FACILE AND EFFICIENT SYNTHESIS OF XANTHENE DERIVATIVES MEDIATED BY LANTHANUM(III) NITRATE HEXAHYDRATE UNDER SOLVENT FREE CONDITIONS

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Abstract: The present paper shows that lanthanum(III) nitrate hexahydrate can be used as mild and environment friendly homogeneous catalyst for an efficient one-pot multi-component synthesis of biologically active 1,8-dioxo-octahydroxanthene and 14H-dibenzo[a,j]xanthene derivatives. The solvent free condensation reaction of aromatic aldehydes and dimedone or \( \beta \)-naphthol was carried out at 70-80ºC during 10-30 min. The obtained compounds were analysed by mass and NMR spectroscopic techniques. The advantages of this eco-friendly synthesis route are numerous, and include the use of an inexpensive catalyst, high to excellent yield, short reaction time and high catalytic activity that can make this method an interesting alternative to multi-step approaches.

Keywords: lanthanum(III) nitrate, xanthene derivative, dimedone, \( \beta \)-naphthol, solvent free condition.

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Introduction

Recently, the synthesis of heterocyclic compounds such as xanthene and benzoxanthene derivatives has received great attention from researchers, because of their important pharmaceutical and biological properties such as anti-malarial [1], anti-inflammatory [2], photodynamic therapy [3]. Furthermore, xanthenes have been used as additives in the food industries [4,5], as dyes [6,7], as fluorescent materials [8], and in laser technologies [9]. In natural plants xanthenes are rare; the majority of them are synthesized or are present as microbial metabolites. To present date, xanthenes have been isolated only from plants of two families, \textit{Fabaceae} and \textit{Compositae}. Natural novel xanthenes, blumeaxanthene (A) and blumeaxanthene (B) have been isolated from \textit{Blumea riparia} (Blume) DC (Compositae family), a Chinese medicinal herb traditionally used to treat gynecological disorders (Figure 1) [10].

Recently, several methods have been developed for the synthesis of xanthenes derivatives using various catalysts, such as succinic acid [11], \( \gamma \)-Fe\textsubscript{2}O\textsubscript{3} hydroxyapatite-Fe\textsuperscript{2+} nanoparticles [12], iron oxide nanoparticles (FeNP@SBA-15) [13], acetic acid [14], sulphamic acid [15,16], succinamide-N-sulphonic acid [17], silica sulphuric acid [18], citric acid [19], lactic acid [20], tartaric acid [21], niobium pentachloride [22], \( p \) -toluenesulphonic acid [23,24], indium(III) chloride and metaphosphoric acid [25], silica functionalized propyl sulphonic acid [26], montmorillonite K\textsubscript{10} [27], iodine [28].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{xanthene.png}
\caption{Examples of natural xanthene.}
\end{figure}
However, all of the synthetic protocols needed longer reaction time, high temperature, expensive and toxic catalyst, excess solvent and offered lower yields as compared to the present developed method; thus, the present work tries to overcome all these disadvantages with excellent yield.

In the past decades, lanthanum(III) nitrate based catalysts have attracted rising interests due to their versatility, and notable chemical and physical properties such high acidity, relevant stability, low toxicity, and easy to handle, low price and availability. The importance of lanthanum(III) nitrate as a homogeneous catalyst in biologically significant organic transformations has been highlighted in the literature [29-35]. Previously, lanthanum(III) nitrate was successfully used in the synthesis of 2-arylbenzothiazoles [36].

As a continuation of the ongoing work, the aim set for the present study was to develop a new method for the synthesis of xanthene derivatives using inexpensive, eco-friendly and non-hazardous homogeneous lanthanum(III) nitrate (10 mol%) as catalyst under solvent-free conditions.

**Experimental**

**Generalities**

The β-naphthol, dimedone, aromatic aldehyde, n-hexane, ethyl acetate and lanthanum(III) nitrate hexahydrate were purchased from Merck, S.D. fine Chem and Sigma-Aldrich.

**Melting point** values of all compounds were recorded using the Contemp Melting Point Apparatus MEPOAP121 by the open tube capillary method; uncorrected values are given and compared with those reported in literature and found to be identical.

