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PAPER

Lewis acid-catalysed one pot synthesis of substituted xanthenes†

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A direct synthesis of substituted xanthenes from salicylaldehydes and cyclohexenones or tetralones has been developed. The reaction is catalysed by Lewis acids like scandium triflate and furnishes substituted xanthenes in good to excellent yields using either microwave or thermal heating. Microwave heating results in significantly shortened reaction times of 30 min and generally higher yields.

Introduction

During the course of our investigations of autooxidative coupling reactions with xanthene,[1] we became interested in using xanthenes with substituents in the aromatic rings but unsubstituted in the 9-position for mechanistic and synthetic studies. We were looking for an efficient synthesis of substituted xanthenes requiring preferably one step from commercially available starting materials whilst avoiding costly reagents. However, the known synthetic protocols were either not considered suitable or proved to be unrewarding in our hands. Here, we present our own development of a Lewis acid-catalysed one-pot synthesis of xanthenes from salicylaldehydes and cyclohexenone derivatives.

Xanthene derivatives are pharmaceutically active compounds, and are used as dyes or fluorescent materials and chiroptical molecular switches; they also occur in natural products.[2] Accordingly, many synthetic methods leading to xanthene derivatives have been described, both with and without substituents in the 9-position.[3–5] Protocols only furnishing 9-substituted xanthenes, giving low yields or requiring multiple steps, were not considered suitable for our project. The reaction of salicylaldehydes with cyclohexanones or cyclohexenones under basic conditions has been widely explored by Bräse *et al.* but only furnished xanthenes in low yields.[4d,5d] Li *et al.* reported the coupling of phenols with *o*-bromo-benzylacetates to xanthenes, including a single product example without substituents in the 9-position,[5b] which we found difficult to reproduce. Jha and Beal have reported the direct synthesis of benzoxanthenes from salicylaldehydes and 2-tetralone catalysed by HCl in acetic acid at around 0 °C.[5e] However, their method did not provide good yields in our hands, and only benzoxanthene products were reported.

We then discovered a largely neglected report by Borsche and Geyer, who investigated acid-mediated reactions between salicylaldehyde and α-methyl cyclohexanone.[5h] They reported that tricyclic benzopyrilium salts, after basic work-up and dry distillation over $ZnCl_2$, gave methyl-substituted xanthene next to di- and tetrahydromethylxanthenes. Prompted by this finding, we investigated the one-pot synthesis of xanthenes from salicylaldehydes using Lewis acids as catalysts.

Results and discussion

We selected 5-methoxysalicylaldehyde (**1a**) and cyclohex-2-enone (**2a**) as test substrates for initial optimisation studies of the reaction (Table 1). Cyclohexenone was chosen as a more suitable starting material, in contrast to the cyclohexanone used by Borsche and Geyer, because it would not require an oxidation step to furnish xanthenes.

Initial studies showed that the desired 2-methoxyxanthene, **3a**, could be formed in 50% yield using catalytic amounts of zinc chloride in refluxing chlorobenzene (Table 1, entry 1). It should be noted that no product formation was observed in the absence of catalyst (Table 1, entry 2). The use of zinc triflate resulted in lower yields of only 23% (Table 1, entry 3). Rare earth metal triflates have been shown to be excellent Lewis acid catalysts in organic transformations.[6] In the above synthesis, they proved to be active Lewis acid catalysts as well, but with yields ranging between 22 and 42% only (Table 1, entries 4–8). Copper triflate was also tested but resulted in only a 23% yield (Table 1, entry 8). An improvement was achieved with scandium triflate, with 55% being the highest yield of the Lewis acids tested (Table 1, entry 9). Scandium catalysts have also been successfully employed in the synthesis of 9-aryl or -alkyl-substituted xanthenes.[4c,5a] Brønsted acids could be used as well, but with less success; triflic acid gave small amounts of the product only (Table 1, entry 10) and sulfuric acid led to substantial decomposition of the starting material. Further optimisations with scandium triflate showed that the catalyst loading could be reduced, and 5 mol% was beneficial with an improved yield of 59% (Table 1, entries 11–13). A high-boiling solvent is needed since toluene, 1,2-dichloroethane and *iso*-hexane gave lower yields that followed the trend of their lower

