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Photochemical Formation and Chemistry of Long-Lived Adamantylidene-Quinone Methides and 2-Adamantyl Cations

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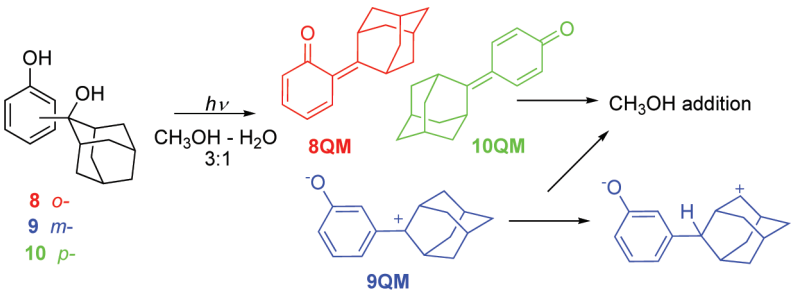
Received September 16, 2009



Hydroxymethylphenols strategically substituted with the 2-hydroxy-2-adamantyl moiety, AdPh **8**-**10**, were synthesized, and their photochemical reactivity was investigated. On excitation to the singlet excited state, AdPh **8** undergoes intramolecular proton transfer coupled with a loss of H_2O giving quinone methide **8QM**. The presence of **8QM** has been detected by laser flash photolysis (CH_3CN-H_2O 1:1, τ = 0.55 s) and UV−vis spectroscopy. Singlet excited states of AdPh **9** and **10** in the presence of H_2O dehydrate giving **9QM** and **10QM**. Photochemically formed QMs are trapped by nucleophiles giving the addition products (e.g., Φ for methanolysis of **8** is 0.55). In addition, the zwitterionic **9QM** undergoes an unexpected rearrangement involving transformation of the 2-phenyl-2-adamantyl cation into the 4-phenyl-2-adamantyl cation ($\Phi \sim 0.03$). An analogous rearrangement was observed with methoxy derivatives **9a** and **10a**. Zwitterionic **9QM** was characterized by LFP in 2,2,2-trifluoroethanol (τ = 1 μs). In TFE, in the ground state, AdPh **10** is in equilibrium with **10QM**, which allowed for recording the ^{1}H and ^{13}C NMR spectra of the QM. Introduction of the adamantyl substituent into the *o*-hydroxymethylphenol moiety increased the quantum yield of the associated QM formation by up to 3-fold and significantly prolonged their lifetimes. Furthermore, adamantyl substituent made the study of the alkyl-substituted quinone methides easier by LFP by prolonging their lifetimes and increasing the quantum yields of formation.

Introduction

Quinone methides (QM) are ubiquitous intermediates in chemistry and biology.[1] The polar nature of these compounds makes them both nucleophilic and electrophilic. Consequently, they are very reactive and therefore usually short-lived. The most common reaction of QMs is with nucleophilic solvent (e.g., water) wherein they behave as Michael systems (e.g., eq 1). Nucleophiles add to the methylene position of QMs, and the driving force of the reaction is the resulting rearomatization of the molecule. Recently, a thorough DFT computational study has been performed to explain the reactivity of QMs as Michael electrophiles with sulfur, nitrogen, and oxygen nucleophiles[2] and pyrimidine bases.[3] In addition, QMs react as dienophiles in [4 + 2]

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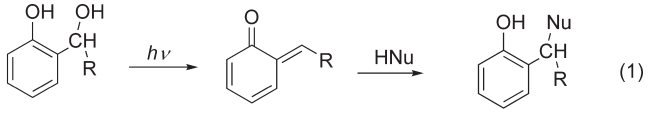
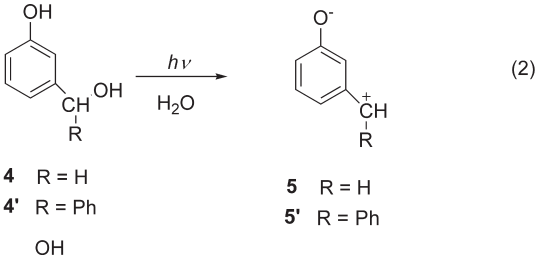
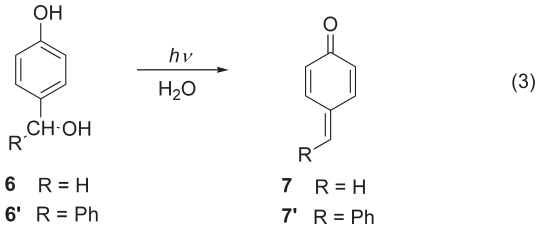
Published on Web 12/03/2009 DOI: 10.1021/jo902004n

cycloadditions, so they have been used as valuable precursors in synthesis.[4]

QMs can be generated in thermal reactions by oxidation of phenols,[5] extrusion of water,[6] or other small molecules from hydroxybenzyl alcohols[7] and fluoride-induced desilylation.[8] The other approach for the generation of QMs under mild conditions is the use of photochemical reactions.[9] Wan et al. developed a general photochemical method for the generation of QMs by dehydration of hydroxymethylphenols (e.g., eqs 1−3).[10,11] The other photochemical methods use Mannich bases,[12] tertiary ammonium derivatives of phenols,[13] or hydroxybenzyl acetate derivatives.[14] Although quantum yields are higher in the later reactions, dehydration of hydroxymethylphenols is still a powerful method, primarily because of the ready availability of the starting materials. On excitation of phenols **1** and **1′**, excited-state intramolecular proton transfer (ESIPT) from the phenol OH to the hydroxyl group, coupled with a loss of H_2O, takes place. That delivers QM **2** and **2′** which react with nucleophilic solvents giving solvolysis products **3** and **3′**, respectively (eq 1).[10,11,15] Due to the presence of the intramolecular H-bond in **1** and **1′**, ESIPT is probably very much facilitated. The quantum yield for the methanolysis reaction is $\Phi = 0.23$ and 0.46, respectively.[11] In case of the meta (**4**, **4′**) and the para derivatives (**6**, **6′**), the distance between the phenol and the hydroxyl group is larger, so ESIPT cannot take place. A protic solvent is required to mediate the excited-state deprotonation of the phenol moiety and the protonation of the alcohol. Overall, formal excited-state proton transfer (ESPT) from the phenol to the alcohol and dehydration gives QMs (**5**, **5′**, **7**, **7′**) which are, however, formed with lower quantum yields (eqs 2 and 3).[10,11,15]







The main reason for the widespread interest in the chemistry of QMs which blossomed two decades ago is their reactivity in biological systems.[1] It has been suggested that QMs play a critical role in the biological action of several classes of antibiotics such as mitomycin and anthracyclines.[16] Furthermore, QMs react with nucleic acids[17] and amino acids.[13] It is now well-established that QMs can act as DNA cross-linking agents.[18] From the discovery of biological activity of QMs, derivatization of the parent structure was performed in order (i) to examine QM reactivity and (ii) to examine their biological applicability.[19] It was shown that introduction of electron-withdrawing groups make QMs more electrophilic and hence shorter-lived, whereas electron-donating groups stabilized the structure.[19] Another way to stabilize such reactive intermediates is the use of a transition-metal approach. Amouri et al. constructed several organometallic π-complexes that contain the ring diene of various *o*-quinone methides with rhodium and iridium metal atoms.[20] Furthermore, introduction of a steric hindrance at the ortho position to the carbonyl group in QM results in lower reactivity of the QM molecules, which has been attributed to the shielding of the carbonyl oxygen from

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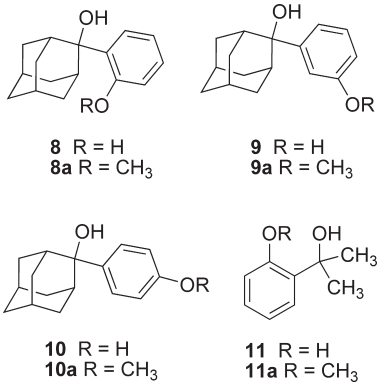
solvent interactions.[21] However, it was also shown that these QMs exhibit high toxicity in the lung tissue of mice.[22] On the other hand, introduction of the steric hindrance at the methylene position of QMs lowered cytotoxic effects.[23] A logical continuation in the research on QMs reactivity and biological activity is further elaboration of the structure−reactivity and the structure−activity pattern by making new derivatives with more significant sterical congestion at the methylene position.



8 R = H
8a R = CH_3

9 R = H
9a R = CH_3

10 R = H
10a R = CH_3

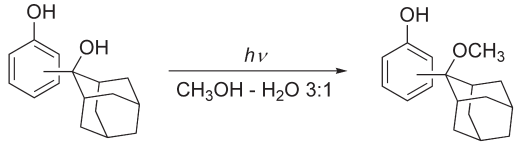
11 R = H
11a R = CH_3

Herein, we report synthesis of three adamantylphenols **8**−**10** that are expected to give rise to sterically congested QMs on photochemical excitation. These QMs should have altered reactivity due to the presence of the bulky adamantyl substituents at the methylene position. We aim to study their reactivity with nucleophiles and compare it to the reactivity of the model compounds (without adamantyl substituents) such as **1** and **11**. Additionally, more insight into the mechanism of the photochemical reactions of **8**−**10** that lead to the formation of QMs will be obtained by performing product studies, fluorescence measurements, and time-resolved absorption spectroscopy. Indeed, by investigating photochemistry of AdPh **9** and methoxy derivatives **9a** and **10a**, we discovered a photoinduced rearrangement of a 2-adamantyl cation.

Results and Discussion

Materials. Adamantylphenols (AdPh **8**−**10**) were prepared by cleavage of the corresponding methyl ether derivatives **8a**−**10a** by use of Lewis acid (BBr_3). The methoxy derivatives **8a**−**10a** were obtained by Grignard reactions of the corresponding bromoanisoles and 2-adamantanone. Compound **11** was prepared from **11a** (obtained by the Grignard reaction of *o*-bromoanisole and acetone) by the methyl ether cleavage in the reaction with sodium ethylthiolate, according to the modification of a known procedure.[24]

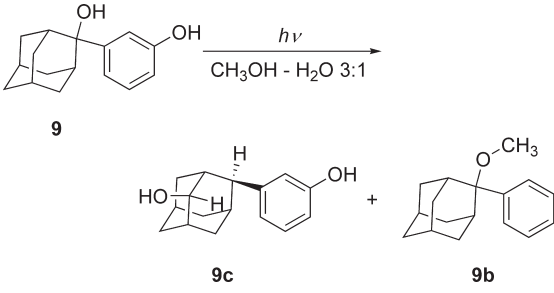
Photochemical Reactions. In view of previously reported photochemical reactions of hydroxymethylphenols,[11,15] it is anticipated that photolysis of AdPh in CH_3OH should give rise to methanolysis products via QM intermediates. Therefore, we performed photolyses (Rayonet reactor, 254 nm, argon purged) of AdPh **8**−**10** and **11** in CH_3OH-H_2O (3:1) and neat CH_3OH. The photochemical reaction in CH_3OH-H_2O (3:1) could be run to completion for **8** (7 lamps, 20 min) and to 70% conversion for **10** (30% of the starting material can be recovered), giving only ethers **8b** and **10b** (eq 4), which were isolated quantitatively, or in 70% yield, respectively. Similarly, photolysis (16 lamps, 1 h) of phenol **11** gave cleanly ether **11b** (66% according to NMR, 40% isolable yield). On the other hand, under the same photolysis conditions **9** gave two products, ether **9b** (10%) and the unexpected rearranged alcohol **9c** (8%) (eq 5). In the low conversion photolysis experiments, the unreacted **9** (70%) could be recovered. Photolysis of **8** in neat CH_3OH was also clean, giving quantitatively ether **8b**. On the other hand, irradiation of **9** in CH_3OH gave ether **9b** (4%) and rearranged alcohol **9c** (20%), whereas **10** gave ether **10b** (20%) and the reduction product **12** (10%). The unreacted **9** or **10** can be recovered by chromatography.



