Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Available online: 04 Mar 2010

To cite this article: Jianjun Li, Jia Li, Jin Fang & Weike Su (2010): Efficient One-Pot Condensation of β-Naphthol, Aldehydes, and Cyclic 1,3-Dicarbonyl Compounds Catalyzed by p-TSA Under Solvent-Free and Sonication Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:7, 1029-1039

To link to this article: http://dx.doi.org/10.1080/00397910903029966

Synthetic Communications®, 40: 1029–1039, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903029966

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EFFICIENT ONE-POT CONDENSATION OF β-NAPHTHOL, ALDEHYDES, AND CYCLIC 1,3-DICARBONYL COMPOUNDS CATALYZED BY *p*-TSA UNDER SOLVENT-FREE AND SONICATION CONDITIONS

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A facile and efficient procedure has been developed by one-pot condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds for the synthesis of 8,9,10,12-tetrahydrobenzo[a]xanthen-11-one or 8,9-dihydrobenzo-[f]cyclopenta[b]chromen-10(11H)-one derivatives catalyzed by p-toluenesulfonic acid under solvent-free and sonication conditions.

Keywords: One-pot condensation; *p*-TSA; solvent-free; ultrasound irradiation

Xanthenes and benzoxanthenes are of considerable interest in industry as well as in academia because of their promising biological and pharmaceutical activities such as antiviral,[1] antibacterial,[2] and anti-inflammatory actions,[3] and they are being used as zoxazolamine[4,5] and in photodynamic therapy.[6,7] Furthermore, these active oxygen-containing heterocyclic compounds can also be employed as dyes,[8,9] in laser technology,[10,11] as pH-sensitive fluorescent materials for the visualization of biomolecules.[12] Thus, the synthesis of this heterocyclic nucleus is of great significance. Lately, only a few procedures for the preparation of 8,9,10,12-tetrahydrobenzo[a]-xanthen-11-one or 8,9-dihydrobenzo-[f]cyclopenta[b]chromen-10(11*H*)-one derivatives have been reported. Catalysts such as $NaHSO_4 \cdot SiO_2$[13] and $Sr(OTf)_2$ have been used for these reactions,[14] but these methods require long reaction times.

Recently, the utilization of multicomponent reactions (MCRs) to generate novel, drug-like scaffolds has received great attention from organic chemists because products can be prepared directly in a single step and diversity can be achieved simply by varying the reaction substrates.[15–19] Previously, it occured to us that dihydropyrimidiones,[20] 1-substituted-1*H*-1,2,3,4-tetrazoles,[21] 2-hydroxy-7,8-dihydroquinolin-5(6*H*)-ones, and 7,8-dihydroquinolin-2,5-(1*H*,6*H*)-diones[22] could

Received March 13, 2009.

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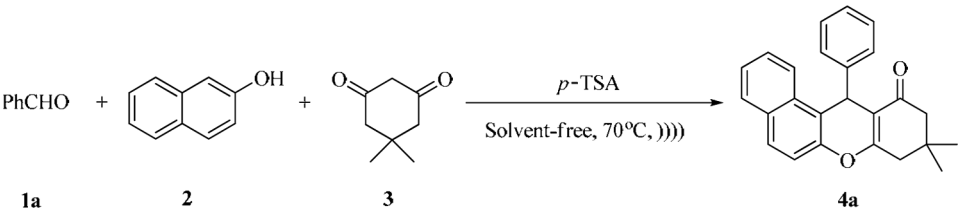
successfully be prepared by MCRs. More recently, we also reported the reaction of the β-naphthol, aldehydes, and amides to form amidoalkyl naphthols.[23]

p-Toluenesulfonic acid (*p*-TSA) is a commercially available and very cheap chemical with good stability. Recently, it has been shown that *p*-TSA can be used as a substitute for conventional acidic catalytic materials. The toxicity and volatile nature of many organic solvents, particularly chlorinated hydrocarbons, that are widely used in huge amounts for organic reactions pose a serious threat to the environment. Thus, design of solventless catalytic reactions has received tremendous attention recently.

Taking these points into consideration, in continuation of our investigations on these active oxygen-containing heterocyclic compounds,[24,14] herein we report a new route to 8,9,10,12-tetrahydrobenzo[a]xanthen-11-one or 8,9-dihydrobenzo-[f]cyclopenta[b]chromen-10(11*H*)-one derivatives with *p*-TSA as catalyst under solvent-free conditions. In addition, all the reactions were carried out under ultrasonic irradiation because it could accelerate the progress of various organic transformations with mild reaction conditions, short reaction times, and good yields.

