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# Acetalization Allows the Photoheterolysis of the Ar–Cl Bond in Chlorobenzaldehydes and Chloroacetophenones

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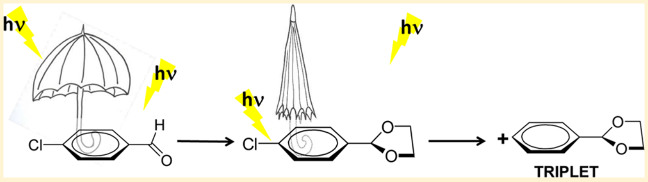
Supporting Information



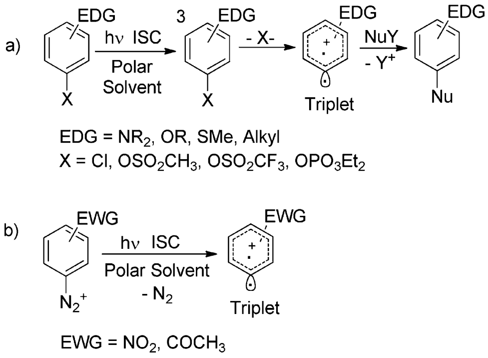
**ABSTRACT:** The nonaccessibility of phenyl cations by irradiation of electron-poor aryl chlorides was circumvented by transforming the carbonyl group of aromatic ketones or aldehydes into the corresponding 1,3-dioxolanes and the carboxyl group of benzoate ester into an orthoester functionality. This transformation allowed the heterolytic photoactivation of the Ar–Cl bond in protic media and the generation of phenyl cations. In the presence of $\pi$-bond nucleophiles, arylated products were obtained in good to excellent yields.

## INTRODUCTION

Phenyl cations, useful intermediates in organic chemistry,[1] are obtained upon heterolysis of an aryl–heteroatom bond under thermal[1] or photochemical[2,3] conditions. In recent years, it has been demonstrated that the second approach is superior for the mild conditions required[3] and because it allows the selective generation of phenyl cations in the triplet state. These intermediates ($^3Ar^+$, $\pi^5\sigma^1$ electronic structure) effectively add onto $\pi$-bond nucleophiles (e.g., alkenes, alkynes, and aromatics), offering a metal-free alternative to transition-metal-catalyzed aryl–carbon bond-forming reactions.[2,3] These cations are generated by heterolysis of the Ar–X bond in the triplet state of aromatic derivatives (X = chloride, phosphate, or sulfonate)[2,3] in polar or protic media. The generation of phenyl cations is favored by the presence of electron-donating groups,[2,3] such as $-NH_2$, $-OR$, $-SMe$, or alkyl groups on the ring[3,4] (Scheme 1a), although it occurs also with parent chlorobenzene in a protic solvent such as 2,2,2-trifluoroethanol (TFE), while homolysis of the Ph–Cl bond remains the main photoprocess in apolar solvents.[5]

This reaction does not extend to electron-poor aryl chlorides, though, where it is limited to compounds bearing an excellent leaving group such as nitrogen in diazonium salts (Scheme 1b).[6] However, disadvantages of this choice are the poor stability of such precursors, the large excess of nucleophile required for the arylation (from 20 up to 150-fold the amount of salt used), and the byproducts formed in some cases.[6] This makes general use of the diazonium salts unsatisfactory. In one instance, the use of diaryl iodonium salts was reported, but a complex mixture resulted.[7] A strategy for activating the heterolysis of the Ar–X bond is thus desirable, and this issue is confronted here for the case of benzaldehyde and acetophenone derivatives. As is well-known,[8] the photochemistry of these compounds generally involves the triplet manifold and results in some of the earliest discovered and most widely investigated reactions, such as the Paternò–Büchi synthesis of oxetanes[9,10] and the reductive dimerization of carbonyls to pinacols.[11,12] As for halogenated derivatives, the photochemical activation of the carbonyl hydrogen in (substituted) benzaldehydes toward C–C[13] and C–O[14] bond formation was likewise feasible, whereas the activation of aryl–Br[15] or of –Cl[16] bonds by a $S_{RN}1$ reaction[17] has been reported only in a couple of cases. Apart from the latter examples, the carbonyl moiety generally prevents any photochemical activation of the other functional groups in the molecule. A possible way around this limitation involves the transformation of the carbonyl into a different functional group (from which it can be regenerated) that is able to promote the activation of the desired chemical bond.[18] A straightforward strategy in the case considered is the acetalization of the carbonyl group that also has the advantage of introducing a substituent that exerts only a small electron-withdrawing effect,[23] thus facilitating aryl–chlorine photoheterolysis. As for the carbonyl groups, the protection/deprotection protocol is widely used in synthetic planning, but this strategy has been used so far only in thermal chemistry.[24] Thus, chlorinated aromatic aldehydes and ketones

**Scheme 1**



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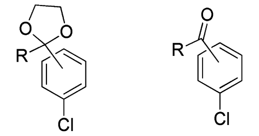
protected as acetals have been successfully employed in transition-metal-catalyzed reactions where the reactivity of the original carbonyl group prevented any cross-coupling reaction with aryl Grignard reagents.[25] Furthermore, the acetal moiety in protected acetophenone derivatives was able to activate selectively the Ar−H bond present in the *ortho* position in lithiation processes.[26] In other cases, the carbonyl protection markedly increased the reactivity of the aryl−chlorine bond in 4-chlorobenzaldehyde in the decarboxylative cross-coupling of isopropyl phthalate with the 1,3-dioxolane derivative of the chloroaromatic, a key step in the synthesis of angiotensin II receptor antagonist telmisartan.[27] A related activation of the Ar−Cl bond was reported in the lithiation of various protected chlorinated benzaldehydes.[28]

## ■ RESULTS

In this work, we chose acetals **1**−**3** in comparison with the corresponding nonprotected derivatives **1a**−**3a** (see Figure 1)



**1**, R = H, 4-Cl
**2**, R = Me, 4-Cl
**3**, R = H, 2-Cl
**3′**, R = H, 3-Cl

**1a**, R = H, 4-Cl
**2a**, R = Me, 4-Cl
**3a**, R = H, 2-Cl
**3′a**, R = H, 3-Cl

**Figure 1.** Chloroaryl acetals (**1**−**3**, **3′**) and their nonprotected derivatives (**1a**−**3a**, **3′a**) considered in the present work.

as suitable models for exploring the derivatization strategy for recovering the carbon-chlorine photoactivation. A combined experimental and computational investigation was carried out. In the case of the meta derivative **3′** the investigation was limited to the computational aspect, since we previously demonstrated that arylations were less successful with meta-substituted cations.[29]

**Computational Results.** The photochemistry of both aromatic carbonyls[8] and aromatic halides[30] proceeds via their lowest energy triplet state. The value of the triplet energy of the protected aryl carbonyl derivatives considered in this study were calculated and reported in Table 1. The triplet energy of 4-chlorobenzaldehyde (**1a**) was likewise calculated for the sake of comparison.

