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Lewis or Brønsted Acid Provoked Rearrangements in ortho-(1,1-Dimethylpropenyl)phenols.

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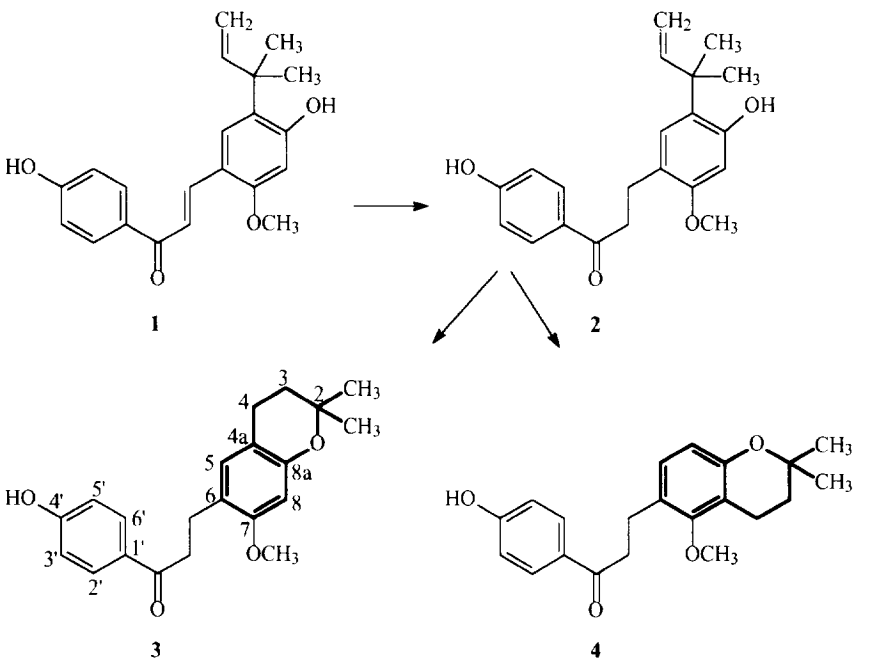
Abstract: Treatment of the o-(1,1-dimethylpropenyl)phenol, dihydrolicochalcone A, with a Brønsted acid affords two isomeric 2,2-dimethyl-4*H*-dihydropyrano[*b*]benzenes. The rearrangement probably involves a [3,5] charge-accelerated rearrangement. Attempts to provoke the same reaction in licochalcone A only afforded poorly defined degradation products. Treatment of dihydrolicochalcone A as well as licochalcone A with Lewis acids afforded 2,3,3-trimethyldihydro-furano[*b*]benzenes and 2,2,3-trimethyldihydrofurano[*b*]benzenes. Proper use of solvents and Lewis acid enables preferential formation of the kinetically favoured product or the thermodynamically more stable product.

The bicyclic residues 2,2-dimethyl-4*H*-1,2-dihydropyrano[*b*]benzene shown in bold in compound **3** and **4**, and 2,3,3-trimethyldihydrofurano[*b*]benzene shown in bold in compound **5** are frequently found in a number of naturally occurring compounds, including xanthones[1], chromones[2], coumarins[3] and flavonoids[4]. The isomeric bicyclic nucleus 2,2,3-trimethyldihydrofurano[*b*]benzene has been found as the 5-propenyl derivative in the essential oil from *Illicium verum*[5] but a later study has indicated that the compound might be an artefact formed by a thermal rearrangement.[6] The biosynthesis of the 2,3,3-trimethyldihydrofurano[*b*]benzene skeleton is generally believed to involve an acid or enzyme catalysed ring closure of an *o*-(1,1-dimethylpropenyl)phenol like licochalcone A (**1**), and *in vitro* experiments have confirmed that the residue might be formed in this way.[7] Similarly, the 2,2-dimethyl-4*H*-1,2-dihydropyrano[*b*]benzene residue can be formed by ring closure of a *o*-(3-methyl-2-butenyl)phenol.

As a part of structure-activity relationships studies over the antiparasitic licochalcone A (**1**) the double bond conjugated with the carbonyl group was reduced using ionic hydrogenation.[8] During the work up of the reaction mixture we noticed the presence of the rearrangement products **3** and **4**, the formation of which had to involve unusual reaction mechanisms. In order to study the mechanisms behind these reactions and thereby elucidate some of the reactions behind formation of furano- and pyranobenzenes the study described in this paper was undertaken.

