Microwave-assisted preparation of graphene quantum dots immobilized nanosilica as an efficient heterogeneous nanocatalyst for the synthesis of xanthenes

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Abstract: Graphene quantum dots (GQDs) immobilized nanosilica was prepared under microwave irradiated green reaction conditions and was used as an efficient heterogeneous acid catalyst. The structure of nano-catalyst was characterized by FT-IR, PL, TEM, XRD, FE-SEM, EDS, TGA, and zeta potential. Xanthene derivatives were synthesized in excellent yields using the freshly prepared catalyst and the catalyst could be easily recovered and recycled for 5 times without significant loss of its catalytic activity. The structures of the resulted products were confirmed by FT-IR, ¹H-NMR, ¹³C-NMR spectroscopic techniques.

Keywords: Graphene quantum dots; heterogeneous nanocatalyst; nanosilica; xanthene. © 2019 ACG Publications. All right reserved.

1. Introduction

Recently carbon based nano materials have moved the attention on nano-carbons toward graphene quantum dots.¹⁻⁶ The inspiration of this area for the interdisciplinary studies, was derived from unique properties of graphene quantum dots such as thermal and electrical conductivity,⁷ fluorescent properties,^{8,9} large surface area,^{10,11} low cytotoxicity and biocompatibility,^{12,13} excellent thermal/chemical stability,¹⁴⁻¹⁷ and size-tunable properties.¹⁸ All these features provide graphene quantum dots a wide range of applications. These applications include: photovoltaic devices,¹⁹ photocatalysis,²⁰ bioimaging,²¹ solar cells,^{19, 22-26} biosensor,²⁷ and environmental monitoring.²⁸

Graphene quantum dots (GQD) with functional groups such as carboxylic, hydroxyl and epoxy could widely be used in synthetic organic chemistry. Very recently we used functionalized GQDs as a reagent and an effective acidic nano-catalyst for the synthesis of xanthene derivatives.²⁹ High solubility properties of GQDs and their difficult and time-consuming separation process from the reaction mixture is a defect of these catalysts. In this report, heterogeneous GQD based nano-catalyst was prepared to resolve this problem, via its immobilization on nanosilica.

2. Experimental

2.1. General

All reagents were purchased from Merck Company. Infrared spectra (FT-IR) were recorded with KBr on a Perkin-Elmer FT-IR spectrometer. Melting points were determined in open glass-capillaries using a Stuart melting point apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker

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Avance AC-300 MHz using CDCl_3 as a deuterated solvent and TMS as an internal standard. Catalyst structure was supported by X-ray diffractometry (XRD; Bruker AXS model D8 Advance). Transmission electron microscopy (TEM) images were obtained by Transmission Electron Microscope Zeiss LEO906. Fluorescence spectra and intensity measurements were carried out using an FP-6200 spectrofluorometer (JASCO Corporation, Tokyo, Japan). The morphology of the catalyst was studied by field emission scanning electron microscopy (FE-SEM; Hitachi, model S-4160), and the elements of the catalyst was confirmed by energy-dispersive X-ray analysis (EDS; Phenom; model ProX) and elemental analysis (CHNS; Eurovector; model EuroEA3000). Thermal gravimetric analysis (TGA) was determined using Linseis Thermal Balance L81/1750. Microwave experiments were conducted in a Milestone MicroSynth apparatus.

2.2. Synthesis of GQDs

GQDs were synthesized via the down-top method under microwave irradiation (Scheme 1).³⁰⁻³²

Scheme 1. Synthesis of graphene quantum dots (GQDs)

Ammonia solution 25% (2 mL) was added to citric acid (15 g) in a closed vessel. Then the reaction mixture was heated at 145°C with full power MWI (1000 W) for 30 min³² after which the reaction mixture was incubated under vacuum at 70°C for 15 min to produce crude GQDs. The size of particles and functional groups were determined by transmission electron microscopy and infrared spectroscopy respectively.

Then, for the preparing of heterogeneous nano-catalyst, GQDs were immobilized on Silica nanoparticles via mixing under microwave irradiation (Scheme 2). This part of the work was conducted with high efficiency under green reaction conditions and the resulted product was quite characterized. To examine the catalytic effectiveness of heterogeneous GQDs-based nano-catalyst and for the comparison with our recently reported method,²⁹ it was used for the synthesis of benzoxanthene derivatives (Scheme 2). Xanthenes are very important oxygen-containing heterocyclic compounds because of their wide applications in pharmacy as antiviral, anticancer, antibacterial and etc.^{29, 34-37} Results showed that the products were efficiently prepared in the presence of the freshly prepared heterogeneous catalyst under green reaction conditions and the catalyst was separated very simply filtration. In addition, recyclability and reusability of the catalyst were studied.