The most relevant properties of $^3$**1** (chosen as model compound) were compared with those of the unprotected aldehyde ($^3$**1a**). Density functional theory (DFT) at the UB3LYP/6-311+G(2d,p) level of theory was adopted to optimize the absolute minimum of these species (see the Supporting Information for details), as in previous studies on phenyl chlorides.[29,32] Solvent effects (MeOH bulk) were included at the same level of theory by single-point calculations using the CPCM method (conductor-like polarizable continuum model).[33] The elongation of the Ar−Cl bond (up to 4.00 Å) has been evaluated as well. Figure 2 gathers the results obtained for $^3$**1** (Figure 2a,b) and $^3$**1a** (Figure 2c,d).

**Table 1. Calculated Triplet Energy of Selected Aryl Chlorides Considered in This Study**

| aryl chloride | $E_T$[a] |
|---|---|
| **1** | 72.2 |
| **1a** | 65.8 (71.7)[b] |
| **3** | 72.1 |
| **3′** | 73.6 |
| **19** | 74.2 |

[a]Triplet energy (kcal mol$^{-1}$) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory (see the Supporting Information). [b]Value measured in nonpolar solvent; see ref 31.

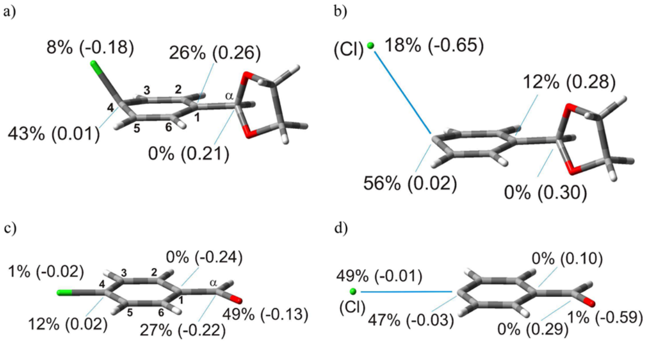


**Figure 2.** Geometries, spin densities, and ESP atomic charges (in parentheses) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory for: (a) $^3$**1** (Ar−Cl bond length: 1.82 Å); (b) $^3$**1** upon stretching the Ar−Cl bond up to 4.00 Å; (c) $^3$**1a** (Ar−Cl bond length: 1.75 Å); (d) $^3$**1a** upon stretching the Ar−Cl bond up to 4.00 Å.

As is apparent from Figure 2a, in $^3$**1** the symmetry of the aromatic backbone is lowered with the $C_4$ atom sticking out of the molecule plane and a partial negative charge is present at the chlorine atom (−0.18) that moves toward the partially positively charged π system. This is in fair agreement with previous findings concerning electron-rich aromatic chlorides.[29,32] Moreover, the spin density is largely localized at $C_4$ (43%) and $C_1$ (26%). Stretching the $C_4$−Cl bond up to 4.00 Å led to a marked charge separation (Cl −0.65; $C_1$ and $C_\alpha$ +0.28 and +0.30, respectively) and only to a minor spin localization (Cl 18%, see Figure 2b). On the contrary, no ring deformation was observed in $^3$**1a**, the Ar−Cl bond lying in the plane of the aromatic ring, with the spin density mainly localized at the carbonyl site (27% on $C_\alpha$ and 49% on the oxygen atom; see Figure 2c). Furthermore, the elongation of the Ar−Cl bond up to 4.00 Å resulted in no significant charge formation and a spin distribution mainly localized at the $C_4$ and Cl atoms (ca. 50% each; see Figure 2d). The energy increase accompanying the above stretch accounted to 18.2 kcal mol$^{-1}$ for $^3$**1** and to 30.6 kcal mol$^{-1}$ for $^3$**1a**. Thus, heterolytic dechlorination in $^3$**1** is viable, analogously to other aryl chlorides, while dechlorination of $^3$**1a** confronts a barrier 12 kcal mol$^{-1}$ higher and, in any case, would proceed via a homolytic pathway. Similar results have been obtained when comparing **3** with **3a** and **3′** with **3′a** (see Figures S3 and S4, Supporting Information).

It is worthy of note that cations $^1$**1**$^+$, $^1$**3**$^+$, and $^1$**3′**$^+$ were planar, and their structures resembled that of the parent singlet phenyl cation (see the Supporting Information). On the contrary, in electron-donating substituted phenyl cations a puckering of the ring and a small out-of-plane displacement were observed.[29] Figure 3 shows the structure of $^{1,3}$**1**$^+$ as representative cases where it is apparent that the $C_3$−$C_4$−$C_5$ moiety has some character of a cumulene in the singlet, whereas the triplet has a geometry close to a regular hexagon as in other substituted triplet cations.[29]

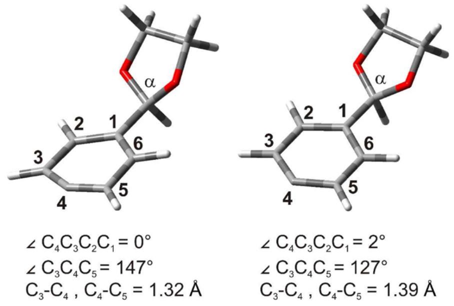
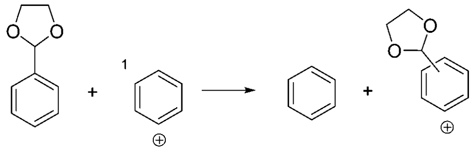


**Figure 3.** Bond lengths (Å), angles (∠, in degrees) and dihedral angles (∠, in degrees) for $^1$**1**$^+$ (left) and $^3$**1**$^+$ (right).

