JOC The Journal of Organic Chemistry

Article

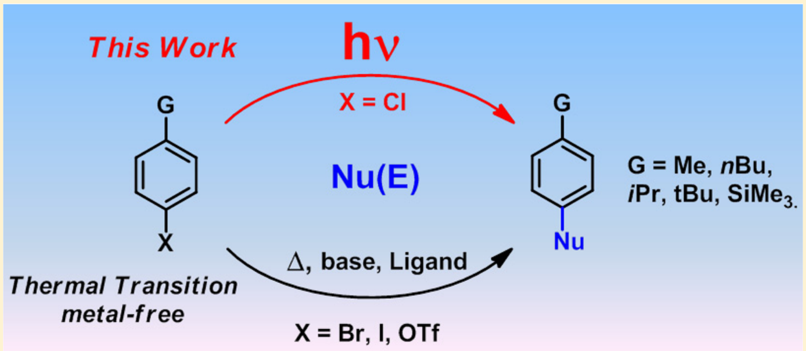
pubs.acs.org/joc

Transition-Metal-Free Arylations via Photogenerated Triplet 4-Alkyl- and 4-Trimethylsilylphenyl Cations

Hisham Qrareya, Carlotta Raviola, Stefano Protti,* Maurizio Fagnoni,* and Angelo Albini

PhotoGreen Lab, Department of Chemistry, University of Pavia, V. Le Taramelli 12, 27100 Pavia, Italy

S Supporting Information

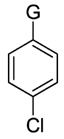


ABSTRACT: The irradiation in protic solvents of 4-chloroalkylbenzenes and 4-chlorophenyltrimethylsilane caused the heterolytic cleavage of aryl−chlorine bonds to give the corresponding triplet phenyl cations. These were exploited for transition-metal-free arylation reactions under mild conditions to give allylbenzenes, γ-benzyl lactones, 3-arylacetals (ketals), and biaryls in moderate to good yields. The path followed was supported by DFT calculations at the UB3LYP/6-311+G(2d,p) level.

■ INTRODUCTION

The synthesis of (poly)functionalized alkyl(hetero)arenes is of considerable importance in organic chemistry due to the possible elaboration of the alkyl chains.[1] A typical approach involves the activation of Ar−X bonds in substituted alkyl aromatics under metal-catalyzed conditions.[2] However, innovative protocols for transition-metal-free arylations have recently emerged and involve relatively weak Ar−X bonds, as in the thermal decomposition of diaryliodonium salts[3a] or in the visible light photocatalytic reduction of arenediazonium salts.[3b] The metal-free activation of the Ar−X bond in alkyl aryl halides (or esters) may be envisaged for a larger scope application in the preparation of biphenyls by reaction with unactivated arenes. This approach has been sparsely reported in the literature,[4,5] but the use of a strong base (e.g., KOtBu) and of a high temperature (up to 200 °C), as well as of a large excess of the arene (from 100 equiv up to neat) were required. Furthermore, these reactions are efficient on phenyl iodides, bromides, and triflates, while being limitedly applied to easily available chlorides,[4a,c,d] contrary to that reported for related transition-metal-catalyzed cross-coupling reactions.[6] An alternative may be sought in the photochemical cleavage of the aryl−chlorine bond. However, the photochemical behavior of *n*-chloroalkylbenzenes has not been extensively documented,[7,8] and application in synthesis is limited to photostimulated S$_{RN}$1 reactions of 4-chlorotoluene (**1**, Chart 1) with diphenyl arsenide[9a] and triphenylstannyl anion[9b] in liquid ammonia (but the same reaction was sluggish in DMSO).[10]

Chart 1



1, G = CH$_3$
2, G = *n*Bu, **2'**, G = Et
3, G = *i*Pr
4, G = *t*Bu
5, G = SiMe$_3$

Increasing attention has been paid to triplet phenyl cations (^{3}Ar$^+$) formed by the photoinduced heterolytic fragmentation of the Ar−Cl bond. Examples are the photoreduction of 4-chloro-*n*-butylbenzene (**2**) in 2-propanol[11] and the arylations occurring upon irradiation of **2** in the presence of π-bond nucleophiles.[12] The formation of a phenyl cation has been also invoked in the photolysis of 2-chloroisopropylbenzene in 2,2,2-trifluoroethanol (TFE), where a mixture of ethers, alkenes, propylbenzene, and indane was obtained.[13]

In view of the above results, further exploration of the potential of phenyl cations photogenerated from *n*-chloroalkylbenzenes for transition-metal-free arylations appeared worthwhile. In parallel with the experimental study, a computational analysis was carried out, since the only data available dealt with **1** in the gas phase (CASSCF level of theory) where a homolytic photodissociation takes place.[14] A combined experimental and computational study of the photochemistry of chlorides **1**−**4** (see Chart 1) as well as of 4-chlorotrimethylsilylbenzene (**5**) was thus performed, as reported below.

Received: April 3, 2013
Published: May 20, 2013

dx.doi.org/10.1021/jo4007046 | *J. Org. Chem.* 2013, 78, 6016−6024

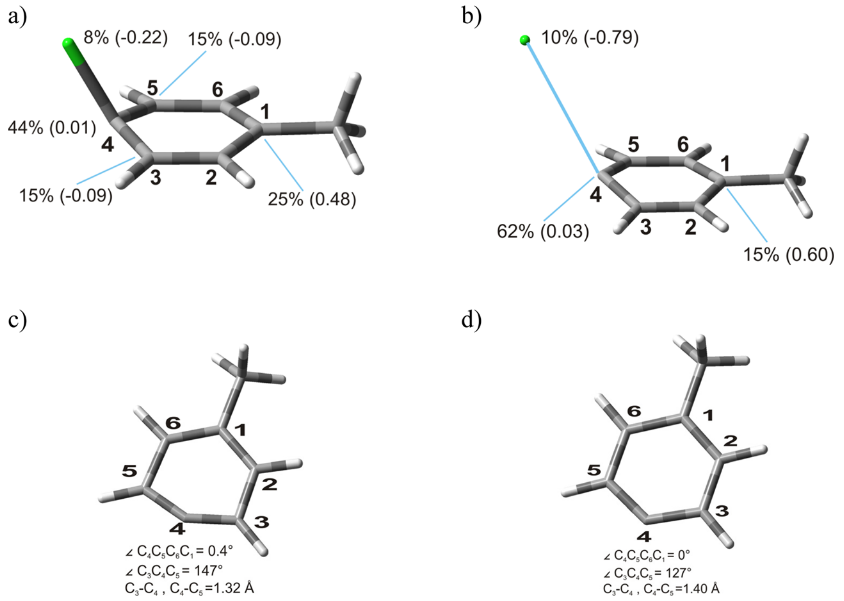


Figure 1. Geometries, spin densities, and ESP atomic charges (in parentheses) calculated in bulk MeOH at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory for (a) ^{3}**1** (Ar−Cl bond length: 1.84 Å) and (b) ^{3}**1** upon stretching the Ar−Cl bond up to 4.00 Å. Bond lengths (Å), angles (∠, in degrees), and dihedral angles (∠, in degrees) for (c) ^{1}**1**$^{+}$ and (d) ^{3}**1**$^{+}$.

