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Ruthenium/Yb(OTf)$_3$-cocatalyzed dehydrogenative synthesis of 14-substituted-14-*H*-dibenzo[*a*,*j*]-xanthenes from β-naphthol and alcohols†

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By employing [P^O]$_2$Cl$_2$Ru/Yb(OTf)$_3$ as a new and efficient catalyst system [P^O = 2-(diphenylphosphino)-2,4-dimethylpentan-3-one], readily available, abundant alcohols were firstly employed for dehydrogenative synthesis of 14-substituted-14-*H*-dibenzo[*a*,*j*]xanthenes. Due to the inherent stability of alcohols compared to aldehydes, the presented synthetic protocol is adaptable to a broad substrate scope, there is no need for stringent protection in the whole preparation process, providing the potential to prepare products that are currently inaccessible or challenging to prepare using conventional methods. It is an important complement to the conventional synthetic methodologies.

Introduction

Due to the gradual depletion of the earth's limited resources, the replacement of conventional reagents with abundant and sustainable feedstocks to synthesize valuable products emerges as a significant important subject in modern synthetic chemistry. In recent years, alcohols have been extensively employed as desirable coupling partners for various synthetic purposes.[1] In general, the dehydrogenation of the alcohols leading to *in situ* formation of aldehydes (or ketones) is considered as the key step for substrate activation, and the search for suitable catalyst system which is compatible to both dehydrogenative process and the formation of the final products is the main challenging point.

Xanthenes derivatives constitute an interesting class of oxygen-containing heterocycles that exhibit diverse biological activities including antibacterial,[2] anti-inflammatory,[3] and antiviral activities.[4] In addition, these compounds have also been widely used as dyes in laser technology,[5] functional materials for visualization of biomolecular assemblies[6] and photodynamic therapy,[7] as well as antagonists for paralyzing the action of zoxazolamine.[8] Given these extensive functions, much attention has been focused on developing different methods for the construction of xanthene derivatives in the past decades, involving the cycloacylation of carbamates,[9] trapping of benzynes by phenols,[10] the coupling or condensation reactions of aryloxymagnesium halides with triethylorthoformate,[11] 2-hydroxyaryl aldehydes with 2-tetralone,[12] β-naphthols with (1) 2-naphthol-1-methanol,[13a] (2) formamide,[13b] (3) carbon monoxide,[13c] (4) acetals[13d] and (5) aldehydes.[14] However, many of these methods suffer from the drawbacks such as the need of pre-functionalization step, the use of less environmentally friendly reagents, the generation of stoichiometric amount of undesirable wastes. Although the condensation of β-naphthols with aldehydes has provided a simple and straightforward pathway to the related end.[14] However, the use of aldehydes as reaction reagents could frequently meet the following problems: (1) the active carbonyl site may easily undergo an oxidation or decarbonylation step, leading to formation of undesirable by-products unless the synthetic operation follows stringent protection under inert gas,[15] or avoids harsh reaction conditions such as high temperature.[16] (2) Some aldehydes are of high cost or not readily available, the method for variation of xanthene derivatives is hence restricted. Given these factors, the search for readily available, inexpensive and stable alternatives of aldehydes would provide new access to the xanthene derivatives.

Considering alcohols could be desirable aldehyde alternatives in some cases, we wish to develop a new method for direct synthesis of 14-aryl (alkyl)-14-*H*-dibenzo[*a*,*j*]xanthenes from alcohols and β-naphthols by employing suitable catalyst system. In such a transformation, the alcohol coupling partners would exhibit some significant advantages such as cost-effectiveness, thermodynamic stability, abundance and sustainability comparing to aldehydes. Most importantly, using alcohols to condense with β-naphthols would provide the potential to prepare the products that are currently inaccessible or challenging to prepare using the conventional methods.

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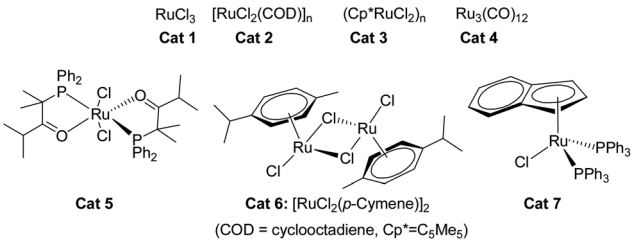
Results and discussion

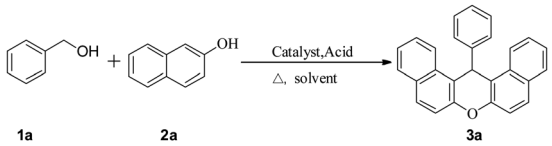
With the aforedescribed idea in mind, we initiate our work by choosing the synthesis of 14-phenyl-14-*H*-dibenzo[*a*,*j*]xanthene **3a** from phenylmethanol **1a** and β-naphthol **2a** as a model reaction to evaluate different reaction parameters, so that we could obtain an efficient catalyst system and the optimal reaction conditions. Firstly, the reaction was performed at 110 °C by using *para*-toluenesulfonic acid (*p*-TSA) as a catalyst and toluene as the reaction solvent, but it failed to give even trace amount of product (Table 1, entry 1). Gratifyingly, a 23% yield of desired product was formed by introducing 1 mol% of $RuCl_3$ to the same reaction system (Table 1, entry 2). However, the reaction resulted in no product detected while $RuCl_3$ was used as a sole catalyst (Table 1, entry 3). Based on these results, the formation of product is believed by cooperative actions of ruthenium-catalysed dehydrogenation of alcohols[1] and acid-catalysed condensation of benzaldehyde with β-naphthol **2a**.[14]

