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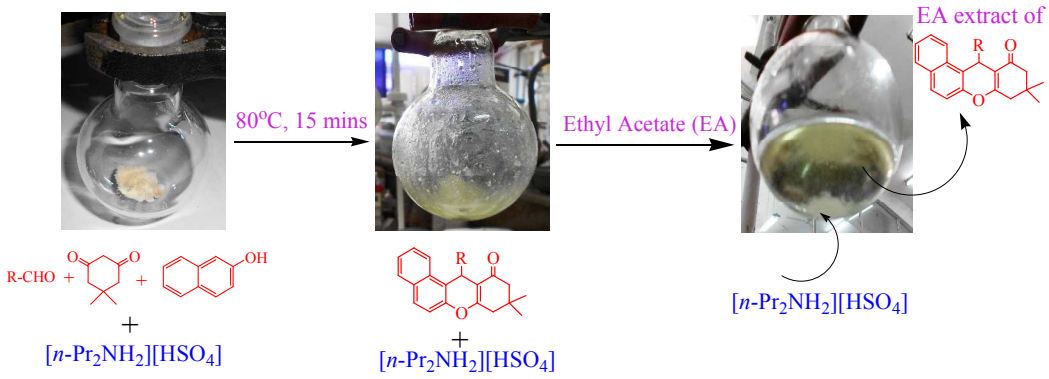
Amine based ionic liquid was reported as an efficient and easily recyclable catalyst for the solvent free environmental benign synthesis of xanthene and benzoxanthene derivatives within 10-30 minutes.



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ARTICLE TYPE

Secondary amine based ionic liquid: an efficient catalyst for solvent free one pot synthesis of xanthenes and benzoxanthenes

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Ionic liquids (IL) prepared from dialkylamines and concentrated sulphuric acid were used in an operationally simple, cost effective, efficient and environmentally benign synthesis of xanthenes and benzoxanthenes. Three ILs were screened for their efficiency as promoter of the synthesis. Results indicate di-*n*-propylammoniumhydrogensulphate to be the most efficient IL. Product recovery is simple and the IL could be recovered for reuse.

Introduction

The use of IL as environmentally benign reaction solvents for synthesis and catalysis has been recognized. Its environmentally favourable qualities such as nonvolatility, high thermal stability, excellent solubility and extended liquid range have contributed to its versatility and increasing applicability.[1] Recently, ILs with different morphology and with improved quality like ionic liquid marbles,[2] stable room temperature ionic liquids,[3] ionic liquid crystals[4], poly (ionic liquid)s,[5] ionic liquids with metal chelate counter anion,[6] and biodegradable ionic liquids[7] were synthesized and have found application in different fields including the transformation of renewable biomass into functional carbon materials by the ionothermal carbonization process.[8]

Xanthene and benzoxanthene are important heterocycles with a variety of applications in the field of pharmaceutical chemistry.[9] The xanthene moiety being a source of brilliant fluorescent dye is widely used in chemical biology as tracers for proteins, DNAs, sugars with high sensitivity and selectivity.[10] Their application in laser technology is well documented.[11] Notable Pharmaceutical activities of xanthene derivatives includes antibacterial,[12] analgesic,[13] antiviral,[14] anti-inflammatory,[15] antimalarial and inhibitory action towards trypanothione reductase enzymes and chloroquine potentiating agent,[16] besides others. The versatility of xanthenes derivatives have attracted attention of synthetic chemists towards their preparation and scaffold manipulation using improved procedure. Condensation of dimedone, aldehyde and 2-naphthol is the usual procedure for library synthesis of xanthene, benzoxanthene and their structural variants. Classical methods of the synthesis include reaction of 2-naphthol with aldehydes or acetals under acidic conditions[17] and the reaction of aryloxymagnesium halides with triethyl orthoformate.[18] Zhao *et al*. synthesized xanthones, thioxanthones by the reaction of silylaryl triflates, CsF and ortho-heteroatom substituted benzoates by the intermolecular nucleophilic coupling followed by intramolecular electrophilic cyclization.[19] Other methods include palladium-catalyzed cyclization of polycyclic aryltrifalte esters,[20] annulation reaction of benzyne with salicylaldehyde,[21] coupling reaction of arynes with aldehydes via ortho-quinone methides[22] and reaction of 2-tetralone and 2-hydroxy aromatic aldehydes under acidic conditions.[23] The target molecules have also been synthesized by a one pot multicomponent reaction using HY zeolite.[24] Li *et al.* used proline triflate as catalyst for the synthesis under reflux condition in water.[25] Other reported catalysts that promoted the reaction are strontium triflate,[26] indium (III) chloride and P_2O_5,[27] silica sulfuric acid,[28] quasi homogeneous magnetic silica-coated Fe_3O_4 nanoparticle supported on 3-sulfobutyl-1-(3-pro pyltriethoxysilane) imidazolium[29] besides others. The synthesis of (9-aryl/alkyl-octahydroxanthene-1, 8-diones) have been reported by Shakibaei *et al.* using Dowex-50W ion exchange resin as reusable catalyst.[30] Kantevari *et al.* compared the catalytic efficiency of $HClO_4$-SiO_2 and polyphosphoric acid-SiO_2 as catalyst in a variety of solvents and observed that in acetonitrile and under solvent free conditions polyphosphoric acid-SiO_2 gave selectively 1,8-dioxooctahydroxanthene whereas $HClO_4$-SiO_2 gave 2,2'-arylmethylene bis (3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) as major products.[31] Other catalysts used for promoting the condensation includes methanesulfonic acid,[32] *p*-dodecylbenzenesulfonic acid (DBSA),[33] $NaHSO_4$-SiO_2[34] tetrabutylammoniumhydrogensulphate (TBAHS),[35] trimethylsilyl chloride (TMSCL)[36] etc. The application of ILs as promoter for the reaction was demonstrated by Kidwai using imidazolium based IL [bmim]PF_6 as solvent,[37] Khaligh applied poly(4-vinylpyridinium) hydrogensulphate as catalyst for the synthesis of three xanthene derivatives namely 14-aryl-14H-dibenzo[a,j]xanthene-8,13-diones, dibenzo[b,i]xanthenetetraones and aryl-14H-dibenzo[a,j]xanthenes by using 2-naphthol, 2-hydroxynaphthalene-1,4-dione and aryl halide as reactant.[38]

