Heterocyclic Letters
Vol. 11| No.4|605-613|August-October|2021
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

CONVENIENT GREEN APPROACH FOR ONE POT SYNTHESIS OF 1, 8 DIOXO-OCTAHYDROXANTHENE DERIVATIVES BY CO_3O_4 NANOPARTICLES CATALYSIS IN AQUEOUS MEDIA

S.V.Thakare,[a]* A.V.Borhade,[b] T.D.Patil[c]

[a]Department of Chemistry K.S.K.W. Arts, Commerce and Science College CIDCO Nashik 422008 Maharashtra India
[b]Department of Chemistry H.P.T. Arts & R.Y.K. Science College Nashik 422 005, Maharashtra India
[c]Colagen Research Pvt. Ltd. Nashik 422013 Maharashtra India
Corresponding author Email: savitathakare@cidcocollegenashik.ac.in

ABSTRACT:
The current work reports an efficient and green methodology to the synthesis of 1,8-dioxo-octahydroxanthene derivatives catalysed by Co_3O_4 nanoparticles in water as green solvent. Stabilized Co_3O_4 nanoparticles were prepared by using $Co(NO_3)_2.6H_2O$ as a metal precursor and anionic surfactant sodium dodecylbenzene sulfonate (NaDBS). The nanoparticles thus formed were characterised by powder Fourier transform infrared spectra, X-ray diffraction(XRD), scanning electron microscopy, energy-dispersive X-ray spectroscopy and transmission electron microscopy. Further we verified the catalytic activity of the pure phase Co_3O_4 nanoparticles for the synthesis of 1,8-dioxo-octahydroxanthene derivatives.

KEYWORDS:
Co_3O_4 nanoparticles, 1, 8 dioxo-octahydroxanthene, Sol-Gel method, sodium dodecylbenzene sulfonate, XRD, SEM, TEM

INTRODUCTION:

Catalysis is the core of large scale organic transformations involved in existing chemical and Pharmaceutical industries. Transition metal oxides at nanoscale have developed as the exceptional substitutes to conventional catalysis. Transition metal oxides shows a broad structural variety like unique morphology with controlled size and large surface area include densely occupied active sites[i].

Transition metal oxide, Co_3O_4 is prominent heterogeneous catalyst for chemical synthesis and surface reactions[ii-iv]. They also retain excellent properties such as antiferromagnetic, p-type semiconductor, gas-sensing, catalytic and electrochemical ones. By reason of these assets, Co_3O_4 nanoparticles have been exploited in field of research and industry[v-viii]. Thus many successful efforts have been taken in the current years to fabricate and investigation of properties of Co_3O_4 nanostructures. A lot of techniques have been practiced for the designing

of cobalt oxide nanoparticles. Out of those, in latest research gives emphasis on wet chemical methods such as sol-gel[ix], hydrothermal[x], co-precipitation[xi], polyol[xii], combustion[xiii], spray-pyrolysis[xiv], micro emulsion[xv] and mechanochemical methods[xvi].Out of them surfactant-mediated sol gel method was exhibited as a finest route to get the Co_3O_4 nanostructures .The measures of this method provides better homogeneity, phase purity as well as sintering at low temperature[xvii-xix].

Recently Xanthene derivatives are found as active moiety within Pharmaceutical, chemical and biological approaches[xx-xxi]. Hence, a variety of reports regarding synthetic studies on xanthene derivatives has been documented. Lewis acid catalysed xanthene Synthesis have not been entirely satisfactory as it encounters harsh experimental conditions such as anhydrous condition, high temperature, prolonged reaction time, expensive, harmful and difficult to handle reagents, low yield, difficult work up[xxii-xxv]. Now there is need to develop environmentally friendly procedures which provides effectual and competent means to synthesize xanthene. With this concern, the usage of nanocatalyst has been encouraged in recent times. There are effective tries of xanthenes synthesis using CuO[xxvi], ZnO[xxvii] and $ZnAl_2O_4$[xxvii] nanocatalyst. Though, in such cases amount of catalyst as well as time required was more to produce xanthenes. Therefore, to sidestep these limitations, the introduction of a novel and efficient process for the synthesis of 1,8-dioxo-octahydroxanthene derivatives in green aqueous media will be a leading exploration.

