Benign and Highly Efficient Synthesis of Indenoquinoline Derivatives from 3-Arylamino-5,5-dimethylcyclohex-2-enone, Arylaldehyde and 1,3-Indenedione in Ionic Liquid Medium

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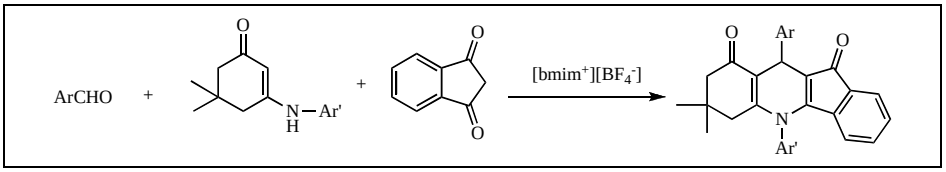

A green and simple syntheses of indeno[1,2-*b*]quinoline derivatives was accomplished in excellent yields *via* the reaction of 3-arylamino-5,5-dimethylcyclohex-2-enone, aromatic aldehyde and 1,3-indenedione in ionic liquid medium of [bmim$^+$][BF_4^-] as a green solvent. It was interesting that one of the protons exhibited doublet within 5.06~5.28 ppm identified as one of the aromatic protons from the indene ring. The reason was perhaps best explained by intramolecular C-H...π stacking interaction, and confirmed by X-ray diffraction analysis in one case.

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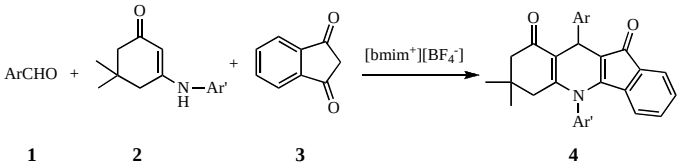
INTRODUCTION

Heteroaromatic rings containing nitrogen atoms often play important roles as the scaffolds of bioactive substances. Quinoline is one of the most popular nitrogen heteroaromatic rings incorporated into the structure of many pharmaceuticals. It is known that many quinoline containing compounds exhibit a wide spectrum of pharmacological activities such as antiplasmodial activity [1], intrinsic activity [2], cytotoxic activity [3], functional activity [4], antibacterial activity [5], antiproliferative activity [6], antimalarial activity [7] and anticancer activity [8]. These promote us to explore a new reaction media for the synthesis the potentially active compound mentioned above. Room temperature ionic liquids, especially those based on the 1-*N*-alkyl-3-methyl-imidazolium cation, have shown great promise as attractive alternatives to conventional solvents [9]. The unique property of room temperature ionic liquids is that they have essentially no vapour pressure, which makes them optimal replacements for the volatile organic solvents traditionally used as industrial solvents [10]. An advantage of an ionic liquid is the ability to reuse them many times, thus making them useful as green solvents. Because of this advantage, ionic liquids have made a significant contribution to green chemistry and have been used widely as a reaction medium in organic chemistry [11]. In this paper, we would like to report the synthesis of indeno[1,2-*b*]quinoline derivatives in ionic liquid *via* a novel reaction of arylaldehyde, 3-arylamino-5,5-dimethyl-cyclohex-2-enone and 1,3-indenedione.

RESULTS AND DISCUSSION

In order to avoid the disadvantages such as toxicity and unstability that many organic solvents inherently have, we selected 1-butyl-3-methylimidazolium tetrafluoroborate [bmim$^+$][BF_4^-] as a green ionic liquid medium. The reaction of arylaldehyde 1, 3-arylamino-5,5-dimethyl-cyclohex-2-enone 2, and 1,3-indenedione 3 proceeded smoothly in ionic liquid medium of [bmim$_+$][BF_4^-] at 90°C (Scheme 1), affording indeno[1,2-*b*]quinoline derivatives **4** in high yield after completion monitored by TLC.

Scheme 1



1 **2** **3** **4**

We began our study of the reaction shown in Scheme 1 by optimizing the reaction conditions for preparation of indeno[1,2-*b*]quinoline derivatives **4**. A summary of the optimization experiment was provided in Table 1. It turned out that at room temperature, no reaction takes place (Table 1, Entry 1) however, to our delighted at 90 ℃ the reaction could be carried out smoothly with high yield. To find the optimum reaction time, the reaction was carried out in ionic liquid [bmim$^+$][BF_4^-] for 3, 6, or 9 hours (Table 1, Entries 3, 4 and 5), resulting in the

isolation of **4a** in 86%, 97% and 97% yield respectively. Thus, a temperature of 90℃ and a reaction time of 6 hours were chosen as optimal conditions. Moreover, different ionic liquids and organic solvents were further studied, from Table 1, we could see different group on the methylimidazolium and anions were chosen as media for this reaction, we could obtained the ionic liquid [bmim$^+$][BF_4^-] was as best reaction media for this reaction.

