Intramolecular Photochemical Reactions of Bichromophoric 3-(Alkenyloxy)phenols and 1-(Alkenyloxy)-3-(alkyloxy)benzene Derivatives. Acid-Catalyzed Transformations of the Primary Cycloadducts

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Irradiation of 3-(alkenyloxy)phenols and 1-(alkenyloxy)-3-(alkyloxy)benzene derivatives, at $\lambda = 254$ nm in acidic media, yields benzocyclobutenes, 3-alkylphenols, 3-alkylanisols, and 4-alkyl-1,2-dialkyloxybenzenes depending on the substitution pattern of the aromatic ring and the olefinic side chain. The final products are derived from an intramolecular [2 + 2] photocycloaddition and acidic rearrangements from a common intermediate.

Introduction

Three types of cycloaddition reactions are usually observed between photochemically excited benzene derivatives and alkenes.[1−3] Depending on the relative redox potentials and on the substitution pattern of the two reaction partners, [2 + 2], [2 + 3], or [2 + 4] cycloadditions can be observed.[4,5] In case of alkoxy-substituted benzene derivatives, [2 + 2] addition and [2 + 3] cycloaddition (meta-cycloaddition), the most frequent process, can have considerable interest for organic synthesis of polycyclic skeletons (e.g., triquinanes).[1,6] Intramolecular [2 + 2] photocycloaddition of (alkenyloxy)-benzenes have been reported to give unstable intermediates in thermal or photochemical equilibrium.[3,7] Until recently, little attention had been paid to the photochemistry of (alkenyloxy)phenols, and only a few examples of intermolecular [2 + 2] cycloaddition of alkenes to phenols have been reported in the literature.[8] Additionally, one example of an intramolecular [2 + 2] photocycloaddition,[9] a photocyclization of allylphenols, and a di-π-methane photorearrangement were also described.[10]

Photolysis of various O-alkenylsalicylic esters in neutral medium was found to give complicated mixtures. However, when the reaction was carried out in the presence of acid, the reaction mixture was simplified and the only isolated product could be explained through a series of thermal and photochemical equilibria, starting from a [2 + 2] cycloaddition. These equilibria could be shifted efficiently to a mixed acetal by an irreversible protonation of an enol ether intermediate.[11]

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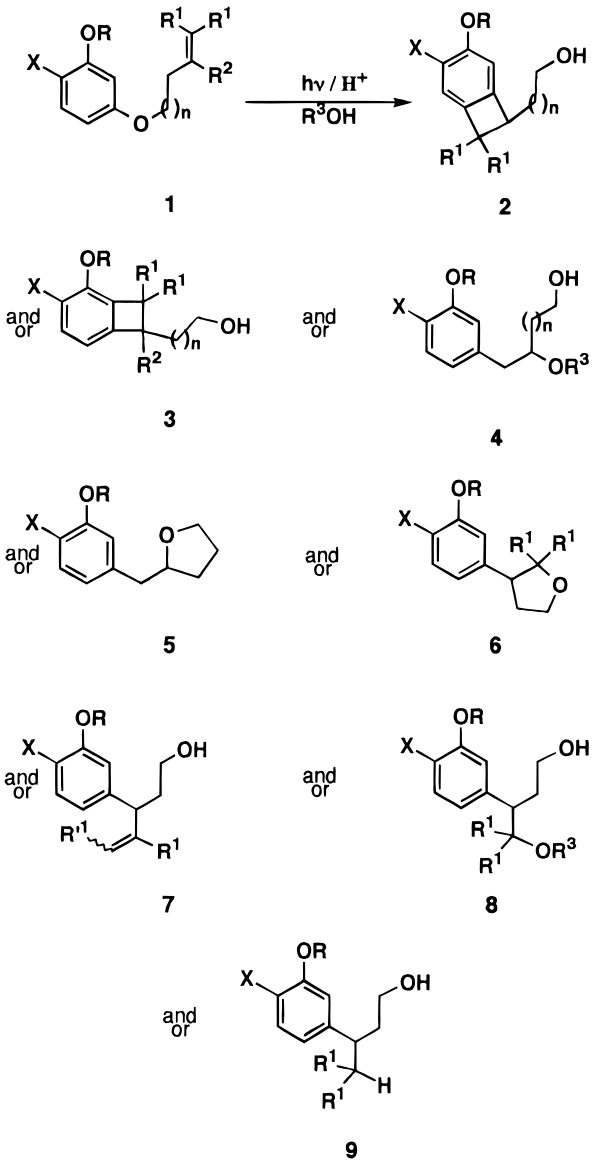
In order to generalize this reaction, and to gain more insight into the effect of acids on the photocycloaddition of alkenes on phenol derivatives, we decided to investigate *O*-(alkenyloxy)phenols. Surprisingly, benzocyclobutene derivatives were obtained in preparative yield.[12] We have now compared the photoreactivity of (alkenyloxy)phenols, (alkenyloxy)(alkyloxy)benzene, and (alkenyloxy)bis(alkyloxy)benzene derivatives in acidic conditions. We also describe our investigation on the effect of substitution at the extremity of the ethylenic double bond on the course of the reaction.

Results and Discussion

When phenol **1a**, having an *O*-butenyl chain in the meta position, was irradiated at $\lambda = 254$ nm, in methanol or ethanol, only very slow transformation and complex mixtures were observed. In contrast, when irradiation was carried out in the presence of H_2SO_4, a faster reaction and a cleaner transformation to isomeric benzocyclobutenes **2a** and **3a** was obtained (Scheme 1, Table 1). Similarly, when phenols **1b** and **1c** having an *O*-pentenyl and *O*-(3-methylbut-3-enyl) chain, respectively, were irradiated under the same conditions, a mixture of benzocyclobutenes **2** and **3** could be isolated as the only new products (runs 1−3). When an alkyl substituent was introduced at the extremity of the ethylenic bond as in **1d** and **1e**, the chemical yield of the corresponding benzocyclobutenes dropped considerably, and only regioisomers **3d** and **3e** could be characterized. Furthermore, **6**, **7**, and **8**, which possess a rearranged skeleton, are the main products isolated from the reaction mixture (runs 4 and 5). These new products result from C−C bond formation between C-3 of the phenol ring and the C-3′ of the original alkenyloxy side chain. They can be explained by an acidic transformation of unstable intermediates. In order to determine if the presence of a hydroxyl group on the benzene ring was needed in these photoreactions, methoxy and 3-(alkenyloxy)benzenes **1f**, **1g**, and **1h** were then irradiated. As for the corresponding 3-(alkenyloxy)phenols, **1f** and **1g** gave mainly benzocyclobutenes **2** and **3**. However, the transformation had become more regioselective, and **2** was sometimes formed almost exclusively. For (alkenyloxy)(alkyloxy)-benzene **1h** having a terminally substituted alkenyl chain, no benzocyclobutene could be isolated and the reaction mixture containing **6h**, **7h**, and **8h** was very similar to the one obtained from the corresponding phenol **1d**.

In very acidic medium, rearranged products **3** and **6**−**8** might be in equilibrium. To verify if the reaction was under kinetic or thermodynamic control, we irradiated **3a**, **6a**, **7a**, and **8a** separately and under the same reaction conditions. We observed a slow degradation of the starting material and a complex mixture of products, which did not contain the expected ones. This observation indicates that **5**−**8** are primary products derived from unstable and nonisolable intermediates. To explain the reaction products, several mechanisms could be envisaged. A first possibility was to consider an initial C-protonation leading to a mixture of photoreactive cyclohexadienones according to Scheme 2. Protonation of the aromatic ring might occur either in the ground state before excitation or in the excited state to produce

Scheme 1. Photochemical Reaction of 3-(Alkenyloxy)phenols and (Alkenyloxy)(alkyloxy)benzene Derivatives



a photoreactive cyclohexadienone-like intermediate. Then absorption of a photon by this intermediate could lead to an intramolecular [2 + 2] photocycloaddition. The observed products would result from an acid-catalyzed transformation of primary cycloadducts in the ground state. Formation of cyclohexadienone-like intermediates might also allow an exchange of the alkoxy groups of the benzene ring simply by modification of the solvent of the reaction. In order to find out if such a C-protonation of the aromatic ring is required in the photoreaction process, we studied the photoreactivity of anisol derivative **1f**, under different solvent conditions. In a mixture of methanol and water, no exchange of the methoxy by a hydroxy group could be detected, either in the recovered starting material or in rearranged products **2**, **3**, and **4**. Similarly, when the reaction was carried out in acidic ethanol, there was no exchange of the methoxy by an ethoxy group on the aromatic ring (runs 7 and 8) but an incorporation of an ethoxy group on the side chain of **4**. Furthermore, when CH_3OH was replaced by CH_3OD while the other conditions remained the same, no significant deuterium incorporation could be detected either in the reactant **1f** or in the products **2f**, **3f**, and **4f**

