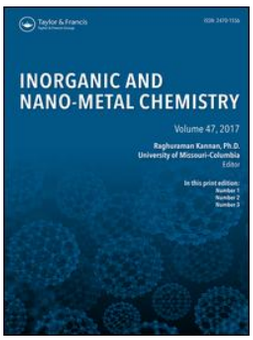

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γ-Fe_2O_3@Si-$(CH_2)_3$@mel@$(CH_2)_4SO_3H$ as a magnetically bifunctional and retrievable nanocatalyst for green synthesis of benzo[c]acridine-8(9*H*)-ones and 2-amino-4*H*-chromenes

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ABSTRACT

The present work describes the synthesis and characterization of melamine functionalized with sulfonic acid supported on the magnetic nanoparticle, γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid nanoparticle as a green and retrievable bifunctional catalyst. This catalyst was assigned by FT-IR, XRD, EDX, TEM, VSM, CHN, and TGA analyses. In addition, the catalytic activity of this new catalyst was investigated for the synthesis of 7,10,11,12-tetrahydrobenzo[c]acridine-8(9*H*)-ones from aliphatic and aromatic aldehydes, dimedone and 1-naphthylamine in excellent yields and 2-amino-4*H*-chromenes were provided using manufactured nanocatalyst in good-to-high yield under mild reaction condition. The γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid heterogeneous catalyst showed the advantages such as very simple and eco-friendly due to use from magnetic nanoparticles as high reusability of the catalyst, magnetically separable catalyst, excellent yield, and mild reaction condition. The synthesis of some new derivatives of dibenzo[*c*]acridines and 2-amino-4H-chromenes in the presence of this nanocatalyst is also reported.

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γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid; nanoparticle; melamine; acridine; chromene

Introduction

Almost the heterocyclic compounds are the most attention in pharmaceutical chemistry. Among heterocyclic compounds, the tricyclic compounds containing acridine skeleton is a significant pharmacophore and interesting structure in pharmacology. Acridine derivatives have antitumor,[1] carcinogenic,[2] and anti-malaria activities.[3] In addition, these organic compounds can be applied for heart defibrillation[4] and as DNA-intercalating anticancer drugs.[5] Therefore, the synthesis of acridine derivatives is principal task in modern organic chemistry. Although numerous methods have been introduced in the providing of benzoacridine derivatives,[6–15] in recent studies, Borah's group successfully synthesized benzoacridine derivatives via *N,N*-disulfo-1,1,3,3-tetramethylguanidinium carboxylate ionic liquids as a catalyst,[16] Murugesan et al. used sulfonic acid functionalized boron nitride as a catalyst in the preparation of acridine derivatives, [17] Wan et al. modified glucose sulfonic acid and applied in the synthesis of acridine derivatives,[18] and Shen et al. synthesized acridine derivatives using imidazolium salts as ionic liquids catalyst,[19] but these methods in spite of advantages have their shortcomings, such as low yield, high reaction temperature, and prolong reaction time.

On the other hand, more progress in the field of green synthesis has reported magnetically recoverable nanocatalysts which possess expansive surface area, high activity, reusability, and long lifetime.[22–29] The use of magnetic nanocatalysts is an interesting area for the development of sustainable and green procedures due to external magnetic separation and no needing to catalyst filtration or centrifugation, and providing simple and practical method for the recovering of these catalysts. Also, multi-component reactions (MCRs) are very powerful weapons in the organic and medicinal chemistry for the preparation of the bulky products in a one-pot and almost one-step from small starting materials. The combination of magnetic nanocatalysts and MCRs will become a merits protocol for the introducing of green procedures in green synthesis.[30] Moreover, on the base of the best our knowledge, γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid as a new, reusable, bifunctional heterogeneous nanoparticles catalyst was first utilized in the one-pot preparation of benzo[c]acridines. In this communication, in the present work, we enclosed the synthetic applicability of a prepared catalyst (magnetic-based butyl sulfonic acid–melamine complex) in the synthesis of benzo[c]acridines in one-pot and under mild reaction condition in ethanol at 60 °C with low reaction times (Scheme 1).

Experimental

Chemicals were purchased from Merck Chemical Company. Drying of the solvents was done using standard methods. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker Advance DPX-300 instrument, Germany country. SEM analysis was determined by using FE-TESCAN, model Mira3-XMU, Czech Republic country at accelerating voltage of 15 KV. TEM analysis was performed using Philips CM30

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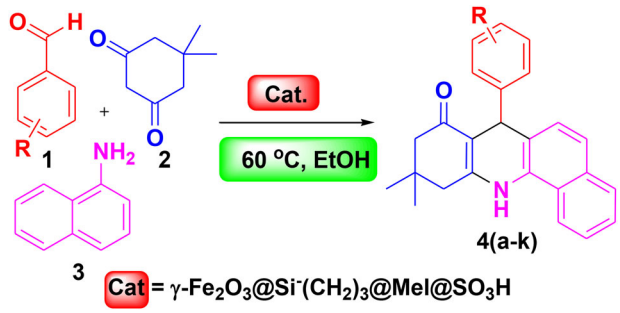
instrument, Nederland country. XRD analysis was measured on a Bruker D8-advance X-ray diffractometer or on an X'Pert Pro MPD diffractometer, Nederland country with Cu Kα ($\lambda = 0.154$ nm) radiation. TGA analysis was recorded using a Shimadzu Thermogravimetric analyzer (TG-50), Japan country. FT-IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer, Japan country. Elemental analysis was performed on a Costech 4010 CHN elemental analyzer, Italy country.

Synthesis of γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid nanoparticle. The synthesis of magnetic Fe_3O_4 nanoparticles, γ-Fe_2O_3@Si-$(CH_2)_3$Cl nanoparticles, and γ-Fe_2O_3@Si-$(CH_2)_3$@melamine nanoparticles were carried out according to the previous procedure reported in the literature.[31,32] Then, the γ-Fe_2O_3@Si-$(CH_2)_3$@melamine nanoparticles (1.0 g) were sonicated in 30 mL of dry THF at 30 min. Next, 1,4-butane sultone (5.0 mmol) was added and refluxed at 24 h. Then, the catalyst was separated using an external magnet, washed with ethanol (3 × 15 mL), water (2 × 15 mL), and dried in a vacuum oven at 50 °C and 4.0 h (Scheme 2).



Scheme 1. Providing of benzo[c]acridin-8(7*H*)-ones.