This research work endeavour to synthesize the cobalt oxide nanoparticles with cobalt nitrate as metal precursor and sodium dodecylbenzene sulfonate (NaDBS) surfactant via the sol-gel method. Developed knowledge is utilized in the synthesis of Xanthene derivatives aided with catalyst cobalt oxide nanoparticles.

EXPERIMENT:

Materials

Cobalt nitrate ($Co(NO_3)_2.6H_2O$) , citric acid ($C_6H_8O_7$) and sodium dodecylbenzene sulfonate (NaDBS), 5,5 dimethyl 1,3 cyclohexanedione, aromatic aldehydes, were analytical grade and all were purchased from Sigma-Aldrich.

Preparation of Co_3O_4 Nanoparticles

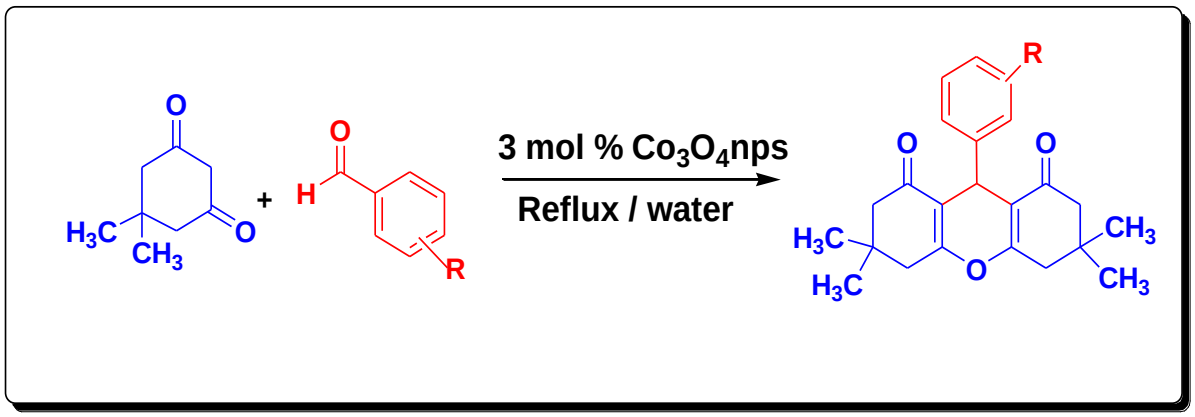
In typical synthesis of Co_3O_4 nanoparticles, Cobalt nitrate $Co(NO_3)_2.6H_2O$ (1M) used as metal precursor and as sodium dodecylbenzene sulfonate (NaDBS) surfactant was dissolved in 100 ml double distilled water. After stirring continuously for 30 minute solution became clear pink in colour. The citric acid (1M) was slowly added to the above reaction mixture in drop wise way under continuous stirring until light pink coloured precipitates of cobalt hydroxide was formed. The precipitate was then treated in a stainless steel autoclave with teflon lining at 120 °C for 24 hours in oven and then endorsed to cool naturally at room temperature. The resulting gel was filtered and washed repeatedly by ethanol. Subsequently, dried the precipitate at 90 °C for 24 h. Finally, precipitate was calcined in the muffle furnace at 550°C for 4 hours. Black color Co3O4 nanoparticles were obtained. Further the synthesized Co3O4 nanoparticles were characterized by FT-IR, XRD, SEM and TEM.

General procedure for preparation of 1, 8 dioxo-octahydroxanthene

In a round-bottom flask, a mixture of 5,5 dimethyl 1,3 cyclohexanedione (2 mmol), aromatic aldehyde (1 mmol) and catalyst Co_3O_4 nanoparticles (0.2 mol) along with 10ml water was added. Then the flask was connected with water condenser. The reaction mixture was stirred and reflux for appropriate time in an oil-bath. The Progress of the reaction was qualitatively checked by TLC. After completion of reaction, the mixture was filtered and the catalyst was separated out. The resulting filtrate was cool to room temperature and solid obtained was

filtered by suction. The crude product was subjected to crystallization with ethanol to get the desired compound in pure form (Scheme.1)

The structure of all products was confirmed by using physical and spectroscopic data such as 1HNMR, 13CNMR and Mass spectra.



Scheme 1: Synthesis of 1, 8 dioxo-octahydroxanthene

RESULT AND DISCUSSION:

Fig. 1. FT-IR spectrum of pure Co_3O_4 nanoparticles displays two characteristic absorption band at 524 cm^{-1} and 648 cm^{-1} which assigned Co-O stretching vibration mode and bridging vibration of O- Co-O respectively.

