



POLYBORATE SUPPORTED PERCHLORIC ACID AS AN EFFICIENT SOLID ACID CATALYST FOR ONE-POTSYNTHESIS OF 12-ARYL-8, 9, 10, 12-TETRAHYDROBENZO[A]XANTHENE-11-ONE DERIVATIVES UNDER SOLVENT-FREE CONDITION

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ABSTRACT:

In the present study, perchloric acid supported on polyborate catalyst was subjected for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one derivatives by one-pot, three-component reaction between aromatic aldehydes, 2-naphthol and dimedone under solvent-free condition. Superiority of the present protocol includes short reaction time, solvent-free condition, excellent yield, high purity, cleaner reaction profiles, easy set-up, mild reaction condition and straightforward experimental procedures. The prepared perchloric polyborate solid acid catalyst was characterized by analytical techniques like energy dispersive x-ray analysis, x-ray diffraction, field emission scanning electron microscopy and fourier transform infrared spectroscopy analysis.

KEYWORDS: Multi-component reaction, perchloric polyborate, solvent-free conditions, green chemistry, xanthenes.

INTRODUCTION:

The multicomponent pathway provide an easy approach for the formation of carbon-carbon bonds, carbon-heteroatom bonds, which occur spontaneously by cyclo addition and condensation that occur sequentially which provides synthetic organic chemistry a systematic and focused orientationⁱ. There are many biologically active heterocyclic compounds developed with help of MCRs which are beneficial to the medicinal and pharmaceutical industriesⁱⁱ.

Oxygen-containing benzo xanthene heterocyclic derivatives possess potent biological activities, which includes anti-malarial, anti-bacterial, anti-HIV, anti-fungal, algicidal, anti-

cancer, anti-ulcer, anti-inflammatory, antioxidant and therapeutic effect on Alzheimer's and diabetes diseaseⁱⁱⁱ. They also exhibit specific applications in dyes, laser technology and photodynamic therapy, used as an antagonist for the paralyzing action of zoxazolamine^{iv}. Multicomponent (MCRs) methodology offers new opportunities for researchers to develop numerous pathways for sustainable protocols that reduce the use of toxic substances or eliminate substances that are harmful to human life or the environment^{v-vi}.

Present method adheres to the green chemistry principles^{vii-ix}. Protocols shorten the reaction period so that the time parameter can be reduced^{x-xi}. It is a method of environmental protection that uses safer solvents, non hazardous materials and less energy while reducing environmental contamination^{xii-xiv}. The 12-aryl-8, 9, 10,12-tetrahydrobenzo[a]xanthene-11-one derivatives are synthesized by different catalytic systems. Among them some includes NiFe₂O₄@SiO₂@amino glucose MNPs^{xv}, [Fe₂O₃@HAP]-supported dual acidic nanocatalyst^{xvi}, TBAHS^{xvii}, Lanthanum (III) chloride/chloroacetic acid^{xviii}, Ascorbic acid^{xix}, Tartaric Acid^{xx}, Ionic CSA^{xxi}, Al₂(SO₄)₃.18H₂O^{xxii}, KF/CP NPs^{xxiii}, Manganese (IV) oxide^{xxiv}, SCMNPs@imine@SO₃H^{xxv}, Sulfated Polyborate^{xxvi}, PDNES^{xxvii}, ZrO₂-SO₃H NPs^{xxviii}, Cu(II)Fe₃O₄@APTMS-DFX^{xxix}, GO-SB-PMo^{xxx}, [TMXH]FeCl₄^{xxxi}, P₂O₅^{xxxii}, CoFe₂O₄@OCMC@Cu(BDC)Manganese(IV) Oxide^{xxxiii}, LAIL@MNP^{xxxiv}, Sodium acetate^{xxxv}, ZnO nanoparticle^{xxxvi}, Fe₃O₄.SiO₂ NPs^{xxxvii}, Boric acid^{xxxviii}, NaHSO₄.SiO₂^{xxxix}, [bmim]BF₄^{xl}, PEG-400^{xli}, Tetrachlorosilane^{xlii}, F₃O₄ NPs^{xliii}, PVPP.OTf^{xliv}, GO/GO-SO₃H^{xlv}.

Derivatives of xanthene are used in antiviral therapy^{xix}. Rose Bengal act as a dye sensitizers for photodynamic treatment^{xx} while pharmacologically active compound such as RO67-4853 and Rhodamine^{xxvi} in **Fig 1**. Most of the reported protocols contain acceptable, environmentally benign features but at the same time have some drawbacks, including lack of reagents suitability that follow green chemistry principles, the need for anhydrous and harsh reaction conditions, the use of expensive reagents, the use of harmful volatile organic reagents and reports that some protocols require excessive amounts of reagents and catalyst, a lengthy workup procedure, long reaction times and poor yields. Therefore there is still need to develop protocol following green chemistry features.

