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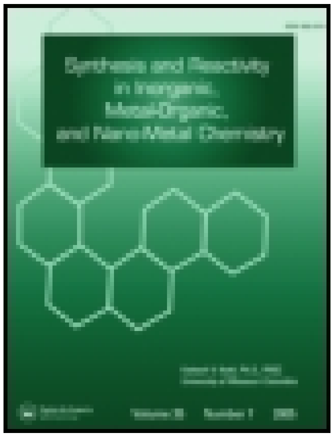

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Sulfonated polyethylene glycol (PEG-SO_3H) as eco-friendly and potent water soluble solid acid for facile and green synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives

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Sulfonated polyethylene glycol (PEG-SO_3H) as eco-friendly and potent water soluble solid acid for facile and green synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives

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Abstract: In this work, a green, simple and highly efficient procedure for the preparation of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives [as biologically active heterocycles, fluorescence materials and Pharmaceutical compounds] is described. Sulfonated Polyethylene glycol (PEG-SO_3H) has been used as an efficient and reusable catalyst for the one-pot multi component domino condensation reaction of dimedone and an aromatic aldehyde without/and a primary amine. The reactions were completed at 80 ^{o}C in water as green solvent. Using this procedure, all the products were obtained in good to excellent yields. The catalyst has been recovered and reused several times without any lose of reactivity.

Keywords: green chemistry; sulfonated polyethylene glycol; 1,8-dioxo-octahydroxanthene; 1,8-dioxo-decahydroacridines; heterocyclic compounds.

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Introduction

Functionalized nitrogen and oxygen containing heterocycles play a predominant role in medicinal chemistry and they have been intensively used as scaffolds for drug development *(1,2)*. Between them, xanthenes and acridinediones are two important classes of biologically active heterocycles *(3,4)*.

Xanthene based compounds exhibit extensive activities in pharmaceutical and biological aspects, for example antibacterial, antiviral and anti-inflammatory activities *(5)* In particular 1,8-dioxo-octahydroxanthene derivatives constitute a structural unit in several natural products *(6)* and through presence of inbuilt reactive pyran ring they are very important synthons in organic synthesis. Xanthene derivatives are also very important organic compounds with widespread applications as dye *(7)*, in laser technologies *(8)*, and fluorescence materials in bio-molecules visualization *(9)*.

Therefore, a great number of synthetic methods have been reported via the condensation of aldehyde with 1,3- cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione in the presence of protonic acids *(10)* or Lewis acids such as $InCl_3$-$4H_2O$ *(11)*, $FeCl_3$-$8H_2O$ *(12)*, $NaHSO_4$ *(13)*, and heterogeneous catalysts, for instance Dowex-50W *(14)*, $NaHSO_4$-SiO_2 *(15)*, silica sulphuric acid *(16)*, polyanilinep- toluenesulfonate *(17)*, PPA-SiO_2 *(18)*, TiO_2/SO_4^{2-} *(19)*, and Amberlyst-15 *(20)* as catalysts. Other catalysts, such as trimethylsilyl chloride *(21)*, p-dodecylbenzenesulfonic acid *(22,23)*, triethylbenzylammonium chloride *(24)*, and NH_2SO_3/SDS *(25)* have also been employed for the preparation of xanthenedione derivatives. Additionally, the above condensation process could proceed in ionic liquid or ethylene glycol *(26)* However, some of these methodologies have some disadvantages, such as low yields *(17,18)*, prolonged reaction time

(11,15,20,21), harsh reaction conditions *(10)*, and the requirement of excess of catalysts *(21)* or special apparatus *(23)*. Thus, the extension of a simple, highly efficient procedure for synthesis of xanthenes remains desired.

The acridinediones are a class of compounds that exhibit wide applicability as photosensitizers and as excellent initiators in photopolymerization *(27)*. They have a high fluorescence quantum yield of about 0.9 *(28)* and have fine lasing action *(29)* which operates in the blue green region with efficiencies comparable to that of coumarin-102 *(30)*. The acridinedione dyes have a bichromophoric structure enabling them to act as both an electron donor and acceptor *(31)* The photochemical behavior of donor-acceptor of these compounds has received considerable attention due to their unique photophysical, photochemical and nonlinear optical properties *(32)*. Also, light-emitting materials based on acridinediones have previously reported that they act as organic light-emitting diodes (OLED) *(4)*. The acridinediones are similar in structure to the 1,4-dihydropyridines (1,4-DHPs) and the biologically important ϐ-dihydronicotinamide adenine dinucleotide (NADH) and its analogues which are vital coenzymes in biological systems *(33)*. The acridinedione dyes have been shown to mimic NADH to a greater extent than the 1,4-DHPs due to the tricyclic structure which is capable of protecting the enamine moiety *(33)*. The presence of several reaction centers in acridinediones opens broad synthetic possibilities *(34)*. Furthermore, the chemical behaviors of acridinediones in catalytic hydrogenation reactions under various conditions have been studied *(35)*.

