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Aryl Imidazylates and Aryl Sulfates As Electrophiles in Metal-Free ArS_N1 Reactions

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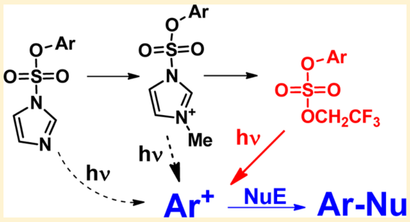
S *Supporting Information*

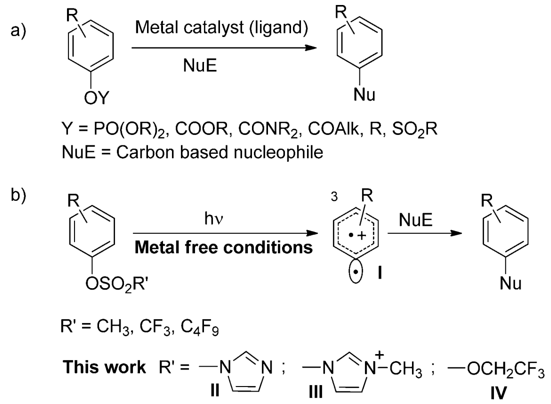
ABSTRACT: Some oxygen-bonded substituents were investigated as leaving groups in photoinduced ArS_N1 reactions. Irradiation of aryl imidazylates and of the corresponding imidazolium salts mainly caused homolysis of the ArO−S bond. However, previously unexplored trifluoroethoxy aryl sulfates were found to undergo efficient metal-free arylation. The sulfates were conveniently generated in situ by dissolving the corresponding imidazolium salts in basic 2,2,2-trifluoroethanol.



INTRODUCTION

Phenols are easily converted into a wide range of aryl electrophiles, including phosphates,[1a] carbonates,[1b] carbamates,[1c] esters and ethers,[1d,e] sulfamates,[1f] and sulfonates, that have been used in various cross-coupling reactions with carbon-based nucleophiles (mainly organometallic species; see Scheme 1a). Sulfonates constitute the most widely used class of compounds, and among them, electron-withdrawing perfluoroalkyl sulfonates such as triflates[2a] and nonaflates ($ArOSO_2C_4F_9$)[2b] have long been used specifically for their excellent reactivity and the mild reaction conditions required. Other fluorine-free sulfonates such as mesylates[3a] and tosylates[3b,c] have been likewise used, despite the lower reactivity in cross-coupling processes due to the high stability of the sulfonate groups.[3a,d,e] A recent advance in aromatic chemistry is the use of the imidazolesulfonate moiety (imidazylate, Imz), previously used in sugar derivatization via aliphatic nucleophilic substitution.[4] Aryl imidazylates have proven to be efficient partners in a wide range of cross-coupling procedures[5] and exhibit higher reactivity with respect to the corresponding aryl tosylates,[5c] pivalates,[5e] and bromides and chlorides.[5h] They also have the advantage of improved stability, cost, and handling properties over traditional aryl triflates.[5c]

Scheme 1. Use of Aryl Esters in (a) Transition-Metal-Catalyzed Reactions and (b) Metal-Free Photochemical Arylations



Little attention has been given, however, to the development of transition-metal-free approaches for activation of the Ar−O bond in aryl imidazylates. To the best of our knowledge, the only case reported deals with the fluoride- induced generation of *o*-benzynes from *o*-(trimethylsilyl)aryl imidazolesulfonates.[6] We recently demonstrated that some aryl sulfonates, namely aryl mesylates,[7a] triflates,[7a] and nonaflates,[7b] can be used as substrates to achieve metal-free arylations via photoheterolytic cleavage of the Ar−O bond. In this process, triplet phenyl cations (**I**, Scheme 1b) are formed photochemically and trapped by carbon nucleophiles (NuE).

We reasoned that (hetero)aromatic sulfonates[4] could function as electrophilic partners for the photogeneration of cations **I**. We therefore tested aryl imidazolesulfonates (**II**, Scheme 1b), for which no photochemical investigations have been reported as yet, thereby replacing an S−C bond by an S−N bond in the leaving group. On the same ground, aryl sulfurylimidazolium salts (**III**) were likewise prepared (by N-methylation of imidazylates **II**) and tested. Subsequently, the corresponding trifluoroethyl sulfates (**IV**, Scheme 1b) were explored (from the preparative point of view, sulfates **IV** are known to be easily prepared from salts **III**, as previously reported for the synthesis of TFE-protected 6-sulfated carbohydrates).[8] The virtually unexplored photochemistry of these aryl sulfates was investigated and gave results radically different from those reported for sulfonates.[9]

RESULTS

The irradiation of aryl imidazylates **1a**−**d** and their corresponding imidazolium salts **9a**−**d** (Chart 1) was explored initially. In analogy with other aryl sulfonates,[7a,10] compounds

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Chart 1

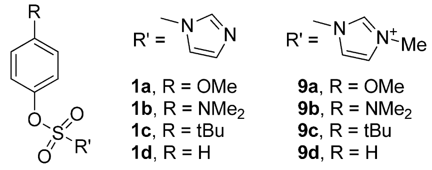
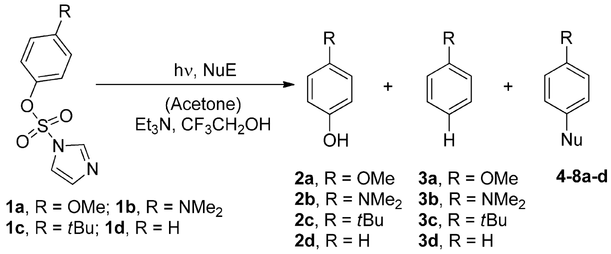