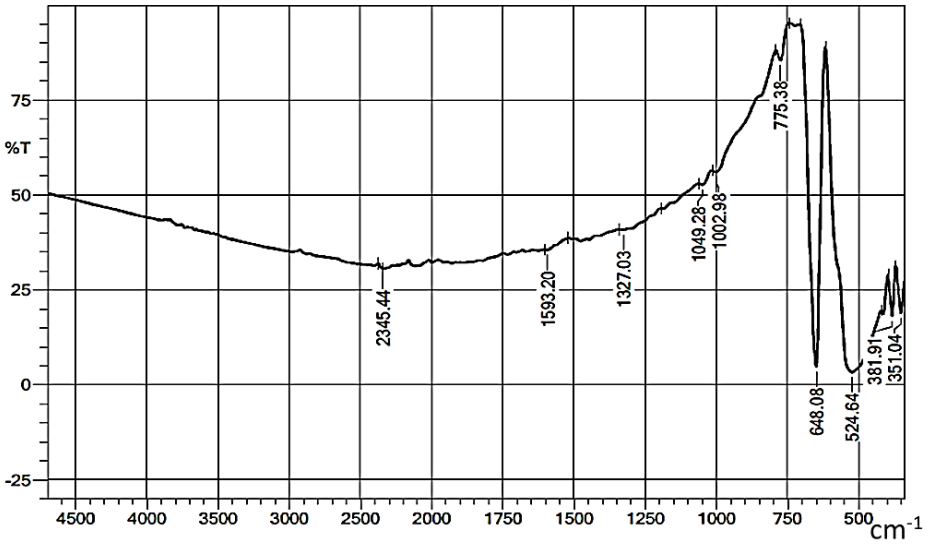


Figure 1. FT-IR spectrum of Co_3O_4 nanoparticles.

Phase purity and crystallinity of the pure Co_3O_4 where investigated through XRD in

Fig.2. The patterns of the produced nanoparticles predict that sample is crystalline as sharp peaks are detected. XRD pattern also results that cobalt oxide has cubic phase structure. The peak positions 2θ =18.93°, 31.33°, 36.93°, 38.66°, 44.93°, 55.79, 59.39° and 65.33°.The relative intensity values matches accurately with typical JCPDS card No: 74-2120

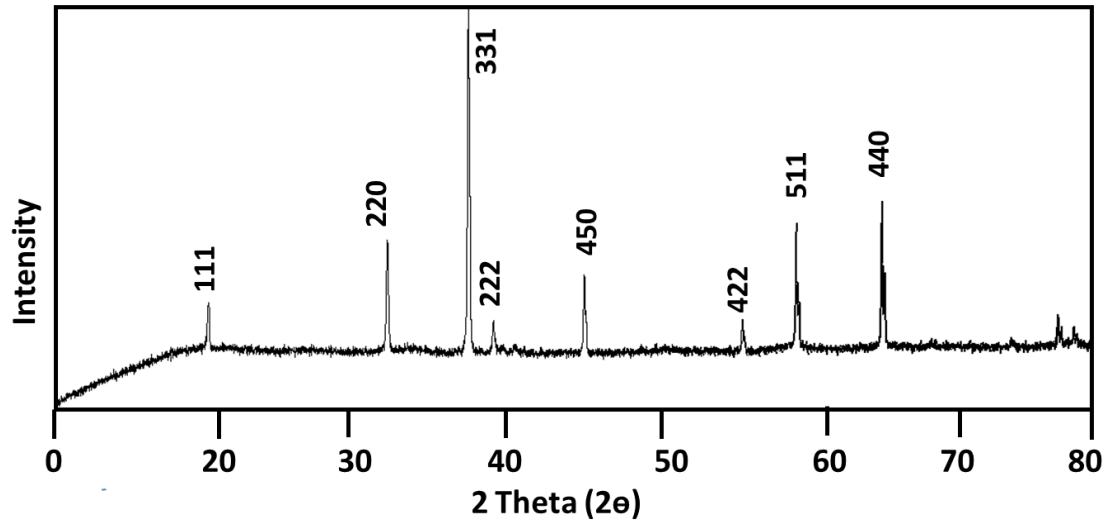


Figure 2. XRD pattern of Co_3O_4 nanoparticles.

