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# Visible Light Promoted Metal- and Photocatalyst-Free Synthesis of Allylarenes

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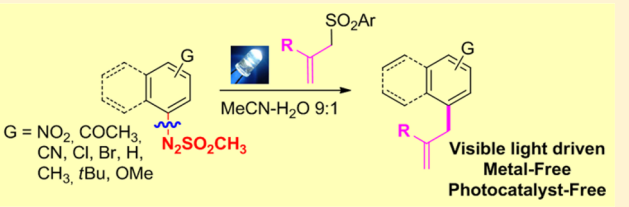
Supporting Information

**ABSTRACT:** The metal- and photocatalyst-free synthesis of substituted allylarenes has been carried out under visible light driven conditions. The process was based on the photogeneration of aryl radicals from arylazo sulfones and their ensuing reaction with allyl sulfones. The developed procedure was very efficient when using substrates bearing electron-withdrawing groups, and allowed for the preparation of $\alpha$-benzyl styrenes and 2-benzyl acrylates in good yields.




Besides the extensive presence of the allylarene motif in biologically active compounds,[1] interest for these molecules arises from its rich chemistry that allows for their chemical conversion to a wide range of functional groups including cinnamaldehydes,[2] cinnamates,[3] alkenyl nitriles,[4] and *N*-allylamides[5] as well as the allyl C($sp^3$)−H site functionalization.[6] For this aim, the development of efficient allylations of arenes is a goal in organic synthesis. Apart from the Lewis acid promoted Friedel−Crafts allylation, which is however affected by a limited substrate scope and selectivity,[7] most of the synthetic protocols described rely on transition metal cross-coupling reactions between aromatic organometallic reagents,[8] aryl boronic acids,[9] and unfunctionalized aromatics[10] with allylic electrophiles (e.g., allyl halides, carboxylates, and carbonates).

In recent decades, however, the demand for synthetic strategies that proceed under mild and environmental benign conditions has become more pressing.[11] In fact, the risk of contamination of the end products by heavy metals (even in trace) is a serious drawback for pharmaceutical and cosmetic applications.[12] Quite surprisingly, allylations represent only a minor part[13] of the large number of metal-free arylation processes developed.[14] Indeed, only a few examples have been reported in the literature making use of rather high temperatures[15] as well as of strong bases.[16]

Photochemistry is a potential sustainable approach that allows for the use of unactivated, thermally stable substrates which are promoted to their excited states by the exclusive intervention of a photon and subsequently converted to high energy intermediates. In this way, the use of aggressive and yet noxious organometallic species, transition metal based catalysts, and harsh conditions may thus be avoided.[17]

Allylarenes can be indeed obtained via photogeneration of a triplet phenyl cation (in turn obtained from aryl chlorides,[18] sulfonates,[19] phosphates,[19] and arenediazonium salts[20]) in the presence of nucleophilic allyltrimethylsilane as the allylating agent (Scheme 1, path a), but when chlorides and esters were used the process was mainly limited to electron-rich substrates.[18,19] On the other hand, in the case of diazonium salts a photosensitizer (e.g., benzophenone) was required in most cases,[20] thus limiting the scope of the process.[21] Furthermore, apart from a few examples,[18c] the use of an artificial, energy demanding UV-light source was mandatory.

Photoredox catalysis has emerged in recent decades as an appealing approach for the synthesis of valuable compounds.[22] In this case, the photoexcited catalyst (typically an organic dye or a transition metal complex) is responsible for the generation of the reactive intermediate (a radical ion or a radical) via monoelectronic reduction/oxidation of the starting substrate. This approach has been exploited by Fensterbank and co-workers for the synthesis of allylarenes from diaryliodonium (Scheme 1, path b)[23] and triarylsulfonium salts.[24] The process was based on the single electron transfer between the -onium salt and the photoreduced catalyst, followed by trapping of the generated aryl radical by an allyl sulfone.

However, a rather expensive transition metal based photocatalyst was used, along with a large amount (2−5 equiv) of tertiary amine as the sacrificial electron donor.[23−26] For this aim, the interest for visible light promoted reactions under photocatalyst-free conditions is currently increasing.[27] We recently reported that arylazo sulfones acted as photochemical precursors of high energy intermediates including radicals.[28] Indeed such compounds that have been prepared from the corresponding anilines bear a colored, thermally stable but photolabile moiety ($-N_2SO_2CH_3$) which undergoes, upon visible light exposition, homolytic cleavage of the N−S bond, affording, after $N_2$ loss, the