Ionic hydrogenation of licochalcone A (**1**) using triethyl silane and trifluoracetic acid as reagents affords the dihydroproduct **2** in high yields if the reaction time is restricted to 2 h. If, however, the reaction time is prolonged to 6 h, the two dominating reaction products are **3** and **4** (Scheme 1).

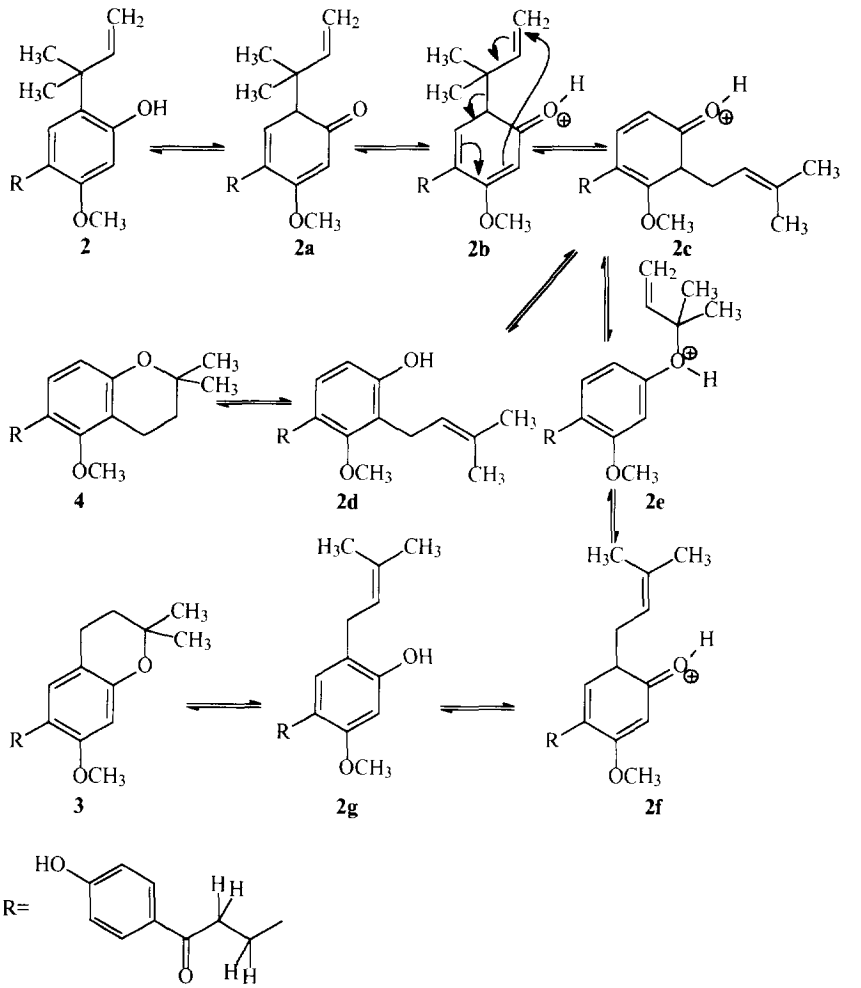
Treatment of **1** with trifluoroacetic acid only leads to a complicated mixture of products beside unreacted **1**, indicating that the starting material for the bicyclic products is **2**. This hypothesis was further confirmed, when it was observed that the two dihydropyranobenzenes were formed in high yields when **2** was treated with the Brønsted acid trifluoroacetic acid. Triethylsilyl trifluoroacetate, a side product formed by the ionic hydrogenation of **1**, has no effect on neither the reaction speed nor the regioselectivity.



Scheme 1.