Table 1

Synthesis of **4a** in ionic liquid under different reaction conditions [a]

Entry	T/℃	ionic liquid	Time/h	Yield[b]/(%)
1	r.t.	[bmim$^+$][BF_4^-]	6	0
2	50	[bmim$^+$][BF_4^-]	6	82
3	90	[bmim$^+$][BF_4^-]	3	86
4	**90**	**[bmim$^+$][BF_4^-]**	**6**	**97**
5	90	[bmim$^+$][BF_4^-]	9	97
6	90	[emim$^+$]Br^-	6	89
7	90	[pmim$^+$]Br^-	6	92
8	90	[bmim$^+$] Br^-	6	92
9	90	[emim$^+$][BF_4^-]	6	95
10	90	[pmim$^+$][BF_4^-]	6	95
11	80	CH_3CN	8	86
12	80	EtOH	8	82
13	90	DMF	6	88

[a] Reaction condition: 5 mL ionic liquid or 10 mL organic solvents, 1 mmol 4-chlorobenzaldehyde and 1 mmol 3-phenylamino-5,5-dimethylcyclohex-2-enone and 1mmol **3**. [b] Isolated yields

At completion monitored by TLC, the reaction mixture was allowed to cool to room temperature, the solid of the products was isolated by filtration, the filtrate of the ionic liquid [bmim$^+$][BF_4^-] could be recovered easily by drying at 80℃ *in vacuo* for several hours. Investigations by using 4-chlorobenzaldehyde and 3-phenylamino-5,5-dimethylcyclohex-2-enone and **3** as model substrates showed that the ionic liquid could be recovered and successively reused. A summary of the reuse of the ionic liquid is shown in Table 2. Even in the fourth round the yield of the product **4a** is fairly high.

Table 2

Study on the reuse of ionic liquid [bmim$^+$][BF_4^-][a]

Round	**1**	**2**	**3**	**4**
Yield/(%)[b]	97	95	94	94

[a] Reaction condition: 5 mL ionic liquid or 10 mL organic solvents, 1 mmol 4-chlorobenzaldehyde, 1 mmol 3-phenylamino-5,5-dimethylcyclohex-2-enone and 1mmol **3**. [b] Isolated yields

The products **4** were completely characterized by IR, ^{1}H NMR and elemental analyses. The analyses were in agreement with their structures. The IR spectra for **4o** exhibited strong bands at 1673, 1644 cm^{-1} (C=O), but there is a peculiarity in the ^{1}H nmr spectra of all products **4a-u** obtained, namely one of the benzene protons appears in a higher filed in the range 5.06-5.28 as shown in Table 3. To elucidate the reason for this phenomenon, X-ray diffraction analysis [12] of one of the products (**4o**) was performed. As expected, the structure we obtained was indeno[1,2-*b*]quinoline **4o** as shown in Figure 1. In the further X-ray diffraction study, we found that the distance from H17 to Cg (the centre of the benzene (C25-C30) is 2.700 Å, the angle of C17–H17…Cg is 147.1°, these results suggest that H15 can form intra-molecular C17-H17…π interaction with phenyl ring (C25-C30) (Figure 1). In addition, the distance of H17-C30 (2.916(1) Å) is statistically near to the value of H17-C25 (3.163 (1) Å) also indicate the C17-H17 group is upon the phenyl ring (C25-C30), so the H17 is in the high shielding degree due to the π-electrons of benzene ring, perhaps this reason is perhaps the best explanation that the H17 exhibiting a low doublet at 5.18 ppm in ^{1}H NMR.

Table 3

Synthesis of **4** in ionic liquida and ppm of C-H involved in C-H…π interaction [a].

Entry	Ar	Ar'	Time (h)	δ ppm	Yield (%)[b]
4a	4-ClC_6H_4	Ph	6	5.11	97
4b	3,4-$Cl_2C_6H_3$	Ph	8	5.09	96
4c	2-$NO_2C_6H_4$	Ph	6	5.10	99
4d	2,4-$Cl_2C_6H_3$	Ph	8	5.06	94
4e	2-ClC_6H_4	4-BrC_6H_4	8	5.25	99
4f	2-$NO_2C_6H_4$	4-BrC_6H_4	6	5.27	98
4g	4-$NO_2C_6H_4$	4-BrC_6H_4	6	5.28	97
4h	3,4-$Cl_2C_6H_3$	4-BrC_6H_4	8	5.26	98
4i	4-$NO_2C_6H_4$	4-$CH_3C_6H_4$	6	5.23	98
4j	2,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	8	5.18	94
4k	3,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	6	5.22	98
4l	3-$NO_2C_6H_4$	4-$CH_3C_6H_4$	6	5.24	97
4m	2-$NO_2C_6H_4$	4-$CH_3C_6H_4$	6	5.22	98
4n	3-ClC_6H_4	4-$CH_3C_6H_4$	6	5.21	98
4o	2-ClC_6H_4	4-$CH_3C_6H_4$	6	5.18	98
4p	4-ClC_6H_4	4-$CH_3C_6H_4$	6	5.20	97
4q	4-ClC_6H_4	4-FC_6H_4	8	5.22	98
4r	4-ClC_6H_4	4-$CH_3OC_6H_4$	6	5.27	97
4s	4-ClC_6H_4	4-ClC_6H_4	8	5.27	95
4t	4-ClC_6H_4	4-IC_6H_4	8	5.26	95
4u	4-ClC_6H_4	4-$NO_2C_6H_4$	10	5.26	92

[a] Reaction condition: 5 mL ionic liquid, 1 mmol arylaldehyde and 1 mmol 3-arylamino-5,5-dimethylcyclohex-2-enone and 1mmol **3**. [b] Isolated yields.

