Scandium triflate-catalyzed one-pot domino approach towards general and efficient syntheses of unsymmetrical 9-substituted xanthene derivatives†‡

Ritesh Singh and Gautam Panda*

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A general and efficient one-pot cascade/tandem approach to synthesize unsymmetrical 9-aryl/heteroaryl xanthenes has been developed under extremely mild reaction conditions using 10 mol% $Sc(OTf)_3$ as a catalyst. This strategy has been further extended to synthesize 9-(thioaryl) xanthenes through tandem carbon–sulfur (C–S) and carbon–carbon (C–C) bond formation. Novel C–C and C–S bond cleavage promoted by $Sc(OTf)_3$ is also discussed during mechanistic investigation.

Introduction

Multi-bond-forming reactions are especially effective in constructing complex molecular architectures from relatively simple starting materials. Thus, domino/tandem reactions are being widely used by organic chemists to synthesize desired molecules in one pot or one vessel due to their well-known advantages, *i.e.* reduction of the number of synthetic steps and high atom economy.[1] One-pot/step strategies to access xanthenes and dibenzo[*a*,*j*]xanthenes, have attracted considerable attention over the years due to their diverse biological properties, such as antiviral,[2] anti-inflammatory[3] and antibacterial activities, as well as their use as dyes and fluorescent materials[4] (Fig. 1). These compounds have also been utilized as antagonists for the paralyzing action of zoxazolamine[5] and in photodynamic therapy (PDT).[6] Recent strategies to synthesize xanthene scaffolds include palladium-catalyzed cyclization of polycyclic aryl triflate esters,[7] intramolecular trapping of benzynes by phenols,[8] reaction of aryloxymagnesium halides with triethylorthoformate[9] and reaction of 2-tetralones with substituted 2-hydroxy arylaldehydes.[10]

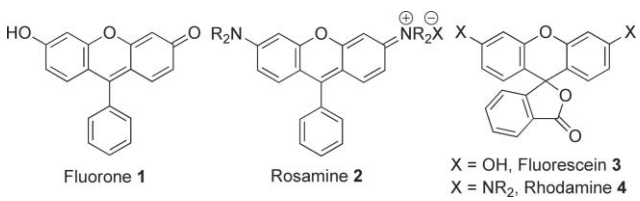

Fig. 1 Structures of some common xanthene dyes.

Very recently, some elegant synthetic protocols to synthesize xanthone scaffolds have also been reported. Larock *et al.*,[11] applied an aryl to imidoyl palladium migration process involving intramolecular C–H activation to access xanthone. Domínguez *et al.*[12] utilized Cu-mediated intramolecular *O*-arylation of *o*-halobenzophenones, and also employed nucleophilic aromatic substitution (S_NAr) reactions, using KOH as the base, starting from *o*-halobenzophenones to synthesize the xanthone skeleton under aqueous conditions.

Though efficient, the above methods have several drawbacks, such as utilization of harsh reaction conditions (strong acidic media, high temperature), stoichiometric amounts of reaction promoters and the moisture sensitiveness of the catalysts used *etc.*, leaving ample scope for the development of new synthetic protocols to assemble such scaffolds.

Over the past several years, we have been involved in the design, synthesis, and antitubercular and anticancer activities of symmetrical and unsymmetrical trisubstituted methanes (TRSMs) by intermolecular diarylmethylation of electron-rich arenes using diaryl carbinols as alkylating agents.[13,14] In continuation of our research programme, we became interested in synthesizing 9-aryl xanthenes as conformationally constrained triarylmethanes (TRAMs).

Although a literature survey gives accounts of several syntheses of symmetrical and unsymmetrical TRAMs using a one-pot sequential intermolecular Friedel–Crafts approach,[15] there are, however, few reports on accessing unsymmetrical 9-aryl/heteroaryl xanthenes in one pot using tandem/domino reactions. Recently, we developed a facile two-step synthetic route to access symmetrical as well as unsymmetrical 9-aryl/heteroaryl xanthenes **7** and diverse related compounds from arenoxybenzaldehydes **5** through carbinols **6** under mild conditions (Scheme 1).[16] Thus, in our pursuit to further improve efficiency and to provide a general, one-pot and highly atom economical protocol for the synthesis of functionalized 9-substituted xanthene derivatives, the idea of employing electron-rich arenes and heteroarenes with various 2-arenoxybenzaldehydes was undertaken. In fact, while compiling our work, Li *et al.*[17] reported a tandem C–C bond formation strategy to access unsymmetrical 9-aryl xanthenes catalyzed by $FeCl_3{\cdot}6H_2O$, which prompted us to reveal our synthetic strategy towards unsymmetrical xanthenes using 10 mol% $Sc(OTf)_3$ as the catalyst.

Results and discussion

Our study began with the synthesis of a series of four 2-arenoxy/2-arylsulfanylbenzaldehydes **11a–d** following a literature procedure, which involved refluxing a solution of 2-fluorobenzaldehydes,

Medicinal and Process Chemistry Division, Central Drug Research Institute, CSIR, Chattar Manzil Palace, Lucknow, 226001, UP, India. E-mail: gautam.panda@gmail.com

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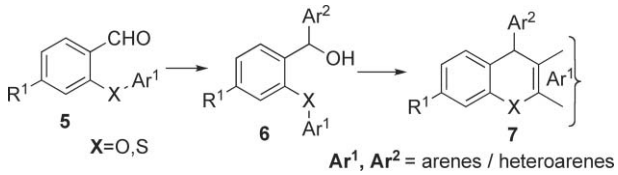
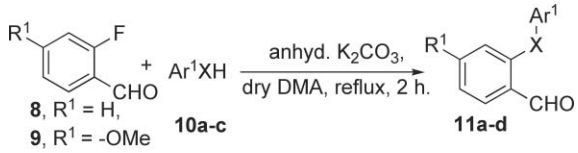


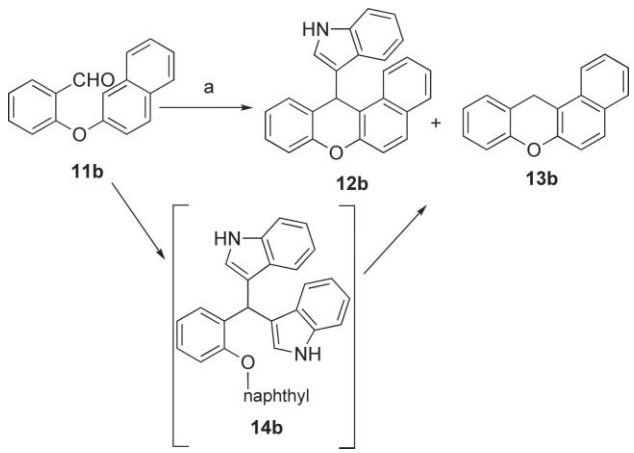
Scheme 1 Two step protocol to synthesize unsymmetrical 9-aryl xanthenes from 2-aryloxy/2-sulfanylbenzaldehyde **5**.