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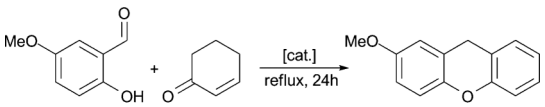
Table 1 Optimisation of the reaction conditions[a]



1a 2a 3a

Entry	1a : 2a	Catalyst	Mol%	Solvent	Yield (%)[b]
1	1 : 1	$ZnCl_2$	20	PhCl	50
2	1 : 1	—	—	PhCl	0
3	1 : 1	$Zn(OTf)_2$	20	PhCl	23
4	1 : 1	$Yb(OTf)_3$	20	PhCl	40
5	1 : 1	$Y(OTf)_3$	20	PhCl	22
6	1 : 1	$Er(OTf)_3$	20	PhCl	42
7	1 : 1	$Sm(OTf)_3$	20	PhCl	23
8	1 : 1	$Cu(OTf)_3$	20	PhCl	23
9	1 : 1	$Sc(OTf)_3$	20	PhCl	55
10	1 : 1	TfOH	20	PhCl	9
11	1 : 1	$Sc(OTf)_3$	15	PhCl	55
12	1 : 1	$Sc(OTf)_3$	5	PhCl	59
13	1 : 1	$Sc(OTf)_3$	3	PhCl	48
14	1 : 1	$Sc(OTf)_3$	5	Toluene	38
15	1 : 1	$Sc(OTf)_3$	5	1,2-DCE	9
16	1 : 1	$Sc(OTf)_3$	5	*iso*-Hexane	7
17	1 : 1.5	$Sc(OTf)_3$	5	PhCl	54
18	1.5 : 1	$Sc(OTf)_3$	5	PhCl	61
19	1.1 : 1	$Sc(OTf)_3$	5	PhCl	63
20[c]	1.1 : 1	$Sc(OTf)_3$	5	PhCl	82

[a] Reaction conditions: 4 mL solvent per 1 mmol **1a**, heating to reflux in an oil bath. [b] Isolated yields. [c] Microwave heating at 180 °C for 30 min.

boiling points (Table 1, entries 14–16). Varying the ratio of the two starting materials revealed that a slight excess of 1.1 equivalents of salicylaldehyde was beneficial to the yield, increasing it up to 63% (Table 1, entries 17–19). A significant improvement could be made by performing the reaction in a sealed tube in a microwave reactor. When performed at a temperature of 180 °C, the reaction took only 30 min to go to completion, giving xanthene **3a** in a yield of 82% (Table 1, entries 20).

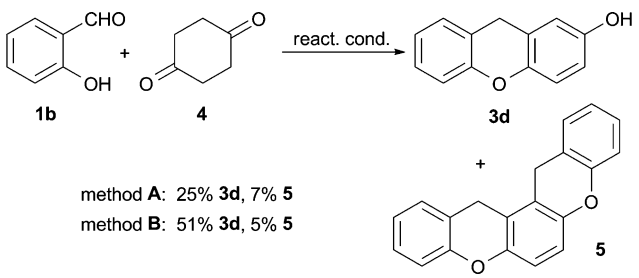
Using the optimised conditions, we synthesised various xanthenes from substituted salicylaldehydes and cyclohexenones or cyclohexenone equivalents such as tetralones (Table 2). Product yields for two different conditions are given, refluxing in chlorobenzene using an oil bath and using a microwave reactor, since the latter might not be available in all laboratories.