Neither of the two products can be formed by a simple ring closure of the *o*-(1,1-dimethylpropenyl)phenol fragment of **2**, since this would lead to either a 4,4-dimethyldihydropyranobenzene or, more likely, a 2,3,3-trimethyldihyrofurano-benzene derivative. Likewise, the positions of the methyl groups exclude the possibility, that the products are formed by a double [3,3] or a [1,5] sigmatropic rearrangement.[9] Instead the reaction might proceed *via* [3,5][10] and [3,3][9] sigmatropic (retro-Claisen) rearrangements as depicted in Scheme 2. Since the reaction takes place at room temperature and proceeds quickly compared to thermal sigmatropic rearrangements it is most likely a charge-accelerated rearrangement catalysed by trifluoroacetic acid.[11]

The initiating step might be a protonation of **2a** to give the intermediate **2b**, which by a [3,5] sigmatropic rearrangement is converted into **2c**. Intermediate **2c** then either might ring close to give **4** or might, *via* a [3,3] sigmatropic rearrangement, be converted into intermediate **2e**, which after another [3,3] rearrangement and ring closure will be converted into **3**.

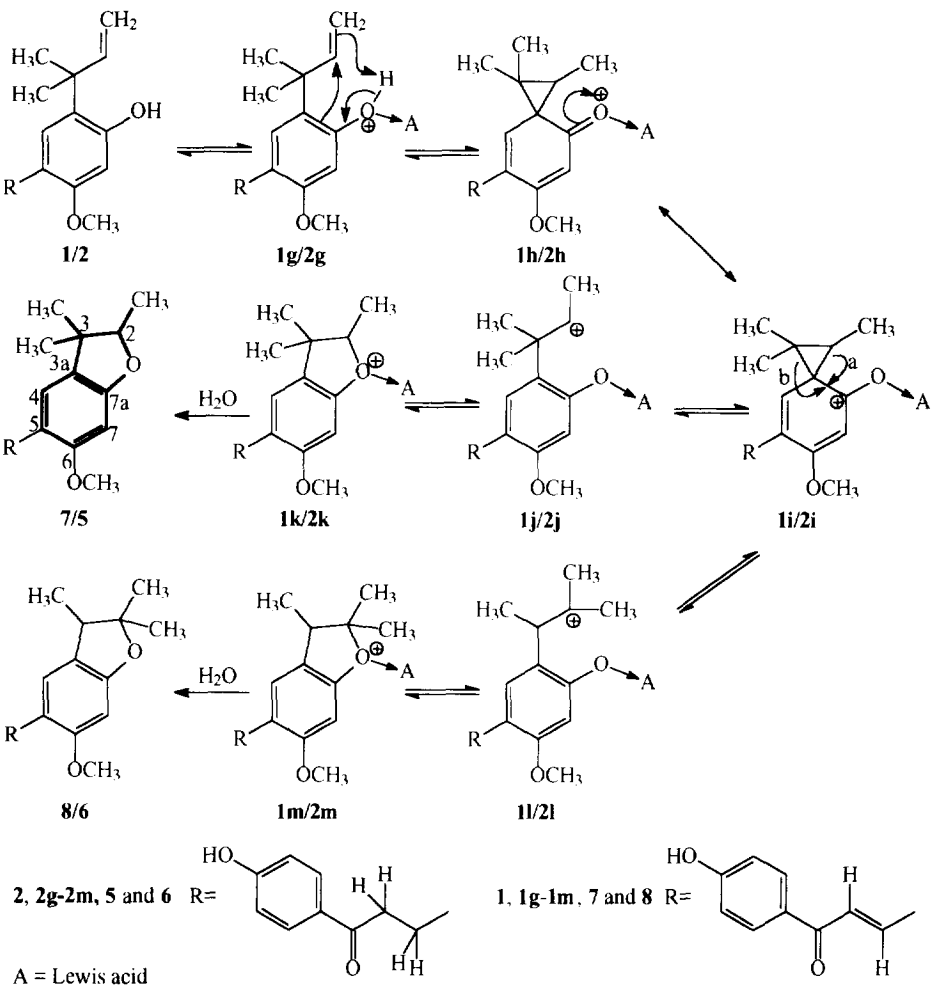


Scheme 2.

Lewis acids, such as anhydrous aluminium chloride or titanium tetrachloride are also known to catalyse sigmatropic rearrangements.[11a] Surprisingly, however, neither of these catalysts afforded the dihydropyranobenzene derivatives **3** or **4** but with both catalysts the dihydrofuranobenzene derivative **5** and **6** were obtained (Scheme 3).

