	2-Napthylphenyl	**6l**	6	94
13	3,4-$(CH_3O)_2C_6H_3$	2-Napthylphenyl	**6m**	8	93
14	2-ClC_6H_4	2-Napthylphenyl	**6n**	5	92
15	3-ClC_6H_4	2-Napthylphenyl	**6o**	7	91
16	4-OHC_6H_4	2-Napthylphenyl	**6p**	8	91

[a] Reaction condition: 10 mL [bmim$^+$][BF_4^-], 1 mmol **1**, 1 mmol **2**, and 1 mmol **5**.
[b] Isolated yields.

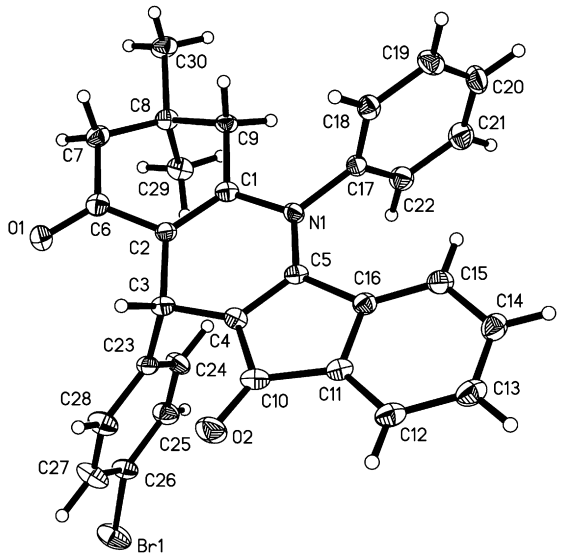


Figure 1. The structure of **6a** showing 50% probability displacement ellipsoids.

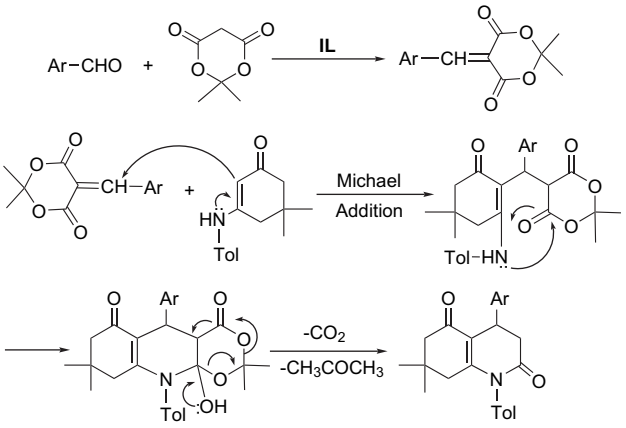
unexpected ring opening of meldrum's acid reaction. However, only the aromatic rings with *ortho*-substituent resulted in this reaction as summarized in Table 4.

Table 4. The reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and meldrum's acid in the ionic liquid[a]

Entry	Ar	Time (h)	Products	Yields[b] (%)
1	2-ClC_6H_4	16	**8a**	88
2	2,4-$Cl_2C_6H_3$	16	**8b**	89
3	2-$NO_2C_6H_4$	12	**8c**	86
4	2-$OCH_3C_6H_4$	20	**8d**	80
5	2-FC_6H_4	16	**8e**	82
6	2-NO_2-4,5-$OCH_2OC_6H_4$	12	**8f**	84

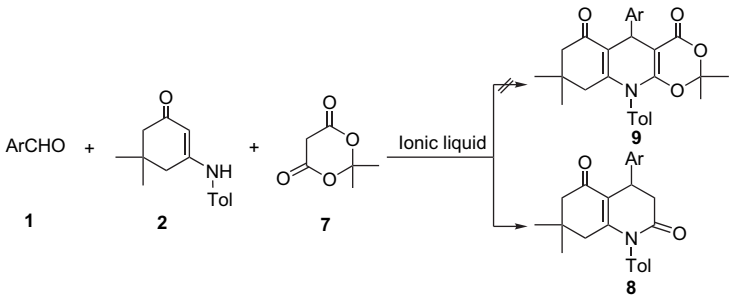
[a] Reaction condition: 10 mL [bmim$^+$][BF_4^-], 1 mmol **1**, 1 mmol **2**, and 1 mmol **7**.
[b] Isolated yields.

Although the detailed mechanism of the above reaction has not been clarified yet, the formation of 4-aryl-7,7-dimethyl-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione derivatives **8** can be explained by the tentative mechanism presented in Scheme 4. Importantly, meldrum's acid readily eliminated CO_2 and acetone when heated.

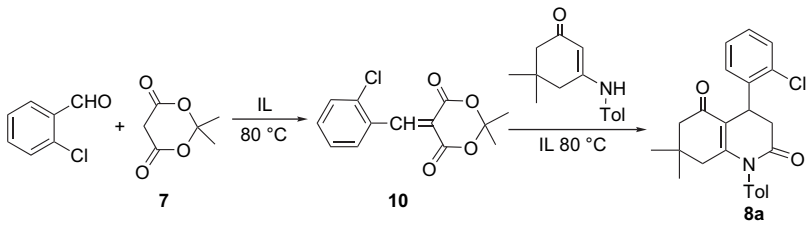


Scheme 4.

To verify the mechanism, we individually performed each separate step. The Knoevenagel condensation product, 5-(2-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **10** was obtained in 62% yield, when the 2-chlorobenzaldehyde (**1**, Ar=2-ClC_6H_4) was treated with meldrum's acid in ionic liquid (Scheme 5). As expected, intermediate **10** smoothly reacted with **2** to give the corresponding quinoline-2,5(1*H*,6*H*)-dione derivatives **8a** (Scheme 5). This result suggests that a Knoevenagel condensation took place during the reaction.



Scheme 3.



Scheme 5.

3. Conclusion

In conclusion, we found a green method for the syntheses of *N*-arylquinoline-3-carbonitrile derivatives, *N*-arylindeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione derivatives, and *N*-tolylquinoline-2,5(1*H*,6*H*)-dione derivatives by the three-component reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and active methylene compounds. The features of this procedure are mild reaction conditions, high yields, operational simplicity, and the environmentally friendly procedure. Meanwhile, [bmim$^+$][BF_4^-] could be reused for several rounds without significant loss of activity.

4. Experimental

4.1. General

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 with Me_4Si as internal standard using an Inova-400 spectrometer. Elemental analyses were carried out using Perkin–Elmer 240 II analyzer. ESI-MS was performed using a FINNIGAN LCQ Advantage mass spectrometer.

4.2. General procedure for the syntheses of 2-amino-1,4-diaryl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4

A dry 50 mL flask was charged with arylaldehyde (1.0 mmol), malononitrile (1.0 mmol), 3-arylamino-5,5-dimethylcyclohex-2-enone (1.0 mmol), and ionic liquid [bmim$^+$][BF_4^-] (10 mL). The reaction mixture was stirred at 90 °C for 4–7 h, and then cooled to room temperature. The generated yellow solid was filtered off, and the ionic liquid in filtrate was then recovered for reuse by evaporating at 80 °C for several hours in *vacuum*. The crude yellow products were washed with water and purified by recrystallization from DMF and water, followed by being dried at 80 °C for several hours in *vacuum* to give **4**.

