

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

Fatemeh Noori Sadeh^a, Maryam Fatahpour^a, Nourallah Hazeri^{a*},
Malek Taher Maghsoodlou^a and Mojtaba Lashkari^b

^a*Department of Chemistry, Faculty of Sciences, University of Sistan and
Baluchestan, P.O. Box 98135-674, Zahedan, Iran*

^b*Faculty of Sciences, Velayat University, Iranshahr, Iran*

Abstract: The synthesis of some biologically important xanthenes, by efficient and convenient approach for one-pot condensation reaction of aldehydes and dimedone or β -naphthol in the presence of lactic acid as an efficient, inexpensive and environmental friendliness catalyst under solvent-free conditions, is presented. The merits of this reaction are higher product yields in shorter reaction time and environmentally benign reaction conditions.

Keywords: xanthenes, environmental friendliness, lactic acid, solvent-free.

Introduction

Critical role of heterocycles is distinguished in the design and synthesis of bioactive small molecules. Among the many heteroaromatic

* Nourallah Hazeri, *e-mail:* n_hazeri@yahoo.com , nhazeri@chem.usb.ac.ir

compounds, xanthenes and benzoxanthenes as one of the important classes of organic compounds have received significant attention for many pharmaceutical and organic researchers essentially due to their vast biological and pharmaceutical potent, such as antiviral,¹ antibacterial,² and antimalarial³. Xanthenes also have been used as dyes,^{4,5} fluorescent materials,⁶ and in laser technologies⁷. According to the literature data, various catalysts have been used for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-octahydroxanthenes such as Dowex-50W,⁸ silica sulfuric acid,⁹ [Et₃N-SO₃H]Cl,¹⁰ 1,3,5-trichloro-2,4,6-triazinetriion,¹¹ *o*-sulfonated poly(4-vinylpyrrolidonium)chloride,¹² acetic acid,¹³ and [*n*-Pr₂NH₂][HSO₄]¹⁴.

In the multi-component reactions (MCRs) protocol, several simple starting substrates are involved in a single reaction vessel to generate molecular complexity which possesses substantial elements of all the reactants.¹⁵ MCRs have demonstrated to be a privileged asset in organic and medicinal chemistry owing to their application in synthesis of multifunctionalized and structurally diverse drug-like chemical entities.¹⁶ These reactions in conjunction with solvent-free conditions as one of the key green chemistry protocols present notable evolutions, such as easier work up, decrease in reaction times, increase in yield, avoiding the use of toxic solvents, and minimizing waste generation.¹⁷

As a part of our ongoing efforts towards the development of greener catalytic systems for important organic conversions,¹⁸⁻²¹ we had recently explored the catalytic potential of lactic acid as an efficient, non toxic, commercially available, high yielding, and inexpensive catalyst for the synthesis of various 1,8-dioxo-octahydroxanthene and 14-aryl-14*H*-

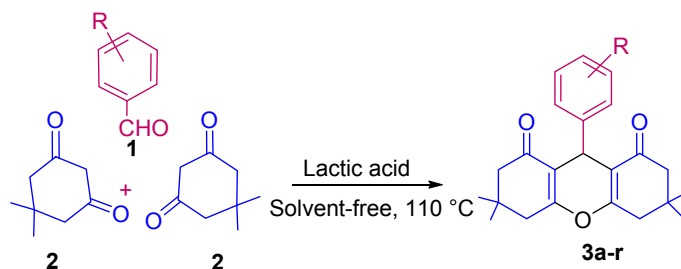
dibenzo[*a,j*]xanthene molecules by one-pot condensation reactions of different benzaldehydes with dimedone or β -naphthol.

Results and Discussion

At first, we focused our attention on the synthesis of 1,8-dioxo-octahydroxanthenes (**3a-r**) (scheme 1). The reaction between benzaldehyde (**1**) and dimedone (**2**) in ratio 1:2 was chosen as a simple model substrate, and optimization studies are shown in Table 1. Further evaluation of the solvent-free reaction conditions using of different temperatures accomplished in the presence of lactic acid as catalyst. As it can be seen in Table 1, the shorter times and excellent yields were gained when the reaction was carried out at 110 °C (Table 1, entry 4).