We initially studied the reaction of benzaldehyde **1a**, β-naphthol **2**, and 5,5-dimethyl-cyclohexane-1,3-dione **3** along with a catalytic amount of *p*-TSA (10 mol%) in several classic solvents chosen as the medium for comparison. The results are summarized in Table 1. 1,2-Dichloroethane (Table 1, entry 5, 93%) and solvent-free conditions (Table 1, entry 6, 95%) afforded the product 9,9-dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one **4a** in excellent yields. Table 1 (entry 7) shows that the reaction time is reduced and yields improve in the absence of

Table 1. Optimization of conditions for the condensation reaction of aldehyde, β-naphthol, and dimedone[a]



1a **2** **3** **4a**

Entry	Solvent	Time (h)	Yields (%)[b]
1	Water	3	30
2	THF	3	45
3	CH_3CH_2OH	3	<10
4	[bpy]BF_4	3	60
5	$(CH_2Cl)_2$	1.5	93
6	None	0.5	95
7	None	1.0	90[c]

[a]Reaction conditions: benzaldehyde **1a** (1 mmol), β-naphthol **2** (1 mmol), 5,5-dimethyl-cyclohexane-1,3-dione **3** (1.2 mmol), *p*-TSA (0.1 mmol), solvent (3 mL), 70°C.

[b]Isolated yield.

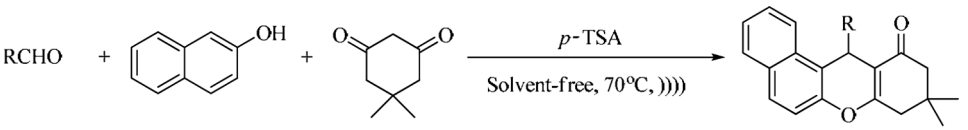
[c]The reaction was carried out by stirring instead of sonic irradiation.

ultrasound irradiation conditions. Taking the reaction yields and environmental impact into consideration, we carried out this reaction under ultrasonic irradiation and solvent-free conditions at 70 °C.

Encouraged by this success, we extended this reaction to a range of aldehydes in the presence of 10 mol% *p*-TSA under solvent-free and ultrasonic irradiation conditions (Table 2). Varoius aromatic aldehydes with electron-donating and electron-withdrawing substituents reacted successfully, and the corresponding products **4a–k** were obtained in good to excellent yields in 0.5–3 h. These results were also obtained in the case of the aliphatic and heterocyclic aldehydes (Table 2, entries 12–14). The desired products were characterized by NMR, infrared (IR), and mass spectroscopy (MS) and also by comparison with authentic samples.

We have not established an exact mechanism for the formation of this kind of compound; however, a reasonable pathway is shown in Scheme 1. The products may be formed either through step 1 → step 2 or through step 3 → step 4 by referring to literature.[13] The role of *p*-TSA comes in step 1, when it catalyzes the Knoevenagel-type coupling of aldehyde **1** with active methylene compound **3**, and in step 2, when it catalyzes the Michael-type addition of β-naphthol **2** and heterodiene **7** to afford the corresponding products **4**.

Table 2. *p*-TSA-promoted one-pot condensation of β-naphthol, aldehydes, and 5,5-dimethyl-cyclohexane-1,3-dione[a]



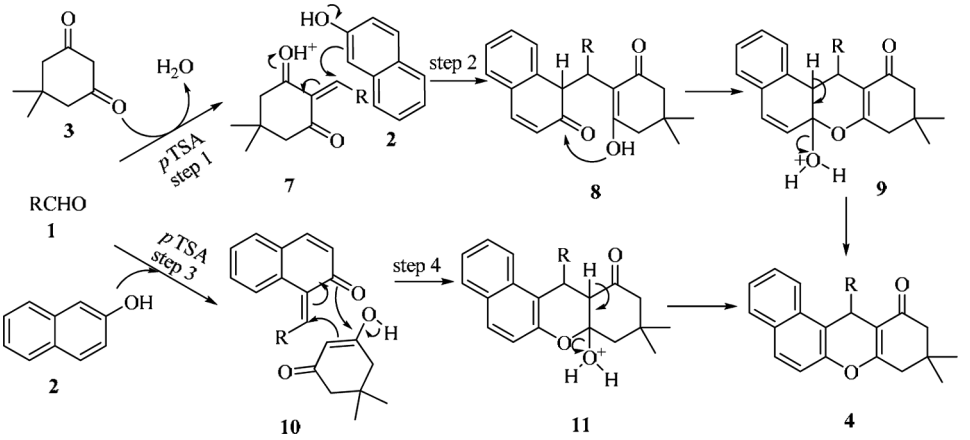
1 **2** **3** **4**

Entry	1	R	Time (h)	Product	Yields (%)[b]
1	1a	C_6H_5	0.5	**4a**	95
2	1b	3-F-C_6H_4	0.5	**4b**	96
3	1c	3-Cl-C_6H_4	0.5	**4c**	95
4	1d	3-OH-C_6H_4	0.5	**4d**	97
5	1e	3-NO_2-C_6H_4	0.5	**4e**	94
6	1f	3-OCH_3-C_6H_4	0.5	**4f**	91
7	1g	3-OMe-4-OH-C_6H_3	2.5	**4g**	90
8	1h	3-Me-4-Me-C_6H_3	1.0	**4h**	92
9	1I	4-OMe-C_6H_4	0.5	**4i**	94
10	1j	4-Cl-C_6H_4	0.5	**4j**	94
11	1k	CH_3CH_2	2.5	**4k**	87
12	1l	$CH_3C(CH_3)_2$	3.0	**4l**	86
13	1m	2-thiophene	2.5	**4m**	85
14	1a	C_6H_5	0.5	**a**	95[c]
15	1j	4-Cl-C_6H_4	0.5	**j**	96[c]

