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An efficient one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9,11-dione derivatives under solvent free condition

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ABSTRACT

Indium(III) chloride catalyzed one-pot synthesis of 12-aryl/alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one and 8,10-dimethyl-12-aryl-8,12-dihydro-7-oxa-8,10-diazabenzo[*a*]anthracene-9,11-dione derivatives have been achieved by three component cyclocondensation of aldehydes, β-naphthol and cyclic 1,3-dicarbonyl compounds under solvent free condition in high yields. P_2O_5 too has been found as an effective catalyst towards this transformation.

1. Introduction

In the mainstream of current interest, multi-component processes have recently gained considerable economic and ecological interest as they address fundamental principles of synthetic efficiency and reaction design. Multi-component reactions (MCRs) have been proven to be a very elegant and rapid way to access complex structures in a single synthetic operation from simple building blocks and show high atom economy and high selectivity.[1] As a one-pot reaction, MCRs generally afford good yields and are fundamentally different from two-component reactions in several aspects[2] and permitted rapid access to combinatorial libraries of organic molecules for efficient lead structure identification and optimization in drug discovery.[3] Over the past decade, various advanced sequential MCRs have been developed where 1,3-dicarbonyl derivatives are important synthetic intermediates due to its multiple functionalities that can be involved either as nucleophilic or electrophilic species in a large variety of synthetic transformations.[4] There versatility and effectiveness as potential multicomponent substrate has been used in various MCRs such as Hantzsch 1,4-dihydropyridine synthesis,[5] Biginelli reaction,[6] Schopf's tropinone synthesis,[7] Tietze's reaction[8] and Michael addition reaction.[9]

Xanthenes and benzoxanthenes are important biologically active heterocyclic compounds, which possess antiviral,[10] anti-inflammatory[11] and antibacterial[12] activities. These are being utilized as antagonists for paralyzing action of zoxazolamine[13] and in photodynamic therapy.[14] Furthermore, these compounds can be used as dyes,[15] in laser technologies[16] and as pH sensitive fluorescent materials for visualization of biomolecules.[17]

It is evident from the recent literature that indium trichloride[18] has invoked enormous interest as a green and potential Lewis acid catalyst to construct carbon-carbon and carbon–heteroatom bonds in various organic transformations such as Mukaiyama aldol condensation,[19] Diels–Alder reactions,[20] aza-Michael reactions[21] and ring opening reactions of epoxides with nucleophiles.[22] It has received considerable attention due to its low toxicity, cost effectiveness, air and water compatibility, ease of handling, good reactivity, experimental simplicity and remarkable ability to suppress side reactions in acid sensitive substrates.

The condensation of phenol with aldehyde in the presence of acid or base catalyst is believed to proceed via *ortho*-quinone methide (*o*-QM) intermediate,[23] which has been used in many tandem processes[24] and [4+2] cycloaddition with variety of dienophiles.[25] However, with carbon nucleophiles only limited work has been appeared.[26] We have developed an efficient tandem process that would allow the reaction of *o*-QM intermediate with carbon nucleophiles in situ to provide xanthene derivatives under solvent free and simple reaction conditions. Herein, we are reporting the reaction of aldehydes, 2-naphthol and cyclic 1,3-dicarbonyl

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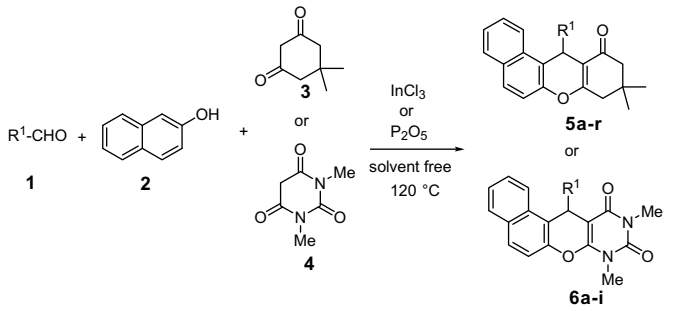
compounds for the formation of tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9,11-dione derivatives in presence of catalytic amount of $InCl_3$ or P_2O_5 under solvent free conditions (Scheme 1). To the best of our knowledge, this methodology has not been reported in the literature. These catalysts not only make the synthetic process clean, safe and inexpensive, but also afford the products in excellent yield.



Scheme 1. $InCl_3$ and P_2O_5 catalyzed condensation of aldehydes, β-naphthol and cyclic 1,3-dicarbonyl compounds.

2. Result and discussion

Xanthenes and its derivatives are an important structural motif in biologically relevant compounds and pharmaceuticals. Previously tetrahydrobenzo[*a*]xanthenes have been synthesized under reflux for 4–5 h in dichloromethane or 1,2-dichloroethane in the presence of acid catalysts such as $BF_3 \cdot Et_2O$,[27] silica supported $NaHSO_4$,[28] $Sr(OTf)_2$[29] and TBAF.[30] These synthetic methods afforded good yields however, have limitations of long reaction time, harsh reaction conditions and often expensive catalysts. Moreover, the synthesis has been usually carried out in solvent leading to complex isolation and recovery procedures. Consequently, there is a scope of further improvement towards lower reaction time and improved yields. The three-component condensation of aldehyde, β-naphthol and dimedone (5,5-dimethyl-1,3-cyclohexanedione) was performed in the presence of cerium(IV) ammonium nitrate (CAN) in dichloromethane (DCM); however, the yield of **5** was low along with long reaction time and various by-products. A by-product, aryl-14*H*-dibenzo[*a*,*j*]xanthene was obtained as a major product when phosphorous pentoxide (P_2O_5) was used as catalyst in the refluxing DCM. Carrying out the condensation in refluxing dichloromethane catalyzed by $InCl_3$ resulted **5** in good yield without side product but it requires long reaction time. Then, it was decided to carry out the reactions under solvent free conditions with above catalysts separately, and it was found that the reactions proceeded smoothly in shorter reaction time giving higher yields. In all cases $InCl_3$ was found a better catalyst than P_2O_5 and provides the desired products exclusively.