Table 1 Synthesis of 2-arenoxy/2-arylsulfanyl benzaldehydes **11a-d**



Entry	Aldehyde	Ar^{1}XH	Product (yield (%))
1	**8**	**Ar**^{1} = Ph, **X** = O **10a**	**11a** (90)
2	**8**	**Ar**^{1} = 2-naphthyl, **X** = O **10b**	**11b** (93)
3	**8**	**Ar**^{1} = 2-naphthyl, **X** = S **10c**	**11c** (91)
4	**9**	**Ar**^{1} = 2-naphthyl, **X** = O **10b**	**11d** (85)

8 and **9**, and aromatic hydroxy/aromatic thiols **10a–c** in dry DMA, in the presence of anhydrous K_2CO_3 as a base (Table 1).[7,18] With 2-arenoxy/2-arylsulfanylbenzaldehydes **11a–d** in hand, we turned our attention towards our next immediate goal: to execute the one-pot addition of electron-rich arenes and heteroarenes, followed by cyclization to access 9-substituted xanthene derivatives. Initially, we chose indole and 2-(naphthalen-2-yloxy)benzaldehyde **11b** as the model reaction substrates to demonstrate domino/tandem reactions, synthesizing the 9-indole xanthene derivative **12b** (Scheme 2). Without much ado, we preferred the same catalytic and solvent system as was used for the intramolecular Friedel–Crafts reaction in our previous report.[9] Thus, indole (1 equiv.) was reacted with**11b** at rt in anhydrous dichloromethane (DCM) using 10 mol% of $FeCl_3$ (entry 5, Table 2).



Scheme 2 Synthesis of 9-substituted xanthene derivative **12b**. ***Reagents and conditions***: (a) indole (1 equiv.), $FeCl_3$, anhydrous DCM, rt.

Table 2 Optimization studies for the synthesis of **12b**

Entry	Catalyst	Conditions	Yield (%)[a]
1	Conc. H_2SO_4	Dry benzene, reflux, 15 h.	65
2	$AlCl_3$ (1.2 equiv.)	Dry CH_2Cl_2, rt, 30 h	68
3	TfOH (20 mol%)	Dry CH_2Cl_2, rt, 20 h	72
4	$Sc(OTf)_3$ (10 mol%)	Dry CH_2Cl_2, rt, 18 h	88
5	$FeCl_3$ (10 mol%)	Dry CH_2Cl_2, rt, 24 h	48
6	$FeCl_3$ (1.2 equiv.)	Dry CH_2Cl_2, rt, 24 h	57
7	Ag(OTf) (10 mol%)	Dry CH_2Cl_2, rt, 30 h	32
8	$AuCl_3 \cdot 3H_2O$ (10 mol%)	Dry CH_2Cl_2, rt, 48 h	24

[a] Isolated yield of **12b** after silica gel column chromatography.

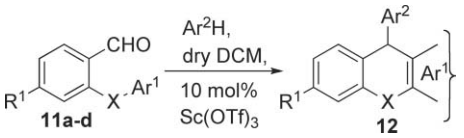
Delightfully, we obtained the desired xanthene derivative **12b** in 48% yield, along with a little amount of xanthene **13b** (18% yield) and unreacted starting materials after 24 h. This observation encouraged us to find the optimal catalyst for the domino/tandem cyclization. When the $FeCl_3$ loading was increased to 1.2 equiv., the starting material was consumed after 18 h, and we obtained **12b** and **13b** in 57% and 31% yields, respectively. Subsequently, various other catalytic systems were screened, which are summarized in Table 2. $AlCl_3$ as the catalyst provided the desired products **12b** and **13b** in 68% and 27% yield respectively. Among the Brønsted acids, TfOH provided **12b** in 72% yield with **13b** (14%). A catalytic amount of conc. H_2SO_4 also initiated the reaction, which furnished **12b** in 65% yield. Milder Lewis acids like $AuCl_3 \cdot 3H_2O$ and Ag(OTf) gave the desired product **12b** in 24–32% yield. However, 10 mol% $Sc(OTf)_3$ proved to be the catalyst of choice, as it provided the coveted **12b** in very high yield (88%) at room temperature. While monitoring the reaction we also observed **14b**, after just 15 min of the reaction, which had gradually converted to **12b** by 18 h.

It is noteworthy that the reactions with $FeCl_3$, $AlCl_3$, TfOH, H_2SO_4 and other Lewis acids, except $Sc(OTf)_3$, as catalysts were performed strictly under inert atmosphere, as these catalysts immediately react with water/moisture rather than substrates, and get deactivated or decomposed under normal atmospheric conditions at room temperature. However, in contrast, just 10 mol% $Sc(OTf)_3$ was sufficient in catalyzing the reaction under normal atmospheric conditions[19] at rt. In recent years, $Sc(OTf)_3$ has emerged as a powerful Lewis acid for a number of organic syntheses, as only a small amount of catalyst is required, thus increasing the catalytic turnover number, compared to $AlCl_3$, $FeCl_3$, *etc.*, which are generally required in stoichiometric amounts. In fact, many organic transformations like the aldol,[20a,b] Diels–Alder,[20c] Mannich,[20d,e] Michael[20f,g] and Friedel–Crafts acylation[20h] reactions have been performed using $Sc(OTf)_3$ as a catalyst, in aqueous as well as organic solvents.

Based on these facts and the above optimization results, we then turned our attention to exploring the scope of $Sc(OTf)_3$-catalyzed tandem addition/cyclization of electron-rich arenes with various aldehydes containing a tethered arenoxy/arylsulfanyl group **11a–d**. Towards this objective, a series of electron-rich arenes and heteroarenes were added to aldehydes **11a–d** in dry DCM at rt, using 10 mol% $Sc(OTf)_3$ under normal atmospheric conditions, which furnished 9-substituted xanthene derivative **12** in 68–87% yields (Table 3).

The reaction was acquiescent to a variety of substituted aromatic rings for the synthesis of unsymmetrical/symmetrical

