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Molecular Iodine-Catalyzed One-Pot Synthesis of Tetrahydrobenzo[a]xanthene-11-one and Diazabenzo[a]anthracene-9,11-dione Derivatives

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MOLECULAR IODINE–CATALYZED ONE-POT SYNTHESIS OF TETRAHYDROBENZO[*a*]XANTHENE-11-ONE AND DIAZABENZO[*a*]ANTHRACENE-9,11-DIONE DERIVATIVES

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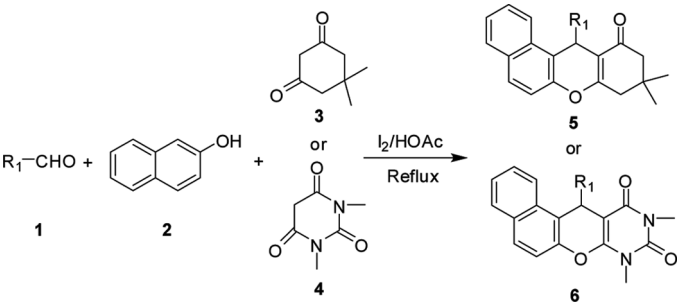
GRAPHICAL ABSTRACT



Abstract *An efficient one-pot condensation of* β*-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds has been achieved with molecular iodine as a catalyst, thus a variety of tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9,11-dione derivatives were prepared in good yields.*

Keywords Cyclic 1,3-dicarbonyl compounds; molecular iodine; β-naphthol; one-pot synthesis

INTRODUCTION

Xanthenes and benzoxanthenes have attracted considerable interest because they possess various biological activities such as antibacterial,[1] anti-inflammatory,[2] and antiviral[3] activities. 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

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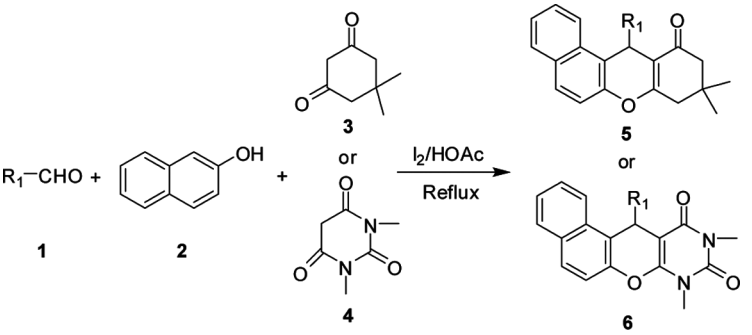


Scheme 1. I_2-catalyzed condensation of aldehydes, β-naphthol, and cyclic 1,3-dicarbonyl compounds.

synthetic candidates, thereby accentuating the need to develop newer synthetic routes for scaffold manipulation of xanthene derivatives. The synthesis of tetrahydrobenzo[a]xanthen-11-ones has been reported in the presence of strontium triflate[9] and $NaHSO_4$-SiO_2 under reflux in halogenated solvents for long times,[10] with a catalyst of *para*-tolunesulfonic acid (p-TSA) in ionic liquid ([bmim]BF_4), and in solvent-free media.[11] They also had been catalyzed by $InCl_3$ or P_2O_5 under solvent-free conditions.[12] These synthetic methods afforded good yields but have limitations of long reaction time, harsh reaction conditions, and expensive catalysts.

Recently, molecular iodine[13] has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic transformations to afford the corresponding products in excellent yields. In this article, we report an efficient one-pot method for the three-component condensation of β-naphthol, benzaldehyde, and cyclic-1,3-dicarbonyl compound to synthesis tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9,11-dione derivatives using molecular iodine as the catalyst in acetic acid at reflux (Scheme 1).

RESULTS AND DISCUSSION

The reaction of benzaldehyde **1a**, β-naphthol **2**, and 5,5-dimethylcyclohexane-1,3-dione **3** catalyzed by iodine in acetic acid at reflux has been considered as a standard model reaction.