The reaction of 4-nitrobenzaldehyde (1.0 mmol), 2-naphthol (1.0 mmol) and dimedone (1.2 mmol) in refluxing DCM was performed as a model reaction in the presence of catalysts such as CAN (50 mol %, 48 h), P_2O_5 (20 mol %, 24 h) and $InCl_3$ (30 mol %, 20 h) separately, resulting desired product in 50%, 22% and 78% yields, respectively. When P_2O_5 was used as catalyst in DCM the reaction profile was clean but the by-product aryl-14*H*-dibenzo[*a*,*j*]xanthene was obtained in maximum yield (70%). The above model reaction was performed in the absence of solvent with the above respective catalysts to give 45%, 80% and 88% yields. In the absence of solvent the reaction completed within 30–40 min at 120 °C. We carried out another set of reaction under similar conditions taking benzaldehyde, 2-naphthol and dimedone. The desired product was obtained in 60%, 76% and 84% yields using catalysts CAN, P_2O_5 and $InCl_3$ respectively. The results show that under solvent free condition, the catalytic activity of P_2O_5 and $InCl_3$ increases and very less amount of by-product was formed. $InCl_3$ was thus found to be the catalyst of choice.

A test reaction using 4-nitrobenzaldehyde, 2-naphthol and dimedone at 120 °C in the absence of solvent and without any catalyst was performed in order to establish the real effectiveness of the catalysts. It was found that only 15% conversion to product was obtained even after 2.5 h of heating. To optimize the catalyst loading, 5 mol %, 10 mol %, 15 mol % and 25 mol % of $InCl_3$ was tested but the yields were not good. A 30 mol % loading of $InCl_3$ was sufficient to push the reaction forward and higher amounts of catalyst did not increase the yields significantly. The best results were obtained when the reactions were carried out with 30 mol % of $InCl_3$ at 120 °C. To explore the generality of the reaction, we extended our study using $InCl_3$ (30 mol %) and P_2O_5 (20 mol %) as catalysts separately under solvent free condition with different aliphatic as well as aromatic aldehydes to prepare a series of benzo[*a*]xanthene-11-one derivatives (Table 1). Various aromatic aldehydes containing electron-withdrawing and electron-donating substituent at *ortho*, *meta* or *para*-positions show equal ease towards the product formation in good to high yields. Interestingly, aliphatic aldehydes also gave the expected xanthene-11-one derivatives in good yields.

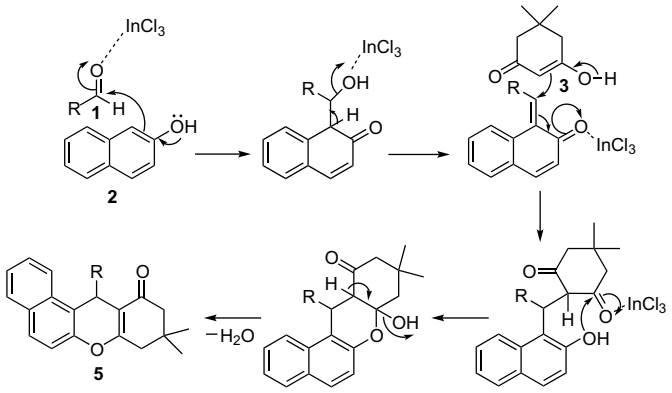
Table 1
$InCl_3$ and P_2O_5 catalyzed condensation of 2-naphthol, aldehyde and 1,3-dicarbonyl compound to give **5** and **6**

Entry	R^1	Diketone	Method A ($InCl_3$)[a]	Method B (P_2O_5)[a]
			Time (min)/ yield[b] (%)	Time (min)/ yield[b] (%)
5a	C_6H_5	**3**	30/84	40/76
5b	*p*-$NO_2C_6H_4$	**3**	30/88	36/80
5c	*m*-$NO_2C_6H_4$	**3**	30/80	45/77
5d	*o*-$NO_2C_6H_4$	**3**	55/81	60/75
5e	*p*-$OMeC_6H_4$	**3**	45/76	55/71
5f	*o*-$OMeC_6H_4$	**3**	35/87	40/80
5g	*p*-ClC_6H_4	**3**	30/80	40/76
5h	*o*-ClC_6H_4	**3**	60/83	65/74
5i	2,4-$Cl_2C_6H_3$	**3**	25/85	30/78
5j	*p*-OHC_6H_4	**3**	65/70	70/68
5k	*m*-OHC_6H_4	**3**	60/68	65/64
5l	5-Br-2-OHC_6H_3	**3**	35/76	40/71
5m	5-NO_2-2-OHC_6H_3	**3**	30/73	35/70
5n	2-OH-3-$OMeC_6H_3$	**3**	50/82	60/73
5o	2-OH-3-$OEtC_6H_3$	**3**	55/80	55/74
5p	*p*-MeC_6H_4	**3**	50/74	55/71
5q	–CH=CH·C_6H_5	**3**	60/73	65/62
5r	$-CH(CH_3)_2$	**3**	75/70	80/62
6a	*p*-$NO_2C_6H_4$	**4**	75/65	80/58
6b	*p*-ClC_6H_4	**4**	70/63	70/58
6c	C_6H_5	**4**	60/68	65/60
6d	*p*-MeC_6H_4	**4**	60/70	60/62
6e	2,4-$Cl_2C_6H_3$	**4**	65/65	65/61
6f	*o*-ClC_6H_4	**4**	70/67	75/62
6g	*o*-$NO_2C_6H_4$	**4**	65/69	70/65
6h	4-BrC_6H_4	**4**	65/70	65/62
6i	4-FC_6H_4	**4**	60/72	65/67