Table 1. Irradiation of Aryl Sulfonates **1a−d** in the Presence of π-Bond Nucleophiles[a]



nucleophile NuE	byproducts (%)[b]	ArNu (%)[c]
	1a, Φ_{-1} = 0.081[d]	
0.5 M ATMS	**2a** (8), **3a** (5)	**4a** (4)[b]
0.5 M 4-pentenoic acid	**3a** (18)	**5a** (17)
1 M benzene	**3a** (2)	**6a** (60)
1 M benzene[e]	**2a** (4)	**6a** (12)
1 M mesitylene		**7a** (60)
0.5 M 1-hexyne	**3a** (2)	**8a** (34)
	1b, Φ_{-1} = 0.54[d]	
0.5 M ATMS	**2b** (28)	**4b**
0.5 M 4-pentenoic acid	**2b** (15)	**5b**
1 M benzene	**2b** (18)	**6b**
1 M mesitylene	**2b** (35), **3b** (<1)	**7b** (19)
0.5 M 1-hexyne	**2b** (15), **3b** (<1)	**8b**
	1c, Φ_{-1} = 0.072[d]	
0.5 M ATMS	**2c** (19), **3c** (8)	**4c** (9)
0.5 M 4-pentenoic acid	**2c** (10)	**5c**
1 M benzene	**2c** (2), **3c** (2)	**6c** (39)
1 M mesitylene	**2c** (5)	**7c** (16)
0.5 M 1-hexyne	**2c** (6), **3c** (11)	**8c** (1)[b]
	1d, Φ_{-1} = 0.087[d]	
0.5 M ATMS	**2d** (55)	**4d** (7)[b]
0.5 M 4-pentenoic acid		**5d** (4)[b]
1 M benzene	**2d** (34)	**6d** (14)[b]
1 M mesitylene		**7d** (9)[b]

[a] Reaction conditions: A nitrogen-saturated solution of sulfonate **1a−d** (0.05 M), Et_3N (0.05 M), and the chosen nucleophile in TFE was irradiated at 310 nm; see Supporting Information. t_{irr} = 24 h (**1a**, **1c**, **1d**) or 4 h (**1b**). Acetone (10% v/v) was added in experiments with aryl sulfonates **1a**, **1c**, and **1d**. [b] Yields determined by gas chromatographic (GC) analysis. [c] Isolated yields. [d] Measured in TFE at 254 nm (**1a**, **1c**, **1d**, 0.015 M) or 310 nm (**1b**, 0.01 M). [e] Irradiation carried out in the absence of acetone.

1a−d absorbed in the UV region at a peak wavelength depending on the nature of the substituent (from 308 nm for **1b** to 255 nm for **1d**), with a low emission yield (Φ_F up to 0.02; see Table S1 in Supporting Information).

The photoreactivity of these substrates was investigated in 2,2,2-trifluoroethanol (TFE), in the presence of various π-bond nucleophiles: allyltrimethylsilane (ATMS), 4-pentenoic acid, benzene, mesitylene, and in selected cases 1-hexyne. A base (triethylamine, TEA) was added in order to buffer the acid released during the irradiation. Acetone (10% v/v) was used as a triplet sensitizer for compounds **1a**, **1c**, and **1d**, also compensating for the insufficient absorption at 310 nm. The disappearance quantum yield (Φ_{-1}) was 0.54 for **1b** and ca. 0.1 for the other aryl imidazylates (Table 1). Control experiments were conducted, demonstrating that **1a−d** were not consumed when tubes containing these solutions were covered with aluminum foil and placed in a multilamp apparatus for 24 h. The results obtained are gathered in Table 1.

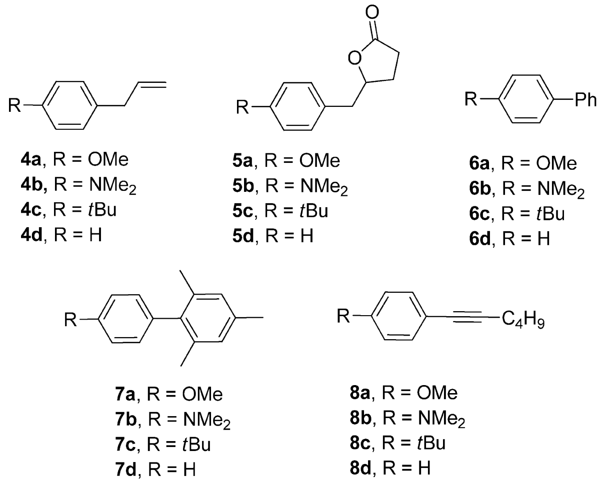
Photolysis of **1a** in TFE in the presence of a π-bond nucleophile yielded phenylated compounds ArNu in amounts that varied considerably with the nucleophile (Chart 2). The best yields were obtained in the reaction with aromatics to form biphenyls **6a** and **7a** (ca. 60% isolated yield). On the other hand, when **1a** is irradiated in the absence of acetone as sensitizer, a strong decrease in the yield of **6a** (down to 12% yield) was observed, along with the formation of some phenol **2a**. Irradiation of **1b**, however, gave no phenylated products other than **7b** (20% yield), producing instead only the deprotected aminophenol **2b** along with traces of *N*,*N*-dimethylaniline (**3b**). Analogous results were observed for sulfonates **1c** and **1d**, for which both the yield of arylated products **4−8c,d** and the resulting mass balance were unsatisfactory in most cases; the corresponding phenols **2** were the main, or exclusive, products observed. The data above suggest that the product distribution obtained from aryl imidazylates **1a−d** is determined by competition between ArO−S bond photohomolysis (which leads to phenol **2**) and Ar−OS bond heterolysis (which leads to reduced **3** and to trapping products **4−8**), with the former pathway largely preferred.

At this point we turned to salts **9a−d**, not previously investigated either in arylation reactions or in photochemistry. The photophysics of **9a−d** are similar to those of demethylated **1a−d** (Table S1, Supporting Information). Blank experiments carried out on **9a**, however, demonstrated that this compound was thermally unstable under the conditions used in Table 1, since it was converted to sulfate **10a** with a rate depending on the strength of the base used (Scheme 2).

As a matter of fact, in the presence of Cs_2CO_3 the conversion took place in a few minutes, whereas with TEA a complete conversion was achieved in 1 h. We then isolated **10a** from **9a** by treatment with basic 2,2,2-trifluoroethanol. The photophysics of **10a** were similar to those of **1a** or **9a** or other methoxyphenyl sulfonates,[7] whereas Φ_{-1} (**10a**) < Φ_{-1} (**1**) (in neat 2,2,2-trifluoroethanol, the measured Φ_{-1} for **10a** was ca. 0.03; Table 2). Irradiation of **10a** in TFE in the presence of π-bond nucleophiles led to the phenylated products **4−8a** in yields higher (up to >97%) than those observed from the irradiation of **1a**, and in some cases (see Table 2) a smaller amount of nucleophile maintained the same yield. We note that this is the first report of generation of a phenyl cation from an aryl sulfate. Compounds **9b−d** were likewise easily converted into sulfates **10b−d** in basic TFE, as demonstrated by gas chromatographic−mass spectrometric (GC-MS) analyses (see Supporting Information).