We studied the catalyst loading on the model reaction. We varied the amount of catalyst: 5, 10, 15, 20, and 25 mol%. The results revealed that when the reaction was carried out in the presence of 5, 10, and 15 mol% of catalyst, it gave lower yield of product even after prolonged reaction time. At the same time, when the amount of catalyst was 20 mol%, we got excellent yields of product in a short span. Even after increasing the catalyst loading to 25 mol%, the yields of the products were constant. So, the use of 20 mol% of catalyst appears to be optimal. The results obtained are summarized in Table 1.

To study the generality of this procedure, a series of aldehydes and 5,5-dimethylcyclohexane-1,3-dione were applied. The results are shown in Table 2. Various aromatic aldehydes containing electron-withdrawing and electron-donating

Table 1. Effect of catalyst concentration on model reaction[a]

Entry	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	5	2.5	30
2	10	2.5	49
3	15	2.5	66
4	20	2.5	87
5	25	2.5	87

[a]Reaction of benzaldehyde, β-naphthol, and 5,5-dimethylcyclohexane-1,3-dione in the presence of iodine in acetic acid at reflux.
[b]Isolated yield.

substituent at *ortho, meta*, or *para* positions show equal ease in forming the product in good to excellent yields.

With the successful condensation of aromatic aldehydes, β-naphthol, and 5,5-dimethylcyclohexane-1,3-dione **3**, we further studied the reaction of aromatic aldehydes, β-naphthol, and 1,3-dimethylbarbituric acid under similar conditions. It was found that the corresponding tetrahydrobenzo[*a*]xanthen-11-one **5** and diazabenzo[*a*]anthracene-9,11-diones **6** could also be obtained in good yields (Table 2).

To further confirm the structures of the products, we also present the crystal structure of **5a** (Fig. 1). X-ray analysis of 5a: Empirical formula $C_{25}H_{22}O_2$, F.W. 354.43, $T = 296(2)$ K, monoclinic, space group $P2_1/n$, $a = 6.2308(11)$ Å, $b = 18.099(3)$ Å, $c = 17.063(3)$ Å, $\beta = 93.566(2)^\circ$, $V = 1920.4(6)$ Å^3, $Z = 4$, $D_c = 1.226$ gcm^{-3}, $F(000) = 752$, $\lambda(\mathrm{Mo/K}\alpha) = 0.71073$ Å, $\mu = 0.76\,\mathrm{cm}^{-1}$, $4 < 2\theta < 52^\circ$, $R = 0.0457$, $R_w = 0.1052$

Table 2. I_2-catalyzed condensation of aldehydes, β-naphthol, and cyclic 1,3-dicarbonyl compounds to give **5** and **6** in acetic acid at reflux

Entry	R_1	Time (h)	Yield[a] (%)	Mp (observed/reported[ref]) (°C)
5a	C_6H_5	2.5	87	152–154/151–153[12]
5b	4-MeC_6H_4	2.5	88	173–175/176–178[12]
5c	4-$OMeC_6H_4$	2.5	77	201–203/204–205[12]
5d	2-ClC_6H_4	3	89	173–174/179–180[12]
5e	4-ClC_6H_4	2.5	87	177–179/180–182[12]
5f	4-$NO_2C_6H_4$	2.5	85	179–181/178–180[12]
5g	4-OHC_6H_4	3	70	221–223/223–225[12]
5h	2-FC_6H_4	2.5	76	230–232/not rep.
5i	3,4-$(OCH_2O)C_6H_3$	2.5	89	203–205/not rep.
6a	C_6H_5	3	70	227–229/226–228[12]
6b	4-MeC_6H_4	3	74	199–201/196–198[12]
6c	2-ClC_6H_4	3.5	70	271–273/270–272[12]
6d	4-$NO_2C_6H_4$	3.5	68	283–285/288–290[12]
6e	2-FC_6H_4	3	66	287–289/not rep.
6f	3,4-$(OCH_2O)C_6H_3$	3	73	204–206/not rep.