Numerous acridinediones have been prepared by the reactions between ϐ-diketones with various aldehydes and appropriate amines, in most cases primary amine, to form a fluorescent heterocyclic system *via* various methods *(36,37)*. In addition, these synthetic methods have been catalyzed by utilizing various catalysts such as *p*-dodecylbenzenesulfonic acid (DBSA) under microwave irradiation *(38)*, Brønsted acidic imidazolium salts containing perfluoroalkyl tails *(39)*, and 1-Methylimidazolium triflouroacetate ([Hmim]TFA) *(10)*.

In recent years, there has been rapid growth in the development of novel polymer-supported compounds *(40)*, such as supported catalysts, reagents, and scavengers. These species allow rapid and simplified procedures, and their use has become widespread in solution-phase organic synthesis and combinatorial chemistry *(41)*. In this context, soluble polymers have recently been the subject of an intense research activity; allowing the reaction to be carried out in homogeneous solution they would secure higher chemical and stereochemical efficiency than insoluble polymer *(42)*. Among the soluble polymeric matrixes employed, poly(ethylene glycol)s (PEGs) are the most successful. Provided that their Mw is >2000 Da, PEGs are soluble in many, mostly polar solvents (including water) and insoluble in a few nonpolar solvents (hexanes, diethyl ether, tert-butyl methyl ether). Because of this solubility profile, PEG-based supports combine the advantageous features of homogeneous solution chemistry (high reactivity, lack of diffusion phenomena, analytical simplicity) and of solid phase methods (ready isolation and purification of products) *(26,40)*.

Use of aqueous media as a reaction solvent has attracted much attention in synthetic organic chemistry for several reasons *(43)*. In comparison with organic solvents, water is cheap, safe and reduces the use of harmful organic solvents and leads to the development of environmentally friendly chemical processes *(44)*. In addition, reactions in aqueous media illustrate unique reactivities and selectivities that are not usually observed in organic media *(45)*. However, organic solvents are still used instead of water for mainly two reasons; first, most organic substrates are not soluble in water, and as a result, water cannot function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are sensitive towards water and are decomposed or deactivated in aqueous media. A possible new way to improve the solubility of substrates is the use of surface-active compounds that can form micelles *(46)* or vesicular structures. Polyethylene glycols are soluble in water by continues repeated (-OCH_2CHO-) units that have lipophilic properties and can work as surfactant reagent that is able to provide micelles of water insoluble reactant to encourage the organic reactions in aqueous media (Figure **1**).

In continues of our recent studies about use of green protocols in organic synthesis *(47-55)*, herein we report the use of sulfonated polyethylene glycol as a potent and eco-friendly catalyst for facile and green synthesis of 1,8-dioxo-octahydroxanthene derivatives under solvent-free condition and also synthesis 1,8-dioxo-decahydroacridines derivatives at the present sulfonated polyethylene glycol as potent water soluble solid acid catalyst in water (Scheme **1**).

Results and Discussion

To achieve the best results we examined the efficiency of different reaction media and catalyst amounts for the condensation reactions of 5,5-dimethy-1,3-cyclohexanedione (**1**) and benzaldehyde (**2**) as a model reaction (Scheme **2**) and obtained result was reported in table **1**. For each reaction condition, conversion of 5,5-dimethy-1,3-cyclohexanedione (2 mmol) and benzaldehyde (1 mmol) to 3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (**3a**) was monitored by thin layer chromatography (TLC) using hexane-ethyl acetate (5:1) as eluent. As it can be seeing from table **1**, significant rate enhancement and improved yields were observed using about (20 mol% in order of active H^+) of PEG-SO_3H under solvent-free condition at 80 ^oC.

The experimental procedure for this reaction is remarkably simple and does not require the use of organic solvents or inert atmospheres. Use of PEG-SO_3H as catalyst provided very simple work up procedure. After completion of the reaction, water was added and the insoluble products was separated by simple filtration and purified by recrystalization from ethanol.

