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$[Et_3NH][HSO_4]$-Catalyzed Efficient, Eco-Friendly, and Sustainable Synthesis of Quinoline Derivatives via Knoevenagel Condensation

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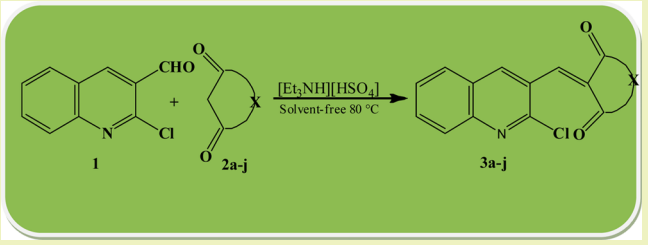
ABSTRACT: An efficient, eco-friendly, and sustainable protocol was described for the synthesis of new quinolinyl alkenes via Knoevenagel condensation of 2-chloro-3-formyl-quinoline with different active methylene compounds using $[Et_3NH][HSO_4]$ as a catalyst and an environmentally benign solvent eliminating the need for a volatile organic solvent and additional catalyst. This ionic liquid is air and water stable and easy to prepare from amine and acid. Structures of the newly synthesized compounds had been elucidated on the basis of elemental analysis and spectral data (IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry).The ionic liquid was also characterized by ^{1}H NMR and ^{13}C NMR. The present methodology is a green protocol as it eliminates the need for a volatile organic solvent and additional catalyst and offers several advantages such as shorter reaction time, excellent yield of products, mild reaction conditions, simple operational procedure, and recyclablility up to seven cycles without any appreciable loss in catalytic activity.



KEYWORDS: *$[Et_3NH][HSO_4]$, Acidic Brönsted ionic liquid, Knoevenagel condensation, 2-Chloro-3-formylquinoline, Quinolinyl alkenes*

INTRODUCTION

In recent years, ionic liquids have been the subject of considerable interest in the context of green synthesis because of their adjustable physical and chemical properties.[1] They have been introduced as alternative green reaction media due to their unique chemical and physical properties such as low vapor pressure, high thermal and chemical stability, good solvating ability, ease of recyclability, and controlled miscibility.[2−8] Ionic liquids also have various applications such as sensors,[9] fuel cells,[10] batteries,[11] capacitors,[12] thermal fluids,[13] plasticizers,[14] lubricants,[15] extractants,[16,17]and solvents in synthesis and catalysis.[18−22] Furthermore, after the first industrial process involving ionic liquids by BASF (BASIL10 process) in 2003,[23] the potential of ionic liquids for new chemical processes is being recognized. Therefore, there is a need for exploring the cheap and easily available ionic liquids in organic synthesis. In this regard, acidic Brönsted ionic liquid $[Et_3NH][HSO_4]$ would be a good candidate as it is prepared via a simple and atom economic acid−base neutralization reaction from cheap amine and acid.[24] Moreover, acidic Brönsted ionic liquids (ABILs) are of special importance because they possess simultaneously the proton acidity and the characteristic properties of an ionic liquid.[25] Acidic Brönsted or Lewis ionic liquids, offer environmentally friendly catalyst properties due to the combination of the advantages of liquid acids and solid acids, such as uniform acid sites, stability in water and air, easy separation, and reusability. This ionic liquid has been proved to be a very excellent catalyst as well as solvent for many organic transformations.[26−37]

It is pertinent to mention that Knoevenagel reaction is a facile and versatile method for the formation of carbon−carbon bonds,[38] with numerous applications in the synthesis of intermediates of fine chemicals,[39] hetero-Diels−Alder reactions,[40] and in the synthesis of carbocyclic as well as heterocyclic compounds of biological significance.[41] The reaction has been utilized in the preparation of coumarin derivatives,[42] cosmetics,[43] perfumes,[44] and pharmaceutical chemicals.[45] A variety of ionic liquids have been employed for this condensation reaction such as [C6-mim]PF_6,[46] [bmim]Cl·x$AlCl_3$ and [bpy]Cl·x$AlCl_3$,[47] [Bmim]BF_4,[48] guanidinium lactate ionic liquid,[49] ethylammonium nitrate (EAN),[50] [bmIm]OH,[51] glycine in ionic acid,[52] HMTA−AcOH,[53] [C4-choline][Ac],[54] ethylenediammonium diacetate,[55] 2-hydroxyethylammonium formate,[56,57] 2-HEAA,[58] etc.

