Guanidine Hydrochloride: A Highly Efficient Organocatalyst for the Synthesis of 12-Aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones Under Solvent-Free Conditions

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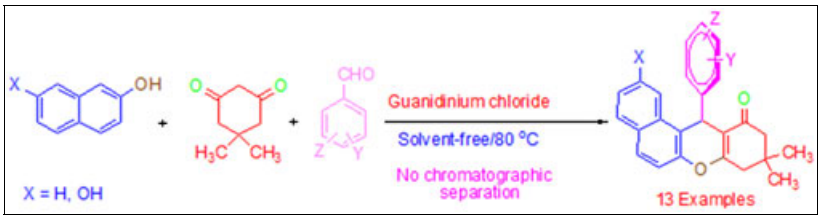

A new green protocol has been developed for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones using guanidine hydrochloride as an organocatalyst under solvent-free conditions. Operational simplicity, mild reaction conditions, enhanced rates, high isolated yields of the pure products, and purification of products by nonchromatographic methods are significant advantages of the protocol presented here.

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INTRODUCTION

Xanthenes and benzoxanthenes are important heterocycles that are known to possess multiple biological activities. Although not widely found in nature, xanthenes and compounds based on these core templates exhibit a broad spectrum of pharmaceutical activities such as antibacterial [1], anti-inflammatory [2], and antiviral [3]. These structural motifs have also found a niche as antagonists for paralyzing the action of zoxazolamine [4] and demonstrate efficacy in photodynamic therapy [5]. In addition, these compounds have been employed as dyes [6] and pH-sensitive fluorescent materials for visualization of biomolecular assemblies [7] and utilized in laser technologies [8]. Thus, a broad utility range has made xanthenes prime synthetic candidates thereby accentuating the need to develop newer synthetic routes for scaffold manipulation of xanthene derivatives. Previously, tetrahydrobenzo[*a*]xanthenes have been synthesized under reflux for 4–5 h for long hours in dichloromethane or 1,2-dichloroethane in the presence of acid catalysts such as $Sr(OTf)_2$ [9], $InCl_3$ or P_2O_5 [10], pTSA in ionic liquid [11], 2,4,6-trichloro-1,3,5-triazine [12], $BF_3.Et_2O$ [13], tetrabutylammonium fluoride (TBAF) [14], and $NaHSO_4$—SiO_2 [15].

These synthetic methods afforded good yields but have limitations of long reaction time, harsh reaction conditions, and often expensive catalysts. Moreover, the synthesis has been usually carried out in the solvent leading to complex isolation and recovery procedures. Consequently, the development of new and simple synthetic methods such as further improvement towards lower reaction time and improved yields for the preparation of heterocyclic compounds containing xanthene fragment remains an interesting challenge.

Organocatalysts have been used widely in many reactions as mono and bifunctional catalysts because of economic and environmental considerations. Among many organocatalysts, hydrogen-bonding compounds such as guanidine derivatives are becoming powerful tools for activation of the carbonyl functionality in organic transformations. Recently, guanidinium salts have been successfully employed as novel chiral phase-transfer catalyst in the conjugate addition of nitroalkanes with enones [16]. Moreover, these organocatalysts provide an environment to the process activating the nucleophile, the electrophile, or both reagents through weak interactions, such as hydrogen bonding or ion pairing or much stronger interactions such as covalent bonding.

Because of our interest in developing solvent-free multicomponent reactions [17–19], we report here a simple and facile protocol for the synthesis of a series of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives from aldehydes, naphthols, and dimedone using guanidine hydrochloride as a catalyst under solvent-free conditions. To the best of our knowledge in the open literature, one-pot synthesis of xanthenone derivatives catalyzed by guanidine hydrochloride has not previously been reported.