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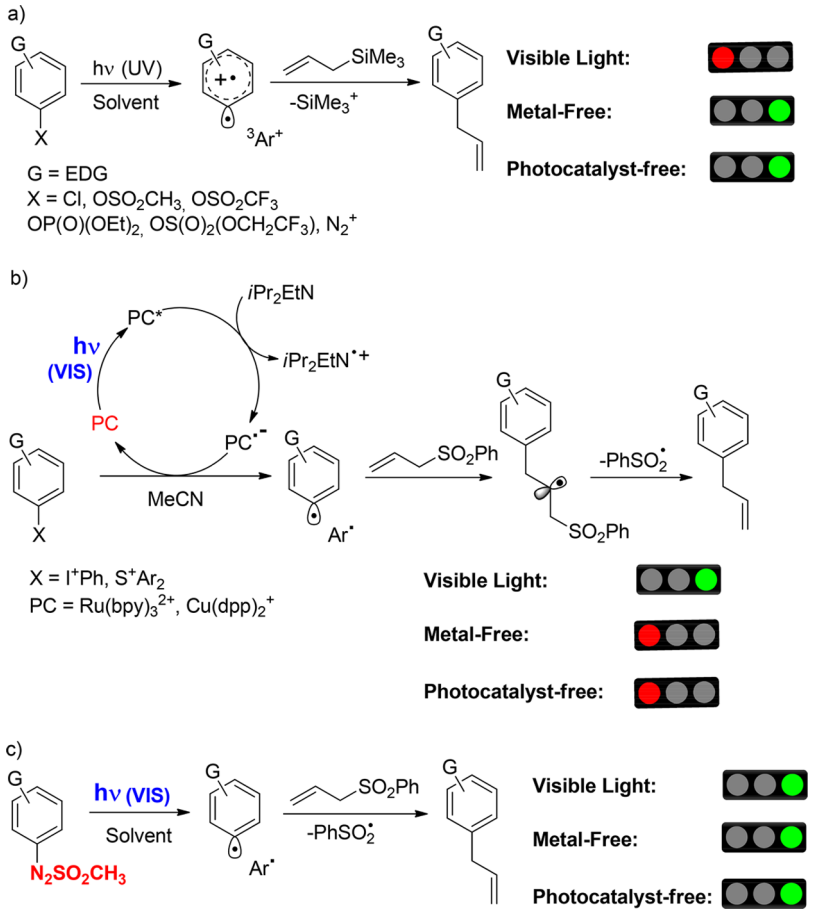
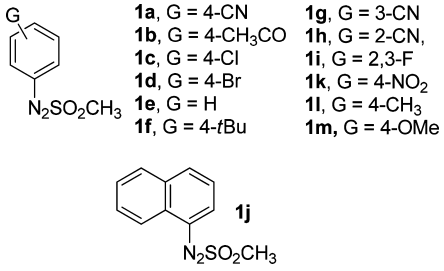
**Scheme 1. Photochemical/Photocatalyzed Synthesis of Allylarenes**




corresponding aryl radicals. We thus reasoned that such compounds can be exploited in the visible light promoted, metal-, photocatalyst-, and additive-free synthesis of allylarenes via aryl radicals (Scheme 1, path c).

We initially synthesized a set of substituted arylazo sulfones (compounds **1a**–**m**, see Chart 1), and we investigated the photoreactivity of a model compound (1-(methylsulfonyl)-2-(4-cyanophenyl)diazene, **1a**) in the presence of allyl phenyl sulfone **2** as a model reaction. The obtained results are depicted in Table 1.

**Chart 1. Arylazo Sulfones Used in the Present Study**




Preliminary experiments have been performed by means of a solar simulator equipped with a 1500 W xenon lamp. Irradiation of **1a** (0.05 M) in dichloromethane in the presence of an excess of **2** (4 equiv, 0.2 M) led to the formation of benzonitrile **1aH** along with only a minor amount of 4-allylbenzonitrile (**5a**, 6% yield, entry 1). However, when raising the concentration of **2** (up to 0.5 M, entry 2), the desired **5a** was obtained in 32% yield, though **1aH** remained predominant. The use of esters viz. ethyl acetate and diethyl carbonate (entries 3, 4) as the media led to the obtainment of a comparable amount of **1aH** and **5a**, whereas in DMSO photoreduction was preferred (entry 5). Notably, when acetone and acetonitrile were used as the solvent, arylation became the main path (entries 6, 7), and **5a** was formed in 24% and 26% yield, respectively. The efficiency of the process further increased by replacing part of the organic medium with water, with **5a** isolated in up to 38% yield (entries 8, 9). We finally investigated the role of the light source. The sun emission spectrum includes both UV and visible light, but the former is not suitable for the generation of aryl radicals from arylazo sulfones as it was previously demonstrated.[28] In contrast, a visible light source (a 1 W LED, $\lambda_{em}$ = 410 nm) led to a significant increase of the arylation efficiency, and **5a** was isolated in 70% yield, along with a significant amount (19%) of benzonitrile **1aH** (entry 10). On the other hand, no consumption of **1a** was detected in the absence of irradiation (entry 11). The protocol described in entry 10 was thus adopted to investigate the synthetic scope of the reaction. Unfortunately, when moving to substrates bearing electron-donating groups, such as 1-(methylsulfonyl)-2-(4-methoxyphenyl)diazene (**1m**), estragole **5m** was obtained only in modest yields (along with a significant amount of anisole **1mH**), even under the optimal reaction conditions (entry 12). However, due to the scarce reactivity of allyl phenyl solfone **2** in free radical processes,[24] we focused on substituted allyl sulfones **3**, **4** (Tables 2, 3).



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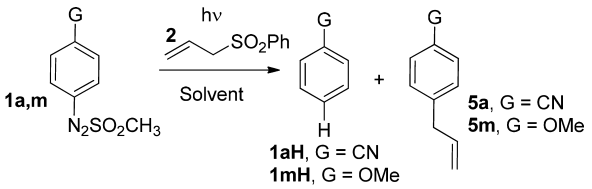
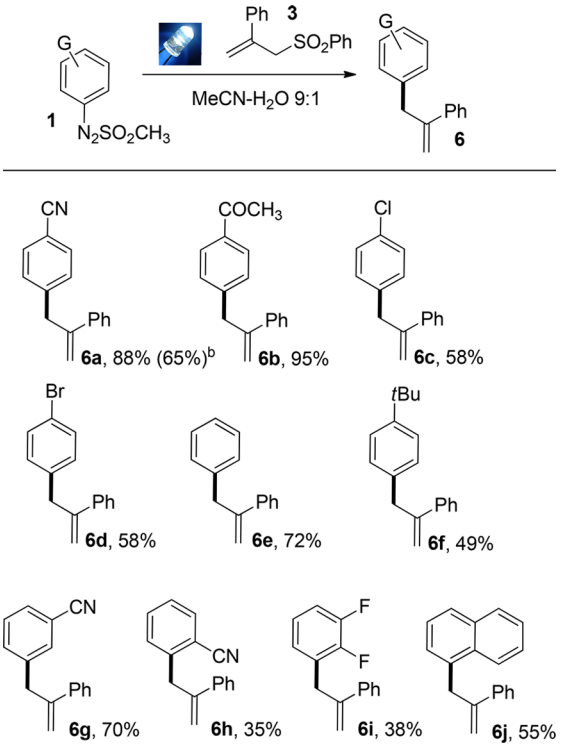
**Table 1. Optimization of the Reaction Conditions**




