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Synthesis novel pigments by the α-phenylhydrazation of 2-ketomethylquinoline derivatives

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Abstract

Azo dyes with the general formula X–N=N–Y are well known to be important dyestuffs. Dyes with a hydroxy group are known to exhibit an azo–hydrazone tautomerism and NMR measurements are well suited to investigate this type of tautomerism. In particular multinuclear studies form the basis of a powerful investigation technique.

The azo-coupling products have been prepared from derivatives of 2-ketomethylquinoline and aryldiazonium ions. Structure of the products obtained was studied by means of multinuclear NMR spectroscopy in $CDCl_3$ solution, IR and Mass spectroscopy. Products are only present as hydrazone forms in both the solution and the solid state.
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Keywords: Azo-coupling; 2-Ketomethylquinoline; Diazonium ions; Multinuclear NMR; Hydrazone form

1. Introduction

In recent decades, organic color chemistry is undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and non-linear optics, reprography, sensors, and biomedical uses [1].

Azo dyes are the largest and most versatile class of dyes [2,3]. Aliphatic azo compounds in which the carbon containing the azo group is attached to hydrazones that are the products of the reaction.

If a C–H bond is acidic enough, it couples with diazonium salts in the presence of a base, most often aqueous sodium acetate [4]. The reaction is commonly carried out on compounds of the form ZCH_2Z', where Z and Z′ may be COOR, CHO, COR, $CONR_2$, CN, NO_2, SOR, SO_2R, or similar groups e.g., β-ketoesters, malonicester groups [5]. When the reaction is carried out on a compound of the form ZCH_2Z', so that the azo compound has no tautomerizable hydrogen, if at least one Z is acyl or carboxyl, this group usually cleaves. So the product in this case is also the hydrazone, and not the azo compound. In fact, the azo compounds having an acyl or carboxyl group are seldom isolable from the reaction, though this has been accomplished [6]. The overall process in this case is called the Japp Klingeman reaction [7] and involves conversion of a ketone or carboxylic acid to hydrazones.

When an acyl and a carboxyl group are both present, the leaving group order has been reported to be MeCO > COOH > PhCO [8]. When there is no acyl or carboxyl group present, the aliphatic azo compound is stable. Aromatic diazonium ions normally couple only with active substrates such as amines and phenols [9]. Many of the products of this reaction are used as dyes (azo dyes) [10].

In our lab we applied 2-ketomethylquinolines (**1**) and prepared the diazonium ion by treating aryl amine with sodium nitrite and acid. When primary aromatic amines

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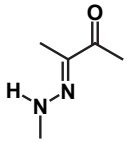
($ArNH_2$) are treated with nitrous acid (HONO), they are converted into diazonium cations, ArN_2^+. In solution, nitrous acid is in equilibrium with its anhydride, dinitrogen trioxide (N_2O_3), which is the actual diazotizing agent. The primary amine reacts with the dinitrogen trioxide to form a nitrous amine. The nitrous amine is in equilibrium with its tautomer, a diazonium salt. Diazonium salts are explosive when dry, and therefore are generally not isolated [11–16].

2. Results and discussion

2-Ketomethylquinoline is an important component in organic chemistry because of the applications of these compounds in heterocyclic synthesis and chemical transformations [17–22]. The synthesizing of 2-ketomethylquinolines (**1**) in order to α-hydrazate them caused to synthesize α-phenylhydrazones (**2**) (Scheme 1).

Thus, 2-ketomethylquinolines are hydrazated using sodium nitrite and derivatives of aniline in the presence of acid and then initially formed hydrazo compounds are converted to the corresponding α-hydrazoketones (**3**) under the reaction conditions (Scheme 2). The hydrazation reactions are carried out under the mild and completely heterogeneous conditions at 5 °C and give quantitative yields.

Since these derivatives have eniminone structure, IR and NMR data have been affected.



Eniminone structure

The eniminone structure exists as several resonance forms that led to reduce percent of double bond carbonyl group in compound, which appeared in adsorbtion lower than carbonyl groups in common ketones (1715 cm^{-1}) (Scheme 3).

