A convenient one-pot preparation of spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives

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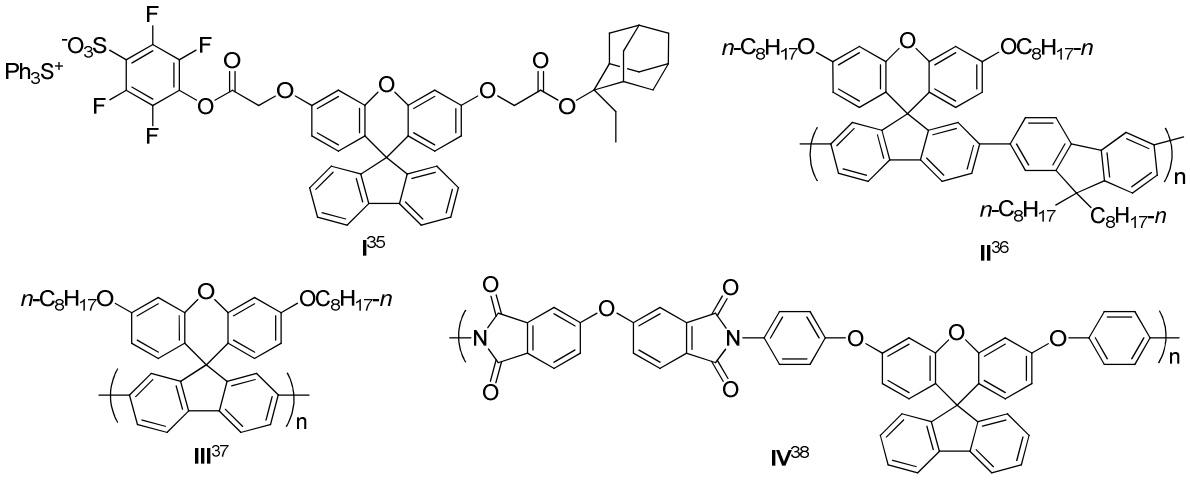
Abstract
Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives were prepared via the condensation reaction of fluorenones with resorcinol using *p*-toluenesulfonic acid as catalyst. A series of substituted spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives with halogen, alkyl, phenyl, and ester were prepared by this one-pot method in good yield.

Keywords: Spiro[fluorene-9,9'-xanthene]-3',6'-diol, fluorenone, resorcinol, *p*-toluenesulfonic acid

Introduction

Polyfluorene (PF) derivatives have attracted much attention as promising materials in organic electronic devices such as light-emitting diodes (LEDs),[1-5] photovoltaic cells,[6-9] and field-effect transistors (FETs)[10-13] for their high quantum yields, excellent solubility, and film-formation ability. However, it is difficult for PF to obtain pure and stable blue light emission due to the presence of undesirable green emission upon exposure to heat or during device operation. Two explanations have been given for the green emission: one was the keto defect,[14-17] and the other was the formation of interchain excimers.[18-20] The introduction of spiro structures is thought as one of the most promising solutions to the problem.[21-23] In recent years, spiro compounds as organic molecular materials have become promising candidates for optoelectronic devices.[24-30] In addition, spiro compounds with fluorene structures also serve as monomers in the preparation of thermally stable polyesters.[31-34] As an important class of spirofluorene derivatives, spiro[fluorene-9,9'-xanthene] (**SFX**) has also received much attention in recent years (Figure 1).[35-41] In the early literatures, SFXs were arduously synthesized by means of multistep routes with poor yield.[42,43] Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives can be obtained *via* the condensation reaction of 9-fluorenones with resorcinol using $ZnCl_2$/HCl[37,44] or gaseous HCl[31] as

a condensing reagent at high temperature. In 2006, Huang[45] reported an expedient one-pot method to synthesize **SFX** through a thermodynamic-controlled process involving excessive acid catalyst, which represents an efficient and convenient approach for the preparation of **SFX**. Nevertheless, most of these methods suffer from long reaction times, high temperatures, or the use of excess acidic catalysts. In addition, some procedures may cause the introduction metallic ions or halogens which are strictly restricted on residual amount in material preparation. Thus, the convenient method to prepare **SFX** derivatives under mild conditions is still highly desirable. Herein, we report an efficient method to prepare spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives catalyzed by *p*-toluenesulfonic acid in one-pot. And this metallic salts and chlorides free procedure is more suitable for the demand of material research.



