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ARTICLE TYPE

Water mediated reactions: TiO₂ and ZnO Nanoparticles catalyzed Multi component domino reaction in the synthesis of tetrahydroacridinediones, acridindiones, xanthenones and xanthenes

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The eco-accomodating TiO₂ 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, photosensitizers 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)₂·7H₂O,¹⁴ CeCl₃·7H₂O,¹⁵ silica bonded sulfonic acid,¹⁶ sovent free methanesulfonic acid catalysed,^{17,18} In(OTf)₃,¹⁹ p-dodecylbenzenesulfonic acid in aq medium,²⁰ ionic liquids- 1-n-butyl-3-methylimidazolium bromide ([bmim]Br),^{22,23} Amberlyst-15,^{24,25} ammonium chloride,²⁶ P₂O₅,²⁸ [B(C₆F₅)₃],²⁹ L-proline³⁰ along these lines on³¹⁻³⁹. All the techniques delineated above, incorporated the synthesis of symmetrical acridinediones and simply few report is known on unsymmetrical acridinediones⁴⁰⁻⁴² 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 (TiO₂) of meso, micro, nano materials nature found to have remarkable electronic and optical properties⁴³⁻⁴⁵, various endeavors has been made for their synthesis particularly due to their high surface area, uniform pore size which find enormous applications in photocatalysis⁴⁶, solar cells⁴⁷, lithium-ion batteries⁴⁸, sensors⁴⁹ and catalyst supports as well as in numerous fields⁵⁰. In continuation of our research engages in synthetic strategies for the assorted biologically imperative motifs utilizing heterogeneous catalysts⁵¹⁻⁷² utilized TiO₂ 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

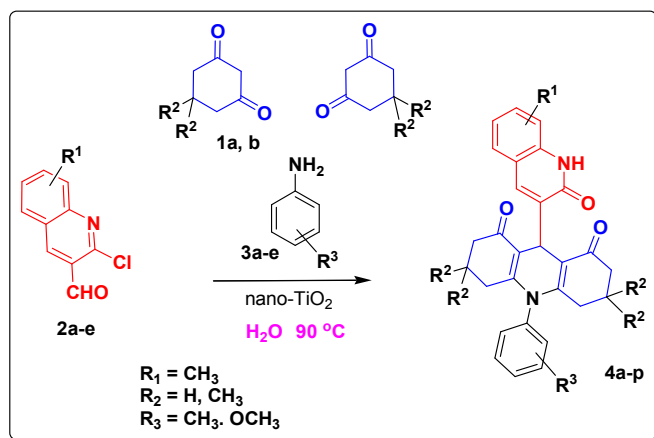
demonstrated, a domino synthesis of 9-(quinolin-2(1*H*)-one)-xanthene-1,8(5*H*,9*H*)-dione derivatives in aqueous medium whilst, the present work exhibit the four component one pot reaction (Scheme 1, 2). The hydrolysis of the chloro functionality of the reactant to oxo functionality under the applied 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, antiviral⁷³, antibacterial⁷⁴ and anti-inflammatory activities⁷⁵. Further, these compounds have been utilized as dyes⁷⁶, in laser technology⁷⁷, pH-sensitive fluorescent materials for the visualization of biomolecular assemblies⁷⁸. Basically, it is moreover noteworthy that dibenzoxanthenes derivatives have been utilized as sensitizers as a part of photodynamic therapy⁷⁹. Acridine-1, 8-diones containing a 1, 4-dihydropyridine parent core has potential pharmacological action, for instance, against malaria⁸⁰, cancer⁸¹ and leishmania⁸².

The synthesis of xanthenes and acridine derivatives has been enhanced in the presence of an acidic catalyst, for instance, sulfamic acid⁸³, Amberlyst-15⁸⁴, AcOH-H₂SO₄⁸⁵, *p*-TSA⁸⁶ and silica sulfuric acid⁸⁷. There are similar reports incorporating TBAHSO₄ in aqueous dioxane⁸⁸, wet cyanuric chloride⁸⁹, TiO₂-SO₄⁻²⁹⁰, polyaniline *p*-toluenesulfonate⁹¹, PPA-SiO₂⁹², NaHSO₄-SiO₂⁹³, Fe⁺³-montmorillonite⁹⁴, 1-methylimidazolium trifluoroacetate⁹⁵, quaternary ammonium alkyl sulfonate⁹⁶, polytungstozincate acid⁹⁷, cellulose-sulfuric acid⁹⁸, microwave irradiation^{99,100}, ionic liquid^{101,102}, LiBr, ZrOCl₂·8H₂O¹⁰³, proline¹⁰⁴, silica-bonded *S*-sulfonic acid¹⁰⁵, ceric ammonium nitrate¹⁰⁶, methanesulfonic acid¹⁰⁷ and in aqueous media¹⁰⁸⁻¹¹⁰.

