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Lewis Acid Catalyzed Synthesis of Quinophthalone Pigments Under Solvent-Free Conditions

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Abstract. *A simple and very efficient synthesis of quinophthalones has been achieved with the use of phthalic anhydride and 2-methylquinoline derivatives as starting materials and BF_3/Et_2O as a catalyst under solvent-free and reflux conditions.*

Keywords: *Quinophthalone; Quinoline yellow; Pigments; Solvent-free conditions; Lewis acid.*

INTRODUCTION

Quinophthalones have achieved great significance in organic synthesis [1-3]. Many researchers have shown that these compounds (quinophthalone) are considered as applicable sources for pharmaceuticals [4-5]. Their ability to act as ligands that form stable complexes with different cations, such as Co, Ni and Cu, is also well known [6-8]. Some Quinophthalone derivatives have been used in liquid crystal monitoring [9] as dyestuffs for printing inks and for the bulk dyeing of thermoplastics such as polystyrene, polyvinylcholoride, polyesters and polyamids [10]. Quinophthalone dyes are fascinating due to their color brilliance and light fastness [11], being a highly important yellow dye. Quinoline yellow (quinophthalone), which was first discovered by Jacobsen and Reimer in 1883, is probably the most widely used yellow compound for the trichromatic dyeing of bulk textile goods made from polyester fibers [12]. Several methods for the preparation of quinophthalones have been reported such as the treatment of phthalic anhydrides as a mixture of quinaldine with nitrobenzene [13], $ZnCl_2$ [14-16], sodium hydride [17] or silica gel (microwave condition) [18] and reactions of quinoline N-oxides/β-diketones [19].

In this article, preparation of quinophthalone by the condensation of phthalic anhydride derivatives with 2-methylquinoline derivatives under solvent-free and reflux conditions (in the presence of lewis acid) are reported (Scheme 1).

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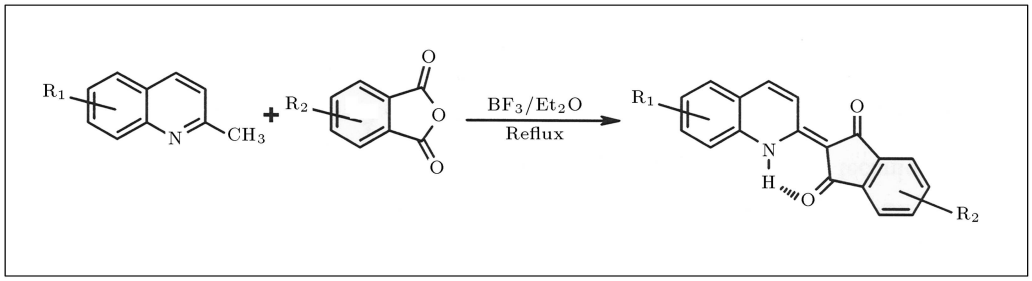
RESULT AND DISCUSSION

In order to choose the appropriate catalyst, some common Lewis acids such as BCl_3/THF, BF_3/Et_2O, $ZrCl_4$, $SnCl_4$ and $AlCl_3$ were selected and, then, a comparative study was done using 2-methylquinoline and phthalic anhydride as starting materials (Table 1).

Quinophthalone derivatives were prepared from phthalic anhydride and 2-methylquinoline derivatives under reflux and solvent-free conditions in the presence of catalysts. The results in Table 1 indicate that the application of BF_3/Et_2O as a catalyst (due to having a selective product at high yield and with a low reaction time and any byproducts) was selected for subsequent experiments. In order to obtain the best reaction conditions and to optimize reactions, several concentrations of BF_3/Et_2O were used. It was observed that the reaction mixture without the intervention of Lewis acid

Table 1. Quinophthalone formation in the presence of various catalysts.

Entry	Catalyst	Time (min)	Yield (%)
(1)	BCl_3/THF	12	30
(2)	BF_3/Et_2O	12	70
(3)	$ZrCl_4$	20	25
(4)	$SnCl_4$	15	50
(5)	$AlCl_3$	20	25

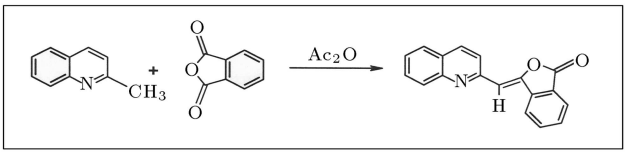


Scheme 1: Synthesis of quinophthalone.

does not produce any product. The results in Table 2 indicate that in 0.2 mmol of catalysts, the yield of the reaction is best. In the presence of acetic anhydride as a catalyst, the reaction process changes into another product, namely isobenzofuranone [20] (Scheme 2).