4.2.1. 2-Amino-7,7-dimethyl-4-(4-fluorophenyl)-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4a. Pale yellow crystals, mp 263–265 °C.

IR (KBr, ν, cm^{-1}): 3454, 3339, 3053, 2959, 2958, 2888, 2177, 1651, 1639, 1592, 1558, 1504, 1489, 1417, 1371, 1340, 1257, 1216, 1153, 1046, 929, 849, 781, 764, 702.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.70 (d, J=17.6 Hz, 1H, CH), 2.01 (d, J=16.0 Hz, 1H, CH), 2.17–2.22 (m, 2H, 2CH), 4.48 (s, 1H, CH), 5.38 (s, 2H, NH_2), 7.15 (t, J=8.8 Hz, 2H, ArH), 7.29–7.32 (m, 2H, ArH), 7.41 (d, J=6.8 Hz, 2H, ArH), 7.57–7.62 (m, 3H, ArH).

LC–MS (ESI$^+$, *m*/*z*): 797 [(2M+Na$^+$), 5%], 386 [(M−1), 87%].

Anal. Calcd for $C_{24}H_{22}FN_3O$: C 74.40, H 5.72, N 10.85; found: C 74.28, H 5.77, N 10.93.

4.2.2. 2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4b. Pale yellow crystals, mp 275–277 °C (lit.[11b] 270 °C).

IR (KBr, ν, cm^{-1}): 3464, 3329, 3060, 2956, 2902, 2867, 2178, 1652, 1593, 1567, 1489, 1372, 1314, 1258, 1172, 1144, 1069, 1040, 1008, 840, 810, 757, 697.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.70 (d, J=17.6 Hz, 1H, CH), 2.01 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=16.8 Hz, 2H, 2CH), 4.46 (s, 1H, CH), 5.40 (s, 2H, NH_2), 7.24 (d, J=8.0 Hz, 2H, ArH), 7.41 (d, J=6.4 Hz, 2H, ArH), 7.53 (d, J=8.0 Hz, 2H, ArH), 7.57–7.66 (m, 3H, ArH).

4.2.3. 2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4c. Pale yellow crystals, mp 268–269 °C.

IR (KBr, ν, cm^{-1}): 3465, 3329, 2960, 2871, 2179, 1651, 1618, 1592, 1523, 1417, 1374, 1349, 1257, 1146, 1072, 810, 734, 710, 693.

^{1}H NMR (DMSO-d_6) δ: 0.72 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.73 (d, J=17.6 Hz, 1H, CH), 2.02 (d, J=16.0 Hz, 1H, CH), 2.22 (d, J=16.0 Hz, 1H, CH), 2.24 (d, J=17.6 Hz, 1H, CH), 4.65 (s, 1H, CH), 5.55 (s, 2H, NH_2), 7.42 (d, J=6.8 Hz, 2H, ArH), 7.57–7.70 (m, 4H, ArH), 7.79 (d, J=7.6 Hz, 1H, ArH), 8.09–8.11 (m, 2H, ArH).

Anal. Calcd for $C_{24}H_{22}N_4O_3$: C 69.55, H 5.35, N 13.52; found: C 69.48, H 5.36, N 13.44.

4.2.4. 2-Amino-1-(4-bromophenyl)-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4d. Pale yellow crystals, mp 271–274 °C.

IR (KBr, ν, cm^{-1}): 3479, 3382, 2957, 2924, 2870, 2180, 1642, 1566, 1489, 1412, 1374, 1259, 1179, 1148, 1073, 1011, 895, 808, 746, 696.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.76 (d, J=17.6 Hz, 1H, CH), 2.00 (d, J=16.0 Hz, 1H, CH), 2.17 (d, J=16.0 Hz, 1H, CH), 2.25 (d, J=17.6 Hz, 1H, CH), 4.63 (s, 1H, CH), 5.72 (s, 2H, NH_2), 7.38 (d, J=8.4 Hz, 2H, ArH), 7.64–7.69 (m, 1H, ArH), 7.79–7.81 (m, 3H, ArH), 8.07–8.11 (m, 2H, ArH).

Anal. Calcd for $C_{24}H_{21}BrN_4O_3$: C 58.43, H 4.29, N 11.36; found: C 58.40, H 4.20, N 11.48.

4.2.5. 2-Amino-1-(4-bromophenyl)-7,7-dimethyl-4-(4-fluorophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4e. Pale yellow crystals, mp 253–255 °C.

IR (KBr, ν, cm^{-1}): 3467, 3331, 3066, 2967, 2951, 2868, 2181, 1654, 1620, 1601, 1505, 1486, 1415, 1373, 1256, 1219, 1153, 1070, 1011, 858, 811, 769, 739.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.72 (d, J=17.6 Hz, 1H, CH), 2.01 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=16.0 Hz, 1H, CH), 2.21 (d, J=17.6 Hz, 1H, CH), 4.46 (s, 1H, CH), 5.53 (s, 2H, NH_2), 7.12 (t, J=8.8 Hz, 2H, ArH), 7.27–7.31 (m, 2H, ArH), 7.37 (d, J=8.4 Hz, 2H, ArH), 7.77 (d, J=8.4 Hz, 2H, ArH).

Anal. Calcd for $C_{24}H_{21}BrFN_3O$: C 61.81, H 4.54, N 9.01; found: C 61.90, H 4.58, N 8.97.

4.2.6. 2-Amino-1,4-di(4-bromophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4f. Pale yellow crystals, mp 276–278 °C.

IR (KBr, ν, cm^{-1}): 3460, 3323, 3058, 2962, 2867, 2179, 1652, 1621, 1571, 1486, 1415, 1371, 1313, 1256, 1146, 1069, 1009, 858, 842, 803.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.72 (d, J=17.6 Hz, 1H, CH), 1.99 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=16.0 Hz, 1H, CH), 2.21 (d, J=17.6 Hz, 1H, CH), 4.44 (s, 1H, CH), 5.56 (s, 2H, NH_2), 7.23 (t, J=8.4 Hz, 2H, ArH), 7.37 (t, J=8.4 Hz, 2H, ArH), 7.51 (d, J=8.4 Hz, 2H, ArH), 7.77 (d, J=8.4 Hz, 2H, ArH).

Anal. Calcd for $C_{24}H_{21}Br_2N_3O$: C 54.67, H 4.01, N 7.97; found C 54.55, H 4.20, N 7.94.

4.2.7. 2-Amino-1-(4-bromophenyl)-4-(3,4-dichlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4g. Pale yellow crystals, mp 277–279 °C.

IR (KBr, ν, cm^{-1}): 3464, 3334, 3059, 2957, 2888, 2870, 2178, 1650, 1620, 1570, 1487, 1466, 1398, 1371, 1256, 1147, 1071, 1044, 1022, 1010, 881, 850, 812.

