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Acid-Catalyzed Condensation of Citronellal and Electron Rich Phenols: Mechanism and Functionalization of the Adducts

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Abstract—Citronellal was condensed with a number of electron rich phenols, affording either adducts of the benzo(di)furan or benzo-(di)oxocane type. Functionalities could be introduced on the benzodifuran at the 8-position by using either 2-substituted resorcinols or by reactions of preformed benzodifuran. The mechanism of the formation of the adducts was investigated.

Introduction

In an attempt to prepare chiral resorcinarenes, we serendipitously found that citronellal and resorcinol form an unusual non chiral [2+1] benzodifuran adduct **1** by acid-catalyzed condensation. Citronellal and hydroquinone on the other hand gave a different, but not less unusual [2+1] adduct **4** that had a benzodioxocane structure. Both structures were proven by NMR and X-ray crystallography in our earlier communication.[1] In this work we propose a more detailed study of these systems.

Results

Benzo(di)furan type adducts

The bis(spirocyclohexane)benzodifuran **1a** has an extended structure which can be compared to a 3,5-bis(*t*-butyl)phenyl group. The latter has been used extensively in supramolecular and macromolecular chemistry as a solubilizing moiety.[2] We can imagine that the solubility of macromolecular systems based on **1a** would be even greater as the cyclohexane rings will prevent self-association even more. Since the adduct **1a** is formed in high yield in one step from cheap commercial products, we thought it would be worthwhile to investigate the preparation of some of its derivatives. Normally the condensation reactions are carried out in an ethanol/hydrochloric acid mixture. We tried to perform these reactions using different acid conditions (sulfuric acid, *p*-toluenesulfonic acid and trifluoroacetic acid instead of hydrochloric acid) and solvents. None of these modifications were successful. We used the racemic citronellal in all experiments unless mentioned otherwise.

Firstly, we wanted to find out if the preparation of a [1+1] adduct of citronellal and a phenol would be possible. Therefore, we allowed 3-methoxyphenol to react with citronellal. The latter reaction indeed afforded the benzofuran derivative **2**. However, a similar condensation with umbelliferone (7-hydroxycoumarin) did not yield the furocoumarin adduct. Clearly, the coumarin ring is not electron rich enough to react with citronellal.

The simplest way to introduce functionalities in structure **1a** is to take 2-substituted resorcinols as the substrates. Thus, the 1-hydroxy-[1] or 1-methylbenzodifurans (**1b**, **1c**) were prepared from citronellal and pyrogallol or 2-methylresorcinol, respectively. On the other hand, 5-methylresorcinol gave no defined product under the same conditions, probably due to steric hindrance.

The number of readily available 2-substituted resorcinols is limited and therefore we considered functionalizing unsubstituted **1a**. An obvious way seems to be the lithiation of the 1-position in analogy to similar reactions with 1,3-dimethoxybenzene.[3] Reaction of **1a** with butyllithium, followed by quenching with dimethylformamide only lead to the recovery of the starting material, whereas in the model reaction 2,6-dimethoxybenzaldehyde was formed in high yield. Probably the lithium derivative is not formed due to sterical hindrance. It was possible to increase the reactivity by using the 1-bromo compound **1d** which is readily obtained from **1a** by treatment with bromine in chloroform solution. We saw that in the latter reaction, an equivalent

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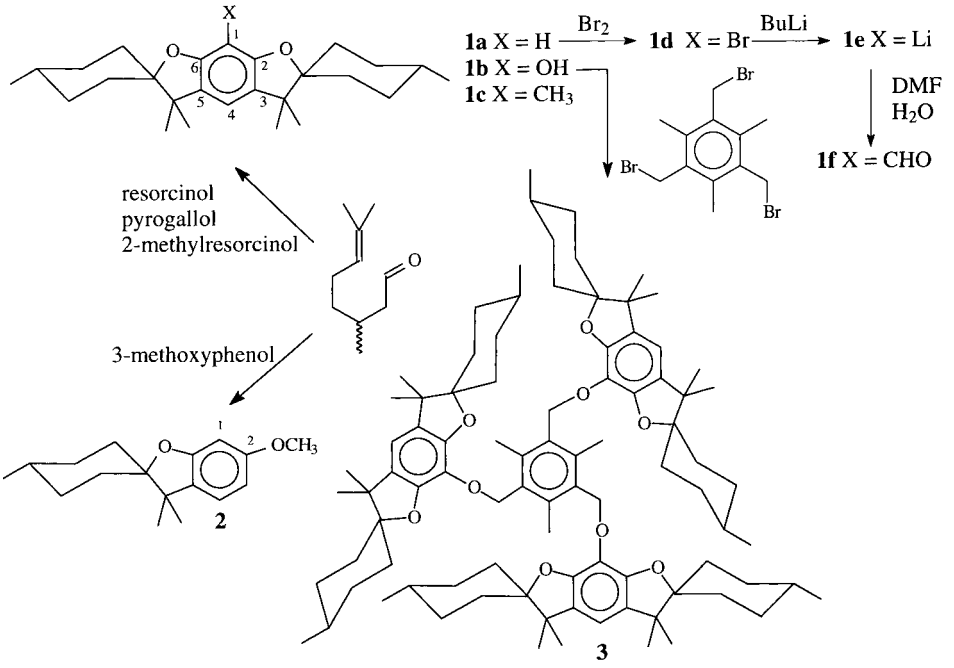


Scheme 1.

triethylamine base is necessary to obtain a good yield, as the benzodifuran system **1a** seems to be very sensitive to strong acid (HBr in this case). This was the reason why other electrophilic substitution reactions, such as nitration, failed. Bromide **1d** was smoothly lithiated and the lithium derivative **1e** was converted to the aldehyde **1f** in good overall yield.

Attempts to convert the aldehyde **1f** into the corresponding tetrakis(aryl)porphyrin by [4+4] condensation with pyrrole failed. The aldehyde **1f** was not found back in the highly colored reaction mixture, probably because the Lewis acid catalyst ($BF_3{\cdot}Et_2O$) had promoted its decomposition. Apparently, building up larger structures from **1a** and its derivatives is rather difficult in acid conditions. On the contrary, in basic conditions it was possible to combine **1b** successfully with the 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene[4] yielding compound **3**, having a molecular mass of 1350. As expected, **3** had excellent solubility in organic solvents (Scheme 1).