The parent compound xanthene (**3b**) could be made in 56% yield by microwave heating and in 50% yield by heating in an oil bath (Table 2, entry 1). Various substituted salicylaldehydes could be employed to synthesise the corresponding xanthenes in low to good yield (Table 2, entries 2–6). Good yields were achieved with methoxy- or methyl-substituted aldehydes (Table 2, entries 2, 3 and 5), while hydroxy or chloro substituents gave lower yields. Microwave heating proved to be especially beneficial in these cases, nearly doubling the yield compared to conventional heating (Table 2, entries 4 and 6). Nitrosalicylaldehyde did not furnish any of the desired product, indicating that strongly electron-withdrawing substituents are not suitable for this method. 3,5-Dimethylcyclohexenone **2b** could be employed with similar results as cyclohexenone itself, giving 1,3-dimethylxanthenes **3g** and **3h** (Table 2, entries 7 and 8). Instead of cyclohexenone, α- and β-tetralone (**2c** and **2d**) could be employed as well, giving benzo-fused xanthenes in excellent yields (Table 2, entries 9–12). Using hydroxynaphthaldehyde **1g**, dibenzoxanthene **3k** could be synthesised (Table 2, entry 11). A methoxy group could also be introduced into the tetralone component, again in high yield (Table 2, entry 12). Attempts to introduce substituents into the 9-position by using *o*-hydroxyacetophenone or benzophenone were unsuccessful. The limitation to xanthene products without substituents in the 9-position makes this method complementary to xanthene syntheses giving predominantly 9-substituted products.[4b,5a,b]

Interestingly, microwave heating did not provide consistently higher yields. In the case of products **3g**, **3h** and **3j** (Table 2, entries 7, 8 and 10), yields were lower compared with conventional oil bath heating. Conducting the reactions at 200 °C instead of 180 °C could improve the yields to similar levels as oil bath heating. Attempts to further optimise the yields of these products were not made. The shorter reaction time of just 30 min still makes the microwave method advantageous.

The reactions are air- and moisture tolerant. Initially, we performed the reactions under an atmosphere of argon, but later we did not find any difference in yield for reactions performed in air. Also, the removal of water is not necessary to obtain high yields, although two molecules of water per molecule of product are formed during the reaction. Experiments with Dean–Stark traps did not improve the reaction yields, and the intentional addition of water to the reaction (10 vol%) was tolerated without having an effect on the yield. Surprisingly, the addition of molecular sieves to the reaction mixture was actually detrimental, and resulted in very low conversion and only 6% yield of the product after 24 h.

We also tested 1,4-cyclohexanedione in the reaction with salicylaldehyde, expecting this combination to provide an alternative route to 2-hydroxyxanthene (**3d**). We could indeed isolate **3d** in 51% yield using microwave heating (method **B**), comparable to the synthesis from hydroxysalicylaldehyde **1d** and **2a** (Table 2, entry 4). Additionally, a second product was isolated, which turned out to be the result of two salicylaldehydes reacting with cyclohexadione. Analysis of the INEPT-INADEQUATE NMR spectrum[7] revealed the structure to be the non-linear double xanthene **5** (Scheme 1). Using conventional heating (method **A**), only 25% of **3d** was isolated together with 7% of **5**.

