Selectivity in the photo-Fries rearrangement of some aryl benzoates in green and sustainable media. Preparative and mechanistic studies.

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Complete List of Authors:	Siano, Gastón; Universidad de Buenos Aires Facultad de Ciencias Exactas y Naturales, Química Orgánica Crespi, Stefano; Universita degli Studi di Pavia, Department of Chemistry Mella, Mariella; Universita degli Studi di Pavia, of Chemistry Bonesi, Sergio; Univerisity of Buenos Aires, Organic Chemistry

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Selectivity in the photo-Fries rearrangement of some aryl benzoates in green and sustainable media. Preparative and mechanistic studies.

Gastón Siano[a], Stefano Crespi[b], Mariella Mella[b] and Sergio M. Bonesi[*,a,b]

[a] *Departamento de Química Orgánica, CIHIDECAR – CONICET, 3er Piso, Pabellón 2, Ciudad Universitaria, Facultad de Ciencias Exactas y Naturales, University of Buenos Aires, Buenos Aires, 1428, Argentina. Phone:+541145763346.*

[b] *Dipartimento di Chimica, Sezione Chimica Organica, v.le Taramelli 12, 27100, University of Pavia, Pavia, Italy.*

E-mail: smbonesi@qo.fcen.uba.ar

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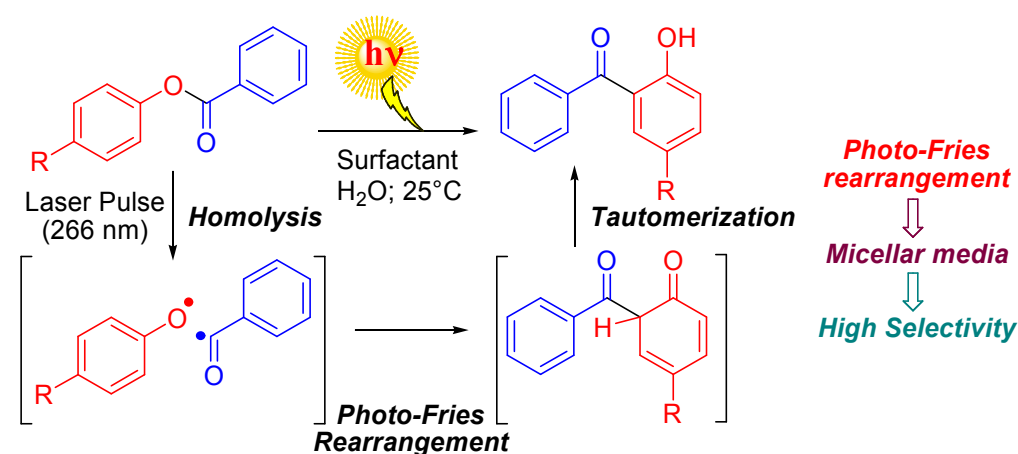
Abstract. Irradiation of a series of *p*-substituted aryl benzoates under N_2 atmosphere in homogeneous and micellar media was investigated by means of steady-state condition and of time-resolved spectroscopy. A notable selectivity in favor of the 2-hydroxybenzophenone derivatives was observed in micellar media. The benzophenone derivatives were the main photoproduct. On the other hand, in

homogeneous media (cyclohexane, acetonitrile, and methanol) the observed product distribution was entirely different, viz. substituted 2-hydroxybenzophenones, *p*-substituted phenols, benzyl and benzoic acid were found. The binding constants in the surfactant were also measured and NOESY experiments showed that the aryl benzoates were located in the hydrophobic core of the micelle. Laser flash photolysis experiments led to the characterization of both *p*-substituted phenoxy radical and substituted 2-benzoylcyclohexadienone transients in homogeneous and micellar environment.

Introduction.

Photochemical reactions grant access to a variety of scaffolds difficult, if not impossible, to access through thermal chemistry. However, the energetic advantage of populating the excited states is often paid with a lack of selectivity in product formation. For this reason, reactions involving intermediates such as radical pairs or radical-ion pairs represent a significant challenge regarding product distribution for the synthetic organic photochemist. Zeolites, micelles, polyolefin films, cavitands, dendrimers, etc., as a useful heterogeneous media, can be helpful to direct the selectivity of photoproducts in photoinduced reactions.[1]

Surfactants are amphiphilic molecules and aggregation in solution to form micelles can be achieved when their concentration is 100 times higher than the critical micellar concentration (*cmc*). Then, micelles solubilize efficiently hydrophobic compounds in water, albeit micelles are not static species showing a dynamic equilibrium.[2] Also, micelle can concentrate guest molecules into relatively small effective volumes promoting their re-encounter consequently.[1c] Inside the homophobic core of the micelles, significant cage effects are observed when compared to homogeneous media, with magnitudes impossible to explain considering the sole microviscosity in the constrained environment. The main reason for this behavior is based on the hydrophobicity of the solutes where inhibition of their diffusion into the aqueous phase is noteworthy. Thus, the reaction intermediates show a high lifetime in the restricted hydrophobic core of the micelle. For example, geminate radical pairs that are

produced photochemically within the micellar core, have their rotational and translational mobility constrained inside the micelles.[2] Indeed, the mobility restricted within the hydrophobic cores of radicals, radical cations, or other reactive intermediates limits unwanted reactions (*e.g.* radical–radical self-quenching reactions) and the access of adventitious reagents (*e.g.* water and oxygen) that would cause their collapse in solution. Therefore, micellar solution can induce a product distribution and a relative chemical yield that can be significantly different when compared with homogeneous conditions.[1,2]

There has been many studies on the control of the reactivity of radical species generated within the hydrophobic core of the micelle and some physical parameters (e.g. electrostatic, polarity, hydrophobic interactions, viscosity, as well as hydrogen-bonding solvation) may be involved in determining their reactivities.[3] Also, several studies directed to analyze and quantify the reactivity, selectivity, and efficiency of micellar cage on photochemical reactions in water have been carried out.

Among the vast number of photochemical transformations, a particular example is represented by the photo-Fries rearrangement. Anderson and Reese[4] have discovered the photoreaction where a homolytic fragmentation of a carbon–heteroatom bond is involved, *i.e.*, C-O, C-S and C-N, of esters, thioesters and amides, respectively.[5] The photo-Fries rearrangement proceeds via a well-established radical mechanism, mainly occurring through the excited singlet state.[1b,6] Typically, the photoinduced Fries rearrangement reaction of (hetero)aryl benzoates in homogeneous media affords *ortho-* and *para-* regioisomers as well as the corresponding phenols (Scheme 1).[7,1b]
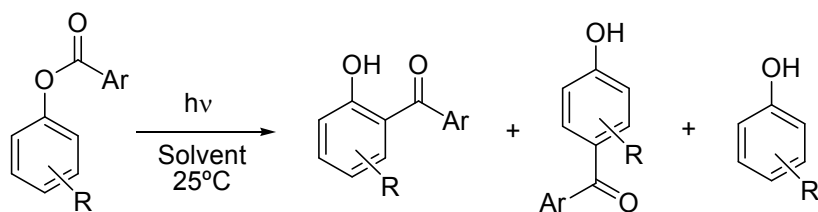
Scheme 1. Photochemisytry of aryl benzoates.

The product distribution of the photo-Fries rearrangement underlines the competition between in-cage radical recombination versus out-of-cage diffusion and, consequently, aryl esters, as model substrates, have been chosen to study heterogeneous environments.[8] In these studies, SDS (sodium dodecyl sulfate) was the preferred surfactant to be tested. In the literature, there are examples of photo-Fries reactions, i.e. irradiation of benzamides in SDS solution and irradiation of aqueous solutions of acetanilides confined in cyclodextrin.[8b,8d] Recently, we have studied the photo-Fries rearrangement of a variety of substituted acetanilides in micellar solution showing the high selectivity of the photoreaction in favor of the *ortho*-rearranged photoproducts, viz. substituted 2-aminoacetophenones.[9] The preparation of benzoyloxy benzophenone derivatives requires the use of 2-hydroxybenzophenones as key compounds, demonstrating biological activity and pharmaceutical properties (*e.g.* anti-inflammatory and estrogenic activity).[10] Therefore, we carried out the systematic study the photo-Fries rearrangement of a series of *p*-substituted phenyl benzoates in surfactant solutions with the aim to evaluate the selectivity towards the formation of 5-substituted 2-hydroxy benzophenones in constrained environment. Scheme 2 shows the structures of the surfactants as well as the aryl benzoates employed in this systematic study.

(a) Structures of aryl benzoates.
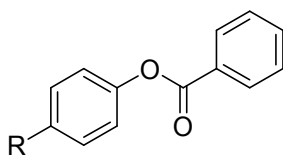
1 R = OCH$_3$; **2** R = OPh; **3** R = CH$_3$; **4**; R = *t*-Bu;
5 R = H; **6** R = Ph; **7** R = CN; **8** R = NO$_2$
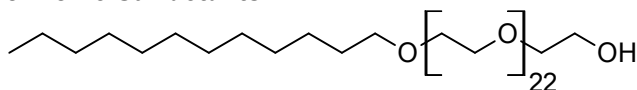
(b) Structures of surfactants.

Anionic Surfactant.
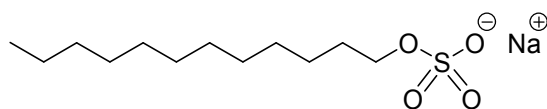
Sodium dodecyl sulfate (SDS)
*cmc*: 8.2 mM

Non-ionic Surfactants.

Polyoxyethylene(22)lauryl ether (Brij P35)
cmc: 0.09 mM

Scheme 2. Structures of surfactants and aryl benzoates.

In the present article, we describe the results on the photo-Fries rearrangement of several *para*-substituted aryl benzoates in homogeneous and micro heterogeneous media. The binding constants (K_b) and the location of the substrates within the micelles are measured through spectroscopic methods. From a preparative point of view, the use of anionic and neutral surfactant micelles shows a high selectivity in favor of the formation of the 2-hydroxy benzophenone derivatives achieving yields higher than 90%. From a mechanistic viewpoint, it is furnished the characterization of both *p*-substituted phenoxy radical and substituted 2-benzoylcyclohexadienone transients in homogeneous and micellar environment. The in-cage and out-of-cage rate constants (k_R and k_E, respectively) of *p*-substituted phenoxy radical are measured for the first time by means of laser flash photolysis.

Results.

Steady-state Photolysis. Photoirradiation of aryl benzoates in homogeneous media. Irradiation of aryl benzoates (**1** − **8**) in cyclohexane, MeOH and MeCN which were chosen as representative non-polar, protic polar and aprotic polar solvents, with $\lambda_{exc} = 254$ nm under N_2 atmosphere provided the expected photoproducts from the photo-Fries rearrangement, viz. formation of 2-hydroxybenzophenone derivatives (**1a** − **8a**), the corresponding phenols (**1b** − **8b**) and benzoic acid. The photochemical reaction is depicted in Scheme 3. The formation of benzoic acid was attributed to the oxidation of benzaldehyde, which is the primary photoproduct formed, because of the presence of residual molecular oxygen in the reaction mixture.[11] In all the performed reactions, the yield of benzoic acid was between 5 to 15%.
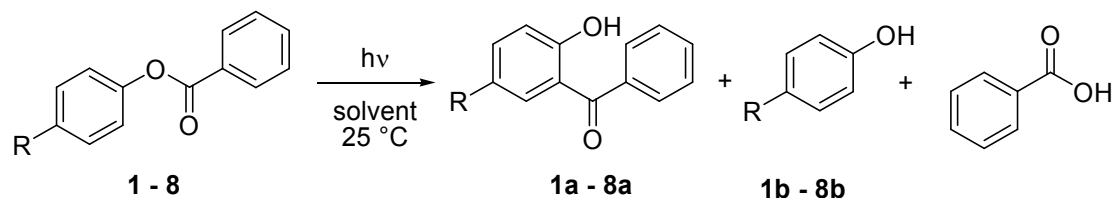
Scheme 3. The photoinduced Fries rearrangement of aryl benzoates (**1** − **8**).

When esters are consumed, the chemical yields collected in Table 1 show that benzophenones **1a – 8a** are the main photoproducts in up to 94% yield. Furthermore, the product distribution did not change significantly with the nature of the solvent and poor selectivity in favor of the benzophenone derivatives was observed.