Subsequently, we tried to improve the reaction efficiency by screening the combinations of other six ruthenium catalyst precursors (Scheme 1, **Cat 2–Cat 7**) with *p*-TSA (Table 1, entries 4–9). The results showed that the bis(P^O) ruthenium(II) complex (Scheme 1, **Cat 5**) gave the best activity in the formation of **3a** upon GC analysis (Table 1, entry 7). By using **Cat 5** as the preferred ruthenium catalyst, various other acidic catalysts were then tested for model reaction (Table 1, entries 10–13), $Yb(OTf)_3$ gave a highest product yield. Next, we combined **Cat 5** with $Yb(OTf)_3$, several other organic solvents were further evaluated for the synthesis of **3a**. However, the results indicated that these solvents are less effective than that of toluene (Table 1, entries 14–16). Finally, the decrease of reaction temperature or the catalyst loading led to decreased product yields (Table 1, entries 17, 18 and 21). In contrast, the increase of these reaction parameters could not afford improved yields (Table 1, entries 19, 20 and 22). Hence, the optimized reaction conditions are as follows: 1 mol% of **Cat 5**, 10 mol% of $Yb(OTf)_3$, toluene as the reaction solvent, and at 110 °C (Table 1, entry 13).



Scheme 1 Catalysts employed for optimization of reaction conditions.

Table 1 Optimization of reaction conditions[a]

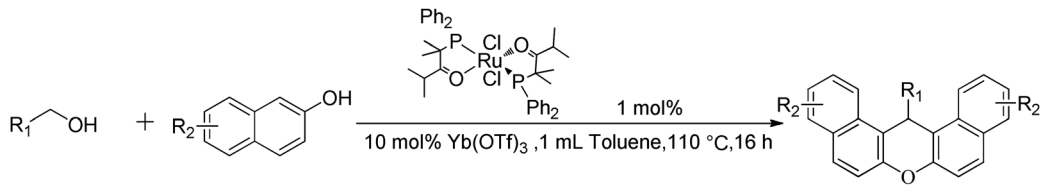


Entry	Ru-cat	Acid-cat	Solvent	**3a**, yield[b]%
1	—	*p*-TSA	Toluene	—
2	**Cat 1**	*p*-TSA	Toluene	23
3	**Cat 1**	—	Toluene	—
4	**Cat 2**	*p*-TSA	Toluene	26
5	**Cat 3**	*p*-TSA	Toluene	<5
6	**Cat 4**	*p*-TSA	Toluene	35
7	**Cat 5**	*p*-TSA	Toluene	56
8	**Cat 6**	*p*-TSA	Toluene	50
9	**Cat 7**	*p*-TSA	Toluene	33
10	**Cat 5**	NH_2SO_3H	Toluene	<5
11	**Cat 5**	$FeCl_3$	Toluene	<5
12	**Cat 5**	AgOTf	Toluene	32
13	**Cat 5**	$Yb(OTf)_3$	Toluene	83
14	**Cat 5**	$Yb(OTf)_3$	Dioxane	21
15	**Cat 5**	$Yb(OTf)_3$	DMSO	<10
16	**Cat 5**	$Yb(OTf)_3$	DMF	<10
17[c]	**Cat 5**	$Yb(OTf)_3$	Toluene	70
18[d]	**Cat 5**	$Yb(OTf)_3$	Toluene	76
19[e]	**Cat 5**	$Yb(OTf)_3$	Toluene	79
20[f]	**Cat 5**	$Yb(OTf)_3$	Toluene	83
21[g]	**Cat 5**	$Yb(OTf)_3$	Toluene	72
22[h]	**Cat 5**	$Yb(OTf)_3$	Toluene	82

[a] Reaction conditions: unless otherwise specified, all reactions were carried out without inert gas protection by using **1a** (1.5 mmol), **2a** (1 mmol), catalyst (1 mol%), solvent (1 mL), temperature (110 °C), acid (10 mol%), reaction time (16 h). [b] GC yield using hexadecane as an internal standard. [c] Reaction temperature (100 °C). [d] Loading of **Cat 5** (0.8 mol%). [e] Reaction temperature (120 °C). [f] Loading of **Cat 5** (1.5 mol%). [g] Acid catalyst loading (5 mol%). [h] Acid catalyst loading (15 mol%).