^{1}H NMR (DMSO-d_6) δ: 0.74 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.75 (d, J=17.2 Hz, 1H, CH), 2.02 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=16.4 Hz, 2H, 2CH), 4.49 (s, 1H, CH), 5.64 (s, 2H, NH_2), 7.28 (dd, J=8.4 Hz, J'=2.0 Hz, 1H, ArH), 7.37 (t, J=8.4 Hz, 2H, ArH), 7.44 (d, J=2.0 Hz, 1H, ArH), 7.60 (d, J=8.4 Hz, 1H, ArH), 7.78 (d, J=8.4 Hz, 2H, ArH).

Anal. Calcd for $C_{24}H_{20}BrCl_2N_3O$: C 55.73, H 3.90, N 8.12; found: C 55.60, H 3.99, N 8.23.

4.2.8. 2-Amino-7,7-dimethyl-4-(3,4-dichlorophenyl)-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4h. Pale yellow crystals, mp 270–272 °C.

IR (KBr, ν, cm^{-1}): 3463, 3330, 3084, 3034, 2960, 2940, 2889, 2871, 2178, 1652, 1619, 1509, 1468, 1416, 1398, 1371, 1343, 1313, 1257, 1175, 1145, 1125, 1108, 1046, 1025, 880, 847, 812, 726, 671.

^{1}H NMR (DMSO-d_6) δ: 0.74 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.74 (d, J=17.6 Hz, 1H, CH), 2.02 (d, J=16.0 Hz, 1H, CH), 2.18 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=17.6 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 4.50 (s, 1H, CH), 5.43 (s, 2H, NH_2), 7.26–7.30 (m, 3H, ArH), 7.40 (d, J=8.4 Hz, 2H, ArH), 7.44 (d, J=2.0 Hz, 1H, ArH), 7.61 (d, J=8.4 Hz, 1H, ArH).

Anal. Calcd for $C_{25}H_{23}Cl_2N_3O$: C 66.38, H 5.12, N 9.29; found: C 66.44, H 5.10, N 9.12.

4.2.9. 2-Amino-7,7-dimethyl-1-(4-methylphenyl)-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4i. Pale yellow crystals, mp 281–283 °C.

IR (KBr, ν, cm^{-1}): 3483, 3383, 3032, 2960, 2927, 2870, 2179, 1643, 1612, 1564, 1529, 1510, 1412, 1375, 1348, 1302, 1259, 1146, 1043, 896, 809, 741, 698.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.76 (d, J=17.6 Hz, 1H, CH), 2.01 (d, J=16.0 Hz, 1H, CH), 2.22 (d, J=16.0 Hz, 1H, CH), 2.24 (d, J=17.6 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 4.64 (s, 1H, CH), 5.51 (s, 2H, NH_2), 7.29 (d, J=7.6 Hz, 2H, ArH), 7.42 (d, J=7.6 Hz, 2H, ArH), 7.65–7.69 (m, 1H, ArH), 7.77 (d, J=7.6 Hz, 1H, ArH), 8.08–8.10 (m, 2H, ArH).

Anal. Calcd for $C_{25}H_{24}N_4O_3$: C 70.08, H 5.65, N 13.08; found: C 70.25, H 5.60, N 13.00.

4.2.10. 2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4j. Pale yellow crystals, mp 260–262 °C.

IR (KBr, ν, cm^{-1}): 3441, 3306, 2959, 2927, 2870, 1651, 1621, 1557, 1510, 1469, 1442, 1408, 1373, 1258, 1243, 1152, 1110, 1034, 847, 820.

^{1}H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.73 (d, J=17.6 Hz, 1H, CH), 2.00 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=16.08 Hz, 2H, 2CH), 2.41 (s, 3H, CH_3), 4.47 (s, 1H, CH), 5.33 (s, 2H, NH_2), 7.27–7.30 (m, 4H, ArH), 7.38–7.41 (m, 4H, ArH).

Anal. Calcd for $C_{25}H_{24}ClN_3O$: C 71.85, H 5.79, N 10.05; found: C 71.98, H 5.80, N 9.91.

4.2.11. 2-Amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4k. Pale yellow crystals, mp 267–269 °C.

IR (KBr, ν, cm^{-1}): 3470, 3339, 2965, 2929, 2871, 2174, 1651, 1626, 1584, 1557, 1466, 1419, 1371, 1316, 1260, 1245, 1203, 1154, 1101, 1042, 847, 807, 757, 738.

^1H NMR (DMSO-d_6) δ: 0.80 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.78 (d, J=17.6 Hz, 1H, CH), 1.96 (d, J=16.0 Hz, 1H, CH), 2.17 (d, J=16.4 Hz, 2H, 2CH), 2.41 (s, 3H, CH_3), 4.98 (s, 1H, CH), 5.30 (s, 2H, NH_2), 7.32 (d, J=8.4 Hz, 2H, ArH), 7.37–7.42 (m, 4H, ArH), 7.53 (s, 1H, ArH).

Anal. Calcd for $C_{25}H_{23}Cl_2N_3O$: C 66.38, H 5.12, N 9.29; found: C 66.42, H 5.01, N 9.35.

4.2.12. 2-Amino-4-(4-chloro-2-nitrophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4l. Pale yellow crystals, mp 274–276 °C.

IR (KBr, ν, cm^{-1}): 3468, 3373, 2954, 2870, 2188, 1653, 1600, 1566, 1521, 1508, 1489, 1472, 1417, 1371, 1352, 1293, 1256, 837, 810, 756.

^1H NMR (DMSO-d_6) δ: 0.71 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.78 (d, J=17.2 Hz, 1H, CH), 1.93 (d, J=16.0 Hz, 1H, CH), 2.09–2.14 (m, 2H, ArH), 2.42 (s, 3H, CH_3), 5.20 (s, 1H, CH), 5.51 (s, 2H, NH_2), 7.32 (d, J=8.0 Hz, 2H, ArH), 7.44 (d, J=8.0 Hz, 2H, ArH), 7.52–7.54 (m, 2H, ArH), 7.87 (d, J=9.6 Hz, 1H, ArH).

Anal. Calcd for $C_{25}H_{23}ClN_4O_3$: C 64.86, H 5.01, N 12.10; found: C 64.80, H 5.22, N 12.11.

4.2.13. 2-Amino-7,7-dimethyl-1,4-di(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4m. Pale yellow crystals, mp 252–254 °C.

IR (KBr, ν, cm^{-1}): 3459, 3331, 3032, 3007, 2954, 2866, 2179, 1655, 1620, 1557, 1509, 1413, 1372, 1257, 1146, 1042, 1017, 848, 797.

^1H NMR (DMSO-d_6) δ: 0.74 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.73 (d, J=17.6 Hz, 1H, CH), 1.99 (d, J=16.0 Hz, 1H, CH), 2.18 (d, J=16.0 Hz, 1H, CH), 2.19 (d, J=17.6 Hz, 1H, CH), 2.17 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.41 (s, 1H, CH), 5.24 (s, 2H, NH_2), 7.12 (d, J=8.0 Hz, 2H, ArH), 7.15 (d, J=8.0 Hz, 2H, ArH), 7.25 (d, J=8.0 Hz, 2H, ArH), 7.39 (d, J=8.0 Hz, 2H, ArH).

Anal. Calcd for $C_{26}H_{27}N_3O$: C 78.56, H 6.85, N 10.57; found: C 78.77, H 6.70, N 10.50.