We carried on our endeavors for improvement in the result. So model reactants were allowed to react at a higher or lower catalyst loading (entries 5-8) that the optimum yield of 1,8-dioxo-octahydroxanthene was obtained in the presence of 20 mol % of lactic acid.

After optimized the reaction conditions, we evaluated the reaction scope using a various aryl aldehydes; results are summarized in Table 2. As shown in Table 2, the reaction of aryl aldehydes either with electron-withdrawing groups or electron-donating groups gave the corresponding products with good to excellent yields.



Scheme 1. One-pot synthesis of 1,8-dioxo-octahydroxanthenes using lactic acid as catalyst.

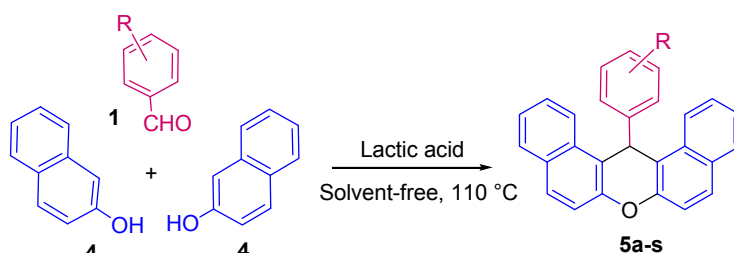
Table 1. Optimization of reaction condition between benzaldehyde (1.0 mmol) and dimedone (2.0 mmol) in the presence of lactic acid under solvent-free conditions.

Entry	Temperature (°C)	Catalyst (mol %)	Time (min)	Yield (%)
1	80	20	90	87
2	90	20	60	85
3	100	20	45	85
4	110	20	30	95
5	110	5	30	70
6	110	10	30	84
7	110	15	30	92
8	110	30	30	95

Table 2. 1,8-Dioxo-octahydroxanthene derivatives of pseudo three-component coupling reaction catalysed by lactic acid under solvent-free conditions.

Entry	R	Product	Time (min)	Yield (%)	Mp (°C)	
					Found	Reported ^{Ref}
1	H	3a	30	95	204-206	203-205 ¹¹
2	2-Cl	3b	25	90	226-227	225-227 ¹¹
3	3-Cl	3c	30	92	185-187	185-186 ¹⁴
4	4-Cl	3d	25	95	234-236	233-235 ¹¹
5	2,4- di Cl	3e	25	95	179-181	175-177 ²⁷
6	4-F	3f	20	95	225-227	226-227 ¹¹
7	3-Br	3g	35	85	278-281	281-282 ¹²
8	4-Br	3h	30	95	237-238	235-237 ¹²
9	2-NO ₂	3i	25	89	249-251	251-252 ¹²
10	3-NO ₂	3j	25	91	170-172	168-170 ¹¹
11	4-NO ₂	3k	20	95	226-228	226-228 ²⁹
12	3-OH	3l	25	93	224-227	220-222 ²⁸
13	4-OH	3m	25	95	248-250	250-254 ¹⁴
14	3-Me	3n	35	85	205-207	205-207 ³⁰
15	4-Me	3o	25	91	210-212	215-217 ¹¹
16	3-OMe	3p	35	83	298-301	308-310 ²⁹
17	4-OMe	3q	20	95	248-249	243-245 ²⁸
18	3,4- di OMe	3r	25	82	179-181	175-177 ²⁸

In the next step, lactic acid was used in the condensation of β -naphthol (**4**) with aldehydes (**1**) leading to 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**) (scheme 2). Our observations showed that under the same conditions used for the preparation of 1,8-dioxo-octahydroxanthenes, this reaction was completed; the respective results are summarized in Table 3. Evidences indicate that, lactic acid is one of the efficient catalyst for one-pot synthesis of 1,8-dioxo-octahydroxanthenes (**3a-r**) and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**) under solvent-free conditions that confirms the efficiency of this method.