With these encouraging indications in hand, we decided to generate sulfates **10a−d** in situ by carrying out the arylation reactions on **9a−d** in basic (Cs_2CO_3) TFE solution (Table 3). Arylations of **9a** gave **4a−7a** in similar or slightly lower yields, compared to experiments starting with pure **10a**. Efficient arylation (in most cases in >70% yield) was likewise found for sulfates **10b,c** (except in synthesis of the allylated compounds **4c,d**), despite the non-negligible presence of byproducts **2b** and

Chart 2



Scheme 2

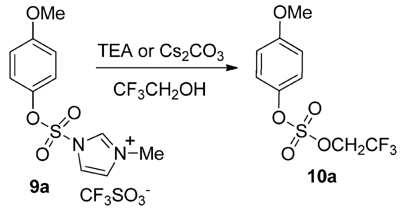
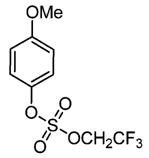


Table 2. Irradiation of 10a in the Presence of π-Bond Nucleophiles[a]

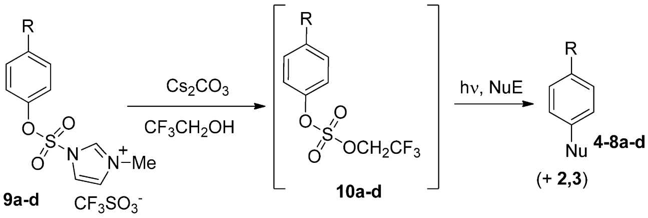
10, Φ_{-1}	Nucleophile (NuE), M	Byproducts (%)[b]	ArNu (%)[c]
	0.5 M ATMS	**2a**, 9 (10)[e]; **3a**, 4 (4)[e]	**4a**, 87 (86)[e]
	0.5 M 4-pentenoic acid	**2a**, -	**5a**, 58
	1 M Benzene	**3a**, 14	**6a**, 86
	1 M Mesitylene	**3a**, - (3)[f]	**7a**, >99 (97)[f]
10a, 0.027[d]	0.5 M 1-hexyne	**3a**, 11	**8a**, 86

[a]Reaction conditions: A nitrogen-saturated solution of **9a** (0.05 M), Cs_2CO_3 (0.05 M), acetone (10% v/v), and the chosen nucleophile in TFE was irradiated at 310 nm for 24 h. [b]Yields determined by GC analysis. [c]Isolated yields. [d]Measured at 254 nm (0.01 M **9a**). [e]0.25 M ATMS. [f]0.5 M mesitylene.

3b in the case of **10b**. Apparently, the presence of the sulfate leaving group allowed for formation of the phenyl cation. Indeed, a modest arylation was achieved even from sulfate **10d**, in which no electron-donating group is present.[11]

These findings suggested that imidazylates **1a–d** could likewise be used for in situ formation of sulfates **10a–d** by replacing TEA with cesium carbonate (Cs_2CO_3). In fact, compounds **1a–d** were slowly (in a few hours) converted (albeit in part) to sulfates **10a–d** in TFE in the presence of 0.05 M Cs_2CO_3 (higher amounts of base could be detrimental in this case), in competition with hydrolysis. We then repeated the same arylation reactions, starting from **10a–d** generated in situ directly from **1a–d**. The results, gathered in Table 4, show that in most cases the arylation yields were intermediate between those reported in Tables 1 and 3 but consistently lower than those obtained starting from **9a–d**. Finally, aryl imidazylate **1a** was found to release acid upon irradiation, thus behaving as a photoacid generator (see Supporting Information for details).

Table 3. Irradiation of in Situ Generated Aryl Sulfates 10a–d from Arylsulfonylimidazolium Triflates 9a–d in the Presence of π-Bond Nucleophiles[a]



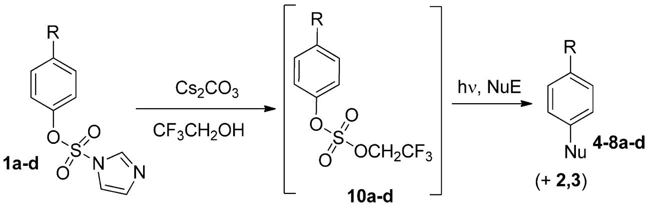
nucleophile, NuE	byproducts (%)[b]	ArNu (%)[c]
	9a → **10a**	
0.5 M ATMS	**2a** (8), **3a** (4)	**4a** (77)
0.5 M 4-pentenoic acid	**2a** (8)	**5a** (58)
1 M benzene	**2a**, **3a** (5)	**6a** (79)
1 M mesitylene	**3a** (0, 1[d])	**7a** (94, 77[d])
0.5 M 1-hexyne	**3a** (7.5, 5[e])	**8a** (63, 73[e])
	9b → **10b**	
0.5 M ATMS,	**2b** (11), **3b** (5)	**4b** (72)
0.5 M 4-pentenoic acid	**2b** (11), **3b** (1)	**5b** (79)
1 M benzene	**2b** (11), **3b** (10)	**6b** (78)
1 M mesitylene	**2b** (10), **3b** (4)	**7b** (70)
	9c → **10c**	
0.5 M ATMS	**2c** (13), **3c** (1)	**4c** (7)
0.5 M 4-pentenoic acid		**5c** (52)
1 M benzene	**3c** (5)	**6c** (68)
1 M mesitylene		**7c** (73, 55[d])
0.5 M 1-hexyne	**2c** (4), **3c** (4)	**8c** (30, 54[e])
	9d → **10d**	
0.5 M ATMS	**2d** (31)	**4d** (14)
0.5 M 4-pentenoic acid		**5d** (39)
1 M benzene	**2d** (15)	**6d** (57)
1 M mesitylene		**7d** (33)

[a]Reaction conditions: A nitrogen-saturated solution of **9a–d** (0.05 M), Cs_2CO_3 (0.05 M), and the chosen nucleophile in TFE was irradiated with 10 × 15 W Hg phosphor-coated lamps (λ_{em} = 310 nm, t_{irr} = 24 h for **9a**, **9c**, and **9d** and 4 h for **9b**). Acetone (10% v/v) was added in the experiments with **9a**, **9c**, and **9d**. [b]Yields determined by GC analysis. [c]Isolated yields. [d]0.5 M mesitylene. [e]1 M 1-hexyne.