The results summarized in Table 3 indicate that in the presence of the electron withdrawing substitution on the phthalone ring, the resonance and inductive effects of substitution have an influence on reaction time. The electron releasing substitution on the 6-position of the quinoline ring inhibit the nucleophilic attack of the methyl group of 2-methylquinoline; therefore, the yield of the reaction is influenced by it and is decreased. The structure of the quinophthalone products were confirmed by their spectroscopic data. In all the ^{1}H-NMR spectra of the quinophthalone products, the NH group appeared in the δ 14-15 ppm region as a broad singlet. The integral of this signal was proportional to one proton and no signal was observed in the aliphatic region corresponding to a C-H. From this data, it is concluded that the compounds are exclusively in the enaminone form [21-25]. With $CDCl_3$ as the solvent, the structure of (B) is major (Figure 1).

The ^{13}C-NMR data was also consistent with the proposed structures in all cases. In IR spectra, the C=O groups were observed around 1640 and 1680 cm^{-1}. Different frequencies of carbonyl group refer to intramolecular hydrogen bonding with NH in enaminone form [26].



Scheme 2: Synthesis of isobenzofuranone.

Table 2. The effect of catalyst concentration on yield of product (3a)*.

Entry	BF_3 (mmol)	Yeild (%)
(1)	0	0
(2)	0.05	25
(3)	0.07	47
(4)	0.09	70
(5)	0.1	85
(6)	0.2	91
(7)	0.3	91
(8)	0.4	91

* The concentration of initial material is constant.

Table 3. The reaction of quinaldine derivatives with phthalic anhydride derivatives under reflux condition.

Entry	R_1	R_2	Product	Time (min)	Yield (%)*
(1)	H	H	3a	14	91
(2)	H	Cl_4	3b	13	79
(3)	H	Br_4	3c	13	68
(4)	H	3-NO_2	3d	15	64
(5)	H	4-NO_2	3e	17	66
(6)	6-CH_3	H	3f	15	76
(7)	6-CH_3	Cl_4	3g	13	70
(8)	6-CH_3	Br_4	3h	15	67
(9)	6-CH_3	3-NO_2	3i	14	61
(10)	6-CH_3	4-NO_2	3j	15	54

* Yields refers to isolated pure product after purification.

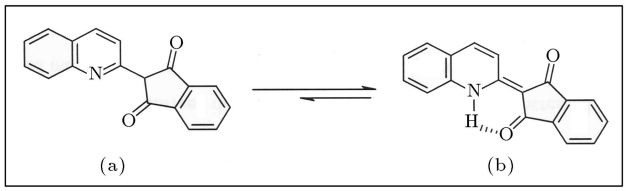


Figure 1. Tautomeric form of quinophthalone.

CONCLUSION

The facile protocol has been developed for the synthesis of quinophthalone in any solvent with intervention of lewis acid under reflux conditions. In this research, it was found that lewis acid activates the carbonyl group of phthalic anhydride toward the nucleophilic attack reaction by the methyl group of 2-methylquinoline, and the effect of substitution on the reaction time and yield of the reaction was illustrated. The redundancy of extra preparation in the isolation of products is another important advantage of this research. We believe that the reported method offers a mild, simple and efficient route for preparation of quinophthalone pigments. Its ease of work up, high yields and short reaction times make it a useful addition to modern synthetic methodologies.

EXPERIMENTAL SECTION

General

Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus. IR spectra were recorded using a Perkin-Elmer FT-IR 550 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer for the sample, as indicated by tetramethylsilane as the internal reference. UV spectra were recorded on a Hitachi 200-20 spectrophotometer using spectrophotometeric grade chloroform (Baker). MS spectra were recorded on a Finnigan MAT 44S with an ionization voltage of 70 eV. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer, carried out on a Perkin-Elmer 240c analyzer.