The progress of the reaction and the purity of the compounds were monitored by thin-layer chromatography (TLC), using analytical silica gel plates (Merck 60 F254).

The 1H and 13C NMR spectra were registered on a Bruker Avance Spectrometer 500 and 125 MHz, respectively, in CDCl3 solvent and with tetramethylsilane (TMS) as internal standard. Chemical shift values were recorded as parts per million (ppm) and the coupling constants (J) were expressed in Hertz (Hz).

Mass spectra were recorded on a Bruker IMPACT HD mass spectrometer, applying the electrospray ionization (ESI) method. Also, the structures of some products were confirmed by 1H and 13C NMR and mass spectral data.

**General procedure for the synthesis of 14H-dibenzo[a,j]xanthene derivatives (Table 2, entry 1-6)**

The reaction mixture of one of aromatic aldehydes 1a-i (1 mmol), β-naphthol (2) (2 mmol) and lanthanum(III) nitrate (10 mol%) was prepared and heated at 80°C for an appropriate time. After completion of the reaction, the mixture was washed with cold water and the solid was separated by filtration. The crude product was recrystallized with ethanol.

**14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene (3b).** 1H NMR: δ 4.73 (1H, br. s., OH), 6.42 (1H, s, CH), 6.56 (2H, d, J= 8.8, Ar-H), 7.35-7.58 (8H, m, Ar-H), 7.76-7.82 (4H, m, Ar-H), 8.34 (2H, d, J= 8.4, Ar-H). 13C NMR: δ 37.0, 115.2, 117.4, 118.0, 122.6, 124.2, 126.7, 128.7, 128.8, 129.3, 131.0, 131.3, 137.4, 148.6, 153.8. MS: m/z= 375 (M+H).

**14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (3e).** 1H NMR: δ 6.65 (1H, s, CH), 7.07 (2H, d, J= 9.3, ArH), 7.39-7.83 (12H, m, ArH), 8.29 (2H, d, J=9.5, ArH). 13C NMR: δ 37.3, 116.7, 118.0, 122.4, 124.3, 126.9, 128.6, 128.9, 129.0, 129.4, 131.0, 131.2, 132.0, 143.4, 148.7. MS: m/z= 393 (M+H).

**14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthene (3e).** 1H NMR: δ 6.58 (1H, s, CH), 7.25-7.85 (13H, m, ArH), 8.28 (2H, d, J= 7.5, ArH), 8.40 (1H, s, ArH). 13C NMR: δ 37.7, 115.8, 118.4, 121.7, 122.0, 122.7, 124.5, 127.2, 129.0, 129.5, 131.0, 134.2, 146.9, 148.2, 148.8. MS: m/z= 404 (M+H).

**14-(3,4-Dimethoxyphenyl)-14H-dibenzo[a,j]xanthene (3f).** 1H NMR: δ 3.68 (3H, s, OCH3), 3.72 (3H, s, OCH3), 6.44 (1H, s, CH), 6.65 (1H, d, J= 8.3, ArH), 6.91(1H, d, J= 1.7, ArH), 7.11-7.13 (1H, dd, J= 8.3, 1.8, ArH), 7.39-7.58 (6H, m, ArH), 7.77-7.83 (4H, m, ArH), 8.40 (2H, d, J= 8.4, ArH). 13C NMR: δ 37.4, 55.7, 110.7, 111.6, 117.4, 117.9, 120.3, 122.7, 124.2, 126.7, 128.7, 128.8, 131.1, 131.4, 137.6, 147.5, 148.7, 149.0. MS: m/z= 419 (M+H).

**General procedure for the synthesis of 1,8-dioxo-octahydroxanthene derivatives (Table 2, entry 7-12)**

The reaction mixture of one of aromatic aldehydes 1a-i (1 mmol), dimedone (4) (2 mmol) and lanthanum(III) nitrate (10 mol%) was heated at 80°C for an appropriate time. After completion of the reaction, the mixture was washed with cold water and the solid was separated by filtration. The crude product was recrystallized with ethanol.

