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ZnO Nanoparticles: A Highly Effective and Readily Recyclable Catalyst for the One-Pot Synthesis of 1,8-dioxo-decahydroacridine and 1,8-dioxooctahydro-xanthene Derivatives

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Abstract. ZnO nanoparticles as a worthwhile and recyclable catalyst have been used for the one-pot synthesis of 1,8-dioxo-decahydroacridines and 1,8-dioxooctahydro-xanthenes *via* multi-component reactions under solvent-free conditions. The presented method is mild, environmentally friendly, inexpensive and highly effective to give the products in good to excellent yields.
Keywords: Nanoparticles, ZnO, Multi-component reaction, 1,8-dioxooctahydro-xanthenes, 1,8-dioxo-decahydroacridines, solvent-free, one-pot synthesis.

Resumen. Las nanopartículas de ZnO se han utilizado como catalizador valioso y reciclable para la síntesis de un solo paso de 1,8-dioxo decahidroacridinas y 1,8-dioxooctahydro xantenos a través de reacciones multicomponentes bajo condiciones libres de disolvente. El método presentado es suave, respetuoso del medio ambiente, de bajo costo y altamente eficaz para dar los productos en rendimientos de buenos a excelentes.
Palabras clave: Nanopartículas, ZnO, reacción multicomponente, 1,8-dioxooctahidro-xantenos, 1,8-dioxo-decahidroacridinas, libre de disolvente, síntesis en un paso.

Introduction

Multi-component reactions (MCRs) are valuable device for assembling three or more reactants and converting them into higher molecular weight compounds. In recent years MCRs have become a powerful synthetic strategy, and the synthetic applications of these protocols are further made more attractive when the reactions are carried out under solvent free conditions [1].

Recently, metal oxides as efficient heterogeneous catalysts have been used in various organic transformations [2]. The development of new catalysts by nano-scale design has emerged as a fertile field for research and innovation [3, 4]. The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive nanocatalysts. Although metal oxide surface exhibits both Lewis acid and base properties, the nature of metal cation and surface area of the metal oxides have extensively amplify their catalytic properties. Zinc oxide is a low-priced metal oxide which has been used in both industrial and nano type as a professional catalyst in various organic transformations [5-9].

Nitrogen-containing heterocyclic compounds are widespread in Nature and their applications in biologically active pharmaceuticals, agrochemicals and functional materials are becoming more and more important [10-12]. Therefore, the development of new efficient methods for synthesis of *N*-heterocycles is one of the major interests of modern synthetic organic chemistry [13-16]. Recently, the synthesis of 1,8-dioxo-decahydroacridines via three-component coupling of aldehydes, dimedone and amines has been reported using MCRs in the presence of diverse catalysts including ceric ammonium nitrate (CAN)[17], fluorotailed acidic imidazolium salts[18], 1-*n*-butyl-3-methylimidazolium bromide [bmim]Br [19], 1-methylimidazolium triflouroacetate [Hmim]TFA [20], proline [21], amberlyst-15 [22], carbon-based solid acid (CBSA) [23], silica-bonded N-propyl sulfamic acid (SBNPSA) [24], 4-dodecylbenzenesulfonic acid (DBSA)[25] and $Zn(OAc)_2.2H_2O$ [26].

Xanthenes are one of the important classes of organic compounds which have been used as dyes, fluorescent material and in laser technologies [27]. Xanthenes have also received significant attention for many pharmaceutical and organic chemists essentially due to the broad spectrum of their biological and pharmaceutical properties such as antiviral [28], antibacterial [29], and antinociceptive activities [30]. Some progresses for the synthesis of 1,8-dioxooctahydro-xanthene derivatives have been reported in the literature *via* the condensation of two equivalent of dimedone with various aromatic aldehydes in the presence of different catalysts including $InCl_3.4H_2O$ in ionic liquid [31], *p*-dodecylbenzenesulfonic acid in water [32], Fe^{3+}-montmorilonite [33], $NaHSO_4$- SiO_2 or silica chloride [34], and amberlyst-15 [35].

However, some of these methods have some drawbacks, such as long reaction times, unsatisfactory yields and use of expensive catalysts. Therefore, it is necessary to develop a simple and green method for the synthesis of 1,8-dioxo-decahydroacridines and 1,8-dioxooctahydro-xanthenes without these problems.

