

# BiVO<sub>4</sub>-NPs as a new and efficient nano-catalyst for the synthesis of 1,8-dioxo-octahydro xanthenes

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**Abstract** BiVO<sub>4</sub>-NPs can be used as a new and efficient nano-catalyst for the promotion of the synthesis of 1,8-dioxo-octahydro xanthenes derivatives. The structures of the products were characterized by their physical properties, comparison with authentic samples and IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. Easy preparation of the catalyst, mild reaction conditions, easy work-up procedure, excellent yields and short reaction times are some of the advantages of this work.

**Keywords** BiVO<sub>4</sub>-NPs · Nano-particles · 1,8-dioxo-octahydro xanthenes · Aldehyde · Reusable catalyst

## Background

Xanthenes and their derivatives have received special attention due to their diverse array of biological activities such as anti-inflammatory, antibacterial and antiviral activities [1–3]. Furthermore, these compounds can be used as leuco dyes [4], in laser technology [5] and pH-sensitive fluorescent materials for the visualization of biomolecular assemblies [6]. Because of their wide range of synthetic, industrial and pharmacological applications, there are

several reports in the literature for the synthesis of xanthene derivatives.

1,8-Dioxo-octahydro xanthene derivatives are among the most important types of xanthenes and for this reason several methods are reported for the synthesis of 1,8-dioxo-octahydro xanthenes using a variety of catalysts and reagents [7–17].

However, these methods suffer from one or more disadvantages such as: long reaction times, low yields, the use of toxic solvents, requirement of excess of reagents/catalysts and harsh reaction conditions. Therefore, it is important to find more efficient catalysts and methods for the synthesis of these types of compounds.

In recent years and because of the unique properties of nano-particles, synthetic chemists focused on the synthesis and characterization of these types of catalysts with lower dimensions named as nano-catalysts [18].

## Results and discussion

In recent years, a considerable amount of our research program is focused on the development of new methods and use of new reagents for the synthesis of xanthenes derivatives [19–25]. In continuation of these studies, we have found that BiVO<sub>4</sub>-NPs as a newly reported reagent [26] is efficiently able to catalyze the synthesis of 1,8-dioxo-octahydro xanthenes. All reactions are performed under mild reaction conditions in good to high yields.

At the first step and to optimize the reaction conditions, the prepared catalyst was used for the promotion of the condensation of benzaldehyde with dimedone, as a model reaction, and compared the effect of different solvents and solvent-free conditions and also the effect of the catalyst load on the reaction yield and time at thermal conditions

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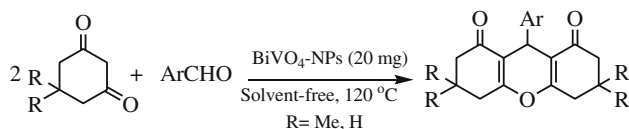
(Table 1). On the basis of these studies, we concluded that the best result can be obtained under the conditions showed in Scheme 1.

**Table 1** The effect of different conditions on the model reaction

Entry	Conditions	BiVO <sub>4</sub> -NPs (mg)	Time (min)	Conversion (%) <sup>a</sup>
1	EtOH (reflux)	20	60	100
2	H <sub>2</sub> O (reflux)	20	60	0
3	Solvent-free (60 °C)	20	60	70
4	Solvent-free (100 °C)	20	45	90
5	Solvent-free (120 °C)	20	30 s	100
6	Solvent-free (120 °C)	10	15	80

Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol)

<sup>a</sup> GC



**Scheme 1** Synthesis of 1,8-dioxo-octahydro xanthenes

After optimization of the reaction conditions and to show the general applicability of the method, different types of aromatic aldehydes were subjected to the same reaction under the determined conditions. The obtained results showed that these conversions also were occurred with excellent yields during very short times (Table 2).

It seems that the electronic nature of the functional group on the ring of the aldehyde exerted a slight influence on the reaction time.

A plausible mechanism for the synthesis of 1,8-dioxo-octahydro xanthenes catalyzed by BiVO<sub>4</sub>-NPs is shown in Scheme 2 [34, 35].