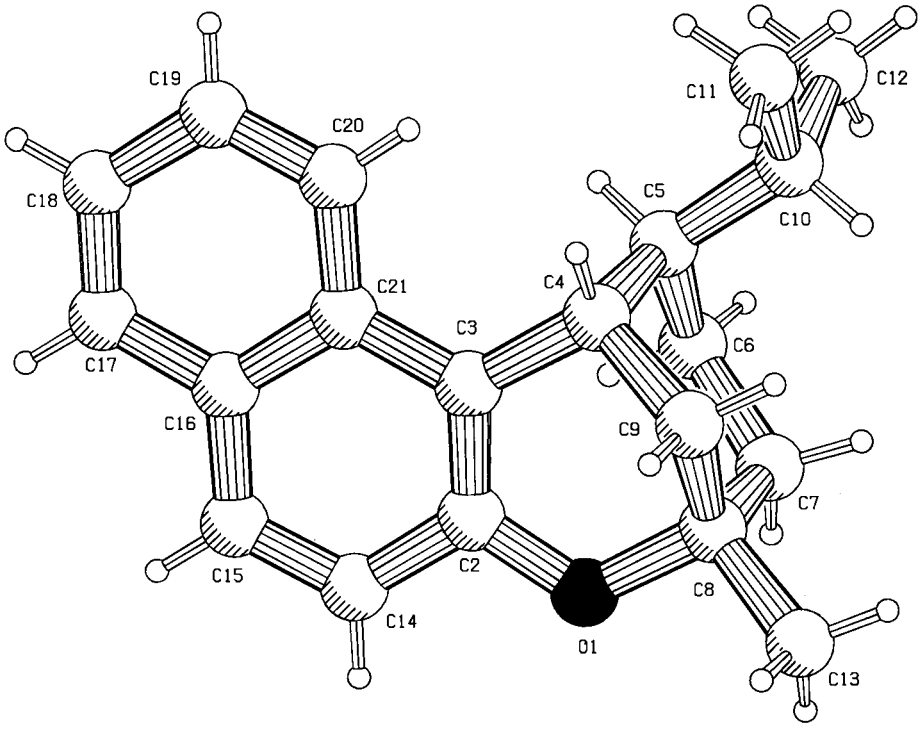
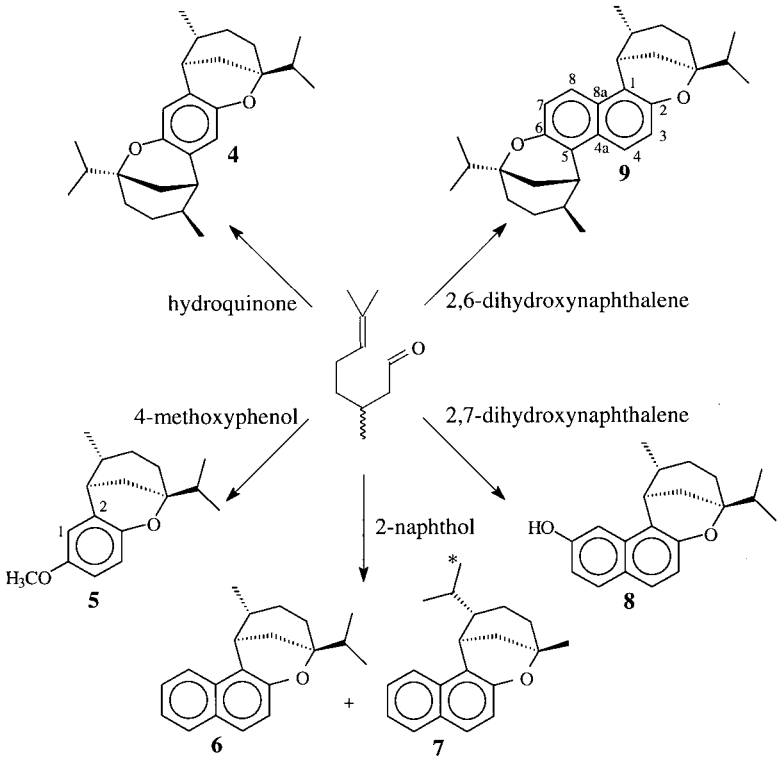


Figure 1.



Scheme 2.

Oxocane adducts

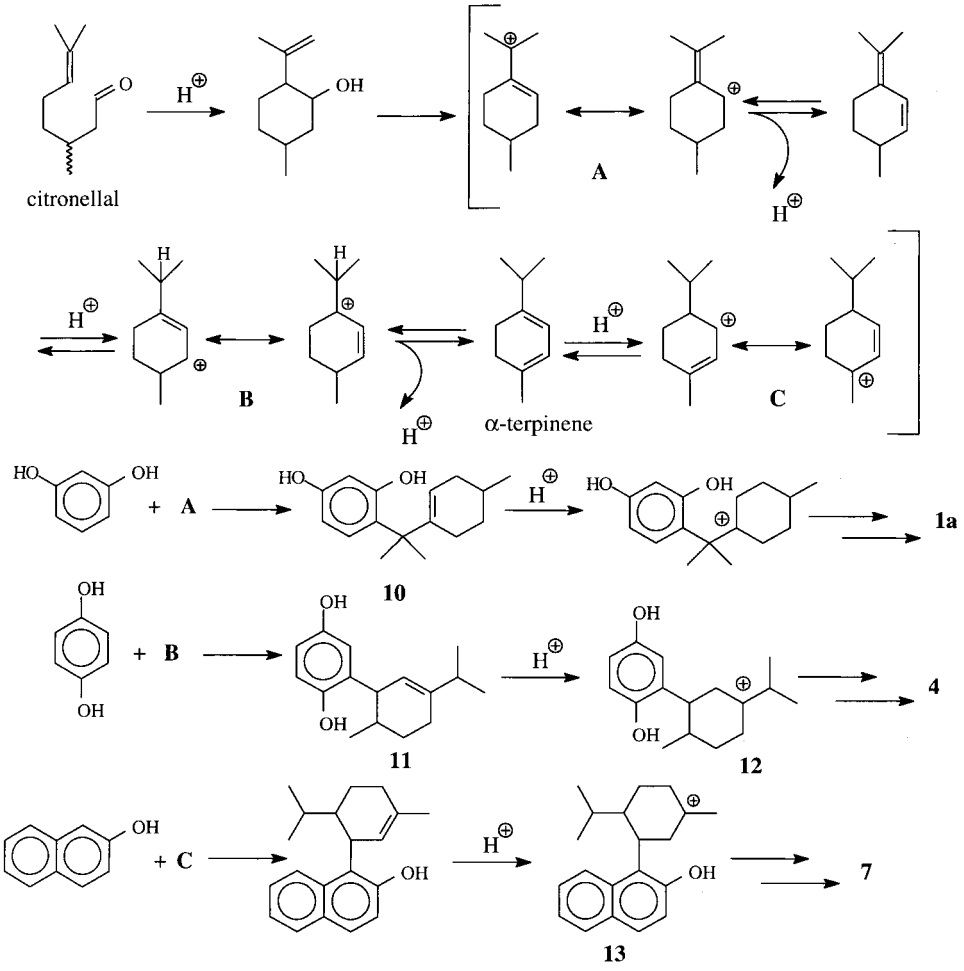
Previously,[1] we had obtained a [2+1] adduct **4** (72%) by the acid-catalyzed condensation of citronellal and hydroquinone. We now found that 4-methoxyphenol and citronellal analogously gave a [1:1] benzooxocane adduct **5**.