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 safety¹¹¹ 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 applications¹¹². As of late, bulk zinc oxide has been employed as a heterogeneous catalyst for distinctive organic transformations¹¹³. The late literature survey uncovers that nano ZnO¹¹⁴ 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 etc¹¹⁵⁻¹²⁵ through thermal treatment of Zn(OH)₄²⁻ or Zn(NH₃)₄²⁻ precursor in aqueous solvent utilizing structure directing agents or through solvothermal processing¹²⁶⁻¹²⁸. Consequently, to our greatest advantage on heterocycles⁵¹⁻⁶², is represented water intervened, eco-accommodating microwave irradiated, flower shaped ZnO catalyzed synthesis of xanthene and acridine derivatives (Scheme 3, 4).



Results and Discussion

In this paper, we concentrated on the application of TiO₂ 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(CH₃)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 $2\theta = 25.28^\circ$ (101), $2\theta = 37.94^\circ$ (004), $2\theta = 47.82^\circ$ (200), $2\theta = 54.39^\circ$ (105) and $2\theta = 62.45^\circ$ (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 (TiO₂) morphology (**Figure 1**). The TEM images demonstrated the well crystalline TiO₂ 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 (Ti⁴⁺-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 Ti⁴⁺ in the anatase TiO₂.

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 TiO₂ 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, SnO₂, CuO, NiO, TiO₂. Amongst the explored oxides, interestingly in TiO₂, 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 SnO₂, 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 TiO₂ catalyst, catalyst loading was investigated. Fittingly, amongst the different tested solvents (Table 1 and entries 8-12), water was found to be best, cheap and offered high yield of products. Correspondingly the nano TiO₂ 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 TiO₂ 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 TiO₂ assumes a catalytic role in water at 90 °C, accelerating the reaction rate and in increasing the product yield.