[a] For the experimental procedure see Section 4.2.
[b] Yield of isolated and pure product.

Encouraged by the successful condensation of aldehydes, 2-naphthol and dimedone under solvent-free condition to give benzoxanthene derivatives, we next attempted the reaction with 1,3-dimethylbarbituric acid, aromatic aldehydes and 2-naphthol under the optimized reaction conditions, which led to the exclusive formation of diazabenzo[*a*]anthracene-9,11-diones (**6**) in good yields. However, when some aliphatic aldehydes such as cinnamaldehyde, isobutyraldehyde and cyclohexanaldehyde were used in this protocol under the above optimized conditions, unfortunately, the expected products could not be obtained. The results are shown in Table 1.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. We supposed that the reaction may proceed via the *ortho*-quinone methides intermediate, which was formed by the nucleophilic addition of 2-naphthol to aldehyde catalyzed by $InCl_3$. Subsequent Michael addition of the *o*-QM with cyclic 1,3-dicarbonyl and followed by addition of the phenolic hydroxy moiety to the carbonyl of ketone provides cyclic hemiketal which on dehydration afforded **5**. All the products **5** and **6** were characterized by mp, IR and NMR spectra.



Scheme 2. Tentative mechanism for the formation of tetrahydrobenzo[*a*]xanthene-11-ones (**5**).

3. Conclusion

In conclusion, we have developed a solvent free, efficient and environmentally benign methodology for the synthesis of 12-aryl/alkyl-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, multi-component reaction. The advantages of this method over other existing methods are reduced reaction times, higher yields, mild reaction condition, easy purification and economic viability of the catalyst. We feel that this economically viable procedure will find practical utility for the one-pot synthesis of novel xanthenes and anthracenes. Further applications of $InCl_3$ and P_2O_5 on the extension of this protocol are ongoing in our group.

4. Experimental

4.1. General

All reagents were purchased from Merck, Aldrich, CDH and Fluka and used without further purification. NMR spectra were recorded on JEOL AL 300 FT NMR spectrometer. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. CHN analyses were performed on Exeter Analytical Inc. 'Model CE-400 CHN Analyzer'. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck $60F_{254}$). Melting points were determined with BUCHI B-540 melting point apparatus and are uncorrected.

4.2. General procedure for synthesis of 12-aryl/alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (5) and 8,10-dimethyl-12-aryl-8,12-dihydro-7-oxa-8,10-diazabenzo[*a*]anthracene-9,11-dione (6)

The aldehyde (1.0 mmol), cyclic-1,3-dicarbonyl compound (1.2 mmol) and 2-naphthol (1.0 mmol) were grinded in a mortar. The catalyst $InCl_3$ (30 mol %) or P_2O_5 (20 mol %) was added to the reaction mixture and grinded further for additional 15 min. The whole reaction mixture was heated in an oil bath at 120 °C for the stipulated period of time (Table 1) till the completion of the reaction (monitored by TLC). Water (30 mL) was added to the reaction mixture to remove unreacted reactants and the product was extracted with ethyl acetate (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under vacuum. The residue obtained was purified by column chromatography on silica gel to afford the pure product. Finally the products were recrystallized from methanol.

*4.2.1. 9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-one (**5a**)*

White solid; R_f=0.50 (1:9 EtOAc/Hexane), mp 151–153 °C. IR (KBr, cm^{-1}): 3055, 2954, 2884, 1651, 1374, 1229, 1178, 1076, 811. ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J=8.1 Hz, 1H), 7.78–7.74 (m, 2H), 7.42–7.04 (m, 8H), 5.70 (s, 1H), 2.57 (s, 2H), 2.33 (d, J=16.2 Hz, 1H), 2.26 (d, J=16.2 Hz, 1H), 1.11 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 163.8, 147.7, 144.7, 131.4, 131.3, 128.7, 128.4, 128.3, 128.1, 126.9, 126.1, 124.8, 123.6, 117.6, 117.0, 114.2, 50.8, 41.3, 34.6, 32.2, 29.2, 27.1. MS (FAB): m/z=355 $[M+H]^+$. Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.62; H, 6.50.