The isodesmic reaction reported in eq 1 (see the Supporting Information for details) was then calculated in solution



(1)

(MeOH) and used to evaluate the energy of the isomeric phenyl cations **1**$^+$, **3**$^+$, **3′**$^+$ and, accordingly, the (de)stabilization imparted by the 1,3-dioxolane group with respect to the parent singlet phenyl cation taken as the reference point. Figure 4 shows the relative energy of the six isomeric phenyl cations. In all of the cases, the singlets are the lower energy states and their energy is close to that of the unsubstituted phenyl cation. The triplets were displaced upward by a relevant amount (ca. 20 kcal mol$^{-1}$) only in the case of the meta derivative (**3′**$^+$).

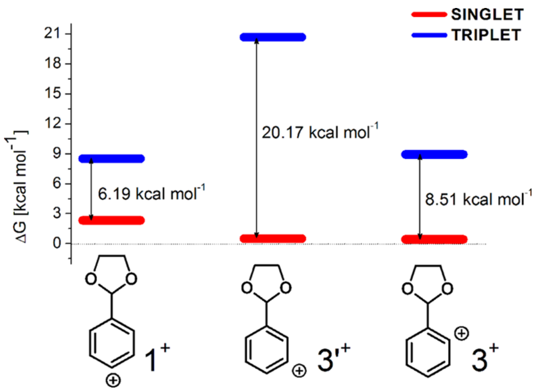


**Figure 4.** Relative Gibbs free energies (see Tables S4 and S5, Supporting Information, for details) of singlet (red) and triplet (blue) phenyl cations **1**$^+$, **3**$^+$, and **3′**$^+$ in solution (MeOH) according to the isodesmic reaction reported in eq 1.

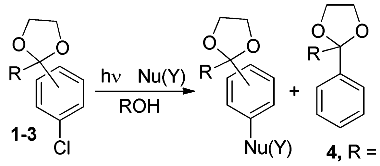
**Experimental Results.** The absorption spectra of **1**−**3** are blue-shifted with respect to the corresponding **1a**−**3a** (see Figures S1 and S2 in the Supporting Information), and acetals **1**−**3** exhibit low fluorescence (see Table S1, Supporting Information). Irradiation experiments were carried out in the presence of an equimolar amount of base ($Cs_2CO_3$ or $Et_3N$) in order to avoid that the HCl liberated in the process[34] caused the deprotection of the carbonyl group.[35] The dioxolanes reacted only slowly in nonprotic solvents, as demonstrated by the reaction of **1** in ethyl acetate (not shown), and fast in methanol (see $\Phi_{-1}$ in Table 2), in any case with reductive dechlorination to give products **4** and **5** as the only process. Irradiation of **1**−**3** (0.05 M) in methanol and in TFE caused the formation of the corresponding phenyl cations that were efficiently trapped by a series of $\pi$-bond nucleophiles (0.5 M, Table 2). It should be noted that the irradiation of the corresponding deprotected derivatives **1a**−**3a** under the same conditions led to a significant consumption of these compounds, but neither reductive dechlorination nor arylation in the presence of $\pi$-bond nucleophiles were observed.

As shown in Tables 2 and S2 (Supporting Information), in most cases, the arylation yield was between 70% and quantitative, with only a few percent of the reduction products. The end products included allylbenzenes **6**, **12**, and **17** by irradiation of acetals **1** and **3** and ketal **2** in the presence of allyltrimethylsilane (ATMS) in TFE (yields 63 to 99%) as well as $\gamma$-benzyl lactones **7** (quantitative from **1** and 4-pentenoic acid, entry 2) and **13** from the corresponding reaction of **2** (79%) (entry 9). A series of mixed acetals were obtained from **1** with ethyl vinyl ether in MeOH and TFE (**8** and **9**, 78 and 68% yields, respectively) and with 2-methoxypropene in TFE (**10** in 78% yield), as well as from **2** (**14**−**16** with ethyl vinyl ether or 2-methoxypropene in the two alcohols, yields from 43 to 77%) and **3** (**18** with 2-methoxypropene in TFE, 70%). Biphenyl **11** was obtained by irradiation of **1** (0.025M) in the presence of benzene (the consumption of the starting material was limited to 70% after 15 h irradiation in this case and the reaction was too slow with a larger concentration of the starting acetal). The photoreaction of compound **2** in the presence of ATMS was likewise tested under different conditions, namely in the presence of oxygen, by using a longer wavelength (310 nm) and a triplet sensitizer (acetone). In every case, the arylation yield for the same irradiation time was lower (entries 7 and 8). Moreover, the crude mixture obtained from the photoreaction between **2** and ATMS was treated with *p*-toluenesulfonic acid and deprotected 4-allylacetophenone (**12′**) was then isolated in 80% yield (see the Experimental Section).

In view of the positive results obtained for protected aromatic aldehydes and ketones, the photoreactivity of 1-(4-chlorophenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**19**, Scheme 2), where a −COOR group has been protected as orthoester, was next examined. Computational investigations performed on $^3$**19** (in MeOH bulk, except where otherwise noted) predicted a situation similar to that of $^3$**1**, with the C−Cl bond sticking out of the aromatic plane (see Figure 5a). Moreover, stretching of the Ar−Cl bond up to 4.00 Å (Figure 5b) resulted in the development of a partial negative charge at the chlorine atom (from −0.18 to −0.57) with the positive charge mainly localized at $C_1$ and $C_\alpha$ (0.26 and 0.56, respectively). An energy increase of 20.4 kcal mol$^{-1}$, somewhat larger than that found for $^3$**1**, has been observed upon stretching of the C−Cl bond. The influence of the solvent has also been tested; TFE and water gave similar results to those observed in methanol (see the Supporting Information).

The occurrence of heterolytic cleavage of the Ar−Cl bond in orthoester **19** was experimentally confirmed by irradiation in TFE in the presence of ethyl vinyl ether and ATMS (Scheme 2). The corresponding 3-aryl acetal **20** and allylated derivative **22** were deprotected during workup, and the corresponding hydroxy esters **21** and **23** were obtained in a modest yield (24 and 20%, respectively).