Preparation of Quinophthalone (3a-3j)

A mixture of 2-methylquinoline (1 mmol), phthalic anhydride (1.2 mmol) and BF_3/Et_2O (0.2 mmol) were well mixed in a flask and were refluxed at 200°C. A thin layer chromatography (TLC) on commercial silica gel plates 60 F_{254} was used to monitor the progress of the reaction. After 14 minutes, the reaction was completed. At the end of the reaction, the reaction mixture was cooled to room temperature and a saturated solution of $NaHCO_3$ (10 ml) was added and the mixture was stirred for 20 min to neutralize an excess of phthalic anhydride. The mixture was filtered using a filter glass and was washed carefully with petroleum ether (2×10 mL). The residue obtained after removal of the solvent was crystallized from ethanol. The crystallization yielded 2-[2(1H)quinolinylidene]-1H-indene-1,3-(2H)-dione (3a).

2-(2(1H) quinolinylidene)-1H-indene-1,3-(2H) -dione (3a)

Yield: 91%, mp : 240-242°C. IR (KBr): $\overline{v}$ cm^{-1} : 1680 (C=O), 1640 (C=O), 1616 (C=C), 1453 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.18 (s, 1H, NH enaminone form), 8.62 (d, 1H, ^{3}J= 9Hz, =C-H), 8.05 (d, 1H, ^{3}J= 9Hz, =C-H), 7.65-7.75 (m, 4H, Ar), 7.5-7.6 (m, 3H, Ar), 7.41 (d, 1H, ^{3}J= 8Hz, ^{4}J= 1Hz, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 194.2 (C=O), 188.0 (C=O), 151.0 (C), 148.3 (CH), 139.7 (C), 139.3 (C), 136.2 (C), 132.6 (CH), 132.2 (CH), 131.8 (CH), 128.0 (CH), 124.9 (C), 123.7 (CH), 121.0 (CH), 120.4 (CH), 119.4 (CH), 117.5 (CH), 99.2 (C). MS (m/z): 273 ($M^{+\cdot}$, 100), 217 (26), 143 (16), 108 (22), 77 (48), 50 (23). UV ($CDCl_3$): λ_{max}= 440, 420, 290 nm. Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.10; H, 4.05; N, 5.58. Found: C, 79.25; H, 4.01; N, 5.49.

4,5,6,7-Tetrachloro-[2-(2(1H) quinolinylidene)] -1H-indene-1,3-(2H)-dione (3b)

Yield: 79%, mp : > 350°C. IR (KBr): $\overline{v}$ cm^{-1} : 1688 (C=O), 1637 (C=O), 1613 (C=C), 1450 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 14.02 (s, 1H, NH enaminone form), 8.55 (d, 1H, ^{3}J= 9.1Hz, =C-H), 8.07(d, 1H, ^{3}J= 9.1Hz, , =C-H), 7.65-7.85 (m, 3H, Ar), 7.48 (d, 1H, ^{3}J= 8.2Hz, ^{4}J= 1.1Hz, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 195.6 (C=O), 189.7 (C=O), 153.1 (C), 140.5 (CH), 140.2 (C), 139.7 (C), 137.0 (C), 136.9 (C), 135.2 (C), 132.8 (CH), 129.4 (CH), 126.6 (C), 125.6 (C), 125.0 (C), 123.3 (CH), 120.5 (CH), 118.4 (CH), 96.4 (C). MS (m/z): 413 (M+2, 33), 411 ($M^{+\cdot}$, 74), 376 (83), 374 (87), 355 (95), 318 (23), 238 (43), 248 (27), 212 (45), 173 (35), 140 (100), 114 (46), 75 (35). UV ($CDCl_3$): λ_{max}= 443, 413, 288 nm. Anal. Calcd for $C_{18}H_7NO_2Cl_4$: C, 52.59; H, 1.71; N, 8.80. Found: C, 52.20; H, 1.78; N, 8.69.