In accordance with above-mentioned importance of multi-component reaction in heterocyclic synthesis and in the continuation of our research on the application of nanocatalysts in MCRs [36-39], we report here an efficient one-pot preparation of acridine and xanthene derivatives using ZnO nanoparticles (ZnO NPs) as a green and reusable catalyst under solvent-free conditions (Scheme 1).

Results and Discussions

In the preliminary experiments nano crystalline was and characterized by IR, SEM, XRD, BET and EDX analysis.

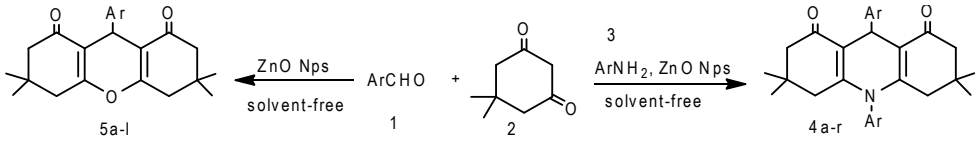
The chemical purification of samples as well as their stoichiometry was tested by EDX studies. As shown Figure 1A zinc and oxygen are the only elementary components of the prepared nanoparticles.

The crystalline nature of the synthesized ZnO nanoparticles was further verified by X-ray diffraction pattern (XRD). The XRD pattern of the ZnO NPs is shown in Figure 1B. All of the reflection peaks in Figure 1B can be easily indexed to pure Hexagonal phase of ZnO with P63mc group (JCDPS No. 36-1451). The crystallite size diameter (D) of the ZnO nanoparticles has been calculated by Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$), where β FWHM (full-width at half-maximum or half-width) is in radian and θ is the position of the maximum of diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength (1.5406 Å for Cu Kα). Crystallite size of ZnO has been found to be 24 nm.

In order to study the morphology and particle size of ZnO nanoparticles, SEM image of ZnO NPs was applied which is shown in Figure 2A. These results show that spherical ZnO NPs were gained from $Zn(CH_3COO)_2$ and $H_2C_2O_4.2H_2O$ with particle size between 20-30 nm under solvent-free conditions.

In FT-IR spectrum of ZnO NPs (Figure 2B) the band from 500-600 cm^{-1} is assigned to the stretching vibrations of (Zn–O) bond. The broad band with low intensity at 3422 cm^{-1} is related to vibration mode of (OH) group, indicating the presence of little amount of water adsorbed on the zinc oxide nanoparticles surfaces.

In addition, the specific surface area was measured by nitrogen physisorption (the BET method), the specific surface



Scheme 1. ZnO nanoparticles catalysed synthesis of acridine and xanthene derivatives.

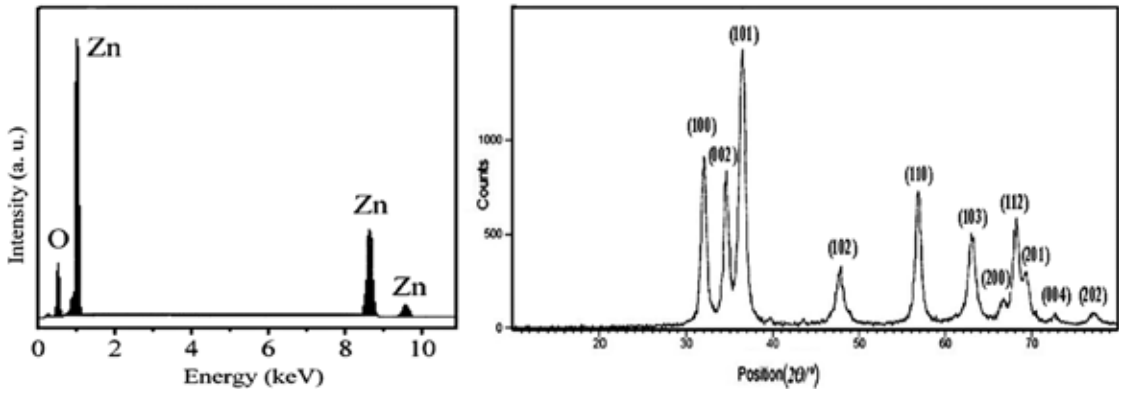


Fig. 1. EDX (A) and XRD (B) of ZnO nanoparticles.