Table 3 Synthesis of 9-arylxanthenes **12**



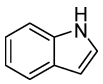
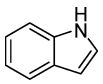
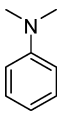
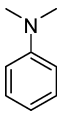
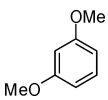
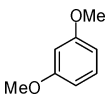
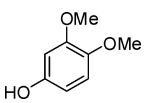
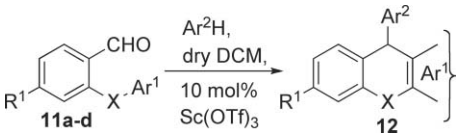
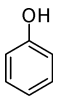
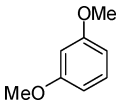
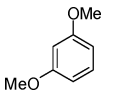
Entry	Aldehyde	Ar^2H	**12** (yield (%))
1[a]	**11c**		R^1 = H,X=S Ar^1 = Ar^2 = 3-indyl **12a, 84%**
2[c]	**11d**		R^1 =OMe,X=O Ar^1 = Ar^2 = 3-indyl **12c, 87%**
3[b]	**11b**		R^1 = H,X=O Ar^1 = Ar^2 = 4-(N,N dimethyl)C_6H_4 **12d, 82%**
4[b]	**11c**		R^1 = H,X=S Ar^1 = Ar^2 = 4-(N,N dimethyl)C_6H_4 **12e, 80%**
5[c]	**11b**		R^1 = H,X=O Ar^1 = Ar^2 = 2-thienyl **12f, 72%**
6[c]	**11a**		R^1 = H,X=O Ar^1 = Ar^2 = 4-OMeC_6H_4 **12g, 70%**
7[c]	**11c**		R^1 = H,X=S Ar^1 = Ar^2 = 4-OMeC_6H_4 **12h, 72%**
8[a]	**11b**		R^1 = H,X=O Ar^1 = Ar^2 = 2,4-OMeC_6H_3 **12i, 74%**
9[a]	**11c**		R^1 = H,X=S Ar^1 = Ar^2 = 2,4-OMeC_6H_3 **12j, 73%**
10[a]	**11d**		R^1 = OMe,X=O Ar^1 = Ar^2 = (4,5-OMe)(2-OH)C_6H_2 **12k, 75%**

Table 3 (*Contd.*)



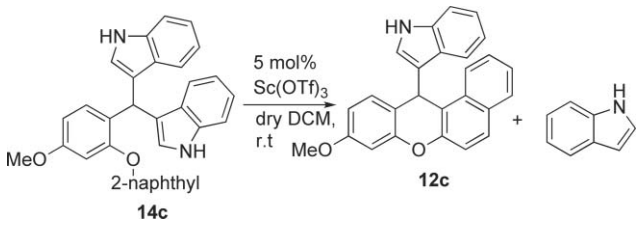
Entry	Aldehyde	Ar^2H	**12** (yield (%))
11[b]	**11a**		R^1 = H,X=O Ar^1 = Ar^2 = 4-OHC_6H_4 **12l, 68%**
12[c]	**11a**		R^1 = H,X=O Ar^1 = Ar^2 = 2,4-OMeC_6H_3 **12m, 69%**
13[a]	**11d**		R^1 = OMe,X=O Ar^1 = Ar^2 = 2,4-OMeC_6H_3 **12n, 71%**

[a] Isolated yield after 24 h at rt. [b] Isolated yield at 50 °C, with 10 mol% $Sc(OTf)_3$ after 24 h. [c] Isolated yield at rt, 24 h, 20 mol% $Sc(OTf)_3$.

9-aryl xanthenes. The diverse collection of 9-aryl xanthenes synthesized demonstrates the potential to utilize any 2-arenoxy/arylsulfanyl benzaldehyde as a common precursor for a library of 9-arylxanthenes. Thus, careful choice of electron-rich arenes/heteroarenes could allow us to access symmetrical as well as unsymmetrical 9-(hetero)aryl xanthenes/thioxanthenes in high yield, which was only possible by the mild reaction conditions.

While investigating the mechanism for the above one-pot strategy, we came across Li *et al.*'s report[17] in which they mention that a 9-arylxanthene derivative could be formed through an intermediate triarylmethane (TRAM) derivative.[11] We also isolated one of the intermediates (**14c**), which, on treatment with 5 mol% of $Sc(OTf)_3$ in dry DCM at rt under normal atmospheric conditions, was converted to **12c** (Scheme 3), confirming the hypothesis that C–C bond cleavage might be taking place first, followed by the intramolecular Friedel–Crafts reaction, to provide the desired cyclized product **12c**. It was assumed that $Sc(OTf)_3$, as an electrophile, associates at the 3-position of the indole (**15c**), and the required push from the oxygen of OAr^1 leads to cleavage of the strong C–C bond, resulting in a stabilized carboxonium ion intermediate (**16c**). Thereafter, the intramolecular attack by the tethered aryloxy group generated the product **12c** and a little amount of indole, which gets reused in the whole process. However, during the catalyst optimization process (Scheme 2), reactions were performed with Lewis acids like $AlCl_3$ and $FeCl_3$, furnishing a little amount of **13b**, of which there was no mention in Li *et al.*'s manuscript.

In fact, there are several reports in the literature where alkylation, dealkylation and realkylation in TRAM derivatives are known during the addition of electron-rich arenes to aromatic aldehydes in the presence of Lewis and Brønsted acids.[21] So, it can be alleged that in the presence of $FeCl_3$ or $AlCl_3$, 9-substituted

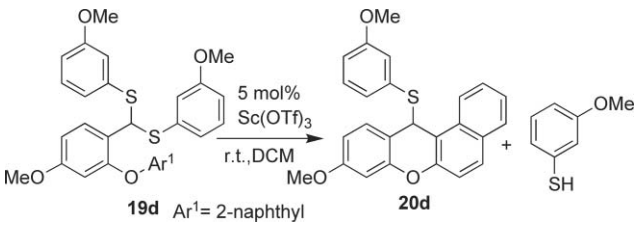


Scheme 3

xanthene derivative **12c** could be attacked by $FeCl_3/AlCl_3$ (Scheme 4), to give intermediate **17c**, which through further C–C bond cleavage gives **18c**, leading finally to **13c**. However, it was noticeable that formation of **13c** could not be observed from **12c** with $Sc(OTf)_3$ as the catalyst.

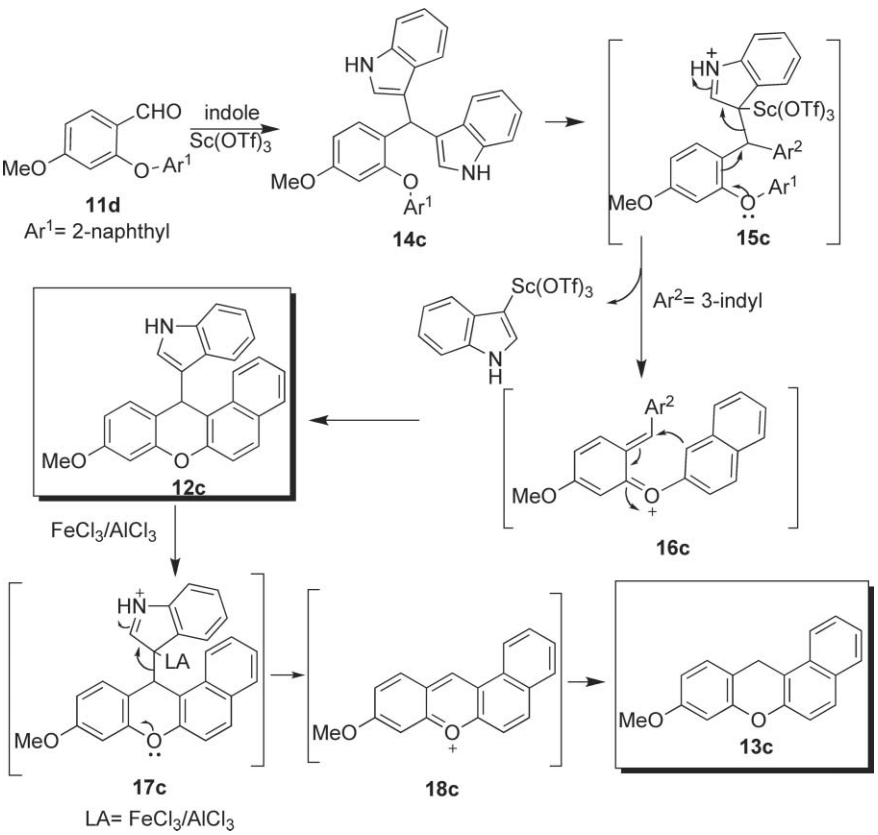
Elated by the above observations, we endeavoured to apply this approach to provide a mild and general route to a new class of 9-(arylthio)-substituted xanthenes/thioxanthenes. 9-(Lupinylthio)xanthene/thioxanthenes bearing a thia group at their 9-position, are known to inhibit the angiotensin II-induced contractions of the guinea pig ileum. Some of these compounds are also moderately active *in vitro* as tracheal relaxants.[22] Thus, this synthetic protocol seemed well poised to provide new aryl analogues of 9-(lupinylthio)xanthene, by using aromatic/heteroaromatic thiols as nucleophiles. Keeping these things in mind, we reacted several aromatic thiols with the previously described aldehydes **11b–d** under the optimized reaction conditions.