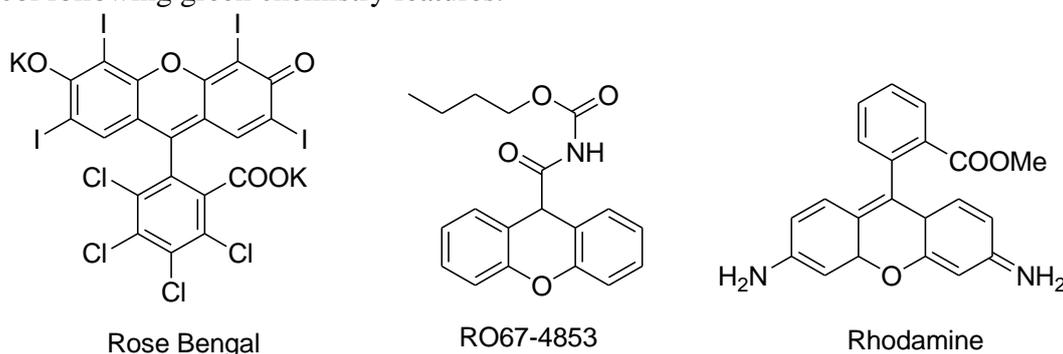


Figure 1. Some Medicinally important drugs containing xanthenes scaffold

Our earlier study on supported polyborate catalysts served as an efficient green strategy for a variety of multicomponent reactions^{xlvi-l}. Catalysts assisted by perchloric acid play a key role in multicomponent organic transformation^{li-lii}. In the current work, polyborate supported perchloric acid was synthesized and used as a solid acid catalyst in multicomponent processes with a green approach.

EXPERIMENTAL:

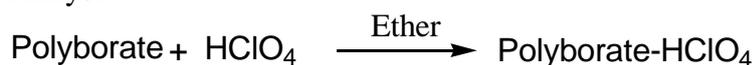
All compounds were purchased from loba and spectrochem and were used exactly as they were received, with no further purification. Ethyl acetate and n-hexane were used as eluting agents in thin layer chromatography on Merck silica gel G₆₀ F₂₅₄ plates. UV-light was used to visualize the thin layer chromatography plates. High resolution mass spectrometry on a waters Q ToF Micromass spectrometer, proton nuclear magnetic resonance spectroscopy, and carbon nuclear magnetic resonance spectroscopy were used to study selected synthesized compounds. The NMR spectra of materials were obtained using a Bruker Avance Neo 500 MHz and 125 MHz frequency NMR spectrometer, SAIF, P.U., with TMS as an internal standard in CDCl₃. Fourier transform infrared spectra were collected using a Perkin-Elmer 400 FT-IR spectrometer. The SEM and EDAX analysis were recorded on JEOL JSM-6100 Scanning Electron Microscope and X-ray diffraction analysis was performed on (PANalytical X'Pert Pro, X-ray diffractometer). Melting points were measured using EQ 730 equiptronics digital melting points equipment.

Synthesis of catalyst:

The polyborate was prepared as per reported in our previous work and its supported catalyst formation was proved by spectral techniques FT-IR, SEM, EDS and XRD etc^{xlvi}.

Synthesis of Perchloric Polyborate Catalyst:

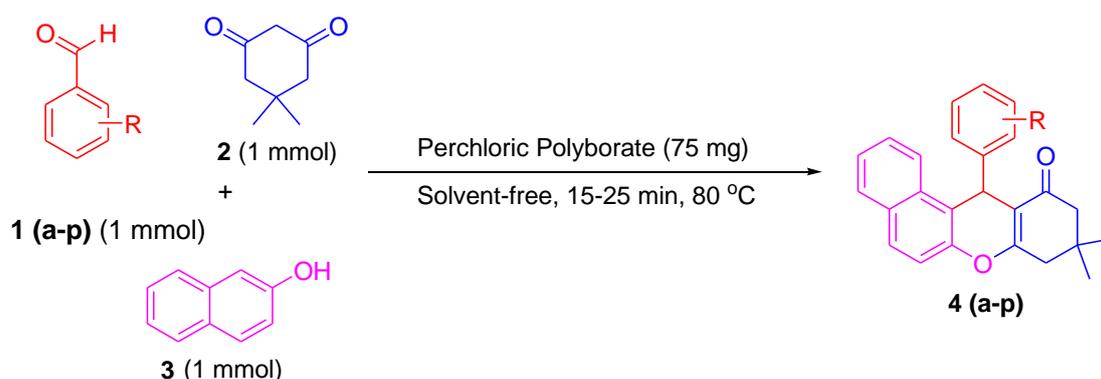
Polyborate (20.50 gm) was taken in 100 mL of dry ether. The temperature of the flask was maintained between 10-15°C by stirring the mixture over magnetic stirrer. To this mixture perchloric acid (8.605 gm) was added drop wise over period of 30 min. The resulting reaction mixture was further stirred for 2 hours at room temperature. After completion of stirring the ether solvent was allowed to evaporate and the resulting solid catalyst was washed several times by acetone and dried at room temperature to get solid powder of perchloric polyborate catalyst.



Scheme 1. Preparation of perchloric polyborate acid catalyst

General synthesis of 2-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives

A 50 ml round-bottomed flask mounted in an oil bath under solvent-free condition at 80°C was charged with a mixture of 2-naphthol (1 mmol), substituted aromatic aldehydes (1 mmol) and dimedone (1 mmol). TLC was used to monitor the progress of reaction and ethyl acetate:n-hexane (7:3) as an eluent. To obtain pure products they recrystallized from ethanol. Compounds were characterized by spectral techniques such as FT-IR, NMR and HRMS.



