

Self-condensation of *ortho*-Hydroxy- $\beta$ -chloro- $\beta$ -nitrostyrenes:  
 Synthesis of some *Z*-11-Nitromethylene-11*H*-  
 benzofuro[3,2-*b*][1]benzopyrans†  
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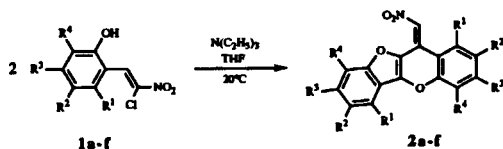
The triethylamine-promoted self-condensation of several 2-(2-chloro-2-nitroethenyl)phenols gives the so far unknown *Z*-11-Nitromethylene-11*H*-benzofuro[3,2-*b*][1]benzopyrans.

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We have recently described a four step procedure to prepare 3-nitroflavones starting from various 2-hydroxy-benzaldehydes and a wide range of *Z*-(2-chloro-2-nitroethenyl)benzenes [1,2]. In the course of our continuing interest in this field, and with the aim of broadening the scope of this synthesis, we have attempted the base-promoted condensation of salicylaldehyde with 2-(2-chloro-2-nitroethenyl)phenols **1** [3] in order to provide access to 3-nitroflavones bearing an hydroxyl group at the 2'-position. Surprisingly, the expected formation of 3-chloro-3,4-dihydro-4-hydroxy-2-(2-hydroxyphenyl)-3-nitro-2*H*-1-benzopyrans did not take place, and the only products isolated were the hitherto unknown title tetracyclic compounds **2** resulting from the reaction between two molecules of 2-hydroxy- $\beta$ -chloro- $\beta$ -nitrostyrenes **1**, whereas the salicylaldehyde remained unaffected.

This fact led us to investigate the synthesis of these *Z*-11 nitromethylene-11*H*-benzofuro[3,2-*b*][1]benzopyrans **2** starting from various 2-(2-chloro-2-nitroethenyl)phenols **1**. However, in spite of numerous optimization trials, the obtained yields are moderate and the best results were obtained by performing the reaction, at room temperature, in the presence of an excess of triethylamine, under inert atmosphere, using anhydrous tetrahydrofuran as solvent (Scheme I).

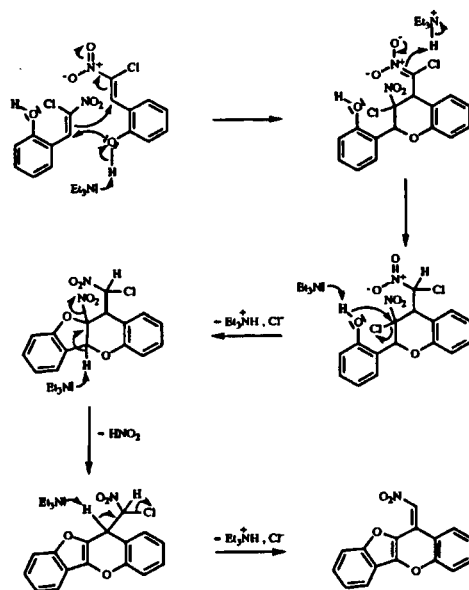
Scheme I



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<b>2a</b>	H	H	H	H
<b>2b</b>	H	Br	H	H
<b>2c</b>	H	H	H	OCH <sub>3</sub>
<b>2d</b>	H	OCH <sub>3</sub>	H	H
<b>2e</b>	H	OCH <sub>3</sub>	H	OCH <sub>3</sub>
<b>2f</b>	Br	H	H	OCH <sub>3</sub>

A proposed mechanism to account for the formation of the tetracyclic derivatives **2** is depicted in Scheme II:

Scheme II



It is worth pointing out that a survey of the literature reveals that the previously reported syntheses of benzofuro[3,2-*b*][1]benzopyrans derivatives are rather few and limited in scope [4], in spite of the fact that this tetracyclic framework is present in the structures of some interesting natural products such as Cyanomaclurin [5] or Sanggenons [6].