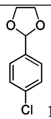
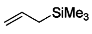
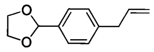
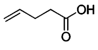
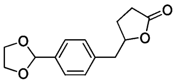
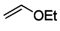
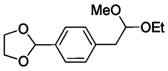
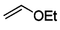
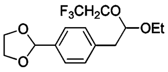
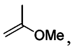
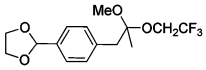
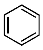
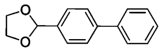
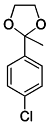
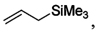
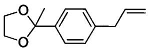
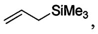
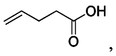
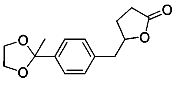
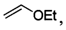
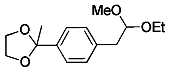
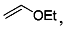
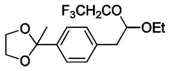
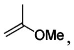
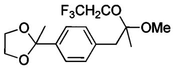
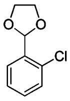
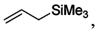
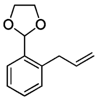
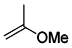
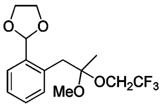
Table 2. Irradiation of **1**−**3** in Neat Solvent and in the Presence of $\pi$-Bond Nucleophiles[a]



**1-3** Cl

Nu(Y)
**6-18**

**4**, R = H
**5**, R = CH$_3$

| Entry | Ar-Cl[b] | Nu(Y), solvent | Products, %[c] |
|---|---|---|---|
| 1 |  **1**,<br>$\Phi_{-1}$ (MeOH) = 0.085 | ,<br>$CF_3CH_2OH$ |  **6**, 67 |
| 2 | “ | ,<br>$CF_3CH_2OH$ |  **7**, 100 |
| 3 | “ | ,<br>$CH_3OH$ |  **8**, 78 |
| 4 | “ | ,<br>$CF_3CH_2OH$ |  **9**, 68 |
| 5 | “ | ,<br>$CF_3CH_2OH$ |  **10**, 78 |
| 6[d] | “ | ,<br>$CF_3CH_2OH$ |  **11**, 87; **4**, 10 |
| 7 |  **2**,<br>$\Phi_{-1}$ (MeOH) = 0.027 | ,<br>$CF_3CH_2OH$ |  **12**, 99, 66[e] |
| 8[f] | “ | ,<br>$CF_3CH_2OH$ | **12**, 70, 43[g] |
| 9 | “ | ,<br>$CF_3CH_2OH$ |  **13**, 79 |
| 10 | “ | ,<br>$CH_3OH$ |  **14**, 77; **5**, 7 |
| 11 | “ | ,<br>$CF_3CH_2OH$ |  **15**, 52; **5**, 2 |
| 12 | “ | ,<br>$CF_3CH_2OH$ |  **16**, 43; **5**, 4 |
| 13 |  **3**,<br>$\Phi_{-1}$ (MeOH) = 0.17 | ,<br>$CF_3CH_2OH$ |  **17**,63; **4**, 3 |
| 14 | “ | ,<br>$CF_3CH_2OH$ |  **18**, 70; **4**, 17 |

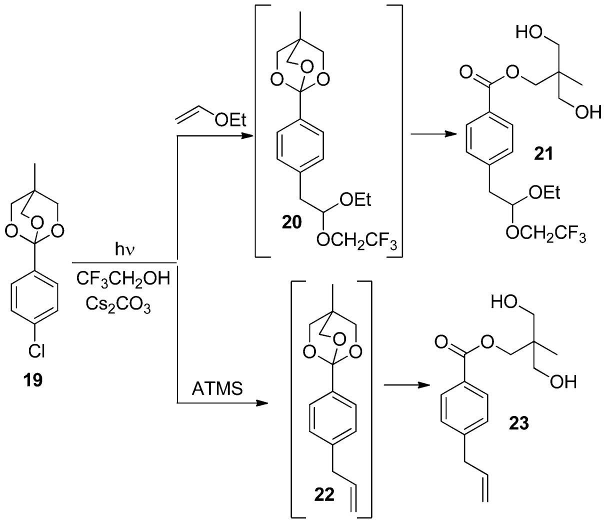
[a] ArCl 0.05 M in the presence of the chosen nucleophile (0.5 M) and $Cs_2CO_3$ (0.03 M) irradiated at $\lambda$ = 254 nm. [b] Quantum yields of photodecomposition in neat MeOH measured by irradiating at $\lambda$ = 254 nm a 5 × $10^{-3}$ M solution of **1**−**3** in the presence of an equimolar amount of $Et_3N$. [c] Yield based on the consumption of ArCl; see the Supporting Information for details. [d] **1** (0.025 M) and benzene 1 M were used. [e] Reaction carried out under aerated conditions. [f] Irradiated at $\lambda$ = 310 nm. [g] Acetone (20% v/v) added.

## ■ DISCUSSION

The above results support the reasoning that transforming carbonyl and carboxyl groups into acetals and orthoesters shifts the barrier to heterolytic cleavage of the aryl−chlorine bond as supported by both computational and experimental results. As is apparent from Table 1 for the case of 4-chlorobenzaldehyde, protection of the carbonyl group significantly increases the triplet energy (up to 72 kcal mol$^{-1}$), and the three dioxolane isomers and the orthoester have similar triplet energies that marginally differ from that of chlorobenzene (experimental 81.5 kcal mol$^{-1}$).[36] Apparently, ISC is effective also in these compounds (no advantage from attempted acetone sensitization, experimental $E_T$ acetone =78.9 kcal mol$^{-1}$).[36] In protic solvents, such as alcohols, the hoped for fragmentation occurs with a reasonable quantum yield (3−17%), comparable to that observed with chloroanisoles.[3] The triplet phenyl cation is thus formed, and the reactions expected from this intermediate do occur under these conditions. Thus, in neat alcohols hydrogen abstraction to give dechlorinated **4** and **5** takes place (path $R_D$ in Scheme 3), whereas in the presence of $\pi$-bond nucleophiles (Nu(Y)) efficient trapping occurs (path $A_R$) leading to the corresponding arylated products (**6**−**18**, **20**, and **22**)[3,4] as the only or (in a few cases) main products. With a poor trap (see benzene in the reaction of **1**) or when a somewhat hindered cation[29] (such as the *o*-chlorophenyl derivative from **3**) was generated, trapping was less efficient and the amount of the reduction product **4** was more significant.