The generality of the method has been shown by the preparation of a series of 1,8-dioxo-octahydroxanthene derivatives using various aromatic aldehydes bearing electron withdrawing and electron releasing substituents and 1,3-5,5-dimethyl-1,3-cyclohexanedione (Table **2**). The influence of electron-withdrawing and electron-donating substituents on the aromatic ring of aldehydes upon the reaction yields was investigated. The results showed that both electron-withdrawing and electron- releasing substituents had no significant effect on the reaction yields. Moreover, the presence of halogen on the aromatic ring of aldehydes had negligible effect on the reaction results. We also successfully applied acid sensitive heteroaromatic aldehydes and the corresponding products were obtained without any by-products or side reactions.

Our methodology for synthesis of *1,8*-dioxo-octahydroxanthene derivatives also shown very good chemoselectivity. The use of PEG-SO_3H as a water soluble solid acid catalyst showed rate enhancements, high yields and good reaction times. However, one of the important points regarding the adaptable catalyst is its ability to recovering from reaction media and stability of their reactivity toward the eternal uses. From every reaction the PEG-SO_3H catalytic system have been recovered by evaporation of water after filtration of insoluble products. Table **3** shows the results of five consecutive runs of the reaction of 5,5-dimethyl-1,3-cyclohexanedione with benzaldehyde and shows that catalyst could be reused several times without noticeable loss of activity. This reusability demonstrates the high stability and turnover of PEG-SO_3H catalytic system under operating condition.

In the other way, the catalytic effects of PEG-SO_3H for the synthesis of 1,8-dioxo-decahydroacridines were studied. For this propose, dimedone (2 mmol), benzaldehyde (1 mmol) and aniline (1 mmol) were selected as a model reaction to achieve 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(*2H*,*5H*)-dione **5a** in different conditions and the results are summarized in Table **4** (Scheme **3**).

After extensive screening, we found that the optimized best yields and time profiles were obtained with 10 mol % of PEG-SO3H in water as solvent at 90 ^{o}C. It is noticeable that neither water nor aqueous solutions of H_2SO_4 have been shown efficiency for this reaction under same conditions.

Using the optimum conditions including the utilization of primary aromatic amine (1 mmol), dimedone (2 mmol), an aromatic aldehydes (1 mmol) and catalytic amount of PEG-SO3H (10 mol %) in water as solvent at 90 °C were tested (Table **5**). As can be seen from table **5** (**5a-q**), steric and electronic variation in the aromatic aldehyde were tolerated and did not change the efficiency of the reaction in the presence of aromatic amine. Besides the introduction of key functional group such as halides, alkyl, nitro, methoxy and nitrile, several aromatic aldehydes bearing two functional groups were also tested and resulted in the corresponding products.

From every reaction the PEG-SO_3H catalytic system have been recovered by evaporation of water after filtration of insoluble products. Table **6** shows the results of five consecutive runs of the reaction of 5,5-dimethyl-1,3-cyclohexanedione, benzaldehyde with aniline and shows that catalyst could be reused several times without noticeable loss of activity. This reusability demonstrates the high stability and turnover of PEG-SO_3H catalytic system under operating condition.

Experimental section

All chemicals were purchased from Merck or Fluka Chemical Companies. All compounds are known, and their structures were identified by comparing their melting points and ^{1}H and ^{13}C NMR data with those reported in the literature. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (ŭ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Preparation of PEG-SO$_3$H

At 0 °C, chlorosulfonic acid (1.16 g, 10 mmol) was added to a solution of PEG-4000 (6.0 g, 1 mmol) in CH_2Cl_2 (10 mL). Then the resulting solution was stirred at room temperature overnight, and the solution was concentrated under vacuum. Appropriate ether (50 ml) was added, and the precipitate filtered and washed with ether (30 ml) three times to afford the PEG-SO$_3$H *(61)*.

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

,5-dimethyl-1,3-cyclohexanedione (2 mmol) and aromatic aldehyde (1 mmol) were mixed with PEG-SO3H (1.2 g, 0.2 mmol) and the obtained mixture was stirred magnetically at 80 °C. After the completion of reaction (as monitored by TLC) warm water (5 ml) was added and the mixture stirred for about 5 min. The insoluble crude product was filtered and recrystallized from EtOH and the pure product was obtained. In order to recover the catalyst, the filtrate was dried under reduced pressure and recovered catalyst was washed with diethyl ether and reused after drying under reduced pressure.

