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BENZYLIC OXIDATION AND FUNCTIONALIZATIONS OF XANTHENES BY LIGAND TRASFER REACTIONS OF HYPERVALENT IODINE REAGENTS

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Abstract – The benzylic oxidation, amidation, and unprecedented heteroarylation proceed at room temperature using iodosobenzene, (sulfonylimido)iodobenzenes, and diaryliodonium(III) salts are described for the direct Csp^3-H functionalizations of xanthene molecules. This study has demonstrated that hypervalent iodine reagents serve as unified synthetic tools for versatile xanthene Csp^3-H transformations based on the radical and SET oxidation processes.

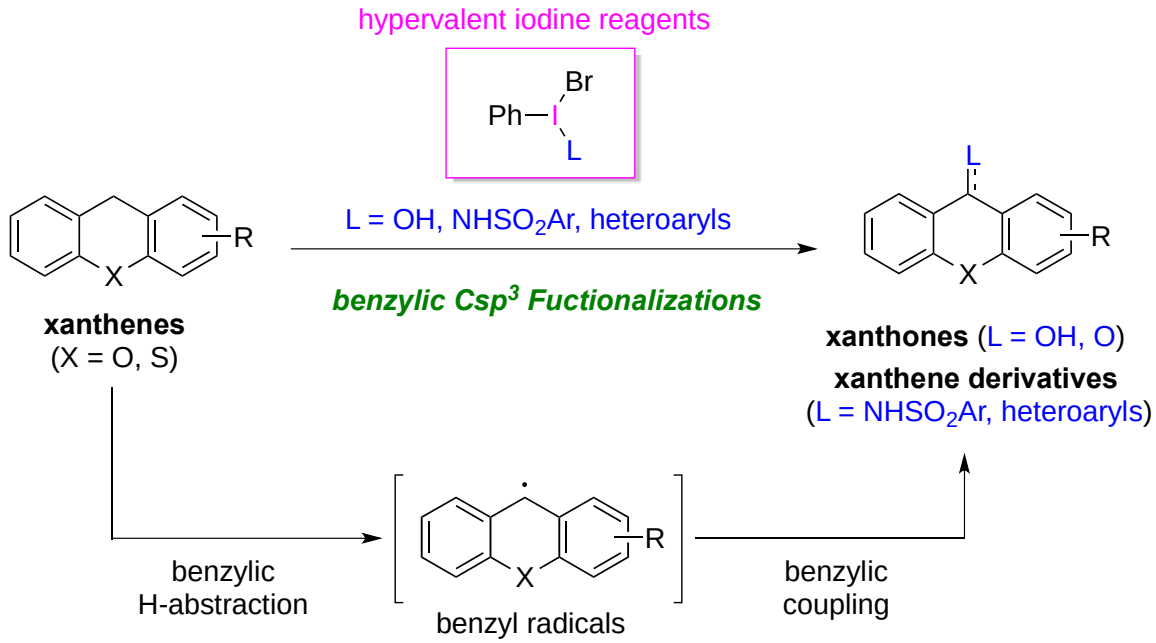
In Celebration of HETEROCYCLES 100th Special Issue

INTRODUCTION

Xanthenes and their derivatives are a unique class of heterocyclic compounds showing a broad range of biological activities and having practical applications as organic functional materials, such as dyes and pH responsive fluorescent compounds.[1] In this context, the benzylic functionalization of xanthenes is an important way to furnish the structural diversity of the molecules.[2] The synthesis of these compounds from xanthenes was sometimes stepwise carried out through the benzylic oxidation products, that is, xanthones, as the intermediate.[3,4] In addition, several oxidative Csp^3-H functionalization strategies that

can directly install specific nucleophiles[5,6] and aromatic molecules[7] at the xanthene 9-*H* positions have newly emerged in recent years for their synthetic access.

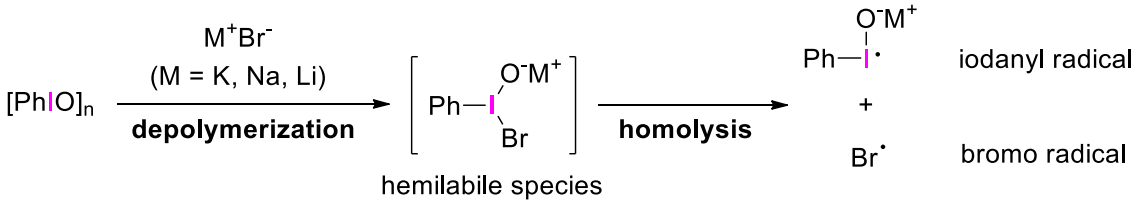
Hypervalent iodine reagents, such as iodosobenzene (PhIO), phenyliodine(III) diacetate (PIDA), and [phenyliodine(III) bis(trifluoroacetate)] (PIFA), are the useful oxidant and coupling agent in view of their low toxicity, ready availability, high stability, easy handling, inertness, ease of recovery and recyclability.[8] The reactivities of these reagents are similar to the lead(IV), mercury(II), and thallium(III) salts, and thus one expected use is replacing these toxic heavy-metal oxidizers in chemical transformations by a safer one in order to obtain the high-purity products.[9] Interestingly, hypervalent iodine(III) reagents typically showing two-electron-transfer oxidations would cause single-electron-transfer (SET) oxidations and radical reactions depending on the substrates, reaction conditions, and activation methods.[10] Utilizing the radical reactivities of the hypervalent iodine(III) reagent suitably activated by inorganic bromides,[11] we have previously developed the benzylic C-H oxidation and functionalizations that can work under both aqueous and nonaqueous conditions for the synthesis of aryl ketones, carboxylates, and lactones.[12] As an extended study, we now report the benzylic oxidations and new Csp^3-H functionalization methods of xanthenes to give xanthones, xanthene sulfonamides, and some heteroaryl xanthenes based on the unique activations of iodosobenzene, phenyliodine(III) diacetate, and specific thienyl- and indolyl-iodonium(III) salts (Scheme 1).