| entry | solvent | conditions | light source | products (% yield) |
|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | **1a** (0.05 M), **2** (0.2 M) | SolarBox[a] | **1aH**, 31; **5a**, 6 |
| 2 | $CH_2Cl_2$ | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 44; **5a**, 32 |
| 3 | $(EtO)_2CO$ | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 17; **5a**, 16 |
| 4 | Ethyl acetate | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 15; **5a**, 27 |
| 5 | DMSO | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 16; **5a**, 8 |
| 6 | Acetone | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 18; **5a**, 24 |
| 7 | $CH_3CN$ | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 10; **5a**, 26 |
| 8 | Acetone/$H_2O$ 9:1 | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 5; **5a**, 32 |
| 9 | $CH_3CN/H_2O$ 9:1 | **1a** (0.05 M), **2** (0.5 M) | SolarBox[a] | **1aH**, 11; **5a**, 38 |
| 10 | $CH_3CN/H_2O$ 9:1 | **1a** (0.05 M), **2** (0.5 M) | 410 nm[b] | **1aH**, 19; **5a**, 70 |
| 11 | $CH_3CN/H_2O$ 9:1 | **1a** (0.05 M), **2** (0.5 M) | –[c] | – |
| 12 | $CH_3CN/H_2O$ 9:1 | **1m** (0.05 M), **2** (0.5 M) | 410 nm[b] | **1mH**, 16; **5m**, 36 |

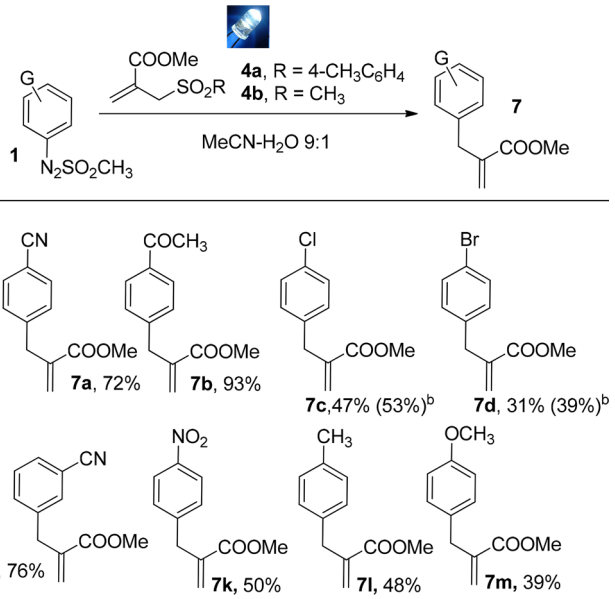
[a]Irradiation carried out in a SolarBox equipped with a Xe lamp, 500 $Wm^{-2}$, $t_{irr}$ = 16 h. [b]Irradiation carried out by means of a 1W LED, $t_{irr}$ = 24 h. [c]Blank experiment, no consumption of **1a** observed.

**Table 2. Visible Light Promoted Synthesis of α-Benzyl Styrenes 6[a]**




[a]A solution of **1a–j** (0.05 M) in acetonitrile/water 9/1 mixture in the presence of **3** (0.5 M) irradiated for 24 h (1 W LED, $\lambda_{em}$ = 410 nm). [b]Reaction carried out under exposition to natural sunlight, 24 h (3 days).

**Table 3. Visible Light Promoted Synthesis of 2-Benzyl Acrylates 7[a]**




[a]A solution of arylazosulfone **1** (0.05 M) in acetonitrile/water 9/1 mixture in the presence of **4a** (0.5 M) irradiated for 24 h (1 W LED, $\lambda_{em}$ = 410 nm). [b]Sulfone **4b** (0.5 M) adopted.

α-Benzyl styrenes **6a–j** were obtained in moderate to highly satisfactory yields, and the best results were obtained when using substrates bearing an electron-withdrawing substituent in both the para- (see for instance products **6a,b**) and meta-position (**6g**). In the case of **6a**, a 65% yield of the arylated product was isolated when carrying out the process under natural sunlight (3 days, 6 h exposition for day). Unsubstituted 2,3-diphenyl propylene **6e** was also isolated in 72% yield. In contrast, 4-*tert*-butyl substituted **1f**, as well as ortho substituted 2-cyanophenyl (**1h**) and 2,3-difluorophenyl (**1i**) derivatives, afforded the arylated products only in modest amounts (35–49%). It should be noted that the large excess of **3** employed could be partially recovered during the isolation step (74% of the unreacted material in the case of **6f**; see the Experimental Section). Finally, the 1-naphthylazo derivative (**6j**) was likewise obtained in 55% yield.

We then moved to allyl sulfone **4a**, and again, good yields of the corresponding 2-benzyl acrylates **7** were generally obtained



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with electron-poor **1a,b** and **1g,k**, and the reaction with halogenated **1c,d** occurred with a lower efficiency. Finally, under the same reaction conditions, 4-methyl and 4-methoxyderivative **7l,m** were obtained in moderate amounts (48% and 39% yield, respectively). As in the case of **3**, the excess of **4a** employed was efficiently recovered during the isolation step of **7b** (73% of the unreacted material). In the case of halogenated derivatives **1c,d**, we also investigated the chance to replace tosyl derivative **4a** with allyl methyl sulfone **4b** as the radical trap, in order to increase the atom economy of the process. Interestingly, acrylates **7c,d** were obtained with yields (53% and 39%, respectively) comparable to those observed for **4a**.