[a]Reaction conditions: aldehyde **1** (1 mmol), β-naphthol **2** (1 mmol), 5,5-dimethyl-cyclohexane-1,3-dione **3** (1.2 mmol), *p*-TSA (0.1 mmol), 70°C.

[b]Isolated yield.

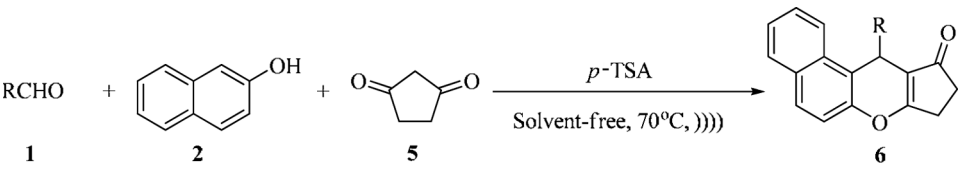
[c]Cyclopentane-1,3-dione was substituted for 5,5-dimethyl-cyclohexane-1,3-dione **3**.

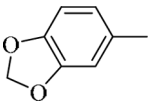


Scheme 1. Possible mechanism for the formation of compound **4**.

Next, we extended this reaction to phenols and α-naphthol under similar conditions. However, in the case of phenol and α-naphthol, the reaction did not proceed or gave only traces of the expected products under similar conditions after 24 h. A by-product was characterized, which was formed from the condensation of 2 equiv. of 5,5-dimethyl-cyclohexane-1,3-dione **3** and 1 equiv. of aldehydes because of their weaker nucleophilicity compared to β-naphthol.

Table 3. *p*-TSA-promoted one-pot condensation of β-naphthol, aldehydes, and cyclopentane-1,3-dione[a]



Entry	1	R	Time (h)	Product	Yields (%)[b]
1	1a	C_6H_5	0.5	**6a**	95
2	1d	3-OH-C_6H_4	0.5	**6d**	96
3	1f	3-OCH_3-C_6H_4	0.5	**6f**	93
4	1h	3-Me-4-Me-C_6H_3	0.5	**6h**	92
5	1j	4-Cl-C_6H_4	0.5	**6j**	94
6	1k	CH_3CH_2	2.5	**6k**	85
7	1n	2-Furan	2.5	**6n**	80
8	1o	2-OMe-4-OMe-C_6H_3	1.0	**6o**	90
9	1p		0.5	**6p**	91
10	1q	$C_6H_5CH_2$	1.0	**6q**	86

[a]Reaction conditions: aldehyde **1** (1 mmol), β-naphthol **2** (1 mmol), cyclopentane-1,3-dione **5** (1.2 mmol), *p*-TSA (0.1 mmol), 70°C.
[b]Isolated yield.

We next tried to observe the effect of substituents in 5,5-dimethyl-1,3-cyclohexanedione **3** using cyclopentane-1,3-dione **5**. Both aromatic and aliphatic aldehydes **1** reacted well with **2** and **5** in the presence of 10 mol% of *p*-TSA to afford **6** in good to high yields under similar conditions (Table 3).

In summary, we have developed a facile and efficient method for the synthesis of 8,9,10,12-tetrahydrobenzo[a]xanthen-11-one or 8,9-dihydrobenzo-[f]cyclopenta[b]chromen-10(11*H*)-one derivatives. The easy workup procedure, short reaction times, solvent-free conditions, and good yields make this method an important addition to the existing methodologies.

EXPERIMENTAL

All reagents are commercially available and were used without any purification. Melting points were recorded on a Büchi B-540 capillary melting-point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus-400 instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS; the coupling constants *J* are given in hertz. IR spectra were recorded on an Avatar 370 Fourier transform (FT)–IR spectrophotometer. MS were measured with Finnigan Trace DSQ (EI, CI) or Thermo Finnigan LCQ-Advantage (ESI).

General Procedure for the Synthesis of Product 4 or 6

A mixture of aldehyde **1** (1.0 mmol), β-naphthol **2** (1.0 mmol), dimedone **3** or **5** (1.2 mmol), and *p*-TSA (10 mol%) were irradiated at 70 °C in the presence of ultrasonic waves for a certain time as shown in Tables 2 and 3. The progress of the reaction was monitored by thin-layer chromatography (TLC) until the disappearance of aldehyde. After the completion of the reaction, water (15 mL) was added and the crude product was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried ($MgSO_4$) and evaporated, and the crude product was purified through crystallization from ethanol to afford a pure product.