In contrast to the Brønsted acid, trifluoroacetic acid, which degraded **1**, rearrangements analogous to the reactions provoked with **2** proceeded when **1** was treated with the two Lewis acids affording the two reaction products **7** and **8**. In the case of **1** as well as **2** experiments with prolonged reaction time afforded preponderance of **8** and **6**, respectively.

Analogously, treatment of the products **5** and **7** with the Lewis acids converted these products into **6** and **8**, respectively. These observations prove that the 2,3,3-trimethyldihydrofuranobenzenes (**5** and **7**) or intermediates on the reaction path for these compounds are temporarily accumulated, but upon additional treatment with the Lewis acids they are converted into the 2,2,3-trimethyl derivatives **6** and **8**.



Scheme 3.

The formation of the two 2,2,3-trimethyldihydrofuranobenzenes (**6** and **8**) is difficult to explain without assuming intermediate phenonium ions like **1h** resonating with **1i**, and **2h** resonating with **2i**.[12] Analogous phenonium ions have been suggested for thermal rearrangements.[13]

By accepting these intermediates, however, the reaction path might be depicted as shown in Scheme 3. The complexes between the Lewis acid and the phenols (**1g** or **2g**, respectively) rearrange into the phenonium ions. The intermediates **1i** or **2i**, respectively, might open the cyclopropane ring either by cleaving bond a to give intermediate **1j** or **2j**, respectively, or by cleaving bond b to give **1l** or **2l**, respectively. The finding that **5** and **7** by prolonged treatment with Lewis acids are converted into **6** and **8**, respectively, indicates, that intermediates **1l** and **2l**, being tertiary carbocations, are thermodynamically more stable than the secondary carbocations **1j** and **2j**, respectively. The quicker formation of **5** and **7** indicates that intermediates **1j** and **2j** are the kinetically easier formed ions.

The finding, that the dihydrochalcone **2** was converted into the rearrangement products **5** and **6** much faster than the chalcone **1** was transformed into the analogous rearrangement products **7** and **8**, might relate to the poorer electron density in the cyclopropane ring in **1i** compared to **2i** because of the greater delocalization of the electrons in the chalcone skeleton. The poorer electron density will cause decreased possibility for stabilising the phenonium intermediate.

The different rate of formation of the 2,3,3-trimethyldihydrofuranobenzenes (*e.g.* **5** or **7**) and the 2,2,3-trimethylfuranobenzens (*e.g.* **6** and **8**) makes it possible to favour formation of the desired isomer. The use of a solvent, which slow down the reaction (*e.g.* nitrobenzene) and a less reactive catalyst (*e.g.* titanium tetrachloride) will make the reaction path b (Scheme 3) very slow and thus enable isolation of the 2,3,3-trimethylfuranobenzenes **5** or **7** in high yield. Solvents that speed up the reaction (*e.g.* dichloromethane) and reactive catalysts (*e.g.* aluminium chloride) will favour formation of the 2,2,3-trimethylfuranobenzenes **6** and **8**.

EXPERIMENTAL

^{1}H NMR, ^{13}C NMR and DEPT (135°) spectra were recorded on a Bruker AC-200F spectrometer. Chemical shifts are reported in parts per million (PPM, δ) using tetramethylsilane as internal standard. Splitting pattern are described as singlet (s), doublet (d), triplet (t), quartet (q) and broad (b). A * indicates that signals with similar shifts might be interchanged. Mass spectra were recorded on a Jeol AX505W mass spectrometer. Melting points are determined on a Electrothermal melting point apparatus, and are not corrected. Column chromatography was performed on silica gel (Merck, 0.040-0.063 mm) using a mixture of toluene and ethyl acetate as eluent.

*Synthesis of 3-(7-methoxy-2,2-dimethyl-4*H*-1,2-dihydropyrano[b]phenyl-6)-1-(4-hydroxyphenyl)-propanon-1 (3) and 3-(5-methoxy-2,2-dimethyl-4*H*-1,2-dihydropyrano[b]phenyl-6)-1-(4-hydroxyphenyl)-propanon-1 (4).*

Trifluoroacetic acid (0.230 ml, 2.99mmol) was slowly added to a stirred suspension of Licochalcone A[14] (**1**) (0.06g, 0.18mmol) in dichloromethane (2ml) and triethylsilane (60ml, 0.38mmol).