As already reported,[1] phenol itself gave only unidentified products, probably because reaction can also occur at the 4-position where cyclization with the phenol function is not possible. We decided to use the more reactive 2-naphthol and were surprised to find two isomeric [1+1] adducts **6** (55%) and **7** (22%) having a naphthooxocane structure. These two products could be distinguished by their ^{1}H NMR spectra: compound **6** showed methyl and bridgehead methine resonances at δ=1.24 (d) and 3.78 ppm, which were similar values as obtained for [2+1] adduct **4** or [1+1] adduct **5**. Isomer **7** showed these resonances at δ=1.40 (s) and 3.39 ppm. The rest of the signals were rather similar. In both cases a strong NOE was seen between the aromatic H_8 proton and the methine bridgehead as expected in a *peri* interaction. Based on these results we could tentatively assign the structures **6** and **7**. To get confirmation, crystals of **7** were analyzed by X-ray diffraction. The tetrahydropyran of **7** had a clear envelope conformation with the methyl group attached in the equatorial position. The cyclohexane ring, oriented axially towards the tetrahydropyran, has a chair conformation, with the isopropyl group in the axial position. There are reports of similar structures in the literature[5] (Fig. 1).

These results motivated us to investigate the condensation reaction of dihydroxynaphthalenes with citronellal. With 2,7-dihydroxynaphthalene the [1+1] adduct **8** was formed. Clearly the 8-position of this product was too hindered for further reaction. On the other hand, 2,6-dihydroxynaphthalene was converted to the diadduct **9**. 1-Naphthol and 1,5-dihydroxynaphthalene gave no defined reaction products, probably due to similar reasons as for unsubstituted phenol (Scheme 2).

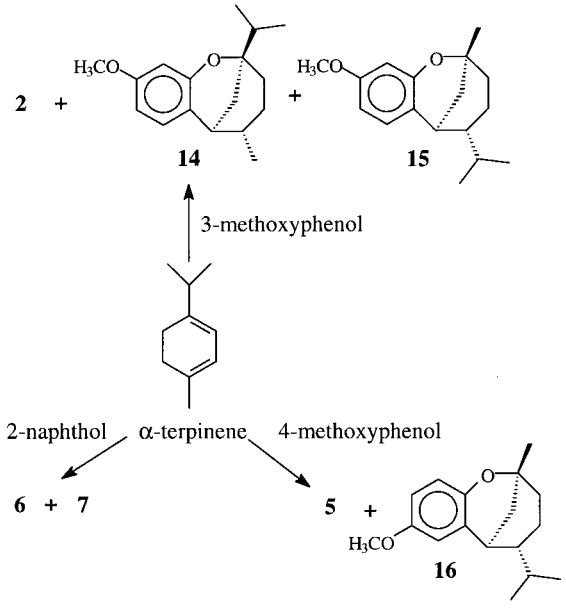
Discussion

The results described above allowed us to propose the following mechanism for the condensation reactions. First, citronellal cyclizes to isopulegol,[6] which via acid catalyzed isomerizations forms an equilibrated mixture of intermediates, including cationic species **A**, **B**, and **C**. Indeed, the use of isopulegol in these reactions instead of citronellal gives the same products in comparable yields. The tertiary allyl cation **A** is more stable than the secondary allyl cations **B** and **C**. The equilibrium will thus be shifted to cation **A**. Molecules that are highly susceptible towards electrophilic attack such as resorcinol will react with cation **A**, with the formation of the intermediate of type **10**. The latter, after protonation, will cyclize with its phenol function, affording compound **1a**. This effectively traps intermediate **A** before the more reactive intermediates **B** and **C** can be formed from citronellal. It is interesting to note, that even when the reactants are combined in a 1:1 ratio, only the [2+1] adduct **1a** is obtained. Apparently, the intermediate [1+1] adduct is significantly more reactive than resorcinol itself. Less reactive molecules, such as hydroquinone, can only react with more reactive intermediate **B**. Thus, hydroquinone reacts with cation **B**, and the intermediate **11** will be protonated selectively with the formation of the tertiary carbenium ion **12**, and ultimately ring close, affording the bridged



Scheme 3.

compound **4**. 2-Naphthol also reacts with the even more reactive cation **C**. The latter has time to form because 2-naphthol is less reactive towards electrophilic substitution than hydroquinone, as (1) there is only one electron donating group present, and (2) the 1-position has an sterically unfavourable *peri* interaction. Since the reaction of optically active citronellal with 2-naphthol only yields non optically active reaction products (**6** and **7**), we have a strong argument for the presence of intermediate **13** in the reaction mixture (Scheme 3).



Scheme 4.

Moreover, to prove that α-terpinene is really an intermediate in this sequence, we allowed 3-methoxyphenol, 4-methoxyphenol and 2-naphthol to react with it under the same conditions. Starting from 3-methoxyphenol, we obtained the three kinds of cyclized products (**2**, **14** and **15** in a ratio of 1:1:2), which demonstrates that (1) α-terpinene is an intermediate molecule, and (2) the rates to install the equilibrium between **A**, **B**, **C** starting from α-terpinene are comparable with the rate of the condensation reactions of **B** and **C**. In the light of these findings it was not surprising that the reaction of α-terpinene with 4-methoxyphenol and 2-naphthol afforded molecules **5** and **16** (2:1 ratio) and compounds **6** and **7** (1:1 ratio), respectively (Scheme 4).

Conclusion

We showed that citronellal can be condensed with a number of electron rich phenols, affording either adducts of the benzo(di)furan or benzo(di)oxocane type. Since

functionalities could be easily introduced both directly and indirectly, the adducts can be used to build up larger structures. The mechanism of the condensation reactions was clarified.

Experimental

General

All starting materials were obtained from ACROS Organics and were used without further purification. THF, diethyl ether and acetone were dried using standard methods.

General procedure

The appropriate phenol or dihydroxyarene (0.040 mol) was dissolved in a mixture of ethanol (20 mL) and concentrated hydrochloric acid (10 mL). After the solution became homogeneous, it was chilled at 0°C, and citronellal (or an equivalent amount of isopulegol or α-terpinene) (0.082 mol, 12.8 g) was added over 10 min. The mixture was heated at reflux overnight, cooled and stripped of the solvent. The residue was dissolved in dichloromethane, washed with water and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a crude product which was purified by column chromatography on silica gel eluting with an appropriate mixture of dichloromethane and petroleum ether. The solid products were subsequently crystallized from a mixture of acetone/methanol (1/1). All yields are those found after chromatographic separation, and when appropriate, crystallization.