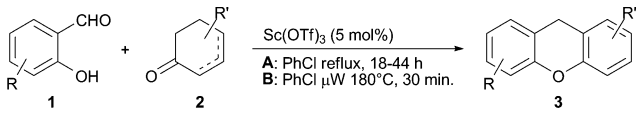


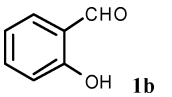
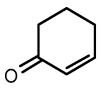
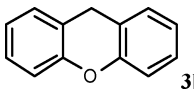
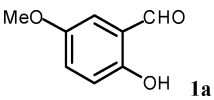
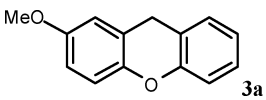
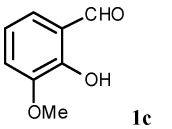
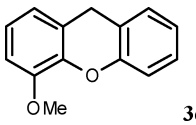
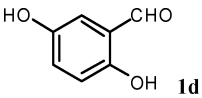
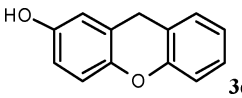
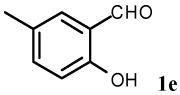
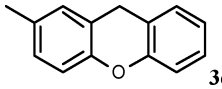
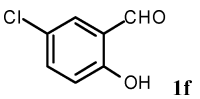
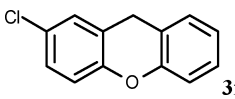
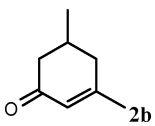
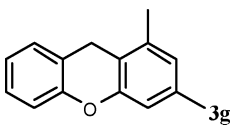
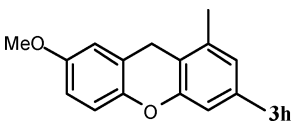
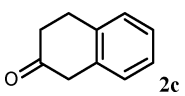
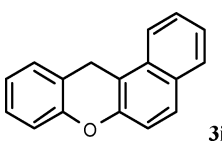
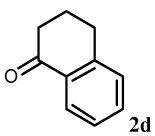
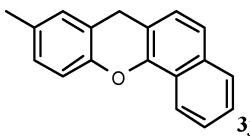
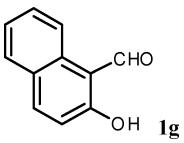
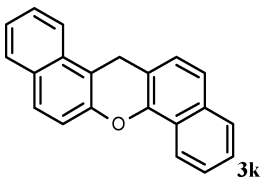
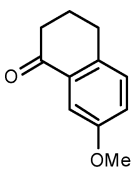
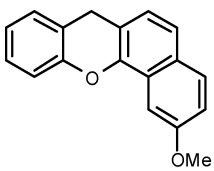
Scheme 1 The reaction with cyclohexadione.

The mechanism of this reaction is believed to proceed by an acid-catalyzed condensation reaction *via* benzopyrilium salts **6** and a subsequent sigmatropic hydrogen shift, similar to a mechanism suggested by Jha,[5e] as indicated in Scheme 2. The occurrence of salts like **6** could explain the various colours observed in the different reactions.[5h]

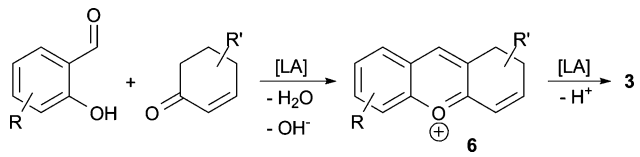
The substitution pattern of the xanthenes follows from this mechanistic proposal, and has been established by single crystal

Table 2 Synthesis of xanthenes[a]



Entry	Salicylaldehyde	Cyclohexenone or derivative	Product	*t*/h **A**	Yield **A** (%)[b]	Yield **B** (%)[b]
1	 **1b**	 **2a**	 **3b**	24	50	56
2	 **1a**	**2a**	 **3a**	24	63	82
3	 **1c**	**2a**	 **3c**	24	54	62
4	 **1d**	**2a**	 **3d**	24	30	55
5	 **1e**	**2a**	 **3e**	44	63	88
6	 **1f**	**2a**	 **3f**	24	18	30
7	**1b**	 **2b**	 **3g**	42	60	56[c]
8	**1a**	**2b**	 **3h**	42	62	69[c]
9	**1b**	 **2c**	 **3i**	18	89	95
10	**1e**	 **2d**	 **3j**	44	84	77[c]
11	 **1g**	**2d**	 **3k**	24	83	96
12	**1b**	 **2e**	 **3l**	20	80	96

[a] Reaction conditions: 1 mmol of **2**, 1.1 mmol of **1**, 0.05 mmol $Sc(OTf)_3$ in 4 mL PhCl. Method **A**: oil bath heating, reflux; method **B**: microwave heating, 180 °C, 30 min. [b] Isolated yields. [c] Microwave heating at 200 °C.



Scheme 2 Mechanistic suggestion for xanthene synthesis proceeding *via* intermediate benzopyrilium salts **6**.

X-ray analysis of xanthenes **3h** and **3j** (Fig. 1 and Fig. 2)† or by a comparison with literature data in the cases of **3e**[5b] and **3i**.[5a]

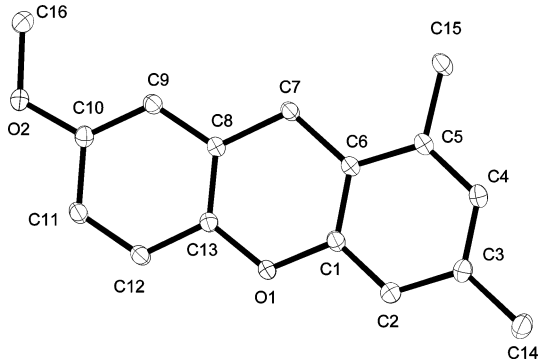


Fig. 1 X-Ray crystal structure of xanthene **3h**.