Data

9,9-Dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4a). Mp 154–155 °C. ν_{max} (KBr)/cm^{-1} 3125, 2954, 1651, 1595, 1398, 1375, 1228, 1176, 1025, 808, 743, 699, 510. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 (1H, d, $J = 8.4$ Hz, Ar-H), 7.79–7.75 (2H, m, Ar-H), 7.45–7.31 (5H, m, Ar-H), 7.19–7.15 (2H, m, Ar-H), 7.07–7.03 (1H, m, Ar-H), 5.71 (1H, s, CH), 2.57 (2H, s, CH_2), 2.27 (2H, m, CH_2), 1.12 (3H, s, CH_3), 0.96 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 196.9, 163.9, 147.8, 144.7, 131.5, 131.4, 128.8, 128.4, 128.2, 127.0, 126.2, 124.9, 123.7, 117.7, 117.0, 114.3, 50.9, 41.4, 34.7, 32.2, 29.3, 27.1. MS (ESI) m/z 355 ([M + 1]$^+$, 100), 274 (20).

12-(3-Fluorophenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4b). Mp 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (1H, d, $J = 8.0$ Hz, Ar-H), 7.80–7.77 (2H, m, Ar-H), 7.46–7.32 (3H, m, Ar-H), 7.26–7.11

(2H, m, Ar-H), 7.00–6.96 (1H, m, Ar-H), 6.77–6.75 (1H, m, Ar-H), 5.72 (1H, s, CH), 2.57 (2H, s, CH_2), 2.28 (2H, m, CH_2), 1.12 (3H, s, CH_3), 0.97 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 196.8, 164.1, 164.0, 161.6, 147.8, 147.2, 147.1, 131.5, 131.2, 129.6, 129.5, 129.1, 127.1, 125.0, 124.1, 123.4, 117.0, 116.9, 115.4, 115.2, 113.7, 113.3, 113.1. MS (EI) m/z 372.2 (M^+, 30), 277.1 (100). HRMS (EI): calcd. for $C_{25}H_{21}FO_2$ [M^+]: 372.1526; found: 372.1515.

12-(3-Chlorophenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4c). Mp 180–181 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.91 (1H, d, $J = 8.0$ Hz, Ar-H), 7.80–7.77 (2H, m, Ar-H), 7.47–7.25 (5H, m, Ar-H), 7.11 (1H, t, $J = 8.0$ Hz, Ar-H), 7.05–7.02 (1H, m, Ar-H), 5.69 (1H, s, CH), 2.57 (2H, s, CH_2), 2.28 (2H, m, CH_2), 1.12 (3H, s, CH_3), 0.97 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 196.7, 164.1, 147.8, 146.7, 134.1, 131.5, 131.2, 129.4, 129.1, 128.4, 127.1, 126.8, 126.5, 125.0, 123.4, 117.0, 116.8, 113.7, 50.8, 41.4, 36.2, 34.5, 32.2, 29.2, 27.1, 18.4. MS (ESI) m/z 389.1 ([M + 1]$^+$, 100). HRMS (EI): calcd. for $C_{25}H_{21}ClO_2$ [M^+]: 388.1230; found: 388.1238.

12-(3-Hydroxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4d). Mp 240–242 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H 9.22 (1H, s, OH), 8.02 (1H, d, J 8.8 Hz, Ar-H), 7.92 (2H, d, J 9.2 Hz, Ar-H), 7.53–7.42 (3H, m, Ar-H), 6.93 (1H, m, Ar-H), 6.73 (1H, d, $J = 8.4$ Hz, Ar-H), 6.65 (1H, s, Ar-H), 6.44 (1H, d, $J = 8.4$ Hz, Ar-H), 5.49 (1H, s, CH), 2.63 (2H, m, CH_2), 2.33 (1H, d, $J = 15.6$ Hz, CH_2), 2.15 (1H, d, $J = 16.8$ Hz, CH_2), 1.06 (3H, s, CH_3), 0.91 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 195.8, 163.7, 157.1, 147.2, 146.2, 131.0, 130.7, 129.0, 128.5, 127.1, 124.9, 123.2, 118.9, 117.4, 117.1, 115.1, 113.2, 50.1, 33.9, 31.9, 28.8, 26.3. MS (ESI) m/z 369.3 ([M − 1]$^+$, 100). HRMS (EI): calcd. for $C_{25}H_{22}O_3$ [M^+]: 370.1569; found: 370.1577.

9,9-Dimethyl-12-(3-nitrophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4e). Mp 169–170 °C. ν_{max} (KBr)/cm^{-1} 3125, 2954, 2864, 1649, 1596, 1529, 1375, 1344, 1225, 1025, 812, 748, 683, 510. ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.12–7.79 (6H, m, 7.47–7.35 (4H, m, Ar-H), 5.82 (1H, s, CH), 2.61 (2H, s, CH_2), 2.29 (2H, m, CH_2), 1.13 (3H, s, CH_3), 0.95 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 196.8, 164.6, 148.4, 147.8, 146.8, 134.9, 131.6, 131.0, 129.7, 129.1, 128.7, 127.4, 125.2, 123.3, 123.1, 121.6, 117.3, 116.0, 113.1, 50.8, 41.4, 34.8, 32.3, 29.3, 27.1. MS (EI) m/z 399 (M^+, 8), 165 (56), 221 (40), 277 (100).