As shown in Table 3, we can see a 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, alkoxyl group), reacted well with **3** to give the corresponding products **4** in high yields under the same reaction medium so we concluded that no obvious effects of electronic and nature of substituents on the aromatic ring were observed.

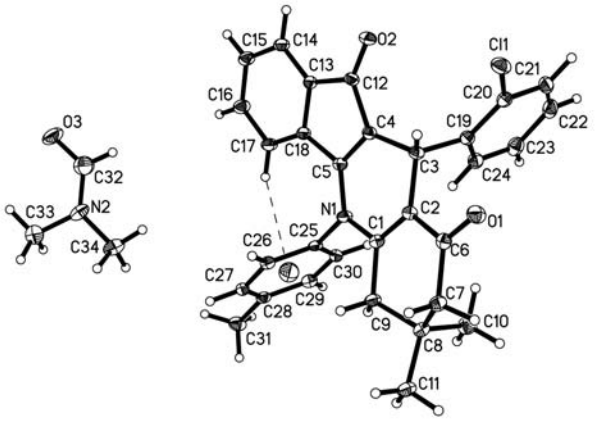
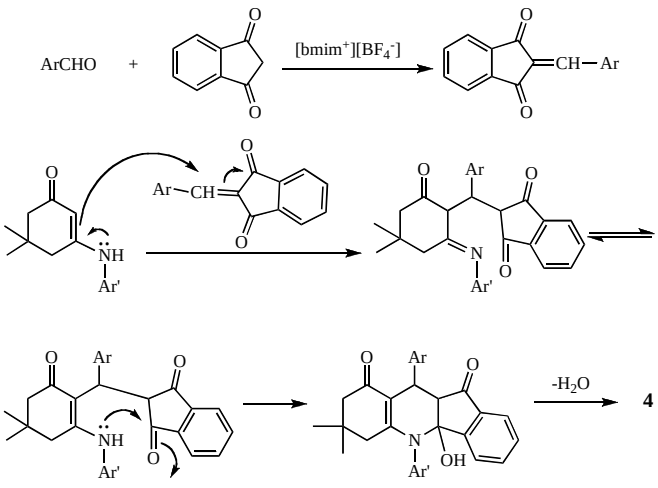


Figure 1. ORTEP diagram of **4o** as a DMF solvate.

Although a detailed mechanism of the above reaction has not been clarified yet, the formation of indeno[1,2-*b*]-quinoline derivatives **4** can be explained by the possible mechanism presented in Scheme 2.

Scheme 2



In conclusion, we have developed a novel synthetic method for the synthesis of indeno[1,2-*b*]quinoline derivatives in excellent yields in ionic liquid medium [bmim$^+$][BF_4^-]. Meanwhile, the ionic liquid medium [bmim$^+$][BF_4^-] was chosen as green solvent, which could be reused for several rounds without significant loss of activity.

EXPERIMENTAL

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 for solution in DMSO-d_6 with Me_4Si as internal standard using an Inova-400 spectrometer. Elemental analyses were carried out using Carlo Erba 1110 analyzer. X-ray diffraction was measured on a Rigaku Mercury diffractometer.

Reaction of arylaldehyde (1), 3-arylamino-5,5-dimethylcyclohex-2-enone (2) and 1,3-indenedione (3) in ionic liquid medium [bmim$^+$][BF_4^-]

Typical Procedure. A mixture of arylaldehyde (**1**, 1.0 mmol), 3-arylamino-5,5-dimethylcyclohex-2-enone (**2**, 1.0 mmol), 1,3-indenedione (0.15 g, 1.0 mmol) and in ionic liquid medium [bmim$^+$][BF_4^-] (5 mL) was stirred at 90°C for several hours to complete the reaction (monitored by TLC), then cooled to room temperature. The red solid was collected by filtration and the ionic liquid [bmim$^+$][BF_4^-] filtrate was then recovered for reuse by drying at 80 ℃ several hours *in vacuo*. The crude red products were washed with water and purified by recrystallization from DMF and water, followed by being dried at 80 ℃ several hours *in vacuo* to give **4**.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-phenyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4a). This compound was obtained as red crystals, mp 272 ~ 274 ℃; ir (KBr): ν_{max} 3056, 2960, 2870, 1697, 1648, 1632, 1597, 1559, 1489, 1455, 1394, 1363, 1254, 1224, 1191, 1169, 1141, 1104, 1014, 976, 940, 888, 842, 765, 736, 700; ^{1}H nmr (DMSO-d_6): δ 0.81 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 2.01 (d, J = 17.2 Hz, 1H, CH), 2.06 (d, J = 16.0 Hz, 1H, CH), 2.28 (d, J = 16.0 Hz, 1H, CH), 2.41 (d, J = 17.2 Hz, 1H, CH), 4.86 (s, 1H, CH), 5.11 (d, J = 7.2 Hz, 1H, ArH), 7.09-7.13 (m, 1H, ArH), 7.18-7.26 (m, 2H, ArH), 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.71 (b, 5H, ArH). Anal. Calcd for $C_{30}H_{24}ClNO_2$: C, 77.33; H, 5.19; N, 3.01. Found: C, 77.20; H, 5.25; N, 3.12.