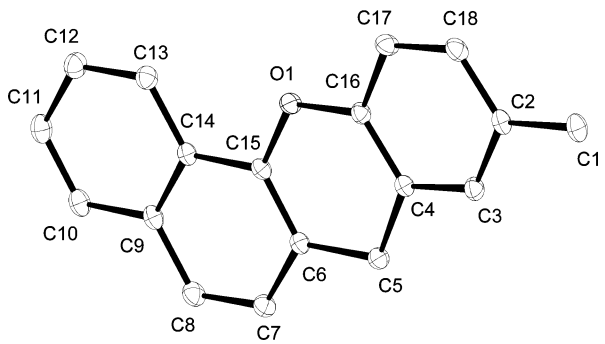


Fig. 2 X-Ray crystal structure of xanthene **3j**.

Conclusion

In summary, we have developed an economical and fast one-step synthesis of substituted xanthenes from commercially available starting materials. A range of simple Lewis acids can be used as catalysts, with 5 mol% of scandium triflate being found to be optimal. Good to excellent yields are achieved within 30 min using microwave heating, but conventional heating in an oil bath can be used instead.

Experimental

Unless otherwise indicated, all reagents and solvents were purchased from commercial distributors and used as received. Solvents used for column chromatography were of technical grade and used after distillation in a rotary evaporator. TLC was performed on Macherey-Nagel Polygram Sil G/UV254 thin layer plates. TLC was used to check the reactions for full conversion and spots were visualized by UV light irradiation. Flash column chromatography was carried out using Merck Silica Gel 60 (40–63 μm). Yields refer to pure isolated compounds. ^{1}H and ^{13}C NMR spectra were measured by Bruker AV 500 and AV 600 spectrometers. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks. ^{1}H NMR chemical shifts are designated using the following abbreviations, as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. High resolution mass spectra were recorded using either a Bruker APEX III FTICR-MS, a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument. Infrared spectra were measured by a Perkin-Elmer Spectrum 100 FT-IR spectrometer on a diamond ATR unit. Microwave reactions were carried out in a CEM Discover microwave with a power up to 300 W. The reaction temperature (IR surface flask, air cooling upon heating), pressure (non-invasive pressure transducer) and microwave power was remotely controlled.

General procedure A—oil bath heating

Substituted salicylaldehyde **1** (1.1 mmol) and cyclohexenone derivative **2** (1.0 mmol) were quickly added to a suspension of scandium(III) triflate (24.61 mg, 0.05 mmol) in chlorobenzene (4.0 mL). The reaction mixture was refluxed for 24 h and allowed to cool to room temperature. CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ (20 mL) were added to the reaction mixture, and the two layers separated. The aqueous phase was extracted with CH_2Cl_2 (3× 20 mL) and the combined organic layers were dried over $MgSO_4$, filtered and the solvent removed by a rotary evaporator. Crude xanthene **3** was purified by flash chromatography using mixtures of pentane and ethyl acetate.

General procedure B—microwave heating

Substituted salicylaldehyde **1** (1.1 mmol) and cyclohexenone derivative **2** (1.0 mmol) were quickly added to a suspension of scandium(III) triflate (24.61 mg, 0.05 mmol) in chlorobenzene (4.0 mL). The reaction mixture was heated in a microwave tube at 180 °C for 30 min. After compressed air cooling to room temperature, CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ (20 mL) were added to the reaction mixture, and the two layers separated. The aqueous phase was extracted with CH_2Cl_2 (3× 20 mL) and the combined organic layers were dried over $MgSO_4$, filtered and the solvent removed by a rotary evaporator. Crude xanthene **3** was purified by flash chromatography using mixtures of pentane and ethyl acetate.