Scheme 2. Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones derivatives 4 (a-p)

Characterization data of some synthesized compounds:

9, 9 -Dimethyl- 1 2-phenyl-8, 9, 10, 12-tetrahydrobenzo[a]-xanthen-11-one(4a):

White crystals, m.p. 148-149°C; FT-IR (cm⁻¹): 3055, 3025, 3002, 2955, 2884 (C-H), 1650 (C=O), 1596 (C=C), 1373, 1227 (C-O), 1183, 810, 698, 747; ¹H NMR (CDCl₃, 500 MHz, δ ppm): 0.93 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 2.20 (dd, 2H, CH₂), 2.53 (s, 2H, CH₂), 5.70 (s, 1H, CH), 7.01 (t, 1H, ArH), 7.13 (t, 2H, ArH), 7.29 (m, 4H, ArH), 7.38 (t, 1H, ArH), 7.71 (t, 2H, ArH), 7.97 (d, 1H, ArH); ¹³C NMR (CDCl₃, 125 MHz, δ ppm): 27.18, 29.34, 32.28, 34.76, 41.43, 50.93, 114.30, 117.08, 117.74, 123.71, 124.93, 126.28, 127.04, 128.28, 128.43, 128.47, 128.87, 131.44, 131.53, 144.80, 147.78, 163.94, 196.93; M. F: C₂₅H₂₂O₂, calculated mass 354.4410, [M⁺ + H] = 355.1701.

12-(2-chlorophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one(4b):

white crystals, m.p. 179-180°C; FT-IR (cm⁻¹): 3058, 3017, 2947, 2867 (C-H), 1652 (C=O), 1622, 1596 (C=C), 1370, 1228 (C-O), 1180, 835 (C-Cl), 812, 745; ¹H NMR (CDCl₃, 500 MHz, δ ppm): 0.98 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.20 (dd, 2H, CH₂), 2.58 (s, 2H, CH₂), 5.98 (s, 1H, CH), 6.95 (t, 1H, ArH), 7.02 (t, 1H, ArH), 7.24 (t, 3H, ArH), 7.34 (t, 1H, ArH), 7.45 (t, 1H, ArH), 7.72 (t, 2H, ArH), 8.20 (d, 1H, ArH); ¹³C NMR (CDCl₃, 125 MHz, δ ppm): 27.13, 29.40, 32.18, 32.98, 41.49, 50.90, 113.47, 117.09, 117.43, 123.97, 124.96, 126.92, 127.15, 127.67, 128.42, 129.14, 130.01, 131.39, 131.66, 131.71, 132.96, 142.19, 147.71, 164.26, 196.75; M. F: C₂₅H₂₁ClO₂, calculated mass-388.8860, [M⁺ + H] = 389.1371.

12-(4-bromophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one(4g):

White solid, m.p. 185-187°C; FT-IR (cm⁻¹): 3062, 2958, 2946, 2896, 2868 (C-H), 1642 (C=O), 1592 (C=C), 1512, 1373, 1222 (C-O), 1172, 836, 754, 661 (C-Br); ¹H NMR (CDCl₃, 500 MHz, δ ppm): 0.94 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 2.21 (dd, 2H, CH₂), 2.54 (s, 2H, CH₂), 5.66 (s, 1H, CH), 7.20 (t, 2H, ArH), 7.26 (d, 2H, ArH), 7.30 (d, 1H, ArH), 7.35 (t, 1H, ArH), 7.40 (t, 1H, ArH), 7.74 (t, 2H, ArH), 7.88 (d, 1H, ArH); ¹³C NMR (CDCl₃, 125 MHz, δ ppm): 27.17, 29.34, 32.27, 34.30, 41.41, 50.87, 76.83, 113.76, 117.00, 117.07, 120.15, 123.47, 125.06, 127.16, 128.53, 129.15, 130.23, 131.23, 131.37, 131.54, 143.80, 147.75, 164.09, 196.88; M. F: C₂₅H₂₁BrO₂, calculated mass-433.3370, [M⁺ + H] = 433.0818.

12-(4-Nitrophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one(4h):

White solid; mp 177-178°C; FT-IR (cm⁻¹): 3076, 2954, 2892, 2872 (C-H), 1646 (C=O), 1595 (C=C), 1516 (NO₂), 1376, 1344 (NO₂), 1223 (C-O), 1181, 830, 748; ¹H NMR (CDCl₃, 500 MHz, δ ppm): 0.93 (s, 3H, CH₃), 1.12 (s, 3H, CH₃), 2.22 (dd, 2H, CH₂), 2.58 (s, 2H, CH₂), 5.80 (s, 1H, CH), 7.34 (d, 1H, ArH), 7.40 (m, 2H, ArH), 7.49 (d, 2H, ArH), 7.78 (d, 3H, ArH), 8.00 (d, 2H, ArH); ¹³C NMR (CDCl₃, 125 MHz, δ ppm): 27.07, 29.32, 32.28, 41.42, 50.79, 112.99, 116.05, 117.12, 123.13, 123.64, 125.27, 127.40, 128.69, 129.39, 129.66, 131.04, 131.59, 146.35, 147.80, 151.90, 164.68, 196.78; M. F: C₂₅H₂₁NO₄, calculated mass-399.4385, [M⁺ + H] = 400.1594.