However, $[Et_3NH][HSO_4]$ has not been explored yet for Knoevenagel condensation. Therefore, in continuation of our work on the development of novel synthetic methodologies for organic transformations,[59,60] we employed $[Et_3NH][HSO_4]$ as an acidic Brönsted ionic liquid as a green, efficient, and recyclable catalyst as well as a solvent for the synthesis of quinoline derivatives.

Quinolines and their derivatives represent a major class of heterocycles and are widely found in natural products.[61,62] The quinoline ring is endowed with various activities, such as antimicrobial,[63] antituberculosis,[64] antimalarial,[65] anti-inflammatory,[66] anticancer,[67] antibiotic,[68] antihypertensive,[69] tyro kinase PDGF-RTK inhibiting agents,[70] antiHIV,[71] and anticonvulsant.[72] Among the various activities of their

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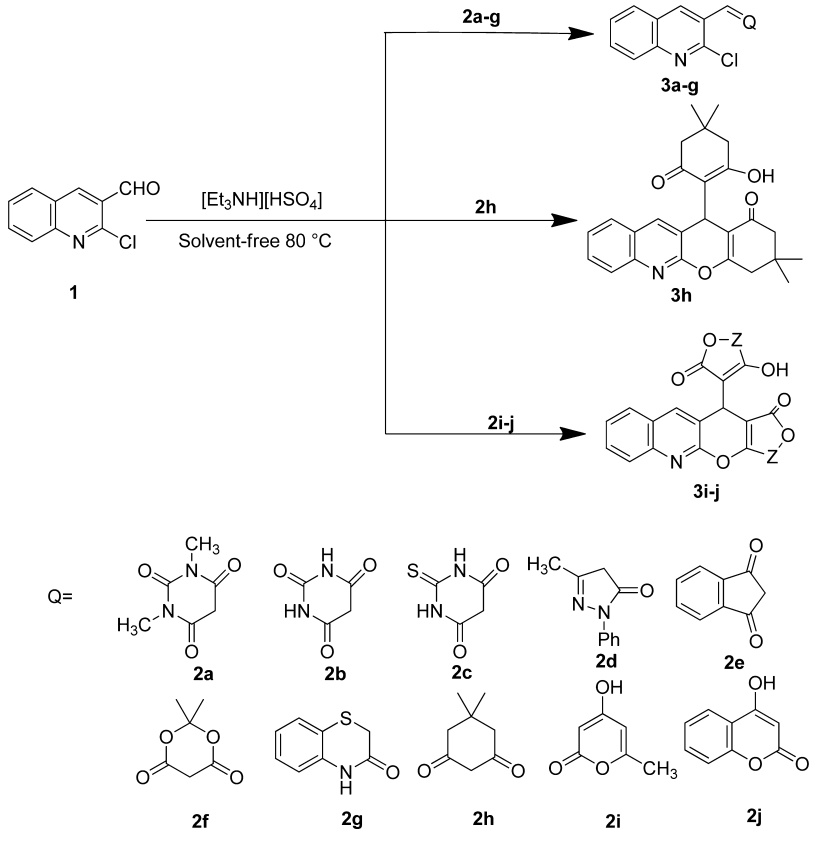
Table 1. Optimization of Reaction Conditions for Synthesis of the Quinoline Derivative Catalyzed by $[Et_3NH][HSO_4]$[a]

entry	solvent	temperature (°C)	time (min)[b]	catalysts (mol %)	yield (%)[c]
1	MeOH	reflux	6h	20	70
2	EtOH	reflux	7h	20	69
3	$(CH_3)_2CHOH$	reflux	14h	20	57
4	H_2O	reflux	3h	20	Trace
5	CH_3CN	reflux	7h	20	41
6	THF	reflux	9h	20	trace
7	$C_6H_5CH_3$	reflux	15h	20	Trace
8	solvent-free	room temperature	1.5h	20	42
9	solvent-free	40	45	20	51
10	solvent-free	60	20	20	74
11	solvent-free	80	5	20	99
12	solvent-free	100	5	20	99
13	solvent-free	110	5	20	97
14	solvent-free	80	24h	no catalyst	20
15	solvent-free	80	10	5	90
16	solvent-free	80	8	10	92
17	solvent-free	80	5	15	97
18	solvent-free	80	5	20	99
19	solvent-free	80	5	25	99