**9-(4-Methoxyphenyl)-1,8-dioxo-octahydroxanthene (5b).** 1H NMR: δ 0.99 (6H, s, 2CH3),
1.09 (6H, s, 2CH₃), 2.18(4H, d, J= 18.2, 2CH₂), 2.45 (4H, d, J= 16.2, 2CH₂), 3.73 (3H, s, OCH₃), 4.69 (1H, s, CH), 6.76 (2H, d, J= 8.8, Ar-H), 7.20 (2H, d, J= 8.8, Ar-H). ¹³C NMR: δ 27.3, 29.2, 30.9, 32.2, 40.8, 50.7, 55.1, 113.4, 115.8, 129.3, 136.5, 157.9, 162.0, 196.5. MS: m/z= 381 (M+H).

9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (5d). ¹H NMR: δ 0.99 (6H, s, 2CH₃), 1.12 (6H, s, 2CH₃), 2.15-2.27 (4H, d, J= 18.2, 2CH₂), 2.49 (4H, d, J= 16.2, 2CH₂), 4.82 (1H, s, CH), 7.48 2H, (d, J= 8.6, Ar-H), 8.08 (2H, d, J= 8.8, Ar-H). ¹³C NMR: δ 27.2, 29.2, 32.2, 32.3, 40.8, 50.6, 114.5, 123.4, 129.3, 146.4, 151.5, 162.9, 196.2. MS: m/z= 396 (M+H).

Results and discussion

Lanthanum(III) nitrate hexahydrate reagent was explored for the synthesis of 1,8-dioxo-octahydroxanthene and 14H-dibenzo[a,j]xanthene derivatives as an efficient catalyst. The solvent

free condensation reaction of aromatic aldehydes 1a-i and dimedone (4) or β-naphthol (2) was carried out at 80°C. Initially, for reaction conditions optimization, the condensation reaction of dimedone (4) (2 mmol) and p-chlorobenzaldehyde (1c) (1 mmol) at 70-80°C under solvent-free condition was used as a model reaction (Scheme 1). When the reaction of p-chlorobenzaldehyde (1c) (1 mmol) was carried out with dimedone (4) (2 mmol) at 70°C in absence of lanthanum(III) nitrate catalyst, no significant amount of product formed (Table 1, entry 1). This means that the involvement of catalyst is necessary for the initiation of the reaction. By increasing the amount of catalyst used from 2 to 10 mol%, the yield gradually increased from 45 to 95% (Table 1, entries 2-6). The obtained results show that the best yield for the synthesis of compound 5e were observed when using 10 mol% of the catalyst, the reaction completes in 10 min with a yield of 95% at 80°C (Table 1, entry 6).

Increasing the concentration from 10 to 20 mol% of lanthanum(III) nitrate, at 80°C, does not result in any noticeable changes in the reaction time or yields (Table 1, entries 7-9). Moreover, when the reaction temperature was increased, no improvement in the yield of the product was observed (Table 1, entries 5-7).

Reagent and conditions: i) lanthanum(III) nitrate, solvent free, 80°C, 10 min, 95%.

Scheme 1. Synthesis of 9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (5c).

| Entry | Catalyst (mol%) | Temperature (°C) | Time (min) | Yield (%) |
|-------|----------------|-----------------|------------|-----------|
| 1     | -              | 70              | 60         | No reaction |
| 2     | 2              | 70              | 40         | 45        |
| 3     | 5              | 70              | 30         | 75        |
| 4     | 7              | 70              | 20         | 85        |
| 5     | 10             | 70              | 15         | 94        |
| 6     | 10             | 80              | 10         | 95        |
| 7     | 10             | 90              | 10         | 95        |
| 8     | 15             | 80              | 10         | 95        |
| 9     | 20             | 80              | 10         | 94        |

*Reaction conditions: p-chlorobenzaldehyde (1c) (1 mmol), dimedone (4) (2 mmol), lanthanum(III) nitrate (10 mol%) under solvent-free conditions. †Isolated yield.
Based on the optimized reaction conditions, the scope of this cyclization reaction was explored. The reaction of β-naphthol (2) or dimedone (4) with various aldehydes bearing electron-withdrawing and electron-donating groups was carried out in the presence of lanthanum(III) nitrate under solvent-free reaction condition (Scheme 2). Aromatic aldehydes bearing both electron-withdrawing substituents and electron-donating substituents showed better activity. All results are summarized in Table 2.