Results and discussions

Although some acid catalysts were found to be efficient for the

synthesis of xanthenes derivatives most procedures suffer from one or more disadvantages notably prolonged reaction time, tedious work up procedures, use of VOCs and hazardous reaction

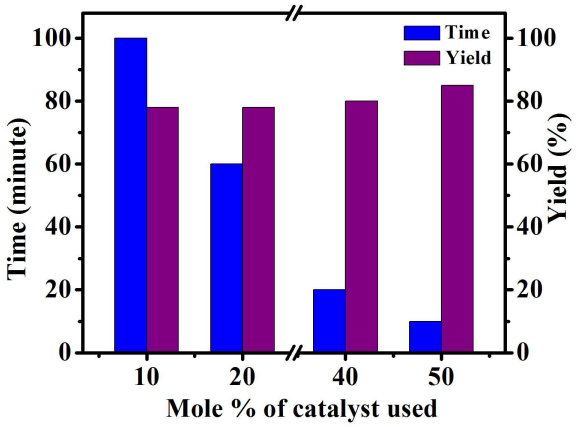
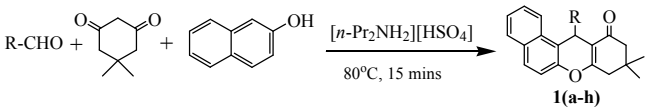
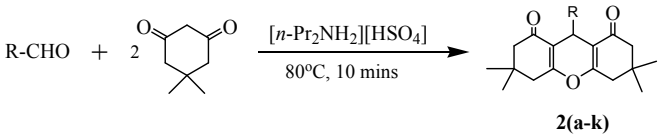


Figure 1: Effect of amount of [(*n*-propyl)$_2$NH$_2$][HSO$_4$] IL on the synthesis of **2c**

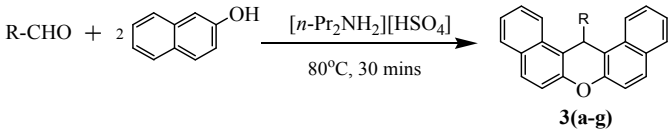
conditions. Chemoselectivity can be a problem in the presence of acid sensitive groups. A few instances of the use of ILs as solvents as well as promoter in the synthesis have been reported, but high cost of imidazole, thiazole and pyridine based IL and concomitant use of costly catalyst for the synthesis have been the essential drawbacks. To overcome these disadvantages, herein is reported simple yet efficient procedures for the synthesis of the xanthenes derivatives particularly 9, 9-dimethyl-12-aryl-8, 9, 10, 12-tetrahydro-benzo[a]xanthenes-11-one, 3, 3, 6, 6-tetramethyl-9-aryl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-xanthene-1,8-dione and 14-Aryl-14[H]-dihydro-dibenzo[a,j]xanthenes using environmental benign, cheap and easily preparable IL derived from a dialkylamines which perform the role of a catalyst. The VOC free synthetic protocol reported here offers additional advantage of simple work up and easy product recovery. The IL could be easily recovered and recycled. Three ILs namely [Et$_2$NH$_2$][HSO$_4$](diethylammonimhydrogensulphate),[(*n*-propyl)$_2$ NH$_2$][HSO$_4$](di-*n*-propylammon-iumhydrogensulphate and [(*iso*-propyl)$_2$NH$_2$][HSO$_4$] (di-*iso*-propylammoniumhydrogen sulphate) were synthesized from the appropriate dialkylamine and concentrated sulphuric acid. The essentiality of acidic IL catalyst to promote the reaction is established by the observation that in the absence of IL the reaction did not proceed. Further the three ILs were screened for their efficiency in a representative reaction of 4-nitrobenzaldehyde and dimedone for the formation of **2b** (**Table 1**) and on the basis of reaction time and yield it was observed that [Et$_2$NH$_2$][HSO$_4$] and [(*n*-propyl)$_2$NH$_2$][HSO$_4$] were more efficient than [(*iso* -propyl)$_2$NH$_2$][HSO$_4$]. However thermal stability of [(*n*-propyl)$_2$NH$_2$][HSO$_4$] compared to [Et$_2$NH$_2$][HSO$_4$] at the optimum temperature encouraged us to use [(*n*-propyl)$_2$NH$_2$][HSO$_4$] as the IL of choice in all our reactions. Consequent to this observation, this IL was used in carrying out the syntheses reported here **(Table 2)**.



Scheme 1: Synthesis of 9, 9-dimethyl-12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthenes-11-one



Scheme 2: Synthesis of 3, 3, 6, 6-tetramethyl-9-aryl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-xanthene-1, 8-dione



Scheme 3: Synthesis of 14-Aryl- 14[H]-dihydrodibenzo[a,j]xanthenes

Table 1: Screening for efficiency of the ionic liquids on the synthesis of **2b** (50 mol% IL was used)

Entry	Ionic Liquid	Time(mins)	Yield(%)[a]
1	[Et$_2$NH$_2$][HSO$_4$]	10	83
2	[(*n*-propyl)$_2$NH$_2$][HSO$_4$]	10	85
3	[(*iso*-propyl)$_2$NH$_2$][HSO$_4$]	10	72
4	none	120	0

a. Isolated product

To determine the optimum amount of the [(*n*-propyl)$_2$NH$_2$][HSO$_4$] IL necessary for less reaction time and maximum yield, the model reaction of dimedone and *p*-anisaldehyde for the formation of **2c** (**Table 2**) was selected. The mol% of the IL was changed and the optimum quantity of IL required for maximum yield and shortest reaction time was found to be 50 mol% **(Figure 1)**.