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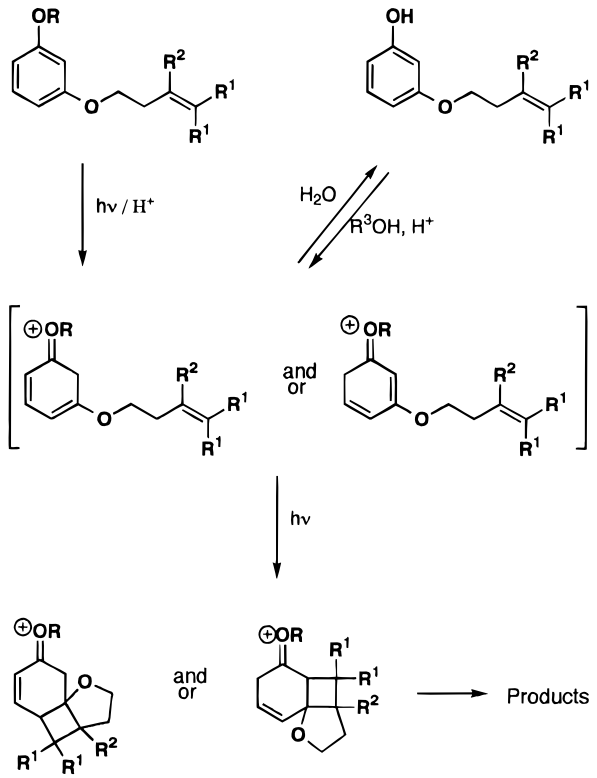
Table 1. Results of the Photochemical Reaction of 3-(Alkenyloxy)phenols and (Alkenyloxy)(alkyloxy)benzene Derivatives

run	1	X	OR	*n*	R_1	R_2	solvent	conversion, %[a]	yield, %[a] 2	3[b]	4	5	6	7	8	9
1	**a**	H	OH	1	H	H	MeOH	83	45	5						
2	**b**	H	OH	2	H	H	MeOH	77	39	20						
3	**c**	H	OH	1	H	Me	MeOH	50	50	10						
4	**d**	H	OH	1	Me	H	MeOH	73		13			10	10	37	*i*
5	**e**	H	OH	1	Et	H	MeOH	86		11			20	40[c]	15	*i*
6	**f**	H	OMe	1	H	H	MeOH	86	41	2	20[d]					
7							EtOH	84	31		18[e]					
8							MeOH−H_2O (5/1)	94	28		17/4[f]					
9	**g**	H	OMe	2	H	H	MeOH	100	33	8	23	4				
10							MeCN	82	20	6		25				
11	**h**	H	OMe	1	Me	H	MeOH	>97					4	15	33	
12	**i**	OCH_2O		1	H	H	MeOH	100			55					
13	**j**	OCH_2O		2	H	H	MeOH	54			23[g]	17/6[h]				
14							MeCN	70				42				
15	**k**	OCH_2O		1	Me	H	MeOH	100					10	14	42	5[j]
16	**l**	OMe	OMe	1	H	H	MeOH	93			58					20

[a] On the basis of transformed starting material. [b] Isolated as a mixture with **2**. [c] Two stereoisomers; cis/trans ratio 1.3/1. [d] $R^3 = CH_3$. [e] $R^3 = C_2H_5$. [f] $R^3 = CH_3/R^3 = H$ 17/4. [g] Isolated with **5j** (X = OR = OH). [h] **5j**: X, OR = OCH_2O, 17%; X = OR = OH, 6%. [i] Unidentified product ~2%. [j] Isolated as a mixture with **7k**.

Scheme 2



(detection limit 5−10%). These results indicate that intermediacy of cyclohexadienone-like intermediates and the mechanism of Scheme 2 are improbable.

In order to obtain more information on the origin of the observed photoreactivity, we examined the influence of the ethylenic bond and of acidic conditions on the fluorescence spectra of dialkoxybenzene derivatives. The results are reported in Figures 1 and 2. Only a small quenching of the fluorescence was observed at an H_2SO_4 concentration of 0.1 mol·L^{-1}. Furthermore, no significant difference was observed for 1,3-dimethoxybenzene (Figure 1) and **1f** (Figure 2), and within the described concentration range, the presence of acid had no influence on the UV spectra.

We next considered the possibility of an initial [2 + 2] photocycloaddition on an O-protonated dialkoxybenzene.

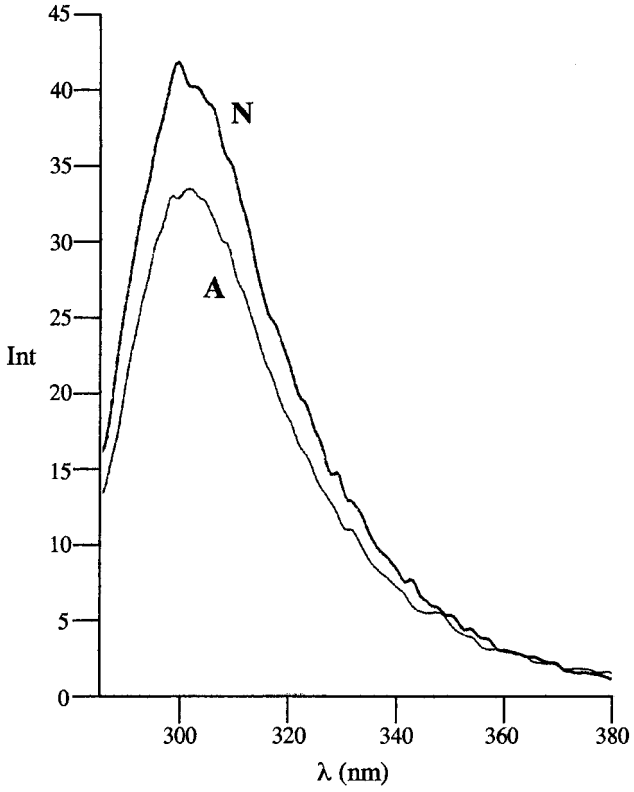


Figure 1. Fluorescence spectra of 1,3-dimethoxybenzene in the presence (**A**) and the absence (**N**) of acid.

The need for an acidic medium to allow a [2 + 2] photocycloaddition was evident from the following observation: a very slow photoreaction of **1f** and a less selective formation of the expected products was detected in neutral methanol and an increase of the conversion was observed in the presence of increasing amounts of sulfuric acid, according to Figure 3.

Formation of the final products can be explained through acid-catalyzed processes and rearrangements, as summarized in Scheme 3.

Intramolecular [2 + 2] photocycloaddition of the alkene moiety onto the aromatic ring is regioselective and leads to tricyclic and protonated isomers **2′** and **3′**. Ring opening of the protonated tetrahydrofuran moiety of **2′**

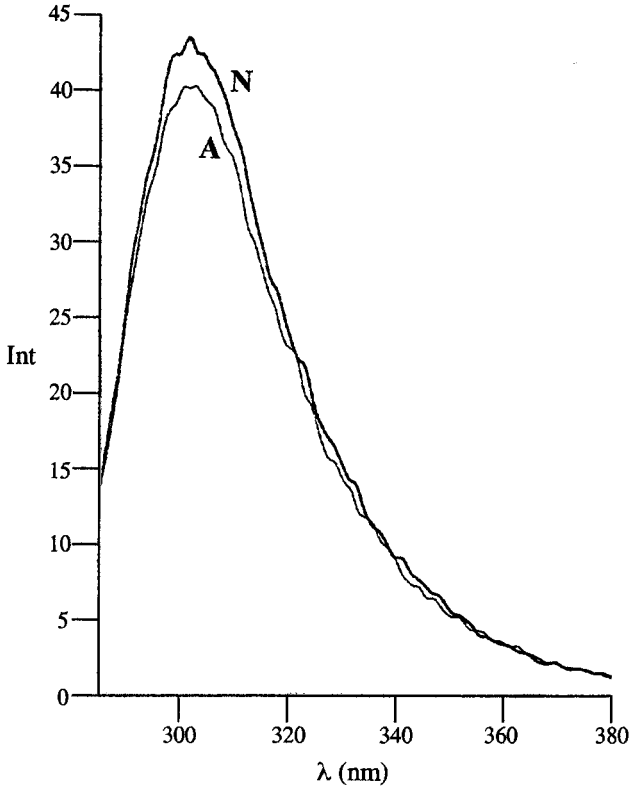


Figure 2. Fluorescence spectra of **1f** in the presence (**A**) and the absence (**N**) of acid.