The versatility of the reaction sequence in Table 4 can be explained by the fact that heteroaromatic thiols can also be introduced into the xanthene system (entry 6), albeit with lower yield. In the reaction process, we observed dithioacetal intermediate **19d**, similar to **14c** (Scheme 4), when electron-rich arenes were used. Thereafter, to investigate the mechanism, one of the intermediates (**19d**) was isolated and treated with 5 mol% $Sc(OTf)_3$, at rt in dry DCM under normal atmospheric conditions, furnishing the desired cyclized product **20d** (Scheme 5). Isolation of 3-methoxy benzenethiol demonstrated that **20** was being formed through tandem C–S bond cleavage and C–C bond formation by an intramolecular Friedel–Crafts reaction, similar to the aforementioned mechanism for electron-rich arene/heteroarene systems.



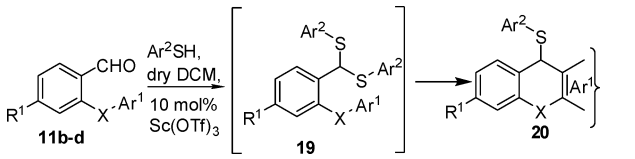
Scheme 5

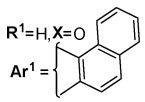
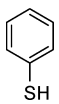
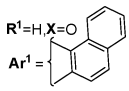
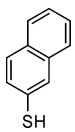
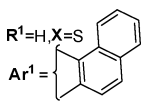
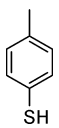
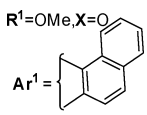
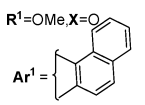
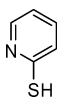
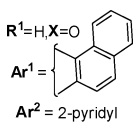
In the tentative mechanism shown in Scheme 6, it was assumed that $Sc(OTf)_3$, as an electron-deficient species, complexes with the basic sulfur, and the required push coming from the oxygen of OAr^1 (**21d**) results in cleavage of the C–S bond, which in



Scheme 4 Proposed mechanism for the tandem one-pot addition/cyclization sequence for **12** and **13**.

Table 4 Synthesis of 9-(arylthio) xanthenes **20**



Entry	Aldehyde	Ar^2SH	**20** (yield(%))[a]
1	**11b**		 Ar^2 = 3-$OMeC_6H_4$ **20a, 79%**
2	**11b**		 Ar^2 = Ph **20b, 72%**
3	**11c**		 Ar^2 = 2-naphthyl **20c, 74%**
4	**11d**		 Ar^2 = 4-MeC_6H_4 **20d, 71%**
5	**11d**		 Ar^2 = 3-$OMeC_6H_4$ **20e, 76%**
6	**11b**		 Ar^2 = 2-pyridyl **20f, 58%**

[a] All reactions at rt.

turn stabilizes the intermediate **22d** as an oxocarbonium ion. Subsequently, tandem intramolecular attack by the tethered aryloxy (OAr^1) group provided xanthene **20d** (Scheme 6). To the best of our knowledge, this is the first example of selective C–S bond cleavage in diaryl dithioacetals using $Sc(OTf)_3$ under such mild reaction conditions.

Conclusions

In conclusion, we have developed a new, facile and very mild tandem, one-pot synthetic route to synthesize 9-substituted xanthene derivatives using 10 mol% $Sc(OTf)_3$ starting from various 2-aryloxy benzaldehydes and electron-rich arenes. Biologically significant thioxanthenes, as well as a new series of 9-(arylthio) xanthenes, were also synthesized employing this strategy. Besides, we were able to discover for the first time a new C–C and C–S bond cleavage reaction by catalytic $Sc(OTf)_3$.

Utilization of $Sc(OTf)_3$ as a reaction promoter makes this protocol environmentally benign and convenient to handle, as the reactions could be performed in the absence of an inert gas at room temperature. $Sc(OTf)_3$ is well-known to tolerate aqueous conditions, can retain its catalytic efficiency for longer periods, with high catalytic turnover frequency,[19] consequently reducing the formation of undesired side products, as is the case with conventional Lewis acids ($FeCl_3$/$AlCl_3$). Further exploration and mechanistic investigation of this synthetic strategy is currently under way in our lab and will be reported in due course.