After optimizing the reaction conditions, we examined the generality of our synthetic protocol. Various aryl methanols were firstly reacted with β-naphthols to generate the corresponding 14-aryl-14-*H*-dibenzo[*a*,*j*]xanthenes. As shown in Table 2, all the reactions proceeded smoothly and gave the desired products in moderate to excellent yields upon GC analyses (Table 2, see **3a–3n**). It was found that the substituents on the aryl ring of the aldehydes slightly affected the product yields. Comparing to electron-rich benzylic alcohols (*i.e.* –Me) (Table 2, entries 7 and 14), the ones containing an electron-withdrawing group (such as –Cl, $-NO_2$) furnished the products in relatively higher yields (Table 2, entries 2–6 and 9–13). On the other hand, the reactions using nitro-substituted aryl methanols (see **1e** and **1f**) afforded lower product yields than that of chloro-substituted aryl methanols (see **1b–1d**), which is attributed to the *in situ* generated nitrobenzaldehydes arising from ruthenium-catalysed dehydrogenation of nitro-substituted aryl methanols are less stable than chloro-benzaldehyde intermediates (Table 2, comparing entries 2–4 with entries 5 and 6, entries 9–11 with entries 12 and 13). Notably, the products possessing halogenated groups have the potential for further elaboration of complex molecules *via* the classical coupling reactions. To further expand the substrate scope, we next tested the utilization of simple, abundant and readily-available primary alkyl alcohols as the coupling partners for the synthesis of 14-alkyl-14-*H*-dibenzo[*a*,*j*]xanthenes. Interestingly, all the reactions underwent

Table 2 Efficient synthesis of 14-substituted-14-*H*-dibenzo[*a*,*j*]xanthenes from β-naphthol and alcohols[a]



1 2 3

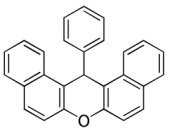
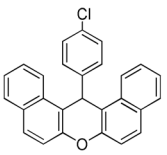
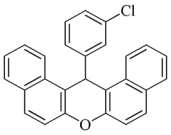
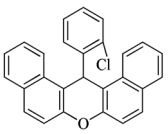
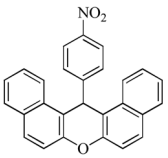
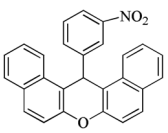
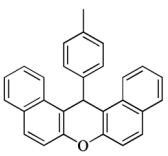
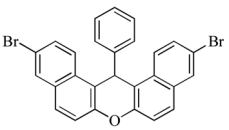
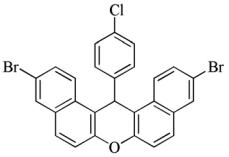
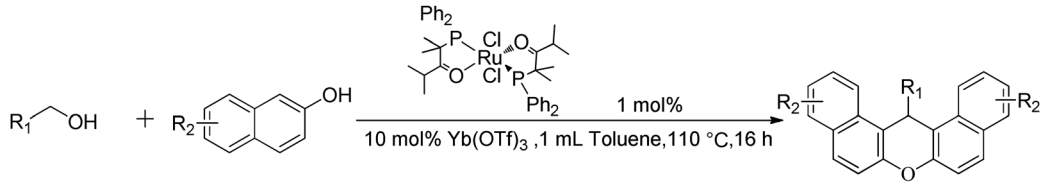
Entry	Alcohol **1**	β-Naphthol **2**	Product **3**	Yield[b] (%)
1	**1a:** R^1 = Ph	**2a:** R^2 = H		**3a,** 83
2	**1b:** R^1 = 4-Cl–C_6H_4	**2a**		**3b,** 85
3	**1c:** R^1 = 3-Cl–C_6H_4	**2a**		**3c,** 80
4	**1d:** R^1 = 2-Cl–C_6H_4	**2a**		**3d,** 78
5	**1e:** R^1 = 4-NO_2–C_6H_4	**2a**		**3e,** 71
6	**1f:** R^1 = 3-NO_2–C_6H_4	**2a**		**3f,** 74
7	**1g:** R^1 = 4-CH_3–C_6H_4	**2a**		**3g,** 66
8	**1a**	**2b:** R^2 = 6-Br		**3h,** 77
9	**1b**	**2b**		**3i,** 78

Table 2 (*Contd.*)