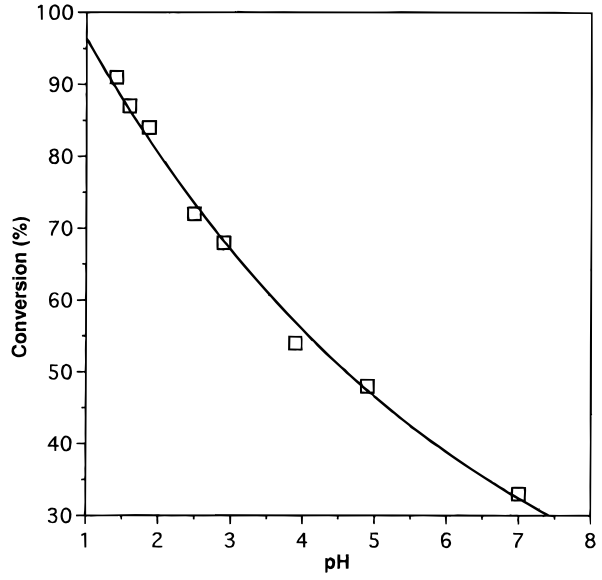


Figure 3. Dependence of the conversion of **1f** from pH after 2.5 h of irradiation.

and **3′** involves the breaking of a C−O bond. Rearomatization by deprotonation of the system according to path a describes the formation of benzocyclobutenes **2** and **3**. The regioselectivity of the benzocyclobutene formation was found to be higher with diethers **1f** and **1g** (runs 6−10) than with the corresponding (alkenyloxy)phenols **1a**, **1b**, and **1c** (entries 1−3). This change might reflect a difference in steric hindrance between the hydroxy or the methoxy substituent and a preference for a bond-forming step at the *para* rather than the *ortho* position. When R^1 is an alkyl group and when the alkenyl chain is trisubstituted, two rearomatization processes now compete (runs 4, 5, 11, and 15). Besides a deprotonation pathway producing small amounts of **3** (runs 4 and 5), an opening of the cyclobutane ring leads to rearranged products. A C−C bond between the benzene ring and the unsaturated chain replaces the original and vinylic C−O bond (path b). Depending on the deprotonation process, and by intra- or intermolecular trapping of the tertiary carbocation intermediate **4′**, products **7**, **6**, and **8** are formed, respectively. From resorcinol diethers **1f** and **1g** with a terminal alkene, products **4** and **5** can be explained only if we assume that a C−C bond between the benzene ring and *ω*-carbon of the alkenyloxy group replaces the vinylic O−C3 bond of the starting material. Rearrangement of **3′** with cyclobutane contraction and formation of spiranic cyclopropylcarbinyl carbocation **5′** [13] could explain the formation of products **4** and **5** (path c). That **4** and **5** could not be isolated from the corresponding (alkenyloxy)phenols (runs 1−5) is indicative of a higher preference of path a in the presence of a 1-hydroxyl group.

The unexpected photoreactivity of resorcinol diethers led us to compare their reactivity with the corresponding trihydroxybenzene derivatives **1i**, **1j**, and **1l**. Two main differences between resorcinol and trihydroxybenzene derivatives were observed. No benzocyclobutene was detected, but rearranged products **4** and **5** could be isolated in high yield from **1i** and **1l** (runs 12 and 16). Second, and unexpectedly, reduction product **9** could also be isolated in yields up to 20% (run 16).

In acetonitrile an increase of the chemical yield of the tetrahydrofuranyl derivative **5** should be observed. As expected, the formation of **5j**, resulting from an intramolecular trapping of the cationic intermediate by the terminal hydroxyl group, was favored when intermolecular trapping was impossible under these conditions (runs 9, 10, 13, and 14). Products **4** and **5** were not observed from (alkenyloxy)phenols **1a**−**e**, as well as when the alkenyl side chain of **1h** and **1k** was substituted in the terminal position (runs 1−5, 11, and 15). Furthermore, **4** and **5** were the sole products when an additional alkyloxy substituent was present in the para position of the butenyloxy or pentenyloxy side chain of *ω*-(alkenyloxy)benzenes (runs 12, 13, and 14).

From the observed results, it can be concluded that the respective stability of the cationic intermediates, which can be formed from an opening of the primary cycloadducts, is steering the reaction mixture (Scheme 4). When $R^1 = X = H$, no stabilized carbocation can be expected from an opening of the cyclobutane ring, and deprotonation through path a is the preferred process. When R^1 is an alkyl group, cleavage of a cyclobutane bond which leads to a tertiary cation competes favorably with the deprotonation process (path b). From starting compounds **1i**−**l**, bearing one additional alkoxy group on the benzene ring, rearrangement of intermediate **2′** can produce **5′**, stabilized by the electron-donating ability of X. In absence of alkyl substituents ($R^1 = H$), formation of **5′** and then of **4** and **5** is now preferred to the other processes.

Formation of rearranged compounds **9** (entries 15 and 16) was very surprising and involves a reduction step.

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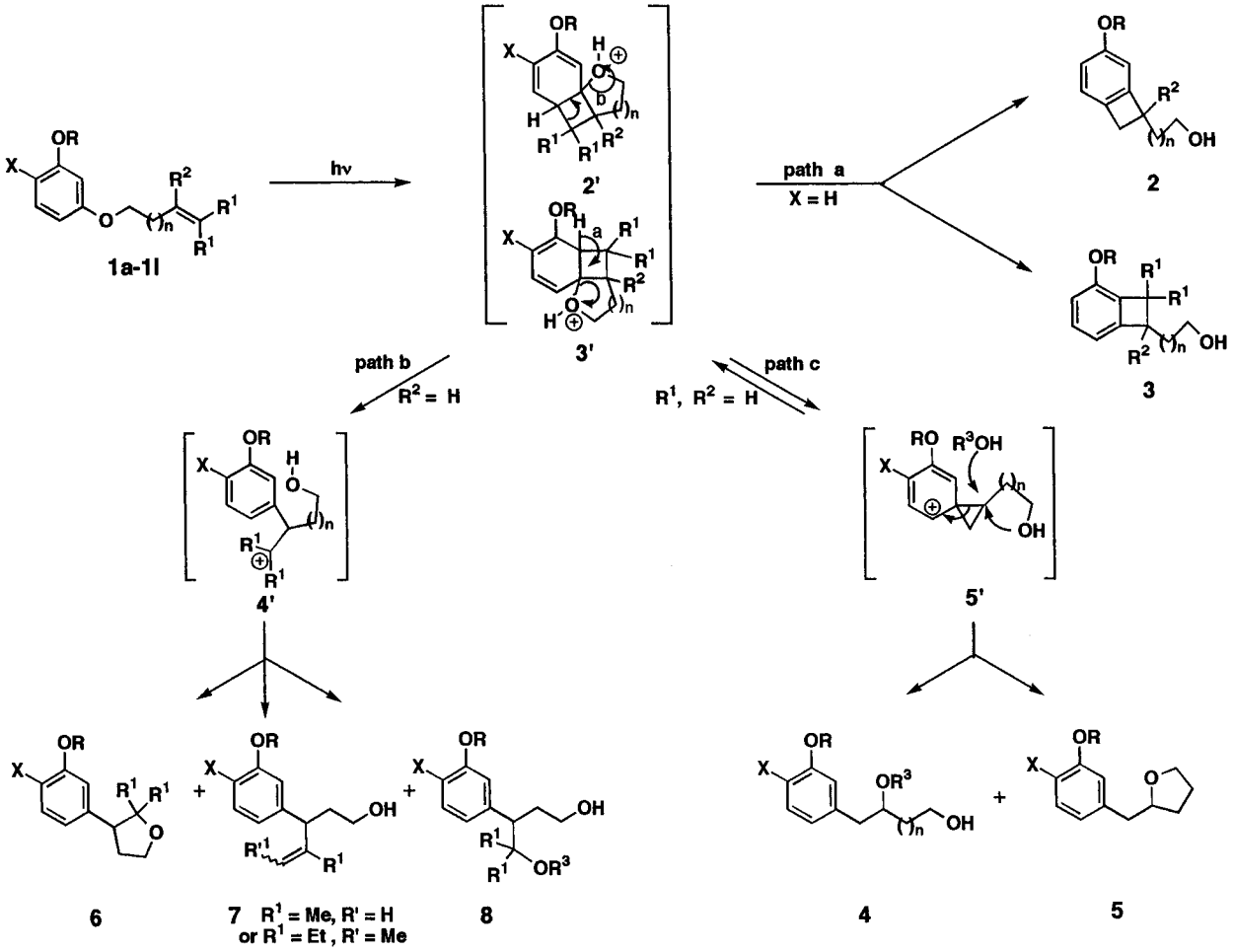
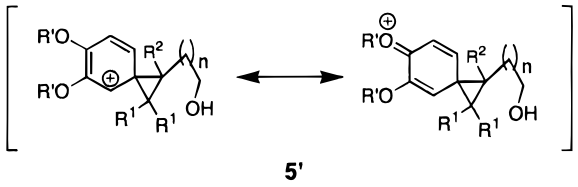
Scheme 3. Mechanism for the Formation of Different Products in the Reaction of 3-(Alkenyloxy)phenols and (Alkenyloxy)(alkyloxy)benzene Derivatives in Acidic Media



Scheme 4



Although we have verified that **9** is not obtained from a reduction of **8** under the reaction conditions, further experiments are still needed to explain its formation.

Conclusion

In contrast to the very slow transformation observed when the reaction was carried out in neutral conditions, benzocyclobutenes **2** and **3** and rearranged products **4**−**9** were obtained when **1** was irradiated in acidic media at $\lambda = 254$ nm. Formation of the reaction products can be explained by a sequence initiated by a [2 + 2] cycloaddition and followed by an acid-catalyzed rearomatization of the corresponding intermediates.

Further work to determine the limits of this photoreactivity and to apply the benzocyclobutenes to the synthesis of natural products analogs are now in progress.