In conclusion, we extended the generation of phenyl cations to electron-poor aromatics. Although the photochemistry of chlorobenzaldehyde or chloroacetophenone derivatives involves the carbonyl function exclusively, an expeditious transformation into acetals reintroduces the heterolytic photofragmentation of the aryl−Cl bond. The phenyl cation chemistry is thus accessible and clean arylation reactions can be obtained. Similar results were obtained when a chlorobenzoate orthoester was used.

**Scheme 2. Irradiation of 19 in TFE in the Presence of Ethyl Vinyl Ether and Allyltrimethylsilane ATMS**



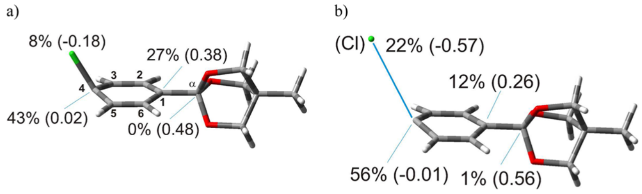
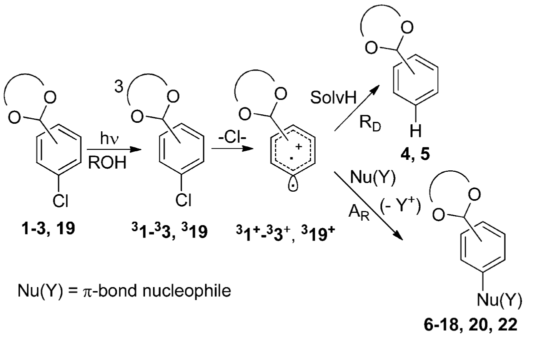


**Figure 5.** Geometries, spin density, and ESP atomic charges (in parentheses) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level for: (a) $^3$**19** (Ar−Cl bond length: 1.82 Å); (b) $^3$**19** upon stretching the Ar−Cl bond up to 4.00 Å.

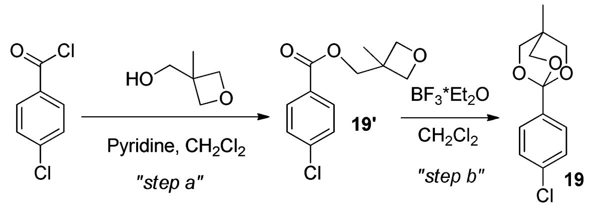
**Scheme 3. Photoreactivity of Phenyl Chlorides 1−3 and 19**



## EXPERIMENTAL SECTION

**General Methods.** NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of $^1$H and $^{13}$C NMR as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes in a multilamp reactor equipped with 4 Hg lamps, 15 W (emission centered at 254 nm) for the irradiation (or 10 phosphor coated lamps, 15 W each, emission centered at 310 nm, see Table 2). The reaction course was followed by GC analyses. Workup of the raw photolyzed mixtures involved concentration in vacuo (80−100 Torr) and chromatographic separation using silica gel. 4-Chlorobenzaldehyde (**1a**), 4-chloroacetophenone (**2a**), 2-chlorobenzaldehyde (**3a**), 4-chlorobenzoyl chloride, and all of the π-bond nucleophiles are commercially available and were used as received, except for ethyl vinyl ether, which was freshly distilled before use. Solvents of HPLC purity grade were employed in the photochemical reactions. Quantum yields were measured at 254 nm (1 Hg lamp, 15 W). The acetals **1**−**3** (or **4**−**5**) were prepared from the corresponding carbonyl derivatives **1a**−**3a** (benzaldehyde or acetophenone) by azeotropic water elimination from a toluene-ethylene glycol solution in the presence of *p*-toluenesulfonic acid monohydrate and redistillation (or column chromatography purification for **2**).

**Synthesis of 1-(4-Chlorophenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (19).** Orthoester **19** was prepared from 4-chlorobenzoyl chloride by following a procedure used in the synthesis of 1-*n*-amyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane.[37]



***Step a.*** 4-chlorobenzoyl chloride (2 g, 11.4 mmol) was added to a solution of (3-methyloxetan-3-yl)methanol (1.20 mL, 11.4 mmol) and pyridine (0.90 mL, 11.5 mmol) in $CH_2Cl_2$ (5 mL) at 0 °C. The resulting mixture was stirred for 5 h at 0 °C. The mixture was then diluted with $CH_2Cl_2$ and the organic layer washed with brine and water, dried with $Na_2SO_4$, and then concentrated to afford 2.02 g of (3-methyloxetan-3-yl)methyl 4-chlorobenzoate (**19′**, white solid, 74% yield, mp = 47−48 °C). The crude ester was employed for the following step without further purification. **19′**: $^1$H NMR ($CD_3COCD_3$) δ 1.40 (s, 3H), 4.35−4.40 (d, 2H, *J* = 6 Hz), 4.45 (s, 2H), 4.55−4.60 (d, 2H, *J* = 6 Hz), 7.55−8.05 (AA′BB′, 4H, *J* = 11 Hz); $^{13}$C NMR ($CD_3COCD_3$) δ 21.7, ($CH_3$), 40.4, 70.4 ($CH_2$), 80.0 ($CH_2$), 130.1 (CH), 130.3, 132.4 (CH), 140.2, 166.4; IR (KBr), ν/cm$^{-1}$ 2924, 1730, 1264, 1102, 759.

***Step b.*** Crude **19′** (766 mg, 3.18 mmol) was dissolved in 5 mL of dry $CH_2Cl_2$. The resulting solution was cooled at −15 °C and boron trifluoride etherate (100 μL, 0.80 mmol) was added. After 24 h GC analysis revealed a 90% consumption of the starting material. Triethylamine (TEA, 0.44 mL, 3.18 mmol) was added and the reaction mixture was diluted with diethyl ether (20 mL) and filtered to remove the resulting TEA-$BF_3$ complex. The filtrate was concentrated and the residue purified by chromatographic separation by using silica gel (eluant: $CH_2Cl_2$ with 0.2% v/v TEA) to afford 306 mg of **19** (white solid, 40% yield, mp = 102−105 °C). **19**: $^1$H NMR ($CD_3COCD_3$) δ 0.90 (s, 3H), 4.05 (s, 6H), 7.35−7.55 (AA′BB′, 4H, *J* = 8.5 Hz); $^{13}$C NMR ($CD_3COCD_3$) δ 14.6 ($CH_3$), 31.5, 74.1 ($CH_2$), 108.1, 128.9 (CH), 129.0 (CH), 135.4, 138.8; IR (KBr) ν/cm$^{-1}$ 2924, 1788, 1594, 1094, 831, 760. Anal. Calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44. Found: C, 59.9; H 5.4.