General procedure for the synthesis of 7,10,11,12-tetrahydrobenzo[c]acridine-8(9H)-ones using γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid. A mixture of 1-naphthylamine (1.0 mmol), dimedone (1.0 mmol), aldehydes (1.0 mmol), and prepared magnetic nanoparticle (0.004 g) in ethanol (2.0 mL) was taken in a flask and the reaction mixture was mixed at 60 °C for appreciating times in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed with an external magnet and then water poured to the reaction mixture to obtain precipitation. Finally, the isolated precipitation recrystallized with ethanol to attained absolute product in 95% yield.

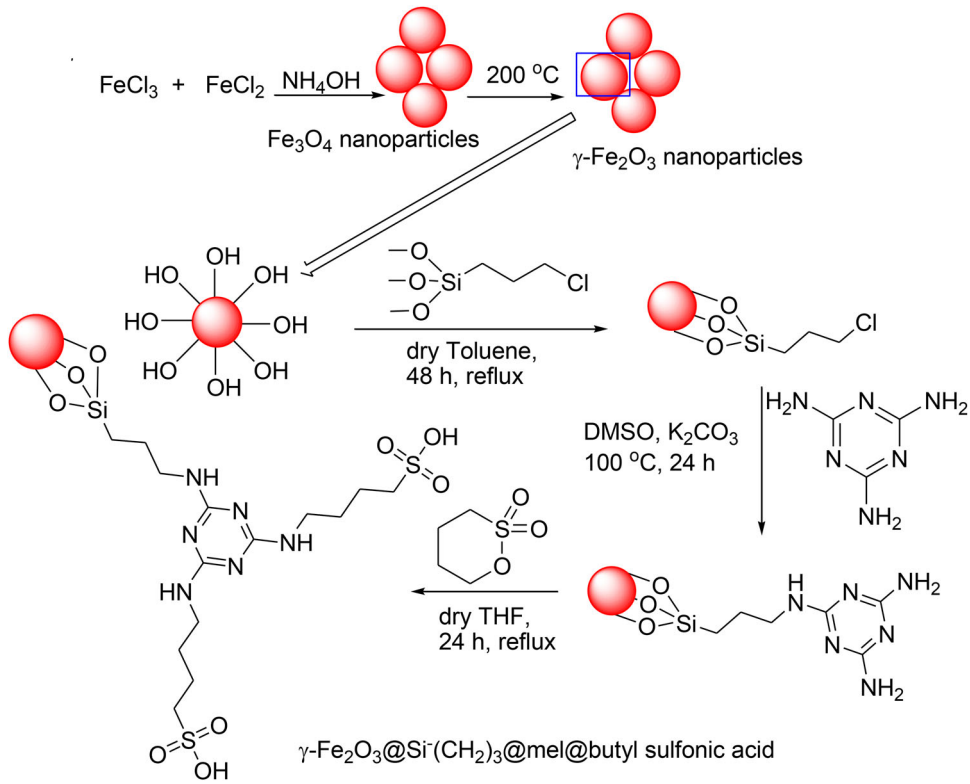
Reusability of the catalyst

The reusability of the catalyst was examined in the synthesis of **4a**. At the end of the reaction, the catalyst was removed with an external magnet and washed with ethanol (2 × 5 mL) and then used it without further purification. The separated catalyst was reused three times in the preparation of **4a** without considerable loss of its catalytic activity (entry 1, Table 1; 95%, 95%, and 94%). In addition, FT-IR analysis was exhibited that the catalytic activity of the catalyst was the same as those of the freshly used catalyst (Figure 1).

Results and discussion

Characterization of the nanocatalyst

The FT-IR spectra of the intermediate nanoparticles and final catalyst are shown in Figure 2. The band at 1025 cm^{-1}



Scheme 2. Manufactured of γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid nanoparticle.

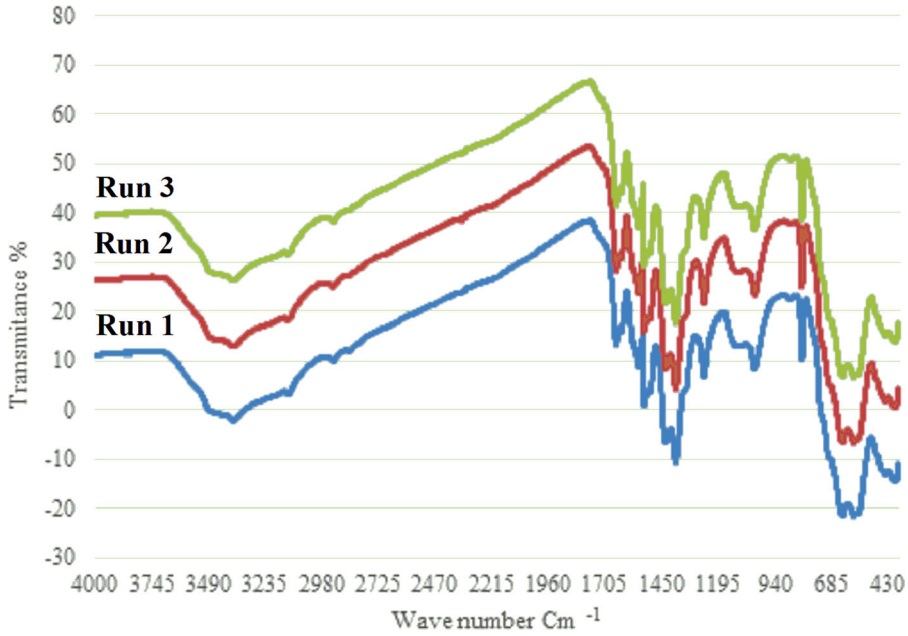


Figure 1. FT-IR spectra of the recovered γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H after three runs.