[a]Model reaction: 1 mmol of 3-chloro-3-formylquinoline and 1 mmol of 1,3-dimethylbarbituric acid. [b]Reaction progress monitored by TLC. [c]Isolated yield.

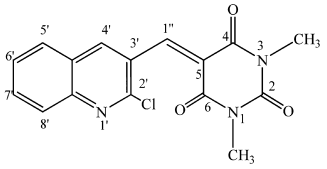
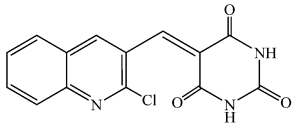
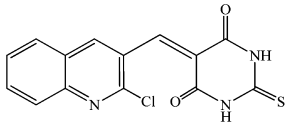
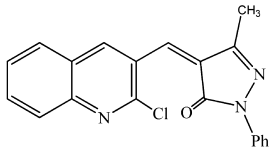
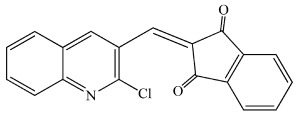
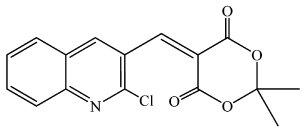
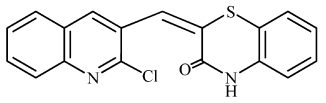
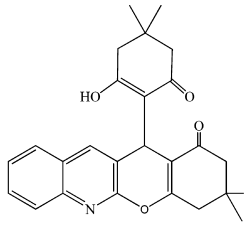
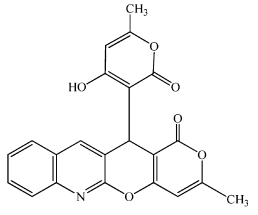
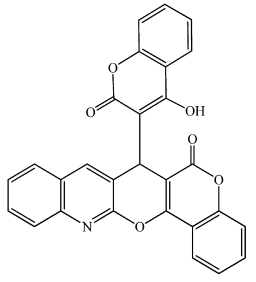
Scheme 1. Synthesis of Quinoline Derivatives



derivatives, antimicrobial and antimalarial activity is noteworthy.

Keeping in mind the biological properties of quinolines and our continued interest in green synthesis, we report herein the synthesis of quinolinyl alkenes through Knoevenagel condensation using $[Et_3NH][HSO_4]$ as an eco-friendly solvent and as a highly efficient catalyst. To the best of our knowledge, there seems to be no report on the synthesis of quinolinyl derivatives via Knoevenagel condensation in an $[Et_3NH]$-$[HSO_4]$ ionic liquid as an eco-friendly solvent as well as catalyst.

Table 2. $[Et_3NH][HSO_4]$-Catalyzed Synthesis of Quinolinyl Alkene 3a−j

Entry	Product	Time (min)[a]	Yield (%)[b]	M.P (°C)
3a.		5	99	280
3b.		6	95	>300
3c.		6	95	>300
3d.		7	96	171-180
3e.		5	91	>300
3f.		6	90	207-215
3g.		8	95	>300
3h.		7	91	>300
3i.		9	90	>300
3j.		10	90	>300

[a]Reaction progress monitored by TLC. [b]Isolated yield.