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

PEG-OSO$_3$H (0.6 g, 0.1 mmol) was dissolved in water (5 ml) and heated to 90 ^{o}C and then 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aromatic aldehyde (1 mmol) and primary amine were added and obtained mixture was stirred. After the completion of reaction (as monitored by TLC), insoluble products was separated by simple filtration and then was recrystalized from EtOH to obtain pure products. In order to recover the catalyst, the filtrate was dried under reduced pressure and recovered catalyst was washed with diethyl ether and reused after drying under reduced pressure.

Selected spectral data of the products

9-(4-fluorophenyl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-10-p-tolylacridine-1,8(2H,5H,9H,10H)-dione (5l). White powder (M.P.= 258-261 ^{o}C) gmax (KBr): 3400, 2950, 1620, 1480, 1440, 1370, 1270, 1080, 1010, 880, 540 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 500 MHz) ŭ: 0.83 (s, 6H), 0.98 (s, 6H), 1.87 (d, *J*=17.5 Hz, 2H), 2.11, (d, *J*=17.5 Hz, 2H), 2.16 (d, *J*=16.0 Hz, 2H), 2.23 (d, *J*=16.0 Hz, 2H), 2.52 (s, 3H), 5.28 (s, 1H), 6.96 (t, *J*=8.7 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 7.38 (d, *J*=7.5 Hz, 2H), 7.41-7.44 (m, 2H) ppm. Calculated for $C_{30}H_{32}FNO_2$: C, 78.75; H, 7.05; N, 3.06%. Found: C, 78.53; H, 7.26; N, 2.91%.

Conclusion

In conclusion, we have developed a simple, green and efficient procedure for synthesis of *1,8*-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives catalyzed by PEG-SO$_3$H. The use of mild conditions, simple work-up, high yield, and recyclability of the catalyst make our methodology a valid contribution to the existing processes in the field of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives synthesis. Furthermore, the method was successfully applied for aldehydes bearing powerful electron releasing substituents and their corresponding 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine derivatives were obtained in good yields.

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Table 1. Comparison of the reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) under various conditions and in the presence of different amounts of PEG-SO_3H.

Entry	Solvent	Catalyst amount (mol%)	Temperature (°C)	Time (min)	Yield[a] (%)
1	$CHCl_3$	20	reflux	450	50
2	THF	20	reflux	450	Trace
3	MeOH	20	reflux	90	85
4	EtOH	20	reflux	270	75
5	CH_2Cl_2	20	reflux	280	60
6	EtOAc	20	reflux	300	70
7	H_2O	20	reflux	480	25
8	Solvent-free	20	100	70	90
9	Solvent-free	20	90	65	91
10	Solvent-free	20	80	60	92
11	Solvent-free	20	70	240	89
12	Solvent-free	20	50	420	87
13	Solvent-free	20	r.t.	600	Trace
14	Solvent-free	5	80	330	70
15	Solvent-free	10	80	180	75

16	Solvent-free	15	80	120	82
17	Solvent-free	25	80	65	92

[a] Isolated Yield

Table 2. Preparation of 1,8-dioxo-octahydroxanthene derivatives via condensation of dimedone (2 mmol) and aromatic aldehydes (1 mmol) under solvent-free condition in the presence of PEG-SO_3H (20 mol %) at 80 °C.

Entry	Ar	Product	Time (min)	Yield[a] (%)	M.P. Found (Reported) (ref)
1	C_6H_5	**3a**	60	92	202-204 (201-203) (21)
2	4-Br-C_6H_4	**3b**	165	81	238-240 (240-242) (21)
3	4-Cl-C_6H_4	**3c**	30	91	228-230 (230-232) (21)
4	3-Cl-C_6H_4	**3d**	210	89	184-186 (185-187) (18)
5	2-Cl-C_6H_4	**3e**	120	96	223-225 (224-226) (11)
6	4-F-C_6H_4	**3f**	90	98	226-227 (224-226) (11)
7	4-Me-C_6H_4	**3g**	45	89	213-215 (210-212) (11)
8	4-isopropyl-C_6H_4	**3h**	160	94	170-172 (170-171) (56)
9	4-NO_2-C_6H_4	**3i**	95	86	221-223 (222-224) (11)
10	3-NO_2-C_6H_4	**3j**	60	96	167-169 (168-170) (22)
11	4-OMe-C_6H_4	**3k**	210	90	242-244 (241-243) (11)
12	4-CN-C_6H_4	**3l**	190	90	215-217 (217-218) (57)
13	2-NO_2-C_6H_4	**3m**	375	83	252-254 (250-252) (57)
14	3-Br-C_6H_4	**3n**	215	84	188-190 (190-192) (56)
15	3,4-$(OMe)_2$-C_6H_3	**3o**	135	89	176-179 (175-176) (57)
16	3,4,5-$(OMe)_3$-C_6H_2	**3p**	75	97	207-209 (210-212) (57)
17	-CH=CH-C_6H_5	**3q**	160	95	174-176 (174-176) (58)
18	2-furyl	**3r**	75	89	61-63 (62-64) (56)