1 **2** **3**

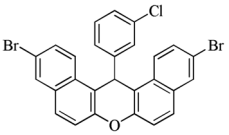
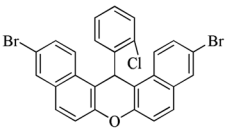
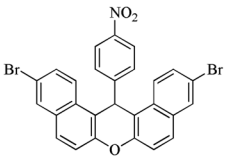
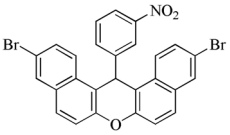
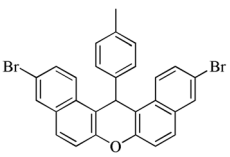
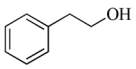
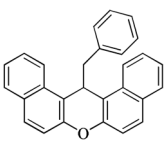
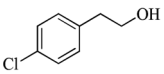
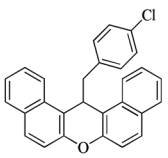
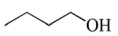
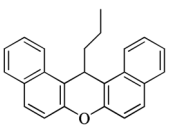
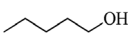
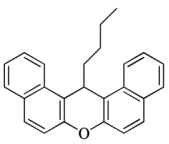
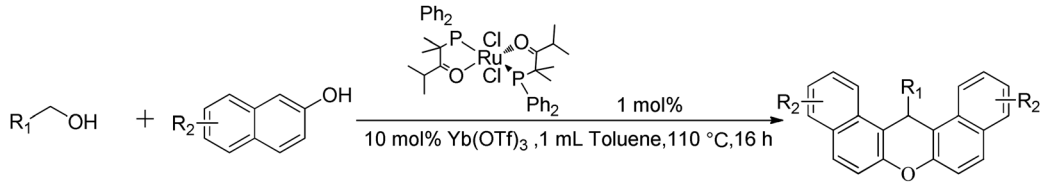
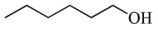
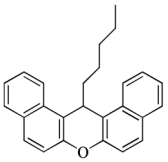
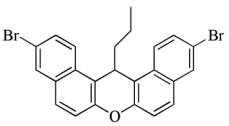
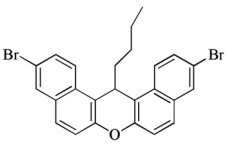
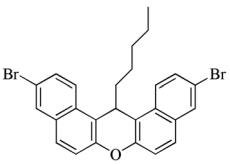
Entry	Alcohol **1**	β-Naphthol **2**	Product **3**	Yield[b] (%)
10	**1c**	**2b**		**3j**, 72
11	**1d**	**2b**		**3k**, 70
12	**1e**	**2b**		**3l**, 65
13	**1f**	**2b**		**3m**, 68
14	**1g**	**2b**		**3n**, 60
15	**1k**: 	**2a**		**3o**, 58
16	**1l**: 	**2a**		**3p**, 62
17	**1h**: 	**2a**		**3q**, 60
18	**1i**: 	**2a**		**3r**, 63

Table 2 (*Contd.*)



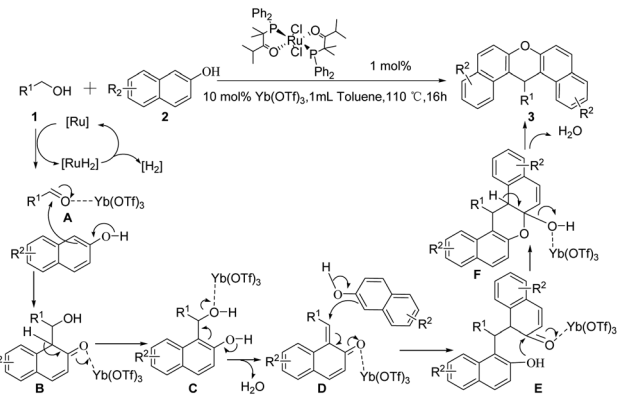
1 **2** **3**

Entry	Alcohol **1**	β-Naphthol **2**	Product **3**	Yield[b] (%)
19	**1j**: 	**2a**		**3s**, 61
20	**1h**	**2b**		**3t**, 57
21	**1i**	**2b**		**3u**, 59
22	**1j**	**2b**		**3v**, 56

[a] Reaction conditions: unless otherwise specified, all reactions were performed without inert gas protection by using **1** (1.5 mmol), **2** (1 mmol), **Cat 5** (1 mol%), $Yb(OTf)_3$ (10 mol%), toluene (1 mL), temperature (110 °C), reaction time (16 h). [b] GC yield using hexadecane as an internal standard.

efficiently to furnish the expected products in moderate to good yields upon GC analyses (Table 2, entries 15–22). Given these findings, our synthetic protocol is suitable for the application of both aryl methanols and alkyl primary alcohols.

On the basis of the above-described experimental facts as well as the acid-catalysed condensation of aryl aldehydes with β-naphthols,[14] a plausible reaction is depicted in Scheme 2. The reaction initiates with the dehydrogenation of alcohols catalyzed by ruthenium catalyst. The *in situ* formed aldehyde **A** is activated by Lewis acid $Yb(OTf)_3$, then followed by a nucleophilic attack of the α-carbon in the β-naphthol to form intermediate **B**. 1,3-Hydrogen shift of **B** would afford **C**. Enone **D** is then produced *via* elimination of one molecule of water from **C**, which is activated by $Yb(OTf)_3$ and acts as a Michael acceptor. Afterwards, the Michael addition of another molecule of β-naphthols to the carbon–carbon double bond of **D** would afford intermediate **E**. The subsequent nucleophilic addition of hydroxyl group to the activated carbonyl group generates a polycyclic intermediate **F**. Finally, thermodynamic favourable dehydration of **F** releases the desired product **3**.