Compound **1a** was obtained according the general procedure (resorcinol, citronellal) but using direct crystallization of the residue, without previous chromatography, in 75% yield. mp=181°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.61 (1H, s, $\mathbf{H}_{4arom}$) 6.18 (1H, s, $\mathbf{H}_{1arom}$) 1.86 (4H, d, J=12 Hz, $CH_3CHCH_2C\mathbf{H}_{2,equatorial}$) 1.54 (4H, m, $CH_3CHC\mathbf{H}_2CH_{2,equatorial}$) 1.25–1.45 (10H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{,axial}$) 1.10 (12H, s, $C(C\mathbf{H}_3)_2$) 0.93 (6H, d, J=5.8 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 157.0 ($\mathbf{C}_{arom}$–O) 129.4 ($\mathbf{C}_{arom}C(CH_3)_2$) 115.5 ($\mathbf{C}_{4arom}$) 93.4 ($\mathbf{C}_{1arom}$) 91.8 ($\mathbf{C}_{spiro}$) 45.7 ($\mathbf{C}(CH_3)_2$) 32.1 ($\mathbf{C}HCH_3$) 31.0 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 24.2 ($C(\mathbf{C}H_3)_2$) 22.3 ($CH\mathbf{C}H_3$); MS (E) m/z 382 (M^+); EA (%C, %H) Calculated: 81.60%, 10.0% Found: 81.85%, 9.72%.

Compound **1b** was obtained following the standard procedure using pyrogallol, but using direct crystallization of the residue, without previous column chromatography, in 63% yield; mp=203°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.26 (1H, s, $\mathbf{H}_{4arom}$) 5.1 (1H, s, O**H**) 1.90 (4H, d, J=12 Hz, $CH_3CHCH_2C\mathbf{H}_{2,equatorial}$) 1.56 (4H, m, $CH_3CHC\mathbf{H}_2CH_{2,equatorial}$) 1.25–1.50 (10H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{,axial}$) 1.10 (12H, s, $C(C\mathbf{H}_3)_2$) 0.94 (6H, d, J=5.8 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 143.5 ($\mathbf{C}_{arom}$–O) 130.8 ($\mathbf{C}_{arom}C(CH_3)_2$) 126.3 ($\mathbf{C}_{1arom}$) 106.6 ($\mathbf{C}_{4arom}$) 93.1 ($\mathbf{C}_{spiro}$) 46.5 ($\mathbf{C}(CH_3)_2$) 32.1 ($\mathbf{C}HCH_3$) 31.0 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 24.1 ($C(\mathbf{C}H_3)_2$) 22.2 ($CH\mathbf{C}H_3$); MS (EI) m/z 398 (M^+).

Compound **1c** was obtained according to the general procedure using 2-methylresorcinol in 50% yield. The product was purified chromatographically with a 60/40 mixture of petroleum ether and dichloromethane. mp=179–181°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.47 (1H, s, $\mathbf{H}_{4arom}$) 2.06 (3H, s, $CC\mathbf{H}_3$) 1.87 (4H, d, J=12 Hz, $CH_3CHCH_2C\mathbf{H}_{2,equatorial}$) 1.53 (4H, m, $CH_3CHC\mathbf{H}_2CH_{2,equatorial}$) 1.20–1.45 (10H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{,axial}$) 1.09 (12H, s, $C(C\mathbf{H}_3)_2$) 0.94 (6H, d, J=5.9 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 155.2 ($\mathbf{C}_{arom}$–O) 128.7 ($\mathbf{C}_{arom}C(CH_3)_2$) 112.4 ($\mathbf{C}_{4arom}$) 103.2 ($\mathbf{C}_{1arom}$) 91.2 ($\mathbf{C}_{spiro}$) 46.1 ($\mathbf{C}(CH_3)_2$) 32.2 ($\mathbf{C}HCH_3$) 31.2 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 24.4 ($C(\mathbf{C}H_3)_2$) 22.4 ($CH\mathbf{C}H_3$) 8.56 ($C_{arom}$–$\mathbf{C}H_3$); MS (E) m/z 396.58 (M^+); EA (%C, %H) Calculated: 81.75%, 10.18% Found: 81.60%, 10.18%.

Preparation of 1d. A solution of **1a** (2.6 mmol, 1 g) and triethylamine (1.2 mmol, 0.17 mL) in tetrachloromethane (15 mL) was chilled to 0°C. Liquid bromine (0.12 mL) in tetrachloromethane (10 mL) was added dropwise under stirring over 10 min. The reaction mixture was allowed to reach room temperature and was further stirred for 1 h. The solvent was removed under low pressure and dichloromethane (150 mL) was added to the residue. The solution was washed with water (100 mL), sodium bisulfite (100 mL, 10% in water), sodium hydroxide (100 mL, 10% in water), dried ($MgSO_4$), filtered and concentrated to afford the crude 1-bromo bis(spirocyclohexane)benzodifuran that was purified chromatographically on silica gel eluting with a 70/30 mixture of dichloromethane and petroleum ether. Yield: 70%; mp=159°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.55 (1H, s, $\mathbf{H}_{arom}$) 1.88 (4H, d, J=11.6 Hz, equatorial H $CC\mathbf{H}_2CH_2$) 1.54 (4H, m, $CCH_2C\mathbf{H}_{2,equatorial}$) 1.32–1.50 (10H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{,axial}$) 1.11 (12H, s, $C(C\mathbf{H}_3)_2$) 0.95 (6H, d, J=6.3 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 154.2 ($\mathbf{C}_{arom}$–O) 130.4 ($\mathbf{C}_{arom}C(CH_3)_2$) 114.2 ($\mathbf{C}_{4arom}$) 93.0 ($\mathbf{C}_{spiro}$) 86.8 ($\mathbf{C}_{arom}$Br) 47.0 ($\mathbf{C}(CH_3)_2$) 32.1 ($\mathbf{C}HCH_3$) 31.0 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 24.2 ($C(\mathbf{C}H_3)_2$) 22.3 ($CH\mathbf{C}H_3$); MS (E) m/z 462 (M^+); EA (%C, %H) Calculated: 67.60%, 8.10% Found: 67.30%, 8.13%.

Preparation of 1f. A solution of **1d** (1.95 mmol, 0.9 g) in dry diethyl ether (30 mL) was treated with *n*-butyllithium (2.15 mmol, 0.86 mL of a 2.5 M solution in hexane) at 0°C. The mixture was stirred at this temperature for 10 min and dimethylformamide (2 mmol, 0.15 mL) was added. After the usual work-up, the product was purified by column chromatography on silica gel eluted with a 50/50 mixture of dichloromethane and petroleum ether to afford **1f** (62% yield); mp=188°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.28 (1H, s, C**H**O) 6.84 (1H, s, $\mathbf{H}_{4arom}$) 1.90 (4H,d, J=11.6 Hz, $CC\mathbf{H}_2CH_{2,equatorial}$) 1.70 (4H, m, $CCH_2C\mathbf{H}_{2,equatorial}$) 1.26–1.56 (10H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{,axial}$) 1.1 (12H, s, $C(C\mathbf{H}_3)_2$) 0.95 (6H, d, J=6.2 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 187.0 (**C**HO) 158.0 ($\mathbf{C}_{arom}$–O) 130.3 ($\mathbf{C}_{arom}C(CH_3)_2$) 122.1 ($\mathbf{C}_{4arom}$) 94.3 ($\mathbf{C}_{spiro}$) 45.1 ($\mathbf{C}(CH_3)_2$) 32.1 ($\mathbf{C}HCH_3$) 31.0 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 24.2 ($C(\mathbf{C}H_3)_2$) 22.2 ($CH\mathbf{C}H_3$); MS (E) m/z 410.27 (M^+); EA (%C, %H) Calculated: 78.97%, 9.35% Found: 79.35%, 9.56%.