Table 1. Irradiation of aryl benzoates in homogeneous solution. Yield of photoproducts,[a] reaction quantum yield (ϕ_r)[b] and fluorescence quantum yield (ϕ_f).[c]

| Aryl benzoates | Solvent | Photoproduct yield (%) | | ϕ_r | ϕ_f |
		Benzophenones **(a)**	Phenols **(b)**		
1	Cyclohexane	46	27	0.30	0.08
	MeCN	62	17	0.36	0.03
	MeOH	66	17	0.33	0.10
2	Cyclohexane	55	28	0.37	0.002
	MeCN	69	19	0.71	0.013
	MeOH	73	23	0.44	0.002
3	Cyclohexane	42	22	0.40	0.25
	MeCN	94	5	0.62	0.07
	MeOH	80	20	0.31	0.11
4	Cyclohexane	59	27	0.50	0.001
	MeCN	95	5	0.35	0.025
	MeOH	75	25	0.63	0.002
5	Cyclohexane	40[e]	30	0.36	0.001
	MeCN	60[e]	33	0.14	0.005
	MeOH	58[e]	26	0.14	0.002
6	Cyclohexane	41	23	0.59	0.012
	MeCN	73	18	0.32	0.035
	MeOH	85	14	0.31	0.033
7	Cyclohexane	38	19	0.51	0.002
	MeCN	84	15	0.82	0.025

	MeOH	75	26	0.93	0.002
8	Cyclohexane	31	34	0.02	NF[d]
	MeCN	60	40	0.07	NF
	MeOH	50	52	0.07	NF

[a] Yield of photoproducts determined by ^{1}H-NMR spectroscopy in the reaction mixture. Concentration of aryl benzoates: 5.0×10^{-3} M. [b]Actinometer: KI (0.6 M), KIO$_3$ (0.1 M) and Na$_2$B$_4$O$_7$.10H$_2$O (0.01 M) solution in water; $\phi(I_3^-) = 0.74$; $\lambda_{exc} = 254$ nm.[12]; Error: ± 0.01. [c]Actinometer: 4-chloroanisole acetonitrile solution under Ar atmosphere; $\phi_f = 0.019$[13]; Error: ±0.002. [d]NF: non-fluorescent substrate. [e] 4-Hydroxybenzophenone is also formed: Cyclohexane 30%; MeCN 7%; MeOH 15%.

The quantum yields of consumption of the aryl benzoates (ϕ_r) in polar and non-polar solvents were measured (see Table 1). The ϕ_r values were found to be higher than 0.30, implying that the photo-Fries rearrangement reaction occurred efficiently. Moreover, in every solvent, a marked increase of the ϕ_r values was observed, moving from esters bearing electron-donor to esters substituted with electron-acceptor substituents. The only exception found was ester **8**. The ϕ_r values measured for compound **8** are lower than 0.10 in all the solvents studied. The aryl benzoates are all poorly fluorescent chromophores (see Table 1) with the exception of benzoate **8** that was found to be non-fluorescent. The spin coupling effect of the nitro group explains the peculiarity of ester **8**.[14,15] Indeed, intersystem crossing pathway competes with both the photo-Fries rearrangement reaction and the fluorescence emission.

UV-visible and NMR spectroscopies were used to follow the photochemical reaction and aryl benzoates **1**, **2**, **3** and **7** have been chosen as representative examples for such spectroscopic studies. Figure 1(a) showed the time-resolved UV-visible absorption spectrum of the photoreaction of *p*-methylphenyl benzoate (**3**) in cyclohexane showing the growth of a new band located at 352 nm during the irradiation time. This band was assigned to the *n,π** transition of the carbonyl group of benzophenone **3a**[14] and was also observed in MeOH and MeCN. However, no significant solvent effect was observed in the maximum wavelength of the *n,π** transition band upon change of the solvent polarity. A similar solvent effect on the maximum wavelength of the *n,π** band of the 2-hydroxy

benzophenone derivatives (**1a**, **2a**, **4a** – **8a**) was also observed (see Figure S1 in Supporting Information). On the other hand, a noticeable substituent effect on the n,π^* band of the substituted 2-hydroxy benzophenones (**1a** – **8a**) was observed. In fact, a hypsochromic effect ($\Delta\lambda$ = -73 nm) ascribed to the n,π^* band was measured changing the substituent from the electron-donor MeO (λ_{max} = 378 nm) to the electron-accepting NO_2 (λ_{max} = 305 nm). The course of the photoreaction of ester **1** is detailed in Figure 1(b), where the benzoyl [1;3]-migration to form benzophenone **1a** is shown to be the primary process. Figures 1(c) and 1(d) show the relative formation of benzophenones **2a** and **7a** (starting from the corresponding esters **2** and **7**), respectively, in non-polar and polar solvents. The relative rates of formation of **2a** are similar in MeCN and cyclohexane while in MeOH is somewhat lower implying that in protic polar solvent radiative and non-radiative decay rates compete with the photoreaction pathway. The rates of formation of benzophenone **7a** are quite similar in all the solvents tested. For the other esters studied the relative rates of formation of the corresponding benzophenone derivatives showed a similar behavior (see Figure S2 in Supporting Information).
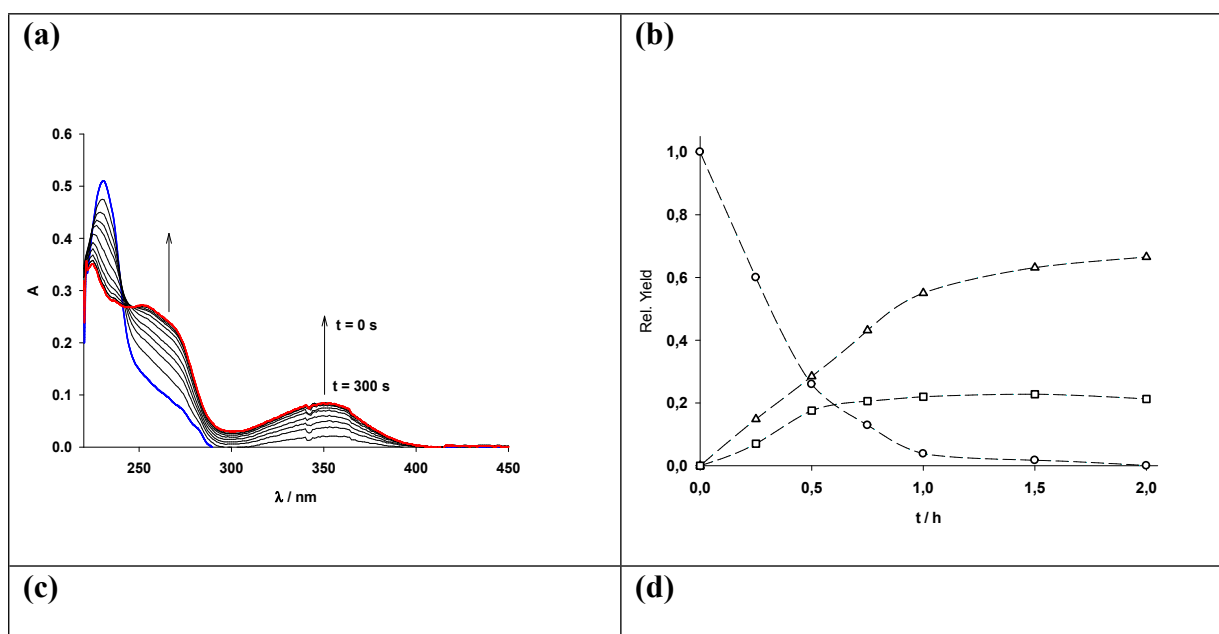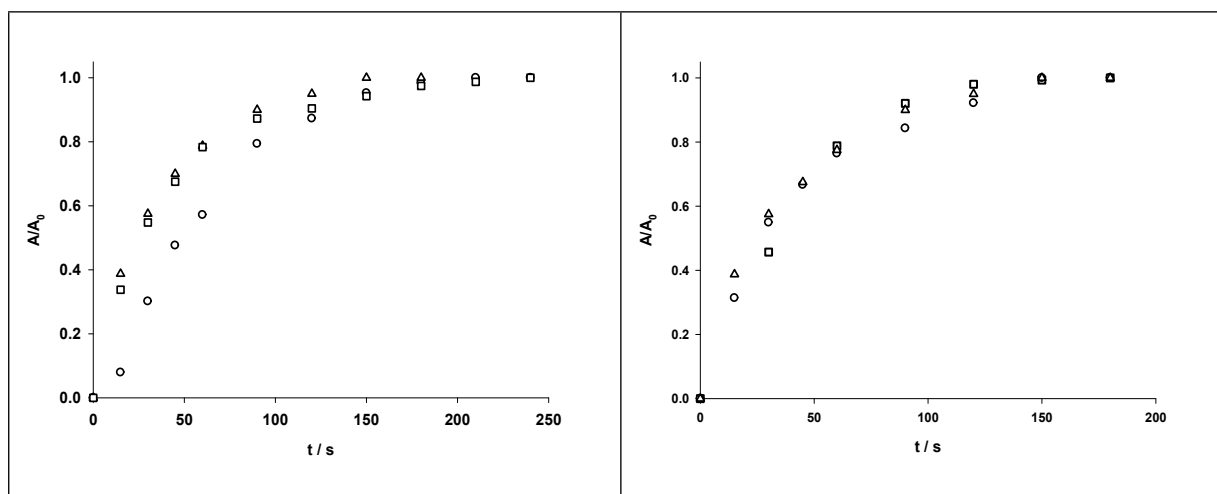
Figure 1. (a) Time-resolved UV-visible absorption spectrum of **3** in cyclohexane. Blue line: initial time; red line: 300 s. (b) Relative yield profile vs time of **1** in MeOH: ester **1** (circles); benzophenone **1a** (triangles); phenol **1b** (square). (c) Relative absorbance at 358 nm (A/A_∞) of formation of **2a** in: MeOH (circles); MeCN (triangles); cyclohexane (square). (d) Relative absorbance at 333 nm (A/A_∞) of formation of **7a** in: MeOH (circles); MeCN (triangles); cyclohexane (square).

The ^{1}H-NMR spectra of the photoreaction mixture (6 h irradiation) of 4-cyanophenyl benzoate (**7**) in cyclohexane under N$_2$ atmosphere were also recorded (see Figure S3 in Supporting Information). As expected, the formation of the photoproducts benzophenone **7a** and phenol **7b** were confirmed through their diagnostic signals (see Figure S3 in Supporting Information) along with the unreacted ester **7**. The experiments demonstrated poor selectivity of the photoreaction in homogeneous media and this trend was observed for all the esters (**1 – 8**) studied (see Table 1).

Photoirradiation of aryl benzoates in micellar media. Irradiation of aryl benzoates (**1 – 8**) in aqueous SDS (0.10 M) with λ_{exc} = 254 nm under air caused the selective generation of 2-hydroxybenzophenone derivatives (**1a – 8a**) in high yields along with lower amounts of the corresponding phenols (**1b – 8b**) (for structures, refer to Scheme 3). In these experiments consumption up to 95% of aryl benzoates (**1 – 8**) was obtained. The chemical yields of benzophenone derivatives (**1a – 8a**) are collected in Table 2.

Table 2. Irradiation of aryl benzoates in micellar solution. Yield of 5-substituted-2-hydroxybenzophenones[a] and reaction quantum yield (ϕ_r)[b] and fluorescence quantum yield (ϕ_f)[c] of aryl benzoates.

	Photoproduct yield (%)		ϕ_r		ϕ_f
Benzophenones	SDS	Brij-P35	SDS	Brij-P35	SDS
1a	94	95	0.13	0.12	0.026
2a	76	85	0.79	0.21	0.026
3a	70	92	0.55	0.41	0.024
4a	85	89	0.54	0.26	0.025
5a	90[e]	92[e]	0.50	0.21	0.029
6a	87	90	0.53	0.21	0.062
7a	80	78	0.45	0.10	0.024
8a	44	56	0.13	0.01	NF[d]

[a] Yield of photoproducts determined by ^{1}H-NMR spectroscopy in the reaction mixture. Concentration of aryl benzoates: 5.0×10^{-3} M. [b] Actinometer: KI (0.6 M), KIO$_3$ (0.1 M) and Na$_2$B$_2$O$_7$.10H$_2$O (0.01 M) solution in water; $\phi(I_3^-) = 0.74$; $\lambda_{exc} = 254$ nm.[12] Error: $\pm$ 0.01. [c] Actinometer: 4-chloroanisole acetonitrile solution under Ar atmosphere; $\phi_f = 0.019$[13]; Error: ±0.002. [d] NF: non-fluorescent substrate. [e] 4-Hydroxybenzophenone is also formed in 8 − 10%.