2-Methoxy-9*H*-xanthene (3a). ^{1}H NMR (500 MHz, DMSO): δ 7.25–7.18 (m, 2H), 7.06–6.98 (m, 3H), 6.83–6.77 (m, 2H), 4.01 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, DMSO): δ 155.0, 151.6, 145.2, 129.1, 127.7, 122.9, 121.4, 120.1, 116.8, 116.0, 113.5, 113.3, 55.4, 27.3; HRMS-(EI) (*m*/*z*): M^+ calc. for $C_{14}H_{12}O_2$, 212.083728; found 212.083561.

9*H*-Xanthene (3b). ^{1}H NMR (500 MHz, DMSO): δ 7.27–7.20 (m, 4H), 7.09–7.04 (m, 4H), 4.04 (s, 2H); ^{13}C NMR (125 MHz, DMSO): 151.31, 129.17, 127.75, 123.23, 120.61, 116.04, 26.90; HRMS-(EI) (*m*/*z*): M^+ calc. for $C_{13}H_{10}O$, 182.073166; found 182.072975.

4-Methoxy-9*H*-xanthene (3c). ^{1}H NMR (500 MHz, DMSO): δ 7.26–7.19 (m, 2H), 7.10–7.04 (m, 2H), 7.02–6.97 (m, 1H), 6.94–6.90 (m, 1H), 6.83–6.79 (m, 1H), 4.02 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, DMSO): 151.2, 147.6, 140.6, 129.1, 127.7, 123.3, 122.9, 121.3, 120.5, 120.4, 116.2, 110.5, 55.6, 27.0; HRMS-(EI) (m/z): M$^+$ calc. for $C_{14}H_{12}O_2$, 212.083730; found 212.083684.

9*H*-Xanthen-2-ol (3d). ^{1}H NMR (500 MHz, DMSO): δ 9.18 (s, 1H), 7.25–7.17 (m, 2H), 7.06–6.99 (m, 2H), 6.90–6.89 (m, 1H), 6.64–6.59 (m, 2H), 3.96 (s, 2H); ^{13}C NMR (125 MHz, DMSO): 153.03, 151.74, 144.08, 129.10, 127.61, 122.74, 121.22, 120.24, 116.68, 115.94, 114.64, 114.48, 27.30; HRMS-(EI) (m/z): M$^+$ calc. for $C_{13}H_{10}O_2$, 198.068079; found 198.067949

2-Methyl-9*H*-xanthene (3e). ^{1}H NMR (500 MHz, DMSO): δ 7.26–7.19 (m, 2H), 7.07–6.99 (m, 4H), 6.97–6.93 (m, 1H), 4,00 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, DMSO): δ 151.4, 149.2, 132.1, 129.4, 129.2, 128.2, 127.7, 123.1, 120.5, 120.2, 116.0, 115.8, 26.9, 20.2; HRMS-(EI) (m/z): M$^+$ calc. for $C_{14}H_{12}O$, 196.088811; found 196.088659.

2-Chloro-9*H*-xanthene (3f). ^{1}H NMR (500 MHz, DMSO): δ 7.34–7.32 (m, 1H), 7.27–7.21 (m, 3H), 7.09–7.04 (m, 3H), 4.04 (s, 2H); ^{13}C NMR (125 MHz, DMSO): δ 150.9, 150.1, 129.1, 128.7, 127.9, 127.6, 126.7, 123.5, 122.8, 119.9, 117.8, 116.1, 26.7; HRMS-(EI) (m/z): M$^+$ calc. for $C_{13}H_9OCl_1$, 216.034193; found 216.034201.

1,3-Dimethyl-9*H*-xanthene (3g). ^{1}H NMR (500 MHz, DMSO): δ 7.26–7.17 (m, 2H), 7.05–6.98 (m, 2H), 6.73 (s, 1H), 6.68 (s, 1H), 3.88 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, DMSO): 150.95, 150.80, 136.88, 136.45, 129.49, 127.71, 125.04, 122.93, 120.06, 115.83, 115.81, 113.94, 24.53, 20.56, 18.64; HRMS-(EI) (m/z): M$^+$ calc. for $C_{15}H_{14}O$, 210.104467; found 210.104383.