To illustrate the efficiency of the present method, Table 3 compares some of our results obtained from the synthesis of xanthene derivatives with the same results reported by the other groups. This Table clearly shows the applicability and efficiency of the present method. Table 3 also compares the TOF (turnover frequency) of these catalysts in this reaction. As it is clear BiVO<sub>4</sub>-NPs is superior in terms of TOF to the compared catalysts.

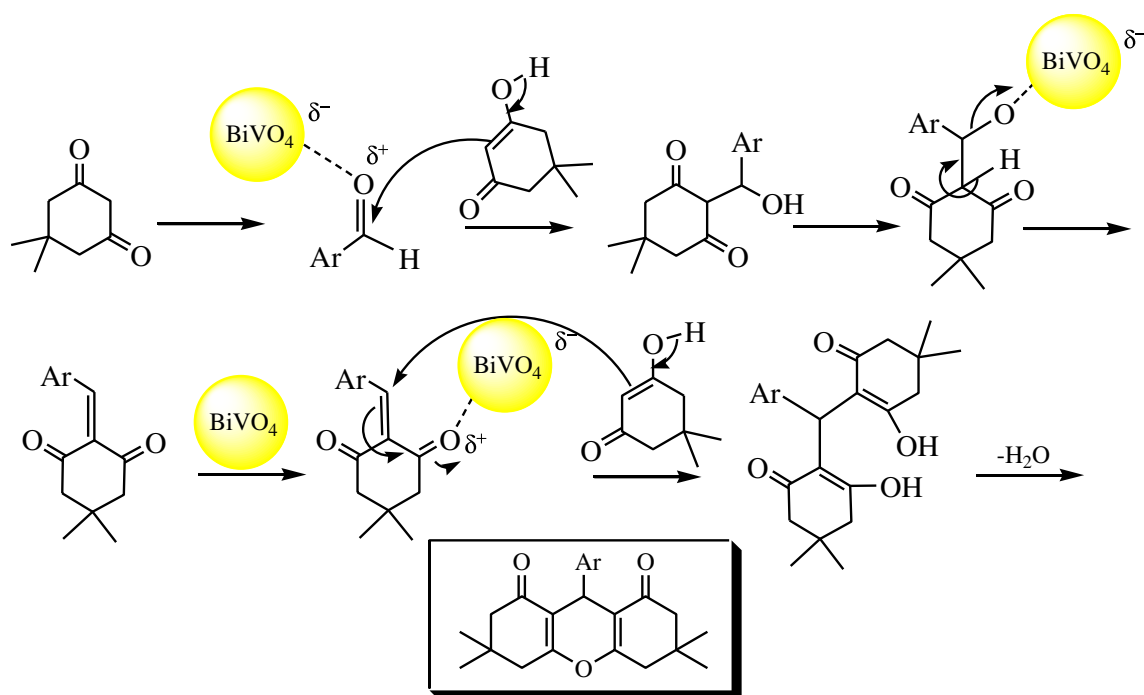
In addition, we decided to study the catalytic activity of the recycled catalyst for the synthesis of xanthenes derivatives. After the separation of the product, the catalyst was