The structural elucidations of the new compounds **2a-f** were accomplished on the basis of <sup>1</sup>H nmr, <sup>13</sup>C nmr, microanalysis as well as mass spectra. With regard to the <sup>13</sup>C nmr spectra, the assignments were made by analogy with the previously reported chemical shifts for related compounds [7,8] and with the aid of the increment values depending on the substituents borne by the aryl moieties [9]. Furthermore, the structure of these novel *Z*-11-nitromethylene-11*H*-benzofuro[3,2-*b*][1]benzopyrans has

been unequivocally confirmed by a X-ray crystal study of **2a** selected as a representative of its class of products (Figure I).

Such tetracyclic coplanar compounds can be regarded as potential DNA-intercalating agents. In this context, several chemical transformations (in particular the reduc-

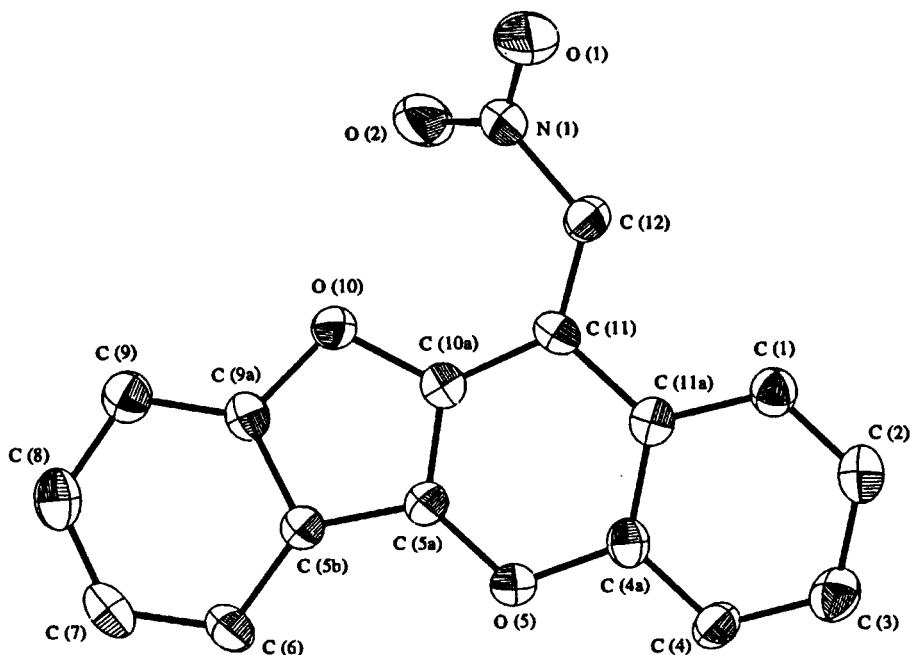


Figure I. Molecular structure of **2a** with the atomic numbering scheme (Hydrogen atoms have been omitted for clarity).

Table I  
Crystal and Refinement Parameters for Compound **2a**.

Molecular formula	$C_{16}H_{11}NO_4$
Molecular weight	279.25
Crystal system	Triclinic
Space group	P-1
a, Å	8.841 (9)
b, Å	9.120 (1)
c, Å	9.267 (6)
$\alpha$ , deg.	85.97 (7)
$\beta$ , deg.	66.74 (7)
$\gamma$ , deg.	65.20 (9)
$V, \text{Å}^3$	619 (4)
Z	2
$\rho$ calc., g.cm <sup>-3</sup>	1.50
F(000)	292
Temperature, °C	18
Crystal size, mm	0.45 x 0.30 x 0.25
Scan type	$\omega-2\theta$
Scan width	$0.8 + 0.34 \tan \theta$
$\theta$ range, deg.	1-25
$\mu$ , cm <sup>-1</sup>	1.02
Nb. of measured reflections	2166
Nb. of reflections used $I \geq 2\sigma(I)$	913
Min. and max. height in final $\Delta\rho$ , e Å <sup>-3</sup>	-0.24, 0.20
Nb. of refined parameters	191
$R = [\sum \Delta F  / \sum F_o ]$	0.058
$R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$	0.058
w=1	