In order to find out the efficiency and greenness of the method, obtained results for the synthesis of xanthene derivative 3a were compared with the pre- eminent data from the literature as shown in Table 3. It was noted that many of the formerly reported methodologies experience from one or more disadvantages such as necessity of excess amount of catalyst, high temperature, prolonged reaction time, use of volatile and toxic organic solvents. The present method helps avoiding the disadvantages within the formerly reported methodologies.

**Scheme 2. General procedure for the synthesis of xanthene derivatives (5).**

Reagent and conditions: i) lanthanum(III) nitrate, solvent free, 70-80°C, 10-30 min.

**Table 2**

| Entry | Aromatic aldehyde | Compound | Product | Time (min) | Yield (%) | Melting point values (ºC) |
|-------|-------------------|----------|---------|------------|-----------|--------------------------|
|       |                   |          |         | Found      | Reported [Ref.] | |
| 1     | C₆H₅               | 2        | 3a      | 25         | 92        | 181-182                  |
| 2     | p-OH-C₆H₄          | 2        | 3b      | 30         | 88        | 138-140                  |
| 3     | p-Cl-C₆H₄          | 2        | 3c      | 20         | 94        | 287-290                  |
| 4     | p-NO₂-C₆H₄         | 2        | 3d      | 20         | 94        | 307-309                  |
| 5     | m-NO₂-C₆H₄         | 2        | 3e      | 22         | 92        | 212-213                  |
| 6     | m, p-OCH₃-C₆H₃     | 2        | 3f      | 22         | 85        | 170-172                  |
| 7     | C₆H₅               | 4        | 5a      | 10         | 94        | 202-204                  |
| 8     | p-OCH₃-C₆H₄        | 4        | 5b      | 12         | 94        | 247-249                  |
| 9     | p-Cl-C₆H₄          | 4        | 5c      | 10         | 95        | 230-232                  |
| 10    | p-NO₂-C₆H₄         | 4        | 5d      | 10         | 95        | 228-230                  |
| 11    | o, p-Cl-C₆H₃       | 4        | 5e      | 14         | 88        | 255-257                  |
| 12    | p-CH₃-C₆H₄         | 4        | 5f      | 10         | 92        | 215-216                  |

*aReaction conditions: aromatic aldehyde (1 mmol), β-naphthol (2) or dimedone (4) (2 mmol), lanthanum(III) nitrate (10 mol%) under solvent free conditions.

*Isolated yield.
Table 3

| Entry | Catalysts                        | Conditions/T (°C) | Time (h) | Yield % [Ref.] |
|-------|---------------------------------|-------------------|----------|----------------|
| 1     | Sulphamic acid                  | Solvent free/125  | 8        | 93 [15]        |
| 2     | Silica sulphuric acid           | Solvent free/80   | 0.75     | 89 [18]        |
| 3     | Niobium pentachloride           | DCM/ ambient temperature | 48 | 90 [22]        |
| 4     | Montmorillonite K10             | Solvent free/120  | 3        | 75 [27]        |
| 5     | Lanthanum(III) nitrate hexahydrate | Solvent free/80  | 0.41     | 92 [Present work] |

Scheme 3. Proposed mechanism for the synthesis of xanthene derivatives 5.

A plausible mechanism for the synthesis of xanthene derivatives was proposed in Scheme 3. Due to the strong oxophilicity, lanthanum(III) nitrate appears to play a more efficient catalytic role. Initially, the carbonyl group of the aromatic aldehyde coordinates with lanthanum ion and facilitates the nucleophilic attack. Then, the carbon atom of the carbonyl group of aldehydes is attacked by the nucleophilic dimedone (4) to form Knoevenagel product 6. Next, the subsequent addition of 6 with 4 gives the acyclic adduct intermediates, followed by intramolecular cyclization with the participation of two hydroxyl groups to give the xanthene derivative 5.

Conclusions

An efficient and green protocol for the synthesis of xanthene derivatives was developed. The advantage of this method is the use of a one-pot multi-component reaction catalyzed by 10 mol% lanthanum(III) nitrate hexahydrate. Due to the strong oxophilicity, lanthanum(III) nitrate appears to play a more efficient catalytic role in the synthesis of xanthenes derivatives. The obtained compounds were confirmed by mass and NMR spectroscopic techniques. The merit of the present synthesis protocol is the use of non-toxic catalyst, eco-friendliness, shorter reaction time, excellent yield and high catalytic activity which can made the proposed method an interesting alternative to multi-step approaches.