■ DISCUSSION

As one might expect, changes in the side group affect the mode and rate of cleavage in the ground and excited states (Scheme 3). The behavior of imidazylates **1a–d** is similar to that reported for other alkyl aryl sulfonates, where two competing paths were observed upon irradiation.[7,9,10] In this case phenols **2** are observed as the main products resulting from direct homolysis[10] from the singlet states (^{1}**1a–d**) to give phenoxy radicals (**12a–d**, Scheme 3, path a). Heterolytic Ar–OS bond cleavage[11] (from triplets ^{3}**1a–d**) to afford triplet phenyl cations (^{3}**11$^+$a–d**, path b) is observed only as minor path since intersystem crossing (ISC, from singlets ^{1}**1a–d** to triplets ^{3}**1a–d**) is slower than the formation of **12a–d**. An exception, however, is the case of **1a**, where heterolysis competes to some extent and arylated compounds were formed in variable amounts (up to 17% yield for **4** and **5** and 60% yield for biphenyls **6** and **7**; Scheme 3 and Table 1). In the latter case, the low yield obtained when alkenes were used as nucleophiles

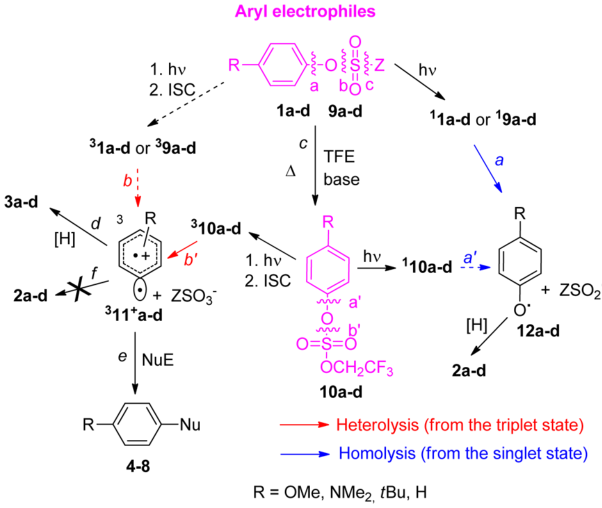
Table 4. Irradiation of in Situ Generated Aryl Sulfates 10a−d from Aryl Imidazylates 1a−d in the Presence of π-Bond Nucleophiles[a]



nucleophile NuE	byproducts (%)[b]	ArNu (%)[b]
	1a → **10a**	
0.5 M ATMS	**2a** (18), **3a** (5)	**4a** (42)
0.5 M 4-pentenoic acid	**3a** (30)	**5a** (16)
1 M benzene	**2a** (2)	**6a** (27)
1 M mesitylene		**7a** (55)
	1b → **10b**	
0.5 M ATMS	**2b** (58), **3b** (1)	**4b** (12)
0.5 M 4-pentenoic acid	**2b** (41)	**5b** (7)
1 M benzene	**2b** (46), **3b** (6)	**6b** (16)
1 M mesitylene	**2b** (42), **3b** (1)	**7b** (19)
	1c → **10c**	
0.5 M ATMS	**2c** (16), **3c** (4)	**4c** (27)
0.5 M 4-pentenoic acid	**2c** (8)	**5c** (7)
1 M benzene	**2c** (2), **3c** (10)	**6c** (33)
1 M mesitylene		**7c** (28)
0.5 M 1-hexyne	**2c** (6), **3c** (5)	**8c** (7)
	1d → **10d**	
0.5 M ATMS	**2d** (38)	**4d** (24)
0.5 M 4-pentenoic acid		**5d** (4)
1 M benzene	**2d** (17)	**6d** (5)
1 M mesitylene		**7d** (9)

[a]Reaction conditions: A nitrogen-saturated solution of **1a**−**d** (0.05 M), Cs_2CO_3 (0.05 M), and the chosen nucleophile in TFE was stirred for 1−2 h and then irradiated with 10 × 15 W Hg phosphor-coated lamps (λ_{em} = 310 nm; t_{irr} = 24 h for **1a**, **1c**, and **1d** and 4 h for **1b**). Acetone (10% v/v) was added in the experiments with **1a**, **1c**, and **1d**. [b]Yields determined by GC analysis.

Scheme 3. Efficient and Inefficient Pathways[a] **in Irradiation of Aryl Sulfonates 1a−d and 9a−d and Aryl Sulfates 10a−d**



[a]Efficient pathways are shown with solid arrows; inefficient ones are shown with dashed arrows.

could be explained by the competitive reaction of Me_2CO^{3*} with ATMS (or 4-pentenoic acid) as previously observed in the photochemistry of related aryl sulfonates[7] and caused by the inefficient energy transfer between Me_2CO^{3*} and the aromatic.

Methylation of the imidazole moiety to form imidazolium salts **9a**−**d** did not substantially modify the photoreactivity of the resulting aryl sulfonates, and homolysis (path a) remained the main pathway. The imidazylates (**1a**−**d**) and trifluoroethoxysulfates (**10a**−**d**) are thermally stable, whereas the imidazolium salts (**9a**−**d**) acted as sulfating agents for the in situ preparation of trifluoroethyl sulfates **10a**−**d** along path c. Gratifyingly, in contrast to the aryl imidazylates **1a**−**d** (**9a**−**d**), the photohomolysis of the ArO-S bond in **10a**−**d** played only a marginal role (path a′), whereas heterolytic cleavage of the Ar−OS bond took place efficiently (path b′) from the triplet excited state. The lack of homolysis in sulfates **10a**−**d** can be safely attributed to an efficient energy-transfer ISC from singlets ^{1}**10a**−**d** to triplets ^{3}**10a**−**d**[10,16] rather than to a different stability of the alkoxysulfonyl radical formed, since it has been previously reported to have similar structural characteristics and reactivity as the alkanesulfonyl radicals.[12]

The triplet phenyl cation intermediate generated underwent reduction to **3a**−**d** (path d), but in the presence of π-bond nucleophiles, trapping became the main (often exclusive) path and arylation occurred efficiently (path e, see Table 3). The formation of phenols **2** by reaction of adventitious water to ^{3}**11**$^+$**a**−**d** (path f) can be safely excluded, since solvolysis is typical of a singlet but not of a triplet phenyl cation as previously demonstrated.[7a] Sulfates **10** were likewise formed by the unprecedented transformation of aryl imidazylates **1** under basic conditions, although the lack of complete conversion lowered the arylation yields.