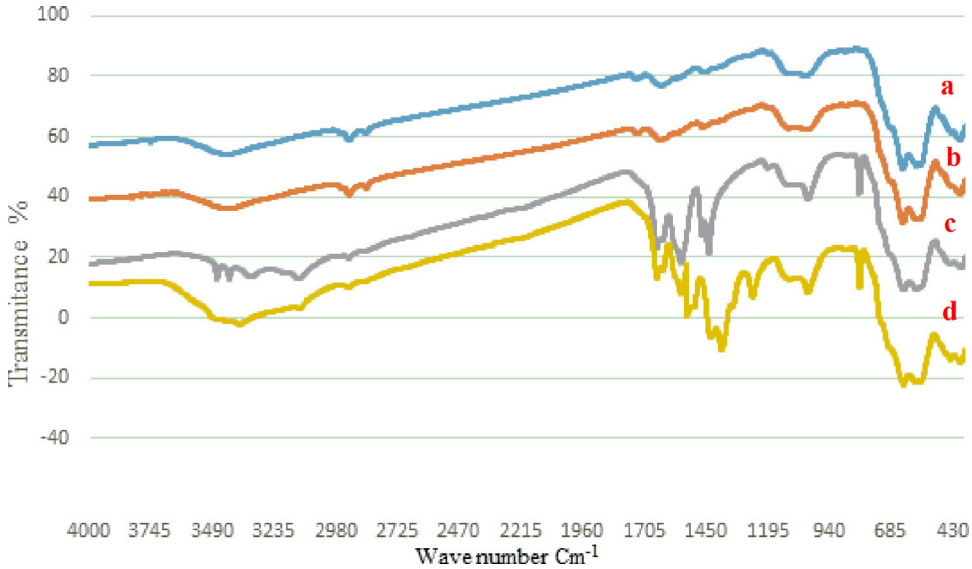


Figure 2. FT-IR spectra of intermediate nanoparticles and prepared catalyst: γ-Fe_2O_3 (a), γ-Fe_2O_3@Si-$(CH_2)_3$Cl (b), γ-Fe_2O_3@Si-$(CH_2)_3$@Mel (c), and γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H (d).

relatives to SiO of γ-Fe_2O_3@Si-$(CH_2)_3$ the nanoparticles, and that at 2921 cm^{-1} is related to CH_2 of propyl in γ-Fe_2O_3@Si-$(CH_2)_3$ nanoparticles. The band at 3424 and 3415 cm^{-1} confirms the presence of NH_2 group of melamine, loaded on the surface of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel. The broadband at 3380 cm^{-1} corresponds to the OH group, and that at 1653 cm^{-1} is related to S = O of SO_3H in γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

The TGA curve of the synthesized catalyst is indicated in Figure 3. The first mass loss up to 160 °C (region A) is due to the release of adsorbed water; the second from 200 to 515 °C is related to the decomposition of organic matter on the γ-Fe_2O_3 core (region B). Region C attributes to γ-Fe_2O_3. The TGA curve of the synthesized catalyst demonstrates high thermal stability, with decomposition starting at around 200 °C under a nitrogen atmosphere.

Also, the XRD pattern of the catalyst is shown in Figure 4. The reflection planes of (220), (311), (400), (422), (511), and (440) at $2\theta = 30.3$, 35.7, 43.4, 53.8, 57.4, and 63.0, which are attributed to the diffraction scattering of γ-Fe_2O_3 were readily recognized from the XRD pattern. These characteristic peaks adopted with those of standard γ-Fe_2O_3 (JCPDS file No 04-0755). The observed diffraction peaks were indicated that γ-Fe_2O_3 mostly exist in a face-centered cubic structure.

The SEM and TEM images of the synthesized magnetic nanocatalyst are shown in Figures 5–7. As can be seen from SEM images (Figure 5), the geometric shape of the nanoparticles is spherical. To investigate the morphology and topography of the described catalyst, TEM was carried out as shown in Figure 6. As it is clearly approved the spherical uniform of the catalyst particles and confirmed that the catalyst has nanosize particles.

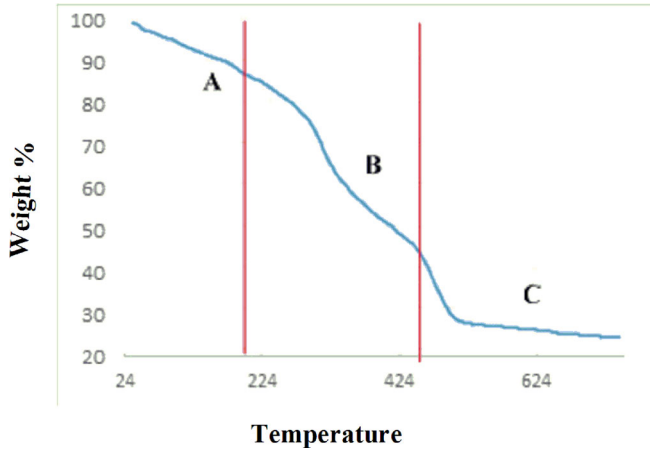


Figure 3. TGA analysis of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H. **A)** γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H without H_2O; **B)** γ-Fe_2O_3@Si-$(CH_2)_3$@Mel, γ-Fe_2O_3@Si-$(CH_2)_3$; **C)** γ-Fe_2O_3.

The cumulative distribution function shows that the nanoparticles have sizes between 12 and 24 nm that the utmost of nanoparticle size was 17 nm (Figure 7), respectively, that according to research, the smaller and uniform particles exhibited better physical and magnetic properties.[28]

The loading amount of melamine on γ-Fe_2O_3@Si-$(CH_2)_3$@melamine was determined by elemental analysis, and the C, N, and H contents of γ-Fe_2O_3@Si-$(CH_2)_3$@melamine was quantified 9.56, 9.88, and 1.55, respectively, that it can result from 1.2 mmol melamine on the surface of γ-Fe_2O_3@Si-$(CH_2)_3$. Thus γ-Fe_2O_3@Si-$(CH_2)_3$@melamine can react with 4.8 mmol 1,4-butan sultone to achieve SO_3H functionalized theoretically, whereas the S content of γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@SO_3H was 4.1 mmol approximately based on EDAX analysis (Figure 8).

To evaluate the magnetic properties of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H and to investigate the effect of Si-$(CH_2)_3$@Mel@butylSO_3H on the magnetic feature of