As is apparent from Table 2, SDS and Brij-P35 micellar solutions promoted a high selectivity on the photo-Fries rearrangement of the aryl benzoates **2 − 8**, favoring the formation of the corresponding substituted benzophenones (**2a − 8a**) over the *p*-substituted phenols. The observed selectivity was attributed to the confinement of the aryl benzoates and the radicals formed after the C-O bond cleavage within the hydrophobic core provided by the micellar medium. Moreover, the *p*-substituted phenols were formed in a minor extent or not formed at all, evidencing the suppression of products arising from cage escape. It is worth noticing that the irradiation of *p*-nitrophenyl benzoate (**8**) gave 2-hydroxy-5-nitrobenzophenone (**8a**) only in 44 % yield (the consumption of the starting material was 66 % after 6 h of irradiation). No *p*-nitrophenol was detected in the reaction mixture. Competitive deactivation of the singlet state of *p*-nitrophenyl benzoate (**8**) through intersystem crossing accounted for the observed chemical yield of benzophenone **8a**.[14] The competitive process populates the triplet excited state, due to the spin-orbit coupling provided by the nitro group, which is an unproductive excited state of benzoate **8**.

Quantum yields of consumption of the aryl benzoates (ϕ_r, see Table 2) were measured in micellar media, viz. SDS and Brij-P35, and were found to be of the same order of magnitude. However, the quantum yields measured in SDS solution were larger than in Brij-P35 solutions. This behavior can be attributed to an enhancement of the non-radiative pathway from the singlet state of the aryl benzoates in Brij-P35 solutions. The high-consumption quantum yields and low or no fluorescence emission from aryl benzoates (**1 – 8**) was consistent with a fast reaction from the singlet state. However, non-radiative and intersystem crossing pathways from the singlet state compete with the photo-Fries rearrangement.

UV-visible spectroscopy was used for following the photoreaction and *p*-methoxyphenyl benzoate (**1**) was selected as a representative aryl benzoate. Thus, the reaction of **1** in SDS (0.10 M) was followed by UV-visible absorption spectroscopyand the UV-visible spectral change vs time is shown in Figure 2(a). It is apparent from the UV-visible spectra that the photo-Fries rearrangement of compound **1** to form 2-hydroxy-5-methoxy benzophenone (**1a**) is the primary process, according to the appearance of the characteristic n,π^* band of the carbonyl group located at 372 nm. Similar behavior was observed for compounds **2 – 8** (see Figure S1 in Supporting Information).

The course of the photoreaction of ester **1** is depicted in Figure 2(b) and clearly shows that the benzoyl [1;3]-migration to form benzophenone **1a** is the main process. On the other hand, we selected aryl benzoates **7** and **4** as examples of aryl benzoates to show the relative formation of benzophenones **7a** and **4a**, respectively, in cyclohexane and 0.10 M SDS and 0.01 M Brij-P35 solutions (see Figures 2(c) and 2(d)). The relative rates of formation of **7a** in surfactant media (see Figure 2(c)) are slightly lower than in cyclohexane and can be attributed to the radiative and non-radiative decay rates that compete with the photoreaction pathway. Similar behavior is observed for the rates of formation of benzophenone **4a** (see Figure 2(d)) as well as with for the other benzophenone derivatives (see Figure S2 in Supporting Information).
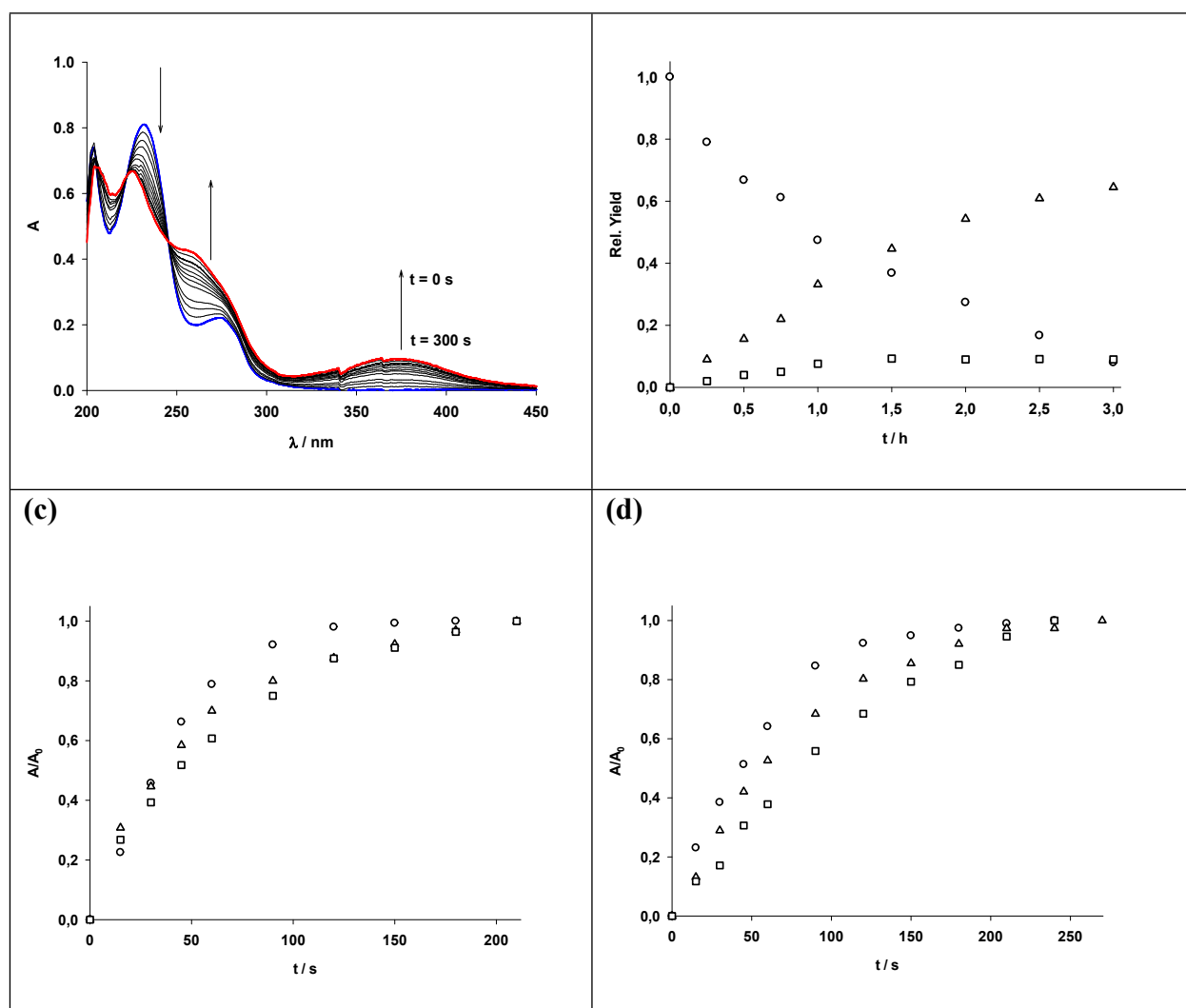
(a)	(b)

Figure 2. (a) UV-visible spectral change vs time of **1** in SDS 0.10 M in water. Blue line: initial time; red line: 300 s. (b) Relative yield profile vs time of **1** in MeOH: ester **1** (circles); benzophenone **1a** (triangles); phenol **1b** (square). (c) Relative absorbance at 375 nm (A/A_∞) of formation of **7a** in: Cyclohexane (circles); 0.10 M SDS solution (triangles); 0.10 m Brij-P35 solution (square). (d) Relative absorbance at 355 nm (A/A_∞) of formation of **4a** in: Cyclohexane (circles); 0.10 M SDS solution (triangles); 0.10 m Brij-P35 solution (square).

The photoreaction of compound **1** in micellar environment (SDS 0.10 M) was also followed by NMR spectroscopy. The ^{1}H-NMR spectra of the reaction mixture of benzoate **1** in SDS (0.10 M) irradiated during 6 h with λ_{exc}= 254 nm (see Figure S4 in Supporting Information) showed that benzophenone **1a** was formed in 94 % yield along with *p*-methoxyphenol and benzoic acid in yields lower than 5%. In the same spectra, the signals belonging to the surfactant (SDS) were also observed. The consumption of

benzoate **1** was quantitative. Similar results were obtained with all the aryl benzoates studied (**2 – 8**) and the photoproduct yields are collected in Table 2.

Binding constants (K_b) of aryl benzoates in micellar media. When ionic and neutral surfactant solutions are used as micro reactors to perform photoreactions the knowledge of the reactant's location in the micellar system is required. In order to know the reactant's positioning within micelles, UV-visible and ^{1}H NMR studies of guest molecules (aryl benzoates) in micellar solution were conducted. UV-visible spectroscopy was used to determine the binding constant (K_b) between micelles and aryl benzoates applying a methodology that have been reported earlier for aryl acetamide.[9] Both bathochromic and hyperchromic shifts of the lower energy absorption band of the aryl benzoates were observed by addition of increasing amounts of surfactant, demonstrating the binding of the substrates to the micelle that took place within the hydrophobic core of the micelle. Indeed, the binding of the aryl benzoates to the micelle can be described as equilibrium, K_b can be written according to equation 1, where S represents the benzoates, Surf the surfactants and [S-Surf] the complex formed between benzoates and the surfactants.

$$[S] + [Surf] \xrightleftharpoons{K_b} [S\text{-}Surf] \qquad\qquad K_b = \frac{[S\text{-}Surf]}{[S]\,[Surf]} \tag{1}$$
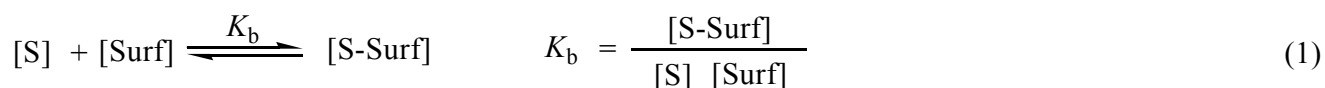
Equation 2 was obtained after application of Lambert-Beer law on equation 1. A_0 and A are the absorbances at the maximum wavelength in the absence and presence of surfactant, respectively. The molar absorptivity of the complex and the benzoates are dubbed accordingly ε_C and ε_S. A linear relationship is observed between $(A - A_0)^{-1}$ and the reciprocal of the concentration of the surfactant in equation 3 which was obtained after rearranging equation 2.

$$\frac{(A - A_0)}{A_0} = \frac{\varepsilon_C . K_b . [Surf]}{\varepsilon_S . (1 + K_b . [Surf])} \tag{2}$$

$$\frac{A_0}{(A - A_0)} = \frac{\varepsilon_S}{\varepsilon_C} + \frac{\varepsilon_S}{\varepsilon_C . K_b} \frac{1}{[Surf]} = A_0 \frac{1}{\Delta A} \tag{3}$$