*4.2.2. 9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (**5b**)*

White solid; R_f=0.32 (1:9 EtOAc/Hexane), mp 178–180 °C. IR (KBr, cm^{-1}): 3077, 2934, 1645, 1597, 1516, 1377, 1343, 1225, 1177, 1026, 827. ^1H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J=8.4 Hz, 2H), 7.82–7.79 (m, 3H), 7.52–7.33 (m, 5H), 5.81 (s, 1H), 2.59 (s, 2H), 2.36 (d, J=16.2 Hz, 1H), 2.26 (d, J=16.2 Hz, 1H), 1.13 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 164.5, 151.8, 147.7, 146.2, 131.5, 130.9, 129.5, 129.3, 128.6, 127.3, 125.2, 123.5, 123.0, 117.0, 115.9, 112.9, 50.7, 41.3, 34.8, 32.2, 29.2, 27.0. MS (FAB): 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, 75.23; H, 5.32; N, 3.66.

*4.2.3. 9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (**5c**)*

White solid; R_f=0.35 (1:9 EtOAc/Hexane), mp 168–170 °C. IR (KBr, cm^{-1}): 3071, 2955, 1649, 1528, 1372, 1356, 1224, 1172, 1025, 809. ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.95–7.80 (m, 5H), 7.47–7.35 (m, 4H), 5.81 (s, 1H), 2.61 (s, 2H), 2.36 (d, J=16.2 Hz, 1H), 2.26 (d, J=16.2 Hz, 1H), 1.13 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 164.5, 148.3, 147.7, 146.7, 134.7, 131.5, 130.9, 129.6, 129.0, 128.6, 127.3, 125.1, 123.1, 123.0, 121.5, 117.1, 115.9, 113.1, 50.7, 41.3, 34.7, 32.2, 29.2, 27.1. MS (FAB): 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, 75.46; H, 5.42; N, 3.86.

*4.2.4. 9,9-Dimethyl-12-(2-nitrophenyl)-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (**5d**)*

Pale yellow solid; R_f=0.30 (1:9 EtOAc/Hexane), mp 223–225 °C. IR (KBr, cm^{-1}): 3069, 2957, 2926, 1651, 1526, 1369, 1227, 1170, 1028, 823. ^1H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, J=8.1 Hz, 1H), 7.86–7.77 (m, 3H), 7.46–7.03 (m, 6H), 6.58 (s, 1H), 2.60 (d, J=17.4 Hz, 1H), 2.52 (d, J=17.4 Hz, 1H), 2.29 (d, J=16.2 Hz, 1H), 2.19 (d, J=16.2 Hz, 1H), 1.11 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 164.5, 148.6, 142.1, 132.9, 131.6, 131.5, 131.0, 129.9, 129.0, 128.3, 127.6, 127.2, 126.5, 124.3, 123.7, 117.5, 117.0, 113.2, 50.4, 41.3, 34.8, 32.3, 29.3, 27.1. MS (FAB): 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, 75.42; H, 5.59; N, 3.56.

*4.2.5. 12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5e**)*

White solid; R_f=0.50 (1:9 EtOAc/Hexane), mp 204–205 °C. IR (KBr, cm^{-1}): 3057, 2949, 1643, 1227, 1172, 1024. ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J=8.1 Hz, 1H), 7.77–7.72 (m, 2H), 7.44–7.22 (m,

5H), 6.70 (d, *J*=8.4 Hz, 2H), 5.65 (s, 1H), 3.68 (s, 3H), 2.55 (s, 2H), 2.33 (d, *J*=16.2 Hz, 1H), 2.26 (d, *J*=16.2 Hz, 1H), 1.11 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 163.1, 156.7, 146.5, 136.0, 133.6, 130.4, 130.2, 128.3, 127.3, 126.6, 125.2, 123.8, 122.2, 117.0, 116.8, 115.9, 113.3, 112.5, 53.9, 49.7, 40.3, 32.7, 31.2, 28.2, 26.0. MS (FAB): *m*/*z*=385 $[M+H]^+$. Anal. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.41; H, 6.07.

4.2.6. 12-(2-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5f**)

White solid; R_f=0.48 (1:9 EtOAc/Hexane), mp 163–165 °C. IR (KBr, cm^{-1}): 3072, 2930, 1649, 1376, 1231, 1170, 1029. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J*=8.4 Hz, 1H), 7.74–7.67 (m, 2H), 7.45–7.25 (m, 4H), 7.05 (t, *J*=7.2 Hz, 1H), 6.81–6.74 (m, 2H), 5.95 (s, 1H), 3.94 (s, 3H), 2.58 (s, 2H), 2.32 (d, *J*=16.2 Hz, 1H), 2.22 (d, *J*=16.2 Hz, 1H), 1.12 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 164.2, 156.3, 147.6, 133.2, 131.8, 131.2, 130.5, 128.3, 128.1, 127.5, 126.7, 124.6, 123.9, 120.6, 118.2, 116.9, 113.6, 111.4, 55.8, 50.8, 41.4, 32.9, 32.2, 29.4, 27.0. MS (FAB): *m*/*z*=385 $[M+H]^+$. Anal. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.42; H, 6.31.

4.2.7. 12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5g**)

White solid; R_f=0.50 (1:9 EtOAc/Hexane), mp 180–182 °C. IR (KBr, cm^{-1}): 3072, 2925, 1645, 1374, 1226, 1174, 1088. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J*=8.1 Hz, 1H), 7.79–7.75 (m, 2H), 7.45–7.11 (m, 7H), 5.67 (s, 1H), 2.56 (s, 2H), 2.34 (d, *J*=16.2 Hz, 1H), 2.26 (d, *J*=16.2 Hz, 1H), 1.12 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 164.5, 151.6, 147.4, 146.3, 131.7, 130.5, 129.5, 129.2, 128.6, 127.3, 125.1, 123.4, 123.0, 116.9, 115.9, 112.9, 50.7, 41.3, 34.8, 32.2, 29.2, 27.0. MS (FAB): *m*/*z*=389 $[M+H]^+$. Anal. Calcd for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44. Found: C, 77.32; H, 5.53.