12-(3-Methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4f). Mp 169–170 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.00 (1H, d, $J = 8.4$ Hz, Ar-H), 7.76 (2H, m, Ar-H), 7.45–7.30 (7.08 (1H, t, $J = 8.0$ Hz, Ar-H), 6.94–6.89 (2H, m, Ar-H), 5.69 (1H, s, CH), 3.70 (3H, s, CH_3), 2.56 (2H, s, CH_2), 2.27 (2H, d, $J = 5.6$ Hz, CH_2), 1.11 (3H, s, CH_3), 0.97 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 196.8, 163.9, 159.4, 147.7, 146.3, 131.4, 129.0, 128.8, 128.3, 126.9, 124.8, 123.6, 121.0, 117.5, 117.0, 114.6, 114.1, 111.2, 55.0, 50.9, 41.4, 34.6, 32.2, 29.2, 27.2. MS (ESI) m/z 385.3 ([M + 1]$^+$, 100). HRMS (EI): calcd. for $C_{26}H_{24}O_3$ [M^+]: 384.1725; found: 384.1735.

12-(4-Hydroxy-3-methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo-[a]xanthen-11(12*H*)-one (4g). Mp 164–166 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H

7.98 (1H, d, $J = 8.4$ Hz, Ar-H), 7.79–7.74 (2H, m, Ar-H), 7.45–7.35 (2H, m, Ar-H), 7.31 (1H, d, $J = 9.2$ Hz, Ar-H), 7.00 (1H, m, Ar-H), 6.68–6.63 (2H, m, Ar-H), 5.64 (1H, s, CH), 3.82 (3H, s, CH_3), 2.56 (2H, s, CH_2), 2.28 (2H, d, $J = 5.2$ Hz, CH_2), 1.11 (3H, s, CH_3), 0.98 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 197.2, 163.8, 147.7, 146.1, 143.8, 137.0, 131.5, 131.4, 128.7, 128.4, 126.9, 124.9, 123.7, 121.0, 117.8, 117.0, 114.1, 111.4, 55.9, 50.9, 41.4, 34.1, 32.2, 29.3, 27.1. MS (ESI) m/z 399.3 ($[M-1]^+$, 100).

12-(3,4-Dimethylphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4h). Mp 181–182 °C. ν_{max} (KBr)/cm^{-1} 3125, 2958, 1650, 1593, 1398, 1371, 1237, 1226, 1172, 819, 747, 478. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.04 (1H, d, $J = 8.5$ Hz, Ar-H), 7.77–7.72 (2H, m, Ar-H), 7.43–7.25 (3H, m, 7.10–7.03 (2H, m, Ar-H), 6.91 (1H, d, $J = 8.0$ Hz, Ar-H), 5.63 (1H, s, CH), 2.56 (2H, m, CH_2), 2.27 (2H, m, CH_2), 2.13 (3H, s, CH_3), 2.09 (3H, s, CH_3), 1.11 (3H, s, CH_3), 0.99 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 196.2, 163.8, 147.7, 142.3, 136.2, 134.4, 131.5, 129.7, 129.5, 128.7, 128.4, 127.0, 125.9, 124.9, 123.8, 118.1, 117.1, 114.5, 51.0, 41.4, 34.3, 32.4, 29.2, 27.4, 20.0, 19.4. MS (EI) m/z 382 (M^+, 40), 277 (100).

12-(4-Methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4i). Mp 205–206 °C. ν_{max} (KBr)/cm^{-1} 3121, 2958, 1652, 1607, 1507, 1462, 1382, 1218, 1143, 1028, 834, 747, 661, 539. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 (1H, d, $J = 8.4$ Hz, Ar-H), 7.78–7.73 (2H, m, Ar-H), 7.45–7.24 (5H, m, Ar-H), 6.71–6.69 (2H, m, Ar-H), 5.66 (1H, s, CH), 3.68 (3H, s, CH_3), 2.56 (2H, s, CH_2), 2.27 (2H, m, CH_2), 1.11 (3H, s, CH_3), 0.97 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 197.0, 163.7, 157.8, 147.7, 137.2, 131.5, 131.4, 129.4, 128.7, 128.4, 127.0, 124.9, 123.7, 117.9, 117.1, 114.4, 113.6, 55.1, 50.9, 41.4, 33.9, 32.3, 29.3, 27.2. MS (EI) m/z 384 (M^+, 40), 277 (100).

