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ARTICLE TYPE

Water mediated reactions: TiO_2 and ZnO Nanoparticles catalyzed Multi component domino reaction in the synthesis of tetrahydroacridinediones, acridindiones, xanthenones and xanthenes

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The eco-accomodating TiO_2 nanorods in the four component Domino reaction for the framing of 9-(2-oxo-1,2-dihydroquinolin-3-yl)-10-phenyl-3,4,6,7-tetrahydroacridine-1,8 (2*H,*5*H,*9*H,*10*H*)-diones, **4** from 1,3-cyclohexanedione or/and dimedone, **1** 2-chloro-3-formylquinoline, **2** and anilines, **3** in water at 90 °C is accounted for. The present methodology offers domino reaction strategy, high yield, simple operations, recyclable and being eco-friendly. In like manner, a productive, highly chemo selective ZnO catalyzed, water mediated, microwave aided synthesis of functionalized xanthenes and xanthenones, **7** acridinediones, **8** in excellent yields is reported through environmentally benevolent strategy.

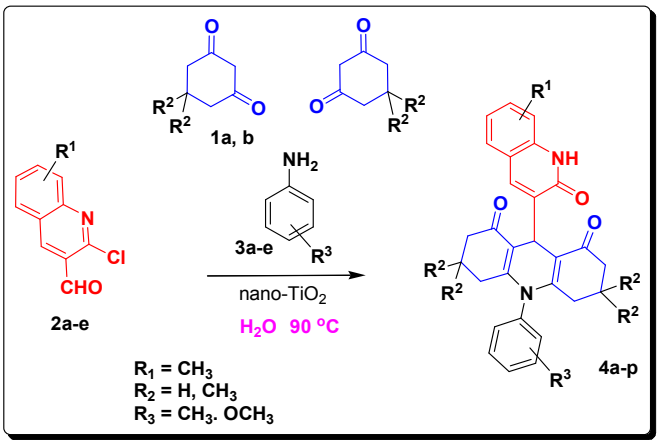
Introduction

The 1,8-acridinediones and their derivatives are adaptable intermediates with potential pharmaceutical action against cardiovascular ailment, hypertension, Alzheimer's infection, tumor, cancer and are utilized as laser, fluorescent dyes, photo-sensitizers with photo physical and electrochemical properties.[1-10] Many strategies have been developed including catalytic systems, for instance, ceric ammonium nitrate,[11,12] microwave irradiation,[13] $Zn(OAc)_2{\cdot}7H_2O$,[14] $CeCl_3{\cdot}7H_2O$,[15] silica bonded s-sulfonic acid,[16] sovent free methanesulfonic acid catalysed,[17,18] In(OTf) [19] p-dodecylbenzenesulfonic acid in aq medium,[20,21] ionic liquids- 1-n-butyl-3-methylimidazolium bromide ([bmim]Br),[22,23] Amberlyst-15,[24,25] ammonium chloride,[26,] P_2O_5[28,] $[B(C_6F_5)_3]$,[29] L-proline [30] along these lines on[31-39]. All the techniques delineated above, incorporated the synthesis of symmetrical acridinediones and simply few report is known on unsymmetrical acridinediones[40-42] and they experience from one or distinctive downsides including low yield, longer reaction time, time, multistep methodology, side products, perilous organic solvents and extravagant catalysts, troublesome in recuperation and reusability of the catalyst. Consequently, there is a need of gainful strategy which is pragmatic, cheap, faster, operationally straightforward and high yielding procedure. The titanium dioxide (TiO_2) of meso, micro, nano materials nature found to have remarkable electronic and optical properties[43-45], various endeavors has been made for their synthesis particularly due to their high surface area, uniform pore size which find enormous applications in photocatalysis[46], solar cells[47], lithium-ion batteries[48], sensors[49] and catalyst supports as well as in numerous fields[50]. In continuation of our research engages in synthetic strategies for the assorted biologically imperative motifs utilizing heterogeneous catalysts[51-72] utilized TiO_2 for the one-pot four component tandem-cascade reaction in the synthesis of acridine-1,8-dione under ambient conditions. As of late, we have demonstrated, a domino synthesis of 9-(quinolin-2(*1H*)-one)-xanthene-1,8(*5H,9H*)-dione derivatives in aqueous medium whilst, the present work exhibit the four component one pot reaction (**Scheme 1, 2**). The hydrolysis of the chloro functionality of the reactant to oxo functionality under the applied reaction conditions is well discussed in our previous work.

In the like way, the synthesis of xanthene and acridine derivatives pulled in chemists' enthusiasm due to their broad variety of biological and pharmaceutical properties, for instance, antiviral[73], antibacterial[74] and anti-inflammatory activities[75]. Further, these compounds have been utilized as dyes[76], in laser technology[77], pH-sensitive fluorescent materials for the visualization of biomolecular assemblies[78]. Basically, it is moreover noteworthy that dibenzoxanthenes derivatives have been utilized as sensitizers as a part of photodynamic therapy[79]. Acridine-1, 8-diones containing a 1, 4-dihydropyridine parent core has potential pharmacological action, for instance, against malaria80, cancer[81] and leishmania[82].

The synthesis of xanthenes and acridine derivatives has been enhanced in the presence of an acidic catalyst, for instance, sulfamic acid[83], Amberlyst-15[84], AcOH-H_2SO4[85], *p*-TSA[86] and silica sulfuric acid[87]. There are similar reports incorporating $TBAHSO_4$ in aqueous dioxane[88], wet cyanuric chloride[89], TiO_2–SO_4^{-2} [90], polyaniline p-toluenesulfonate[91], PPA–SiO_2[92], $NaHSO_4$–SiO_2[93], Fe^{+3}–montmorillonite[94], 1-methylimidazolium trifluoroacetate[95], quaternary ammonium alkyl sulfonate[96], polytungstozincate acid[97], cellulose-sulfuric acid[98], microwave irradiation[99,100], ionic liquid[101,102], LiBr, $ZrOCl_2.8H_2O$ [103], proline[104], silica-bonded *S*-sulfonic acid[105], cericammonium nitrate[106], methanesulfonic acid[107] and in aqueous media[108–110]. The majority of the reported procedures have downsides including low product yields, delayed reaction, lavish reagents or catalysts and usage of dangerous organic solvents. Henceforth, there is an exceptional interest for the advancement of an