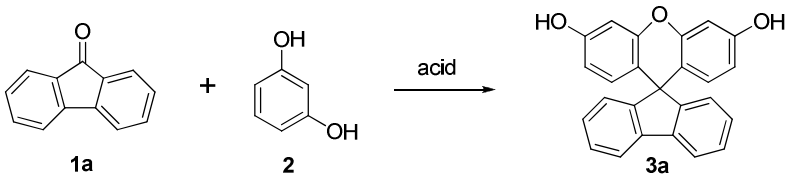
I[35] II[36] III[37] IV[38]

Figure 1. Representative **SFX** derivatives.

Results and Discussion

The reaction of 9-fluorenone (**1a**) and resorcinol was investigated in presence of acid catalysts (Table 1). To our delight, the reaction was possible and provided the desired product spiro[fluorene-9,9'-xanthene]-3',6'-diol (**3a**) in promising yield, when sulfuric acid were employed (Table 1, Entry 1). For initial optimization of the reaction conditions, we tested several protic acids and Lewis acids, and found the *p*-toluenesulfonic acid (*p*-TsOH) gave the best results (Table 1, entry 8). Stronger acids such as sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, and polyphosphoric acid (PPA) also served as catalysts, but the yields were relatively low (Table 1, entries 1–4). When sulfuric acid, trifluoromethanesulfonic acid, and PPA were used, the reaction mixtures became dark-brown and many byproducts were generated. Trifluoroacetic acid, aluminum chloride and zinc chloride were not efficient catalysts for the reaction under this conditions (Table 1, entries 5–7).

Table 1. Preparation of **3a** with different acid catalysts and solvents[a]



Entry	Cat.	Solvent	**1a/2** (mol/mol)	Time/h	Temp./°C	Yield/%[b]
1	H_2SO_4	toluene	1/2.4	6	reflux	53.9
2	$MeSO_3H$	toluene	1/2.4	6	reflux	71.5
3	CF_3SO_3H	toluene	1/2.4	6	reflux	38.7
4	PPA	toluene	1/2.4	6	reflux	43.3
5	CF_3COOH	toluene	1/2.4	6	reflux	Trace[c]
6	$AlCl_3$	toluene	1/2.4	6	reflux	Trace[c]
7	$ZnCl_2$	toluene	1/2.4	6	reflux	Trace[c]
8	*p*-TsOH	toluene	1/2.4	6	reflux	74.5
9	*p*-TsOH	*n*-$C_{10}H_{22}$	1/2.4	6	110	39.3
10	*p*-TsOH	CCl_4	1/2.4	8	reflux	42.4
11	*p*-TsOH	AcOH	1/2.4	6	reflux	19.4[c]
12	*p*-TsOH	MeCN	1/2.4	8	reflux	Trace[c]
13	*p*-TsOH	THF	1/2.4	8	reflux	Trace[c]
14	*p*-TsOH	PhCl	1/2.4	6	110	65.9
15	*p*-TsOH	dimethylbenzene	1/2.4	6	110	67.2
16	*p*-TsOH	$CHCl_3$	1/2.4	8	reflux	66.6
17	*p*-TsOH	benzene	1/2.4	8	reflux	75.2
18	*p*-TsOH	toluene	1/2	6	reflux	62.5
19	*p*-TsOH	toluene	1/3	6	reflux	80.1
20	*p*-TsOH	toluene	1/4	6	reflux	85.5
21	*p*-TsOH	toluene	1/6	6	reflux	86.6

[a]Reaction condition: 0.3 mmol **1**, with 10 mol% catalyst in 2 mL solvent.
[b]The yield was detected by HPLC with 2-naphthol as internal standard.
[c]A large amount of substrates was unchanged.