■ RESULTS

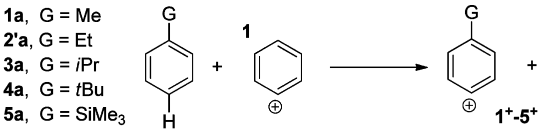
Density functional theory (DFT) at the UB3LYP/6-311+G-(2d,p) level was adopted in this work to optimize the absolute minima of phenyl chlorides **1**−**5**, their triplets ^{3}**1**−^{3}**5**, and the resulting cations ^{1,3}**1**$^{+}$−^{1,3}**5**$^{+}$ (see the Supporting Information for details), analogously to previous studies on substituted chlorobenzenes.[15] For simplicity, the ethyl derivative **2**′ was taken as a model for the butyl analogue **2**, and the calculations were extended to chlorobenzene (**Ph-Cl**), in order to assess the effect of the alkyl groups. Solvent effects (bulk MeOH) were included at the same level of theory by single-point calculations using the C-PCM method (conductor-like polarizable continuum model).[15] As for parent triplet ^{3}**1**, computational data obtained in the gas phase essentially confirmed what was previously reported,[14] that is the aryl−chlorine bond was elongated and stuck out from the ring plane. In bulk methanol, calculations revealed a significant partial negative charge at the chlorine atom (−0.22, Figure 1a), with the spin density mainly localized on C_4 (44%) and only 8% on Cl. A further stretching of the Ar−Cl bond in ^{3}**1** up to 4.00 Å (Figure 1b) resulted in a marked charge separation (Cl −0.79; C_4 0.03). The spin localization on the chlorine atom remained almost unchanged (10%), while energy increased by ca. 15 kcal mol^{-1} with respect to the equilibrium geometry. Similar data were obtained for triplet aromatics with more branched alkyl substituents viz. ethyl, *i*-Pr, and *t*-Bu (see Figures S1−S2, Supporting Information and Table 1). The results for silyl derivative ^{3}**5** were similar to those obtained for the isosteric *t*-Bu-substituted benzene (^{3}**4**, see Figure S2, Supporting Information, for comparison). The calculated triplet energies (E_T, 72.9−73.6 kcal mol^{-1}) and $\Delta E_{stretch}$ (the energy required to stretch the Ar−Cl bond up to 4 Å) for ^{3}**1**−^{3}**5** are reported in Table 1. With **Ph-Cl**, $\Delta E_{stretch}$ = 18.7 kcal mol^{-1} (the highest in the series), the charge separation is less pronounced (C_4 = −0.01, Cl = −0.60), and 20% of the spin density remains localized on the chlorine atom (see Figure S3, Supporting Information, and Table 1). Further studies were likewise performed on both singlet and triplet phenyl cations. The geometry was characteristic. Thus, singlets ^{1}**1**$^{+}$−^{1}**5**$^{+}$ were planar with a cumulative double-bond character at the C_3−C_4−C_5 moiety (see Figures 1c and S4a, Supporting Information), while the corresponding triplets ^{3}**1**$^{+}$−^{3}**5**$^{+}$ were planar and close to a regular hexagon (Figure 1d), with the only exception of 4-trimethylsilylphenyl cation (^{3}**5**$^{+}$), where a small out-of-plane displacement (∠C_4−C_5−C_6−C_1 = 2.9°) of the Ar−Si bond occurred (Figure S4b, Supporting Information).

Table 1. Calculated E_T and $\Delta E_{stretch}$ of Triplet Aryl Chlorides Considered in This Study

aryl chloride	E_T[a]	$\Delta E_{stretch}$[b]
1	73.1	15.6
2′	73.4	15.4
3	73.1	15.0
4	72.9	15.2
5	73.6	17.7
Ph−Cl	76.3	18.7

[a] Triplet energy (kcal mol^{-1}) calculated in bulk MeOH at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory; [b] Energy required to stretch the Ar−Cl bond up to 4 Å for ^{3}**1**−^{3}**5**.

The isodesmic reaction shown in eq 1 was adopted to evaluate the energy of the phenyl cations formed (calculated in MeOH, see Supporting Information) with respect to the reduced form **1a**−**5a**. In all cases, alkyl and trimethylsilyl groups imparted a slight stabilization to the singlets with respect to the parent singlet phenyl cation taken as the reference point and a larger stabilization (>4 kcal mol^{-1}) to the triplets (Figure 2). Singlets are the ground state of these cations, with a triplet/singlet energy gap ranging from ca. 14 (**1**$^{+}$−**4**$^{+}$) to 19.2 kcal mol^{-1} (**5**$^{+}$).



(1)

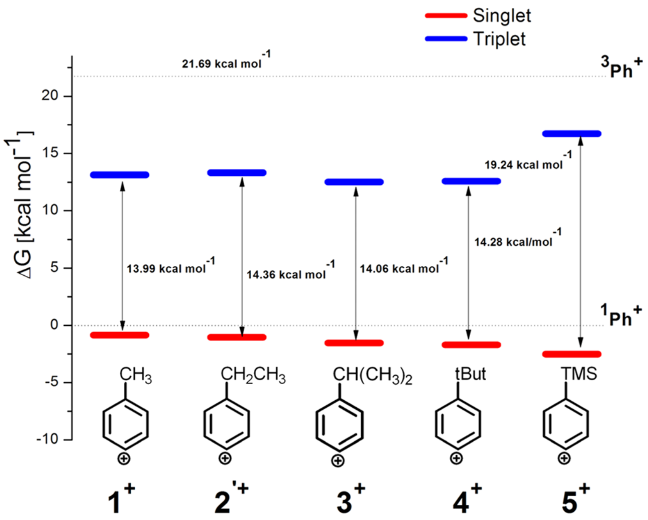


Figure 2. Relative Gibbs free energies (see Tables S1 and S2, Supporting Information) of singlet (red) and triplet (blue) phenyl cations in solution (MeOH) according to the isodesmic reaction in eq 1.

Turning to the experiment, compounds **1**−**5** exhibit low fluorescence (see Table S3, Supporting Information). Irradiation of **1** in MeOH (254 nm) led to a mixture of the dechlorinated toluene (**1a**, 80% yield based on the consumption of **1**) and 4-methylanisole (**1b**, 18%). In order to assess whether both products arose from the same intermediate, the reaction was repeated in the presence of increasing amounts of allyltrimethylsilane (ATMS), a known trap of phenyl cations.[16] The irradiation time required for the conversion did not change significantly, while as shown in Figure 3, the yields of both photoproducts depended on [ATMS] and decreased in a parallel way with the increase of the trapping product, 4-allyltoluene (**6**).

The successful trapping by ATMS fostered a more extended investigation on the reaction of the examined chlorides with π-bond nucleophiles and its synthetic potential. The phenyl chlorides employed were commercially available or easily accessible from the corresponding 4-alkylanilines as in the case of **3** and **4** (see the Experimental Section). Irradiation has been tested for the synthesis of allylbenzenes (by reaction with ATMS),[16] γ-benzyl lactones (by using 4-pentenoic acid as the nucleophile),[12b] 3-arylacetals and ketals (by reaction with vinyl ethers),[12a] and biaryls (in the presence of aromatics).[16] Photolysis of **1**−**5** has been carried out at 254 nm for direct irradiation, applied with alkenes, and at 310 nm under sensitized conditions (acetone 20%$_{v/v}$) when a trap absorbing at 254 nm was employed (e.g., benzene, mesitylene). The use of a base (Et_3N or Cs_2CO_3) to buffer the HCl released[17] was also tested. The phenyl chlorides mostly reacted quantitatively, except when benzene and mesitylene were used as the nucleophiles (see below and the Experimental Section). Gratifyingly, the results obtained (see Tables 2−4) demonstrated that smooth arylation reactions starting from alkyl(silyl) substituted phenyl chlorides under metal-free conditions were feasible.

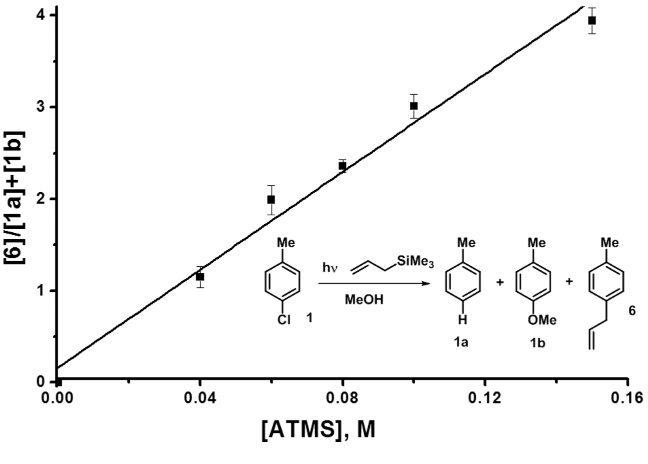


Figure 3. Ratio between the yield of 4-allyltoluene (**6**) and that of the other photoproducts (toluene **1a** and 4-methylanisole **1b**) from the irradiation of 4-chlorotoluene (**1**) in MeOH in the presence of an increasing amount of allyltrimethylsilane (ATMS).

Irradiation of a mixture of **1**−**5** (0.05 M) and ATMS (0.5 M) in water/acetonitrile 1/5$_{v/v}$ gave the corresponding 4-allylarenes **6**−**10** in a satisfactory yield (53−72%, Table 2a). In the preparation of allylated **6** and **7**, yields were lower when shifting to 2,2,2-trifluoroethanol as the solvent. Aqueous acetonitrile was the chosen medium for the arylation of 4-pentenoic acid, and the corresponding γ-benzyl lactones **11**−**15** were isolated in satisfying amounts (Table 2b). A partial ring-opening of lactones **14**−**15** to the corresponding 5-phenyl-4-hydroxypentenoic acids has been observed after the isolation.

A three-component reaction was likewise accomplished by irradiation of **1**−**5** in methanol at 254 nm in the presence of ethyl vinyl ether or 2-methoxypropene. This gave 3-aryl acetals (**16**−**20**) or ketals (**21**−**25**), respectively (Table 3). In the synthesis of **16** and **17**, a lower excess of the nucleophile (0.25 M) was likewise tested, and the yields were still satisfactory at least in the first case. A 3-arylketal (a protected ketone) was the only product observed in the reaction between **1** and 2-methoxypropene. However, addition of aqueous HCl (equimolar to **1**) to the photolyzed solution resulted in the efficient one-pot preparation of the corresponding α-aryl ketone **21′** (Scheme 1).