RESULTS AND DISCUSSION

On the basis of the green chemistry approach, we report an efficient and environmentally benign protocol for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives by multicomponent condensation of naphthols, aromatic aldehydes, and dimedone catalyzed by guanidine hydrochloride under solvent-free neat conditions. The

products were obtained in high to excellent yields by a simple work-up. The condensation of salicylaldehyde (1.0 mmol), 2-naphthol (1.0 mmol), and dimedone (1.0 mmol) using 10 mol% of catalyst was attempted at various temperatures. Our investigation demonstrated that 80°C is an effective temperature in terms of reaction time and yield obtained. The reaction was then attempted under similar conditions in the presence of different catalyst concentrations. The reactions were carried out in the presence of 2, 5, 8, 10, and 15 mol% of catalyst. The yield of the product improved remarkably to 90% after heating the components at 80°C in the presence of catalytic amount of guanidine hydrochloride. After optimizing the conditions, several syntheses of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives from the condensation of 2-naphthol (**2**) and 2,7-dihydroxynaphthalene (**3**) with a wide range of aromatic aldehydes (**1**) and dimedone utilizing guanidine hydrochloride as organocatalyst under solvent-free conditions at 80°C were examined (Scheme 1). All reactions were complete within 15–60 min, as indicated in Table 1; in all cases, the reactions afforded the desired products in high to excellent yields.

Concerning the reaction mechanism, we proposed that guanidine hydrochloride is a polyfunctional catalyst. The catalyst initially acts as a hydrogen-bond donor to activate aldehyde by formation of six-membered ring with aldehyde oxygen. Subsequently, the reaction proceeds through the nucleophilic addition of naphthol to aldehyde that is further attacked by dimedone. Then, deprotonation of the hydroxyl group on naphthol occurred by the amine of guanidine hydrochloride (as the base), and naphthoxy ion is formed. Finally, the reaction proceeds through the nucleophilic addition of naphthoxy ion to carbonyl of dimedone, and dehydration occurred in the presence of hydrochloride of guanidine hydrochloride (as the acid) to give the final product. Various aromatic aldehydes containing electron-withdrawing and electron-donating substituent at ortho, meta, or para-positions show equalease towards the product formation in good to high yields. Also, aliphatic aldehydes were used for the production of the expected xanthenes-11-one derivatives, but the desirable products were obtained in moderate yields, and the reaction times are too long. It should be noted that, in these reactions, steric factors play a major role in the product formation, and electronic factors play a limited role.

All products were well characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR, mass spectra, elemental analyses, and melting point. For example, the ^{1}H-NMR spectrum of synthesized compounds contained two singlet signals at about δ 0.90 and 1.06 ppm corresponding to two chemically different methyl protons. Moreover, methylene protons appeared as two AB quartet patterns at about δ 2.10 and 2.30 ppm (J = 16.0 Hz) and at δ 2.50 and 2.70 ppm (J = 17.2 Hz) corresponding to two chemically different moieties. Methine and aromatic protons showed as a sharp singlet at about δ 5.50 and multiplet at about δ 6.50–7.70 ppm, respectively. Hydroxyl protons appeared as a sharp singlet at δ 9.90 ppm. To the best of our knowledge, synthesis of compounds **5d–g** has not previously been reported in literature.

CONCLUSION

In summary, a novel and highly efficient method for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones by condensation reaction of naphthols with aromatic aldehydes and dimedone catalyzed by guanidine hydrochloride has been described. The attractive features of this protocol are simple experimental procedure, solvent-free reaction conditions, utilization of an inexpensive and readily available organocatalyst, short reaction time, and its adaptability for synthesis of a diverse set of benzoxanthenone derivatives. To the best of our knowledge, this is the first report on synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones with guanidine hydrochloride.

EXPERIMENTAL

All commercially available chemicals and reagents were used without further purification. Melting points were determined with

Scheme 1. Guanidinium chloride promoted one-pot synthesis of xanthenones (**4**, **5**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