As *p*-TsOH proved to be the most effective acid, further experiments were focused on the screening of solvents. When *n*-decane and carbon tetrachloride were performed as solvents, dark red gum was generated for poor solubility of resorcinol in these solvents (Table 1, entries 9 and 10). The conversions were much low when the reactions were carried out in acetic acid, acetonitrile and THF (Table 1, entries 11–13). In all kinds of the tested solvents, toluene and benzene gave the best results (Table 1, entries 8, 17). Herein, we do not prefer to choose benzene

in view of toxicity. In that condition, the crude product deposited from the reaction solution in the course of the reaction. The yield of the crude product, which contained a chief byproduct (15% percent, HPLC λ = 275 nm), was about 95% with a purity of 80% (HPLC λ = 275 nm). Fortunately, the byproduct (**4**) does not dissolve in EtOH or *i*-PrOH while our desired product **3a** possesses good solubility, so it is easy to separate **3a** from the crude product. The byproduct **4** was identified by MS and ^{1}H NMR, and its structure was shown in Figure 2. Its formation was attributed to the competing reaction of **3a** with resorcinol and fluorenone, so it was suggested that it may be reduced by modifying the relative amount of the starting materials. The experiments confirmed our supposition. The yield of **3a** was lower when theoretic stoichiometry of resorcinol (2 equivalents, Table 1, entry 18) was used, and the percentage of **4** rose to 20%. In contrast, the yield of **3a** was increased as additional resorcinol was used (Table 1, entries 19–21). The product **3a** was obtained in 85.5% yield with the percentage of **4** decreased to 7%, when 4 equivalents of resorcinol were employed (Table 1, entry 20). Since a large amount of resorcinol remained, it gave gum instead of solid after the reaction. Nevertheless, a powder was obtained after superfluous resorcinol was washed off with water, and **3a** was isolated in 80% yield after chromatography.

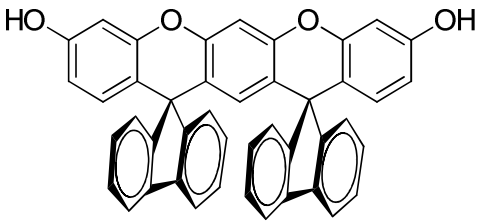
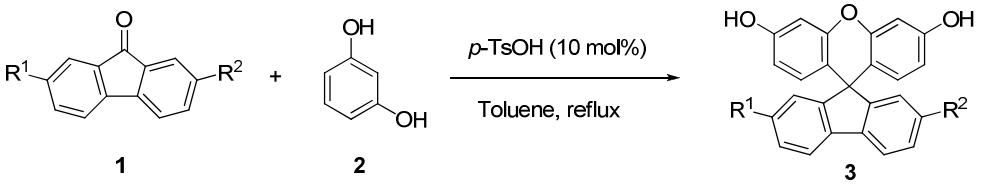


Figure 2. Structure of the byproduct (**4**).

To further survey the scope of this process to prepare 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] derivatives, a series of substituted 9-fluorenones with halogen, alkyl, phenyl, and ester were examined (Table 2). Each substance reacted at a comparable rate, and gave the corresponding product in moderate to good yield. Ester group was tolerant well in the reaction (Table 2, entry 10). The electron-poor 9-fluorenones (Table 2, entries 1–4, 10) gave better results than the electron-rich ones (Table 2, entries 5–9).

Table 2. Preparation of spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives[a]



1 2 3

Entry	Product	R^1	R^2	Time/h	Yield/%[b]
1	**3b**	Cl	Cl	6	86
2	**3c**	Cl	H	6	83
3	**3d**	Br	Br	6	81
4	**3e**	Br	H	6	80
5	**3f**	Me	Me	10	76
6	**3g**	Me	H	10	73
7	**3h**	Ph	Ph	10	72
8	**3i**	Ph	H	10	78
9	**3j**	*t*-Bu	*t*-Bu	10	73
10	**3k**	COOMe	H	6	83

[a]Reaction condition: 3.0 mmol of **1**, 12.0 mmol of **2**, 10 mol% *p*-TsOH in 20 mL toluene, reflux.
[b]Isolated yield.

Conclusions

We have developed an easy, efficient, metallic salts and chlorides free procedure for the synthesis of 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] derivatives in one-pot. The condensation reaction of 9-fluorenones with resorcinol using *p*-TsOH as catalyst gave the corresponding 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] derivatives in good yield. The functional groups such as halogen, alkyl, phenyl, and ester were tolerant well in the reaction. The electron-poor 9-fluorenones gave better results than the electron-rich ones.

