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# An expeditious synthesis of polyhydroxylated 2-arylbenzo[*b*]furans

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**Abstract**—An expeditious synthesis of polyhydroxylated 2-arylbenzo[*b*]furans is described. The key steps are the conversion of the corresponding polymethoxylated stilbenes into diarylethanoid molecules (epoxide or alcohol) that were demethylated and cyclised using boron tribromide to give the target polyhydroxylated 2-arylbenzo[*b*]furans. © 2001 Elsevier Science Ltd. All rights reserved.

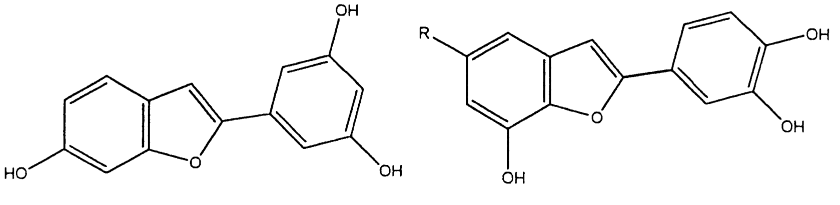
## 1. Introduction

Natural polyphenols containing a 2-phenylbenzo[*b*]furan unit such as moracins[1] or norlignans[2] (Scheme 1) often exhibit interesting biological activities. This has stimulated numerous studies[3] on the synthesis of the 2-phenylbenzo[*b*]-furan skeleton.

As a part of our studies on the synthesis of new biologically active polyhydroxylated compounds,[4] we have shown that boron tribromide may promote a tandem deprotection–cyclisation of 2-methoxyphenylacetones[5] and 2-hydroxy-3-arylpropenoic acids[6] leading respectively to 2-methyl and 2-carboxybenzo[*b*]furans in moderate yields. These results led us to evaluate the synthesis of natural or synthetic polyhydroxylated 2-phenylbenzo[*b*]furans from 1,2-diarylethanoid units and boron tribromide. The acid-catalysed tandem deprotection–cyclisation of diarylethanoid units is well documented[7] but the reported procedure generally requires hard conditions (concentrated acid, high temperature) and gives variable yields. Our new approach might be of particular interest due to the limited number of steps involved (five steps from the commercially available benzyl alcohols) and its simplicity.

## 2. Results and discussion

In order to design the best 1,2-diarylethanoid unit, we synthesised three model molecules, i.e. 2-(2-methoxyphenyl)-1-(4-methoxyphenyl)ethanone **1a**, 1,2-epoxy-1-(2-methoxyphenyl)-2-(4-methoxyphenyl)ethane **2a** and 2-(3-chlorobenzoyloxy)-1-(2-methoxyphenyl)-2-(4-methoxy phenyl)ethanol **3a** (Scheme 2). We have chosen these models since the known 2-(4-hydroxyphenyl)benzofuran **5a**[8] presents an easily interpretable $^1$H NMR spectrum. The proton H3 appears as a doublet at 7.04 ppm with a coupling constant of $^5J$=0.85 Hz, the phenyl protons as two doublets at 6.97 and 7.78 ppm ($^3J$=8.8 Hz) and the other aromatic protons as two broad singlets at 7.14–7.31 and 7.48–7.59 ppm. Compound **1a** was prepared according to Clader et al.[9] Compounds **2a** and **3a** were obtained from the reaction of the corresponding *E*-stilbene **4a** and mcpba.[10] The structure of **3a** was unambiguously established from the NMR data ($^1$H, $^{13}$C and $^1$H–$^{13}$C correlation). Compound **3a** was obtained from the nucleophilic substitution of the epoxide **2a** by *m*-chlorobenzoic acid. Under neutral conditions, this reaction is known to follow a second-order kinetics and the nucleophile reacts on the less hindered position to give **3a**. The crude product



Moracin M

Norlignans

**Scheme 1.**

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*Keywords*: boron and compounds; dealkylation; cyclisation; benzofurans.