5-(3,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-10-phenyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4b). This compound was obtained as red crystals, mp 254 ~256 ℃; ir (KBr): ν_{max} 3050, 2953, 2929, 2875, 1690, 1645, 1630, 1586, 1558, 1492, 1455, 1393, 1360, 1299, 1257, 1224, 1191, 1171, 1142, 1101, 1061, 1028, 941, 887, 764, 742, 695; ^{1}H nmr (DMSO-d_6): δ 0.82 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 2.02 (d, J = 17.2 Hz, 1H, CH), 2.08 (d, J = 16.0 Hz, 1H, CH), 2.27 (d, J = 16.0 Hz, 1H, CH), 2.39 (d, J = 17.2 Hz, 1H, CH), 4.86 (s, 1H, CH), 5.09 (d, J = 7.2 Hz, 1H, ArH), 6.99-7.03 (m, 1H, ArH), 7.19-7.26 (m, 2H, ArH), 7.39 (dd, J = 8.4 Hz, J' = 1.6 Hz, 1H, ArH), 7.54 (d, J = 8.4 Hz, 1H, ArH), 7.57 (d, J = 1.6 Hz, 1H, ArH), 7.69-7.77 (m, 5H, ArH). Anal. Calcd for $C_{30}H_{23}Cl_2NO_2$: C, 72.00; H, 4.63; N, 2.80. Found: C, 71.89; H, 4.70; N, 2.73.

7,8-Dihydro-7,7-dimethyl-5-(2-nitrophenyl)-10-phenyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4c). This compound was obtained as red crystals, mp 285 ~ 287 ℃; ir (KBr): ν_{max} 3052, 2954, 2873, 1690, 1649, 1633, 1586, 1558, 1527, 1492, 1454, 1394, 1362, 1301, 1253, 1226, 1192, 1172, 1141, 1104, 1062, 979, 890, 859, 833, 767, 747, 723, 707; ^{1}H nmr (DMSO-d_6): δ 0.75 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.98 (d, J = 16.8 Hz, 2H, 2CH), 2.22 (d, J = 16.0 Hz, 1H, CH), 2.34 (d, J = 17.2 Hz, 1H, CH), 5.10 (d, J = 7.2 Hz, 1H, ArH), 5.71 (s, 1H, CH), 7.00-7.03 (m, 1H, ArH), 7.19-7.24 (m, 2H, ArH), 7.37-7.41 (m, 1H, ArH), 7.62-7.65 (m, 1H, ArH), 7.70-7.73 (m, 5H, ArH), 7.81-7.87 (m, 2H, ArH). Anal. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.45; H, 5.17; N, 5.94.

5-(2,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-10-phenyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4d). This compound was obtained as red crystals, mp 295 ~ 297 ℃; ir (KBr): ν_{max} 3060, 2959, 2868, 1689, 1652, 1633, 1588, 1561, 1492, 1466, 1454, 1395, 1362, 1254, 1226, 1193, 1172, 1141, 1102, 978, 889, 850, 765, 715, 701; ^{1}H nmr (DMSO-d_6): δ 0.83 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.99 (d, J = 17.6 Hz, 1H, CH), 2.01 (d, J = 16.0 Hz, 1H, CH), 2.25 (d, J = 16.0 Hz, 1H, CH),

2.36 (d, J = 17.6 Hz, 1H, CH), 5.06 (d, J = 7.6 Hz, 1H, ArH), 5.22 (s, 1H, CH), 6.98-7.02 (m, 1H, ArH), 7.18-7.22 (m, 2H, ArH), 7.34 (dd, J = 8.0 Hz, J' = 2.0 Hz, 1H, ArH), 7.47 (d, J = 2.0 Hz, 1H, ArH), 7.53 (d, J = 8.0 Hz, 1H, ArH), 7.69-7.75 (m, 5H, ArH). Anal. Calcd for $C_{30}H_{23}Cl_2NO_2$: C, 72.00; H, 4.63; N, 2.80. Found: C, 71.90; H, 4.68; N, 2.88.

10-(4-Bromophenyl)-5-(2-chlorophenyl)-7,8-dihydro-7,7-dimethyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4e). This compound was obtained as red crystals, mp 284 ~ 286 ℃; ir (KBr): ν_{max} 3053, 2958, 2866, 1683, 1667, 1636, 1590, 1564, 1488, 1455, 1395, 1365, 1303, 1256, 1226, 1193, 1171, 1142, 1101, 1063, 1013, 889, 850, 763, 750, 736, 703; ^{1}H nmr (DMSO-d_6): δ 0.84 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 1.99 (d, J = 17.6 Hz, 1H, CH), 2.01 (d, J = 16.0 Hz, 1H, CH), 2.24 (d, J = 16.0 Hz, 1H, CH), 2.35 (d, J = 17.6 Hz, 1H, CH), 5.24 (s, 1H, CH), 5.25 (d, J = 8.0 Hz, 1H, ArH), 7.06-7.28 (m, 5H, ArH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.50 (dd, J = 7.6 Hz, J' = 1.2 Hz, 1H, ArH), 7.71 (b, 2H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH); Anal. Calcd for $C_{30}H_{23}ClBrNO_2$: C, 66.13; H, 4.25; N, 2.57. Found: C, 66.03; H, 4.31; N, 2.60.