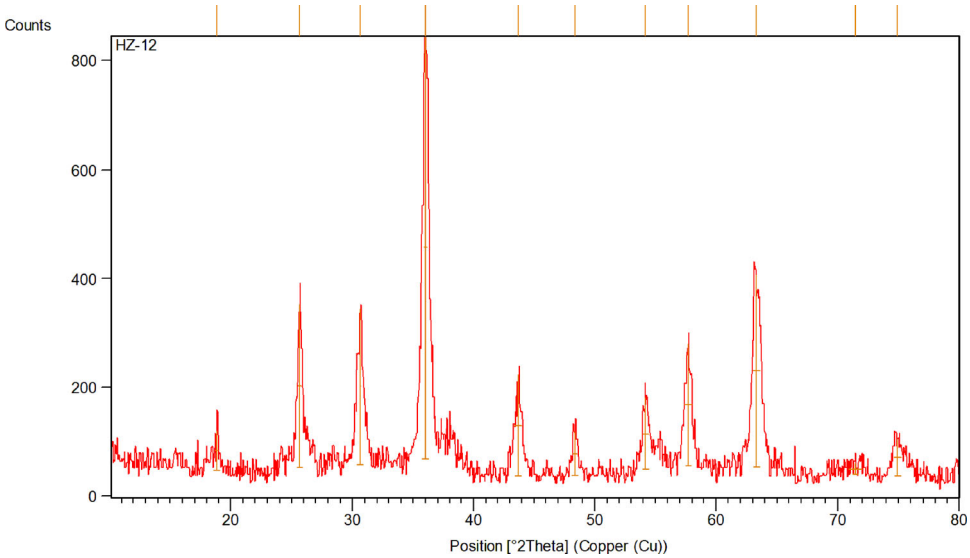


Figure 4. XRD analysis of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

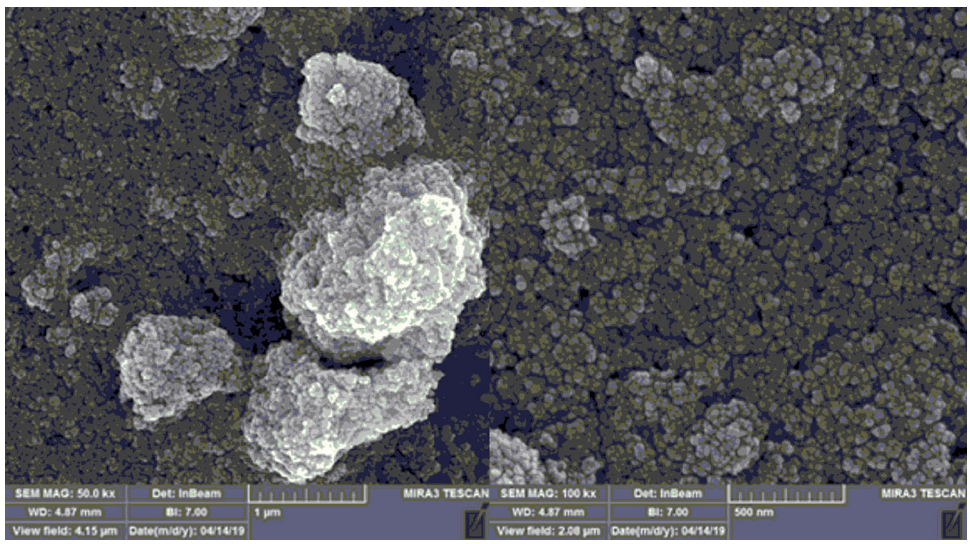


Figure 5. SEM analysis of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

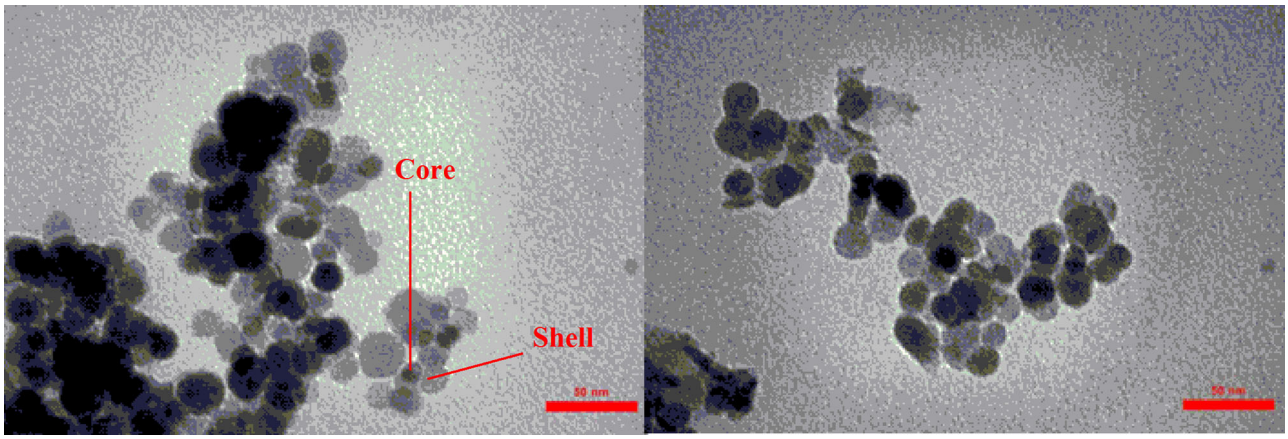


Figure 6. TEM analysis of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

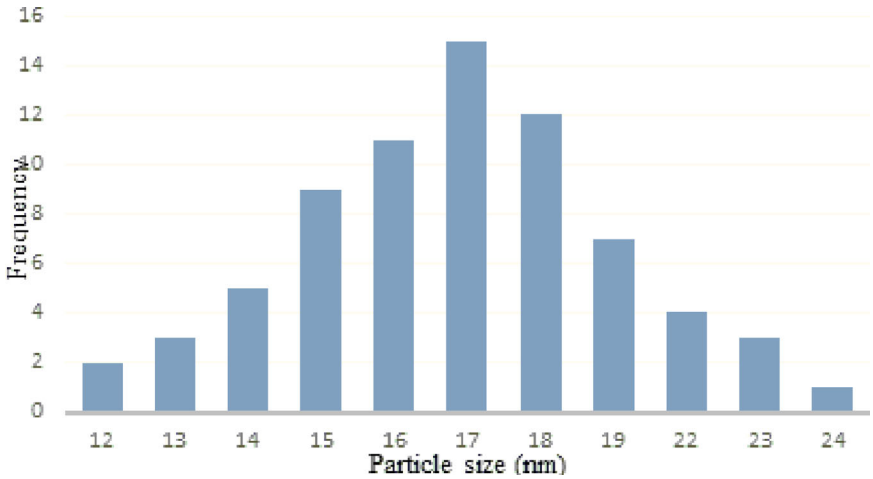


Figure 7. Particle size of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

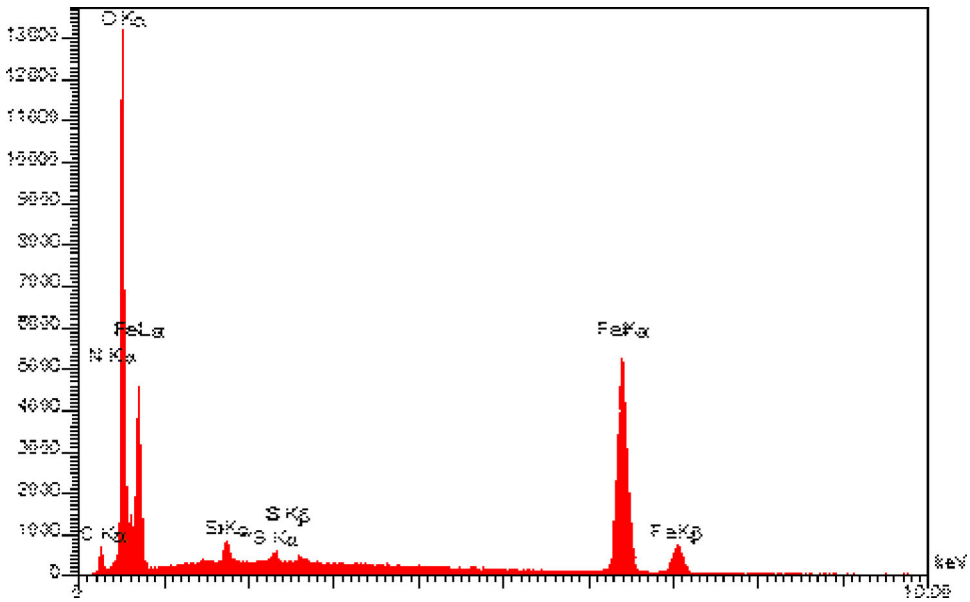


Figure 8. EDX analysis of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H.

γ-Fe_2O_3, the magnetic property of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H was performed *via* VSM analysis and compared with that of γ-Fe_2O_3. The results, in Figure 9 showed that upon bounding between Si-$(CH_2)_3$@Mel@butylSO_3H and γ-Fe_2O_3, the magnetic property decreased from 95 to 65 $emug^{-1}$. This result is not beyond expectation as incorporation of nonmagnetic component, Si-$(CH_2)_3$@Mel@butylSO_3H, can decrease the

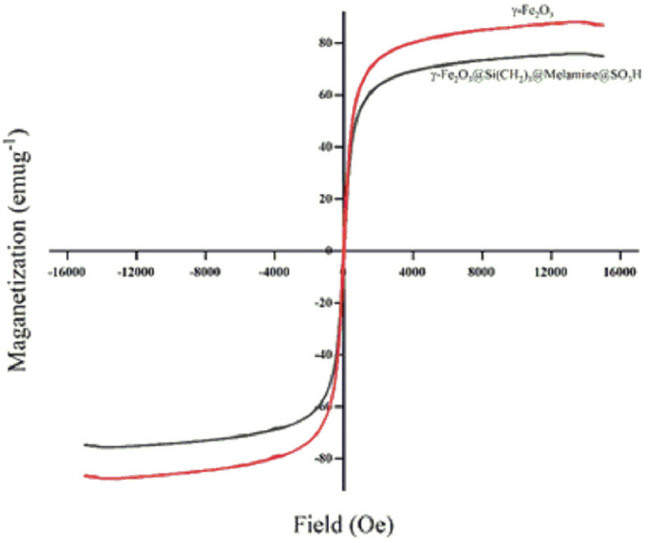


Figure 9. VSM analyses of γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H and γ-Fe_2O_3.

magnetic property. Despite the decrease of the magnetic property, γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H could be magnetically recovered *via* using an external magnet.

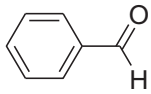
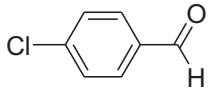
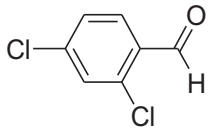
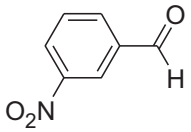
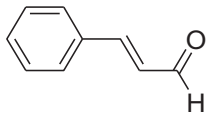
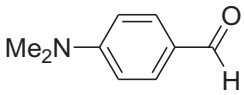
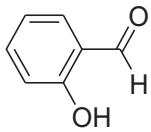
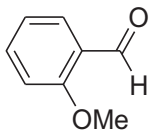
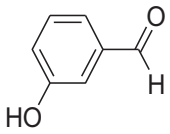
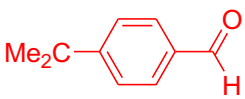
Catalytic activity evaluation

To examine the solvent type effect on the reaction yield and time, the model reaction for the providing of **4a** was subjected in various solvents including dimethylformamide (DMF), water, tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and ethanol, n-hexane, dichloromethane, ethyl acetate, and without solvent. The results are presented in Table 2. The reaction was first carried out at room temperature and 60 °C under solvent-free condition in 120 min and the product was resulted in 10% and 35% yield. When the benchmark reaction was