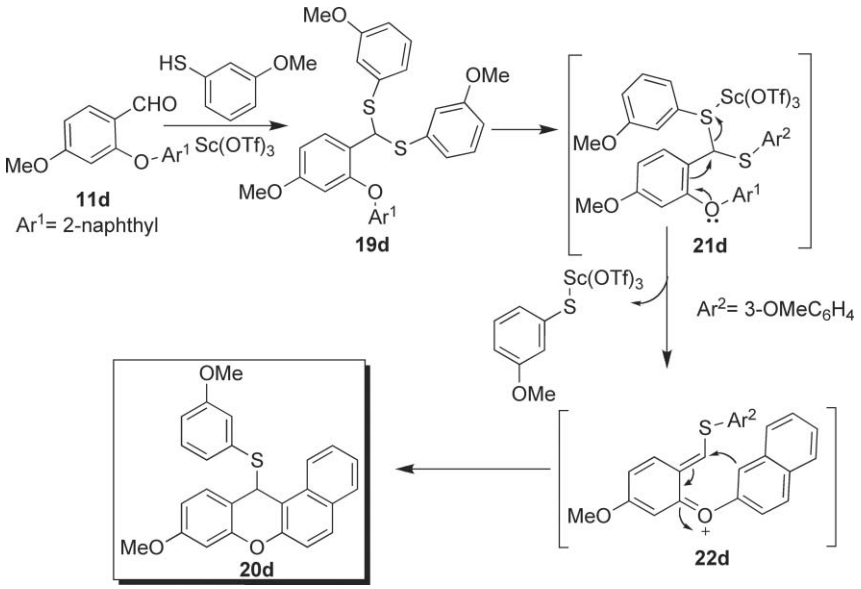
Experimental

General methods

All reactions were carried out under normal atmospheric pressure in oven-dried glassware using standard gas-light syringes, cannulas and septa. All reagents and solvents were dried prior to use according to standard methods. Commercial reagents were used without further purification unless otherwise stated. Reactions were monitored on silica gel TLC plates (coated with TLC grade silica gel). The detecting agents used for TLC were iodine vapors and/or spraying with an aqueous solution of vanillin in 10% sulfuric acid, followed by heating at 150 °C. Column chromatography was performed over silica gel (60–120 mesh) using freshly distilled solvents. Mass spectra were recorded using electron spray ionization (ESI-MS) or fast atom bombardment spectra (FAB-MS) using argon/xenon as the FAB gas. Elemental analyses were done on Varian EL-III C H N analyzer. Melting points were determined and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on DPX-300 spectrometer (operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as the solvent. Tetramethylsilane (0.00 ppm) served as an internal standard in ^{1}H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. All spectra were recorded at 25 °C. Coupling constants (*J* values) are given in Hertz (Hz). Chemical shifts are expressed in parts per million.

Characterization data of compounds and general method for the one pot cascade cyclization

3-(12*H*-Benzo[*a*]thioxanthen-12-yl)-1*H*-indole (12a). To a stirred solution of **11c** (100 mg, 0.37 mmol) in dry DCM (10 ml) was added indole (43 mg, 0.37 mmol) in dry DCM (10 ml) and $Sc(OTf)_3$(10 mol%). The reaction mixture was stirred at room temperature until completion of the reaction (as observed on TLC). After the usual work-up (with DCM (3 × 10 ml) and water, washing with brine and drying over Na_2SO_4), the reaction mixture was concentrated *in vacuo*. It was then charged over silica gel, which, after elution with ethyl acetate–hexane (2 : 98), furnished **12a** (84%, 115 mg) as a colorless solid. M.p. 180–181 °C IR (KBr): 3491, 2360, 1612, 760, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 1H, J = 8.3), 7.86-7.72 (m, 5H), 7.56-7.38 (m, 4H), 7.33-7.04 (m, 5H), 6.54 (s, 1H), 6.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 136.4, 132.6, 132.5, 132.4, 131.6, 130.8, 129.4, 128.8, 127.1, 126.9, 126.9, 126.6, 126.5, 126.2, 125.3, 122.9, 122.5,



Scheme 6 Tentative mechanism for the formation of 9-(arylthio) xanthenes/thioxanthenes **20**.

121.7, 119.5, 119.1, 114.8, 111.2, 40.1. MS (ESI): *m/z* 362 [M – 1]$^+$. Anal. calcd. for $C_{25}H_{17}NS$: C, 82.61; H, 4.71; N, 3.85. Found: C, 82.53; H, 4.84; N, 3.96.

3-(12*H*-Benzo[*a*]xanthen-12-yl)-1*H*-indole (12b). As described for **12a**, **11b** (100 mg, 0.40 mmol), indole (47 mg, 0.40 mmol) and $Sc(OTf)_3$(10 mol%) furnished **12b** (88%, 123 mg) as a colorless solid. M.p. 230–231 °C. IR (KBr): 3490, 2912, 2360, 1601, 670 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, 1H, J = 7.7), 7.86-7.83 (m, 1H), 7.76 (s, 1H), 7.74 (s, 1H), 7.70 (s, br, 1H), 7.46 (d, 1H, J = 7.5), 7.41(d, 1H, J = 8.7), 7.35-7.26 (m, 2H), 7.19-7.07 (m, 5H), 6.99-6.34 (m, 1H), 6.79 (d, 2H, J = 2.4), 6.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5, 149.4, 136.4, 131.9, 130.9, 129.3, 128.8, 128.5, 127.4, 126.6, 125.9, 125.3, 123.9, 123.5, 123.1, 122.1, 122.3, 122.0, 119.8, 118.9, 117.9, 116.5, 116.1,111.2. MS (ESI): *m/z* 346 [M – 1]$^+$. Anal. calcd. for $C_{25}H_{17}$ NO: C, 86.43; H, 4.93; N, 4.03. Found: C, 86.23; H, 5.12; N, 3.91.

3-(9-Methoxy-12*H*-benzo[*a*]xanthen-12-yl)-1*H*-indole (12c). As described for **12a**, **11d** (100 mg, 0.35 mmol), indole (42 mg, 0.35 mmol) and $Sc(OTf)_3$(10 mol%) furnished **12c** (87%, 118 mg) as a colorless solid. M.p. 221–222 °C. IR (KBr): 2359, 1614, 1012, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 1H, J = 7.4), 7.82-7.78 (m, 4H), 7.42-7.22 (m, 5H), 7.13 (s, 2H), 6.87 (s, 1H), 6.71 (s, 1H), 6.58 (d, 1H, J = 8.3), 6.08 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 136.4, 131.9, 129.7, 128.7, 128.4, 126.5, 123.9, 123.2, 122.6, 121.9, 121.8, 119.7, 118.9, 117.8, 116.1, 111.2, 110.4, 101.3, 55.4, 32.2. MS (ESI): *m/z* 376 [M-1]$^+$. Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.58; H, 4.94; N, 3.85.

4-(12*H*-Benzo[*a*]xanthen-12-yl)-*N*,*N*-dimethylaniline (12d). As described for **12a**, **11b** (100 mg, 0.40 mmol), *N*,*N*-dimethylaniline (48 mg, 0.40 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12d** (82%, 116 mg) as a colorless solid. M.p. 201–202 °C. IR (KBr): 3012, 2360, 1609, 763 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 1H, J = 8.4), 7.78-7.73 (m, 2H), 7.43-7.30 (m, 4H), 7.16-7.11 (m, 4H), 7.04-6.99 (m, 1H), 6.55 (s, 1H), 6.52 (s, 1H), 5.71 (s, 1H), 2.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 149.4, 149.1, 134.9, 131.8, 130.8, 129.3, 128.7, 128.5, 127.9, 127.3, 126.6, 125.7, 123.9, 123.6, 123.3, 117.9, 116.5, 116.4, 112.9, 40.9, 40.6. MS (ESI): *m/z* 352 [M + H]$^+$. Anal. calcd. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.56; H, 5.91; N, 3.86.

4-(12*H*-Benzo[*a*]thioxanthen-12-yl)-*N*,*N*-dimethylaniline (12e). As described for **12a**, **11c** (100 mg, 0.37 mmol), *N*,*N*-dimethylaniline (44 mg, 0.37 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12e** (80%, 111 mg) as a colorless solid. M.p. 170–171 °C. IR (KBr): 2259, 1590, 763, 671 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, 1H, J = 8.6), 7.85 (d, 1H, J = 8.1), 7.73 (d, 1H, J = 8.6), 7.59-7.43 (m, 5H), 7.29 (t, 1H, J = 7.4), 7.25-7.20 (m, 1H), 6.84 (d, 2H, J = 8.5), 6.48 (d, 2H, J = 8.6), 6.22 (s, 1H), 2.80 (s, 6H). MS (ESI): *m/z* 368 [M + H]$^+$. Anal. calcd. for $C_{25}H_{21}$ NS: C, 81.70; H, 5.76; N, 3.81. Found: C, 81.82; H, 5.89; N, 3.96.