Scheme 2 Plausible mechanism for the formation of product **3**.

Conclusions

In summary, we have presented a new and straightforward $[P^O]_2Cl_2Ru/Yb(OTf)_3$-cocatalyzed synthesis of 14-aryl- and 14-alkyl-14-*H*-dibenzo[*a*,*j*]xanthenes by using stable, abundant, readily-available and sustainable alcohols as the reaction partners. All the dehydrogenative cyclization process underwent efficiently to furnish the desired products in moderate to excellent isolated yields. The method is adaptable to a broad substrate scope, and has the potential to prepare the compounds that are currently inaccessible or challenging to prepare using the conventional methods. In addition, the whole work-up procedure is operationally simple and there is no need for special protection. Hence, we believe this new synthetic protocol is of high importance that complements the existing synthetic methodologies. Given the importance of 14-aryl- and 14-alkyl-14-*H*-dibenzo[*a*,*j*]xanthenes in various fields, our presented method has the potential to be frequently used for many synthetic purposes.

Experimental

General information

All the obtained products were characterized by melting points (mp), ^{1}H-NMR, ^{13}C-NMR infrared spectra (IR), the ^{1}H-NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, the new products were further determined by high resolution mass spectra (HR-MS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; all the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for the synthesis of 3a

In a schlenk tube equipped with a magnetic stirrer bar, benzyl alcohol **1a** (1.5 mmol, 162.2 mg), β-naphthol **2a** (1 mmol, 144.2 mg), $[P^O]_2Cl_2Ru$ (**Cat 5**, 0.005 mmol, 3.8 mg) and $Yb(OTf)_3$ (0.05 mmol, 31.0 mg) and toluene (1 mL) were introduced successively. The resulting mixture was stirred at 110 °C for 16 h without insert any gas protection. After cooling down to room temperature, the reaction solvent was removed under vacuum, the residue was directly purified by flash chromatography on silica gel eluting with petroleum ether : ethyl acetate (30 : 1) to give 14-phenyl-14-*H*-dibenzo[*a*,*j*]xanthene **3a** as a white solid.

Analytic data of obtained compounds

14-Phenyl-14-*H*-dibenzo[*a*,*j*]xanthene (3a). White solid, mp: 191–192 °C (lit.[14f] 185 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.5 Hz, 2H), 7.80 (dd, J = 14.3, 8.5 Hz, 4H), 7.62–7.42 (m, 6H), 7.39 (t, J = 7.4 Hz, 2H), 7.13 (t, J = 7.7 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.48 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.76, 145.01, 131.48, 131.08, 128.86, 128.80, 128.48, 128.27, 126.79, 126.39, 124.24, 122.70, 118.02, 117.35, 38.05; IR (KBr): 3075, 1592, 1458, 1243, 964, 827, 803, 745, 701 cm^{-1}.

14-(4-Chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3b). Light yellow solid, mp: 296 °C (lit.[14f] 289 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.5 Hz, 2H), 7.81 (dd, J = 14.3, 8.5 Hz, 4H), 7.57 (t, J = 7.7 Hz, 2H), 7.52–7.35 (m, 6H), 7.09 (d, J = 8.4 Hz, 2H), 6.46 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.72, 143.47, 132.10, 131.27, 131.07, 129.49, 129.09, 128.92, 128.64, 126.91, 124.37, 122.41, 118.01, 116.77, 37.38; IR (KBr): 3069, 1592, 1475, 1240, 1103, 832, 807, 741 cm^{-1}.

14-(3-Chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3c). White solid, mp: 204–205 °C (lit.[14n] 210–211 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.5 Hz, 2H), 7.79 (dd, J = 13.9, 8.5 Hz, 4H), 7.57 (t, J = 7.7 Hz, 2H), 7.51–7.35 (m, 6H), 7.05 (t, J = 8.1 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.79, 146.89, 134.42, 131.28, 131.07, 129.60, 129.16, 128.90, 128.34, 126.96, 126.75, 126.40, 124.38, 122.40, 118.07, 116.58, 37.75; IR (KBr): 3067, 1591, 1456, 1246, 1082, 964, 813, 746 cm^{-1}.

14-(2-Chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3d). White solid, mp: 201–202 °C (lit.[14f] 215 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 8.5 Hz, 2H), 7.83–7.73 (m, 4H), 7.59 (t, J = 7.1 Hz, 2H), 7.49–7.34 (m, 5H), 7.25–7.21 (m, 1H), 6.88 (pd, J = 7.2, 1.8 Hz, 2H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.99, 143.60, 131.80, 131.79, 130.93, 129.61, 129.06, 128.64, 127.93, 127.85, 126.91, 124.42, 123.46, 118.09, 118.03, 34.69; IR (KBr): 3056, 1593, 1472, 1108, 827, 811, 749 cm^{-1}.