12-(4-Chlorophenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4j). Mp 181–182 °C. ν_{max} (KBr)/cm^{-1} 3133, 2958, 1648, 1596, 1483, 1400, 1375, 1224, 1139, 1009, 841, 747, 535. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.90 (1H, d, $J = 8.5$ Hz, Ar-H), 7.79–7.76 (2H, m, Ar-H), 7.45–7.25 (5H, m, Ar-H), 7.14–7.12 (2H, m, Ar-H), 5.68 (1H, s, CH), 2.56 (2H, s, CH_2), 2.28 (2H, m, CH_2), 1.12 (3H, s, CH_3), 0.96 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 196.9, 164.1, 147.7, 143.3, 131.9, 131.5, 131.2, 129.8, 129.1, 128.5, 128.4, 127.2, 125.0, 123.5, 117.1, 113.9, 50.9, 41.4, 34.2, 32.3, 29.3, 27.1. MS (EI) m/z 388 (M^+, 15), 221 (20), 277 (100).

12-Ethyl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4k). ν_{max} (KBr)/cm^{-1} 3130, 2960, 1651, 1595, 1394, 1225, 1177, 1145, 813, 748, 649, 480. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.10 (1H, d, $J = 8.0$ Hz, Ar-H), 7.82 (1H, d, $J = 8.0$ Hz, Ar-H), 7.70 (1H, d, $J = 9.0$ Hz, Ar-H), 7.56–7.53 (1H, m, Ar-H), 7.45–7.42 (1H, m, Ar-H), 7.20 (1H, d, $J = 8.5$ Hz, Ar-H), 4.74 (1H, t, $J = 4.0$ Hz, CH), 2.55 (2H, d, $J = 3.5$ Hz, Ar-H), 2.37 (2H, d, $J = 4.5$ Hz, Ar-H), 1.86–1.83 (2H, m, CH_2), 1.20 (3H, s, CH_3), 1.16 (3H, s, CH_3), 0.61 (3H, t, $J = 7.5$ Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 197.6, 166.3, 148.7, 131.5, 131.2, 128.6, 128.0, 126.7, 124.8, 123.3, 117.7, 116.8, 112.1, 51.1, 41.4, 32.2, 29.7, 28.7, 27.4, 27.3, 9.0. MS (EI) m/z 305 ($[M-1]^+$, 2), 85 (100), 124 (60), 221 (65), 275 (90).

12-*tert*-Butyl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4l). Mp 110–111 °C. ν_{max} (KBr)/cm^{-1} 3125, 2962, 1642, 1592, 1394, 1220, 1176, 1005, 812, 750, 616, 490. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.21 (1H, d, $J = 9.0$ Hz, Ar-H), 7.80 (1H, d, $J = 8.0$ Hz, Ar-H), 7.72 (1H, d, $J = 9.0$ Hz, Ar-H), 7.52–7.49 (1H, m, Ar-H), 7.43–7.40 (1H, m, Ar-H), 7.28 (1H, d, $J = 9.0$ Hz, Ar-H), 4.62 (1H, s, CH), 2.65 (1H, d, $J = 18.0$ Hz, CH_2), 2.52 (1H, d, $J = 18.0$ Hz, CH_2), 2.42 (1H, d, $J = 16.5$ Hz, CH_2), 2.28 (1H, d, $J = 16.5$ Hz, CH_2), 1.27 (3H, s, CH_3), 1.14 (3H, s, CH_3), 0.78 (9H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 197.2, 167.6, 150.6, 132.7, 131.3, 128.2 (CH), 127.8, 126.0, 124.6, 118.4, 116.8, 113.9, 51.0, 41.6, 40.0, 35.9, 31.7, 30.1, 27.8, 27.4. MS (EI) m/z 277 ([M − 57]$^+$, 100), 165 (45), 221 (30).

9,9-Dimethyl-12-(thiophen-2-yl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (4m). Mp 180–181 °C. ν_{max} (KBr)/cm^{-1} 3105, 2958, 1651, 1593, 1376, 1224, 1177, 1147, 1009, 813, 746, 700, 661, 507. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.04 (1H, d, $J = 8.5$ Hz, Ar-H), 7.82–7.78 (2H, m, Ar-H), 7.51–7.30 (3H, m, Ar-H), 7.01–7.00 (1H, m, CH), 6.77–6.74 (2H, m, CH), 6.04 (1H, s, CH), 2.57 (2H, s, CH_2), 2.35 (2H, s, CH_2), 1.14 (3H, s, CH_3), 1.05 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 196.8, 164.6, 148.6, 147.8, 131.4, 129.1, 128.4, 127.2, 126.3, 125.1, 125.0, 124.0, 123.5, 117.2, 117.1, 113.8, 50.9, 41.4, 32.3, 29.4, 29.3, 27.2. MS (EI) m/z 360 (M$^+$, 75), 165 (55), 221 (50), 277 (100), 327 (60).