12-(Thiophen-2-yl)-12*H*-benzo[*a*]xanthene (12f). As described for **12a**, **11b** (100 mg, 0.40 mmol), thiophene (34 mg, 0.40 mmol) and $Sc(OTf)_3$ (20 mol%) furnished **12f** (72%, 90 mg) as a colorless solid. M.p. 166–167 °C.IR (KBr): 2923, 2362, 1624, 1582, 1486, 1456, 1250, 811, 753, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4): δ 7.88 (d, 1H, J = 8.5), 7.68-7.63 (m, 2H), 7.37-7.31 (m, 2H), 7.27-7.22 (m, 2H), 7.14-7.04 (m, 2H), 7.00-6.95 (m, 1H), 6.86 (dd, 1H, J_1 = 1.0, J_2 = 5.0), 6.62-6.59 (m, 1H), 6.55-6.54 (m, 1H), 5.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4): δ 150.7, 149.9, 149.4, 131.6, 130.8, 129.3, 129.2, 128.6, 128.0, 126.9, 126.6, 124.3, 124.2, 124.1, 123.9, 123.7, 122.8, 118.1, 116.8, 115.6, 36.6. MS (ESI): *m/z* 313 [M – 1]$^+$. Anal. calcd for $C_{21}H_{14}OS$: C, 80.22; H, 4.49. Found: C, 80.17; H, 4.63.

9-(4-Methoxyphenyl)-9*H*-xanthene (12g). As described for **12a**, **11a** (100 mg, 0.50 mmol), anisole (54 mg, 0.50 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12g** (70%, 102 mg) as a colorless solid. M.p. 91–92 °C. IR (KBr): 2356, 1606, 1485, 1261, 769, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-7.04 (m, 2H), 7.01-6.97 (m, 4H), 6.92-6.81 (m, 4H), 6.69-6.66 (m, 2H), 5.07 (s,1H),

3.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4): δ 158.3, 151.1, 138.8, 129.7, 129.4, 127.7, 124.7, 123.1, 116.5, 114.1, 55.1, 43.6. MS (ESI): m/z 287 $[M - 1]^+$. Anal. calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59 Found: C, 83.26; H, 5.69.

12-(4-Methoxyphenyl)-12*H*-benzo[*a*]thioxanthene (12h). As described for **12a**, **11c** (100 mg, 0.37 mmol), anisole (41 mg, 0.37 mmol) and $Sc(OTf)_3$ (20 mol%) furnished **12h** (72%, 96 mg) as a colorless solid. M.p. 135–136 °C. IR (KBr): 3012, 2359, 1603, 763, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, 1H, J = 8.7), 7.89 (d, 1H, J = 8.1), 7.77 (d, 1H, J = 8.5), 7.63-7.48 (m, 5H), 7.36-7.24 (m, 2H), 6.93 (d, 2H, J = 8.5), 6.68-6.65 (m, 2H), 6.28 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4): δ 158.2, 137.1, 132.9, 132.8, 132.7, 132.3, 131.9, 131.4, 129.8, 128.9, 128.5, 127.2, 127.1, 126.9, 126.8, 125.5, 125.3, 122.5, 113.6, 54.9, 46.4. MS (ESI): m/z 353 $[M - 1]^+$. Anal. calcd. for $C_{24}H_{18}OS$: C, 81.32; H, 5.12. Found: C, 81.23; H, 5.20.

12-(2,4-Dimethoxyphenyl)-12*H*-benzo[*a*]xanthene (12i). As described for **12a**, **11b** (100 mg, 0.40 mmol), 1,3-dimethoxybenzene (55 mg, 0.40 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12i** (74%, 109 mg) as a colorless solid. M.p. 251–152 °C. IR (KBr): 3019, 2318, 1612, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, 1H, J = 8.3), 7.77-7.73 (m, 2H), 7.46 (d, 1H, J = 7.4), 7.42-7.29 (m, 3H), 7.18-7.11 (m, 2H), 7.01-6.96 (m, 1H), 6.78 (d, 1H, J = 8.4), 6.47 (d, 1H, J = 2.3), 6.33 (s, 1H), 6.17 (dd, 1H, J_1 = 2.4, J_2 = 8.5), 4.05 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 155.8, 150.3, 149.8, 131.8, 130.7, 129.9, 129.1, 128.6, 128.3, 128.2, 127.3, 126.7, 125.9, 123.9, 123.5, 123.1, 117.8, 116.7, 116.3, 105.0, 98.4, 55.7, 55.1, 32.8. MS (ESI): m/z 368 $[M + H]^+$. Anal. calcd. for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.62; H, 5.61.

12-(2,4-Dimethoxyphenyl)-12*H*-benzo[*a*]thioxanthene (12j). As described for **12a**, **11c** (100 mg, 0.37 mmol), 1,3-dimethoxybenzene (51 mg, 0.37 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12j** (73%, 106 mg) as a colorless solid. M.p. 195–196 °C. IR (KBr): 2261, 1615, 762, 671 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, 1H, J = 8.6), 7.79-7.69 (m, 3H), 7.50-7.32 (m, 4H), 7.19-7.08 (m, 3H), 6.67 (s, 1H), 6.44 (d, 1H, J = 2.4), 6.16 (dd, 1H, J_1 = 2.4, J_2 = 8.5), 4.03 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 156.2, 136.7, 132.6, 132.0, 131.7, 130.7, 129.9, 129.2, 128.7, 127.3, 126.9, 126.5, 126.3, 126.2, 125.1, 124.8, 124.5, 122.7, 104.5, 98.6, 55.5, 55.1, 39.2. MS (ESI): m/z 385 $[M + H]^+$. Anal. calcd. for $C_{25}H_{20}O_2S$: C, 78.09; H, 5.24. Found: C, 77.94; H, 5.38.

4,5-Dimethoxy-2-(9-methoxy-12*H*-benzo[*a*]xanthen-12-yl)phenol (12k). As described for **12a**, **11d** (100 mg, 0.35 mmol), 3,5-dimethoxyphenol (54 mg, 0.35 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12k** (75%, 111 mg) as a colorless solid. M.p. 232–233 °C. IR (KBr): 3350, 3018, 2360, 1596, 793, 679 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, 1H, J = 8.4), 7.81-7.77 (m, 2H), 7.46-7.34 (m, 4H), 6.73 (s, br,1H), 6.65 (d, 1H, J = 8.4), 6.44 (s, 1H), 6.34 (s, 1H), 6.24 (s, 1H), 5.02 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 150.9, 149.5, 147.8, 144.8, 131.8, 130.7, 129.9, 128.8, 128.4, 126.7, 124.1, 123.2, 117.7, 112.7, 110.7, 101.0, 100.6, 56.2, 55.8, 55.4, 33.3. MS (ESI): m/z 415 $[M + H]^+$. Anal. calcd. for $C_{26}H_{22}O_5$: C, 75.35; H, 5.35. Found: C, 75.49; H, 5.48.