The procedure described herein is, to the best of our knowledge, the first example of the synthesis of allylarenes under both metal- and photocatalyst-free conditions enabled by visible light. The process took place in reasonable irradiation times (24 h), by means of low energy demanding LEDs, and the arylated products were obtained in discrete to highly satisfactory yields. The conditions we adopted are comparable to those described in literature for other aryl radical based allylation processes, where an excess of allyl phenyl sulfone (up to 10 equiv) was required.[23−25] However, purification by column chromatography allowed for the recovery of more than the 70% of the unreacted allylating agent, thus lowering the amount of waste produced and, as a consequence, the environmental and economical impact of the process.

## EXPERIMENTAL SECTION

**General.** $^1$H and $^{13}$C NMR spectra were recorded on a 300 MHz spectrometer, chemical shifts were reported in ppm downfield from TMS, and the attributions were made on the basis of $^1$H and $^{13}$C signals, as well as DEPT-135 experiments. The reaction course was followed by means of TLC, GC, and HPLC analyses (C-18 column; eluant: MeOH/water mixture). GC-MS analyses were carried out using a Thermo Scientific DSQII single quadrupole GC/MS system. A Restek Rtx-5MS (30 m × 0.25 mm × 0.25 $\mu$m) capillary column was used for analytes separation with helium as the carrier gas at 1 mL min$^{-1}$. The injection in the GC system was performed in split mode, and the injector temperature was 250 °C. The GC oven temperature was held at 60 °C for 5 min, increased to 250 °C by a temperature ramp of 10 °C min$^{-1}$, and held for 10 min. The transfer line temperature was 270 °C, and the ion source temperature, 250 °C. Mass spectral analyses were carried out in full scan mode. Compounds **1aH** (benzonitrile) and **2mH** (anisole) were characterized by comparison with authentic samples, and their yields were calculated by means of GC calibration curves. Allyl phenyl sulfone **2** was commercially available and used as received, while olefins **3**[29] and **4a,b**[30] have been prepared by following reported procedures. Compounds **1a−c**, **1e−h**, and **1m** were previously synthesized by our research group.[28]

**Synthesis of Arylazo Mesylates 1d, 1e, 1i−l.** Diazonium salts were prepared just before use from the corresponding anilines[31] and purified by dissolving in acetone and precipitation by adding cold diethyl ether. To a cooled (0 °C) suspension of the chosen diazonium salt (1 equiv., 0.3 M) in $CH_2Cl_2$ was added sodium methanesulfinate (1 equiv, except where indicated) in one portion. The temperature was allowed to rise to room temperature, and the solution stirred overnight. The resulting mixture was then filtered, and the obtained solution was evaporated. The raw product was purified by dissolving in $CH_2Cl_2$ and precipitation by adding cold *n*-hexane.

*1-(Methylsulfonyl)-2-(4-bromophenyl)diazene (**1d**).* From 4-bromophenyldiazonium tetrafluoroborate[32] (1.0 g, 3.69 mmol) and 385 mg (1 equiv) of sodium methanesulfinate in 13 mL of dichloromethane. Recrystallization afforded 533 mg of **1d** as a yellow powder (55% yield, mp: 133.2−134.7 °C dec.). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.86−7.83 (d, 2H, $J$ = 9 Hz), −7.77−7.74 (d, 2H, $J$ = 9 Hz), 3.25 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 147.6, 133.1 (CH), 130.5, 125.7 (CH), 34.8 ($CH_3$). IR (NaCl, $\nu$/cm$^{-1}$): 3056, 2931, 1328, 1265, 1161, 737. Anal. Calcd for $C_7H_7BrN_2O_2S$: C, 32.0; H, 2.7; N, 10.6. Found: C, 32.1; H, 2.8; N, 10.7.

*1-(Methylsulfonyl)-2-(2,3-difluorophenyl)diazene (**1i**).* From 2,3-difluorophenyldiazonium tetrafluoroborate[33] (1.5 g, 6.58 mmol) and 745 mg (1.1 equiv) of sodium methanesulfinate in 22 mL of dichloromethane. Recrystallization afforded 666 mg of **1i** as a yellow powder (46% yield, mp: 71.1−72.4 °C dec.). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.59−7.52 (m, 2H), 7.29−7.27 (m, 1 H), 3.26 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 151.4 (dd, $J$ = 249 Hz, 11 Hz), 149.6 (dd, $J$ = 266 Hz, 14 Hz), 138.2 (d, $J$ = 4 Hz), 124.2 (m, CH), 123.7 (d, $J$ = 17 Hz, CH), 113.3 (m, CH), 34.7 (s, $CH_3$). IR (NaCl, $\nu$/cm$^{-1}$): 3044, 2939, 1499, 1342, 1273, 1160, 796. Anal. Calcd for $C_7H_6F_2N_2O_2S$: C, 38.2; H, 2.8; N, 12.7. Found: C, 38.2; H, 2.7; N, 12.6.

*1-(Methylsulfonyl)-2-(α-naphthyl)diazene (**1j**).* From the corresponding α-naphthyldiazonium tetrafluoroborate[34] (1.5 g, 6.20 mmol) and 957 mg (1.5 equiv) of sodium methanesulfinate in 22 mL of dichloromethane. After three recrystallizations we obtained 435 mg of **1j** as a red powder (30% yield, mp: 96.6−98.2 °C dec.). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 8.70−8.67 (d, $J$ = 9 Hz, 1H), 8.22−8.19 (d, $J$ = 8 Hz, 1H), 8.03−7.98 (t, $J$ = 8 Hz, 2H), 7.76−7.6 (m, 3H), 3.35 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 143.8, 136.2 (CH), 134.3, 131.4, 128.6 (CH), 128.3 (CH), 127.2 (CH), 125.3 (CH), 122.4 (CH), 115.0 (CH), 35.1 ($CH_3$). IR (NaCl, $\nu$/cm$^{-1}$): 1337, 1153, 892, 770. Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.4; H, 4.3; N, 12.0. Found: C, 56.3; H, 4.4; N, 12.0.