(4)

8 *o*-
10 *p*-

8b *o*-
10b *p*-



(5)

9

9c **9b**

The structure of the rearranged alcohol **9c** was determined by spectroscopic methods. In the aliphatic region of the ^1H NMR spectrum, two characteristic signals are present at δ 3.86 and 3.10 ppm corresponding to the H atoms at positions 2 and 4 of the adamantane ring. Furthermore, in the ^{13}C NMR spectrum in the aliphatic region six doublets and four triplets are seen (as compared to one quarternery carbon, three doublets, and three triplets for **9**). 2D homonuclear and heteronuclear spectra are fully in accordance with the assigned structure. The stereochemistry of the product was determined from the NOESY spectrum and NOE difference spectra. Namely, there is no NOE interaction between the H-atoms at positions 2 and 4 of the adamantane ring. On the other hand, there is an NOE interaction between the H atom adjacent to the adamantyl OH group and the phenyl H atoms.

In the ^1H NMR spectrum of **12** a characteristic broad singlet appears at δ 2.9 ppm that is assigned to the signal of the adamantyl-benzylic H atom. In addition, in the aliphatic region of the ^{13}C NMR spectrum four doublets and three

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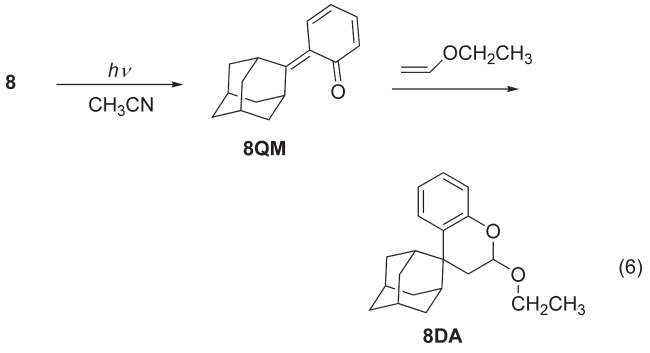
triplets are seen. However, there is no signal in the aliphatic region of the spectrum corresponding to the quarternary carbon atom, all in accordance with the assigned structure **12**.

Irradiation of **8** and **10** was also performed in CH_3CN with ethanolamine as nucleophile. In both reactions the corresponding ethanolamine adducts were formed. On photolysis of **8**, the adduct **13** was formed quantitatively so it was isolated and fully characterized. Additionally, irradiation of AdPh **8** in CH_3CN in the presence of excess of ethyl vinyl ether gave Diels−Alder adduct **8DA**, 50% (eq 6). The isolation of the Diels−Alder adduct undoubtedly indicate the intermediacy of the quinone methide **8QM** in the photolysis of **8**.



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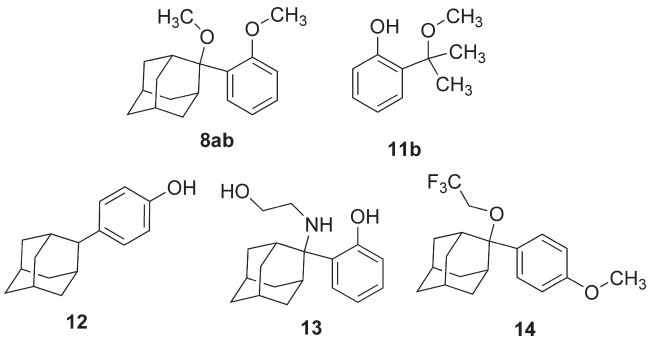


Since we observed formation of the rearranged alcohol **9c** on photolysis of **9**, irradiations of **8** and **10** were also carried out in CH_3CN-H_2O 3:1 to check for the possibility of rearranged alcohols due to an analogous rearrangement. However, 1 h irradiation (CH_3CN and CH_3CN-H_2O 3:1) gave no observable products from **8** and **10**, whereas alcohol **9c** was formed from **9** in 30% yield (70% of the starting material was recovered). Furthermore, assuming that the phenolic OH in AdPh is essential in the excited-state proton transfer giving rise to QMs that subsequently give methanolysis products **8b**−**10b**, the corresponding methoxy derivatives **8a**−**10a** should under the irradiation in CH_3OH remain unreactive. Indeed, they were significantly less reactive than the corresponding phenols. Only photolysis (CH_3OH-H_2O 3:1, 16 lamps 254 nm, 2 h) of **8a** gave rise to dimethoxy compound **8ab** (10%), whereas **9a** and **10a** gave rearranged alcohols **9ac** (20%) and **10ac** (30%), respectively (eq 7). The unreacted starting materials can be recovered from these experiments by chromatography.

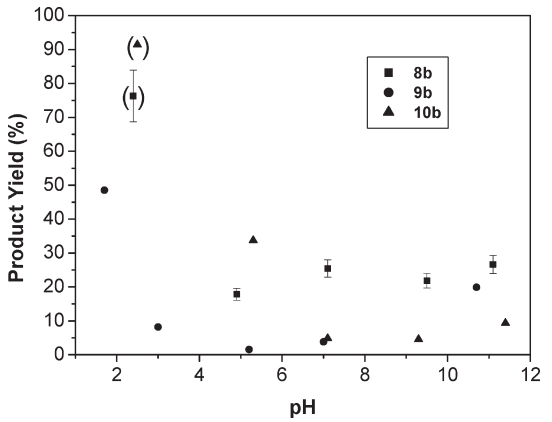
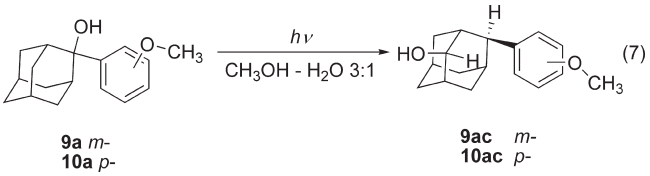


FIGURE 1. Methanolysis product yields as a function of the acidity of the irradiated solution. Irradiation was performed in CH_3OH-H_2O (3:1), by using 7 lamps, 254 nm for 20 min (three lamps, 3 min for **8**). pH of the aqueous part was measured by pH-meter and adjusted by addition of NaOH or H_2SO_4. The composition of the solution was analyzed by HPLC. The points in parentheses correspond to thermally formed methanolysis products.



(7)

Formation of the rearranged alcohols **9c**, **9ac**, and **10ac** suggests the intermediacy of the carbocations that could arise via an acid-catalyzed protonation of the alcohol moiety and dehydration (vide infra). Since that represents a competing, not thoroughly investigated pathway in the photosolvolysis of hydroxymethylphenols, we performed additional experiments to probe for the influence of acidity to the photosolvolysis. Therefore, photochemical reactions of AdPh **8**−**10** were carried out in CH_3OH-H_2O (3:1) at different acidities. The pH of the aqueous part was measured by a pH-meter and adjusted by the addition of NaOH or H_2SO_4. The composition of the irradiated solutions was analyzed by HPLC. Control experiments were performed in which the solution was kept in the dark to check for the possible competing thermal methanolysis pathway. The results are summarized in Figure 1. It should be noted that at low pH (< 2.5) methanolysis products **8b** and **10b** are formed in a thermal reaction. On the other hand, thermal methanolysis at pH 2.2 for the meta isomer **9** was possible, but it was much slower compared to the photochemical. Photolysis of **9** (CH_3OH-H_2O 3:1, pH 2.2, 7 lamps, 20 min) gave **9b** in 48% yield, whereas at the same time the thermal reaction gave only 1.6% of **9b**. Prolonged stirring of the solution of **9** gave 40% of **9b** in 2 days, and to achieve the total conversion, 10 days were required. The photolysis results at different pH indicate that the efficiency of the photochemical formation of **8b** is not influenced by acidity in the range studied, whereas **9b** and **10b** can also be formed by an acid catalyzed pathway.

Since photolyses at different acidities indicated the possibility of an acid-catalyzed pathway for the formation of the methanolysis products, we carried out irradiations of **9**, **10**,

TABLE 1. Quantum Yields of Photochemical Reactions, Φ_R[a]

compd	Φ_R
1	0.23[b]
8	0.51
9	(0.06)[c,d]
10	0.19
11	0.16
8a	(< 0.002)
9a	(0.02)[c,e]
10a	(0.06)[c,e]

[a]Quantum yields were determined using methanolysis of **1** as a secondary actinometer. Photolyses were performed in CH_3OH-H_2O 3:1. Composition of the irradiated solution was analyzed by NMR and HPLC; estimated errors on the reported values are 10%. [b]Taken from ref 11. [c]Estimated value obtained in the experiment wherein compound is photolyzed longer than the actinometer. [d]Quantum yield for the formation of **9b** and **9c**. [e]Quantum yield for the formation of rearranged alcohol products.

9a, and **10a** in 2,2,2-trifluoroethanol (TFE), which is a more acidic but less nucleophilic solvent than H_2O. Irradiations were preformed in analytical quantities by irradiating 2−3 mL of solution in UV−vis cuvettes. In all cases after the removal of the solvent, the characteristic multiplets at δ 3.2 ppm were observed that are associated to the methylene group adjacent to the CF_3 of the corresponding ethers. In addition, we performed control experiments by keeping the solutions in the dark to check for the possibility of thermal reaction. For derivatives **10** and **10a**, no exposure to irradiation was necessary to induce formation of the trifluoroethyl ether. Indeed, formation of the ether from **10a** was so efficient and clean that evaporation of the solvent afforded pure ether **14**.

Quantum yields of the photochemical reactions were determined using a secondary actinometer, the methanolysis of compound **1**.[11] To avoid absorption of the light by products, photolyses were performed to low conversions (< 30%). The composition of the irradiated solution was analyzed by NMR and HPLC. For the reactions with low quantum yields (photolysis of **9** and **8a**−**10a**), longer photolysis was required than for compound **1**, so only approximated results are reported. The results are compiled in Table 1.

Fluorescence. It is generally accepted that ESIPT and ESPT reactions of phenols are singlet excited-state processes.[11] Therefore, we studied fluorescence properties of **8**−**11** to gain more insight into their reactivity. Generally, fluorescent properties of **8**−**11** in CH_3CN (Table 2) are comparable to other alkylphenols.[15] They are moderately fluorescent and show maxima in the emission spectra at $\lambda \sim 300$ nm. The excitation spectra resemble the absorption spectra with maxima at 275. Singlet state lifetimes in CH_3CN were measured by the single-photon timing technique. Whereas decay of the fluorescence of **10** and **11** can be well-fitted to a single-exponential function giving lifetimes of 4.7 and 3.6 ns, respectively, two-exponential functions were required to fit the decays of **8** and **9**. Two decay times might be ascribed to the presence of conformers which have different singlet state lifetimes, due to the bulky adamantane. However, no unambiguous assignment can be made at this point.

TABLE 2. Fluorescence Properties of AdPh 8−10 and 11

compd	Φ_f (CH_3CN)[a]	Φ_f (CH_3CN-H_2O 1:4)	τ_f (CH_3CN)[b]/ns
8	0.085 ± 0.005	0.13 ± 0.02	4.0 ± 0.1 0.2 ± 0.1
9	0.24 ± 0.05	0.18 ± 0.08	4.1 ± 0.1 0.3 ± 0.1
10	0.22 ± 0.03	0.13 ± 0.03	4.70 ± 0.01
11	0.30 ± 0.02	0.15 ± 0.02	3.60 ± 0.05

[a]Measured using anisole in cyclohexane as a reference (Φ_f = 0.29).[28] [b]Measured using single-photon timing technique.

It is known that in the neutral aqueous media singlet excited-state phenols deprotonate, whereas in CH_3CN it does not occur since CH_3CN cannot solvate protons.[25] Therefore, addition of H_2O to the CH_3CN solution of *o*-hydroxymethylphenols can in principle change the mechanism of the proton transfer from intrinsic ESIPT to H_2O-mediated ESPT giving rise to phenolates. In addition, for the meta and the para derivatives, H_2O-mediated ESPT giving rise to dehydration and QMs can become operative.[15,26] The influence of added H_2O and the change of the photochemical reaction mechanism is evidenced from fluorescence which is being quenched.[27]

To investigate the influence of added H_2O on the photochemistry of AdPh, the fluorescence titrations of the CH_3CN solutions of **8**−**10** and **11** with H_2O were performed. On addition of H_2O no changes to the maxima in the absorption spectra could be detected. The emission maxima shifted 2 nm batochromically due to a weak stabilization of the excited state by H-bonding. Interestingly, on addition of H_2O in the concentration range 0−20 M the fluorescence of **11** was quenched, whereas no quenching for **8**−**10** could be detected. In contrast, fluorescence of **8** and **10** increased (Figure 2). The increase of the fluorescence for the ortho derivative **8** may be ascribed to the disruption of the intramolecular H-bond between the phenol OH and the alcohol, which decreases quantum yield of the intrinsic ESIPT. However, that cannot explain the fluorescence behavior of **9** and **10**. It should be recalled that adamantane is a very big and lipophilic substituent. Therefore, AdPh derivatives are probably more solvated by CH_3CN than by H_2O molecules. Hence, the dependence of fluorescence on H_2O content in **8**−**10** cannot be compared to typical phenol behavior.