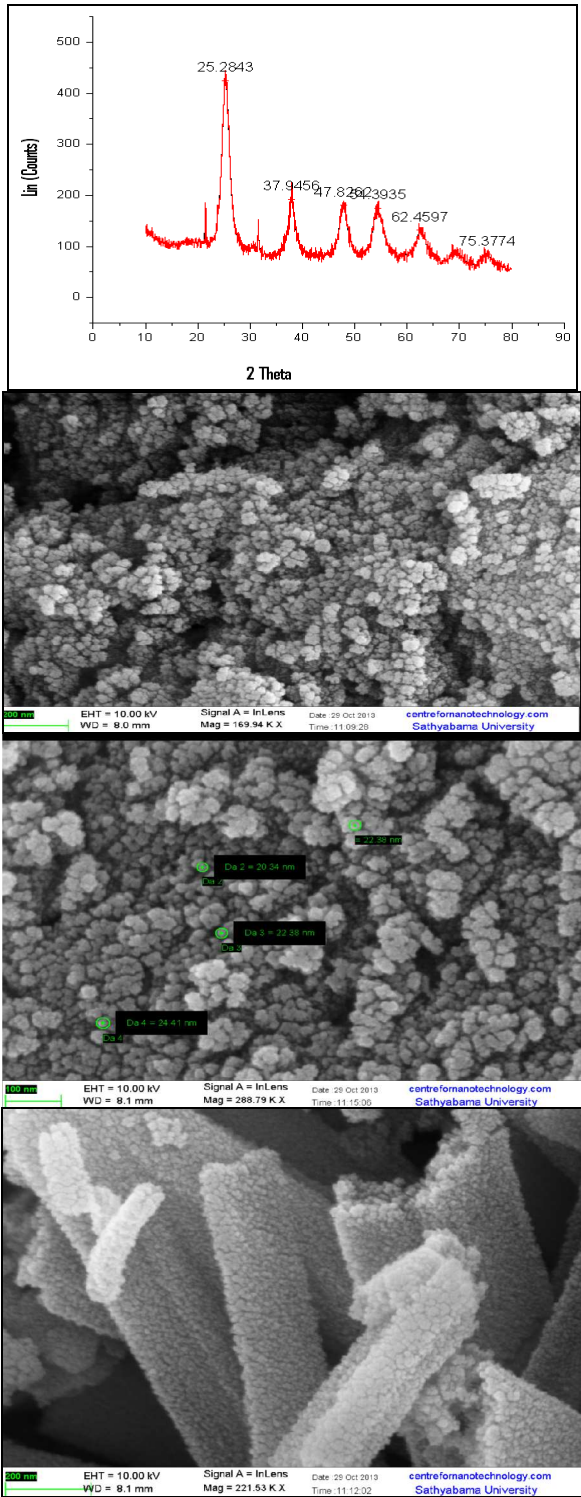


Figure 1 XRD and SEM images of TiO₂ nano

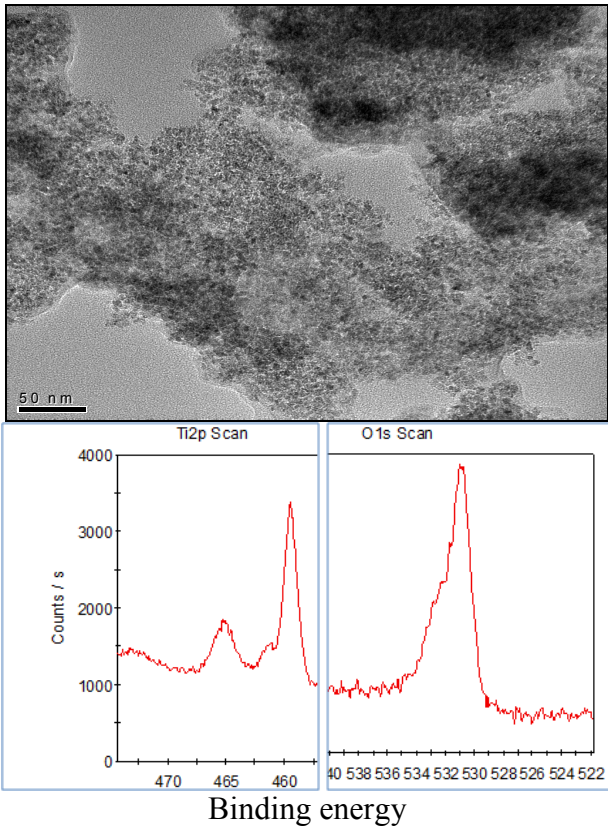


Figure 2 TEM and XPS images of TiO₂ nano

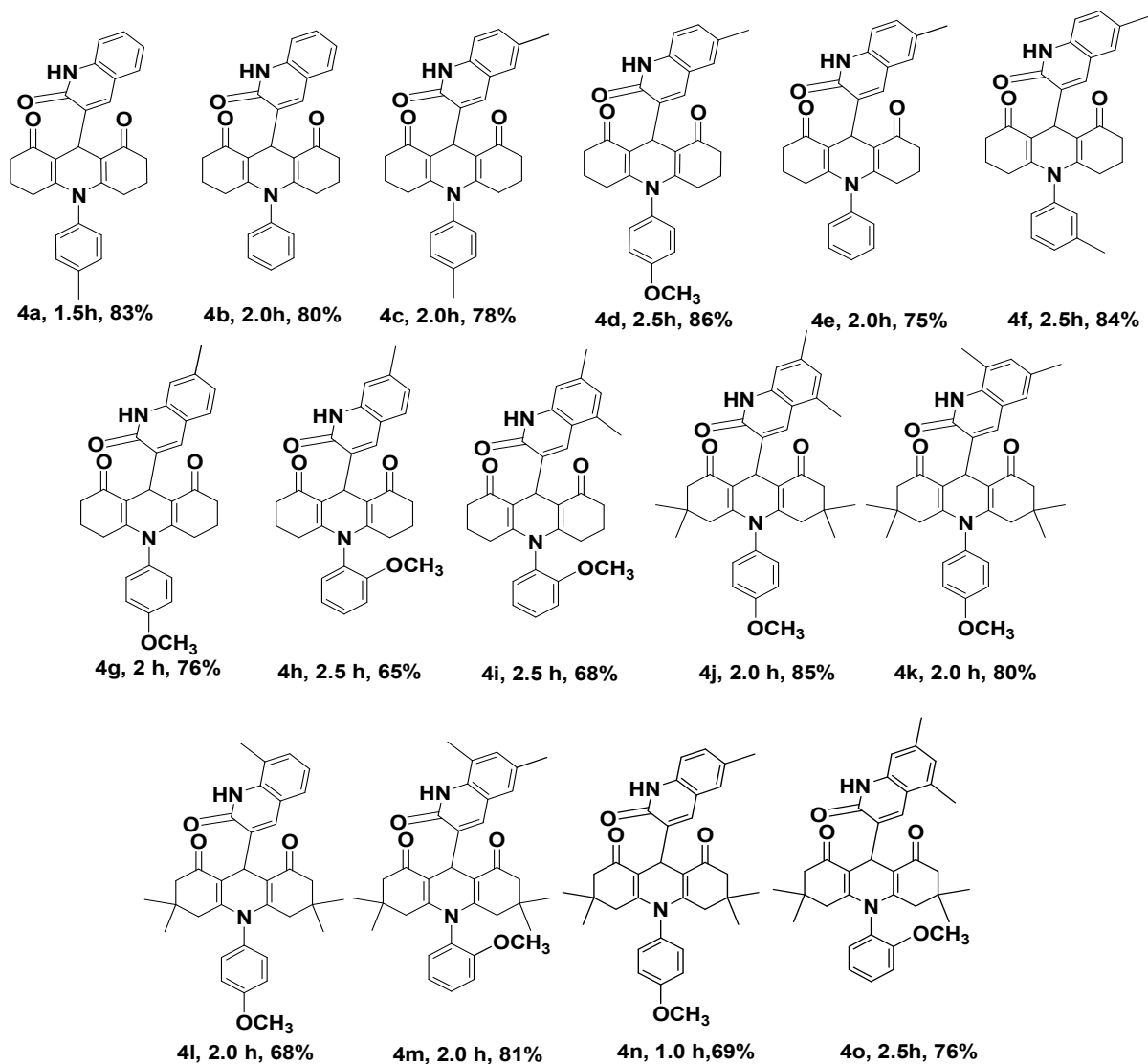
With these generally upgraded results in hand, the scope of reaction was examined utilizing unsubstituted 2-chloro-3-formylquinoline and those containing methyl substituent at different positions, substituted anilines and dimedone or 1,3-cyclohexanedione. The advancement of the reactions was checked 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, ¹H NMR, ¹³C 