Scheme 1. Benzylic oxidation and functionalizations using hypervalent iodine(III) reagent through the formation of xanthene radicals

RESULTS AND DISCUSSION

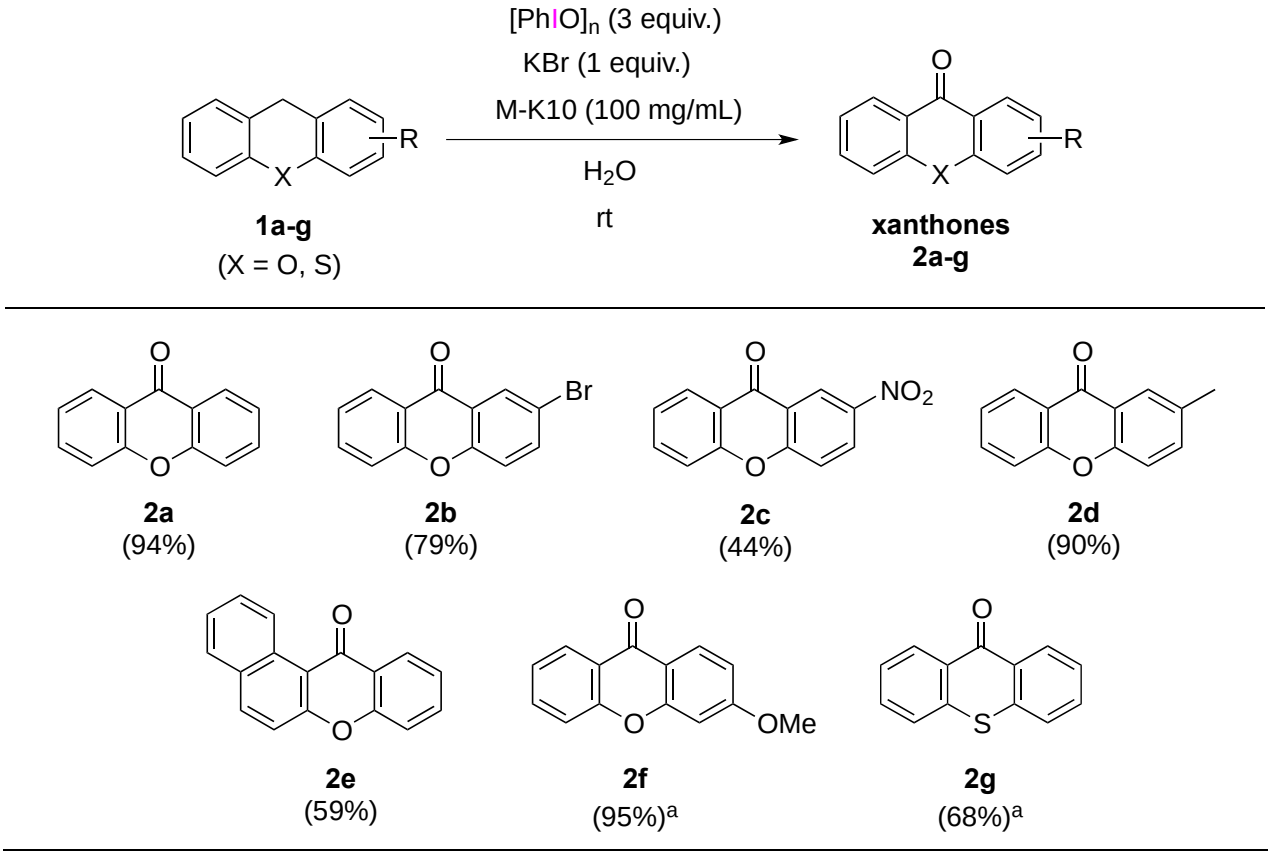
The treatment of a hypervalent iodine reagent, such as iodosobenzene, with an inorganic bromide produces the unique iodanyl radical[13] together with the generation of a bromo radical. For iodosobenzene ([PhIO]$_n$), depolymerization of the network would occur due to the inorganic bromide to develop monomeric hypervalent iodine species having the homolytic I(III)-Br bond,[14] which can initiate radical reactions as illustrated in Scheme 2. These radicals appeared to selectively abstract the benzylic hydrogen of organic substrates in the presence of a wide variety of functional groups. Thus, we reported the aqueous benzylic oxidations of a series of aromatic hydrocarbons using the iodosobenzene-inorganic bromide radical reaction system in the presence of montmorillonite-K10 (M-K10).[12a] The alternative I(III)-Br species and related hypervalent iodine radical initiators can also be generated by the ligand exchange of PIDA and its derivatives.[15]



Scheme 2. Generation of iodanyl and bromo radicals from iodosobenzene and inorganic bromide

We have now found that our reaction conditions employing iodosobenzene with potassium bromide for aqueous benzylic oxidations to give aryl ketones[12a] are also applicable to xanthenes and their derivatives. The green oxidations not using an organic solvent smoothly proceeded at room temperature for xanthene **1a**, and after 3 h, the corresponding benzylic oxidation product, xanthone **2a**, was obtained in high yield from the clean reaction mixture (Scheme 3). Similarly, xanthones bearing an electron-donating substituent at the aromatic ring, such as **2d** and **2f**, were effectively produced from the methyl and methoxy xanthenes, **1d** and **1f**, respectively. On the other hand, the reaction rates were somewhat lower when an electron-withdrawing group is present on the xanthenes, and the yield of 2-nitroxanthone **2c** was only 44% after the reaction for 24 h. Unfortunately, the yield was not improved at an elevated reaction temperature due to the over-oxidation of the product and partial ring-bromination of the xanthene aromatic ring. For the methyl-substituted xanthene **1d**, the reaction was highly chemoselective at the xanthene benzylic position and the methyl group was not oxidized at all at room temperature. The naphthalene ring, which is reactive to hypervalent iodine reagents,[16] was tolerant during the reaction, but accompanied by decompositions. Thus, benzoxanthone **2e** was obtained in 59% yield after isolation. Under mild reaction conditions, the xanthone formation was preferred to the sulfide oxidation for the thioxanthene as shown by the product **2g**. In these reactions, the added M-K10 seems to well assist in the

depolymerization and solubilization of iodosobenzene in water, while it would slowly cause ring bromination and oxidations of the electron-rich aromatic ring and sulfur group for such xanthenes, **1f** and **1g**.