4.2.8. 12-(2-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5h**)

White solid; R_f=0.45 (1:9 EtOAc/Hexane), mp 179–180 °C. IR (KBr, cm^{-1}): 3075, 2930, 1648, 1372, 1229, 1179, 1030, 748. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J*=8.4 Hz, 1H), 7.76–7.72 (m, 2H), 7.49–7.26 (m, 5H), 7.07–6.96 (m, 2H), 5.98 (s, 1H), 2.60 (s, 2H), 2.34 (d, *J*=16.2 Hz, 1H), 2.24 (d, *J*=16.2 Hz, 1H), 1.13 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 164.1, 147.6, 142.1, 132.9, 131.6, 131.5, 131.3, 129.9, 129.0, 128.3, 127.6, 127.0, 126.8, 124.9, 123.9, 117.3, 117.0, 113.4, 50.8, 41.4, 32.9, 32.1, 29.3, 27.0. MS (FAB): *m*/*z*=389 $[M+H]^+$. Anal. Calcd for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44. Found: C, 77.49; H, 5.56.

4.2.9. 12-(2,4-Dichlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5i**)

White solid; R_f=0.50 (1:9 EtOAc/Hexane), mp 178–180 °C. IR (KBr, cm^{-1}): 3058, 2952, 2869, 1652, 1369, 1227, 1103, 1024, 751. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J*=8.4 Hz, 1H), 7.78–7.74 (m, 2H), 7.48–7.36 (m, 2H), 7.29–7.19 (m, 3H), 7.04 (d, *J*=6.9 Hz, 1H), 5.93 (s, 1H), 2.60 (s, 2H), 2.35 (d, *J*=16.2 Hz, 1H), 2.25 (d, *J*=16.2 Hz, 1H), 1.14 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 164.4, 147.6, 140.7, 133.6, 132.5, 132.4, 131.4, 131.3, 129.6, 129.3, 128.4, 127.3, 127.2, 125.0, 123.6, 117.0, 116.7, 112.9, 50.8, 41.4, 32.6, 32.1, 29.3, 27.0. MS (FAB): *m*/*z*=423 $[M+H]^+$. Anal. Calcd for $C_{25}H_{20}Cl_2O_2$: C, 70.93; H, 4.76. Found: C, 70.72; H, 4.85.

4.2.10. 12-(4-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5j**)

White solid; R_f=0.30 (1:4 EtOAc/Hexane), mp 223–225 °C. IR (KBr, cm^{-1}): 3305, 2957, 1638, 1572, 1378, 1225, 1176, 1024. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J*=8.1 Hz, 1H), 7.78–7.73 (m, 2H), 7.45–7.15 (m, 5H), 6.61 (d, *J*=8.4 Hz, 2H), 5.63 (s, 1H), 5.49 (s, 1H), 2.56 (s, 2H), 2.34 (d, *J*=16.2 Hz, 1H), 2.27 (d, *J*=16.2 Hz, 1H), 1.12 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 164.5, 154.5, 147.4, 136.3, 131.4, 131.3, 129.4, 128.6, 128.3, 126.9, 124.8, 123.7, 117.8, 116.9, 115.3, 114.4, 50.7, 41.3, 33.8, 32.2, 29.1, 27.0. MS (FAB): *m*/*z*=371 $[M+H]^+$. Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 81.26; H, 6.12.

4.2.11. 12-(3-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5k**)

White solid; R_f=0.35 (1:4 EtOAc/Hexane), mp 240–241 °C. IR (KBr, cm^{-1}): 3409, 3054, 2951, 1640, 1589, 1371, 1222, 1170, 1023. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J*=8.1 Hz, 1H), 7.79–7.74 (m, 2H), 7.45–7.30 (m, 3H), 7.04 (t, *J*=7.8 Hz, 1H), 6.93 (s, 1H), 6.83 (d, *J*=7.5 Hz, 1H), 6.56 (d, *J*=6.0 Hz, 1H), 5.69 (s, 1H), 5.43 (s, 1H), 2.56 (s, 2H), 2.36 (d, *J*=16.2 Hz, 1H), 2.30 (d, *J*=16.2 Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.3, 164.5, 148.4, 147.6, 146.3, 134.5, 131.5, 130.9, 129.6, 129.1, 128.7, 127.5, 125.1, 123.4, 123.0, 121.7, 117.3, 115.7, 113.6, 50.7, 41.3, 34.7, 32.2, 29.2, 27.0. MS (FAB): *m*/*z*=371 $[M+H]^+$. Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 81.20; H, 6.06.