tested by the above mention solvents, the desired product was yielded in better condition than without solvent. As can be seen in Table 2, the best solvent was ethanol. To more investigate the catalyst amount effect on the reaction time, the obtained optimum solvent was repeated in the different amount of the catalyst including to 0.002, 0.004, 0.006 g, and without the catalyst. As one can see, in the absence of catalyst, even with a time greater than 15 min, the yield is low (45%). Also, increasing the catalyst amount to 0.006 g did not effect on reaction time and yield. So, the catalyst is essential component for the progress of the reaction. Therefore, entry 9, Table 2 was used as the best optimum reaction condition.

Also, the model reaction was examined for the synthesis of **4a** in the presence of γ-Fe_2O_3, γ-Fe_2O_3@Si-$(CH_2)_3$Cl, γ-Fe_2O_3@Si-$(CH_2)_3$@Mel and the results were compared with those of using γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H. As shown in Table 1, the best result was obtained by γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H (entry 5, Table 3).

To generalize this model reaction, the optimum reaction condition was fixed for a series of aliphatic and aromatic aldehydes with electron-withdrawing and electron-donating groups for the synthesis of the corresponding dibenzo[c] acridines. Found in Table 1, in all cases, the yields were excellent. Therefore, this protocol is suitable for both aliphatic and aromatic aldehydes bearing electron-releasing and electron-withdrawing groups. Also, cinnamaldehyde and acetaldehyde were subjected as aliphatic aldehydes under reaction condition and the reaction was carried out well in good yields and short reaction times (entry 5 and 9, Table 1). In addition, the method is easy to operate, very simple, and eco-friendly due to use from magnetic nanoparticle as

Table 1. Synthesis of 7,10,11,12-tetrahydrobenzo[*c*]acridine-8(9*H*)-ones using γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid nanoparticle.

Entry	Aldehyde	Product	Time (min)	Yield%[a]	m.p (°C) [ref.]
1		4a	15	95	258–261[10]
2		4b	15	90	260–260[13]
3		4c	10	98	284–286[7]
4		4d	10	95	268–270[14]
5		4e	25	95	175–178 [14]
6		4f	30	92	277–279 [33]
7		4g	50	93	219–221[14]
8		4h	60	91	267–270[6]
9		4i	30	90	190–192 [34]
10		4j	40	94	187–191[14]
11		4k	35	90	214–216 (new)

[a]Isolated yield.