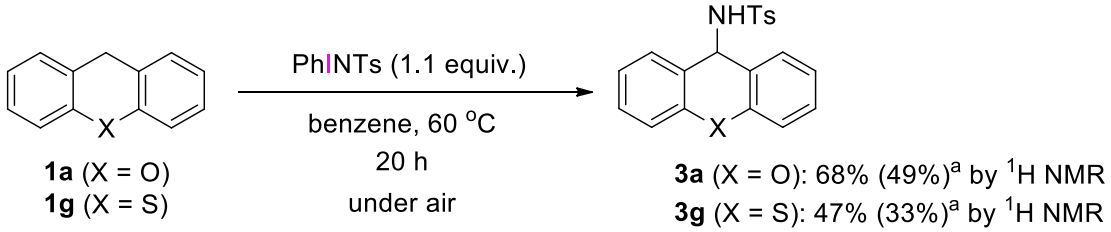


[a]In the absence of M-K10.

Scheme 3. Aqueous benzylic oxidation of xanthenes using a combination of iodosobenzene and potassium bromide

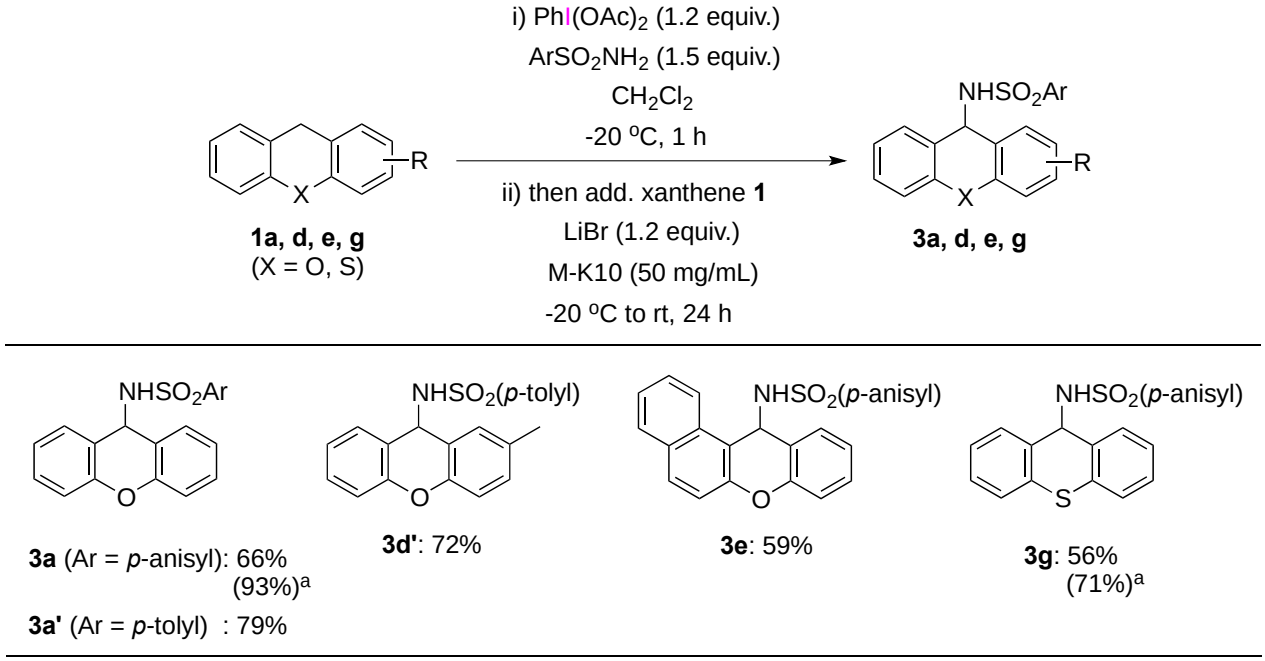
Very recently, de Bruin and co-workers discussed the thermal imido-group transfer of (tosylimino)phenyl iodinane, PhINTs, into the Csp^3-H bond of xanthene **1a** and thioxanthene **1g** at 60 °C for the oxidative amidation to give the *N*-9*H*-functionalized xanthene sulfonamides (the yields were determined by ^{1}H NMR without isolation).[6e] The reaction is believed to involve generation of the xanthylium cation-tosylamido anion pair through the oxidation by PhINTs and hydride transfer to the tosylamido group from the xanthene, which subsequently undergoes conjugate addition to produce the observed benzylic C-H amidation product (Scheme 4). However, xanthenes and the products are susceptible to other types of oxidations and decompositions, respectively, due to the reactive benzylic positions, which would produce oxygenated xanthones, dehydrogenated xanthene sulfonylimines, and some unidentified products, during the oxidation reactions and even isolations. Hence, the catalytic strategy of the C-H amination processes

that employs a transition metal instead using a mild oxidant to lower the reaction temperature and milder conditions has been investigated in these types of xanthene transformations for broadening the substrate scope.[6a-d]



Scheme 4. Bruin's work: Catalyst-free oxidative C-H functionalization using imino-λ^3-iodinane ([a]Yields in parentheses concern reactions using *in situ* generated PhINTs, generated from $TsNH_2$ and $PhI(OPiv)_2$ in the presence of magnesium oxide.)