**Table 2** Preparation of 1,8-dioxo-octahydro xanthenes in the presence of BiVO<sub>4</sub>-NPs

Entry	Aldehydes	R	Time (min)	Yield (%) <sup>a</sup>	M.p. (°C)	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub> CHO	Me	30 s	99	197–198	199–201 [15]
2	4-ClC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	99	227–229	229–231 [15]
3	3-ClC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	98	186–187	186–187 [15]
4	2-ClC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	98	224–225	225–227 [27]
5	4-BrC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	97	239–240	240–242 [28]
6	3-BrC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	95	281–282	281–283 [21]
7	4-FC <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	98	259–260	259–262 [21]
8	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	Me	4	94	223–224	224–226 [15]
9	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	Me	30 s	96	164–165	164–166 [15]
10	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	Me	4	93	251–252	251–252 [27]
11	3-MeOC <sub>6</sub> H <sub>4</sub> CHO	Me	4	95	190–191	192–194 [21]
12	3-MeC <sub>6</sub> H <sub>4</sub> CHO	Me	5	98	205–206	206–208 [9]
13	Cinnamaldehyde	Me	3	90	170–172	172–174 [15]
14	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	Me	3	96	220–221	221–223 [29]
15	C <sub>6</sub> H <sub>5</sub> CHO	H	30 s	99	203–204	203–205 [27]
16	4-ClC <sub>6</sub> H <sub>4</sub> CHO	H	30 s	99	228–229	229–232 [27]
17	4-BrC <sub>6</sub> H <sub>4</sub> CHO	H	30 s	97	227–228	229–231 [27]
18	3-BrC <sub>6</sub> H <sub>4</sub> CHO	H	30 s	95	280–281	281–283 [21]
19	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	H	30 s	94	263–264	263–265 [23]
20	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	H	30 s	96	280–281	281–282 [19]
21	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	H	30 s	96	238–240	238–240 [19]
22	4-OHC <sub>6</sub> H <sub>4</sub> CHO	H	30 s	98	245–246	245–247 [30]
23	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	H	6	95	200–201	200–201 [19]

<sup>a</sup> Isolated yields





**Scheme 2** Proposed mechanism for the synthesis of 1,8-dioxo-octahydro xanthenes catalyzed by  $\text{BiVO}_4$ -NPs

**Table 3** Comparison of the results of the reaction of dimedone with 4- $\text{ClC}_6\text{H}_4\text{CHO}$  using  $\text{BiVO}_4$ -NPs with some of those reported in the literature

Entry	Catalyst (mol%)	Conditions	Time (h)	Yield (%)	TOF ( $\text{h}^{-1}$ )	Refs.
1	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (10)	Solvent-free, 120 °C	0.66	95	14.4	[9]
2	MCM-41- $\text{SO}_3\text{H}$ (5)	$\text{H}_2\text{O}$ , 60 °C	1	86	17.2	[12]
3	<i>N</i> -Sulfonic acid poly(4-vinyl pyridinium) chloride (4)	Solvent-free, 100 °C	0.05	98	490	[23]
4	1-Butyl-3-methylimidazolium hydrogen sulfate (72)	Solvent-free, 80 °C	3.5	95	0.38	[28]
5	Silica sulfuric acid (7.8)	Solvent-free, 80 °C	0.5	92	23.6	[31]
6	$\text{ZrO}(\text{OTf})_2$ (1)	Solvent-free, 90 °C	0.066	94	1,424	[32]
7	Silicabonded <i>N</i> -propyl sulfamic acid (1.02)	EtOH, reflux	3	91	29.7	[33]
8	$\text{Fe}_3\text{O}_4$ NPs (10)	Solvent-free, 100 °C	0.33	88	26.7	[34]
9	ZnO NPs (10)	Solvent-free, 80 °C	0.25	96	38.4	[35]
10	$\text{BiVO}_4$ -NPs (6.2)	Solvent-free, 120 °C	30 s	99	956	This work

washed with acetone and derived at 70 °C. As shown in Fig. 1,  $\text{BiVO}_4$ -NPs can be recycled at least six times without significant decrease in its catalytic activity (Table 2, entry 2).

## Conclusion

In conclusion, we have introduced an efficient and convenient approach for the synthesis of 1,8-dioxo-octahydro xanthenes using  $\text{BiVO}_4$ -NPs as a novel nano-catalyst.

This method has several advantages such as: ease of preparation and handling of the catalyst, simplicity and

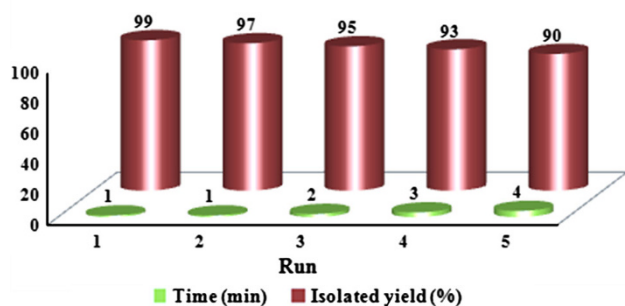
easy work-up, high reaction rates, excellent yields and effective reusability of the catalyst for several times without considerable decrease in yields.