In the first instance, the three component reaction of 2-naphthol, demidone and aldehyde was carried out in di-*n*-propylammoniumhydrogensulphate to give the 9, 9-dimethyl-12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthenes-11-one in high yield **(Scheme 1)**. In a subsequent reaction using only the demidone and aldehyde as the substrates in the molar ratio 2:1 and the product obtained was 3, 3, 6, 6-tetramethyl-9-aryl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-xanthene-1, 8-dione **(Scheme 2)** and finally a reaction of 2-naphthol and aldehyde in the molar proportion of 2:1 gave the 14-Aryl-14[H]-dihydro-dibenzo[a,j]xanthenes **(Scheme 3)**. In comparision to aromatic aldehydes, aliphatic aldehydes are found to be less reactive under this reaction conditions giving reasonably low yields

Experimental procedure for all the three reactions involve mixing the substrates and IL in the right proportions, grinding to give a oily homogeneous mixture followed by thermal heating at 80°C in an oil bath for 10-30 minutes in the absence of solvents. The oily homogeneous mixture solidified on completion of the reaction as indicted by TLC. Addition of ethylacetate to the crude product precipitated the insoluble IL which could be recovered in high state of purity by simple filtration and reused for three successive run without any appreciable loss of activity

(all these representative steps are shown in **Figure S1** in supporting information). The products were crystallized from

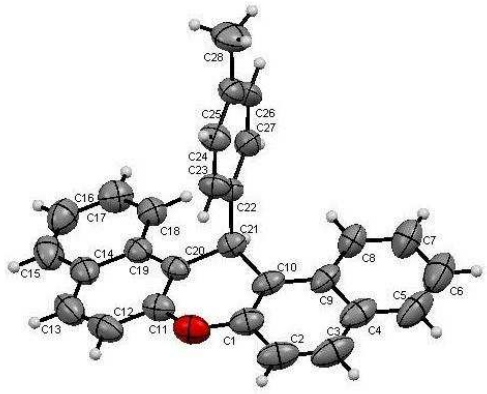


Figure 2: ORTEP diagram of 3c

ethylacetate extract. The results are summarized in **Table 2**.

Table 2: Synthesis of xanthene derivatives catalysed by [(*n*-propyl)$_2$NH$_2$][HSO$_4$] ionic liquid

Entry	R	Product	Time (min)	Yield (%)[a]
1	4-ClC_6H_4	1a	15	80
2	4-$NO_2C_6H_4$	1b	15	79
3	4-$CH_3C_6H_4$	1c	15	82
4	4-$OCH_3C_6H_4$	1d	15	82
5	C_6H_5	1e	15	78
6	2-naphthyl	1f	15	78
7	2- $OCH_3C_6H_4$	1g	15	82
8	iso-$CH(CH_3)_2$	1h	20	65[b]
9	4-ClC_6H_4	2a	10	85
10	4-$NO_2C_6H_4$	2b	10	85
11	4-$OCH_3C_6H_4$	2c	10	85
12	4-OHC_6H_4	2d	10	82
13	4-$CH_3C_6H_4$	2e	10	86
14	3-Cl C_6H_4	2f	10	83
15	2,6-$Cl_2C_6H_3$	2g	10	82
16	2,5-$(OH)(NO_2)C_6H_3$	2h	10	83
17	CH_3	2i	20	72[b]
18	$C_6H_5CH_2CH_2$	2j	10	87[c]
19	iso-$CH(CH_3)_2$	2k	20	70[b]
20	4-ClC_6H_4	3a	30	67
21	4-$NO_2C_6H_4$	3b	30	65
22	4-$CH_3C_6H_4$	3c	30	69
23	4-OHC_6H_4	3d	30	69
24	2- $OCH_3C_6H_4$	3e	30	70
25	CH_3	3f	30	69[b]
26	iso-$CH(CH_3)_2$	3g	25	65[b]
27	2- $OCH_3C_6H_4$	1g	15	82[d]
28	2- $OCH_3C_6H_4$	1g	15	82[e]
29	2- $OCH_3C_6H_4$	1g	15	82[f]

a. Isolated product
b. 0.2 ml of aldehyde used
c. New compound
d. Catalyst reused: 1st run
e. Catalyst reused: 2nd run
f. Catalyst reused: 3rd run

It can be seen from Table 2 that a variety of aldehydes both aromatic as well as aliphatic aldehydes respond similarly and give similar products under identical reaction conditions. However, we observed that with aliphatic aldehydes, the % yield is generally lower than those obtained from aromatic aldehydes and requires higher reaction time. Further, among the aromatic aldehydes, the % yield and the reaction time is not influenced by the nature and electronic effects of the substituents present in the phenyl ring .

All products obtained were characterized by IR, ^{1}H NMR, ^{13}C NMR, Mass spectrometry and by comparing the melting points with those reported in literature. Single crystal X-ray analysis of one of the product namely 14-(4-Methylphenyl)-14[H]-dihydro-dibenzo[a,j]xanthenes (**3c**) confirms the structure (**Figure 2**).

Table 3: Crystallographic parameter of compound **3c**

Chemical formula	$C_{28}H_{20}O$
Formula mass	372.44
Crystal system	orthorhombic
Space group	Pna2(1)
T(K)	296
a/Å	14.015(4)
b/Å	17.350(6)
c/Å	7.950(2)
α/deg	90.00
β/deg	90.00
γ/deg	90.00
Unit cell volume/ Å^3	1933.2(10)
D_{calcd} (g cm^{-3})	1.280
μ (mm^{-1})	0.076
Z	4
Reflns collected	9212
Unique reflns	4050
Observed reflns	2410
$R_1[I > 2\sigma(I)]$	0.0607
wR2(all)	0.1219
Goodness-of-fit	1.082
Diffractometer	SMART Bruker Apex-II
CCDC number	1025707

A comparison of results obtained in this study with some reported procedures is presented in **Table 4**. Data indicate the superiority of the present procedure over others in terms of yield, time, reaction conditions and ease of product recovery.