Compound **2** was obtained as an oil in 35% yield using the standard procedure (only 1.1 equiv. of citronellal was used). The crude product was purified chromatographically on

silica gel eluting with a 60/40 mixture of dichloromethane and petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.90 (1H, d, J=12.8 Hz, $\mathbf{H}_{4arom}$) 6.37 (2H, m, $\mathbf{H}_{1-3arom}$) 3.75 (3H, s, $OC\mathbf{H}_3$) 1.87 (2H, d, J=11.6 Hz, $CH_3CHCH_2C\mathbf{H}_{2,equatorial}$) 1.56 (2H, m, $CH_3CHC\mathbf{H}_2CH_{2,equatorial}$) 1.17–1.40 (5H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{axial}$) 1.1 (6H, s, $C(C\mathbf{H}_3)_2$) 0.94 (3H, d, J=5.7 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 160.1 ($\mathbf{C}_{6arom}$) 158.4 ($\mathbf{C}_{2arom}$) 128.3 ($\mathbf{C}_{5arom}$) 122.4 ($\mathbf{C}_{4arom}$) 105.3 ($\mathbf{C}_{3arom}$) 96.8 ($\mathbf{C}_{1arom}$) 92.4 ($\mathbf{C}_{spiro}$) 55.4 ($CO\mathbf{C}H_3$) 45.6 ($\mathbf{C}(CH_3)_2$) 32.0 ($\mathbf{C}HCH_3$) 30.9 ($\mathbf{C}H_2CHCH_3$) 30.6 ($\mathbf{C}H_2CH_2CHCH_3$) 23.9 ($C(\mathbf{C}H_3)_2$) 22.3 ($CH\mathbf{C}H_3$); MS (EI) m/z 260 (M^+).

Preparation of 3. A solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene[4] (0.16 mmol, 65 mg), **1b** (0.63 mmol, 250 mg), potassium carbonate (0.72 mmol, 100 mg) in dry acetone under argon atmosphere was refluxed overnight. After the usual work-up, the residue was purified chromatographically on silica gel eluting with a 80/20 mixture of dichloromethane and petroleum ether affording 180 mg of compound **3** as an oil (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.38 (3H, s, $\mathbf{H}_{4arom}$) 5.24 (6H, s, Ar–C$\mathbf{H}_2$–O) 2.75 (9H, s, Ar–C$\mathbf{H}_3$) 1.90 (12H, d, J=12.6 Hz, $CH_3CHCH_2C\mathbf{H}_{2,equatorial}$) 1.56 (12H, m, $CH_3CHC\mathbf{H}_2CH_{2,equatorial}$) 1.25–1.50 (30H, m, $C\mathbf{H}_2C\mathbf{H}_2C\mathbf{H}_{axial}$) 1.10 (36H, s, $C(C\mathbf{H}_3)_2$) 0.94 (18H, d, J=6.3 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 148.6 ($\mathbf{C}_{arom}$–O) 140.0 ($\mathbf{C}_{1arom}$) 132.3 (O–CH_2–$\mathbf{C}_{arom}$) 131.0 ($\mathbf{C}_{arom}C(CH_3)_2$) 129.2 ($CH_3$–$\mathbf{C}_{arom}$) 109.5 ($\mathbf{C}_{4arom}$) 92.2 ($\mathbf{C}_{spiro}$) 69.2 (Ar–$\mathbf{C}H_2$–O) 46.1 ($\mathbf{C}(CH_3)_2$) 32.2 ($\mathbf{C}HCH_3$) 31.1 ($\mathbf{C}H_2CHCH_3$) 30.7 ($\mathbf{C}H_2CH_2CHCH_3$) 24.2 ($C(\mathbf{C}H_3)_2$) 22.5 ($CH\mathbf{C}H_3$) 16.0 (Ar–$\mathbf{C}H_3$); MS (ES) m/z 1350 (M^+).

Compound **4** was obtained using the general procedure without column chromatography in 72% yield; mp=235°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.41 (2H, s, $\mathbf{H}_{arom}$) 2.60 (2H, br q, $C\mathbf{H}_{bridge\ head}$) 1.89, 1.54 (4H, m, $C\mathbf{H}_{2bridge}$) 1.76 (2H, sept, $C\mathbf{H}(CH_3)_2$) 1.65 (4H, $C\mathbf{H}_2CHCH_3$) 1.60–1.16 (4H, m, $C\mathbf{H}_2CH_2CHCH_3$) 1.10 (6H, d, J=7.2 Hz, $CHC\mathbf{H}_3$) 0.96 (12H, d, $CH(C\mathbf{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 149.1 ($\mathbf{C}_{2arom}$) 127.1 ($\mathbf{C}_{3arom}$) 113.2 ($\mathbf{C}_{1arom}$) 74.8 ($\mathbf{C}CH(CH_3)_2$) 38.7 ($C\mathbf{H}_{bridge\ head}$) 37.9 ($\mathbf{C}H(CH_3)_2$) 34.7 ($\mathbf{C}HCH_3$) 29.2 ($\mathbf{C}H_2CHCH_3$) 25.0 ($\mathbf{C}_{bridge}$) 24.0 ($\mathbf{C}H_2CH_2CHCH_3$) 17.2 ($CH\mathbf{C}H_3$) 17.1 ($CH(\mathbf{C}H_3)_2$);MS (E) m/z 382 (M^+); EA (%C, %H) Calculated: 81.60%, 10.00% Found: 81.55%, 10.08%.

Compound **5** was obtained as an oil in 35% yield following the general procedure (only 1.1 equiv. of citronellal was used). The crude product was purified by column chromatography on silica gel eluting with a 50/50 mixture of dichloromethane and petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.67 (2H, m, $\mathbf{H}_{1-5arom}$) 6.55 (1H, d, J=2.9 Hz, $\mathbf{H}_{2arom}$) 3.7 (3H, s, $OC\mathbf{H}_3$) 2.65 (1H, br d, $C\mathbf{H}_{bridge\ head}$) 1.89, 1.55 (2H, m, $C\mathbf{H}_{2bridge}$) 1.79 (1H, sept, $C\mathbf{H}(CH_3)_2$) 1.64 (2H, m, $C\mathbf{H}_2CHCH_3$) 1.60–1.17 (2H, m, $C\mathbf{H}_2CH_2CHCH_3$) 1.12 (3H, d, J=7.1 Hz, $CHC\mathbf{H}_3$) 0.96 (6H, m, $CH(C\mathbf{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 152.3 ($\mathbf{C}_{6arom}$) 150.7 ($\mathbf{C}_{3arom}$) 128.7 ($\mathbf{C}_{4arom}$) 112.9–115.3 ($\mathbf{C}_{1,2,5arom}$) 78.6 ($\mathbf{C}CH(CH_3)_2$) 55.7 ($CO\mathbf{C}H_3$) 39.1($C\mathbf{H}_{bridge\ head}$) 37.7 ($\mathbf{C}H(CH_3)_2$) 34.6 ($\mathbf{C}HCH_3$) 29.5 ($\mathbf{C}H_2CHCH_3$) 24.5 ($\mathbf{C}_{bridge}$) 23.9 ($\mathbf{C}H_2CH_2CHCH_3$) 17.7 ($CH\mathbf{C}H_3$) 17.0 ($CH(\mathbf{C}H_3)_2$); MS (EI) m/z 260.42 (M^+).