Experimental Section

Synthesis of Compounds 1. Phenol (45 mmol) and the corresponding alkenyl tosylate (45 mmol) were dissolved in DMF (50 mL) followed by the addition of K_2CO_3 (15 g). The mixture was stirred at 80 °C for 2 h. Most of the DMF was then evaporated, and the residue was treated with water and ether. The aqueous phase was extracted twice with ether. The combined organic phases were dried over $MgSO_4$. After evaporation of the ether, the crude material was purified by flash silicagel chromatography (eluent, petroleum ether and ethyl acetate). For the preparation of the (alkenyloxy)phenols, resorcinol was added in excess (82 mmol) in order to reduce the proportion of the bisalkylated product in the presence of K_2CO_3 (15 g) and 70 mL of DMF (70 mL). After extraction of the alkaline mixture with ether, the aqueous phase was carefully acidified with concentrated HCl and extracted again with ether (3×).

3-(But-3-enyloxy)phenol (1a). Yield: 48%. Yield of dialkylated product: 23%. UV: λ_{max} (ϵ) = 205 (18400), 220 (7000), 275 (2200) nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.10 (1H, t, J = 8.5), 6.4−6.5 (3H, m), 5.88 (1H, ddt, J = 10, 17, 6.5), 5.05−5.20 (2H, m), 3.95 (2H, t, J = 7.5), 2.51 (2H, qt, J = 6.5, 1.5). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.20, 156.93, 134.36, 130.05, 116.96, 107.92, 106.96, 102.25, 67.26, 33.53. IR (film): ν 3374, 3073, 2936, 1591, 1491, 1290, 1154. MS m/z (rel intensity): 164 (M^+, 55), 136 (14), 123 (18), 120 (15), 118 (15), 111 (14), 110 (100). HRMS m/z calcd for $C_{10}H_{12}O_2$: 164.0837, found 164.0840.

3-(Pent-4-enyloxy)penol (1b). Yield: 38%. Yield of the dialkylated product: 30%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.11 (1H, t, J = 8.0), 6.37−6.52 (3H, m), 5.85 (1H, ddt, J = 10.0, 17.0, 6.5), 4.95−5.10 (2H, m), 3.94 (2H, t, J = 7), 2.22 (2H, q, J = 7), 1.87 (2H, p, J = 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.46, 156.71, 137.79, 130.09, 115.17, 107.68, 107.13, 102.14, 67.26, 30.07, 28.38. IR (film): ν 3399, 3073, 2948, 1591, 1491, 1291, 1140. MS m/z (rel intensity): 178 (M^+, 100), 123 (11), 111 (42), 110 (65), 93 (14), 82 (20), 81 (29), 69 (47). HRMS m/z calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.0990.

3-((3-Methylbut-3-enyl)oxy)penol (1c). Yield: 38%. Yield of the dialkylated product: 34%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.10 (1H, t, J = 8.5), 6.38−6.52 (3H, m), 5.22 (1H, s), 4.83 (1H, s), 4.78 (1H, s), 4.04 (2H, t, J = 7), 2.48 (2H, t, J = 7), 1.80 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.23, 156.73, 142.12, 130.09, 111.97, 107.84, 107.08, 102.23, 66.53, 37.10, 22.76. IR (film): ν 3399, 3073, 2936, 1591, 1505, 1290, 1154. MS m/z (rel intensity): 178 (M^+, 77), 150 (12), 123 (15), 111 (33), 110 (100), 93 (15), 87 (15), 85 (74), 83 (94), 69 (40). HRMS m/z calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.0976.

3-((4-Metylpent-3-enyl)oxy)phenol (1d). Yield: 36%. Yield of the dialkylated product: 11%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.12 (1H, t, J = 8.5), 6.40−6.55 (3H, m), 5.55 (1H, s), 5.16−5.27 (1H, m), 4.78 (2H, m), 3.91 (2H, t, J = 7), 2.47 (2H, q, J = 7), 1.75 (3H, s), 1.67 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.24, 156.67, 134.44, 130.06, 119.48, 107.77, 107.06, 102.17, 67.73, 28.14, 25.69, 17.81. IR (film): ν 3387, 2973, 2923, 2872, 1591, 1491, 1291, 1154. MS m/z (rel intensity): 192 (M^+, 100), 165 (35), 151 (15), 149 (16), 136 (10), 124 (17), 123 (55), 121 (17), 112 (40), 111 (63), 110 (63). HRMS m/z calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1170.

3-((4-Ethylhex-3-enyl)oxy)phenol (1e). Yield: 30%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.12 (1H, t, J = 8), 6.51 (1H, ddd, J = 0.7, 2.5, 8), 6.40−6.46 (2H, m), 5.20 (1H, s), 5.15 (2H, t, J = 7), 3.91 (2H, t, J = 7), 2.50 (2H, q, J = 7), 2.00−2.15 (4H, m), 1.02 (3H, t, J = 7), 1.00 (1H, t, J = 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.36, 156.70, 145.77, 130.06, 117.35, 107.68, 107.06, 102.16, 67.98, 29.16, 27.71, 23.32, 13.20, 12.72. IR (film): ν 3387, 2961, 2872, 1591, 1491, 1291, 1140. MS m/z (rel intensity): 220 (M^+, 60), 179 (18), 165 (21), 149 (10), 136 (13), 123 (20), 111 (100), 110 (38), 95 (30), 81 (45). HRMS m/z calcd for $C_{14}H_{20}O_2$: 220.1463, found 220.1456.

3-(But-3-enyloxy)-1-methoxybenzene (1f). Yield: 61%. UV: λ_{max} (ϵ) = 205 (25000), 220 (8000), 275 (2200) nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.15 (1H, t, J = 8), 6.44−6.52 (3H, m), 5.89 (1H, ddt, J = 17, 10, 7), 5.06−5.21 (2H, m), 3.99 (2H, t, J = 7), 3.77 (3H, s), 2.52 (2H, q, J = 6.5). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.90, 160.21, 134.45, 129.81, 116.95, 106.80, 106.36, 101.14, 67.23, 55.21, 33.61. IR (film): ν 3079, 2936, 2836, 1605, 1491, 1291, 1154. MS m/z (rel intensity): 178 (M^+, 52), 150 (7), 137 (24), 124 (100), 107 (28). HRMS m/z calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.1007.

1-Methoxy-3-(pent-4-entyloxy)benzene (1g). Yield: 79%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.16 (1H, t, J = 8), 6.45−6.52 (3H, m), 5.85 (1H, ddt, J = 17, 10, 6.5), 4.95−5.11 (2H, m), 3.95 (2H, t, J = 6.5), 3.78 (3H, s), 2.18−2.29 (2H, m), 1.81−1.94 (2H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.89, 160.37, 137.82, 129.81, 115.13, 106.80, 106.20, 101.09, 67.21, 55.24, 30.11, 28.46. IR (film): ν 3073, 2936, 2836, 1605, 1491, 1291, 1154. MS m/z (rel intensity): 192 (M^+, 40), 125 (29), 124 (100), 107 (8). HRMS m/z calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1121.

1-Methoxy-3-((4-methylpent-3-enyl)oxy)benzene (1h). Yield: 42%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.15 (1H, dt, J = 1, 8), 6.44−6.53 (3H, m), 5.20 (1H, d/sep, J = 7, 1.5), 3.91 (2H, t, J = 7), 3.78 (3H, s), 2.43 (1H, q, J = 7), 1.73 (3H, d, J = 1.5), 1.65 (3H, d, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.78, 160.24, 134.32, 129.74, 119.74, 106.68, 106.18, 100.97, 61.23, 55.18, 28.20, 25.66, 17.78. IR (film): ν 2922, 1591, 1491, 1291. MS m/z (rel intensity): 206 (M^+, 12), 137 (10), 125 (64), 124 (100), 111 (12), 107 (18). HRMS m/z calcd for $C_{11}H_{14}O_2$: 206.1307, found 206.1324.

5-(But-3-enyloxy)benzo[1,3]dioxole (1i). Yield: 50%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.70 (1H, d, J = 8.5), 6.51 (1H, d, J = 2.5), 6.34 (1H, dd, J = 8.5, 2.5), 5.91 (2H, s), 5.90 (1H, ddt, J = 16.5, 10, 6.5), 5.05−5.22 (2H, m), 3.95 (2H, t, J = 7), 2.52 (2H, tq, J = 1.5, 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 154.46, 141.65, 134.47, 121.33, 116.92, 107.90, 105.92, 101.07, 98.25, 68.27, 33.67. IR (film): ν 3073, 2886, 2772, 1630, 1491, 1190, 1040. MS m/z (rel intensity): 192 (M^+, 45), 138 (100), 137 (53), 107 (12). HRMS m/z calcd for $C_{11}H_{12}O_3$: 192.0786, found 192.0772.