Table II  
Fractional Coordinates and Thermal Parameters for  
Non-hydrogen Atoms of **2a**

Atom	x/a	y/b	z/c	U (eqv)
O(1)	-0.5982(9)	0.6570(9)	0.8801(8)	0.0932
O(2)	-0.5221(8)	0.8554(8)	0.8488(7)	0.0813
O(5)	0.2091(6)	0.5755(6)	0.5410(5)	0.0450
O(10)	-0.2426(6)	0.8299(6)	0.5887(5)	0.0449
N(1)	-0.4848(9)	0.710(1)	0.8520(8)	0.0598
C(1)	0.021(1)	0.371(1)	0.8696(8)	0.0493
C(2)	0.177(1)	0.260(1)	0.8766(9)	0.0555
C(3)	0.348(1)	0.248(1)	0.770(1)	0.0567
C(4)	0.348(1)	0.3613(9)	0.6637(9)	0.0511
C(4a)	0.191(1)	0.4725(9)	0.6556(8)	0.0436
C(5a)	0.0552(9)	0.6867(9)	0.5341(8)	0.0396
C(5b)	0.0442(9)	0.7987(9)	0.4212(8)	0.0407
C(6)	0.167(1)	0.835(1)	0.2906(8)	0.0505
C(7)	0.095(1)	0.957(1)	0.2098(9)	0.0561
C(8)	-0.091(1)	1.040(1)	0.2502(9)	0.0559
C(9)	-0.217(1)	1.0088(9)	0.3803(8)	0.0539
C(9a)	-0.143 (1)	0.8872 (9)	0.4599 (8)	0.0431
C(10a)	-0.1145(9)	0.7070(8)	0.6322(8)	0.0404
C(11)	-0.1499(9)	0.6024(9)	0.7488(7)	0.0366
C(11a)	0.019(1)	0.4825(9)	0.7580(8)	0.0379
C(12)	-0.309(1)	0.5945(9)	0.8419(9)	0.0493

Table III  
Interatomic Bond Lengths (Å) for Compound 2a

O(1) - N(1)	1.222(8)	O(2) - N(1)	1.224(8)
O(5) - C(4a)	1.374(7)	O(5) - C(5a)	1.337(8)
O(10) - C(9a)	1.394(8)	O(10) - C(10a)	1.391(8)
N(1) - C(12)	1.439(9)	C(1) - C(2)	1.35(1)
C(1) - C(11a)	1.401(9)	C(2) - C(3)	1.40(1)
C(3) - C(4)	1.37(1)	C(4) - C(4a)	1.36(1)
C(4a) - C(11a)	1.408(9)	C(5a) - C(5b)	1.412(9)
C(5a) - C(10a)	1.351(9)	C(5b) - C(9a)	1.403(9)
C(6) - C(7)	1.36(1)	C(6) - C(5b)	1.402(9)
C(7) - C(8)	1.39(1)	C(8) - C(9)	1.39(1)
C(9) - C(9a)	1.365(9)	C(11) - C(12)	1.355(9)
C(11) - C(10a)	1.420(8)	C(11) - C(11a)	1.466(9)