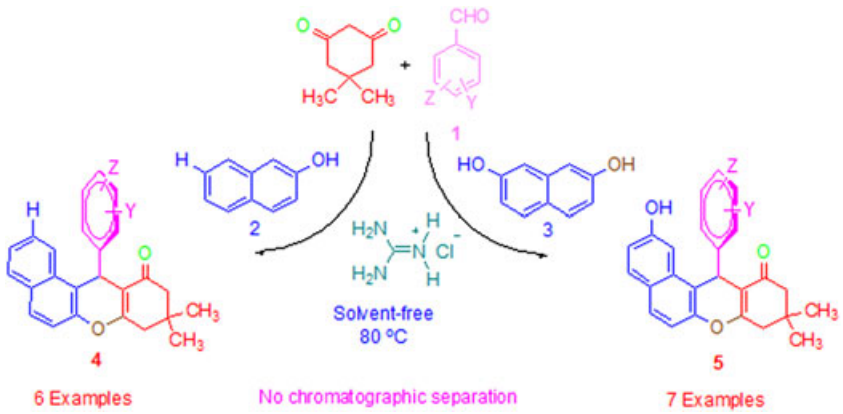
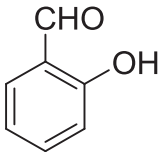
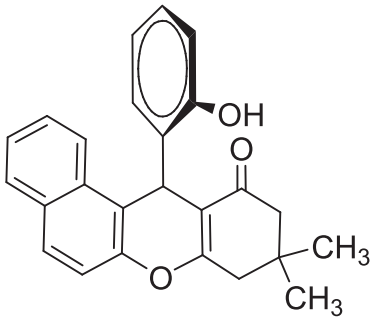
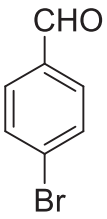
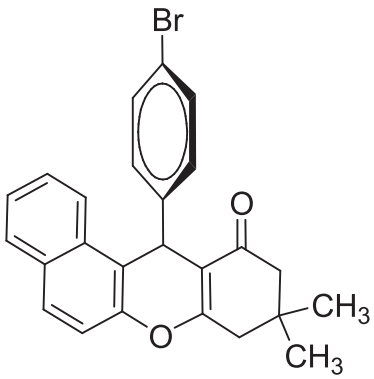
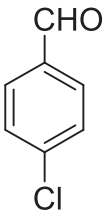
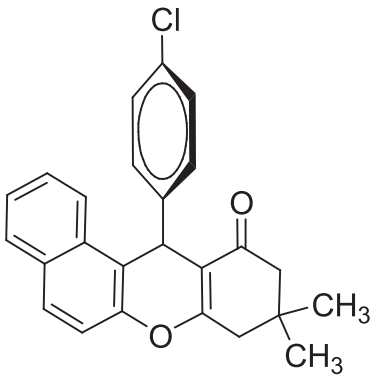


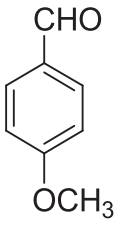
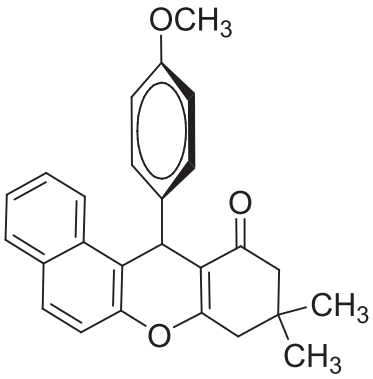
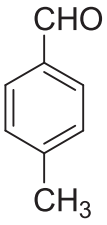
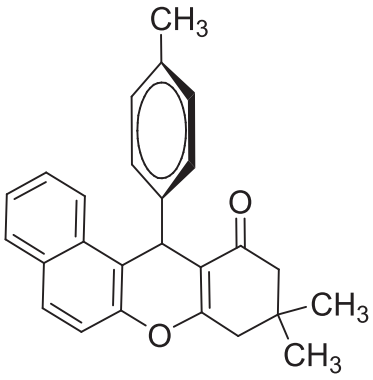
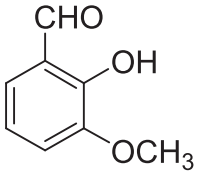
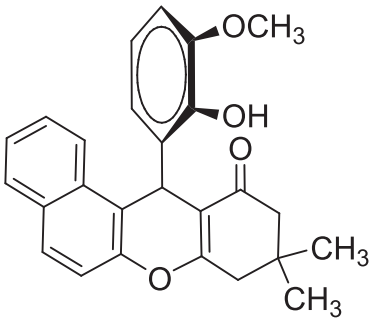
Table 1

Guanidine hydrochloride catalyzed one-pot synthesis of xanthenones.