Scheme 2. Heterogeneous GQDs-based catalyst for the synthesis of xanthenes

2.3. Synthesis of silica nanoparticles

Mixture of ammonia solution 25% (750 μ L, 10 mmol), water (1.98 mL) and absolute methanol (100 mL) were added into a 250 mL round-bottom flask. Then, tetraethoxysilane (11 mL, 50 mmol) was added dropwisely into the mixture and the stirring was continued for 3 days at room temperature. The particles size and functional groups were examined using scanning electron microscopy and infrared spectroscopy respectively.

2.4. GQDs immobilization on silica nanoparticles

GQDs and freshly prepared Silica nanoparticles were simultaneously poured into the microwave vessel and the mixture was heated at 125°C with full power MWI (1000 W) for 15 min. After this, the contents of the vessel were left to cool. For the separation of the heterogeneous catalyst, water was added to the reaction mixture and mixture was stirred vigorously and then the nanoparticles were separated out by centrifugation. This process was repeated several times. The morphology of nano-catalyst and functional groups were confirmed by scanning electron microscopy and infrared spectroscopy respectively.

2.5. General procedure for the synthesis of 14H-dibenzoxanthene derivatives

The mixture of 2-naphthol (2 mmol), benzaldehyde derivative (1 mmol) and heterogeneous nano-catalyst (20 mg) was heated at 90°C with full power MWI (400 W) for 10 min. The end of reaction was followed by thin layer chromatography, after which ethyl acetate (20 mL) was added to the mixture and stirred thoroughly. Heterogeneous nano-catalyst was separated via filtration and was washed several times with ethyl acetate and reused. Ethyl acetate was removed from the filtrate under vacuum conditions and crude product was separated. Further purifications were performed by recrystallization on ethyl acetate/n-hexane to afford the pure products in high yields.

3. Results and Discussions

3.1. Characterization of GQDs

The morphology of GQDs was investigated by TEM. As it can be seen from figure 2A, the monodisperse particles were uniform and size of particles were distributed around 15 nm. XRD pattern of GQDs is shown in Figure 1B. In this pattern, a broad peak which appeared at $2\theta = 20^\circ$, is corresponded to the interlayer spacing of GQDs (4.43 Å). GQDs were synthesized via the down-top method and the size of the particles is smaller in comparison with the particle size via our reported top-down method²⁹.

Figure 1. (A) TEM image of GQDs and (B) XRD pattern of GQDs

FT-IR spectrum of GQDs (Figure 2A) confirms the presence of the hydroxyl and carbonyl functional groups on graphene quantum dots. The signals at 1729 cm^{-1} and 3193 cm^{-1} (broad) are respectively related to the absorption band of stretching vibrations of C=O and stretching vibrations of OH groups. FTIR (KBr, cm^{-1}): 3427 (O–H), 1729 (C=O), 1408 (O–H), 1193 (C–O).

Figure 3B displays the photoluminescence spectrum of GQDs while the excited was set in 388 nm and the emission at 502 nm.

Figure 2. (A) FT-IR spectrum of GQDs and (B) Photoluminescence spectrum of GQDs

3.2. Characterization of nanosilica

The FE-SEM image of silica nanoparticles is shown in Figure 3A. Nanosilica particle size was measured about 25-35 nm. Signals at 3423 cm^{-1} and 1082 cm^{-1} in FT-IR spectrum of SiO_2 nanoparticles confirmed the presence of O-H and Si-O functional groups respectively (Figure 3B).

Figure 3. (A) FE-SEM image of silica nanoparticles and (B) FT-IR spectrum of silica nanoparticles

3.3. Characterization of nano-catalyst

At first the surface modification of nanosilica was confirmed by comparison of the FE-SEM images and the FT-IR spectra of nanosilica and nanocatalyst (Figures 4A, 4B and 4C). Morphology of nanocatalyst is different from nanosilica because of the existence of hydrogen bonds and increasing of the particles size average that is presented in Figures 4A and 4B. In the FT-IR spectrum of nanocatalyst two peaks at 1717 and 3437 cm^{-1} were observed, which are related to the C=O and OH groups (Figure 5C). FTIR (KBr, cm^{-1}): 3437 (O–H), 1717 (C=O), 1087 (O–H).