Table 4: Comparison of the efficiency of Ionic Liquid ([(*n*-propyl)$_2$NH$_2$][HSO$_4$]) with some reported catalyst for the synthesis of xanthenes and benzoxanthenes

Entry	Catalyst	Temp. (°C)	Time	Yield (%)	Ref.
1	$InCl_3/P_2O_5$	120	25-80min.	58-88	27
2	[n-WO_3-SO_3H]	100	75-100min.	83-94	44
3	AIL@MNP	90	30-65min.	80-94	29
4	HY Zeolite	80	1-24h	70-95	24
5	Dowex-50W	100	1.5-5h	78-91	30
6	$NaHSO_4.SiO_2$,	reflux	6-6.5h	90-98	45
7	[Hmim]TFA	80	2.5-4h	80-94	46
8	Nano-TiO_2	100	15-90min.	81-96	47
9	Amberlite IR-120H	reflux	1.5-3h	70-94	48
10	ZrTPA	130	1-5h	54-98	49
11	$P_2O_5/InCl_3$	80	30-75min.	50-94	50
12.	$CoPy_2Cl_2$	85	1.5-8h	65-97	51
13.	Heteropoly acid	100	1-1.5h	81-94	52
14	*p*-TSA	125	2.5-6h	80-96	53
15	I_2	90	2-5h	85-95	54
16	[(*n*-propyl)$_2$$NH_2$][$HSO_4$]	80	10-30min.	65-86	

Conclusion

Experiments indicate that a solvent free multicomponent reaction of demidone, aldehyde and 2-naphthol can be carried out by using the easily prepared IL namely the di-*n*-propylammoniumhydrogensulphate which performs the role of a

catalyst. The nature of the products varied with the variation in the composition of the reaction mixture. The reactions were simple and efficient for both aromatic and aliphatic aldehydes which widen the scope of the present protocol. The reactions could be completed in short reaction time of 10-30 minutes. Isolation of the products was easy and the IL used could be easily recovered for reuse.

Experimental

Melting points were recorded in open capillaries. ^{1}H-NMR and ^{13}C NMR spectra recorded in a Bruker 300 MHz spectrometer and Bruker ascend 600 MHz spectrometer and Varian AS 400 (400MHz) in $CDCl_3$ with TMS as the internal standard. IR spectra were recorded in Perkin Elmer FT-IR 1600 spectrometer using KBr pallets. High resolution mass spectra were recorded on a Micromass QTOF ESI-MS instrument (model HAB273).

Preparation of IL: The classical ionic liquid was prepared by a method reported earlier.[39]

General procedure for synthesis of 9, 9-dimethyl-12-aryl-8, 9, 10, 12-tetrahydro-benzo[a]xanthenes-11-one

5, 5-Dimethyl-cyclohexane-1, 3-dione (Dimedone) (1 mmol), 2-Naphthol (1 mmol), aldehyde (1 mmol) and 50 mol% of di-*n*-propylammonium hydrogensulphate were mixed, ground to a homogeneous mixture taken in a 100mL RBF and heated to 80°C with stirring in an oil bath for 15 minute. After completion of the reaction, indicated by TLC, the crude product was extracted with ethyl acetate, washed with water and dried in anhydrous Na_2SO_4. Product was crystallized on slow evaporation of solvent at room temperature. The ethyl acetate insoluble IL was recovered by simple filtration of product mixture and stored in desiccator for reuse.

General procedure for synthesis of 3, 3, 6, 6-tetramethyl-9-aryl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-xanthene-1, 8-dione

5,5-Dimethyl-cycloheaxan-1,3-dione (Dimedone) (2 mmol), aldehyde (1 mmol) and 50 mol% IL was grounded to a homogeneous mixture taken in a 100 mL RBF and the mixture heated with stirring in an oil bath at 80°C for 10 minutes. After completion of the reaction indicated by TLC, the crude product extracted with ethyl acetate, washed with water and then dried with anhydrous Na_2SO_4. Product was crystallized on room temperature evaporation of solvent. The ethyl acetate insoluble IL was recovered by simple filtration of product mixture and stored in desiccator for reuse.

General procedure for synthesis of 14-aryl- 14[H]-dihydro-dibenzo[a,j]xanthenes

2-Naphthol (2 mmol), aldehyde (1 mmol) and IL (50 mol%) grounded to a homogeneous mixture taken in a 100 mL RBF and heated with stirring in an oil bath at 80°C for 30 minutes. After completion of the reaction as indicated by TLC, the crude product was extracted with ethyl acetate, washed with water and dried with anhydrous Na_2SO_4. The product was crystallized on slow evaporation of solvent at room temperature. The ethyl acetate insoluble IL was recovered by simple filtration of the product mixture and stored in desiccator for reuse.

In all the reactions, the products were obtained in pure form and did not require further purification.

Recycling of Ionic Liquid

After completion of the reactions, ethyl acetate was added to the reaction mixture. The IL was found to be insoluble in ethyl acetate, precipitated out and recovered by simple filtration. Being hygroscopic, recovered IL was stored in desiccator and reused. The IL did not undergo any change during the reaction as confirmed by ^{1}H NMR of the recovered IL (Figure **S2** in supporting information). Amount of the recovered IL is 0.0982g (98.69%).

Experimental Data

*9,9-dimethyl-12-(4-chlorophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthe-11-one(**1a**):* mp: 182 °C (Ethylacetate) (lit[26]: 181-182°C); IR(KBr): ν 2950(Ar-H), 2872 (C-H), 1657 (C=O), 1587 (C=C), 1362 (CH_3), 1015 (C-O), 828 (Ar-H, out of plane bending), 748 (C-Cl) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.943-7.144 (10H, m, ArH) 5.709 (1H, s, CH), 2.567 (2H, s, CH_2), 2.355-2.224 (2H, m, CH_2), 1.123 (3H, s, CH_3), 0.097 (3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 196.94, 164.10, 147.72, 143.29, 131.93, 131.51, 131.21, 129.84, 129.14, 128.53, 128.43, 127.15, 125.06, 123.47, 117.08, 113.80, 50.85, 41.37, 34.21, 32.27, 29.36, 27.12. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{21}ClO_2$ 411.1128, found 411.1131.

*9,9-dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one(**1b**):* mp: 176-177 °C (Ethylacetate) (lit[27]: 178-180°C); IR(KBr): ν 2952 (Ar-H), 2873 (C-H), 1650 (C=O), 1589 (C=C), 1509 (N=O), 1370 (CH_3), 1223 (C-O), 1018 (C-O), 833 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.045-7.348 (10H, m, ArH), 5.822 (1H, s, CH), 2.602 (2H, s, CH_2), 2.370-2.220 (2H, m, CH_2), 1.139 (3H, s, CH_3), 0.955 (3H, s, CH_3). ^{13}C NMR δ ppm 196.70, 164.62, 151.87, 147.80, 146.36, 131.59, 131.03, 129.63, 129.36, 128.66, 127.38, 125.24, 123.61, 123.11, 117.09, 116.04, 113.00, 50.79, 41.42, 34.87, 32.24, 29.28, 27.06. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{21}NO_4$ 422.1368, found 422.1369.

