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Intramolecular excited-state interactions in phenol–styrene bicromophoric systems: a photochemical and photophysical study

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Abstract—The intramolecular excited state interaction between phenol and styrene in a series of *trans*-2-cinnamylphenols bearing electron-donating substituents at the phenolic ring has been directly observed as an exciplex emission in acetonitrile. The photochemical reactivity and the relatively low fluorescence quantum yields as compared with model compounds are additional evidences for the phenol/styrene interaction. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Bichromophoric compounds are interesting models for the study of energy and electron transfer processes. They also have application for the development of new materials (i.e. photoconducting polymers) and for mimicking some biological processes such as photosynthesis.[1,2]

trans-2-Cinnamylphenols are bichromophoric compounds containing phenol and styrene moieties connected through a methylenic spacer. The introduction of suitable substituents allows to reproduce at will a wide range of intramolecular proton, electron or energy transfer processes.[3–10]

In general, photocyclisation of *trans*-2-cinnamylphenols to dihydrobenzofurans and dihydrobenzopyrans occurs mainly via intramolecular excited state proton transfer, through zwitterionic intermediates (Fig. 1, path a). However, introduction of electron-donating substituents at the phenolic nucleus enhances the contribution of excited state intramolecular electron transfer, which becomes the predominating mechanism of photocyclisation (Fig. 1, path b).

We have recently communicated the first direct observation of an intramolecular excited state interaction between phenol and styrene, detected as an exciplex emission.[10] Although such interaction has been described for a single compound (*trans*-2-cinnamyl-4-methoxyphenol **1a**), in the present work we show that other analogues with electron donating substituents at the phenolic ring exhibit similar photophysical and photochemical properties. This is remarkable; as such phenol/olefin intramolecular exciplexes were unknown. The most closely related examples have been found by Lewis et al. in bichromophoric amine/styrene systems,[11] where the conformation of chemically reactive intramolecular exciplexes appears to control the regioselectivity of the observed photocyclisation reactions.

2. Results and discussion

The structures of the substrates studied are given in Chart 1. *trans*-2-Cinnamylphenols **1a–d** were prepared as described in the literature for the parent compound *trans*-2-cinnamylphenol.[12] The corresponding propanes **1aH–dH**, required for comparative photophysical studies, were obtained by catalytic hydrogenation of **1a–d**. Compounds **1a–d**,[13–16] **1aH,bH**[15] and **1dH**[17] were known, and their structures were unambiguously confirmed by comparison of their spectroscopic data with those reported in the literature.

2.1. Photophysical studies

The emission properties of **1a–d** are summarised in Table 1, together with those measured under the same conditions for their corresponding hydrogenated derivatives **1aH–dH**, where the styrenic chromophore has been suppressed and the emission takes place exclusively from the phenolic moiety. Data for β-methylstyrene have also been included for comparison.[18]

The fluorescence spectra of **1a** (Table 1, entry 1) in hexane displayed a single band with λ_{max}=320 nm, clearly attributable to emission from the lowest lying phenolic singlet (compare trace B, Fig. 2(a) with trace A, Fig. 2(b)). The same result was obtained by exciting either at 250 nm

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Keywords: *trans*-2-cinnamylphenols; bichromophoric compounds; exciplex; intramolecular interaction; photocyclisation.