Molecules **6** and **7** were obtained in 55% and 22% yield, respectively, according to the general procedure (only 1.1 equiv. of citronellal was used). When 1.1 equiv. of α-terpinene was used, the yields were 41 and 35%, respectively. Purification was carried out by column chromatography eluting with a 97.5/2.5 mixture of dichloromethane and ethyl acetate. **6**: mp=69–71°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.80 (1H, d, J=8.4 Hz, $\mathbf{H}_8$) 7.74 (1H, d, J=7.6 Hz, $\mathbf{H}_5$) 7.59 (1H, d, J=8.8 Hz, $\mathbf{H}_4$) 7.44 (1H, t, $\mathbf{H}_7$) 7.27 (1H, t, $\mathbf{H}_6$) 7.06 (1H, d, J=8.9 Hz, $\mathbf{H}_3$) 3.39 (1H, s, $C\mathbf{H}_{bridge\ head}$) 2.12 (1H, dd, $C\mathbf{H}_{bridge}$) 2.1 (1H, m, $C\mathbf{H}CH_3$) 1.87 (1H, m, $C\mathbf{H}(CH_3)_2$) 1.80 (1H, m, $CHCH_3CH_2C\mathbf{H}_{2,axial}$) 1.73 (1H, m, $CHCH_3CH_2C\mathbf{H}_{2,equatorial}$) 1.61 (1H, dm, $C\mathbf{H}_{bridge}$) 1.60 (1H, m, $CHCH_3C\mathbf{H}_{2,axial}$) 1.24 (3H, d, J=7.2 Hz, $CHC\mathbf{H}_3$) 1.22 (1H, m, $CHCH_3C\mathbf{H}_{2,equatorial}$) 1.04 (3H, d, J=7.1 Hz, $CH(C\mathbf{H}_3)_2$) 1.02 (3H, d, J=7.5 Hz, $CH(C\mathbf{H}_3)_2$);^{13}C NMR (100 MHz, $CDCl_3$) δ_C 154.1 ($\mathbf{C}_{ipso-O}$) 131.7 ($\mathbf{C}_{8a,\ arom}$) 128.6 ($\mathbf{C}_{5arom}$) 128.5 ($\mathbf{C}_{4a\ arom}$) 127.5 ($\mathbf{C}_{4arom}$) 126.1 ($\mathbf{C}_{7arom}$) 122.4 ($\mathbf{C}_{6arom}$) 121.3 ($\mathbf{C}_{8arom}$) 118.9 ($\mathbf{C}_{1arom}$) 118.3 ($\mathbf{C}_{3arom}$) 78.9 ($\mathbf{C}CH(CH_3)_2$) 37.6 ($\mathbf{C}H(CH_3)_2$) 33.7 ($\mathbf{C}H_{bridge\ head}$) 32.2 ($\mathbf{C}HCH_3$) 29.9 ($\mathbf{C}H_2CH_2CHCH_3$) 24.7 ($\mathbf{C}_{bridge}$) 24.6 ($\mathbf{C}H_2CHCH_3$) 17.8 ($CH(\mathbf{C}H_3)$) 17.1 ($CH(\mathbf{C}H_3)_2$); MS (EI) m/z 280 (M^+). EA (%C, %H) Calculated: 85.65%, 8.64% Found: 85.39%, 8.74%; **7**: mp=97°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.81 (1H, d, J=8.5 Hz, $\mathbf{H}_8$) 7.74 (1H, d, J=8.1 Hz, $\mathbf{H}_5$) 7.59 (1H, d, J=8.9 Hz, $\mathbf{H}_4$) 7.44 (1H, t, $\mathbf{H}_7$) 7.27 (1H, t, $\mathbf{H}_6$) 7.04 (1H, d, J=8.9 Hz, $\mathbf{H}_3$) 3.76 (1H, s, $C\mathbf{H}_{bridge\ head}$) 2.08 (1H, dd, $C\mathbf{H}_{bridge}$) 1.95 (1H, m, $C\mathbf{H}(CH_3)_2$) 1.81 (1H, m, $(CH_3)_2CHCHCH_2C\mathbf{H}_{2,equatorial}$) 1.67 (1H, dm, $C\mathbf{H}_{bridge}$) 1.66 (1H, m, $(CH_3)_2CHCHCH_2C\mathbf{H}_{2,axial}$) 1.53–1.47 (2H, m, $(CH_3)_2CHCHC\mathbf{H}_2CH_2$) 1.45 (1H, m, $(CH_3)_2CHC\mathbf{H}$) 1.40 (3H, s, $C\mathbf{H}_3$) 1.27 (3H, d, J=6.6 Hz, $CH(C\mathbf{H}_3)_2$) 0.97 (3H, d, J=6.5 Hz, $CH(C\mathbf{H}^*_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 154.2 ($\mathbf{C}_{ipso-O}$) 131.8 ($\mathbf{C}_{8a\ arom}$) 128.7 ($\mathbf{C}_{5arom}$) 128.6 ($\mathbf{C}_{4a\ arom}$) 127.6 ($\mathbf{C}_{4arom}$) 126.2 ($\mathbf{C}_{7arom}$) 122.4 ($\mathbf{C}_{6arom}$) 121.2 ($\mathbf{C}_{8arom}$) 118.2 ($\mathbf{C}_{1arom}$) 118.1 ($\mathbf{C}_{3arom}$) 74.4 ($\mathbf{C}(CH_3)$) 44.5 ($\mathbf{C}HCH(CH_3)_2$) 35.9 ($\mathbf{C}H_2CH_3$) 30.6 ($\mathbf{C}_{bridge}$) 29.7 ($\mathbf{C}H_{bridge\ head}$) 29.15 ($\mathbf{C}H_3$) 26.5 ($\mathbf{C}H(CH_3)_2$) 22.05 ($CH(\mathbf{C}H^*_3)_2$) 21.3 ($CH(\mathbf{C}H_3)_2$) 20.8 ($\mathbf{C}H_2CH_2CH_3$); MS (E) m/z 280 (M^+). EA (%C, %H) Calculated: 85.65%, 8.64% Found: 85.50%, 8.64%.