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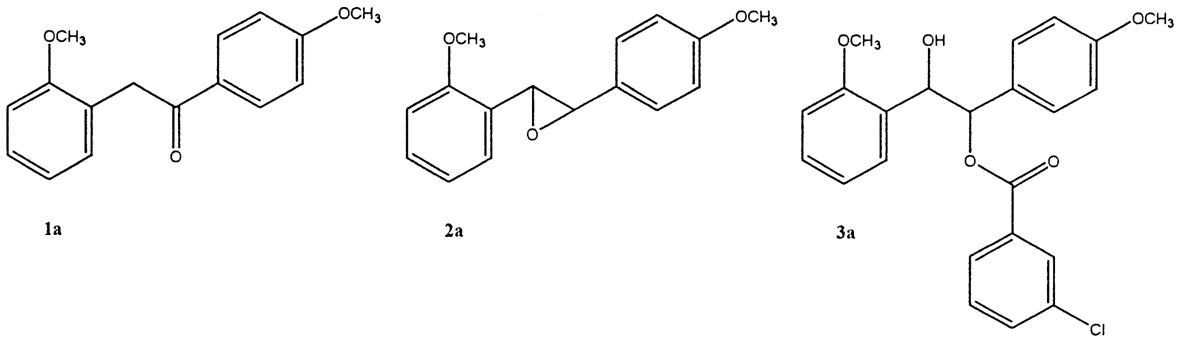


**1a** **2a** **3a**

**Scheme 2.**

**Table 1.** Stilbenes **4** and 2-arylbenzo[*b*]furans **5** prepared

| Entry | Yield in **4**[a] | Starting material | $R_3$[b] | $R_4$ | $R_5$ | $R'_3$ | $R'_4$ | Yield in **5**[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | | **1a** | H | H | H | H | OMe | 13 |
| 2 | 71 | **2a** | H | H | H | H | OMe | 58 |
| 3 | 71 | **3a** | H | H | H | H | OMe | 65 |
| 4 | 71 | **2a**+**3a** | H | H | H | H | OMe | 50 |
| 5 | 70 | **2b** | OMe | H | H | H | OMe | 51 |
| 6 | 80 | **2c** | H | H | OMe | H | OMe | 21 |
| 7 | 72 | **3d** | H | OMe | OMe | H | OMe | 64 |
| 8 | 84 | **3e** | H | H | H | OMe | OMe | 40 |
| 9 | 71 | **2f** | OMe | H | H | OMe | OMe | 48 |
| 10 | 86 | **3g** | H | H | OMe | OMe | OMe | 66 |

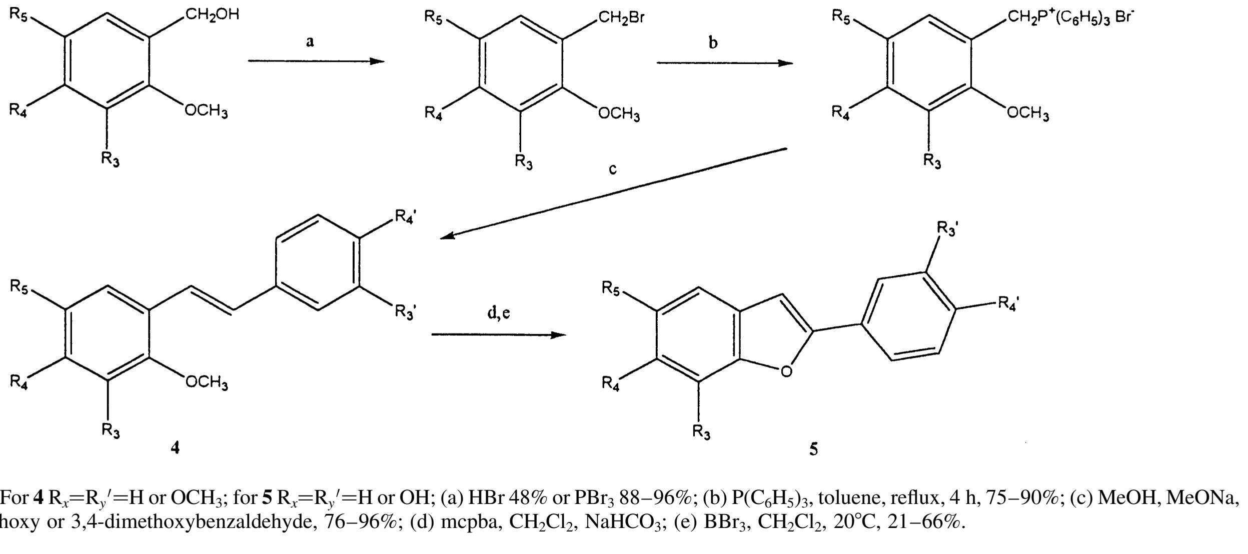
[a] Unoptimised yields in crude stilbenes **4** form the corresponding commercially available benzylalcohols.