Scheme 2. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using lactic acid as catalyst.

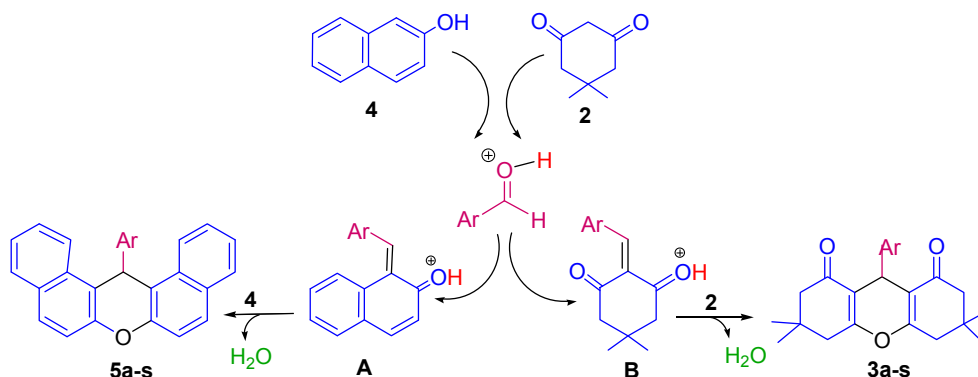
Table 3. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives using lactic acid as catalyst under solvent-free conditions.

Entry	R	Product	Time (min)	Yield (%)	Mp (°C)	
					Found	Reported ^{Ref}
1	H	5a	45	85	185-188	184-186 ¹²
2	2-Cl	5b	50	90	214-216	214-216 ²²
3	3-Cl	5c	45	94	206-209	207-209 ²³
4	4-Cl	5d	30	95	292-295	290-292 ²²
5	2,4- di Cl	5e	40	90	225-227	229-230 ²⁴
6	4-F	5f	30	90	247-249	250-252 ²⁵
7	3-Br	5g	40	84	193-195	190-192 ²⁶
8	4-Br	5h	30	95	297-299	297-298 ²²
9	2-NO ₂	5i	25	85	214-216	214-216 ¹¹
10	3-NO ₂	5j	50	90	226-228	233-234 ²⁵

Table 3. Continued

11	4-NO ₂	5k	20	90	318-320	313-315 ¹²
12	3-OH	5l	45	82	247-253	250-253 ²⁴
13	4-OH	5m	30	85	136-139	135-137 ¹²
14	2-Me	5n	40	80	259-262	258-259 ³¹
15	3-Me	5o	40	80	253-255	250-253 ²⁴
16	4-Me	5p	40	80	230-233	230-231 ²²
17	3-OMe	5q	40	88	171-173	170-171 ¹²
18	4-OMe	5r	30	90	202-205	204-205 ²²
19	4-OH-3- OMe	5s	40	80	198-200	198-201 ²⁵

A plausible mechanism, illustrating the role of lactic acid in the synthesis of 1,8-dioxo-octahydroxanthenes (**3a-r**) and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**). Initially, aldehyde is activated by the proton from lactic acid. Next, the carbonyl group aldehyde is attacked by the nucleophilic β -naphthol (**4**) or dimeone (**2**) to create the intermediated products (**A**, **B**). The subsequent addition of (**4**) or (**2**) to these intermediates, gives the acyclic adduct product, which undergoes intramolecular cyclization with elimination of one H₂O molecule to afford the desired xanthene derivatives.



Scheme 3. The proposed mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes catalysed by lactic acid.

Experimental

General

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a FT-IR-JASCO-460 plus spectrometer, respectively. ^1H NMR spectra of known compounds were recorded on a Bruker DRX-400 Avance instrument in CDCl_3 operating at 400 MHz. All reagents were purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) and used without further purification.