[a]Isolated yield.

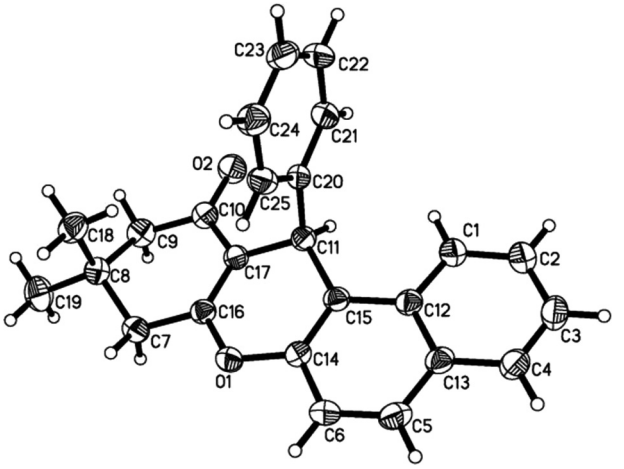
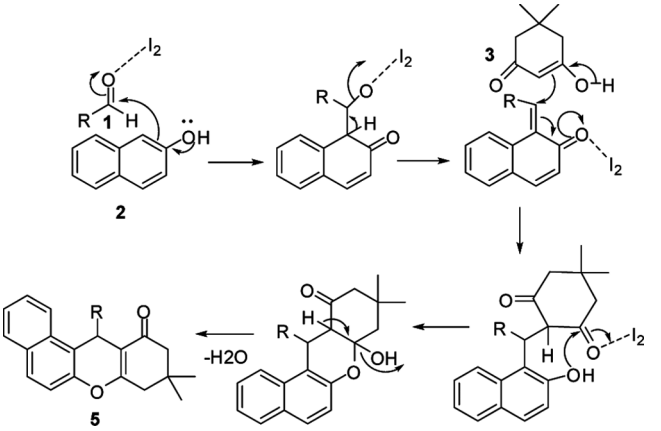


Figure 1. Molecular structure of **5a**, with 30% probability displacement ellipsoids.



Scheme 2. Tentative mechanism for the formation of compound **5**.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2.[12] We supposed that the reaction may proceed via the *ortho*-quinone methides (o-QM) intermediate, which was formed by the nucleophilic addition of β-naphthol to aldehyde catalyzed by I_2. Subsequent Michael addition of the o-QM with cyclic 1,3-dicarbonyl and followed by addition of the phenolic hydroxyl moiety to the carbonyl of ketone provides cyclic hemiketal, which on dehydration afforded **5**.

CONCLUSIONS

In conclusion, we have developed an efficient and environmentally benign methodology for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones

and 8,10-dimethyl-12-aryl-8,12-dihydro-7-oxa-8,10-diazabenzo[*a*]anthracene-9,11-diones by a one-pot, multicomponent reaction. The advantages of this method over other existing methods are mild reaction condition, better yields, easy purification, and economic viability of the catalyst. We believe that this economically viable procedure will find practical utility for the one-pot synthesis of novel xanthenes and anthracenes.

EXPERIMENTAL

Melting points were determined in a WRS-1B digital melting-point instrument and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 Fourier transform (FT)–IR instrument. ^{1}H NMR were measured on a Burke 400-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Mass spectra (MS) were recorded on an LCQ Advantage instrument. X-ray diffraction was measured on a Brucker Smart 1000 X diffractometer. All the reagents are commercially available.

General Procedure

Iodine (0.2 mmol) in acetic acid (3 ml) was added to a mixture of aromatic aldehyde (1 mmol), β-naphthol (1 mmol), and cyclic-1,3-dicarbonyl compound (1.2 mmol). The mixture was stirred at reflux for the given time (Table 2). The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was treated with aquecus $Na_2S_2O_3$ solution and stirred at room temperature for 10 min. The precipitate formed was collected by filtration at the pump, washed with water, and dried. The crude product was recystallized from methanol.