Figure 4. (A) FE-SEM image of nanosilica, (B) FE-SEM image of nanocatalyst and (C) FT-IR spectra of nanosilica and nanocatalyst

The surface modification of nanosilica was also confirmed by the comparison of TGA diagrams, EDX analysis and Zeta Potential analysis of Silica nanoparticles and nanocatalyst. The TGA diagrams clearly showed the distinction in the structures of the three compounds namely GQDs, Silica nanoparticles and nanocatalyst (Figure 5). As it can be seen from Figure 5, demolition of silica nanoparticles was shown above 220°C in which staircase destruction for nano-catalyst and a clear degradation for the GQDs could be seen.

Figure 5. TGA diagrams of (A), Silica nanoparticles (B) and Nanocatalyst and (C) GQDs

The EDX analysis showed the existence of Si and O elements in the nanosilica and C, N, Si and O in the nanocatalyst (Figure 6A, 6B).

Figure 6. EDX analysis of (A) nanosilica and (B) nanocatalyst

The surface charge of the nanocatalyst and nanosilica was determined by zeta potential analysis. The results show that the electrical conductivity of the nanocatalyst is about ten-fold in comparison with nanosilica (Figure 7A, 7B).

Figure 7. ZP analysis of (a) nanosilica and (b) nanocatalyst

3.4. Reaction of 2-naphthol with arylaldehydes

The freshly prepared heterogeneous acidic nanocatalyst was examined on the model reaction of 2-naphthol (2 mmol) with benzaldehyde (1 mmol) under MWI (400 W) solvent-free conditions. The

experimental optimization was performed for assignment of ratio of the catalyst (g)/ benzaldehyde (mmol) and the best result was found in the ratio of 0.02/1 in 4 min at 90°C (entry 9, Table 1).

Table 1. Optimization of the reaction conditions for the product (**2a**)

Entry	Temperature (°C)	Catalyst (mg)	Aldehyde (mmol)	Time (min)	Yield ^a (%)
1	70	10	1	2	5
2	70	10	1	4	18
3	70	10	1	6	18
4	70	20	1	4	20
5	70	20	1	6	20
6	70	25	1	4	≈20
4	80	20	1	2	25
5	80	20	1	4	43
6	80	20	1	6	≈45
7	80	25	1	4	45
8	90	20	1	2	68
9	90	20	1	4	92
10	90	20	1	6	93
11	90	10	1	4	63
12	90	25	1	4	92
13	100	20	1	4	≈91
14	100	20	1	6	92
15	100	25	1	4	≈91

^aIsolated yield.

Product **2a** was prepared in 92% yield under optimized conditions and its structure was confirmed by FT-IR, ¹H-NMR and ¹³C-NMR spectra. For the examination of the generality of this method, the reaction of a variety of aldehyde derivatives were evaluated for the synthesis of the related 14*H*-dibenzoxanthene derivatives (Table 2).

FT-IR spectra of freshly prepared and recycled nanocatalyst for the typical reaction of 2-naphthol with benzaldehyde was compared and no significant differences is observed as shown in Figure 8.

Figure 8. FT-IR spectra of nanocatalyst: freshly prepared (a), after 6 run (b)

Table 2. Synthesis of the 14*H*-dibenzo xanthene derivatives using heterogeneous catalyst.

Entry	Aldehyde	Reactant number	Product	Product Number
1		1a		2a
2		1b		2b
3		1c		2c
4		1d		2d
5		1e		2e
6		1f		2f

Table 2 Continued..

7		1g		2g
8		1h		2h
9		1i		2i
10		1j		2j

In continue, for the influence of nanocatalyst in this reaction, results were compared with previously reported data. These results showed that the reaction times and yields of current products are significantly improves compared to that of previously reported data (Table 3).

Table 3. Comparison of the reaction times and yields of products with reported values.