[b] For the structures of compounds **2**, **3**, **4** and **5** see Scheme 3.

[c] Overall yields in 2-arylbenzo[*b*]furans **5** calculated from the purified starting material (entries 1–3) or from the crude stilbenes **4** (other entries).

(mixture of **2a** and **3a**) of the reaction of crude **4a** (*E*/*Z*=4) was also tested in order to evaluate the relevance of an exhaustive purification at this early step. The results reported in Table 1 (entries 1–3) led us to choose the 'epoxide/alcohol' strategy since **1a** gave **5a** in only 13% yield whereas **5a** was obtained in 58 and 65% yields from **2a** and **3a**, respectively. The unseparated products of the oxidation of **4a** with mcpba were converted into **5a** in 50% yield (entry 4). Consequently, stilbene **4** was not separated from its *Z* isomer before oxidation and the oxidation products (**2** and **3**) were not purified prior to cyclisation. The yields in **5** are given for the transformation **4**→**5**. Oxidation of **4** with mcpba gave variable amounts of epoxide **2** (the *trans* isomer was the major product in the same proportions than the *E* isomer of the starting stilbene **4**) and alcohol **3** (as mixtures of diastereoisomers and in some cases regioisomers). The main product is indicated in Table 1, column 2.

Stilbenes **4** were synthesised in three steps from the commercially available benzyl alcohols as depicted in Scheme 3. The known benzyl bromides[11–15] were obtained from the reaction of the corresponding benzyl alcohols with 48% aqueous HBr[16] or with phosphorus tribromide[15] in 88–96% yields. The phosphonium bromides were obtained by treatment of the corresponding benzyl bromides



**Scheme 3.** For **4** $R_x$=$R_y'$=H or $OCH_3$; for **5** $R_x$=$R_y'$=H or OH; (a) HBr 48% or $PBr_3$ 88–96%; (b) $P(C_6H_5)_3$, toluene, reflux, 4 h, 75–90%; (c) MeOH, MeONa, then 4-methoxy or 3,4-dimethoxybenzaldehyde, 76–96%; (d) mcpba, $CH_2Cl_2$, $NaHCO_3$; (e) $BBr_3$, $CH_2Cl_2$, 20°C, 21–66%.

with triphenylphosphine in refluxed toluene[17] in 75–90% yields. The stilbenes **4**[18–22] were obtained by a classical Wittig reaction[22] in variable mixtures of *E* and *Z* isomers. The crude stilbenes were used without further purification except for **4a**. The epoxidation of the stilbenes was carried out according to Moyna et al.[10] to give variable mixtures of epoxides **2** (*cis* and *trans* isomers) and alcohols **3** (*erythro* and *threo* isomers). The epoxidation products were used without further purification except for **2a** and **3a**.