Based on the situation, we speculated that the catalysis of the inorganic bromide of our benzylic oxidation system becomes beneficial for activating the imino-λ^3-iodinanes and for performing the oxidative Csp^3-H xanthene amidation at room temperature. As for the reaction factor, several inorganic bromides[12] were screened for the *in situ* prepared $PhINSO_2Ar$ (Ar = *p*-anisyl or tolyl) from PIDA and sulfonamides using xanthene **1a** as a model substrate, which suggested that the metal ion plays a distinct role in the activation of imino-λ^3-iodinanes and the hard lithium is a better candidate in this case among the alkali metal (M = Li, Na, K, and Cs) bromides. As a result, the reaction conditions using M-K10 in dichloromethane (~0.1 M of the reaction substrate) at room temperature were optimized to 1.2 equiv. of finely powdered LiBr and PIDA with a slight excess amount of sulfonamides (see Scheme 5). Gratefully, the ^{1}H NMR monitoring indicated that our new protocol would apparently improve the product yields of the oxidative Csp^3-H amidation of xanthenes by $PhINSO_2Ar$; a 93% formation of the target product **3a** (Ar = *p*-anisyl) was detected after the reaction of xanthene **1a**. The xanthene *p*-tolylsulfonamide **3a'** was more stable than *p*-anisyl **3a** during the workup and isolation, and it was obtained in 79% isolated yield by silica-gel column chromatography. Likewise, for the benzylic oxidation by iodosobenzene, this xanthene *N*-functionalization selectively occurred for the methyl-substituted xanthene **1d** and benzoxanthene **1e** to give the products **3d'** and **3e** in 72% and 59% yields. The yield of thioxanthene sulfonamide **3g** was also increased in our reaction system compared to the non-catalytic C-H amidation (see Scheme 4).[17]



[a] NMR yield using 1,1,2,2-tetrachloroethane (d = 6.95 ppm in DMSO-d_6) as an internal standard.

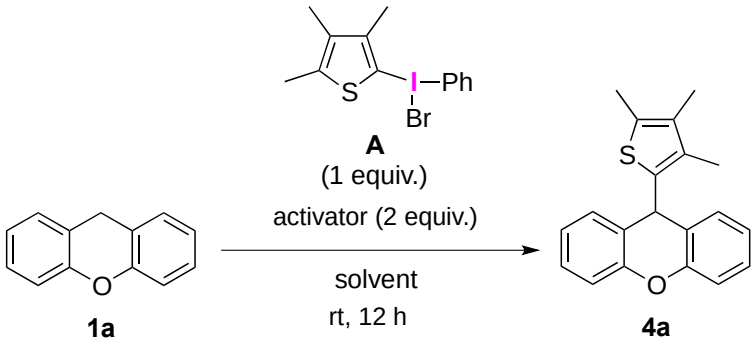
Scheme 5. Benzylic C-H amidation of xanthenes by activation of imino-λ^3-iodinane with lithium bromide

The diaryliodonium(III) salts expressed by the general formula, $ArI^+Ar'X^-$ (Ar, Ar' = aryl, X^- = counterion), constitute a unique class of hypervalent iodine compounds having practical applications as a reactive coupling agent and photo-acid generator in the material sciences.[18] Since 2009, we have pioneered the metal-free oxidative coupling reactions utilizing diaryliodonium(III) salts as unique aryl transfer agents.[19,20] Based on this renaissance, hypervalent iodine chemistry has faced significant advances in recent years in the area of the oxidative coupling reactions and syntheses as a new strategic choice.[9,10] Aiming to extend our strategy for the introduction of heteroaromatics to xanthenes, we have now examined the reaction of heteroaromatic diaryliodonium(III) bromide[21,22] based on the SET activation (Table 1).[23] Note that several methods for the oxidative benzylic arylations of xanthenes were recently reported, one of which uses a hypervalent iodine reagent for coupling with a Grignard reagent,[7a] while others deal with the dehydrogenative couplings toward the arene C-H bonds by means of the oxidative coupling catalysts.[7b,c]

The results in Table 1 indicated that strong SET activation conditions employing trimethylsilyl triflate (TMSOTf) in hexafluoroisopropanol (HFIP)[10a] is suitable for the diaryliodonium(III) salt **A** to transfer the thienyl group into xanthene **1a** (see entries 1-4). Interestingly, the formation of biaryls did not occur, but instead, 9*H*-aryl xanthene **4a** was produced as the sole coupling product. Hence, the reaction of xanthene **1a** with the TMS-activated thienyliodonium(III) salt **A** under the optimized conditions (entry 2) gave Csp^3-aryl xanthene **4a** in 78% yield. Among the screened Brønsted acids, trifluoromethanesulfonic acid

(TfOH) acted as a good activator for the arylation, but the yield was not further improved (entry 5). Other Lewis and Brønsted acids, such as $BF_3{\cdot}Et_2O$ and trifluoroacetic acid, and the thienyliodonium(III) salt having other ligands, *i.e.*, triflate and tosylate, were also tested but with negative results.

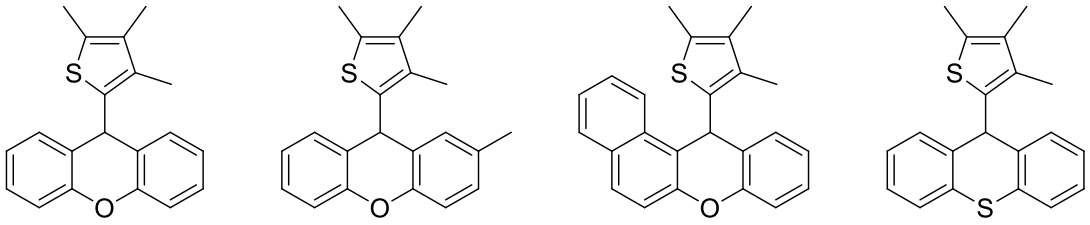
Table 1. Benzylic C-H arylation of xanthenes using diaryliodonium(III) salt **A**: Optimization



entry	activator (acid)	solvent	arylation product **4a**
1	TMSBr	hexafluoroisopropanol	26%
2	TMSOTf	hexafluoroisopropanol	78%
3	TMSOTf	trifluoroethanol	trace
4	TMSOTf	CH_2Cl_2	trace
5	TfOH	hexafluoroisopropanol	64%
6	$C_6F_5CO_2H$	hexafluoroisopropanol	trace