The experimental data obtained for some aryl benzoates and SDS and Brij-P35 are shown in Figure 3 and the best linear regression curves are also included in the same figure. The plots for the other systems are collected in Figure S5 (see Supporting Information). The K_b values for $1 - 8$ calculated from the ratio between the slope and the intercept of the regression curve are shown in Table 3. From these data it is apparent that the benzoates bind to the micelles and the ones possessing hydrophobic character, i.e. benzoates **1** and **4** in SDS micellar solution, show high K_b values. Likewise, benzoates **1**, **4** and **7** possess greater K_b compared to the other substrates in the case of Brij-P35 micellar solution. Generally, the K_b values obtained for benzoates $1 - 8$ are typical of aromatic solutes as it pointed out by Quina, Treiner and co-workers.[16] Estimation of K_b values ≤ 100 M^{-1} in SDS for weakly hydrophobic substrates such as phenyl chloroformate have also been reported.[17] Likewise, K_b values have been reported for the binding of Brij-P35 surfactant and a series of benzoyl chloride derivatives and they were found to be higher than those obtained for other surfactants such as SDS and CTAC.[18] Estimation of a minimum value around 190 M^{-1} for the binding constant (K_b) of Brij-P35 surfactant was reported and accounts for a more apolar environment when pyrene was used as a micropolarity probe.[18]
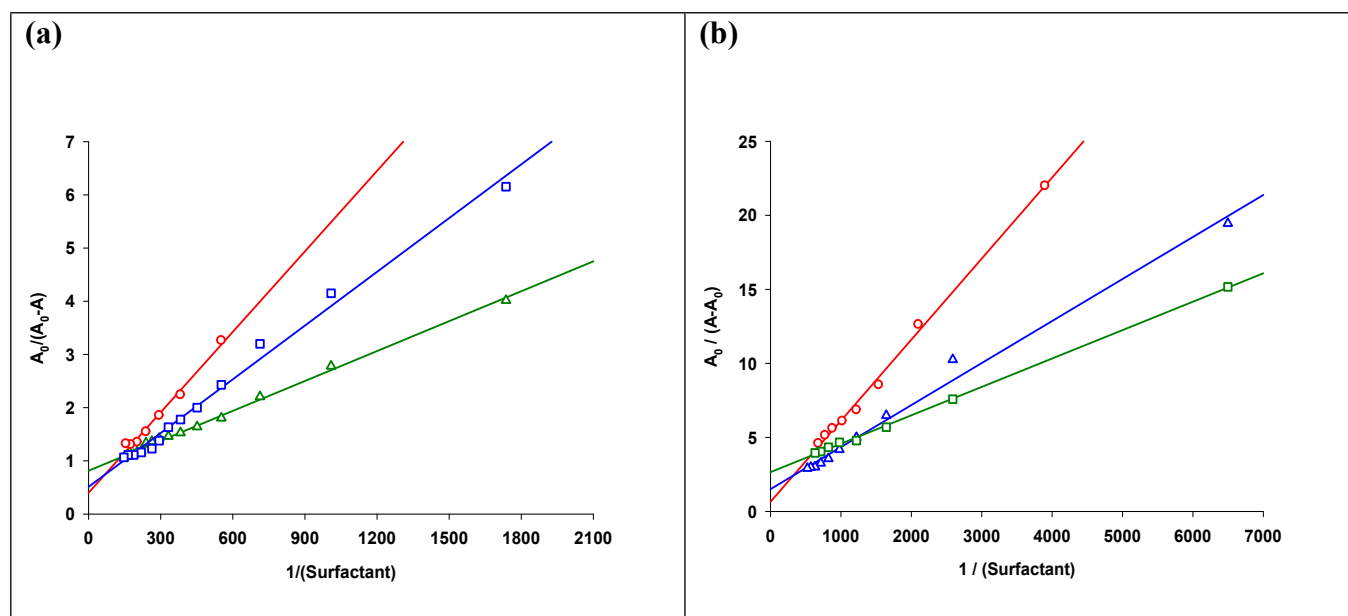
Figure 3. Reciprocal plotting (($A_0/(A-A_0)$ vs concentration of surfactants) in water at room temperature: **(a)** SDS (circles: **2**; squares: **4**; triangles: **7**) and **(b)** Brij-P35 (circles: **2**; squares: **4**; triangles: **1**). In all the linear fitting regressions: $r^2 > 0.99$.

Table 3. Binding constant (K_b) in water of surfactants (SDS and Brij-P35) and aryl benzoates.

Aryl benzoates	K_b / M^{-1}							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
SDS	1402	80	127	539	42	10	18	74
Brij-P35	1398	581	69	423	63	26	1394	181

2D NMR spectroscopy has been recorded to confirm qualitatively the location of the aryl benzoates within the micelle. NOESY experiments have been often used to determine the localization of substrates inside the micelle as well as to determine the extent of co-aggregation between two different kinds of surfactants in water.[19] Positive results are achieved when cross-peaks between diagnostic signals of the substrate and the surfactants, respectively, are observed in the corresponding contour plots.[9] Thus, the NOESY experiments were performed in D_2O and Figure 4 shows the 2D NMR spectrum for a solution of SDS (7 mM) in the presence of benzoate **1** (10 mM). The inset red frames recognize the NOE (Nuclear Overhauser Effect) between the signals of the surfactant SDS (bulk hydrogens and α hydrogen) and the signals belonging to the aromatic protons (H-2/H-6, H-3/H-5, H-10/H-14, H-12 and H-12/H-13) of *p*-cyanophenyl benzoate **7**. Also, Figure 6 shows the labels of the protons of the surfactant SDS and the aryl benzoate **7,** respectively. Similar spectroscopic behavior was observed for solutions of SDS and Brij-P35 in D_2O in the presence of aryl benzoates **1** and **3** (see Figures S6, S7 and S8 in Supporting Information). The cross-peaks of diagnostic signals observed in the 2D NMR contour plots are in agreement with and reinforce the UV-visible spectroscopic analyses.
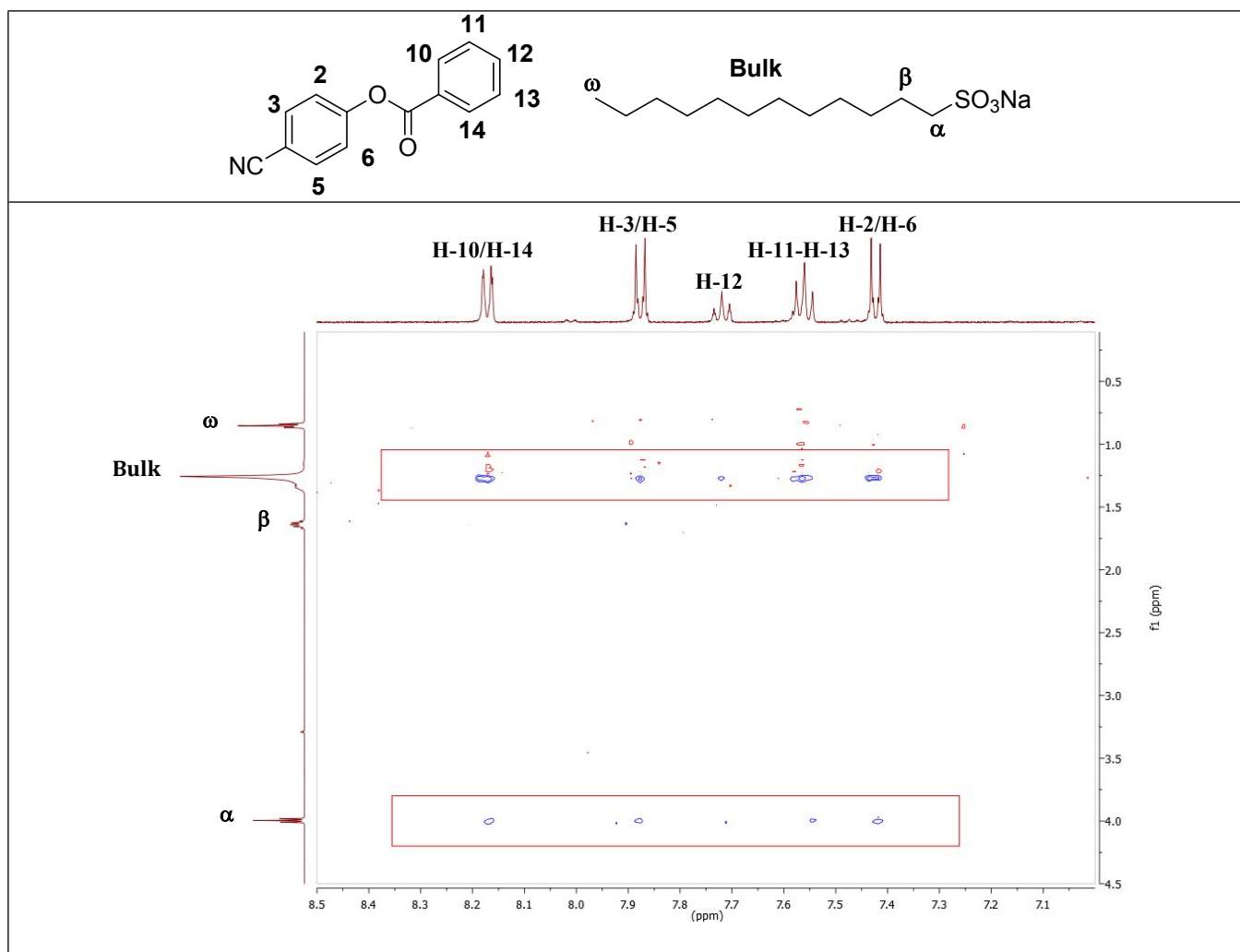
Figure 4. 2D NOESY contour plot of a solution of SDS (7 mM) and **7** (10 mM) in D$_2$O at room temperature.

However, we cannot estimate the location of the benzoates with accuracy but we can suggest that the benzoates are located inside the hydrophobic core of the micelle because the proton nuclei of the aryl benzoates correlate nicely with the proton nuclei of the surfactants as can be seen through the cross-peaks of the contour plots.

Laser Flash photolysis of aryl benzoates. Irradiation of *p*-methoxyphenyl benzoate (**1**) in acetonitrile and cyclohexane solutions with a laser pulse (266 nm) under nitrogen atmosphere gives the transient absorption spectra shown in Figures 5(a) and (b). Four absorption bands with maximum wavelength at 290, 340, 400 and 720 nm were observed in the transient spectra. According to the data reported in the literature, we attributed the bands located at 290 nm and 400 nm to the *p*-methoxyphenoxyl radical

while those bands centred at 340 nm and 720 nm were attributed to cyclohexadienone transient.[20] Two

consecutive pathways from the singlet excited state of ester **1** are involved in the formation of both

transients after the pulse (266 nm): (i) homolytic fragmentation of the C-O bond of the ester group

affording *p*-methoxyphenoxy and benzoyloxy radical species in the solvent cage (intermediates **A** and

B, respectively, in Scheme 4), and then, (ii) coupling of both radical species to give the 4-methoxy-2-

benzoylcyclohexadienone intermediate (**C** in Scheme 4). Also, in Figures 5(c) and (d) are reported the

transient absorption spectra of compounds **6** and **2** in acetonitrile after the laser pulse (266 nm). Two

characteristic bands located around 340 and 400 nm are observed which were assigned to the

substituted 2-benzoylcyclohexadienone and substituted phenoxy radical intermediates, respectively.

Noteworthy similar results are obtained for the other aryl benzoates studied (see Figure S9 in

Supporting Information).
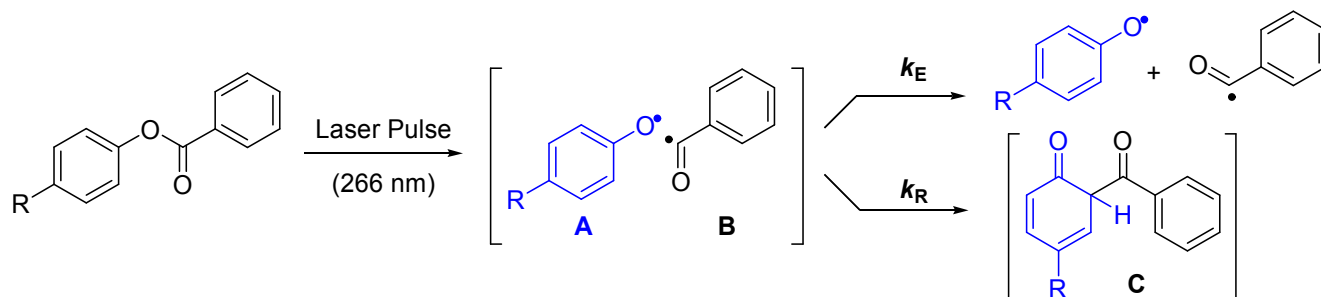
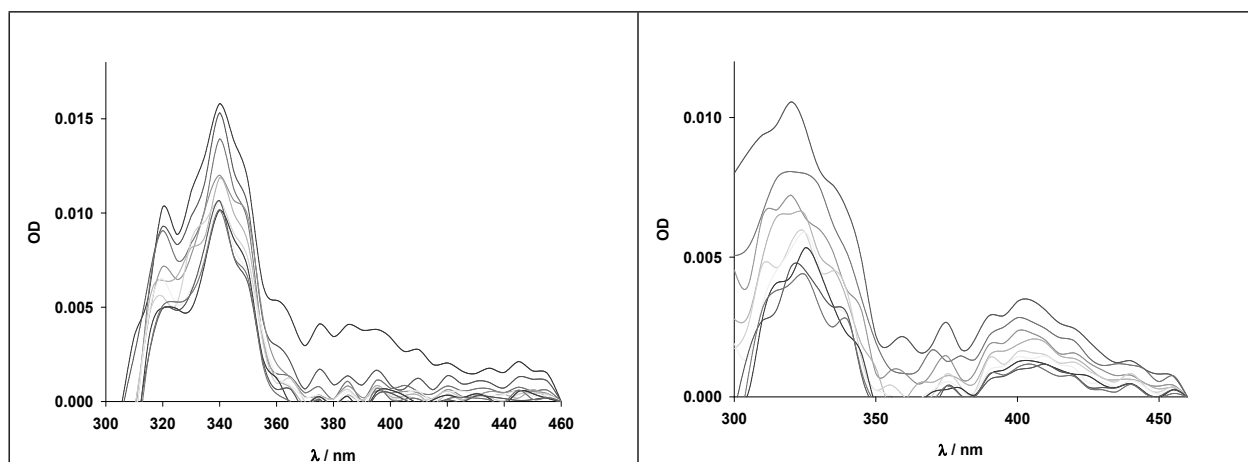Scheme 4. Formation of transient species after the laser pulse (266 nm).
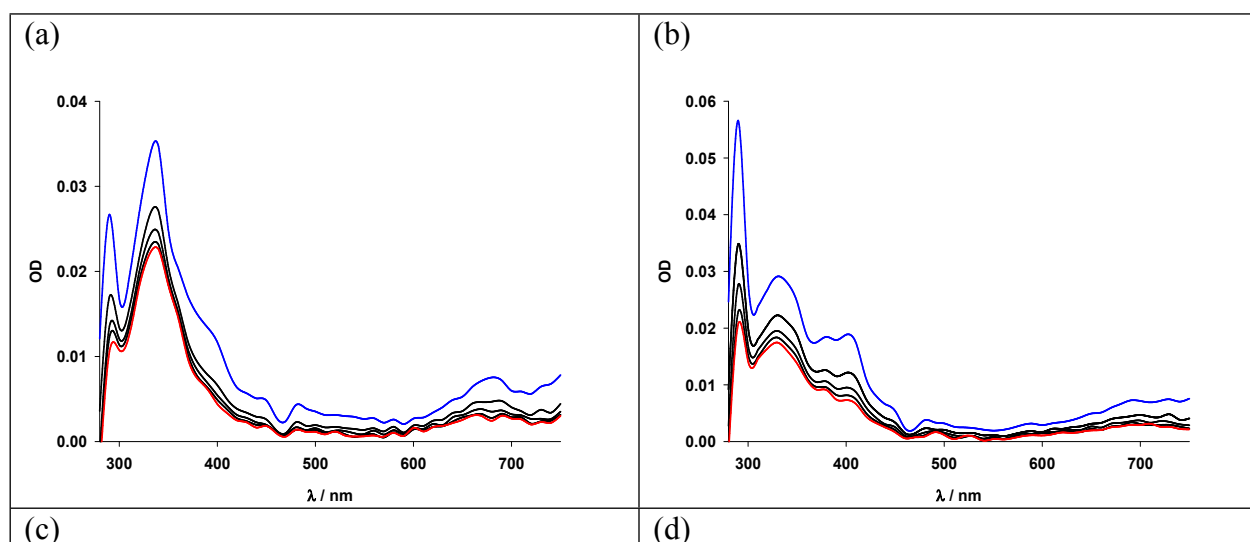
Figure 5. Transient absorption spectra obtained after a laser pulse (100 µs; λ_{exc}: 266 nm) of solutions (5.1x10⁻⁴ M) of: (a) **1** in cyclohexane; (b) **1** in acetonitrile; (c) **6** in acetonitrile and (d) **2** in acetonitrile under nitrogen atmosphere.