Morphology of pure Co_3O_4 nanoparticles studied by SEM image analysis **(Fig. 3a)**. It was suggested that nanoparticles are agglomerated and evenly sized with spherical shape. **Fig. 3b** shows EDX spectrum confirm composition and purity of cobalt oxide nanoparticles. The details of atomic and weight % of Co and O elements are showed in Table 1.

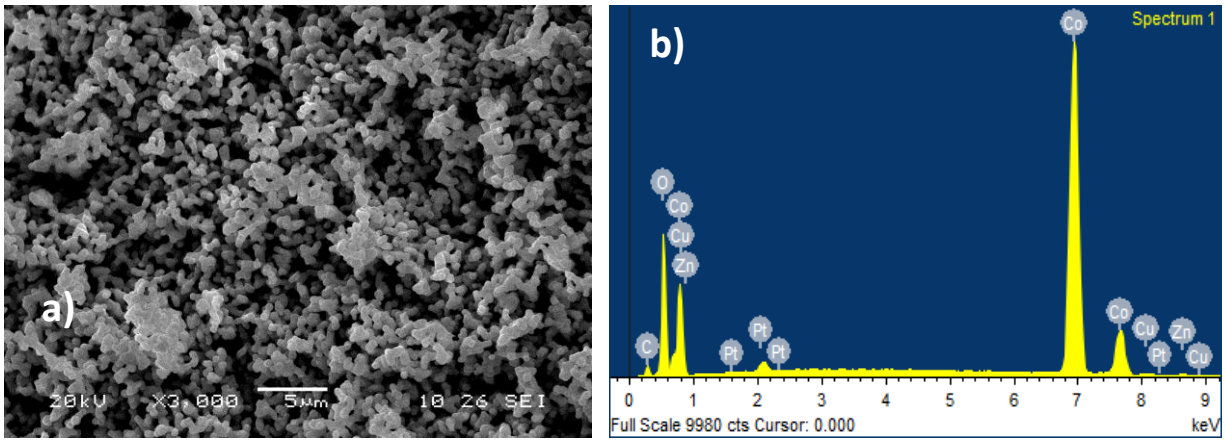


Figure 3. a) SEM image of Co_3O_4 nanoparticles b) EDX of Co_3O_4 nanoparticles.

Table 1. The compositions generated from EDX

Element	Weight%	Atomic%
C K	9.87	22.77
O K	27.90	47.94
Co K	61.50	28.76
Cu K	0.16	0.29
Zn K	0.27	0.24

Fig.4 shows TEM image predicted that average size of Co_3O_4 nanoparticles is 20nm with spherical morphology. SAED pattern shows numerous discrete spots line up and forming rings that indicates polycrystalline nature of nanoparticles.

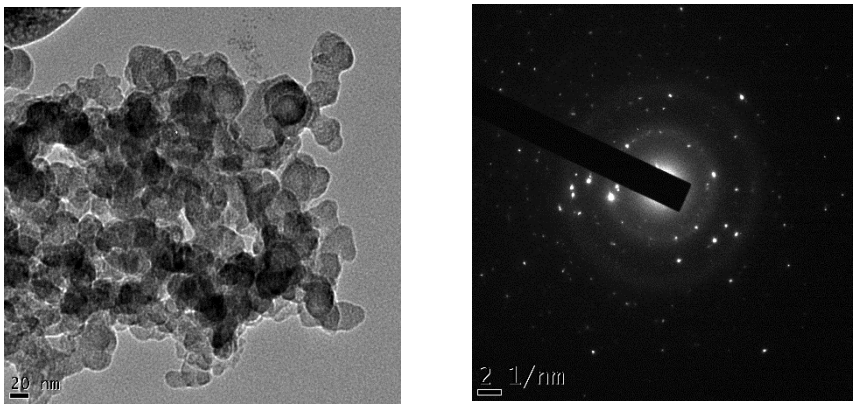
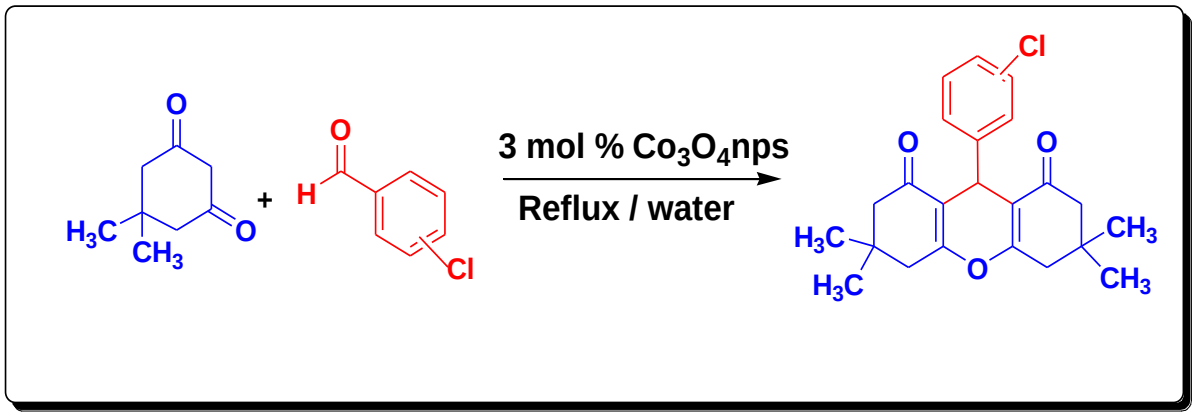