*9,9-dimethyl-12-(4-methylphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one(**1c**)*: mp: 177-179°C (Ethylacetate) (lit[27]: 176-178°C); IR(KBr): ν 2945(Ar-H), 2860 (C-H), 1650 (C=O), 1579 (C=C), 1445 (CH_3), 1369 (CH_3), 1219 (C-O), 1015 (C-O), 814 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.026 (1H, d, *J*= 8.1 Hz, ArH), 7.794-7.743 (2H, m, ArH), 7.473-7.235 (5H, m, CH_2), 6.991 (2H, d, *J* = 7.8 Hz, ArH), 5.686 (1H, s, CH), 2.576 (2H, s, CH_2), 2.353-2.223 (2H, m, CH_2), 2.210 (3H, s, CH_3), 1.126 (3H, s, CH_3), 0.989 (3H, s, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.96, 163.76, 147.58, 141.79, 135.61, 131.41, 131.34, 128.88, 128.66, 128.31, 128.21, 126.92, 124.80, 123.61, 117.81, 116.99, 114.30, 50.84, 41.33, 34.22, 32.24, 29.22, 27.21, 20.95. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{24}O_2$ 391.1674, found 391.1678.

*9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one(**1d**):* mp: 203-205 °C (Ethylacetate) (lit[26]: 205-206°C); IR(KBr): ν 2948(Ar-H), 2863 (C-H), 1655 (C=O), 1570 (C=C), 1443 (CH_3), 1351 (CH_3), 1240 (C-O), 1027 (C-O), 824 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δH ppm 7.996 (1H, d, *J*= 8.1 Hz, ArH), 7.795-7.742 (2H, m, ArH), 7.443-7.243 (5H, m, ArH),

6.712 (2H, d, *J* = 8.4 Hz, ArH), 5.663 (1H, s, CH), 3.692 (3H, s, OCH_3), 2.570 (2H, s, CH_2), 2.349-2.218 (2H, m, CH_2), 1.122 (3H, s, CH_3), 0.978 (3H, s, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 197.08, 163.71, 157.71, 147.62, 137.13, 131.44, 131.33, 129.32, 128.68, 128.35, 126.92, 124.82, 123.65, 117.83, 117.00, 114.36, 113.53, 55.03, 50.87, 41.34, 33.77, 32.25, 29.26, 27.16. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{24}O_3$ 407.1623, found 407.1624.

*9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one(**1e**):* mp: 155 °C (Ethylacetate) (lit[26]: 154-155°C); IR(KBr): ν 2945 (Ar-H), 2870 (C-H), 1651 (C=O), 1591 (C=C), 1368 (CH_3), 1229 (C-O), 804 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.031-7.068 (11H, m, ArH), 5.286 (1H, s, CH), 2.579 (2H, s, CH_2), 2.353-2.225 (2H, m, CH_2), 1.126 (3H, s, CH_3), 0.973 (3H, s, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.84, 163.81, 147.59, 144.62, 131.35, 131.26, 128.71, 128.30, 128.11, 126.88, 126.12, 124.77, 124.14, 123.54, 117.56, 116.92, 114.12, 50.75, 41.26, 34.57, 32.14, 29.18, 27.02. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{22}O_2$ 377.1517, found 377.1519.

*9,9-dimethyl-12-naphthyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one(**If**)*: mp: 234-236 °C (Ethylacetate) (lit[40]: 231-233°C); IR(KBr): ν 2955 (Ar-H), 2869 (C-H), 1648 (C=O), 1582 (C=C), 1375 (CH_3), 1222 (C-O), 1021 (C-O), 791 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 9.214 (1H, d, *J*= 7.2 Hz, ArH), 7.916 (1H, d, *J*= 8.1 Hz, ArH), 7.819-7.211 (11H, m, ArH), 6.455 (1H, s, CH), 2.638 (2H, s, CH_2), 2.320-2.161 (2H, m, CH_2), 1.132 (3H, s, CH_3), 0.944 (3H, s, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 197.12, 163.71, 147.54, 142.64, 133.49, 131.69, 131.33, 130.85, 128.62, 128.53, 128.28, 127.72, 127.14, 127.01, 126.21, 125.47, 125.40, 124.76, 124.57, 123.66, 119.48, 117.13, 115.10, 50.72, 41.46, 32.08, 30.16, 29.23, 27.11. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{29}H_{24}O_2$ 427.1674, found 427.1675.

*9,9-dimethyl-12-(2-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one(**1g**):*
mp: 165-167°C (Ethylacetate) (lit[27]: 163-165°C); IR(KBr): ν 2955 (Ar-H), 2872 (C-H), 1658 (C=O), 1578 (C=C), 1445 (CH_3), 1363 (CH_3), 1245 (C-O), 1031 (C-O), 825 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δH ppm 8.285 (1H, d, *J*= 8.4 Hz, ArH), 7.739-7.683 (2H, m, ArH), 7.430-7.251 (3H, m, ArH), 7.035-7.022 (1H, m, ArH), 6.812-6.768 (2H, m, ArH), 5.960 (1H, s, CH), 3.945 (3H, s, OCH_3), 2.625-2.555 (2H, m, CH_2), 2.281-2.190 (2H, m, CH_2), 1.125 (3H, s, CH_3), 1.001 (3H, s, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 197.18, 164.59, 156.53, 147.84, 133.49, 132.05, 131.45, 130.79, 128.52, 128.36, 127.81, 126.92, 124.83, 124.16, 120.90, 118.49, 117.12, 113.84, 111.70, 56.04, 51.07, 41.63, 32.39, 29.68, 29.60, 27.16. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{24}O_3$ 407.1623, found 407.1626.

