

## A Novel and Efficient Synthesis of New Dixanthonenes

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**ABSTRACT:** The facile and high yield synthesis of a new series of dibenzophenones in the presence of polyphosphoric acid (PPA) together with their cyclization to corresponding mono- and dixanthonenes are described. The aromatic nucleophilic substitution of these new compounds are also studied.

**KEY WORDS:** Dixanthonenes, Synthesis, Dibenzophenones, Aromatic nucleophilic substitution.

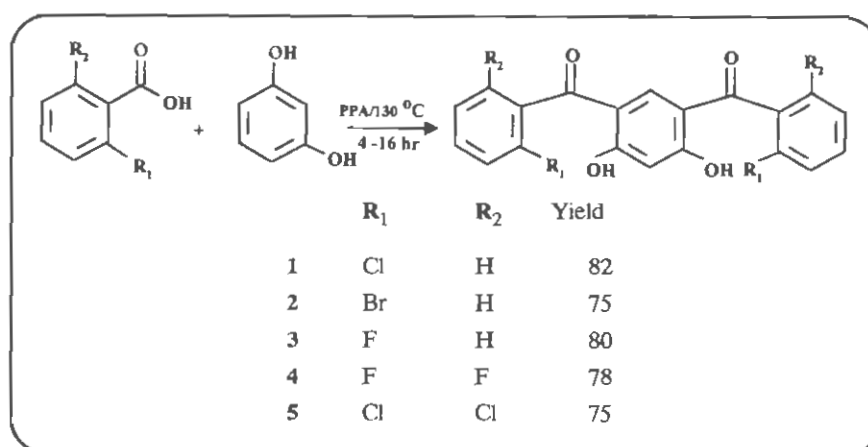
### INTRODUCTION

Xanthonenes are one of the most important natural occurring compounds. Beside a wide variety of chemical and industrial applications, synthetic derivatives of xanthonenes as well as naturally occurring derivatives have been used for medical purpose [1-7]. The biological and photochemical behaviour of this family of xanthone derivatives made these substance attractive for synthetic studies [8,9].

In a preceding report the preparation of benzo-

phenones from benzoic acid derivatives and phenols in the presence of polyphosphoric acid (PPA) [10], was described. Synthesis of the first dibenzophenones series (1-5) is reported in this paper.

The first dibenzophenone was 4,6-di-(2-chlorobenzoyl) resorcinol (**1**) obtained unexpectedly by condensation of 2-chlorobenzoic acid and resorcinol in PPA at 130°C. The product was isolated in 82% yields. Under similar conditions, 2-bromo, 2-fluoro,



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2,6-difluoro and 2,6-dichloro benzoic acid were condensed with resorcinol to afford the corresponding dibenzophenones (2-5). Dihydroxy and dimethoxy benzoic acid were decarboxylated under these conditions.

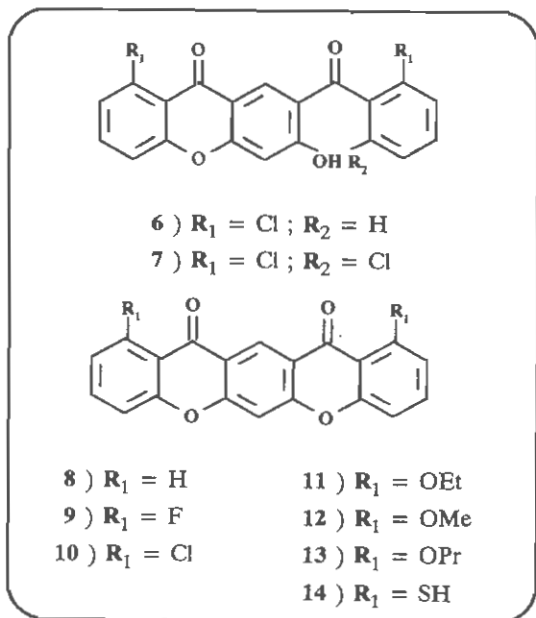
Three methods were tested to cyclize the dibenzophenones. The first was the Ulman-Schmidt procedure [11,12] (8% aq NaOH; reflux 48 h) for xanthenes synthesis. Cyclization of 1 and 5 in this condition generated the two new monocyclic xanthenes (6, 7) in 72% and 70% yield respectively. However when bromo, fluoro- and 2,6-difluorodibenzophenones (2-4) were subjected to identical conditions, biscyclization was occurred and corresponding dixanthenes (8, 9) were obtained in 80-90% yield. Among these products, compound 8 has been synthesized in 1921 [13] through several steps and in low yield. The second method that applied for xanthone synthesis from the benzophenone precursors, was the refluxing of dibenzophenone 1 with equimolar of Na<sub>2</sub>S in DMF [14]. Cyclization of 1 under this condition afforded the dixanthone (8) in 90% yield. However at this condition compound 5 was not cyclized to its corresponding dixanthone (10).