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(2*H*,5*H*,9*H*,10*H*)-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^aCyclohexanedione (2mmol), 2-Chloro-3-formylquinolines (1mmol), aniline (1mmol), 5 ml of appropriate solvent; ^b1,8-

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	SnO ₂	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

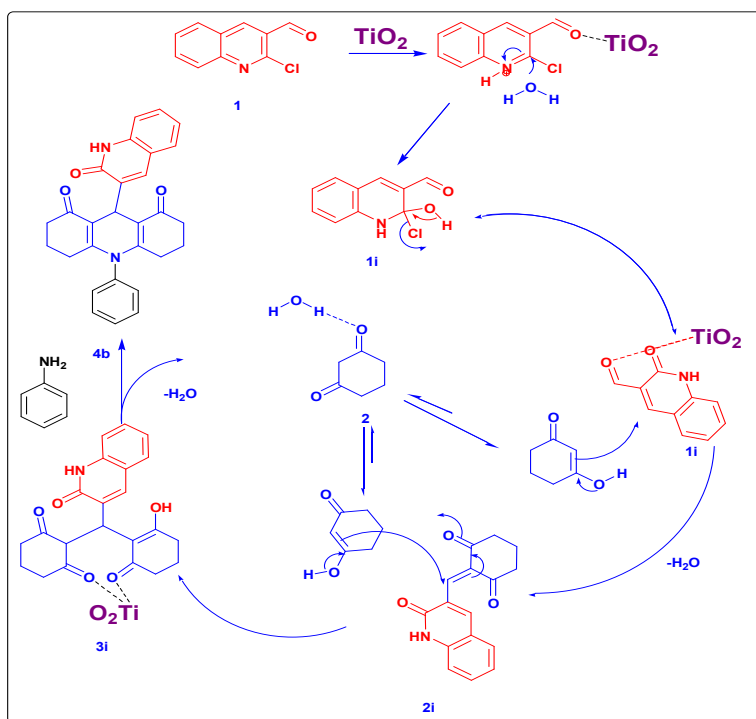
^c50, 54, 49, 47, 56 % for MeOH, EtOH, iPrOH, nBuOH, water respectively, ^d56, 58, 62 % for 5, 8, 10 mol %, respectively ^e76, 83, 79, 77, 89 % for MeOH, EtOH, iPrOH, nBuOH respectively, ^f89, 90, 92% for 5, 8, 10 mol % respectively, ^g89, 86, 83, 83 % for cycles 1-4 respectively.