Entry	Product number	Time (min)	MP (°C)		Yield ^a (%)	
			Measured	Reported [ref.]	Measured	Reported [ref.]
1	2a	6	188-190	186-187 [33]	93	88 [40]
2	2b	4	314-316	311-313 [34]	94	95 [41]
3	2c	6	293-294	291-292 [33]	94	86 [40]
4	2d	6	262-263	258-259 [35]	98	97 [42]
5	2e	8	212-214	210-212 [36]	90	73 [43]
6	2f	5	291-293	290-292 [37]	97	95 [44]
7	2g	5	249-251	250-252 [38]	95	90 [44]
8	2h	6	296-298	297-298 [37]	97	95 [44]
9	2i	10	213-215	214-216 [39]	91	85 [44]
10	2j	9	214-216	214-216 [37]	93	90 [44]

^a Isolated yield.

Recyclability of nanocatalyst was also evaluated for six periods. For this purpose, the separated catalyst was washed with hot EtOH or acetone to remove the previous reaction mixtures and then used. As it can be seen from Table 4, no significant decrease in the yield of product was observed in six run and the efficiency of the catalyst was appropriately close to each other.

Table 4. The recyclability test of nanocatalyst.

Run	1	2	3	4	5
Yield (%)	93	91	90	88	88
Standard Error	0.84				

4. Conclusion

In summary, in this study GQDs based heterogeneous nanocatalyst was prepared and used in the preparation of xanthene derivatives. All reactions were performed in green conditions. Xanthene derivatives were produced with high yields in short reaction time under mild solvent-free conditions. The catalyst could be easily recovered and recycled for 5 times without significant loss of its catalytic activity.

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Supporting Information

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References

- [1] Geim, A.K.; Novoselov, K.S. The rise of graphene. *Nat. Mater.* **2007**, *6*, 183.
- [2] Park, S.; Vosguerichian, M.; Bao, Z. A review of fabrication and applications of carbon nanotube film-based flexible electronics. *Nanoscale*. **2013**, *5*, 1727-1752.
- [3] Eda, G.; Lin, Y. Y.; Mattevi, C.; Yamaguchi, H.; Chen, H. A.; Chen, I.; Chen, C. W.; Chhowalla, M. Blue photoluminescence from chemically derived graphene oxide. *Adv. Mater.* **2010**, *22*, 505-509.
- [4] Yavari, F.; Koratkar, N. Graphene-based chemical sensors. *J. Phys. Chem. Lett.* **2012**, *3*, 1746-1753.
- [5] Terrones, M. Science and technology of the twenty-first century: synthesis, properties, and applications of carbon nanotubes. *Annu. Rev. Mater. Res.* **2003**, *33*, 419-501.
- [6] Avouris, P.; Chen, Z.; Perebeinos, V. Carbon-based electronics. *Nat. Nanotechnol.* **2007**, *2*, 605.
- [7] Choi, J.T.; Kim, D. H.; Ryu, K. S.; Lee, H.-i.; Jeong, H. M.; Shin, C. M.; Kim, J. H.; Kim, B. K. Functionalized graphene sheet/polyurethane nanocomposites: effect of particle size on physical properties. *Macromol Res.* **2011**, *19*, 809-814.