ponding dixanthenes in high yields. In the case of compound 4, we found that both-F groups have been substituted by -OEt together with cyclization to the corresponding dixanthone (11) in 90% yield. When dixanthone 9 was treated with sodium in ethanol, compound 11 was obtained in high yield.

In contrast to 4, the dichlorodibenzophenone 5 was cyclized to dichlorodixanthone 10 and no aromatic nucleophilic substitution took place. Similarly dichlorodixanthone 10 remained unreactive in the reaction with sodium and ethanol.

The reaction of 4 with methanol and sodium proceeded at reflux temperature and after 2 h, the dimethoxydixanthone (12) was obtained in 95% yield. By subsequent reaction of 4 with propanol and sodium, the reaction time is extended to 12 h. to give dipropoxydixanthone (13) in 40% yield. It is remarkable that by the reaction of 4 with Na<sub>2</sub>S in refluxing DMF, dithiodixanthone (14) was obtained in 80% yield, dichlorodibenzophenone 5 did not react under similar condition.

All of the dixanthenes have high melting points and special thermal behaviour of them is expected.



In the third method compound 5 was refluxed with Na in ethanol for 3 h, to give dixanthone 10 in 80% yield. By this method all of the dibenzophenones (1-3, 5) except 4, were converted to their corres-

## EXPERIMENTAL

Solvents and reagents were obtained from Merck and Fluka. Melting points were determined in open capillary tubes in a Buchi 510 circulating oil melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. <sup>1</sup>H NMR spectra were obtained on a Jeol-Ex 90 Q in CDCl<sub>3</sub> with tetramethylsilane as internal standard. Mass spectra (MS) were performed with a GC-MS Trie 1000 spectrometer and GCMS-QP 1000EX at 70 eV. UV spectra were recorded on a UV/Vis spectrophotometer Pu 8750. Thin layer chromatography were carried out on silica gel 60 F-254 analytical sheets obtained from Merck.

### Preparation of dibenzophenones 1-5

#### General procedure

A mixture of phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>, 8 g) and orthophosphoric acid (5 mL) was heated on an oil bath until a clear and fresh solution of PPA was obtained. Then 2-substituted or 2,6-disubstituted-

benzoic acid (0.01 mol) and resorcinol (0.01 mol; 1.11 g) were added and the reaction mixture was vigorously stirred at 130°C for 7-15 h. After cooling the reaction mixture was added to crushed ice (400 g) and stirred for 1 h, the dibenzophenones were isolated either by filtration or by extraction with chloroform (2×500 mL). In the latter case the organic layer was washed with 10% sodium bicarbonate (3 × 250 mL) and water (3×250 mL), dried with CaCl<sub>2</sub> and the solvent was evaporated.