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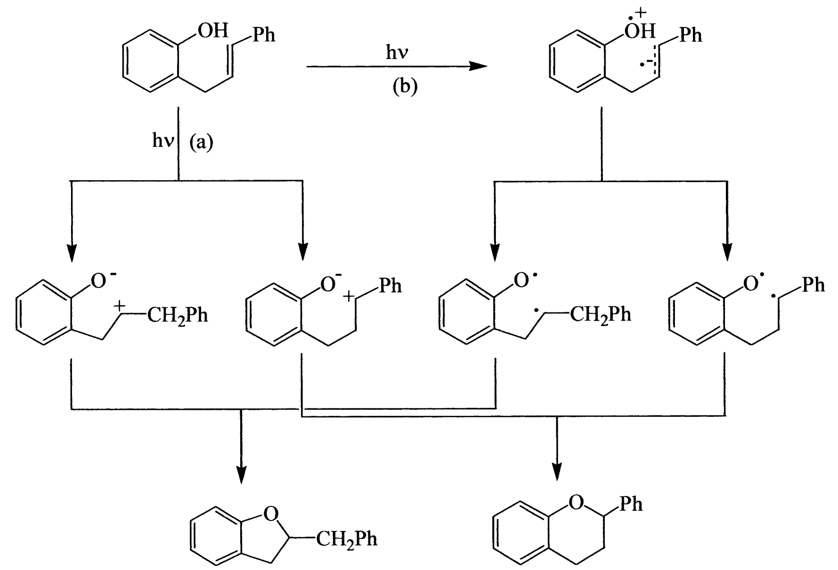

Figure 1. Photocyclisation pathways of cinnamylphenol: (a) via excited state proton transfer (b) or excited state electron transfer.

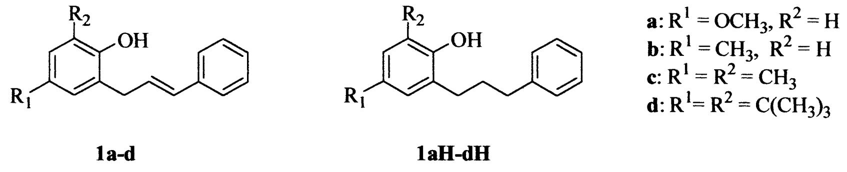

Chart 1.

Table 1. Photophysical data of **1a–d** and **1aH–dH**

Entry	Compound	λ_{max} (em)[a]	ϕ_F[a]	τ_F (ns)[b]
1	**1a**	320 (420)	0.056 (0.051)	5.1
2	**1aH**	320 (320)	0.197 (0.342)	2.5
3	**1b**	310 (360)	0.010 (0.012)	0.5
4	**1bH**	310 (310)	0.100 (0.327)	0.7 (14%), 3.0 (86%)
5	**1c**	310 (310,360)	0.024 (0.057)	1.2 (67%), 6.8 (33%)
6	**1cH**	310 (310)	0.127 (0.364)	1.5 (13%), 5.8 (87%)
7	**1d**	310 (310)	0.012 (0.012)	1.7 (35%), 5.2 (65%)
8	**1dH**	310 (310)	0.063 (0.327)	3.4
9	β-methylstyrene[c]	308 (307)	0.35	8.1

The data have been obtained upon excitation at 290 nm.

[a] The emission maxima and the fluorescence quantum yields have been measured in hexane and acetonitrile (in parentheses).

[b] λ(exc)=280 nm, solvent acetonitrile. The data in hexane are not included, because a number of them were near the time resolution of our instrumentation.

[c] Data taken from Ref. 18.

(styrene) or at 290 nm (phenol), due to efficient energy transfer between the excited singlets of both chromophores. By contrast, a completely different behaviour was observed in the more polar solvent acetonitrile (Table 1, entry 1, data in parentheses). The most remarkable result was the presence of a much longer wavelength band centred at 420 nm and the concomitant disappearance of the phenolic emission at 320 nm (see Fig. 2(b)). For compound **1aH** (which does not possess styrenic subunit), the emission wavelength (λ_{max}=320 nm) does not depend on the polarity of the solvent (Table 1, entry 2).

The band observed for **1a** in acetonitrile is clearly attributable to a charge-transfer exciplex, whose formation would be exergonic according to the Rehm–Weller Eq. (1)[19]

$$\Delta G(\text{kcal mol}^{-1}) = 23.06(E_{D/D^{+\cdot}} - E_{A/A^{-\cdot}}) - E^{*} \qquad (1)$$

where $E_{D/D^{+\cdot}}$ and $E_{A/A^{-\cdot}}$ are the redox potentials of the donor and acceptor moieties and E^{*} is the singlet energy of the phenolic chromophore. Using the excitation energy determined from the intersection between normalised excitation and emission spectra and the reported literature values for the redox potentials,[20] the resulting Gibbs free energy associated with exciplex formation would be ca. -25 kcal mol^{-1}.