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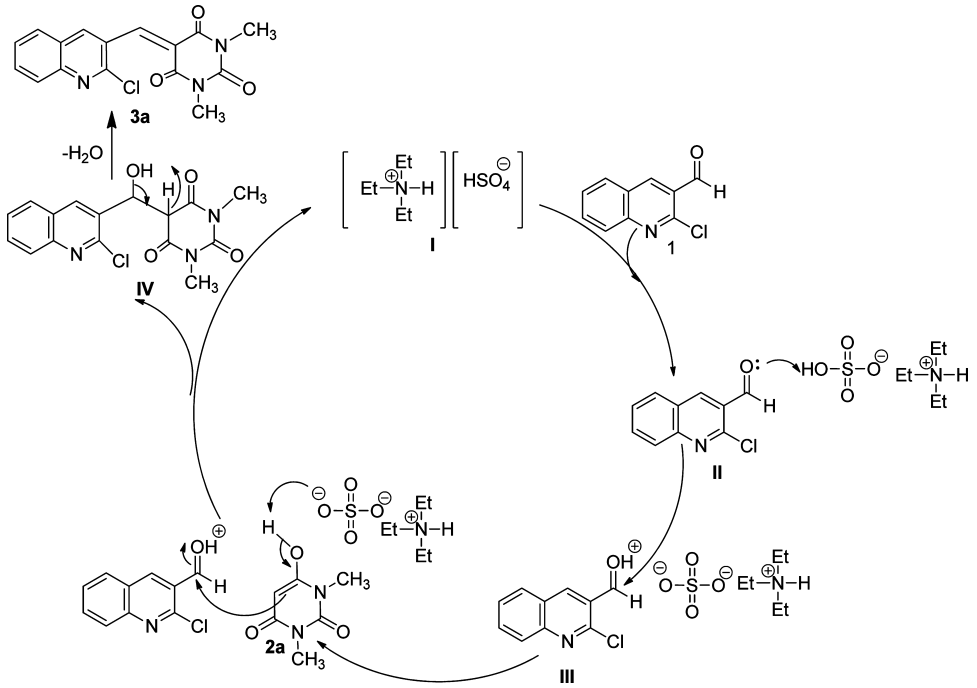
Scheme 2. Probable Mechanism for the Synthesis of Quinolinyl Alkene (3a) via Knoevenagel Condensation of 2-Chloro-3-formylquinoline (1) and Active Methylene Compound (2a) Catalyzed by $[Et_3NH][HSO_4]$



RESULTS AND DISCUSSION

In our preliminary experiments, we investigated the optimum reaction conditions regarding the solvent, amount of catalyst, and temperature of reaction. For this purpose, 2-chloro-3-formylquinoline **1** and 1,3-dimethylbarbituric acid **2a** were chosen as model substrates for the synthesis of representative compound **3a**. First, we performed the reaction using model substrates and 20 mol % of $[Et_3NH][HSO_4]$ as catalyst in different solvents (Table1) under reflux condition. In MeOH, EtOH, and $(CH_3)_2CHOH$ (Table 1, entries 1, 2 and 3), the reaction took a longer time (6−14 h) with moderate yield of the products, whereas in water (Table1, entry 4), the product was obtained in trace amount only after 3 h. In CH_3CN (Table 1, entry 5), a lower yield of the product was obtained with a long reaction time. Conducting the reaction in THF and $C_6H_5CH_3$ (Table1, entries 6, 7), again only a trace amount of the product was obtained. However, when the model reaction was carried out under a solvent-free condition, there was significant increase in the yield of the product in a shorter time period. Thus, it is concluded that solvent-free is the best condition for this Knoevenagel condensation. To get an optimum temperature, the model reaction was carried out at different temperatures (Table1, entries 8, 9, 10, 11, 12, 13). The yield of the product increased when the reaction temperature was raised from room temperature to 80 °C. However, no increase in the yield of product **3a** was observed when the reaction temperature was raised from 80 to 100 °C. Therefore, all further reactions were carried out at 80 °C.

To get the optimum concentration of catalyst, the model reaction was investigated at 5, 10, 15, 20, and 25 mol % (Table1, entries 15, 16, 17, 18, 19) of $[Et_3NH][HSO_4]$ at 80 °C under solvent-free conditions. The product was obtained in 90%, 92%, 97%, 99%, and 99% yield, respectively. Thus, it is concluded that 20 mol % of $[Et_3NH][HSO_4]$ is sufficient for the best result. Therefore, all reactions were carried out at 80 °C in the presence of 20 mol % of $[Et_3NH][HSO_4]$ under solvent-free conditions.