Compound **8** was prepared following the general procedure, in 30% yield. Column chromatography was carried out with a 70/30 mixture of dichloromethane and petroleum ether; mp=46–48°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.63 (1H, d, J=8.7 Hz, $\mathbf{H}_5$) 7.51 (1H, d, J=8.8 Hz, $\mathbf{H}_4$) 7.10 (1H, s, $\mathbf{H}_8$) 6.91 (1H, m, $\mathbf{H}_3$) 6.85 (1H, m, $\mathbf{H}_6$) 4.91 (1H, s, O$\mathbf{H}$) 3.22 (1H, s, $C\mathbf{H}_{bridge\ head}$) 2.10 (1H, m, $C\mathbf{H}CH_3$) 2.09 (1H, m, $\mathbf{H}_{bridge}$) 1.58 (1H, m, $\mathbf{H}_{bridge}$) 1.86 (1H, m, $C\mathbf{H}(CH_3)_2$) 1.80–1.56 (3H, m, $C\mathbf{H}_2C\mathbf{H}_2CHCH_3$) 1.27 (1H, m, $CH_2C\mathbf{H}_2CHCH_3$) 1.21 (3H, d, J=7.2 Hz, $CHC\mathbf{H}_3$) 1.01;1.03 (6H, dd, $CH(C\mathbf{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) 154.8 ($\mathbf{C}_{7arom}$) 153.9 ($\mathbf{C}_{2arom}$) 133.1 ($\mathbf{C}_{8a,arom}$) 130.5, 127.3 ($\mathbf{C}_{6,8arom}$) 123.9 ($\mathbf{C}_{1arom}$) 117.6 ($\mathbf{C}_{4a,arom}$) 116.0, 113.7 ($\mathbf{C}_{3,6arom}$) 104.0 ($\mathbf{C}_{5arom}$) 78.9 ($\mathbf{C}CH(CH_3)_2$) 37.5 ($\mathbf{C}_{bridgehead}$) 33.8 ($\mathbf{C}H(CH_3)_2$) 31.8 ($\mathbf{C}HCH_3$) 29.9 ($\mathbf{C}H_2CH(CH_3)$) 24.6 ($\mathbf{C}H_2CH_2CH(CH_3)$) 24.7 ($\mathbf{C}_{bridge}$) 17.7 ($CH\mathbf{C}H_3$) 17.1;17.0 ($CH(\mathbf{C}H_3)_2$); MS (CI) m/z 297

(M^+). EA (%C, %H) Calculated: 81.03%, 8.18% Found: 80.82%, 8.13%.

Compound **9** was obtained according to the general procedure in 20% yield. The crude product was purified chromatographically eluting with a 20/80 mixture of dichloromethane and petroleum ether; mp=181°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.6 (2H, d, $\mathbf{H}_3$) 7.06 (2H, d, J=8 Hz, $\mathbf{H}_4$) 3.34 (2H, d, J=11.3 Hz, $\mathbf{CH}_{\text{bridge head}}$) 2.13 (2H, br, $\mathbf{CH}CH_3$) 2.09 (2H, d, $\mathbf{CH}_{\text{bridge}}$) 1.86 (2H, m, $\mathbf{CH}(CH_3)_2$) 1.80–1.60 (6H, m, $CHCH_3\mathbf{CH_2}\mathbf{CH_2}$) 1.55 (2H, m, $\mathbf{CH}_{\text{bridge}}$) 1.24 (6H, m, $CH\mathbf{CH}_3$ and $CHCH_3CH_2\mathbf{CH_2}$) 1.02 (12H, m, $CH(\mathbf{CH}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 151.8 ($\mathbf{C}_{\text{arom}-O}$) 126.4 ($\mathbf{C}_{4\text{arom}}$) 120.7 ($\mathbf{C}_{3\text{arom}}$) 119.9 ($\mathbf{C}_{5\text{arom}}$) 118.1 ($\mathbf{C}_{4\text{arom}}$) 78.4 ($\mathbf{C}CH(CH_3)_2$) 37.6 ($\mathbf{C}H(CH_3)_2$) 32.3 ($\mathbf{C}HCH_3$) 33.9 ($\mathbf{C}H_{\text{bridge head}}$) 30.1 ($\mathbf{C}H_2CHCH_3$) 24.7 ($\mathbf{C}H_2CH_2CHCH_3$) 24.6 ($\mathbf{C}_{\text{bridge}}$) 17.8 ($CH(\mathbf{C}H_3)$) 17.1 ($CH(\mathbf{C}H_3)_2$); MS (CI) m/z 433.10 (M^+).