environmentally benign technique in the synthesis of xanthenes and acridine derivatives. It must be noted that the aqua-mediated reactions have gotten much consideration on account of their environmental safety[111] and the usage of universal solvent, heterogeneous reusable catalysts is an influential green chemical approach ensuing negligible pollution and waste material which could have major industrial applications[112]. As of late, bulk zinc oxide has been employed as a heterogeneous catalyst for distinctive organic transformations[113] The late literature survey uncovers that nano ZnO[114] as a heterogeneous catalyst, has gotten impressive consideration because of its inexpensive, non-toxic nature and has environmental preferences i.e., minimum execution time, low corrosion, waste minimization, recycling of the catalyst, easy transport and disposal of the catalyst. Different ZnO nanostructures have been prepared including nanoflower, nanorods, nanowhiskers etc[115-125] through thermal treatment of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2-}$ precursor in aqueous solvent utilizing structure directing agents or through solvothermal processing[126-128]. Consequently, to our greatest advantage on heterocycles[51-62], is represented water intervened, eco-accommodating microwave irradiated, flower shaped ZnO catalyzed synthesis of xanthene and acridine derivatives (**Scheme 3, 4**).



Scheme 1 Synthesis of 9-(2-oxo-1,2-dihydroquinolin-3-yl) acridine-1,8-diones, **4**

Results and Discussion

In this paper, we concentrated on the application of TiO_2 nanorods in the synthesis of titled compounds (Scheme 1). The present methodology stresses the clean, safe, exceptional yield, shoddy strategy and the reusability of the heterogeneous catalysts. In this study, titania nanorods were successfully acquired by a sol–gel process, employing titanium (IV) tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$; TIP) precursor in ethanol. The as-procured mesoporous titania was calcined at 600 °C to give the thermally stable anatase crystallites. X-ray diffraction studies demonstrated the crystalline nature with peaks lying at 2θ = 25.28° (101), 2θ = 37.94° (004), 2θ = 47.82 ° (200), 2θ = 54.39° (105) and 2θ = 62.45 ° (204 and the diffraction information were in good concurrence with JCPDS files # 21-1272. Scanning electron microscopy exhibits the crystalline, anatase and titanium dioxide nanorods (TiO_2) morphology (**Figure 1**). The TEM images demonstrated the well crystalline TiO_2 NPs of size ranging from 10-20 nm (**Figure 2**).The XPS spectrum of Ti 2p shows doublet peaks corresponding to the binding energy of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ was at 464.9 eV and 458.9 eV, respectively. The peak of O 1s is centred at 530.8 eV, which is ascribed to O atoms bound to titanium (Ti^{4+}–O).The splitting data (spin–orbital doublet splitting) between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ core levels is 6.0 eV, indicating a normal state of Ti^{4+} in the anatase TiO_2.

Previously, the symmetrical acridindiones were obtained through one pot four component reactions comprising of arylaldehydes, anilines and diketones or by three component reaction involving the arylaldehyde, diketone and enamines. The above reactions included either catalyst-systems, or without solvent/catalyst. With this information in hand, the four component reaction of 2-chloro-3-formylquinolines, diketones, amines were endeavored to accomplish the unreported acridindiones through the TiO_2 nanorods (Scheme 1). At first, a mixture of 1,3-cyclohexanedione, **1a** 2-chloro-3-formylquinoline, **2a** and aniline**, (3a)** in the 2: 1: 1 molar ratio in ethanol was refluxed in the presence and without the various metal oxides including ZnO, SnO_2 CuO, NiO, TiO_2. Amongst the explored oxides, interestingly in TiO_2, the reaction offered the product, **4a** with a noteworthy yield of 50% (Scheme 1, Table 1 and entries 1-7). It ought to be noted that SnO_2, CuO and NiO neglects to offer the acridone-1,8-dione compound much after prolonged reaction time however gave the xanthenediones. The reaction product, **4a** was affirmed by an additional NH proton peak and N-C=O carbon peak respectively at δ 12.59 in proton and carbon NMR spectra, and by the IR and HRMS data. With this perception, to accomplish the streamlined conditions, variety of solvent, nano TiO_2 catalyst, catalyst loading was investigated. Fittingly, amongst the different tested solvents **(**Table 1and entries 8-12**),** water was found to be best, cheap and offered high yield of products. Correspondingly the nano TiO_2 catalyst with a loading of 1 mol % was the best improved condition (Table 1, entry 10) among the different catalyst loading of 1-10 mol % (Table 1, entry 10,11**).** The reusability of nano TiO_2 reveals that the catalyst is capable for the four sequential cycle runs without any noteworthy product loss. The reusable catalysts did not show any noteworthy change in its morphology and size as affirmed by their SEM, TEM analysis. The Nano TiO_2 assumes a catalytic role in water at 90 °C, accelerating the reaction rate and in increasing the product yield.