Figure 4. TEM image and SAED of Co_3O_4 nanoparticles

To assess the catalytic performance of Co_3O_4 nanoparticles, we have attempted model test reaction, condensation of 5,5 dimethyl 1,3 cyclohexanedione and 4-chlorobenzaledheyde (Scheme 2).

In order to get maximum conversion and yield of the product, we examined reaction parameters such as the reaction temperature, reaction time, amount of catalyst and effect of solvent.



Scheme 2: Model reaction

The result summarized in Table 2 clearly shows that with respect to yield and reaction time Co_3O_4 is an effective catalyst for this two component reaction. The reaction was incomplete in absence of catalyst .The moderate yield were obtained with long time when we used P_2O_5 and PCl_3 as a catalyst . Water was proven as finest solvent among all tried solvents for reaction.

Further we have optimized parameters like mol % of catalyst and temperature to get maximum yield in short time. 3 mol% of catalyst is sufficient to produce excellent yield of the product Further the same reaction was carried out at various temperature and it was found that at reflux condition provides improvement in reaction with respect to yield and time. Thus Co_3O_4 was found effective catalyst as it leads to high yield (about 96%) in less time (at 15 min) (entry 10).

Table 2. Optimization of the reaction conditions

Entry	Catalyst	Mol (%) of Catalyst	Solvent	Temparature(^{O}C)	Time (Min)	Yield (%)
1	Without catalyst	-	Ethanol	60	180	Reaction incomplete
2	P_2O_5	0.5	Ethanol	60	90	45
3	PCl_3	0.5	Ethanol	60	180	40
4	Co_3O_4 nps	0.5	Ethanol	60	60	62
5	Co_3O_4 nps	0.5	THF	70	55	59
6	Co_3O_4 nps	0.5	Methanol	80	30	60
7	Co_3O_4 nps	0.5	water	Reflux	30	78
8	Co_3O_4 nps	1	water	Reflux	30	80
9	Co_3O_4 nps	2	water	Reflux	35	84
10	**Co_3O_4 nps**	**3**	**water**	**Reflux**	**15**	**96**

Table 3. Synthesis of different 9-phenyl 1, 8 dioxo-octahydroxanthene derivatives catalysed by Co_3O_4 nps.

Entry	R group	Time (min)	Yield (%)	MP (^{0}C) (Observed)
3a	H	20	88	204-206
3b	4-Cl	15	96	225-227
3c	4-F	10	94	226-227
3d	4-Br	10	92	241-243
3e	4-OH	15	95	247-248
3f	4Me	20	92	194-196
3g	4-OMe	15	93	240-242
3h	2,5-OMe	10	95	201-202
3i	2-NO_2	05	94	214-216
3j	2-OH	20	90	238-240

After optimizing the reaction conditions, we investigated applicability of this reaction with a range of aromatic aldehyde including electron-donating or electron-withdrawing groups. Then we analysed series of reaction of 5,5 dimethyl 1,3 cyclohexanedione(2mmol) with wide range of structurally diverse aromatic aldehydes (1mmol) in presence of Co_3O_4 nanoparticles catalyst under similar reaction conditions (Table 3). The synthesis with structurally diverse aldehyde results excellent yields of 1, 8 dioxo-octahydroxanthene derivatives but the outcome related to time showed a marginal impact on of the reaction rate. It is observed that aromatic aldehyde substituted with electron withdrawing group gives product more rapidly than those with electron-donating groups.