*1-(Methylsulfonyl)-2-(4-nitrophenyl)diazene (**1k**).* From 4-nitrophenyldiazonium tetrafluoroborate[35] (1.50 g, 6.33 mmol) and 645 mg (1 equiv) of sodium methanesulfinate in dichloromethane (21 mL). Recrystallization afforded 1.02 g of **1k** as a yellow powder (70% yield, mp: 115.9−116.6 °C dec). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 8.48−8.45 (d, 2H, $J$ = 9 Hz), 8.15−8.12 (d, 2H, $J$ = 9 Hz), 3.31 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 151.8, 150.9, 125.0 (4CH), 34.9 ($CH_3$). IR (NaCl, $\nu$/cm$^{-1}$): 3094, 1532, 1353, 1157. Anal. Calcd for $C_7H_7N_3O_4S$: C, 36.7; H, 3.1; N, 18.3. Found: C, 36.9; H, 3.1; N, 18.2.

*1-(Methylsulfonyl)-2-(4-methylphenyl)diazene (**1l**).* From 4-methylphenyldiazonium tetrafluoroborate[36] (1.00 g, 4.85 mmol) and 545 mg (1.1 equiv) of sodium methanesulfinate in dichloromethane (16 mL). Recrystallization afforded 0.28 g of **1l** as a yellow powder (29% yield, mp: 107.1−108.0 °C dec). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.88−7.85 (d, 2H, $J$ = 9 Hz), 7.40−7.37 (d, 2H, $J$ = 9 Hz), 3.22 (s, 3H), 2.5 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 147.0, 146.9, 130.3 (CH), 124.6 (CH), 34.6 ($CH_3$), 21.8 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 1464, 828. ESI-MS ($m/z$): 236.9 ($M^+$ + $K^+$), 201.8 ($M^+$ + $Na^+$). Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.5; H, 5.1; N, 14.1. Found: C, 48.6; H, 5.2; N, 14.1.

**Photochemical Synthesis of Allylarenes 5−7.** A solution (5 mL) of aryl azosulfone **1a−m** (0.25 mmol, 0.05 M) and allyl sulfone **2−4** (2.5 mmol, 0.5 M) in MeCN−$H_2O$ 9:1 was divided into two portions and poured into two Pyrex vials, purged for 2 min with nitrogen, and irradiated at 410 nm for 24 h. The photolyzed solution was washed with *n*-pentane (3 × 20 mL), and the organic phases were collected and concentrated in vacuo (max 600 mbar). The crude residue was purified by column chromatography (eluant: pentane/diethyl ether mixture).

*4-Allylbenzonitrile (**5a**).* From 51 mg (0.25 mmol, 0.05 M) of **1a** and 456 mg of allyl phenyl sulfone (**2**, 2.5 mmol, 0.5 M) in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 19.5 mg of **5a** (pale yellow oil, 55% yield). 14% of benzonitrile **1aH** was also detected by GC analyses. The spectroscopic data of **5a** were in accordance with the literature.[37]

*4-Allylanisole (**5m**).* From 54 mg (0.25 mmol, 0.05 M) of **1m** and 456 mg of allyl phenyl sulfone (**2**, 2.5 mmol, 0.5 M) in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 15 mg of **5m** (colorless oil, 36% yield). 16% of anisole **1mH** was also detected by GC analyses. The spectroscopic data of **5m** were in accordance with the literature.[38]

*4-(2-Phenylallyl)-benzonitrile (**6a**).* From 51 mg (0.25 mmol, 0.05 M) of **1a** and 680 mg of 1-methyl-4-((2-phenylallyl)sulfonyl)benzene (**3**, 2.5 mmol, 0.5 M) in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 8:2) afforded 44 mg of **6a** (pale yellow oil, 88% yield). The spectroscopic data of **6a** were in accordance with the literature.[39] The same reaction afforded **6a** in 65% yield upon solar exposition (3 days, 8 h day$^{-1}$).



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*1-(4-(2-Phenylallyl)phenyl)ethan-1-one (**6b**).* From 57 mg (0.25 mmol, 0.05 M) of **1b** and 680 mg (2.5 mmol, 0.5 M) of **3** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 8:2) afforded 56 mg of **6b** (pale yellow oil, 95% yield). The spectroscopic data of **6b** were in accordance with the literature.[40]

*1-Chloro-4-(2-phenylallyl)benzene (**6c**).* From 54.3 mg (0.25 mmol, 0.05 M) of **1c** and 680 mg (2.5 mmol, 0.5 M) of **3** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane) afforded 33 mg of **6c** (colorless oil, 58% yield). The spectroscopic data of **6c** were in accordance with the literature.[40]

*1-Bromo-4-(2-phenylallyl)benzene (**6d**).* From 67.5 mg (0.25 mmol, 0.05 M) of **1d** and 680 mg (2.5 mmol, 0.5 M) of **3** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane) afforded 39.5 mg of **6d** (pale yellow oil, 58% yield). The spectroscopic data of **6d** were in accordance with the literature.[41]

*Prop-2-ene-1,2-diyldibenzene (**6e**).* From 46 mg (0.25 mmol, 0.05 M) of **1e** and 680 mg (2.5 mmol, 0.5 M) of **3** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane) afforded 35 mg of **6e** (colorless oil, 72% yield). The spectroscopic data of **6e** were in accordance with the literature.[42]

*1-(tert-Butyl)-4-(2-phenylallyl)benzene (**6f**).* From 60 mg (0.25 mmol, 0.05 M) of **1f** and 680 mg (2.5 mmol, 0.5 M) of **3** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane) afforded 30.5 mg of **6f** (pale yellow oil, 49% yield) along with 462 mg of **3** (75% of the unreacted material recovered) that were isolated by column chromatography. $^1$H NMR (300 MHz, $CD_3COCD_3$) $\delta$ 7.51−7.54 (m, 2H), 7.18−7.33 (m, 7H), 5.52 (s, 1H), 5.10 (s, 1H), 3.86 (s, 2H), 1.28 (s, 9H). $^{13}$C NMR (75 MHz, $CD_3COCD_3$) $\delta$ 149.8, 148.6, 141.9, 137.8, 129.7 (CH), 129.5 (CH), 128.7 (CH), 127.4 (CH), 126.3 (CH), 115.0 ($CH_2$), 41.8 ($CH_2$), 35.2, 32.1 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 2963, 2866, 1515, 898. GC-MS ($m/z$): 250 ($M^+$, 5), 236 (9), 235 (48), 194 (28), 193 (100), 192 (52), 117 (38), 115 (47). Anal. Calcd for $C_{19}H_{22}$ C, 91.1; H, 8.9. Found: C, 90.8; H, 9.0.