The emission spectra were also obtained for solutions of **1a**

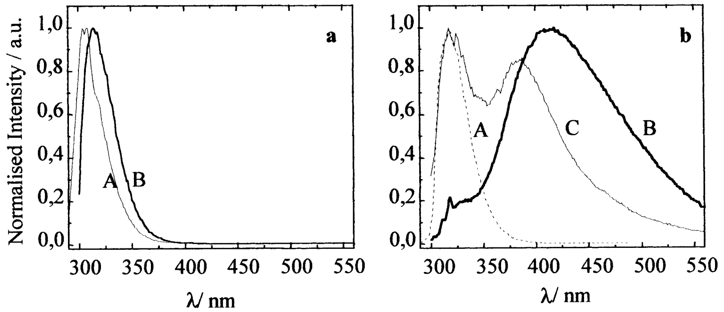

Figure 2. Fluorescence spectra of: (a) the isolated β-methylstyrene (trace A) and **1aH** (trace B); (b) **1a** in hexane (trace A), in acetonitrile (trace B) and in a 9:1 dichloromethane–acetonitrile mixture (trace C).

in solvents of intermediate polarity and in a variety of solvent mixtures. For instance, using CH_2Cl_2/CH_3CN (9:1, v:v), both the monomer and the exciplex bands were observed (see trace C, Fig. 2(b)). As expected for a charge transfer exciplex, the position of the longer wavelength band clearly depended on the solvent polarity (data not shown).[21,22]

Likewise, the shape and the position of the emission band for **1b** (Table 1, entry 3) changed with the solvent polarity, being the wavelength shift associated with the exciplex formation less pronounced (50 nm) than in the case of **1a** (100 nm).

The fluorescence spectrum of **1c** (Table 1, entry 5) in acetonitrile displayed two maxima: the monomer emission at shorter wavelength (310 nm), identical to that obtained in hexane and a second one appearing at 360 nm, due to exciplex emission.

Although in principle the *t*-butyl derivative **1d** could also give rise to an exciplex, the spectra recorded for this compound in polar and non polar solvent (Table 1, entry 7) were superimposable (λ_{max} 310 nm). The lack of exciplex emission is still unclear although it could be due to steric reasons.

In general, the fluorescence quantum yields of **1a–d** were markedly lower than those for the hydrogenated derivatives **1aH–dH** and for β-methylstyrene. On the other hand, the obtained values for **1aH–dH** were higher in acetonitrile than in hexane, as expected for simple phenols.[23]

The fluorescence lifetimes in acetonitrile are also given in Table 1 (last column). Although the trends are far from being clearcut, it appears that the exciplexes live longer when the phenolic nuclei are more strongly activated (for instance, $\tau_{F(\mathbf{1a}\text{ or }\mathbf{1c})}>\tau_{F(\mathbf{1b})}$).

As a summary of the photophysical studies, the interchromophoric interaction in the excited states of the studied *trans*-2-cinnamylphenols is evidenced by: (1) formation of intramolecular exciplexes in polar solvents and/or (2) the sharp decrease of the fluorescence quantum yield as compared to model compounds.

2.2. Photochemical studies

After determining the photophysical properties of **1a–d**, their preparative photochemistry was investigated. Although the absorption spectra of **1a–d** showed their most intense maximum below 300 nm, irradiation using quartz-filtered light gave rise to a high degree of polymerisation. In order to prevent this problem, a pyrex filter was used for the photolysis experiments. All the samples were exhaustively deoxygenated before irradiation, and the solvents used were hexane (as non-polar solvent), acetonitrile (as polar solvent) and acetone (triplet-photosensitised irradiations).