5-(Pent-4-enyloxy)benzo[1,3]dioxole (1j). Yield: 72%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.68 (1H, d, J = 8), 6.49 (1H, d, J = 2.5), 6.32 (1H, dd, J = 8, 2.5), 5.90 (2H, s), 5.85 (1H, ddt, J = 17, 10, 6.5), 4.95−5.11 (2H, m), 3.89 (2H, t, J = 6.5), 2.15−2.28 (2H, m), 1.85 (2H, tt, J = 6.5, 7.5). ^{13}C NMR (62 MHz, $CDCl_3$): δ 154.63, 148.22, 141.54, 137.82, 115.11, 107.90, 105.80, 101.04, 98.13, 68.20, 30.08, 28.48. IR (film): ν 3079, 2880, 2774, 1634, 1473, 1186, 1040. MS m/z (rel intensity): 206 (M^+, 40), 192 (30), 139 (15), 138 (100), 137 (75), 121 (8), 107 (17). HRMS m/z calcd for $C_{12}H_{14}O_3$: 206.0943, found 206.0933.

5-((3-Methylbut-3-enyl)oxy)benzo[1,3]dioxole (1k). Yield: 57%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.69 (1H, d, J = 8.5), 6.49 (1H, d, J = 2.5), 6.33 (1H, dd, J = 8.5, 2.5), 5.90 (2H, s), 5.19 (1H, t/sep, J = 7, 1.5), 3.85 (2H, t, J = 7), 2.44 (2H, q, J = 7), 1.73 (3H, s), 1.65 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 154.57, 148.21, 141, 134.30, 119.63, 107.90, 105.83, 101.04, 98.16, 68.67, 28.30, 17.82. IR (film): ν 2973, 2880, 1630, 1190, 1040. MS m/z (rel intensity): 220 (M^+, 25), 139 (15), 138 (100), 137 (30), 121 (7), 107 (7). HRMS m/z calcd for $C_{13}H_{16}O_3$: 220.1099, found 220.1103.

3-(But-3-enyloxy)-1,6-dimethoxybenzene (1l). Yield: 69%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.77 (1H, d, J = 8.5), 6.52 (1H, d, J = 2.5), 6.41 (1H, dd, J = 8.5, 2.5), 5.91 (2H, s), 5.90 (1H, ddt, J = 17, 10, 6.5), 5.08−5.22 (2H, m), 3.97 (2H, t, J = 6.5), 3.85 (3H,s), 3.83 (3H, s), 2.53 (2H, tq, J = 1.5, 6.5). ^{13}C NMR (62 MHz, $CDCl_3$): δ 153.60, 149.95, 143.59, 134.50, 116.85, 112.09, 104.05, 101.14, 67.79, 55.49, 55.80, 33.70. IR (film): ν 3075, 2936, 2836, 1597, 1516, 1229, 1028. MS m/z (rel intensity): 208 (M^+, 100), 182 (11), 167 (6), 154 (98), 139 (88), 125 (22), 120 (18), 118 (18), 111 (21). HRMS m/z calcd for $C_{12}H_{16}O_3$: 208.1099, found 208.1109.

Irradiation of Compounds 1a−l. Solutions (16 mL) of 0.5 mmol of **1** and 0.1 mmol of H_2SO_4 were irradiated at λ = 254 nm (Rayonet, T = 35 °C). After 4 h, the reaction was stopped and $NaHCO_3$ was added to the solution. After evaporation of the solvent, the residue was purified by flash silica gel chromatography with petroleum ether/ethyl acetate.

8-(2-Hydroxyethyl)bicyclo[4.2.0]octa-1,3,5-trien-3-ol (2a). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.9 (1H,s), 6.83 (1H, d, J = 8), 6.60−6.68 (2H, m), 3.65−3.76 (3H, m), 3.40−3.55 (1H, m), 3.18 (1H, dd, J = 5.5, 13.5), 2.64 (1H, dd, J = 2.5, 13.5), 1.87 (2H, q, J = 6.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 157.59, 151.03, 134.33, 124.52, 115.23, 110.40, 61.43, 40.29, 38.52, 35.50. IR (KBr): ν 3387, 3048, 2923, 1591, 1454, 1366, 1015. MS m/z (rel intensity): 164 (M^+, 74), 145 (30), 133 (100), 131 (53), 120 (37), 115 (46), 107 (40), 105 (80), 103 (42). HRMS m/z calcd for $C_{10}H_{12}O_2$: 164.0837, found 164.0825.

7-(2-Hydroxyethyl)bicyclo[4.2.0]octa-1,3,5-trien-2-ol (3a). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.05 (1H, t, J = 8.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 129.30, 114.83, 114.50, 40.59, 34.59.

8-(3-Hydroxypropyl)bicyclo[4.2.0]octa-1,3,5-trien-3-ol (2b). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.0 (1H,s), 6.85 (1H, d, J = 7.5), 6.57−6.70 (2H, m), 3.55−3.75 (3H, m), 3.16 (1H, m), 3.10−3.27 (2H, m), 2.58 (1H, t, J = 13), 1.65−1.78 (4H, m) ^{13}C NMR (62 MHz, CD_3COCD_3): δ 157.54, 151.33, 134.23, 124.54, 115.20, 110.22, 62.51, 43.08, 35.41, 32.13, 31.63. IR (film): ν 3324, 2924, 2851, 1591, 1466, 1253, 1053. MS m/z (rel intensity): 178 (M^+, 55), 163 (19), 161 (10), 159 (8), 147 (74), 145 (40), 134 (33), 133 (60), 132 (100), 131 (40), 127 (19), 121 (25), 119 (27), 117 (16), 115 (32), 107 (40), 105 (35), 103 (23). HRMS m/z calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.0972.

7-(3-Hydroxypropyl)bicyclo[4.2.0]octa-1,3,5-trien-2-ol (3b). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.30 (1H, s), 7.01 (1H, t, J = 8), 2.64 (1H, d, J = 12.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 129.24, 127.84, 114.82, 114.34, 62.51, 43.42, 34.50.

8-(2-Hydroxyethyl)-8-methylbicyclo[4.2.0]octa-1,3,5-trien-3-ol (2c). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.93 (1H,s), 6.85 (1H, d, J = 8), 6.64 (1H, dd, J = 8, 2.5), 6.59 (1H, d, J = 2.5), 3.64 (2H, q, J = 6.5), 3.42 (1H, t, J = 5), 2.95 (1H, d, J = 13), 2.72 (1H, d, J = 13), 1.92 (1H, t, J = 6.5), 1.91 (1H, t, J = 6.5), 1.37 (3H, s). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 157.54, 155.08, 132.04, 125.22, 115.49, 113.87, 109.08, 60.23, 43.26 (2), 35.41, 24.91. IR (film): ν 3349, 2953, 2921, 1597, 1466, 1366, 1265, 1204, 1053. MS m/z (rel intensity): 178 (M^+, 65), 163 (30), 160 (50), 147 (69), 145 (100), 135 (22), 133 (37), 132 (50), 131 (46), 121 (22), 119 (27), 117 (50), 115 (35),

107 (66), 105 (25), 103 (27). HRMS *m*/*z* calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.0995.

7-(2-Hydroxyethyl)-7-methylbicyclo[4.2.0]octa-1,3,5-trien-2-ol (3c). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.2 (1H, s), 7.01 (1H, t, J = 7.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 46.57.

8,8-Dimethyl-7-(2-hydroxyethyl)bicyclo[4.2.0]octa-1,3,5-trien-2-ol (3d). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.9 (1H,s), 6.97 (1H, dd, J = 7.5, 8.5), 6.61 (1H, d, J = 7.5), 6.59 (1H, d, J = 8.5), 3.70−3.82 (3H, m), 3.10 (1H, t, J = 7.5), 1.85−1.97 (1H, m), 1.65−1.80 (1H, m), 1.45 (3H, s), 1.34 (3H, s). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 151.60, 148.62, 129.13, 115.32, 114.95, 61.75, 51.68, 46.58, 34.12, 27.51, 21.91. IR (KBr): ν 3438, 3148, 2948, 1593, 1454, 1263, 1014. MS *m*/*z* (rel intensity): 192 (M^+, 24), 177 (19), 161 (17), 159 (50), 147 (52), 135 (30), 133 (100), 131 (70), 128 (22), 121 (23), 115 (32), 110 (22), 107 (39), 105 (22), 103 (17). HRMS *m*/*z* calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1155.

8,8-Diethyl-7-(2-hydroxyethyl)bicyclo[4.2.0]octa-1,3,5-trien-2-ol (3e). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.9 (1H,s), 6.83 (1H, dd, J = 7.5, 8.), 6.43−6.52 (2H, m), 3.59−3.70 (2H, m), 3.54 (1H, t, J = 5), 3.02 (1H, dd, J = 5.5, 10), 1.42−1.88 (6H, m), 0.96 (3H, t, J = 7.5), 0.78 (3H, t, J = 7.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 151.95, 149.63, 136.58, 128.97, 115.29, 114.76, 61.92, 55.41, 49.33, 33.80, 25.85, 10.36, 9.89. IR (KBr): ν 3538, 3212, 2961, 2880, 1591, 1455, 1291, 1010. MS *m*/*z* (rel intensity): 220 (M^+, 37), 191 (20), 176 (29), 173 (60), 161 (50), 159 (37), 147 (100), 145 (96), 133 (48), 131 (43), 128 (40), 119 (16), 117 (25), 115 (50), 107 (33), 105 (22), 103 (13). HRMS *m*/*z* calcd for $C_{14}H_{20}O_2$: 220.1463, found 220.1461.