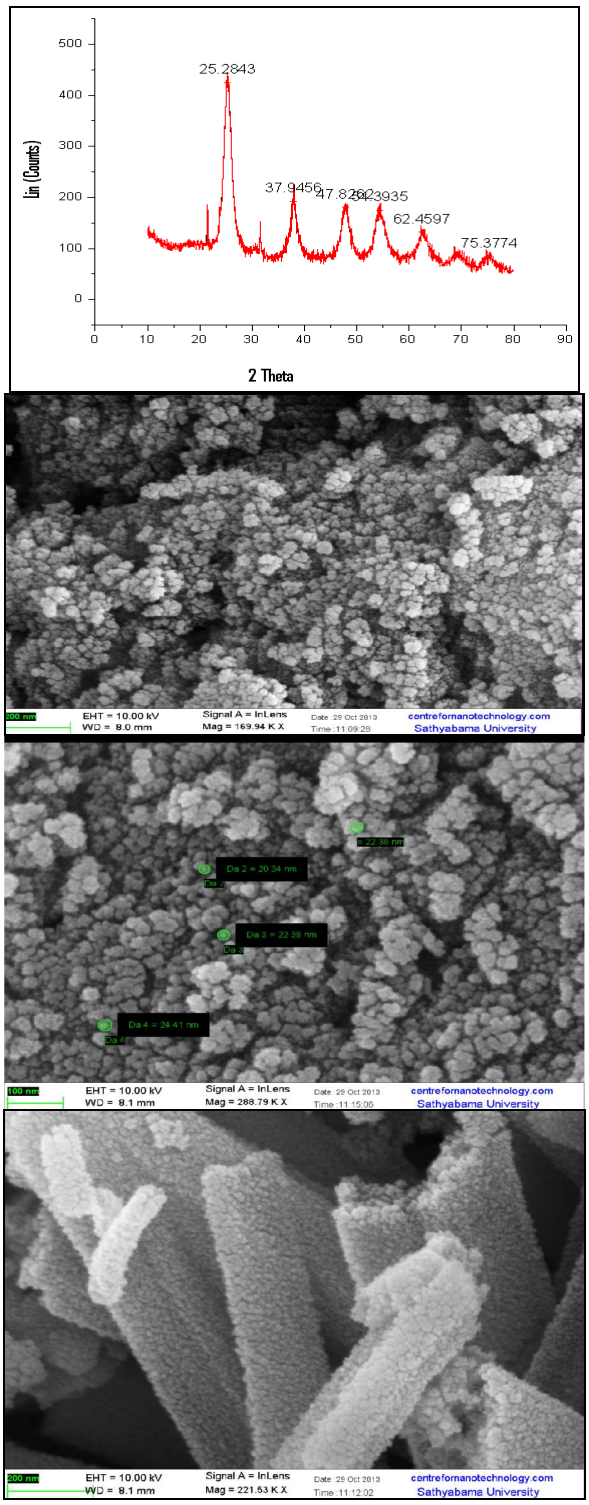


Figure 1 XRD and SEM images of TiO_2 nano

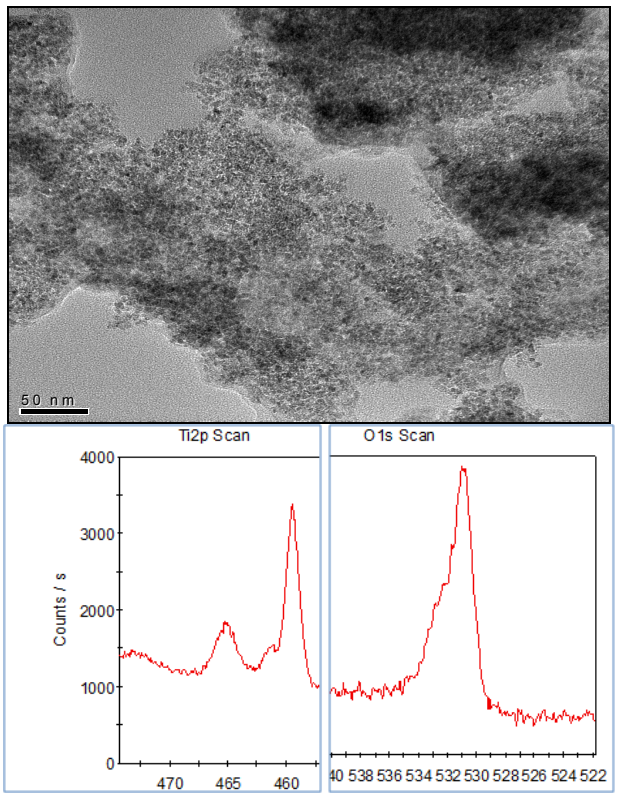


Figure 2 TEM and XPS images of TiO_2 nano

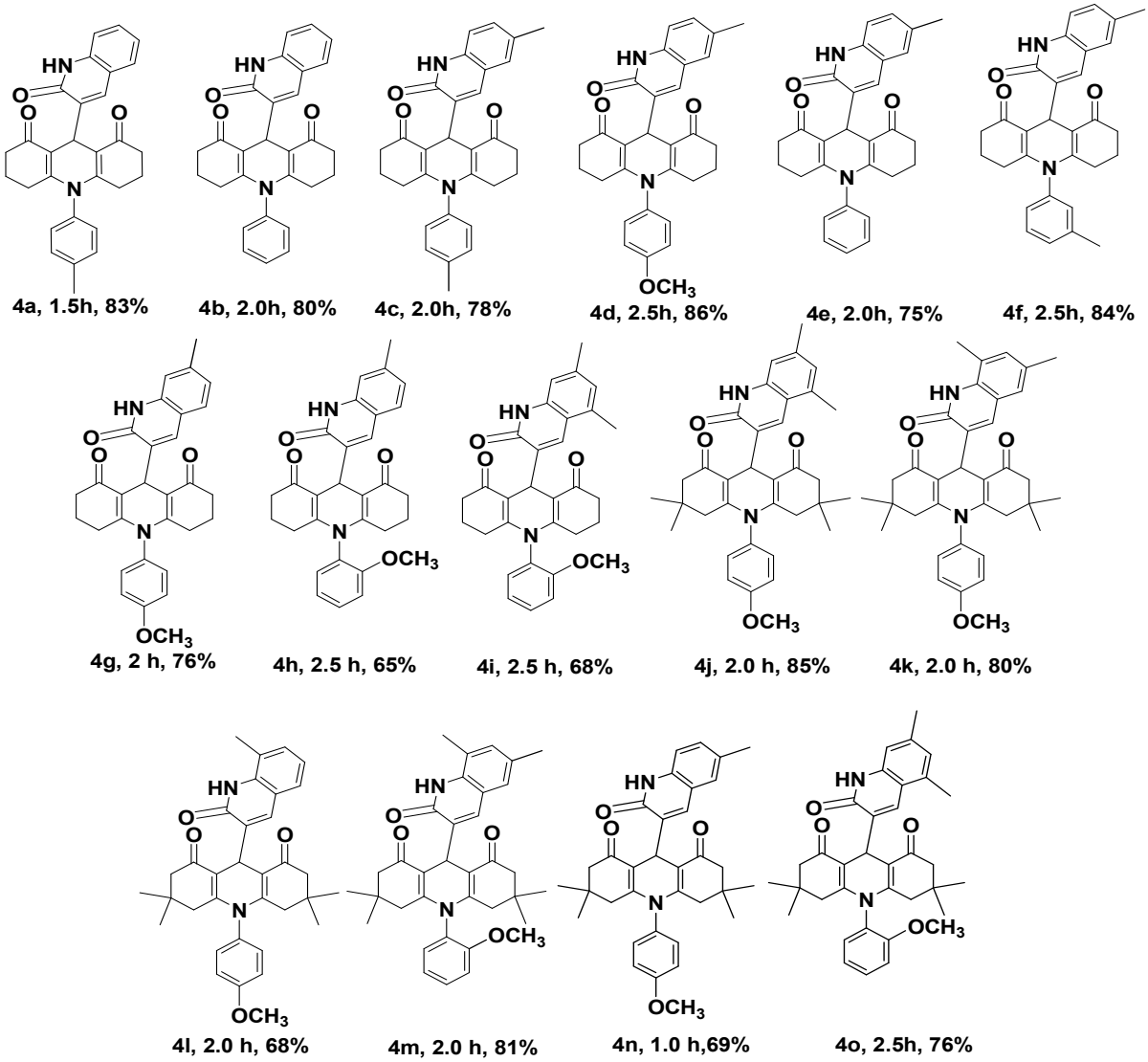
With these generally upgraded results in hand, the scope of reaction was examined utilizing unsubstituted 2-chloro-3-formylquinoline and those containing methyl subsistent at different positions, substituted anilines and dimedone or 1,3-cyclohexanedione. The advancement of the reactions was checked by thin layer chromatography and with the vanishing aldehydes. The isolated yields are summarized (Table 2). All the incorporated compounds were well characterized by various spectroscopic methods like FTIR, ^{1}H NMR, ^{13}C NMR and HRMS. A conceivable mechanism for the domino synthesis of 3,4,6,7-tetrahydro-9-(1,2-dihydro-2-oxoquinolin-3-yl)-10-phenylacridine-1,8(*2H,5H,9H,10H*)-dione was portrayed in **Scheme 2** Initially, 2-chloro-3-formylquinoline gets hydrolyzed to 2-oxo-3-formylquinoline which react with first 1,3-cyclohexanedione to give an intermediate **1i** that further react with second molecule of 1,3-cyclohexanedione to form a diketone intermediate **3i.** The diketone then condense with anilines with the elimination of molecules of water to offer the desired acridone-1,8-dione product, **4b.**