Activation of the Ar−OS bond in aryl sulfates has rarely been exploited in synthesis. To the best of our knowledge, only diaryl sulfates have been used as electrophiles in transition metal arylation procedures and only rarely: in the Kumada synthesis of biaryls via nickel-catalyzed coupling with Grignard reactants[13a] and in the direct C−H ortho arylation of heterobiaryls catalyzed by a Ru(II) carboxylate complex.[13b] The latter reactions, however, always required the use of transition metal catalysts and, in some cases, of aggressive nucleophiles.[13a] On the other hand, cleavage of the $ArOSO_2O$−R bond in alkyl aryl sulfates (e.g., R = Me)[14] is more common in aliphatic nucleophilic substitution reactions, though the related activation of the Ar−OSO_2OR bond has been not yet reported. The adoption of a metal-free approach in synthesis has gained increased attention in recent years and is hoped to overcome limitations, related to the synthesis and the use of not readily available and relatively expensive organometallic reactants, while avoiding the release of stoichiometric amounts of metal waste as byproducts.[15]

■ CONCLUSION

In the present paper, we report the discovery of a class of new photoactive substrates, 2,2,2-trifluoroethyl aryl sulfates **10**, capable of photogenerating aggressive phenyl cations that are smoothly trapped by a wide range of π-bond nucleophiles, including aromatics, alkynes, and alkenes, to afford valuable arylation products in a satisfying yield. Interestingly, the synthesis and isolation of sulfates **10** is not mandatory, since these electrophiles are quantitatively generated in situ from sulfonates **9** and (in part) from **1**. As a side issue, the photohomolysis of aryl imidazylates **1** could potentially be exploited for the photoinduced release of strong acid, as demonstrated during the photolysis of **1a** (see Supporting Information).

■ EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as distortionless enhancement by polarization transfer (DEPT)-135 experiments; chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes. Irradiations were performed in a multilamp reactor fitted with 10 15-W phosphor-coated lamps (emission maximum 310 nm). Quantum yields (Φ_{-1}) of compounds **1a**−**d** and **10a** have been measured on a 0.015 M (**1a**, **1c**, **1d**) or 0.01 M (**1b**, **10a**) solution in TFE (irradiation 1 × 15 W Hg lamp). Workup of the photolytes involved concentration in vacuo and chromatographic separation on silica gel. Solvents of HPLC purity were employed in the photochemical reactions. All the employed π bond nucleophiles [allyltrimethylsilane (ATMS), 4-pentenoic acid, 1-hexyne, benzene, and mesitylene] were commercially available and used as received.

Synthesis of Aryl Imidazolesulfonates 1a−d. Compounds **1a**−**d** were prepared from the corresponding phenols as previously reported.[5b] A 50 mL round-bottom flask was charged with the corresponding phenol **2a**−**d** (3.47 mmol), 1,1′-sulfonyldiimidazole[5b] (Im$_2$SO$_2$, 6.94 mmol), and cesium carbonate (Cs$_2$CO$_3$, 1.87 mmol) in tetrahydrofuran (THF, 10 mL). The reaction was stirred at room temperature for 16 h, and then the solvent was evaporated. Ethyl acetate (20 mL) was added to the resulting residue, and the obtained solution was cooled to 0 °C and treated with saturated aqueous NH$_4$Cl. The layers were separated and the aqueous layer was washed further with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with brine (10 mL) and water (10 mL) and dried over MgSO$_4$, and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography (eluant cyclohexane/ethyl acetate).

*4-Methoxyphenyl 1H-Imidazole-1-sulfonate (**1a**).* From 4-methoxyphenol (**2a**, 430 mg, 3.47 mmol), Im$_2$SO$_2$ (1.375 g, 6.94 mmol), and Cs$_2$CO$_3$ (0.565 g, 1.87 mmol) in THF (10 mL). Purification via column chromatography (eluant cyclohexane/ethyl acetate 9:1) afforded 775 mg of **1a** (viscous oil, 88% yield). Spectroscopic data for **1a** are in accordance with the literature.[5d] Anal. Calcd for C$_{10}$H$_{10}$N$_2$O$_4$S: C, 47.24; H, 3.96; N, 11.02. Found: C,47.2; H, 4.0; N, 11.0.

*4-(N,N-Dimethylamino)phenyl 1H-Imidazole-1-sulfonate (**1b**).* From 476 mg (3.47 mmol) of 4-(*N*,*N*-dimethylamino)phenol (**2b**),[16] 1.375 g (6.94 mmol) of Im$_2$SO$_2$, and 565 mg (1.87 mmol) of Cs$_2$CO$_3$ in THF (10 mL). Purification via column chromatography (eluant cyclohexane/ethyl acetate 9:1) afforded 650 mg of **1b** (colorless solid, mp = 62−64 °C, 70% yield). ^{1}H NMR (CD$_3$COCD$_3$, δ) 7.70 (s, 1H), 7.25−7.30 (s, 1H), 7.20 (s, 1H), 6.80−6.60 (4H, AA′BB′), 2.95 (s, 6H). ^{13}C NMR (CD$_3$COCD$_3$, δ) 149.5, 139.8, 137.5 (CH), 131.0 (CH), 121.7 (CH), 118.2 (CH), 112.9 (CH), 40.7 (CH$_3$). IR (neat, ν/cm^{-1}) 3320, 2924, 1416, 1048, 947. Anal. Calcd for C$_{11}$H$_{13}$N$_3$O$_3$S: C, 49.43; H, 4.90; N, 15.72. Found: C, 49.5; H, 4.8; N, 15.7.

*4-tert-Butylphenyl 1H-Imidazole-1-sulfonate (**1c**).* From 4-*tert*-butylphenol (**2c**, 521 mg, 3.47 mmol), Im$_2$SO$_2$ (1.375 g, 6.94 mmol), and Cs$_2$CO$_3$ (565 mg, 1.87 mmol) in THF (10 mL). Purification by column chromatography (eluant cyclohexane/ethyl acetate 9:1) afforded 700 mg of **1c** (colorless solid, mp = 45−47 °C, 72% yield). ^{1}H NMR (CD$_3$COCD$_3$, δ) 7.90 (s, 1H), 7.40−7.35 (2H, part of the AA′BB′ system), 7.35−7.30 (s, 1H), 7.20 (s, 1H), 7.09−6.95 (2H, part of the AA′BB′ system), 1.30 (s, 9H). ^{13}C NMR (CD$_3$COCD$_3$, δ) 153.1, 148.3, 137.5 (CH), 131.2 (CH), 127.1 (CH), 120.5 (CH), 118.2 (CH), 34.6, 31.1 (CH$_3$). IR (neat, ν/cm^{-1}) 3131, 2966, 1504, 1428, 886. Anal. Calcd for C$_{13}$H$_{16}$N$_2$O$_3$S: C, 55.70; H, 5.75; N, 9.99. Found: C, 55.6; H, 5.8; N, 9.9.