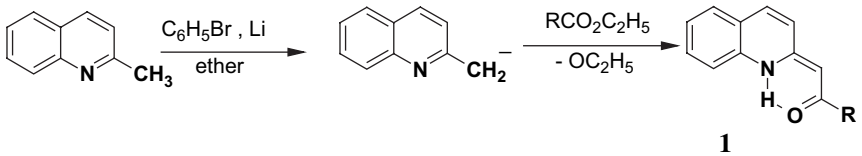
R group connected to carbonyl group and kind of X substitution in absorbing place (observed in spectra) are effective for carbonyl group. Presence of an acceptor electron in R position causes an increase in absorbing frequency of carbonyl group mentioned (1680 cm^{-1} in compound **3a**) and reducing acceptor electron in R substitution, absorbing frequency of carbonyl group has been reduced (1635 cm^{-1} in compound **3c**).

This point is right for X substitution. Presence of acceptor electron groups causes increase in the absorbing frequency of carbonyl group in derivatives. IR data of derivatives α-phenylhydrazone can be seen in Table 1. Products were found to be stable and thus suitable for studies of intra-molecular hydrogen bonding. The ^1H NMR and ^{13}C NMR chemical shifts for these derivatives are summarized in Tables 2 and 3, respectively.

3. Experimental

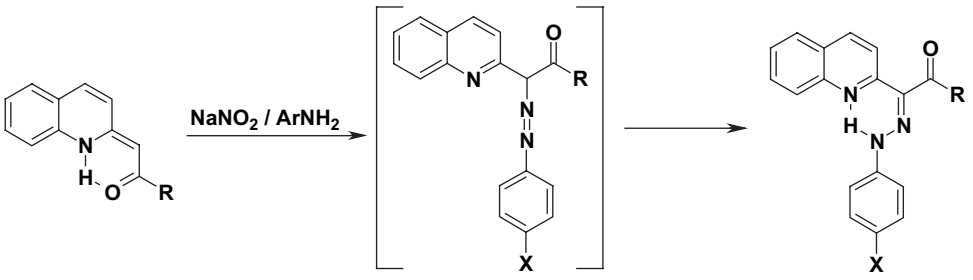
In a typical procedure chemical reagents were purchased from Merck chemical company. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded by Bruker DRX 500 Avance spectrometer Multiplicities of proton resonance and were designated as singlet (s), doublet (d), and triplet (t). Tetramethylsilane (TMS) was used as an internal reference. A Magna-550 Nicolet recorded IR spectra. Spectra of hydrazone were carried out with KBr pellet and CH_2Cl_2 solvent. Vibrational transition frequencies were reported as wave numbers (cm^{-1}). Band intensities were designated as weak (w), medium (m), sprang (s), and broad (br). A mass spectrum was recorded by QP 1100EX Shimadzu spectrometer. Solid compound reported in this paper gave satisfactory C, H, N microanalyses with a Perkin–Elmer Model 240 Analyzer. Melting point was obtained with an Electrothermal micro melting point apparatus and is uncorrected.

In the first stage, 1 mmol of derivatives 2-ketomethylquinoline was dissolved in 15–20 ml water and some concentrated sulfuric acid, then 1 g of sodium acetate dissolved in some water in a vial and was added to the solution (part a). In order to prepare sodium nitrite solution, 1 mmol (~0.069 g) of this salt was dissolved in water, and was cooled in an ice bath (part b). Then, 1 mmol of primary amine was dissolved in minimum volume of concentrated sulfuric acid (part c). Further, sodium nitrite solution (b) was added to primary amine solution (c) and then the solution of part a, was added to it. In this reaction, temperature was kept below 5 °C. After completion of the reaction, the products were filtered off, washed with water until acid-free, dried at 50 °C in an oven to give hydrazone compounds **3(a–i)**, which were recrystallised from suitable solutions.



1

Scheme 1.