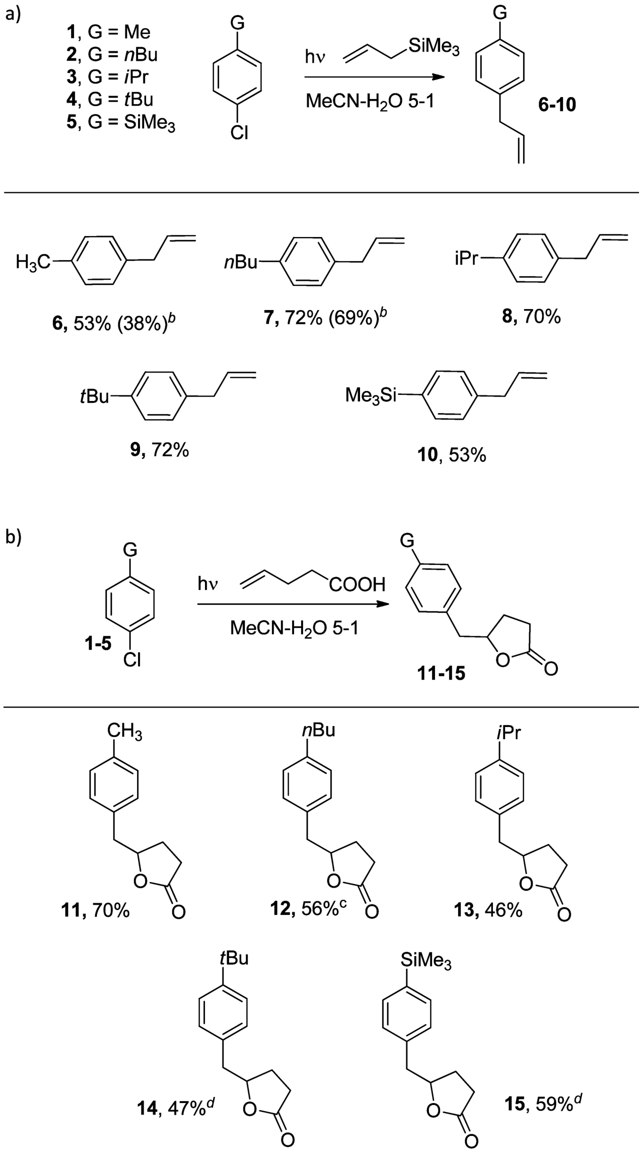
Finally, biaryls **26**−**35** were synthesized in discrete yields by photoreaction between the chosen chlorides and benzene or mesitylene (Table 4). In this case, a longer irradiation time (50 h) was required to achieve a significant consumption of the substrate (particularly when benzene was used), and TFE was required to have a satisfying arylation yield. However, a faster reaction roughly maintaining the same yields can be obtained by lowering the concentration of chlorides (see Table 4 and the Experimental Section).

■ DISCUSSION

The photochemical behavior of **PhCl** and of the corresponding alkylated derivatives depends on the medium used. Accordingly, irradiation of **PhCl** in alkanes caused an efficient dechlorination via homolysis of the Ar−Cl bond.[18a] On the contrary, the consumption of **1** when photolyzed in 9:1 acetonitrile−water mixture was negligible ($\Phi_r = 3.7 \times 10^{-3}$),[18b] whereas it was consistently larger in MeOH ($\Phi_r = 0.09$) where both toluene and 4-methylanisole were formed.[19]

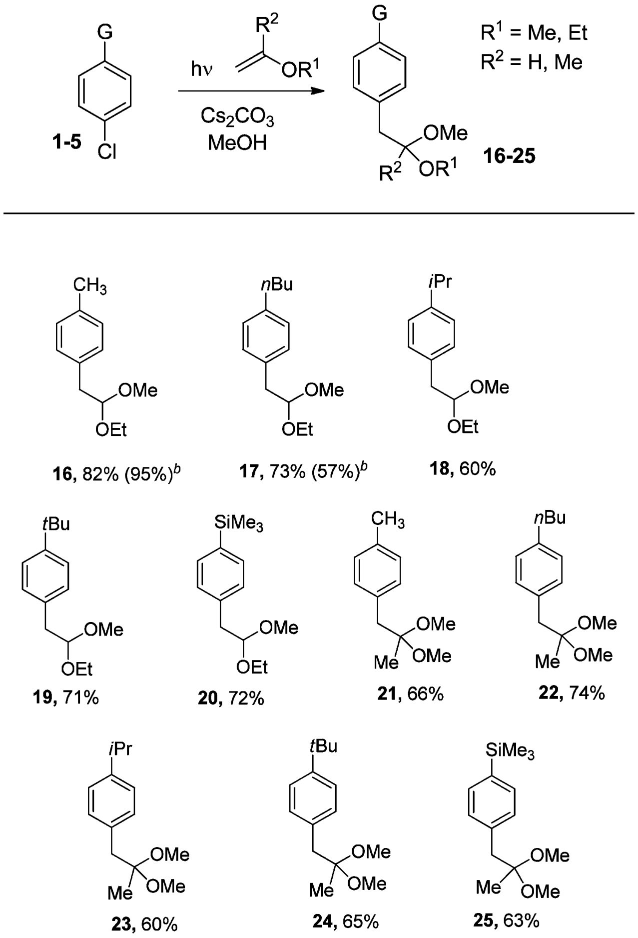
Triplet phenyl cations as synthetic intermediates were initially characterized upon photolysis of chloro- and (less efficiently) fluoroanilines.[20] Later, it was demonstrated that the photoheterolytic cleavage was likewise feasible for a wide range of electron-rich aromatic halides and esters.[12] On the basis of the present results, it appears that the reaction is rather general,

Table 2. Synthesis of (a) Allylbenzenes 6−10 and (b) γ-Benzyl Lactones 11−15[a]



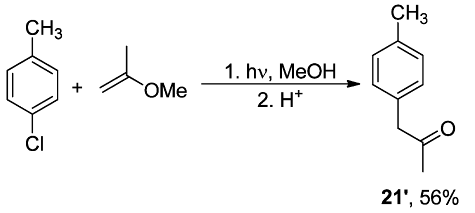
[a]Reaction conditions: 0.05 M solution of **1**−**5** in water/acetonitrile 1/$5_{v/v}$ irradiated at 254 nm for 18 h in the presence of the chosen nucleophile (ATMS or 4-pentenoic acid, 0.5 M); arylation yields based on the consumption of the phenyl chloride. [b]Reaction carried out in 2,2,2-trifluoroethanol, Cs_2CO_3 0.05 M. [c]See ref 12b. [d]Partial hydrolysis to the corresponding 5-aryl-4-hydroxypentanoic acid has been observed.

Table 3. Synthesis of 3-Arylacetals and 3-Arylketals 16−25[a]



[a]Reaction conditions: 0.05 M solution of **1**−**5** and 0.05 M Cs_2CO_3 in MeOH irradiated at 254 nm for 18 h in the presence of 0.5 M ethyl vinyl ether (products **16**−**20**) or 2-methoxypropene (products **21**−**25**); [b]Reaction carried out by using 0.25 M of ethyl vinyl ether.

Scheme 1. One-Pot Synthesis of α-Aryl Ketone 21′

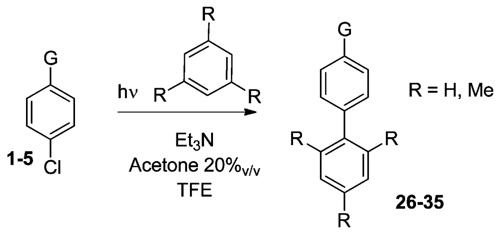


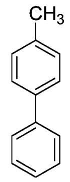
provided that a polar protic solvent 5:1 acetonitrile−water mixture, MeOH, or TFE is used. The presence of a mild electron-donating substituent (an alkyl or to a lesser extent a $SiMe_3$ group, compare the σ values for Et = −0.15; Me = −0.17; $SiMe_3$ = −0.07)[21] contributes to drive the reaction toward heterolysis. Actually, calculations confirmed that the energy required to stretch the Ar−Cl bond in **PhCl** (ca. 19 kcal mol^{-1}) is 3 kcal mol^{-1} higher than those of alkyl-substituted **1**−**4** (Table 1).

Intersystem crossing in **1**−**5** is known to be quite efficient (Scheme 2, path a),[7,14] and direct irradiation is a viable choice provided that the trap does not absorb competitively. If this is the case (aromatics), acetone sensitization (E_T = 80 kcal mol^{-1}) was successful, although a longer irradiation time (ca. 50 h) was required. Photoheterolysis of the Ar−Cl bond from the triplet states ^{3}**1**−^{3}**5** (path b) is supported by computational results (see Figure 1).