4.2.14. 2-Amino-4-(bromophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile 4n. Pale yellow crystals, mp 261–263 °C.

IR (KBr, ν, cm^{-1}): 3460, 3320, 3055, 2950, 2866, 2180, 1653, 1619, 1569, 1509, 1483, 1413, 1371, 1257, 1173, 1145, 1041, 1007, 842, 805, 785.

^1H NMR (DMSO-d_6) δ: 0.73 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.74 (d, J=17.6 Hz, 1H, CH), 2.01 (d, J=16.0 Hz, 1H, CH), 2.17–2.21 (m, 2H, 2CH), 2.41 (s, 3H, CH_3), 4.45 (s, 1H, CH), 5.36 (s, 2H, NH_2), 7.23 (d, J=8.0 Hz, 2H, ArH), 7.28 (d, J=8.0 Hz, 2H, ArH), 7.40 (d, J=8.0 Hz, 2H, ArH), 7.52 (d, J=8.0 Hz, 2H, ArH).

Anal. Calcd for $C_{25}H_{24}BrN_3O$: C 64.94, H 5.23, N 9.09; found: C 64.90, H 5.28, N 9.22.

4.3. General procedure for the syntheses of 5,10-diaryl-7,8-dihydro-7,7-dimethyl-5-phenyl-5*H*-indeno[1,2-*b*]-quinolin-9,11(6*H*,10*H*)-dione 6

A dry 50 mL flask was charged with arylaldehyde (1.0 mmol), 1,3-indenedione (1.0 mmol), 3-arylamino-5,5-dimethylcyclohex-2-enone (1.0 mmol), and ionic liquid [$bmim^+$][BF_4^-] (10 mL). The reaction mixture was stirred at 90 °C for 5–8 h, and then cooled to room temperature. The generated red solid was filtered off and the ionic liquid in filtrate was then recovered for reuse by drying at 80 °C for several hours in *vacuum*. The crude red products were washed with water and purified by recrystallization from DMF and water, followed by being dried at 80 °C for several hours in *vacuum* to give **6**.

4.3.1. 10-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-5-phenyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6a). Red crystals, mp 280–283 °C.

IR (KBr, ν, cm^{-1}): 3047, 2952, 2871, 1686, 1640, 1586, 1559, 1485, 1453, 1391, 1368, 1317, 1256, 1224, 1193, 1169, 1139, 1100, 1061, 1009, 938, 888, 845, 768, 734, 710.

^1H NMR (DMSO-d_6) δ: 0.81 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 2.00 (d, J=17.2 Hz, 1H, CH), 2.06 (d, J=16.4 Hz, 1H, CH), 2.27 (d, J=16.0 Hz, 1H, CH), 2.41 (d, J=17.6 Hz, 1H, CH), 4.84 (s, 1H, CH), 5.10 (d, J=7.2 Hz, 1H, ArH), 7.00 (t, J=7.6 Hz, 1H, ArH), 7.17–7.25 (m, 2H, ArH), 7.35 (d, J=8.0 Hz, 2H, ArH), 7.47 (d, J=8.0 Hz, 2H, ArH), 7.71 (br, 5H, ArH).

Anal. Calcd for $C_{30}H_{24}BrNO_2$: C 70.59, H 4.74, N 2.74; found: C 70.48, H 4.92, N 2.80.

4.3.2. 5,10-Di(4-bromophenyl)-7,8-dihydro-7,7-dimethyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6b). Red crystals, mp 271–273 °C.

IR (KBr, ν, cm^{-1}): 3089, 2959, 2883, 1692, 1645, 1608, 1590, 1559, 1487, 1455, 1395, 1365, 1301, 1254, 1223, 1191, 1169, 1141, 1100, 1070, 1010, 976, 888, 841, 791, 763, 705.

^1H NMR (DMSO-d_6) δ: 0.80 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.98 (d, J=17.6 Hz, 1H, CH), 2.05 (d, J=16.0 Hz, 1H, CH), 2.26 (d, J=16.0 Hz, 1H, CH), 2.38 (d, J=17.6 Hz, 1H, CH), 4.82 (s, 1H, CH), 5.26 (d, J=7.6 Hz, 1H, ArH), 7.07–7.12 (m, 1H, ArH), 7.19–7.26 (m, 2H, ArH), 7.34 (d, J=8.0 Hz, 2H, ArH), 7.45 (d, J=8.0 Hz, 2H, ArH), 7.72 (br, 2H, ArH), 7.90 (d, J=8.4 Hz, 2H, ArH).

LC–MS (ESI^+, m/z): 1201 [(2M+Na^+), 100%].

Anal. Calcd for $C_{30}H_{23}Br_2NO_2$: C 61.14, H 3.93, N 2.38; found: C 61.00, H 3.98, N 2.49.

4.3.3. 10-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-5-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6c). Red crystals, mp 263–265 °C.

IR (KBr, ν, cm^{-1}): 3059, 2957, 2933, 2857, 1673, 1644, 1637, 1590, 1558, 1511, 1456, 1439, 1365, 1321, 1301, 1223, 1189, 1170, 1140, 1110, 1058, 976, 888, 766, 756, 700.

^{1}H NMR (DMSO-d_6) δ: 0.83 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 2.00 (d, J=16.8 Hz, 2H, 2CH), 2.24 (d, J=16.4 Hz, 1H, CH), 2.36 (d, J=17.6 Hz, 1H, CH), 2.50 (s, 3H, CH_3), 5.18 (d, J=7.6 Hz, 1H, ArH), 5.24 (s, 1H, CH), 6.98–7.03 (m, 1H, ArH), 7.13–7.20 (m, 3H, ArH), 7.25–7.32 (m, 2H, ArH), 7.49–7.58 (m, 5H, ArH).

Anal. Calcd for $C_{31}H_{26}ClNO_2$: C 77.57, H 5.46, N 2.92; found: C 77.45, H 5.60, N 3.01.

4.3.4. 10-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-1-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6d). Red crystals, mp 288–290 °C.

IR (KBr, ν, cm^{-1}): 3061, 2954, 2868, 1683, 1852, 1631, 1590, 1562, 1488, 1454, 1391, 1362, 1261, 1249, 1226, 1128, 1086, 1014, 1005, 889, 841, 785, 767, 732, 699.

^{1}H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.80 (s, 3H, CH_3), 1.94 (d, J=16.8 Hz, 1H, CH), 2.09 (d, J=16.0 Hz, 1H, CH), 2.21 (d, J=16.8 Hz, 1H, CH), 2.24 (d, J=16.0 Hz, 1H, CH), 4.67 (d, J=7.6 Hz, 1H, ArH), 4.97 (s, 1H, CH), 6.74 (t, J=7.6 Hz, 1H, ArH), 7.05–7.09 (m, 1H, ArH), 7.19 (d, J=6.8 Hz, 1H, ArH), 7.35 (d, J=8.4 Hz, 2H, ArH), 7.48 (d, J=8.4 Hz, 2H, ArH), 7.64–7.69 (m, 2H, ArH), 7.79–7.85 (m, 2H, ArH), 8.03 (d, J=7.2 Hz, 1H, ArH), 8.20 (d, J=8.4 Hz, 1H, ArH), 8.34 (d, J=8.0 Hz, 1H, ArH).