1 **2** **3**

3	*R*	*X*	*% Yield*
a	CO_2Et	Br	75
b	C_6H_5	Br	73
c	$C(CH_3)_3$	Br	82
d	$2\text{-}C_6H_4N$	NO_2	85
e	CO_2Et	NO_2	99.9
f	C_6H_5	NO_2	99
g	$C(CH_3)_3$	NO_2	91
h	$C(CH_3)_3$	CH_3	63
i	C_6H_5	CH_3	68

Scheme 2.

*3.1. Ethyl (3E)-3-[(4-bromophenyl)hydrazono]-2-oxo-3-quinoline-2-yel poropanoate (**3a**)*

$C_{20}H_{16}BrN_3O_3$

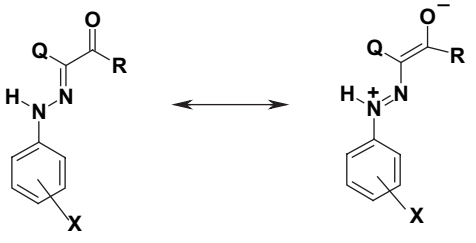
Yield: 75%; mp (°C): 120–123 (ethanol).

FDMS: *m/z* (%) = 427, 323, 217, 171.

IR (KBr, cm^{-1}) = 1750(w), 1680(m), 1620(m), 1590(m), 1530(m).

Elemental analysis (%); Theory: C, 56.35; H, 3.78; N, 9.86; Found: C, 56.33; H, 3.78; N, 9.89.

^{1}H NMR δ (ppm): 1.45 (3H, t, $J = 6.2$ Hz, CH_3); 4.47 (2H, q, $J = 6.2$ Hz, CH_2); 7.19 (2H, d, $J = 7.4$ Hz, $2 \times$ CH); 7.46 (2H, d, $J = 7.4$ Hz, $2 \times$ CH); 7.52 (1H, dd, $J = 6.4$ Hz, CH); 7.73 (1H, d, CH); 7.74 (1H, dd, $J = 7.5$, $J = 4$ Hz, CH); 7.90 (1H, d, $J = 7.5$ Hz, CH); 8.14 (1H, d, $J = 8.4$ Hz, CH), 8.62 (1H, d, $J = 8.4$ Hz, CH); 16.63 (1H, s, NH).



Scheme 3.

^{13}C NMR δ (ppm): 14.45 (CH_3); 61.61 (CH_2); 117.38 (2CH), 117.84 (C), 120.83 (CH), 127.07 (C), 127.52 (CH); 127.65 (CH); 127.77 (CH); 128.75 (C), 130.32 (CH), 132.53 (2CH), 137.04 (CH), 141.17 (C), 144.82 (C), 151.97 (C), 166.72 (C), 186.78 (C).

*3.2. (2E)-1-phenyl-2-quinoline-3-yel ethanone-1,2-dione-2-[(4-bromophenyl)hydrazone] (**3b**)*

$C_{23}H_{16}BrN_3O$

Yield: 73%; mp (°C): 189–190 (ethanol).

FDMS: *m/z* (%) = 396 (98), 395 (100), 246 (30).

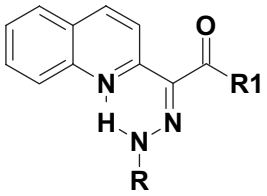
IR (KBr, cm^{-1}) = 1660(m), 1600(m), 1540(m), 1500(m).

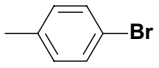
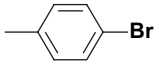
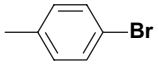
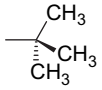
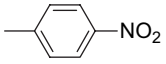
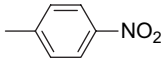
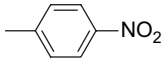
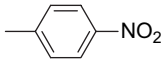
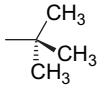
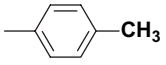
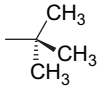
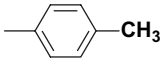
Elemental analysis (%); Theory: C, 64.20; H, 3.75; N, 9.77; Found: C, 64.23; H, 3.76; N, 9.76.