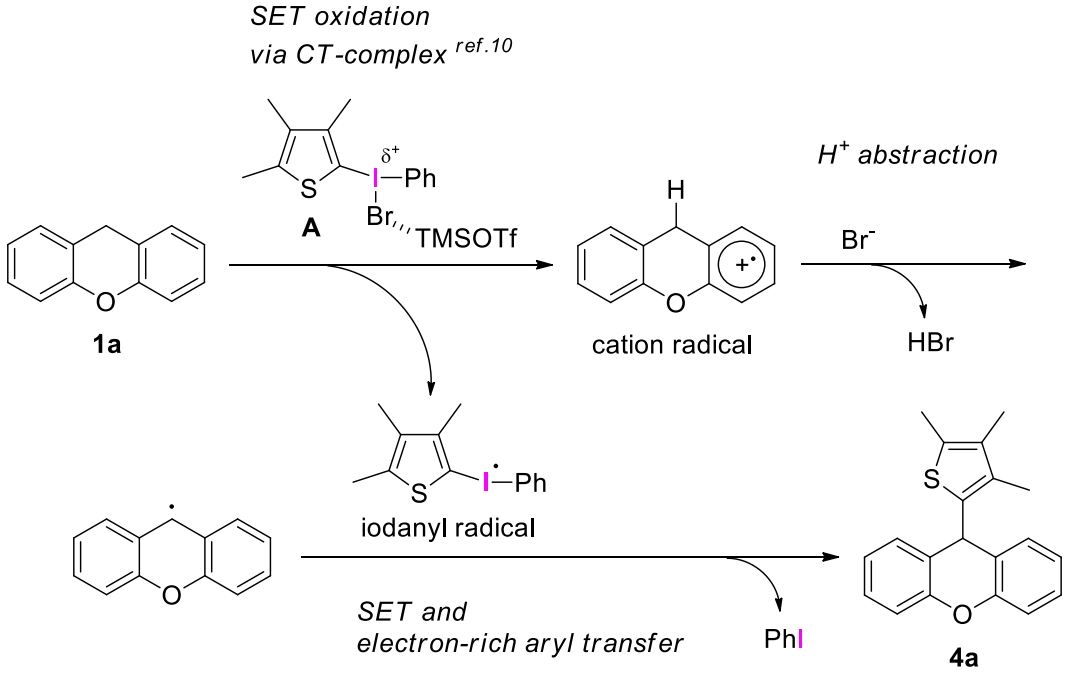
hexafluoroisopropanol: $(CF_3)_2CHOH$ (HFIP), trifluoroethanol: CF_3CH_2OH

We have confirmed that a series of xanthenes **1** selected for our already-mentioned study can be similarly transformed into the arylated products **4** by the thienyliodonium(III) salt **A**[22] under SET oxidizing conditions (Scheme 6). Based on the result of the product **4d** yield, this oxidative Csp^3 arylation initiated by the SET oxidation of the xanthene ring seems sensitive to the aromatic substituent compared to the radical benzylic functionalization pathways (see the products **2d** and **3d** in Schemes 3 and 5 using iodosobenzene and imino-λ^3-iodinanes). Although the naphthalene ring is expected to accommodate the smooth charge-transfer (CT) complexation with the hypervalent iodine reagent and successive SET oxidation,[16] the yield of the product **4e** somewhat decreased in comparison to the reaction of the simple xanthene **1a**. On the other hand, thioxanthene becomes a rather good substrate and the corresponding 9*H*-thienyl thioxanthene **4g** was obtained in good yield. In each case, the electron-rich thienyl group was exclusively transferred to the xanthene ring and no phenyl group-transfer product was detected during the reaction.



Scheme 6. Metal-free thienyl-group transfer to xanthene Csp^3-H group using diaryliodonium(III) salt **A**

The outline of the reaction mechanism for the thienyl group-transfer from the diaryliodonium(III) salt **A** to the xanthene Csp^3-H group is believed to involve the SET oxidation pathway (Scheme 7).[10] Without any activation, the diaryliodonium(III) bromide **A** itself cannot react with aromatic compounds. Prior to the SET oxidation, a Lewis acid, TMSOTf, would support the CT-complex formation[23] of the iodonium(III) bromide toward the aromatic ring of xanthene **1a** by enhancing the electrophilicity of the iodine(III) atom. The xanthene aromatic cation radical was then transformed into a neutral radical species by abstraction of the benzylic proton.

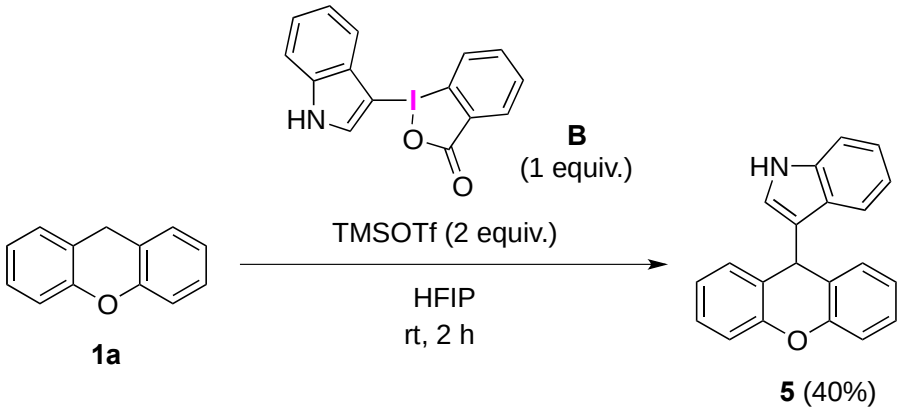


Scheme 7. Outline of the reaction mechanism for aryl ligand transfer reaction of diaryliodonium(III) salt **A** to the xanthene benzylic C-H group

Although the detailed reaction mechanism has not yet been determined, the formed xanthene radical was possibly further oxidized to some benzylic electrophilic species by the persistent iodanyl radical through

the second SET oxidation event to which the electron-rich thienyl ring concomitantly transferred as a nucleophilic counterpart to produce the aryl xanthene **4a**. To the best of our knowledge, this is the first example in the literature dealing with the aryl ligand-transfer from a diaryliodonium(III) salt into the Csp^3-H bond of organic compounds without the use of a transition metal catalysis.