Water (2ml) was added after stirring for 6 h. The aqueous phase was extracted twice with dichloromethane (2 ml) and the combined organic phases were concentrated *in vacuo*. The residue was purified by column chromatography to give **3** (0.023g, 37.5%) and **4** (0.012g, 19.1%) as colourless oils.

3: ^{1}H NMR ($CDCl_3$) δ 7.92 (AA' part of a AA'MM' system, H2', H6'), 6.95 (MM' part of a AA'MM' system, H3', H5'), 6.80 (s, H5), 6.30 (s, H8), 3.71 (s, -OCH_3), 3.19 (bt, *J* 7Hz, Hα), 2.92 (bt, *J* 7 Hz, Hβ), 2.62 (t, *J* 7 Hz, H4), 1.72 (t, *J* 7 Hz, H3), 1.29 (s, -CH_3). ^{13}C NMR ($CDCl_3$) δ 200.3 (C=O), 160.9* (C4'), 156.7* (C7), 153.0* (C8a), 130.9 (C2', C6'), 130.5 (C5), 129.5 (C1'), 120.8 (C6), 115.4 (C3', C5'), 112,1 (C4a), 99.7 (C8), 74.3 (C2), 55.3 (-OCH_3), 39.2 (Cα), 33.0 (Cβ), 26.8 (-CH_3), 25.7 (C4), 21.6 (C3). HRMS (FAB+): 340.1690 (Calc. $C_{21}H_{24}O_4$: 340.1675).

4: ^{1}H NMR ($CDCl_3$) δ 7.89 (AA' part of a AA'MM' system, H2', H6'), 6.96 (d, *J* 8 Hz, H7), 6.87 (MM' part of a AA'MM' system, H3', H5'), 6.55 (d, *J* 8 Hz, H8), 3.77 (s, -OCH_3), 3.20 (bt, *J* 7 Hz, Hα), 2.96 (bt, *J* 7 Hz, Hβ), 2.77 (t, *J* 7 Hz, H4), 1.78 (t, *J* 7 Hz, H3), 1.33 (s, -CH_3). ^{13}C NMR ($CDCl_3$) d 199.3 (C=O), 160.7* (C5), 155.9* (C4'), 152.5* (C8a), 130.8 (C2', C6'), 128.7 (C1'), 128.2 (C7), 124.6 (C6), 115.4 (C3', C5'), 114.5 (C4a), 113.2 (C8), 73.9 (C3''), 60.4 (-OCH_3), 39.7 (Cα), 32.3 (Cβ), 26.7 (-CH_3), 24.8 (C4), 17.5 (C3). HREIMS: 340.1677 (Calc. $C_{21}H_{24}O_4$: 340.1675). EIMS *m/z* (rel.int.): 340 ([M]$^+$,83), 296(17), 205(100), 161(22), 149(22), 121(46).

*Synthesis of 3-(7-methoxy-2,2-dimethyl-4*H*-1,2-dihydropyrano[b]phenyl-6)-1-(4-hydroxyphenyl)-propanon-1 (3) and 3-(5-methoxy-2,2-dimethyl-4*H*-1,2-dihydropyrano[b]phenyl-6)-1-(4-hydroxyphenyl)-propanon-1 (4).*

Trifluoroacetic acid (0.230 ml, 2.99mmol) was slowly added to a stirred solution of **2** (0.06g, 0.18mmol) in dichloromethane (2ml). Water (2ml) was added after stirring for 2 h. The aqueous phase was extracted twice with dichloromethane (2 ml) and the combined organic phases were concentrated *in vacuo*. The residue was purified by column chromatography to give **3** (0.032g, 53.1%) and **4** (0.018g, 29.1%) as colourless oils. The ^{1}H NMR and ^{13}C NMR spectra of **3** and **4** were superimposable to those obtained previously.

Synthesis of 3-(6-methoxy-2,3,3,trimethyl-2,3-dihydrofurano[b]phenyl-6)-1-(4-hydroxyphenyl)propanon-1 (5).

