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Wavelength Selective Generation of Aryl Radicals and Aryl Cations for Metal-Free Photoarylations

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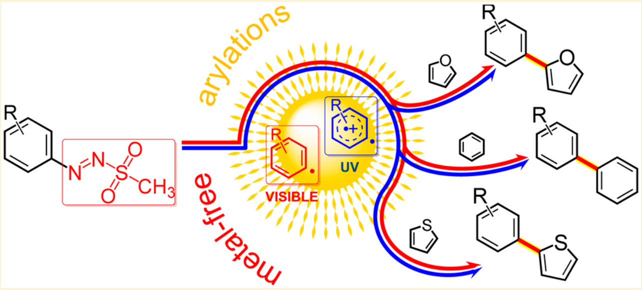
Supporting Information

ABSTRACT: Photochemical reactions have become an important tool for organic chemists. Visible (solar) light can be conveniently adopted, however, only when using colored organic compounds or in photocatalyzed processes induced by visible light absorbing photocatalysts. Herein we demonstrate that a photolabile, colored moiety could be incorporated in a colorless organic compound with the aim of generating highly reactive intermediates upon exposure to visible (solar) light. Arylazo sulfones, colored thermally stable derivatives of aryl diazonium salts, were used as valuable substrates for the photoinduced metal-free synthesis of (hetero)biaryls with no need of a (photo)catalyst or of other additives to promote the reaction. Noteworthy, selective generation of aryl radicals and aryl cations can be attained at will by varying the irradiation conditions (visible light for the former and UVA light for the latter).



INTRODUCTION

The majority of organic compounds are colorless. Nonetheless, the use of solar and visible light to promote key photochemical steps in organic synthesis has rapidly grown in recent years.[1] Two approaches have been followed, and in both cases the presence of suitable moieties in the starting compounds has the role of directing the reactivity. In the first case, an organic molecule is activated by a chemical interaction with a visible light absorbing catalyst via an electron[1] or a hydrogen atom transfer process.[2] Transition metal photoredox catalysis has been the most rapidly growing field in the past decade (see a general scheme in Figure 1a).[1] The incorporation in the starting substrates of redox sensitive moieties (X) is required to facilitate the monoelectronic oxidation/reduction step (path a). These moieties, known as electroauxiliary groups,[3] have the further advantage to be easily eliminated at the end of the process by fragmentation of the resulting radical ions ($R{-}X^{\bullet+}$ or $R{-}X^{\bullet-}$, path b) to give reactive radicals.

In the second approach a photocleavable colored moiety (responsible for the absorption of visible light) is introduced in the starting substrate.[4] However, this approach is limited to few examples, such as Barton esters[5] where stable carboxylic acids are converted into colored photoactive thiohydroxamate esters (Figure 1b). Photohomolysis of the labile N−O bond in these esters gave (substituted) carbon-centered (aliphatic) radicals (upon carbon dioxide loss from carbonyloxy radicals).[4,5]

In some instances uncatalyzed processes can be carried out under solar light irradiation even for colorless compounds[6] or by the in situ formation of colored electron donor−acceptor (EDA) complexes.[7]

Nonetheless, key motivations in devising photolabile visible light absorbing groups are that no (expensive) photocatalysts are required to carry out reactions under solar/visible irradiation.

We describe herein the application of arylazo sulfones in metal-free photochemical arylations (Figure 1c). These substrates were easily prepared from colorless anilines and have been sparsely described[8] as suitable precursors of chemical intermediates, including phenyl radicals and cations, upon heating (>80 °C) or by treatment with a strong acid (e.g., CF_3COOH) or a base (pyridine as solvent).[9a−e] Heating of substituted arylazo sulfones in the presence of potassium iodide or *N*,*N*-dimethylformamide gave iodoarenes and desulfonylated arenes, respectively.[9f] More attention has been given to the electrophilic character of the N═N bond in the reaction with nucleophiles (e.g., with selenolate ion[9g] or Grignard reagents[9h]). Recently, aryl azosulfones have been employed in desulfonylative [3 + 2] cycloadditions for the synthesis of substituted pyrazoles,[9i] where, however, the azo moiety was maintained in the final product.