*Phenyl 1H-Imidazole-1-sulfonate (**1d**).* From phenol (**2d**, 327 mg, 3.47 mmol), Im$_2$SO$_2$ (1.375 g, 6.94 mmol), and Cs$_2$CO$_3$, (565 mg, 1.87 mmol) in THF (10 mL). Purification by column chromatography (eluant cyclohexane/ethyl acetate 85:15) afforded 557 mg of **1d** (colorless solid, mp = 36−38 °C, lit.[17] mp 32−33 °C, 72% yield). Spectroscopic data for **1d** are in accordance with the literature.[5d] Anal. Calcd for C$_9$H$_8$N$_2$O$_3$S: C, 48.21; H, 3.60; N, 12.49. Found: C, 48.1; H, 3.6; N, 12.5.

Synthesis of 1-Aryloxysulfonyl-3-Methyl-1*H*-imidazol-3-ium Trifluoromethanesulfonates 9a−d and Sulfate 10a. Compounds **9a**−**d** were synthesized from the corresponding aryl 1*H*-imidazolesulfonates **1a**−**d** by adapting a known procedure.[17] A solution of the chosen imidazylate **1a**−**d** (2 mmol) in dry diethyl ether (8 mL) was cooled to 0 °C, and then methyl trifluoromethanesulfonate (MeOTf, 2 mmol) was added dropwise. The resulting solution was stirred for 2 h, and the obtained precipitate was isolated by filtration and washed repeatedly with cold ether.

*1-[(4-Methoxyphenoxy)sulfonyl]-3-methyl-1H-imidazol-3-ium Trifluoromethanesulfonate (**9a**).* From **1a** (508 mg, 2 mmol) and 0.21 mL (2 mmol) of MeOTf in dry ether (8 mL). The obtained precipitate was filtered and washed with dry cold ether, affording 678 mg of **9a** (colorless solid, mp =70−72 °C, 81% yield). Spectroscopic data for **9a** are in accordance with the literature.[17] IR (neat, ν/cm^{-1}) 3143, 1594, 1502, 1453, 1258, 1031, 896, 640. Anal. Calcd for C$_{12}$H$_{13}$F$_3$N$_2$O$_7$S$_2$: C, 34.45; H, 3.13; N, 6.70. Found: C, 34.4; H, 3.1; N, 6.6.

*1-{[4-(N,N-Dimethylamino)phenoxy]sulfonyl}-3-methyl-1H-imidazol-3-ium Trifluoromethanesulfonate (**9b**).* From **1b** (535 mg, 2 mmol) and 0.21 mL (2 mmol) of MeOTf in dry ether (8 mL), to afford 768 mg of **9b** (colorless solid, decomposes above 85 °C, 89% yield). ^{1}H NMR (CD$_3$OD, δ) 9.75 (br s, 1H), 8.15 (br s, 1H), 7.85 (br s, 1H), 7.15−6.75 (AA′BB′, 4H), 4.0 (s, 3H), 3.0 (s, 6H). ^{13}C NMR (CD$_3$OD, δ) 152.5, 141.9, 141.5 (CH), 127.7 (CH), 125.4 (CH), 123.2 (CH), 114.9 (CH), 41.3 (CH$_3$), 38.2 (CH$_3$). IR (neat, ν/cm^{-1}) 2924, 1596, 1446, 1269, 1160, 1031, 814. Anal. Calcd for C$_{13}$H$_{16}$F$_3$N$_3$O$_6$S$_2$: C, 36.19; H, 3.74; N, 9.74. Found: C, 36.2; H, 3.7; N, 9.7.

*1-[(4-tert-Butylphenoxy)sulfonyl]-3-methyl-1H-imidazol-3-ium Trifluoromethanesulfonate (**9c**).* From **1c** (561 mg, 2 mmol) and 0.21 mL (2 mmol) of MeOTf in dry ether (8 mL). The obtained precipitate was filtered and washed with dry cold ether to give 818 mg of **9c** (colorless solid, mp =149−151 °C, 90% yield). ^{1}H NMR (CD$_3$OD, δ) 9.80 (s, 1H), 8.10 (s, 1H), 7.90 (s, 1H), 7.60−7.15 (AA′BB′, 4H), 4.00 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (CD$_3$OD, δ) 154.6, 148.9, 141.3 (CH), 129.4 (CH), 127.7 (CH), 122.9 (CH), 122.0 (CH), 38.1 (CH$_3$), 36.0, 31.8 (CH$_3$). IR (neat, ν/cm^{-1}) 3180, 2923, 1448, 1262, 837. Anal. Calcd for C$_{15}$H$_{19}$F$_3$N$_2$O$_6$S$_2$: C, 40.54; H, 4.31; N, 6.30. Found: C, 40.5; H, 4.3; N, 6.3.

*3-Methyl-1-(Phenoxysulfonyl)-1H-imidazol-3-ium Trifluoromethanesulfonate (**9d**).* From **1d** (449 mg, 2 mmol) and MeOTf (0.21 mL, 2 mmol) in dry ether (8 mL). The obtained precipitate was filtered and washed with dry cold ether to afford 583 mg of **9d** (colorless solid, mp = 80−82 °C, lit.[17] mp 79−80 °C, 86% yield. Spectroscopic data for **9d** are in accordance with the literature.[17] IR (neat, ν/cm^{-1}) 2924, 1654, 1269, 1161, 1032, 874, 692. Anal. Calcd for C$_{11}$H$_{11}$F$_3$N$_2$O$_6$S$_2$: C, 34.02; H, 2.86; N, 7.21. Found: C, 33.9; H, 2.9; N, 7.2.