To investigate the reusability of the catalyst Co_3O_4 nanoparticles, After completion of the reaction catalyst was recovered by filtration ,washed with alcohol and dried in the oven at 120^{0}C for 4h.This regenerated and activated catalyst used in next reaction cycle under similar

reaction condition showed similar catalytic activity till 4th reaction cycle which indicate effectiveness of fabricated catalyst **Fig.5**.

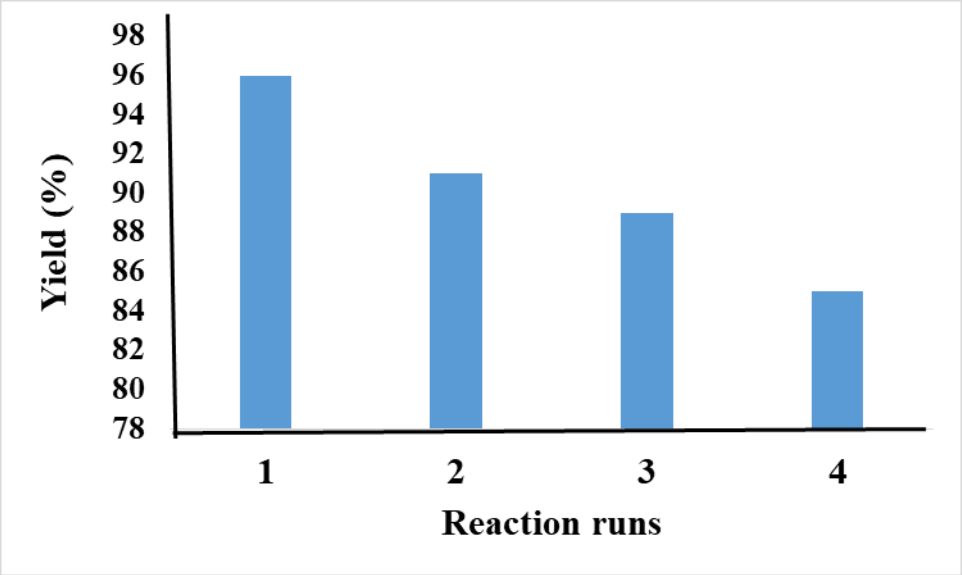


Figure 5. Reusability of catalyst in synthesis of 1, 8 dioxo-octahydroxanthene

CONCLUSION:

The cobalt oxide (Co_3O_4) nanoparticles were prepared by using sol-gel technique assisted with anionic surfactant sodium dodecylbenzene sulfonate. Co_3O_4 nanoparticles were characterized by using FT-IR, XRD, SEM, EDX and TEM .The characterization confirm the uniform and spherical crystal structure of the Co_3O_4 nanoparticles with an average size of 20 nm. The present catalytic synthesis method of 1, 8 dioxo-octahydroxanthene derivatives can be commercially advantageous for large scale industrial fabrication of Co_3O_4 nanoparticles.

ACKNOWLEDGEMENTS:

We are thankful to Management and Principal of our college for providing all necessary facility. The authors are thankful to Savitribai Phule Pune University, Pune and SAIF Chandigarh for providing analysis facility.

SPECTRAL DATA OF PREPARED COMPOUND

3,3,6,6 Tetramethyl-9 phenyl 1,8 dioxo-octahydroxanthene **3a**

^{1}HNMR $CDCl_3$ 400MHz δ(ppm) 1.26(s,6H) 2.31-2.51(m,8H) 5.57(s,1H) 7.13-7.27(m,5H) ^{13}C NMR (100 MHz, CDCl3); δC (ppm): 27.37, 29.33, 31.82, 32.19, 40.93, 50.75, 115.76, 126.39, 128.04, 128.38, 144.04, 162.01, 195.96 HRMS (m/z):350.458