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References

1. Chibale, K.; Visser, M.; Van Schalkwyk, D.; 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(13), pp. 2289-2296. DOI: https://doi.org/10.1016/S0040-4020(03)00240-0
2. Poupelin, J.P.; Saint-Ruf, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lacroix, R.
Synthesis and antiinflammatory properties of bis(2-hydroxy-1-naphthyl)methane derivatives. I. Monosubstituted derivatives. European Journal of Medicinal Chemistry, 1978, 13(1), pp. 67-71. DOI: https://doi.org/10.1016/0022-2862(78)85002-6

3. Neckers, D.C. Rose Bengal. Journal of Photochemistry and Photobiology A: Chemistry, 1989, 47(1), pp. 1-29. DOI: https://doi.org/10.1016/0166-3816(89)85003-8

4. Tanaka, T. Reproductive and neurobehavioural toxicity study of erythrosine administered to mice in the diet. Food and Chemical Toxicology, 2001, 39(5), pp. 447-454. DOI: https://doi.org/10.1016/S0278-4917(00)00163-0

5. Chequer, F.M.D.; Venancio, V.P.; Bianchi, M.L.P.; Antunes, L.M.G. Genotoxic and mutagenic effects of erythrosine B, a xanthene food dye, on HepG2 cells. Food and Chemical Toxicology, 2012, 50(10), pp. 3447-3451. DOI: https://doi.org/10.1016/j.fct.2012.07.042

6. Menchen, S.M.; Benson, S.C.; Lam, J.Y.; Zhen, W.; Sun, D.; Rosenblum, B.B.; Khan, S.H.; Taing, M. Sulfonated diarylthiadiazine dyes. US Patent, 2003, 6583168. https://patents.justia.com/patent/6583168

7. Bhowmik, B.B.; Ganguly, P. Photophysics of xanthene dyes in surfactant solution. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2005, 61(9), pp. 1997-2003. DOI: https://doi.org/10.1016/j.saa.2004.07.031

8. Knight, C.G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles. Biochemical Journal, 1989, 258(3), pp. 683-687. DOI: https://doi.org/10.1042/bj2580683

9. Ahmad, M.; King, T.A.; Ko, D.K.; Cha, B.H.; Lee, J. Performance and photostability of xanthene and pyromethene laser dyes in sol-gel phases. Journal of Physics D: Applied Physics, 2002, 35(13), pp. 1473-1476. DOI: https://doi.org/10.1088/0022-3773/35/13/303

10. Ravindranath, B.; Seshadri, T.R. Structural studies on santalin permethyl ether. Phytochemistry, 1973, 12(11), pp. 2781-2788. DOI: https://doi.org/10.1016/0031-9422(73)85099-X

11. Mohamadpour, F. Green and solvent-free protocol promoted facile one-pot synthesis of xanthene derivatives using succinic acid as a bio-based, biodegradable and versatile di-functional Bronsted acid catalyst. Indian Journal of Chemistry – Section B, 2019, 58(B07), pp. 832-841. http://nopr.niscair.res.in/handle/123456789/49107

12. Hosseinzadeh-Khanamiri, R.; Vessally, E.; Shahverdizadeh, G.H.; Babazadeh, M.; Edjlali, L. γ-Fe2O3@HAP-Fe2+ NPs: an efficient and eco-friendly catalyst for the synthesis of xanthene derivatives in water. Iranian Journal of Chemistry and Chemical Engineering, 2018, 37(3), pp. 51-62. http://www.ijccej.ac.ir/article_30765.html

13. Rajabi, F.; Abdollahi, M.; Diarjani, E.S.; Osmolowsky, M.G.; Osmolovskaya, O.M.; Gomez-Lopez, P.; Puente-Santiago, A.R.; Luque, R. Solvent-free preparation of 1,8-dioxo-octahydroxanthenes employing iron oxide nanomaterials. Materials, 2019, 12(15), pp. 2386. DOI: https://doi.org/10.3390/ma12152386