Experimental Section

General. Melting points were measured on a X-4 micro melting point apparatus (Beijing Tech Instrument Co. Ltd, China). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively on a Varian VA400MHz spectrometer (Varian, USA) with DMSO-d_6 as solvent. Chemical shift (δ) were reported in parts per million (ppm) relative to the residual solvent signal. Mass spectra were recorded on a HP1100 high Performance Liquid Chromatography/Mass

Selective Detector (HP, USA). Elemental analyses for C and H were obtained using a Vario EL III (Elementar, German) elemental analysis instrumentation. Column chromatography was performed on silica gel (100 – 200 mesh) using petroleum ether/EtOAc (3:1) as an eluent. Reagents were purchased from commercial sources and used directly.

General procedure for the synthesis of 3. To a three-necked flask were added 9-fluorenone (3.0 mmol), resorcinol (12.0 mmol), *p*-TsOH (0.3 mmol) and toluene (20 mL). The mixture was refluxed for 6 h or 10 h, and then cooled to room temperature. After water (10 mL) was added, the mixture was stirred for 0.5 h. The crude product **3** precipitated from the reaction mixture, and was isolated as a yellow solid by filtration. The crude product was dissolved into alcohol (10 mL) and filtrated to remove insoluble impurity (**4**). The organic solution was concentrated, purified by chromatography on silica gel using petroleum ether/EtOAc (3:1) as an eluant, and dried in vacuum at 100 °C for 5 h to afford product **3** as a white solid.

Spiro[fluorene-9,9'-xanthene]-3',6'-diol (**3a**).[38] White solid, yield 80%, 873 mg; mp 262-264 °C, MS (API-ES, Negative), *m/z*: 363 ([M–H]$^-$), 399 ([M+Cl]$^-$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.63 (s, 2H, OH), 7.92 (2H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.36 (2H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.22 (2H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.02 (2H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.59 (2H, d, $^4J_{HH}$ 2.0 Hz, ArH), 6.26 (2H, dd, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 2.0 Hz, ArH), 6.03 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH).

The byproduct of the reaction of 9-fluorenone and resorcinol (4). It was isolated as a white solid with about 40 mol% residual EtOAc (see ^{1}H NMR spectra in SI). mp > 300 °C; MS (APCI, Negative), *m/z*: 617 ([M–H]$^-$), 653 ([M+Cl]$^-$). ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ_H: 9.33 (2H, s, OH), 7.63 (4H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.20 (4H, m, ArH), 7.11 (1H, s, ArH), 6.98 – 7.08 (4 H, m, ArH), 6.82 (4H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.63 (2H, d, $^4J_{HH}$ 2.0 Hz, ArH), 6.22 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 5.96 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH), 5.35 (1H, s, ArH). Anal. Calcd. for $C_{44}H_{26}O_4$ (618.2): C, 85.42; H, 4.24. Found (after correction): C, 85.31; H, 3.98. It is difficult to obtain its ^{13}C NMR data for the poor solubility.

2,7-Dichlorospiro[fluorene-9,9'-xanthene]-3',6'-diol (3b). White solid, yield 86%, 1111 mg; mp > 300 °C. MS (APCI, Negative), *m/z*: 431 ([M–H]$^-$), 467 ([M+Cl]$^-$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.71 (2H, s, OH), 7.99 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.45 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.00 (2H, d, $^4J_{HH}$ 1.6 Hz, ArH), 6.60 (2H, d, $^4J_{HH}$ 2.4 Hz, ArH), 6.31 (2H, dd, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.06 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 158.2, 157.5, 151.8, 137.4, 133.5, 128.7, 128.6, 125.5, 122.8, 113.5, 112.4, 103.3, 53.4. Anal. Calcd. for $C_{25}H_{14}Cl_2O_3$ (432.0): C, 69.30; H, 3.26. Found: C, 69.31; H, 2.98.