Using these optimized reaction conditions, the scope and efficiency of this approach were explored for the synthesis of other quinoline derivatives Scheme 1, and the obtained results are summarized in Table 2.

It was observed that due to higher reactivity of lactones (**2i−j**) and dimedone (**2h**) the reaction did not stop at the Knoevenagel condensation stage and proceeded further for Michael addition with another molecule of **2h−j** to the double bond of the initially formed Knoevenagel intermediates followed by cyclization to give the products (**3h−j**) as reported earlier.[73]

A plausible mechanism for the synthesis of quinoline derivatives via Knoevenagel condensation catalyzed by $[Et_3NH][HSO_4]$ is shown in Scheme 2. As $[Et_3NH][HSO_4]$ is a protic ionic liquid, initially aldehyde (**1**) was protonated to form intermediate III. It facilitated the nucleophilic attack of the active methylene compound (**2a**) for C−C bond formation. The final Knoevenagel product **3a** was formed by the elimination of a water molecule from IV and an ionic liquid I regenerated.

The reusability of the catalyst is a significant advantage particularly for commercial applications. Thus, the recovery and reusability of $[Et_3NH][HSO_4]$ were also investigated (Table 3). After the completion of the reaction, cold water was added to the reaction mixture, and the products were isolated by filtration. The ionic liquid was recovered by removing the water under reduced pressure and was reused at least seven times without any appreciable decrease in yield.

To show the superiority of $[Et_3NH][HSO_4]$, the model reaction was also carried out in the presence of other acidic Brönsted ionic liquids (Table 4). The catalytic activity of the ionic liquid with the HSO_4^- anion (Table 4 entry 1) was higher than the other two (Table 4, entries 2, 3). This is primarily due to higher acidity of the former as compared to the other two.

Table 3. Reusability of Catalyst for Model Reaction

entry	run	time[a] (min)	yield[b] (%)
1	1	5	99
2	2	5	99
3	3	5	99
4	4	5	99
5	5	5	98
6	6	5	97
7	7	5	95

[a]Reaction progress monitored by TLC. [b]Isolated yield.

Table 4. Comparison of Efficiency of $[Et_3NH][HSO_4]$ for Synthesis of 3a[a]

entry	catalyst	time[b] (min)	yield[c] (%)
1	$[Et_3NH][HSO_4]$	5	99
2	$[Et_3NH][H_2PO_4]$	9	97
3	$[Et_3NH][CH_3COO]$	12	86
4	$[Me_3NH][HSO_4]$	8	96
5	$[Me_3NH][H_2PO_4]$	13	91
6	$[Me_3NH][CH_3COO]$	16	81

[a]Reaction conditions: 3-chloro-3-formylquinoline (1 mmol), 1,3-dimethylbarbituric acid (1 mmol), ionic liquids (20 mol %), solvent-free at 80 °C. [b]Reaction progress monitored by TLC. [c]Isolated yield.

When the $[Me_3NH][HSO_4]$ ionic liquid was used (Table 4, entry 4), the yield of the reaction decreased as compared to $[Et_3NH][HSO_4]$. The efficiency of $[Et_3NH][HSO_4]$ was also compared with other ionic liquids reported earlier for Knoevenagel condensation. The data summarized in Table 5 showed the advantages of this method in terms of reaction rate and yield as compared with those reported in the literature. Additionally, the present catalyst is more beneficial from the economical and accessibility point of view and is stable both in air and water.

EXPERIMENTAL SECTION

Melting points were taken in Riechert Thermover instrument and are uncorrected. The IR spectra were recorded on a Perkin-Elmer RXI spectrometer in KBr, ^{1}HNMR on Bruker DRX-300, and Bruker Avance II 400 spectrometer using tetramethyl silane (TMS) as the internal standard and DMSO-d_6/$CDCl_3$ as solvent. ESI-MS were recorded on a Quattro II (ESI) spectrometer. The microanalytical data were collected on Elementar vario EL III elemental analyzer. The purity of all compounds was checked by TLC on glass plates coated with silica gel (E-Merck G254, 0.5 mm thickness). The plates were run in a chloroform−methanol (4:1) mixture and were visualized by iodine vapors. 3-Methyl-1-phenylpyrazole-5-one, barbituric acid, thiobarbituric acid, and 1,3-dimethylbarbituric acid were purchased from Sigma-Aldrich Chemicals Pvt., Ltd. Other chemicals were of commercial grade and used without further purification. 2-Chloro-3-formylquinoline was synthesized by using DMF/$POCl_3$ according to the reported method.[83]