*9,9-dimethyl-12-isopropyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (**1h**):* mp: 115-117°C (Ethylacetate) (lit[27]:116-117°C); IR(KBr): ν 2961(Ar-H), 2849 (C-H), 1660 (C=O), 1559 (C=C), 1363 (CH_3), 1200 (C-O) cm^{-1}. ^{1}H NMR (600MHz, $CDCl_3$): δ_H ppm 8.106 (1H, d, *J*= 8.4 Hz, ArH), 7.812 (1H, d, *J*= 7.8 Hz, ArH), 7.699 (1H, d, *J*= 9 Hz, ArH), 7.547-7.521 (1H, m, ArH), 7.439-7.413 (1H, m, ArH), 7.224 (1H, d, *J*= 9 Hz, ArH), 4.711(1H, d, *J*= 3.6 Hz, CH), 2.622-2.296 (4H, m, $2CH_2$), 2.113-2.062 (1H, m, CH), 1.236 (3H, s, CH_3), 1.143 (3H, s, CH_3), 0.905 (3H, d, *J* = 7.2 Hz, CH_3), 0.669 (3H, d, *J* = 6.6Hz, CH_3). ^{13}C NMR (150MHz, $CDCl_3$): δ ppm 197.78, 167.33, 149.25, 131.66, 128.64, 128.00, 126.73, 124.90, 123.69, 119.11, 116.89, 111.84, 51.20, 41.73, 35.52, 33.08, 31.97, 30.10, 29.37, 27.42, 21.02, 18.42. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}O_2$ 321.1855, found 321.1849.

*3,3,6,6-tetramethyl-9-(4-chlorophenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione(**2a**):* mp: 230-231°C (Ethylacetate) (lit[27]: 230-232°C); IR(KBr): ν 2955 (Ar-H), 2877 (Ar-H), 2820 (C-H), 1662 (C=O), 1593 (C=C), 1362 (CH_3), 1196 (C-O), 1161 (C-O), 840 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.252-7.148 (4H, m, ArH), 4.711 (1H, s, CH), 2.574 (4H, s, $2CH_2$), 2.271-2.134 (4H, m, $2CH_2$), 1.104 (6H, s, $2CH_3$), 0.988 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.41, 162.43, 142.64, 131.98, 129.73, 128.85, 128.35, 128.18, 126.87, 117.00, 115.20, 50.62, 40.78, 32.17, 31.41, 29.24, 27.23. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{25}ClO_3$ 407.1390, found 407.1392.

*3,3,6,6-tetramethyl-9-(4-nitrophenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione(**2b**):* mp: 225-226°C (Ethylacetate) (lit[27]: 223-224°C); IR(KBr): ν 2949 (Ar-H), 2868 (Ar-H), 2823 (C-H), 1666 (C=O), 1597 (C=C), 1512 (N=O), 1354 (CH_3), 1200 (C-O), 1134 (C-O), 829 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.083 (2H, d, *J*= 8.4 Hz, ArH), 7.472 (2H, d, *J*= 8.4 Hz, ArH), 4.808 (1H, s, CH), 2.495 (4H, s, $2CH_2$), 2.277-2.120 (4H, m, $2CH_2$), 1.106 (6H, s, $2CH_3$), 0.974 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.32, 162.95, 151.49, 146.29, 129.28, 123.33, 114.35, 50.46, 40.67, 32.26, 32.14, 29.15, 27.14. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{25}NO_5$ 418.1630, found 418.1634.

*3,3,6,6-tetramethyl-9-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**2c**):* mp: 241-242°C (Ethylacetate) (lit[35]: 240-242°C); IR(KBr): ν 2951 (Ar-H), 2882 (Ar-H), 2835 (C-H), 1666 (C=O), 1608 (C=C), 1362 (CH_3), 1250 (C-O), 1192 (C-O), 840 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.202 (2H, d, *J*= 8.4 Hz, ArH), 6.755 (2H, d, *J*= 8.4 Hz, ArH), 4.693 (1H, s, CH), 3.733 (3H, s, OCH_3), 2.455 (4H, s, $2CH_2$), 2.265-2.134 (4H, m, $2CH_2$), 1.098 (6H, s, $2CH_3$), 0.992 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.57, 162.07, 157.89, 136.43, 129.28, 115.73, 113.42, 55.08, 50.71, 40.81, 32.18, 30.91, 29.26, 27.30. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{28}O_4$ 403.1885, found 403.1887.

*3,3,6,6-tetramethyl-9-(4-hydroxyphenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**2d**):* mp: 252-254°C (Ethylacetate) (lit[27]: 249-251°C); IR(KBr): ν 3455 (O-H), 2952 (Ar-H), 2875 (Ar-H), 2830 (C-H), 1655 (C=O), 1595 (C=C), 1360 (CH_3), 1220 (C-O), 1128 (C-O), 820 (Ar-H, out of plane bending) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.102 (2H, d, *J*= 7.8 Hz, ArH), 6.613 (2H, d, *J*= 8.1 Hz, ArH), 4.667 (1H, s, CH), 2.457 (4H, s, $2CH_2$), 2.273-2.145 (4H, m, $2CH_2$), 1.097 (6H, s, $2CH_3$), 0.996 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.95, 162.27, 154.41, 135.95, 129.39, 115.81, 115.11, 50.73, 40.83, 32.22, 30.93, 29.20, 27.33. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{26}O_4$ 389.1729, found 389.1731.

*3,3,6,6-tetramethyl-9-(4-methylphenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**2e**):* mp: 216-217°C (Ethylacetate) (lit[27]: 213-215°C); IR(KBr): ν 2939 (Ar-H), 2886 (Ar-H), 2825 (C-H), 1652 (C=O), 1616 (C=C), 1358 (CH_3), 1200 (C-O), 1134

(C-O), 833 (Ar-H, out of plane bending) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.175 (2H, d, *J*= 7.8 Hz, ArH), 7.017 (2H, d, J= 7.5 Hz, ArH), 4.706 (1H, s, CH), 2.460 (4H, s, $2CH_2$), 2.238 (3H, s, CH3), 2.205-2.125 (4H, m, $2CH_2$), 1.096 (6H, s, $2CH_3$), 0.991 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.42, 162.07, 141.12, 135.68, 128.71, 128.16, 115.65, 50.67, 40.77, 32.12, 31.35, 29.20, 27.28, 20.99. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{28}O_3$ 387.1936, found 387.1937.