*3-(2-Phenylallyl)benzonitrile (**6g**).* From 51 mg (0.25 mmol, 0.05 M) of **1g** and 680 mg (2.5 mmol, 0.5 M) of **4** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 8:2) afforded 38 mg of **6g** (pale yellow oil, 70% yield). $^1$H NMR (300 MHz, $CD_3COCD_3$) $\delta$ 7.66−7.48 (m, 5H), 7.34−7.24 (m, 4H), 5.57 (s, 1H), 5.17 (s, 1H), 4.01 (s, 2H). $^{13}$C NMR (75 MHz, $CD_3COCD_3$) $\delta$: 147.7, 142.8, 141.2, 134.8, 133.5 (CH), 131.1 (CH), 130.6 (CH), 129.6 (CH), 128.9 (CH), 127.4 (CH), 119.8 (CH), 115.9 ($CH_2$), 113.4, 41.7 ($CH_2$). IR (NaCl, $\nu$ cm$^{-1}$): 2229, 1627, 1600, 1582. GC-MS ($m/z$): 219 ($M^+$, 17), 204 (6), 141 (24), 103 (100). Anal. Calcd for $C_{16}H_{13}N$: C, 87.6; H, 6.0; N, 6.4. Found C, 87.8; H, 5.9; N, 6.3.

*2-(2-Phenylallyl)benzonitrile (**6h**).* From 51 mg (0.25 mmol, 0.05 M) of **1h** and 680 mg (2.5 mmol, 0.5 M) of **4** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 8:2) afforded 19 mg of **6h** (colorless oil, 35% yield). $^1$H NMR (300 MHz, $CD_3COCD_3$) $\delta$ 7.77−7.60 (m, 1H), 7.55−7.29 (m, 8H), 5.54 (s, 1H), 4.99 (s, 1H), 4.11 (s, 2H). $^{13}$C NMR (75 MHz, $CD_3COCD_3$) $\delta$: 35.4 ($CH_2$), 109.0, 113.7 ($CH_2$), 113.6, 122.1 (CH), 123.2 (CH), 123.8 (CH), 124.4 (CH), 126.3 (CH), 128.8 (CH), 136.3, 139.2, 142.1, 36.4 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 2924, 2218, 1488, 1441, 901. GC-MS ($m/z$): 219 ($M^+$, 22), 218 (10), 141 (12), 117 (14), 103 (100). Anal. Calcd for $C_{16}H_{13}N$: C, 87.6; H, 6.0; N, 6.4. Found C, 87.4; H, 5.8; N 6.5

*2,3-Difluoro-3-(2-phenylallyl)benzene (**6i**).* From 55 mg (0.25 mmol, 0.05 M) of **1i** and 680 mg (2.5 mmol, 5 M) of **4** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 95:5) afforded 22 mg of **6i** (colorless oil, 38% yield). $^1$H NMR (300 MHz, $CD_3COCD_3$) $\delta$ 7.54−7.51 (m, 2H), 7.37−7.28 (m, 3H), 7.12−7.08 (m, 3H), 5.53 (s, 1H), 5.05 (s, 1H), 3.96 (s, 2H). $^{13}$C NMR (75 MHz, $CD_3COCD_3$) $\delta$: 152.0 (dd, $J$ = 120 and 12.7 Hz), 150.0 (d, $J$ = 134 Hz), 146.9, 141.4, 130.4 (d, $J$ = 12.7 Hz), 129.6 (CH), 129.0 (CH), 127.4 (t, $J$ = 12.7 Hz), 125.5 (m, CH), 116.4 (CH, $J$ = 75 Hz), 115.3 (CH), 134.7 ($CH_2$) 34.7 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 2921, 2847, 901. GC-MS ($m/z$): 230 (19), 210 (5), 152 (28), 103 (100), 77 (25). Anal. Calcd for $C_{15}H_{12}F_2$: C, 78.2; H, 5.2. Found C, 78.1; H, 5.1.

*2-(2-Phenylallyl)naphthalene (**6j**).* From 58.5 mg (0.25 mmol, 0.05 M) of **1j** and 680 mg (2.5 mmol, 5 M) of **4** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: neat pentane) afforded 33.5 mg of **6j** (pale yellow oil, 55% yield). The spectroscopic data of **6j** were in accordance with the literature.[42]

*Methyl 2-(4-Cyanobenzyl)acrylate (**7a**).* From 51 mg (0.25 mmol, 0.05 M) of **1a** and 636 mg of methyl 2-(tosylmethyl)acrylate (**4a**, 2.5 mmol, 0.5 M) in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 36 mg of **7a**[43] (pale yellow oil, 72% yield).

$^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.62−7.59 (d, 2H, $J$ = 9 Hz) 7.35−7.32 (d, 2H, $J$ = 9 Hz), 6.31 (s, 1H), 5.57 (s, 1H), 3.74 (s, 3H), 3.70 (s, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 144.4, 138.6, 132.1 (CH), 129.6 (CH), 127.2 ($CH_2$), 118.8, 110.3, 52.0 ($CH_2$), 38.2 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 2230, 1719, 1632. ESI-MS ($m/z$): 202.2 ($M^+ + H^+$). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.8; H, 5.7; N, 6.8.