#### 4,6-Di(2-chlorobenzoyl) resorcinol (1)

1 was obtained from 2-chlorobenzoic acid and resorcinol following the general procedure for 7 h in 82% yield; white needles (from ethanol); mp= 170-172°C; R<sub>f</sub> = 0.38 (CH<sub>2</sub>Cl<sub>2</sub> - CCl<sub>4</sub>/50-50); IR(KBr): 3500-2700(b), 1640(s), 1595(s) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 90 MHz): δ 6.5(s, 1H), 7.1- 7.4(m, 9H), 12.55 (s, 2H, 2×OH); UV(CHCl<sub>3</sub>), λ(ε<sub>max</sub>): 271(90000), 290(8542); MS: m/z= 387(M<sup>+</sup>, C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>Cl<sub>2</sub>, 10), 111 (C<sub>6</sub>H<sub>4</sub>Cl, base peak); Found: C, 62.2; H, 3.3, C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>Cl<sub>2</sub> requires C, 62.01, H, 3.1%.

#### 4,6-Di(2-bromobenzoyl) resorcinol (2)

2 was obtained from 2-bromobenzoic acid and resorcinol following the general procedure for 5 h in 75% yield as white needles (from ethanol); mp= 190-192°C; R<sub>f</sub> =0.36(CH<sub>2</sub>Cl<sub>2</sub>-CCl<sub>4</sub>/50-50); IR(KBr): 3200-2800(b), 1650(s), 1605(weak) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 90 MHz): δ 6.5(s, 1H), 7.0-7.4(m, 9H), 12.5(s, 2H, 2×OH); UV(CHCl<sub>3</sub>), λ(ε<sub>max</sub>): 270(87000), 290(7200); MS: m/z= 476(C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>, 15), 475 (C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>, 5), 134(C<sub>7</sub>H<sub>2</sub>O<sub>3</sub>, base peak); Found: C, 50.1; H, 2.5; C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>Br<sub>2</sub> requires C, 50.42; H, 2.52.

#### 4,6-Di(2-fluorobenzoyl) resorcinol (3)

3 was obtained from 2-fluorobenzoic acid and resorcinol following the general procedure for 7 h in 80% yield as white needles (from ethanol); mp= 150-152°C; R<sub>f</sub> =0.34(CH<sub>2</sub>Cl<sub>2</sub> -CCl<sub>4</sub>/50-50); IR(KBr): 3500-2600(b), 1630(s), 1600(s) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 90 MHz): δ 6.5(s, 1H), 6.7-7.6(m, 9H), 12.7(s, 2H, 2×OH); UV(CH<sub>3</sub>OH), λ(ε<sub>max</sub>): 270 nm (96100); MS: m/z= 355 (C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>F<sub>2</sub>, 17.5), 354(M<sup>+</sup>, C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>F<sub>2</sub>, 78.6), 353 (C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>F<sub>2</sub>, 67.5), 95(C<sub>6</sub>H<sub>4</sub>F, base peak);

Found: C, 67.4; H, 3.2, C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>F<sub>2</sub> requires C, 67.8; H, 3.38%.

#### 4,6-Di(2,6-difluorobenzoyl) resorcinol (4)

4 was obtained from 2,6-difluorobenzoic acid and resorcinol following the general procedure for 12 h in 78% yield, white needles (from ethanol); mp= 239-240°C, R<sub>f</sub> = 0.29(CH<sub>2</sub>Cl<sub>2</sub> - CCl<sub>4</sub>/50-50). IR(KBr): 3500-2700(b), 1640(s), 1620(b), 1595(s) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 90 MHz): δ 6.55(s, 1H), 6.7- 7.6(m, 7H), 12.5(s, 2H, 2×OH); UV(CH<sub>3</sub>OH), λ(ε<sub>max</sub>): 268 (74350); MS: m/z= 391(C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>F<sub>4</sub>, 14), 390(M<sup>+</sup>, C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>F<sub>4</sub>, 60.3), 389(C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>F<sub>4</sub>, 17.4), 371 (C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>F<sub>3</sub>, base peak); Found: C, 61.2; H, 2.6; C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>F<sub>4</sub> requires C, 61.53; H, 2.56%.