*3,3,6,6-tetramethyl-9-(3-chlorophenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione **(2f)**:* mp: 185-186°C (Ethylacetate) (lit[33]: 183-184°C); IR(KBr): ν 2953 (Ar-H), 2877 (Ar-H), 2816 (C-H), 1666 (C=O), 1589 (C=C), 1365 (CH_3), 1201 (C-O), 1165 (C-O), 843 (Ar-H, out of plane bending), 751 (C-Cl) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.222-6.963 (4H, m, ArH), 5.487 (1H, s, CH), 2.505-2.282 (8H, m, $4CH_2$), 1.234 (6H, s, $2CH_3$), 1.102 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 190.60, 189.40, 140.42, 134.13, 129.34, 127.15, 126.00, 124.91, 115.06, 46.98, 46.36, 32.61, 31.40, 29.52, 27.33. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{25}ClO_3$ 407.1390, found 407.1392.

*3,3,6,6-tetramethyl-9-(2,6-dichlorophenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione **(2g)**:* mp:315-317°C (Ethylacetate) (lit[43]:318-320°C); IR(KBr): ν 2958 (Ar-H), 2872 (Ar-H), 2822 (C-H), 1661 (C=O), 1595 (C=C), 1359 (CH_3), 1192 (C-O), 1160 (C-O), 839 (Ar-H, out of plane bending), 757 (C-Cl) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 7.382-6.984 (3H, m, ArH), 5.526 (1H, s, CH), 2.535 (4H, s, $2CH_2$), 2.264-2.129 (4H, m, $2CH_2$), 1.105 (6H, s, $2CH_3$), 1.051 (6H, s, $2CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 196.71, 163.87, 129.48, 128.74, 128.35, 127.83, 112.34, 50.71, 40.78, 31.85, 30.02, 29.16, 27.54. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{24}Cl_2O_3$ 441.1000, found 441.1004.

*3,3,6,6-tetramethyl-9-(2-hydroxy-5-nitrophenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione **(2h)**:* mp: 194-196°C (Ethylacetate) (lit: ---); IR(KBr): ν 3440 (O-H), 2934 (Ar-H), 2858 (Ar-H), 2830 (C-H), 1672 (C=O), 1581 (C=C), 1509 (N=O), 1355 (CH_3), 1222 (C-O), 1125 (C-O), 831 (Ar-H, out of plane bending) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 10.325 (1H, s, OH), 8.059 (1H, dd, *J*= 3.0, 3.0 Hz, ArH), 7.941 (1H, d, *J*= 2.4 Hz, ArH), 7.130 (1H, d, *J*= 9 Hz, ArH), 4.675 (1H, s, CH), 2.631-2.363 (6H, m, $3CH_2$), 2.046-1.958 (2H, m, $1CH_2$), 1.035 (3H, s, $1CH_3$), 1.001 (3H, s, $1CH_3$), 0.996 (6H, s, $2CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 201.14, 196.05, 172.20, 168.14, 155.65, 144.54, 126.13, 123.96, 123.82, 117.88, 116.65, 111.18, 50.80, 50.10, 43.41, 41.44, 32.57, 31.37, 29.87, 29.40, 28.15, 27.27, 26.86. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{25}NO_6$ 411.1128, found 411.1131.

*3,3,6,6-tetramethyl-9-methyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione**(2i)**:* mp: 176 °C (Ethylacetate) (lit[55]:174 °C); IR(KBr): ν 2834 (C-H), 1678 (C=O), 1590 (C=C), 1351 (CH_3), 1175 (C-O) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 3.631(1H, q, *J*= 6.6 Hz, CH), 2.343 (4H, s, $2CH_2$), 2.259 (4H, d, *J*= 3Hz, $2CH_2$), 1.085 (3H, d, *J*= 3.6 Hz, CH_3), 1.007(12H, s, $4CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 197.32, 162.94, 116.97, 51.17, 41.05, 32.30, 29.48, 27.44, 21.97, 21.08. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{24}O_3$ 289.1804, found 289.1789.

*3,3,6,6-tetramethyl-9-phenethyl-1,2,3,4,5,6,7,8-octahydro-xanthene-1,8-dione**(2j)**: (New Compound)* mp: 172-174 °C (Ethylacetate) (lit: -); IR(KBr): ν 2951 (Ar-H), 2838 (C-H), 1675 (C=O), 1585 (C=C), 1381 (CH_3), 1171 (C-O) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 7.271-7.246 (2H, m, ArH), 7.176-7.126 (3H, m, ArH), 3.998 (1H, t, *J*= 7.8 Hz, CH), 2.498-2.471 (2H, m, CH_2), 2.349-2.243 (10H, m, $5CH_2$), 1.070 (6H, s, $2CH_3$), 1.052 (6H, s, $2CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 190.23, 142.00, 128.57, 126.09, 116.56, 47.23, 46.42, 35.64, 31.67, 31.40, 29.92, 29.82, 26.96. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{30}O_3$ 379.2273, found 379.2222.

*3,3,6,6-tetramethyl-9-isopropyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione**(2k)**:* mp: 147-149 °C (Ethylacetate) (lit[27]: 146-147°C); IR(KBr): ν 2825 (C-H), 1675 (C=O), 1572 (C=C), 1353 (CH_3), 1179 (C-O) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 3.455 (1H, d, *J*= 11.4 Hz, CH), 2.976-2.893 (1H, m, CH), 2.334-2.246 (8H, m, $4CH_2$), 1.007 (6H, s, $2CH_3$), 1.054 (6H, s, $2CH_3$), 0.840 (6H, d, *J*= 6 Hz, $2CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 190.57, 116.67, 47.21, 46.49, 38.29, 31.30, 30.17, 27.06, 25.93, 22.50. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{28}O_3$ 317.2117, found 317.2105.

*14-(4-chlorophenyl)-7,14-dihydro-dibenzo[a,j]xanthene**(3a)**:* mp: 287°C (Ethylacetate) (lit[41]: 288°C); IR(KBr):ν 2920 (Ar-H), 2820 (Ar-H), 1590 (C=C), 803 (Ar-H, out of plane bending)cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.457 (2H, d, *J*= 8.4 Hz, ArH), 7.905-7.844 (4H, m, ArH), 7.664-7.450 (8H, m, ArH), 7.155 (2H, d, *J*= 8.4 Hz, ArH), 6.579 (1H, s, CH). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 147.22, 142.73, 130.52, 129.86, 129.69, 128.47, 127.95, 127.64, 127.31, 125.88, 123.34, 121.53, 116.77, 115.51, 35.76. HRMS (ESI): m/z $[M]^+$ calcd for $C_{27}H_{17}ClO$ 392.0968, found 392.0971.