Preparation of $[Et_3NH][HSO_4]$. Sulfuric acid (19.6 g, 0.2 mol) 98% solution in water was dropped into triethylamine (20.2 g, 0.2 mol) while stirring at 60 °C for 1 h. After the addition, the reaction mixture was stirred for another 1 h at 70 °C. Water was removed by heating the residue at 80 °C in high vacuum until the weight of the residue remained constant.

^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.27 (t, 9H), 3.10 (m, 6H), 8.60 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 100 MHz) δ 45.8, 8.4 ppm.

General Procedure for Synthesis of Quinolinyl Alkene Under Solvent-Free Conditions. To a mixture of 2-chloro-3-formylquinoline **1** (1.00 mmol) and active methylene compounds **2a−j** (1.00 mmol), 20 mol % $[Et_3NH][HSO_4]$ was added, and the mixture was heated on an oil bath at 80 °C with good stirring. During the reaction process, the mixture spontaneously solidified. After completion of the reaction (monitored by TLC), the reaction was cooled to room temperature, water was added, and the mixture was stirred for 5 min. The solid obtained was removed by filtration and recrystallized from methanol. Filtrate was dried under reduced pressure to recover ionic liquid, which was reused in subsequent cycles.

CONCLUSION

In conclusion, we have developed a simple, efficient, mild, and environmentally benign method for the synthesis of new quinolinyl alkenes. The green protocol offers advantages such as excellent yields of products, shorter reaction time period, simple operational procedure, easy preparation of catalyst from cheap amines, and reusability of the catalyst.

Spectroscopic Data of Compounds. *5(2-Chloroquinolin-3-yl)methylene-1,3-dimethyl-2,4,6-pyrimidinetrione (**3a**).* Yellow solid, mp: 280 °C. IR (KBr) (υ_{max}, cm^{-1}): 1693 (C═O), 1580 (C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.10 (1H, s), 8.54 (1H, s), 7.78 (1H, d, J = 9.5 Hz, arom. H), 7.65 (1H, m, arom. H), 7.35 (1H, d, J = 8.2 Hz, arom. H), 7.25 (1H, s, arom. H), 3.24 (3H, s, N−CH_3), 3.20 (3H, s, N−CH_3), ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 115.3, 118.3, 119.9, 122.6, 124.5, 149.4, 140.2, 129.9, 151.1, 145.5, 133.3, 162.0, 160.7, 161.6, 28.6, 28.1 ppm. ESI-MS: (m/z) 330 (M^+ + 1). Anal. Calcd. for $C_{16}H_{12}ClN_3O_3$; C 58.41, H, 3.67, N, 12.82. Found: C, 58.40, H, 3.51, N, 12.79.

*5-(2-Chloroquinolin-3-yl)methylene-2,4,6-pyrimidinetrione (**3b**).* White solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 3443 (N−H), 1716 (C═O), 1537 (C═C). ^{1}H NMR

Table 5. Comparison of Ionic Liquids Used as Catalysts for Knoevenagel Condensation[a]

entry	ionic liquids	time	yield (%)	ref
1	n-butylpyridinium nitrate	15 min	81	74
2	[emim][BF4]	12 h	97	75
3	[bmim] PF6	6 h	96	76
4	EAN	3 h	94	50
5	[DBU][Lac]	30 min	96	77
6	[bmIm]OH	10 min	93	51
7	[Hmim]Tfa	4 h	91	78
8	[2-aemim][PF6]	30 min	96	79
9	[bnmim]Cl	20 min	93	80
10	$[^iPr_2N(CH_2)_2(OCH_2CH_2)_2\text{-}N_{112}][NTf_2]$	20 min	91	81
11	BIL	30 min	100[b]	82

[a]Reported reactions. [b]% conversion.