**Preparative Irradiations.** A solution of **1**−**3** or **19** (1.5 mmol, 0.05 M except where otherwise indicated), $Cs_2CO_3$ (0.9 mmol, 0.03 M), and π-bond nucleophiles (15 mmol, 0.5 M) in the chosen alcohol (TFE or methanol, 30 mL) was nitrogen purged in quartz tubes and irradiated by means of a multilamp reactor equipped with 4 Hg lamps, 15 W (emission centered at 254 nm). The reaction course was followed by GC analysis. GC yields of compounds **4** and **5** have been determined by comparison with authentic samples. The photolyzed solution was concentrated in vacuo at 80−100 Torr, and the resulting residue purified by silica gel column chromatography (eluant: pentane/diethyl ether mixture with 0.2% v/v triethylamine or pentane/dichloromethane mixture).

*2-(4-Allylphenyl)-1,3-dioxolane (**6**):* 6 h irradiation, 78% consumption of **1**; eluant: pentane/diethyl ether 9:1, oil, 67% yield based on the consumption of **1**; $^1$H NMR ($CD_3COCD_3$) δ 3.40−3.45 (d, 2H, *J* = 7 Hz), 3.95−4.10 (m, 4H), 5.00−5.10 (m, 2 H), 5.70 (s, 1H), 5.90−6.05 (m, 1H), 7.20−7.40 (AA′BB′ system, 4H, *J* = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) δ 40.9 ($CH_2$), 66.2 ($CH_2$), 104.7 (CH), 116.4 ($CH_2$), 128.0 (CH), 129.5 (CH), 137.8, 138.8 (CH), 142.2; IR (neat) ν/cm$^{-1}$ 2890, 1702, 1605, 1084, 838. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76, H, 7.42. Found: C, 75.6; H, 7.6.

*5-(4-(1,3-Dioxolan-2-yl)benzyl)dihydrofuran-2(3H)-one* (**7**)*:* 6 h irradiation, 90% consumption of **1**; eluant: from pentane/diethyl ether 9:1 to pentane/diethyl ether 7:3. oil, 100% yield based on the consumption of **1**; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.95−2.00 (m, 1H), 2.30−2.35 (m, 1H), 2.40−2,45 (m, 2H), 3.00−3.05 (m, 2H), 3.95−4.10 (m, 4H), 4.70−4.80 (qui, 1H, $J$ = 6.5 Hz), 5.70 (s, 1H), 7.30−7.40 (AA′BB′ 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 28.3 ($CH_2$), 29.3 ($CH_2$), 42.0 ($CH_2$), 66.2 ($CH_2$), 81.6 (CH), 104.6 (CH), 128.0 (CH), 130.5 (CH), 138.4, 139.2, 177.4; IR (neat) $\nu$/cm$^{-1}$ 2925, 1774, 1176, 1080. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.7; H, 6.5.

*2-(4-(2-Ethoxy-2-methoxyethyl)phenyl)-1,3-dioxolane* (**8**)*:* 20 h irradiation, 100% consumption of **1**; eluant: pentane/diethyl ether 9:1, oil, 78% yield; $^1$H NMR ($CDCl_3$) $\delta$ 1.15−1.20 (t, 3H, $J$ = 7 Hz), 2.90−2.95 (d, 2H, $J$ = 6 Hz), 3.35 (s, 3H), 3.40−3.70 (m, 2H), 4.00−4.15 (m, 4H), 4.55−4.60 (t, 1H, $J$ = 6 Hz), 5.80 (s, 1H), 7.25−7.40 (AA′BB′ system, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 15.1 ($CH_3$), 40.0 ($CH_2$), 53.2 ($CH_3$), 61.9 ($CH_2$), 65.2 ($CH_2$), 103.6 (CH), 104.4 (CH), 126.3 (CH), 129.4 (CH), 135.8, 138.2; IR (neat), $\nu$/cm$^{-1}$ 2888, 1275, 1080, 820. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.7; H, 8.0.

*2-(4-(2-(2,2,2-Trifluoroethoxy)-2-ethoxyethyl)phenyl)-1,3-dioxolane* (**9**)*:* 20 h irradiation, 100% consumption of **1**; eluant: from pentane/diethyl ether 99:1 to pentane/diethyl ether 96:4, oil, 68% yield; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.10−1.15 (t, 3H, $J$ = 7 Hz), 2,95−3.00 (d, 2H, $J$ = 6 Hz), 3.45−3.50 (m, 1H) 3.70−3.75 (m, 1H), 3.95−4.15 (m, 6H), 4.85−4.90 (t, 1H, $J$ = 6 Hz), 5.70 (s, 1H), 7.30−7.40 (AA′BB′, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 15.7 ($CH_3$), 40.9 ($CH_2$), 63.0 ($CH_2$), 63.5 (q, $CH_2$, $J$ = 34 Hz), 66.2 ($CH_2$), 104.7 (CH), 105.0 (CH), 127.8 (CH), 127.4 (q, $CF_3$, $J$ = 240 Hz), 130,6 (CH), 138.2, 138.8; IR (neat) $\nu$/cm$^{-1}$ 2889, 1280, 1162, 1088, 968, 823. Anal. Calcd for $C_{15}H_{19}F_3O_4$: C, 56.25; H, 5.98. Found: C, 56.2; H, 5.9.