*14-(4-nitrophenyl)-7,14-dihydro-dibenzo[a,j]xanthene**(3b)**:* mp: 312-314°C (Ethylacetate) (lit[41]: 315°C); IR(KBr): ν 2941 (Ar-H), 2831 (Ar-H), 1595 (C=C), 1518 (N=O), 818 (Ar-H, out of plane bending) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.291 (2H, d, *J*= 8.4 Hz, ArH), 8.008 (2H, d, *J*= 8.7 Hz, ArH), 7.874-7.831 (4H, m, ArH), 7.700-7.421 (8H, m, ArH), 6.612 (1H, s, CH). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 148.72, 131.03, 129.55, 129.02, 128.92, 127.15, 124.54, 123.83, 121.98, 118.02, 115.71, 37.82. HRMS (ESI): m/z $[M]^+$ calcd for $C_{27}H_{17}NO_3$ 403.1208, found 403.1209.

*14-(4-methylphenyl)-7,14-dihydro-dibenzo[a,j]xanthene**(3c)**:* mp: 229-230°C (Ethylacetate) (lit[41]: 227°C); IR(KBr): ν 2909 (Ar-H), 2824 (Ar-H), 1593 (C=C), 1392 (CH_3), 810 (Ar-H, out of plane bending) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.434 (2H, d, *J*= 8.4 Hz, ArH), 8.089-7.417 (12H, m, ArH), 6.997(2H, d, *J*= 7.8 Hz, ArH), 6.481 (1H, s, CH), 2.196 (3H, s, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 148.66, 142.15, 135.90, 131.46, 131.08, 129.19, 128.79, 128.12, 126.76, 124.22, 122.73, 118.01, 117.45, 37.64, 20.91. HRMS (ESI): m/z $[M]^+$ calcd for $C_{28}H_{20}O$ 372.1514, found 372.1517.

*14-(4-hydroxyphenyl)-7,14-dihydro-dibenzo[a,j]xanthene**(3d)**:* mp: 145°C (Ethylacetate) (lit[41]: 141°C); IR(KBr): ν 3459 (O-H), 2915 (Ar-H), 2830 (C-H), 1595 (C=C), 1230 (C-O), 804 (Ar-H, out of plane bending) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H ppm 8.325 (2H, d, *J* = 8.4 Hz, ArH), 7.860-7.796 (4H, m, ArH), 7.616-7.409 (8H, m, ArH), 7.112 (2H, d, *J*= 8.4 Hz, ArH), 6.472 (1H, s, CH). ^{13}C NMR (75MHz, $CDCl_3$): δ ppm 148.74, 143.52, 132.13, 131.30, 131.10, 129.55, 129.14, 128.97, 128.70, 126.97, 124.42, 122.46, 118.07, 116.80, 37.43. HRMS (ESI): m/z $[M]^+$ calcd for $C_{27}H_{18}O_2$ 374.1307, found 374.1309.

*14-(2-methoxyphenyl)-7,14-dihydro-dibenzo[a,j]xanthene**(3e)**:* mp: 260°C (Ethylacetate) (lit[42]:258-259°C); IR(KBr): ν 2911 (Ar-H), 2828 (Ar-H), 1589 (C=C), 1395 (CH_3), 815 (Ar-H, out of

plane bending) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 8.575 (2H, d, *J*= 8.4 Hz, ArH), 7.794 (2H, d, *J*= 8.4 Hz, ArH),7.758 (2H, d, *J*= 9Hz, ArH), 7.543-7.518(2H, m, ArH), 7.467 (2H, d, *J*= 9 Hz, ArH), 7.385 (2H, t, *J*= 7.8Hz, ArH), 6.969-6.942 (1H, m, ArH), 6.901 (1H, s, CH), 6.861 (1H, d, *J*= 7.8Hz, ArH), 6.633 (1H, t, *J*= 7.8Hz, ArH), 4.271 (3H, s, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 153.95, 149.05, 132.25, 131.05, 128.65, 127.74, 126.83, 124.36, 123.50, 121.92, 118.72, 118.19, 110.78, 55.94, 30.45. HRMS (ESI): m/z $[M]^+$ calcd for $C_{28}H_{20}O_2$ 388.1463, found 388.1465.

*14-methyl-7,14-dihydro-dibenzo[a,j]xanthenes(**3f**):*

mp: 174 °C (Ethylacetate) (lit[53]: 173 °C); IR(KBr): ν 2951 (Ar-H), 1565 (C=C), 1385 (CH_3) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H ppm 8.246 (2H, d, *J*= 8.4 Hz, ArH), 7.881 (2H, d, *J*= 8.4 Hz, ArH), 7.773 (2H, d, *J*= 8.8 Hz, ArH), 7.636 (2H, t, *J*= 7.6 Hz, ArH), 7.466 (2H, t, *J*= 7.6 Hz, ArH), 7.380 (2H, d, *J*= 9.2 Hz, ArH), 5.446 (1H, q, *J*= 6.4 Hz, CH), 1.625 (3H, d, *J*= 7.2 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3$): δ ppm 149.017, 131.492, 131.202, 129.074, 128.388, 126.939, 124.315, 122.386, 118.428, 118.031, 110.222, 26.538, 23.655. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{16}O$ 297.1279, found 297.0925.

*14-isopropyl-7,14-dihydro-dibenzo[a,j]xanthene(**3g**):*

mp: 152-153°C (Ethylacetate) (lit[50]: 152-153°C); IR(KBr): ν 2939 (Ar-H), 1581 (C=C), 1372 (CH_3), cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ_H ppm 8.296 (2H, d, *J*= 8.4 Hz, ArH), 7.863 (2H, d, *J*= 8.4 Hz, ArH), 7.776 (2H, d, *J*= 8.4 Hz, ArH), 7.604-7.577 (2H, m, ArH), 7.449-7.406 (4H, m, ArH), 5.442 (1H, d, *J*= 4.2 Hz, CH), 2.312-2.248 (1H, m, CH), 0.819 (6H, d, *J*= 6.6 Hz, $2CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 151.10,132.41, 131.24, 128.89, 128.23, 126.45, 124.20, 123.20, 117.79, 117.42, 37.24, 36.47, 20.55. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{20}O$ 325.1592, found 325.1616.

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