(DMSO-d_6, 400 MHz) δ: 8.25 (1H, s), 8.11(1H, s), 7.96 (3H, m, arom. H), 7.55 (1H, s, arom. H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 115.2, 118.3, 119.6, 122.4, 124.4, 129.8, 150.9, 140.23, 149.67, 145.5, 132.9, 161.8, 161.0, 160.5 ppm. ESI-MS: (m/z) 302 (M^+ + 1). Anal. Calcd. for $C_{14}H_8ClN_3O_3$; C 55.86, H, 2.67, N, 14.01. Found: C, 55.90, H, 2.71, N, 14.23.

*5-(2-Chloroquinolin-3-yl)methylene-2-mercapto-4,6-pyrimidinedione (**3c**).* Yellow solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 3443 (N−H), 1716 (C═O), 1537 (C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.80 (s, 1H), 8.22 (s, 1H), 7.84 (d, J = 7.2 Hz, 1H, arom. H), 7.38 (m, 1H, arom. H), 7.31 (m, 1H, arom. H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 127.1, 127.3, 127.4, 127.7, 127.9, 128.1, 129.4, 129.9, 149.8, 140.9, 133.4, 163.2, 188.8 ppm. ESI-MS: (m/z) 318 (M^+ + 1). Anal. Calcd. for $C_{14}H_8ClN_3O_2S$; C 53.04, H, 2.54, N, 13.31. Found: C, 53.09, H, 2.61, N, 13.35

*2-(2-Cholroquinoli-3-yl)methylene-3-methyl-1-phenylpyrazol-5-one (**3d**).* White solid, mp: 171−180 °C. IR (KBr) (υ_{max}, cm^{-1}): 1692 (C═O), 1545 (C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.28 (1H, s), 7.75−7.71 (5H, m), 7.56−7.52 (1H, m), 7.41−7.33 (2H, m), 7.32−7.21 (1H, m), 7.17 (1H, s), 2.36 (3H, s) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 20.2, 111.5, 114.6, 119.3, 121.2, 124.7, 126.8, 127.1, 129.1, 131.8, 138.3, 139.0, 144.5, 159.3, 160.9, 164.1 ppm. ESI-MS: (m/z) 348 (M^+ + 1). Anal. Calcd. for $C_{20}H_{14}ClN_3O$; C, 69.22, H, 4.06, N, 12.16. Found: C, 69.50, H, 4.09, N, 12.20.

*2-(2-Chloroquinolin-3-yl)methylene-1,3-indanedione (**3e**).* Yellow solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 1692(C═O), 1545(C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.80 (1H, s), 8.59 (1H, s), 8.32 (1H, Harom.), 8.04 (3H, m, Harom.), 7.86 (1H, m, Harom.), 7.70 (1H, m, Harom.), 7.38 (d, J = 8.1, 1H, Harom.), 7.31 (1H, m) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 120.6, 123.7, 124.7, 125.3, 125.3, 126.0, 127.3, 128.5, 135.7, 137.0, 144.5, 145.9, 153.9, 155.8, 159.3, 189.12 ppm. ESI-MS: (m/z) 320(M^+ + 1). Anal. Calcd. for $C_{19}H_{10}ClNO_2$; C, 71.53, H, 3.15, N, 4.40. Found: C, 71.49, H, 3.19, N, 4.38.

*5-(2-Chloroquinolin-3-yl)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**3f**).* Yellow solid, mp: 201−215 °C. IR (KBr) (υ_{max}, cm^{-1}): 1692 (C═O), 1545 (C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.99 (1H, s), 8.42 (1H, m), 7.97 (1H, s), 7.71 (1H, m), 7.43 (2H, m) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 35.8, 30.7, 112.9, 115.8, 116.3, 122.7, 123.5, 124.5, 131.8, 132.6, 152.0, 152.3, 159.6, 161.1, 161.9 ppm. ESI-MS: (m/z) 318 (M^+ + 1). Anal. Calcd. for $C_{16}H_{12}ClNO_4$; C 62.19, H, 3.58, N, 13.65.Found: C, 62.31, H, 3.62, N, 13.31.