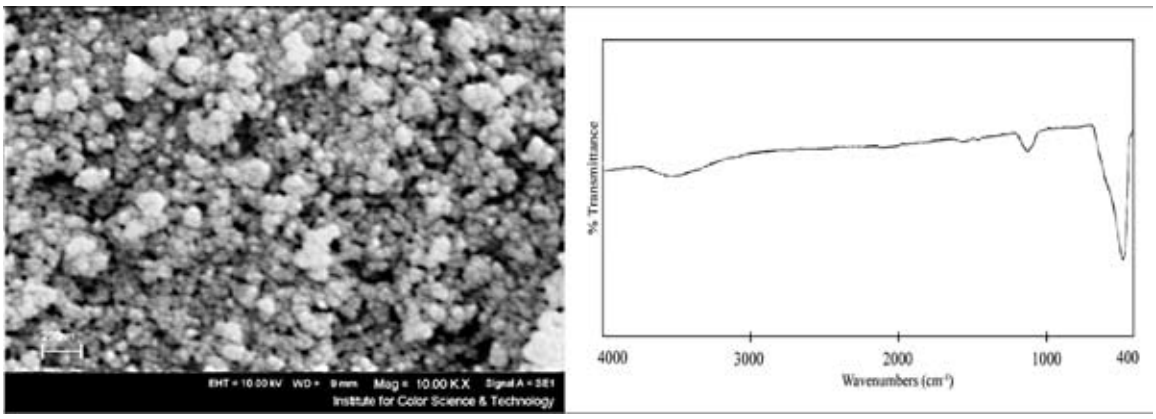


Fig. 2. SEM image (A) and FT-IR (B) of ZnO nanoparticles.

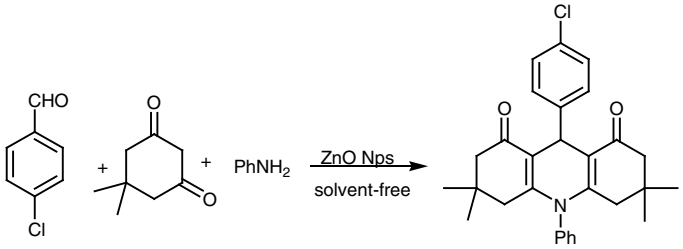
area was approximately 64 m^2/g. Also the theoretical particle size was calculated from the surface area and zinc oxide density (5.61 g/cm^3) from the equation was 21.1 nm.

$$D_{BET} = \left(\frac{6000}{\rho \times S}\right)$$

Firstly, in order to optimize the reaction conditions, the model reaction was carried out by using 4-chlorobenzaldehyde, dimedone and aniline under solvent-free conditions (Scheme 2).

Initially, to show the merits of the present work, a comparative study of the catalytic efficiency of ZnO with other catalysts was examined in the model study (Table 1). It was observed that ZnO exhibited high activity and the corresponding product was performed in high yield. Here, the higher catalytic activity of ZnO may be attributed to the surface area which is available for greater adsorption of the reactants on its surface. With in hand results, we encouraged to use ZnO nanoparticles instead of bulk ZnO in the test reaction. As result of this experiment we found that while ZnO nanoparticles used the reaction time decreased considerably. It seems that high surface area and better dispersion of nanoparticles in the reaction mixture are reasons for better activities of ZnO NPs.

Afterward, optimization of catalyst amounts was carried out in the model study by using different amounts of the ZnO NPs. The higher yield was obtained with increasing the amountof catalyst from 10 mol% to 12 mol%. However, further increase of the molar amount of the catalyst from 12 mol% to 20 mol% did not significantly increase the yield of the product



Scheme 2. The model reaction for the synthesis of acridine.

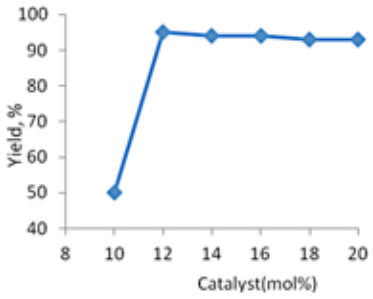


Fig. 3. Influence of the amount of the catalyst on the model reaction.