*Methyl 2-(4-Acetylbenzyl)acrylate (**7b**).* From 57 mg (0.25 mmol, 0.05 M) of **7b** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 51 mg of **7b** (yellow oil, 93% yield) along with 419 mg of **4a** (73% of the unreacted material recovered) were isolated by column chromatography. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.93−7.90 (d, 2H, $J$ = 9 Hz) 7.33−7.30 (d, 2H, $J$ = 9 Hz), 6.29 (s, 1H), 5.54 (s, 1H), 3.75 (s, 3H), 3.70 (s, 2H), 2.60 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 197.7, 166.9, 144.4, 139.3, 135.4, 129.0 (CH), 128.5 (CH), 126.8 ($CH_2$), 51.9 ($CH_2$), 38.0 ($CH_3$), 26.5 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 1720, 1640. GC-MS ($m/z$): 218 ($M^+$, 28), 203 (66), 158 (16), 143 (100). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5. Found: C, 71.4; H, 6.4.

*Methyl 2-(4-Chlorobenzyl)acrylate (**7c**).* From 54.3 mg (0.25 mmol, 0.05 M) of **1c** and 635 mg (2.5 mmol, 5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 25 mg of 7c (colorless oil, 47% yield). The spectroscopic data of **7c** were in accordance with the literature.[44] The same reaction carried out by using allyl methylsulfone **4b** instead of **4a** afforded **7c** in 53% yield.

*Methyl 2-(4-Bromobenzyl)acrylate (**7d**).* From 67.5 mg (0.25 mmol, 0.05 M) of **1d** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 20 mg of **7d** (yellow oil, 31% yield). The spectroscopic data of **7d** were in accordance with the literature.[44] The same reaction carried out by using **4b** instead of **4a** afforded **7d** in 39% yield.

*Methyl 2-(3-Cyanobenzyl)acrylate (**7g**).* From 52 mg (0.25 mmol, 0.05 M) of **1g** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane) afforded 38.2 mg of **7g** (colorless oil, 76% yield). Spectroscopic data of **7g** were in accordance with the literature.[45]

*Methyl 2-(4-Nitrobenzyl)acrylate (**7k**).* From 57 mg (0.25 mmol, 0.05 M) of **1k** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 27.6 mg of **7k**[46] (yellow oil, 50% yield). $^1$H NMR (300 MHz, $CD_3COCD_3$) $\delta$: 8.20−8.17 (d, 2H, $J$ = 9 Hz), 7.56−7.53 (d, 2H, $J$ = 9 Hz), 6.28 (s, 1H), 5.76 (s, 1H), 3.81 (s, 2H), 3.70 (s, 3H). $^{13}$C NMR (75 MHz, $CD_3COCD_3$) $\delta$: 167.6, 148.6, 140.4, 131,2 (CH), 128.1 (CH), 124.7 ($CH_2$), 52.6 ($CH_2$), 38.8 ($CH_3$). IR (NaCl, $\nu$ cm$^{-1}$): 1721, 1519, 1633. GC-MS ($m/z$): 221 ($M^+$, 16), 204 (30), 174 (18), 161 (62), 116 (57), 115 (100). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.7; H, 5.0; N, 6.3. Found: 59.5, H; 4.9, N, 6.4.

*Methyl 2-(4-Methylbenzyl)acrylate (**7l**).* From 50 mg (0.25 mmol, 0.05 M) of **1l** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 23 mg of **7l** (colorless oil, 48% yield). The spectroscopic data of **7l** were in accordance with the literature.[44]

*Methyl 2-(4-Methoxybenzyl)acrylate (**7m**).* From 53.5 mg (0.25 mmol, 0.05 M) of **1m** and 635 mg (2.5 mmol, 0.5 M) of **4a** in MeCN−$H_2O$ 9:1 (5 mL). Purification by column chromatography (eluant: pentane/diethyl ether 9:1) afforded 20 mg of **7m** (colorless oil, 39% yield). The spectroscopic data of **7m** were in accordance with the literature.[47]



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## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01532.

Copy of $^{1}H$ and $^{13}C$ NMR spectra for compounds **1**−**5** (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) See for reviews: (a) Guo, S. S.; You, C. X.; Liang, J. Y.; Zhang, W. J.; Geng, Z. F.; Wang, C. F.; Du, S. S.; Lei, N. *Molecules* **2015**, *20*, 15735−15747. (b) Ni, G.; Zhang, Q. J.; Zheng, Z. F.; Chen, R. Y.; Yu, D. Q. *J. Nat. Prod.* **2009**, *72*, 966−968. (c) Parmar, V. S.; Jain, S. C.; Bisht, K. P.; Jain, R.; Taneja, P.; Jha, A.; Tyagi, O. D.; Prasad, A. K.; Wengel, J.; Olsen, C. E.; Boll, P. M. *Phytochemistry* **1997**, *46*, 597−673.

(2) (a) Wang, T.; Xiang, S.-K.; Qin, C.; Ma, J.-A.; Zhang, L.-H.; Jiao, N. *Tetrahedron Lett.* **2011**, *52*, 3208−3211. (b) Chen, H.; Jiang, H.; Cai, C.; Dong, J.; Fu, W. *Org. Lett.* **2011**, *13*, 992−994.

(3) Chang, S.; Lin, S. Y.; Chan, C. K. *Synlett* **2013**, *24*, 487−490.

(4) Qin, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 15893−15895.

(5) Liu, G.; Yin, G.; Wu, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4733−4736.

(6) (a) Jia, T.; Bellomo, A.; Montel, S.; Zheng, B.; Walsh, P. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 260−264. (b) Zhou, R.; Liu, H.; Tao, H.; Yu, X.; Wu, J. *Chem. Sci.* **2017**, *8*, 4654−4659.

(7) (a) Ricci, J.; Poulain-Martini, S.; Duñach, E. *C. R. Chim.* **2009**, *12*, 916−921. (b) Rueping, M.; Nachtsheim, B. J. *Beilstein J. Org. Chem.* **2010**, *6*, doi: 10.3762/bjoc.6.6.