10-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-5-(2-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4f). This compound was obtained as red crystals, mp 290 ~291 ℃; ir (KBr): ν_{max} 3064, 2954, 2872, 1685, 1637, 1591, 1564, 1520, 1489, 1453, 1397, 1368, 1301, 1257, 1226, 1193, 1172, 1155, 1103, 1063, 1013, 978, 889, 849, 829, 767, 749, 725, 702; ^{1}H nmr (DMSO-d_6): δ 0.75 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 1.97 (d, J = 17.6 Hz, 1H, CH), 1.98 (d, J = 16.0 Hz, 1H, CH), 2.20 (d, J = 16.0 Hz, 1H, CH), 2.31 (d, J = 17.6 Hz, 1H, CH), 5.27 (d, J = 7.2 Hz, 1H, ArH), 5.70 (s, 1H, CH), 7.09-7.13 (m, 1H, ArH), 7.23-7.26 (m, 2H, ArH), 7.37-7.41 (m, 1H, ArH), 7.60-7.64 (m, 1H, ArH), 7.67-7.73 (m, 2H, ArH), 7.81-7.93 (m, 4H, ArH); Anal. Calcd for $C_{30}H_{23}BrN_2O_4$: C, 64.87; H, 4.17; N, 5.04. Found: C, 64.59; H, 4.22; N, 5.12.

10-(4-Bromophenyl)-7,8-dihydro-7,7-dimethyl-5-(4-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4g). This compound was obtained as red crystals, mp 294 ~ 296 ℃; ir (KBr): ν_{max} 3073, 2958, 2873, 1677, 1634, 1591, 1562, 1516, 1488, 1454, 1393, 1365, 1343, 1302, 1256, 1224, 1193, 1171, 1141, 1101, 1060, 1012, 889, 830, 765, 753, 725, 703; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 2.02 (d, J = 17.6 Hz, 1H, CH), 2.06 (d, J = 16.0 Hz, 1H, CH), 2.27 (d, J = 16.0 Hz, 1H, CH), 2.38 (d, J = 17.6 Hz, 1H, CH), 4.97 (s, 1H, CH), 5.28 (d, J = 7.2 Hz, 1H, ArH), 7.09-7.13 (m, 1H, ArH), 7.21-7.28 (m, 2H, ArH), 7.67-7.93 (m, 6H, ArH), 8.14 (d, J = 8.4 Hz, 2H, ArH). Anal. Calcd for $C_{30}H_{23}BrN_2O_4$: C, 64.87; H, 4.17; N, 5.04. Found: C, 64.62; H, 4.28; N, 5.17.

10-(4-Bromophenyl)-5-(3,4-dichlorophenyl)-7,8-dihydro-7,7-dimethyl-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4h). This compound was obtained as red crystals, mp 251 ~ 253 ℃; ir (KBr): ν_{max} 3048, 2958, 2929, 2871, 1693, 1670, 1634, 1583, 1562, 1489, 1463, 1392, 1365, 1301, 1255, 1226, 1195, 1142, 1099, 1061, 1013, 890, 848, 823, 764, 739, 702; ^{1}H nmr (DMSO-d_6): δ 0.83 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 2.02 (d, J = 17.6 Hz, 1H, CH), 2.07 (d, J = 16.0 Hz, 1H, CH), 2.26 (d, J = 16.0 Hz, 1H, CH), 2.35 (d, J = 17.6 Hz, 1H, CH), 4.84 (s, 1H, CH), 5.26 (d, J = 7.2 Hz, 1H, ArH), 7.08-7.12 (m, 1H, ArH), 7.21-7.27 (m, 2H, ArH), 7.39 (dd, J = 8.4 Hz, J' = 1.6 Hz, 1H, ArH), 7.52 (d, J = 8.4 Hz, 1H, ArH), 7.57 (d, J = 1.6 Hz, 1H, ArH), 7.68 (b, 1H, ArH), 7.79 (b, 1H, ArH), 7.90 (d, J = 8.0 Hz, 2H, ArH). Anal. Calcd for $C_{30}H_{22}BrCl_2NO_2$: C, 62.20; H, 3.83; N, 2.42. Found: C, 62.09; H, 3.89; N, 2.50.