#### 4,6-Di(2,6-dichlorobenzoyl) resorcinol (5)

5 was obtained from 2,6-dichlorobenzoic acid and resorcinol following the general procedure for 15 h in 75% yield, white needles (from ethanol); mp= 250-251°C, R<sub>f</sub> = 0.4(CH<sub>2</sub>Cl<sub>2</sub> - CCl<sub>4</sub>/50-50); IR(KBr): 3500-2700(b), 1640(s), 1595(s) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 90 MHz): δ 6.5(s, 1H), 6.7-7.6(m, 7H), 12.1(s, 2H, 2 × OH); UV(CH<sub>3</sub>OH), λ(ε<sub>max</sub>): 264(72266); MS: m/z= 458 (C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub>, 14.4), 457(C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub>, 7), 456(M<sup>+</sup>, C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub>, 28.4), 454(C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>4</sub>, 22), 421(C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>3</sub>, base peak), Found: C, 52.2; H, 2.3, C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub> requires C, 52.63; H, 2.19%.

#### Cyclization procedure for dibenzophenones (1-5)

##### General Procedure

A) A mixture of dibenzophenone (0.001 mol) and NaOH (0.8 g, 0.02 mol) in water (5 mL) was refluxed for 40-50 h. After cooling and acidification with hydrochloric acid (2 M, 20 mL) the product was isolated either by filtration or by extraction with chloroform (3×300 mL). In the latter case the organic layer was washed with 10% sodium bicarbonate (3×150 mL), water (3×200 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed and the precipitate recrystallized.

B) A mixture of dibenzophenone (0.001 mol) and Na<sub>2</sub>S (0.001 mol) in DMF (10 mL) was refluxed for 8 h. Then water was added, the precipitate was filtered off and after washing with water recrystallized.

C) To a stirring solution of sodium (0.004 mol, 0.10 g) in ethanol (25 mL) was added dibenzophenone (0.001 mol). After refluxing the reaction mixture for 3 h, the mixture was cooled and treated with crushed ice (100 g) and the precipitate was filtered off, washed (water, 50 mL) and then recrystallized.

#### 2-(2-Chlorobenzoyl)-3-hydroxyxanthone (6)

6 was obtained from 1 by following the general cyclization method A in 72% yield, white needles (from ethyl acetate-*n*-hexane/50-50); mp= 209-210°C,  $R_f = 0.68(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 3300-2800 (b), 1670(s), 1640(s), 1590(m)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 90 \text{ MHz})$ :  $\delta$  6.95(s, 1H), 7.1-7.7(m, 7H), 8.18 (dd, 1H,  $J_1 = 6 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ ), 8.25(s, 1H), 12.4(s, 1H, OH); UV(CHCl<sub>3</sub>),  $\lambda(\epsilon_{\text{max}})$ : 280(8200); MS: m/z= 351 (C<sub>20</sub>H<sub>11</sub>O<sub>4</sub>Cl, 35), 139(C<sub>6</sub>H<sub>4</sub>OCl, base peak); Found: C, 68.1; H, 3.0, C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl requires C, 68.37; H, 2.85%.

#### 2-(2,6-Dichlorobenzoyl)-3-hydroxyxanthone (7)

7 was obtained from 5 by following the general cyclization procedure A in 70% yield, white needles (from EtOH-MeOH/80-20); mp=190-191°C,  $R_f = 0.7(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 3500-3010(b), 1670 (m), 1640(s), 1595(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 90 \text{ MHz})$ :  $\delta$  6.5(s, 1H), 6.8-7.6(m, 6H), 8.2(dd, 1H,  $J_1 = 6 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ ), 12.2(s, 1H, OH); UV(MeOH),  $\lambda(\epsilon_{\text{max}})$ : 265(9325); MS: m/z= 420 (M<sup>+</sup>), C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>3</sub>, 25), 419(C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>3</sub>, 14.8), 418 (C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>3</sub>, 23.4), 383(C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>, base peak); Found: C, 57.4; H, 2.0, C<sub>20</sub>H<sub>9</sub>O<sub>4</sub>Cl<sub>3</sub> requires C, 57.28; H, 2.15%.