General procedure for preparation of 1,8-dioxo-octahydroxanthenes and 14-aryl-14H-dibenzo[a,j]xanthenes

A mixture of different aldehydes (**1**) (1.0 mmol) with dimedone (**2**) or β -naphthol (**4**) (2.0 mmol) and lactic acid (20 mol %) was stirred at 110 °C under solvent-free conditions. The completion of reactions was monitored through thin layer chromatography (TLC). The reaction mixture was cooled to room temperature, then ethanol (5 mL) was added to the reaction mixture and the precipitate formed was filtered off. The crude products were recrystallized from ethanol to afford the pure xanthene derivatives.

Characterization data of selected compounds

9-(3-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3l): White solid; IR (KBr, cm^{-1}): 3364, 3054, 2963, 1671, 1658, 1452, 1359, 1256, 1137; ^1H NMR (400 MHz, CDCl_3): δ 1.03 (s, 6H, 2 CH_3), 1.13 (s, 6H, 2 CH_3), 2.22 (d, $J = 16.4$ Hz, 2H, 2 CH_2), 2.28 (d, $J = 16.4$ Hz, 2H, 2 CH_2), 2.49 (s, 4H, 2 CH_2), 4.77 (s, 1H, CH), 6.59-7.10 (m, 4H, Ar-H).

3,3,6,6-tetramethyl-9-(m-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3n): White solid; IR (KBr, cm^{-1}): 3098, 2956, 1672, 1662, 1464, 1358, 1233, 1135; ^1H NMR (400 MHz, CDCl_3): δ 1.02 (s, 6H, 2 CH_3),

1.13 (s, 6H, 2CH₃), 2.20 (d, $J = 16.4$ Hz, 2H, 2CH₂), 2.26 (d, $J = 16.0$ Hz, 2H, 2CH₂), 2.31 (s, 3H, CH₃), 2.49 (s, 4H, 2CH₂), 4.74 (s, 1H, CH), 6.92-7.16 (m, 4H, Ar-H).

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3o): White solid; IR (KBr, cm⁻¹): 3039, 2958, 1679, 1664, 1467, 1357, 1198, 1137; ¹H NMR (400 MHz, CDCl₃): δ 1.02 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.18 (d, $J = 16.2$ Hz, 2H, 2CH₂), 2.26 (d, $J = 16.2$ Hz, 2H, 2CH₂), 2.26 (s, 3H, CH₃), 2.48 (s, 4H, 2CH₂), 4.73 (s, 1H, CH), 7.04 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.20 (d, $J = 8.1$ Hz, 2H, Ar-H).

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3q): White solid; IR (KBr, cm⁻¹): 3028, 2958, 1678, 1665, 1461, 1358, 1260, 1234, 1164; ¹H NMR (400 MHz, CDCl₃): δ 1.02 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.19 (d, $J = 16.0$ Hz, 2H, 2CH₂), 2.26 (d, $J = 16.4$ Hz, 2H, 2CH₂), 2.48 (s, 4H, 2CH₂), 3.75 (s, 3H, OCH₃), 4.72 (s, 1H, CH), 6.78 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.23 (d, $J = 8.8$ Hz, 2H, Ar-H).

9-(3,4-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3r): White solid; IR (KBr, cm⁻¹): 3007, 2957, 1666, 1627, 1465, 1360, 1262, 1228, 1139; ¹H NMR (400 MHz, CDCl₃): δ 1.02 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.20 (d, $J = 16.2$ Hz, 2H, 2CH₂), 2.27 (d, $J = 16.5$ Hz, 2H, 2CH₂), 2.48 (s, 4H, 2CH₂), 3.81 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 4.27 (s, 1H, CH), 6.73 (d, $J = 8.1$ Hz, 2H, Ar-H), 6.78 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.92 (s, 1H, Ar-H).