## 3. Conclusion

We have successfully obtained by this method seven hydroxylated 2-phenylbenzo[*b*]furans in 17–57% overall yields (from the corresponding benzyl alcohols) in five steps. This strategy may be easily applied to the synthesis of some norlignans that possess a 2-phenylbenzo[*b*]furan skeleton. This expeditious, inexpensive and simple method for the synthesis of polyhydroxylated 2-phenylbenzo[*b*]furans may be of particular interest in the obtention of potentially biologically active synthetic polyphenols. Some of them are currently being tested as HIV-integrase inhibitors.

## 4. Experimental

### 4.1. General

TLC analyses were performed on a 3×10 cm plastic sheet precoated with silica gel 60F254 (Merck) (Solvent system: ethyl acetate/hexane 1:4). $SiO_2$, 200–400 mesh (Merck) was used for column chromatography. Melting points were obtained on a Reichert Thermopan melting point apparatus, equipped with a microscope and are uncorrected. NMR spectra were obtained on an AC 200 Bruker spectrometer in the appropriate solvent with TMS as internal reference. Mass spectra were recorded on a Ribermag R 10-10 spectrometer (Electron Impact, 60 eV) or on a Finnigan MAT Vision 2000 spectrometer [for the MALDI (mass assisted laser desorption ionisation)]. Elemental analyses were performed by CNRS laboratories (Vernaison) and were within 0.4% of the theoretical value.

**4.1.1. (*E*)-2,5,4′-Trimethoxystilbene 4c.** 97% yield; yellow oil: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.82 (3H, s, OMe), 3.83 (3H, s, OMe), 3.85 (3H, s, OMe), 6.81–6.83 (2H, m), 6.93 (2H, d, $^3J$=8.9 Hz), 7.11 (1H, d, $^3J$=16.5 Hz), 7.21 (1H, d, $^4J$=2.55 Hz), 7.42 (1H, d, $^3J$=16.5 Hz), 7.52 (2H, d, $^3J$=8.9 Hz); Elemental analysis calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; found: C, 75.45; H, 6.76.

**4.1.2. (*E*)-2,3′4′-Trimethoxystilbene 4e.** 96% yield; white powder: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.897 (3H, s, OMe), 3.903 (3H, s, OMe), 3.95 (3H, s, OMe), 6.85 (d, 1H, $^3J$=8.2 Hz), 6.90 (1H, dd, $^3J$=8.2 Hz, $^4J$=1.6 Hz), 6.97 (1H, tdd, $^3J$=7.55 Hz, $^4J$=1.2 Hz, $^4J$=0.45 Hz), 7.06 (1H, m), 7.07(1H, d, $^3J$=16.45 Hz), 7.10(1H, d, $^4J$=1.60 Hz), 7.24(1H, ddd, $^3J$=8.2 Hz, $^3J$=7.4 Hz, $^4J$=1.7 Hz), 7.34(1H, d, $^3J$=16.45 Hz), 7.58(1H, dd, $^3J$=7.65 Hz, $^4J$=1.75 Hz); Elemental analysis calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; found: C, 75.15; H, 6.65.

**4.1.3. (*E*)-2,5,3′4′-Trimethoxystilbene 4g.** 96% yield; pale yellow powder: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.81 (3H, s, OMe), 3.84 (3H, s, OMe), 3.89 (3H, s, OMe), 3.94 (3H, s, OMe), 6.78–6.87 (3H, m), 6.99–7.14 (4H, m), 7.31 (1H, d, $^3J$=16.2 Hz); Elemental analysis calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71; found: C, 72.02; H, 6.89.