3,3,6,6 Tetramethyl-9(4-chlorophenyl)1,8dioxo-octahydroxanthene **3b**

^{1}HNMR $CDCl_3$ 400MHz δ(ppm)0.98 (s,6H) 1.10(s,6H) 2.14-2.25 (m,8H) 4.71(s,1H) 7.16-7.26(m,4H) ^{13}C NMR (100 MHz, $CDCl_3$); δC (ppm): 27.41, 29.60, 31.42, 32.21, 32.40, 46.42, 47.04, 115.33, 128.19, 129.77, 131.58, 136.69,189.44 HRMS (m/z):385.1568

3,3,6,6 Tetramethyl-9(2-nitrophenyl) 1,8dioxo-octahydroxanthene **3i**

^{1}HNMR $CDCl_3$ 400MHz δ(ppm) 1.25 (s,12H) 2.19-2.57(s,8H) 6.03(s,1H) 7.23-7.55 (m,4H) ^{13}C NMR (100 MHz, $CDCl_3$); δC (ppm):27.41, 29.42, 32.30, 40.99, 50.61, 114.75,123.44, 129.39, 146.71, 151.23,162.45, 195.43 HRMS (m/z):396.1797

REFERENCES:

I. Dey S.; Dhal G. C.; Mohan D.; Prasad R.; Advances in transition metal oxide catalysts for carbon monoxide oxidation: a review; Adv. Compos. Hybrid Mater.; 2019, **2**,626.

II. Mate V. R.; Shirai M.; Rode C. V.;Heterogeneous Co3O4 catalyst for selective oxidation of aqueous veratryl alcohol using molecular oxygen; Catal. Commun.; 2013,**33**,66.

III. Kong C.; Liu F.; Sun H.; Zhang Z.; Zhu B.; Wei Z.; Li W.; Co3O4/GO catalyst as efficient heterogeneous catalyst for degradation of waste water containing polyacrylamide(PAM); Wat. Cyc.; 2021,**2**, 15.

IV. Tuyen N.H.; Kim H.G.; Yoon Y.S.; Effect of Co3O4 Nanoparticles on Improving Catalytic Behavior of Pd/Co3O4@MWCNT Composites for Cathodes in Direct Urea Fuel Cells; Nanomaterials; 2021, **11**, 1017.

V. Packiaraj R.; Devendran P.; Venkatesh K.S.; Asath bahadur S.; Manikandan A.; Nallamuthu N.; Electrochemical investigations of magnetic Co3O4 nanoparticles as an active electrode for supercapacitor applications; J. Supercond. Nov. Magn.; 2018, **32**, 2427

VI. Ravi Dhas C.; Venkatesh R.; Jothivenkatachalam, K.; Nithya A.; Suji Benjamin, B.; Moses Ezhil Raj A.; Jeyadheepan K.; Sanjeeviraja C.; Visible light driven photocatalytic degradation of Rhodamine B and Direct Red using cobalt oxide nanoparticles. Ceram. Int.; 2015, **41**, 9301.

VII. Xing L.L.; Chen Z. H.; Xue X. Y.; Controllable synthesis Co3O4 nanorods and nanobelts and their excellent lithium storage performance.
Solid State Sci.; 2014, **32**, 88.

VIII. Yin M.L.; Liu S.Z.; Synthesis of Co3O4 Multilayer Nanosheet Material and its Promising Gas Sensing Property; Adv. Mater. Res.; 2014, **937**, 231.

IX. Vennela A.B.; Mangalaraj D.; Muthukumarasamy N.; Agilan S.; Hemalatha K.V.; Structural and optical properties of Co3O4 nanoparticles prepared by sol-gel technique for photocatalytic application; Int. J. Electrochem. Sci.; 2019, **14**, 3535.

X. Hekmat F.; Shahrokhian s.; Rahimia S.; 3D flower-like binary nickel cobalt oxide decorated coiled carbon nanotubes directly grown on nickel nanocones and binder-free hydrothermal carbons for advanced asymmetric supercapacitors; Nanoscale, 2019,**11**, 2901.

XI. Anuradha C. T.; Raji P.; Synthesis, Characterization and anti-Microbial activity of oxalate-assisted CO3O4 nanoparticles derived from homogeneous Co-precipitation method ;Int. J. Nanosci.; 2019,**18**, 1950002.

XII. Izu N. ; Matsubara I.; Uchida T.; Itoh T.; Shin W.;Synthesis of spherical cobalt oxide nanoparticles by a polyol method; J. Ceram. Soc. Jpn. ; 2017, **125**, 701.