4.2.12. 12-(5-Bromo-2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5l**)

White solid; R_f=0.45 (1:4 EtOAc/Hexane), mp 266–268 °C. IR (KBr, cm^{-1}): 3116, 2957, 2927, 1624, 1590, 1382, 1225, 1143, 1030. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83–7.80 (m, 2H), 7.60–7.26 (m, 4H), 7.10 (d, *J*=6.0 Hz, 1H), 6.91 (d, *J*=8.4 Hz, 1H), 6.65 (s, 1H), 5.71 (s, 1H), 4.73 (s, 1H), 2.70 (d, *J*=17.7 Hz, 1H), 2.61 (d, *J*=17.7 Hz, 1H), 2.45 (d, *J*=17.1 Hz, 1H), 2.36 (d, *J*=17.1 Hz, 1H), 1.15 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 167.3, 152.1, 147.7, 134.9, 134.8, 131.6, 131.2, 130.8, 129.5, 128.3, 127.6, 125.4, 123.1, 120.9, 120.8, 116.6, 113.6, 113.3, 50.1, 41.5, 32.4, 29.6, 28.8, 27.3. MS (FAB): *m*/*z*=449 $[M+H]^+$. Anal. Calcd for $C_{25}H_{21}BrO_3$: C, 66.82; H, 4.71. Found: C, 67.01; H, 4.95.

4.2.13. 12-(5-Nitro-2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5m**)

White solid; R_f=0.50 (1:4 EtOAc/Hexane), mp 263–265 °C. IR (KBr, cm^{-1}): 3316, 2940, 1631, 1492, 1373, 1334, 1231, 1026, 830. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (s, 1H), 7.93–7.79 (m, 3H), 7.49–7.37 (m, 5H), 7.09 (d, *J*=9.0 Hz, 1H), 5.75 (s, 1H), 2.73 (d, *J*=17.7 Hz, 1H), 2.65 (d, *J*=17.7 Hz, 1H), 2.49 (d, *J*=17.1 Hz, 1H), 2.41 (d, *J*=17.1 Hz, 1H), 1.17 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.1, 168.2, 159.4, 147.9, 142.0, 133.1, 131.7, 130.5, 130.0, 128.6, 127.7, 125.5, 125.1, 124.2, 122.6, 119.2, 116.8, 115.7, 112.7, 50.0, 41.5, 32.3, 29.0, 28.2, 27.1. MS (FAB): *m*/*z*=416 $[M+H]^+$. Anal. Calcd for $C_{25}H_{21}NO_5$: C, 72.28; H, 5.10; N, 3.37. Found: C, 72.36; H, 5.21; N, 3.57.

4.2.14. 12-(2-Hydroxy-3-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5n**)

White solid; R_f=0.40 (1:4 EtOAc/Hexane), mp 213–215 °C. IR (KBr, cm^{-1}): 3283, 3077, 2951, 1622, 1377, 1237, 1069. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.83–7.73 (m, 3H), 7.40–7.25 (m, 3H), 6.59–6.57 (m, 2H), 6.32 (d, *J*=4.5 Hz, 1H), 5.82 (s, 1H), 3.85 (s, 3H), 2.59 (s, 2H), 2.42 (d, *J*=16.2 Hz, 1H), 2.34 (d, *J*=16.2 Hz, 1H), 1.13 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.8, 166.3, 149.1, 147.6, 142.2, 132.7, 131.3, 131.2, 128.9, 128.1, 127.3, 125.1, 123.5, 120.7, 120.6, 117.5, 116.5, 113.7, 109.4, 55.7, 50.2, 41.5, 32.3, 29.0, 28.1, 27.1. MS (FAB): *m*/*z*=401 $[M+H]^+$. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 78.10; H, 6.33.

4.2.15. 12-(2-Hydroxy-3-ethoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5o**)

White solid; R_f=0.40 (1:4 EtOAc/Hexane), mp 190–192 °C. IR (KBr, cm^{-1}): 3215, 3059, 2962, 2927, 1629, 1386, 1226, 1121, 1057. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.91 (d, *J*=8.1 Hz, 1H), 7.75–7.73 (m, 2H), 7.44–7.25 (m, 3H), 6.60–6.52 (m, 2H), 6.38 (dd, *J*=1.8, 6.9 Hz, 1H), 5.83 (s, 1H), 4.07 (q, *J*=6.9 Hz, 2H), 2.59 (s, 2H), 2.41 (d, *J*=16.2 Hz, 1H), 2.33 (d, *J*=16.2 Hz, 1H), 1.49 (t, *J*=6.9 Hz, 3H), 1.13 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.2, 165.9, 148.0,

147.5, 142.4, 132.4, 131.3, 131.2, 128.7, 128.0, 127.2, 124.9, 123.5, 120.8, 120.4, 117.5, 116.5, 113.6, 110.5, 64.1, 50.2, 41.3, 32.1, 29.0, 28.2, 27.0, 14.8. MS (FAB): m/z=415 $[M+H]^+$. Anal. Calcd for $C_{27}H_{26}O_4$: C, 78.24; H, 6.32. Found: C, 78.52; H, 6.60.

4.2.16. 9,9-Dimethyl-12-p-tolyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5p**)

White solid; R_f=0.50 (1:9 EtOAc/Hexane), mp 176–178 °C. IR (KBr, cm^{-1}): 3071, 2949, 2865, 1648, 1510, 1372, 1230, 1071, 814. ^1H NMR (300 MHz, DMSO-d_6): δ 8.04–7.88 (m, 3H), 7.46–7.42 (m, 3H), 7.17–7.15 (m, 2H), 6.98 (d, J=7.2 Hz, 2H), 5.52 (s, 1H), 2.72 (d, J=17.4 Hz, 1H), 2.60 (d, J=17.4 Hz, 1H), 2.41 (d, J=16.2 Hz, 1H), 2.30 (d, J=16.2 Hz, 1H), 2.14 (s, 3H), 1.06 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 163.0, 153.1, 146.5, 140.7, 134.6, 133.6, 130.3, 128.5, 127.9, 127.2, 126.6, 125.9, 123.8, 122.6, 117.1, 116.8, 115.9, 113.3, 49.7, 40.3, 33.2, 31.2, 28.2, 26.1, 19.9. MS (FAB): m/z=369 $[M+H]^+$. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.52; H, 6.38.