Table 1. Optimization of one pot four component reaction[a]

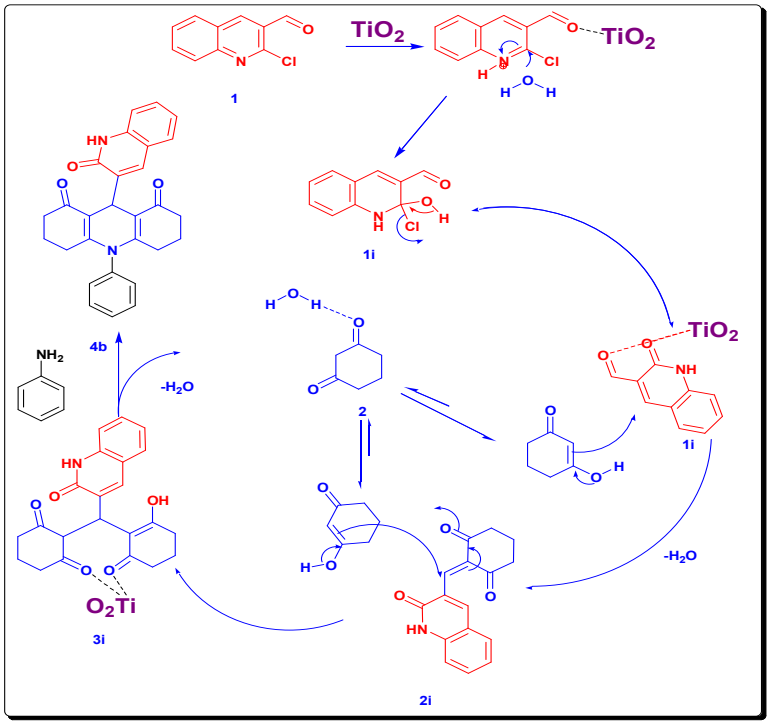
[a]Cyclohexanedione (2mmol), 2-Chloro-3-formylquinolines (1mmol), aniline (1mmol), 5 ml of appropriate solvent; [b]1,8-xanthenediones, [c]50, 54, 49, 47, 56 % for MeOH, EtOH, iPrOH, nBuOH, water respectively, [d]56, 58, 62 % for 5, 8. 10 mol %, respectively [e]76, 83, 79, 77, 89 % for MeOH, EtOH, iPrOH, nBuOH respectively, [f]89, 90,92% for 5, 8. 10 mol % respectively, [g]89, 86, 83, 83 % for cycles 1-4 respectively.

S. No	Catalyst (% mol)	Solvent	Time (h)	Yield (%)[b]
1	Nil	Ethanol	3	30
2	Nil	Nil	6	trace
3	ZnO	Ethanol	12	32 [b]
4	SnO2	Ethanol	12	43 [b]
5	CuO	Ethanol	12	42 [b]
6	NiO	Ethanol	12	33 [b]
7	Bulk TiO_2	Nil	6	35
8	Bulk TiO_2 (1)	Water	6	56[c]
9	Bulk TiO_2 (5-10)	Water	6	62[d]
10	Nano TiO_2 (1)	Water	1.5	89[e]
11	Nano TiO_2 (5-10)	Water	1.5	92[f]
12	Nano TiO_2 (5)	Water	1.5	89[g]

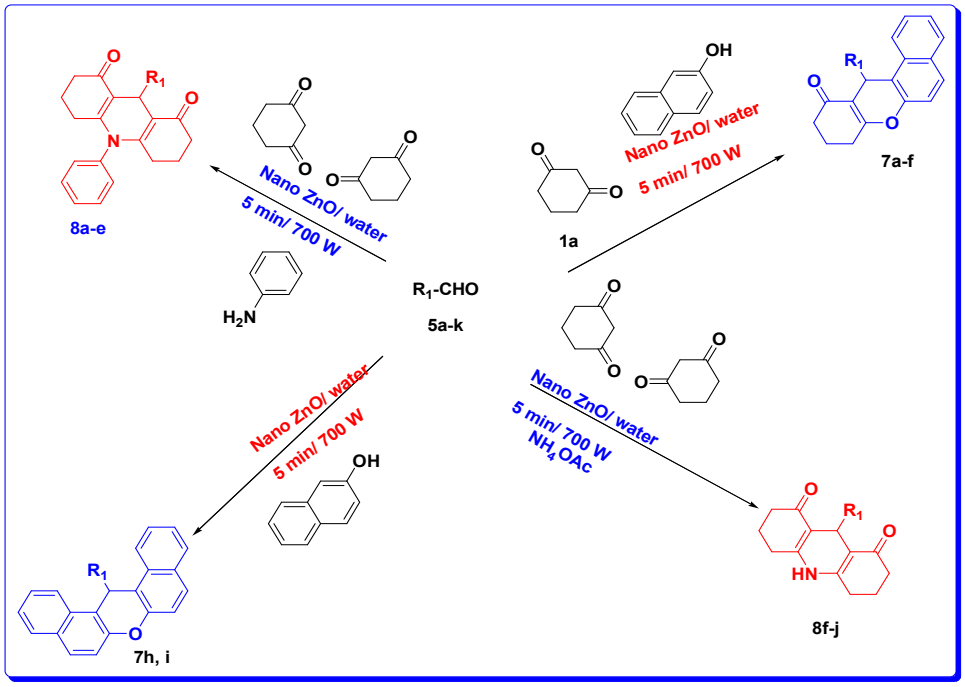
Table 2: Synthesis of acridine-1,8-diones[a]