The decay traces of the transient signal assigned to 4-substituted phenoxyl radicals were also measured at 400 nm in N₂-saturated cyclohexane and acetonitrile solutions (after a laser pulse at 266 nm). The experiment was done with the aim of determining both the rate constants of radical out-of-cage escape (k_E) and *ortho* coupling reaction (k_R) (see Scheme 4). Some selected examples of the decay traces are shown in Figure 6. The decay traces of 4-substituted phenoxyl radicals show biexponential decay fitting with r^2 values > 0.998 independent of the solvent used. Two half lifetime values were obtained from the nonlinear fittings, τ_E and τ_R: the short lifetime (τ_R) was assigned to in-cage coupling process while the large lifetime (τ_E) was assigned to the phenoxyl radical out-of-cage process by comparison with earlier reported data regarding thiyl radicals.[20e,21] This biexponential behaviour can be interpreted considering the two competitive pathways the 4-substituted phenoxyl radical can undergo, viz. out-of-cage escape and in-cage coupling pathways, (see Scheme 4). This behavior can be described according to equation 4 where ArO$^\bullet$ represents the substituted phenoxy radical and PhCO$^\bullet$ represents the benzoyl radical.

$$- \frac{d[ArO\bullet]}{dt} = k_E\,[ArO\bullet] + k_R\,[ArO\bullet]\,[Ph\overset{\bullet}{C}O] \tag{4}$$
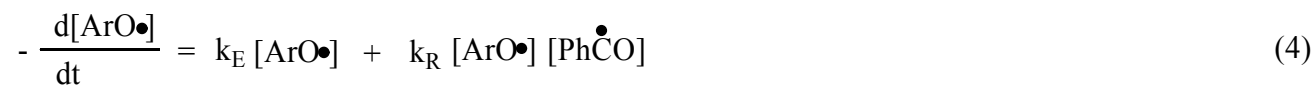
The out-of-cage escape of the substituted phenoxy radical is a unimolecular pathway. Therefore, the rate constant (k_E) of this process can be calculated from the reciprocal of the lifetime, $k_E = 1 / \tau_E$ (see Table 4). The in-cage coupling rate constants (k_R) were obtained by plotting the reciprocal of the concentration of the substituted phenoxy radicals against time and excellent linear correlations were observed (see Figure S11 in Supporting Information for the linear correlations). Then, after applying a linear regression fitting the in-cage coupling rate constants (k_R) were obtained from the slopes and these data are also shown in Table 4. As can be seen in Table 4, it is apparent that the out-of-cage rate constants (k_E) for the unimolecular escape process of 4-substituted phenoxyl radicals are quite similar in all the solvents studied (1.5 to 8.3 $\times 10^5$ s^{-1}) and somewhat independent of the substituent. On the other hand, the bimolecular in-cage coupling of 4-substituted phenoxyl and benzoyl radicals was found to be a second-order rate constant (k_R) of $10^9 - 10^{10}$ M^{-1}.s^{-1} in N$_2$-saturated solvents with no significant substituent effect associated to it.
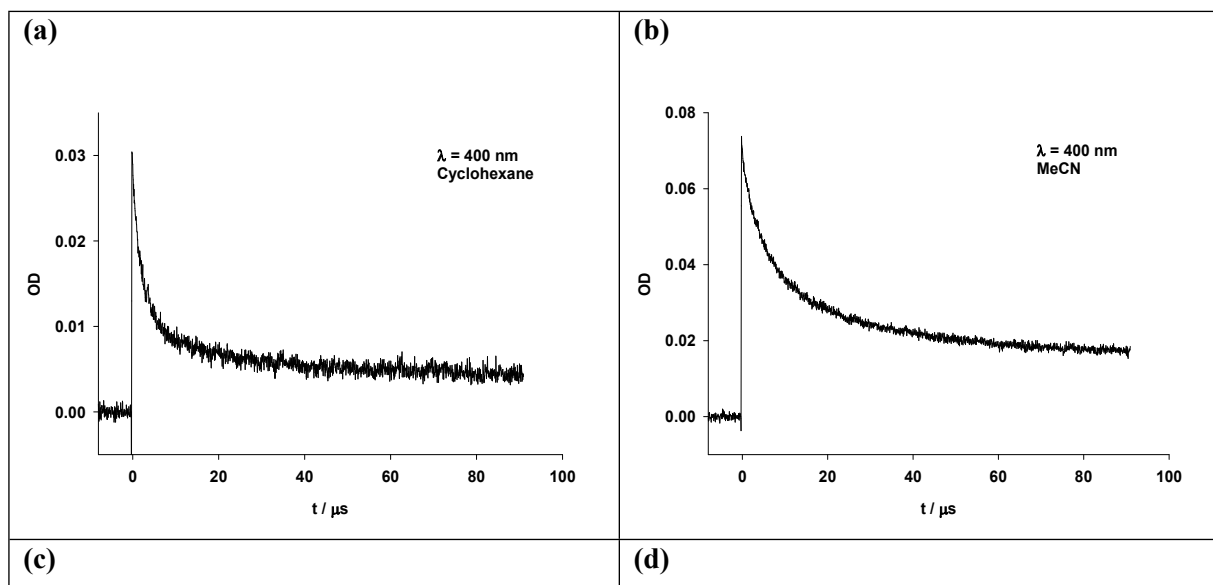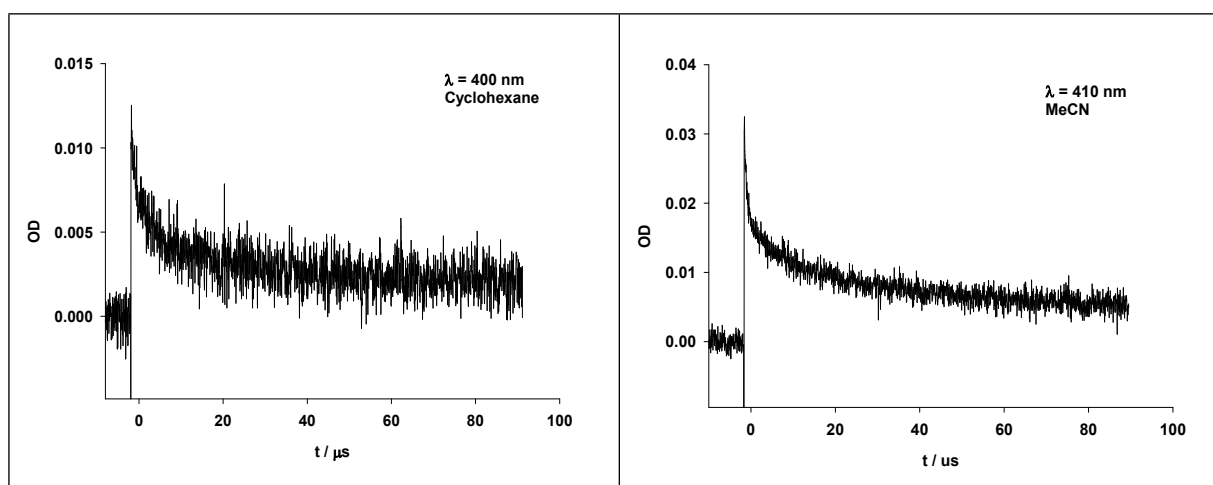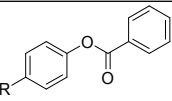
Figure 6. Decay traces of 4-substituted phenoxyl radical recorded at 400 nm after the laser pulse (λ_{exc}: 266 nm) of solutions (5.1×10^{-4} M) of: (a) 4-methoxyphenyl benzoate (**1**) in cyclohexane; (b) 4-methoxyphenyl benzoate (**1**) in acetonitrile; (c) 4-tert-butylphenyl benzoate (**4**) in cyclohexane; (d) 4-phenoxyphenyl benzoate (**2**) in acetonitrile under N_2 atmosphere.

Table 4. Out-of-cage (k_E) and in-cage coupling (k_R) rate constants of 4-substituted phenoxyl radicals measured by laser flash photolysis (266 nm) in different solvents under N_2 atmosphere.[a]

	Rate constants						
	MeCN		MeOH		Cyclohexane		SDS (0.10 M)
R	$k_E \times 10^{-5}$ / s^{-1}	$k_R \times 10^{-9}$ / $M^{-1}.s^{-1}$	$k_E \times 10^{-5}$ / s^{-1}	$k_R \times 10^{-9}$ / $M^{-1}.s^{-1}$	$k_E \times 10^{-5}$ / s^{-1}	$k_R \times 10^{-9}$ / $M^{-1}.s^{-1}$	$k_R \times 10^{-9}$ / $M^{-1}.s^{-1}$
OMe (**1**)	2.2±0.1	5.5±0.1	2.8±0.1	15±1	4.5±0.1	8.9±0.1	3.9±0.1
OPh (**2**)	8.3±0.2	14±1	1.0±0.2	24±1	2.2±0.2	46±1	25±1
Me (**3**)	3.0±0.1	1.4±0.1	6.7±0.1	1.7±0.1	2.5±0.1	7.3±0.1	3.0±0.1
t-Bu (**4**)	1.5±0.1	28±1	3.4±0.1	12±1	3.4±0.1	3.4±0.1	26±1
Ph (**6**)	5.0±0.2	4.6±0.1	1.0±0.2	6.1±0.1	Insoluble		1.2±0.1
CN (**7**)	4.8±0.2	9.5±0.1	2.3±0.2	9.9±0.1	1.3±0.2	36±1	17±1

[a] Concentration of aryl benzoates: 5.0×10^{-4} M.