7,8-Dihydro-7,7-dimethyl-10-(4-methylphenyl)-5-(4-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4i). This compound was obtained as red crystals, mp 276 ~ 278 ℃; ir (KBr): ν_{max} 3054, 2958, 2870, 1684, 1634, 1589, 1560, 1498, 1454, 1394, 1366, 1350, 1256, 1225, 1192, 1171, 1141, 1102, 1060, 1017, 890, 830, 765, 723, 700; ^{1}H nmr (DMSO-d_6): δ 0.81 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 2.03 (d, J = 17.6 Hz, 1H, CH), 2.06 (d, J = 16.0 Hz, 1H, CH), 2.29 (d, J = 16.0 Hz, 1H, CH), 2.40 (d, J = 17.6 Hz, 1H, CH), 2.51 (s, 3H, CH_3), 4.98 (s, 1H, CH), 5.23 (d, J = 7.2 Hz, 1H, ArH), 7.02-7.06 (m, 1H, ArH), 7.18-7.25 (m, 2H, ArH), 7.51-7.58 (m, 3H, ArH), 7.67 (d, J = 8.4 Hz, 3H, ArH), 8.15 (d, J = 8.4 Hz, 2H, ArH), Anal. Calcd for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.81; H, 5.38; N, 5.92.

5-(2,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4j). This compound was obtained as red crystals, mp 284 ~ 286 ℃; ir (KBr): ν_{max} 3062, 2957, 2867, 1686, 1673, 1650, 1634, 1591, 1560, 1511, 1459, 1393, 1364, 1255, 1224, 1191, 1171, 1142, 1102, 1061, 1045, 1019, 977, 888, 849, 765, 729, 702; ^{1}H nmr (DMSO-d_6): δ 0.83 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 2.01 (d, J = 16.4 Hz, 2H, CH), 2.24 (d, J = 16.4 Hz, 1H, CH), 2.35 (d, J = 17.2 Hz, 1H, CH), 2.51 (s, 3H, CH_3), 5.18 (d, J = 7.6 Hz, 1H, ArH), 5.22 (s, 1H, CH), 7.00-7.04 (m, 1H, ArH), 7.17-7.22 (m, 2H, ArH), 7.34 (dd, J = 8.4 Hz, J' = 1.6 Hz, 1H, ArH), 7.46 (d, J = 1.6 Hz, 1H, ArH), 7.48-7.61 (m, 5H, ArH). Anal. Calcd for $C_{31}H_{25}Cl_2NO_2$: C, 72.38; H, 4.90; N, 2.72. Found: C, 72.29; H, 4.90; N, 2.78.

5-(3,4-Dichlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4k). This compound was obtained as red crystals, mp 226 ~228 ℃; ir (KBr): ν_{max} 3052, 2955, 2873, 1693, 1671, 1635, 1588, 1559, 1512, 1464, 1392, 1366, 1300, 1256, 1226, 1193, 1172, 1142, 1099, 1062, 1027, 928, 891, 840, 765, 743; ^{1}H nmr (DMSO-d_6): δ 0.83 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 2.03 (d, J = 17.2 Hz, 1H, CH), 2.08 (d, J = 16.0 Hz, 1H, CH), 2.27 (d, J = 16.0 Hz, 1H, CH), 2.37 (d, J = 17.2 Hz, 1H, CH), 2.50 (s, 3H, CH_3), 4.86 (s, 1H, CH), 5.22 (d, J = 7.6 Hz, 1H, ArH), 7.02-7.05 (m, 1H, ArH), 7.18-7.26 (m, 2H, ArH), 7.38 (dd, J = 8.4 Hz, J' = 2.0 Hz, 1H, ArH), 7.48-7.62 (m, 6H, ArH). Anal. Calcd for $C_{31}H_{25}Cl_2NO_2$: C, 72.38; H, 4.90; N, 2.72. Found: C, 72.34; H, 4.96; N, 2.86.

7,8-Dihydro-7,7-dimethyl-10-(4-methylphenyl)-5-(3-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4l). This compound was obtained as red crystals, mp 239 ~241 ℃; ir (KBr): ν_{max} 3067, 3032, 2955, 2871, 1689, 1648, 1607, 1590, 1561, 1525, 1456, 1397, 1365, 1302, 1259, 1224, 1190, 1172, 1139, 1102, 1057, 1017, 978, 887, 841, 812, 764, 742, 724, 706, 679; ^{1}H nmr (DMSO-d_6): δ 0.82 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 2.05 (d, J = 17.2 Hz, 1H, CH), 2.08 (d, J = 16.0 Hz, 1H, CH), 2.29 (d, J = 16.0 Hz, 1H, CH), 2.42 (d, J = 17.2 Hz, 1H, CH), 2.51 (s, 3H, CH_3), 5.00 (s, 1H, CH), 5.24 (d, J = 7.6 Hz, 1H, ArH), 7.02-7.06 (m, 1H, ArH), 7.18-7.25 (m, 2H, ArH), 7.49-7.62 (m, 5H, ArH), 7.87 (d, J = 7.6 Hz, 1H, ArH), 8.04 (dd, J = 8.0 Hz, J' = 1.2 Hz, 1H, ArH), 8.18 (s, 1H, ArH). Anal. Calcd for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.78; H, 5.30; N, 5.82.