[a]2-Chloro-3-formylquinolines (1mmol), cyclohexane-1,3-dione or dimedone (2mmol), anilines (1mmol), 5ml of ethanol, reflux, [5] .



Scheme 2. Plausible mechanism for the formation of acridine-1,8-dione



Scheme 3. General scheme for the synthesis of 2-substituted xanthenediones and acridindiones

The ZnO required for the present study is adequately prepared from the Zinc acetate precursor and sodium hydroxide as a precipitating agent through the sol-gel strategy. Typically, a 21.94 g Zinc acetate dihydrate was dissolved in 100 mL (0.149M) double distilled water in a flat bottomed flask under steady magnetic stirring conditions and homogenized for 30 minutes, the NaOH 3.33M (30ml) of was then included drop-wise to the flask. The colloidal milky solution formed was stirred for an hour and a while later setup on water bath kept at 65 °C and allowed for an hour, then cooled and centrifuged at 4000 rpm. It must be noted that the basic pH of the reaction mixture was found to be 12.5, and at a pH of 11.9 the flower-shaped ZNP was formed. The white precipitate got was washed with double distilled water and then with methanol, dried at room temperature for 24h. The procured powder was calcined at 500 °C for 2h. The chemical reactions included are as follows.

The morphology and microstructure of flower-like ZnO nanostructure have been depicted by X-ray diffraction (XRD), scanning electron microscopy (SEM) (**Figure 3**). The crystalline structure and the nano size are adjusted with the XRD pattern. The sharp diffraction peaks at $2\theta = 32.009^{o}$ (100), 34.4746^{o} (002), 36.3087^{o} (101), 47.6093^{o} (102), 56.6418^{o} (110), 62.8936^{o} (103) demonstrate the incredible crystalinity of the ZnO NPs. The high intensity of (100) peak at 32 demonstrate the development of ZnO NPs along the direction of crystallization. The ZnO NPs crystallite size was figured from the Debye–Scherrer equation:

$$D = k\lambda/\beta \cos\theta$$

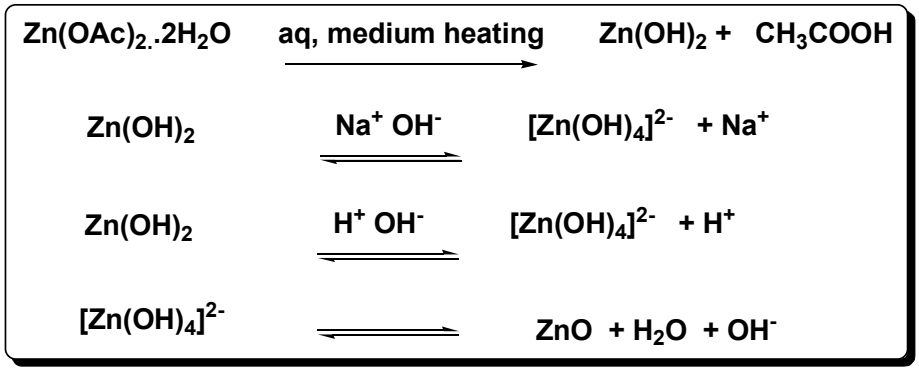
utilizing highest astounding peak (101), where k = proportionality constant = 0.9; λ = X-ray wavelength Cu-Kα= 1.54178 Å; β= full width at half maxima; θ = Braggs' angle in degrees. The FT-IR spectroscopy of the flower-like ZnO nanostructures was analyzed to recognize its structure and quality. The spectra revealed bands of 505 cm^{-1} identifying with the Zn-O stretching vibration and broad absorption at 3200-3600 cm^{-1} demonstrate the hydroxyl mode of vibration on the surface of the ZnO samples.

The morphology and the size of the ZnO particles were recognized from the SEM images which show abundant flower-shaped bundles of ZnO NPs with long and pointed rods and the SEM patterns concur well with the XRD results. The lengths of the flower-shaped ZnO nanostructures are in the range of 0.8–2 mm with the petal widths change from the tip to the premise. The TEM images showed well crystalline ZnO, nanostructures are in the range of 70-100 nm (**Figure 4**).

The XPS survey sweep of the ZnO nanoparticles exhibit the peaks credited to Zn, O and C elements and the HRXPS of O 1s and Zn 2p core level (Figure 4). XPS spectra show their corresponding binding energies. The peak centered at 530.2 eV is related to the O_2^- ions encompassed by the Zn atoms. The other nearby peak located at 531.1 eV is identified with OH group ingested onto the surface of the ZnO nanoparticles. The Zn2p core-level of ZnO NPs reveals two peaks at around 1043.7 and 1020.7 eV identifying with Zn2p1/2 and Zn2p3/2. The ratio of Zn/O is marginally lower than unity affirming pure ZnO as accommodated by XRD results.

At first, when a reaction between aryl aldehydes, **5a**, diketone, **1**and beta naphthol, **6a** in the equimolar ratio is completed without a catalyst under ethanol reflux condition for 6h, the reaction was continued to offer low yield product xanthenone, **7a** (Table 3, entry 1). By then, the reaction progress in the presence of catalytic amount (5mol %) of distinctive metal oxide including SnO_2, CuO, TiO_2, ZnO was investigated in ethanol reflux condition for 6h. Amongst the tested metal oxides the ZnO was found to be best catalyst with 77 % product yield and after that the TiO_2 with 56 % yield (Table 3, entry 3, 5). Supported by these result, the variety of catalyst from bulk to nano materials, catalyst loading, heating strategies, for instance, conventional and microwave irradiation (synthetic microwave oven) has been looked into. The result revealed that the ZnO NPs has risen out as a best catalyst among the different bulk and nano material catalyst (Table 3, entry 4, 6).