Little is known on the photoreactivity of arylazo sulfones and arylazo sulfonates.[8−10] At least in principle, a phenyl radical[10] or a phenyl cation may be generated upon irradiation in what seems to be a solvent dependent process. As an example, the photodecomposition of *p*-alkylphenylazo sulfonates used as photolabile surfactants was investigated in micellar systems.[11] A heterolytic cleavage occurred in bulk aqueous phase to yield a phenyl cation, whereas in micelles homolytic cleavage forming the corresponding phenyl radical took place.[11,12] Photolysis of phenylazo-*p*-tolyl sulfones in aromatic solvents under visible light irradiation was suggested to proceed via aryl radicals.[10]

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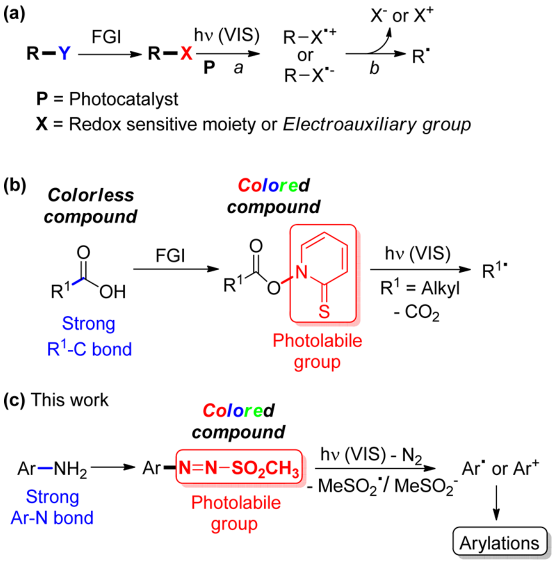


Figure 1. Visible light generation of intermediates. (a) Photoredox catalysis is mainly based on the presence of a redox sensitive moiety (an electroauxiliary group, X) that makes organic molecules more oxidizable and reducible, thus facilitating an electron transfer reaction with a photoexcited photocatalyst. These X groups have the further advantage to be lost in the reaction to give radicals. (b) A colored moiety could be introduced in an organic compound by a functional group interconversion (FGI) to allow the generation of reactive intermediates by converting a strong bond to a weak photolabile bond. (c) The introduction of an azosulfone group in colorless stable anilines formed colored photolabile arylazo mesylates for the photogeneration of either aryl radicals or aryl cations.

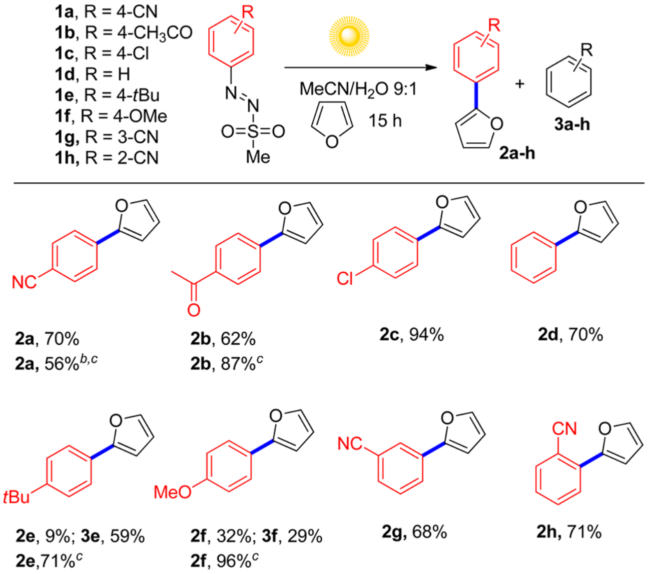
As for the above, azosulfones can be viewed as the *colored* and *stable* form of the corresponding highly reactive and rather unstable aromatic diazonium salts. We reasoned that the use of such azosulfones may widen the application of diazonium salts (recently adopted for the photoredox catalytic generation of aryl radicals[13]), overcoming, at the same time, their limitations related to their electrophilicity and difficult handling.