4-(9*H*-Xanthen-9-yl)phenol (12l). As described for **12a**, **11a** (100 mg, 0.50 mmol), phenol (47 mg, 0.50 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12l** (68%, 94 mg) as a colorless solid. M.p. 88–89 °C. IR (KBr): 3361, 1603, 761, 689 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.06 (m, 2H), 7.12-7.09 (m, 2H), 7.06-7.03 (m, 4H), 6.99-6.93 (m, 2H), 6.73-6.70 (m, 2H), 5.18 (s, 1H), 4.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 151.02, 138.9, 129.7, 129.6, 127.8, 124.7, 123.2, 116.5, 115.5, 43.5. MS (ESI): m/z 275 $[M + H]^+$. Anal. calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.09; H, 5.25.

9-(2,4-Dimethoxyphenyl)-9*H*-xanthene (12m). As described for **12a**, **11a** (100 mg, 0.50 mmol), 1,3-dimethoxybenzene (69 mg, 0.50 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12m** (69%, 110 mg) as a colorless solid. M.p. 108–109 °C. IR (KBr): 2971, 2330, 1614, 768 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (d, 1H, J = 1.6), 7.12-7.09 (m, 5H), 6.98-6.93 (m, 2H), 6.85 (d, 1H, J = 8.4), 6.48 (d, 1H, J = 2.3), 6.37 (dd, 1H, J_1 = 2.4, J_2 = 8.4), 5.72 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H). MS (ESI): m/z 319 $[M + H]^+$. Anal. calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.34; H, 5.56.

12-(2,4-Dimethoxyphenyl)-9-methoxy-12*H*-benzo[*a*]xanthene (12n). As described for **12a**, **11d** (100 mg, 0.35 mmol), 1,3-dimethoxybenzene (48 mg, 0.35 mmol) and $Sc(OTf)_3$ (10 mol%) furnished **12n** (71%, 101 mg) as a colorless semisolid. IR (KBr): 2332, 1616, 769 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, 1H, J = 7.9), 7.77-7.73 (m, 2H), 7.41-7.29 (m, 4H), 6.75 (d, 1H, J = 8.3), 6.68 (d, 1H, J = 2.2), 6.60-6.58 (m, 1H), 6.47 (s, 1H), 6.26 (s, 1H), 6.18 (d, 1H, J = 8.3), 4.05 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 158.9, 155.8, 151.0, 149.7, 131.9, 130.7, 129.8, 129.6, 128.6, 128.5, 128.3, 126.6, 123.9, 123.2, 118.2, 117.7, 116.9, 110.6, 105.1, 101.1, 98.4, 55.7, 55.4, 55.2, 32.3. MS (ESI): m/z 399 $[M + H]^+$. Anal. calcd. for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.24; H, 5.69.

12*H*-Benzo[*a*]xanthene (13b). As described for **12a**, **11b** (100 mg, 0.40 mmol), indole (47 mg, 0.40 mmol) and $FeCl_3$ (10 mol%) furnished **13b** (18%, 16 mg) as a colorless solid, after elution (1% ethyl acetate in hexane) of the crude product. M.p. 93–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-7.85 (m, 2H), 7.76 (d, 1H, J = 8.7), 7.64-7.58 (m, 1H), 7.50-7.45 (m, 1H), 7.35-7.26 (m, 3H), 7.16-7.10 (m, 2H), 4.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.0, 148.7, 132.1, 130.1, 129.4, 128.4, 128.2, 127.7, 126.6, 124.1, 123.1, 122.2, 119.5, 117.9, 116.5, 111.5, 24.7. MS (ESI): m/z 231 $[M - 1]^+$. Anal. calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.79; H, 5.35.

9*H*-Xanthene (13g). Isolated as a colorless solid by silica gel column chromatography (1% ethyl acetate in hexane) of the crude product. M.p. 98–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.22 (m, 4H), 7.14-7.07 (m, 4H), 4.10 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 128.8, 127.6, 122.9, 120.5, 116.4, 27.8. MS (ESI): m/z 181 $[M - 1]^+$. Anal. calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.81; H, 5.41.

3,3′-((4-Methoxy-2-(naphthalen-2-yloxy)phenyl)methylene)bis-(1*H*-indole) (14c). Isolated as a colorless semisolid by silica gel column chromatography (4% ethyl acetate in hexane) of the crude product. IR (KBr): 1614, 760, 678 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-7.71 (m, 4H), 7.59 (d, 1H, J = 7.9), 7.42-7.35 (m, 5H), 7.28-7.22 (m, 3H), 7.15-7.10 (m, 3H), 6.95 (t, 2H,

J = 7.4), 6.72 (s, 2H), 6.64-6.58 (m, 3H), 6.20 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 155.8, 154.7, 136.7, 130.9, 129.8, 129.5, 127.9, 127.6, 127.0, 127.0, 126.3, 124.3, 123.6, 121.8, 120.0, 119.4, 119.2, 119.1, 112.8, 110.9, 109.7, 106.0, 55.4, 32.9. MS (ESI): m/z 493 $[M - 1]^+$. Anal. calcd. for $C_{34}H_{26}N_2O_2$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.69; H, 5.19; N, 5.52.

((4-Methoxy-2-(naphthalen-2-yloxy)phenyl)methylene)bis((3-methoxyphenyl)sulfane) (19d). Isolated as a colorless liquid by silica gel column chromatography (3% ethyl acetate in hexane) of the crude product. IR (KBr): 1614, 760, 678 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H), 7.78-7.71 (m, 2H), 7.52-7.42 (m, 2H), 7.25-7.11 (m, 4H), 6.98 (d, 2H, J = 7.7), 6.92-6.91 (m, 2H), 6.78-6.75 (m, 3H), 6.43 (d, 1H, J = 2.5), 6.10 (s, 1H), 3.72 (s, 3H), 3.67 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3,159.5, 154.6, 154.3, 136.0, 134.2, 130.2, 130.1, 129.8, 129.5, 127.6, 127.2, 126.5, 124.8, 124.1, 123.0, 119.5, 116.7, 114.1, 113.7, 109.9, 104.7, 55.4, 55.1, 52.5. MS (ESI): m/z 261, 262. Anal. calcd. for $C_{32}H_{28}S_2O_4$: C, 71.08; H, 5.22. Found: C, 71.21; H, 5.09.