Selected Data

Compound 5a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $J = 8.0$ Hz, 1H), 7.79–7.74 (m, 2H), 7.44–7.18 (m, 8H), 5.72 (s, 1H), 2.58 (s, 2H), 2.35 (d, $J = 16.4$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 1.13 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3155, 2957, 2886, 1650, 1374, 1229, 1178, 1066, 811. MS (ESI): $m/z = 355$ $[M + H]^+$. Anal. calcd. for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.65; H, 6.44.

Compound 5b. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.87 (m, 3H), 7.46–7.41 (m, 3H), 7.17–7.14 (m, 2H), 6.99 (d, $J = 7.6$ Hz, 2H), 5.54 (s, 1H), 2.72 (s, 2H), 2.56 (d, $J = 16.4$ Hz, 1H), 2.41 (d, $J = 16.4$ Hz, 1H), 2.14 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3086, 2949, 2868, 1648, 1372, 1228, 1071, 816. MS (ESI): $m/z = 369$ $[M+H]^+$. Anal. calcd. for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.91; H, 6.68.

Compound 5c. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.78–7.72 (m, 2H), 7.44–7.20 (m, 5H), 6.70 (d, $J = 8.0$ Hz, 2H), 5.66 (s, 1H), 3.68 (s, 3H), 2.56 (s, 2H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 1.12 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3055, 2949, 1644, 1376, 1227, 1172, 1026, 814. MS (ESI): $m/z = 385$ $[M + H]^+$. Anal. calcd. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.11; H, 6.45.

Compound 5d. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, $J = 8.0$ Hz, 1H), 7.76–7.72 (m, 2H), 7.46–7.22 (m, 5H), 7.05–6.96 (m, 2H), 5.96 (s, 1H), 2.58 (s, 2H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.24 (d, $J = 16.4$ Hz, 1H), 1.13 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3075, 2934, 1648, 1372, 1229, 1175, 1028, 786. MS (ESI): $m/z = 389$ $[M + H]^+$. Anal. calcd. for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44. Found: C, 77.09; H, 5.61.

Compound 5e. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.79–7.71 (m, 2H), 7.46–7.14 (m, 7H), 5.68 (s, 1H), 2.56 (s, 2H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.24 (d, $J = 16.4$ Hz, 1H), 1.12 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3074, 2928, 1645, 1374, 1226, 1175, 1082. MS (ESI): $m/z = 389$ $[M + H]^+$. Anal. calcd. for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44. Found: C, 77.12; H, 5.28.

Compound 5f. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $J = 8.0$ Hz, 2H), 7.80–7.74 (m, 3H), 7.49–7.34 (m, 5H), 5.78 (s, 1H), 2.59 (s, 2H), 2.36 (d, $J = 16.4$ Hz, 1H), 2.25 (d, $J = 16.4$ Hz, 1H), 1.13 (s, 3H), 1.02 (s, 3H). IR (KBr, cm^{-1}): 3076, 2934, 1645, 1597, 1374, 1228, 1175, 1026, 825. MS (ESI): $m/z = 400$ $[M+H]^+$. Anal. calcd. for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found C, 75.02; H, 5.55; N, 3.72.

Compound 5g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.76–7.73 (m, 2H), 7.46-7.17 (m, 5H), 6.62 (d, $J = 8.2$ Hz, 2H), 5.65 (s, 1H), 5.48 (s, 1H), 2.58 (s, 2H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 1.12 (s, 3H), 1.01 (s, 3H). IR (KBr, cm^{-1}): 3306, 2958, 1640, 1572, 1378, 1226, 1175, 1024, 818. MS (ESI): $m/z = 371$ $[M+H]^+$. Anal. calcd. for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found C, 81.21; H, 5.75.