To a stirred solution of **2** (0.075 g, 0.22 mmol) in nitrobenzene (9ml) was added titanium(IV) chloride (24 µl, 0.22 mmol). After stirring for 30 sec, water (10ml) was added and the aqueous phase was extracted with nitrobenzene (10 ml). The combined organic phases were concentrated *in vacuo* and purified by column chromatography to give **5** (0.062g, 82.3%) as a colourless oil.

^{1}H-NMR ($CDCl_3$): δ 7.92 (AA' part of a AA'MM' system, H2', H6'), 6.91 (MM' part of a AA'MM' system, H3', H5'), 6.85 (s, H4), 6.37 (s, H7), 4.36 (q, *J* 7 Hz, H2), 3.76 (s, -OCH_3), 3.18 (bt, *J* 6Hz, Hα), 2.95 (bt, *J* 6 Hz, Hβ), 1.35 (d, *J* 7Hz, C2-CH_3), 1.25 (s, C3-CH_3), 1.04 (s, C3-CH_3). ^{13}C-NMR ($CDCl_3$): δ 200.0 (C=O), 160.63* (C4'), 157.3* (C6), 157.1* (C7a), 130.8 (C2', C6'), 129.3 (C1'), 128.2 (C3a), 123.5 (C4), 120.9 (C5), 115.3 (C3', C5'), 93.5 (C7), 89.5 (C2), 55.4 (-OCH_3), 43.1 (C3), 39.1 (Cα), 26.5 (Cβ), 26.0 (C3-CH_3), 23.3 (C3-CH_3), 14.5 (C2-CH_3). HRMS (FAB+): 340.1719 (Calc. $C_{21}H_{24}O_4$: 340.1675).

*Synthesis of 3-(6-methoxy-2,2,3,trimethyl-2,3-dihydrofurano[b]phenyl-6)-1-(4-hydroxyphenyl)propanon-1 (**6**).*

To a stirred solution of **2** (0.030 g, 0.09 mmol) in dichloromethane (5ml) was added anhydrous aluminium chloride (12mg, 0.09 mmol). After stirring for 30 min water (1ml) was added and the aqueous phase was extracted with dichloromethane (5 ml). The combined organic phases were concentrated *in vacuo* and purified by column chromatography to give **6** (0.028g, 94.2%) as a colourless oil.

^{1}H-NMR ($CDCl_3$): δ 7.94 (AA' part of a AA'MM' system, H2', H6'), 6.92 (MM' part of a AA'MM' system, H3', H5'), 6.80 (s, H4), 6.35 (s, H7), 3.77 (s, -OCH_3), 3.19 (bt, *J* 6Hz, Hα), 3.08 (q, *J* 7 Hz, H3), 2.94 (bt, *J* 6 Hz, Hβ), 1.43 (s, C2-CH_3), 1.29 (s, C2-CH_3), 1.16 (d, *J* 7Hz, C3-CH_3). ^{13}C-NMR ($CDCl_3$): δ 199.4 (C=O), 160.3* (C4'), 157.2* (C6), 156.9* (C7a), 130.4 (C2', C6'), 129.3 (C1'), 124.8 (C4), 123.1 (C3a), 120.3 (C5), 115.0 (C3', C5'), 93.3 (C7), 89.9 (C2), 55.3 (-OCH_3), 45.2 (C3), 39.3 (Cα), 28.0 (C2-CH_3), 26.3 (Cβ), 21.8 (C2-CH_3), 15.1 (C3-CH_3). HRMS (FAB+): 340.1691 (Calc. $C_{21}H_{24}O_4$: 340.1675).

*Transformation of (**5**) into (**6**).*

To a stirred solution of **5** (0.010 g, 0.03 mmol) in dichloromethane (1ml) was added anhydrous aluminium chloride (4mg, 0.03 mmol). After stirring for 30 minutes, water (1ml) was added and the aqueous phase was extracted with dichloromethane (5 ml). The combined organic phases were concentrated *in vacuo* and purified by column chromatography to give **6** (0.009g, 85.2%).

The ^{1}H NMR and ^{13}C NMR spectra of **6** were superimposable to those obtained previously.

Synthesis of 3-(6-methoxy-2,3,3,trimethyl-2,3-dihydrofurano[b]phenyl-6)-1-(4-hydroxyphenyl)prop-2-enon-1 **(7)**.