In general, irradiation of **1a–d** led to the *cis* isomers **2a–d** together with the cyclic ethers **3a–d** and **4a–d** (Fig. 3). Compounds **4a–d** were known.[16,24,25]

The results are summarised in Table 2. Irradiation of **1a** in hexane and acetonitrile (Table 2, entries 1 and 2) resulted in the almost complete consumption of the starting material, accompanied by formation of the six-membered ring compound **4a** as the major photoproduct. Minor amounts of the *cis* isomer **2a** and the five-membered ring product **3a** were also obtained in hexane. Acetone-photosensitised irradiation of **1a** (Table 2, entry 3) led exclusively to the *cis* isomer **2a**. Similar photolysis results were obtained for **1b–d**.

As the predominating formation of dihydrobenzopyrans **4** is considered to be an indication for the involvement of

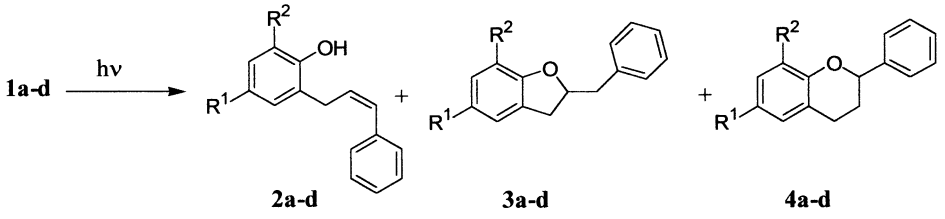

Figure 3. Products obtained upon irradiation of **1a–d**.

Table 2. Photolysis of *trans*-2-cinnamylphenols **1a–d**

Entry	Substrate	Conditions[a]	Conversion	Product distribution (%)		
				2	**3**	**4**
1	**1a**	A	94	4	10	86
2	**1a**	B	96	Traces	Traces	99
3	**1a**	C	63	100	–	–
4	**1b**	A	70	37	18	45
5	**1b**	B	58	20	–	80
6	**1b**	C	42	100	–	–
7	**1c**	A	67	30	5	65
8	**1c**	B	73	Traces	Traces	99
9	**1c**	C	100	100	–	–
10	**1d**	A	100	Traces	9	91
11	**1d**	B	51	22	8	70
12	**1d**	C	59	100	–	–

[a] A: hexane, B: acetonitrile, C: acetone.

intramolecular excited state electron transfer (Fig. 1, path b), detection of a charge transfer exciplex is compatible with the preparative photochemistry of the *trans*-2-cinnamylphenols. This is further supported by the fact that the yield of **4** increases in the more polar solvent acetonitrile in the cases where an exciplex is detected. The lower regioselectivity towards product **4** in hexane might be an indication for the participation of the proton transfer mechanism (Fig. 1, path a) to some extent.

Finally, formation of **2a–d** upon irradiation in acetone is consistent with the previously established mechanism, where *trans*/*cis* isomerisation of cinnamylphenols is accepted to occur from the styrenic triplet.[3]

As a summary of the photochemical studies, the charge transfer interchromophoric interaction in the excited state of **1a–d** is evidenced by the photocyclisation to six-membered ring products.

3. Conclusions

The intramolecular excited state interaction between phenol and styrene in *trans*-2-cinnamylphenols bearing electron-donating substituents at the phenolic ring has been directly observed as an exciplex emission. The photochemical reactivity and the relatively low fluorescence quantum yields as compared with model compounds are additional evidences for the phenol/styrene interaction.