14-(4-Nitrophenyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3e). Light yellow solid, mp: 327–329 °C (lit.[14f] 310 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.84 (t, J = 7.6 Hz, 4H), 7.73–7.55 (m, 4H), 7.54–7.33 (m, 4H), 6.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.00, 148.80, 146.33, 131.09, 129.59, 129.06, 128.96, 127.19, 124.58, 123.86, 122.04, 118.06, 115.78, 37.86; IR (KBr): 3071, 1592, 1515, 1340, 1239, 1107, 827, 808, 750 cm^{-1}.

14-(3-Nitrophenyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3f). Light yellow solid, mp: 223–225 °C (lit.[14f] 211 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (t, J = 1.8 Hz, 1H), 8.21 (d, J = 8.5 Hz, 2H), 7.73 (q, J = 8.1 Hz, 6H), 7.56–7.48 (m, 2H), 7.41 (d, J = 8.9 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.17 (d, J = 8.3 Hz, 1H), 6.50 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.84, 148.26, 146.93, 134.22, 131.07, 131.04, 129.56, 129.49, 129.06, 127.24, 124.57, 122.71, 122.02, 121.68, 118.12, 115.90, 37.72; IR (KBr): 3080, 1621, 1593, 1458, 1097, 825, 808, 723 cm^{-1}.

14-(4-Tolyl)-14-*H*-dibenzo[*a*,*j*]xanthenes (3g). Yellow solid, mp: 228–229 °C (lit.[14f] 229 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.5 Hz, 2H), 7.79 (dd, J = 15.9, 8.5 Hz, 4H), 7.56 (t, J = 7.7 Hz, 2H), 7.53–7.32 (m, 6H), 6.94 (d, J = 7.6 Hz, 2H), 6.45 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.70, 142.12, 135.89, 131.46, 131.09, 129.17, 128.78, 128.74, 128.09, 126.75,

124.20, 122.71, 118.00, 117.46, 37.62, 20.88; IR (KBr): 3071, 2917, 1621, 1591. 1458, 1248, 1107, 961, 808, 739 cm^{-1}.

3,11-Dibromo-14-phenyl-14-*H*-dibenzo[*a*,*j*]xanthene (3h). White solid, mp: 249–251 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, $J = 9.0$ Hz, 2H), 7.98 (d, $J = 1.7$ Hz, 2H), 7.79–7.57 (m, 4H), 7.48 (dd, $J = 13.1$, 8.2 Hz, 4H), 7.17 (t, $J = 7.7$ Hz, 2H), 7.04 (t, $J = 7.4$ Hz, 1H), 6.35 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.66, 144.39, 132.28, 130.74, 130.09, 129.91, 128.64, 128.06, 126.72, 124.40, 119.12, 118.25, 117.19, 38.11; IR (KBr): 3060, 1583, 1500, 1451, 1247, 1107, 961, 892, 796 cm^{-1}; HRMS calcd for $C_{27}H_{16}Br_2O$: 513.96, found: 513.9568.

3,11-Dibromo-14-(4-chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3i). White solid, mp: 295–297 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, $J = 9.0$ Hz, 2H), 7.98 (d, $J = 1.9$ Hz, 2H), 7.74–7.59 (m, 4H), 7.47 (d, $J = 8.9$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.33 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.66, 142.80, 132.53, 132.29, 130.89, 130.24, 129.73, 129.28, 128.84, 128.32, 124.11, 119.15, 118.39, 116.67, 37.44; IR (KBr): 3075, 1584, 1455, 1253, 1105, 964, 838, 800 cm^{-1}; HRMS calcd for $C_{27}H_{15}Br_2ClO$: 547.92, found: 547.9176.

3,11-Dibromo-14-(3-chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3j). White solid, mp: 263–264 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, $J = 9.0$ Hz, 2H), 7.96 (d, $J = 2.0$ Hz, 2H), 7.74–7.57 (m, 4H), 7.47 (d, $J = 8.9$ Hz, 2H), 7.35 (dd, $J = 8.8$, 4.8 Hz, 2H), 7.09 (t, $J = 7.8$ Hz, 1H), 7.03–6.94 (m, 1H), 6.30 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.69, 146.27, 134.68, 132.27, 130.87, 130.26, 129.77, 129.71, 128.38, 128.16, 127.10, 126.17, 124.08, 119.19, 118.40, 116.44, 37.77; IR (KBr): 3071, 1585, 1454, 1250, 1107, 961, 872, 805 cm^{-1}; HRMS calcd for $C_{27}H_{15}Br_2ClO$: 547.92, found: 547.9178.

3,11-Dibromo-14-(2-chlorophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3k). White solid, mp: 217–219 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, $J = 9.1$ Hz, 2H), 7.90 (d, $J = 2.0$ Hz, 2H), 7.65–7.59 (m, 4H), 7.41 (d, $J = 8.9$ Hz, 2H), 7.22 (d, $J = 4.3$ Hz, 2H), 6.93–6.85 (m, 2H), 6.53 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.79, 142.94, 132.10, 131.63, 130.57, 130.21, 130.19, 129.89, 129.70, 128.23, 128.18, 128.10, 125.21, 119.15, 118.52, 117.76, 34.56; IR (KBr): 3060, 1631, 1588, 1458, 1259, 1105, 964, 881, 837, 738 cm^{-1}; HRMS calcd for $C_{27}H_{15}Br_2ClO$: 547.92, found: 547.9176.