(Figure 3). Hence, the optimum concentration of ZnO NPs was chosen 12 mol% in the model reaction.

To improve the yield of the target product, we carried out the test reaction in presence of various solvents and the results are presented in Table 2. As can be seen from this table, solvent-free conditions accelerated the rate of reaction and also high yields were obtained for all products.

After optimization of the reaction conditions, we were encouraged to perform the reaction of 5,5-dimethyl-1,3-cyclohexanedione and aromatic aldehydes in the presence of ZnO NPs (12 mol%) under solvent-free condition. Therefore, a series of experiments were carried out and as a result of these reactions we produced some 1,8-dioxooctahydro-xanthene derivatives in excellent yields within a good period of time. So in this research we successfully prepared a small library of 1,8-dioxo-decahydroacridines and 1,8-dioxooctahydro-xanthenes in the presence of zinc oxide nanoparticles. As shown in Table 3 aromatic aldehydes with electron-withdrawing groups such as: NO_2 and Cl reacted faster than those with electron-releasing groups including OMe and Me as expected. Sterically hindered aromatic aldehydes required longer reaction times in comparison with *p*-substituted aryl aldehydes. The rate of reactions of these aldehydes decreased in comparison to aldehydes with electron-donating groups, but the yield of the corresponding products was higher than benzaldehydes with electron-donating groups. Also, aromatic amines containing electron-donating groups in *para* position reacted smoothly compared with other substituents (Table 3).

Table 1. The model study for the one-pot synthesis of acridine in the presence of various catalysts.

Entry	Catalyst	Catalyst (mol%); conditions	Time	Yield,[a]%
1	amberlyst-15[20]	200 mg; reflux conditions	4.5h	90
2	SBNPSA[22]	0.03 g; reflux conditions	2h	93
3	CBSA[21]	0.03 g; solvent-free, 100°C	30 min	84
4	Ceric ammonium nitrate (CAN)[15]	5 mol%; solvent PEG 400, 50°C	4h	98
5	Brønsted acidic imidazolium salts[16]	1.5 mol%; reflux conditions	4h	86
6	CuO	15 mol%; solvent-free, 120°C	1h	88
7	ZnO	15 mol%; solvent-free, 100°C	40 min	90
8	ZnO NPs[b]	12 mol%; solvent-free, 90°C	**7 min**	**95**

[a] Isolated yields.
[b] This work.

Table 2 Test reaction using different solvents.

Entry	Solvent	Time (min)	Yield[a],%
1	Ethanol	30	62
2	Methanol	30	59
3	CH_3CN	30	57
4	$CHCl_3$	30	53
5	Toluene	30	45
6[b]	Solvent-free condition	**7**	**95,94,94,93**

[a] Isolated yields.
[b]Catalyst was reused four times.

The reusability of the catalyst was examined by repeating of the model reaction using ZnO NPs 12 mol% nanoparticles under optimized reactions. The results of these experiments showed that the catalytic activity of nano ZnO did not decrease significantly even after five catalytic cycles.

In order to determine the catalytic behavior of zinc oxide nanoparticles, the possible mechanism for the coupling of aldehydes, dimedone and amines in the presence of ZnO NPs as an efficient catalyst is shown in Scheme 3. To the best of our knowledge, ZnO NPs catalyzes the reaction by electrophilic activation of the carbonyl groups of aldehyde and dimedone; this makes them susceptible to nucleophilic attack.