#### Dixanthone (8)

8 was obtained from 1, 2 and 3 by following the general procedure C, as white solids (from nitrobenzene) in 80-90% yield; mp= 350-352°C (lit[11] 353°C),  $R_f = 0.55(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 1670(s), 1600 (s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 100 \text{ MHz})$ :  $\delta$  8.6(s, 1H), 8.2(dd, 2H,  $J_1 = 7 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ ), 6.7-7.8(m, 7H); UV(CH<sub>3</sub>OH),  $\lambda(\epsilon_{\text{max}})$ : 233(6178), 266 (8821), 314 (2252), 347(2547); MS: m/z= 315 (C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>, 23.1), 314(M<sup>+</sup>, C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>, base peak); Found: C, 68.4; H, 2.3, C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>F<sub>2</sub> requires C, 68.57; H, 2.28%.

#### Difluorodixanthone (9)

9 was obtained from 4 by following the general procedure A in 80% yield; white solids (from ethanol); mp= 390-392°C;  $R_f = 0.59(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 1670, 1600(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 100 \text{ MHz})$ :  $\delta$  9.2(s, 1H), 6.7-7.8(m, 7H); UV(CH<sub>3</sub>OH),  $\lambda(\epsilon_{\text{max}})$ : 235(6607), 268(10071), 348 (2428); MS: m/z= 350(M<sup>+</sup>, C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>F<sub>2</sub>, base peak); Found: C, 62.5; H, 2.2, C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub> requires C, 62.66; H, 2.09%.

#### Dichlorodixanthone (10)

10 was obtained from 5 by following the general cyclization procedure C in 80% yield; pale yellow solids; mp= 387-390°C,  $R_f = 0.49(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 1670, 1595(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 100 \text{ MHz})$ :  $\delta$  9.1(s, 1H), 6.7-7.7(m, 7H); UV(CH<sub>3</sub>OH),  $\lambda(\epsilon_{\text{max}})$ : 240(1668), 274(2250), 351 nm (643); MS: m/z= 384(C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>, 62.4), 383 (M<sup>+</sup>, C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>, 25.9), 382(C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>, base peak);  $^{13}\text{C NMR}(\text{DMSO}-d_6, 62.89 \text{ MHz})$ :  $\delta$  113, 118.62, 121, 125, 126.53, 135, 136.36, 147, 155.99, 177, Found: C, 62.5; H, 2.2, C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub> requires C, 62.66; H, 2.09%.

#### Diethoxydixanthone (11)

11 was obtained from 4 through two procedures, first by following the general cyclization procedure C in 90% yield, secondly obtained from refluxing a solution of difluorodixanthone 9 (0.001 mol, 350 mg) and sodium (0.1 g, 0.004 mol) in ethanol (25 mL). After cooling and filtration, 11 was obtained in 90% yield as white solids (from ethanol); mp= 297-300°C,  $R_f = 0.3(\text{CH}_2\text{Cl}_2 - \text{MeOH}/95-5)$ ; IR(KBr): 2910 (m), 1670(s), 1600(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}(\text{CDCl}_3, 100 \text{ MHz})$ :  $\delta$  9.25(s, 1H), 7.57(t,  $J = 7 \text{ Hz}$ , 2H), 7.43(s, 1H), 7.0(dd,  $J_1 = 9 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ , 2H), 6.8(dd,  $J_1 = 9 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ , 2H), 4.2(q,  $J = 7 \text{ Hz}$ , 4H), 1.6(t,  $J = 7 \text{ Hz}$ , 6H); UV(CH<sub>3</sub>OH),  $\lambda(\epsilon_{\text{max}})$ : 228(2575), 250(3373), 272 (4707), 363.5 (1757); MS: m/z= 402 (M<sup>+</sup>, C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>, 74.7), 387(C<sub>23</sub>H<sub>15</sub>O<sub>6</sub>, base peak); Found: C, 71.3; H, 4.2, C<sub>24</sub>H<sub>18</sub>O<sub>6</sub> requires C, 71.64; H, 4.48%.