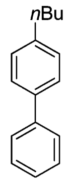
Singlet phenyl cations ^{1}**1**$^+$−^{1}**5**$^+$ are planar and have a structure similar to those reported for analogues bearing a moderate donating substituent, e.g., $CH(OR)_2$,[15] and different from cations substituted with more electron-rich groups, such as OMe or NMe_2, where a puckering of the ring was observed.[22] The triplets ^{3}**1**$^+$−^{3}**5**$^+$ has a regular hexagonal shape as in other (substituted) triplet phenyl cations. Singlets ^{1}**1**$^+$-^{1}**5**$^+$, are more stable than the corresponding triplets (by at least 14 kcal mol^{-1}) and are accessible from them by intersystem crossing (ISC, Scheme 2, path c). Thus, in neat solvent, the chemistry occurring results from the competition

Table 4. Synthesis of Biphenyls 26−35[a]

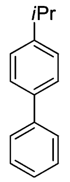




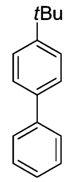
26, 52%(62%)[b]



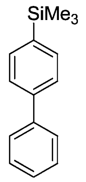
27, 63%(49%)[b]



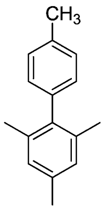
28, 55%(68%)[b]



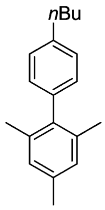
29, 67%(72%)[b]



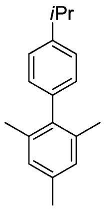
30, 76% (48%)[b]



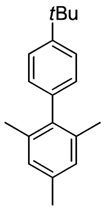
31, 88%



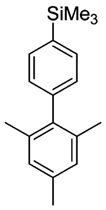
32, 51%



33, 50%



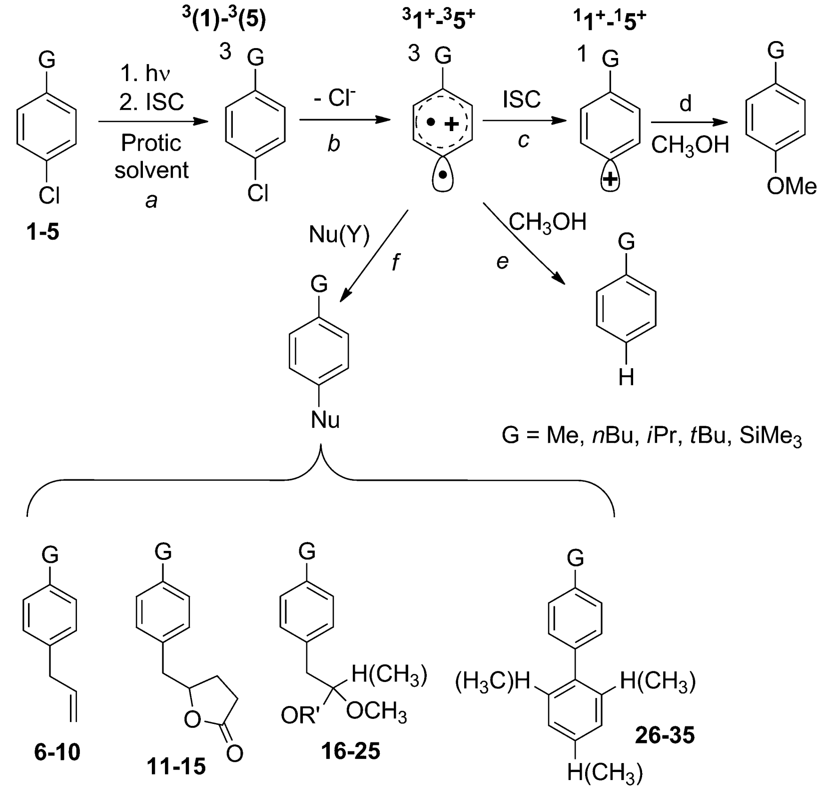
34, 61%



35, 60%

[a] Reaction conditions: 0.05 M solution of **1**−**5** and 0.05 M Et$_3$N in TFE/acetone 8/2 mixture irradiated at 310 nm for 50 h in the presence of 1.0 M benzene (products **25**−**30**) or mesitylene (products **31**−**35**). Yields based on the consumption of phenyl chlorides. [b] 0.025 M **1**−**5** were used.

Scheme 2. Irradiation of Phenyl Chlorides 1−5 in Neat Protic Solvents and in the Presence of π-Bond Nucleophiles



between hydrogen abstraction (path e) and ISC to the singlets leading to solvolysis (path d).

On the other hand, in the presence of a sufficiently high concentration (0.5 M) of a π-bond nucleophile, trapping of the triplet cation (Scheme 2, path f) and formation of an Ar—C bond was exclusive. The efficiency of the photoreaction in neat solvents and in the presence of a trap did not vary, supporting the idea that the cation is formed through a unimolecular fragmentation, not requiring the intermediacy of an exciplex, at least under the present conditions.[23] Moreover, the intermediacy of an aryl radical ($Ar^{\bullet}$) formed by photohomolysis of the Ar—X bond[24] or from cleavage of $Ar{-}X^{\bullet -}$ in turn obtained by a photoinduced electron transfer reaction (PET) between Ar—Cl* and the nucleophile[24] is likewise ruled out. The former path has a role only in nonpolar solvents[18a] or when using aryl halides having a more labile Ar—halogen bond such as Ar—I or Ar—Br.[24] A PET reaction is reasonably excluded since the reaction between ^{3}**1** and ATMS (the most oxidizable nucleophile among those tested) was calculated to be slightly endoergonic (ΔG_{ET} = +3.3 kcal mol^{-1}).[25] In addition, the attempted reaction between mesitylene and a substituted phenyl radical was recently reported but the arylation failed due to the high steric hindrance of the alkyl aromatic.[28]

Thus, all of the previously found classes of addition by using electron-rich substituted phenyl cations have been carried out successfully also with halides **1**—**5** (alkene addition followed by elimination with ATMS, or by intramolecular nucleophilic attack with pentenoic acid, or by intermolecular trapping, with enol ethers and methanol; arylation via benzenium ion intermediate with benzene or mesitylene).[16]

A peculiar case is represented by silane **5** that bears two potential leaving groups (viz. nucleofugal Cl and electrofugal $SiMe_3$). Both of these groups were activated under metal-catalyzed conditions. Thus, the Ar—Cl bond in **5** was cleaved in the Pd-catalyzed α-arylation of aliphatic aldehydes[29] whereas the Ar—$SiMe_3$ bond was activated in gold-catalyzed cross-coupling reactions with unactivated arenes to form biaryls.[30]

We recently studied the chemistry of photogenerated phenyl cations having 14b group-based substituents (viz. a trimethylsilyl or trimethylstannyl) in the *ortho* position with respect to the positive charge.[22,31] A β-silicon (or β-tin) effect operated and intersystem crossing of the triplet cation to the singlet was favored also in the presence of π bond nucleophiles. In the present case, however, neither experimental nor computational data showed a significant difference between silane **5** and alkylbenzenes **1**—**4**, except for a lower stabilization imparted to the triplet cation (that had the higher triplet-singlet gap of the series, ca. 19 kcal mol^{-1}, Figure 2). As expected, no δ-silicon effect operated, which allowed us to prepare substituted arylsilanes prone to further elaboration through metal catalysis.[30,32,33]

CONCLUSIONS

The results presented here (see Tables 2—4) again strengthen the role of triplet phenyl cations as intermediates for transition-metal-free arylations under mild conditions. The generation of the cations, previously limited to electron-rich aromatics,[16] is now extended to easily available alkyl (or silyl) substituted phenyl chlorides. Although an excess of a nucleophile has to be used, particularly in the preparation of biphenyl derivatives, the method proposed competes with transition-metal-free reactions[4,5] where the nucleophile was mostly used as the reaction medium.

EXPERIMENTAL SECTION

^{1}H and ^{13}C 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. Irradiations were performed in a multilamp reactor fitted with ten 15 W phosphor coated lamps (maximum of emission 310) or with four low pressure Hg lamps (maximum of emission at 254 nm). The π bond nucleophiles (allyltrimethylsilane (ATMS), ethyl vinyl ether, 2-methoxypropene, 4-pentenoic acid, benzene, and mesitylene) were commercially available and were used as received, except for ethyl vinyl ether, which was freshly distilled before use. Aryl chlorides **1**, **2**, and **5** were commercially available. Toluene (**1a**) and 4-methylanisole (**1b**) have been characterized by comparison with authentical samples, and their yield calculated by means of calibration curves. Compounds **3** (oil) and **4** (oil) have been synthesized from the corresponding anilines through a Sand-Mayer reaction by following a known procedure[35] and obtained in 40% (665 mg) and 43% (801 mg) yield, respectively.