Table IV  
Interatomic Angles (deg.) for Compound 2a

C(5a)-O(5)-C(4a)	116.6(5)	C(10a)-O(10)-C(9a)	105.5(5)
O(2)-N(1)-O(1)	122.7(7)	C(12)-N(1)-O(1)	115.8(8)
C(12)-N(1)-O(2)	121.1(8)	C(11a)-C(1)-C(2)	122.5(7)
C(3)-C(2)-C(1)	121.6(7)	C(4)-C(3)-C(2)	116.9(7)
C(4a)-C(4)-C(3)	121.6(7)	C(4)-C(4a)-O(5)	116.4(7)
C(11a)-C(4a)-O(5)	121.3(7)	C(11a)-C(4a)-C(4)	122.3(7)
C(5b)-C(5a)-O(5)	125.5(6)	C(10a)-C(5a)-O(5)	125.2(6)
C(10a)-C(5a)-C(5b)	109.3(6)	C(5a)-C(5b)-C(6)	136.8(7)
C(9a)-C(5b)-C(6)	118.5(6)	C(9a)-C(5b)-C(5a)	104.8(6)
C(5b)-C(6)-C(7)	117.2(7)	C(8)-C(7)-C(6)	122.7(7)
C(9)-C(8)-C(7)	121.9(7)	C(9a)-C(9)-C(8)	114.6(7)
C(9)-C(9a)-O(10)	124.6(6)	C(5b)-C(9a)-O(10)	110.3(6)
C(5b)-C(9a)-C(9)	125.1(6)	C(5a)-C(10a)-O(10)	110.1(5)
C(11)-C(10a)-O(10)	126.2(6)	C(5a)-C(10a)-C(11)	123.3(7)
C(10a)-C(11)-C(12)	130.2(7)	C(11a)-C(11)-C(12)	118.5(6)
C(11a)-C(11)-C(10a)	111.2(6)	C(4a)-C(11a)-C(1)	115.0(7)
C(11)-C(11a)-C(1)	122.8(7)	C(4a)-C(11a)-C(11)	122.2(6)
C(11)-C(12)-N(1)	124.2(7)		

tion of the nitro group and further modifications) are planned in order to provide access to biologically attractive derivatives.

## EXPERIMENTAL

The melting points were measured on a Köfler hot stage apparatus and are uncorrected. Mass spectra were obtained with a Nermag-Ribermag R10-10C spectrometer under electron impact conditions (70 eV). The  $^1\text{H}$  (250 MHz) and  $^{13}\text{C}$  (50 MHz) nmr spectra were determined with a Bruker AC 250 apparatus or a Bruker AC 200 spectrometer with tetramethylsilane as the internal reference. Microanalyses were carried out by the "Service Central d'Analyse du C.N.R.S., Vernaison." Reactions were monitored by analytical thin layer chromatography performed on Merck 60F<sub>254</sub> precoated plates and products were visualized by uv light. Anhydrous tetrahydrofuran was obtained by distillation from benzophenone/sodium. Starting 2-(2-chloro-2-nitroethenyl)phenols 1 were synthesized according to a previously described procedure [3]. Triethylamine was purified by distillation from calcium hydride prior to use. Silica gel Merck (230-400 Mesh ASTM) was used for column chromatography.

## General Procedure for the Preparation of Z-11-Nitromethylene-11H-benzofuro-[3,2-b][1]benzopyrans 2a-f.

A solution of the appropriate 2-(2-chloro-2-nitroethenyl)phenol 1a-f, (15 mmoles) in anhydrous tetrahydrofuran (20 ml) was placed, under an inert atmosphere, in a dried two-necked 50 ml round-bottomed flask equipped with a septum inlet. The mixture was efficiently stirred, at room temperature, with a magnetic bar. When the starting material was completely dissolved, triethylamine (5.06 g, 6.97 ml, 50 mmoles) was added with a syringe. The reaction mixture was stirred at 20° for seventy two additional hours, then taken up with dichloromethane (100 ml) and water (50ml). The organic phase was separated. The aqueous layer was extracted with dichloromethane (3 x 30 ml). The combined organic extracts were dried (Magnesium sulfate), filtered, then evaporated under reduced pressure to leave a residue which was flash-chromatographed on a silica gel column (150 g, eluent dichloromethane). Removal of the solvent *in vacuo* gave pure 2a-f which were further recrystallized under appropriate conditions.