The hybridization of the indole structure with xanthenes is of continuous interest in the pharmaceutical sciences and the development of new organic materials and sensors.[24] As a new synthetic tool of the diaryliodinium(III) salts, a safer, stable, and readily available cyclic indolyl iodonium(III) salt **B** was recently independently introduced by Waser[25] and Yoshikai.[26] Thus, we evaluated the cyclic indolyl iodonium(III) salt **B** under our aryl-transfer conditions by treatment with xanthene **1a**, which caused the selective indole transfer to afford the benzylic coupling product, 9*H*-indolyl xanthene **5**, in a 40% yield (Scheme 8). Though the product formation was moderate, our method merits the synthetic step for the transformation of xanthenes into indole-hybrid compounds because the 9*H*-xanthen-9-ols should be prepared before introduction of the indole group to the xanthene structures by conventional methods.[27,28]



Scheme 8. Indole-group transfer from cyclic diaryliododnium(III) salt **B**

CONCLUSION

In this study, we have developed the benzylic oxidation, amidation, and heteroarylation of xanthenes at room temperature using a hypervalent iodine reagent as a unified synthetic tool. The benzylic oxidation of xanthenes was demonstrated by extending our aqueous radical reaction system based on the activation of iodosobenzene with potassium bromide. This strategy is also valuable for activating imino-λ^3-iodanes to initiate radical reactions, and the effective benzylic Csp^3-H sulfonamidations utilizing the *in situ* generated $PhINSO_2Ar$ are realized by selection of lithium bromide as a suitable inorganic salt. In addition to these radical oxidation processes, the unprecedented aryl-group transfer to the benzylic Csp_3-H bond from diaryliodonium(III) salts was first discovered by the SET activation of heteroaryl iodonium(III) **A** and **B**. Hence, it is expected that the radical and SET oxidation strategies using the hypervalent iodine

reagent will become versatile approaches for the functionalizations of xanthenes. We are currently studying the extension of our Csp^3-H functionalization system to utilize less reactive substrates and other types of organic molecules.

EXPERIMENTAL

Melting points (mp) are uncorrected. All ^1H NMR and ^{13}C NMR spectra of the products were recorded on JEOL JMN-300 or 400 spectrometers operating at 400 or 300 MHz (100 or 75 MHz for ^{13}C NMR, 25 °C) with tetramethylsilane (δ 0.00 for ^1H and ^{13}C) as an internal standard. The data are reported as follows: chemical shift in parts per million (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters for the representative peaks. Analytical TLC was performed on MERCK silica gel (grade 60 F_{254}) using hexane/ethyl acetate as eluent; the spots were detected by UV irradiation (254, or 365 nm) and/or by staining with 5% phosphomolybdic acid followed by heating. Flash column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh)).

Materials

Iodosobenzene and phenyliodine(III) diacetate are commercially available and used as-received. Thienyl and iodolyliodonium(III) salts **A** and **B** were prepared according to the synthetic methods reported by us[22] and others,[25,26] respectively. The solid acid catalyst, montmorillonite-K10 (M-K10), was purchased from the Sigma-Aldrich Co. LLC (cat.; 28, 152-2). Regarding xanthenes **1b-f** and acridine **1h**, these compounds were prepared according to the literatures.[29a] Unless otherwise noted, all other chemicals used in this study were commercially available and used as-received without further purification.

General procedure for the benzylic oxidation of xanthenes 1 and their derivatives (Scheme 3)

To a suspension of xanthene **1a** (24.0 mg, 0.20 mmol) in water (1 mL) was added iodosobenzene (132 mg, 0.60 mmol, 3 equiv.) and potassium bromide (23.8 mg, 0.20 mmol, 1 equiv.) at room temperature. Montmorillonite-K10 (M-K10, 100 mg) was then added and the resulting mixture was stirred for 3 h. The reaction was quenched by aqueous saturated sodium carbonate, and then extracted with CH_2Cl_2. The organic phase was dried over anhydrous sodium sulfate and then concentrated *in vacuo*. Purification of the residue by column chromatography on silica-gel gave a benzylic oxidation product, xanthene-9-one **2a** (25.8 mg, 0.19 mmol), in 94% yield. Gram-scale preparation of xanthene **2** was possible by using the same procedure.

Xanthen-9-one (2a)[29b]

white powder; mp 176-177 ºC; IR (KBr, cm^{-1}): 1659, 1607, 1481, 1460, 1333, 758; ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32 (t, *J* = 7.1 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.66 (m, 2H), 8.29 (dd, *J* = 8.1, 1.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 117.8, 121.6, 123.7, 126.5, 134.6, 155.9, 176.9.

2-Bromoxanthen-9-one (2b)[29c]

Pale yellow solid; mp 149-151 ºC; IR (KBr, cm^{-1}): 1665, 1458, 1315, 757; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34-7.41 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.69-7.79 (m, 2H), 8.30 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.42 (d, *J* = 2.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 117.2, 118.2, 120.1, 121.6, 123.2, 124.4, 126.9, 129.3, 135.3, 137.8, 155.0, 156.1, 176.1.

2-Nitroxanthen-9-one (2c)[29d]

white solid; mp 199-200 ºC; IR (KBr, cm^{-1}): 1670, 1613, 1533, 1464, 1347, 767, 747; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45-7.50 (m, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 9.3 Hz, 1H), 7.79-7.84 (m, 1H), 8.34 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.55 (dd, *J* = 9.3, 2.9 Hz, 1H), 9.20 (d, *J* = 2.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 118.4, 119.8, 121.5, 121.8, 123.7, 125.4, 127.1, 129.2, 136.1, 144.0, 156.0, 159.3, 175.9.

2-Methylxanthen-9-one (2d)[29e]

white solid; mp 120-122 ºC; IR (KBr, cm^{-1}): 1657, 1608, 1489, 1469, 1319, 761; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.46 (s, 3H), 7.30-740 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.66-7.74 (m, 1H), 8.11 (d, *J* = 1.5 Hz, 1H), 8.33 (dd, *J* = 8.3, 2.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 21.0, 117.9, 118.1, 121.6, 121.9, 123.8, 126.1, 126.8, 133.8, 134.8, 136.2, 154.5, 156.3, 177.4.

1,2-Benzoxanthone (2e)[29e]

pale yellow solid; mp 138-140 ºC; IR (KBr, cm^{-1}): 1646, 1518, 1467, 768, 752; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39-7.45 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.67-7.74 (m, 1H), 7.74-7.80 (m, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 9.3 Hz, 1H), 8.42 (dd, *J* = 8.3, 1.5 Hz, 1H), 10.08 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 114.6, 117.6, 118.1, 123.7, 124.4, 126.2, 126.8, 127.1, 128.5, 129.6, 130.2, 131.2, 134.0, 136.8, 154.7, 157.7, 178.6.