Compounds **2**, **14** and **15** were obtained, following the standard procedure (using 3-methoxyphenol and 1.1 equiv. of α-terpinene). The product mixture was separated chromatographically eluting with a 60/40 mixture of petroleum ether and dichloromethane. This afforded **2** (8% yield); **14**, oil (8% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.84 (1H, d, J=8.7 Hz, $\mathbf{H}_{4\text{arom}}$) 6.38 (1H, d, $\mathbf{H}_{5\text{arom}}$) 6.35 (1H, s, $\mathbf{H}_{1\text{arom}}$) 2.65 (1H, s, $\mathbf{CH}_{\text{bridge head}}$) 3.73 (3H, s, $OC\mathbf{H}_3$) 1.86 (1H, dd, $\mathbf{CH}_{\text{bridge}}$) 1.77 (1H, m, $\mathbf{CH}(CH_3)_2$) 1.70 (1H, m, $(CH_3)_2CHCHCH_2\mathbf{CH}_{2,\text{equatorial}}$) 1.60 (1H, dm, $\mathbf{CH}_{\text{bridge}}$) 1.57 (1H, m, $(CH_3)_2CHCHCH_2\mathbf{CH}_{2,\text{axial}}$) 1.52–1.44 (2H, m, $(CH_3)_2CHCH\mathbf{CH}_2CH_2$) 1.46 (1H, m, $(CH_3)_2CH\mathbf{CH}$) 1.34 (3H, d, $\mathbf{CH}_3$) 0.99 (3H, d, J=5.8 Hz, $CH(\mathbf{CH}^*_3)_2$) 0.94 (3H, d, J=5.8 Hz, $CH(\mathbf{CH}^*_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.2 ($\mathbf{C}_{6\text{arom}}$) 157.4 ($\mathbf{C}_{2\text{arom}}$) 130.5 ($\mathbf{C}_{5\text{arom}}$) 120.7 ($\mathbf{C}_{4\text{arom}}$) 105.5 ($\mathbf{C}_{3\text{arom}}$) 100.0 ($\mathbf{C}_{1\text{arom}}$) 79.2 ($\mathbf{C}CH(CH_3)_2$) 55.1 ($CO\mathbf{C}H_3$) 37.9 ($\mathbf{C}H_{\text{bridge head}}$) 37.6 ($\mathbf{C}H(CH_3)_2$) 34.8 ($\mathbf{C}HCH_3$) 29.3 ($\mathbf{C}H_2CHCH_3$) 24.7 ($\mathbf{C}_{\text{bridge}}$) 23.7 ($\mathbf{C}H_2CH_2CHCH_3$) 17.6 ($CH\mathbf{C}H_3$) 17.1 ($CH(\mathbf{C}H_3)_2$) MS (EI) m/z 260.42 (M^+); **15**, oil (16% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.84 (1H, d, J=7.9 Hz, $\mathbf{H}_{4\text{arom}}$) 6.39 (1H, d, 3.75 (3H, s, $OC\mathbf{H}_3$) $\mathbf{H}_{5\text{arom}}$) 6.37 (1H, s, $\mathbf{H}_{1\text{arom}}$) 2.98 (1H, s, $\mathbf{CH}_{\text{bridge head}}$) 1.86 (1H, dd, $\mathbf{CH}_{\text{bridge}}$) 1.77 (1H, m, $\mathbf{CH}(CH_3)_2$) 1.70 (1H, m, $(CH_3)_2CHCHCH_2\mathbf{CH}_{2,\text{equatorial}}$) 1.60 (1H, dm, $\mathbf{CH}_{\text{bridge}}$) 1.57 (1H, m, $(CH_3)_2CHCHCH_2\mathbf{CH}_{2,\text{axial}}$) 1.52–1.44 (2H, m, $(CH_3)_2CHCH\mathbf{CH}_2CH_2$) 1.46 (1H, m, $(CH_3)_2CH\mathbf{CH}$) 1.34 (3H, s, $\mathbf{CH}_3$) 1.05 (3H, d, J=6.6 Hz, $CH(\mathbf{CH}_3)_2$) 0.94 (3H, d, J=6.5 Hz, $CH(\mathbf{CH}^*_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.2 ($\mathbf{C}_{6\text{arom}}$) 157.4 ($\mathbf{C}_{2\text{arom}}$) 128.4 ($\mathbf{C}_{4\text{arom}}$) 120.1 ($\mathbf{C}_{5\text{arom}}$) 105.9 ($\mathbf{C}_{3\text{arom}}$) 100.0 ($\mathbf{C}_{1\text{arom}}$) 74.7 ($\mathbf{C}(CH_3)$) 55.2 ($O\mathbf{C}H_3$) 47.4 ($\mathbf{C}HCH(CH_3)_2$) 35.1 ($\mathbf{C}H_2CH_3$) 30.9 ($\mathbf{C}_{\text{bridge}}$) 33.9 ($\mathbf{C}H_{\text{bridge head}}$) 29.3 ($\mathbf{C}H_3$) 26.3 ($\mathbf{C}H(CH_3)_2$) 22.0 ($CH(\mathbf{C}H^*_3)_2$) 21.2 ($CH(\mathbf{C}H_3)_2$) 19.9 ($\mathbf{C}H_2CH_2CHCH_3$); MS (EI) m/z 260 (M^+).

Compounds **5** and **16** were prepared following the standard procedure (using 1.1 equiv. of α-terpinene). The mixture was separated chromatographically eluting with a 60/40 mixture of petroleum ether and dichloromethane. This afforded **5**, (25% yield); **16**, oil (12% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.68 (1H, s, $\mathbf{H}_{5\text{arom}}$) 6.67 (1H, d, J=8 Hz, $\mathbf{H}_{1\text{arom}}$) 6.52 (1H, d, J=8 Hz, $\mathbf{H}_{2\text{arom}}$) 3.75 (3H, s, OCH_3) 2.98 (1H, s, $\mathbf{CH}_{\text{bridge head}}$) 1.84 (1H, dd, $\mathbf{CH}_{\text{bridge}}$) 1.75 (1H, m, $\mathbf{CH}(CH_3)_2$) 1.70 (1H, m, $(CH_3)_2CHCHCH_2\mathbf{CH}_{2,\text{equatorial}}$) 1.60 (1H, dm, $\mathbf{CH}_{\text{bridge}}$) 1.58 (1H, m, $(CH_3)_2$ $CHCHCH_2\mathbf{CH}_{2,\text{axial}}$) 1.55–1.46 (2H, m, $(CH_3)_2$ $CHCH\mathbf{CH}_2CH_2$) 1.48 (1H, m, $(CH_3)_2CH\mathbf{CH}$) 1.32 (3H, s, $\mathbf{CH}_3$) 1.06 (3H, d, J=6.6 Hz, $CH(\mathbf{CH}_3)_2$) 0.95 (3H, d, J=6.5 Hz, $CH(\mathbf{CH}^*_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 152.6 ($\mathbf{C}_{6\text{arom}}$) 150.8 ($\mathbf{C}_{3\text{arom}}$) 128.2 ($\mathbf{C}_{4\text{arom}}$) 115.3;113.2; 112.9 ($\mathbf{C}_{1,2,5\text{arom}}$) 74.2 ($\mathbf{C}(CH_3)$) 55.8 ($O\mathbf{C}H_3$) 47.3 ($\mathbf{C}HCH(CH_3)_2$) 35.3 ($\mathbf{C}H_2CH_3$) 34.9 ($\mathbf{C}_{\text{bridge}}$) 30.6 ($\mathbf{C}H_{\text{bridge head}}$) 29.4 ($\mathbf{C}H_3$) 26.3 ($\mathbf{C}H(CH_3)_2$) 21.9 ($CH(\mathbf{C}H^*_3)_2$) 21.2 ($CH(\mathbf{C}H_3)_2$) 20.4 ($\mathbf{C}H_2CH_2CHCH_3$); MS (EI) m/z 260 (M^+).

X-Ray diffraction study of 7. Crystals were grown from an acetone/methanol mixture. Crystal Data: $C_{20}H_{24}O$, Mr=280.39, Triclinic, space group P-1, lattice parameters: a=8.887(3), b=10.220(4), c=10.372(3) Å, α=85.57(2), β=67.88(2), γ=68.20(2)°, Z=2, V=808.1(5)Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centered reflections, λ=0.71073 Å), D_c= 1.152 g/cm^3, $F(000)$=304, crystal size: 0.15×0.20× 0.40 mm. Data Collection and Processing: Siemens P4-PC diffractometer, graphite-monochromated MoKα radiation, T=289K, ω-scan, $\Delta\omega$=0.6°, $2.0 \leq \omega \leq 60.0°$ min^{-1}, $4.2 \leq 2\theta \leq 50.0°$, 3438 reflections collected, 2002 unique reflections, $R_{(\text{int})}$=0.030. Three checks measured every 100 reflections showed no significant decrease in intensity. Structure Analysis and Refinement: Structure solved by direct methods and refined by full-matrix least-squares techniques on F^2, with all non-hydrogen atoms anisotropic, and riding hydrogen atoms with fixed isotropic temperature factors (1.2 times U_{eq} of the carrying atom). Final R indices: R_1=0.0601 for 1383 reflections with $F>4\sigma(F)$ and R_1=0.1437, wR_2=0.1713 for all data. The program package SHELXTL was used for all calculations,[7] the figure was drawn with PLATON.[8] Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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