Compound 5h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.77 (m, 2H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.44–7.28 (m, 3H), 7.04–7.01 (m, 2H), 6.64–6.61 (m, 2H), 5.79 (s, 1H), 2.63 (s, 2H), 2.44 (d, $J = 16.4$ Hz, 1H), 2.37 (d, $J = 16.4$ Hz, 1H), 1.17 (s, 3H), 1.02 (s, 3H). IR (KBr, cm^{-1}): 3196, 2957, 2891, 1628, 1380, 1229, 1180, 1032, 811. MS (ESI): $m/z = 373$ $[M+H]^+$. Anal. calcd. for $C_{25}H_{21}FO_2$: C, 80.62, H, 5.68. Found: C, 80.55; H, 5.82.

Compound 5i. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.81–7.76 (m, 2H), 7.49–7.28 (m, 3H), 6.88–6.80 (m, 2H), 6.63 (d, $J = 8.0$ Hz, 1H), 5.81 (s, 2H), 5.65 (s, 1H), 2.58 (s, 2H), 2.28 (s, 2H), 1.14 (s, 3H), 1.02 (s, 3H). IR (KBr, cm^{-1}): 3132, 2959, 2878, 1645, 1399, 1226, 1174, 1034, 823. MS (ESI): $m/z = 399$ $[M+H]^+$. Anal. calcd. for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.53; H, 5.62.

Compound 6a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, $J = 7.8$ Hz, 1H), 7.86 (m, 2H), 7.45–7.36 (m, 5H), 7.21–7.14 (m, 3H), 6.00 (s, 1H), 3.62 (s, 3H), 3.38 (s, 3H). IR (KBr, cm^{-1}): 2926, 1706, 1650, 1485, 1232, 1179. MS (ESI): $m/z = 371$ $[M+H]^+$. Anal. calcd. for $C_{23}H_{18}N_2O_3$: C, 74.58, H, 4.90; N, 7.56. Found: C, 74.41; H, 4.75; N, 7.71.

Compound 6b. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, $J = 7.8$ Hz, 1H), 7.86–7.80 (m, 2H), 7.45–7.36 (m, 3H), 7.26–7.08 (m, 4H), 5.98 (s, 1H), 3.60 (s, 3H), 3.32 (s, 3H), 2.21 (s, 3H). IR (KBr, cm^{-1}): 2924, 1702, 1646, 1487, 1232,

1179. MS (ESI): $m/z = 385$ $[M+H]^+$. Anal. calcd. for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.72; H, 5.35; N, 7.41.

Compound 6c. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, $J = 7.8$ Hz, 1H), 7.84–7.80 (m, 2H), 7.51–7.30 (m, 5H), 7.08–7.04 (m, 2H), 6.10 (s, 1H), 3.64 (s, 3H), 3.32 (s, 3H). IR (KBr, cm^{-1}): 3058, 2950, 1704, 1655, 1456, 1275, 1184. MS (ESI): $m/z = 405$ $[M+H]^+$. Anal. calcd. for $C_{23}H_{17}ClN_2O_3$: C, 68.23; H, 4.23; N, 6.92. Found: C, 68.15; H, 4.31; N, 7.11.

Compound 6d. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, $J = 7.8$ Hz, 1H), 7.89–7.76 (m, 3H), 7.55–7.41 (m, 5H), 6.01 (s, 1H), 3.62 (s, 3H), 3.31 (s, 3H). IR (KBr, cm^{-1}): 3070, 2925, 1706, 1665, 1596, 1227, 1175. MS (ESI): $m/z = 416$ $[M+H]^+$. Anal. calcd. for $C_{23}H_{17}N_3O_5$: C, 66.50, H, 4.12, N; 10.12. Found: C, 66.38; H, 4.33; N, 10.25.