*2-(4-(2-(2,2,2-Trifluoroethoxy)-2-methoxypropyl)phenyl)-1,3-dioxolane* (**10**)*:* 6 h irradiation, 77% consumption of **1**; eluant: pentane/diethyl ether 98:2, oil, 78% yield based on the consumption of **1**; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.20 (s, 3H), 3.00−3.05 (d, 2H, $J$ = 3 Hz), 3.30 (s, 3H), 3.95−4.10 (m, 6H), 5.70 (s, 1H), 7.30−7.40 (AA′BB′, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 22.1 ($CH_3$), 43.9 ($CH_2$), 49.4 ($CH_3$), 59.8 ($CH_2$, q, $J$ = 35 Hz), 104.0, 104.7 (CH), 127.6 (CH), 129.0 ($CF_3$, q, $J$ = 275 Hz), 131.3 (CH), 138.2, 139.2; IR (neat) $\nu$/cm$^{-1}$ 2952, 1162, 1083, 1050, 971, 868. Anal. Calcd for $C_{15}H_{19}F_3O_4$: C, 56.25; H, 5.98. Found: C, 56.2; H, 5.9.

*2-(Biphenyl-4-yl)-1,3-dioxolane* (**11**)*:* 15 h irradiation, 70% consumption of **1**; eluant: pentane/diethyl ether 95:5, colorless solid, 87% yield based on the consumption of **1**, mp = 53−54 °C (lit.[38] mp 57 °C). Spectroscopic data of **11** are in accordance with the literature.[38] Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.6; H, 6.2.

*2-(4-Allylphenyl)-2-methyl-1,3-dioxolane* (**12**)*:* 18.5 h irradiation, 77% consumption of **2**; eluant: from neat pentane to pentane/diethyl ether 7:3, oil, 99% yield based on the consumption of **2**: $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.50 (s, 3H), 3.35−3.40 (d, 2H, $J$ = 7 Hz), 3.70−4.00 (m, 4H), 5.00−5.10 (m, $CH_2$), 5.90−6.00 (m, CH), 7.15−7.40 (AA′BB′, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 28.4 ($CH_3$), 40.8 ($CH_2$), 65.4 ($CH_2$), 109.6, 116.3 ($CH_2$), 126.5 (CH), 129.4 (CH), 138.9 (CH), 140.8. 142.9; IR (neat) $\nu$/cm$^{-1}$ 2953, 1685, 1638, 1268, 1158, 1041, 958, 917, 839. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.3; H, 8.0.

The reaction was repeated under the same conditions, and crude **12** was deprotected in situ by adding *p*-toluenesulfonic acid.[39] In detail, water (0.17 mL), *p*-toluensulfonic acid monohydrate (17 mg, 0.09 mmol), and acetone (1.7 mL) were added to the photolyzed solution. The resulting mixture was stirred overnight at room temperature and diluted with toluene and a saturated sodium hydrogen carbonate solution. The toluene phase was separated and washed with brine, dried over $MgSO_4$, and concentrated in vacuo at 80−100 Torr. The resulting residue was purified by silica gel column chromatography (eluant: hexane with 0.2% v/v triethylamine) affording 148 mg of 4-allylacetophenone (**12′**, oil, 80% yield). Spectroscopic data of **12′** are in accordance with the literature.[40] Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.5; H, 7.6.

*5-(4-(2-Methyl-1,3-dioxolan-2-yl)benzyldihydrofuran-2(3H)-one* (**13**)*:* 19 h irradiation, 100% consumption of **2**; eluant: from pentane/diethyl ether 9:1 to pentane/diethyl ether 5:5, oil, 79% yield; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.55 (s, 3H) 1.95−2.00 (m, 1H), 2.30−2.35 (m, 1H), 2.40−2.50 (m, 2H) 2.95−3.00 (m, 2H), 3.70−4.00 (m, 4H), 4.70−4.80 (qui, 1H, $J$ = 7 Hz), 7.25−7.40 (AA′BB′, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 28.3 ($CH_3$), 28.4 ($CH_2$), 29.3 ($CH_2$), 42.0 ($CH_2$) 65.5 ($CH_2$), 81.8 (CH), 109.6, 126.6 (CH), 130.4 (CH), 137.9, 143.5, 177.4; IR (neat) v/cm$^{-1}$ 2928, 1773, 1175, 1035. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.7; H, 6.9.

*2-(4-(2-Ethoxy-2-methoxyethyl)phenyl)-2-methyl-1,3-dioxolane* (**14**)*:* 20 h irradiation, 100% consumption of **2**; eluant: pentane/diethyl ether 99:1, oil, 77% yield; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.10−1.15 (t, 3H, $J$ = 7 Hz), 1.55 (s, 3H), 2.85−2.90 (d, 2H, $J$ = 6 Hz), 3.30 (s, 3H), 3.40−3.50 (m, 1H), 3.60−3.65 (m, 1H), 3.70−4.00 (m, 4H), 4.60−4.65 (t, 1H, $J$ = 6 Hz), 7.25−7.40 (AA′BB′, 4H, $J$ = 8 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 15.9 ($CH_3$), 28.4 ($CH_3$), 40.7 ($CH_2$), 53.4 ($CH_3$), 62.5 ($CH_2$), 65.4 ($CH_2$), 105.5 (CH), 109.6, 126.2 (CH), 130.5 (CH), 138.2, 142.9; IR (neat) $\nu$/cm$^{-1}$ 2979, 1199, 1124, 1041, 737. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.6; H, 8.3.

*2-(4-(2-Ethoxy-2-(2,2,2-trifluoroethoxy)ethyl)phenyl)-2-methyl-1,3-dioxolane* (**15**)*:* 19 h irradiation, 100% consumption of **2**; eluant: pentane/diethyl ether 98:2, oil, 52% yield; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.10−1.15 (t, 3H, $J$ = 7 Hz), 1.55 (s, 3H), 2.95−3.00 (d, 2H, $J$ = 6 Hz), 3.50−3.60 (m, 2H), 3.70−4.10 (m, 6H), 4.85−4.90 (t, 1H, $J$ = 6 Hz), 7.25−7.40 (AA′BB′, 4H, $J$ = 8.5 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 15.7 ($CH_3$), 28.3 ($CH_3$), 40.7 ($CH_2$), 63.4 ($CH_2$), 63.5 (q, $CH_2$, $J$ = 33 Hz), 65.5 ($CH_2$), 105.1 (CH), 109.6, 125.9 (q, $CF_3$, $J$ = 275 Hz), 126.4 (CH), 130.5 (CH), 137.4, 143.2; IR (neat) $\nu$/cm$^{-1}$ 2981, 1280, 1161, 1077, 1040, 870. Anal. Calcd for $C_{16}H_{21}F_3O_4$: C, 57.48; H, 6.33. Found: C, 57.5; H, 6.3.