Fluorescence was also recorded for the solutions of **8**−**11** containing 80% of H_2O. In these solutions, quantum yields of fluorescence were lower (except for **8**) than in neat CH_3CN (Table 2), in accordance with previous reports. Wan reported[15] that addition of H_2O to the CH_3CN solution of **1′** results in initial increase of the fluorescence which is quenched on addition of sufficient amount of H_2O, which can mediate formation of phenolates and the formal long-range proton transfer from the phenol to the hydroxyl group.[15] However, no emission from the phenolates from **8**−**11** could be detected, indicating that phenolates are not emissive in the aqueous solution. Indeed, no emission from the solutions (CH_3CN-H_2O 1:3) of **8**−**10** could be detected when the pH of the aqueous part was adjusted to 12 (higher than pK_a of alkylphenols ~10−10.5).

(25) (a) Solntsev, K. M.; Huppert, D.; Agmon, N.; Tolbert, L. M. *J. Phys. Chem. A* **2000**, *104*, 4658–4669. (b) Tolbert, L. M.; Solntsev, K. M. *Acc. Chem. Res.* **2002**, *35*, 19–27. (c) Agmon, N. *J. Phys. Chem. A* **2005**, *109*, 13–35.

(26) (a) Fisher, M.; Wan, P. *J. Am. Chem. Soc.* **1998**, *120*, 2680–2681. (b) Lukeman, M.; Wan, P. *J. Am. Chem. Soc.* **2002**, *124*, 9458–9464. (c) Brousmiche, D. W.; Xu, M.; Lukeman, M.; Wan, P. *J. Am. Chem. Soc.* **2003**, *125*, 12961–12970.

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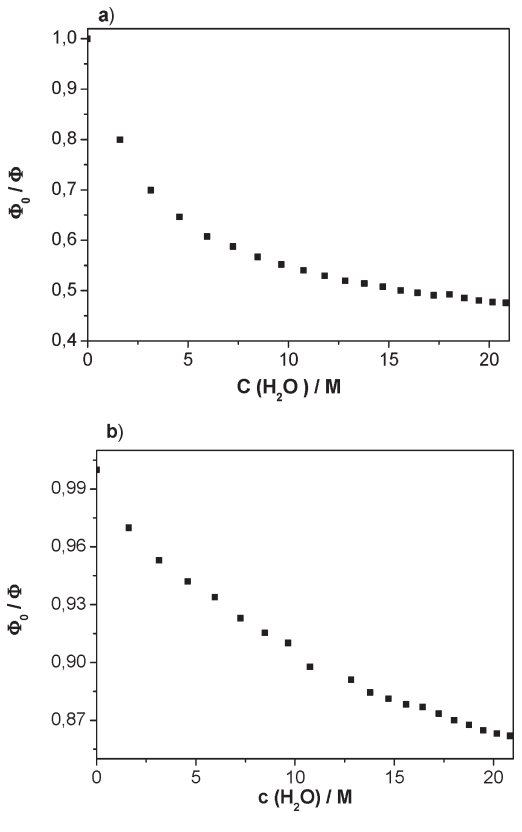


FIGURE 2. Stern−Volmer plots: fluorescence of **8** (a) and **10** (b) in CH_3CN as a function of H_2O concentration.

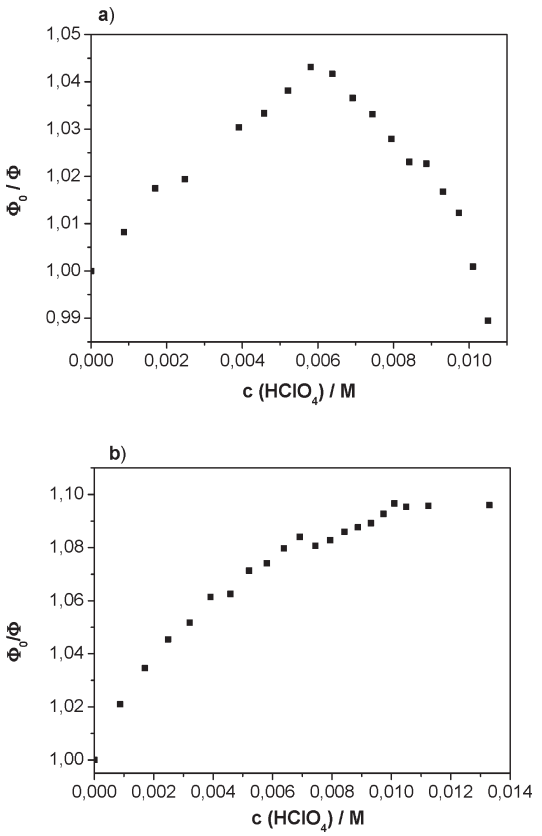


FIGURE 3. Stern−Volmer plots: fluorescence of **9** (a) and **10** (b) in CH_3CN-H_2O (1:4) as a function of $HClO_4$ concentration.

Since we found that acid can catalyze photosolvolysis of **9** and **10** (vide supra), we investigated influence of the added acid to the fluorescence properties of these AdPh. Therefore, solutions (CH_3CN-H_2O 1:4) of **9** and **10** were titrated with 0.03 M $HClO_4$. Initial addition induced quenching of the fluorescence for both AdPh, which for **10** leveled off reaching a plateau (at ~0.01 M), whereas for **9** started showing an increase (Figure 3). This fluorescence behavior clearly indicates two different mechanisms. At lower acidity, fluorescence of **9** and **10** is probably quenched due to the protonation of the excited state. The linear part of the Stern−Volmer plots can be used to estimate bimolecular quenching constant (taking the mean value of the decay time for **9** $\tau = 1.5$ ns), $k_q = 4.7 \times 10^9$ M^{-1} s^{-1} and $k_q = 3.2 \times 10^9$ M^{-1} s^{-1} for **9** and **10**, respectively. The adamantyl is an electron donating group (e.g., tert butyl $\sigma_m = -0.10$ and $\sigma_p = -0.10$).[29] According to the well-known meta-effect in photochemistry,[30] the adamantylphenyl in the singlet excited state is probably more electron donating in the meta position than in the para. Hence, **9** is probably less acidic in the singlet excited state than **10**. Thus, as the acidity of the solution of **9** is approaching the equilibrium pK_a*, the phenol moiety should deprotonate less in the excited state, resulting in the increase of the fluorescence. No reverse behavior of the fluorescence was observed for **10**, in accordance with the probable higher acidity in the excited state. We did not study influence of the further acidity increase (above 0.01 M $HClO_4$) where the thermal acid catalyzed pathways would also be possible (vide supra).

UV−vis and NMR Study. AdPh derivatives **8**−**10**, their corresponding methoxy derivatives **8a**−**10a**, and phenols **1** and **11** were studied by UV−vis spectrometry and NMR in CH_3CN and CH_3CN-H_2O (and the corresponding deuterated solvents for NMR) to test if photolysis could give rise to long-lived transient species (presumably QMs) that could be detected without the use of nanosecond laser flash photolysis. CH_3CN solutions ($c = 3-5 \times 10^{-4}$ M) were placed in UV−vis quartz cuvettes or NMR tubes and irradiated in a merry-go-round in the Rayonet reactor using 254 nm lamps. After each exposure to irradiation, UV−vis or NMR spectra were recorded. Irradiations of methoxy derivatives **8a**−**10a**, or aqueous solutions did not result in any observable changes. In addition, no changes were observed on irradiation of **9** in CH_3CN. These findings are in accordance with the inability of the methoxy compounds to form QMs, or the short lifetimes of the zwitterionic QMs that are derived from the meta isomers.

Contrary to the experiments with methoxy or meta derivatives and aqueous solutions, already a short exposure of the CH_3CN solution of **8** to 254 nm irradiation produced a strong new absorption band with a maximum at 400 nm (Figure 4) and changed the color to yellow. This transient absorption decayed with kinetics that could be described by first order ($\tau \sim 130$ min) and was quenched by H_2O, CH_3OH,

(28) Berlman, I. B. *Handbook of Fluorescent Spectra of Organic Molecules*; Academic Press: New York, 1971.

(28) Berlman, I. B. *Handbook of Fluorescent Spectra of Organic Molecules*; Academic Press: New York, 1971.

(29) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of photochemistry*; CRC Taylor and Francis: Boca Raton, 2006; p 627.

(30) (a) Zimmermann, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915–922. (b) Zimmermann, H. E. *J. Am. Chem. Soc.* **1995**, *117*, 8988–8991.

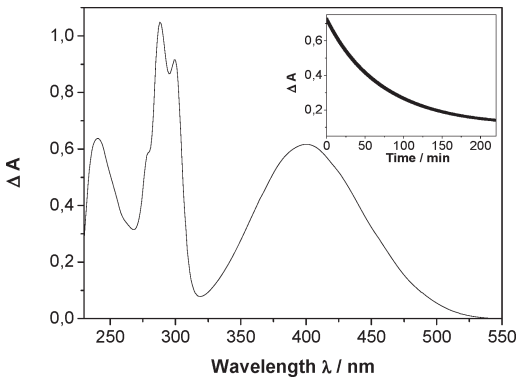
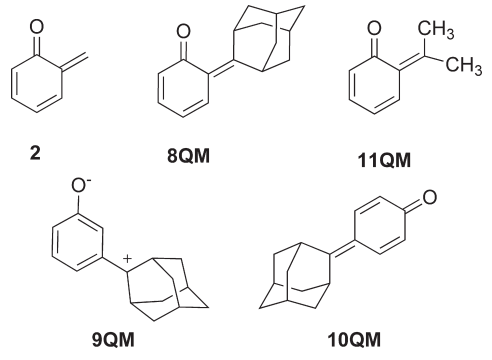


FIGURE 4. Difference absorption spectrum obtained by UV−vis spectrometer after photolysis (3 min, 16 lamps, 254 nm) of **8** in CH_3CN; inset: decay kinetics at 400 nm.

and ethyl vinyl ether (EVE). Hence, we assign the transient to **8QM**. The quenching with EVE was performed in the concentration range 0−2 M and revealed the relatively low value of the second-order quenching constant $k_q = 3.5 \times 10^{-4}$ M^{-1} s^{-1}. The low value of the quenching constant is in accordance with the steric congestion of the QM moiety and the difficulty to attain planar 6π transition state in the Diels−Alder reaction. Since **2** and **8QM** have similar chromophores, the difference absorption spectrum obtained by UV−vis spectrometer on photolysis of **8** (Figure 4) resembles the one assigned to **2** obtained on LFP of **1**.[13] Analogous ortho derivatives without the adamantane (**1** and **11**) did not produce as distinct transient absorptions detectable by UV−vis spectrometer with a maximum at 400 nm. However, much weaker transients were detected with maxima at ∼300 nm and shoulders stretching to longer wavelengths. This, however, allowed for the estimation of the lifetimes of the associated transient species (compiled in Table 3).

UV−vis study of the para derivative **10** in CH_3CN also gave rise to a transient species. A new band was apparent in the absorption spectrum with a maximum at 350 nm. Although we were not able to record a representative spectrum that could be associated only with the presence of **10QM**, this transient absorption decayed with kinetics that could be described as first order ($\tau \sim 200$ min) and was quenchable by CH_3OH and H_2O.



The surprising finding was the absorption spectrum observed for AdPh **10** in TFE. Whereas the corresponding methoxy derivative **10a** shows the maximum of absorption in TFE at 270 nm, the absorption for **10** was shifted to 350 and only a weak band at 270 nm could be observed (Figure 5).

TABLE 3. Lifetimes of Transient Species Observed by UV−vis Spectroscopy after Photolysis of Phenols in CH_3CN Solutions[a]

irradiated phenol	τ/min
1	0.80 ± 0.05
8	130 ± 20
10	100−300
11	6.3 ± 0.3

[a]The reported values correspond to the mean of 3−5 decays.