RESULTS

We therefore deemed it worthwhile to investigate the photochemistry of a set of arylazo mesylates (**1a**−**h**, Table 1). Compounds **1a**−**h** were easily obtained as yellow/orange crystalline solids from the corresponding anilines (see Supporting Information for further details). The electronic spectra of azosulfones **1** exhibit a low intensity band in the visible ($\varepsilon = 10^2\ \mathrm{M^{-1}\ cm^{-1}}$) and an intense band in the UV region ($\varepsilon = 10^4\ \mathrm{M^{-1}\ cm^{-1}}$),[8] the latter considerably red-shifted when an electron-donating group is present (see Table S1 and Figure S1). These bands were safely attributed to the nπ* and the $\pi\pi$* transitions, respectively.[8,10]

Photochemical Arylation of (Hetero)aromatics via Arylazo Mesylates. We carried out preliminary irradiation experiments on **1a** in the presence of furan. We found it convenient to adopt a solar simulator (Solarbox) equipped with a Xe lamp (500 W) as the light source. A MeCN/water 9:1 mixture was found to be the best solvent to obtain the corresponding arylated furan and to minimize the undesired formation of byproducts (mainly benzonitrile, Table S2). The reaction was tested on arylazo mesylates **1a**−**h**, and in each case heterobiaryls **2a**−**h** were obtained in satisfactory yields. Noteworthy, in the case of **1a** the reaction can be likewise carried out under natural sunlight (3 days irradiation, 56% yield, see further Figure S2).

Table 1. Solar Light Induced Synthesis of 2-Arylfurans 2a−h[a]



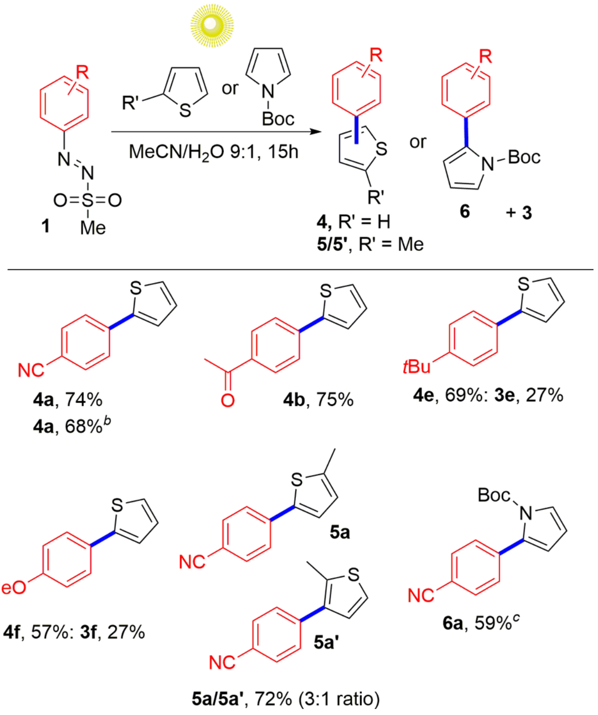
[a]Reactions were performed on 5 mL solutions placed in glass vessels in a Solarbox apparatus; **1** (0.1 M), furan (1 M). Letters in the products refer to the same substituents as in compounds **1**. [b]Reaction carried out by exposing the reaction vessel under natural sunlight (3 days, 8 h a day). [c]**1** (0.05 M) and furan (2 M).

We then investigated the arylation of other electron-rich heteroaromatics such as thiophene, 2-methylthiophene, and *N*-Boc-pyrrole (Table 2). Irradiation of azosulfones **1a**,**b** in the presence of thiophene led to the corresponding 2-arylthiophenes **4a**,**b** in more than 70% yield. Sunlight was again convenient to induce the synthesis of **4a**. Azosulfones bearing an electron-donating group on the aromatic ring (**1e**,**f**) gave again the corresponding arylated products but accompanied by a significant amount of **3e**,**f** (ca. 30%). Arylation of 2-methylthiophene with **1a** gave a mixture of 2-aryl-5-methylthiophene (**5a**) and 2-methyl-3-arylthiophene (**5a′**) in 72% overall yield (**5a**/**5a′** 3:1 ratio). In a single case, *N*-Boc-pyrrole was arylated (compound **6a**, isolated as the exclusive isomer, 59% yield), and the use of LED irradiation (λ = 450 nm) was found convenient in this case.

The challenging arylation of unactivated arenes was then tested (Table 3). Arylation of benzene, though satisfactory in some cases, is not a clean process (**3** and acetanilide **9** as the byproducts). However, when photolysis was carried out in neat benzene, or upon sunlight irradiation, biaryls **7** were exclusively formed. Biaryls **8a** and **8b** were obtained in 56% and 32% yields, respectively by the reaction between electron-poor azosulfones **1a**,**b** and mesitylene. In the latter case, however, the adoption of a 366 nm phosphor coated Hg lamp as the light source improved the arylation yields up to 70% (Table 3).