- [8] Shen, J.; Zhu, Y.; Yang, X.; Zong, J.; Zhang, J.; Li, C. One-pot hydrothermal synthesis of graphene quantum dots surface-passivated by polyethylene glycol and their photoelectric conversion under near-infrared light. *New J. Chem.* **2012**, *36*, 97-101.
- [9] Pan, D.; Zhang, J.; Li, Z.; Wu, M. Hydrothermal route for cutting graphene sheets into blue- luminescent graphene quantum dots. *Adv. Mater.* **2010**, *22*, 734-738.
- [10] Zhou, K.; Zhu, Y.; Yang, X.; Li, C. One-pot preparation of graphene/Fe₃O₄ composites by a solvothermal reaction. *New J. Chem.* **2010**, *34*, 2950-2955.
- [11] Zhou, K.; Zhu, Y.; Yang, X.; Li, C. Preparation and application of mediator- free H₂O₂ biosensors of graphene- Fe₃O₄ composites. *Electroanalysis*. **2011**, *23*, 862-869.
- [12] Yang, S.-T.; Cao, L.; Luo, P. G.; Lu, F.; Wang, X.; Wang, H.; Meziani, M. J.; Liu, Y.; Qi, G.; Sun, Y.-P. Carbon dots for optical imaging in vivo. *J. Am. Chem. Soc.* **2009**, *131*, 11308-11309.
- [13] Baker, S.N.; Baker, G.A. Luminescent carbon nanodots: emergent nanolights. *Angew. Chem. Int. Ed.* **2010**, *49*, 6726-6744.
- [14] Zhou, K.; Zhu, Y.; Yang, X.; Li, C. Electrocatalytic Oxidation of Glucose by the Glucose Oxidase Immobilized in Graphene- Au- Nafion Biocomposite. *Electroanalysis*. **2010**, *22*, 259-264.
- [15] Geim, A.K. Graphene: status and prospects. *science*. **2009**, *324*, 1530-1534.
- [16] Stankovich, S.; Dikin, D. A.; Dommett, G. H.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-based composite materials. *nature*. **2006**, *442*, 282.
- [17] Xie, X.; Bai, H.; Shi, G.; Qu, L. highly strain-responsive graphene sheets. *J. Mater. Chem.* **2011**, *21*, 2057-2059.
- [18] Umrao, S.; Jang, M.-H.; Oh, J.-H.; Kim, G.; Sahoo, S.; Cho, Y.-H.; Srivastva, A.; Oh, I.-K. Microwave bottom-up route for size-tunable and switchable photoluminescent graphene quantum dots using acetylacetone: New platform for enzyme-free detection of hydrogen peroxide. *Carbon*. **2015**, *81*, 514-524.
- [19] Yan, X.; Cui, X.; Li, B.; Li, L.-s. solution-processable graphene quantum dots as light absorbers for photovoltaics. *Nano Lett.* **2010**, *10*, 1869-1873.
- [20] Zhuo, S.; Shao, M.; Lee, S. Upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis. *ACS Nano*. **2012**, *6*, 1059.
- [21] Zhu, S. t. Strongly green-photoluminescent graphene quantum dots for bioimaging applications. *Chem Comm.* **2011**, *47*, 6858-6860.
- [22] Yan, X.; Cui, X.; Li, L.-s. Synthesis of large, stable colloidal graphene quantum dots with tunable size. *J. Am. Chem. Soc.* **2010**, *132*, 5944-5945.
- [23] Hamilton, I.P.; Li, B.; Yan, X.; Li, L.-s. Alignment of colloidal graphene quantum dots on polar surfaces. *Nano Lett.* **2011**, *11*, 1524-1529.
- [24] Li, L.-s.; Yan, X. Colloidal graphene quantum dots. *J. Phys. Chem. Lett.* **2010**, *1*, 2572-2576.
- [25] Mueller, M.L.; Yan, X.; McGuire, J. A.; Li, L.-s. Triplet states and electronic relaxation in photoexcited graphene quantum dots. *Nano Lett.* **2010**, *10*, 2679-2682.
- [26] Mueller, M.L.; Yan, X.; Dragnea, B.; Li, L.-s. Slow hot-carrier relaxation in colloidal graphene quantum dots. *Nano Lett.* **2010**, *11*, 56-60.
- [27] Ran, X.; Sun, H.; Pu, F.; Ren, J.; Qu, X. Ag nanoparticle-decorated graphene quantum dots for label-free, rapid and sensitive detection of Ag⁺ and biothiols. *Chem Comm.* **2013**, *49*, 1079-1081.
- [28] Dong, Y.; Li, G.; Zhou, N.; Wang, R.; Chi, Y.; Chen, G. Graphene quantum dot as a green and facile sensor for free chlorine in drinking water. *Anal. Chem.* **2012**, *84*, 8378-8382.
- [29] Shomali, A.; Valizadeh, H.; Banan, A.; Mohammad-Rezaei, R. Efficient synthesis of xanthene derivatives using carboxyl functionalized graphene quantum dots as an acidic nano-catalyst under microwave irradiation. *RSC ADV.* **2015**, *5*, 88202-88208.
- [30] Tang, L.; Ji, R.; Cao, X.; Lin, J.; Jiang, H.; Li, X.; Teng, K. S.; Luk, C. M.; Zeng, S.; Hao, J. Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots. *ACS nano*. **2012**, *6*, 5102-5110.
- [31] Liu, R.; Wu, D.; Feng, X.; Müllen, K. Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology. *J. Am. Chem. Soc.* **2011**, *133*, 15221-15223.
- [32] Dong, Y.; Shao, J.; Chen, C.; Li, H.; Wang, R.; Chi, Y.; Lin, X.; Chen, G. Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid. *Carbon*. **2012**, *50*, 4738-4743.
- [33] Skibo, E.B.; Islam, I.; Heileman, M. J.; Schulz, W. G. Structure-activity studies of benzimidazole-based DNA-cleaving agents, Comparison of benzimidazole, pyrrolobenzimidazole, and tetrahydropyridobenzimidazole analogs. *J. Med. Chem.* **1994**, *37*, 78-92.
- [34] Ryu, C.-K.; Choi, K. U.; Shim, J.-Y.; You, H.-J.; Choi, I. H.; Chae, M. J. Synthesis and antifungal activity of 6-arylthio-/6-Arylamino-4, 7-dioxobenzothiazoles. *Bioorg. Med. Chem.* **2003**, *11*, 4003-4008.
- [35] Ryu, C.-K.; Kang, H.-Y.; Yi, Y.-J.; Shin, K.-H.; Lee, B.-H. Synthesis and antifungal activities of 5/6-arylthio-/5/6-Arylamino-4, 7-dioxobenzothiazoles. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1589-1591.