## Methods

### General

All chemicals were purchased from Merck or Fluka Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants and comparison with authentic samples. The purity





**Fig. 1** Reusability of BiVO<sub>4</sub>-NPs in the reaction of 4-chlorobenzaldehyde with dimedone

determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates. The FT-IR spectra were run on a VERTEX 70 Bruker company (Germany). The <sup>1</sup>H NMR (300, 400 and 500 MHz) and <sup>13</sup>C NMR (100 MHz) were run on a Bruker Avance DPX-400 FT-NMR spectrometer ( $\delta$  in ppm).

#### General procedure

##### *Synthesis of 1,8-dioxo-octahydro xanthenes derivatives*

A mixture of dimedone or cyclohexadione (2 mmol), aldehyde (1 mmol) and BiVO<sub>4</sub>-NPs (20 mg) was stirred at 120 °C under solvent-free conditions for the appropriate time. After completion of the reaction [monitored by TLC: EtOAc: *n*-hexane (2:8)], the reaction was cooled to room temperature, ethanol (5 mL) was added and the mixture was filtered. Evaporation of the solvent, followed by recrystallization of the residue from EtOH:H<sub>2</sub>O (95:5) afforded the pure products in good to high yields. The physical and spectral data of the known compounds were in agreement with those reported in the literature.

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#### References

- Chatterjee, S., Iqbal, M., Kauer, J.C., Mallamo, J.P., Senadhi, S., Mallya, S., Bozyczko-Coyne, D., Siman, R.: Xanthenes derived potent nonpeptidic inhibitors of recombinant human calpain I. *Bioorg. Med. Chem. Lett.* **6**, 1619–1622 (1996)
- Vieira, E., Huwyler, J., Jolidon, S., Knofach, F., Mutel, V., Wichmann, J.: Synthesis 12-aryl or 12-alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives catalyzed by dodecatungstophosphoric acid. *Bioorg. Med. Chem. Lett.* **15**, 4628–4631 (2005)