12-(4-Methylphenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one(4i):

White solid, m.p. 176-178°C; FT-IR (cm⁻¹): 3041, 3015, 2950, 2894, 2867 (C-H), 1647 (C=O), 1596 (C=C), 1511, 1371, 1228 (C-O), 812, 753; ¹H NMR (CDCl₃, 500 MHz, δ ppm): 0.96 (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 2.18 (s, 3H, CH₃), 2.21 (dd, 2H, CH₂), 2.54 (s, 2H, CH₂), 5.66 (s, 1H, CH), 6.95 (d, 2H, ArH), 7.21 (t, 2H, ArH), 7.29 (d, 1H, ArH), 7.34 (t, 1H, 1H), 7.39 (t, 1H, ArH), 7.72 (t, 2H, ArH), 7.99 (d, 1H, ArH); ¹³C NMR (CDCl₃, 125 MHz, δ ppm): 21.01, 27.30, 29.29, 32.31, 34.32, 41.44, 50.94, 114.41, 117.06, 117.91, 123.71, 124.87, 126.98, 128.30, 128.39, 128.73, 128.96, 131.45, 131.51, 135.68, 141.88, 147.70, 163.81, 196.97; M. F: C₂₆H₂₄O₂, calculated mass-368.4468, [M⁺ + H] = 369.1863.

12-(4-chlorophenyl)-9, 9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one(4m):

White crystals, m.p. 180-181°C; FT-IR (cm⁻¹): 3075, 3019, 2952, 2894, 2869 (C-H), 1648 (C=O), 1598 (C=C), 1370, 1227 (C-O), 1183, 751, 835 (C-Cl); ¹H NMR (CDCl₃, 500 MHz, δ

ppm): 0.95 (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 2.22 (dd, 2H, CH₂), 2.55 (s, 2H, CH₂), 5.67 (s, 1H, CH), 7.12 (d, 2H, ArH), 7.25 (t, 2H, Ar-H), 7.30 (d, 1H, ArH), 7.37-7.44 (m, 2H, ArH), 7.75 (t, 2H, ArH), 7.89 (d, 1H, ArH); ¹³C NMR: (CDCl₃, 125 MHz, δ ppm), 27.15, 29.32, 32.27, 34.20, 41.41, 50.87, 113.84, 117.06, 123.48, 125.04, 127.14, 128.41, 128.50, 129.11, 129.82, 131.23, 131.53, 131.94, 143.26, 147.75, 164.08, 196.90; M. F.: C₂₅H₂₁ClO₂, calculated mass 388.886, [M⁺ + H] = 389.1371.

RESULTS AND DISCUSSION:

Characterization of catalyst:

FT-IR analysis of perchloric polyborate catalyst

The FT-IR spectrum of catalyst exhibits peak at 3215-3746 cm⁻¹ due to O-H stretching, band at 3215 cm⁻¹ corresponds to O-H stretching of B-O-H, band at 1451 cm⁻¹ for B-O stretching and band at 640 cm⁻¹ indicate O-B-O stretching of polyborate catalyst. The bands at 1193.5 cm⁻¹ attributed to the asymmetric stretching whereas bands at 806 cm⁻¹, 674 cm⁻¹ and 546 cm⁻¹ were due to the symmetric stretching and rocking vibration of HClO₄^{liii}.

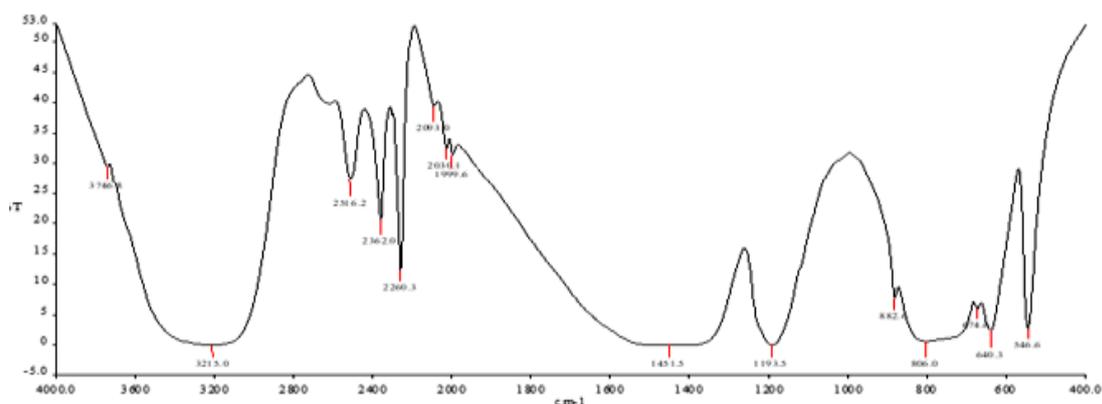


Figure 2. FT-IR Spectrum of perchloric polyborate

XRD analysis of perchloric polyborate catalyst

Powder XRD pattern of perchloric polyborate catalyst shown significant peaks positioned at 2θ=28.15° which confirms the presence of B-O bonds in the crystalline structure of the perchloric polyborate catalyst. The remaining significant peaks in the range from 32.3 to 64.4 were due to HClO₄ group^{liv}.