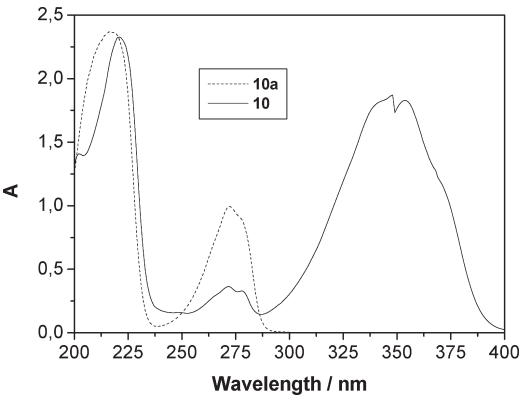
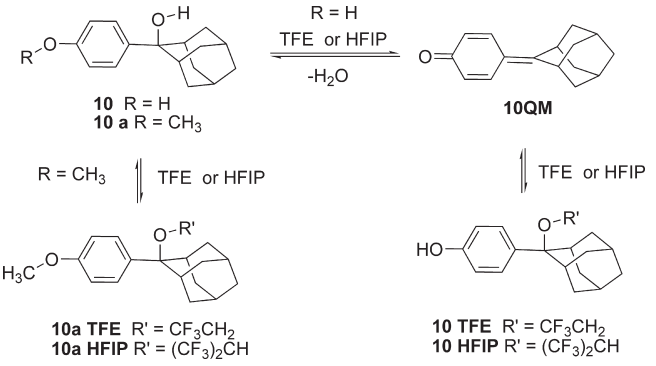


FIGURE 5. Absorption spectra of the solutions of **10** (full line) and **10a** (dash line) in 2,2,2-trifluoroethanol ($c = 8 \times 10^{-4}$ M).

SCHEME 1



This finding suggests that in TFE in the ground state there is an equilibrium between phenol **10**, ether **10TFE**, and **10QM** (Scheme 1), with the QM being the dominant species. Since TFE is an acidic and ionizing solvent, in principle it can protonate the alcohol and form a cation via a loss of H_2O. No light is needed to initiate formation of **10QM**. The other two AdPh derivatives **8** and **9** did not show this behavior in TFE. The inability of **8QM** to exist as a stable molecule in TFE might be ascribed to a higher basicity of the carbonyl oxygen in **8QM** (as compared to **10QM**). However, no unambiguous conclusion can be made at this point. In addition, **9QM**, which is a zwitterion, also probably does not exist as a stable species in TFE.

To verify the existence of the equilibrium and to show that absorption at 350 nm is due to **10QM**, we recorded ^1H and ^{13}C NMR spectra of **10** and **10a** in 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 (HFIP) which is a readily available deuterated, acidic, and non-nucleophilic solvent. In the ^1H NMR spectrum of the solution of **10a**, two species were detected that were associated to **10a** and the solvolysis product **10aHFIP**. Therefore, the aromatic part of the spectrum shows two

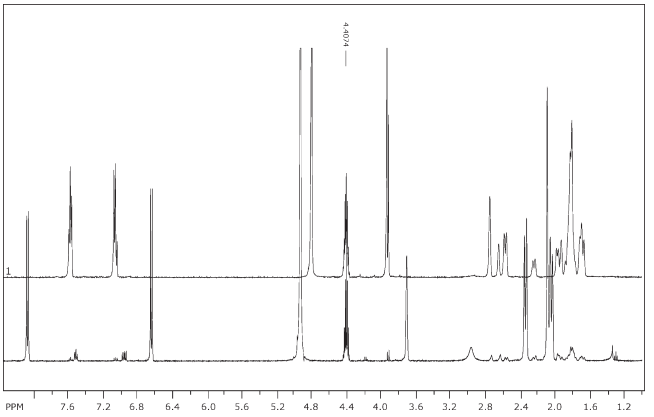


FIGURE 6. ^{1}H NMR spectra obtained on recording the solutions of **10** (bottom) and **10a** (top) in 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 (the multiplet at δ 4.40 ppm corresponds to the solvent $(CF_3)_2$C**D**OD). The dominant species in the bottom spectrum corresponds to **10QM**, whereas the top spectrum indicates the presence of a mixture of **10a** and **10aHFIP**.

multiplets at δ ~7.59 and 7.07 ppm (Figure 6). On the other hand, in the ^{1}H NMR spectrum of the solution of **10** in HFIP, signals at δ ~7.59 and 7.07 ppm correspond to minor species **10** and **10HFIP** (10%). The dominant species that corresponds to **10QM** shows proton resonances appearing as two doublets at δ ~8.08 and 6.65 ppm (J = 9.9 Hz), in accordance with published NMR data for other related QMs.[31] In addition, the aliphatic part of the spectrum appears as two broad singlets and two doublets, indicating increased symmetry of the adamantyl part of the molecule. The ^{13}C NMR DEPT spectrum of the HFIP solutions of **10** shows in the aromatic region two doublets at δ 138.2 and 124.6 ppm, whereas in the aliphatic region two triplets at δ 40.9 and 35.4 and two doublets at 38.1 and 27.6 ppm can be seen, all consistent with the structure of **10QM**.

Laser Flash Photolysis (LFP). Studying reactions by UV−vis spectroscopy can indicate the intermediacy of long-lived transient species (e.g., QMs) but cannot give insight in the early events after excitation of the sample or the presence of short-lived species such as zwitterionic QMs or carbonium ions. Therefore, we performed a study of **8**−**11** by LFP. LFP of **8** was carried out in CH_3CN and CH_3CN-H_2O 1:1. After the laser pulse, in both solvent systems transients were observed with the maximum of absorption at 400 nm. The transient decaying with the rate constant $k = 3.3 \times 10^5$ s^{-1} (τ 3 μs) in N_2-purged CH_3CN-H_2O 1:1 that was quenched by O_2 (O_2 purged CH_3CN-H_2O 1:1, $k = 2.5 \times 10^7$ s^{-1}, τ = 40 ns) was assigned to the triplet state of **8**. The persistent transient that remained after decay of the triplet was not quenched by O_2. Its absorption spectrum (Figure 7) resembled the one collected after the photolysis in CH_3CN (Figure 4). Since this transient was quenched by CH_3OH and ethanolamine (the quenching constants are compiled in Table 5) it was assigned to **8QM**. In O_2-purged CH_3CN-H_2O 1:1, **8QM** decays with the rate constant $k = 2$ s^{-1}, whereas in CH_3CN it is too long-lived to measure its decay kinetics by LFP. However, its

(31) (a) Dyall, L. K.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2196–2199. (b) Kurata, H.; Shimoyama, T.; Matsumoto, K.; Kawase, T.; Oda, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1327–1332.

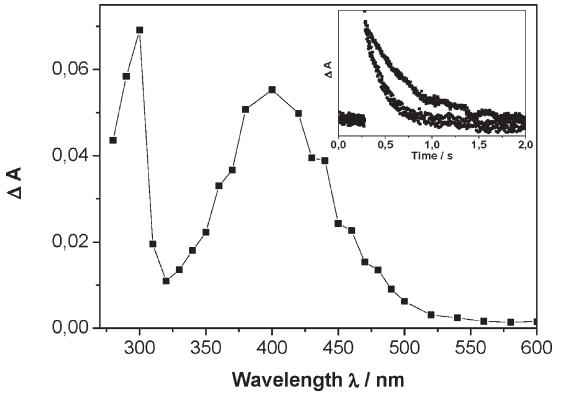


FIGURE 7. Transient absorption spectrum of **8** in CH_3CN recorded 17 μs after the laser pulse. Inset: decay kinetics in CH_3CN-H_2O 1:1 at 380 nm without CH_3OH and with addition of 10% of CH_3OH.

TABLE 4. Lifetimes and Relative Quantum Yield of Formation (Φ_{rel}) of QMs 2, 8QM, and 11QM in CH_3CN-H_2O 1:1[a]

QM	τ/s[a]	Φ_{rel}[b]
2	0.2	0.27
8QM	0.50 ± 0.05	1
11QM	0.35	0.36

[a] N_2 purged. [b] Assuming that **2**, **8QM**, and **11QM** have the same molar absorption coefficients, Φ_{rel} are obtained from the intensities of the ΔA of optically matched solutions of **1**, **8**, and **11**, respectively; the absolute value of Φ for methanolysis of **8** was estimated at 0.51.

TABLE 5. Bimolecular Quenching Constants of 8QM and 9QM by Ethanolamine and Methanol

k_q/QM	**8QM**[a]	**9QM**[b]
k_q (CH_3OH)/M^{-1} s^{-1}	1.4	6.1×10^6
k_q ($H_2NCH_2CH_2OH$) M^{-1} s^{-1}	3.7×10^2	4.1×10^6

[a] In CH_3CN-H_2O 1:1. [b] In TFE.

decay kinetics in CH_3CN was measured by a UV−vis spectrometer (Table 3).

The transients observed by LFP of **1** and **11** are similar to those from **8**. The presence of triplets was detected at 380−400 nm, that in N_2-purged CH_3CN-H_2O 1:1 decayed with rate constants $k = 1.7 \times 10^5$ s^{-1} (τ 5.7 μs) and $k = 2.2 \times 10^5$ s^{-1} (τ 4.6 μs) for **1** and **11**, respectively. The triplets were quenched by O_2, but longer lived transients that remained after the triplet had decayed were not quenched. Their maxima of absorption was at 400 nm, and decay kinetics was much slower (Table 4), all consistent with being due to **2** and **11QM**. Assuming that **2**, **8QM**, and **11QM** have the same molar absorption coefficients, the relative intensities of the transient absorptions obtained from optically matched solutions of **1**, **8**, and **11**, respectively, are directly proportional to the relative quantum yields of the QM formation (Φ_{rel}, Table 4). It can be seen that **8QM** is formed with the quantum yield 2.5 times higher than QMs without the adamantane, in accordance with the quantum yields of methanolysis (vide supra, Table 1). In addition, **8QM** is 2−3 times longer lived than QMs without adamantyl substituents at the methylene position.

The LFP results of **9** and **10** turned out to be more complex. The observed transient spectra in CH_3CN and CH_3CN-H_2O 1:1 in early times after the laser pulse were

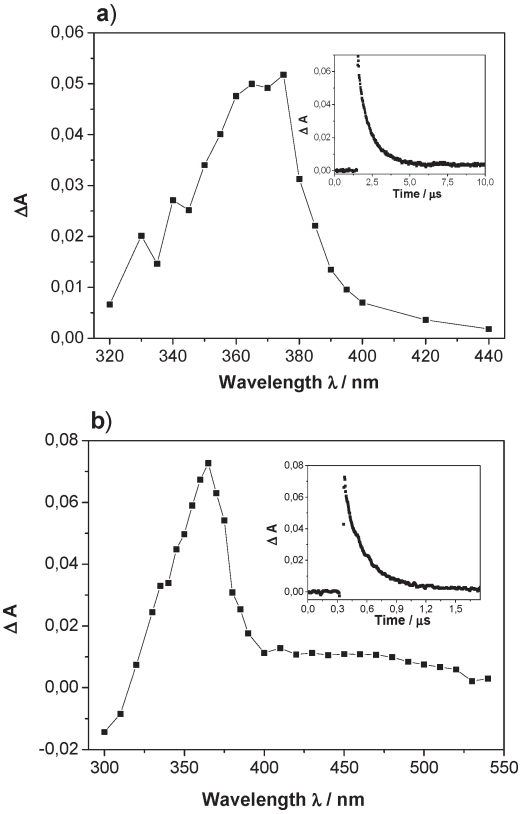
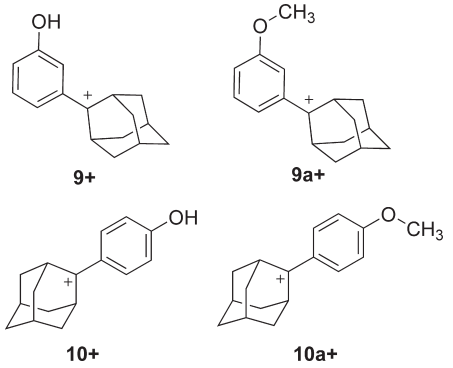


FIGURE 8. Transient absorption spectrum of (a) **9** in TFE and (b) **9a** in TFE recorded at 200 ns after the laser pulse. Insets: decays at 370 nm.

obscured due to the overlapping with the signals of triplets with maxima at 400 nm. The triplets of **9** and **10** decayed in N_2 purged CH_3CN-H_2O 1:1 with the rate constants $k = 3.3 \times 10^5\ s^{-1}$ (τ 3 μs) and $k = 3.1 \times 10^5\ s^{-1}$ (τ 3.2 μs), respectively. In addition to triplets, transients were observed with maxima at 400 nm and shoulders stretching to longer wavelengths (600 nm) that were more persistent and may be associated to phenoxy radicals and/or species from the secondary photochemical processes. However, the intensity of the residual transient absorption of **10** in CH_3CN-H_2O 1:1 at longer times (after decay of triplets and secondary photochemical species) that may be associated to **10QM** was too weak for recording reliable spectra and decay kinetics. The low intensity of the transient absorption is consistent with its low quantum yield of formation.