4,5,6,7-Tetrabromo-[2-(2(1H) quinolinylidene)] -1H-indene-1,3-(2H)-dione (3c)

Yield: 68%, mp : > 350°C. IR (KBr): $\overline{v}$ cm^{-1} : 1694 (C=O), 1642 (C=O), 1608 (C=C), 1428 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 14.14 (s, 1H, NH enaminone form), 8.60 (d, 1H, ^{3}J= 9.0Hz,=C-H), 8.01 (d, 1H, ^{3}J= 9.0Hz, , =C-H), 7.65-7.81 (m, 3H, Ar), 7.45 (dt, 1H, ^{3}J= 8.1Hz, ^{4}J= 1.2Hz, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 194.1 (C=O), 188.7 (C=O), 152.7 (C), 141.7 (C), 141.2 (C), 139.7 (CH), 137.6 (C), 136.1 (C), 135.2 (C), 133.8 (CH), 131.8 (CH), 128.5 (C), 126.0 (CH), 123.1 (C), 122.3 (C), 121.5 (CH),

119.3 (CH), 99.0 (C). MS (m/z): 585 ($M^{+\cdot}$, 100), 217 (26), 143 (16), 108 (22), 77 (48), 50 (23). UV ($CDCl_3$): λ_{max}= 440, 412, 290 nm. Anal. Calcd for $C_{18}H_7NO_2Br_4$: C, 36.71; H, 1.18; N, 2.37. Found: C, 36.54; H, 1..16; N, 2.37.

5-Nitro-[2-(2(1H) quinolinylidene)]-1H-indene -1,3-(2H)-dione (3d)

Yield: 64%, mp : 217-219°C. IR (KBr): $\overline{v}$ cm^{-1} : 1674 (C=O), 1636 (C=O), 1620 (C=C), 1453 (C=C), 1550 (N=O), 1330 (N-O). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.32 (s, 1H, NH enaminone form), 8.60 (d, 1H, ^{4}J= 1.5 Hz, Ar), 8.41 (dd, 1H, ^{3}J= 8.2Hz, ^{4}J= 1.5Hz, Ar), 8.11 (d, 1H, ^{3}J= 9.1Hz, , =C-H), 7.91 (d, 1H, ^{3}J= 8.2Hz, Ar), 7.55-7.71 (m, 4H, Ar), 7.43 (d, 1H, ^{3}J= 7.1Hz, , =C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) : 194.0 (C=O), 190.3 (C=O), 152.2 (C), 146.4 (C), 145.1 (C), 141.3 (CH), 140.8 (C), 137.1 (C), 133.4 (CH), 130.5 (CH), 128.6 (C), 126.4 (CH), 125.0 (CH), 123.0 (CH), 121.8 (CH), 119.2 (CH), 118.7 (CH), 103.3 (C). MS (m/z): 273 ($M^{+\cdot}$, 100), 217 (26), 143 (16), 108 (22), 77 (48), 50 (23). UV ($CDCl_3$): λ_{max}= 442, 420, 292 nm. Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.10; H, 4.05; N, 5.58. Found: C, 79.25; H, 4.01; N, 5.49. Anal. Calcd for $C_{18}H_{10}N_2O_4$: C, 67.92; H, 3.16; N, 8.80. Found: C, 67.61; H, 3.05; N, 8.68.

4-Nitro-[2-(2(1H) quinolinylidene)]-1H-indene -1,3-(2H)-dione (3e)

Yield: 66%, mp: 231-234°C. IR (KBr): $\overline{v}$ cm^{-1} : 1674 (C=O), 1636 (C=O), 1620 (C=C), 1453 (C=C), 1553 (N=O), 1330 (N-O). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 14.26 (s, 1H, NH enaminone form), 8.65 (dd, 1H, ^{3}J= 8.0Hz, ^{4}J= 1.1Hz, Ar), 8.15 (d, 1H, ^{3}J= 9.1Hz, , =C-H), 7.75 (dd, 1H, ^{3}J= 8.3Hz, ^{4}J=1.1 Hz, Ar),7.3-7.4 (m, 2H, Ar), 7.53-7.68 (m, 3H, Ar), 7.46 (d, 1H, ^{3}J= 9.1Hz, , =C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 194.0 (C=O), 190.3 (C=O), 152.2 (C), 146.4 (C), 145.1 (CH), 141.3 (C), 140.8 (CH), 137.0 (C), 133.4 (C), 130.5 (CH), 128.6 (CH), 126.4 (CH), 125.6 (C), 123.2 (CH), 121.8 (CH), 119.2 (CH), 118.7 (CH), 103.3 (C). MS (m/z): 273 ($M^{+\cdot}$, 100), 217 (31), 143 (20), 108 (22), 77 (50), 50 (26). UV ($CDCl_3$): λ_{max}= 444, 420, 290 nm. Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.10; H, 4.05; N, 5.58. Found: C, 79.25; H, 4.01; N, 5.49. Anal. Calcd for $C_{18}H_{10}N_2O_4$: C, 67.92; H, 3.16; N, 8.80. Found: C, 67.44; H, 3.04; N, 8.71.