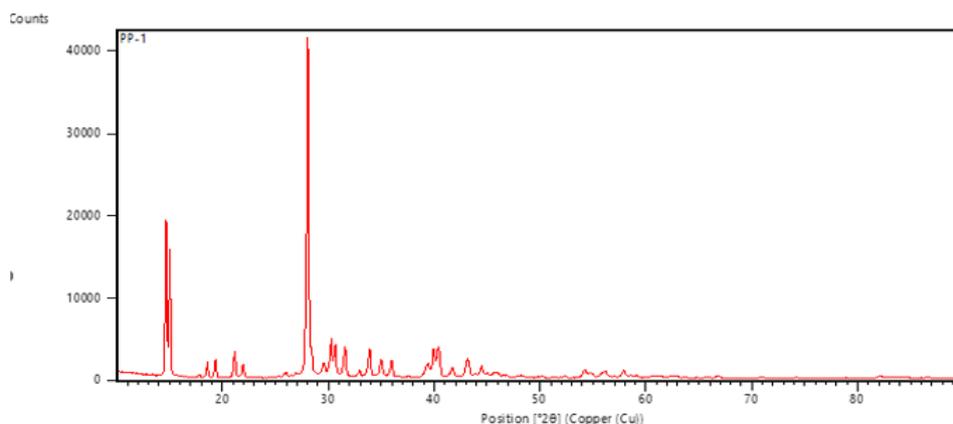


Figure 3. XRD spectrum of perchloric polyborate catalyst

EDS analysis of perchloric polyborate catalyst

EDS analysis of the catalyst indicates presence of the expected elements in the perchloric polyborate catalyst which supports its formation.

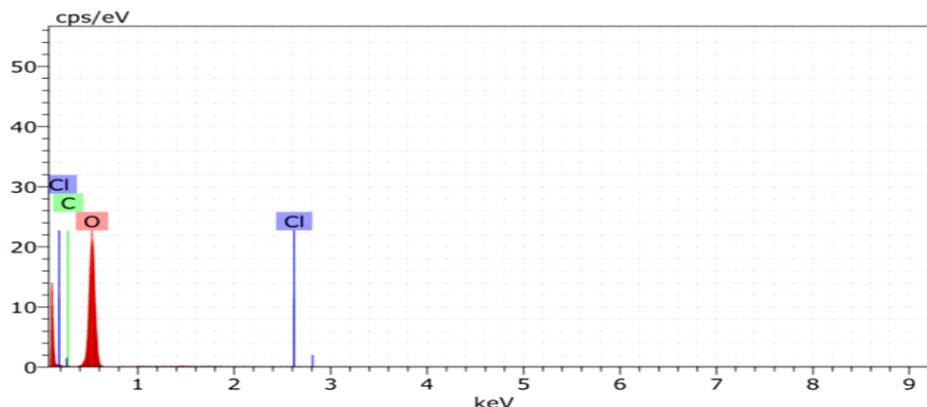


Figure 4. EDS of perchloric polyborate catalyst

SEM analysis of perchloric polyborate catalyst

Surface morphology of synthesized catalyst was examined by SEM analysis which highlights crystalline nature of catalyst with different shapes and sizes of the particles.

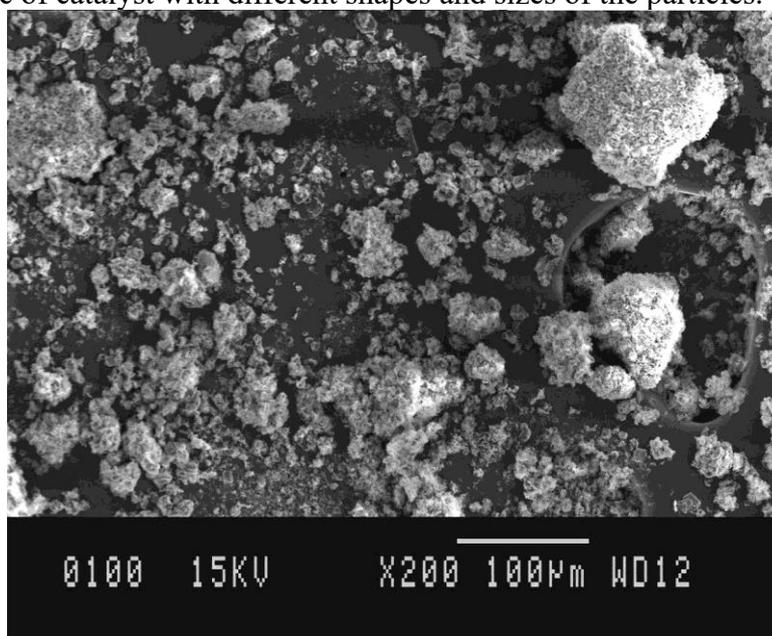
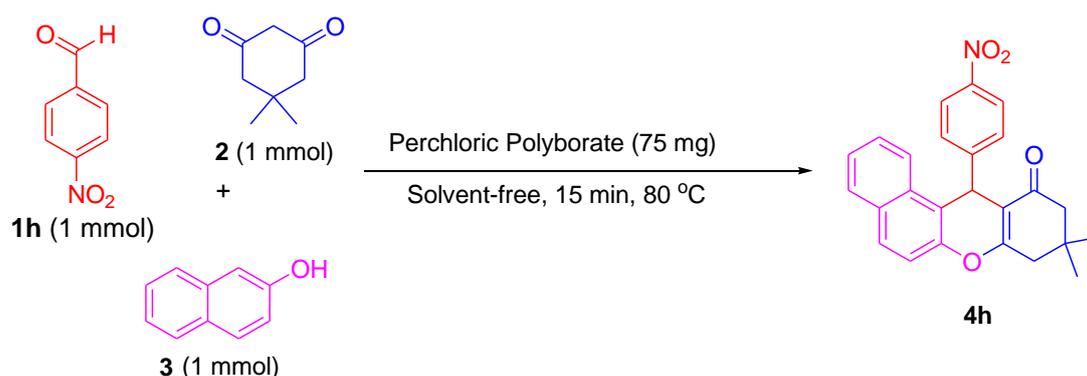