The lifetime of zwitterionic **9QM** that is anticipated intermediate from **9** is probably too short-lived in aqueous solvent to be detected by nanosecond LFP. Therefore, we carried out LFP of **9** in TFE. Since it is significantly less nucleophilic solvent than aqueous CH_3CN, zwitterionic **9QM** could be detectable. Thus, after the laser pulse in N_2-purged solution we observed transient absorption with a maximum at 370 nm that decayed with the rate constant $k = 6.2 \times 10^5\ s^{-1}$ (τ 1.6 μs) that was partly overlapped with the triplet of **9**. However, in O_2-purged solution at 370 nm, the same transient was observed (Figure 8a) that decayed with the rate constant $k = 1.0 \times 10^6\ s^{-1}$. This transient was quenched by CH_3OH and ethanolamine (quenching constants are compiled in Table 5). Such a transient is consistent with being due to zwitterion **9QM** or cation $\mathbf{9}^+$. Depending on the substitution on the phenyl ring the maxima of benzyl cation absorptions are generally in the range 350−400 nm, and their decay kinetics ranges from 100 ns to 100 μs.[32] Furthermore, 2-adamantyl cation (without stabilizing phenyl substituent) has also been studied by LFP, and it has lifetime in TFE of 0.33 ns.[33]

Therefore, we performed LFP of **9a** in TFE whereupon we can expect formation of cation $\mathbf{9a}^+$, but not the QM. The transient absorption spectrum from **9a** in TFE (Figure 8b) resembles the one from **9**, with a maximum at 370 nm. However the transient from **9a** decays faster than the one from **9**; in N_2- and O_2-purged TFE the rate constant is $k = 4.8 \times 10^6\ s^{-1}$ (210 ns). Furthermore, we should take into account that the phenyl ring with the methoxy or hydroxy group in the meta position is an electron-withdrawing group ($\sigma_m = +0.12$), whereas the phenoxide (O^-) in the meta position is an electron-donating group ($\sigma_m = -0.47$).[29] Consequently, decay kinetics obtained on LFP of **9** and **9a** are consistent with the assignation of the transients as being due to **9QM** and cation $\mathbf{9a}^+$, respectively. We also attempted to detect cation $\mathbf{10a}^+$ that is expected to be formed on LFP of **10a** in TFE. Cation $\mathbf{10a}^+$ should be longer lived than $\mathbf{9a}^+$ due to the stabilizing effect of the p-methoxy group ($\sigma_p = -0.27$).[29] However, in O_2-purged solution, besides the triplet which decayed with rate constant $k = 3.3 \times 10^7\ s^{-1}$ (30 ns) no other transient was observed.



Mechanism of Reaction. The phenolic OH group in AdPh **8** is intramolecularly hydrogen bonded to the oxygen atom of the alcohol OH group, as clearly indicated from the NMR spectrum of AdPh **8** recorded in $CDCl_3$. Namely, the signal corresponding to the phenolic OH in **8** shows the resonance at δ 7.8 ppm whereas for **9** and **10** it is at 4.6−4.8 ppm. The presence of the intramolecular H-bond suggests that on excitation of **8**, an efficient ESIPT takes place. Indeed, dehydration of **8** giving rise to **8QM** is an efficient process. The lower limit for the quantum yield of the photochemical formation of **8QM** is 0.51, as determined for the methanolysis reaction giving **8b**. The corresponding methoxy derivative **8a** is significantly less reactive (Table 1) showing that the free phenolic OH is required for the efficient formation of the photosolvolysis products. In addition, H_2O is probably not

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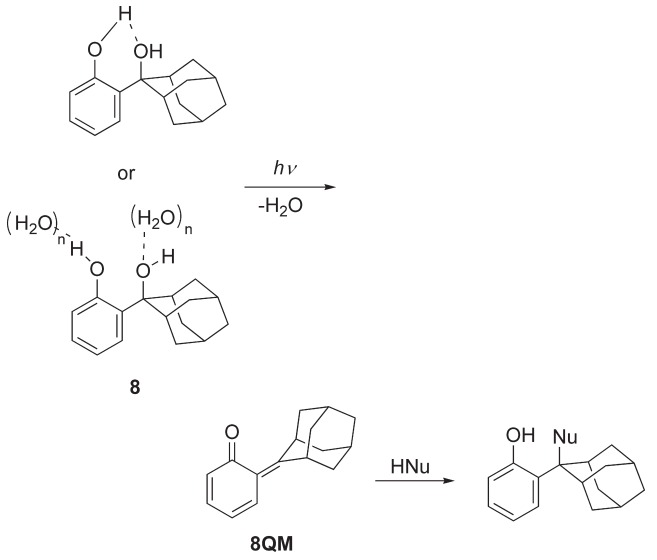
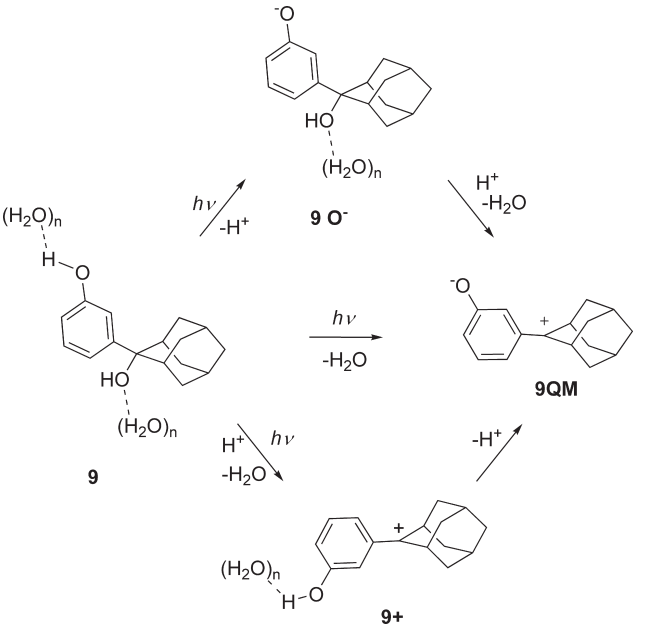
(33) Pezacki, J. P.; Shukla, D.; Lusztyk, J.; Warkentin, J. *J. Am. Chem. Soc.* **1999**, *121*, 6589–6598.

SCHEME 2



SCHEME 3



required to mediate this process. Furthermore, comparing photochemical reactivity of **1**, **8**, and **11** (judged by the values of the quantum yield for the QM formation), clearly shows that **8** is the most reactive. That may be ascribed to the electron-donating effect of the adamantyl substituent which stabilizes the QM structure.

On addition of H_2O to the system containing **8**, the intramolecular H-bonding is partly disrupted which probably leads to the decreased quantum yield of ESIPT. That is indicated from (a) the decrease of the intensity of the transient absorption (in CH_3CN-H_2O 1:1 the intensity of the ΔA decreases 50%) and (b) the fluorescence quantum yield which increases. Contrary to previous reports for the ortho-hydrogen bonded systems, in this case we have not observed quenching of the fluorescence by H_2O even with 80% of H_2O. That may be ascribed to the different solvation of the AdPh, which is very lipophilic and preferably solvated by CH_3CN. However, the mechanism shown in Scheme 2, wherein H_2O molecules participate in the formation of **8QM**, cannot be completely ruled out, although it probably does not contribute much to the overall formation of **8QM**. The independence of the solvolysis quantum yield on acidity additionally corroborates the intrinsic ESIPT pathway.

Comparing reactivity of QMs **2**, **8QM**, and **11QM**, as judged from the lifetimes in CH_3CN and CH_3CN-H_2O, clearly shows that **8QM** is the least reactive. Lower reactivity is in accordance with its selectivity in reaction with nucleophiles, being 2 orders of magnitude more reactive with amino-nucleophile (ethanolamine) than with oxygen nucleophiles (CH_3OH and H_2O). That finding may be of importance in biological systems regarding cytotoxicity of QMs.[23] Furthermore, it is interesting to note that neither **8** nor **8a** undergoes rearrangement of the adamantyl skeleton that was seen with meta and para derivatives.

The mechanism of photochemical reaction of **9** and **10** clearly has to be different from **8**, since the phenolic OH is further away from the alcohol moiety. Intramolecular hydrogen bonding cannot exist; hence, the presence of a protic solvent is required to ferry the proton from the acidic to the basic site. We have not observed quenching of the fluorescence of **9** on addition of H_2O. However, that could be ascribed to the unusual solvation due to the lipophilic adamantyl substituent. Wan and co-workers[11,15] suggested that in the *m*-benzhydrol systems deprotonation of the phenol moiety by H_2O molecules takes place almost simultaneously with the loss of hydroxyl group, giving rise to zwitterionic QMs. However, it was also suggested that deprotonation of the phenol is essential to trigger the expulsion of the hydroxyl moiety.[15] Neither of these processes can be disregarded in the case of **9**. However, the high rate constant of the fluorescence quenching by acid (although inefficient) and higher efficiencies of the methanolysis at low pH indicate that an acid-catalyzed pathway (as shown in Scheme 3) should be possible. That is, in the excited state AdPh **9** can be protonated and on loss of H_2O give cation $\mathbf{9}^+$ that is subsequently stabilized by deprotonation (in the excited state or the ground state) giving **9QM**. Formation of rearrangement product **9c** on irradiation of **9** in CH_3CN also suggests that heterolysis pathway via cation $\mathbf{9}^+$ can operate at pH 7, although probably less efficiently than the simultaneous loss of OH^- and H^+. In addition, it is very suggestive that formation of the rearranged product **9ac** on photolysis of **9a** has to stem from the pathway that involves acid-catalyzed formation of cation $\mathbf{9a}^+$.

What is the mechanism for the unusual rearrangement leading to 2,4-disubstituted adamantanes? The thermal solvolysis reactions of 2-substituted adamantanes that involve 2-adamantyl cations have been intensively studied.[34] Many

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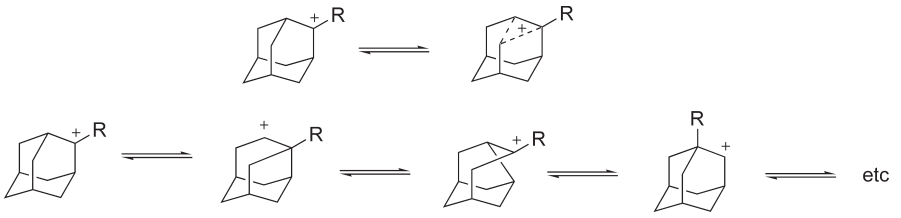
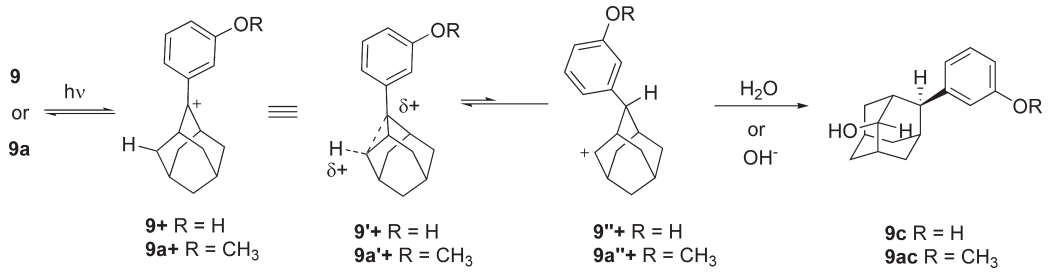
SCHEME 4



SCHEME 5



authors suggest that the 2-adamantyl cation exist as σ-bridged or as an equilibrium between 2-adamantyl and protoadamantyl structures (Scheme 4).[35] Such a description of the 2-adamantyl cation can best account for some experimental findings, especially those involving rearrangement to the protoadamantyl system. However, it has been shown by theoretical calculations[36] and X-ray structural analysis[37] that the actual structure of the 2-adamantyl cation does not involve bridging, but rather hyperconjugation,[38] and the distortion of the bridge bearing the positive charge. Thus, photochemical reaction of **9** or **9a** is expected to give rise to cations $\mathbf{9}^+$ (or **9QM**), or $\mathbf{9a}^+$, respectively, that are the most accurately represented by drawings $\mathbf{9'}^+$ and $\mathbf{9a'}^+$ (Scheme 5). If a tunneling of the proton takes place in such a cation it would give rise to structures $\mathbf{9''}^+$ and $\mathbf{9a''}^+$ that are actually less stable than the starting $\mathbf{9'}^+$ and $\mathbf{9a'}^+$. However, when these rearranged cations are trapped by nucleophiles, products of the reactions can not revert to the starting material. That is, the rearranged alcohols are photochemically stable. Therefore, although rearrangement takes place with low quantum yield, it is possible since it is irreversible.