3: ^{1}H NMR ($CDCl_3$) δ 7.30—7.15 (AA′BB′, J = 8 Hz, 4H), 2.90—2.75 (m,1H), 1.3—1.25 (d, J = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 147.2, 131.2, 128.3 (CH), 127.7 (CH), 33.5 (CH), 24.0 (CH_3); IR (neat) ν/cm^{-1} 2961, 1493, 1092, 1013, 825. Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17. Found: C, 69.8; H, 7.3.

4: spectroscopic data were in accordance with the literature.[36] Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77. Found: C, 71.1; H, 7.9.

General Procedure for the Synthesis of 4-Alkyl-1-allylbenzenes 6—10. *Method A.* A solution of the aryl chlorides (**1**—**5**, 1.5 mmol, 0.05 M) and allyltrimethylsilane (ATMS, 15 mmol, 0.5 M) in MeCN/H_2O 5:1 (30 mL) was nitrogen purged in quartz tubes, serum capped, and irradiated at 254 nm for 18 h until complete consumption of the aromatic. The photolyzed mixture was extracted with diethyl ether (3 × 20 mL), the organic phases were reunited, dried over $MgSO_4$, evaporated, and the residue was purified by column chromatography (eluant: *n*-hexane).

Method B. A solution of the aryl chlorides (**1**—**5**, 1.5 mmol, 0.05 M), allyltrimethylsilane (ATMS, 15 mmol, 0.5 M), and Cs_2CO_3 0.05 M (1.5 mmol) in TFE (30 mL) was nitrogen purged in quartz tubes, serum capped, and irradiated at 254 nm for 18 h until complete consumption of the aromatic (except where indicated). The photolyzed solution were evaporated under vacuum, and the residue was purified by column chromatography (eluant: *n*-hexane).

*1-Allyl-4-methylbenzene (**6**):* oil, 105 mg, 53% yield from method A and 68 mg, 38% yield (based on the 90% consumption of **1**) from method B. The spectroscopic data of compound **6** were in accordance with the literature.[37] Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.8; H, 9.1.

*1-Allyl-4-butylbenzene (**7**):* oil, 188 mg, 72% yield from method A and 180 mg 69% yield from method B. The spectroscopic data of compound **7** were in accordance with the literature.[38] Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.6; H, 10.4.

*1-Allyl-4-isopropylbenzene (**8**):* oil, 168 mg, 70% yield from method A; ^{1}H NMR ($CDCl_3$)[39] δ 7.25—7.15 (AA′BB′, 4H, J = 8 Hz), 6.05—6.00 (m, 1H), 5.20—5.10 (m, 2H), 3.45—3.40 (d, 2H, J = 6.5 Hz), 3.00—2.95 (m, 1H), 1.35—1.30 (d, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 146.5, 137.6 (CH), 137.3, 128.4 (CH), 126.2 (CH), 115.5 (CH_2), 39.8 (CH_2), 36.6 (CH), 23.9 (CH_3); IR (neat) ν/cm^{-1} 2963, 1515, 1248, 1064, 836. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.9; H, 10.3.

*1-Allyl-4-tert-butylbenzene (**9**):* oil, 188 mg, 72% yield from method A. The spectroscopic data of compound **9** were in accordance with the literature.[40] Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.6; H, 10.3.

*(4-Allylphenyl)trimethylsilane (**10**):* oil, 151 mg, 53% yield from method A. The spectroscopic data of compound **10** were in accordance with the literature.[41] Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.6; H, 9.6.

General Procedure for the Photochemical Synthesis of γ-Benzyl Lactones 11—15. A solution of aryl chlorides (**1**—**5**, 1.5

mmol, 0.05 M) and 4-penten-1-oic acid (15 mmol, 0.5 M) in MeCN/H_2O 5:1 (30 mL) was purged for 5 min with nitrogen, serum capped, and irradiated with four 15-W Hg lamps (emission centered at 254 nm) for 18 h. The photolyzed mixture was thus neutralized with aqueous $NaHCO_3$ 5% and extracted with diethyl ether (3 × 20 mL). The organic phase were collected, dried over $MgSO_4$, evaporated, and the residue purified by column chromatography (eluant: cyclohexane/ethyl acetate mixture).

*5-(4-Methylbenzyl)dihydrofuran-2(3H)-one (**11**):* oil, 200 mg, 70% yield (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 75:25); ^1H NMR (CD_3COCD_3) δ 7.20−7.10 (AA′BB′, *J* = 8 Hz, 4H), 4.80−4.70 (qui, *J* = 7 Hz, 1H), 2.95−2.80 (dd, *J* = 6 and 14 Hz, 2H), 2.55−2.40 (m, 2H), 2.30 (s, 3H), 2.30−2.25 (m, 1H), 2.00−1.90 (m, 1H); ^{13}C NMR (CD_3COCD_3) δ 177.5, 137.2, 135.2, 130.6 (CH), 130.2 (CH), 81.8 (CH), 41.9 (CH_2), 29.3 (CH_2), 28.2 (CH_2), 21.4 (CH_3); IR (neat) ν/cm^{-1} 2925, 1773, 1516, 1179, 919, 807. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.7; H, 7.4.

*5-(4-Isopropylbenzyl)dihydrofuran-2(3H)-one (**13**):* oil, 151 mg, 46% yield (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 8:2); ^1H NMR (CD_3COCD_3) δ 7.30 (s, 4H), 4.80−4.70 (qui, *J* = 7 Hz, 1H), 3.00−2.90 (m, 3H), 2.50−2.20 (m, 3H), 2.00−1.95 (m, 1H), 1.25 (d, *J* = 6 Hz, 6H); ^{13}C NMR (CD_3COCD_3) δ 177.5, 148.3, 135.7, 130.6 (CH), 127.6 (CH), 81.9 (CH), 41.9 (CH_2), 34.8 (CH), 29.3 (CH_2), 28.3 (CH_2), 24.7 (CH_3); IR (neat) ν/cm^{-1} 2960, 1776, 1514, 1178, 1020, 920, 818. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.0; H, 8.3.

*5-(4-tert-Butylbenzyl)-dihydrofuran-2(3H)-one (**14**):* oil, 164 mg, 47% yield (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 8:2); ^1H NMR (CD_3COCD_3) δ 7.40−7.20 (AA′BB′, *J* = 8 Hz, 4H), 4.80−4.70 (qui, *J* = 7 Hz, 1H), 3.00 (dd, *J* = 6 and 11 Hz, 2H), 2.50−2.40 (m, 2H), 2.30−2.10 (m, 2H), 2.05−1.95 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (CD_3COCD_3) δ 177.5, 150.5, 135.3, 130.3 (CH), 126.6 (CH), 81.9 (CH), 41.8 (CH_2), 34.1, 32.0 (CH_3), 29.3 (CH_2), 28.3 (CH_2); IR (neat) ν/cm^{-1} 2962, 1774,1512, 1364, 1178, 832. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.6; H, 8.9. After isolation a partial hydrolysis of **14** to 5-(4-*tert*-butylphenyl)-4-hydroxypentenoic acid has been observed as pointed out by the signals at 4.20−4.30 (m, 1H) in the ^1H NMR spectra and at 64.8 (CH) in the ^{13}C NMR.

*5-(4-(Trimethylsilyl)benzyl)-dihydrofuran-2(3H)-one (**15**):* oil, 220 mg, 59% yield (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 7:3); ^1H NMR (CD_3COCD_3) δ 7.55−7.30 (AA′BB′, *J* = 8 Hz, 4H), 4.80−4.70 (qui, *J* = 7 Hz, 1H), 3.05−2.95 (m, 2H), 2.50−2.25 (m, 3H), 2.15−2.0 (m, 1H). 0.3 (s, 9H); ^{13}C NMR (CD_3COCD_3) δ 177.4, 139.2, 139.1, 134.6 (CH), 130.1 (CH), 81.7 (CH), 42.3 (CH_2), 29.4 (CH_2), 28.4 (CH_2), −0.66 (CH_3); IR (neat) ν/cm^{-1} 2954, 1772, 1602, 1248, 1178, 839, 692. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found. C, 67.7; H, 8.3. After isolation a partial hydrolysis of **15** to 5-(4-trimethylsilylphenyl)-4-hydroxypentenoic acid has been observed as pointed out by the signals at 4.20−4.30 (m, 1H) in the ^1H NMR spectra and at 64.6 (CH) in the ^{13}C NMR.

General Procedure for the Synthesis of 3-Arylacetals or Ketals (16−25. A solution of the aryl chloride (**1**−**5**, 1.5 mmol, 0.05 M), ethyl vinyl ether, or 2-methoxypropene (15 mmol, 0.5 M) and Cs_2CO_3 (1.5 mmol, 0.05 M) in methanol (30 mL) was nitrogen purged in quartz tubes and irradiated at 254 nm until complete consumption of the aromatic (except where indicated). The solvent was thus removed under vacuum and the residue purified by column chromatography (hexane/ethyl acetate mixtures with 1% Et_3N as the eluant).