Anal. Calcd for $C_{34}H_{26}ClNO_2$: C 79.14, H 5.08, N 2.71; found: C 79.22, H 5.13, N 2.70.

4.3.5. 10-(3,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-1-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6e). Red crystals, mp 284–286 °C.

IR (KBr, ν, cm^{-1}): 3050, 2958, 2871, 1689, 1653, 1634, 1589, 1559, 1507, 1465, 1456, 1393, 1363, 1261, 1226, 1191, 1171, 1133, 1029, 1004, 891, 784, 766, 738, 699.

^{1}H NMR (DMSO-d_6) δ: 0.80 (s, 3H, CH_3), 0.91 (d, J=8.0 Hz, 3H, CH_3), 2.00–2.14 (m, 2H, 2CH), 2.24 (d, J=16.0 Hz, 1H, CH), 2.26 (d, J=17.2 Hz, 1H, CH), 4.68 (d, J=7.6 Hz, 1H, ArH), 4.99 (s, 1H, CH), 6.73–6.77 (m, 1H, ArH), 7.08 (t, J=7.2 Hz, 1H, ArH), 7.20 (d, J=7.2 Hz, 1H, ArH), 7.47 (dd, J=8.4 Hz, J'=2.0 Hz, 1H, ArH), 7.56 (d, J=8.4 Hz, 1H, ArH), 7.65–7.68 (m, 3H, ArH), 7.80–7.85 (m, 2H, ArH), 8.06 (d, J=7.6 Hz, 1H, ArH), 8.20 (d, J=7.6 Hz, 1H, ArH), 8.34 (d, J=8.4 Hz, 1H, ArH).

Anal. Calcd for $C_{34}H_{25}Cl_2NO_2$: C 74.18, H 4.58, N 2.54; found: C 74.02, H 4.66, N 2.60.

4.3.6. 10-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-1-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6f). Red crystals, mp 289–291 °C.

IR (KBr, ν, cm^{-1}): 3054, 2964, 2871, 1687, 1653, 1633, 1588, 1560, 1541, 1521, 1455, 1391, 1362, 1261, 1225, 1191, 1167, 1125, 1103, 1067, 1009, 889, 863, 804, 784, 766, 729.

^{1}H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.80 (s, 3H, CH_3), 2.09 (d, J=17.2 Hz, 1H, CH), 2.10 (d, J=16.8 Hz, 1H, CH), 2.21 (d, J=16.8 Hz, 1H, CH), 2.24 (d, J=17.2 Hz, 1H, CH), 4.67 (d, J=7.6 Hz, 1H, ArH), 4.96 (s, 1H, CH), 6.71–6.76 (m, 1H, ArH), 7.05–7.09 (m, 1H, ArH), 7.19 (d, J=8.8 Hz, 1H, ArH), 7.42 (d, J=8.4 Hz, 2H, ArH), 7.49 (d, J=8.4 Hz, 2H, ArH), 7.63–7.68 (m, 2H, ArH), 7.79–7.85 (m, 2H, ArH), 8.03 (d, J=7.2 Hz, 1H, ArH), 8.20 (d, J=8.0 Hz, 1H, ArH), 8.34 (d, J=8.4 Hz, 1H, ArH).

Anal. Calcd for $C_{34}H_{26}BrNO_2$: C 72.86, H 4.68, N 2.50; found: C 72.80, H 4.52, N 2.54.

4.3.7. 10-(2,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-1-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6g). Red crystals, mp 285–288 °C.

IR (KBr, ν, cm^{-1}): 3058, 2954, 2867, 1692, 1650, 1633, 1587, 1560, 1507, 1466, 1391, 1364, 1259, 1226, 1192, 1171, 1133, 1103, 1047, 1004, 939, 891, 863, 782, 766, 732, 703.

^{1}H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.82 (s, 3H, CH_3), 2.01 (d, J=17.2 Hz, 1H, CH), 2.04 (d, J=16.4 Hz, 1H, CH), 2.22 (d, J=16.4 Hz, 2H, 2CH), 4.66 (d, J=7.6 Hz, 1H, ArH), 5.36 (s, 1H, CH), 6.75 (t, J=7.6 Hz, 1H, ArH), 7.06–7.10 (m, 1H, ArH), 7.17 (d, J=6.8 Hz, 1H, ArH), 7.37 (dd, J=8.4 Hz, J'=2.0 Hz, 1H, ArH), 7.50 (d, J=2.0 Hz, 1H, ArH), 7.63 (d, J=8.4 Hz, 1H, ArH), 7.66–7.69 (m, 2H, ArH), 7.80–7.91 (m, 2H, ArH), 8.02 (d, J=6.8 Hz, 1H, ArH), 8.19–8.21 (m, 1H, ArH), 8.34 (d, J=8.4 Hz, 1H, ArH).

Anal. Calcd for $C_{34}H_{25}Cl_2NO_2$: C 74.18, H 4.58, N 2.54; found: C 74.10, H 4.70, N 2.55.

4.3.8. 7,8-Dihydro-7,7-dimethyl-5-naphthalen-1-yl-10-(4-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6h). Red crystals, mp 268–270 °C.

IR (KBr, ν, cm^{-1}): 3059, 2958, 2929, 2869, 1694, 1673, 1634, 1589, 1562, 1514, 1455, 1390, 1363, 1261, 1227, 1193, 1171, 1134, 1006, 891, 829, 781, 761, 712, 702.

^{1}H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.80 (s, 3H, CH_3), 1.96 (d, J=17.2 Hz, 1H, CH), 2.10 (d, J=16.4 Hz, 1H, CH), 2.25 (d, J=16.4 Hz, 2H, 2CH), 4.69 (d, J=7.6 Hz, 1H, ArH), 5.12 (s, 1H, CH), 6.73–6.78 (m, 1H, ArH), 7.06–7.10 (m, 1H, ArH), 7.20 (d, J=6.8 Hz, 1H, ArH), 7.66–7.89 (m, 6H, ArH), 8.10 (d, J=7.2 Hz, 1H, ArH), 8.17–8.30 (m, 3H, ArH), 8.35 (d, J=8.4 Hz, 1H, ArH).

Anal. Calcd for $C_{34}H_{26}N_2O_4$: C 77.55, H 4.98, N 5.32; found C 77.46, H 4.90, N 5.39.

4.3.9. 7,8-Dihydro-7,7-dimethyl-10-(4-methylphenyl)-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6i). Red crystals, mp 271–273 °C.

IR (KBr, ν, cm^{-1}): 3046, 2957, 2870, 1688, 1645, 1626, 1589, 1557, 1509, 1455, 1396, 1364, 1256, 1222, 1192, 1171, 1140, 1091, 1056, 872, 763.

^1H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.99 (d, J=17.6 Hz, 1H, CH), 2.05 (d, J=16.4 Hz, 1H, CH), 2.25 (s, 3H, CH_3), 2.28 (d, J=16.4 Hz, 1H, CH), 2.46 (d, J=17.6 Hz, 1H, CH), 4.86 (s, 1H, CH), 5.02 (d, J=7.2 Hz, 1H, ArH), 6.83–6.87 (m, 1H, ArH), 7.11–7.14 (m, 3H, ArH), 7.22 (d, J=7.2 Hz, 1H, ArH), 7.32 (d, J=7.2 Hz, 2H, ArH), 7.71–7.76 (m, 2H, ArH), 7.79 (d, J=8.4 Hz, 1H, ArH), 8.19–8.35 (m, 4H, ArH).