Table 2. The optimization of reaction condition for the preparation of **4a** using γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid nanoparticle.

Entry	Catalyst (g)	Solvent	Temp. (°C)	Time (min)	Yield[a]%
1	0.004	Free	r.t	120	10
1	0.004	Free	60	120	35
2	0.004	H_2O	100	15	60
3	0.004	EtOH	r.t.	300	75
4	0.004	THF	60	120	40
5	0.004	DMF	60	60	55
6	0.004	DMSO	60	60	60
7	–	EtOH	60	120	45
8	0.002	EtOH	60	20	90
9	0.004	EtOH	60	15	95
10	0.006	EtOH	60	15	95
11	0.004	n-Hexane	Reflux	180	10
12	0.004	CH_2Cl_2	Reflux	180	10
13	0.004	EtOAc	Reflux	180	75

[a]Reaction condition: 1-naphthylamine (1 mmol), dimedone (1 mmol), benzaldehyde (1 mmol) catalyst in solvent (5 mL) at different times.

Table 3. The optimization of reaction condition for the preparation of **4a** using different of nanoparticle catalysts.

Entry	Catalyst	Yield[a]%
1	Free	35
2	γ-Fe_2O_3	40
3	γ-Fe_2O_3@Si-$(CH_2)_3$Cl	40
4	γ-Fe_2O_3@Si-$(CH_2)_3$@Mel	55
5	γ-Fe_2O_3@Si-$(CH_2)_3$@Mel@butylSO_3H	95

[a]Reaction condition: 1-naphthylamine (1 mmol), dimedone (1 mmol), benzaldehyde (1 mmol), catalyst (0.004 g) in ethanol (5 mL) at 60 °C and in 15 min.

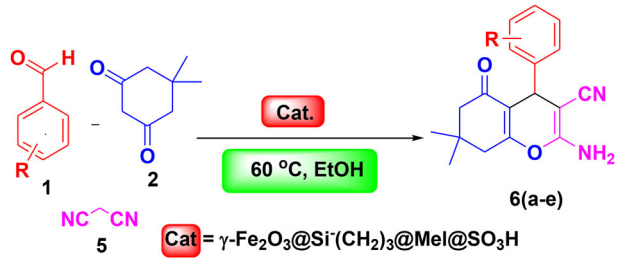
high reusability of the catalyst, magnetically separable catalyst, excellent yield, and mild reaction condition. All compounds have been characterized based on physical and spectral data and were good matched with authentic samples in the literature (Table 1). Also, when we used 4-isopropyl benzaldehyde, we obtained a new derivative of benzo[c]acridines in good yield (entry 11, Table 1).

Owing to wide range of useful biological activities in the field of medicinal chemistry[35] and to have anti-cancer and anti-coagulant activities[36] of 2-amino-4*H*-chromenes and, to evaluate catalytic activity of prepared catalyst, the synthesis of 2-amino-4*H*-chromenes was studied using aryl aldehydes, dimedone, and malononitrile in the presence of prepared nanocatalyst in good-to-high yield (Scheme 3).

The results have been shown in Table 4. The main advantages of this synthesis method are mild reaction condition, separation of the catalyst using external magnet, eco-friendly, non-corrosive, and reusable catalytic system at least five times without loss of activity with high isolated yield of the products and the synthesis of two new derivatives of 2-amino-4H-chromene (entry 5 and 6, Table 4).

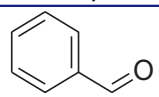
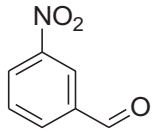
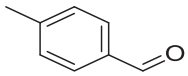
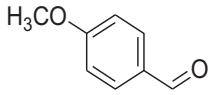
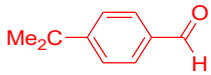
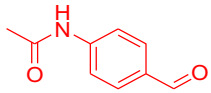
The suggested mechanism for the preparation of 7,10,11,12-tetrahydrobenzo[c]acridine-8(9*H*)-ones has been depicted in Scheme 4. As shown in Scheme 4, the enolic form of dimedone **1** attacks to activated-magnetic nanocatalyst aldehyde **2** to form intermediate **3**. Dehydration of **3** obtains Knoevenagel product **4**. Michel like-addition of 1-naphtyl amine **5** to **4** and following cyclization and assisted-dehydration *via* basic part of the catalyst give intermediate **8** that is tatumerized to **4**.

To show the merits of this procedure in comparison with the previously reported protocols, we compared the



Scheme 3. Synthesis of 2-amino-4*H*-chromenes.

Table 4. Preparation of 2-amino-4H-chromene.