Experimental

General

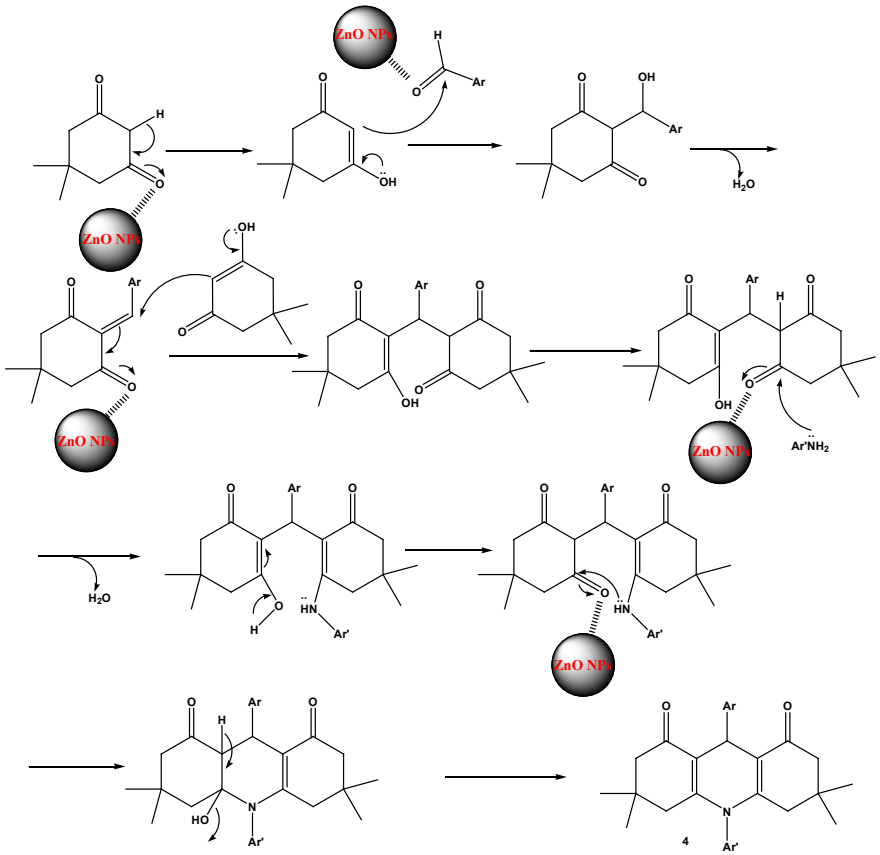
Chemicals were purchased from Fluka and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. Zinc oxide nanoparticles were prepared according to the procedure reported by Shen *et al.* [40]. All products were characterized by comparison of their FT-IR and NMR spectra and physical data with those reported in the literature. All yields refer to the isolated products. Progress of reactions was followed by TLC on silica-gel Polygram SILG/UV 254 plates. IR spectra were obtained on a Shimadzu FT-IR- 8300 spectrophotometer. NMR spectra were recorded on a Bruker Avance DRX instrument (400 MHz). The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. The N_2 adsorption/desorption analysis (BET) was performed at −196 ^oC using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Microscopic morphology of products was visualized by SEM (LEO 1455VP). PowderX-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation (λ = 1.5406 Å).The compositional analysis was done by energy dispersive analysis of X-ray (EDX, Kevex, Delta Class I).

Table 3. Preparation of 1,8-dioxo-decahydro-acridines (4**a-r**) and 1,8-dioxo-octahydro-xanthenes (5**a-l**) using ZnO NPs under solvent-free conditions.

Entry	Ar	Ar'	Product	Time (min)	Yield, %
1	C_6H_5	C_6H_5	**4a**	10	88
2	*o*-MeC_6H_4	C_6H_5	**4b**	25	70
3	*m*-MeC_6H_4	C_6H_5	**4c**	20	85
4	*p*-MeC_6H_4	C_6H_5	**4d**	15	85
5	*o*-$OMeC_6H_4$	C_6H_5	**4e**	15	75
6	*p*-$OMeC_6H_4$	C_6H_5	**4f**	10	80
7	*m*-$NO_2C_6H_4$	C_6H_5	**4g**	9	90
8	*p*-$NO_2C_6H_4$	C_6H_5	**4h**	5	95
9	*p*-ClC_6H_4	C_6H_5	**4i**	7	95
10	*p*-BrC_6H_4	C_6H_5	**4j**	7	90
11	C_6H_5	*p*-MeC_6H_4	**4k**	10	88
12	*p*-$NO_2C_6H_4$	*p*-MeC_6H_4	**4l**	5	90
13	*m*-$NO_2C_6H_4$	*p*-MeC_6H_4	**4m**	9	92
14	*p*-ClC_6H_4	*p*-MeC_6H_4	**4n**	5	97
15	*m*-ClC_6H_4	*p*-MeC_6H_4	**4o**	8	95
16	*p*-MeC_6H_4	*p*-$OMeC_6H_4$	**4p**	10	90
17	*p*-CNC_6H_4	*p*-$OMeC_6H_4$	**4q**	9	92
18	C_6H_5	*p*-$OMeC_6H_4$	**4r**	10	90
19	C_6H_5	-	**5a**	10	92
20	*p*-MeC_6H_4	-	**5b**	15	87
21	*p*-$OMeC_6H_4$	-	**5c**	15	85
22	*p*-$NO_2C_6H_4$	-	**5d**	5	97
23	*p*-ClC_6H_4	-	**5e**	7	95
24	*p*-BrC_6H_4	-	**5f**	7	90
25	*p*-OHC_6H_4	-	**5g**	12	80
26	*o*-$NO_2C_6H_4$	-	**5h**	10	85
27	*p*-CNC_6H_4	-	**5i**	12	90
28	*p*-$SMeC_6H_4$	-	**5j**	15	86
29	*p*-$CH(CH_3)_2C_6H_4$	-	**5k**	20	80
30	*p*-$CHOC_6H_4$	-	**5l**	10	90