Anal. Calcd for $C_{35}H_{29}NO_2$: C 84.82, H 5.90, N 2.83; found: C 84.99, H 5.73, N 2.90.

4.3.10. 10-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6j). Red crystals, mp 262–264 °C.

IR (KBr, ν, cm^{-1}): 3050, 2954, 1685, 1649, 1635, 1588, 1560, 1541, 1507, 1486, 1456, 1389, 1361, 1255, 1222, 1191, 1140, 762.

^1H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.91 (d, J=8.4 Hz, 3H, CH_3), 1.97 (d, J=16.8 Hz, 1H, CH), 2.07 (d, J=16.4 Hz, 1H, CH), 2.29 (d, J=16.0 Hz, 1H, CH), 2.45 (d, J=17.6 Hz, 1H, CH), 4.88 (s, 1H, CH), 5.04 (d, J=7.2 Hz, 1H, ArH), 6.85–6.89 (m, 1H, ArH), 7.12–7.16 (m, 1H, ArH), 7.24 (d, J=6.8 Hz, 1H, ArH), 7.38–7.42 (m, 2H, ArH), 7.48–7.52 (m, 2H, ArH), 7.70–7.87 (m, 3H, ArH), 8.06–8.13 (m, 1H, ArH), 8.17 (d, J=7.6 Hz, 1H, ArH), 8.23–8.39 (m, 2H, ArH).

Anal. Calcd for $C_{34}H_{26}BrNO_2$: C 72.86, H 4.68, N 2.50; found: C 72.80, H 4.49, N 2.65.

4.3.11. 7,8-Dihydro-7,7-dimethyl-5-naphthalen-2-yl-10-(4-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6k). Red crystals, mp 231–233 °C.

IR (KBr, ν, cm^{-1}): 3050, 2958, 2867, 1688, 1647, 1636, 1591, 1562, 1519, 1456, 1392, 1362, 1255, 1223, 1193, 1171, 1092, 875, 764, 724.

^1H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.92 (d, J=9.2 Hz, 3H, CH_3), 1.99–2.13 (m, 2H, 2CH), 2.30 (d, J=16.0 Hz, 1H, CH), 2.46 (d, J=17.6 Hz, 1H, CH), 5.04 (s, 1H, CH), 5.06 (d, J=8.0 Hz, 1H, ArH), 6.87–6.91 (m, 1H, ArH), 7.14–7.17 (m, 1H, ArH), 7.25 (d, J=7.2 Hz, 1H, ArH), 7.72–7.95 (m, 5H, ArH), 8.06–8.12 (m, 1H, ArH), 8.17–8.21 (m, 3H, ArH), 8.24–8.45 (m, 2H, ArH).

Anal. Calcd for $C_{34}H_{26}N_2O_4$: C 77.55, H 4.98, N 5.32; found: C 77.40, H 4.92, N 5.51.

4.3.12. 10-(2,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6l). Red crystals, mp 295–297 °C.

IR (KBr, ν, cm^{-1}): 3058, 2952, 1682, 1637, 1591, 1558, 1508, 1468, 1396, 1365, 1255, 1222, 1191, 1174, 1142, 1097, 1059, 874, 846, 760.

^1H NMR (DMSO-d_6) δ: 0.83 (d, J=6.0 Hz, 3H, CH_3), 0.90 (d, J=9.2 Hz, 3H, CH_3), 1.98–2.11 (m, 2H, 2CH), 2.26 (d, J=16.0 Hz, 1H, CH), 2.40–2.44 (m, 1H, CH), 5.01 (t, J=6.8 Hz, 1H, ArH), 5.27 (s, 1H, CH), 6.84–6.88 (m, 1H, ArH), 7.12–7.16 (m, 1H, ArH), 7.21 (d, J=7.2 Hz, 1H, ArH), 7.34–7.40 (m, 1H, ArH), 7.49 (dd, J=6.0 Hz, J'=2.0 Hz, 1H, ArH), 7.58–7.61 (m, 1H, ArH), 7.71–7.87 (m, 3H, ArH), 8.06–8.19 (m, 2H, ArH), 8.23–8.38 (m, 2H, ArH).

Anal. Calcd for $C_{34}H_{25}Cl_2NO_2$: C 74.18, H 4.58, N 2.54; found: C 74.29, H 4.60, N 2.48.

4.3.13. 7,8-Dihydro-7,7-dimethyl-10-(3,4-dimethoxylphenyl)-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6m). Red crystals, mp 251–254 °C.

IR (KBr, ν, cm^{-1}): 3059, 2999, 2956, 2931, 2897, 2870, 2832, 1688, 1638, 1589, 1558, 1510, 1452, 1414, 1392, 1365, 1256, 1221, 1189, 1139, 1092, 1030, 871, 804, 765, 750, 717, 693.

^1H NMR (DMSO-d_6) δ: 0.84 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 2.01 (d, J=17.2 Hz, 1H, CH), 2.08 (d, J=16.0 Hz, 1H, CH), 2.31 (d, J=16.0 Hz, 1H, CH), 2.51 (d, J=17.2 Hz, 1H, CH), 3.72 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 4.85 (s, 1H, CH), 5.03 (d, J=7.6 Hz, 1H, ArH), 6.83–6.97 (m, 4H, ArH), 7.11–7.14 (m, 1H, ArH), 7.24 (d, J=6.8 Hz, 1H, ArH), 7.70–7.80 (m, 3H, ArH), 8.09–8.30 (m, 4H, ArH).

Anal. Calcd for $C_{34}H_{25}Cl_2NO_2$: C 74.18, H 4.58, N 2.54; found: C 74.33, H 4.54, N 2.55.

4.3.14. 10-(2-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6n). Red crystals, mp 286–288 °C.

IR (KBr, ν, cm^{-1}): 3063, 2953, 1693, 1647, 1637, 1589, 1561, 1508, 1470, 1440, 1395, 1366, 1257, 1223, 1174, 1141, 1095, 1037, 874, 754, 736, 699.

^1H NMR (DMSO-d_6) δ: 0.82 (s, 3H, CH_3), 0.90 (d, J=8.4 Hz, 3H, CH_3), 1.95–2.10 (m, 2H, 2CH), 2.27 (d, J=16.4 Hz, 1H, CH), 2.42 (d, J=17.2 Hz, 1H, CH), 5.00 (t, J=7.2 Hz, 1H, ArH), 5.29 (s, 1H, CH), 6.86 (t, J=7.6 Hz, 1H, ArH), 7.11–7.21 (m, 3H, ArH), 7.28–7.36 (m, 2H, ArH), 7.55–7.59 (m, 1H, ArH), 7.70–7.84 (m, 3H, ArH), 8.06–8.38 (m, 4H, ArH).

Anal. Calcd for $C_{34}H_{26}ClNO_2$: C 79.14, H 5.08, N 2.71; found: C 79.10, H 5.21, N 2.64.