4.2.17. 9,9-Dimethyl-12-styryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5q**)

White solid; R_f=0.35 (1:9 EtOAc/Hexane), mp 148–150 °C. IR (KBr, cm^{-1}): 3080, 2927, 1648, 1464, 1383, 2225, 908. ^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J=8.4 Hz, 1H), 7.83–7.75 (m, 2H), 7.53–7.17 (m, 8H), 6.45 (dd, J=6.3 Hz, 1H), 6.17 (d, J=15.9 Hz, 1H), 5.33 (d, J=6.3 Hz, 1H), 2.56 (s, 2H), 2.37 (s, 2H), 1.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 165.0, 147.8, 137.0, 131.2, 130.8, 130.6, 128.7, 128.3, 128.2, 127.1, 127.0, 126.2, 124.9, 123.7, 117.0, 112.1, 50.9, 41.4, 32.3, 31.2, 29.2, 27.5. MS (FAB): m/z=381 $[M+H]^+$. Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 85.45; H, 6.30.

4.2.18. 12-Isopropyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**5r**)

White solid; R_f=0.40 (1:9 EtOAc/Hexane), mp 116–117 °C. IR (KBr, cm^{-1}): 3066, 2956, 1646, 1384, 1218, 1172, 817, 544. ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J=8.4 Hz, 1H), 7.82 (d, J=8.1 Hz, 1H), 7.71 (d, J=8.7 Hz, 1H), 7.55 (t, J=7.5 Hz, 1H), 7.44 (t, J=7.5 Hz, 1H), 7.23 (d, J=9.0 Hz, 1H), 4.71 (d, J=3.0 Hz, 1H), 2.64 (d, J=18.0 Hz, 1H), 2.54 (d, J=18.0 Hz, 1H), 2.44 (d, J=16.5 Hz, 1H), 2.33 (d, J=16.5 Hz, 1H), 2.11 (m, 1H), 1.23 (s, 3H), 1.14 (s, 3H), 0.91 (d, J=6.9 Hz, 3H), 0.68 (d, J=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 167.0, 149.0, 131.4, 128.4, 127.8, 126.5, 124.5, 123.4, 118.8, 116.7, 111.5, 102.5, 50.9, 41.4, 35.3, 32.8, 31.7, 29.9, 27.1, 20.8, 18.2. MS (FAB): m/z=321 $[M+H]^+$. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.78; H, 7.86.

4.2.19. 8,10-Dimethyl-12-(4-nitrophenyl)-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6a**)

White solid; R_f=0.35 (1:4 EtOAc/Hexane), mp 288–290 °C. IR (KBr, cm^{-1}): 3070, 2924, 2855, 1709, 1667, 1596, 1227, 1175. ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, J=8.4 Hz, 2H), 7.91–7.79 (m, 3H), 7.56–7.42 (m, 5H), 5.90 (s, 1H), 3.63 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.7, 152.4, 150.7, 150.4, 147.1, 146.5, 131.7, 130.4, 130.2, 129.2, 128.7, 127.8, 125.7, 123.7, 123.3, 116.3, 115.7, 89.9, 36.0, 29.1, 28.2. MS (FAB): 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, 66.82; H, 4.40; N, 10.38.

4.2.20. 8,10-Dimethyl-12-(4-chlorophenyl)-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6b**)

White solid; R_f=0.40 (1:4 EtOAc/Hexane), mp 270–272 °C. IR (KBr, cm^{-1}): 2924, 2855, 1708, 1671, 1648, 1225, 1174, 1081. ^1H NMR (300 MHz, $CDCl_3$): δ 7.88–7.81 (m, 3H), 7.47–7.14 (m, 7H), 5.78 (s, 1H), 3.60 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 152.2, 150.5, 147.1, 142.3, 132.5, 131.7, 130.7, 129.7, 129.6, 128.5, 127.6, 125.6, 123.7, 116.7, 116.3, 90.9, 35.4, 29.1, 28.2. MS (FAB): 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, 68.54; H, 4.63; N, 7.12.

4.2.21. 8,10-Dimethyl-12-phenyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6c**)

White solid; R_f=0.35 (1:4 EtOAc/Hexane), mp 226–228 °C. IR (KBr, cm^{-1}): 2928, 1706, 1651, 1485, 1233, 1179. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J=7.8 Hz, 1H), 7.85 (m, 2H), 7.46–7.35 (m, 5H), 7.23–7.10 (m, 3H), 5.81 (s, 1H), 3.61 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 152.2, 150.6, 147.1, 143.8, 131.7, 130.9, 129.4, 128.5, 128.4, 128.2, 127.4, 126.7, 125.4, 123.9, 117.4, 116.2, 91.4, 35.9, 29.0, 28.1. MS (FAB): 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, 74.92; H, 5.12; N, 7.89.