19	2-pyrolyl	**3s**	110	83	88-90 (88-90) (59)
20	2-thienyl	**3t**	80	89	163-165 (164-165) (57)

[a] Isolated Yield

Table 3. Reusability of the catalyst for a series of five consecutive runs of the reaction of dimedone (2 mmol) with benzaldehyde (1 mmol).

Entry	Time (min)	Conversion (%)	Yield[a] (%)
1	90	100	92
2	90	100	92
3	90	100	92
4	100	100	92
5	120	100	92

[a] Isolated Yield

Table 4. Comparison of the reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) and anilin (1 mmol) under various conditions.

Entry	Solvent	Catalyst (mol%)	Temperature (°C)	Time (min)	Yield[a] (%)
1	$CHCl_3$	PEG-SO_3H (10)	reflux	480	20
2	THF	PEG-SO_3H (10)	reflux	480	Trace
3	MeOH	PEG-SO_3H (10)	reflux	480	75
4	EtOH	PEG-SO_3H (10)	reflux	360	80
5	CH_3CN	PEG-SO_3H (10)	reflux	480	47
6	EtOAc	PEG-SO_3H (10)	reflux	480	10
7	H_2O	PEG-SO_3H (10)	reflux	235	80
8	H_2O	PEG-SO_3H (10)	r.t.	480	Trace
9	H_2O	PEG-SO_3H (10)	50	480	35
10	H_2O	PEG-SO_3H (10)	70	480	71
11	H_2O	PEG-SO_3H (10)	90	240	82
12	H_2O	PEG-SO_3H (5)	90	480	73
13	H_2O	PEG-SO_3H (15)	90	240	82
14	H_2O	PEG-SO_3H (20)	90	230	82
15	H_2O	Catalyst-free	90	480	Trace
16	Solvent-free	PEG-SO_3H (10)	90	480	----[b]
17	H_2O	aqueous H_2SO_4	90	180	38

(10)

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[a] Isolated Yield

[b] Mixture of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(*2H*)-dione **3a** and 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(*2H*,*5H*)-dione **5a**

Table 5. Preparation of 1,8-dioxo-decahydroacridine derivatives via condensation of dimedone (2 mmol), aromatic aldehydes (1 mmol) and primary amine (1 mmol) in the presence of PEG-SO_3H in water and 90 °C.

Entry	Ar	Ar'	Product	Time (min)	Yield[a] (%)	M.P. Found (Reported) (ref)
1	C_6H_5	C_6H_5	**5a**	240	82	255-256 (255-256) (20)
2	4-OMe-C_6H_4	C_6H_5	**5b**	300	81	219-222 (220-222) (20)
3	3-NO_2-C_6H_4	C_6H_5	**5c**	240	85	278-281 (276-278) (60)
4	C_6H_4	4-Me-C_6H_4	**5d**	240	89	266-268 (265-267) (60)
5	4-Cl-C_6H_4	4-Me-C_6H_4	**5e**	210	83	273-276 (270-271) (60)
6	3-Cl-C_6H_4	4-Me-C_6H_4	**5f**	240	87	318-320 (315-317) (60)
7	3-NO_2-C_6H_4	4-Me-C_6H_4	**5g**	180	87	289-291 (285-287) (60)
8	4-OH-C_6H_4	4-Me-C_6H_4	**5h**	360	83	352-354 (350-352) (60)
9	4-OMe-C_6H_4	4-Me-C_6H_4	**5i**	270	81	282-285 (285-287) (60)
10	4-Me-C_6H_4	4-Me-C_6H_4	**5j**	240	85	296-298 (293-294) (60)
11	4-Cl-C_6H_4	3-OH-C_6H_4	**5k**	300	79	268-270 (267ï 269) (58)
12	4-F-C_6H_4	4-Me-C_6H_4	**5l**	240	83	258-261
13	4-NO_2-C_6H_4	2-OH-C_6H_4	**5m**	180	84	296-298 (>300) (58)
14	3-NO_2-C_6H_4	3-CN-C_6H_4	**5n**	240	82	267-269 (266ï 268) (58)
15	3-OH-C_6H_4	3-CN-C_6H_4	**5o**	300	81	309-311 (>300) (58)
16	4-SMe-C_6H_4	4-Me-C_6H_4	**5p**	240	73	240-242 (239) (58)
17	3-CN-C_6H_4	4-Me-C_6H_4	**5q**	240	82	254-257 (256ï 257) (58)