7,8-Dihydro-7,7-dimethyl-10-(4-methylphenyl)-5-(2-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4m). This compound was obtained as red crystals, mp 284 ~286 ℃; ir (KBr): ν_{max} 3040, 2954, 2872, 1685, 1637, 1589, 1562, 1517, 1454, 1400, 1368, 1258, 1226, 1194, 1155, 1103, 890, 844, 767, 748, 702; ^{1}H nmr (DMSO-d_6): δ 0.75 (s, 3H, CH_3), 0.92 (s, 3H,

CH_3), 1.98 (d, J = 16.0 Hz, 1H, CH), 2.00 (d, J = 17.2 Hz, 1H, CH), 2.21 (d, J = 16.0 Hz, 1H, CH), 2.33 (d, J = 17.2 Hz, 1H, CH), 2.51 (s, 3H, CH_3), 5.22 (d, J = 7.6 Hz, 1H, ArH), 5.71 (s, 1H, CH), 7.01-7.05 (m, 1H, ArH), 7.17-7.22 (m, 2H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.48-7.71 (m, 6H, ArH), 7.82 (d, J = 8.4 Hz, 1H, ArH). Anal. Calcd for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.76; H, 5.44; N, 5.75.

5-(3-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4n). This compound was obtained as red crystals, p 182 ~184 ℃; ir (KBr): ν_{max} 3063, 2961, 2871, 1686, 1655, 1633, 1590, 1558, 1510, 1472, 1455, 1398, 1363, 1301, 1254, 223, 1191, 1172, 1139, 1101, 1059, 979, 888, 789, 764, 738, 729, 708; ^{1}H nmr (DMSO-d_6): δ 0.82 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 2.03 (d, J = 17.6 Hz, 1H, CH), 2.07 (d, J = 16.0 Hz, 1H, CH), 2.27 (d, J = 16.0 Hz, 1H, CH), 2.39 (d, J = 17.6 Hz, 1H, CH), 2.50 (s, 3H, CH_3), 4.85 (s, 1H, CH), 5.21 (d, J = 7.2 Hz, 1H, ArH), 7.01-7.05 (m, 1H, ArH), 7.18-7.26 (m, 3H, ArH), 7.30-7.37 (m, 3H, ArH), 7.48-7.57 (m, 4H, ArH). Anal. Calcd for $C_{31}H_{26}ClNO_2$: C, 77.57; H, 5.46; N, 2.92. Found: C, 77.48; H, 5.52; N, 2.90.

5-(2-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4o). This compound was obtained as red crystals, mp 263 ~ 265 ℃; ir (KBr): ν_{max} 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.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methylphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4p). This compound was obtained as red crystals, mp 257 ~ 258 ℃; ir (KBr): ν_{max} 3044, 2958, 2871, 2838, 1673, 1633, 1588, 1559, 1511, 1488, 1455, 1397, 1362, 1254, 1224, 1191, 1102, 1090, 1060, 1015, 889, 839, 767, 731, 701; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.99 (d, J = 17.6 Hz, 1H, CH), 2.05 (d, J = 16.0 Hz, 1H, CH), 2.27 (d, J = 16.0 Hz, 1H, CH), 2.40 (d, J = 17.6 Hz, 1H, CH), 2.50 (s, 3H, CH_3), 4.84 (s, 1H, CH), 5.20 (d, J = 7.6 Hz, 1H, ArH), 7.11-7.15 (m, 1H, ArH), 7.18-7.23 (m, 2H, ArH), 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.39 (d, J = 8.4 Hz, 2H, ArH), 7.48-7.61 (m, 4H, ArH). Anal. Calcd for $C_{31}H_{26}ClNO_2$: C, 77.57; H, 5.46; N, 2.92. Found: C, 77.40; H, 5.55; N, 2.99.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-fluorophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4q). This compound was obtained as red crystals, mp 240 ~ 242 ℃; ir (KBr): ν_{max} 3074, 2955, 2889, 1684, 1647, 1633, 1589, 1563, 1508, 1487, 1453, 1396, 1368, 1257, 1224, 1191, 1153, 1101, 1012, 889, 844, 763, 732, 702; ^{1}H nmr (DMSO-d_6): δ 0.81 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.99 (d, J = 17.6 Hz, 1H, CH), 2.06 (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), 4.84 (s, 1H, CH), 5.22 (d, J = 7.6 Hz, 1H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.19-7.26 (m, 2H, ArH), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.52-7.56 (m, 2H, ArH), 7.79-7.84 (m, 2H, ArH). Anal. Calcd for $C_{30}H_{23}ClFNO_2$: C, 74.45; H, 4.79; N, 2.89. Found: C, 74.21; H, 4.80; N, 2.90.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-methoxyphenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4r). This compound was obtained as red crystals, mp 233 ~ 235 ℃; ir (KBr): ν_{max} 3050, 2996, 2956, 2886, 2840, 1685, 1634, 1606, 1588, 1561, 1496, 1486, 1454, 1295, 1250, 1190, 1169, 1102, 1030, 1001, 889, 764, 732, 703; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 2.02 (d, J = 17.2 Hz, 1H, CH), 2.05 (d, J = 16.0 Hz, 1H, CH), 2.26 (d, J = 16.0 Hz, 1H, CH), 2.39 (d, J = 17.2 Hz, 1H, CH), 3.91 (s, 3H, CH_3O), 4.84 (s, 1H, CH), 5.27 (d, J = 7.6 Hz, 1H, ArH), 7.06-7.08 (m, 1H, CH), 7.19-7.25 (m, 4H, ArH), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.39 (d, J = 8.4 Hz, 2H, ArH), 7.59 (d, J = 8.0 Hz, 1H, ArH), 7.64 (d, J = 8.0 Hz, 1H, ArH). Anal. Calcd for $C_{31}H_{26}ClNO_3$: C, 75.07; H, 5.28; N, 2.82. Found: C, 75.12; H, 5.25; N, 2.88.