A similar spectroscopic analysis was carried out with aryl benzoates in aqueous SDS (0.10 M) solutions after irradiation with a pulse at 266 nm. Two characteristic bands (340 – 360 nm and 400 nm) are observed in the transient absorption spectra and 4-substituted phenoxyl radicals showed second order kinetic decay traces. The in-cage coupling rate constants (k_R) were obtained by plotting the

reciprocal of the concentration of the 4-substituted phenoxyl radicals against time and, after applying a

linear regression fitting, the rate constants (k_R) were obtained from the slopes (see Table 4). No

significant substituent effect on the rate constants (k_R) was observed when the solvent was a micellar

solution (SDS 0.10 M) which gave a similar trend that was observed in homogeneous media.

Because phenyl benzoate (**5**) has no substituent in *para* position, two possible *ortho-* and *para-*

benzoylcyclohexadienone regioisomers can be proposed (see Scheme 5). Therefore, we have recorded

the transient absorption spectra and transient decay traces of compound **5** in different N_2-saturated

solvents with a laser pulse at 266 nm systematically. Figure 7(a) shows both the transient absorption

spectra and decay trace recorded at 400 nm in MeCN. The band located at 400 nm in the transient

absorption spectra was assigned to the phenoxyl radical while the large structured band located

between 330 and 385 nm was assigned to *ortho*-benzoylcyclohexadienone and *para-*

benzoylcyclohexadienone transients (see Scheme 5).
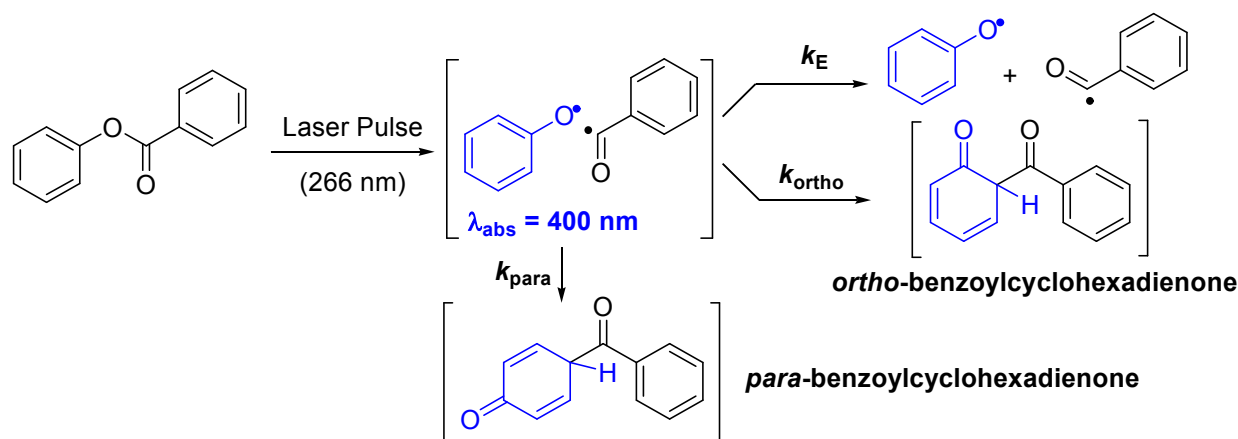
Scheme 5. Formation of transient species after the laser pulse (266 nm) from phenyl benzoate.

On the other hand, Figure 7(b) shows the decay trace of phenoxyl radical measured at 400 nm in N_2-

saturated acetonitrile solution after the laser pulse (266 nm). Biexponential decay was observed after a

non-linear fitting. This biexponential behaviour can be interpreted considering the competitive

pathways the phenoxyl radical can take viz. out-of-cage escape and *ortho* and *para* in-cage coupling

pathways (see Scheme 5). The rate constant (k_E) of the out-of-cage escape pathway was calculated from the reciprocal of the lifetime, $k_E = 1/\tau_E$. The rate constants thus obtained are shown in Table 5. In addition, the *ortho* and *para* in-cage coupling constants, k_{ortho} and k_{para}, were obtained by plotting the reciprocal of the concentration of the phenoxy radical against time and two nice linear correlations were observed (see Figure S12 Supporting Information for the linear correlations). Then, after applying a linear regression fitting to the linear correlations, the in-cage coupling constants were obtained from the slopes and these data are also shown in Table 5. No significant solvent effect on the rate constants was observed. However, the in-cage *para*-coupling pathway is rather lower than the *ortho*-coupling pathway.
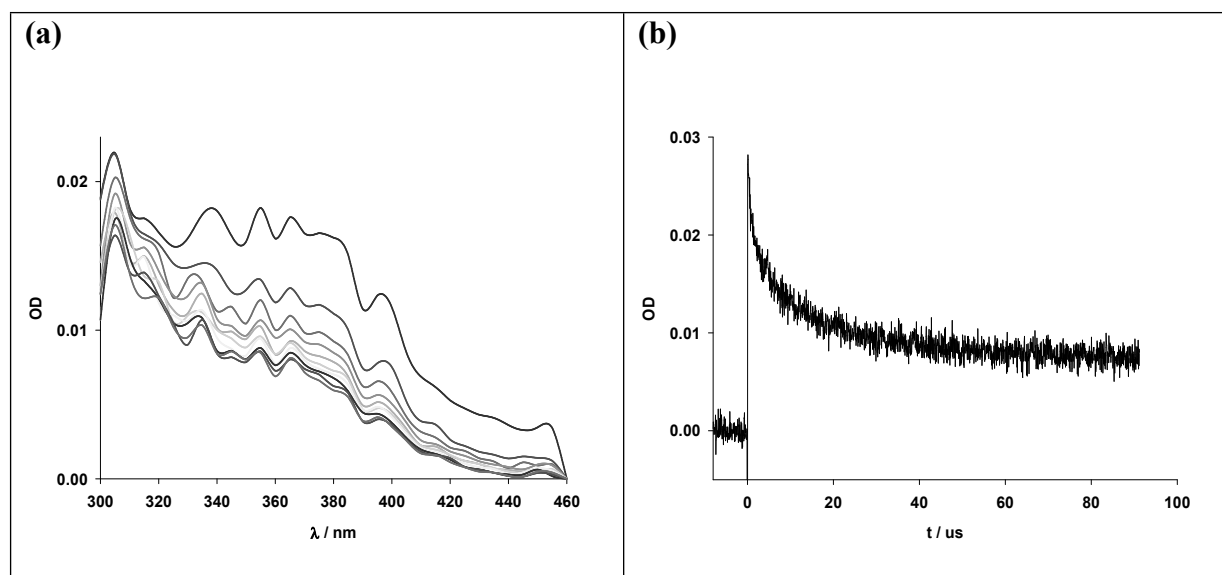

Figure 7. (a) Transient absorption spectra of phenyl benzoate (**5**) recorded in N_2-saturated acetonitrile solution (5.1×10^{-4} M) and (b) decay trace of phenoxyl radical recorded at 400 nm after the laser pulse (100 μs; λ_{exc}: 266 nm) of N_2-saturated acetonitrile solution (5.1×10^{-4} M) of phenyl benzoate (**5**).

Table 5. Out-of-cage (k_E) and in-cage coupling (k_{ortho} and k_{para}) rate constants of phenoxyl radicals measured by laser flash photolysis (266 nm) in different solvents under N_2 atmosphere.[a]

	Rate constants		
Solvents	$k_E \times 10^{-5}$ / s^{-1}	$k_{ortho} \times 10^{-9}$ / $M^{-1}.s^{-1}$	$k_{para} \times 10^{-9}$ / $M^{-1}.s^{-1}$
Cyclohexane	4.8±0.1	8.7±0.1	4.1±0.1

| MeCN | 4.8±0.1 | 8.4±0.1 | 3.2±0.1 |
| MeOH | 3.1±0.1 | 2.7±0.1 | 1.4±0.1 |
| SDS (0.10 M) | --- | 5.5±0.2 | 1.5±0.2 |

[a] Concentration of phenyl benzoates: 5.0×10^{-4} M.

Discussion.

As it was described above, direct irradiation (254 nm) of aryl benzoates in homogeneous media (cyclohexane, MeCN and MeOH) as well as in micro heterogeneous media (SDS and Brij-P35 aqueous solutions) under N_2 atmosphere took place efficiently (see Figures 1 and 2). During the irradiation of aryl benzoates a noticeable selectivity in favour of the benzophenone derivatives was observed in micellar media. In this case, the formation of the corresponding substituted phenols was lower than 2 % because of the confined hydrophobic core of the micelle (compare the data shown in Tables 1 and 2). The reaction mechanism depicted in Scheme 6 was sustained by the results obtained under steady-state conditions and laser flash photolysis experiments. When aryl benzoates are irradiated at 254 nm, population of the singlet state is achieved efficiently. This excited state is the photo reactive state of the photoreaction as it was reported in the literature.[5] Two pathways are involved in the deactivation of the singlet state, (i) homolytic fragmentation of the C-O bond (*path (a)*; Scheme 6) affording aryl phenoxy (ArO•) and benzoyl (PhCO•) radicals that evolves to 5-substituted-2-hydroxybenzophenone and 4-substituted phenol and (ii) photophysical deactivation (k_d; Scheme 3) of the singlet state involving fluorescence emission and internal conversion pathways that give the aryl benzoates in their ground state. In the case of ester **8**, intersystem crossing pathway must be considered as a process involved in the physical deactivation pathway estimating a ϕ_T value around 0.50.[14,15] Irradiation of aryl benzoates in N_2-saturated solutions with a laser pulse (λ_{exc} = 266 nm) gave the transient absorption of 4-substituted phenoxyl radical and 5-substituted-2-benzoylcyclohexadienone and these transients were formed immediately at 10 μs after the incident light (see, for example, Figure 5 for compounds **1**, **2** and

6) demonstrating that C-O homolytic fragmentation (***path (a)*** in Scheme 6) and in-cage coupling pathway (***path (d)*** in Scheme 6) occurred efficiently.

The decay traces of the phenoxyl radical transients were obtained at 400 nm in homogeneous media under inert atmosphere and biexponential decay was observed. Second-order kinetics (k_R) of 10^9 to 10^{10} $M^{-1}.s^{-1}$ were obtained (see Table 4 and Figure 6) and were attributed to the in-cage coupling of the substituted phenoxy radical and benzoyl radical (***path (d)*** in Scheme 6) providing the substituted 2-benzoylcyclohexadienone intermediates **C**. These last intermediates, i.e. intermediates **C,** are long-lived species showing lifetime values higher than 200 μs. The [1;3]-hydrogen migration and aromatization reaction pathway (***path (e)*** in Scheme 6) were estimated to occur with first-order kinetics (k_H) lower than $5x10^3$ s^{-1} providing the substituted 2-hydroxybenzophenone derivatives as the main photoproducts (see Table 1). On the other hand, first-order kinetics (k_E) of 10^5 s^{-1} were also obtained (see Table 4) which were assigned to the escape of the phenoxy radical from the solvent cage (***path (b)*** in Scheme 6) that in turn evolved to the 4-substituted phenol by abstraction of hydrogen from the reaction solvent (***path (c)*** in Scheme 6; SH: solvent).
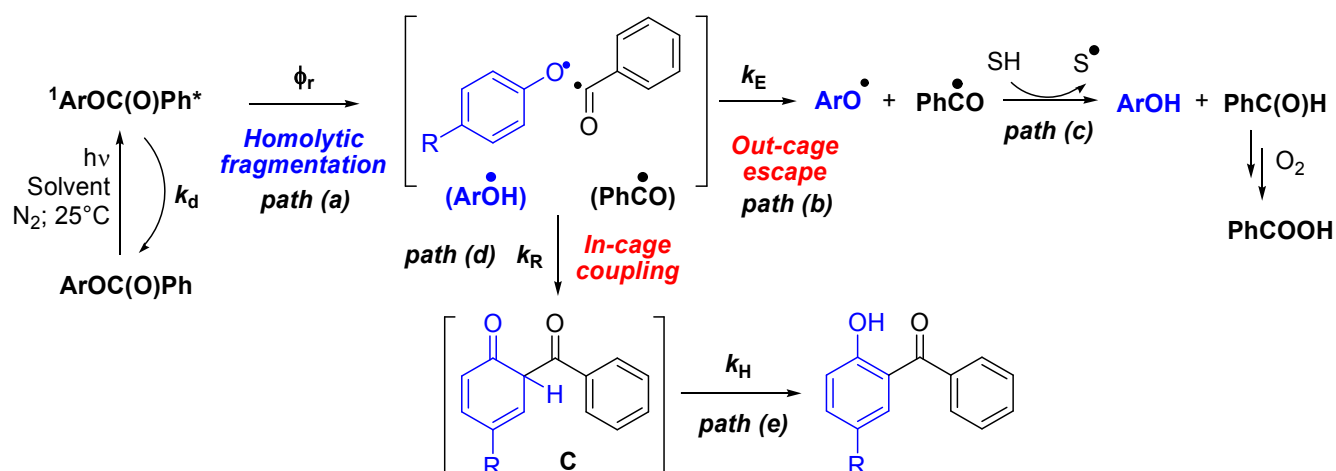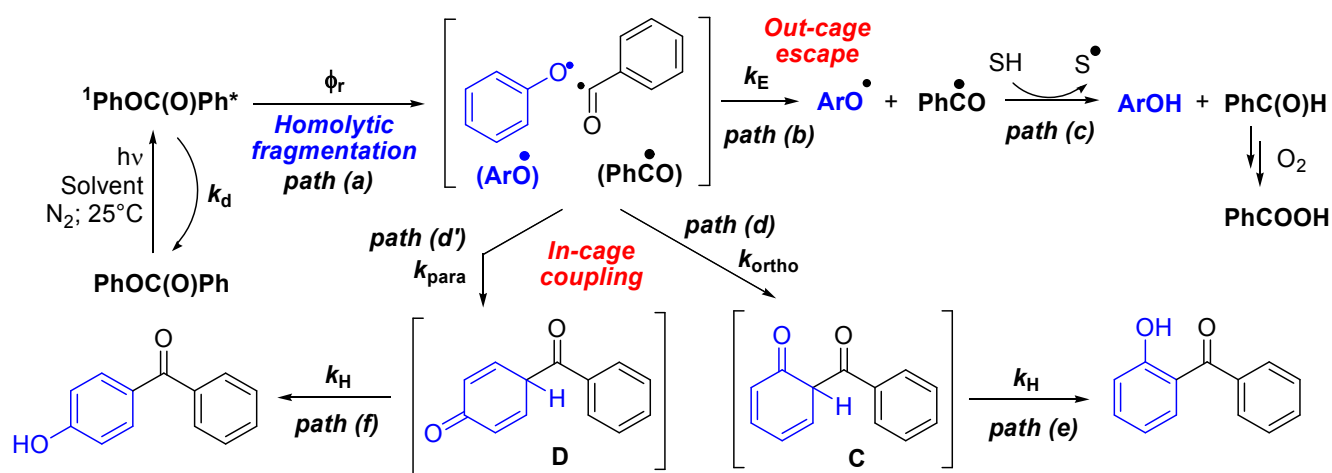