The recyclability of the catalyst has been investigated after separting the catalyst from the reaction mixture, washing with the organic solvent, dichloromethane, drying the catalyst. The reaction was successful in five successive runs without the lost of catalyst efficiency.



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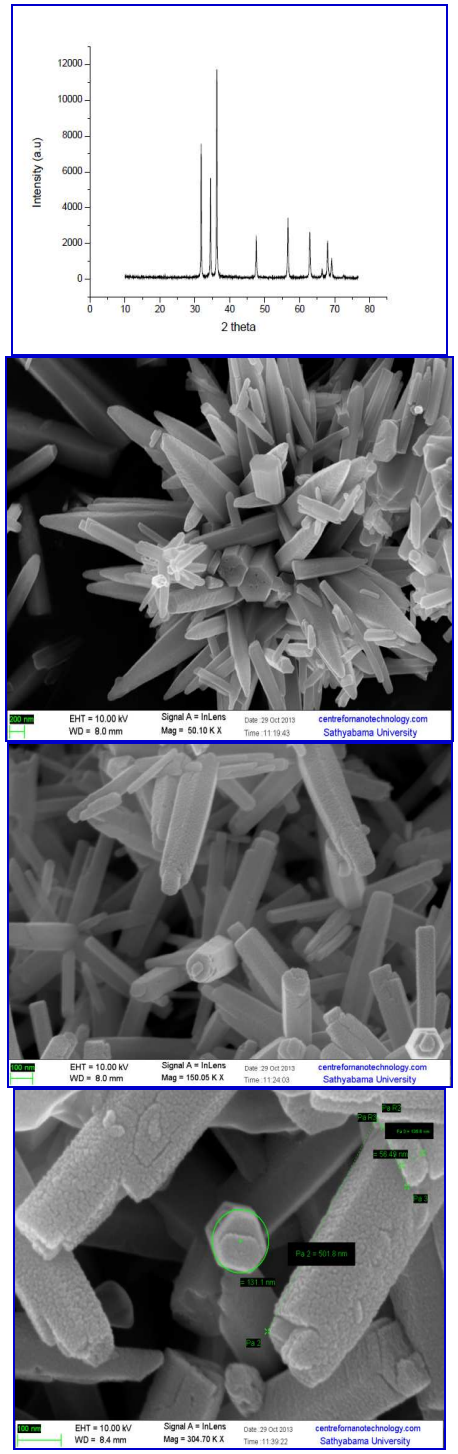


Figure 3 XRD and SEM images of ZnO nano

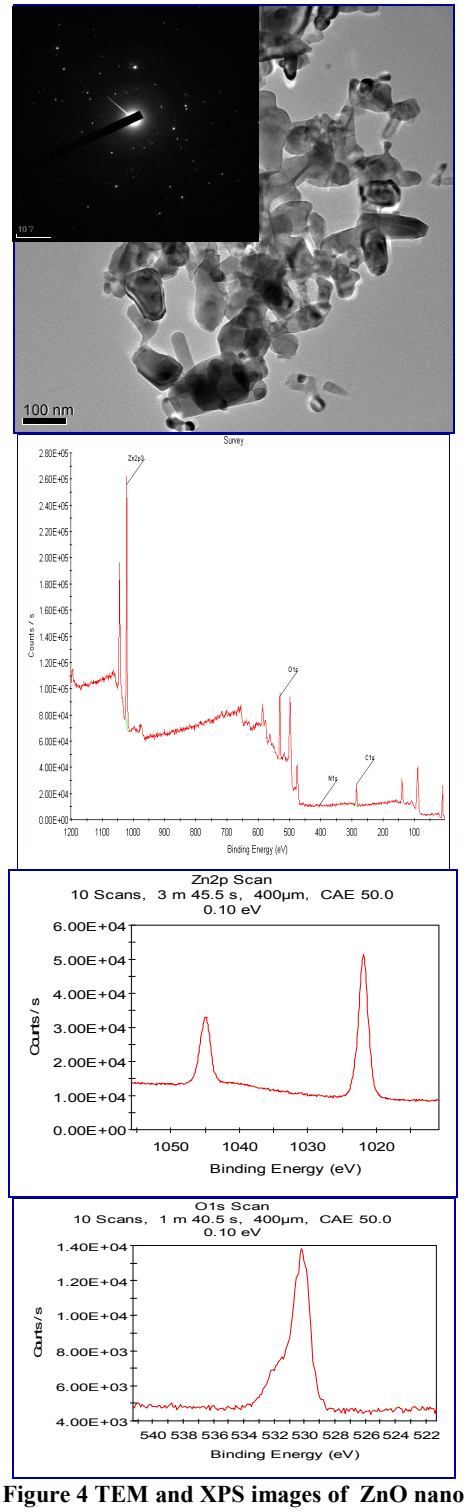


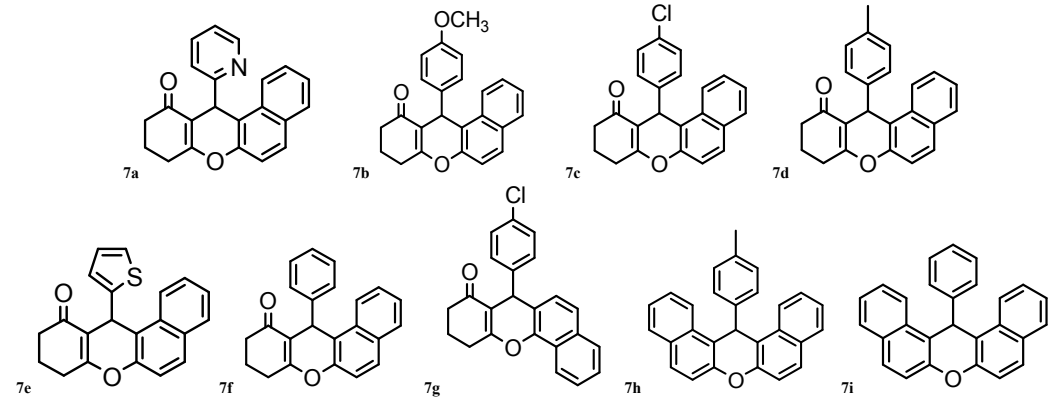
Figure 4 TEM and XPS images of ZnO nano

Table 3. Optimization of reaction conditions[a]