*4-Methoxyphenyl 2,2,2-Trifluoroethyl Sulfate (**10a**).* Compound **9a** (510 mg, 1.22 mmol) was treated with 467 mg (1.22 mmol) of Cs$_2$CO$_3$ in TFE (24.5 mL). The resulting solution was stirred for 1 h, and then the solvent was evaporated. Purification of the residue by column chromatography (eluant neat hexane) afforded 316 mg of **10a** (90% yield, colorless oil). ^{1}H NMR (CD$_3$COCD$_3$) δ 7.35−6.90 (AA′BB′, 4H), 4.75−4.65 (q, 2H, J = 8 Hz), 3.80 (s, 3H). ^{13}C NMR (CD$_3$COCD$_3$) δ 158.7, 143.3, 122.0 (CH), 114.9 (CH), 67.7 (CH$_2$), 55.6 (CH3). IR (neat, ν/cm^{-1}) 2954, 1504, 1417, 1170, 892, 838. GC-MS (m/z) 286 (15), 123 (100), 95 (20), 83 (5). Anal. Calcd for C$_9$H$_9$F$_3$O$_5$S: C, 37.77; H, 3.17. Found: C, 37.8; H, 3.2. Quantitative formation of sulfates **10b**−**d** from **9b**−**d** in TFE in the presence of Cs$_2$CO$_3$ has been confirmed by GC-MS analyses of the resulting solutions. **10b**: GC-MS (m/z) 299 (18), 136 (100), 108 (10), 65 (5). **10c**: GC-MS (m/z) 312 (10), 297 (100), 267 (10), 91 (5). **10d**: GC-MS (m/z) 256 (50), 93 (100), 77 (10), 65 (90).

Preparative Irradiations. *Irradiation of Aryl Imidazylates* ***1a–d***. A 0.05 M solution of sulfonates **1a–d**, the chosen π-bond nucleophile (0.5–1.0 M), 0.05 M Et$_3$N, and, when required, acetone (10% v/v) in TFE was nitrogen-purged in a quartz tube and then irradiated at 310 nm. The reaction course was followed by means of GC and HPLC analyses. GC yields of compounds **2a–d**, **3a–d**, **5d**, and **7d** were determined by comparison with either commercial standards or synthesized compounds.

Irradiation of Sulfonates ***9a–d***. A 0.05 M solution of sulfonate **9a–d**, the chosen π-bond nucleophile (0.5–1.0 M), 0.03 M Cs$_2$CO$_3$, and, when required, acetone (10% v/v) in TFE was nitrogen-purged in a quartz tube and then irradiated at 310 nm. The reaction course was followed by means of GC and HPLC analyses. GC yields of compounds **2a–d**, **3a–d**, **5d**, and **7d** were determined by comparison with either commercial standards or synthesized compounds.

Synthesis of 4-Methoxy Compounds 4a–8a. *1-(2-Propenyl)-4-methoxybenzene (**4a**).* From 628 mg of **9a** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 2.4 mL of ATMS (15 mmol, 0.5 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (neat cyclohexane) afforded 171 mg of **4a** (oil, 77% yield). Spectroscopic data for **4a** are in accordance with the literature.[18] Anal. Calcd for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16. Found: C, 81.0; H, 8.2.

*5-(4-Methoxybenzyl)dihydrofuran-2(3H)-one (**5a**).* From 628 mg of **9a** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (0.05 M, 1.5 mmol), 3 mL of acetone (10% v/v), and 1.3 mL of 4-pentenoic acid (15 mmol, 0.5 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 8:2) afforded 180 mg of **5a** (oil, 58% yield). Spectroscopic data for **5a** are in accordance with the literature.[19] Anal. Calcd for C$_{12}$H$_{14}$O$_3$: C, 69.88; H, 6.84. Found: C, 69.9; H, 6.9.

*4-Methoxybiphenyl (**6a**).* From 628 mg of **9a** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 2.67 mL of benzene (30 mmol, 1 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 97:3) afforded 219 mg of **6a** (colorless solid, mp = 87–89 °C, lit.[20] mp 86–88 °C, 79% yield). Spectroscopic data for **6a** are in accordance with the literature.[21] Anal. Calcd for C$_{13}$H$_{12}$O: C, 84.75; H, 6.57. Found: C, 84.7; H, 6.6.

*4′-Methoxy-2,4,6-trimethyl-1,1′-biphenyl (**7a**).* From 628 mg of **9a** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 4.17 mL of mesitylene (30 mmol, 1.0 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 97:3) afforded 318 mg of **7a** (colorless solid, mp = 68–70 °C, lit.[22] mp 69–71 °C, 94% yield). Spectroscopic data for **7a** are in accordance with the literature.[22] Anal. Calcd for C$_{16}$H$_{18}$O: C, 84.91; H, 8.02. Found: C, 84.9; H, 8.0. Compound **7a** was obtained in 77% yield when 0.5 M mesitylene was used.

*1-(Hex-1-ynyl)-4-methoxybenzene (**8a**).* From 628 mg of **9a** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 1.7 mL of 1-hexyne (15 mmol, 0.5 M) in TFE (30 mL). The solution was nitrogen-purged in quartz tubes and then irradiated for 24 h. Purification by column chromatography (eluant neat hexane) afforded 178 mg of **8a** (oil, 63% yield). Spectroscopic data for **8a** are in accordance with the literature.[23] Anal. Calcd for C$_{13}$H$_{16}$O: C, 82.94; H, 8.57. Found: C, 83.0; H, 8.6. Compound **8a** was obtained in 73% yield when 1 M 1-hexyne was used.

Synthesis of 4-(*N*,*N*-Dimethylamino) Compounds 4b–7b. *4-(Propen-2-yl)-N,N-dimethylanisole (**4b**).* From 647 mg (1.5 mmol, 0.05 M) of **9b**, 488 mg (1.5 mmol, 0.05 M) of Cs$_2$CO$_3$, and 2.4 mL (15 mmol, 0.5 M) of ATMS in TFE (30 mL), irradiated for 4 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 98:2) afforded 174 mg of **4b** (oil, 72% yield). Spectroscopic data for **4b** are in accordance with the literature.[24a] Anal. Calcd for C$_{11}$H$_{15}$N: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.9; H, 9.5; N, 8.7.

*5-(N,N-Dimethyl-4-aminobenzyl)dihydrofuran-2-one (**5b**).* From 488 mg of **9b**, (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), and 1.3 mL of 4-pentenoic acid (15 mmol, 0.5 M) in TFE (30 mL), irradiated for 4 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 95:5) afforded 260 mg of **5b** (colorless solid, mp = 51–53 °C, lit.[24b] mp 54–57 °C, 79% yield). Spectroscopic data for **5b** are in accordance with the literature.[19] Anal. Calcd for C$_{13}$H$_{17}$NO$_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.3; H, 7.8; N, 6.4.