Compound 6e. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.81 (m, 2H), 7.69 (d, $J = 7.8$ Hz, 1H), 7.45–7.41 (m, 3H), 7.09–7.04 (m, 2H), 6.66–6.58 (m, 2H), 6.02 (s, 1H), 3.64 (s, 3H), 3.41 (s, 3H). IR (KBr, cm^{-1}): 3151, 2956, 1710, 1625, 1488, 1231, 1176. MS (ESI): $m/z = 389$ $[M+H]^+$. Anal. calcd. for $C_{23}H_{17}FN_2O_3$: C, 71.13; H, 4.41; N, 7.21. Found: C, 71.36; H, 4.65; N, 7.05.

Compound 6f. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, $J = 8.2$ Hz, 1H), 7.86–7.83 (m, 2H), 7.50–7.28 (m, 4H), 6.93–6.65 (m, 2H), 6.10 (s, 2H), 5.86 (s, 1H), 3.42 (s, 3H), 3.40 (s, 3H). IR (KBr, cm^{-1}): 3128, 2960, 1724, 1671, 1454, 1282, 1151. MS (ESI): $m/z = 415$ $[M+H]^+$. Anal. calcd. for $C_{24}H_{18}N_2O_5$: C, 69.56; H, 4.38; N, 6.76. Found: C, 69.39; H, 4.62; N, 6.60.

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REFERENCES

1. Hideo, T.; Teruomi, J. (Sankyo Co.) Benzopyrano[2,3-b]xanthene derivatives and its preparation. Jpn. Patent 56005480, 1981.
2. Poupelin, J. P.; Saint-Ruf, G.; Foussard-Blanpin, O.; Marcisse, G.; Uchida-Ernouf, G.; Lacroix, R. Synthesis and anti-inflammatory properties of bis(2-hydroxy-1-naphthyl)-methane derivatives, I: Monosubstituted derivatives. *Eur. J. Med. Chem.* **1978**, *13*, 67.
3. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. Pyrimidine nucleosides. PCT Int. Appl. WO9706178, 1997.
4. Saint-Ruf, G.; De, A.; Hieu, H. T.; Poupelin, J. P. Effect of dibenzoxanthenes on paralyzing action of zoxazolamine. *Naturwissenschaften* **1975**, *62*, 584.
5. Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K. The incorporation of various porphyrins into blood cells measured via flow cytometry, absorption, and emission spectroscopy. *Acta Biochim. Pol.* **1998**, *45*, 833.
6. (a) Banerjee, A.; Mukherjee, A. K. Chemical aspects of santalin as a histological stain. *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. Sulfonated diarylrhodamine dyes. U.S. Patent 6,583,168, 2003.