^{1}H NMR δ (ppm): 7.26 (2H, d, $J = 8.7$ Hz, $2 \times$ CH), 7.53 (2H, dd, $J = 7.5$, 7.5 Hz, $2 \times$ CH), 7.65 (2H, dd, $2 \times$ CH), 7.83 (1H, dd, $J = 7.5$, 7.5 Hz, CH), 7.88 (1H, d, $J = 8.0$ Hz, CH), 8.06 (1H, d, $J = 9.0$ Hz, CH), 8.07 (1H, d, CH), 8.10 (2H, d, $J = 8.5$ Hz, $2 \times$ CH), 8.20 (2H, d, $J = 9.0$ Hz, $2 \times$ CH), 8.27 (1H, d, $J = 8.5$ Hz, CH), 16.13 (1H, s, NH).

^{13}C NMR δ (ppm): 114.24 (2CH), 122.16 (CH), 125.84 (2CH), 127.28 (C), 127.72 (CH), 127.89 (CH), 128.00 (2CH), 128.24 (CH), 130.44 (CH), 130.62 (2CH),

Table 1
IR data derivatives α-phenylhydrazone 2-ketomethylquinoline



3	R	R1	C=O	C=O/C=N	C=N/C=C	C=N/C=O	Ar
a			1750	1680	1620	1590	1530
b			—	1660	1600	1540	1500
c			—	1635	1595	1560	1525
d			—	1680	1670	1597	1499
e			1736	1683	1620	1600	1580
f			—	1650	1625	1600	1525
g			—	1676	1624	1560	1505
h			—	1663	1610	1530	1500
i			—	1675	1615	1580	1550

132.59 (CH), 136.16 (C), 136.96 (CH), 138.17 (C), 142.47 (C), 145.46 (C), 148.41 (C), 152.62 (C), 192.43 (C).

3.3. (1E)-3,3-dimethyl-1-quinoline-3-yel buthane-1,2-dione-1-[(4-bromophenyl)hydrazone] (**3c**)

$C_{21}H_{20}BrN_3O$

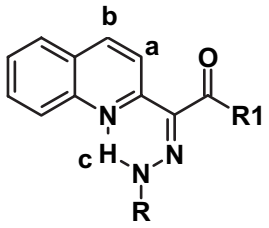
Yield: 82%; mp (°C): 165–164 (ethanol).
FDMS: m/z (%) = 411(M^+), 359, 239, 155, 128, 57, 41.
IR (KBr, cm^{-1}) = 1635(m), 1595(m), 1560(m), 1525(m).

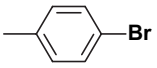
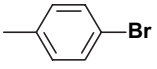
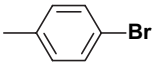
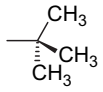
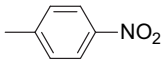
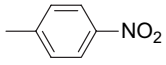
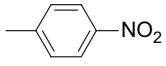
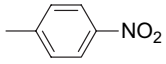
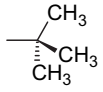
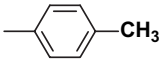
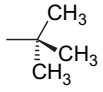
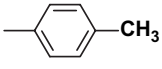
Elemental analysis (%); Theory: C, 61.74; H, 4.91; N, 10.24; Found: C, 61.77; H, 4.93; N, 10.22.

^{1}H NMR δ (ppm): 1.52 (9H, s, CH_3); 7.36 (2H, d, $J = 8.5$ Hz, 2 × CH); 7.62 (1H, d, CH); 7.64 (1H, dd, CH); 7.81 (1H, dd, $J = 7.5$, 7.5 Hz, CH); 7.86 (1H, d, $J = 8.0$ Hz, CH); 8.07 (1H, d, $J = 8.5$ Hz, CH); 8.23 (1H, d, $J = 8.5$ Hz, CH); 8.27 (2H, d, $J = 8.5$ Hz, 2 × CH); 15.63 (1H, s, NH).