11-Phenyl-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6a). Mp 237–238 °C. ν_{max} (KBr)/cm^{-1} 3391, 3125, 1705, 1667, 1596, 1377, 1232, 1101, 1011, 942, 811, 747, 696, 528, 509. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84–7.77 (3H, m, Ar-H), 7.40–7.38 (3H, m, Ar-H), 7.28–7.26 (2H, m, Ar-H), 7.21–7.18 (2H, m, Ar-H), 7.12–7.09 (1H, m, Ar-H), 5.58 (1H, s, CH), 2.84–2.73 (2H, m, CH_2), 2.55–2.45 (2H, m, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 202.5, 177.1, 149.2, 143.6, 131.8, 131.7, 129.6, 128.5, 128.4, 128.2, 127.2, 126.6, 125.2, 124.2, 118.9, 117.4, 116.1, 36.0, 33.8, 25.4. MS (EI) m/z 312 (M$^+$, 20), 235 (100).

11-(3-Hydroxyphenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6d). Mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.23 (1H, s, OH), 7.99–7.86 (3H, m, Ar-H), 7.54–7.42 (4H, m, Ar-H), 7.00–6.96 (1H, m, Ar-H), 6.69 (1H, d, $J = 8.0$ Hz, Ar-H), 6.55–6.46 (2H, m, Ar-H), 5.41 (1H, s, CH), 2.90–2.76 (2H, m, CH_2), 2.51–2.41 (2H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 201.4, 176.8, 157.2, 148.4, 145.3, 131.3, 131.1, 129.6, 129.1, 128.4, 127.0, 125.1, 123.9, 118.8, 117.9, 117.4, 116.0, 114.9, 113.4, 35.1, 33.5, 24.7. MS (ESI) m/z 329.1 ([M + 1]$^+$, 100). HRMS (EI): calcd. for $C_{22}H_{16}O_3$ [M$^+$]: 328.1099; found: 328.1106.

11-(3-Methoxyphenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6f). Mp 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83–7.78 (3H, m, Ar-H), 7.41–7.36 (3H, m, Ar-H), 7.13–7.09 (1H, m, Ar-H), 6.85–6.83 (2H, m, Ar-H), 6.66–6.64 (1H, m, Ar-H), 5.55 (1H, s, CH), 3.71 (3H, s, CH_3), 2.80–2.75 (2H, m, CH_2), 2.51–2.49 (2H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 202.3, 177.1, 159.6, 149.2, 145.1, 131.8, 131.7, 129.5, 129.3, 128.4, 127.1, 125.1, 124.1, 120.6, 118.7, 117.3, 115.9, 114.3, 111.6, 55.1, 35.9, 33.7, 25.3. MS (ESI) m/z 343.2 ([M + 1]$^+$, 100). HRMS (EI): calcd. for $C_{23}H_{18}O_3$ [M$^+$]: 342.1256; found: 342.1267.

11-(3,4-Dimethylphenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6h). Mp 223–224 °C. ν_{max} (KBr)/cm^{-1} 3407, 3131, 1709, 1670, 1591, 1396, 1237, 943, 825, 746, 498. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.83–7.79 (3H, m, Ar-H), 7.40–7.36 (3H, m, Ar-H), 7.03–6.93 (3H, m, Ar-H), 5.50 (1H, s, CH), 2.79–2.75 (2H, m, CH_2), 2.50–2.47 (2H, m, CH_2), 2.13 (3H, s, CH_3), 2.12 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 202.5, 177.1, 149.2, 141.2, 136.6, 134.8, 131.9, 131.8, 129.7, 129.4, 129.3, 128.4, 127.1, 125.5, 125.1, 124.2, 119.2, 117.4, 116.5, 35.5, 33.8, 25.3, 19.9, 19.4. MS (EI) m/z 340 (M^+, 10), 178 (22), 235 (100).

11-(4-Chlorophenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6j). Mp 233–234 °C. ν_{max} (KBr)/cm^{-1} 3426, 3131, 1699, 1658, 1396, 1233, 1088, 1013, 9445, 819, 744, 527. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.85–7.82 (2H, m, Ar-H), 7.71–7.69 (1H, m, Ar-H), 7.41–7.38 (3H, m, Ar-H), 7.21–7.15 (4H, m, Ar-H), 5.55 (1H, s, CH), 2.84–2.75 (2H, m, CH_2), 2.56–2.45 (2H, m, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 202.4, 177.2, 149.2, 142.0, 132.4, 131.8, 131.6, 129.9, 129.5, 128.7, 128.6, 127.3, 125.3, 124.0, 118.3, 117.4, 115.5, 35.5, 33.8, 25.4. MS (EI) m/z 346 (M^+, 10), 141 (20), 235 (100).