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

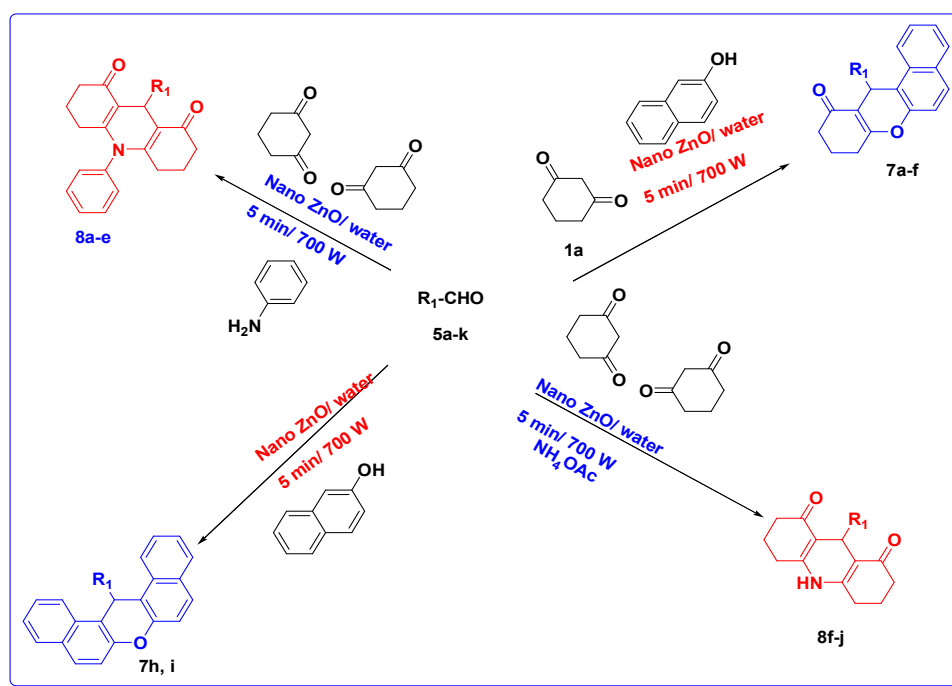


^a2-Chloro-3-formylquinolines (1mmol), cyclohexane-1,3-dione or dimedone (2mmol), anilines (1mmol), 5ml of ethanol, reflux,

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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 $2\theta = 32.009^\circ$ (100), 34.4746° (002), 36.3087° (101), 47.6093° (102), 56.6418° (110), 62.8936° (103) demonstrate the incredible crystallinity 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-K α = 1.54178 Å; β = full width at half maxima; θ = Bragg's 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.

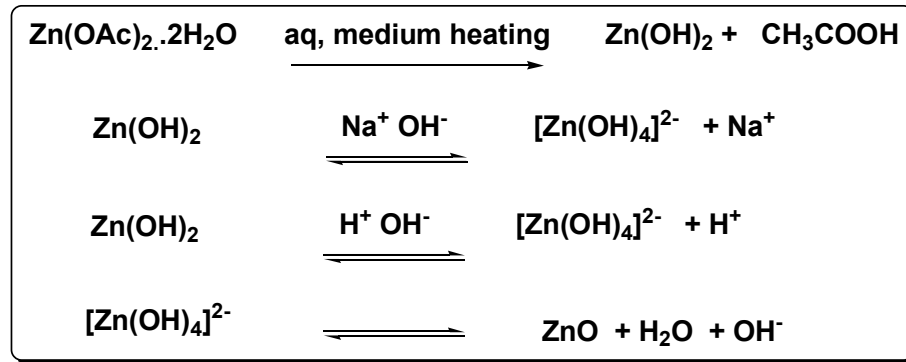
The morphology and the size of the ZnO particles were recognized from the SEM images which show abundant flower-shaped bundles of ZnO NPs with long and pointed rods and the