4.3.15. 10-(3-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (6o). Red crystals, mp 227–229 °C.

IR (KBr, ν, cm^{-1}): 3050, 2951, 2882, 1684, 1647, 1636, 1591, 1559, 1508, 1472, 1457, 1395, 1365, 1257, 1222, 1192, 830, 734, 684.

^1H NMR (DMSO-d_6) δ: 0.81 (s, 3H, CH_3), 0.91 (d, J=6.4 Hz, 3H, CH_3), 1.98–2.13 (m, 2H, 2CH), 2.29 (d, J=16.0 Hz, 1H, CH), 2.45 (d, J=16.8 Hz, 1H, CH), 4.90 (s, 1H, CH), 5.03 (d, J=6.8 Hz, 1H, ArH), 6.85–6.89 (m,

1H, ArH), 7.13–7.17 (m, 1H, ArH), 7.25 (d, J=6.8 Hz, 2H, ArH), 7.35–7.43 (m, 3H, ArH), 7.69–7.86 (m, 3H, ArH), 8.06–8.39 (m, 4H, ArH).

Anal. Calcd for $C_{34}H_{26}ClNO_2$: C 79.14, H 5.08, N 2.71; found: C 79.25, H 5.06, N 2.62.

4.3.16. 7,7-Dimethyl-10-(4-hydroxylphenyl)-7,8-dihydro-5-naphthalen-2-yl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*, 10*H*)-dione (6p). Red crystals, mp >300 °C.

IR (KBr, ν, cm^{-1}): 3325, 3054, 2957, 2869, 1684, 1646, 1635, 1591, 1561, 1510, 1456, 1395, 1365, 1253, 1223, 1195, 1170, 1099, 874, 831, 763, 709.

^{1}H NMR (DMSO-d_6) δ: 0.79 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.94 (d, J=17.6 Hz, 1H, CH), 2.05 (d, J=16.0 Hz, 1H, CH), 2.28 (d, J=16.0 Hz, 1H, CH), 2.45 (d, J=17.6 Hz, 1H, CH), 4.79 (s, 1H, CH), 5.01 (d, J=6.8 Hz, 1H, ArH), 6.69 (d, J=7.2 Hz, 2H, ArH), 6.85 (t, J=7.6 Hz, 1H, ArH), 7.12 (t, J=7.6 Hz, 1H, ArH), 7.21–7.23 (m, 3H, ArH), 7.69–7.79 (m, 3H, ArH), 8.07–8.34 (m, 4H, ArH), 9.24 (s, 1H, OH).

Anal. Calcd for $C_{34}H_{27}NO_3$: C 82.07, H 5.47, N 2.81; found: C 82.19, H 5.53, N 2.77.

4.4. General procedure for the syntheses of 4-aryl-7,7-dimethyl-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione 8

A dry 50 mL flask was charged with arylaldehyde (1 mmol), meldrum's acid (1.0 mmol), 3-arylamino-5,5-dimethylcyclohex-2-enone (1.0 mmol), and ionic liquid [bmim$^+$][BF_4^-] (10 mL). The reaction mixture was stirred at 90 °C for 12–20 h, and then cooled to room temperature. The generated yellow solid was filtered off and the ionic liquid in filtrate was then recovered for reuse by drying at 80 °C for several hours in *vacuum*. The crude yellow products were washed with water and purified by recrystallization from DMF and water, followed by being dried at 80 °C for several hours in *vacuum* to give **8**.

4.4.1. 4-(2-Chlorophenyl)-7,7-dimethyl-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8a). Colorless crystals, mp 249–250 °C.

IR (KBr, ν, cm^{-1}): 2960, 2889, 2869, 1704, 1642, 1625, 1570, 1510, 1467, 1441, 1416, 1378, 1341, 1313, 1294, 1265, 1193, 1144, 1034, 815, 755.

^{1}H NMR (DMSO-d_6) δ: 0.98 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 2.02 (d, J=17.6 Hz, 1H, CH), 2.17 (d, J=16.0 Hz, 1H, CH), 2.31–2.37 (m, 5H, CH_3+2CH), 2.61 (d, J=16.0 Hz, 1H, CH), 3.28 (dd, J=16.0 Hz, J'=8.0 Hz, 1H, CH), 4.60 (d, J=8.0 Hz, 1H, CH), 7.14–7.17 (m, 2H, ArH), 7.26–7.37 (m, 5H, ArH), 7.51 (d, J=7.6 Hz, 1H, ArH).

Anal. Calcd for $C_{24}H_{24}ClNO_2$: C 73.18, H 6.14, N 3.56; found: C 73.29, H 6.08, N 3.55.

4.4.2. 4-(2,4-Dichlorophenyl)-7,7-dimethyl-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8b). Colorless crystals, mp 251–253 °C.

IR (KBr, ν, cm^{-1}): 2961, 2926, 2870, 1706, 1641, 1625, 1585, 1556, 1510, 1468, 1389, 1370, 1340, 1310, 1294, 1264, 1212, 1194, 1146, 1137, 1104, 1045, 984.

^{1}H NMR (DMSO-d_6) δ: 0.97 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.00 (d, J=17.6 Hz, 1H, CH), 2.16 (d, J=16.0 Hz, 1H, CH), 2.30–2.37 (m, 5H, CH_3+2CH), 2.59 (d, J=14.0 Hz, 1H, CH), 3.32 (dd, J=14.0 Hz, J'=7.6 Hz, 1H, CH), 4.56 (d, J=7.6 Hz, 1H, CH), 7.16 (d, J= 8.0 Hz, 2H, ArH), 7.26–7.32 (m, 3H, ArH), 7.43 (dd, J=8.4 Hz, J'=2.0 Hz, 1H, ArH), 7.69 (d, J=2.0 Hz, 1H, ArH).

LC–MS (ESI$^+$, m/z): 879 [(2M+Na$^+$), 68%].

Anal. Calcd for $C_{24}H_{23}Cl_2NO_2$: C 67.29, H 5.41, N 3.27; found: C 67.43, H 5.35, N 3.40.

4.4.3. 7,7-Dimethyl-4-(2-nitrophenyl)-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8c). Pale yellow crystals, mp 279–281 °C.

IR (KBr, ν, cm^{-1}): 3068, 3053, 2962, 2928, 2885, 1703, 1658, 1625, 1530, 1510, 1451, 1418, 1378, 1341, 1259, 1213, 1195, 1157, 1138, 982, 854, 788, 750, 695.

^{1}H NMR (DMSO-d_6) δ: 0.93 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.02 (d, J=17.6 Hz, 1H, CH), 2.13 (d, J=16.0 Hz, 1H, CH), 2.25 (d, J=16.0 Hz, 1H, CH), 2.30 (d, J=17.6 Hz, 1H, CH), 2.38 (s, 3H, CH_3), 2.66 (d, J=16.0 Hz, 1H, CH), 3.43 (dd, J=16.0 Hz, J'=8.4 Hz, 1H, CH), 4.64 (d, J=8.4 Hz, 1H, CH), 7.18 (d, J=8.0 Hz, 1H, CH), 7.26 (d, J=8.0 Hz, 1H, CH), 7.31–7.36 (m, 2H, ArH), 7.45 (d, J=8.0 Hz, 1H, CH), 7.51–7.55 (m, 1H, ArH), 7.76–7.72 (m, 1H, ArH), 7.97 (d, J=8.0 Hz, 1H, ArH).