8-(2-Hydroxyethyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-triene (2f). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.99 (1H, d, J = 8), 6.78 (1H, dd, J = 8, 2), 6.72 (1H, d, J = 2), 3.82 (2H, t, J = 7), 3.78 (3H, s), 3.48−3.60 (1H, m), 3.10 (1H, dd, J = 5, 13), 2.73 (1H, dd, J = 13, 2.5), 1.99 (2H, q, J = 7), 1.8 (1H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.18, 149.69, 135.07, 123.92, 113. 65, 108.08, 61.66, 55.41, 39.34, 37.12, 35.02. IR (film): ν 3349, 2923, 2836, 1605, 1476, 1273, 1167, 1030. MS *m*/*z* (rel intensity): 178 (M^+, 49), 163 (11), 159 (10), 149 (23), 147 (100), 145 (15), 135 (20), 132 (23), 122 (22), 117 (24), 115 (44), 107 (17), 104 (27), 103 (32). HRMS *m*/*z* calcd for $C_{11}H_{14}O_2$: 178.0934, found 178.0970.

7-(2-Hydroxyethyl)-2-methoxybicyclo[4.2.0]octa-1,3,5-triene (3f). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.14 (1H, t, J = 7.5), 3.88 (3H, s), 2.90 (1H, dd, J = 2, 13), 2.00 (2H, q, J = 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 128.55, 114.66, 113.10, 55.99, 40.19, 35.68.

8-(3-Hydroxypropyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-triene (2g). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.95 (1H, d, J = 8), 6.73 (1H, dd, J = 8, 2.5), 6.66−6.71 (1H, m), 3.75 (3H, s), 3.62−3.70 (2H, m), 3.33−3.46 (1H, m), 3.23 (1H, dd, J = 13.5, 5), 2.65 (1H, dd, J = 13.5, 2.5), 2.0 (1H, s), 1.70−1.80 (4H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.08, 150.09, 135.07, 123.86, 113.50, 107.96, 62.68, 55.37, 42.28, 34.99, 31.14, 30.42. IR (film): ν 3399, 2932, 2851, 1604, 1480, 1271, 1167, 1057. MS *m*/*z* (rel intensity): 192 (M^+, 100), 177 (44), 161 (87), 159 (39), 148 (46), 147 (76), 146 (74), 135 (40), 131 (42), 121 (51), 115 (48), 105 (28), 103 (48). HRMS *m*/*z* calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1135.

7-(3-Hydroxypropyl)-2-methoxybicyclo[4.2.0]octa-1,3,5-triene (3g). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.10 (1H, t, J = 8), 3.84 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 129.28, 114.54, 113.03, 55.95, 43.13, 35.67.

3-Methoxy-4-(3-methoxyphenyl)butan-1-ol (4f) (R^3 = Me). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.19 (1H, dd, J = 7, 9), 6.71−6.81 (3H, m) 3.80 (3H, s), 3.70−3.79 (2H, m), 3.56−3.70 (1H, m), 3.39 (3H, s), 2.95 (1H, dd, J = 13, 5.5), 2.68 (1H, dd, J = 13, 7), 2.65 (1H, s), 1.58−1.81 (2H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.61, 139.89, 129.29, 121.78, 115.31 111.40, 82.01, 60.76, 56.99, 55.10, 39.84, 35.74. IR (film): ν 3412, 2940, 2836, 1603, 1489, 1261, 1051. MS *m*/*z* (rel intensity): 210 (M^+, 100), 178 (32), 165 (34), 161 (48), 147 (47), 135 (42), 121 (94), 120 (69), 117 (19), 115 (30), 107 (26), 105 (31), 103 (27). HRMS *m*/*z* calcd for $C_{12}H_{18}O_3$: 210.1255, found 210.1230.

3-Ethoxy-4-(3-methoxyphenyl)butan-1-ol (4f) (R^3 = Et). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20 (1H, dd, J = 7, 8.5), 6.72−6.82 (3H, m), 3.68−3.80 (3H, s), 3.59 (1H, dq, J = 9, 7), 2.94 (1H, dd, J = 13.5, 5.5), 2.76 (1H, s), 2.68 (1H, dd, J = 13.5, 7), 1.60−1.80 (2H, m), 1.18 (3H, t, J = 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.53, 140.01, 129.21, 121.76, 115.22 111.37, 80.47, 64.84, 60.91, 55.06, 55.10, 40.53, 35.93, 15.48.

3-Hydroxy-4-(3-methoxyphenyl)butan-1-ol (4f) (R^3 = H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.22 (1H, dt, J = 1.5, 7.5), 6.74−6.83 (3H, m), 4.02−4.14 (1H, m), 3.75−3.93 (2H, m), 3.79 (3H, s), 2.78 (1H, dd, J = 14, 5.5), 2.77 (1H, dd, J = 8, 14), 2.35 (2H, s), 1.65−1.85 (2H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.80, 139.61, 129.56, 121.67, 115.13 111.91, 72.74, 61.53, 55.12, 44.35, 37.87.

4-Methoxy-5-(3-methoxyphenyl)pentan-1-ol (4g). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.19 (1H, dd, J = 7.5, 8.5), 6.70−6.81 (3H, m) 3.78 (3H, s), 3.58 (2H, t, J = 6), 3.35−3.46 (1H, m), 3.33 (3H, s), 2.87 (1H, dd, J = 14, 6), 2.66 (1H, dd, J = 14, 7), 2.40 (1H, s), 1.41−1.78 (4H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.46, 140.29, 129.12, 121.67, 115.14 111.25, 82.14, 62.63, 56.78, 55.99, 39.84, 29.99, 28.51. IR (film): ν 3399, 2936, 1603, 1489, 1262, 1154, 1055. MS *m*/*z* (rel intensity): 244 (M^+, 21), 192 (96), 165 (31), 161 (38), 147 (32), 138 (30), 122 (100), 121 (73), 115 (24), 107 (22), 105 (27), 103 (97). HRMS *m*/*z* calcd for $C_{13}H_{20}O_3$: 224.1412, found 224.1441.

4-(Benzo[1,3]dioxol-5-yl)-3-methoxybutan-1-ol (4i). ^{1}H NMR (250 MHz, C_6D_6): δ 6.67 (1H, d, J = 1.5), 6.64 (1H, d, J = 8), 6.49 (1H, dd, J = 1.5, 8), 5.40 (2H, s), 3.64 (1H, dt, J = 11, 6), 3.59 (1H, dt, J = 11, 6), 3.36 (1H, p, J = 6), 3.06 (3H, s), 2.63 (1H, dd, J = 6, 14), 2.50 (1H, s), 2.47 (1H, dd, J = 6, 14), 1.55 (2H, q, J = 6). ^{13}C NMR (62 MHz, C_6D_6): δ 148.08, 146.47, 132.81, 122.70, 110.21, 108.31, 100.81, 81.27, 60.04, 56.65, 39.85, 36.44. IR (film): ν 3399, 2934, 2890, 1608, 1491, 1246, 1040. MS *m*/*z* (rel intensity): 244 (M^+, 12), 206 (35), 192 (17), 138 (100), 137 (45), 135 (42), 118 (10), 116 (11), 107 (10). HRMS *m*/*z* calcd for $C_{12}H_{16}O_4$: 224.1049, found 224.1049.

5-(Benzo[1,3]dioxol-5-yl)-4-methoxypentan-1-ol (4j). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.71 (1H, d, J = 7.5), 6.69 (1H, d, J = 1.5), 6.63 (1H, dd, J = 1.5, 7.5), 5.93 (2H, s), 3.60 (2H, t, J = 6), 3.23−3.41 (1H, m), 3.33 (3H, s), 2.80 (1H, dd, J = 6, 14), 2.62 (1H, dd, J = 7, 14), 2.49 (1H, s), 1.40−1.71 (4H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.43, 145.81, 132.31, 122.14, 109.62, 108.02, 100.69, 82.32, 62.71, 56.83, 39.34, 29.91, 28.49.

4-(3,4-Dimethoxyphenyl)-3-methoxybutan-1-ol (4l). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.70−6.83 (3H, m), 3.87 (3H, s), 3.85 (3H, s), 3.70−3.79 (2H, m), 3.52−3.65 (1H, m), 2.90 (1H, dd, J = 6, 14), 2.65 (1H, dd, J = 7, 14), 2.35 (1H, s, broad), 1.59−1.81 (2H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 148.80, 147.54, 130.88, 121.33, 112.73, 111.28, 82.11, 60.72, 57.03, 55.83 (2), 39.39, 35.68. IR (film): ν 3426, 2936, 2836, 1591, 1520, 1265, 1142. MS *m*/*z* (rel intensity): 240 (M^+, 67), 195 (13), 165 (10), 152 (40), 151 (100), 138 (15), 137 (15), 120 (17), 118 (17), 107 (17). HRMS *m*/*z* calcd for $C_{13}H_{20}O_4$: 240.1362, found 240.1365.