Mechanistic Investigations on the Photoreactivity of Azosulfones 1. Experiments were carried out to investigate the mechanism of the reaction. No appreciable thermal decomposition occurred when the solutions of **1a**−**h** were irradiated in the Solarbox protected from light. Azosulfones **1a**,**b**,**e**,**f** were irradiated in the Solarbox in neat MeCN−H_2O 9:1. Interestingly, along with **3**, solvolysis products, namely, acetanilide **9** and phenol **10**, were obtained in a significant

Table 2. Metal-Free Synthesis of Heterocycles 4–6[a]



4a, 74%
4a, 68%^{b}

4b, 75%

4e, 69%: **3e**, 27%

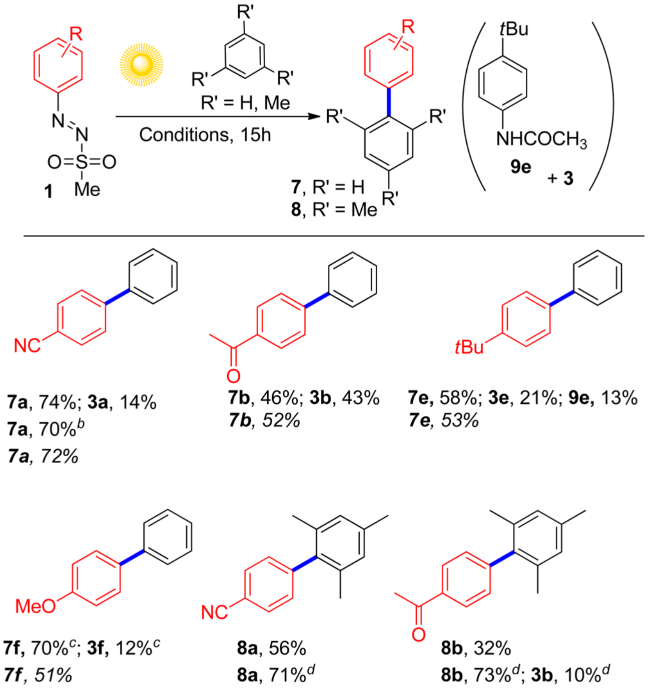
4f, 57%: **3f**, 27%

5a/5a', 72% (3:1 ratio)

6a, 59%^{c}

^{a}Reactions were performed on 5 mL solutions placed in glass vessels in a Solarbox apparatus; **1** (0.05 M), heteroaromatics (2 M). Compound **3** detected in <10% yield except where indicated. ^{b}Reaction carried out by exposing the reaction vessel under natural sunlight (3 days, 8 h a day). ^{c}Reaction carried out on 1 mL of solution by using 450 nm LED as the light source.

Table 3. Synthesis of Biaryls 7, 8[a]



7a, 74%; **3a**, 14%
7a, 70%^{b}
7a, *72%*

7b, 46%; **3b**, 43%
7b, *52%*

7e, 58%; **3e**, 21%; **9e**, 13%
7e, *53%*

7f, 70%^{c}; **3f**, 12%^{c}
7f, *51%*

8a, 56%
8a, 71%^{d}

8b, 32%
8b, 73%^{d}; **3b**, 10%^{d}

^{a}Conditions (see Table 2): **1** (0.05 M), benzene or mesitylene (2 M) irradiated in MeCN–H$_2$O 9:1. In italics: reaction carried out in neat benzene. ^{b}Reaction carried out by exposing the reaction vessel under natural sunlight (3 days, 8 h a day). ^{c}MeCN used as the solvent. ^{d}The solution was irradiated in a 1 mm quartz cuvette for 5 h by using a 366 nm phosphor coated Hg lamp as the light source (GC yields).

amount, except for **1b**, where acetophenone **3b** was exclusively formed (Table 4). The nature of the products obtained resembles that found previously by our group in the irradiation of benzenediazonium tetrafluoroborate salts.[14] Ion chromatograph analyses of the photolyzed solutions revealed the presence of methanesulfinic acid (CH_3SO_2H, 63% yield in the case of **1a**).