4. Experimental

4.1. General

UV spectra were recorded in hexane in a Shimadzu UV-160A; λ_{max} (nm) and log ε values (in parentheses) are given for each absorption band. IR spectra were obtained with a FTIR Hewlett–Packard 5965 instrument; ν_{max} (cm^{-1}) is given for all the absorption bands. ^{1}H RMN and ^{13}C NMR spectra were measured in $CDCl_3$ with a 300-MHz Varian Gemini-300 instrument; chemical shifts are reported in δ (ppm) values, using TMS as internal standard. Mass spectra were obtained under electron impact using a Hewlett–Packard 5988 A spectrometer; the ratio *m*/*z* and the relative intensities (%) are indicated for the significant peaks. Isolation and purification were done by conventional column chromatography on silica gel Merck 60 PF_{254} using dichloromethane as eluent and by means of an isocratic HPLC Waters equipment provided with a semipreparative μporasil™ column (10 μm, 125 Å), using hexane (99–95%)/ethyl acetate (1–5%) as eluent (1.5 ml min^{-1}). Fluorescence spectra were recorded with an Edinburgh instrument.

4.2. General procedure for the fluorescence measurements

Emission spectra were recorded in hexane or acetonitrile at 25°C. The samples (absorbance between 0.1 and 0.3) were thoroughly purged with argon prior to fluorescence measurements. Phenol was used as standard for determining the fluorescence quantum yields.[23]

4.3. General irradiation procedure

Solutions of **1a–d** (5 mM) in 20 ml of the appropriated solvents were placed into pyrex tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium-pressure Hg lamp and irradiated under Ar for 1 h. The course of the reaction was followed by GC and ^{1}H NMR; the degrees of conversion, the product distributions and the mass balances were determined using adequate standards. The reaction mixtures were submitted to chromatographic separation, in order to obtain the pure photoproducts.

4.4. Synthesis of the substrates

Compounds **1a–d** were prepared following a previously described literature method for the parent compound *trans*-2-cinnamylphenol.[12] The sodium salt obtained from 40.0 mmol of 4-methoxy-, 4-methyl-2,4-dimethyl- or 2-4-di-*t*-butylphenol was added to *trans*-cinnamyl chloride (6.10 g, 40.0 mmol) in 100 ml of benzene. After refluxing for 5 h, the solvent was distilled and the residue was treated with 100 ml of Claisen's alkali (35.00 g of potassium hydroxide in 25 ml of water and methanol up to 100 ml). The alkaline solution was washed with hexane, acidified with HCl and extracted with dichloromethane. Evaporation of the solvent gave a residue, which was submitted to column chromatography.

For the preparation of **1aH–dH**, the cinnamylphenols **1a–d** (10 mmol) in ethyl acetate (25 ml) were hydrogenated in the presence of palladium/charcoal (11%) until consumption of the adequate volume of hydrogen. The solution was filtered and on evaporation afforded pure **1aH–dH** in quantitative yield.

4.5. Spectral data of the new compounds

4.5.1. 4,6-Dimethyl-2-(3-phenylpropyl)phenol (1c-H). Oil. FTIR 3624, 3029, 2924, 2859, 1478, 1450, 1196, 800, 695; ^{1}H NMR 7.32–7.15 (m, 5H, ArH), 6,79 (s, 2H, 3,5-ArH), 4.39 (s, 1H, OH), 2.62 (m, 4H, C*H*$_2$CH$_2$C*H*$_2$), 2.20, 2.22 (s+s, 6H, 4,6-ArCH$_3$), 1.94 (m, 2H, CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR 149.5 (1-COH), 142.3 (1′-C), 129.3–122.8 (3,5-CH, 2′,3′,4′,5′,6′-CH),35.7 (*C*H$_2$1-C′), 31.3, 29.6 (2-C*C*H$_2$*C*H$_3$), 20.5, 15.9 (4,6-C*C*H$_3$); MS 240 (M$^+$, 91), 149 (16), 148 (12), 136 (100), 135 (55), 121 (22), 105 (16), 91 (33); Exact mass calcd for $C_{17}H_{20}O$ 240.1514, found 240.1516.