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 O₂⁻ 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 Zn2p_{1/2} and Zn2p_{3/2}. 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, **1a** 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 SnO₂, CuO, TiO₂, 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 TiO₂ 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 separating 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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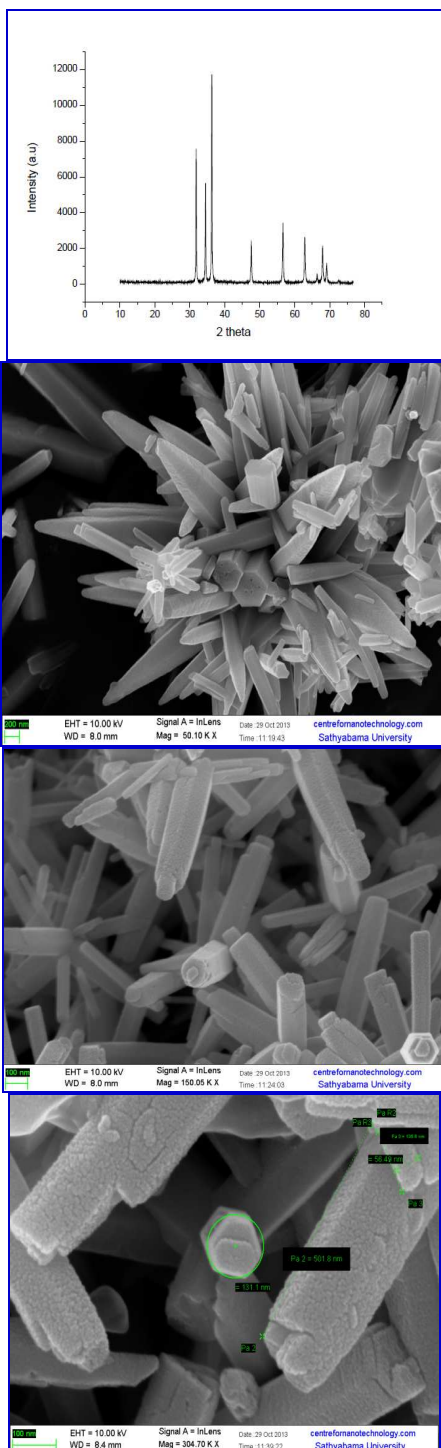