*2-(Chloroquinolin-3-yl)methylene-2H-benzothiazin-3(4H)-one (**3g**).* Yellow solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 3388 (N−H), 1631 (C═O), 1516 (C═C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.79 (s,1H), 8.60 (s,1H), 8.08 (m, 1H), 7.98 (1H, d, J = 8.3 Hz, Harom.), 7.82 (1H, m, Harom.), 7.67 (2H, m, Harom.), 7.52 (1H, d, J = 8.0 Hz, Harom.), 7.28 (1H, m, Harom.), 7.10 (1H, m, Harom.) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 115.5, 117.1, 118.1, 118.9, 122.5, 122.6, 125.5, 126.7, 127.1, 130.6, 133.3, 137.3, 141.2, 155.6, 158.9, 161.5, 164 ppm. ESI-MS: (m/z) 339 (M^+ + 1). Anal. Calcd. for $C_{18}H_{11}ClN_2OS$; C 63.96, H, 3.27, N, 8.32. Found: C, 63.79, H, 3.23, N, 8.28.

*6-(1-hydroxy-5,5-dimethyl-3-oxocyclohex-1-en-2-yl)-9,9-dimethyl-7,8,9,10-tetrahydro-1H-chromeno[2,3-b]quinolin-7-one (**3h**).* White solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 1664(C═O). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 11.30(1H, s), 7.78 (1H,s), 7.57 (1H, d, J = 8.0 Hz, Harom.), 7.37 (1H, t, J = 8.0 Hz, Harom.), 7.25 (1H, d, J = 8.0 Hz, Harom), 7.11 (1H, m, Harom.), 4.62 (1H, s), 2.44 (4H, d, J = 17.5 Hz), 2.24 (2H, d, J = 16.2 Hz), 2.10 (2H, d, J = 16.2 Hz) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 196.3, 164.1, 160.9, 139.0, 138.3, 131.9, 129.1, 127.4, 121.3, 119.3, 114.6, 111.5, 50.6, 31.8, 30.4, 29.1, 26.6 ppm. ESI-MS: (m/z) 418 (M^+ + 1). Anal. Calcd. for $C_{26}H_{27}NO_4$; C 74.80, H, 6.52, N, 3.35. Found: C, 74.82, H, 6.49, N, 3.38.

*6-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)quinolino-[2,3:5,6]-6H-pyrano[2,3-c]-8-methylpyran-7-one (**3i**).* Light yellow solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 1664 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 11.40 (1H, s), 7.91 (1H,s), 7.63 (1H, m), 7.41 (1H, m), 7.30 (1H, m), 7.16 (1H, m), 6.18 (2H, s), 4.62 (1H, s), 2.24 (6H, s) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 19.3, 19.1, 32.4, 99.4, 100.7, 101.0, 122.5, 124.9, 126.6, 127.1, 127.7, 128.0, 138.9, 148.0, 148.9, 159.8, 160.5, 161.4, 161.6, 164.7, 166.1, 188.6, 189.0 ppm. ESI-MS: (m/z) 412 (M^+ + 23). Anal. Calcd. for $C_{22}H_{15}NO_6$; C 67.92, H, 3.88, N, 3.61. Found: C, 67.91, H, 3.80, N, 3.59.

*6-(4-hydroxy-2-oxo-2H-chromeno-3-yl)quinolino[2,3:5,6]-6H-pyrano[2,3-c]-1-benzopyran-7-one (**3j**).* White solid, mp: >300 °C. IR (KBr) (υ_{max}, cm^{-1}): 3308 (OH), 1721 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 11.41(1H. s), 8.6(1H, s), 8.25(2H, m), 8.02(2H, m), 7.82(1H, m), 7.73(2H, m), 7.60(1H, m), 7.52(4H, m), 5.94(1H,s)ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 113.0, 114.8, 116.5, 118.9, 121.7, 123.1, 124.7, 128.0, 130.0, 132.9, 138.5, 140.6, 152.0, 154.6, 33.2, 102, 159.7, 99.4, 160.4 ppm. ESI-MS: (m/z) 484 (M^+ + 23). Anal. Calcd. for $C_{28}H_{15}NO_6$; C 72.95, H, 3.27, N, 3.05. Found: C, 72.96, H, 3.22, N, 3.08.

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Notes

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