[a] Isolated Yield

Table 6. Reusability of the catalyst for a series of five consecutive runs of the reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) and aniline (1 mmol).

Entry	Time (min)	Conversion (%)	Yield[a] (%)
1	240	100	82
2	240	100	80
3	260	100	81
4	300	100	82
5	350	100	80

[a] Isolated Yield

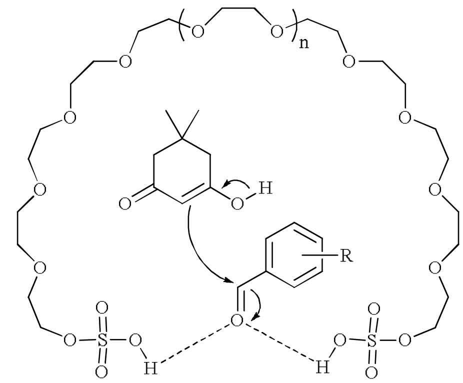
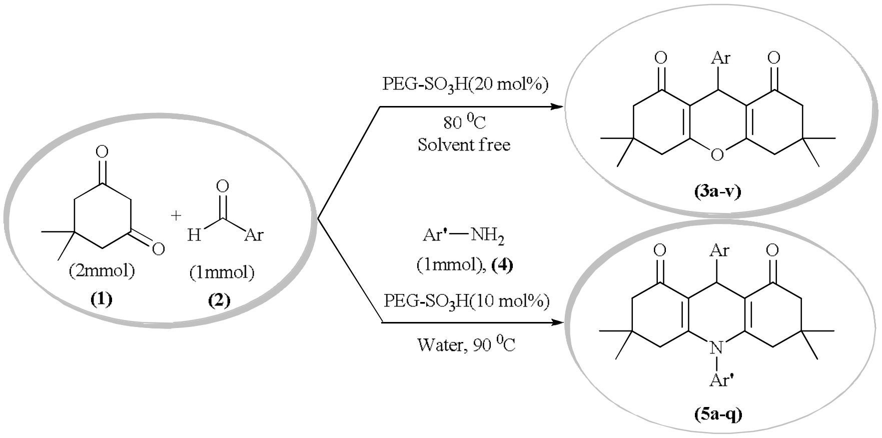
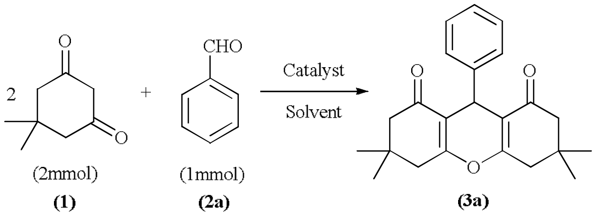


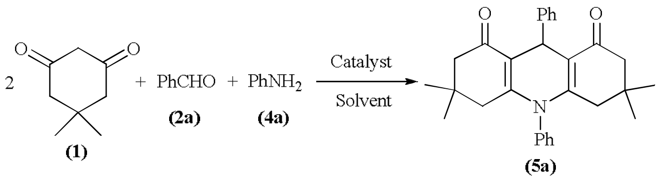
Figure 1. Performance of PEG-SO_3H as a surfactant reagent in water.



Scheme 1. Preparation of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridines derivatives.



Scheme 2. Synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(*2H*)-dione **3a** using dimedone and benzaldehyde in different conditions.



(5a)

Scheme 3. Synthesis of 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(*2H,5H*)-dione **5a** using aniline, dimedone and benzaldehyde in different conditions.