Figure 3 XRD and SEM images of ZnO nano

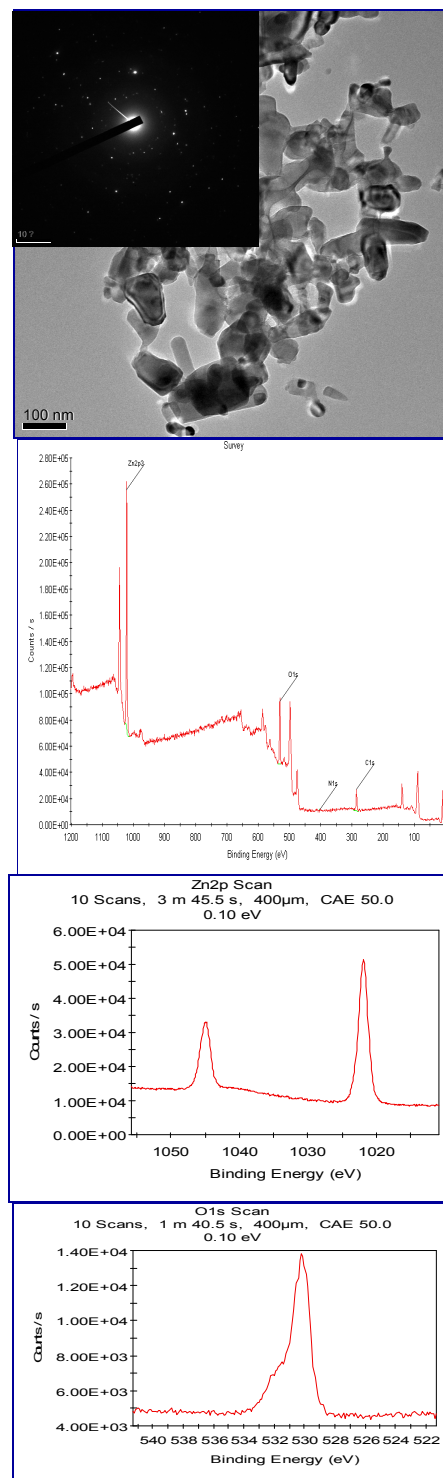


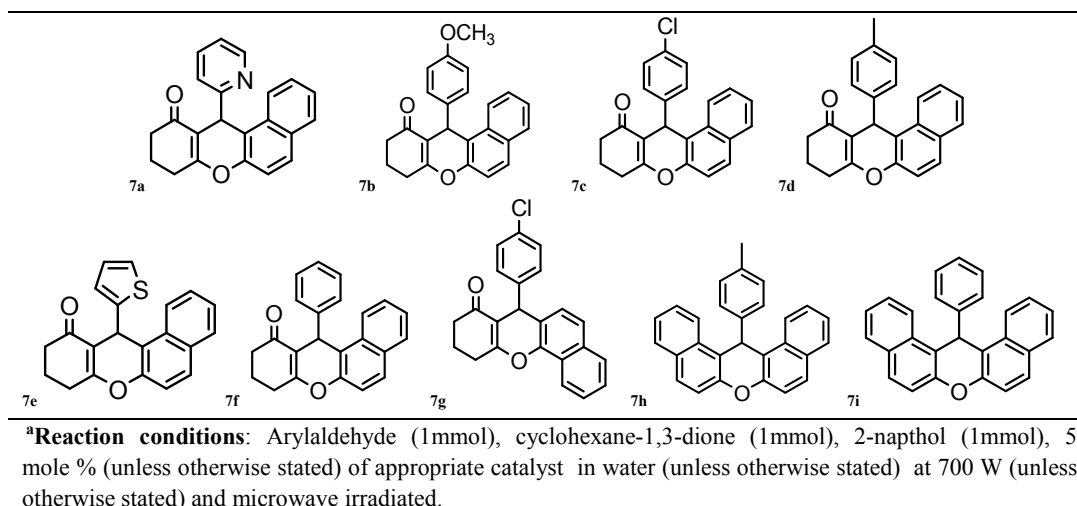
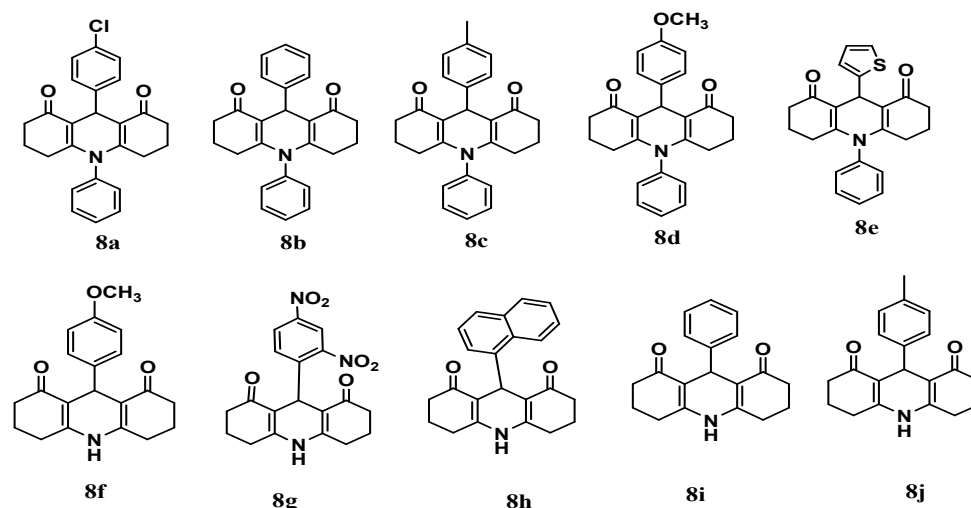
Figure 4 TEM and XPS images of ZnO nano

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10 Table 3. Optimization of reaction conditions^a

Sl. No.	Catalyst	Yield ^b %	
		7a	
1.	No catalyst	trace	15
2.	SnO ₂ (Bulk)	12	20
3.	CuO (Bulk)	30	25
4.	TiO ₂ (Bulk)	56	
5.	TiO ₂ (Nano)	60	30
6.	ZnO (Bulk)	77	
7.	ZnO Nano (5)	80	35
8.	ZnO Nano (10)	85	
9.	ZnO Nano (15)	88	40
10.	ZnO Nano (20)	86	45
11.	ZnO Nano (ethanol)	70	
12.	ZnO Nano (methanol)	72	50
13.	ZnO Nano (n-butanol)	62	
14.	ZnO Nano (isopropanol)	65	55
15.	ZnO Nano (100W)	45	
16.	ZnO Nano (200W)	56	60
17.	ZnO Nano (400W)	63	
18.	ZnO Nano (600W)	77	65

^aReaction conditions: Arylaldehyde (1mmol), cyclohexane-1,3-dione (1mmol), 2-naphthol (1mmol), 5 mole % (unless otherwise stated) of appropriate catalyst in water (unless otherwise stated) at 700 W (unless otherwise stated) and microwave irradiated;
^bIsolated yield

Table 4 Synthesis of xanthenones and xanthenes, 7^aTable 5 Synthesis of acridindiones, 8^a

^aReaction 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.