Entry	Aldehyde	Product		Time (min)	Yield %
1			**4a**	60	90
2			**4b**	60	88
3			**4c**	35	92

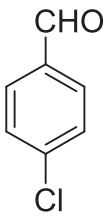
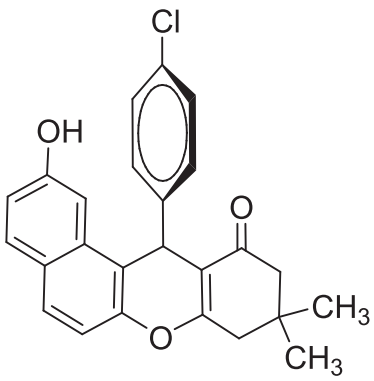
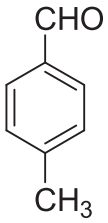
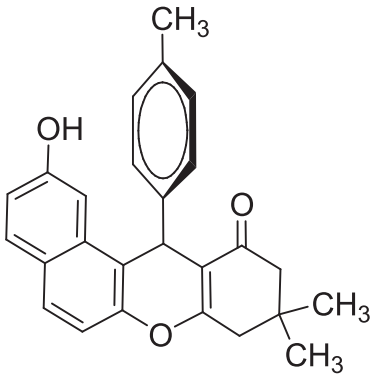
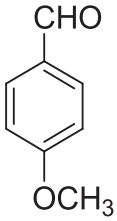
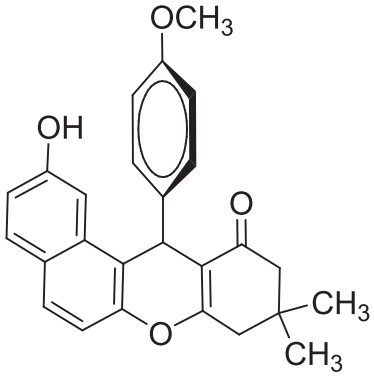
(*Continued*)

Table 1
(*Continued*)

Entry	Aldehyde	Product		Time (min)	Yield %
4			**4d**	30	89
5			**4e**	25	91
6			**4f**	30	93

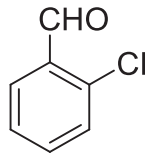
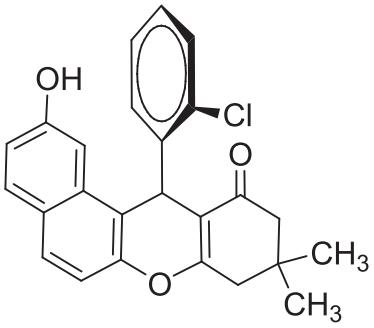
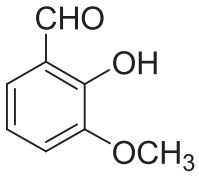
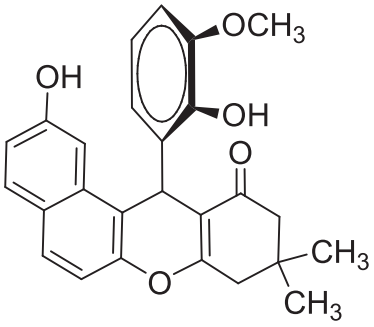
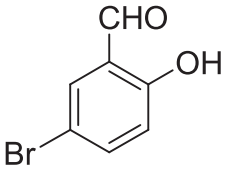
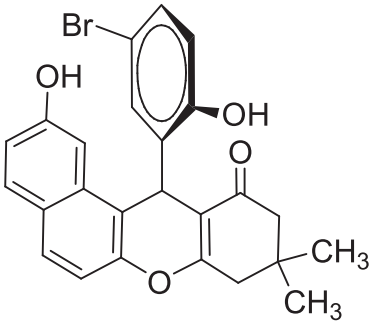
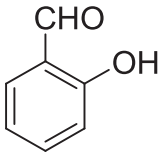
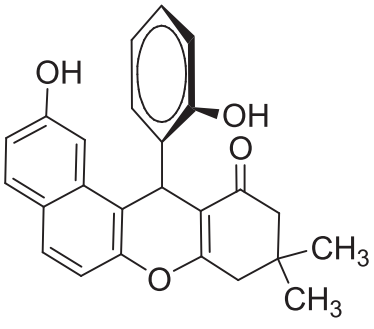
(*Continued*)

Table 1
(*Continued*)

Entry	Aldehyde	Product		Time (min)	Yield %
7			**5a**	15	89
8			**5b**	20	90
9			**5c**	20	93

(*Continued*)

Table 1
(*Continued*)

Entry	Aldehyde	Product		Time (min)	Yield %
10			**5d**	20	95
11			**5e**	30	91
12			**5f**	25	88
13			**5g**	15	89

an Electrothermal model 9100 apparatus (Bibby Scientific Limited, UK) and are uncorrected. IR spectra were recorded on a Shimadzu 4300 spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD). The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in DMSO-d_6 on Bruker DRX-400 AVANCE spectrometers (Bruker Optics Inc., Billerica, MA). Chemical shifts (δ) are reported in parts per million and are referenced to the NMR solvent. Mass spectra of the products were obtained with an high performing Agilent 5973 Mass Selective Detector (Palo Alto, CA). Elemental analyses were carried out by a Carbon-Hydrogen-Nitrogen (CHN)-Rapid Heraeus elemental analyzer (Wellesley, MA).