2-[6-methyl-2(1H) quinolinylidene]-1H-indene -1,3-(2H)-dione (3f)

Yield: 76%, mp : 236-238°C. IR (KBr): $\overline{v}$ cm^{-1} : 1675 (C=O), 1623 (C=O), 1585 (C=C), 1418 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 14.16 (s, 1H, NH enaminone form), 8.58 (d, 1H, ^{3}J= 9Hz, =C-H), 8.09 (d, 1H, ^{3}J= 9Hz, =C-H), 7.65-7.75 (m, 4H, Ar), 7.51-7.60 (m, 3H, Ar), 2.96 (s, 3H, -C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 193.8 (C=O), 190.7 (C=O), 152.7 (C), 141.3 (CH), 140.0 (C), 139.3 (C), 136.2 (C), 133.7 (CH), 132.8 (CH), 128.9 (CH), 127.6 (CH), 126.2 (C), 124.1 (C), 123.8 (CH), 121.2 (CH), 119.9 (CH), 117.9 (CH), 99.7 (C), 21.3 (CH_3). MS (m/z): 287 ($M^{+\cdot}$, 44), 272 (60), 243 (35), 115 (28), 104 (60), 76 (100), 50 (39). UV ($CDCl_3$): λ_{max}= 444, 420, 290 nm. Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.14; H, 4.89; N, 4.85. Found: C, 78.93; H, 4.78; N, 4.91.

4,5,6,7-Tetrachloro-2-[6- methyl-2(1H) quinolinylidene]-1H -indene-1, 3-(2H)-dione (3g)

Yield: 70%, mp : > 350°C. IR (KBr): $\overline{v}$ cm^{-1} : 1682 (C=O), 1635 (C=O), 1612 (C=C), 1426 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.16 (s, 1H, NH enaminone form), 8.50 (d, 1H, ^{3}J= 9.1Hz, , =C-H), 7.60-7.71 (m, 3H, Ar), 2.96 (s, 3H, -C-H), 7.4 (d, 1H, ^{3}J= 9.1, =C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) : 196.8 (C=O), 192.7 (C=O), 154.7 (C), 143.3 (CH), 142.0 (C), 141.7 (C), 138.2 (C), 135.7 (C), 134.8 (C), 129.8 (CH), 129.0 (CH), 128.2 (C), 126.1 (C), 125.8 (C), 123.2 (C), 121.9 (CH), 118.8 (CH), 95.7 (C), 24.1 (CH_3). MS (m/z): 273 ($M^{+\cdot}$, 100), 217 (26), 143 (16), 108 (22), 77 (48), 50 (23). UV ($CDCl_3$): λ_{max}= 446, 418, 294 nm. Anal. Calcd for $C_{19}H_9NO_2Cl_4$: C, 53.55; H, 2.36; N, 3.28. Found: C, 52.90; H, 2.00; N, 2.95.

4,5,6,7-Tetrabromo-2-[6- methyl-2(1H) quinolinylidene]-1H -indene-1, 3-(2H)-dione (3h)

Yield: 67%, mp : > 350°C. IR (KBr): $\overline{v}$ cm^{-1} : 1684 (C=O), 1638 (C=O), 1623 (C=C), 1435 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.11 (s, H, NH enaminone form), 8.71 (d, 1H, ^{3}J= 9.0Hz, , =C-H), 7.65-7.80 (m, 3H, Ar), 2.78 (s, 3H, -C-H), 7.4 (d, 1H, ^{3}J= 9.0 Hz, , Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) : 196.4 (C=O), 190.2 (C=O), 150.2 (C), 143.3 (CH), 141.2 (C), 140.4 (C), 137.9 (C), 133.9 (C), 132.4 (C), 130.0 (CH), 128.8 (CH), 125.2 (C), 124.1 (C), 123.0 (C), 121.8 (C), 119.8 (CH), 118.1 (CH), 95.7 (C), 23.6 (CH_3). MS (m/z): 579 ($M^{+\cdot}$, 100), 217 (26), 143 (16), 108 (22), 77 (48), 50 (23). UV ($CDCl_3$): λ_{max}= 446, 418, 296 nm. Anal. Calcd for $C_{19}H_9NO_2Br_4$: C, 37.85; H, 1.49; N, 2.32. Found: C, 37.80; H, 1.51; N, 2.34.