Scheme 6. The reaction mechanism for the irradiation of aryl benzoates with λ_{exc} = 254 nm.

Second-order rate constants (k_R) in the range of 10^9 to 10^{10} $M^{-1}.s^{-1}$ were obtained (see Table 4) from the fitting analysis of the decay traces of the phenoxyl radicals measured at 400 nm in micellar media (SDS and Brij-P35) under N_2 atmosphere. These values describe the in-cage coupling within the core of the micelle of the substituted phenoxy radical (ArO$^\bullet$) and benzoyl radical (PhC(O)$^\bullet$) (see ***path (d)*** in Scheme 6). This pathway afforded the substituted 2-benzoylcyclohexadienone intermediates **C**, also formed within the hydrophobic core of the micelle, that evolved through a [1;3]-hydrogen migration and aromatization reactions to substituted 2-hydroxybenzophenone. Because intermediates **C** are also long-lived species in micellar media ($\tau > 200$ μs) the rate constants k_H were estimated to be lower than 5×10^3 s^{-1} as it was observed in homogeneous media.

It is worth to mention that the only photoproducts detected in micellar media were the 2-hydroxybenzophenone derivatives **1a** – **8a** formed with chemical yields up to 95 % (see Table 2) the yield of substituted phenols were lower than 5 %. Therefore, we suggest that the escape of the phenoxy radical from the hydrophobic core of the micelle (***path (b)*** in Scheme 6) is not a productive pathway. The decay traces of phenoxy radicals in micellar media did not show biexponential decay traces as it was observed in homogeneous media but second-order kinetics that is in agreement with the in-cage coupling pathway (***path (d)*** in Scheme 6).

Additional comments about the irradiation of phenyl benzoate (**5**) in homogeneous and micellar media are needed. The results obtained under steady-state conditions and time-resolved spectroscopy on phenyl benzoate led us to advance the different reaction pathways depicted in Scheme 7. Irradiation of phenyl benzoate populated the singlet excited state efficiently and competitive physical deactivation (k_d) and homolytic fragmentation (***path (a)*** in Scheme 7) pathways occurred.

Scheme 7. Proposed reaction mechanism for direct irradiation of phenyl benzoate (**5**).

After fragmentation phenoxy and benzoyl radical species were formed in the solvent cage, then, escape of the radical species from the solvent cage (***path (b)***) and hydrogen abstraction from the solvent (***path (c)***) gave the conventional products. Laser flash photolysis experiments provided rate constants (k_E) in cyclohexane, MeCN and MeOH (see Table 5) following the decay trace of phenoxy radical at 400 nm. No escape of the radical species was detected in micellar solution. Because phenyl benzoate has no substituent in *para* position, two possible *ortho*- and *para*-benzoylcyclohexadienone regioisomers viz. intermediates **C** and **D** were formed through the in-cage coupling of the radical species (***path (d)*** and ***path (e)*** in Scheme 7). Both intermediates **C** and **D** were observed in the absorption transient spectra (see Figure 7) with characteristic bands located in the range of 340 – 380 nm. Besides, the k_{ortho} and k_{para} values in the order of 10^9 M^{-1}.s^{-1} belonging to in-cage coupling pathways (***paths (d)*** and ***(d')*** in Scheme 7) implied that the coupling reaction occurred efficiently in all the solvents studied. Then, intermediates **C** and **D** formed in the solvent cage evolved to the regioisomers 2-hydroxybenzophenone and 4-hydroxybenzophenone through the sequence [1;3]-hydrogen migration and aromatization pathways (***path (e)*** and ***path (f)*** in Scheme 7). Again, intermediates **C** and **D** showed lifetimes higher than 200 µs and the rate constants k_H was estimated to be lower than 10^3 s^{-1}. These photoproducts were

formed with 30 – 60 % yields together with the corresponding phenol in homogeneous media (see Table 1) while in micellar solution were formed in up to 95 % yield and no phenol was detected in the micellar reaction mixture.

Conclusions.

The photochemical reaction of aryl benzoates examined in this paper takes place efficiently in homogeneous and micellar media. High selectivity in the formation of the 5-substituted-2-hydroxybenzophenone derivatives was observed in micellar media providing these photoproducts in yields up to 95 % without the formation of the corresponding phenols. Location of the aryl benzoates with 2D NOESY NMR spectroscopy in the shell or in the hydrophobic core of the micelle and measurement of the binding constants (K_b) between the benzoates and the surfactants account for the selective behaviour observed where diffusion of the radical species from the micelle is inhibited. On the other hand, benzophenone derivatives, as the main photoproducts, and the *p*-substituted phenols were formed when the irradiations were carried out in homogeneous media such as cyclohexane, MeCN and MeOH but no selectivity was observed.

Laser flash photolysis led to characterize two intermediates viz. the substituted phenoxy radical and the 5-substituted-2-benzoylcyclohexadienone transients. These intermediates were formed in the cage solvent within 10 μs after the laser pulse. Also, the phenoxy radical escapes from the solvent cage with first-order rate constants (k_E) of 10^5 s^{-1} that in turn evolve to the corresponding phenols by hydrogen abstraction from the reaction solvent (see Schemes 6 and 7). The kinetic parameters (k_R) for in-cage coupling pathways of the radical species viz. substituted phenoxy and benzoyl radicals were also measured in all the solvents studied, providing the corresponding 5-substituted-2-benzoylcyclohexadienone intermediates (intermediate **C** in Scheme 6 and intermediates **C** and **D** in Scheme 7). These species which are formed in the solvent cage evolved to the regioisomeric 5-substituted 2-hydroxybenzophenone derivatives through the sequence [1;3]-hydrogen migration and

aromatization pathways (**path (e)** in Scheme 6 and **paths (f)** in Scheme 7). Because, these intermediates showed lifetimes higher than 200 μs the rate constants k_H were estimated to be lower than 10^3 s^{-1} in all the solvents studied.

Finally, the finding that the selectivity observed in the photo-Fries rearrangement of some aryl benzoates in green and sustainable micellar media gives 5-substituted-2-hydroxybenzophenone derivatives in yields up to 95 % could be applied in the preparation of a new wide variety of substituted-2-hydroxybenzophenoe derivatives.

Experimental.

Materials and equipment. *p*-Substituted phenols, benzoyl chloride, pyridine, sodium dodecyl sulfonate and Brij-P35 were obtained from commercial sources. Spectroscopic grade solvents were used as received. Pyridine was distilled and stored over KOH pellets. Melting Points were determined with a Fisher Jones apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a 300 MHz spectrometer; chemical shifts (δ) are reported in part per million (ppm), relative to signal of tetramethylsilane, used as internal standard. 2D NOESY spectra were recorded in D$_2$O on a 500 MHz spectrometer, using NOESY-ph pulse sequence with a 600 ms mixing time and a recovery delay of 1.5 s. 2K data points were collected for 512 increments of 16 scans, using TPPI f1quadrature detection; chemical shifts (δ) are reported in part per million (ppm), relative to the signal of trimethylsilylpropionic acid, used as internal standard. Coupling constant (*J*) values are given in Hz. The measurements were carried out using standard pulse sequences. GC analysis was carried out on a Hewlett Packard 5890 gas chromatograph using an Ultra 2 capillary chromatographic column. The chromatograms were recorded with the following program: *initial temperature*: 100 ºC, 2 minutes; *gradient rate*: 10 ºC.min^{-1}; *final temperature*: 250 ºC, 10 minutes. The UV-visible spectra were

measured with a Shimadzu UV-1203 spectrophotometer using two-faced stoppered quartz cuvettes (1

mm x 1 mm) at 298 K.

Determination of the binding constants (K_b) of phenyl benzoates in micellar media. Solutions of phenyl

benzoates were prepared in deionized water (MilliQ) and their concentration varied between 5.5×10^{-5} M

and 1.0×10^{-4} M. An aliquot (2 mL) of the phenyl benzoate solution was placed in fluorescence

stoppered quartz cuvette provided with a stirring bar and the UV-visible spectrum was recorded. The

initial absorbance value at the maximum absorption wavelength (A_0) was read. Subsequently, aliquots

of concentrated surfactant solution (10 μL) were added. The UV-visible spectra were registered,

recording for each solution the A value at the maximum absorption wavelength. After each addition of

surfactant solution was stirred for 20 minutes before measuring the absorbance. With the values of A_0

and A in hands, the values of ($A_0/(A - A_0)$) *versus* the reciprocal of the concentration of the micellar

surfactant were plotted and the data were fitted with a linear regression program. The K_b values were

obtained calculating the ratio of the slope and the origin.

Laser Flash Photolysis. The laser pulse photolysis apparatus consisted of a Flash lamp-pumped Q-

switched SpitLight-100 Nd:YAG laser from InnoLas, used at the fourth harmonic of its fundamental

wavelength. The LP920-K monitor system (supplied by Edinburgh Instruments), arranged in a cross-

beam configuration, consisted of a high-intensity 450 W ozone free Xe arc lamp (operating in pulsed

wave), a Czerny-Turner with Triple Grating Turret monochromator, and a five-stage dynode

photomultiplier. The signals were captured by means of a Tektronix TDS 3012C digital phosphor

oscilloscope, and the data was processed with the L900 software supplied by Edinburgh Instruments.

The solutions to be analysed were placed in a fluorescence cuvette (d = 10 mm).

Synthesis of phenyl benzoates 1 – 8. To a solution of the substituted phenols (0.010 mol) in pyridine

(10 mL) cooled in an ice-bath, benzoyl chloride (0.012 mol) were added dropwise in 10 minutes under

stirring. Subsequently, the reaction mixture was kept under stirring for 60 minutes. After total

consumption of the starting material was confirmed by TLC, the reaction mixture was extracted with dichloromethane (10 mL) and washed with a solution of diluted HCl (10 mL). The organic phase was then washed with water, dried on Na_2SO_4, filtrated and evaporated under pressure. The phenyl benzoates were purified from the solid residue by recrystallization using ethanol − water mixtures giving the corresponding phenyl benzoates in excellent yields (> 90 %). The aryl benzoates **1** – **8** were characterized comparing the physical constant (m.p.) and spectroscopic data (^{1}H-NMR and ^{13}C-NMR) with the ones reported in the literature.