We were then interested to ascertain if a wavelength dependent reactivity of the azosulfone exists. Accordingly, we repeated some experiments on sulfone **1f** by using a phosphor coated Hg lamp (λ = 366 nm) and a LED (λ = 450 nm) in order to reach selectively the $\pi\pi^*$ and $n\pi^*$ states, respectively.

Irradiation at these two wavelengths in neat MeCN–H$_2$O 9:1 led to a markedly different distribution of products (at 366 nm the main product is acetanilide **9f**), but the presence of ascorbic acid (a reducing agent) led exclusively to anisole **3f** in both cases. Arylation of furan is not wavelength dependent, which is different from the case of allyl phenyl sulfone, where estragole **11f** (48%) was isolated as the major product in the irradiation of **1f** at 450 nm but not at 366 nm.

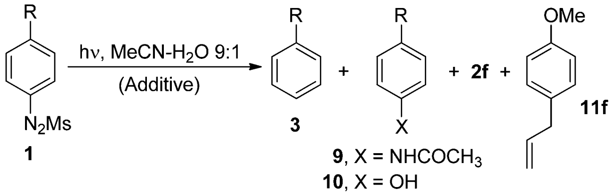
Experiments carried out in the presence of triplet quencher 3,3,4,4-tetramethyl-1,2-diazetine dioxide (TMDD, $E_T \leq 42.0$ kcal mol^{-1}, 0.025 M)[15] demonstrated that while no effect was observed at 450 nm, a dwarfing in the consumption of **1f** (from 86% down to 13%) was apparent at 366 nm. Finally, a comparison with the photoreactivity of 4-methoxyphenyldiazonium tetrafluoroborate (4-MeOC$_6$H$_4$N$_2$BF$_4$) was carried out at 366 nm in the presence of furan, but, contrary to what was observed for **1f** under the same conditions, no arylation took place.

DISCUSSION

The obtained data suggest that a wavelength dependent generation of intermediates is involved in the photoreactivity of **1** (Scheme 1). Thus, irradiation at 450 nm populates the $^1n\pi^*$ state (path a), and homolysis of the S–N bond (path b) occurs to afford the aryl radical (**Ar**$^\bullet$)/methanesulfonyl radical ($CH_3SO_2^\bullet$) pair. In neat solvent, both radicals undergo hydrogen abstraction from the solvent to give **3**[16] and sulfinic acid (CH_3SO_2H)[17] (path c). However, when a radical trap (furan in Scheme 1) is present at a sufficient concentration, trapping of **Ar**$^\bullet$ (path d) to form radical adduct **12**$^\bullet$ competes efficiently with reduction.[18] Hydrogen abstraction from **12**$^\bullet$ by $CH_3SO_2^\bullet$ then affords the heterobiaryl **2** (path e). The intervention of an aryl radical is further supported by the reaction of **1f** with allyl phenyl sulfones (a typical selective trap for aryl radicals[19]), which gives estragole **11f** as the main product. On the other hand, irradiation at 366 nm populates the $^1\pi\pi^*$ state (path f). In this case, intersystem crossing to $^3\pi\pi^*$ (path g) is followed by heterolytic cleavage of the S–N bond to generate an excited aryl diazonium salt in the same multiplicity ($^3ArN_2^+$, path h). The intermediacy of a triplet state is confirmed here by the efficient quenching observed in the presence of TMDD (path g′), not observed upon irradiation at 450 nm (Table 4).

Reduction of $^3ArN_2^+$ by ascorbic acid to the corresponding radical,[20] however, leads efficiently to **3** (path c′). Heterolysis of the Ar–N bond in $^3ArN_2^+$[14,21] generates a triplet aryl cation ($^3Ar^+$, path i) that is then reduced to **3** by the solvent (path j).[14,22] The presence of solvolysis products **9**, **10** (path l) is diagnostic of the formation of a singlet aryl cation $^1Ar^+$ (by ISC from $^3Ar^+$, path k)[23] that depends on the nature of the aromatic