The presence of the zwitterion **9QM**, and cation $\mathbf{9a}^+$ has been detected by LFP in TFE. Although we were not able to study their rearrangement by spectroscopic methods, LFP data gave insight into the reactivity of the zwitterion **9QM** with nucleophiles. Generally, one can see low selectivity of this QM in reactions with N and O nucleophiles, which is not surprising taking into account the zwitterionic nature.

In view of the above findings and previous reports it is clear that photochemistry of **10** has to be similar to that of **9**; that is, H_2O is required to mediate the ESPT. In addition, the observed fluorescence quenching by acid and equilibrium (phenol and QM) seen in the ground state in TFE strongly suggests that acid catalyzed pathway (via cation $\mathbf{10}^+$, Scheme 6) can compete with H_2O-mediated simultaneous loss of both, H^+ and OH^-. However, if $\mathbf{10}^+$ was formed in the excited state, it is reasonably to assume that it would very rapidly deprotonate giving **10QM**. Therefore, it is not surprising that we have not observed the rearranged products on photolysis of **10**, whereas it was the case on photolysis of methoxy derivative **10a**.

Conclusion

The results presented for AdPh derivatives suggest that the intrinsic ESIPT coupled with a dehydration gives rise to **8QM**, and H_2O-mediated formal ESPT and dehydration gives rise to **9QM** and **10QM**. The incorporation of the adamantyl substituent into the hydroxymethylphenol moiety increased the quantum yield of the photochemical reactivity by up to 3 times and significantly prolonged lifetimes of the associated QMs. The fluorescence of **8**−**10** is not quenched by H_2O, suggesting different solvation than for the usual phenol derivatives. On the contrary, fluorescence quenching by acid for **9** and **10**, as well as results of photolyses at low pH suggest that an acid catalyzed pathway giving rise to solvolysis products can compete with H_2O-mediated

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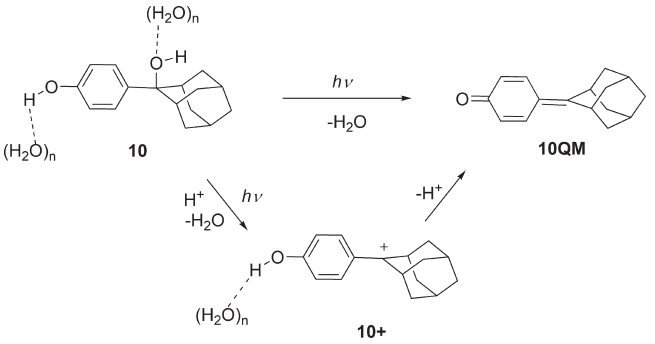
SCHEME 6



proton transfer. Hence, from the methoxy derivatives **9a** and **10a**, photoinitiated acid catalyzed heterolysis gives 2-adamantyl cations that undergo rearrangements giving 2,4-disubstituted adamantyl derivatives. The same type of rearrangement was observed for AdPh **9** giving **9c**, probably taking place on the zwitterion **9QM**, Furthermore, in the TFE acidic media, in the ground state, phenol **10** is in the equilibrium with **10QM** which allowed for the recording of the associated UV−vis, ^{1}H NMR, and ^{13}C NMR spectra. The results reported herein show that photolsyes of AdPh **9** and the methoxy derivatives **9a** and **10a** represent a new method to generate adamantyl cations and probe for their intramolecular (viz. rearrangements) and intermolecular reactivity with nucleophiles. Finally, a new class of QMs bearing sterical hindrance at the methylene position is described, that may find importance in the biological systems due to higher selectivity in nucleophilic additions, and potentially, lower cytotoxicity.

Experimental Section

Grignard Reaction: General Procedure. The reaction was carried out in dry THF. The Grignard reagent was prepared from bromoanisole (2.75 g, 14.63 mmol) and magnesium (0.36 g, 14.63 mmol) and reacted with 2-adamantanone (2 g, 13.31 mmol). The crude products were purified by crystallization from hexane.

2-Hydroxy-2-(2-methoxyphenyl)adamantane (8a): 1.86 g (54%); colorless crystals; mp 87 − 88 °C; IR (KBr) ν_{max}/cm^{-1} 3543, 2965, 2899, 2854, 2842; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.44 (dd, 1H, J = 1.5 Hz, J = 7.7 Hz), 7.21 (dt, 1H, J = 1.5 Hz, J = 8.1 Hz), 6.93 (dt, 1H, J = 1.5 Hz, J = 7.7 Hz), 6.90 (d, 1H, J = 8.1 Hz), 3.85 (s, 3H), 3.42 (s, 1H, OH), 2.66 (br s, 2H), 2.54 (br s, 1H), 2.50 (br s, 1H), 1.65−1.90 (m, 8H), 1.61 (d, J = 12.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, APT) δ/ppm 157.6 (s), 133.5 (s), 128.0 (d), 127.8 (d), 120.3 (d), 111.4 (d), 76.5 (s), 54.8 (q), 37.9 (t), 35.4 (d, 2C), 35.3 (t, 2C), 33.1 (t, 2C), 27.3 (d), 26.9 (d); MS (EI) m/z 259 (9, M$^+$), 258 (46, M$^+$), 240 (13), 137 (42), 135 (100), 121 (7); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, obsd 258.16217.

2-Hydroxy-2-(3-methoxyphenyl)adamantane (9a): 2.77 g (66%); colorless crystals; mp 122 − 123 °C; IR (KBr) ν_{max}/cm^{-1} 3519, 2931, 2911, 2878, 2852; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.30 (dd, 1H, J = 8.0 Hz, J = 8.8 Hz), 7,13 (d, 1H, J = 8.0 Hz), 7.09 (dd, 1H, J = 2.2 Hz, J = 1.7 Hz), 6.81 (dd, 1H, J = 8.1 Hz, J = 2.2 Hz), 3.81 (s, 3H), 2.53 (br s, 2H), 2.42 (br s, 1H), 2.38 (br s, 1H), 1.50−1.95 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz, APT) δ/ppm 159.8 (s), 147.0 (s), 129.5 (d), 117.6 (d), 112.0 (d), 111.8 (d), 75.5 (s), 55.1 (q), 37.5 (t), 35.6 (d, 2C), 34.8 (t, 2C), 32.9 (t, 2C), 27.2 (d), 26.8 (d); MS (EI) m/z 259 (19, M$^+$), 258 (100, M$^+$), 240 (11), 137 (23), 136 (18), 135 (89), 121 (7), 107 (9); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, obsd 258.16184.

2-Hydroxy-2-(4-methoxyphenyl)adamantane (10a):[39] 2.29 g (67%); colorless crystals.

2-(2-Metoxyphenyl)-2-propanol (11a).[40] Grignard reagent was prepared from 2-bromoanisole (3.56 mL, 28.5 mmol) and magnesium (0.72 g, 29.6 mmol) and reacted with acetone (10 mL, 136 mmol). The reaction furnished 5.4 g of the crude product that was additionally purified on a column with silica gel using dichloromethane as eluent: 3.52 g (74%) of **11a**.

General Procedure for Removal of the Methyl Ether Group from Phenols with BBr_3. The reaction was carried out under N_2 inert atmosphere in a three-neck round-bottom flask (250 mL) equipped with a septum and a syringe. In the flask was placed the methoxy derivative **8**−**10** (10 mmol), dissolved in dry CH_2Cl_2 (100 mL), and the solution cooled to 0 °C by ice bath. To the cooled solution, by use of a syringe, was added dropwise a solution of BBr_3 in CH_2Cl_2 (1 M, 50 mL) during 1 h. After addition was completed, the stirring was continued 1 h at 0 °C and at rt overnight. The next day, to the reaction mixture was added 100 mL of cold water, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, solid was removed by filtration, and solvent was removed on a rotary evaporator. The obtained crude product was purified on a column filled with silica gel by use of CH_2Cl_2 and CH_2Cl_2-EtOAc 4:1 as eluent.

2-Hydroxy-2-(2-hydroxyphenyl)adamantane (8).[41] Reaction with 2-hydroxy-2-(2-methoxyphenyl)adamantane (1.26 g, 4.88 mmol) and a solution of BBr_3 (24.42 mL) gave 1.34 g of the crude product that was purified by chromatography to furnish 0.60 g (45%) of the pure product in the form of colorless crystals.

2-Hydroxy-2-(3-hydroxyphenyl)adamantane (9). Reaction with 2-hydroxy-2-(3-methoxyphenyl)adamantane (1.43 g, 4.54 mmol) and a solution of BBr_3 (27.73 mL) gave 1.42 g of the crude product that was purified by chromatography to furnish 1.14 g (85%) of the pure product in the form of colorless crystals: mp 160−161 °C; IR (KBr) ν_{max}/cm^{-1} 3567, 3378, 3075, 2901, 2885; ^{1}H NMR (DMSO-d_6, 600 MHz) δ/ppm 9.17 (s, 1H, OH), 7.11 (t, 1H, J = 7.7 Hz), 6.87−6.90 (m, 2H), 6.60 (ddd, 1H, J = 0.9 Hz, J = 2.3 Hz, J = 7.7 Hz), 4.48 (s, 1H, OH), 2.37 (br s, 3H), 2.35 (br s, 1H), 1.79 (br s, 1H), 1.52−1.68 (m, 9H); ^{13} C NMR (DMSO-d_6, 150 MHz, APT) δ/ppm 157.2 (s), 147.7 (s), 128.9 (d), 116.2 (d), 113.2 (d), 112.7 (d), 73.4 (s), 37.4 (t), 34.9 (d, 2C), 34.3 (t, 2C), 32.6 (t, 2C), 26.9 (d), 26.6 (d); MS (EI) m/z 244 (100, M$^+$), 243 (20, M$^+$), 151 (10), 121 (95); HRMS calcd for $C_{16}H_{20}O_2$ 244.14633, obsd 244.14653.

2-Hydroxy-2-(4-hydroxyphenyl)adamantane (10). Reaction with 2-hydroxy-2-(3-methoxyphenyl)adamantane (1.50 g, 5.81 mmol) and a solution of BBr_3 (29 mL) gave 1.42 g of the crude product that was purified by chromatography to furnish 1.26 g (94%) of the pure product in the form of colorless crystals: mp 301−302 °C; IR (KBr) ν_{max}/cm^{-1} 3408, 3254, 3025, 2913, 2901, 2856; ^{1}H NMR (DMSO-d_6, 300 MHz) δ/ppm 9.20 (s, 1H, OH), 7.24 (d, 2H, J = 8.6 Hz), 6.71 (d, 2H, J = 8.6 Hz), 4.30 (s, 1H, OH), 2.37 (br s, 3H), 2.31 (br s, 1H), 1.78 (br s, 1H), 1.50−1.68 (m, 9H); ^{13} C NMR

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(DMSO-d_6, 75 MHz, APT) δ/ppm 155.6 (s), 136.6 (s), 126.7 (d, 2C), 114.7 (d, 2C), 73.1 (s), 37.6 (t), 35.0 (d, 2C), 34.4 (t, 2C), 32.6 (t, 2C), 27.1 (d), 26.6 (d); MS (EI) m/z 245 (5, M^+), 244 (28, M^+), 227 (23), 226 (100), 158 (7), 123 (19), 121 (55), 120 (14), 106 (14), 91 (10), 79 (13); HRMS, calculated for $C_{16}H_{20}O_2$ 244.14633; obsd 244.14641.