General procedure for the preparation of ZnO nanoparticles

In a typical procedure, zinc acetate (9.10 g, 0.05 mol) and oxalic acid (5.4 g, 0.06 mol) were combined by grinding in an agate mortar for 1h at room temperature. Afterwards, the as-prepared $ZnC_2O_4.2H_2O$ nanoparticles were calcinated at 450^oC for 30 min to produce ZnO nanoparticles under thermal decomposition conditions. The prepared ZnO NPs have been structurally characterized by IR, XRD, EDX, BET and SEM analysis.



Scheme 3. Proposed mechanism pathway for the ZnO NPs catalyzed synthesis of acridines.

General procedure for the preparation of 1,8-dioxo-decahydroacridine derivatives

A mixture of dimedone **1** (2 mmol), aromatic aldehyde **2** (1 mmol), aromatic amines **3** (1 mmol), and ZnO NPs (12 mol%, 0.11 mmol) was heated in the oil bath at 90 °C for 5-25 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be recycled by a simple filtration. The product was then collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give pure compounds 4a-r in high yields.

General procedure for the preparation of 1,8-dioxo-octahydro-xanthene derivatives

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (0.14 g, 1 mmol), aldehydes (0.5 mmol) and ZnO NPs (12 mol%, 0.11 mmol) was heated at 100 °C for 5-20 min. After complete conversion as monitored by TLC, the system was cooled to room temperature and dissolved in 10 mL of dichloromethane. The catalyst was insoluble in CH_2Cl_2 and separated by a simple filtration. The solvent was evaporated and the solid obtained recrystallized from ethanol to afford the pure 1,8-dioxo-octahydro-xanthenes.

3,3,6,6-Tetramethyl-9-(2-methylphenyl)-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (4b). Yellow powder: mp 225-227°C; IR (KBr) υ_{max} 2952, 2875, 1644 (C=O), 1572 (C=C), 1366 (C-N), 1224, 845 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.81 (6H, s, 2 × CH_3), 0.95 (6H, s, 2 × CH_3), 1.79-1.84 (2H, d, J = 16 Hz, 2 × CH), 2.05-2.09 (2H, d, J = 16.5 Hz, 2 × CH), 2.12-2.16 (2H, d, J = 16.5 Hz, 2 × CH), 2.18-2.22 (2H, d, J = 16 Hz, 2 × CH), 2.32 (3H, s, CH_3), 5.25 (1H, s, CH), 7.13-7.31 (5H, m, ArH), 7.55-7.57 (4H, m, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.15, 26.86, 29.71, 32.33, 32.39, 41.51, 51.33, 112.11, 114.76, 127.43, 128.85, 129.41, 130.12, 131.55, 135.22, 139.09, 144.80, 150.11, 195.72; EI MS *m/z*: 439 $[M]^+$. *Anal.* C 81.82%, H 7.65%, N 3.28%, Calcd. For $C_{30}H_{33}NO_2$, C 81.97%, H 7.57%, N 3.19%.