Table 4. Investigation on the Wavelength Dependent Behavior of Azosulfones 1[a]



compd	light source	additive	1 (% cons.)	3 (%)[b]	9/10[b] (%)	arylated[b] (%)
1a	Solarbox[c]		100	**3a**, 57	**9a**, 15; **10a**, 6	
1b	Solarbox[c]		100	**3b**, 67		
1e	Solarbox[c]		100	**3e**, 22	**9e**, 20; **10e**, 8	
1f	Solarbox[c]		100	**3f**, 34	**9f**, 28, **10f**, 14	
1f	LED (450 nm)[d]		70	**3f**, 56		
1f	Hg (366 nm)[e]		87	**3f**, 7	**9f**, 57; **10f**, 12	
1f	LED (450 nm)[d]	ascorbic acid[f]	100	**3f**, 48		
1f	Hg (366 nm)[e]	ascorbic acid[f]	100	**3f**, 50		
1f	LED (450 nm)[d]	furan[g]	100	**3f**, 21		**2f**, 68
1f	Hg (366 nm)[e]	furan[g]	100	**3f**, 16	**9f**, 5	**2f**, 58
1f	LED (450 nm)[d]	allyl phenyl sulfone[h]	100	**3f**, 23		**11f**, 48
1f	Hg (366 nm)[e]	allyl phenyl sulfone[h]	100	**3f**, 8	**9f**, 46	**11f**, 11
1f	LED (450 nm)[d]	TMDD[i]	64	**3f**, 56		
1f	Hg (366 nm)[e]	TMDD[i]	13	**3f**, <5		
4-MeOC$_6$H$_4$N$_2$BF$_4$	Hg (366 nm)[e]	furan[g]	100	**3f**, <5	**9f**, 25	**2f**, <5

[a] Conditions: **1** or diazonium salt (0.05 M) in MeCN–H$_2$O 9:1. [b] Yields based on the consumption of **1**. [c] 1 mL of solution irradiated for 15 h in a vial in the Solarbox. [d] The solution was irradiated in a 1 mm quartz cuvette for 5 h. [e] The solution was irradiated in a 1 mm quartz cuvette for 1.5 h. [f] Ascorbic acid 0.025 M. [g] Furan 2 M. [h] Allyl phenyl sulfone 0.2 M. [i] 4,4-Tetramethyl-1,2-diazetine dioxide (TMDD) 0.025 M.

substituents. A singlet cation reactivity is almost exclusively observed when irradiating the 4-methoxyphenyldiazonium tetrafluoborate salt evidencing a role of the azosulfone group in the population of $^3ArN_2^+$ (Table 4). However, in the presence of π-bond nucleophiles, such as (hetero)aromatics, efficient trapping of $^3Ar^+$ occurs and heterobiaryls (**2** in Scheme 1) are obtained via Wheland intermediate **12**$^+$ (paths m, m′). In contrast, the presence of a radical trap, namely, allyl phenyl sulfone, gives allylated **11f** only as a minor product. When using a xenon lamp (such as that present in the Solarbox apparatus), both **Ar**$^\bullet$ and $^3Ar^+$ are generated in solution, and this successfully leads to (hetero)aromatics. To improve the yields, however, a more selective generation of one of these intermediates was adopted (see Tables 2, 3).

Importance of the Method. The development of metal-free arylation procedures for the synthesis of (hetero)biaryls is a pioneering field in organic chemistry.[13a,24] Common strategies involve the generation of reactive intermediates such as aryl cations or radicals. Triplet aryl cations are obtained via UV irradiation of aryl halides (mainly chlorides) and esters in protic solvents,[22] but the process is limited to electron-rich substrates. Diazonium salts are likewise used as $^3Ar^+$ precursors, but in the case of electron-rich aromatics, the use of a triplet photosensitizer (e.g., benzophenone) is mandatory.[14]