12-(3-Methoxyphenylthio)-12*H*-benzo[*a*]xanthene (20a). As described for **12a**, **11b** (100 mg, 0.40 mmol), 3-methoxybenzenethiol (56 mg, 0.40 mmol) and Sc(OTf)$_3$ (10 mol%) furnished **20a** (79%, 117 mg) as a colorless solid. M.p. 161–162 °C. IR (KBr): 2358, 1605, 761, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, 1H, J = 8.5), 7.87 (d, 1H, J = 8.0), 7.75 (d, 1H, J = 8.9), 7.72-7.67 (m, 1H), 7.54-7.49 (m, 1H), 7.43 (dd, 1H, J_1 = 1.4, J_2 = 7.6), 7.28-7.23 (m, 1H), 7.18-7.12 (m, 1H), 7.09 (d, 1H, J = 8.9), 6.98-6.93 (m, 2H), 6.83 (dd, 1H, J_1 = 1.7, J_2 = 8.3), 6.34 (d, 1H, J = 7.5), 6.17 (t, 1H, J = 1.8), 6.15 (s, 1H), 3.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 151.8, 150.4, 131.8, 130.7, 130.6, 129.5, 129.4, 129.0, 128.8, 128.7, 128.2, 126.9, 124.4, 123.5, 122.9, 121.3, 120.5, 117.4, 116.2, 115.9, 112.1, 54.9, 44.9. MS (ESI): m/z 231, 369 $[M - 1]^+$. Anal. calcd. for $C_{24}H_{18}O_2S$: C, 77.81; H, 4.90. Found: C, 77.92; H, 5.02.

12-(Phenylthio)-12*H*-benzo[*a*]xanthene (20b). As described for **12a**, **11b** (100 mg, 0.40 mmol), benzenethiol (44 mg, 0.40 mmol) and Sc(OTf)$_3$ (10 mol%) furnished **20a** (72%, 98 mg) as a colorless solid. M.p. 199–200 °C. IR (KBr): 3015, 2361, 1609, 771, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, 1H, J = 8.3), 7.87 (d, 1H, J = 8.1), 7.75 (d, 1H, J = 8.9), 7.71-7.67 (m, 1H), 7.54-7.49 (m, 1H), 7.41-7.38 (m, 1H), 7.29-7.22 (m, 2H), 7.16-7.02 (m, 4H), 6.95 (d, 1H, J = 8.0), 6.70 (d, 2H, J = 7.6), 6.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.7, 150.4, 136.8, 132.4, 130.9, 130.7, 130.6, 130.1, 129.4, 129.4, 128.9, 128.7, 128.2, 128.1, 126.9, 124.4, 123.5, 122.9, 121.3, 117.4, 115.9, 112.1, 44.8. MS (ESI): m/z 231. Anal. calcd. for $C_{23}H_{16}OS$: C, 81.14; H, 4.74. Found: C, 81.02; H, 4.61.

12-(Naphthalen-2-ylthio)-12*H*-benzo[*a*]thioxanthene (20c). As described for **12a**, **11c** (100 mg, 0.37 mmol), naphthalene-2-thiol (59 mg, 0.37 mmol) and Sc(OTf)$_3$ (10 mol%) furnished **20c** (74%, 113 mg) as a colorless solid. M.p. 218–219 °C IR (KBr): 3011, 2361, 1621, 769, 671 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, 1H, J = 8.5), 7.85-7.62 (m, 7H), 7.51-7.42 (m, 5H), 7.34 (d, 1H, J = 8.5), 7.25-7.17 (m, 1H), 7.97-6.89 (m, 1H), 6.79 (d, 1H, J = 7.6), 6.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.5, 133.3, 132.9, 132.9, 132.8, 132.6, 132.5, 132.1, 131.0, 130.3, 129.3, 128.9, 128.0, 127.9, 127.8, 127.5, 127.2, 127.1, 126.9, 126.7, 126.2, 125.8, 125.3, 124.8, 121.8, 51.4. MS (ESI): m/z 247. Anal. calcd. for $C_{27}H_{18}S_2$: C, 79.76; H, 4.46. Found: C, 79.89; H, 4.58.

9-Methoxy-12-(*p*-tolylthio)-12*H*-benzo[*a*]xanthene (20d). As described for **12a**, **11d** (100 mg, 0.35 mmol), 4-methylbenzenethiol (43 mg, 0.35 mmol) and Sc(OTf)$_3$ (10 mol%) furnished **20d** (71%, 98 mg) as a colorless solid. M.p. 145–146 °C. IR (KBr): 3014, 2360, 1619, 759, 670 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, 1H, J = 8.1), 7.86 (d, 1H, J = 8.3), 7.73 (d, 1H, J = 8.7), 7.68-7.64 (m, 1H), 7.51-7.46 (m, 1H), 7.24 (s, 1H), 7.07 (d, 1H, J = 9.1), 6.86 (d, 2H, J = 7.5), 6.71 (d, 1H, J = 6.1), 6.61 (d, 2H, J = 7.9), 6.50 (s, 1H) 6.05 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H). MS (ESI): m/z 261. Anal. calcd. for $C_{25}H_{20}O_2S$: C, 78.09; H, 5.24. Found: C, 77.94; H, 5.38.

9-Methoxy-12-(3-methoxyphenylthio)-12*H*-benzo[*a*]xanthene (20e). As described for **12a**, **11d** (100 mg, 0.35 mmol), 3-methoxybenzenethiol (49 mg, 0.35 mmol) and Sc(OTf)$_3$(10 mol%) furnished **20e** (76%, 109 mg) as a colorless solid. M.p. 176–177 °C. IR (KBr): 2360, 1617, 762, 679 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 1H, J = 8.5), 7.85 (d, 1H, J = 7.7), 7.72 (d, 1H, J = 9.2), 7.66-7.61 (m, 1H), 7.51-7.48 (m, 1H), 7.30 (d, 1H, J = 8.5), 7.06 (d, 1H, J = 8.9), 6.92 (d, 1H, J = 7.3), 6.82-6.76 (m, 1H), 6.72 (dd, 1H, J_1 = 2.5, J_2 = 8.2), 6.47 (d, 1H, J = 2.5), 6.35-6.30 (m, 1H), 6.16-6.14 (m, 1H), 6.12 (s, 1H), 3.81 (s, 3H), 3.40 (s, 3H). MS (ESI): m/z 261. Anal. calcd. for $C_{25}H_{20}O_3S$: C, 74.98; H, 5.03. Found: C, 75.11; H, 4.91.

2-(12*H*-Benzo[*a*]xanthen-12-ylthio)pyridine (20f). As described for **12a**, **11b** (100 mg, 0.40 mmol), pyridine-2-thiol (44 mg, 0.40 mmol) and Sc(OTf)$_3$ (50 mol%) furnished **20f** (58%, 77 mg) as a colorless semisolid. IR (KBr): 2358, 1621, 759 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, 1H, J = 8.5), 7.86 (d, 2H, J = 8.6), 7.72 (d, 1H, J = 7.6), 7.63 (d, 1H, J = 7.1), 7.52–6.72 (m, 9H), 6.54 (d, 1H, J = 7.1). MS (ESI): m/z 231 $[M - 110]^+$. Anal. calcd. for $C_{22}H_{15}NOS$: C, 77.39; H, 4.43, N, 4.10. Found: C, 77.51; H, 4.27; N, 3.98.

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