4.5.2. *cis*-2-Cinnamyl-4-methylphenol (2b). Oil. UV 216 (3.97), 245 (4.08), 280 (3.26); FTIR 3651 (OH), 3598 (OH), 3066, 3024, 2931, 1597, 1501, 1438, 1317, 1257, 1180, 1101, 913, 806, 759, 700; ^{1}H NMR 7.76–7.24 (m, 6H, ArH), 6.95 (s, 1H, 3-ArH), 6.90 (d, *J*=8 Hz 1H, 5-ArH), 6.67 (d, *J*=8 Hz, 1H, 6-ArH), 6.63 (d, *J*=12 Hz 1H, CH$_2$CH=C*H*), 5.82 (dt, *J*$_1$=12 Hz, *J*$_2$=7 Hz, 1H, CH$_2$C*H*=CH), 4.67 (s, 1H, OH), 3.63 (d, *J*=7 Hz, 2H, CH$_2$), 2.25 (s, 3H, CH$_3$); ^{13}C NMR: 151.5 (1-COH), 137.0 (1′-*C*CH=CH), 127.0–130.0 (3,5-CH, *C*H=*C*H, 2′,3′,4′,5′,6′-CH), 130.1 (4-*C*CH$_3$), 126.0 (2-*C*CH$_2$), 115.3 (6-*C*H), 29.4 (CH$_2$), 20.5 (CH$_3$); MS 224 (M$^+$, 60), 209 (33), 133 (85), 120 (37), 116 (21), 115 (45), 105 (46), 104 (51), 91 (100), 77 (30). Exact mass calcd for $C_{16}H_{16}O$ 224.1201, found 224.1203.

4.5.3. *cis*-2-Cinnamyl-4,6-dimethylphenol (2c). Oil. UV 216 (4.13), 242 (4.13), 280 (3.51); FTIR 3651 (OH), 3597 (OH), 3067, 3021, 2930, 1598, 1483, 1283, 1194, 1022, 853, 761, 700; ^{1}H NMR 7.37–7.25 (m, 5H, ArH), 6.82 (s, 2H, 3,5-ArH), 6.64 (d, *J*=12 Hz, 1H, CH$_2$CH=C*H*), 5.82 (dt, *J*$_1$=12 Hz, *J*$_2$=7 Hz, 1H, CH$_2$C*H*=CH), 4.56 (s, 1H, OH), 3.62 (d, *J*=7 Hz, 2H, CH$_2$), 2.23 (s, 1H, CH$_3$), 2.19 (s, 1H, CH$_3$); ^{13}C NMR: 150.0 (1-COH), 136.6 (1′CCH=CH), 123.6–130.6 (2-*C*CH$_2$, 3,5-CH, 4*C*–CH$_3$, *C*H=*C*H, 2′,3′,4′,5′,6′-CH), 29.8(CH$_2$), 20.4 (4-C*C*H$_3$), 15.8 (6-C*C*H$_3$); MS 238(M$^+$, 75), 223(14), 147(55), 134(80), 119(13), 115(40), 91(100). Anal. calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61; Found: C, 85.60; H, 7.56.

4.5.4. *cis*-2-Cinnamyl-4,6-ditertbutylphenol (2d). Oil. UV 216 (4.13), 243 (4.16); FTIR 3669 (OH), 3566, (OH), 3069, 3029, 2966, 1597,1476, 1400, 1368, 1288, 1240, 1206, 1118, 967, 876, 736; ^{1}H NMR 7.38–7.23 (m, 5H, ArH), 7.21 (s, 1H, 3- or 5-ArH), 7.04 (s, 1H, 3- or 5-ArH), 6.67 (d, *J*=12 Hz, 1H, CH$_2$CH=C*H*), 5.82 (dt, *J*$_1$=12 Hz, *J*$_2$=7 Hz, CH$_2$C*H*=CH), 4.78 (s, 1H, OH), 3.65 (d, *J*=7 Hz, 2H, CH$_2$), 1.35 (s, 9H, C(CH$_3$)$_3$), 1.27 (s, 9H, C(CH$_3$)$_3$); MS 322 (M$^+$, 18), 308 (13), 307 (53), 203 (100), 161 (12), 145 (10), 117 (22), 115 (28), 91 (77), 57 (60). Anal. calcd for $C_{23}H_{30}O$: C, 85.67; H, 9.34; Found: C, 85.60; H, 9.27.