2-(2-Hydroxyphenyl)-2-propanol (11).[42] Obtained by the modification of the published procudere.[24]

Photolysis Experiments: General. In a quartz vessel was placed a CH_3OH, CH_3OH-H_2O (3:1), or CH_3CN-H_2O solution (100 mL, $c = 4.1 \times 10^{-3}$ M) of adamantane phenol (100 mg, 0.41 mmol) which was irradiated in a Rayonet reactor using 16 lamps (unless stated otherwise) at 254 nm. Prior to and during the irradiation the solution was continuously purged with a stream of Ar and cooled by a coldfinger condenser. After irradiation, the solvent was removed on a rotary evaporator and the residue chromatographed on a thin layer of silica gel using CH_2Cl_2 or CH_2Cl_2-EtOAc (30%) as eluent.

2-Methoxy-2-(2-hydroxyphenyl)adamantane (8b). A methanol solution (25 mL) of AdPh **8** (10 mg, 0.041 mmol) was irradiated in a Rayonet reactor at 254 nm using seven lamps for 20 min. After evaporation of the solvent, pure product **8b** was obtained: colorless crystals; mp 59−60 °C; IR (NaCl) ν_{max}/cm^{-1} 3350, 2904, 2855; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 8.11 (s, 1H, OH), 7.34 (dd, 1H, $J = 1.1$ Hz, $J = 7.9$ Hz), 7.18 (dt, 1H, $J = 1.4$ Hz, $J = 7.4$ Hz), 6.86 (dt, 1H, $J = 1.1$ Hz, $J = 7.9$ Hz), 6.83 (dd, 1H, $J = 1.1$ Hz, $J = 7.4$ Hz), 3.01 (s, 3H, OCH_3), 2.63 (br s, 1H), 2.57 (br s, 1H), 2.50 (d, 1H, $J = 12.6$ Hz), 2.39 (dd, 1H, $J = 2.9$ Hz, $J = 12.9$ Hz), 2.20 (dd, 1H, $J = 2.4$ Hz, $J = 12.4$ Hz), 1.96 (dq, 1H, $J = 2.9$ Hz, $J = 12.9$ Hz), 1.89 (br s, 1H), 1.83 (br s, 1H), 1.73 (br s, 2H), 1.60−1.70 (m, 2H), 1.57 (dq, 1H, $J = 2.4$ Hz, $J = 12.4$ Hz), 1.38 (dd, 1H, $J = 1.9$ Hz, $J = 12.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, APT) δ/ppm 156.1 (s), 129.3 (d), 128.7 (d), 126.6 (q), 118.8 (d), 117.5 (d), 83.7 (s), 48.5 (q), 37.6 (t), 36.0 (t), 35.2 (d), 34.4 (t), 33.0 (t), 32.6 (t), 30.5 (d), 27.0 (d), 26.7 (d); MS (EI) m/z 259 (1, M^+), 258 (3, M^+), 227 (18), 226 (100), 184 (13), 183 (31), 158 (13), 131 (7); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198 obsd 258.16182.

Spiro[2-ethoxychroman-4,2′-adamantane] (8DA). In a quartz vessel was placed a CH_3CN solution (20 mL, $c = 3.3 \times 10^{-3}$ M) of **8** (20 mg, 0.082 mmol) and ethyl vinyl ether (5 mL, 55 mmol). The solution was purged with argon for 15 min, sealed, and irradiated in a Rayonet reactor using four lamps at 254 nm. The solution was irradiated 6 times for 15 min, and after each irradiation the solution was kept in the dark for 3 h. After the irradiations, the solvent was evaporated and the residue chromatographed on a column of silica gel using CH_2Cl_2 as eluent. The chromatography furnished 12 mg (49%) of product **8DA** and 8 mg (40%) of AdPh **8**: 12 mg (49%); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.53 (dd, 1H, $J = 1.2$ Hz, $J = 7.8$ Hz), 7.13 (dt, 1H, $J = 1.5$ Hz, $J = 7.7$ Hz), 6.94 (dt, 1H, $J = 1.5$ Hz, $J = 7.7$ Hz), 6.87 (dd, 1H, $J = 1.2$ Hz, $J = 7.8$ Hz), 5.41 (dd, 1H, $J = 6.1$ Hz, $J = 8.3$ Hz), 4.00 (dd, 1H, $J = 7.0$ Hz, $J = 14.1$ Hz), 3.60 (dd, 1H, $J = 7.0$ Hz, $J = 14.1$ Hz), 2.98 (dd, 1H, $J = 6.1$ Hz, $J = 13.8$ Hz), 2.76 (d, 1H, $J = 12.0$ Hz), 2.35 (br s, 1H), 2.31 (d, 1H, $J = 13.4$ Hz), 2.21 (d, 1H, $J = 13.4$ Hz), 2.04 (br s, 1H), 1.95 (br s, 1H), 1.65−1.90 (m, 6H), 1.54−1.58 (m, 2H), 1.36 (dd, 1H, $J = 8.3$ Hz, $J = 13.8$ Hz), 1.22 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, APT) δ/ppm 153.1 (s), 136.8 (s), 126.8 (d), 126.1 (d), 121.2 (d), 118.6 (d), 99.5 (d), 63.5 (t), 39.9 (t), 38.9 (t), 35.2 (t), 34.2 (s), 33.97 (t), 33.94 (d), 33.89 (t), 33.5 (t), 31.2 (d), 27.7 (d), 27.5 (d), 15.2 (q); MS (FAB) m/z 299 (M^+, 20), 298 (M^+, 70), 265 (100), 190 (75); HRMS calcd for $C_{20}H_{26}O_2 + K$ 337.1564, obsd 337.1558.

Photolysis of 2-Hydroxy-2-(3-hydroxyphenyl)adamantane (9). In a quartz vessel was placed a CH_3CN-H_2O (3:1) solution (100 mL, $c = 4.1 \times 10^{-3}$ M) of AdPh **9** (100 mg, 0.41 mmol) and irradiated in a Rayonet reactor using 16 lamps at 254 nm over 1 h. After irradiation, extraction with CH_2Cl_2 was carried out (3 × 75 mL), and the extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator and the residue chromatographed on a thin layer of silica gel using CH_2Cl_2-EtOAc (30%) as eluent to afford 30 mg of **9c** and recover 70 mg of the starting material.

2-(3-Hydroxyphenyl)-4-hydroxyadamantane (9c): 30 mg (30%); colorless crystals; mp 68−70 °C; IR (NaCl) ν_{max}/cm^{-1} 3368, 2913, 2854; ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 7.16 (t, 1H, $J = 7.8$ Hz), 6.88 (ddd, 1H, $J = 0.7$ Hz, $J = 1.0$ Hz, $J = 7.8$ Hz), 6.81 (dd, 1H, $J = 0.7$ Hz, $J = 1.5$ Hz), 6.63 (ddd, 1H, $J = 0.7$ Hz, $J = 1.0$ Hz, $J = 7.8$ Hz), 5.06 (br s, 1H, OH), 3.86 (t, 1H, $J = 3.1$ Hz), 3.10 (br s, 1H), 2.47 (br s, 1H), 2.38 (br s, 1H), 2.31 (dq, 1H, $J = 2.8$ Hz, $J = 12.8$ Hz), 2.06 (dq, 1H, $J = 2.8$ Hz, $J = 12.8$ Hz), 1.94 (dq, 1H, $J = 2.8$ Hz, $J = 12.2$ Hz), 1.78−1.90 (m, 4H), 1.69 (dq, 1H, $J = 2.8$ Hz, $J = 12.8$ Hz), 1.63 (dq, 1H, $J = 2.4$ Hz, $J = 12.8$ Hz), 1.60 (br s, 1H, OH), 1.52 (dq, 1H, $J = 2.6$ Hz, $J = 12.8$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, COM, DEPT) δ/ppm 155.7 (s), 145.2 (s), 129.3 (d), 118.8 (d), 113.5 (d), 112.3 (d), 69.8 (d), 47.5 (d), 38.7 (t), 37.4 (d), 34.5 (d), 32.1 (t), 31.6 (t), 30.9 (t), 29.7 (d), 26.9 (d); MS (EI) m/z 244 (100, M^+), 243 (20, M^+), 226 (30), 150 (100), 107 (30), 95 (30); HRMS calcd for $C_{16}H_{20}O_2$ 244.14633, obsd 244.14645.

2-Methoxy-2-(3-hydroxyphenyl)adamantane (9b). To the solution of AdPh **9** (100 mg, 0.041 mmol) in CH_3OH-H_2O (3:1) a drop of concentrated sulfuric acid was added and the solution was stirred at rt over 7 days. The progress of the ether formation was monitored by HPLC. When all the starting material disappeared, to the solution was added sodium bicarbonate, methanol was removed on the rotary evaporator and the aqueous residue extracted with CH_2Cl_2 (3 × 50 mL). The extracts were dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator to afford pure product **9b**: colorless crystals; mp 140−142 °C; IR (NaCl) ν_{max}/cm^{-1} 3306, 2910, 2855; ^{1}H NMR (DMSO-d_6, 300 MHz) δ/ppm 9.27 (s, 1H, OH), 7.15 (t, 1H, $J = 7.7$ Hz), 6.82−6.90 (m, 2H), 6.67 (dd, 1H, $J = 1.4$ Hz, $J = 7.7$ Hz), 2.69 (s, 3H), 2.50 (br s, 2H), 2.22 (br s, 1H), 2.18 (br s, 1H), 1.50−1.80 (m, 10 H); ^{13}C NMR (DMSO-d_6, 75 MHz, APT) δ/ppm 157.2 (s), 142.1 (s), 129.8 (d), 117.9 (d), 114.1 (d), 114.0 (d), 79.0 (s), 47.6 (q), 37.2 (t), 34.1 (t, 2C), 32.4 (t, 2C), 32.2 (d, 2C), 27.0 (d), 26.3 (d); MS (EI) m/z 258 (10, M^+), 259 (3, M^+), 244 (10), 229 (30), 227 (100), 165 (10), 137 (15), 121 (10), 107 (13); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, observed 258.16197.

2-Methoxy-2-(4-hydroxyphenyl)adamantane (10b). AdPh **10** (100 mg, 0.41 mmol) was dissolved in CH_3OH-H_2O (3:1, 100 mL) and irradiated in Rayonet reactor at 254 nm using 7 lamps for 20 min. After evaporation of the solvent the residue was chromatographed on a thin layer of silica gel using CH_2Cl_2-EtOAc (30%) to furnish 70 mg of the ether **10b** and 20 mg of the starting material: colorless crystals; mp 124−126 °C; IR (NaCl) ν_{max}/cm^{-1} 3360, 2905, 2854; ^{1}H NMR (DMSO-d_6, 300 MHz) δ/ppm 9.35 (s, 1H, OH), 7.23 (d, 2H, $J = 8.7$ Hz), 6.75 (d, 2H, $J = 8.7$ Hz), 2.66 (s, 3H), 2.53 (br s, 2H), 2.22 (br s, 1H), 2.18 (br s, 1H), 1.50−1.80 (m, 10H); ^{13}C NMR (DMSO-d_6, 75 MHz, APT) δ/ppm 156.1 (s), 130.6 (s), 128.2 (d, 2C), 114.6 (d, 2C), 78.8 (s), 47.3 (q), 37.3 (t), 34.1 (t, 2C), 32.4 (t, 2C), 32.1 (d, 2C), 27.2 (d), 26.3 (d); MS (EI) m/z 259 (1, M^+), 258 (7, M^+), 228 (22), 227 (100), 226 (47), 106 (20); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, obsd 258.16183.

2-(4-Hydoxyphenyl)adamantane (12).[43] AdPh **10** (100 mg, 0.41 mmol) was dissolved in CH_3OH (100 mL) and irradiated in Rayonet reactor at 254 nm using 16 lamps for 20 min. After evaporation of the solvent, the residue was chromatographed on

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a thin layer of silica gel using CH_2Cl_2−EtOAc (30%) to furnish 20 mg of ether **10b**, 10 mg of product **12** (10%), and 50 mg of recovered starting material.

2-(2-Hydroxyphenyl)-2-methoxypropane (11b).[44] Phenol **11** (116 mg, mmol) was dissolved in CH_3OH-H_2O (25%, 100 mL) and irradiated in a Rayonet reactor at 254 nm using 16 lamps for 1 h. After irradiation, extraction with CH_2Cl_2 (3 × 75 mL) was carried out, and the extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator and the residue was chromatographed on a thin layer of silica gel using CH_2Cl_2 to furnish 50 mg (40%) of the product **11b** and 20 mg (17%) of the starting material.