*4-(N,N-Dimethylamino)biphenyl (**6b**).* From 647 mg (1.5 mmol, 0.05 M) of **9b**, 488 mg (1.5 mmol, 0.05 M) of Cs$_2$CO$_3$, and 2.67 mL (30 mmol, 1.0 M) of benzene in TFE (30 mL), irradiated for 4 h. Purification by column chromatography (eluant neat cyclohexane) afforded 231 mg of **6b** (colorless solid, mp = 119–121 °C, lit.[25] mp 120–123 °C, 78% yield). Spectroscopic data for **6b** are in accordance with the literature.[25] Anal. Calcd for C$_{14}$H$_{15}$N: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.3; H, 7.6; N, 7.1.

*4-(N,N-Dimethylamino)-2′,4′,6′-trimethylbiphenyl (**7b**).* From 647 mg (1.5 mmol, 0.05 M) of **9b**, 488 mg (1.5 mmol, 0.05 M) of Cs$_2$CO$_3$, and 4.17 mL (30 mmol, 1.0 M) of mesitylene in TFE (30 mL), irradiated for 4 h. Purification by column chromatography (eluant neat cyclohexane) afforded 252 mg of **7b** (colorless solid, mp = 103–106 °C, lit.[24] mp 105–108 °C, 70% yield). Spectroscopic data for **7b** are in accordance with the literature.[24] ^{13}C NMR (CDCl$_3$, δ) 136.6, 136, 130 (CH), 127.9 (CH), 112.5 (CH), 40.8 (CH$_3$), 20.9 (CH$_3$), 20.8 (CH$_3$). Anal. Calcd for C$_{17}$H$_{21}$N: C, 85.30; H, 8.84; N, 5.85. Found: C, 85.3; H, 8.8; N, 5.9.

Synthesis of 4-*tert*-Butyl Compounds 4c–8c. *1-tert-Butyl-4-allylbenzene (**4c**).* From 667 mg of **9c** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol 0.05 M), 3 mL of acetone (10% v/v), and 2.4 mL of ATMS (15 mmol, 0.5 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant neat hexane) afforded 18 mg of **4c** (oil, 7% yield). Spectroscopic data for **4c** are in accordance with the literature.[26] Anal. Calcd for C$_{13}$H$_{18}$: C, 89.59; H, 10.41. Found: C, 89.5; H, 10.4.

*5-(4-tert-Butylbenzyl)dihydrofuran-2(3H)-one (**5c**).* From 667 mg of **9c** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 1.3 mL of 4-pentenoic acid (15 mmol, 0.5M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 8:2) afforded 181 mg of **5c** (oil, 52% yield). Spectroscopic data for **5c** are in accordance with the literature.[26] Anal. Calcd for C$_{15}$H$_{20}$O$_2$: C, 77.55; H, 8.68. Found: C, 77.5; H, 8.7.

*4-tert-Butylbiphenyl (**6c**).* From 667 mg of **9c** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 2.67 mL of benzene (30 mmol, 1 M) in TFE (30 mL). The solution was nitrogen-purged in quartz tubes and then irradiated for 24 h. Purification by column chromatography (eluant neat hexane) afforded 216 mg of **6c** (colorless solid, mp = 45–47 °C, lit.[26] mp 49–51 °C, 68% yield). Spectroscopic data for **6c** are in accordance with the literature.[26] Anal. Calcd for C$_{16}$H$_{18}$: C, 91.37; H, 8.63. Found: C, 91.4; H, 8.6.

*4′-tert-Butyl-2,4,6-trimethylbiphenyl (**7c**).* From 667 mg of **9c** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 4.17 mL of mesitylene (30 mmol, 1 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant neat hexane) afforded 276 mg of **7c** (colorless solid, mp = 108–110 °C, lit.[26] mp 108–110 °C, 73% yield). Spectroscopic data for **7c** are in accordance with the literature.[21] Anal. Calcd for C$_{19}$H$_{24}$: C, 90.42; H, 9.58. Found: C, 90.4; H, 9.7.

*1-tert-Butyl-4-(hex-1-ynyl)benzene (**8c**).* From 667 mg of **9c** (1.5 mmol, 0.05 M), 488 mg of Cs$_2$CO$_3$ (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 1.7 mL of 1-hexyne (15 mmol, 0.5 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant neat hexane) afforded 96 mg of **8c** (colorless oil, 30% yield). ^{1}H NMR (CDCl$_3$, δ) 7.45–7.25 (AA′BB′, 4H), 2.45–235 (t, 2H, J = 7 Hz), 1.7–1.5 (m, 4H), 1.35 (s, 9H), 1.0–0.9 (t, 3H, J = 7 Hz); 13C NMR (CDCl$_3$, δ) 150.5, 131.1 (CH), 125.0 (CH), 121.0, 89.5, 80.4, 34.5, 31.1 (CH$_3$), 30.8 (CH$_2$), 21.9 (CH$_2$), 19.0 (CH$_2$), 13.5 (CH$_3$). IR (neat, ν/cm^{-1}) 2961, 2250, 1466, 1364, 1269, 834. Anal. Calcd for

$C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.7; H, 10.4. Compound **8c** was obtained in 54% yield when 1 M 1-hexyne was used.

Synthesis of 4-Unsubstituted Compounds 5d and 7d. *5-Benzyldihydrofuran-2(3H)-one (**5d**).* From 582 mg of **9d** (1.5 mmol, 0.05 M), 488 mg of Cs_2CO_3 (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 1.3 mL of 4-pentenoic acid (15 mmol, 0.5 M, 15 mmol) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant cyclohexane/ethyl acetate 8:2) afforded 104 mg of **5d** (oil, 39% yield). Spectroscopic data for **5d** are in accordance with the literature.[27] Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.0; H, 6.9.

*2,4,6-Trimethylbiphenyl (**7d**).* From 582 mg of **9d** (1.5 mmol, 0.05 M), 488 mg of Cs_2CO_3 (1.5 mmol, 0.05 M), 3 mL of acetone (10% v/v), and 4.17 mL of mesitylene (30 mmol, 1 M) in TFE (30 mL), irradiated for 24 h. Purification by column chromatography (eluant neat cyclohexane) afforded 97 mg of **7d** (oil, 33% yield). Spectroscopic data for **7d** are in accordance with the literature.[28] Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found C, 91.8; H, 8.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

One table listing photophysical properties of **1a−d**, **9a−d**, and **10a**; additional text and one figure showing efficiency of acid photorelease from **1a**; ^1H and ^{13}C NMR spectra of **1a−d**, **5d**, **7d**, **8c**, **9a−d**, and **10a**. 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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