2-Chlorospiro[fluorene-9,9'-xanthene]-3',6'-diol (3c). White solid, yield 83%, 992 mg; mp 264-266 °C. MS (APCI, Negative), *m/z*: 397 ([M–H]$^-$), 433 ([M+Cl]$^-$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.73 (2H, s, OH), 7.90 – 8.10 (2H, m, ArH), 7.40 – 7.60 (2H, m, ArH), 7.20 – 7.40 (1H, m, ArH), 7.09 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.05 (1H, d, $^4J_{HH}$ 1.6 Hz, ArH), 6.66 (2H, d, $^3J_{HH}$ 2.4 Hz, ArH), 6.35 (2H, dd, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.11 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 158.0, 157.6, 155.4, 151.9, 138.5, 138.4, 133.0, 129.3,

128.6, 128.5, 128.4, 125.6, 125.4, 122.5, 121.0, 114.4, 112.2, 103.2, 53.4. Anal. Calcd. for $C_{25}H_{15}ClO_3$ (398.1): C, 75.29; H, 3.79. Found: C, 75.31; H, 3.58.

2,7-Dibromospiro[fluorene-9,9'-xanthene]-3',6'-diol (3d).[37] White solid, yield 81%, 1263 mg; mp > 300 °C. MS (APCI, Negative), *m/z*: 519 ($[M–H]^-$), 555 ($[M+Cl]^-$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.73 (2H, s, OH), 7.93 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7. 75 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.11 (2H, s, ArH), 6.59 (2H, s, ArH), 6.30 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH), 6.05 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH).

2-Bromospiro[fluorene-9,9'-xanthene]-3',6'-diol (3e). White solid, yield 80%, 1057 mg; mp 299-300 °C. MS (APCI, Negative), *m/z*: 441 ($[M–H]^-$), 477 ($[M+Cl]^-$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.69 (2H, s, OH), 7.95 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7. 90 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.55 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.35 – 7.45 (1H, m, ArH), 7.20 – 7.30 (1H, m, ArH), 7.10 (2H, d, $^4J_{HH}$ 2.0 Hz, ArH), 7.02 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.59 (2H, d, $^4J_{HH}$ 2.4 Hz, ArH), 6.28 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.04 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 158.0, 157.9, 155.3, 151.9, 138.8, 138.5, 131.3, 129.4, 128.6, 128.4, 128.2, 125.6, 122.9, 121.4, 121.0, 114.4, 112.2, 103.2, 53.4. Anal. Calcd. for $C_{25}H_{15}BrO_3$ (442.0): C, 67.74; H, 3.41. Found: C, 67.45; H, 3.36.

2,7-Dimethylspiro[fluorene-9,9'-xanthene]-3',6'-diol (3f). White solid, yield 76%, 892 mg; mp 272-273 °C. MS (APCI, Positive), *m/z*: 393 ($[M+H]^+$); ^{1}H NMR (400 MHz, DMSO-d_6 +$CDCl_3$) δ_H: 8.44 (2H, s, OH), 7.57 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.09 (2H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.89 (2H, s, ArH), 6.68 (2H, d, $^3J_{HH}$ 2.4 Hz, ArH), 6.25 – 6.35 (2H, m, ArH), 6.15 – 6.25 (2H, m, ArH), 2.23 (6H, s, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6 +$CDCl_3$) δ_C: 155.6, 155.1, 152.0, 137.8, 137.0, 129.3, 128.5, 126.1, 119.3, 117.7, 111.3, 103.2, 53.0, 21.6. Anal. Calcd. for $C_{27}H_{20}O_3$ (392.1): C, 82.63; H, 5.14. Found: C, 82.74; H, 4.77.

2-Methylspiro[fluorene-9,9'-xanthene]-3',6'-diol (3g). White solid, yield 73%, 830 mg; mp 238-239 °C. MS (APCI, Positive), *m/z*: 379 ($[M+H]^+$). ^{1}H NMR (400 MHz, DMSO-d_6 +$CDCl_3$) δ_H: 8.51 (2H, s, OH), 7.70 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.62 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.25 – 7.35 (1H, m, ArH), 7.05 – 7.20 (3H, m, ArH), 6.92 (1H, s, ArH), 6.68 (2H, d, $^4J_{HH}$ 2.4 Hz, ArH), 6.29 (2H, dd, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.19 (2H, d, $^3J_{HH}$ 8.8 Hz, ArH), 2.25 (3H, s, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6 +$CDCl_3$) δ: 156.9, 155.4, 152.0, 145.9, 139.6, 138.0, 136.7, 128.5, 128.3, 127.6, 127.3, 126.0, 125.5, 119.4, 119.3, 115.9, 111.4, 103.0, 53.2, 21.6. Anal. Calcd. for $C_{26}H_{18}O_3$ (378.1): C, 82.52; H, 4.79. Found: C, 82.14; H, 4.42.