**4.1.4. 1,2-Epoxy-1-(2-methoxyphenyl)-2-(4-methoxyphenyl)ethane 2a.** 48% yield; white powder: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.80 (d, 1H, $^4J$=1.90 Hz), 3.834 (s, 3H), 3.841 (s, 3H), 4.33 (d, 1H, $^4J$=1.90 Hz), 6.90–7.08 (m, 2H), 6.96 (d, 2H, $^3J$=8.90 Hz), 7.29–7.39 (m, 2H), 7.35 (d, 2H, $^3J$=8.90 Hz); $\delta_C$(50 MHz, $CDCl_3$; $Me_4Si$): 55.39 (q), 55.43 (q), 58.1 (d), 62.3 (d), 110.2 (d), 114.0 (d), 120.8 (d), 125 (s), 125.9 (d), 127.1 (d), 128.9 (d), 129.6 (s), 158.1 (s), 159.8 (s); MS (EI) *m/z* (%): 256 (13), 227 (40), 151 (68), 135 (42), 121 (100), 91 (17), 77 (18); Elemental analysis calcd for $C_{16}H_{16}O_5$: C, 74.98; H, 6.29; found: C, 75.25; H, 6.08.

**4.1.5. 2-(3-Chlorobenzoyloxy)-1-(2-methoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol 3a.** 31% yield; yellow oil; $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.73 (s, 3H), 3.75 (s, 3H), 5.22 (d, 1H, $^3J$=7.0 Hz), 6.31 (d, 1H, $^3J$=7.0 Hz), 6.73–6.87 (m, 2H), 6.77 (d, 2H, $^3J$=8.90 Hz), 7.10–7.24 (m, 2H), 7.20 (d, 2H, $^3J$=8.90 Hz), 7.36 (dd, 1H, $^3J$=7.95 Hz, $^3J$=7.65 Hz), 7.52 (ddd, 1H, $^3J$=7.95 Hz, $^4J$=1.90 Hz, $^4J$=1.30 Hz), 7.97 (ddd, 1H, $^3J$=7.65 Hz, $^4J$=1.60 Hz, $^4J$=1.30 Hz), 8.08 (dd, 1H, $^4J$=1.90 Hz, $^4J$=1.60 Hz); $\delta_C$(50 MHz, $CDCl_3$; $Me_4Si$): 55.0 (q), 55.1, (q), 73.8 (d), 79.0 (d), 110.3 (d), 113.3 (d), 120.5 (d), 127.8 (d), 128.1 (d), 128.3 (d), 128.6 (d), 128.9 (s), 129.56 (d), 129.63 (d), 132.0 (s), 132.8 (d), 133.3 (s), 134.3 (s), 156.4 (s), 159.2 (s), 164.7 (s); MS (Vision 2000): 257 ($M-C_6H_4ClCO_2$); Elemental analysis calcd for $C_{23}H_{21}ClO_5$: C, 66.93; H, 5.13; found: C, 66.95; H, 5.47.

**4.1.6. 1,2-Epoxy-1-(2,3-dimethoxyphenyl)-2-(4-methoxyphenyl)ethane 2b.** White powder: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.79 (d, 1H, $^3J$=1.90 Hz), 3.81 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 4.23 (d, 1H, $^3J$=1.90 Hz), 6.86–6.94 (m, 2H), 6.92 (d, 2H, $^3J$=8.60 Hz), 7.11 (dd, 1H, $^3J$=8.60 Hz, $^4J$=1.60 Hz), 7.30 (d, 2H, $^3J$=8.60 Hz).

**4.1.7. 1,2-Epoxy-1-(2,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethane 2c.** White powder; $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.69 (d, 1H, $^3J$=1.90 Hz), 3.76 (s, 3H), 3.79 (s, 3H), 3.81 (s, 3H), 4.28 (d, 1H, $^3J$=1.90 Hz), 6.82 (d, 2H, $^4J$=1.60 Hz), 6.90 (d, 1H, $^4J$=1.90 Hz), 6.93 (d, 2H, $^3J$=8.60 Hz), 7.31 (d, 2H, $^3J$=8.60 Hz).