14-(4-hydroxyphenyl)-14-H-dibenzo[a,j]xanthene (5m): White solid; IR (KBr, cm⁻¹): 3414, 3056, 2929, 1622, 1593, 1508, 1428, 1250, 1174, 800, 748; ¹H NMR (400 MHz, CDCl₃): δ 6.46 (s, 1H, CH), 6.61 (d, $J = 8.8$ Hz,

2H, ArH), 7.39-7.62 (m, 8H, ArH), 7.80-7.87 (m, 4H, ArH), 8.39 (d, $J = 8.4$ Hz, 2H, ArH).

14-(3-methylphenyl)-14-H-dibenzo[a,j]xanthene (5o): White solid; IR (KBr, cm^{-1}): 3043, 2918, 1620, 1592, 1514, 1431, 1252, 1172, 808, 747; ^1H NMR (^1H NMR (400 MHz, CDCl_3): δ 2.28 (s, 3H, CH_3), 6.48 (s, 1H, CH), 6.83 (d, $J = 7.2$ Hz, 2H, ArH), 7.42-7.63 (m, 8H, ArH), 7.81-7.87 (m, 4H, ArH), 8.44 (d, $J = 8.4$ Hz, 2H, ArH).

14-(4-methoxyphenyl)-14-H-dibenzo[a,j]xanthene (5r): White solid; IR (KBr, cm^{-1}): 3072, 2927, 1621, 1592, 1509, 1399, 1250, 1177, 808, 742; ^1H NMR (400 MHz, CDCl_3): δ 3.64 (s, 3H, OCH_3), 6.48 (s, 1H, CH), 6.70 (d, $J = 8.0$ Hz, 2H, ArH), 7.39-7.62 (m, 8H, ArH), 7.80-7.86 (m, 4H, ArH), 8.39 (d, $J = 8.0$ Hz, 2H, ArH).

14-(4-hydroxy-3-methoxyphenyl)-14-H-dibenzo[a,j]xanthene (5s): White solid; IR (KBr, cm^{-1}): 3414, 3056, 2929, 1622, 1593, 1508, 1428, 1250, 1240, 1137, 801, 753; ^1H NMR (400 MHz, CDCl_3): δ 3.69 (s, 3H, OCH_3), 6.47 (s, 1H, CH), 6.75 (d, $J = 8.4$ Hz, 1H, ArH), 6.87 (d, $J = 2.4$ Hz, 1H, ArH), 7.18 (dd, $J = 8.4$ Hz, 1H, ArH), 7.43-7.63 (m, 6H, ArH), 7.81-7.87 (m, 4H, ArH), 8.43 (d, $J = 8.4$ Hz, 2H, ArH).

Conclusions

In compendium, we have expanded a very facile and comfortable strategy for one-pot synthesis of biologically 14-aryl-14H-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydroxanthene derivatives in the presence of lactic acid as a commercially available, and eco-compatibility catalyst via pseudo three-component condensation reaction between aldehydes and dimedone or β -naphthol under solvent-free conditions. Good

to excellent yields, simplicity of operation, comfortable purification, and high atom-economy are the key advantages of the present method.

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References

1. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parker, K. E. B.; Thomas, G. J. PCT Int. Appl. WO 9706178, 1997; *Chem. Abstr.* **1997**, *126*, 212377y.
2. Hideo, T. Jpn. Tokkyo Koho JP 56005480, 1981; *Chem. Abstr.* **1981**, *95*, 80922b.
3. Chibale, K.; Visser, M.; Schalkwyk, D. V.; Smith, P. J., Saravanamuthu, A., Fairlamb, A. H. Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents. *Tetrahedron.* **2003**, *59*, 2289-2296.
4. Menchen, S. M.; Benson, S. C.; Lam, J. Y. L.; Zhen, W.; Sun, D.; Rosenblum, B. B.; Khan, S. H.; Taing, M. US Patent. *Chem. Abstr.* **2003**, *139*, 54287f.
5. Bhowmik, B. B.; Ganguly, P. Photophysics of xanthene dyes in surfactant solution. *Spectrochim. Acta, Part A.* **2005**, *61*, 1997-2003.
6. Knight, C. G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles. *J. Biochem.* **1989**, *258*, 683-687.
7. Ahmad, M.; King, T. A.; Ko, D. K.; Cha, B. H.; Lee, J. Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1473.
8. Imani Shakibaei, G.; Mirzaei, P.; Bazgir, A. Dowex-50W promoted synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthene and 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions. *Appl. Catal., A.* **2007**, *325*, 188-192.