Figure 5. SEM analysis of perchloric polyborate catalyst

Catalytic activity study of perchloric polyborate acid catalyst:

The successful synthesis of catalyst motivated us to check its catalytic potential for the multicomponent synthesis of 12-aryl xanthenes using aldehyde, dimedone and β -naphthol. To assess various reaction parameters a model reaction of 4-nitro benzaldehyde, dimedone and β -naphthol was chosen. For any reaction the factors like solvent, amount of catalyst, temperature, time required for completion of reaction are need to evaluated.



Scheme 3. Model reaction of synthesis of 12-aryl-tetrahydrobenzo[a]xanthene-11-ones (4h)

To check the most suitable reaction medium the model reaction was carried out in various solvents as shown in Table 1. The results highlight that among them the solvent-free approach is more suitable for this reaction (Table 1, entry 8).

Table 1. Solvent optimization for the synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives

Entry	Solvent	Temperature	Time (min)	Yields ^a (%)
1	H ₂ O	reflux	30	0
2	EtOH	reflux	30	10
3	CH ₂ Cl ₂	reflux	30	30
4	Toluene	reflux	30	25
5	CHCl ₃	reflux	30	27
6	DMF	80°C	30	35
7	Solvent-free	60°C	20	78
8	Solvent-free	80°C	15	94
9	Solvent-free	100°C	15	94

^aIsolated Yields

In the next part we checked the amount of catalyst essential for the completion of reaction. The results obtained are given in Table 2 which concludes that 75 mg of catalyst is sufficient to carry the reaction with good yield. Further increase in amount of catalyst does not increase the product yield.

Table 2. Optimization of amount of catalyst amount for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one derivatives

Sr. No	Catalyst (gm)	Yield ^a (%)	Time (min)
1	0	0	15
2	0.025	55	15
3	0.050	63	15
4	0.075	94	15
5	0.100	94	15

^aIsolated Yields

After this we optimized the time required for the completion of the reaction. We performed the reaction at various time as shown in Table 3. It is found that 15 minutes is the optimum time required for completion of reaction with good yield. Further increase in reaction time does not alter the product yield.

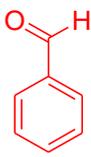
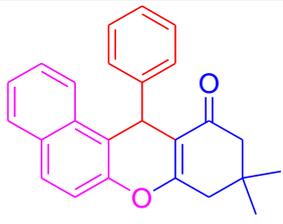
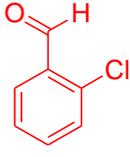
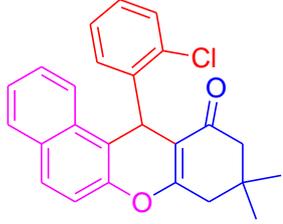
Table 3. The optimization of time required for the synthesis of derivatives of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives

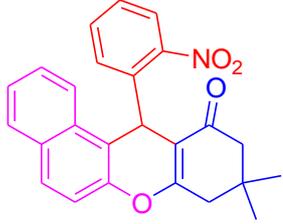
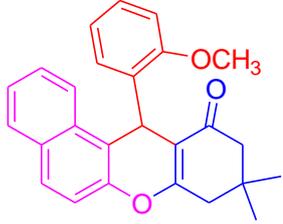
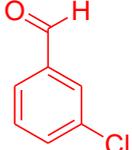
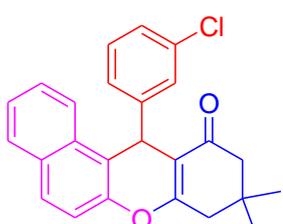
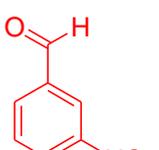
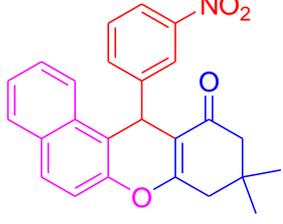
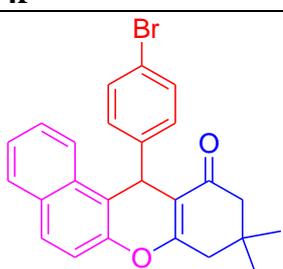
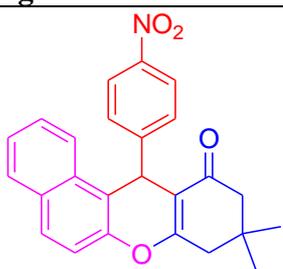
Sr. No.	Amount of catalyst (mg)	Time (min)	Yield ^a (%)
1	75	5	48
2	75	10	66
3	75	15	94
4	75	20	94