### Z-11-Nitromethylene-11H-benzofuro[3,2-b][1]benzopyran (2a).

This compound was obtained in 41% yield, bright red-orange prisms (benzene-cyclohexane), mp 181-183°;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.37-7.46 (m, 2H), 7.60 (s, 1H), 7.55-7.71 (m, 4H), 7.88 (d, 2H, J = 8.2 Hz);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  153.6 and 150.5 (9a-C and 4a-C), 142.4 (11-C), 133.1 (10a-C), 132.5 and 130.1 (3-C and 8-C), 125.6, 125.1 and 124.3 (1-C, 2-C and 7-C), 124.6 (5a-C), 119.5 and 118.6 (4-C and 6-C), 121.5 (=CNO<sub>2</sub>), 116.8 and 115.9 (5b-C and 11a-C), 112.6 (9-C); ms: m/z (%) 279 (M<sup>+</sup>,38), 249 (72), 222 (20), 221 (100), 205 (22), 176 (81), 165 (22), 163 (30), 151 (29), 150 (21), 85 (30), 83 (42), 76 (32), 75 (24), 63 (21).

Anal. Calcd. for C<sub>16</sub>H<sub>9</sub>NO<sub>4</sub>: C, 68.82; H, 3.25; N, 5.02. Found: C, 68.92; H, 3.16; N, 5.11.

### Z-2,7-Dibromo-11-nitromethylene-11H-benzofuro[3,2-b][1]benzopyran (2b).

This compound was obtained in 46% yield, yellow feathery crystals (benzene-cyclohexane), mp 206-209° dec;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.43 (d, 1H, J = 8.9 Hz), 7.47 (s, 1H), 7.50 (dd, 1H, J = 8.9, 0.5 Hz), 7.66 (dd, 1H, J = 8.9, 2.0 Hz), 7.72 (dd, 1H, J = 8.9, 2.3 Hz), 7.94 (d, 1H, J = 2.3 Hz), 7.97 (dd, 1H, J = 2.0, 0.5 Hz);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  152.4 and 149.7 (9a-C and 4a-C), 140.9 (11-C), 133.9 (10a-C), 135.3 and 132.6 (3-C and 8-C), 127.5 (1-C), 122.0 and 123.0 (4-C and 6-C), 123.0 (5a-C), 120.8 (=CNO<sub>2</sub>), 118.8, 118.1, 118.0 and 116.6 (2-C, 5b-C, 7-C and 11a-C), 114.8 (9-C); ms: m/z (%) 439 (M<sup>+</sup> for 2 x  $^{81}\text{Br}$ , 2), 437 (M<sup>+</sup> for  $^{81}\text{Br}$  +  $^{79}\text{Br}$ , 4), 435 (M<sup>+</sup> for 2 x  $^{79}\text{Br}$ , 2), 203 (20), 175 (40), 174 (48), 163 (20), 100 (25), 99 (31), 98 (26), 87 (42), 86 (30), 85 (28), 83 (35), 75 (100), 74 (85), 63 (32), 62 (25), 50 (20).

Anal. Calcd. for C<sub>16</sub>H<sub>7</sub>Br<sub>2</sub>NO<sub>4</sub>: C, 43.97; H, 1.61; N, 3.20. Found: C, 44.02; H, 1.55; N, 3.25.