*2-(4-(2-(2,2,2-Trifluoroethoxy)-2-methoxypropyl)phenyl)-2-methyl-1,3-dioxolane* (**16**)*:* 12 h irradiation, 89% consumption of **2**; eluant: from pentane/diethyl ether 98:2 to pentane/diethyl ether 1:1, oil, 43% yield based on the consumption of **2**; $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.15 (s, 3H), 1,55 (s, 3H), 2.95−3.00 (d, 2H, $J$ = 6 Hz), 3.30 (s, 3H), 3.70−3.80 (m, 2H) 3.90−4.00 (m, 4H), 7.25−7.35 (AA′BB′, 4H, $J$ = 8 Hz); ($CD_3COCD_3$) $\delta$ 22.1 ($CH_3$), 28.3 ($CH_3$), 43.7 ($CH_2$), 49.4 ($CH_3$), 59.8 ($CH_2$, q, $J$ = 34 Hz), 65.5 ($CH_2$), 104.0, 109.6, 126.1 (CH), 128,0 (q, $CF_3$, $J$ = 275 Hz), 131.2 (CH), 137.6, 143.3; IR (neat) $\nu$/cm$^{-1}$ 2933, 1283, 1162, 1077, 1043, 972, 870. Anal. Calcd for $C_{16}H_{21}F_3O_4$: C, 57.48; H, 6.33. Found: C, 57.5; H, 6.3.

*2-(2-Allylphenyl)-1,3-dioxolane* (**17**)*:* 6 h irradiation, 88% consumption of **3**; eluant: pentane/diethyl ether 9:1, oil, 63% yield based on the consumption of **3**; The spectroscopic data of **17** were in accordance with literature data.[41] Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.8; H, 7.4.

*2-(2-(2-Methoxy-2-(2,2,2-trifluoroethoxy)propyl)phenyl)-1,3-dioxolane* (**18**)*:* 8 h irradiation, 73% consumption of **3**; eluant: pentane/diethyl ether 99:1, oil, 70% yield based on the consumption of **3**: $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.20 (s, 3H), 3.20 (s, 2 H), 3.30 (s, 3H), 3−90−4.00 (m, 4H), 4.00−4.10 (m, 2H), 6.10 (s, 1H), 7.25−7.30 (m, 2H), 7.35−7.40 (m, 1H), 7.55−7.60 (dd, 1H, $J$ = 7, 2 Hz); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 22.0 ($CH_3$), 39.4 ($CH_2$), 49.3 ($CH_3$), 60.2 ($CH_2$, q, $J$ = 34 Hz), 66.1 ($CH_2$), 102.7 (CH), 104.4, 127.5 (2 CH), 129.3 (CH), 129.5 ($CF_3$, $J$ = 280 Hz), 132.2 (CH), 136.9, 138.4; IR (neat) $\nu$/cm$^{-1}$ 2891, 1282, 1162, 1084, 970, 758. Anal. Calcd for $C_{15}H_{19}F_3O_4$: C, 56.25; H, 5.98. Found: C, 56.2; H, 5.9.

*Irradiation of* **19** *in TFE in the presence of ethyl vinyl ether:* 14.5 h irradiation, 100% consumption of **19**. Arylated compound **20** thus formed was not stable during the purification procedure (by column chromatography eluant: $CH_2Cl_2$) and hydrolyzed to 3-hydroxy-2-(hydroxymethyl)-2-methylpropyl 4-(2-ethoxy-2-(2,2,2-trifluoroethoxy)ethyl)benzoate (**21**, 141 mg, oil, 24% yield). **21**: $^1$H NMR ($CD_3COCD_3$) $\delta$ 1.10−1.15 (m, 6H), 3.05−3.10 (d, 2H, $J$ = 6 Hz), 3.50−3.55 (m, 1H), 3.60−3.65 (m, 4H) 3.70−3.75 (m, 1H), 3.80−3.85 (t, 2H, OH, $J$ = 5 Hz), 4.10−4.15 (m, 2H), 4.20 (s, 2H), 4.95−5.00 (t, 1H, $J$ = 6 Hz), 7.40−8.00 (AA′BB′, 4H, $J$ = 9 Hz); $^{13}$C

NMR ($CD_3COCD_3$) $\delta$ 15.7 ($CH_3$), 17.5 ($CH_3$), 41.0 ($CH_2$), 41.8 ($CH_2$), 63.2 ($CH_2$, q, $J$ = 33 Hz), 66.3 ($CH_2$), 62.9 ($CH_2$), 104.7 (CH), 127.7 ($CF_3$, q, $J$ = 275 Hz), 130.1, 130.5 (CH), 131.1 (CH), 132.3, 167.2. IR (neat) $\nu$/cm$^{-1}$ 3446, 2980, 1715, 1266, 1165, 739. Anal. Calcd for $C_{18}H_{25}F_3O_6$: C, 54.82; H, 6.39. Found: C, 54.8; H, 6.4.

*Irradiation of **19** in TFE in presence of ATMS:* 24 h irradiation, 100% consumption of **19**. As in the former case, 3-hydroxy-2-(hydroxymethyl)-2-methylpropyl 4-allylbenzoate (**23**, oil, 79 mg, 20% yield) was isolated after workup (column chromatography, eluant: $CH_2Cl_2$/pentane 9:1) in place of compound **22**. **23**: $^1$H NMR ($CDCl_3$) $\delta$ 0.95 (s, 3H), 2.50 (bs, 2H), 3.45−3.50 (d, 2H, $J$ = 6.5 Hz), 3.60−3.65 (m, 4H), 4.45 (s, 2H), 5.10−5.20 (m, 2H), 5.90−5.95 (m, 1H), 7.30−8.00 (AA′BB′, 4H, $J$ = 9.5 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$ 16.8 ($CH_3$), 40.0 ($CH_2$), 41.0 ($CH_2$), 67.0 ($CH_2$), 67.6 ($CH_2$), 116.5 ($CH_2$),128.7 (CH), 129.9 (CH), 136.1, 140.0, 167.4. IR (neat) $\nu$/cm$^{-1}$ 3412, 2955, 1715, 1277, 840. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.2; H, 7.7.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H and $^{13}$C NMR spectra for compounds **1−3**, **6−19**, **21**, and **23**; details of the calculations on intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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