(8) (a) Kacprzynski, A.; May, T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4554−4558. (b) Feng, C.; Kobayashi, Y. *J. Org. Chem.* **2013**, *78*, 3755−3766.

(9) (a) Li, X.-D.; Xie, L.-J.; Kong, D.-L.; Liu, L.; Cheng, L. *Tetrahedron* **2016**, *72*, 1873−1880. (b) Dong, C.; Zhang, L.; Xue, X.; Li, H.; Yu, Z.; Tang, W.; Xu, L. *RSC Adv.* **2014**, *4*, 11152−11158.

(10) Mishra, N. K.; Sharma, S.; Park, J.; Han, S.; Kim, I. S. *ACS Catal.* **2017**, *7*, 2821−2847.

(11) Protti, S.; Albini, A. *Paradigms in Green Chemistry and Technology*; Springer: U.K., 2016.

(12) Roy, J. *AAPS PharmSciTech* **2002**, *3*, 1−8.

(13) (a) Li, X.-D.; Xie, L.-J.; Kong, D.-L.; Liu, L.; Cheng, L. *Tetrahedron* **2016**, *72*, 1873−1880. (b) Ek, F.; Axelsson, O.; Wistrand, L.-G.; Frejd, T. *J. Org. Chem.* **2002**, *67*, 6376−6381.

(14) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114*, 9219−9280.

(15) Ueda, M.; Nishimura, K.; Kashima, R.; Ryu, I. *Synlett* **2012**, *23*, 1085−1089.

(16) Kabalka, G. W.; Yao, M.-L.; Borella, S.; Wu, Z. *Chem. Commun.* **2005**, 2492−2494.

(17) Albini, A.; Fagnoni, M. *Green Chem.* **2004**, *6*, 1−6.

(18) (a) Protti, S.; Fagnoni, M.; Albini, A. *Org. Biomol. Chem.* **2005**, *3*, 2868−2871. (b) Dichiarante, V.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2010**, *75*, 1271−1276.

(19) De Carolis, M.; Protti, S.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1232−1236.

(20) Milanesi, S.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2005**, *70*, 603−610.

(21) Dichiarante, S.; Protti, S.; Fagnoni, M. *J. Photochem. Photobiol., A* **2017**, *339*, 103−113.

(22) (a) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075−10166. (b) Arias-Rotondo, D. M.; McCusker, J. K. *Chem. Soc. Rev.* **2016**, *45*, 5803−5820.

(23) Baralle, A.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. *Chem. - Eur. J.* **2013**, *19*, 10809−10813.

(24) Donck, S.; Baroudi, A.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. *Adv. Synth. Catal.* **2013**, *355*, 1477−1482.

(25) Goddard, J.-P.; Ollivier, C.; Fensterbank, L. *Acc. Chem. Res.* **2016**, *49*, 1924−1936.

(26) A visible light photoredox catalyzed allylation of electron-poor aryl nitriles has been described by Mac Millan and co-workers; see: Cuthbertson, J. D.; MacMillan, D. W. C. *Nature* **2015**, *519*, 74−77.

(27) Candish, L.; Teders, M.; Glorius, F. *J. Am. Chem. Soc.* **2017**, *139*, 7440−7443.

(28) Crespi, S.; Protti, S.; Fagnoni, M. *J. Org. Chem.* **2016**, *81*, 9612−9619.

(29) Harvey, W.; Phillips, E. D.; Whitham, G. H. *Tetrahedron* **1997**, *53*, 6493−6508.

(30) Sawangphon, T.; Katrun, P.; Chaisiwamongkhol, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synth. Commun.* **2013**, *43*, 1692−1707.

(31) Li, Y.; Xie, W.; Jiang, X. *Chem. - Eur. J.* **2015**, *21*, 16059−16065.

(32) Bonin, H.; Delbrayelle, D.; Demonchaux, P.; Gras, E. *Chem. Commun.* **2010**, *46*, 2677−2679.

(33) Sellers, C.; Suschitzky, H. *J. Chem. Soc. C* **1968**, 2317−2319.

(34) Wu, J.; Gu, Y.; Leng, X.; Shen, Q. *Angew. Chem., Int. Ed.* **2015**, *54*, 7648−7652.

(35) Patouret, R.; Kamenecka, T. M. *Tetrahedron Lett.* **2016**, *57*, 1597−1599.

(36) Liras, M.; González-Bejar, M.; Scaiano, J. C. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9757−9762.

(37) Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2008**, *73*, 1165−1168.

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

(39) Dong, C.; Zhang, L.; Xue, X.; Li, H.; Yu, Z.; Tang, W.; Xu, L. *RSC Adv.* **2014**, *4*, 11152−11158.

(40) Lasch, R.; Fehler, S. K.; Heinrich, M. R. *Org. Lett.* **2016**, *18*, 1586−1589.

(41) Alacid, E.; Nájera, C. *Org. Lett.* **2008**, *10*, 5011−5014.

(42) Wu, Q.; Wang, L.; Jin, R.; Kang, C.; Bian, Z.; Du, Z.; Ma, X.; Guo, H.; Gao, L. *Eur. J. Org. Chem.* **2016**, *2016*, 5415−5422.

(43) Kondolff, I.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 8487−8491.

(44) Ramachary, D. B.; Venkaiah, C.; Reddy, Y. V. *Org. Biomol. Chem.* **2014**, *12*, 5400−5406.

(45) Murray, P. M.; Bower, J. F.; Cox, D. K.; Galbraith, E. K.; Parker, J. S.; Sweeney, J. B. *Org. Process Res. Dev.* **2013**, *17*, 397−405.

(46) Camus, N.; Halime, Z.; Le Bris, N.; Bernard, H.; Platas-Iglesias, C.; Tripier, R. *J. Org. Chem.* **2014**, *79*, 1885−1899.

(47) Rao, M. L. N.; Giri, S. *Eur. J. Org. Chem.* **2012**, *2012*, 4580−4589.