### Z-4,9-Dimethoxy-11-nitromethylene-11H-benzofuro[3,2-b][1]benzopyran (2c)

This compound was obtained in 47% yield, yellow tiny needles (benzene-cyclohexane), mp 228-230° dec;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  4.04 (s, 3H), 4.13 (s, 3H), 7.06 (d, 1H, J = 7.9 Hz), 7.15 (dd, 1H, J = 7.8, 0.9 Hz), 7.31 (t, 1H, J = 7.8 Hz), 7.32 (t, 1H, J = 7.9 Hz), 7.40 (dd, 1H, J = 7.8, 0.9 Hz), 7.52 (d, 1H, J

= 7.9 Hz), 7.57 (s, 1H);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  148.9 (4-C), 145.3 (9-C), 143.0, 142.4 and 140.9 (4a-C, 9a-C and 11-C), 133.3 (10a-C), 125.5 and 125.4 (2-C and 7-C), 124.8 (5a-C), 121.5 (=CNO<sub>2</sub>), 118.5 and 116.9 (5b-C and 11a-C), 115.7 (1-C), 113.9 (3-C), 112.3 and 111.1 (6-C and 8-C), 56.3 (2 x CH<sub>3</sub>); ms: m/z (%) 339 (M<sup>+</sup>, 100), 322 (20), 310 (23), 309 (76), 294 (21), 266 (34), 238 (20), 207 (21), 163 (20), 150 (21), 99 (23), 88 (24), 87 (28), 86 (20), 85 (32), 83 (44), 76 (41), 75 (40), 74 (21), 63 (21), 51 (20).

Anal. Calcd. for C<sub>18</sub>H<sub>13</sub>NO<sub>6</sub>: C, 63.72; H, 3.86; N, 4.13. Found: C, 63.81; H, 3.71; N, 4.29.

#### Z-2,7-Dimethoxy-11-nitromethylene-11H-benzofuro[3,2-b]-[1]benzopyran (2d)

This compound was obtained in 40% yield, yellow feathery needles (trichloroethylene-cyclohexane), mp 207-209°;  $^1\text{H}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  3.88 (s, 3H), 3.90 (s, 3H), 7.11-7.22 (dd, 1H, J = 9.2, 2.7 Hz), 7.33 (dd, 1H, J = 9.1, 2.6 Hz), 7.35 (d, 1H, J = 2.6 Hz), 7.59 (d, 1H, J = 2.7 Hz), 7.62 (d, 1H, J = 9.2 Hz), 7.66 (d, 1H, J = 9.1 Hz), 8.16 (s, 1H);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  156.8 and 156.5 (2-C and 7-C), 148.8 and 145.4 (4a-C and 9a-C), 142.8 (11-C), 133.8 (10a-C), 125.1 (5a-C), 121.4 (=CNO<sub>2</sub>), 121.4, 120.1 and 120.0 (1-C, 3-C and 4-C), 117.4 and 116.8 (5b-C and 11a-C), 113.8 (9-C), 106.8 and 100.8 (6-C and 8-C), 56.3 (CH<sub>3</sub>), 56.0 (CH<sub>3</sub>); ms: m/z (%) 339 (M<sup>+</sup>, 81), 309 (71), 308 (42), 281 (28), 266 (39), 250 (20), 238 (61), 223 (22), 222 (28), 220 (29), 207 (26), 195 (27), 179 (20), 163 (38), 139 (22), 125 (22), 107 (21), 106 (21), 101 (26), 100 (26), 99 (38), 98 (37), 91 (20), 89 (22), 88 (39), 87 (52), 86 (31), 85 (20), 83 (22), 82 (33), 78 (42), 77 (28), 76 (25), 75 (42), 74 (26), 69 (20), 63 (100), 62 (25), 55 (23), 54 (40), 53 (22), 52 (29), 41 (32).

Anal. Calcd. for C<sub>18</sub>H<sub>13</sub>NO<sub>6</sub>: C, 63.72; H, 3.86; N, 4.13. Found: C, 63.58; H, 3.93; N, 4.02.