**4.1.8. 2-(3-Chlorobenzoyloxy)-1-(2,4,5-trimethoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol 3d.** Yellow oil; $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.67 (s, 3H), 3.71 (s, 3H), 3.72 (s, 3H), 3.75 (s, 3H), 5.07 (d, 1H, $^3J$=7.0 Hz), 6.36 (d, 1H, $^3J$=7.0 Hz), 6.56 (d, 1H, $^3J$=8.60 Hz), 6.71 (d, 2H, $^3J$=8.90 Hz), 6.98 (d, 1H, $^3J$=8.60 Hz), 7.14 (d, 2H, $^3J$=8.90 Hz), 7.30 (dd, 1H, $^3J$=7.95 Hz, $^3J$=7.65 Hz), 7.46 (ddd, 1H, $^3J$=7.95 Hz, $^4J$=2.20 Hz, $^4J$=1.30 Hz), 7.92 (ddd, 1H, $^3J$=7.65 Hz, $^4J$=1.60 Hz, $^4J$=1.30 Hz), 8.02 (dd, 1H, $^4J$=1.90 Hz, $^4J$=1.60 Hz).

**4.1.9. 2-(3-Chlorobenzoyloxy)-1-(2-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethan-1-ol 3e.** Yellow oil: $\delta_H$

(200 MHz, $CDCl_3$; $Me_4Si$): 3.66 (s, 3H), 3.68 (s, 3H), 3.75 (s, 3H), 5.25 (d, 1H, $^3J$=7.0 Hz), 6.22 (d, 1H, $^3J$=7.0 Hz), 6.63 (d, 1H, $^4J$=1.9 Hz), 6.69 (d, 1H, $^3J$=8.3 Hz), 6.71–6.83 (m, 2H), 6.84 (dd, 1H, $^3J$=8.3 Hz, $^4J$=1.9 Hz), 7.09–7.19 (m, 2H), 7.31 (dd, 1H, $^3J$=7.95 Hz, $^3J$=7.65 Hz), 7.46 (ddd, 1H, $^3J$=7.95 Hz, $^4J$=1.90 Hz, $^4J$=1.30 Hz), 7.93 (ddd, 1H, $^3J$=7.65 Hz, $^4J$=1.60 Hz, $^4J$=1.30 Hz), 8.04 (dd, 1H, $^4J$=1.90 Hz, $^4J$=1.60 Hz).

**4.1.10. 1,2-Epoxy-1-(2,3-dimethoxyphenyl)-2-(3,4-dimethoxyphenyl)ethane 2f.** Yellow oil: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.78 (d, 1H, $^3J$=1.9 Hz), 3.82 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 4.19 (d, 1H, $^3J$=1.9 Hz), 6.83–6.97 (m, 5H), 7.09 (t, 1H, $^3J$=7.95 Hz).

**4.1.11. 2-(3-Chlorobenzoyloxy)-1-(2,5-dimethoxyphenyl)-2-(3,4-dimethoxyphenyl)ethan-1-ol 3g.** Orange oil: $\delta_H$ (200 MHz, $CDCl_3$; $Me_4Si$): 3.66 (s, 3H), 3.72 (s, 3H), 3.76 (s, 3H), 3.82 (s, 3H), 5.17 (d, 1H, $^3J$=7.0 Hz), 6.24 (d, 1H, $^3J$=7.0 Hz), 6.70–6.76 (m, 6H), 7.39 (dd, 1H, $^3J$=7.95 Hz, $^3J$=7.65 Hz), 7.51 (ddd, 1H, $^3J$=7.95 Hz, $^4J$=2.20 Hz, $^4J$=1.3 Hz), 7.97 (ddd, 1H, $^3J$=7.65 Hz, $^4J$=1.6 Hz, $^4J$=1.3 Hz), 8.08 (dd, 1H, $^4J$=1.9 Hz, $^4J$=1.6 Hz).