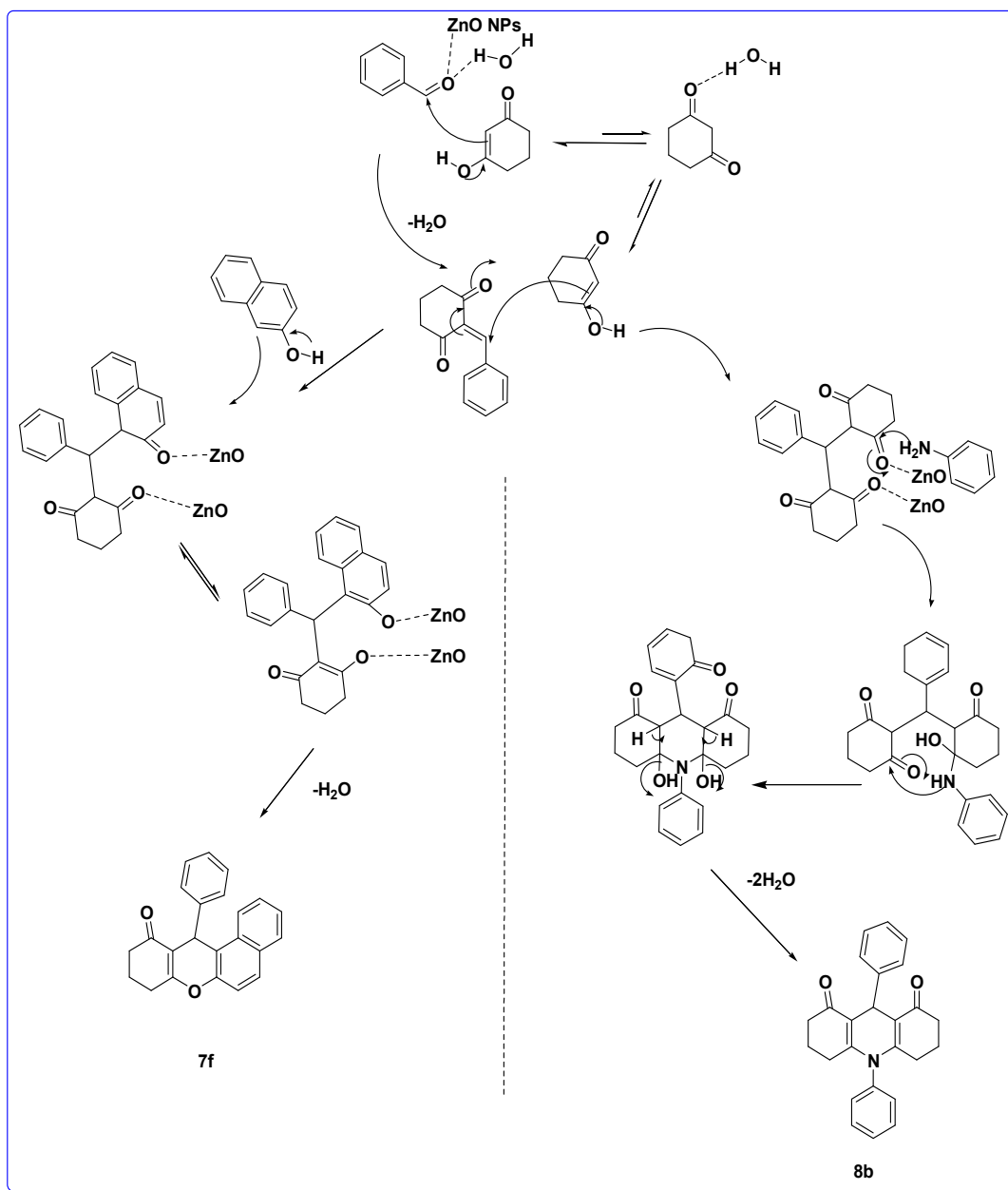
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Scheme 4. Mechanism

10 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, isopropanol, water for the progression of the reaction and better
 15 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
 20 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
 25 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, naphthylamines, 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(1*H*)-one)-xanthene-1,8(5*H*,9*H*)-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(2*H*, 5*H*, 9*H*, 10*H*) -dione derivatives was acquired utilizing TiO₂ 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(2*H*, 5*H*,9*H*, 10*H*) -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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City, Korea. The authors also acknowledge grants from KBSI, no. C34920, P0E013.

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 TiO₂ (1mg) and heated to 90 °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 Xanthenes 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-naphthol (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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