*1-(2-Ethoxy-1-methoxyethyl)-4-methylbenzene (**16**):* oil, 239 mg, 82% yield (after purification by column chromatography, eluant: neat cyclohexane); ^1H NMR ($CDCl_3$) δ 7.20−7.05 (AA′BB′, *J* = 8 Hz, 4H), 4.65−4.60 (t, *J* = 6 Hz, 1H), 3.65−3.55 (AB system, 1H), 3.50−3.40 (AB system, 1H), 3.35 (s, 3H), 2.95−2.85 (d, 2H, *J* = 6 Hz), 2.35 (s, 3H), 1.25−1.15 (t, 3H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 135.7, 134.0, 129.2 (CH), 128.9 (CH), 104.6 (CH), 61.8 (CH_2), 53.1 (CH_3), 39.7 (CH_2), 20.9 (CH_3), 15.2 (CH_3); IR (neat) ν/cm^{-1} 2927, 1516, 1124, 1064. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.2; H, 9.3. The same reaction has been carried out in the presence of 0.25 M ethyl vinyl ether affording 277 mg of **16** (95% yield).

*1-Butyl-4-(2-ethoxy-2-methoxyethyl)benzene (**17**):* oil, 259 mg, 73% yield (after purification by column chromatography, eluant: neat cyclohexane). The spectroscopic data of compound **17** were in accordance with the literature.[12b] Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.3; H, 10.2. The same reaction has been carried out in the presence of ethyl 0.25 M vinyl ether affording 202 mg of **17** (57% yield).

*1-(2-Ethoxy-2-methoxyethyl)-4-isopropylbenzene (**18**):* oil, 200 mg, 60% yield (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 98:2); ^1H NMR ($CDCl_3$) δ 7.30−7.20 (AA′BB′, 4H, *J* = 7 Hz), 4.65−4.55 (t, 1H, *J* = 6 Hz), 3.75 −3.60 (AB system, 1H), 3.55−3.45 (AB system, 1H), 3.35 (s, 3H), 3.00−2.95 (d, 2H, *J* = 7 Hz), 2.95−2.90 (m, 1H), 1.40−1.30 (d, 6H, *J* = 7 Hz),1.30−1.25 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 146.7, 134.3, 129.3 (CH), 126.5 (CH), 104.5 (CH), 61.7 (CH_2), 53.0 (CH_3), 39.6 (CH_2), 33.6 (CH), 23.9 (CH_3), 15.2 (CH_3); IR (neat) ν/cm^{-1} 2958, 1513, 1226, 1127, 1051, 822. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.6; H, 9.9.

*1-tert-Butyl-4-(2-ethoxy-2-methoxyethyl)benzene (**19**):* oil, 211 mg, 71% yield based on 84% consumption of **4** (after purification by column chromatography, eluant: cyclohexane/ethyl acetate 98:2); ^1H NMR ($CDCl_3$) δ 7.35−7.20 (AA′BB′, 4H, *J* = 8 Hz), 4.65−4.55 (t, 1H, *J* = 6 Hz), 3.80−3.70 (AB system, 1H), 3.55−3.45 (AB system, 1H), 3.30 (s, 3H), 3.0−2.90 (d, 2H, *J* = 6 Hz), 1.35 (s, 9H), 1.30−1.20 (t, 3H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 149.0, 134.0, 129.0 (CH), 125.4 (CH), 104.4 (CH), 61.7 (CH_2), 53.0 (CH_3), 39.5 (CH_2), 34.3, 31.3 (CH_3), 15.1 (CH_3); IR (neat) ν/cm^{-1} 2964, 1514, 1364, 1269, 1121, 1064. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.2; H, 10.2.

*(4-(2-Ethoxy-2-methoxyethyl)phenyl)trimethylsilane (**20**):* oil, 248 mg, 72% yield based on 91% consumption of **5** (after purification by column chromatography, eluant: neat cyclohexane); ^1H NMR ($CDCl_3$) δ 7.50−7.20 (AA′BB′, 4H, *J* = 8 Hz), 4.65−4.55 (t, 1H, *J* = 6 Hz), 3.75−3.65 (AB system, 1H), 3.50−3.40 (AB system, 1H), 3.35 (s, 3H), 3.00−2.95 (d, 2H, *J* = 6 Hz), 1.30−1.20 (t, 3H, *J* = 7 Hz), 0.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 137.9, 137.7, 133.2 (CH), 128.8 (CH), 104.3 (CH), 61.7 (CH_2), 53.0 (CH_3), 40.0 (CH_2), 15.2 (CH_3), −1.2 (CH_3); IR (neat) ν/cm^{-1} 2955, 1248, 1110, 1064, 838. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.6; H, 9.6.

*1-(2,2-Dimethoxypropyl)-4-methylbenzene (**21**):* oil, 192 mg, 66% yield (after purification by column chromatography, eluant: neat cyclohexane); ^1H NMR ($CDCl_3$) δ 7.25−7.05 (AA′BB′, 4H), 3.20 (s, 6H), 2.85 (s, 2H), 2.35 (s, 3H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 136.5, 135.9, 131.4 (CH), 129.7 (CH), 102.8, 48.6 (CH_3), 43.3 (CH_2), 21.8 (CH_3), 21.4 (CH_3); IR (neat) ν/cm^{-1} 2944, 1515, 1376, 1126, 1051. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.2; H, 9.3.

*One-Pot Synthesis of 1-p-Tolylpropan-2-one (**21′**).* From 179 μL of 4-chloro toluene (**1**, 0.05 M, 1.5 mmol), 488 mg of Cs_2CO_3 (0.05 M, 1.5 mmol), and 1.45 mL of 2-methoxypropene (0.5 M, 15 mmol) in MeOH (30 mL). A 100 μL portion of 37% aq HCl was added to the photolyzed solution, allowed to stay for 1 h at rt, and evaporated. Purification by column chromatography (eluant: hexane/ethyl acetate 98:2) afforded 124 mg of **21′** (oil, 56% yield). Spectroscopic data of **21′** were in accordance with the literature.[42] Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.1; H, 8.2.

*1-Butyl-4-(2,2-dimethoxypropyl)benzene (**22**):* oil, 262 mg, 74% yield (after purification by column chromatography, eluant: neat hexane); ^1H NMR ($CDCl_3$) δ 7.20−7.05 (AA′BB′, 4H, *J* = 8 Hz), 3.30 (s, 6H), 2.90 (s, 2H), 2.70−2.60 (t, 2H, *J* = 8 Hz), 1.7−1.6 (m, 2H), 1.45−1.35 (m, 2H), 1.20 (s, 3H), 1.0−0.90 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 140.7, 134.4, 129.9 (CH), 128.7 (CH), 101.8, 48.2 (CH_3), 42.2 (CH_2), 35.2 (CH_2), 33.6 (CH_2), 22.3 (CH_3), 21.0 (CH_2), 13.9 (CH_3); IR (neat) ν/cm^{-1} 2931, 1513, 1377, 1127, 1052. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.2; H, 10.1.

*1-Isopropyl-4-(2,2-dimethoxypropyl)benzene (**23**):* oil, 200 mg, 60% yield (after purification by column chromatography, eluant: neat hexane); ^1H NMR (CD_3COCD_3) δ 7.30−7.15 (m, 4H), 3.25 (s, 6H), 2.95 (s, 2H), 2.95−2.90 (m,1H), 1.30−1.25 (d, 6H, *J* = 7 Hz), 1.2 (s, 3H); ^{13}C NMR (CD_3COCD_3) δ 147.6, 136.3, 131,4 (CH), 127.0 (CH), 102.8, 48.6 (CH_3), 43.3 (CH_2), 34.8 (CH), 24.8 (CH_3), 21.8 (CH_3); IR (neat) ν/cm^{-1} 2959, 1513, 1376, 1123, 1064, 819. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.6; H, 9.9.

*1-tert-Butyl-4-(2,2-dimethoxypropyl)benzene (**24**):* oil, 230 mg, 65% yield (after purification by column chromatography, eluant: neat hexane); ^{1}H NMR (CD_3COCD_3) δ 7.35−7.15 (AA′BB′, 4H), 3.25 (s, 6H), 2.85 (s, 2H), 1.35 (s, 9H), 1.10 (s, 3H); ^{13}C NMR (CD_3COCD_3) δ 149.8, 135.9, 131.2 (CH), 125.9 (CH), 102.7, 48.6 (CH_3), 43.2 (CH_2), 35.2 (CH_3), 21.0 (CH_3); IR (neat) ν/cm^{-1} 2961, 1516, 1126, 1052, 826. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.2; H, 10.2.