## 4.2. Reaction of 1a, 2 or 3 with boron tribromide: general procedure

$BBr_3$ (1 M in $CH_2Cl_2$, 15 mL, 15 mmol for **1a**, **2a** and **3a**, 20 mL, 20 mmol for **2b**, **2c** and **2e** or 25 mL, 25 mmol for **3d**, **2f** and **3g**) was added dropwise to a solution of **1a**, **2** or **3** (5 mmol) in $CH_2Cl_2$ (20 mL) at room temperature. The mixture was stirred for 1 h, then water (40 mL) was added dropwise. The solid was filtered off, dried and crystallized from acetone (**5d**, **5f** and **5g**). In the other cases, no solid was obtained and the aqueous layer was extracted twice with ethyl acetate (20 mL). The organic layer was dried ($MgSO_4$), the solvent evaporated and the residue was purified by column chromatography (eluent: hexane/ethyl acetate 1:1).

**4.2.1. 7-Hydroxy-2-(4-hydroxyphenyl)benzo[*b*]furan 5b.** Beige powder; mp=176–178°C; $\delta_H$ (200 MHz, acetone-$d_6$; $Me_4Si$): 6.75 (dd, 1H, $^3J$=6.5 Hz, $^4J$=2.45 Hz), 6.94 (d, 2H, $^3J$=8.8 Hz), 6.97–7.08 (m, 3H), 7.78 (d, 2H, $^3J$=8.8 Hz), 8.91 (s, 1H), 9.00 (s, 1H); $\delta_C$(50 MHz, acetone-$d_6$; $Me_4Si$): 100.4 (d), 111.1 (d), 112.5 (d), 116.6 (d), 123.0 (s), 124.5 (d), 127.2 (d), 132.3 (s), 143.2 (s), 144.1 (s), 157.0 (s), 159.0 (s); MS (EI) *m/z* (%): 226 (100), 197 (12), 113 (19), 110 (13); elemental analysis calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46; found: C, 74.17; H, 4.53.

**4.2.2. 5-Hydroxy-2-(4-hydroxyphenyl)benzo[*b*]furan 5c.** Beige powder; mp=257°C; $\delta_H$ (200 MHz, acetone-$d_6$; $Me_4Si$): 6.78 (dd, 1H, $^3J$=8.7 Hz, $^4J$=2.6 Hz), 6.92 (d, 1H, $^5J$=0.85 Hz), 6.94 (d, 2H, $^3J$=8.7 Hz), 6.99 (dd, 1H, $^4J$=2.6 Hz, $^5J$=0.6 Hz), 7.32 (dt, 1H, $^3J$=8.7 Hz, $^5J$=0.85 Hz, $^5J$=0.6 Hz), 7.74 (d, 2H, $^3J$=8.7 Hz), 8.13 (s, 1H), 8.75 (s, 1H); $\delta_C$(50 MHz, acetone-$d_6$; $Me_4Si$): 100.1 (d), 106.1 (d), 111.7 (d), 113.2 (d), 116.6 (d), 123.1 (s), 127.2 (d), 131.3 (s), 149.9 (s), 154.4 (s), 157.8 (s), 158.9 (s); MS (EI) *m/z* (%):226 (100), 197 (7), 115 (11), 113 (24), 110 (10); elemental analysis calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46; found: C, 74.52; H, 4.41.

**4.2.3. 5,6-Dihydroxy-2-(4-hydroxyphenyl)benzo[*b*]furan 5d.** Brown powder; mp=255°C; $\delta_H$ (200 MHz, acetone-$d_6$; $Me_4Si$): 6.84 (d, 1H, $^5J$=0.85 Hz), 6.91 (d, 2H, $^3J$=8.7 Hz), 6.97 (s, 1H), 7.00 (d, 1H, $^5J$=0.85 Hz), 7.66 (d, 2H, $^3J$=8.7 Hz), 7.82 (s, 1H), 8.02 (s, 1H), 8.65 (s, 1H); $\delta_C$(50 MHz, acetone-$d_6$; $Me_4Si$): 98.4 (d), 100.1 (d), 105.8 (d), 116.5 (d), 122.4 (s), 123.6 (s), 126.5 (d), 143.2 (s), 144.5 (s), 149.9 (s), 155.8 (s), 158.4 (s).; MS (EI) *m/z* (%):242 (100), 241 (11), 226 (16), 139 (15), 121 (30); elemental analysis calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16; found: C, 69.38; H, 4.21.