Anal. Calcd for $C_{24}H_{24}N_2O_4$: C 71.27, H 5.98, N 6.93; found: C 71.50, H 5.89, N 6.84.

4.4.4. 7,7-Dimethyl-4-(2-methoxylphenyl)-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8d). Pale yellow crystals, mp 201–203 °C.

IR (KBr, ν, cm^{-1}): 3060, 3030, 3010, 2959, 2888, 2869, 1704, 1653, 1624, 1599, 1510, 1488, 1457, 1410, 1378, 1342, 1292, 1248, 1222, 1193, 1143, 1122, 1097, 1051, 1030, 958, 815, 756, 675.

^{1}H NMR (DMSO-d_6) δ: 0.97 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 2.01 (d, J=17.2 Hz, 1H, CH), 2.16 (d, J=16.0 Hz, 1H, CH), 2.28 (d, J=17.2 Hz, 1H, CH), 2.31 (d, J=16.0 Hz, 1H, CH), 2.36 (s, 3H, CH_3), 2.62 (d, J=15.6 Hz, 1H, CH), 3.10 (dd, J=15.6 Hz, J'=8.0 Hz, 1H, CH), 3.85 (s, 3H, CH_3), 4.51 (d, J=8.0 Hz, 1H, CH), 6.89–6.93 (m, 1H, ArH), 7.01–7.14 (m, 4H, ArH), 7.22–7.30 (m, 3H, ArH).

Anal. Calcd for $C_{25}H_{27}NO_3$: C 77.09, H 6.99, N 3.60; found: C 76.87, H 7.15, N 3.62.

4.4.5. 7,7-Dimethyl-4-(2-fluorophenyl)-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8e). Pale yellow crystals, mp 183–185 °C.

IR (KBr, ν, cm^{-1}): 3068, 3053, 2960, 2891, 2870, 1203, 1654, 1525, 1583, 1511, 1485, 1455, 1419, 1379, 1344, 1313, 1294, 1262, 1219, 1175, 1140, 1089, 960, 816, 760.

^1H NMR (DMSO-d_6) δ: 0.94 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.02 (d, J=17.6 Hz, 1H, CH), 2.16 (d, J=16.0 Hz, 1H, CH), 2.24–2.32 (m, 2H, ArH), 2.38 (s, 3H, CH_3), 2.57 (d, J=16.0 Hz, 1H, CH), 3.26 (dd, J=16.0 Hz, J'=8.0 Hz, 1H, CH), 4.51 (d, J=8.4 Hz, 1H, CH), 7.06–7.31 (m, 8H, ArH).

Anal. Calcd for $C_{24}H_{24}FNO_2$: C 76.37, H 6.41, N 3.71; found: C 76.30, H 6.28, N 3.70.

4.4.6. 7,7-Dimethyl-4-(2-nitro-4,5-methylenedioxylphenyl)-1-tolyl-3,4,7,8-tetrahydroquinoline-2,5(1*H*,6*H*)-dione (8f). Yellow crystals, mp 218–220 °C.

IR (KBr, ν, cm^{-1}): 3082, 3063, 3032, 2956, 2923, 2894, 2869, 1706, 1655, 1627, 1521, 1483, 1417, 1385, 1366, 1343, 1328, 1291, 1260, 1216, 1174, 1150, 1118, 924, 881, 815, 757, 691.

^1H NMR (DMSO-d_6) δ: 0.92 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.92 (d, J=17.2 Hz, 1H, CH), 2.08 (d, J=16.0 Hz, 1H, CH), 2.32 (d, J=16.0 Hz, 1H, CH), 2.36 (s, 3H, CH_3), 2.39 (d, J=17.2 Hz, 1H, CH), 2.62 (d, J=16.4 Hz, 1H, CH), 3.39 (dd, J=16.4 Hz, J'=8.4 Hz, 1H, CH), 4.69 (d, J=8.4 Hz, 1H, CH), 6.20 (d, J=4.8 Hz, 2H, CH_2), 6.84 (s, 1H, ArH), 7.13–7.17 (m, 2H, ArH), 7.30–7.35 (m, 2H, ArH), 7.62 (s, 1H, ArH).

Anal. Calcd for $C_{25}H_{24}N_2O_6$: C 66.95, H 5.39, N 6.25; found: C 66.75, H 5.50, N 6.36.

4.5. General procedure for the synthesis of 5-(2-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione 10

A mixture of 2-chlorobenzaldehyde (0.42 g, 3.0 mmol) and meldrum's acid (**7**; 0.43 g, 3.0 mmol) in the ionic liquid medium [bmim$^+$][BF_4^-] (5 mL) was stirred at 60 °C for 8 h until the reaction was complete (monitored by TLC). The mixture was then cooled to room temperature, and the yellow solid was collected by filtration. The filtrate of the ionic liquid [bmim$^+$][BF_4^-] was then recovered for reuse by drying at 80 °C for several hours in *vacuum*. The crude yellow product was washed with EtOH; this gave 5-(2-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **10**. A mixture of this intermediate (0.27 g, 1.0 mmol) and 5,5-dimethyl-3-(4-methylanilino)cyclohex-2-enone (0.23 g, 1.0 mmol) in [bmim$^+$][BF_4^-] (5 mL) was stirred at 90 °C for 5 h to complete the reaction (monitored by TLC). The mixture was then cooled to room temperature, the yellow solid was collected by filtration, and the filtrate of the ionic liquid [bmim$^+$][BF_4^-] was then recovered for reuse by drying at 80 °C for several hours in *vacuum*. The crude yellow product was washed with H_2O, purified by recrystallization from DMF–H_2O, and dried at 80 °C for several hours in vacuum, this gave **8a** in 92% yield.

4.5.1. 5-(2-Chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione 10. White powder, mp 133−134 °C (lit.[20] 133 °C).

4.6. Supplementary material

Crystallographic data for the structure of **6a** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with no. CCDC-608551. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Natural Science Foundation (06AXL10) of Xuzhou Normal University and Natural Science Foundation (no. 04KJB150139) of the Education Committee of Jiangsu Province for financial support.

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19. Crystal data for **6a**: $C_{30}H_{24}BrNO_2$; M=510.41, red block crystals, 0.34×0.21×0.04 mm, tetragonal, space group $P2_1/n$, a=10.9821(11), b=17.5795(18), c=12.2340(13) Å, β=91.645(3)°, V=2360.9(4)^3, Z=4, D_c=1.436 g cm^{-3}. F(000)=1048, μ(Mo Kα)=1.770 mm^{-1}. Intensity data were collected on Rigaku Mercury diffractometer with graphite monochromated Mo Kα radiation (λ=0.71070 Å) using ω scan mode with 3.33°<θ<25.35°. Unique reflections of 4307 were measured and 3385 reflections with $I>2\sigma(I)$ were used in the refinement. Structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to R=0.0679 and wR=0.0920.
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