*(4-(2,2-Dimethoxypropyl)phenyl)trimethylsilane (**25**):* oil, 239 mg, 63% yield (after purification by column chromatography, eluant: neat hexane); ^{1}H NMR ($CDCl_3$) δ 7.45−7.25 (AA′BB′, 4H, *J* = 9 Hz), 3.25 (s, 6H), 2.85 (s, 2H), 1.15 (s, 3H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 139.7, 138.5, 134.1 (CH), 131.0 (CH), 102.7, 48.7 (CH_3), 43.8 (CH_2), 21.9 (CH_3), −0.6 (CH_3); IR (neat) ν/cm^{-1} 2944, 1515, 1376, 1126, 1051. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.6; H, 9.6.

General Procedure for the Synthesis of Biaryls 26−35. A solution of the aryl chloride (**1**−**5**) (1.5 mmol, 0.05 M), benzene, or mesitylene (30 mmol 1.0 M), 20% acetone, and TEA 0.05 M (1.5 mmol) in 30 mL of TFE was nitrogen purged in quartz tubes and irradiated at 310 nm for 50 h. The solvent was removed under vacuum and the residue purified by column chromatography (eluant: neat hexane).

*4-Methylbiphenyl (**26**):* colorless solid, 105 mg, 52% yield based on the 80% consumption of **1** (after purification by column chromatography, eluant: neat hexane), mp 41−43 °C (lit.[43] mp 42−43 °C). The spectroscopic data of compound **26** were in accordance with the literature.[44] Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.8; H, 7.2. The same irradiation has been carried out on a 0.025 M solution of **1** affording 71 mg of **26** (62% yield, 90% consumption of **1**).

*4-Butylbiphenyl (**27**):* oil, 137 mg, 63% yield, based on the 69% conversion of **2** (after purification by column chromatography, eluant: neat hexane). The spectroscopic data of compound **27** were in accordance with the literature.[45] Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.4; H, 8.4. The same irradiation has been carried out on a 0.025 M solution of **2** affording 77 mg of **27** (49% yield).

*4-Isopropylbiphenyl (**28**):* oil, 136 mg, 55% yield based on the 84% consumption of **3**, (after purification by column chromatography, eluant: neat hexane). The spectroscopic data of **28** were in accordance with the literature.[44] Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.8; H, 8.2. The same irradiation has been carried out on a 0.025 M solution of **3** affording 100 mg of **28** (68% yield).

*4-tert-Butylbiphenyl (**29**):* colorless solid, 133 mg, 67% yield based on the 63% consumption of **4**, (after purification by column chromatography, eluant: neat hexane), mp 45−47 °C (lit.[46] mp 49−51 °C). The spectroscopic data of compound **29** were in accordance with the literature.[46] Anal. Calcd for $C_{16}H_{18}$: C, 91.37.; H, 8.63. Found: C, 91.4; H, 8.6. The same irradiation has been carried out on a 0.025 M solution of **4** affording 102 mg of **29** (72% yield, 90% consumption of **4**).

*Biphenyl-4-yltrimethylsilane (**30**):* colorless solid, 142 mg, 76% yield based on the 55% consumption of **5** (after purification by column chromatography, eluant: neat hexane), mp 48−50 °C, (lit.[47] mp 52 °C). The spectroscopic data of compound **30** were in accordance with the literature.[47] Anal. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.6.; H, 8.0. The same irradiation has been carried out on a 0.025 M solution of **5** affording 41 mg of **30** (48% yield, 50% consumption of **5**).

*2,4,4′,6-Tetramethylbiphenyl (**31**):* colorless solid, 139 mg, 88% yield based on the 50% consumption of **1** (after purification by column chromatography, eluant: neat hexane), mp 53−56 °C (lit.[48] 58−59 °C). The spectroscopic data of compound **31** were in accordance with the literature.[49] Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.4; H, 8.6.

*4′-Butyl-2,4,6-trimethylbiphenyl (**32**):* oil, 193 mg, 51% yield (after purification by column chromatography, eluant: neat hexane); ^{1}H NMR ($CDCl_3$) δ 7.30−7.05 (AA′BB′, 4H, *J* = 8 Hz), 6.95 (s, 2H), 2.75−2.65 (t, 2H, *J* = 8 Hz), 2.30 (s, 3H), 2.10 (s, 6H), 1.80−1.70 (m, 2H),1.50−1.40 (m, 2H), 1.05−0.95 (t, 3H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 140.9, 139.0, 138.1, 136.3, 136.1, 129.0 (CH), 128.2 (CH), 127.9 (CH), 35.3 (CH_2), 33.5 (CH_2), 22.4 (CH_2), 20.9 (CH_3), 20.7 (CH_3), 13.9 (CH_3); IR (neat) ν/cm^{-1} 2927, 1478, 1377, 1005, 850. Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.4; H, 9.6.

*4′-Isopropyl-2,4,6-trimethylbiphenyl (**33**):* oil, 179 mg, 50% yield (after purification by column chromatography, eluant: neat hexane); ^{1}H NMR ($CDCl_3$) δ 7.35−7.10 (AA′BB′, 4H, *J* = 8 Hz), 7.00 (s, 2H), 3.05−2.95 (m, 1H), 2.40 (s, 3H), 2.10 (s, 6H), 1.40−1.35 (d, 6H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 146.8, 139.0, 138.2, 136.3, 129.0 (CH), 127.9 (CH), 126.2 (CH), 33.7 (CH), 24.0 (CH_3), 20.9 (CH_3), 20.7 (CH_3); IR (neat) ν/cm^{-1} 2960, 1611, 1479, 1056, 850, 833. Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.7; H, 9.3.

*4′-tert-Butyl-2,4,6-trimethylbiphenyl (**34**):* colorless solid, 150 mg, 61% yield based on the 65% consumption of **4** (after purification by column chromatography, eluant: neat hexane); mp 108−110 °C; IR (neat) ν/cm^{-1} 2924, 2854, 1059, 1056, 854. The spectroscopic data of **34** were in accordance with the literature.[50] Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.4; H, 9.6.

*(2′,4′,6′-Trimethylbiphenyl-4-yl)trimethylsilane (**35**):* colorless solid, 208 mg, 60% yield based on the 86% consumption of **5** (after purification by column chromatography, eluant: neat hexane); mp 70−72 °C; ^{1}H NMR ($CDCl_3$) δ 7.50−7.20 (AA′BB′, 4H, *J* = 8 Hz), 7.0 (s, 2H), 2.45 (s, 3H), 2.1 (s, 6H), 0.4 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 141.3, 138.9, 138.1, 136.4, 135.9, 133.2 (CH), 128.5 (CH), 127.9 (CH), 20.9 (CH_3), 20.7 (CH_3), −1.1(CH_3); IR (neat) ν/cm^{-1} 2918, 1605, 1458, 1376, 1033, 849, 690. Anal. Calcd for $C_{18}H_{24}Si$: C, 80.53; H, 9.01. Found: C, 80.5; H, 9.0.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **6**−**11**, **13**−**16**, and **18**−**35**; details of the calculations on intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +390382987316. Fax: +390382987323. E-mail: (M.F.) fagnoni@unipv.it, (S.P.) prottistefano@gmail.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.P. acknowledges MIUR, Rome (FIRB-Futuro in Ricerca 2008 project RBFR08J78Q), for financial support. This work has been supported by the Fondazione Cariplo (Grant No. 2011-1839). We thank Dr. Simone Lazzaroni (University of Pavia) for preliminary experiments.

■ REFERENCES

(1) (a) Elnagdi, M. H.; Hafez, E. A. A.; Erian, A. W. *Rev. Heteroatom Chem.* **1995**, *13*, 179−234. (b) Fischer, R. W.; Roehrscheid, F. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH Verlag: Weinheim, 2002; Vol. *1*, pp 443−467. (c) Elnagdi, M. H.; Soliman Ghozlan, S. A.; Abdelshafy Abdelhamid, I. *ARKIVOC* **2008**, *x*, 54−84. (d) Guan, B.-T.; Wang, B.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 4418−4421.

(2) *Modern Arylation Methods*; Ackermann, L., Ed.; Wiley-VCH Verlag: Weinheim, 2009.

(3) (a) Ackermann, L.; Dell'Acqua, M.; Fenner, S.; Vicente, R.; Sandmann, R. *Org. Lett.* **2011**, *13*, 2358−2360. (b) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958−2961.

(4) See, for instance: (a) Ng, Y. S.; Chan, C. S.; Chan, K. S. *Tetrahedron Lett.* **2012**, *53*, 3911−3914. (b) Qiu, Y.; Liu, Y.; Yang, K.; Hong, W.; Li, Z.; Wang, Z.; Yao, Z.; Jiang, S. *Org. Lett.* **2011**, *13*, 3556−3559. (c) Truong, T.; Daugulis, O. *Org. Lett.* **2011**, *13*, 4172−4175. (d) Wu, Y.; Man Wong, S.; Mao, F.; Long Chan, T.; Yee Kwong, F. *Org. Lett.* **2012**, *14*, 5306−5309.