- Hafez, H.N., Hegab, M.I., Ahmed-Farag, I.S., El-Gazzar, A.B.A.: A facile regioselective synthesis of novel *spiro*-thioxanthenes and *spiro*-xanthenes-9',2-[1, 3, 4]thiadiazole derivatives as potential analgesic and anti-inflammatory agents. *Bioorg. Med. Chem. Lett.* **18**, 4538–4543 (2008)
- Kitahara, Y., Tanaka, K.: Synthesis, crystal structure and properties of thiaheterohelicenes containing phenolic hydroxy functions. *Chem. Commun.* 932–933 (2002)
- Ahmad, M., King, T.A., Ko, D.K., Cha, B.H., Lee, J.: Performance and photostability of xanthenes and pyrromethene laser dyes in sol-gel phases. *J. Phys. D Appl. Phys.* **35**, 1473–1476 (2002)
- Knight, C.G., Stephens, T.: Xanthenes-dye-labelled phosphatidylethanolamines as probes of interfacial pH. *J. Biochem.* **258**, 683–687 (1989)
- Dadhania, A.N., Patel, V.K., Raval, D.K.: Catalyst-free sonochemical synthesis of 1,8-dioxo-octahydroxanthenes derivatives in carboxy functionalized ionic liquid. *C R Chimie.* **15**(5), 378–383 (2012)
- Mulakayala, N., Pavan Kumar, G., Rambabu, D., Aeluri, M., Basaveswara Rao, M.V., Pal, M.: A greener synthesis of 1,8-dioxo-octahydroxanthenes derivatives under ultrasound. *Tetrahedron Lett.* **53**(51), 6923–6926 (2012)
- Lu, H.Y., Li, J.J., Zhang, Z.H.: ZrOCl<sub>2</sub>·8H<sub>2</sub>O: a highly efficient catalyst for the synthesis of 1,8-dioxo-octahydro xanthenes derivatives under solvent-free conditions. *Appl. Organometal Chem.* **23**, 165–169 (2009)
- Oskooie, H.A., Tahershamsi, L., Heravi, M.M., Baghernejad, B.: Cellulose sulfonic acid: an efficient heterogeneous catalyst for the synthesis of 1,8-dioxo-octahydro xanthenes. *J. Chem.* **7**, 717–720 (2010)
- Bigdeli, M.: Clean synthesis of 1,8-dioxo-octahydro xanthenes promoted by DABCO–bromine in aqueous media. *Chin. Chem. Lett.* **21**, 1180–1182 (2010)
- Rostamizadeh, S., Amani, A.M., Mahdavinia, G.H., Amiri, G., Sepehrian, H.: Ultrasound promoted rapid and green synthesis of 1,8-dioxo-octahydro xanthenes derivatives using nanosized MCM-41-SO<sub>3</sub>H as a nanoreactor, nanocatalyst in aqueous media. *Ultrason. Sonochem.* **17**, 306–309 (2010)
- Javid, A., Heravi, M.M., Bamoharram, F.F.: One-pot synthesis of 1,8-dioxo-octahydro xanthenes utilizing silica-supported preyssler nano particles as novel and efficient reusable heterogeneous acidic catalyst. *E-J. Chem.* **8**, 910–916 (2011)
- Mosaddegh, E., Islami, M.R., Hassankhani, A.: ZrOCl<sub>2</sub>·8H<sub>2</sub>O as an efficient and recyclable catalyst for the clean synthesis of xanthenes derivatives under solvent-free conditions. *Arab. J. Chem.* **5**, 77–80 (2012)
- Zolfigol, M.A., Khakyzadeh, V., Moosavi-Zare, A.R., Zare, A., Azimi, S.B., Asgari, Z., Hasaninejad, A.: Preparation of various xanthenes derivatives over sulfonic acid functionalized imidazolium salts (SAFIS) as novel, highly efficient and reusable catalysts. *C R Chimie.* **15**, 719–736 (2012)
- Khaksar, S., Behzadi, N.: Mild and highly efficient method for synthesis of 14-aryl(alkyl)-14H-dibenzo[*a, j*]xanthenes and 1,8-dioxo-octahydro xanthenes derivatives using pentafluorophenyl ammonium triflate as a novel organocatalyst. *Chin. J. Catal.* **33**, 982–985 (2012)
- Venkatesan, K., Pujari, S.S., Lahoti, R.J., Srinivasan, K.V.: An efficient synthesis of 1,8-dioxo-octahydro-xanthenes derivatives promoted by a room temperature ionic liquid at ambient conditions under ultrasound irradiation. *Ultrason. Sonochem.* **15**, 548–553 (2008)
- Shirini, F., Abedini, M.: Application of nanocatalysts in multi-component reactions. *J. Nanosci. Nanotechnol.* **13**, 4838–4860 (2013)
- Shirini, F., Imanzadeh, G.H., Abedini, M., Akbari-Dokhteh-Ghaziani, M., Ghods Ghasemabadi, P., Safarpour Langroodi, M.:

- Introduction of two efficient catalysts for the synthesis of 1,8-dioxo-octahydro xanthene derivatives in the absence of solvent. *Iran. J. Catal.* **2**, 115–119 (2012)
20. Shirini, F., Khaligh, N.G., Ghods Ghasemabadi, P.: 1,3-Dibromo-5,5-dimethylhydantoin (DBH)/kaolin: an efficient reagent system for the synthesis of 14-aryl-14H-dibenzo[a, j]xanthenes under solvent-free conditions. *Chin. Chem. Lett.* **23**, 1145–1148 (2012)
  21. Shirini, F., Khaligh, N.G.: Succinimide-*N*-sulfonic acid: an efficient catalyst for the synthesis of xanthenes derivatives under solvent-free conditions. *Dyes Pigment.* **95**, 789–794 (2012)
  22. Shirini, F., Imanzadeh, G.H., Abedini, M., Ghods Ghasemabadi, P.: 1,3-Dibromo-5,5-dimethylhydantoin (DBH) as a cheap and efficient catalyst for the synthesis of polyhydroquinolines and 12-aryl-8,9,10,12-tetrahydro [a] xanthene-11-ones. *Iran. J. Catal.* **3**, 57–65 (2013)
  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 derivative. *Dyes Pigment.* **99**, 250–255 (2013)
  24. Shirini, F., Akbari-Dadamahaleh, S., Mohammad-Khah, A.: Rice-husk-supported FeCl<sub>3</sub> nano-particles: introduction of a mild, efficient and reusable catalyst for some of the multi-component reactions. *C R Chimie.* **16**, 945–955 (2013)
  25. Shirini, F., Abedini, M., Akbari-Dadamahaleh, S., Rahmaninia, A.: Iranian chemist's efforts to provide various effective methods for the synthesis of xanthenes. *J. Iran. Chem. Soc.* **11**, 791–824 (2014)
  26. Golmojdeh, H., Zanjanchi, M.A.: A facile approach for synthesis of BiVO<sub>4</sub> nano particles possessing high surface area and various morphologies. *Cryst. Res. Technol.* **47**, 1014–1025 (2012)
  27. Maleki, B., Barzegar, S., Sepehr, Z., Keranian, M., Tayebee, R.: A novel polymeric catalyst for the one-pot synthesis of xanthene derivatives under solvent-free conditions. *J. Iran. Chem. Soc.* **9**, 757–765 (2012)
  28. Niknam, K., Damya, M.: 1-Butyl-3-methylimidazolium hydrogen sulfate [bmim]HSO<sub>4</sub>: an efficient reusable acidic ionic liquid for the synthesis of 1,8-dioxo-octahydro xanthenes. *J. Chin. Chem. Soc.* **56**, 659–665 (2009)
  29. Ilangovan, A., Muralidharan, S., Sakthivel, P., Malayappasamy, S., Karuppusamy, S., Kaushik, M.P.: Simple and cost effective acid catalysts for efficient synthesis of 9-aryl-1,8-dioxo-octahydro xanthene. *Tetrahedron Lett.* **54**, 491–494 (2013)
  30. John, A., Yadav, P.J.P., Palaniappan, S.: Clean synthesis of 1,8-dioxo-dodecahydroxanthene derivatives catalyzed by polyaniline-*p*-toluenesulfonate salt in aqueous media. *J. Mol. Catal. A Chem.* **248**, 121–125 (2006)
  31. Seyyedhamzeh, M., Mirzaei, P., Bazgir, A.: Solvent-free synthesis of aryl-14H-dibenzo[a, j]xanthenes and 1,8-dioxo-octahydro xanthenes using silica sulfuric acid as catalyst. *Dyes Pigment.* **76**, 836–839 (2008)
  32. Mohammadpoor-Baltork, I., Moghadam, M., Mirkhani, V., Tangestaninejad, S., Tavakoli, H.R.: Highly efficient and green synthesis of 14-aryl(alkyl)-14H-dibenzo[a, j]xanthene and 1,8-dioxooctahydroxanthene derivatives catalyzed by reusable zirconyl triflate [ZrO(OTf)<sub>2</sub>] under solvent-free conditions. *Chin. Chem. Lett.* **22**, 9–12 (2011)
  33. Rashedian, F., Saberi, D., Niknam, K.: Silica-bonded *N*-propyl sulfamic acid: a recyclable catalyst for the synthesis of 1,8-dioxo-decahydroacridines, 1,8-dioxo-octahydro xanthenes and uinoxalines. *J. Chin. Chem. Soc.* **57**, 998–1006 (2010)
  34. Ghasemzadeh, M.A., Safaei-Ghomi, J., Zahedi, S.: Fe<sub>3</sub>O<sub>4</sub> nanoparticles: a highly efficient and easily reusable catalyst for the one-pot synthesis of xanthene derivatives under solvent-free conditions. *J. Serb. Chem. Soc.* **78**, 769–779 (2013)
  35. Safaei-Ghomi, J., Ghasemzadeh, M.A.: Zinc oxide nanoparticles: a highly efficient and readily recyclable catalyst for the synthesis of xanthenes. *Chin. Chem. Lett.* **23**, 1225–1229 (2012)