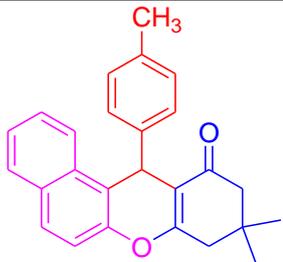
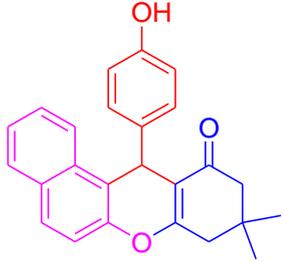
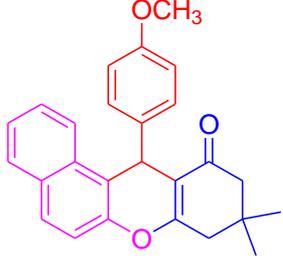
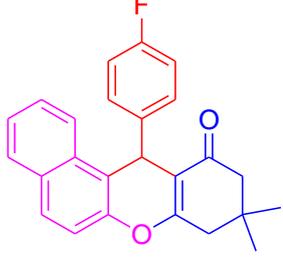
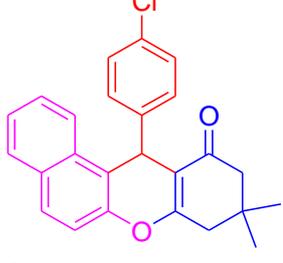
^aIsolated Yields

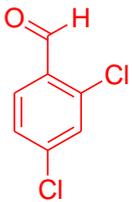
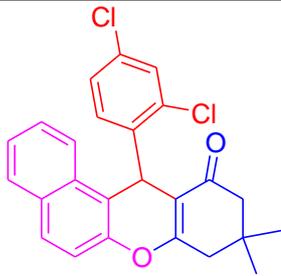
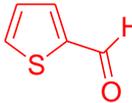
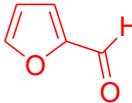
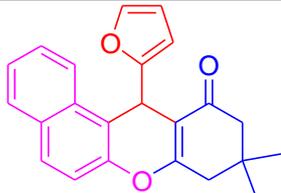
All the above result obtained summaries that solvent-free condition with 75 mg of catalyst at 80°C is the most optimum condition for the synthesis of 12-aryl xanthene derivatives. These results promoted us to check the diversity of the optimized protocol for the synthesis of various other derivatives of xanthenes. We performed the reaction of dimedone (1 mmol), β-naphthol (1 mmol) with variously substituted aromatic aldehydes (1 mmol). The aldehydes possess chloro, nitro, methoxy, bromo, methyl, hydroxyl, fluoro substituents at ortho, meta or para position. All these aldehyde gave satisfactory product yields. We also used heteroaromatic aldehyde 2-thiophene and 2-furfural which also gives good product yields.

Table 4. Synthesis of tetrahydrobenzo[a]xanthene-11-ones (4a-p) catalyzed by perchloric polyborate

Sr. No.	Aldehyde	Products	Time (min)	Yield ^{a,b} (%)	M.P. (°C)	
					Observed	Reported
1		 4a	20	90	148-149	149-151 ^{xvi}
2		 4b	25	89	179-180	177-179 ^{xvi}

3		 4c	20	92	222-223	220-221 ^{xvi}
4		 4d	25	89	165-166	166-167 ^{xvi}
5		 4e	20	87	174-175	173-176 ^{xvi}
6		 4f	15	89	169-170	166-169 ^{xvi}
7		 4g	15	91	185-187	184-186 ^{xvi}
8		 4h	15	94	177-178	173-176 ^{xvi}

9		4i 	20	86	176-178	174-176 ^{xvi}
10		4j 	20	89	224-225	222-224 ^{xvi}
11		4k 	20	88	202-203	202-204 ^{xvi}
12		4l 	20	86	183-184	183-185 ^{xvi}
13		4m 	15	92	180-181	179-181 ^{xvi}

14		 4n	20	90	179-181	180-181 ^{xvi}
15		 4o	20	83	176-177	181-183 ^{xvi}
16		 4p	20	87	171-172	170-172 ^{xvii}

^aIsolated Yields^breaction with dimedone, β -naphthol and substituted aromatic aldehydes in presence of perchloric polyborate under solvent-free condition at 80°C.