^{13}C NMR δ (ppm): 28.14 ($3CH_3$); 44.69 (C); 113.65 (2CH); 122.14 (CH), 125.99 (2CH), 127.11 (C), 127.64 (CH), 127.86 (CH), 128.23 (CH), 130.40 (CH), 136.80

Table 2
^{1}H, chemical shifts of products in $CDCl_3$ at 298 K



3	R	R_1	$^3J_{H3,H4}$	a	b	c	R_1(Aliphatic)
a		$-CO_2Et$	8.4	8.14	8.62	16.63	1.45, 4,47
b			8.8	8.06	8.27	16.13	—
c			8.5	8.07	8.23	15.63	1.52
d			—	7.27	8.56	16.07	—
e		$-CO_2Et$	8.0	7.65	7.88	16.84	1.41, 4.35
f			8.0	7.71	8.05	16.44	—
g			8.5	7.81	8.15	15.90	1.54
h			8.3	8.25	8.66	15.46	1.52
i			8.5	7.71	8.15	15.80	—

(CH), 137.40 (C), 142.04 (C), 145.49 (C), 148.73 (C), 152.38 (C), 207.21 (C).

*3.4. (2E)-1-pyridyn-2-yel-2-quinoline-2-yel ethane-1,2-dione 2-[(4-nitrophenyl)hydrazone] (**3d**)*

$C_{22}H_{15}N_5O_3$

Yield: 85%; mp (°C): 145–147 (ethanol).
IR (KBr, cm^{-1}) = 1680(m), 1670(m), 1597(m), 1499(m).
Elemental analysis (%); Theory: C, 66.49; H, 3.80; N, 17.62; Found: C, 66.45; H, 3.78; N, 17.61.

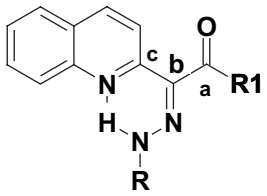
^{1}H NMR δ (ppm): 7.02 (1H, dd, CH); 7.06 (1H, dd, CH); 7.27 (1H, d, CH); 7.35 (1H, dd, CH); 7.48 (2H, d, 2 × CH); 7.75 (3H, d, 3 × CH); 8.01 (3H, d, 3 × CH); 8.13 (2H, dd, 2 × CH); 8.56 (2H, d, 2 × CH); 16.07 (1H, s, NH).

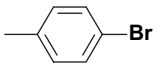
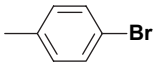
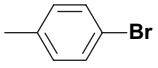
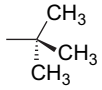
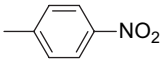
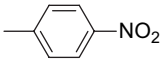
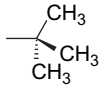
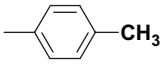
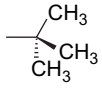
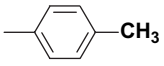
*3.5. Ethyl (3E)-3-[(4-nitrophenyl)hydrazono]-2-oxo-3-quinoline-2-yel poropanoate (**3e**)*

$C_{20}H_{16}N_4O_5$

Yield: 99.9%; mp (°C): 120–123 (ethanol).
FDMS: m/z (%) = 392.3, 319, 155, 128.

Table 3
^{13}C, chemical shifts of products in $CDCl_3$ at 298 K



3	R	R_1	a	b	c	R_1(Aliphatic)
a		$-CO_2Et$	166.72	151.97	144.82	186.78, 61.61, 14.45
b			192.43	152.62	148.41	—
c			207.21	152.38	148.73	44.69, 28.14
f			191.91	152.21	148.63	—
g			206.17	152.68	149.29	44.63, 27.05
h			206.88	150.95	146.62	44.66, 27.97
i			190.97	156.57	149.82	—

IR (KBr, cm^{-1}) = 1736(w), 1683(m), 1620(m), 1600(m), 1580(m).

Elemental analysis (%); Theory: C, 61.22; H, 4.11; N, 14.28; Found: C, 61.23; H, 4.09; N, 14.26.