2,7-Diphenylspiro[fluorene-9,9'-xanthene]-3',6'-diol (3h). White solid, yield 72%, 1110 mg; mp 172-174 °C; MS (APCI, Positive), *m/z*: 517 ($[M+H]^+$). ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.65 (2H, s, OH), 8.06 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.71 (2H, dd, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 2.0 Hz, ArH), 7.52 (4H, m, ArH), 6.35 – 6.40 (4H, m, ArH), 6.25 – 6.32 (4H, m, ArH), 6.64 (2H, d, $^4J_{HH}$ 2.4 Hz, ArH), 6.30 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.18 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 157.8, 156.8, 152.0, 140.8, 140.2, 138.6, 129.4, 128.7, 127.9, 127.1, 127.0, 123.4, 121.5, 115.2, 112.2, 103.2, 53.6. Anal. Calcd. for $C_{37}H_{24}lO_3$ (516.2): C, 86.03; H, 4.68. Found: C, 85.91; H, 4.57.

2-Phenylspiro[fluorene-9,9'-xanthene]-3',6'-diol (3i). White solid, yield 78%, 1025 mg; mp 264-266 °C; MS (APCI, positive), *m/z*: 441 ([M+H]$^+$). ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.83 (2H, s, OH), 7.99 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.93 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.68 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.45 – 7.50 (2H, m, ArH), 7.33 – 7.40 (3H, m, ArH), 7.20 – 7.30 (3H, m, ArH), 7.01 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 6.62 (2H, s, ArH), 6.27 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.08 (2H, d, $^3J_{HH}$ Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 157.8, 156.5, 155.9, 152.0, 140.7, 140.2, 139.07, 139.05, 129.4, 128.9, 128.7, 128.3, 127.9, 126.98, 126.95, 125.6, 123.4, 121.4, 120.9, 115.3, 112.1, 103.1, 53.5. Anal. Calcd. for $C_{31}H_{20}Cl_2O_3$ (440.1): C, 84.53; H, 4.58. Found: C, 84.90; H, 4.38.

2,7-Di-*t*-butylspiro[fluorene-9,9'-xanthene]-3',6'-diol (3j). White solid, yield 73%, 1046 mg; mp > 280 °C (sublimation); MS (APCI, Positive), *m/z*: 477 ([M+H]$^+$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 9.57 (2H, s, OH), 7.76 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.38 (2H, dd, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 6.99 (2H, s, ArH), 6.61 (2H, d, $^4J_{HH}$ 2.4 Hz, ArH), 6.27 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.4 Hz, ArH), 6.04 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH), 1.16 (18H, s, Bu). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 157.6, 155.5, 152.1, 151.1, 137.0, 128.5, 125.2, 121.6, 119.9, 116.2, 112.0, 103.1, 53.6, 35.0, 31.7. Anal. Calcd. for $C_{33}H_{10}O_3$ (476.2): C, 83.16; H, 6.77. Found: C, 83.12; H, 6.63.

Methyl 3',6'-dihydroxyspiro[fluorene-9,9'-xanthene]-2-carboxylate (3k). White solid, yield 83%, 1049 mg; mp 246-249 °C. MS (APCI, Positive), *m/z*: 423 ([M+H]$^+$); ^{1}H NMR (400 MHz, DMSO-d_6 +$CDCl_3$) δ_H: 8.74 (2H, s, OH), 7.96 (1H, d, $^3J_{HH}$ Hz, ArH), 7.73 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.67 (1H, s, ArH), 7.25 – 7.30 (1H, m, ArH), 7.15 – 7.20 (1H, m, ArH), 7.07 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.61 (2H, d, $^3J_{HH}$ 2.0 Hz, ArH), 6.20 (2H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.0 Hz, ArH), 6.06 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH), 3.74 (3H, s, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 166.3, 158.0, 156.3, 156.1, 151.9, 144.3, 138.4, 130.3, 129.7, 128.6, 125.9, 125.8, 121.8, 121.1, 114.3, 112.2, 103.2, 103.1, 53.3, 52.5. Anal. Calcd. for $C_{27}H_{18}O_5$ (422.1): C, 76.77; H, 4.29. Found: C, 76.61; H, 4.38.

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