#### Z-11-Nitromethylene-2,4,7,9-tetramethoxy-11H-benzofuro[3,2-b][1]benzopyran (2e)

This compound was obtained in 38% yield, yellow-green tiny prisms (benzene), mp 239-241°;  $^1\text{H}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  3.88 (s, 3H), 3.90 (s, 3H), 3.98 (s, 6H), 6.66 (d, 1H, J = 2.4 Hz), 6.67 (d, 1H, J = 2.4 Hz), 7.02 (d, 1H, J = 2.4 Hz), 7.14 (d, 1H, J = 2.4 Hz), 8.13 (s, 1H);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide) [12]:  $\delta$  157.0 and 156.9 (2-C and 7-C), 149.9 and 145.9 (4-C and 9-C), 135.1 (4a-C or 9a-C), 121.4 (=CNO<sub>2</sub>), 103.9 and 103.0 (1-C and 3-C), 56.5 (2 x CH<sub>3</sub>), 56.2 (CH<sub>3</sub>), 56.1 (CH<sub>3</sub>); ms: m/z (%) 399 (M<sup>+</sup>, 100), 384 (49), 369 (20), 368 (48), 354 (70), 341 (20), 340 (26), 212 (21), 98 (20), 69 (21).

Anal. Calcd. for C<sub>20</sub>H<sub>17</sub>NO<sub>8</sub>: C, 60.15; H, 4.29; N, 3.51. Found: C, 60.08; H, 4.43; N, 3.62.

#### Z-1,6-Dibromo-4,9-dimethoxy-11-nitromethylene-11H-benzofuro[3,2-b][1]benzopyran (2f)

This compound was obtained in 26% yield, yellow feathery needles (trichloroethylene-heptane), mp 237-239°;  $^1\text{H}$  nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  4.00 (s, 3H), 4.02 (s, 3H), 7.21 (d, 1H, J = 8.5 Hz), 7.35 (d, 1H, J = 8.7 Hz), 7.59 (d, 1H, J = 8.5 Hz), 7.78 (d, 1H, J = 8.7 Hz), 8.39 (s, 1H);  $^{13}\text{C}$  nmr (hexadeuteriodimethyl sulfoxide): [12]  $\delta$  128.4 and 127.7 (2-C and 7-C), 132.0 (10a-C), 121.7 (=CNO<sub>2</sub>), 121.6 and 118.5 (5a-C and 11a-C), 114.9 and 113.0 (3-C and 8-C), 56.9 (CH<sub>3</sub>), 56.6 (CH<sub>3</sub>);

ms: m/z (%) 499 (M<sup>+</sup> for 2 x <sup>81</sup>Br, 3), 497 (M<sup>+</sup> for <sup>81</sup>Br + <sup>79</sup>Br, 6), 495 (M<sup>+</sup> for 2 x <sup>79</sup>Br, 3), 418 (71), 417 (22), 416 (79), 386 (33), 385 (20), 384 (35), 85 (66), 83 (100), 45 (20), 43 (21).

Anal. Calcd. for C<sub>18</sub>H<sub>11</sub>Br<sub>2</sub>NO<sub>6</sub>: C, 43.49; H, 2.23; N, 2.82. Found: C 43.21; H, 2.15; N, 2.89.

#### Single Crystal X-ray Analysis of 2a.

Crystallographic and refinement parameters are summarized in Table I.

The data were collected on a Nonius CAD 4 diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Two standard reflections were measured every two hours, no change was observed. The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by full-matrix least-squares techniques. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms positions were found on difference maps, their coordinates were not refined and they were given an overall isotropic thermal parameter. An absorption correction was applied with the DIFABS program [10] from CRYSTALS [11] which has been used to carry out all the calculations. The final atomic parameters for non-hydrogen atoms are reported in Table II. Bond lengths and bond angles are listed in Table III and IV, respectively.

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#### REFERENCES AND NOTES

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[8] To our knowledge, The  $^{13}\text{C}$  data in hexadeuteriodimethyl sulfoxide solution for the benzofuran itself have never been published. Since we required these chemical shifts for comparison, we have recorded the spectra and collected the following values:  $\delta = 107.7$  (3-C), 112.3 (7-C), 122.4 (4-C), 123.7 (5-C), 125.3 (6-C), 128.4 (3a-C), 146.7 (2-C), 155.7 (7a-C).

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