General procedure for the synthesis of xanthenones (4, 5). To a mixture of aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), and naphthol (1 mmol), guanidinium chloride (10 mol%) was added and heated at 80°C for the appropriate amount of time as indicated in Table 1. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to RT, and EtOH (5 mL) was added until white solid products precipitated. The precipitate was filtered, washed with cold ethanol, and dried. The obtained products **3** were found to be pure upon TLC examination.

9,9-Dimethyl-12-(2-hydroxyphenyl)-8,9,10,12-tetrahydrobenzo-[a] xanthen-11-one (4a). White solid; mp = 221–227°C; IR (KBr): 3199 (OH), 1625 (C═O), 1228 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.94 (s, 3H, *CH*$_3$), 1.08 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.35 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.58 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.72 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 5.75 (s, 1H, *methine-H*), 6.60–8.33 (m, 10H, *Ar—H*), 9.69 (s, 1H, *OH*) ppm.

9,9-Dimethyl-12-(4-bromophenyl)-8,9,10,12-tetrahydrobenzo-[a] xanthen-11-one (4b). White solid; mp = 182–184°C; IR (KBr): 1640 (C═O), 1221 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.88 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.14 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.35 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.59 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.70 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 5.58 (s, 1H, *methine-H*), 7.24–8.02 (m, 10H, *Ar—H*).

9,9-Dimethyl-12-(4-chlorophenyl)-8,9,10,12-tetrahydrobenzo-[a] xanthen-11-one (4c). White solid; mp = 185–187°C; IR (KBr): 1640 (C═O), 1221 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.88 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.14 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.35 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.59 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 2.70 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 5.59 (s, 1H, *methine-H*), 7.24–8.02 (m, 10H, *Ar—H*).

9,9-Dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo-[a] xanthen-11-one (4d). White solid; mp = 200–201°C; IR (KBr): 1645 (C═O), 1227 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.90 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.10 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.34 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.58 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.69 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 3.63 (s, 3H, OCH$_3$), 5.52 (s, 1H, *methine-H*), 6.73–8.05 (m, 10H, *Ar—H*).

9,9-Dimethyl-12-(4-methylphenyl)-8,9,10,12-tetrahydrobenzo-[a] xanthen-11-one (4e). White solid; mp = 175–177°C; IR (KBr): 1645 (C═O), 1231 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.89 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.14 (s, 3H, CH$_3$), 2.34 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.58 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 2.70 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 5.53 (s, 1H, *methine-H*), 6.97–8.05 (m, 10H, *Ar—H*).

9,9-Dimethyl-12-(2-hydroxy-3-methoxyphenyl)-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (4f). White solid; mp = 213–215°C; IR (KBr): 3276 (OH), 1622 (C═O), 1238 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.94 (s, 3H, *CH*$_3$), 1.08 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.35 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.58 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 2.72 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 3.72 (s, 3H, OCH$_3$), 5.80 (s, 1H, *methine-H*), 6.56–8.32 (m, 9H, *Ar—H*), 8.95 (s, 1H, OH).

12-(4-Chlorophenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5a). White solid; mp = 308–310°C; IR (KBr): 3187 (OH), 1626 (C═O), 1231 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.87 (s, 3H, *CH*$_3$), 1.06 (s, 3H, *CH*$_3$), 2.12 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.34 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.56 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 2.67 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 5.35 (s, 1H, *methine-H*), 6.97–7.79 (m, 9H, *Ar—H*), 9.95 (s, 1H, *OH*) ppm.

12-(4-Methylphenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5b). White solid; mp = 298–300°C; IR (KBr): 3173 (OH), 1625 (C═O), 1228 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.88 (s, 3H, *CH*$_3$), 1.06 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.33 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.55 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 2.67 (d, 1H, *J* = 17.6 Hz, *CH*$_2$), 5.30 (s, 1H, *methine-H*), 6.90–7.76 (m, 9H, *Ar—H*), 9.91 (s, 1H, *OH*) ppm.