**4.2.4. 2-(3,4-Dihydroxyphenyl)benzo[*b*]furan 5e.** Brown-grey powder; mp=179–181°C; $\delta_H$ (200 MHz, acetone-$d_6$; $Me_4Si$): 6.96 (d, 1H, $^3J$=8.1 Hz), 7.00 (d, 1H, $^5J$=1.15 Hz), 7.13–7.28 (m, 2H), 7.31 (dd, 1H, $^3J$=8.1 Hz, $^4J$=2.0 Hz), 7.44 (d, 1H, $^4J$=2.0 Hz), 7.46–7.58 (m, 2H), 8.44 (s, 1H), 8.55 (s, 1H); $\delta_C$(50 MHz, acetone-$d_6$; $Me_4Si$): 100.2 (d), 111.5 (d), 112.8 (d), 116.5 (d), 118.0 (d), 121.4 (d), 123.3 (s), 123.7 (d), 124.5 (d), 130.5 (s), 146.4 (s), 147.2 (s), 155.4 (s), 157.3 (s); MS (EI) *m/z* (%): 226 (100), 152 (14), 139 (13), 113 (29), 84 (74), 49 (100); elemental analysis calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46; found: C, 74.28; H, 4.57.

**4.2.5. 2-(3,4-Dihydroxyphenyl)-7-hydroxybenzo[*b*]furan 5f.** Dark powder; mp=99–101°C; $\delta_H$ (200 MHz, methanol-$d_4$; $Me_4Si$): 6.58 (dd, 1H, $^3J$=6.1 Hz, $^4J$=2.8 Hz), 6.741 (d, 1H, $^3J$=8.2 Hz), 6.743 (s, 1H), 6.86 (dd, 1H, $^3J$=7.8 Hz, $^3J$=6.1 Hz), 6.91 (dd, 1H, $^3J$=7.8 Hz, $^4J$=2.8 Hz), 7.17 (dd, 1H, $^3J$=8.2 Hz, $^4J$=2.0 Hz), 7.23 (d, 1H, $^4J$=2.0 Hz); $\delta_C$(50 MHz, methanol-$d_4$; $Me_4Si$): 100.5 (d), 111.0 (d), 112.8 (d), 113.1 (d), 116.6 (d), 118.2 (d), 124.0 (s), 124.5 (d), 132.8 (s), 143.3 (s), 144.6 (s), 146.6 (s), 147.3 (s), 157.6 (s); MS (EI) *m/z* (%): 242 (100), 139 (24), 121 (20), 57 (22); elemental analysis calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16; found: C, 69.48; H, 4.08.

**4.2.6. 2-(3,4-Dihydroxyphenyl)-6-hydroxybenzo[*b*]furan 5g.** Grey powder; mp>230°C; $\delta_H$ (200 MHz, acetone-$d_4$; $Me_4Si$): 6.76 (dd, 1H, $^3J$=9.0 Hz, $^4J$=2.3 Hz), 6.89 (d, 1H, $^5J$=1.1 Hz), 6.91 (d, 1H, $^3J$=8.1 Hz), 6.96 (d, 1H, $^4J$=2.3 Hz), 7.26 (dd, 1H, $^3J$=8.1 Hz, $^4J$=2.0 Hz), 7.29 (bd, 1H, $^3J$=9.0 Hz), 7.35 (d, 1H, $^4J$=2.0 Hz); $\delta_C$(50 MHz, acetone-$d_4$; $Me_4Si$): 105.9 (d), 110.6 (d), 111.6 (d), 112.6 (d), 113.0 (d), 116.4 (d), 127.8 (s), 123.6 (d), 131.2 (s), 146.0 (s), 146.7 (s), 149.8 (s), 150.0 (s), 154.2 (s); MS (EI) *m/z* (%): 242 (100), 139 (32), 121 (27); elemental analysis calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16; found: C, 69.57; H, 4.29.

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