Photoirradiations of phenyl benzoates in homogeneous media. A stock solution of a given benzoates (**1** – **8**, 0.106 mmol in 200 mL cyclohexane) was placed in a stoppered Erlenmeyer quartz flask and degassed with argon for 30 min. The flask was placed in a home made optical bench provided with the possibility to use four or eigth lamps. The solution was stirred during the entire irradiation. Irradiations with λ_{exc} = 254 nm were carried with four germicide lamps (Philips, each of 20 Watts, purchased in Argentina). The reaction progress was monitored by TLC [eluent: hexane–ethyl acetate (8 : 2 v/v); spots were visualized with UV light (254 and 366 nm)] and by GC analysis (Ultra 2 capillary column. When the conversion of the starting material was higher than 90%, the photolyzed solution was carefully evaporated to dryness under reduced pressure. The yellowish solid residue obtained was purified by silica gel column chromatography (eluent: hexane 100% followed by hexane–ethyl acetate mixtures). From the eluted fractions, the photoproducts were isolated and characterized by means of physical and spectroscopic methods.

Photoirradiations of phenyl benzoates in micellar media. Stock solutions of surfactants in deionized water (SDS 0.10 M and Brij-P35 0.05 M) were freshly prepared before each experiment. The aryl benzoate (5 mg) was placed in a stoppered quartz cell provided with a stirring bar (3 ml) and the surfactant stock solution (2 mL) was added. Then, the solution was vigorously stirred for one hour and degassed with argon for 20 min. The quartz cell was placed in a homemade optical bench provided

with two germicide lamps (each of 20 W). The progress of the photoreaction was monitored by two

different methods: (i) UV-visible spectroscopy and GC analysis (Ultra 2 capillary column). The

conversion of the benzoates was kept below 20% to avoid secondary reactions and the formation of by-

products. Previously to the injection into the GC apparatus, the micellar solutions were treated as

follow. The photolyzed solutions were diluted with 2 mL of an aqueous solution of NaCl and then

extracted with ethyl acetate (3x2 mL) while the system was carefully shaken to avoid the formation of

emulsions. The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness under

vacuum. The yellowish solid residue was diluted in dichloromethane (2.00 mL) and this solution was

injected into the GC for chromatographic analysis. The products were characterized by comparison of

physical constant (m.p.) and spectroscopic data (^1H-NMR and ^{13}C-NMR) with the ones reported in the

literature.

p-Methoxyphenyl benzoate (1). White needles (2.24 g; 98 %). M. p.: 89-90°C (lit. 87-88°C[22]). ^1H NMR

(300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.6 Hz, *J* = 1.4 Hz, 2H), 7.66 (dd, *J* = 8.6 Hz, *J* = 1.3 Hz, 2H), 7.53

(t, *J* = 7.8 Hz, *J* = 1.1Hz, 1H), 7.17 (d, *J* = 9.4 Hz, 2H), 6.97 (d, *J* = 9.4 Hz, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$

NMR (75 MHz, $CDCl_3$): δ 165.4, 157.2, 144.3, 133.4, 130.0, 129.6, 128.4, 122.3, 114.4, 55.5.

p-Phenoxyphenyl benzoate (2). White plates (2.84 g; 98 %). M. p.: 100-101°C[23]. ^1H NMR (300 MHz,

$CDCl_3$): δ 8.24 (d, *J* = 7.1, 1.0 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 2H), 7.39 (t, *J* =

8.4 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 7.18 – 7.04 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.2,

157.1, 146.2, 133.5, 130.1, 129.7, 129.4, 128.5, 123.5, 122.7, 119.6, 118.7.

p-Methylphenyl benzoate (3). White needles (2.02 g; 95 %). M. p.: 71°C (lit. 72°C[24]). ^1H NMR (300

MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.2 Hz, *J* = 1.4 Hz, 2H), 7.65 (dd, *J* = 7.4 Hz, *J* = 1.2 Hz, 2H), 7.54 (t, *J* =

7.8Hz, *J* = 1.2 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR

(75 MHz, $CDCl_3$): δ 165.3, 148.6, 135.4, 133.4, 130.1, 129.6, 129.9, 128.4, 121.3, 20.8.

p-t-Butylphenyl benzoate (4). White plates (2.44 g; 96 %). M. p.: 83-84°C (lit. 82-83°C[25]). ^1H NMR

(300 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 8.7 Hz, 1H),

7.47 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 1.35 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ

165.2, 148.6, 148.5, 133.4, 130.0, 129.6, 128.4, 126.3, 120.9, 34.4, 31.6.

Phenyl benzoate (5). White solid (1.94 g; 98 %). M. p.: 69-70°C (lit. 67-69°C[6a]). ^{1}H NMR (300 MHz,

CDCl$_3$): δ 8.25 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 8.1 Hz, 2H), 7.45 (t, J = 8.3,

7.8 Hz, 2H), 7.32 (t, J = 8.1, 7.2 Hz, 1H), 7.24 (d, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ

165.1, 150.9, 133.5, 130.1, 129.5, 129.4, 128.5, 125.8, 121.6.

p-Phenylphenyl benzoate (6). White needles (2.52 g; 92 %). M. p.: 150-151°C.[23] ^{1}H NMR (300 MHz,

CDCl$_3$): δ 8.20 (d, J = 8.2, 1.2 Hz, 2H), 7.72 – 7.61 (m, 5H), 7.57 (t, J = 7.9 Hz, 2H), 7.49 (t, J = 7.8

Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 165.1,

150.3, 140.3, 138.9, 133.5, 130.1, 129.4, 128.7, 128.5, 128.1, 127.3, 127.0, 121.9.

p-Cyanophenyl benzoate (7). White solid (2.01 g; 90 %). M. p.: 94-95°C (lit. 91-92°C[26]). ^{1}H NMR (300

MHz, CDCl$_3$) δ: 8.22 (d, J = 8.4Hz, 2H), 7.74 (d, J = 7,64Hz 2H), 7.70 (t, J = 7.0, 7.64Hz, 2H) 7.56 (t,

J = 7.6 Hz, 2H), 7.4 (d, J = 8.4Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 164.2, 154.1, 134.0, 133.6,

130.1, 128.6, 128.5, 122.8, 118.2, 109.7.

p-Nitrophenyl benzoate (8). Pale yellow needles (2.21 g; 91 %). M. p.: 144-145ºC (lit. 142 – 144°C[27]).

^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.34 (d, J = 9.1 Hz, 2H), 8.23 (dd, J = 7.6, 1.3 Hz, 2H), 7.71 (t, J = 7.5

Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 9.1 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 164.1,

155.6, 145.3, 134.2, 130.2, 128.7, 128.4, 125.2, 122.5.

2-Hydroxy-5-methoxybenzophenone (1a). Pale yellow needles (188 mg; 94 %). M. p.: 83 – 84°C (lit.

84°C[28]). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 11.58 (s, 3H); 7.69 (dd, J = 8.5, 1.6 Hz, 2H), 7.60 (t, J = 7.5

Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 9.0, 2.9 Hz, 1H), 7.06 (d, J = 3.1 Hz, 1H), 7.02 (d. J = 9.0

Hz, 1H), 3.70 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 201.1, 157.7, 151.6, 138.0, 132.1, 130.3,

129.2, 128.5, 124.3, 119.4, 116.5, 56.1.

2-Hydroxy-5-phenoxybenzophenone (2a). Yellow needles (193 mg; 76 %). M. p.: 47 – 48 °C. ^{1}H NMR

(300 MHz, CDCl$_3$) δ: 11.85 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.4, 1H), 7.50 (t, J = 7.6 Hz,

2H), 7.34 – 7.26 (m, 4 H), 7.12 (d, J = 8.7 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ: 200.9, 159.6, 158.6, 147.7, 137.5, 132.2, 129.8, 129.2, 128.9, 128.5, 123.8, 122.8, 119.7, 119.2, 117.3. Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.57; H, 4.90.

2-Hydroxy-5-methylbenzophenone (3a). Pale yellow needles (130 mg; 70 %). M. p.: 83-84°C (lit. 84°C[29]). ^1H NMR (300 MHz, CDCl$_3$) δ: 11.84 (s, 1H), 7.67 (dd, J = 8.4, 1.2 Hz, 2H), 7.60 (t, J = 7.4, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 2.8 Hz, 1 H), 7.32 (dd, J = 8.5, 2.3 Hz, 1H), 6.98 (d, J = 8.54 Hz, 1H), 2.28 (s, 3H).). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ: 201.7, 161.3, 138.2, 137.5, 133.3, 131.9, 129.2, 128.5, 127.9, 118.9, 118.3, 20.6.

2-Hydroxy-5-t-butylbenzophenone (4a). White solid (189 mg; 85 %). M. p.: 67-68°C (lit. 67 – 68°C[25]). ^1H NMR (300 MHz, CDCl$_3$) δ: 11.87 (s, 1 H), 7.72 (dd, J = 1.6, 8.1 Hz, 2H), 7.63 (t, J = 1.3, 7.4, 2H), 7.60 (t, J = 2.5, 8.5 Hz, 1H), 7.55 (t, J = 1.6, 7.2 Hz, 2 H), 7.05 (d, J = 8.3 Hz, 1H), 1.28 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ: 201.6, 161.0, 141.3, 138.1, 133.9, 131.9, 129.8, 129.3, 128.3, 118.4, 117.9, 34.1, 31.3.

2-Hydroxybenzophenone (5a). Yellow needles (156 mg; 90 %). M. p.: 37-38°C (lit. 37 – 38°C[6a]). ^1H NMR (300 MHz, CDCl$_3$) δ: 12.05 (s, 1H), 7.68 (dd, J = 1.4, 8.4 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.53 – 7.48 (m, 3H), 7.08 (dd, J = 1.1, 8.5 Hz, 1 H), 6.88 (dd, J = 1.1, 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ: 201.7, 163.3, 138.0, 136.4, 133.7, 132.0, 129.3, 129.2, 128.5, 119.2, 118.8, 118.5, 118.3.

4-Hydroxybenzophenone. Yellow plates (14 mg; 8 %). M. p.:133-134°C (lit. 133 – 134°C[6a,30]). ^1H NMR (300 MHz, CDCl$_3$) δ: 7.77 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.4, 2H), 7.57 (t, J = 7.4, 1.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2 H), 6.95 (d, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ: 197.2, 161.1, 138.1, 133.3, 132.4, 130.0, 129.5, 128.4, 115.6.

2-Hydroxy-5-phenyl benzophenone (6a). White needles (209 mg; 87 %). M. p.: 91-92ºC (lit. 91 – 92ºC[31]). ^1H NMR (300 MHz, CDCl$_3$) δ: 12.06 (s, 1 H), 7.80 (dd, J = 2.4, 8.6 Hz, 1H), 7.77 (dd, J = 1.5, 8.5, 2H), 7.70 – 7.62 (m, 2H), 7.56 (t, J = 7.7, 1.7 Hz, 2H), 7.49 (dd, J = 8.5, 1.4 Hz, 2 H), 7.44 (t, J =

7.5, 1.5 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 201.7, 162.6, 139.8, 137.9, 135.1, 133.7, 132.1, 132.0, 131.8, 129.3, 128.9, 128.8, 128.5, 119.3, 118.9.

2-Hydroxy-5-cyano benzophenone (7a). Pale yellow needles (156 mg; 80 %). M. p.: 120-121ºC (lit. 120 – 121ºC[32]). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 12.48 (s, 1H), 7.96 (d, J = 2.1, 1H), 7.74 (dd, J = 8.7, 2.1 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.60 – 7.55 (m, 2H), 7.16 (d, J = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 200.6, 166.4, 138.7, 138.4, 136.6, 133.1, 129.3, 129.0, 120.2, 119.4, 118.3, 102.6.

2-Hydroxy-5-nitro benzophenone (8a). Intense yellow plates (94 mg; 44 %). M. p.: 123-124°C (lit.123 – 124°C[33]). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 12.67 (s, 1H), 8.60 (d, J = 2.7 Hz, 1H), 8.40 (dd, J = 9.2, 2.7 Hz, 1H), 7.72 (d, J = 8.4, 1.3 Hz, 2H), 7.69 (t, J = 7.5, 1.3 Hz, 1H), 7.59 (t, J = 7.8, 1.8 Hz, 2H), 7.19 (d, J = 9.2 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 200.7, 168.1, 139.6, 136.5, 133.3, 131.1, 129.8, 129.4, 129.2, 119.7, 118.1.

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Supporting Information.

UV-visible absorption spectra under steady-state and time-resolved spectroscopy. Relative absorption profiles. Determination of the constants of binding K_b. 2D NOESY NMR spectra in micellar media. Determination of the rate constants k_E and k_R in homogeneous and heterogeneous media. Copy of the ^{1}H and ^{13}C spectra of aryl benzoates and of 2-hydroxy-5-substituted benzophenones. This material is available free of charge via the Internet at http://pubs.acs.org.

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