4.2.22. 8,10-Dimethyl-12-p-tolyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6d**)

White solid; R_f=0.37 (1:4 EtOAc/Hexane), mp 196–198 °C. IR (KBr, cm^{-1}): 2924, 1700, 1643, 1487, 1232, 1179. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J=8.4 Hz, 1H), 7.84–7.80 (m, 2H), 7.46–7.37 (m, 3H), 7.26 (d, J=7.5 Hz, 2H), 7.02 (d, J=7.5 Hz, 2H), 5.78 (s, 1H), 3.60 (s, 3H), 3.32 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 152.1, 150.6, 147.1, 140.9, 136.3, 131.7, 130.9, 129.3, 129.1, 128.4, 128.0, 127.3, 125.4, 123.9, 117.5, 116.2, 91.5, 35.5, 28.9, 28.1, 20.9. MS (FAB): 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, 74.88; H, 5.19; N, 7.20.

4.2.23. 12-(2,4-Dichlorophenyl)-8,10-dimethyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6e**)

White solid; R_f=0.35 (1:4 EtOAc/Hexane), mp 222–224 °C. IR (KBr, cm^{-1}): 3060, 2950, 1709, 1658, 1479, 1232, 1181. ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J=8.1 Hz, 1H), 7.84–7.82 (m, 2H), 7.52–7.44 (m, 2H), 7.37–7.31 (m, 3H), 7.08 (d, J=7.8 Hz, 1H), 6.07 (s, 1H), 3.64 (s, 3H), 3.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.6, 152.4, 150.5, 146.9, 139.7, 133.7, 133.0, 132.3, 131.6, 130.9, 129.9, 129.7, 128.6, 127.6, 127.4, 125.5, 123.7, 116.2, 89.9, 33.8, 29.1, 28.1. MS (FAB): m/z=439 $[M+H]^+$. Anal. Calcd for $C_{23}H_{16}Cl_2N_2O_3$: C, 62.88; H, 3.67; N, 6.38. Found: C, 62.82; H, 3.59, N, 6.30.

4.2.24. 12-(2-Chlorophenyl)-8,10-dimethyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6f**)

White solid; R_f=0.32 (1:4 EtOAc/Hexane), mp 270–272 °C. IR (KBr, cm^{-1}): 3058, 2951, 1705, 1655, 1456, 1271, 1183. ^1H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, J=8.4 Hz, 1H), 7.83–7.78 (m, 2H), 7.53–7.29 (m, 5H), 7.09–7.04 (m, 2H), 6.12 (s, 1H), 3.64 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.6, 152.4, 150.6, 146.9, 141.1, 133.0, 131.6, 131.5, 131.1, 130.0, 129.7, 128.4, 128.0, 127.5, 127.0, 125.0, 124.0, 116.9, 116.2, 90.4, 34.1, 29.0, 28.1. MS (FAB): 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, 68.10; H, 4.15; N, 6.85.

4.2.25. 8,10-Dimethyl-12-(2-nitrophenyl)-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6g**)

White solid; R_f=0.25 (1:4 EtOAc/Hexane), mp 288–290 °C. IR (KBr, cm^{-1}): 3062, 2954, 1708, 1651, 1484, 1233, 1177. ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, J=7.8 Hz, 1H), 7.90–7.81 (m, 3H), 7.49–7.38 (m, 3H), 7.29–7.23 (m, 2H), 7.04 (d, J=7.5 Hz, 1H), 6.76 (s, 1H), 3.58 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 151.6, 150.4, 149.1, 147.4, 138.2, 132.9, 131.7, 131.2, 130.9, 130.3, 128.3, 127.8, 127.4, 125.7, 124.6, 124.5, 116.2, 115.7, 90.3, 30.9, 29.0, 28.1. MS (FAB): 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, 66.72; H, 4.09; N, 10.01.

4.2.26. 12-(4-Bromophenyl)-8,10-dimethyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6h**)

White solid; R_f=0.40 (1:4 EtOAc/Hexane), mp 243–245 °C. IR (KBr, cm^{-1}): 2929, 1705, 1646, 1484, 1234. ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (m, 3H), 7.48–7.23 (m, 7H), 5.77 (s, 1H), 3.61 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 152.2, 150.5, 147.1,

142.8, 131.7, 131.5, 130.6, 129.9, 129.7, 128.5, 127.5, 125.5, 123.6, 120.5, 116.6, 116.2, 90.8, 35.5, 29.0, 28.1. MS (FAB): m/z=449 $[M+H]^+$. Anal. Calcd for $C_{23}H_{17}BrN_2O_3$: C, 61.48; H, 3.81; N, 6.23. Found: C, 61.40; H, 3.75; N, 6.10.

*4.2.27. 12-(4-Fluorophenyl)-8,10-dimethyl-8,12-dihydro-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione (**6i**)*

White solid; R_f=0.30 (1:4 EtOAc/Hexane), mp 303–305 °C. IR (KBr, cm^{-1}): 2925, 1706, 1670, 1597, 1452, 1165. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90–7.81 (m, 3H), 7.47–7.30 (m, 5H), 6.90 (t, J=8.7 Hz, 2H), 5.79 (s, 1H), 3.61 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.6, 152.4, 150.4, 147.0, 142.5, 131.4, 131.0, 130.2, 129.8, 129.2, 128.5, 127.5, 125.6, 123.5, 120.3, 116.3, 116.0, 90.5, 35.3, 29.0, 28.2. MS (FAB): 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, 71.10; H, 4.30; N, 7.13.

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