12-(4-Methoxyphenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5c). White solid; mp = 296–297°C; IR (KBr): 3190 (OH), 1625 (C═O), 1232 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.88 (s, 3H, *CH*$_3$), 1.06 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.33 (d, 1H, *J* = 16.4 Hz, *CH*$_2$), 2.55 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.67 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 3.64 (s, 3H, *OCH*$_3$), 5.29 (s, 1H, *methine-H*), 6.75–7.76 (m, 9H, *Ar—H*), 9.20 (s, 1H, *OH*) ppm.

12-(2-Chlorophenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5d). White solid; mp = 280–282°C; IR (KBr): 3396 (OH), 1628 (C═O), 1228 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.90 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.09 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.34 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.57 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.71 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 5.62 (s, 1H, *methine-H*), 7.01–7.77 (m, 9H, *Ar—H*), 9.92 (s, 1H, *OH*) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): 26.54, 29.42, 32.18, 33.29, 50.61, 106.02, 112.61, 114.03, 115.18, 117.47, 125.87, 127.56, 128.51, 129.60, 130.16, 130.64, 132.56, 133.34, 142.02, 148.31, 156.85, 157.02, 158.52, 164.75, 196.20 ppm; MS (EI): *m/z* 406 (M + 2)$^+$, 404 (M)$^+$, 369, 293, 237, 209, 181, 152; *Anal*. Calcd for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.19. Found: C, 74.20; H, 5.23.

12-(2-Hydroxy-3-methoxyphenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5e). White solid; mp = 269–270°C; IR (KBr): 3406 (OH), 1633 (C═O), 1228 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.91 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.10 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.34 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.53 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.68 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 5.57 (s, 1H, *methine-H*), 6.57–7.72 (m, 8H, *Ar—H*), 8.72 (s, 1H, *OH*), 9.79 (s, 1H, *OH*) ppm;P ^{13}C-NMR (100 MHz, DMSO-d_6): 26.64, 28.88, 29.45, 32.10, 32.32, 50.60, 55.92, 106.21, 109.74, 113.32, 114.06, 116.67, 117.33, 119.37, 121.96, 125.84, 128.78, 130.38, 132.02, 133.52, 143.16, 148.12, 156.55, 158.42, 165.14, 197.11 ppm; MS (EI): *m/z* 416 (M)$^+$, 312, 293, 257, 237, 241, 209, 181, 160, 152, 131; *Anal*. Calcd for $C_{26}H_{24}O_5$: C, 75.00; H, 5.77. Found: C, 75.08; H, 5.71.

12-(5-Bromo-2-hydroxyphenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5f). White solid; mp = 308–310°C; IR (KBr): 3381 (OH), 1625 (C═O), 1222 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.94 (s, 3H, *CH*$_3$), 1.07 (s, 3H, *CH*$_3$), 2.11 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.34 (d, 1H, *J* = 16.0 Hz, *CH*$_2$), 2.56 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 2.69 (d, 1H, *J* = 17.2 Hz, *CH*$_2$), 5.47 (s, 1H, *methine-H*), 6.66–7.73

(m, 8H, *Ar—H*), 9.88 (s, 1H, *OH*), 9.94 (s, 1H, *OH*) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): 26.48, 29.47, 29.88, 32.10, 50.60, 106.03, 110.39, 112.42, 114.03, 115.61, 117.33, 117.44, 118.32, 125.83, 129.07, 130.46, 132.99, 133.41, 148.28, 154.01, 156.68, 156.84, 165.22, 196.69 ppm; MS (EI): *m/z* 466 $(M+2)^+$, 464 $(M)^+$, 307, 293, 237, 209, 181, 152; *Anal*. Calcd for $C_{25}H_{21}BrO_4$: C, 64.51; H, 4.51. Found: C, 64.53; H, 4.54.