2-[6- methyl-2(1H) quinolinylidene]-5-nitro-1H -indene-1, 3-(2H)-dione (3i)

Yield: 61%, mp : 248-250°C. IR (KBr): $\overline{v}$ cm^{-1} : 1678 (C=O), 1637 (C=O), 1605 (C=C), 1427 (C=C), 1550 (N=O), 1334 (N-O). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.41 (s, 1H, NH enaminone form), 8.66 (d, 1H, ^{4}J= 1.3Hz, Ar), 8.41 (dd, 1H, ^{3}J= 8.5Hz, ^{4}J= 1.3Hz, Ar), 8.11 (d, 1H, ^{3}J= 9.1Hz, =C-H), 7.50-7.74

(m, 4H, Ar), 7.3 (d, 1H, ^{3}J=9.1, =C-H) 2.84 (s, 3H, -C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) : 194.7 (C=O), 191.6 (C=O), 156.6 (C), 142.2 (C), 141.9 (C), 140.7 (CH), 137.1 (C), 134.6 (C), 133.7 (CH), 129.2 (CH), 128.5 (C), 127.1 (CH), 125.0 (C), 124.4 (CH), 122.1 (CH), 120.8 (CH), 118.8 (CH), 100.5 (C), 22.2 (CH_3). MS (m/z): 332 ($M^{+\cdot}$, 35), 315 (25), 286 (33), 228 (47), 215 (20), 142 (62), 115 (32), 89 (54), 75 (100). UV ($CDCl_3$): λ_{max}= 442, 421, 294 nm. Anal. Calcd for $C_{19}H_{12}N_2O_4$: C, 68.46; H, 3.93; N, 8.40. Found: C, 67.59; H, 3.60; N, 8.53.

2-[6- methyl-2(1H) quinolinylidene]-4-nitro-1H -indene-1, 3-(2H)-dione (3j)

Yield: 54%, mp : 245-246°C. IR (KBr): $\overline{\upsilon}$ cm^{-1} : 1672 (C=O), 1638 (C=O), 1612 (C=C), 1435 (C=C), 1560 (N=O), 1334 (N-O). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) : 14.32 (s, 1H, NH enaminone form), 8.71 (dd, 1H, ^{3}J= 8.3,^{4}J=1.2Hz, Ar), 8.48 (d, 1H, ^{3}J=9.0Hz, =C-H), 8.18 (dd, 1H, ^{3}J= 8.0, ^{4}J=1.2Hz, Ar), 7.81 (dd, 1H, ^{3}J= 8.3, ^{3}J=8.1Hz, Ar), 7.50-7.65 (m, 3H, Ar), 7.3 (d, 1H, ^{3}J=9.0Hz, =C-H), 2.44 (s, 3H, -C-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) : 195.0 (C=O), 189.0 (C=O), 155.3 (C), 143.2 (C), 141.3 (CH), 140.8 (C), 138.2 (CH), 137.1 (C), 136.5 (C), 133.9 (CH), 131.0 (CH), 128.6 (CH), 127.0 (C), 124.1 (CH), 123.8 (CH), 122.7 (CH), 119.2 (CH), 101.0 (C), 21.3 (CH_3). MS (m/z): 332 ($M^{+\cdot}$, 30), 315 (25), 286 (30), 228 (55), 215 (20), 142 (62), 115 (32), 89 (54), 75 (100). UV ($CDCl_3$): λ_{max}= 440, 419, 290 nm. Anal. Calcd for $C_{19}H_{12}N_2O_4$: C, 68.46; H, 3.93; N, 8.40. Found: C, 68.01; H, 3.54; N, 8.34.

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