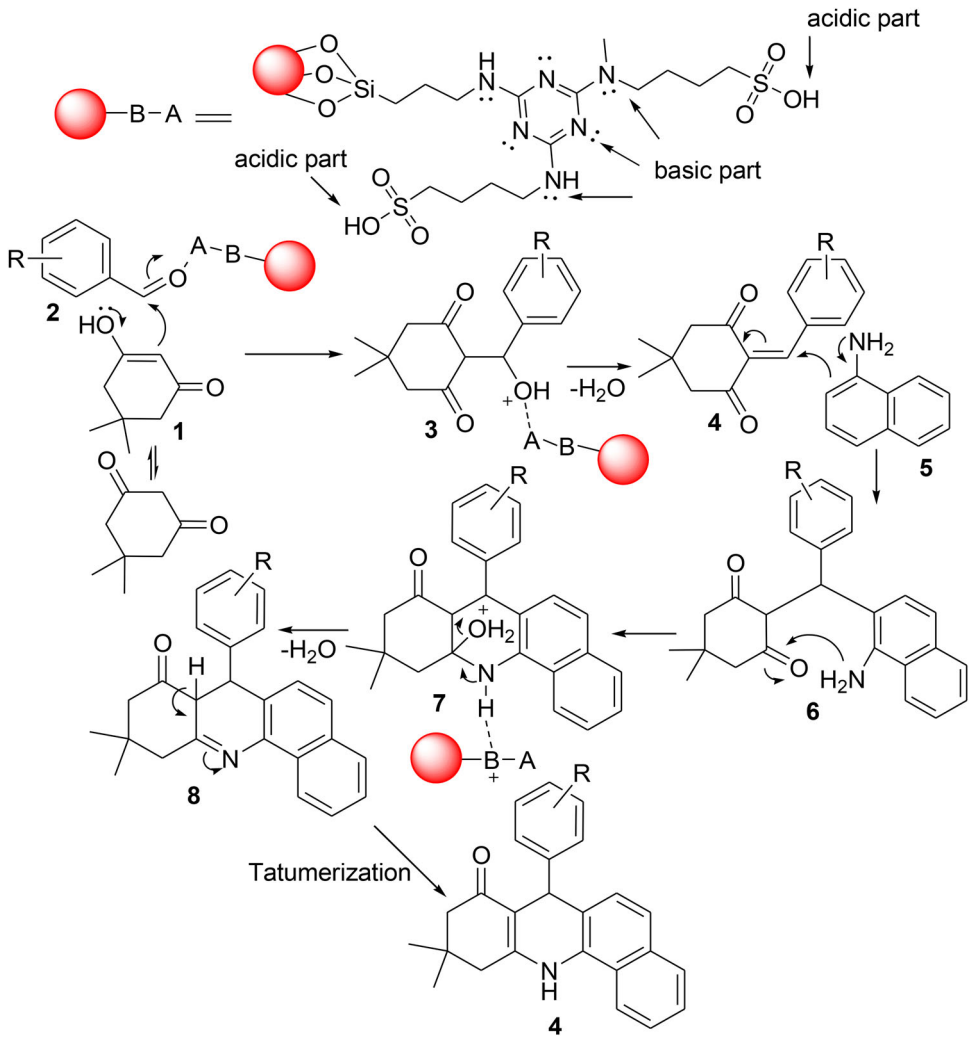
Entry	Aldehyde	Product	Time (min)	Yield%[a]	m.p (°C) [ref.]
1		**6a**	15	92	227–228 [37]
2		**6b**	10	90	201–203[37]
3		**6c**	25	95	210–212[37]
4		**6d**	40	80	202–204[39]
5		**6e**	25	85	208–210 (new)
6		**6f**	45	82	245–247 (new)

[a]Reaction condition: malononitril (1.0 mmol), dimedone (1.0 mmol), benzaldehyde (1.0 mmol) and catalyst (0.004 g) in ethanol (2.0 mL) at 60 °C.

synthesis of 10,10-dimethyl-7-phenyl-7,10,11,12-tetrahydrobenzo [c]acridine-8(9H)-one (**4a**) and 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**6a**) under various conditions (Tables 5 and 6). The advantages of our procedure are the use of γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid as heterogeneous, high reusability of the bifunctional, and magnetically separable catalyst, excellent yield and mild reaction condition, which are very important in the chemical industry.

Conclusion

In summary, the synthesis of dibenzo[*c*]acridines has been developed using a magnetic nanocatalyst catalyst. The reaction is usable to a wide variety of aliphatic and aromatic aldehydes with excellent yields. This synthesis protocol develops an attractive pathway for dibenzo[*c*]acridines production using a magnetic nano bifunctional catalyst, and forming H_2O as the sole byproduct. Also, 2-amino-4*H*-chromenes was synthesized in the presence of prepared nanocatalyst in good-to-high yield under mild reaction condition.



Scheme 4. Proposed mechanism for the synthesis of tetrahydrobenzo[c]acridine-8(9*H*)-ones.

Table 5. Synthesis procedure for the synthesis of **4a** using different catalysts.

Entry	Catalyst	Temp. (°C)	Time (min)	Yield%	Ref.
1	$FePO_4$[a] (10 mol.%)	20	60	90	14
2	*L*-Proline[a] (10 mol.%)	r.t.	60	95	34
3	MW/ 160 w[b]		20	93.5	10
4	Succinimide-*N*-sulfonic acid[a] (4 mol%)	60	30	96	33
5	ultrasonic waves[a]	r.t.	60	85	12
6	$SnCl_2$.$2H_2O$ (20 mol%) / ultrasonic irradiation[a]	r.t.	60	85	13
7	NH_2SO_3H/ $H_6P_2W_{18}O_{62}$.$18H_2O$	110	120	70	15
8	Without catalyst	80	1200	28	6
9	Presented catalyst[a,c] (0.004 g)	60	15	95	This work

[a]Used solvent is EtOH.
[b]Solvent-free.
[c]γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid.

Table 6. Synthesis protocol for the preparation of **6a** using different catalysts.

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield%	Ref.
1	ZnO nanoparticle(0.003 g)	EtOH	Reflux	10	90	38
2	MNPs@Cu (0.01 g)	Free	90	17	91	39
3	*L*-proline (10 mol.%)	EtOH	Reflux	60	93	37
4	$Ba(OTf)_2$(20 mol.%)	PEG-water	r.t.	30	88	40
5	MCM-41@Schif base (0.01 g)/$Co(OAc)_2$ (10 mol%)	H_2O	100	180	94	41
6	Presented catalyst[a] (0.004 g)	EtOH	60	15	92	This work

[a]γ-Fe_2O_3@Si-$(CH_2)_3$@melamine@butyl sulfonic acid.

Another advantage of this method is the synthesis of some new derivatives of dibenzo[*c*]acridines and 2-amino-4*H*-chromenes.

FT-IR spectra data

10,10-Dimethyl-7-phenyl-7,10,11,12-tetrahydrobenzo[c]-acridin-8(9H)-one (**4a**). IR (KBr, cm^{-1}): 3301 (NH), 3083 (CH-aromatic), 2956 (CH-aliphatic), 1689 (C = O), 1595 (C = C aromatic), 1072.

3,3-Dimethyl-9-(4-chlorophenyl)-1,2,3,4,9,10-hexahydro-benzo-[c]acridine-1-one (**4b**).

IR (KBr, cm^{-1}): 3334 (NH), 3030 (CH-aromatic), 2958 (CH-aliphatic), 1605 (C = O), 1572 (C = C aromatic), 1492, 1374, 1262, 1148, 1090, 1014, 851, 822, 757.

3,3-Dimethyl-9-(2,4-dichlorophenyl)-1,2,3,4,9,10-hexahydrobenzo[c]acridine-1-one (**4c**). IR (KBr, cm^{-1}): 3304 (NH), 3065 (CH-aromatic), 2960 (CH-aliphatic), 1684 (C = O), 1590, 1518 (C = C aromatic), 1385, 1262, 1149, 1095, 1037, 880, 807, 754.

3,3-Dimethyl-9-(3-nitrophenyl)-1,2,3,4,9,10-hexahydro-benzo- [c]acridine-1-one (**4d**).

IR (KBr, cm^{-1}): 3310 (NH), 3050 (CH-aromatic), 2956 (CH-aliphatic), 1589 (C = O), 1530 (C = C aromatic), 1387, 1262, 1150, 1093, 831, 807, 758, 611.