3,11-Dibromo-14-(4-nitrophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3l). Yellow solid, mp: 303–305 °C; ^1H NMR (400 MHz, DMSO): δ 8.66 (d, $J = 9.1$ Hz, 2H), 8.25 (d, $J = 1.8$ Hz, 2H), 8.00 (dd, $J = 19.3$, 8.9 Hz, 4H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.77 (dd, $J = 9.0$, 1.9 Hz, 2H), 7.65 (d, $J = 9.0$ Hz, 2H), 6.94 (s, 1H); ^{13}C NMR (101 MHz, DMSO): δ 152.07, 148.20, 145.94, 132.02, 130.49, 129.94, 129.36, 128.94, 128.89, 125.56, 123.79, 119.00, 117.97, 116.34, 36.03; IR (KBr): 3075, 1585, 1515, 1397, 1253, 1108, 957, 834, 797 cm^{-1}; HRMS calcd for $C_{27}H_{15}Br_2NO_3$: 558.94, found: 558.9418.

3,11-Dibromo-14-(3-nitrophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3m). Light yellow solid, mp: 159–161 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.16 (d, $J = 9.0$ Hz, 2H), 8.02 (d, $J = 1.8$ Hz, 2H), 7.92 (d, $J = 8.1$ Hz, 1H), 7.80–7.75 (m, 3H), 7.70 (dd, $J = 9.0$, 1.9 Hz, 2H), 7.54 (d, $J = 8.9$ Hz, 2H), 7.35 (t, $J = 8.0$ Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.80, 148.38, 146.32, 133.90, 132.29, 131.06, 130.56, 129.69, 129.51, 128.79, 123.69, 122.54, 122.00, 119.26, 118.60, 115.83, 37.73; IR (KBr): 3065, 1614, 1586, 1396, 1258, 1112, 960, 890, 815 cm^{-1}; HRMS calcd for $C_{27}H_{15}Br_2NO_3$: 558.94, found: 558.9419.

3,11-Dibromo-14-(*p*-tolyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3n). White solid, mp: 249–251 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (t, $J = 7.5$ Hz, 2H), 7.93 (d, $J = 2.0$ Hz, 2H), 7.67–7.57 (m, 4H), 7.48–7.40 (m, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 7.9$ Hz, 2H), 6.26 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.57, 141.52, 136.35, 132.29, 130.72, 130.04, 129.90, 129.34, 127.97, 127.92, 124.43, 119.11, 118.21, 117.29, 37.70, 20.87; IR (KBr): 3058, 2919, 1584, 1500, 1337, 1249, 1108, 962, 875, 803 cm^{-1}; HRMS calcd for $C_{28}H_{18}Br_2O$: 527.97, found: 527.9724.

14-Benzyl-14-*H*-dibenzo[*a*,*j*]xanthene (3o). White solid, mp: 171–174 °C (lit.[14o] 178 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.9$ Hz, 2H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.5$ Hz, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.93 (t, $J = 7.3$ Hz, 1H), 6.75 (t, $J = 7.5$ Hz, 2H), 6.02 (d, $J = 7.5$ Hz, 2H), 5.70 (t, $J = 4.5$ Hz, 1H), 3.19 (d, $J = 4.6$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.15, 137.58, 131.34, 130.87, 129.77, 128.89, 128.35, 127.21, 126.69, 126.08, 124.04, 122.20, 117.42, 115.33, 41.39, 33.07; IR (KBr): 3064, 2926, 1620, 1591, 1456, 1435, 1244, 1103, 968, 816, 739 cm^{-1}.

14-(4-Chlorobenzyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3p). White solid, mp: 185–187 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, $J = 8.5$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.9$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 2H), 7.07 (d, $J = 8.9$ Hz, 2H), 6.71 (d, $J = 8.3$ Hz, 2H), 5.87 (d, $J = 8.3$ Hz, 2H), 5.72 (t, $J = 4.4$ Hz, 1H), 3.17 (d, $J = 4.5$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.09, 135.92, 132.06, 131.17, 131.01, 130.88, 128.99, 128.51, 127.25, 126.83, 124.14, 122.05, 117.45, 114.64, 40.33, 32.82; IR (KBr): 3062, 2922, 1619, 1591, 1458, 1433, 1242, 1102, 968, 806, 740 cm^{-1}; HRMS calcd for $C_{28}H_{19}ClO$: 406.11, found: 406.1122.