Sl. No.	Catalyst	Yield[b] %
		7a
1.	No catalyst	trace
2.	SnO_2 (Bulk)	12
3.	CuO (Bulk)	30
4.	TiO_2 (Bulk)	56
5.	TiO_2 (Nano)	60
6.	ZnO (Bulk)	77
7.	ZnO Nano (5)	80
8.	ZnO Nano (10)	85
9.	ZnO Nano (15)	88
10.	ZnO Nano (20)	86
11.	ZnO Nano (ethanol)	70
12.	ZnO Nano (methanol)	72
13.	ZnO Nano (n-butanol)	62
14.	ZnO Nano (isopropanol)	65
15.	ZnO Nano (100W)	45
16.	ZnO Nano (200W)	56
17.	ZnO Nano (400W)	63
18.	ZnO Nano (600W)	77

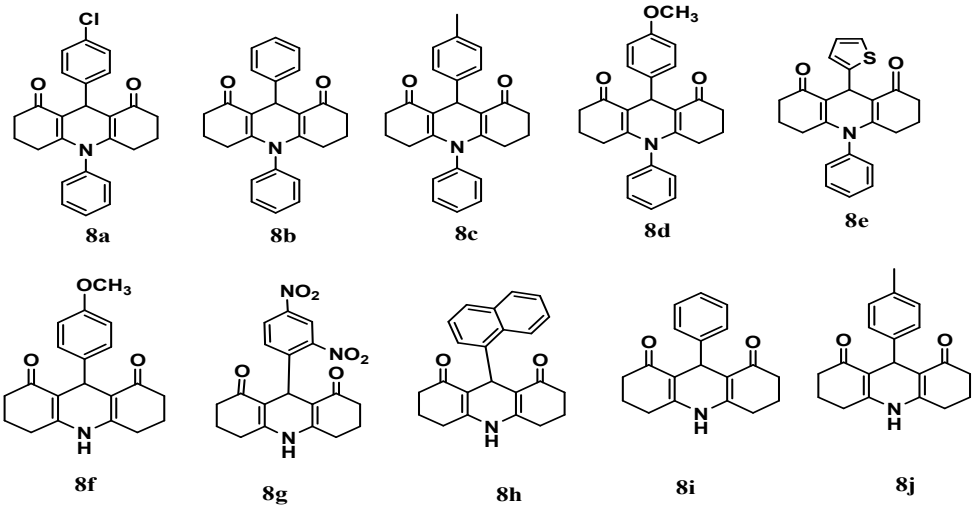
[a]Reaction conditions: Arylaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), 2-napthol (1mmol), 5 mole % (unless otherwise stated) of appropriate catalyst in water (unless otherwise stated) at 700 W (unless otherwise stated) and microwave irradiated; [b]Isolated yield

Table 4 Synthesis of xanthenones and xanthenes, 7 [a]



[a]**Reaction conditions**: Arylaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), 2-napthol (1mmol), 5 mole % (unless otherwise stated) of appropriate catalyst in water (unless otherwise stated) at 700 W (unless otherwise stated) and microwave irradiated.

Table 5 Synthesis of acridindiones, 8 [a]



[a]Reaction conditions: Arylaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), ammonium acetate or aniline (1.2 mmol), 5 mole % of ZnO catalyst in water at 700 W and microwave irradiated.

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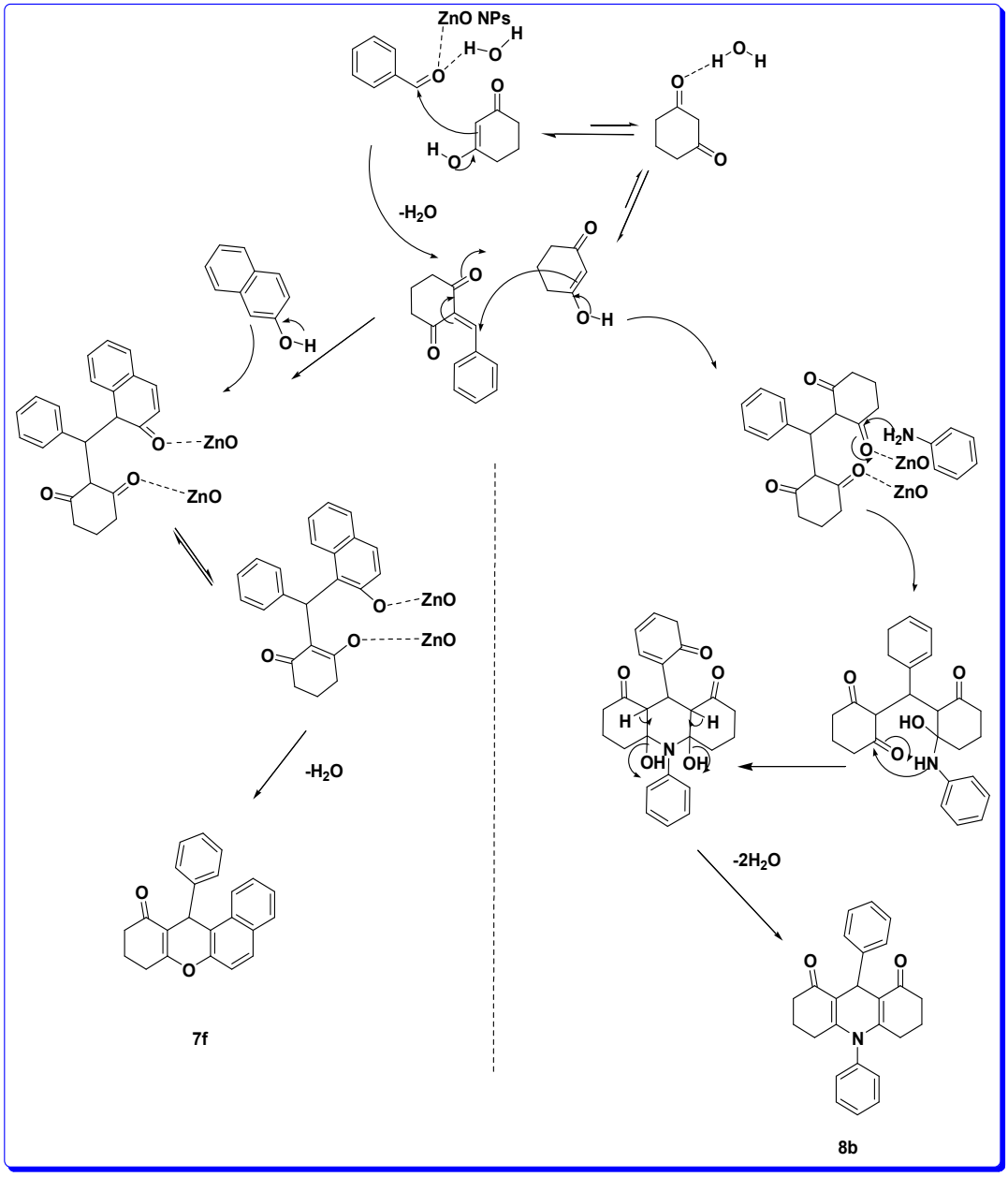