10,10-Dimethyl-7-(2-phenylethenyl)-7,10,11,12-tetrahydrobenzo[c]acridin-8(9H)-one **(4e).** IR (KBr, cm^{-1}): 3342 (NH), 3080 (CH-aromatic), 2956 (CH-aliphatic), 1635 (C = O), 1590, 1557 (C = C aromatic).

10,10-Dimethyl-7-(4-dimethylaminophenyl)-9,10,11,12-tetrahydrobenzo[c]acridin-8(7H)-one (**4f**). IR (KBr, cm^{-1}): 3321 (NH), 3066 (CH-aromatic), 2898 (CH-aliphatic), 1666 (C = O), 1577, 1522 (C = C aromatic), 1435, 1140, 815.

10,10-Dimethyl-7-(2-hydroxyphenyl)-7,10,11,12-tetrahydrobenzo[c]acridin-8(9H)-one (**4 g).** IR (KBr, cm^{-1}): 3500 (NH), 3100 (CH-aromatic), 2997 (CH-aliphatic), 1641 (C = O), 1587, 1515 (C = C aromatic), 1487, 1409, 1260, 1175, 1143, 1026, 845, 819, 755, 746.

7,10,10-Trimethyl-9,10,11,12- tetrahydrobenzo[c]acridin-8(7H)-one (**4 h**). IR (KBr, cm^{-1}): 3336 (NH), 3087 (CH-aromatic), 2987 (CH-aliphatic), 1643 (C = O), 1543, 1532 (C = C aromatic), 1465, 1132, 818.

7-(3-Hydroxyphenyl)-10,10-dimethyl-7,10,11,12-tetrahydrobenzo[c]acridin-8(9H)-one **(4i).** IR (KBr, cm^{-1}): 3314 (NH), 3070 (CH-aromatic), 2956 (CH-aliphatic), 1640 (C = O), 1550, 1520 (C = C aromatic), 1468, 1047.

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6a**). IR (KBr/cm^{-1}): 3395, 3324 (NH_2), 2199 (CN), 1680 (C = O), 1214 (C-O).

2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6 b**). IR (KBr/cm^{-1}): 3429, 3334 (NH2), 2186 (CN), 1680 (C = O), 1210 (C-O).

Ethyl 6-amino-4-(4-methylphenyl)-5-cyano-2- methyl -4H-pyran-3-carboxylate **(6c).** IR (KBr/cm^{-1}): 3382, 3316 (NH_2), 2192 (CN), 1682 (C = O), 1213 (C-O).

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6d**). IR (KBr/cm^{-1}): 3378, 3319 (NH_2), 2196 (CN), 1680 (C = O), 1217 (C-O).

Physical and spectra data for new compounds

10,10-Dimethyl-7-(4-isopropylphenyl)-9,10,11,12-tetrahydrobenzo[c]acridin-8(7H)-one (**4k**). Melting point: 214–216 °C: withe powder, IR (KBr, cm^{-1}): 3321, 3060, 2897, 1667, 1567, 1522, 1435, 1340, 1275, 815; ^{1}H NMR (300 MHz, $CDCl_3$) δ:1.00 (s, 3H), 1.19 (s, 3H), 1.21 (6H, d, J = 7.67 Hz, 2 × CH3), 2.22–2.44 (m, 2H), 2.55–2.80 (m, 2H), 3.11 (1H, m, CH), 5.26 (s, 1H), 7.15–7.77 (m, 9H), 8.77 (d, J= 7.6 Hz, 1H), 9.33 (s, 1H, NH). ^{13}C NMR (DMSO–d6): δ (ppm) = 198, 146,140, 137, 134, 132, 128, 126, 124,118, 108, 51, 42, 36, 31, 30, 27, 23. Combustion analysis for $C_{28}H_{29}NO$: Calculated (%). C, 85.02; H, 7.39; N, 3.54; found (%): C, 85.01; H, 7.36; N, 3.52.

2-amino-7,7-dimethyl-5-oxo-4-(4-isopropylphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6e**): Melting point: 208–2110 °C,: withe powder, IR (KBr/cm^{-1}): 3395, 3324 (NH2), 2199 (CN), 1680 (C = O), 1214 (C-O). ^{1}H NMR (DMSO–d6): δ (ppm) = 0.98 (3H, s, Me), 1.06 (3H, s, Me), 1.23 (6H, d, J = 7.67 Hz, 2 × CH_3), 2.10 (1H, d, J = 16.0 Hz, H-6), 2.25 (1H, d, J = 16.0 Hz, H-6) , 2.49 (2H, brs, CH_2), 3.12 (1H, m, CH), 4.19 (1H, s, H-4), 7.02 (2H, brs, NH_2), 7.10 (2H, d, J = 8.24 Hz,H–Ar), 7.13 (2H, d, J = 8.24 Hz,H–Ar). ^{13}C NMR (DMSO–d6): δ (ppm) = 198, 159, 155, 142,139, 128, 125, 117, 113, 58, 56, 44, 37, 36, 30, 27, 23. Combustion analysis for $C_{21}H_{24}N_2O_2$: Calculated (%). C, 74.97; H, 7.19; N, 8.33; found (%): C, 74.95; H, 7.17; N, 8.30.

N-(4-(2-amino-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4-yl)phenyl)acetamide (**6f**): Melting point: 245–247 °C, withe powder, IR (KBr/cm-1): 3395, 3328 (NH_2), 2199 (CN), 1680 (C = O), 1667 (C = O), 1214 (C-O). ^{1}H NMR (DMSO–d6): δ (ppm) = 0.97 (3H, s, Me), 1.05 (3H, s, Me), 2.00 (3H, s, Me), 2.08 (1H, d, J = 16.0 Hz, H-6), 2.24 (1H, d, J = 16.0 Hz, H-6 0), 2.49 (2H, brs, CH2), 4.10 (1H, s, H-4), 6.98 (2H, brs, NH_2), 7.04 (2H, d, J = 8.0 Hz, H–Ar), 7.24 (2H, d, J = 8.0 Hz, H–Ar), 9.90 (1H, s, NH). ^{13}C NMR (DMSO–d6): δ (ppm) = 198, 168,159, 155, 137,135, 128, 121, 117, 113, 58, 51, 44, 37, 30, 27, 22. Combustion analysis for $C_{20}H_{21}N_3O_3$: Calculated (%). C, 68.36; H, 6.02; N, 11.96; found (%): C, 68.32; H, 6.01; N, 11.93.

Disclosure statement

No potential conflict of interest was reported by the authors.

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