XIII. Ashok A.; Kumar A.; Bhosaleb R. R.; Saleh M.H.; Ghosh U.K.; Marri M. A.; Almomani F. A.; Khader M. M.; Tarlochan F.; Cobalt oxide nanopowder synthesis using cellulose assisted combustion technique;Ceram. Int.; 2016, **42**, 12771.

XIV. Abbas T. A.-H.; Slewa L. H.; Khizir H. A.; Kakil S. A.; Synthesis of cobalt oxide (Co_3O_4) thin films by electrostatic spray pyrolysis technique (ESP); J. Mater. Sci.: Mater. Electron.; 2017, **28**, 1951.

XV. Morsy S.M.I.; Shaban S. A. ; Ibrahim A. M. ; Selim M. M.; Characterization of cobalt oxide nanocatalysts prepared by microemulsion with different surfactants, reduction by hydrazine and mechanochemical method; J.Alloy.Comp.; 2009,**486**, 83.

XVI. Xu R.; Wang J.; Li Q.; Sun G.; Wang E.; Li S.; Gu J.; Ju M.; Porous cobalt oxide (Co3O4) nanorods: Facile syntheses, optical property and application in lithium-ion batteries; J. Solid State Chem.; 2009, **182**, 3177.

XVII. Parashar M., Shukla V. K.; Singh R.; Metal oxides nanoparticles via sol–gel method: a review on synthesis, characterization and applications;J. Mater. Sci.: Mater. Electron.; 2020, **31**, 3729.

XVIII. John D. Mackenzie; Eric P. Bescher; Chemical Routes in the Synthesis of Nanomaterials Using the Sol–Gel Process; Acc. Chem. Res.; 2007, **40**, 810.

XIX. Iravani S.; Varma R.S.; Sustainable synthesis of cobalt and cobalt oxide nanoparticles and their catalytic and biomedical applications; Green Chem.; 2020,22, 2643.

XX. Ghahsare A.G.; Nazifi1 Z.S.; Nazifi S.M.R.;Structure-Bioactivity Relationship Study of Xanthene Derivatives: A Brief Review;Curr. Org. Synth.; 2019, **16**, 1.

XXI. Bhowmik B. B.; Ganguly P.; Photophysics of xanthene dyes in surfactant solution; Spect. Chim. Acta A, 2005, **61**, 1997.

XXII. Karamia B.;Shahin Nejatib S.; Eskandari K.; An adapted route to efficient synthesis of 1,8-dioxooctahydro-xanthene derivatives using InCl3 and (HPO3)n as recyclable catalysts;Curr. Chem. Lett.; 2015, **4**,169.

XXIII. Fang D., Gong K., Liu, Z.-L. (2008). Synthesis of 1,8-Dioxo-octahydroxanthenes Catalyzed by Acidic Ionic Liquids in Aqueous Media. Catalysis Letters; 2008, **127**, 291.

XXIV. Hasaninejad A.; Dadar M.; Zare A.; Silica-Supported Phosphorus-Containing Catalysts Efficiently Promoted Synthesis of 1,8-Dioxo-octahydroxanthenes under Solvent-Free Conditions; Chem. Sci. Trans.; 2012, **1**, 233.

XXV. Rezayat S.; Erfani Z.; Hajinasiri R.;Phospho sulfonic acid as efficient heterogeneous Brønsted acidic catalyst for one-pot synthesis of 14H-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes;Chem. pap.; 2015,**69**,536.

XXVI. Chaudhary G. R.; Bansal P.; Kaura N.; Mehta S. K.; Recyclable CuO nanoparticles as heterogeneous catalysts for the synthesis of xanthenes under solvent free conditions; RSC Adv.; 2014,**4**, 49462.

XXVII. Lasemi Z.; Mehrasbi E.; ZnO nanoparticles: an efficient and reusable catalyst for one-pot synthesis of 1, 8-dioxo-octahydroxanthenes;Res Chem Intermed;2015,**41**,2855.

XXVIII. Mandlimath T.R.; Umamahesh B.; Sathiyanarayanan K.I.;Rapid one pot synthesis of Xanthene derivatives by an efficient and reusable nano ZnAl2O4-an insight into a new process; J. Mol. Catal. A-Chem.;2014, **391**,198.

Received on July15, 2021.