7. Knight, C. G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH: Studies in phospholipid vesicles. *Biochem. J.* **1989**, *258*, 683.
8. (a) Siirkecioglu, O.; Talini, N.; Akar, A. Synthesis of 24-alkyl-14H-dibenzo[*a,j*]xanthenes. *J. Chem. Res., Synop.* **1995**, 502 (b) Ahmad, M.; King, T. A.; Ko, D.-K.; Cha, B. H.; Lee, J. Performance and photostability of xanthene and pyrromethene laser dyes in solgel phases. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1473.
9. Li, J.; Tang, W.; Lu, L.; Su, W. Strontium triflate catalyzed one-pot condensation of β-naphthol, aldehydes and cyclic 1,3-dicarbonyl compounds. *Tetrahedron Lett.* **2008**, *49*, 7117.
10. Das, B.; Laxminarayana, K.; Krishnaiah, M.; Srinivas, Y. An efficient and convenient protocol for the synthesis of novel 12-aryl- or 12-alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives. *Synlett* **2007**, 3107.
11. Jitender, M. K.; Devanshi, M. pTSA-catalyzed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones in ionic liquid and neat conditions. *Tetrahedron Lett.* **2009**, *50*, 4777.
12. Nandi, G. C.; Samai, S. S.; Kumar, R.; Singh, M. S. An efficient one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9-11-dione derivatives under solvent free condition. *Tetrahedron* **2009**, *65*, 7129.
13. (a) Kim, K. M.; Ryu, E. K. Unusual iodine-catalyzed lactonization of γ-methyl-γ,δ-pentenoic acids: A facile synthesis of γ,γ-dimethyl-γ-butyrolactones. *Tetrahedron Lett.* **1996**, *37*, 1441; (b) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Iodine catalyzes efficient and chemoselective thioacetalization of carbonyl functions, transthioacetalization of *O,O*- and *S,O*-acetals and acylals. *J. Org. Chem.* **2001**, *66*, 7527; (c) Ramalinga, K.; Vijayalakshmi, P.; Kaimal, T. N. B. A mild and efficient method for esterification and transesterification catalyzed by iodine. *Tetrahedron Lett.* **2002**, *43*, 879; (d) Firouzabadi, H.; Iranpoor, N.; Sobhani, S. A high-yielding preparation of α-trimethylsilyloxyphosphonates by silylation of α-hydroxyphosphonates with HMDS catalyzed by iodine. *Tetrahedron Lett.* **2002**, *43*, 3653; (e) Yadav, J. S.; Reddy, B. V. S.; Reddy, M. S.; Prasad, A. R. Iodine as novel reagent for the 1,2-addition of trimethylsilyl cyanide to ketones including α, β-unsaturated ketones. *Tetrahedron Lett.* **2002**, *43*, 9703; (f) Bandgar, B. P.; Shaikh, K. A. Molecular iodine–catalyzed efficient and highly rapid synthesis of bis(indolyl)methanes under mild conditions. *Tetrahedron Lett.* **2003**, *44*, 1959; (g) Das, B.; Banerjee, J.; Ramu, R.; Pal, R.; Ravindranath, N.; Ramesh, C. Efficient, selective deprotection of aromatic acetates catalyzed by amberlyst-15 or iodine. *Tetrahedron Lett.* **2003**, *44*, 5465; (h) Saeeng, R.; Sirion, U.; Sahakitpichan, P.; Isobe, M. Iodine catalyzes *C*-glycosidation of d-glucal with silylacetylene. *Tetrahedron Lett.* **2003**, *44*, 6211; (i) Ji, S.-J.; Wang, S.-Y.; Zhang, Y.; Loh, T.-P. Facile synthesis of bis(indolyl)methanes using catalytic amount of iodine at room temperature under solvent-free conditions. *Tetrahedron* **2004**, *60*, 2051; (j) Yadav, J. S.; Reddy, B. V. S.; Shubashree, S.; Sadashiv, K. Iodine/MeOH: A novel and efficient reagent system for thiocyanation of aromatics and heteroaromatics. *Tetrahedron Lett.* **2004**, *45*, 2951; (k) Phukan, P. Iodine as a very powerful catalyst for three component synthesis of protected homoallylic amines. *J. Org. Chem.* **2004**, *69*, 4005; (l) Phukan, P. Iodine as an extremely powerful catalyst for the acetylation of alcohols under solvent-free conditions. *Tetrahedron Lett.* **2004**, *45*, 4785; (m) Sun, J.; Dong, Y.; Wang, X.; Wang, S.; Hu, Y. Highly Efficient chemoselective deprotection of *O,O*-acetals and *O,O*-ketals catalyzed by molecular iodine in acetone. *J. Org. Chem.* **2004**, *69*, 8932; (n) Bhosale, R. S.; Bhosale, S. V.; Wang, T.; Zubaidha, P. K. An efficient, high-yielding protocol for the one-pot synthesis of dihydropyrimidin-2(1*H*)-ones catalyzed by iodine. *Tetrahedron Lett.* **2004**, *45*, 9111; (o) Ke, B.; Qin, Y.; He, Q.; Huang, Z.; Wang, F. Preparation of bisindolylalkanes from *N-tert*-butanesulfinyl aldimines. *Tetrahedron Lett.* **2005**, *46*, 1751; (p) Banik, B. K.; Fernandez, M.; Alvarez, C. Iodine-catalyzed highly efficient Michael reaction of indoles under solvent-free condition. *Tetrahedron Lett.* **2005**, *46*, 2479.