2-(3-Methoxybenzyl)tetrahydrofuran (5g). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.19 (1H, t, J = 8), 6.7−6.85 (3H, m), 4.06 (1H, p, J = 6.5), 3.83−3.94 (1H, m), 3.78 (3H, s), 3.67−3.77 (1H, m), 3.89 (1H, dd, J = 13.5, 6.5), 1.75−2.00 (3H, m), 1.47−1.62 (1H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.51, 140.49, 129.15, 121.53, 114.90, 111.40, 79.85, 67.83, 55.00, 41.88, 30.93, 25.51. IR (film): ν 3426, 2944, 2867, 1603, 1489, 1260, 1061. MS *m*/*z* (rel intensity): 192 (M^+, 100), 181 (7), 169 (6), 147 (7), 134 (11), 131 (12), 124 (79), 122 (42), 121 (62), 115 (11), 107 (14), 103 (9). HRMS *m*/*z* calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1170.

5-(Tetrahydrofuran-2-ylmethyl)benzo[1,3]dioxole (5j). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.63−6.75 (3H, m), 5.90 (2H, s), 3.93−4.06 (1H, m), 3.82−3.93 (1H, m), 3.67−3.78 (1H, m), 2.80 (1H, dd, J = 14, 6.5), 2.67 (1H, dd, J = 14, 6), 1.77−1.98 (3H, m), 145−1.60 (1H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.47, 145.85, 132.76, 121.96, 109.59, 108.03, 100.67, 80.04, 67.83, 41.50, 30.86, 25.54. IR (film): ν 2861, 1489, 1248, 1040. MS *m*/*z* (rel intensity): 206 (M^+, 30), 192 (19), 138 (100), 137 (48), 135 (19), 107 (10). HRMS *m*/*z* calcd for $C_{12}H_{14}O_3$: 206.0943, found 206.0942.

2-(2,4-Dihydroxybenzyl)tetrahydrofuran (5j) (X = OR = OH). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.58 (1H, dd, J = 8, 2), 4.02 (1H, p, J = 6.5), 3.81−3.93 (1H, m), 3.64−3.77 (1H,

m), 2.61 (1H, dd, J = 14, 6.5), 1.75−1.97 (3H, m). ^{13}C NMR (62 MHz, $CDCl_3$): δ 144, 142.61, 130.97, 120.89, 115.98, 114.88, 80.25, 67.73, 41.06, 30.75, 25.44.

3-(2,2-Dimethyltetrahydrofuran-3-yl)phenol (6d). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.12 (1H, t, J = 8), 6.68−6.80 (3H, m), 3.96 (1H, dt, J = 4, 8.5), 3.83 (1H, dd, J = 7.5, 8.5), 3.00 (1H, t, J = 4), 2.17−2.43 (2H, m), 1.26 (3H, s), 0.80 (3H, s). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 158.07, 143.27, 129.81, 120.29, 116.07, 114.26, 82.79, 55.07, 32.30, 28.17, 23.89. IR (KBr): ν 2973, 2886, 1618, 1588, 1285, 1136, 1024. MS m/z (rel intensity): 192 (M^+, 23), 177 (23), 161 (17), 149 (20), 147 (27), 135 (70), 134 (98), 133 (100), 121 (32), 119 (67), 117 (79), 116 (40), 115 (41), 111 (27), 107 (87), 105 (74), 103 (32). HRMS m/z calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1135.

3-(2,2-Diethyltetrahydrofuran-3-yl)phenol (6e). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.12 (1H, dd, J = 7.5, 9.5), 6.68−6.78 (3H, m), 4.08 (1H, dt, J = 4.5, 8.5), 3.92 (1H, q, J = 8.5), 3.20 (1H, t, J = 8), 2.20−2.43 (2H, m), 1.72 (1H, dq, J = 14.5, 7.5), 1.56 (1H, dq, J = 14.5, 7.5), 1.41 (1H, dq, J = 14.5, 7.5), 1.10 (1H, dq, J = 14.5, 7.5), 0.96 (3H, t, J = 7.5), 0.67 (3H, t, J = 7.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 155.99, 142.87, 129.12, 120.66, 115.28, 113.51, 87.77, 65.29, 50.21, 32.41, 27.66, 26.62, 7.98, 7.90. IR (film): ν 3299, 2969, 2880, 1599, 1462, 1151, 1044. MS m/z (rel intensity): 220 (M^+, 6), 191 (10), 134 (100), 133 (41), 124 (30), 117 (12), 107 (15). HRMS m/z calcd for $C_{14}H_{20}O_2$: 220.1463, found 220.1461.

2,2-Dimethyl-3-(3-methoxyphenyl)tetrahydrofuran (6h). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.22 (1H, dd, J = 9, 7.5), 6.75−6.86 (3H, m), 4.05 (1H, dt, J = 4, 8), 3.93 (1H, q, J = 8), 3.80 (3H, s), 3.04 (1H, dd, J = 8, 9.5), 2.22−2.45 (2H, m), 1.30 (3H, s), 0.86 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.45, 142.09, 129.07, 120.73, 114.43, 111.45, 82.55, 64.98, 55.16, 54.40, 31.67, 27.79, 23.41. IR (film): ν 2971, 2880, 1601, 1493, 1157, 1046. MS m/z (rel intensity): 206 (M^+, 25), 191 (9), 161 (10), 149 (27), 148 (100), 147 (52), 133 (35), 121 (21), 117 (65), 105 (74). HRMS m/z calcd for $C_{13}H_{18}O_2$: 206.1307, found 206.1305.

3-(Benzo[1,3]dioxol-5-yl)-2,2-dimethyltetrahydrofuran (6k). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.62−6.78 (3H, m), 5.93 (2H, s), 3.97−4.08 (1H, m), 3.91 (1H, q, J = 8), 2.98 (1H, t, J = 9), 2.20−2.34 (2H, m), 1.30 (3H, s), 0.85 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.46, 146.16, 134.22, 121.21, 108.39, 107.84, 100.80, 82.35, 64.74, 54.05, 31.85, 27.57, 23.25. IR (film): ν 2971, 2886, 1505, 1238, 1042. MS m/z (rel intensity): 220 (M^+, 28), 162 (95), 138 (100), 132 (32), 130 (29), 104 (39). HRMS m/z calcd for $C_{13}H_{16}O_3$: 220.1099, found 220.1093.

3-(3-Hydroxyphenyl)-4-methylpent-4-en-1-ol (7d). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.15 (1H, s), 7.10 (1H, t, J = 8), 6.64−6.75 (3H, m), 4.92 (1H, s), 4.80 (1H,s), 3.44−3.57 (2H, m), 3.40 (2H, t, J = 7.5), 1.80−2.12 (2H, m), 1.55 (3H, s). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 158.27, 148.91, 146.00, 129.94, 119.96, 115.64, 114.04, 110.47, 60.64, 49.36, 36.98, 21.38. IR (film): ν 3324, 3085, 2946, 1590, 1455, 1265, 1042. MS m/z (rel intensity): 192 (M^+, 87), 161 (62), 159 (46), 148 (66), 147 (100), 145 (36), 133 (54), 131 (41), 121 (37), 115 (28), 107 (67), 103 (26). HRMS m/z calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1126.

4-Ethyl-3-(3-hydroxyphenyl)hex-4-en-1-ol (7e). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.15 (1H, s, broad), 7.0−7.12 (1H, m), 6.60−6.76 (3H, m), 5.41 (1H, q, J = 7, cis isomer), 5.32 (1H, tq, J = 1.5, 7, trans isomer), 4.15 (1H, dd, J = 6.5, 9), 3.35−3.64 (3H, m), 3.1 (1H, s, broad), 1.66−2.16 (4H, m), 1.79 (3H, dt, J = 7, 1.5, trans isomer), 1.63 (3H, d, J = 7, cis isomer), 0.84 (3H, t, J = 7.5, trans isomer), 0.82 (3H, t, J = 7.5, cis isomer). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 158.16, 146.94 (cis isomer), 146.47 (trans isomer), 145.25, 129.94, 119.78, 120.24 (cis isomer), 119.76 (trans isomer), 118.39, 115.85 (cis isomer), 115.73 (trans isomer), 60.82, 48.35, 41.57, 37.66 (cis isomer), 35.03 (trans isomer). IR (film): ν 3337, 2963, 2876, 1694, 1590, 1455, 1030. MS m/z (rel intensity): 220 (M^+, 100), 191 (9), 189 (8), 187 (13), 176 (26), 175 (46), 173 (25), 161 (17), 159 (18), 147 (40), 145 (21), 133 (45), 120 (62), 119 (74), 118 (65), 117 (75), 110 (20), 107 (32). HRMS m/z calcd for $C_{14}H_{20}O_2$: 220.1463, found 220.1466.