To a stirred solution of **1** (0.169 g, 0.5mmol) in nitrobenzene (5ml) was added titanium(IV) chloride (55μl, 0.5mmol). After stirring for 30 minutes, water (5ml) was added and the aqueous phase was extracted with nitrobenzene (5 ml). The combined organic phases was concentrated *in vacuo* and purified by column chromatography to give **7** (0.154g, 91.0%) as yellow crystals, m.p.:194.2-195.3°C (ethanol-water).

^{1}H-NMR ($CDCl_3$): δ 8.14 (d, *J* 16Hz, Hβ), 8.00 (AA' part of a AA'MM' system, H2', H6'), 7.51 (d, *J* 16Hz, Hα), 7.33 (s, H4), 6.98 (MM' part of a AA'MM' system, H3', H5'), 6.39 (s, H7), 4.45 (q, *J* 7Hz, H2), 3.83 (s, -OCH_3), 1.38 (d, *J* 7Hz, C2-CH_3), 1.33 (s, C3-CH_3), 1.12 (s, C3-CH_3). ^{13}C-NMR ($CDCl_3$): δ 190.4 (C=O), 162.0* (C4'), 160.6* (C6), 160.3* (C7a), 140.9 (Cβ), 131.1 (C2', C6'), 130.9 (C1'), 129.9 (C3a), 122.8 (Cα), 118.7 (C4), 116.6 (C5), 115.5 (C3', C5'), 93.9 (C7), 90.4 (C2), 55.7 (-OCH_3), 43.0 (C3), 26.3 (C3-CH_3), 23.3 (C3-CH_3), 14.5 (C2-CH_3). Anal. Calcd. for $C_{21}H_{22}O_4$,½H_2O: C, 72.60; H, 6.67. Found: C, 72.59; H, 6.75. EIMS *m/z* (rel. int.): 338([M]$^+$, 38), 323(14), 307(100), 205(21), 121(32).

*Synthesis of 3-(6-methoxy-2,2,3,trimethyl-2,3-dihydrofurano[b]phenyl-6)-1-(4-hydroxyphenyl)prop-2-enon-1 (**8**).*

To a stirred solution of **1** (0.088 g, 0.26 mmol) in dichloromethane (15ml) was added anhydrous aluminium chloride (0.176g, 1.3mmol).

After stirring for 4 h, water (15ml) was added and the aqueous phase were extracted with dichloromethane (15ml). The combined organic phases was concentrated *in vacuo* and purified by column chromatography to give **8** (0.0758 g, 86.1%) as yellow crystals, m.p.:175.7-176.9°C (ethanol-water).

^{1}H-NMR ($CDCl_3$): δ 8.14 (d, *J* 16Hz, Hβ), 7.99 (AA' part of a AA'MM' system, H2', H6'), 7.50 (d, *J* 16Hz, Hα), 7.36 (s, H4), 6.97 (MM' part of a AA'MM' system, H3', H5'), 6.35 (s, H7), 3.83 (s, -OCH_3), 3.12 (q, *J* 7Hz, H3), 1.49 (s, C2-CH_3), 1.30 (s, C2-CH_3), 1.24 (d, *J* 7Hz, C3-CH_3). ^{13}C-NMR ($(CD_3)_2CO$): δ 186.2 (C=O), 160.9* (C4'), 160.3* (C6), 159.1* (C7a), 137.4 (Cβ), 130.0 (C1'), 129.6 (C2', C6'), 124.6 (C3a), 122.5 (Cα), 116.6 (C4), 114.8 (C5), 114.0 (C3', C5'), 92.6 (C7), 90.0 (C2), 54.2 (-OCH_3), 43.6 (C3), 26.3 (C2-CH_3), 20.3 (C2-CH_3), 13.2 (C3-CH_3). Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.76; H, 6.67.

Transformation of (7) into (8).

To a stirred solution of **7** (0.020 g, 0.06 mmol) in dichloromethane (2ml) was added anhydrous aluminium chloride (0.040g, 0.3mmol). After stirring for 4 h, water (2ml) was added and the aqueous phase was extracted with dichloromethane (2ml). The combined organic phases were concentrated *in vacuo* and purified by column chromatography to give **8** (0.019g, 94.7%). The ^{1}H NMR and ^{13}C NMR spectra of **8** were superimposable to those obtained previously.

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