Scheme 4. Mechanism

An enhanced catalyst loading of 5 mol% from the 0, 5, 10, 15, 20 mol% was gainful (table 3, entry 6-10) and water was found to be the best solvent among the methanol, ethanol, butanol, isoprapanol, water for the progression of the reaction and better yield (Table 3, entry 11-14). The microwave irradiation at 700W for 5 min risen out among the tested 100, 200, 400, 600, 700 W and offered the desired product in a phenomenal yield (Table 3, entry 15-18). The reusability of nano ZnO reveals that the separated catalyst (from the reaction mixture by dissolving organic products) is capable for the four sequential cycle runs without any noteworthy product and catalyst efficiency loss. The reusable catalysts did not show any noteworthy change in its morphology and size as affirmed by their SEM, TEM analysis. Having the streamlined result in hand, then examined the scope of the reaction with distinctive aldehydes to give the desired products **7a-f** in good yields (Table 4). By then, the isomeric

xanthenone product has additionally been endeavored utilizing alpha naphthol under upgraded condition to give the desired product **7g** in excellent yields as shown above (**Scheme 3**). In any case, it must be noted that without the diketone, aldehydes can productively reacts with two equivalents of beta-naphthol under the optimized conditions to give the symmetrical xanthenes **7h, 7i** as demonstrated underneath (scheme 2). Further, the scope of the reaction was explored by utilizing the above overhauled condition including the benzaldehyde, diketone, aniline in the 1:2:1 proportion has been attempted to give the desired product **8a**. Distinctive aldehydes have been turned out to be productive for desired products **8a-f** with excellent yields (Table 5). Correspondingly, the reaction between aldehydes, diketone and ammonium acetate in the ratio of 1: 2:1 has been inspected to give the product **8g-l.** The quinoline aldehydes, napthylamines, when attempted under above optimized condition neglected to offer the pure and quantitative yield of the expected product as outlined out beneath and further, alternate approaches to attain the same are under advancement in our research facility.

A conceivable mechanism for the domino synthesis of 9-(quinolin-2(*1H*)-one)-xanthene-1,8(*5H,9H*)-dione was given in **Scheme 4**. At the outset, 2-arylhldehyde and the cyclohexanedione get activated by ZnO NPs. By then, the first molecule of 1,3-cyclohexanedione condenses with aldehydes to form the relating alkylidene intermediate. Further, the active methylene group of second 1,3-cyclohexanedione molecule reacts with intermediate through Michael addition to give an alternate intermediate**.** The intermediate formation steps are facilitated by the ZnO NPs which further experiences intra-molecular cyclodehydration in the presence of aniline to furnish the desired acridindiones, **8b**.

In the like manner, the alkylidene derivative structured in the first step experience condensation with the naphthol molecule to form an intermediate which further experience an intramolecular cyclodehydration to offer the desired benzoaxanthenones, **7f**. The steps are facilitated by the ZnO NPs.

Taking everything into account, an efficient one-pot four component synthesis of 3,4,6,7-tetrahydro-9-(1,2-dihydro-2-oxoquinolin-3-yl)-10-phenylacridine-1,8(*2H, 5H, 9H, 10H*) -dione derivatives was acquired utilizing TiO_2 nanorods catalyst. The present method offers selectively the 9-(2-oxo-1,2-dihydroquinolin-3-yl)-10-phenyl-3,4,6,7-tetrahydro acridine -1,8 (*2H, 5H,9H, 10H*) -diones product in high yield, simple technique, gentle condition and reusable catalytic system.

Moreover, a proficient one-pot synthesis of xanthenes and acridine derivatives were acquired utilizing nanocrystalline ZnO catalyst in water medium by MWI. The present technique offers high return, simple strategy, mellow condition and reusable catalyst. The reaction conversion was good to excellent for all the analogs employed with good isolated yields.

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General procedure for the synthesis of acridine-1,8-diones, 4

In a typical experiment procedure, a mixture of 2-chloro-3-formylquinoline (1.0 mmol), 1,3-cyclohexanedione (2.0 mmol), anilines (1.0 mmol) distilled water (5.0 mL) was taken in 50 mL reaction vial in the presence of nano TiO_2 (1mg) and heated to 90 ^{o}C. Advancement of the reaction was observed by thin layer chromatography. After completion, the reaction mixture was filtered to remove the any catalyst, washed with water. The acquired compound was pure enough for further analysis.

Preparation of Xanthenones and Xanthenes, 7.

Preparation of **7a** is described as a typical procedure.

A mixture of Prydine-2-carboxaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), 2-napthol (1mmol), 5 mole % of ZnO Nps catalyst in water was microwave irradiated at 700 wats (Synthetic microwave oven). After irradiation for 5min, the reaction was extracted with ethyl acetate three times leaving behind the catalyst (separated by filtration). The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane AcOEt 30:1) on silica gel to give the desired xanthenone as a colorless solid.

Likewise procedure was emulated for **7b-i**, however in the case of xanthenes, **7h, 7i** formations, the cyclohexane-1,3-dione was not utilized.

Preparation of Acridinones, 8

Preparation of **8a** is described as a typical procedure.

A mixture of 4-chlorobenzaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), anilines (1mmol), 5 mole % of ZnO Nps catalyst in water was microwave irradiated at 700 wats (Synthetic microwave oven). After irradiations for 5min, the reaction was extracted with ethyl acetate three times leaving behind the catalyst (separated by filtration). The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane AcOEt 30:1) on silica gel to give the desired xanthenone as a colorless solid. Comparative procedure was emulated for **8b-l**, however in the case of xanthenes, **8g-l** formations, ammonium acetate was utilized in the place of anilines

Notes and references

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