^1H NMR δ (ppm): 1.41 (3H, t, $J = 7.0$ Hz, CH_3); 4.35 (2H, q, $J = 7.0$ Hz, CH_2); 7.02 (2H, d, $J = 8.5$ Hz, $2 \times$ CH); 7.65 (1H, d, CH); 7.69 (2H, d, $J = 8.5$ Hz, $2 \times$ CH); 7.84 (1H, dd, $J = 7.0$, 8.0 Hz, CH); 7.88 (1H, d, CH), 8.02 (1H, d, $J = 8.5$ Hz, CH); 8.33 (1H, d, $J = 9.0$ Hz, CH); 8.66 (1H, dd, CH), 16.84 (1H, s, NH).

*3.6. (2E)-1-phenyl-2-quinoline-3-yel ethanone-1,2-dione 2-[(4-nitrophenyl)hydrazone] (**3f**)*

$C_{23}H_{16}N_4O_3$

Yield: 99%; mp (°C): 143–145 (ethanol).

FDMS: m/z (%) = 397, 246, 217, 155, 128, 105, 77.

IR (KBr, cm^{-1}) = 1650(m), 1625(m), 1600(m), 1525(m).

Elemental analysis (%); Theory: C, 69.69; H, 4.07; N, 14.13; Found: C, 69.72; H, 4.06; N, 14.11.

^1H NMR δ (ppm): 7.35 (2H, d, $J = 6.5$ Hz, $2 \times$ CH); 7.45 (2H, dd, $J = 7.0$, 7.0 Hz, $2 \times$ CH); 7.46 (2H, dd, $J = 7.5$, 7.0 Hz, $2 \times$ CH); 7.48 (1H, d, $J = 8.0$ Hz, CH); 7.63 (1H, dd, $J = 7.5$, 8.0 Hz, CH); 7.64 (1H, d, $J = 7.0$ Hz, CH), 7.71 (1H, d, $J = 8.0$ Hz, CH); 7.84 (2H, d, $J = 5.5$ Hz, $2 \times$ CH); 7.93 (2H, d, $J = 7.5$ Hz, $2 \times$ CH); 8.05 (1H, d, $J = 8.0$ Hz, CH); 16.44 (1H, s, NH).

^{13}C NMR δ (ppm): 116.58 (2CH), 119.99 (CH), 121.50 (2CH), 127.11 (C), 127.17 (CH), 127.33 (2CH), 129.45 (CH), 129.70 (CH), 129.79 (CH), 129.91 (2CH), 131.69 (CH), 134.06 (C), 136.25 (CH), 143.82 (C), 144.83 (C), 148.36 (C), 148.63 (C), 152.21 (C), 191.91 (C).

*3.7. (1E)-3,3-dimethyl-1-quinoline-3-yel buthane-1,2-dione-1-[(4-nitrophenyl)hydrazone] (**3g**)*

$C_{21}H_{20}N_4O_3$

Yield: 91%; mp (°C): 126–124 (ethanol).

FDMS: m/z (%) = 376(M^+), 359, 239, 155, 128, 57, 41.

IR (KBr, cm^{-1}) = 1676(w), 1624(m), 1560(m), 1505(m).

Elemental analysis (%); Theory: C, 67.09; H, 5.34; N, 14.85; Found: C, 67.07; H, 5.37, N; 14.83.

UV (CH_2Cl_2) λ_{max}: 384, 365, 262.

^1H NMR δ (ppm): 1.54 (9H, s, CH_3); 7.49 (1H, dd, $J = 7.5$, 7.5 Hz, CH); 7.58 (1H, dd, $J = 8.5$, 6.0 Hz, CH); 7.65 (1H, d, $J = 8.5$ Hz, CH); 7.72 (2H, d, $2 \times$ CH); 7.78 (1H, d, $J = 7.5$ Hz, CH); 7.81 (1H, d, CH); 8.05 (2H, d, $J = 8.0$ Hz, $2 \times$ CH); 8.15 (1H, d, $J = 8.5$ Hz, CH); 15.90 (1H, s, NH).