(5) (a) Liu, H.; Yin, B.; Gao, Z.; Li, Y.; Jiang, H. *Chem. Commun.* **2012**, *48*, 2033−2035.

(6) See, for reviews: (a) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69−82. (b) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211.

(7) Han, K.-L.; He, G.-Z. *J. Photochem. Photobiol. C* **2007**, *8*, 55−66.

(8) (a) Okutsu, T.; Kounose, N.; Nakatsuka, H.; Suzuki, T.; Ichimura, T.; Hiratsuka, H. *J. Photochem. Photobiol. A* **1998**, *115*, 243−247. (b) Freedman, A.; Yang, S. C.; Kawasaki, M.; Bersohn, R. *J. Chem. Phys.* **1980**, *72*, 1028−1033.

(9) (a) Rossi, R. A.; Alonso, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 2498−2502. (b) Yammal, C. C.; Podestà, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720−5725. (c) Córsico, E. F.; Postigo, A.; Rossi, R. A. *Molecules* **2000**, *5*, 1068−1079.

(10) Lockhart, M. T.; Chopa, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1999**, *582*, 229−234.

(11) Dichiarante, V.; Albini, A.; Fagnoni, M. *Green Chem.* **2009**, *11*, 942−945.

(12) (a) Lazzaroni, S.; Protti, S.; Fagnoni, M.; Albini, A. *Org. Lett.* **2009**, *11*, 349−352. (b) Protti, S.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2006**, *128*, 10670−10671.

(13) Hori, K.; Sonoda, T.; Harada, M.; Yamazaki-Nishida, S. *Tetrahedron* **2000**, *56*, 1429−1436.

(14) Liu, Y.-J.; Lunell, S. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3938−3942 and references cited therein.

(15) Raviola, C.; Protti, S.; Ravelli, D.; Mella, M.; Albini, A.; Fagnoni, M. *J. Org. Chem.* **2012**, *77*, 9094−9101.

(16) See, for review: Dichiarante, V.; Fagnoni, M. *Synlett* **2008**, 787−800.

(17) Terpolilli, M.; Merli, D.; Protti, S.; Dichiarante, V.; Fagnoni, M.; Albini, A. *Photochem. Photobiol. Sci.* **2011**, *10*, 123−127.

(18) (a) Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; De Graaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708−3713. (b) Epling, G. A.; Florio, E. *J. Chem. Soc. Chem. Commun.* **1986**, 185−186.

(19) Ichimura, T.; Iwai, M.; Mori, Y. *J. Phys. Chem.* **1988**, *92*, 4047−4052.

(20) Fraboni, A.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2003**, *68*, 4886−4893.

(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(22) Dichiarante, V.; Dondi, D.; Protti, S.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2007**, *129*, 5605−5611. Correction: **2007**, *129*, 11662.

(23) Lazzaroni, S.; Protti, S.; Fagnoni, M.; Albini, A. *J. Photochem. Photobiol. A: Chem.* **2010**, *210*, 140−144.

(24) (a) *Handbook of Synthetic Photochemistry*; Albini, A., Fagnoni, M., Eds.; Wiley-VCH: Weinheim, 2010. (b) Dichiarante, V.; Fagnoni, M.; Albini, A. In *Modern Arylation Methods*; Ackermann, L., Ed.; Wiley-VCH Verlag: Weinheim, 2009; p 513−535.

(25) A PET reaction between excited Ar-Cl and the nucleophile could arise either from ^{1}Ar-Cl or from ^{3}Ar-Cl. The singlet has no role since ISC in compounds **1**−**5** is very efficient and we did not observe a significant quenching of the fluorescence of **1** in the presence of ATMS. The ΔG_{ET} of the PET reaction between ^{3}**1** and ATMS was then calculated by means of the Rehm−Weller equation[26a] where $E(\mathbf{1}/\mathbf{1}^{\bullet-})$ = −2.29 V vs SCE[26b,c] and $E(^3\text{Ar-Cl}/\text{Ar-Cl}^{\bullet-})$ = 1.30 eV (value calculated from the phosphorescence spectrum of **1**[26d]). The $E(\text{R}^{\bullet+}/\text{R})$ of the nucleophiles ranged from 1.50 V vs SCE (for ATMS) to 2.35 vs SCE (for benzene).[27]

(26) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271. (b) Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595−2598. (c) Enemærke, R. J.; Christensen, T. B.; Jensen, H.; Daasbjerg, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1620−1630. (d) Okutsu, T.; Kounose, N.; Tsuchiya, J.; Suzuki, T.; Ichimura, T.; Hiratsuka, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1763−1767.

(27) (a) E^0_{ox} ATMS = 1.5 V vs SCE: Fukuzumi, S.; Fujita, Otera, M.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271−10278. (b) E^0_{ox} 2-methoxypropene = 1.73 V vs SCE; E^0_{ox} ethyl vinyl ether = 1.99 V vs SCE: Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872−2881. (c) E^0_{ox} benzene = 2.35 V vs SCE; E^0_{ox} mesitylene = 1.98 V vs SCE: Fukuzumi, S.; Ohkubo, K.; Suenobu, T.; Kato, K.; Fujitsuka, M.; Ito, S. *J. Am. Chem. Soc.* **2001**, *123*, 8459−8467.

(28) Yong, G.-P.; She, W. L.; Zhang, Y. M.; Li, Y.-L. *Chem. Commun.* **2011**, *47*, 11766−11768.

(29) Martin, R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7236−7239.

(30) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644−1648.

(31) Protti, S.; Dichiarante, V.; Dondi, D.; Fagnoni, M.; Albini, A. *Chem. Sci.* **2012**, *3*, 1330−1337. Abitelli, E.; Protti, S.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2012**, *77*, 3501−3507. Dichiarante, V.; Salvaneschi, A.; Protti, S.; Dondi, D.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2007**, *129*, 15919−15926.

(32) Brenzovich, W. E.; Brazeau, J.-F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728 and references cited therein.

(33) We also reported that a $SiMe_3$ cation can be released from a photogenerated 4-trimethylsilylmethylphenyl cation (a homologue of **5**$^+$) to afford an α,*n*-didehydrotoluene biradical; see ref 34. In this work, however, no loss of electrofugal proton from the benzylic position of ^{3}**1**$^+$−^{3}**3**$^+$ has been observed.

(34) Protti, S.; Ravelli, D.; Mannucci, B.; Albini, A.; Fagnoni, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 8577−8580.

(35) Vogel, A. I. *Vogel's Textbook of Practical Organic Chemistry*, 3rd ed.; Longman Group Ltd.: London, 1956; pp 927−928.

(36) Joshi-Pangu, A.; Wang, C.-Y.; Biscoe, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 8478−8481.

(37) Scrivanti, A.; Beghetto, V.; Bertoldini, M.; Matteoli, U. *Eur. J. Org. Chem.* **2012**, 264−268.

(38) Seomoon, D.; Lee, K.; Kim, H.; Lee, P. H. *Chem.—Eur. J.* **2007**, *13*, 5197−5206.

(39) Okamura, H.; Takei, H. *Tetrahedron Lett.* **1979**, *20*, 3425−3428.

(40) Mayer, M.; Czaplik, W. M.; Von Wangelin, A. J. *Adv. Synth. Catal.* **2010**, *352*, 2147−2152.

(41) Bo, Z.; Schlüter, A. D. *J. Org. Chem.* **2002**, *67*, 5327−5332.

(42) Ackermann, L.; Mehta, V. P. *Chem.—Eur. J.* **2012**, *18*, 10230−10233.

(43) Wang, L.; Cui, X.; Zhu, Z.; Wu, Y.; Li, J.; Wu, Y. *Eur. J. Org. Chem.* **2012**, 595−603.

(44) Schmidt, A.; Rahimi, A. *Chem. Commun.* **2010**, 2995−2997.

(45) Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3190−3198.

(46) Susanto, W.; Ang, W. J.; Lam, Y.; Chu, C.-Y.; Chou, T.-C.; Lo, L.-C. *J. Org. Chem.* **2012**, *77*, 2729−2742.

(47) Iijima, A.; Amii, H. *Tetrahedron Lett.* **2008**, *49*, 6013−6015.

(48) Tamura, Y.; Chun, M.-W.; Inoue, K.; Minamikawa, J. *Synthesis* **1978**, 822−829.

(49) Vallee, F.; Mousseau, J. J.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 1514−1516.

(50) Sreedhar, B.; Yada, D.; Reddya, P. S. *Adv. Synth. Catal.* **2011**, *353*, 2823−2836.