14. Sarma, R.J.; Baruah, J.B. One step synthesis of dibenzoxanthenes. Dyes and Pigments, 2005, 64(1), pp. 91-92. DOI: https://doi.org/10.1016/j.dyepig.2004.03.010

15. Rajitha, B.; Sunil Kumar, B.; Thirupathi Reddy, Y.; Narsimha Reddy, P.; Sreenivasulu, N. Sulfamic acid: a novel and efficient catalyst for the synthesis of aryl-14H-dibenzo[a,j]xanthenes under conventional heating and microwave irradiation. Tetrahedron Letters, 2005, 46(50), pp. 8691-8693. DOI: https://doi.org/10.1016/j.tetlet.2005.10.057

16. Banerjee, A.G.; Kothapalli, L.P.; Sharma, P.A.; Thomas, A.B.; Nanda, R.K.; Shrivastava, S.K.; Khatanglekar, V.V. A facile microwave assisted one pot synthesis of novel xanthene derivatives as potential anti-inflammatory and analgesic agents. Arabian Journal of Chemistry, 2016, 9(1), pp. S480-S489. DOI: https://doi.org/10.1016/j.arabjc.2011.06.001

17. Shirini, F.; Khaligh, N.G. Succinimide-N-sulfonic acid: an efficient catalyst for the synthesis of xanthene derivatives under solvent-free conditions. Dyes and Pigments, 2012, 95(3), pp. 789-794. DOI: https://doi.org/10.1016/j.dyepig.2012.06.022

18. 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 and Pigments, 2008, 76(3), pp. 836-839. DOI: https://doi.org/10.1016/j.dyepig.2007.02.001

19. Navarro, C.A.; Sierra, C.A.; Ochoa-Puentes, C. Aqueous citric acid as “green” reaction media for the synthesis of octahydroxanthenes. Revista Colombiana de Quimica, 2013, 42(2), pp. 5-11. http://www.scielo.org.co/scielo.php?script=sci_arttext&pid=S0120-28402013000200001

20. Sadeh, F.N.; Fatahpour, M.; Hazeri, N.; Maghsoudlu, 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 Chemica Isasi, 2017, 25(1), pp. 24-37. DOI: https://doi.org/10.1515/achi-2017-0004

21. Mohamadpour, F.; Maghsoudlu, M.T.; Lashkari, M.; Heydari, R.; Hazeri, N. Green synthesis of polysubstituted quinolines and xanthene derivatives promoted by tartaric acid as a naturally green catalyst under solvent-free conditions. Chemistry Journal of Moldova, 2018, 13(1), pp. 74-86. DOI: http://dx.doi.org/10.19261/cjm.2017.449

22. Andrade Bartolomeu, A.; Menezes, M.; Silva Filho, L. Efficient one-pot synthesis of 14-aryl-
14H-dibenzo[a,j]xanthene derivatives promoted by niobium pentachloride. Chemical Papers, 2014, 68(11), pp. 1593-1600. DOI: https://doi.org/10.2478/s11696-014-0597-8

23. Mobinikhaledi, A.; Moghianian, H.; Deinavizadeh, M. pTSA-catalyzed condensation of xylenols and aldehydes under solvent-free conditions: One-pot synthesis of 9H-xanthene or bisphenol derivatives. Comptes Rendus Chimie, 2013, 16(11), pp. 1035-1041. DOI: https://doi.org/10.1016/j.crci.2013.03.008

24. Khurana, J.M.; Magoo, D. pTSA-catalyzed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo [a]xanthen-11-ones in ionic liquid and neat conditions. Tetrahedron Letters, 2009, 50(33), pp. 4777-4780. DOI: https://doi.org/10.1016/j.tetlet.2009.06.029

25. Karami, B.; Nejati, S.; Eskandari, K. An adapted route to efficient synthesis of 1,8-dioxooctahydroxanthene derivatives using InCl₃ and (HPO₃)₃ as recyclable catalysts. Current Chemistry Letters, 2015, 4(4), pp. 169-180. DOI: https://doi.org/10.1016/j.j.ccl.2015.05.001