#### Dimethoxydixanthone (12)

12 was obtained from 4 by refluxing a solution of sodium (100 mg, 0.004 mol) and difluorodibenzo-

phenone 4 (0.01 mol, 390 mg) and methanol (25 mL) for 2 h. The mixture was treated with water (50 mL) and the precipitate was filtered off and recrystallized from ethanol to give 12 in 95% yield as white solids, mp = 349-350°C,  $R_f = 0.42$  ( $\text{CH}_2\text{Cl}_2$  - MeOH/95-5); IR(KBr): 2910(m), 1670(s), 1590(s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  9.2(s, 1H), 7.65(t,  $J = 7$  Hz, 2H), 7.6(s, 1H), 7.1(dd,  $J_1 = 7$  Hz,  $J_2 = 2$  Hz, 2H), 6.9(dd,  $J_1 = 7$  Hz,  $J_2 = 2$  Hz, 2H), 4.0(s, 6H); UV ( $\text{CH}_3\text{OH}$ ),  $\lambda(\epsilon_{\text{max}})$ : 224 (4322), 272 (6111), 359 (2550); MS:  $m/z = 374$  ( $\text{M}^+$ ,  $\text{C}_{22}\text{H}_{14}\text{O}_6$ , base peak); Found: C, 70.2; H, 3.4,  $\text{C}_{22}\text{H}_{14}\text{O}_6$  requires C, 70.59; H, 3.74%.

#### Dipropoxydixanthone (13)

Difluorodibenzophenone 4 (390 mg, 0.01 mol) was added to a stirring solution of sodium (100 mg, 0.004 mol) and propanol (25 mL) and refluxed for 12 h. The mixture was treated with water (100 mL) and the pale yellow precipitate was filtered off and after washing with water, recrystallized from ethanol to give 13 in 40% yield as white solids; mp = 350°C (decomposed);  $R_f = 0.28$  ( $\text{CH}_2\text{Cl}_2$  - MeOH/95-5); IR (KBr): 2890 (m), 1670(s), 1600(s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  9.2(s, 1H), 7.6-6.8(m, 7H), 4.25(q,  $J = 7$  Hz, 4H), 1.8-1.3(m, 10H); UV ( $\text{CH}_3\text{OH}$ ),  $\lambda(\epsilon_{\text{max}})$ : 206.9(95000), 219(82000), 356 (41000), MS:  $m/z = 430$  ( $\text{M}^+$ ,  $\text{C}_{26}\text{H}_{22}\text{O}_6$ , 18.5), 401 ( $\text{C}_{24}\text{H}_{17}\text{O}_6$ , base peak); UV ( $\text{CH}_3\text{OH}$ ),  $\lambda(\epsilon_{\text{max}})$ : 206.9 (95000), 219 (82000), 35(41000); Found: C, 72.8; H, 4.9,  $\text{C}_{26}\text{H}_{22}\text{O}_6$  requires C, 72.56; H, 5.12%.

#### Dithioldixanthone (14)

14 was obtained from 4 by following the general cyclization procedure B in 80% yield as white solids; mp >390° (decomposed);  $R_f = 0.5$  ( $\text{CH}_2\text{Cl}_2$  - MeOH/96-4); IR(KBr): 3600-2800(b), 1665(s), 1620(s), 1595 (s)  $\text{cm}^{-1}$ ; MS:  $m/z = 378$  ( $\text{M}^+$ ,  $\text{C}_{20}\text{H}_{10}\text{O}_4\text{S}_2$ , 11.5), UV ( $\text{CH}_3\text{OH}$ ),  $\lambda(\epsilon_{\text{max}})$ : 210(98000), 225(90000), 272 (38200); Found: C, 63.10; H, 2.3,  $\text{C}_{20}\text{H}_{10}\text{O}_4\text{S}_2$  requires

C, 63.49; H, 2.65%.

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