5,10-Di(4-chlorophenyl)-7,8-dihydro-7,7-dimethyl-5*H*-indeno-[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4s). This compound was obtained as red crystals, mp 274 ~ 277 ℃; ir (KBr): ν_{max} 3050, 2996, 2956, 2886, 2840, 1685, 1634, 1606, 1588, 1561, 1496, 1486, 1454, 1295, 1250, 1190, 1169, 1102, 1030, 1001, 889, 764, 732, 703; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 1.99 (d, J = 17.2 Hz, 1H, CH), 2.05 (d, J = 16.0 Hz, 1H, CH), 2.26 (d, J = 16.0 Hz, 1H, CH), 2.39 (d, J = 17.2 Hz, 1H, CH), 4.84 (s, 1H, CH), 5.27 (d, J = 7.6 Hz, 1H, ArH), 7.10 (t, J = 7.6 Hz, 1H, ArH), 7.20-7.26 (m, 2H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.77 (b, 4H, ArH). Anal. Calcd for $C_{30}H_{23}Cl_2NO_2$: C, 72.00; H, 4.63; N, 2.80. Found: C, 71.90; H, 4.70; N, 2.86.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-0-(4-iodo phenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4t). This compound was obtained as red crystals, mp 284 ~ 286 ℃; ir (KBr): ν_{max} 3050, 2951, 2871, 1684, 1649, 1635, 1592, 1566, 1485, 1456, 1397, 1369, 1300, 1256, 1226, 1192, 1153, 1100, 1067, 1008, 889, 843, 764, 737, 703; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.95 (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), 2.37 (d, J = 17.6 Hz, 1H, CH), 4.83 (s, 1H, CH), 5.26 (d, J = 7.6 Hz, 1H, ArH), 7.07-7.11 (m, 1H, ArH), 7.19-7.26 (m, 2H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH), 8.05 (d, J = 8.4 Hz, 2H, ArH). Anal. Calcd for $C_{31}H_{26}ClINO_2$: C, 60.88; H, 3.92; N, 2.37. Found: C, 60.80; H, 4.03; N, 2.41.

5-(4-Chlorophenyl)-7,8-dihydro-7,7-dimethyl-10-(4-nitrophenyl)-5*H*-indeno[1,2-*b*]quinolin-9,11(6*H*,10*H*)-dione (4u). This compound was obtained as red crystals, mp 295 ~ 297 ℃; IR (KBr): 3076, 2955, 2871, 1685, 1647, 1635, 1590, 1528, 1487, 1453, 1396, 1369, 1301, 1254, 1225, 1191, 1171, 1141, 1101, 1060, 1011, 936, 891, 861, 842, 763, 736, 703; ^{1}H nmr (DMSO-d_6): δ 0.80 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.99 (d, J = 17.2 Hz, 1H, CH), 2.07 (d, J = 16.4 Hz, 1H, CH), 2.27 (d, J = 16.4 Hz, 1H, CH), 2.39 (d, J = 17.2 Hz, 1H, CH), 4.85 (s, 1H, CH), 5.26 (d, J = 7.6 Hz, 1H, ArH), 7.04 (t, J = 7.6 Hz, 1H, ArH), 7.19-7.27 (m, 2H, ArH), 7.33 (d, J = 8.4 Hz, 2H, ArH), 7.43 (d, J = 8.4 Hz, 2H, ArH), 8.07 (d, J = 8.8 Hz, 2H, ArH), 8.52 (d, J = 8.8 Hz, 2H, ArH). Anal. Calcd for $C_{30}H_{23}ClN_2O_4$: C, 70.52; H, 4.54; N, 5.48. Found: C, 70.50; H, 4.62; N, 5.56.

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[12] Crystal data for **4o**: $C_{34}H_{33}ClN_2O_3$; M = 553.07, red block crystals, 0.68 × 0.23 × 0.15 mm, triclinic, space group P -1, a = 10.872(2), b = 11.655(2), c = 11.689(2)Å, α = 92.100 (4), β = 99.730 (4)°, γ = 106.147 (4), V = 1396.8 (5) ^{3}, Z = 2, D_c = 1.315 g.cm^{-3}. $F(000)$ = 584, μ(Mo$K\alpha$) = 0.176 mm^{-1}. Intensity data were collected on Rigaku Mercury diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71070Å) using ω scan mode with 3.01°<θ<25.25°. 4222 unique reflections were measured and 3385 reflections with I>2σ(I) were used in the refinement. Structure solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to R = 0.0618 and wR = 0.1494.