9. Seyyedhamzeh, M.; Mirzaei, P.; Bazgir, A. Solvent-free synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as catalyst. *Dyes Pigm.* **2008**, *76*, 836-839
10. Zare, A.; Moosavi-Zare, R.; Merajoddin, M.; Zolfigol, M. A.; Hekmat-Zadeh, T.; Hasaninejad, A.; Khazaei, A.; Mokhlesi, M.; Khakyzadeh, V.; Derakhshan-Panah, F.; Beyzavi, M. H.; Rostami, E.; Argoon, A.; Roohandeh, R. Ionic liquid triethylamine-bonded sulfonic acid {[Et₃N-SO₃H]Cl} as a novel, highly efficient and homogeneous catalyst for the synthesis of β-acetamido ketones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. *J. Mol. Liq.* **2012**, *167*, 69-77.
11. Maleki, B.; Gholizadeh, M.; Sepehr, Z. 1,3,5-Trichloro-2,4,6-Triazinetrion: A Versatile Heterocycle for the One-Pot Synthesis of 14-Aryl- or Alkyl-14*H*-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.
12. Shirini, F.; Najafi Moghadam, P.; Moayedi, S.; Seddighi, M. Introduction of *O*-sulfonated poly(4-vinylpyrrolidonium) chloride as a polymeric and reusable catalyst for the synthesis of xanthene derivatives. *RSC Adv.* **2014**, *4*, 38581-38588.
13. Hazeri, N.; Masoumnia, A.; Mghsoodlou, M. T.; Salahi, S.; Kangani, M.; Kianpour, S.; Kiaee, S.; Abonajmi, J. Acetic acid as an efficient catalyst for synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines. *Res. Chem. Intermed.* **2015**, *41*, 4123-4131.
14. Das, P. J.; Das, J. Secondary amine based ionic liquid: an efficient catalyst for solvent free one pot synthesis of xanthenes and benzoxanthenes. *RSC Adv.* **2015**, *5*, 11745-11752.
15. Naeimi, H.; Rashid, Z.; Zarnani, A. H.; Ghahremanzadeh, R. MnFe₂O₄@NH₂@2AB-Ni: a novel, highly active, stable and magnetically