14-Propyl-14-*H*-dibenzo[*a*,*j*]xanthene (3q). White solid, mp: 155–157 °C (lit.[14j] 152–154 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 8.9$ Hz, 2H), 7.52 (ddd, $J = 8.3$, 6.9, 1.2 Hz, 2H), 7.43–7.22 (m, 4H), 5.46 (t, $J = 4.6$ Hz, 1H), 1.92 (dt, $J = 12.7$, 4.6 Hz, 2H), 1.03–0.83 (m, 2H), 0.51 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.01, 131.49, 131.06, 128.86, 128.16, 126.58, 124.08, 122.48, 117.58, 116.78, 38.27, 31.08, 18.17, 14.10; IR (KBr): 3060, 2953, 1590, 1453, 1398, 1241, 1105, 814, 747 cm^{-1}.

14-Butyl-14-*H*-dibenzo[*a*,*j*]xanthene (3r). White solid, mp: 110–112 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, $J = 8.5$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.9$ Hz, 2H), 7.62–7.54 (m, 2H), 7.45–7.32 (m, 4H), 5.53 (t, $J = 4.6$ Hz, 1H), 2.02 (dt, $J = 7.9$, 4.7 Hz, 2H), 1.01–0.89 (m, 4H), 0.57 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.04, 131.51, 131.07, 128.87, 128.18, 126.60, 124.10, 122.50, 117.62, 116.76, 35.81, 31.03, 26.98, 22.86, 13.91; IR (KBr): 3069, 2929, 1592, 1458, 1397, 1239, 1101, 857, 811 cm^{-1}; HRMS calcd for $C_{25}H_{22}O$: 338.17, found: 338.1670.

14-Pentyl-14-*H*-dibenzo[*a*,*j*]xanthene (3s). Light yellow solid, mp: 104–106 °C (lit.[14p] 98–99 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, $J = 8.5$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H), 7.80 (d, $J = 8.9$ Hz, 2H), 7.69–7.60 (m, 2H), 7.55–7.46 (m, 2H), 7.41 (d, $J = 8.9$ Hz, 2H), 5.59 (t, $J = 4.6$ Hz, 1H), 2.13–2.00 (m, 2H), 1.02 (dd, $J = 15.4$, 5.4 Hz, 6H), 0.65 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.01, 131.49, 131.04, 128.83, 128.14, 126.55, 124.06, 122.46, 117.59, 116.77, 35.96, 31.93, 31.03, 24.52, 22.44, 13.89; IR (KBr): 3067, 2930, 1591, 1458, 1433, 1237, 1105, 857, 809 cm^{-1}.

3,11-Dibromo-14-propyl-14-*H*-dibenzo[*a*,*j*]xanthene (3t). Light yellow solid, mp: 153–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 22.2, 5.4 Hz, 4H), 7.74–7.65 (m, 4H), 7.38 (d, J = 8.9 Hz, 2H), 5.41 (t, J = 4.5 Hz, 1H), 1.95 (dt, J = 12.6, 4.6 Hz, 2H), 0.97 (dt, J = 19.4, 7.4 Hz, 2H), 0.68–0.56 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.97, 132.25, 130.82, 129.91, 129.89, 127.39, 124.18, 118.66, 118.04, 116.71, 38.35, 31.09, 18.11, 14.02; IR (KBr): 3066, 2947, 1586, 1453, 1396, 1258, 1113, 960, 890, 816 cm^{-1}; HRMS calcd for $C_{24}H_{18}Br_2O$: 479.97, found: 479.9720.

3,11-Dibromo-14-butyl-14-*H*-dibenzo[*a*,*j*]xanthene (3u). Light yellow solid, mp: 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 21.5, 5.5 Hz, 4H), 7.73–7.64 (m, 4H), 7.39 (d, J = 8.9 Hz, 2H), 5.45–5.32 (m, 1H), 1.98 (dd, J = 16.3, 4.7 Hz, 2H), 0.98 (ddd, J = 17.8, 14.3, 7.3 Hz, 4H), 0.62 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.00, 132.25, 130.82, 129.90, 127.39, 124.17 (s), 118.69, 118.03, 116.71, 35.87, 31.03, 26.86, 22.72, 13.82; IR (KBr): 3066, 2925, 1585, 1453, 1395, 1255, 1106, 963, 884, 812 cm^{-1}; HRMS calcd for $C_{25}H_{20}Br_2O$: 493.99, found: 493.9881.

3,11-Dibromo-14-pentyl-14-*H*-dibenzo[*a*,*j*]xanthene (3v). Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, J = 19.3, 5.4 Hz, 4H), 7.59–7.52 (m, 4H), 7.25 (d, J = 8.9 Hz, 2H), 5.27 (t, J = 4.5 Hz, 1H), 1.84 (dd, J = 11.5, 7.7 Hz, 2H), 0.90–0.80 (m, 6H), 0.52 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.97, 132.24, 130.81, 129.88, 127.38, 124.17, 118.67, 118.03, 116.68, 36.02, 31.80, 31.04, 24.42, 22.38, 13.86; IR (KBr): 3066, 2929, 1585, 1396, 1253, 1106, 955, 878, 806 cm^{-1}; HRMS calcd for $C_{26}H_{22}Br_2O$: 508.00, found: 508.0036.

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