7-Methoxy-1,3-dimethyl-9*H*-xanthene (3h). ^{1}H NMR (500 MHz, DMSO): 6.96–6.92 (m, 1H), 6.84–6.81 (m, 1H), 6.79–6.75 (m, 1H), 6.72 (s, 1H), 6.66 (s, 1H), 3.88 (s, 2H), 3.72 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, DMSO): 154.78, 151.07, 144.87, 136.81, 136.39, 124.79, 120.80, 116.59, 115.36, 113.87, 113.59, 55.36, 24.99, 20.58, 18.70; HRMS-(EI) (m/z): M$^+$ calc. for $C_{16}H_{16}O_2$, 240.115026; found 240.115225.

12*H*-Benzo[*a*]xanthene (3i). ^{1}H NMR (500 MHz, DMSO): δ 7.97–7.93 (m, 2H), 7.88–7.85 (m, 1H), 7.66–7.61 (m, 1H), 7.52–7.48 (m, 1H),7.43–7.39 (m, 1H), 7.35–725 (m, 2H), 7.17–7.11 (m, 1H), 4.41 (s, 2H); ^{13}C NMR (125 MHz, DMSO): 150.33, 147.95, 131.57, 129.81, 129.68, 128.35, 128.33, 127.87, 126.90, 124.34, 123.42, 122.49, 119.49, 117.51, 116.06, 111.68, 23.87; HRMS-(EI) (m/z): M$^+$ calc. for $C_{17}H_{12}O$, 232.088813; found 232.088790.

9-Methyl-7*H*-benzo[*c*]xanthene (3j). ^{1}H NMR (500 MHz, DMSO) δ 8.30–8.26 (m, 1H), 7.92–7.88 (m, 1H), 7.62–7.51 (m, 3H), 7.36–7.30 (m, 1H), 7.17–7.12 (m, 1H), 7.10–7.04 (m, 2H), 4.13 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, DMSO): 149.00, 145.64, 132.90, 132.43, 129.43, 128.29, 127.67, 127.00, 126.11, 123.40, 122.29, 120.73, 119.91, 116.07, 114.47, 27.13, 20.27; HRMS-(EI) (m/z): M$^+$ calc. for $C_{18}H_{14}O$, 246.104468; found 246.104376.

14*H*-Dibenzo[*a*,*h*]xanthene (3k). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46–8.42 (m, 1H), 7.94–7.78 (m, 4H), 7.64–7.56 (m, 3H), 7.54–7.43 (m, 3H), 7.40–7.37 (m, 1H), 4.51 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 148.70, 145.73, 133.53, 132.23, 130.44, 128.57, 128.41, 127.69, 127.14, 126.85, 126.19, 126.08, 124.35, 124.28, 122.75, 122.53, 121.53, 118.14, 113.61, 111.79, 25.46; HRMS-(EI) (m/z): M$^+$ calc. for $C_{21}H_{14}O$, 282.104462; found 282.104546.

2-Methoxy-7*H*-benzo[*c*]xanthene (3l). ^{1}H NMR (500 MHz, DMSO): δ 7.84–7.80 (m, 1H), 7.62–7.52 (m, 2H), 7.32–7.26 (m, 3H), 7.21–7.15 (m, 2H), 7.13–7.08 (m, 1H), 4.16 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, DMSO): 157.64, 151.18, 144.83, 129.41, 129.22, 128.32, 127.75, 124.47, 124.30, 123.47, 122.32, 120.43, 118.34, 116.41, 115.21, 99.45, 55.23, 27.24; HRMS-(EI) (m/z): M$^+$ calc. for $C_{18}H_{14}O_2$, 262.099378; found 262.099142.

13,14-Dihydrochromeno[3,2*a*]xanthene (5). Isolated as a by-product in the synthesis of **3d** from **1b** and **4**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–7.15 (m, 4H), 7.05–6.98 (m, 4H), 6.88 (s, 2H), 3.96 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 151.61, 147.12, 129.21, 127.98, 122.92, 118.84, 118.69, 116.40, 115.50, 25.6; HRMS-(EI) (m/z): M$^+$ calc. for $C_{20}H_{14}O_2$, 286.099377, found 286.099179.

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