3,3,6,6-Tetramethyl-9-(3-methylphenyl)-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (4c). Yellow powder: mp 208-210°C; IR (KBr) υ_{max} 2954, 2873, 1642 (C=O), 1574 (C=C), 1362 (C-N), 1221, 842 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79 (s, 6H, 2 × CH_3), 0.94 (s, 6H, 2 × CH_3), 1.78-1.85 (d, J = 16.2 Hz, 2H, 2 × CH), 2.05-2.08 (d, J = 16.6 Hz, 2H, 2 × CH), 2.13-2.17 (d, J = 16.6 Hz, 2H, 2 × CH), 2.20-2.46 (d, J = 16.2 Hz, 2H, 2 × CH), 2.31 (s, 3H, CH_3), 5.24 (s, 1H, CH), 6.91(s, 1H, ArH), 7.13-7.26 (m, 3H, ArH), 7.44-7.61 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.12, 26.82, 29.78, 32.29, 32.35, 41.49, 51.41, 112.12, 115.13, 127.45, 128.71, 129.83, 131.11, 132.15, 135.73, 138.99, 145.12, 150.18, 195.65;

EI MS *m/z*: 439 $[M]^+$. *Anal.* C 82.08%, H 7.48%, N 3.11%, Calcd. For $C_{30}H_{33}NO_2$, C 81.97%, H 7.57%, N 3.19%.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-10-(p-tolylphenyl)-1,2,3,4,5,6,7,8,9,10 decahydroacridine-1,8-dione (4l). Yellow powder: mp 272-274°C; IR (KBr) υ_{max} 2956 (C=C), 2873, 1639 (C=O), 1576 (C=C), 1514 (NO2), 1359, 1344 (NO_2), 1222, 863 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (s, 6H, 2 × CH_3), 1.12 (s, 6H, 2 × CH_3), 1.84-1.88 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.07-2.13 (m, 4H, 4 × CH), 2.23-2.28 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.50 (s, 3H, CH_3), 5.34 (s, 1H, CH), 7.09-7.11(d, *J* = 7.2 Hz, 2H, ArH), 7.37-7.39 (d, *J* = 7.2 Hz, 2H, ArH), 7.59-7.61 (d, *J* = 8.1 Hz, 2H, ArH), 8.12-8.14 (d, *J* = 8.1 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.42, 26.72, 29.66, 32.39, 32.88, 41.71, 50.12, 113.52, 116.51, 123.55, 128.83, 129.72, 138.18, 146.22, 148.11, 150.42, 152.91, 195.69; EI MS *m/z*: 484 $[M]^+$. *Anal.* C 74.22%, H 6.78%, N 5.89%, Calcd. For $C_{30}H_{32}N_2O_4$, C 74.36%, H 6.66%, N 5.78%.