12-(2-Hydroxyphenyl)-9,9-dimethyl-2-hydroxy-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (5g). White solid; mp = 276–278°C; IR (KBr): 3316 (OH), 1626 (C═O), 1224 (C—O—C) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 0.92 (s, 3H, *CH$_3$*), 1.07 (s, 3H, *CH$_3$*), 2.10 (d, 1H, *J* = 16.4 Hz, *CH$_2$*), 2.34 (d, 1H, *J* = 16.4 Hz, *CH$_2$*), 2.55 (d, 1H, *J* = 17.2 Hz, *CH$_2$*), 2.69 (d, 1H, *J* = 17.2 Hz, *CH$_2$*), 5.52 (s, 1H, *methine-H*), 6.61–7.72 (m, 9H, *Ar—H*), 9.55 (s, 1H, *OH*), 9.80 (s, 1H, *OH*) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): 26.61, 29.47, 32.32, 40.86, 50.61, 106.27, 113.17, 114.03, 116.34, 116.43, 117.27, 119.59, 125.86, 127.73, 128.73, 130.38, 130.63, 131.43, 135.52, 148.28, 154.28, 156.55, 165.13, 197.03 ppm; MS (EI): *m/z* 386 $(M)^+$, 293, 237, 227, 209, 181, 171, 152; *Anal*. Calcd for $C_{25}H_{22}O_4$: C, 77.72; H, 5.70. Found: C, 77.75; H, 5.78.

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REFERENCES AND NOTES

[1] Hideu, T. JP 56005480, Chem Abstr 1981, 95, 80922b.

[2] Poupelin, J. P.; Saint-Ruf, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Emouf, G.; Lacroix, R. Eur J Med Chem 1978, 13, 67.

[3] Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. PCT Int Appl WO9706178, 1997.

[4] Saint-Ruf, G.; De, A.; Hieu, H. T. Bull Chim Ther 1972, 7, 83.

[5] (a) Ion, R. M. Prog Catal 1997, 2, 55; (b) Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K. Acta Biochim Pol 1998, 45, 833.

[6] (a) Banerjee, A.; Mukherjee, A. K. Stain Technol 1981, 56, 83; (b) Menchen, S. M.; Benson, S. C.; Lam, J. Y. L.; Zhen, W.; Sun, D.; Rosenblum, B. B.; Khan, S. H.; Taing, M. U S Patent 6583168, 2003.

[7] Knight, C. G.; Stephens, T. Biochem J 1989, 258, 683.

[8] (a) Siirkecioglu, O.; Talini, N.; Akar, A. J Chem Res Synop 1995, 502; (b) Ahmad, M.; King, T. A.; Ko, D. K.; Cha, B. H.; Lee, J. J Phys D: Appl Phys 2002, 35, 1473.

[9] Li, J.; Tang, W.; Lu, L.; Su, W. Tetrahedron Lett 2008, 49, 7117.

[10] Nandi, G. C.; Samai, S.; Kumar, R.; Singh, M. S., Tetrahedron 2009, 65, 7129.

[11] (a) Khurana, J. M.; Magoo, D. Tetrahedron Lett 2009, 50, 4777; (b) Khurana, J. M.; Nand, B.; Sneha J Heterocycl Chem 2011, 48, 1388.

[12] Zhang, Z-H.; Zhang, P.; Yang, S-H.; Wang, H-J.; Deng, J. J Chem Sci 2010, 122, 427.

[13] Mashraqui, S. H.; Patil, M. B.; Mistry, H. D.; Ghadigaonkar, S.; Meetsma, A. Chem Lett 2004, 33, 1058.

[14] Gao, S.; Tsai, C. H.; Yao, C. F. Synlett 2009, 949.

[15] Das, B.; Laxminarayana, K.; Krishnaiah, M.; Srinivas, Y. Synlett 2007, 3107.

[16] (a) Davis, A. P.; Dempsey, K. J. Tetrahedron: Asymmetry 1995, 6, 2829; (b) Allingham, M. T.; Howard-Jones, A.; Murphy, P. J.; Thomas, D. A.; Caulkett, P. W. R. Tetrahedron Lett 2003, 44, 8677.

[17] Shockravi, A.; Sadeghpour, M.; Olyaei, A. Synth Commun 2009, 39, 2347.

[18] Olyaei, A.; Chehrehgosha Parashkuhi, E.; Raoufmoghaddam, S.; Sadeghpour, M. Synth Commun 2010, 40, 3609.

[19] Olyaei, A.; Shams, B.; Sadeghpour, M.; Gesmati, F.; Razaziane, Z. Tetrahedron Lett 2010, 51, 6086.