4.5.5. 2-Benzyl-5-methyl-2,3-dihydrobenzofuran (3b). Oil. FTIR 3071, 3030, 2933, 1856, 1607, 1491, 1365, 1337, 1296, 1241, 1115, 983, 921, 851, 807, 745, 700; ^{1}H NMR 7.34–7.23 (m, 5H, ArH), 6.95 (s, 1H, 4-ArH), 6.90, 6.67 (d+d, *J*=8 Hz, 2H, 6,7-ArH), 4.98 (m, 1H, CH), 3.15 (m, 2H, CH$_2$), 2.83 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$): ^{13}C NMR: 157.3 (7a-CO), 137.5 (1′-*C*CH2), 129.6–125.6 (3a-C, 4,6-CH, 5-*C*CH$_3$, 2′3′4′5′6′-*C*H), 109.0 (7-CH), 83.5 (2-*C*HCH$_2$), 42.0, 35.0 (2-CH*C*H$_2$, 3-CH$_2$) 20.7 (CH$_3$); MS 224 (M$^+$,75), 133 (100), 132 (32), 115 (8), 105 (61), 91 (43), 92 (14), 77 (16). Exact mass calcd for $C_{16}H_{16}O$ 224.1201, found 224.1201.

4.5.6. 2-Benzyl-5,7-dimethyl-2,3-dihydrobenzofuran (3c). Oil. FTIR 3070, 3030, 2932, 1606, 1480, 1365, 1320, 1280, 1210, 1137, 1036, 987, 850, 743, 700; ^{1}H NMR 7.34–7.21 (m, 5H, ArH), 6.79, 6.73 (s+s, 2H, 4,6-ArH), 4.95 (m, 1H, CH), 3.17 (m, 2H, CH$_2$), 2.89 (m, 2H, CH$_2$), 2.21 (s, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$); ^{13}C NMR: 155.6 (7a-CO), 137.6 (1′-*C*CH$_2$), 130.2–125.8 (3a-C, 4,6-CH, 5-*C*CH$_3$, 2′3′4′5′6′-CH), 122.9 (7-*C*CH$_3$), 83.1 (2-CH), 42.0, 35.0 (3-CH$_2$, 2-CH*C*H$_2$), 20.7 (5-C*C*H$_3$), 15.2 (7-C*C*H$_3$); MS 238 (M$^+$,26), 147 (100), 131 (7), 119 (36), 117 (8), 115 (10), 91 (37), 77 (10). Anal. calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61; Found: C, 85.64; H, 7.76.

4.5.7. 2-Benzyl-5,7-ditertbutyl-2,3-dihydrobenzofuran (3d). Oil. FTIR 2963, 2850, 1700, 1474, 1365, 1230; ^{1}H NMR 7.55–7.30 (m, 5H, ArH), 7.10, 7.05 (s+s, 2H, 4,6-ArH), 4.98 (m, 1H, CH), 3.17 (m, 2H, CH$_2$), 2.92 (m, 2H, CH$_2$), 1.35 (s, 9H, C(CH$_3$)$_3$), 1.29 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR: 155.7 (7a-CO), 141.2, 139.0 (1′-*C*CH$_2$, 5-*C*C(CH$_3$)$_3$), 130.9 (7-*C*C(CH$_3$)$_3$), 129.5–125.9 (3a-C, 2′3′4′5′6′-CH), 121.6 (4-CH), 119.4 (6-CH), 82.9 (2-CH), 42.1, 35.0 (2-CH*C*H$_2$, 3-CH$_2$) 31.9, 31.8, 29.8, 29.4 (5-C*C*(*C*H$_3$)$_3$, 7-C*C*(*C*H$_3$)$_3$; MS 322 (M$^+$,35), 307 (100), 203 (54), 161 (11), 117 (13), 115 (15), 91 863). Exact mass calcd for $C_{23}H_{30}O$ 322.2296, found 322.2296.

Acknowledgements

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