11-Ethyl-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6k). Mp 166–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (1H, d, $J = 8.4$ Hz, Ar-H), 7.83 (1H, d, $J = 8.0$ Hz, Ar-H), 7.73 (1H, d, $J = 8.4$ Hz, Ar-H), 7.57–7.44 (2H, m, Ar-H), 7.24 (1H, d, $J = 8.0$ Hz, Ar-H), 4.61 (1H, s, CH), 2.92–2.55 (4H, m, CH_2), 2.00–1.89 (2H, m, CH_2), 0.61 (3H, t, $J = 7.6$ Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 203.3, 179.8, 149.4, 131.7, 131.4, 128.6, 126.8, 125.0, 123.3, 117.4, 117.1, 116.8, 33.9, 29.8, 26.6, 25.2, 9.0. MS (ESI) m/z 265.2 ($[M + 1]^+$, 100). HRMS (EI): calcd. for $C_{18}H_{16}O_2$ [M^+]: 264.1150; found: 264.1156.

11-(Furan-2-yl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6n). Mp 220–222 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 (1H, d, $J = 8.4$ Hz, Ar-H), 7.84–7.81 (2H, m, Ar-H), 7.52–7.42 (2H, m, Ar-H), 7.35 (1H, d, $J = 8.8$ Hz, Ar-H), 7.18 (1H, m, CH), 6.20–6.19 (1H, m, CH), 6.08 (1H, d, $J = 7.2$ Hz, CH), 5.68 (1H, s, CH), 2.93–2.76 (2H, m, CH_2), 2.64–2.54 (2H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 202.4, 178.6, 155.2, 149.0, 141.8, 132.1, 131.8, 129.9, 128.7, 127.4, 125.5, 123.8, 117.7, 114.2, 110.5, 106.9, 34.0, 29.7, 25.6. MS (EI) m/z 302.2 (M^+, 30). HRMS (EI): calcd. for $C_{20}H_{14}O_3$ [M^+]: 302. 0943; found: 302.0951.

11-(2,4-Dimethoxyphenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6o). Mp 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.00 (1H, d, J 8.4 Hz, Ar-H), 7.77–7.73 (2H, m, Ar-H), 7.42–7.31 (3H, m, Ar-H), 6.93 (1H, d, $J = 8.4$ Hz, Ar-H), 6.42–6.29 (2H, m, Ar-H), 5.80 (1H, s, CH), 3.93 (3H, s, OCH_3), 3.69 (3H, s, OCH_3), 2.80 (2H, s, CH_2), 2.47 (2H, s, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 202.5, 177.3, 159.4, 157.3, 148.8, 132.0, 131.6, 130.5, 128.8, 128.2, 126.9, 125.4, 124.9, 124.0, 119.3, 117.7, 117.2, 105.3, 99.0, 56.1, 55.1, 33.8, 29.1, 25.3. MS (ESI) m/z 373.1 ($[M + 1]^+$, 100). HRMS (EI): calcd. for $C_{24}H_{20}O_4$ [M^+]: 372.1362; found: 372.1371.

11-(Benzo[d][1,3]dioxol-5-yl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6p). Mp 228–230 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83–7.80 (3H, m, Ar-H), 7.41–7.35 (3H, m, Ar-H), 6.81–6.78 (1H, m, Ar-H), 6.69–6.63 (2H, m,

Ar-H), 5.83 (2H, d, $J = 13.6$ Hz, Ar-H), 5.49 (1H, s, CH), 2.84–2.72 (2H, m, CH_2), 2.52–2.49 (2H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 202.4, 176.9, 149.0, 147.7, 146.1, 137.7, 131.8, 129.5, 128.4, 127.1, 125.1, 124.1, 121.4, 118.8, 117.3, 116.1, 108.7, 108.0, 100.8, 35.6, 33.7, 25.3. MS (ESI) m/z 357.1 ($[M + 1]^+$, 100). HRMS (EI): calcd. for $C_{23}H_{16}O_4$ [M^+]: 356.1049; found: 356.1054.

11-Benzyl-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11*H*)-one (6q). Mp 181–182 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.14 (1H, d, $J = 8.4$ Hz, Ar-H), 7.87 (1H, d, $J = 8.0$ Hz, Ar-H), 7.72 (1H, d, $J = 8.8$ Hz, Ar-H), 7.65–7.61 (1H, m, Ar-H), 7.53–7.49 (1H, m, Ar-H), 7.09–6.96 (4H, m, Ar-H), 6.32 (2H, d, $J = 7.2$ Hz, Hz, Ar-H), 4.89 (1H, t, $J = 3.6$ Hz, CH), 3.21–3.20 (2H, m, CH_2), 2.60–2.44 (4H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 203.1, 179.8, 149.4, 137.4, 131.6, 131.2, 129.6, 128.8, 128.7, 127.3, 127.1, 126.1, 125.1, 123.1, 116.9, 116.4, 115.9, 38.6, 33.7, 30.6, 25.0. MS (ESI) m/z 327.2 ($[M + 1]^+$, 100). HRMS (EI): calcd. for $C_{23}H_{18}O_2$ [M^+]: 326.1307; found: 372.1297.

ACKNOWLEDGMENT

We are grateful to the Science and Technology Projects of Zhejiang (Nos. 2008C11046 and 2007C21111) for financial support.

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