26. Mohammadi Ziarani, G.; Badiel, A.-R.; Azizi, M. The one-pot synthesis of 14-aryl-14H-dibenzo [a,j]xanthene derivatives using sulfonic acid functionalized silica (SiO₂-Pr-SO₃-H) under solvent free conditions. Scientia Iranica, 2011, 18(3), pp. 453-457. DOI: https://doi.org/10.1016/j.scient.2011.05.008

27. Dabiri, M.; Azimi, S.; Bazgir, A. One-pot synthesis of xanthene derivatives under solvent-free conditions. Chemical Papers, 2008, 62, pp. 522-526. DOI:https://doi.org/10.2478/s11696-008-0050-y

28. Pasha, M.A.; Jayashankara, V.P. Molecular iodine catalyzed synthesis of aryl-14H-dibenzo [a,j]xanthenes under solvent-free condition. Bioorganic & Medicinal Chemistry Letters, 2007, 17(3), pp. 621-623. DOI: https://doi.org/10.1016/j.bmcl.2006.11.009

29. Narasimhulu, M.; Mahesh, K.C.; Reddy, T.S.; Rajesh, K.; Venkateswarlu, Y. Lanthanum(III) nitrate hexahydrate or p-toluenesulfonic acid catalyzed one-pot synthesis of 4(3H)-quinazolinones under solvent-free conditions. Tetrahedron Letters, 2006, 47(26), pp. 4381-4383. DOI: https://doi.org/10.1016/j.tetlet.2006.04.096

30. Narasimhulu, M.; Malla Reddy, S.; Rajesh, K.; Suryakiran, N.; Ramesh, D.; Venkateswarlu, Y. A mild and efficient synthesis of chiral tetrahydroquinolinol pyranose derivatives catalyzed by lanthanum(III) nitrate hexahydrate. Heteroatom Chemistry, 2008, 19(4), pp. 429-433. DOI: https://doi.org/10.1002/hc.20441

31. Malla Reddy, S.; Venkat Reddy, Y.; Venkateswarlu, Y. A mild and efficient method for the chemoselective deprotection of acetamides with lanthanum(III) nitrate hexahydrate. Tetrahedron Letters, 2005, 46(43), pp. 7439-7441. DOI: https://doi.org/10.1016/j.tetlet.2005.08.081

32. Chini Mahesh, K.; Narasimhulu, M.; Srikanth Reddy, T.; Suryakiran, N.; Venkateswarlu, Y. A mild and efficient chemoselective protection of amines as N-benzyloxycarbonyl derivatives in the presence of La(NO₃)₃·6H₂O under solvent-free conditions. Tetrahedron Letters, 2007, 48(1), pp. 55-59. DOI: https://doi.org/10.1016/j.tetlet.2006.11.015

33. Srikanth Reddy, T.; Narasimhulu, M.; Suryakiran, N.; Chini Mahesh, K.; Ashalatha, K.; Venkateswarlu, Y. A mild and efficient acetylation of alcohols, phenols and amines with acetic anhydride using La(NO₃)₃·6H₂O as a catalyst under solvent-free conditions. Tetrahedron Letters, 2006, 47(38), pp. 6825-6829. DOI: https://doi.org/10.1016/j.tetlet.2006.07.059

34. Narasimhulu, M.; Srikanth Reddy, T.; Chini Mahesh, K.; Malla Reddy, S.; Vijender Reddy, A.; Venkateswarlu, Y. Lanthanum(III) nitrate hexahydrate or gadolinium(III) chloride hexahydrate catalyzed one-pot synthesis of α-amino nitriles. Journal of Molecular Catalysis A: Chemical, 2007, 264(1-2), pp. 288-292. DOI: https://doi.org/10.1016/j.molcata.2006.09.036

35. Mei, F.; Chen, E.; Li, G. Lanthanum nitrate as an efficient and recoverable homogeneous catalyst for the transesterification of dimethyl carbonate with ethanol. Reaction Kinetics and Catalysis Letters, 2009, 96, pp. 27-33. DOI: https://doi.org/10.1007/s11144-009-5389-8

36. Shaikh, K.A.; Chaudhur, U.N.; Lanthanum(III) nitrate hexahydrate catalyzed one-pot synthesis of 2-arylbenezothiozoles under mild reaction conditions. Organic Communications, 2017, 10(4), pp. 288-297. DOI: http://doi.org/10.25135/acg.oc.29.17.08.044