3-Methoxyxanthen-9-one (2f)[29f]

white solid; mp 126-128 ºC; IR (KBr, cm^{-1}): 1652, 1620, 1466, 1440, 1325, 1259, 762; ^{1}H-NMR (400 MHz, $CDCl_3$): 3.94 (s, 3H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.65-7.73 (m, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.33 (dd, *J* = 7.8, 2.0 Hz, 1H);

^{13}C-NMR (100 MHz, $CDCl_3$): 56.0, 100.3, 113.4, 115.9, 117.8, 122.1, 124.0, 126.8, 128.4, 134.4, 156.3, 158.2, 165.2, 176.4.

Thioxanthen-9-one (2g)[29b]

Pale yellow crystals; mp 208-209 °C; IR (KBr, cm^{-1}): 1643, 1591, 1435, 1321, 731; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45-7.64 (m, 6H), 8.62 (d, *J* = 8.1 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 125.9, 126.2, 129.1, 129.8, 132.2, 137.2, 179.9.

General procedure for the benzylic C-H amidation of xanthenes 1 and their derivatives (Scheme 4)

In a flame-dried two-necked round-bottomed flask, under nitrogen, phenyliodine(III) diacetate (PIDA, 193 mg, 0.24 mmol, 1.2 equiv.) and 4-toluenesulfonamide (51.4 mg, 0.30 mmol, 1.5 equiv.) were subsequently added in dry CH_2Cl_2 (3 mL) at -20 °C, and the resulting solution was stirred for 1 h. Xanthene (0.2 mmol), finely powdered lithium bromide (20.8 mg, 0.24 mmol, 1.2 equiv.) and M-K10 (100 mg) were then added and the resulting mixture was stirred at room temperature. After 24 h, saturated aqueous sodium carbonate was added and the resulting solution was stirred for an additional 5 min. The organic layer was separated, washed again with saturated aqueous sodium carbonate, then with dilute aqueous sodium thiosulfate, and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was subjected to column chromatography on silica-gel (eluents: *n*-hexane/EtOAc) to give the benzylic amination product **3** in the indicated yield.

***N*-Xanthen-9-yl-*p*-toluenesulfonamide (3a)**[29g]

white solid; mp 203-205 °C; IR (KBr, cm^{-1}): 3322, 3043, 1598, 1484, 1459, 1427, 1329, 1264, 1153, 1092, 1029, 875, 814, 754; ^{1}H-NMR (400 MHz, DMSO-d_6): 2.43 (s, 3H), 5.71 (d, *J* = 8.3 Hz, 1H), 6.97-7.05 (m, 3H), 7.08-7.21 (m, 3H), 7.27-7.35 (m, 2H), 7.42 (t, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 8.64 (d, *J* = 8.3 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): 21.0, 47.8, 116.3, 121.2, 123.3, 126.4, 129.1, 129.3, 129.7, 139.6, 142.7, 150.8.

4-Methoxy-*N*-9*H*-xanthen-9-yl-benzenesulfonamide (3a')[29h]

pale yellow solid; mp 187-189 °C; IR (KBr, cm^{-1}): 3313, 2961, 1595, 1485, 1458, 1326, 1261, 1153, 1094, 1027, 802, 756; ^{1}H-NMR (400 MHz, DMSO-d_6): 3.87 (s, 3H), 5.69 (d, *J* = 8.3 Hz, 1H), 6.97-7.08 (m, 4H), 7.10-7.15 (m, 4H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 8.57 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): 47.7, 55.7, 114.4, 116.2, 121.2, 123.3, 128.6, 129.1, 129.3, 134.2, 150.8, 162.2.

4-Methyl-*N*-(2-methyl-9*H*-xanthen-9-yl)benzenesulfonamide (3d)[29i]

pale yellow solid; mp 215-218 ºC; IR (KBr, cm^{-1}): 3314, 2919, 1598, 1488, 1459, 1422, 1330, 1266, 1152, 1092, 1027, 932,885, 822, 763; ^{1}H-NMR (400 MHz, DMSO-d_6): 2.02 (s, 3H), 2.43 (s, 3H), 5.60 (d, *J* = 8.3 Hz, 1H), 6.34 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 7.03-7.09 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.28-7.34 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 8.60 (d, *J* = 8.3 Hz, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): 20.1, 21.0, 47.8, 116.0, 116.2, 120.2, 121.2, 123.2, 126.5, 129.1, 129.3, 129.6, 129.7, 129.8, 131.9, 139.7, 142.7, 148.7, 150.8.

***N*-12*H*-Benzo[*a*]xanthen-12-yl-4-methoxybenzenesulfonamide (3e')**

yellow solid; mp 175-177 ºC; IR (KBr, cm^{-1}): 3277, 3066, 1595, 1497, 1460, 1324, 1255, 1150, 1093, 1024, 817, 750; ^{1}H-NMR (400 MHz, DMSO-d_6): 3.77 (s, 3H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 9.3 Hz, 2H), 6.93-6.98 (m, 1H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.25-7. 33 (m, 2H), 7.38-7. 52 (m, 5H), 7.87-7. 95 (m, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 8.38 (d, *J* = 7.8 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): 45.7, 55.6, 112.0, 113.6, 116.1, 117.5, 120.9, 122.6, 123.2, 124.4, 126.9, 127.9, 128.4, 128.9, 129.8, 130.1, 130.3, 130.9, 134.3, 150.2, 151.0, 161.6.

4-Methoxy-*N*-9*H*-thioxanthen-9-yl-benzenesulfonamide (3g')

Pale yellow solid; mp 176-178 ºC; IR (KBr, cm^{-1}): 3075, 2955, 2835, 1594, 1495, 1463, 1310, 1287, 1254, 1142, 1089, 1024, 972, 834, 805, 752; ^{1}H-NMR (400 MHz, DMSO-d_6): 3.82 (s, 3H), 4.12 (d, *J* = 17.1 Hz, 1H), 4.42 (d, *J* = 17.1 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.64-7.68 (m, 4H), 7.85 (d, *J* = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, DMSO-d_6): 34.5, 55.6, 114.3, 125.5, 128.0 (x 2), 129.3, 131.8, 132.0, 135.2, 135.9, 161.6; HRMS (DART) calcd for $C_{20}H_{18}NO_3S_2$ $[M + H]^+$: 384.0723, found: 384.0725.