- [36] Lin, A.; Coby, L.; Sartorelli, A. Quinones as anticancer agents: potential bioreductive alkylating agents. *Cancer Chemoth. Rep.* **1974**, 4, 23-25.
- [37] Kundu, K.; Nayak, S.K. Camphor-10-sulfonic acid catalyzed condensation of 2-naphthol with aromatic/aliphatic aldehydes to 14-aryl/alkyl-14H-dibenzo [a, j] xanthenes. *J. Am. Chem. Soc.* **2014**, 79, 1051-1058.
- [38] Khaligh, N.G. Poly (4-vinylpyridinium) hydrogen sulfate: a novel and efficient catalyst for the synthesis of 14-aryl-14H-dibenzo [a, j] xanthenes under conventional heating and ultrasound irradiation. *Ultrason Sonochem.* **2012**, 19, 736-739.
- [39] Zhu, A.; Bai, Sh.; Jin, W.; Liu, R.; Li, L.; Zhao, Y and Wang, J. An efficient and reusable ionic liquid catalyst for the synthesis of 14-aryl-14 H-dibenzo [a, j] xanthenes under solvent-free conditions. *RSC ADV.* **2014**, 4, 36031-36035.
- [40] Malek, B. i.; Gholizadeh, M.; Sepehr, Z. 1, 3, 5-Trichloro-2, 4, 6-triazinetriion: a versatile heterocycle for the one-pot synthesis of 14-aryl-or alkyl-14H-dibenzo [a, j] xanthene, 1, 8-dioxooctahydroxanthene and 12-aryl-8, 9, 10, 12-tetrahydrobenzo [a] xanthene-11-one derivatives under solvent-free conditions. *Bull. Korean Chem. Soc.* **2011**, 32, 1697-1702.
- [41] Bansal, P.; Chaudhary, G. R.; Kaur, N.; Mehta, S. An efficient and green synthesis of xanthene derivatives using CuS quantum dots as a heterogeneous and reusable catalyst under solvent free conditions. *RSC ADV.* **2015**, 5, 8205-8209.
- [42] Kiasat, R.A.; Mouradzadegun, A.; Saghanezhad, J.S. Phosphosulfonic acid, an efficient solid acid catalyst for the one-pot preparation of 14-aryl-14H-dibenzo [a, j] xanthenes and 1, 8-dioxo-octahydro-xanthenes under solvent-free conditions. *J. Serb. Chem. Soc.* **2013**, 78, 1291-1299.
- [43] Sajjadifar, S.; Fadaeian, M.; Bakhtiyari, M.; Rezayati, S. One-pot synthesis of xanthene derivatives using silica supported [2-(Sulfooxy) ethyl] sulfamic Acid as a novel and efficient catalyst under solvent-free condition. *Chem. Sci. Trans.* **2014**, 3, 107-116.
- [44] Sadeh, F.N.; Fatahpour, M.; Hazeri, N.; Maghsoodlou, M. T.; Lashkari, M. One-Pot Condensation Approach for the Synthesis of Some 1, 8-Dioxo-octahydroxanthenes and 14-Aryl-14H-dibenzo [a, j] Xanthenes Using Lactic Acid as an Efficient and Eco-Friendly Catalyst. *Acta Chem. Iasi.* **2017**, 25, 24-37.

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