^{13}C NMR δ (ppm): 27.05 ($3CH_3$), 44.63 (C), 119.86 (2CH), 122.09 (CH), 126.92 (C), 127.54 (2CH), 127.61 (CH), 128.22 (CH), 130.20 (CH), 130.24 (CH), 135.66 (C), 136.53 (CH), 144.64 (C), 145.39 (C), 149.29 (C), 152.68 (C), 206.17 (C).

*3.8. (1E)-3,3-dimethyl-1-quinoline-3-yel buthane-1,2-dione-1-[(4-methylphenyl)hydrazone] (**3h**)*

$C_{22}H_{23}N_3O$

Yield: 63%; mp (°C): 107–105 (ethanol).

FDMS: m/z (%) = 345(M^+), 208, 155, 128, 57, 41.

IR (KBr, cm^{-1}) = 1663(w), 1610(m), 1530(m), 1500(m).

Elemental analysis (%); Theory: C, 67.49; H, 6.71; N, 12.16; Found: C, 67.46; H, 6.71; N, 12.14.

^1H NMR δ (ppm): 1.52 (9H, s, CH_3); 7.01 (1H, dd, $J = 7.5$, 8.0 Hz, CH); 7.49 (2H, d, $J = 8.5$ Hz, $2 \times$ CH); 7.64 (1H, dd, $J = 7.5$, 8.7 Hz, CH); 7.80 (1H, d, CH); 8.06 (1H, d, $J = 8.0$ Hz, CH); 8.20 (2H, d, $J = 8.7$ Hz, $2 \times$ CH); 8.25 (1H, d, $J = 8.3$ Hz, CH); 8.66 (1H, d, $J = 8.3$ Hz, CH); 15.46 (1H, s, NH).

^{13}C NMR δ (ppm): 27.97 ($3CH_3$), 44.66 (C), 120.53 (2CH), 121.62 (CH), 126.02 (2CH), 127.16 (C), 127.21 (CH), 129.37 (CH), 130.52 (CH), 133.68 (C), 135.77 (CH), 136.65 (CH), 140.00 (C), 140.92 (C), 146.62 (C), 150.95 (C), 206.88 (C).

*3.9. (2E)-1-phenyl-2-quinoline-3-yel ethanone-1,2-dione 2-[(4-methylphenyl)hydrazone] (**3i**)*

$C_{24}H_{19}N_3O$

Yield: 68%; mp (°C): 88–90 (ethanol).

FDMS: m/z (%) = 366, 246, 217, 155, 128, 105, 77.

IR (KBr, cm^{-1}) = 1675(m), 1615(m), 1680(m), 1550(m).

Elemental analysis (%); Theory: C, 78.88; H, 5.24; N, 11.50; Found: C, 78.89; H, 5.26; N, 11.47.

^1H NMR δ (ppm): 7.27 (2H, d, $J = 6.5$ Hz, $2 \times$ CH); 7.35 (2H, dd, $J = 6.0$, 7.0 Hz, $2 \times$ CH); 7.47 (2H, dd, $J = 7.0$, 7.0 Hz, $2 \times$ CH); 7.59 (1H, dd, $J = 7.5$, 7.0 Hz, CH); 7.71 (1H, d, $J = 8.5$ Hz, CH); 7.79 (2H, d, $J = 6.5$, 7.0 Hz, $2 \times$ CH), 7.90 (1H, d, $J = 6.0$ Hz, CH); 7.92 (1H, d, CH); 7.97 (2H, d, $J = 7.5$ Hz, $2 \times$ CH); 8.15 (1H, d, $J = 8.5$ Hz, CH), 15.80 (1H, s, NH).

^{13}C NMR δ (ppm): 120.17 (2CH), 120.56 (CH), 122.08 (2CH), 124.41 (C), 126.64 (CH), 126.74 (CH), 126.82 (CH), 126.91 (2CH), 128.12 (CH), 128.16 (2CH), 129.13 (CH), 129.95 (CH), 131.26 (C), 131.50 (C), 134.70 (C), 145.00 (C), 149.82 (C), 156.57 (C), 190.97 (C).

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