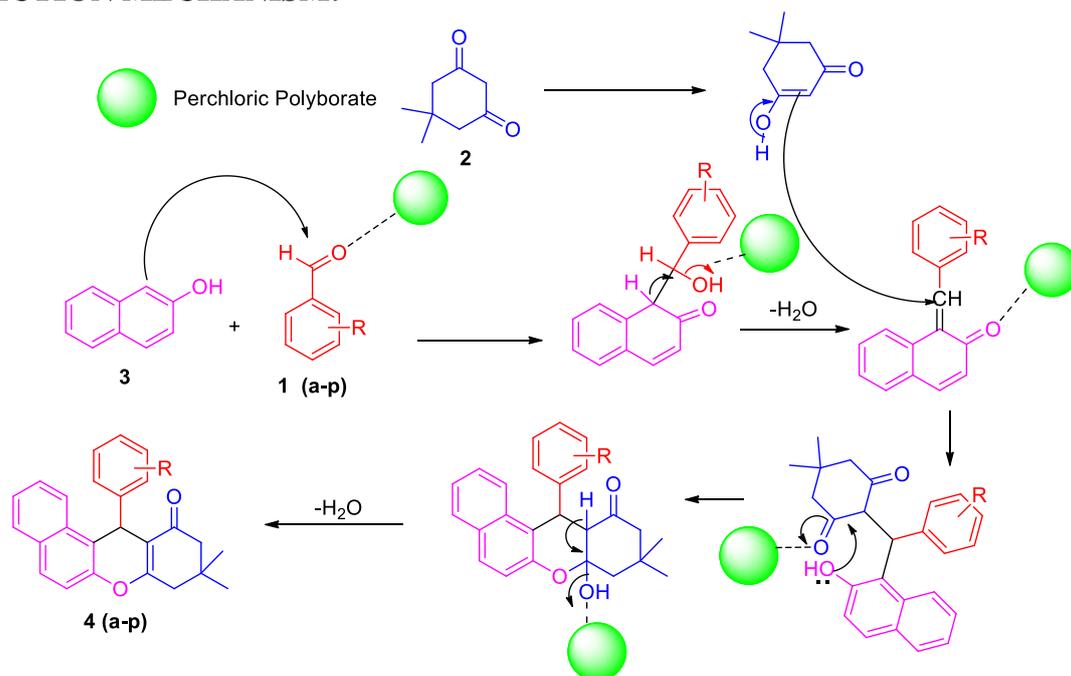
The optimized protocol was compared with the literature reported methods for the synthesis of 12-aryl xanthene derivatives in **Table 5**. The observation is that our reported protocol is superior in term of non-costly and non-toxic solid acid catalyst, solvent-free approach with good product yield.

Table 5. Comparison of reported methods for the synthesis of tetrahydrobenzo[a]xanthene-11-ones

Entry	Catalyst/Solvent/Condition	Catalyst amount	Temp	Time (min)	Yield ^a (%)
1	Tetrabutyl Ammonium Hydrogen Sulphate (TABHS)	10 mol %	60°C	120-300	82-90 ^{xvii}
2	Boric Acid /EtOH	10 mol %	Reflux	120-270	77-92 ^{xxxviii}
3	NaHSO ₄ ·SiO ₂ , CH ₂ Cl ₂	-	Reflux	240-420	71-86 ^{xxxix}
4	[bmim]BF ₄ (0.5 mL), pTSA/ Neat	(0.1 mmol)	80°C	120-210	84-95 ^{xl}
5	PEG-400 (1 mL)	-	120°C	330-450	79-90 ^{xli}
6	Tetrachlorosilane / CH ₂ Cl ₂	2.5 mmol	RT	60-210	92-98 ^{xlii}
7	F ₃ O ₄ NPs/Solvent-Free	5 mol %	90-110°C	120	80-95 ^{xliii}
8	PVPP.OTf / Toluene	30 mg	110°C	300-360	85-95 ^{xliv}
9	GO/GO-SO ₃ H /H ₂ O	0.02 gm	80°C	120-180	83-96 ^{xlv}
10	Perchloric Polyborate / Solvent-Free	0.075 gm	80°C	15-25	83-94

^aIsolated Yields

REACTION MECHANISM:



Scheme 4. Plausible mechanism for the formation of tetrahydrobenzo[a]xanthene-11-ones

CONCLUSION:

In the present work tetrahydrobenzo[a]xanthene-11-ones were synthesized by one-pot multicomponent reaction between substituted aromatic aldehyde, dimeric dione and 2-naphthol using perchloric polyborate solid acid catalyst. The advantages of this method include use of non-toxic solid acid catalyst, mild reaction condition, clean reaction profile, solvent-free approach and good product yields. Overall, an operationally simple, environmentally and economically benign process is been reported.

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CONFLICT OF INTERESTS:

The authors say they have no competing interests.

ABBREVIATIONS:

MCRs = Multicomponent Reactions

NR = No Reaction

SF= Solvent-Free Reactions

FT-IR= Fourier Transform Infrared Spectroscopy

¹H NMR = Proton Nuclear Magnetic Resonance Spectroscopy

¹³C NMR= Carbon Nuclear Magnetic Resonance Spectroscopy

EDS = Energy Disperse Scanning Electron microscopy

SEM= Scanning Electron Microscopy

XRD= X-Ray Diffraction

HRMS = High-Resolution mass spectrometry

TLC = Thin Layer Chromatography

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