3,3,6,6-Tetramethyl-9-(4-cyanophenyl)-10-(4-methoxyphenyl)-1,2,3,4,5,6,7,8,9,10 decahydroacridine -1,8-dione (4q). Yellow powder: mp 233-235°C; IR (KBr) υ_{max} 2957, 2875, 2224 (C≡N), 1640 (C=O), 1574 (C=C), 1510, 1364 (C-N), 1221, 849 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79 (s, 6H, 2 × CH_3), 0.96 (s, 6H, 2 × CH_3), 1.84-1.89 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.06-2.10 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.13-2.22 (m, 4H, 4 × CH), 3.93 (s, 3H, OCH_3), 5.28 (s, 1H, CH), 7.06-7.08(d, *J* = 8.4 Hz, 2H, ArH), 7.11-7.13 (d, *J* = 8.4 Hz, 2H, ArH), 7.54 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.74, 29.68, 32.37, 33.69, 41.81, 50.06, 55.66, 109.56, 113.53, 115.13, 119.34, 128.81, 131.09, 132.00, 150.95, 151.64, 160.00, 195.74; EI MS *m/z*: 480 $[M]^+$. *Anal.* C 77.32%, H 6.65%, N 5.9%, Calcd. For $C_{31}H_{32}N_2O_3$, C 77.47%, H 6.71%, N 5.83%.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-isopropylphenyl)-2H-xanthene-1,8(5H,9H)-dione(5k). Yellow solid: mp 203-206°C; IR (KBr) υ_{max} 3071, 2961, 1665 (C=O), 1624 (C=C), 1359, 1198 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.00 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 1.18 (6H, d, 2 × CH_3), 2.16-2.26 (4H, m, 2 × CH_2), 2.46 (4H, s, 2 × CH_2), 2.78-2.81 (1H, m, CH), 4.73 (1H, s, CH), 7.04-7.06(2H, d, 2 × CH), 7.17-7.19 (2H, d, 2 × CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.9, 27.4, 29.2, 31.3, 32.2, 33.6, 40.8, 50.8, 115.8, 126.1, 128.1, 141.3, 146.5, 162.1, 196.4; EI MS *m/z*: 392 $[M]^+$. *Anal.* C 79.39%, H 8.36%, Calcd. For $C_{26}H_{32}O_3$, C 79.56%, H 8.22%.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-cyanophenyl)-2H-xanthene-1,8(5H,9H)-dione(5i). Yellow solid: mp 216-217°C; IR (KBr) υ_{max} 2960, 2225 (C≡N), 1663 (C=O), 1620 (C=C), 1362, 1199 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.99 (6H, s, 2 × CH_3), 1.12 (6H, s, 2 × CH_3), 2.15-2.28 (4H, m, 2 × CH_2), 2.49 (4H, m, 2 × CH_2), 4.77 (1H, s, CH), 7.41-7.43 (2H, d, 2 × CH), 7.52-7.54 (2H, d, 2 × CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.3, 29.2, 32.2, 32.4, 40.8, 50.6, 110.2, 114.6, 119.0, 129.2, 132.0, 149.4, 162.9, 196.3; EI MS *m/z*: 375 $[M]^+$. *Anal.* C 76.92%, H 6.86%, N 3.82%, Calcd. For $C_{24}H_{25}NO_3$, C 76.77%, H 6.71%, N 3.73%.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-thiomethylphenyl)-2H-xanthene-1,8(5H,9H)-dione(5j). White solid: mp 256-257°C; IR (KBr) υ_{max} 2963, 1661 (C=O), 1621 (C=C), 1368, 1221(C-O) cm^{-1}, ^1H NMR ($CDCl_3$, 400 MHz) δ 1.02 (6H, s, 2 × CH_3), 1.11 (6H, s, 2 × CH_3), 2.14-2.25 (4H, m, 2 × CH_2), 2.45 (4H, m, 2 × CH_2), 2,78 (3H, s, SMe), 4.95 (1H, s, CH), 7.14-7.16 (2H, d, 2 × CH), 7.25-7.27 (2H, d, 2 × CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.3, 29.2, 30.9, 32.1, 40.8, 50.7, 52,1, 113.4, 115.7, 129.3, 136.5, 157.9, 162.1, 196.4; EI MS *m/z*: 396 $[M]^+$. *Anal.* C 72.82%, H 6.99%, Calcd. For $C_{24}H_{28}O_3$, C 72.69%, H 7.12%.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-formylphenyl)-2H-xanthene-1,8(5H,9H)-dione(5l). White solid: mp 211-213°C; IR (KBr) υ_{max} 2959, 2873, 2781, 1728 (C=O), 1663 (C=O), 1618 (C=C), 1517, 1358, 1200 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.99 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.14-2.25 (4H, m, 2 × CH_2), 2.45 (4H, s, 2 × CH_2), 4.70 (1H, s, CH), 7.34-7.36 (2H, d, 2 × CH), 7.75-7.77 (2H, d, 2 × CH), 9.65 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.3, 29.2, 31.5, 32.2, 40.8, 50.76, 115.1, 120.2, 130.1, 131.1, 143.2, 162.4, 196.4, 205.1; EI MS *m/z*: 378 $[M]^+$. *Anal.* C 76.05%, H 7.09%, Calcd. For $C_{24}H_{26}O_4$, C 76.17%, H 6.92%.

Conclusions

We have efficiently synthesized some acridine and xanthene derivatives in the presence of zinc oxide nanoparticles under solvent-free conditions. Zinc oxide nanoparticles as a green, mild and effective catalyst satisfactorily catalyzed the synthesis of some biologically active heterocyclic compounds. Surprisingly, some of the reactions proceeded in the presence of this catalyst under solvent-free conditions and are among the fastest reported in the literature. The catalyst was recyclable and has been reused for five successive runs with little loss of the catalytic activities.

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