- recoverable nanocatalyst and use of this heterogeneous catalyst in green synthesis of spirooxindoles in water. *New J. Chem.* **2014**, *38*, 5527-5535.
16. Veisi, H.; Aminimanesh, A.; Khankhani, N.; Ghorbani-Vagheib, R. Protic ionic liquid [TMG][Ac] as an efficient, homogeneous and recyclable catalyst for one-pot four-component synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones and dihydro-1*H*-pyrano[2,3-*c*]pyrazol-6-one. *RSC Adv.* **2014**, *4*, 25057-25062.
 17. Khazaei, A.; Moosavi-Zare, A. R.; Mohammadi, Z.; Zare, A.; Khakyzadeh, V.; Darvishi, G. Efficient preparation of 9-aryl-1,8-dioxo-octahydroxanthenes catalyzed by nano-TiO₂ with high recyclability. *RSC Adv.* **2013**, *3*, 1323-1326.
 18. Lashkari, M.; Reza Heydari, R.; Mohamadpour, F. Chromium (III) nitrate nonahydrate an environmentally benign and efficient heterogeneous catalyst for facile one-pot Biginelli synthesis of 3,4-dihydropyrimidin-2-(1*H*)-one/thione derivatives under solvent-free conditions. *Acta Chemica Iasi.* **2016**, *24*, 29-42.
 19. Mohamadpour, F.; Maghsoodlou, M.T.; Heydari, R.; Lashkari, M. Copper(II) acetate monohydrate: an efficient and eco-friendly catalyst for the one-pot multi-component synthesis of biologically active spiropyrans and 1*H*-pyrazolo [1,2-*b*]phthalazine-5,10-dione derivatives under solvent-free conditions. *Res Chem Intermed.* **2016**, doi:10.1007/s11164-016-2565-0.
 20. Fatahpour, M.; Hazeri, N.; Maghsoodlou, M. T.; Lashkari, M. Lactic Acid: A New Application as an efficient catalyst for the green one-pot synthesis of 2-hydroxy-12-aryl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthene-11-one and 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one analogs. *Iran. J. Sci. Technol., Trans. A: Sci.* **2016**, doi:10.1007/s40995-016-0064-1.
 21. Mohamadpour, F.; Maghsoodlou, M.T.; Heydari, R.; Lashkari, M. Tartaric acid: a naturally green and efficient di-functional brønsted acid catalyst for the one-pot four-component synthesis of polysubstituted dihydropyrrol-2-ones at ambient temperature. *Iran. J. Sci. Technol., Trans. A: Sci.* **2016**, doi:10.1007/s40995-016-0049-0.

22. Ghaffari Khaligh, N. Poly(4-vinylpyridinium)hydrogen sulfate: A novel and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under conventional heating and ultrasound irradiation. *Ultrason. Sonochem.* **2012**, *9*, 736-739.
23. Shirini, F.; Abedini, M.; Pourhasan, R. *N*-sulfonic acid poly(4-vinylpyridinium) chloride: A novel polymeric and reusable catalyst for the preparation of xanthenes derivatives. *Dyes Pigm.* **2013**, *99*, 250-255.
24. Naeimi, H.; Nazifi, Z. S. Environmentally benign and one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by acyclic brønsted acidic ionic liquid [H-NMP][HSO₄] under green conditions. *C. R. Chim.* **2014**, *17*, 41-48.
25. Zhu, A.; Bai, S.; Jin, W.; Liu, R.; Li, L.; Zhao, Y.; 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.
26. Mokhtary, M.; Refahati, S. Polyvinylpyrrolidone-supported boron trifluoride (PVPP-BF₃): Mild and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo [*a,j*] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives. *Dyes Pigm.* **2013**, *99*, 378-381.
27. Zolfigol, M. A.; Khakyzadeh, V.; Moosavi-Zare, A. R.; Zare, A.; Azimi, B.; Asgari, Z.; Hasaninejad, A. Preparation of various xanthene derivatives over sulfonic acid functionalized imidazolium salts (SAFIS) as novel, highly efficient and reusable catalysts. *C. R. Chim.* **2012**, *15*, 719-736.
28. Zhou, Z.; Deng, X. [Et₃NH][HSO₄] catalyzed efficient and green synthesis of 1, 8-dioxo-octahydroxanthenes. *J. Mol. Catal. A: Chem.* **2013**, *367*, 99-102.
29. Eshghi, H.; Rahimizadeh, M.; Eftekhar, M.; Bakavoli, M. Synthesis, characterization, and application of cobalt hydrogen sulfate as a new heterogeneous, reusable and efficient catalyst in one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxooctahydroxanthenes. *Kinet. Catal.* **2014**, *55*, 428-433.

30. Horning, E. C.; Horning, M. G. Methone derivatives of aldehydes. *J. Org. Chem.* **1946**, *11*, 95-99.
31. Saini, A.; Kumar, S.; Sandhu, J. S. A new LiBr-catalyzed, facile and efficient method for the synthesis of 14-alkyl or aryl-14*H*-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*b*]pyrans under solvent-free conventional and microwave heating. *Synlett.* **2006**, *12*, 1928-1932.