Preparation of thienyliodonium(III) salt A

The thienyliodonium(III) salt **A** was prepared from 2,3,4-trimethylthiophene according to our reported method for the synthesis of diaryliodonium(III) salts in fluoroalcohol solvent.[22]

General procedure for the benzylic C-H heteroarylation of xanthenes 1 and their derivatives using thienyliodonium(III) salt A (Scheme 5)

To a stirred solution of the xanthene (0.20 mmol) and diaryliodonium(III) salt **A** (75.2 mg, 0.20 mmol, 1 equiv.) in 1,1,1,3,3,3-hexafluoroisopropanol (2 mL) was added trimethylsilyl triflate (TMSOTf, 72 μL, 0.40 mmol, 2 equiv.) under nitrogen atmosphere at room temperature. The reaction mixture was then stirred for 12 h. Aqueous saturated sodium hydrogencarbonate was then added to the reaction mixture,

and the aqueous phase was extracted with CH_2Cl_2 twice. The combined extracts were dried over anhydrous sodium sulfate and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (eluents: *n*-hexane/EtOAc) to give the pure benzylic coupling product **4** in the indicated yield.

9-(3,4,5-Trimethyl-2-thienyl)-9*H*-xanthene (4a)

white solid; mp 158-160; IR (KBr, cm^{-1}): 1478, 1447, 1316, 1253, 750; ^{1}H-NMR (400 MHz, DMSO-d_6): 1.94 (s, 3H), 2.14 (s, 3H), 2.18 (s, 3H), 5.76 (s, 1H), 6.99-7.17 (m, 6H), 7.25 (t, J = 6.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 12.4, 12.9, 13.1, 35.9, 116.2, 123.4, 124.3, 128.2, 129.6, 130.2, 132.3, 132.6, 139.5, 150.1; HRMS (DART) calcd for $C_{20}H_{19}OS$ $[M + H]^+$: 307.1151, found: 307.1152

2-Methyl-9-(3,4,5-Trimethyl-2-thienyl)-9*H*-xanthene (4d)

white solid; mp 117-119 ^{o}C; IR (KBr, cm^{-1}): 2916, 1481, 1455, 1312, 1255, 1233, 1213, 813, 750; ^{1}H-NMR (400 MHz, DMSO-d_6): 1.94 (s, 3H), 2.13 (s, 3H), 2.19 (s, 3H), 2.20 (s, 3H), 5.70 (s, 1H), 6.89 (d, J = 1.0 Hz, 1H), 6.98-7.12 (m, 5H), 7.19-7.25 (m, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): 12.4, 12.9, 13.1, 20.3, 36.0, 116.0, 116.1, 123.2, 123.8, 124.3, 128.1, 128.8, 129.5, 129.6, 130.2, 132.2, 132.3 (x 2), 139.7, 148.1, 150.2; HRMS (DART) calcd for $C_{21}H_{21}OS$ $[M + H]^+$: 321.1308, found: 321.1309.

12-(3,4,5-Trimethyl-2-thienyl)-12*H*-Benzo[*a*]xanthene (4e)

pale yellow solid; mp 151-154 ^{o}C; IR (KBr, cm^{-1}): 1488, 1456, 1250, 811, 747; ^{1}H-NMR (400 MHz, DMSO-d_6): 1.89 (s, 3H), 2.00 (s, 3H), 2.45 (s, 3H), 6.34 (s, 1H), 7.08-7.14 (m, 1H), 7.17-7.21 (m, 1H), 7.23-7.28 (m, 1H), 7.38-7.45 (m, 3H), 7.50-7.56 (m, 1H), 7.90 (t, J = 7.8 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6): 12.4, 12.8, 13.4, 33.4, 116.0, 116.3, 117.7, 122.7, 123.9, 124.4, 125.1, 127.1, 128.0, 128.6, 129.3, 129.4, 129.7, 130.3, 130.9, 131.1, 132.4, 140.6, 148.4, 149.4; HRMS (DART) calcd for $C_{24}H_{21}OS$ $[M + H]^+$: 357.1308, found: 357.1308.

9-(3,4,5-Trimethyl-2-thienyl)-9*H*-thioxanthene (4g)

white solid; mp 144-146 ^{o}C; IR (KBr, cm^{-1}): 2913, 1467, 1441, 747; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.04 (s, 3H), 2.18 (s, 3H), 2.27 (s, 3H), 5.50 (s, 1H), 7.23 (t, J = 6.4 Hz, 2H), 7.34 (dd, J = 6.8 Hz, 4H), 7.47 (t, J = 6.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 12.7, 13.2, 14.3, 46.7, 126.5, 126.8, 128.8, 132.4, 133.0, 133.3, 133.7, 137.1; HRMS (DART) calcd for $C_{20}H_{19}S_2$ $[M + H]^+$: 323.0923, found: 323.0920.

Benzylic coupling of xanthene 1a with indole using indolyliodonium(III) salt B (Scheme 7)

Instead using indolyliodonium(III) salt **B**,[25,26] the indole coupling product **5a** was obtained according to

the procedure similar to that described for the thienyliodonium(III) salt **A**.

3-(9*H*-Xanthen-9-yl)-1*H*-indole (5a)[24d]

Pale purple solid; mp 144-146 ºC; IR (KBr, cm^{-1}): 3422, 3053, 2921, 1600, 1574, 1478, 1455, 1254, 1094, 903, 748; ^{1}H-NMR (400 MHz, $CDCl_3$): 5.55 (s, 1H), 6.89-7.01 (m, 3H), 7.09-7.22 (m, 8H), 7.35 (t, *J* = 8.3 Hz, 2H), 8.02 (brs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 35.7, 111.3, 119.8 (x 2), 120.6, 122.3, 122.9, 123.2, 124.5, 126.0, 127.8, 129.6, 136.9, 151.5.

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