***N*-(2-Hydroxyethyl)-2-(2-hydroxyphenyl)-2-aminoadamantane (13).** AdPh **8** (8.2 mg, 0.033 mmol) was dissolved in CH_3CN (2100 mL) and to the solution was added ethanolamine (100 μL, 1.63 mmol). The solution was irradiated in a Rayonet reactor at 254 nm using 16 lamps for 5 min. After irradiation, the solvent was removed on a rotary evaporator and to the residue H_2O (50 mL) was added. Extraction with CH_2Cl_2 was carried out (3 × 50 mL), and extracts were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent pure product was obtained quantitatively: colorless crystals; mp 130−132 °C; IR (NaCl) ν_{max}/cm^{-1} 3368, 2910, 2855; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.31 (dd, 1H, J = 1.3 Hz, J = 7.7 Hz), 7.12 (dt, 1H, J = 1.6 Hz, J = 7.3 Hz), 6.73−6.82 (m, 2H), 3.55−3.70 (m, 2H), 2.65−2.75 (m, 2H), 2.65 (br s), 2.52 (br s, 2H), 2.02−2.14 (m, 3H), 1.86−1.96 (m, 2H), 1.68−1.84 (m, 6H), 1.61 (dq, 1H, J = 3.0 Hz, J = 12.8 Hz), 1.43 (dd, 1H, J = 2.3 Hz, J = 12.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, COM, DEPT) δ/ppm 157.4 (s), 129.4 (d), 128.10 (d), 128.06 (s), 118.1 (d), 117.6 (d), 62.6 (s), 62.3 (t), 42.1 (t), 38.2 (t), 35.3 (t), 34.5 (t), 34.0 (d), 32.8 (t), 32.3 (t), 30.3 (d), 27.3 (d), 26.4 (d); MS (EI) m/z 287 (30, M^+), 288 (10, M^+), 267 (30), 258 (25), 252 (25), 226 (100), 183 (20); HRMS calcd for $C_{18}H_{25}NO_2$ 287.18853, obsd 287.18858.

2-Methoxy-2-(2-methoxyphenyl)adamantane (8ab). Methoxyphenol **8a** (102 mg, 0.39 mmol) was dissolved in CH_3OH-H_2O (3:1, 100 mL) and irradiated in Rayonet reactor at 254 nm using 16 lamps for 2 h. After evaporation of the solvent the residue was chromatographed on a thin layer of silica gel using CH_2Cl_2 to furnish 70 mg of the starting material and 20 mg (20%) of the product: colorless crystals; mp 64 − 66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.36 (dd, 1H, J = 1.3 Hz, J = 8.0 Hz), 7.24 (dt, 1H, J = 1.7 Hz, J = 8.1 Hz), 6.88−6.95 (m, 2H), 3.79 (s, 3H, OCH_3), 3.36 (br s, 1H), 2.85 (s, 3H), 2.64 (br s, 1H), 2.38 (d, 1H, J = 12.4 Hz), 2.23 (dd, 1H, J = 2.7 Hz, J = 12.3 Hz), 1.94 (dd, 1H, J = 2.5 Hz, J = 12.3 Hz), 1.60−1.85 (m, 7H), 1.54 (dq, 1H, J = 2.7 Hz, J = 12.4 Hz), 1.44 (d, 1H, J = 12.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, COM, DEPT) δ/ppm 159.6 (s), 130.5 (d), 128.4 (d), 128.2 (s), 119.6 (d), 112.5 (d), 81.7 (s), 55.5 (q), 48.4 (q), 37.7 (t), 35.2 (t), 34.7 (t), 34.4 (d), 33.0 (t), 32.9 (t), 31.2 (d), 27.5 (d), 26.7 (d); MS (EI) m/z 273 (2, M^+), 272 (12, M^+), 242 (20), 241 (100), 151 (24), 121 (20); HRMS calcd for $C_{18}H_{24}O_2$ 272.17763, obsd 272.17753.

2-Hydroxy-4-(3-methoxyphenyl)adamantane (9ac). Methoxyphenol **9a** (107 mg, 0.41 mmol) was dissolved in CH_3OH-H_2O (3:1, 100 mL) and irradiated in Rayonet reactor at 254 nm using 16 lamps for 2 h. After evaporation of the solvent the residue was chromatographed on a thin layer of silica gel using CH_2Cl_2 to furnish 60 mg of the starting material and 20 mg (20%) of the product: colorless oil: IR (NaCl) ν_{max}/cm^{-1} 3400, 2911, 2852; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.22 (t, 1H, J = 7.8 Hz), 6.92 (d, 1H, J = 8.1 Hz), 6.87 (br s, 1H), 6.70 (dd, 1H, J = 2.4 Hz, J = 8.1 Hz), 3.85 (t, 1H, J = 2.8 Hz), 3.78 (s, 3H), 3.13 (br s, 1H), 2.48 (br s, 1H), 2.40 (br s, 1H), 2.31 (dq, 1H, J = 2.8 Hz, J = 12.6 Hz), 2.07 (dq, 1H, J = 2.8 Hz, J = 12.6 Hz), 1.95 (dq, 1H, J = 2.8 Hz, J = 12.2 Hz), 1.78−1.90 (m, 4H), 1.56−1.75 (m, 3H), 1.52 (dq, 1H, J = 2.1 Hz, J = 12.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, COM, DEPT) δ/ppm 159.7 (s), 144.9 (s), 129.1 (d), 118.8 (d), 112.9 (d), 110.1 (d), 69.7 (d), 55.0 (q), 47.7 (d), 38.7 (t), 37.6 (d), 34.5 (d), 32.1 (t), 31.6 (t), 31.0 (t), 29.6 (d), 27.0 (d); MS (EI) m/z 259 (19, M^+), 258 (100, M^+), 150 (71), 135 (9), 122 (26), 121 (18), 108 (55), 107 (10), 106 (10), 91 (10); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, obsd 258.16184.

2-Hydroxy-4-(2-methoxyphenyl)adamantane (10ac). Methoxyphenol **10a** (114 mg, 0.44 mmol) was dissolved in CH_3OH-H_2O (3:1, 100 mL) and the mixture irradiated in Rayonet reactor at 254 nm using 16 lamps for 2 h. After evaporation of the solvent, the residue was chromatographed on a thin layer of silica gel using CH_2Cl_2 to furnish 70 mg of the starting material and 30 mg (30%) of the product: colorless crystals; mp 66 − 68 °C; IR (NaCl) ν_{max}/cm^{-1} 3368, 29051, 2851; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.22 (d, 2H, J = 8.7 Hz), 6.84 (d, 2H, J = 8.7 Hz), 3.85 (t, 1H, J = 2.7 Hz), 3.78 (s, 3H), 3.10 (br s, 1H), 2.47 (br s, 1H), 2.38 (br s, 1H), 2.31 (dq, 1H, J = 2.7 Hz, J = 12.8 Hz), 2.06 (dq, 1H, J = 2.8 Hz, J = 12.8 Hz), 1.72−1.98 (m, 5H), 1.48−1.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, COM, DEPT) δ/ppm 157.2 (s), 135.0 (s), 127.2 (d), 113.5 (d), 69.6 (d), 55.1 (q), 47.0 (d), 38.7 (t), 37.5 (d), 34.6 (d), 32.1 (t), 31.4 (t), 31.0 (t), 29.6 (d), 26.9 (d); MS (EI) m/z 258 (100, M^+), 259 (20, M^+), 150 (20), 135 (10), 121 (30); HRMS calcd for $C_{17}H_{22}O_2$ 258.16198, obsd 258.16180.

2-(4-Methoxyphenyl)-2-(2,2,2-trifluoroethoxy)adamantane (14). Methoxyphenol **10a** (10 mg, mmol) was dissolved in 5 mL of trifluoroethanol and stirred at rt overnight. The next day, solvent was removed on a rotary evaporator to furnish the pure product: colorless crystals; mp 56−58 °C; IR (NaCl) ν_{max}/cm^{-1} 2906, 2856; ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.36 (d, 2H, J = 8.8 Hz), 6.88 (d, 2H, J = 8.8 Hz), 3.81 (s, 3H), 3.20 (q, $J_{H-F}{}^3$ = 8.8 Hz), 2.55 (br s, 2H), 2.34 (br s, 1H), 2.30 (br s, 1H), 1.88 (br s, 1H), 1.60−1.80 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, COM, DEPT) δ/ppm 158.8 (s), 137.7 (s), 128.4 (d, 2C), 124.4 (q, J_{CF} = 278 Hz), 113.5 (d, 2C), 81.0 (s), 59.2 (qd, $J_{CF}{}^3$ = 34 Hz), 55.1 (q), 37.5 (t), 34.2 (t, 2C), 33.2 (d, 2C), 32.5 (t, 2C), 27.5 (d), 26.6 (d); MS (EI) m/z 340 (10, M^+), 341 (3, M^+), 242 (20), 241 (100), 219 (100), 135 (5), 121 (10); HRMS calcd for $C_{19}H_{23}F_3O_2$ 340.16501, obsd 340.16486.

4-(Adamantan-2-ylidene)cyclohexa-2,5-dienone (10QM). AdPh **10** (10 mg, 0.041 mmol) was dissolved in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 (HFIP), and NMR spectra were taken: ^{1}H NMR (HFIP-d_2, 500 MHz) δ/ppm: 8.08 (d, 2H, J = 9.9 Hz), 6.65 (d, 2H, J = 9.9 Hz), 3.70 (br s, 2H), 2.33 (d, 4H, J = 12.4 Hz), 2.08 (br s, 4H), 2.03 (d, 4H, J = 12.4 Hz); ^{13}C NMR (HFIP-d_2, 125 MHz) δ/ppm 197.8 (s), 191.3 (s), 138.2 (d, 2C), 124.6 (d, 2C), 124.2 (s), 40.9 (t, 4C), 38.1 (d, 2C), 35.4 (t), 27.6 (d, 2C).

Laser Flash Photolysis (LFP). All LFP studies were conducted at the University of Victoria LFP facility employing a YAG laser, with a pulse width of 10 ns and excitation wavelength 266 nm. Static cells (0.7 cm) were used and solutions were purged with nitrogen or oxygen for 20 min prior to measurements. The absorbance of the solutions at 266 nm was ∼0.4−0.6.

Steady-State and Time-Resolved Fluorescence Measurements. The samples were dissolved in CH_3CN, and the concentrations were adjusted to have optical densities of < 0.1 at the excitation wavelength (270 nm). Solutions were purged with nitrogen for 15 min prior to analysis. The measurements were performed at 20 °C and were not corrected. Fluorescence quantum yields were determined by comparison of the integral of emission bands with the one of anisole (Φ = 0.29).[28] Typically, three absorption traces and three fluorescence emission traces

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were recorded, exciting at three different wavelengths (260, 265, and 270 nm). Three quantum yields were calculated and the mean value reported.

Fluorescence decay histograms were obtained on an instrument equipped with hydrogen flash lamp, using time-correlated single-photon timing technique in 1023 channels. Histograms of the instrument response functions (using LUDOX scatterer) and sample decays were recorded until they typically reached 3×10^3 counts in the peak channel. The half width of the instrument response function was typically ~1.3 ns. The time increment per channel was 0.04883 ns. Obtained histograms were fitted as sums of exponential using Gaussian-weighted nonlinear least-squares fitting based on Marquardt−Levenberg minimization implemented in the software package of the instrument. The fitting parameters (decay times and pre-exponential factors) were determined by minimizing the reduced chi-square χ_g^2. Additional graphical method was used to judge the quality of the fit that included plots of surfaces ("carpets") of the weighted residuals vs channel number.

Acknowledgment. We thank the Ministry of Science Education and Sports of the Republic of Croatia (Grant No. 098-0982933-2911), the Croatian Academy of Sciences and Arts (HAZU), the Natural Sciences and Engineering Research Council (NSERC) of Canada, and the University of Victoria for financing. N.B. thanks N. Cindro for help with the synthesis of phenols **11** and **11a**.

Supporting Information Available: General and detailed experimental procedures, characterization of compounds, ^{1}H and ^{13}C NMR spectra, and fluorescence and LFP data. This material is available free of charge via the Internet at http://pubs.acs.org.