3-(3-Methoxyphenyl)-4-methylpent-4-en-1-ol (7h). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.19 (1H, t, J = 7.5), 6.63−6.85 (3H, m), 4.93 (1H, s), 4.85 (1H,s), 3.78 (3H, s), 3.58 (2H, t, J = 6.5), 3.56 (1H, t, J = 6.5), 3.38 (1H, t, J = 7.5), 2.09 (1H, p, J = 7), 1.89−2.02 (1H, m), 1.85 (1H, s), 1.59 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.61, 147.56, 144.70, 129.18, 120.26, 113.75, 111.37, 110.47, 61.06, 55.05, 48.92, 35.70, 20.96. IR (film): ν 3362, 2946, 2838, 1607, 1485, 1264, 1046. MS m/z (rel intensity): 206 (M^+, 100), 175 (60), 173 (44), 161 (98), 160 (70), 147 (56), 135 (45), 129 (23), 121 (43), 115 (31), 105 (19). HRMS m/z calcd for $C_{13}H_{18}O_2$: 206.1307, found 206.1306.

3-(Benzo[1,3]dioxol-5-yl)-4-methylpent-4-en-1-ol (7k). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.65−6.77 (3H, m), 5.93 (2H, s), 4.92 (1H, s), 4.86 (1H,s), 3.50−3.65 (2H, m), 3.33 (1H, t, J = 7.5), 2.09 (1H, dq, J = 7, 14), 1.83−1.98 (1H, m), 1.60 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.86, 147.56, 145.99, 136.92, 120.85, 110.28, 107.96 (2), 100.79, 61.13, 48.59, 35.93, 21.00. IR (film): ν 3374, 2967, 2890, 1645, 1611, 1487, 1248, 1044. MS m/z (rel intensity): 220 (M^+, 100), 179 (62), 175 (62), 159 (27), 149 (51), 145 (98), 135 (64), 131 (47), 117 (52).

3-(3-Hydroxyphenyl)-4-methoxy-4-methylpentan-1-ol (8d). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.20 (1H, s), 7.07 (1H, t, J = 8), 6.78−6.81 (1H, m), 6.75 (1H, d, J = 8), 6.65 (1H, ddd, J = 8, 2.5, 1), 3.63 (1H, s), 3.20−3.48 (2H, m), 3.19 (3H, s), 2.82 (1H, dd, J = 11.5, 1.5), 2.03−2.21 (1H, m), 1.81−1.98 (1H, m), 1.05 (6H, s). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 157.71, 144.60, 129.38, 121.84, 117.45, 114.01, 77.20, 61.35, 51.52, 49.08, 33.27, 24.10, 22.76. IR (KBr): ν 3287, 3162, 2951, 1586, 1483, 1281, 1134, 1069. MS m/z (rel intensity): 224 (M^+, 10), 181 (10), 177 (18), 175 (27), 159 (16), 147 (27), 133 (45), 131 (47), 121 (79), 120 (73), 119 (47) 115 (30), 111 (24), 107 (100), 105 (32), 103 (44). HRMS m/z calcd for $C_{13}H_{20}O_3$: 224.1412, found 224.1422.

4-Ethyl-3-(3-hydroxyphenyl)-4-methoxyhexan-1-ol (8e). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.06 (1H, t, J = 8), 6.83 (1H, t, J = 2.5), 6.78 (1H, dt, J = 8, 2.5), 6.68 (1H, ddd, J = 1, 2.5, 8), 3.30−3.35 (2H, m), 3.22 (3H, s), 3.10 (1H, dd, J = 2.5, 12), 2.93 (1H, dd, J = 2.5, 12), 2.06−2.20 (1H, m), 1.90 (1H, dddd, J = 4, 6.5, 12, 13), 1.40−1.75 (4H, m), 0.83 (3H, t, J = 7.5), 0.78 (3H, t, J = 7.5). ^{13}C NMR (62 MHz, CD_3COCD_3): δ 157.81, 144.66, 129.35, 122.21, 117.80, 113.95, 80.48, 61.26, 49.71, 48.96, 34.09, 27.42, 27.29, 9.07, 8.86. IR (film): ν 3349, 2946, 2886, 1587, 1455, 1258, 1051. MS m/z (rel intensity): 252 (M^+, 10), 222 (35), 220 (100), 191 (67), 175 (76), 173 (55), 161 (40), 147 (82), 145 (54), 133 (90), 121 (76), 107 (92). HRMS m/z calcd for $C_{15}H_{24}O_3$: 252.1725, found 252.1713.

4-Methoxy-3-(3-methoxyphenyl)-4-methylpentan-1-ol (8h). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.17 (1H, t, J = 7), 6.71−6.85 (3H, m), 3.78 (3H, s), 3.49 (1H, ddd, J = 5, 7, 11.5), 3.36 (1H, ddd, J = 6, 8, 11.5), 3.22 (3H, s), 2.82 (1H, dd, J = 4, 10.5), 2.33 (1H, s), 2.15 (1H, dddd, J = 4, 7, 8, 13.5), 1.92 (1H, dddd, J = 5, 6, 10.5, 13.5), 1.11 (3H, s), 1.05 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.15, 143.46, 128.65, 122.05, 115.66, 111.25, 76.87, 61.38, 54.96, 51.39, 48.89, 32.58, 23.75, 21.81. IR (film): ν 3387, 2942, 2834, 1601, 1487, 1256, 1049. MS m/z (rel intensity): 238 (M^+, 35), 221 (72), 207 (100), 189 (75), 175 (32), 166 (31), 145 (34), 135 (90), 121 (42), 115 (47), 105 (50). HRMS m/z calcd for $C_{14}H_{22}O_3$: 238.1569, found 238.1552.

3-(Benzo[1,3]dioxol-5-yl)-4-methoxy-4-methylpentan-1-ol (8k). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.77 (1H, d, J = 1.5), 6.71 (1H, d, J = 8), 6.66 (1H, dd, J = 1.5, 8), 5.91 (2H, s), 3.52 (1H, ddd, J = 5, 6.5, 10.5), 3.38 (1H, ddd, J = 6, 8.5, 10.5), 3.22 (3H, s), 2.76 (1H, dd, J = 4, 11), 2.14 (1H, dddd, J = 4, 6.5, 8.5, 14), 1.96 (1H, s), 1.87 (1H, dddd, J = 5, 6, 11, 14), 1.08 (3H, s), 1.06 (3H, s). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.28, 146.02, 135.64, 122.80, 109.50, 107.67, 100.76, 77.00, 61.57, 51.33, 49.05, 32.80, 23.78, 21.86. IR (film): ν 3399, 2973, 2888, 2830, 1611, 1487, 1244, 1040. MS m/z (rel intensity): 252 (M^+, 94), 205 (17), 203 (17), 180 (86), 176 (20), 173 (19), 165 (47), 161 (18), 149 (67), 148 (97), 147 (91), 135 (100), 118 (45), 103 (34). HRMS m/z calcd for $C_{14}H_{22}O_4$: 252.1362, found 252.1380.

3-(Benzo[1,3]dioxol-5-yl)-4-methylpentan-1-ol (9k). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.88 (3H, d, J = 6.5), 0.65 (3H, d, J = 7). ^{13}C NMR (62 MHz, $CDCl_3$): δ 147.53, 137.72, 121.42, 108.18, 100.71, 61.49, 49.30, 36.05, 33.59, 20.88, 20.62.

3-(3,4-Dimethoxyphenyl)butan-1-ol (9l). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.71−6.85 (3H, m), 3.87 (3H, s), 3.85 (3H, s),

3.50−3.62 (1H, m), 2.83 (1H, sex, J = 6.5), 1.82 (2H, q, J = 6.5), 1.65 (1H, s, broad), 1.26 (3H, d, J = 6.5). ^{13}C NMR (62 MHz, $CDCl_3$): δ 149.00, 147.37, 139.61, 118.70, 111.43, 110.40, 61.16, 55.89, 55.84, 41.09, 36.09, 22.47. IR (film): ν 3426, 2961, 2837, 1593, 1520, 1264, 1144, 1032. MS m/z (rel intensity): 210 (M^+, 62), 179 (10), 166 (31), 165 (100), 151 (30), 145 (16), 135 (18), 121 (21), 105 (10), 103 (11). HRMS m/z calcd for $C_{12}H_{18}O_3$: 210.1256, found 210.1257.

Fluorescence Studies. The spectra were acquired in a 1 cm path length cuvette using a Perkin-Elmer LS 50 luminescence spectrometer. λ_{ex} = 274 nm, λ_{em} = 306 nm. Methanolic solutions of 30.8 mmol/L of **1f** and 27.8 mmol/L of 1,3-dimethoxybenzene were messured in absence and presence of H_2SO_4 (103 mmol/L).

Quantification of the Influence of Acid on the Rate of Conversion. Methanolic solutions (16 mL) of 0.5 mmol of **1f** and different concentrations of H_2SO_4 were irradiated at λ = 254 nm (Rayonet, T = 35 °C). After 2.5 h, the reaction had stopped. A methanolic solution containing 3.3 mg of 1,3-dimethoxybenzene was added (internal standart). The solutions were then treated with $NaHCO_3$ and evaporated. A mixture of ethyl acetate and petroleum ether (1/1) was added. The resulting mixture was filtred with silica gel (eluent, petroleum ether/ethyl acetate 1/1). The samples were analyzed by GC: HP 6890 series (Hewlett-Packard); column, HP-1 (cross-linked methylsiloxane: 30 m × 0.25 mm × 0.25 mm film thickness).

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Supporting Information Available: ^{13}C NMR sprecta of all described compounds and mixtures of compounds (41 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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