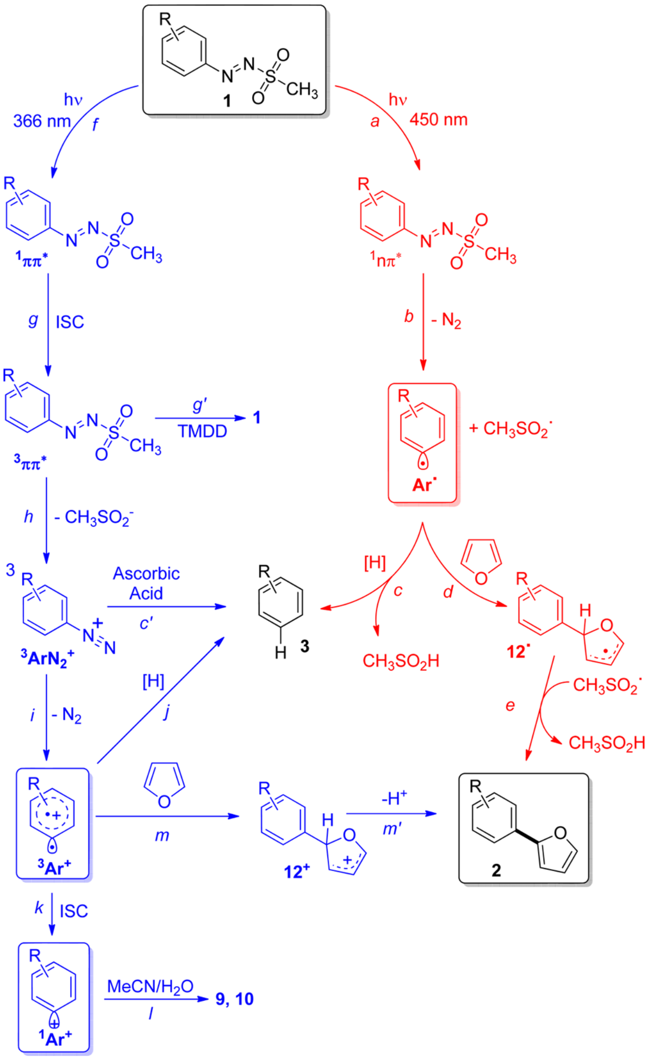
On the other hand, aryl radicals can be formed under metal-free conditions by following either thermal or photochemical approaches. The generation of aryl radicals is reported via radical mediated halide atom abstraction from aryl iodides taking place at room temperature in the presence of $(TMS)_3SiH$ as chain carrier.[25] The most recent proposals, however, involve the monoelectronic reduction of aryl halides (mainly iodides and bromides) followed by halide ion loss. The process occurs at >80 °C in the presence of a strong base (usually *t*BuOK) and organic catalysts such as quinolines,[26a] phenylhydrazine,[26b] and pyridone based macrocycles.[26c] The in situ generated aryl radical then reacts via $S_{RN}1$ mechanism with an unactivated arene (in most cases, benzene) that acts as reagent and solvent. A milder approach makes use of ascorbic acid to reduce the starting diazonium salts to give aryl radicals.[18]

As for metal-free photochemical approaches, aryl radicals can be accessed by Eosin Y photocatalyzed reduction of aryl[13a] and (hetero)aryl[27a] diazonium salts or by two photon perylene bisimide photocatalyzed reduction of aryl halides in the presence of triethylamine as the electron donor.[27b] The uncatalyzed formation of aryl radicals can be promoted by UV irradiation of the in situ generated diazo anhydrides.[27c] Finally, the photoinduced metal-free borylation of aryl halides and ammonium salts was suggested to proceed via either aryl radicals or triplet aryl cations.[27d]

As a common feature of these processes, the addition of the aryl radical onto a heteroaromatic is particularly successful when the radical bears an electron-withdrawing substituent on the aromatic ring.[13a,20,27b,c] The arylation of simple arenes is likewise feasible but only in the presence of a large excess of the arene.[13g] The same holds even in the present case, as is apparent in Tables 1–3.

In the present work we showed that aryl azosulfones are versatile substrates for the uncatalyzed metal-free arylation of heterocycles and unactivated arenes with no need for additives (e.g., bases) at ambient temperature. The introduction of an azosulfone group allows for the wavelength selective formation of aryl radicals and aryl cations albeit both species are generated upon solar light irradiation. Furthermore, aryl azosulfones are not simply a stable colored form of diazonium salts. The presence of the azosulfonyl group is able to change the photoreactivity of the corresponding salts as shown in the case

Scheme 1. Wavelength Selective Generation of Aryl Radicals (Ar$^•$) and Aryl Cations (^{3}Ar$^+$)



of **1f** (Table 4). This opens the way to the use of such versatile azosulfones in a wide range of metal-free synthetic protocols.

■ EXPERIMENTAL SECTION

Aromatics used in the experiments (furan, thiophene, 2-methylthiophene, *N*-Boc-pyrrole, benzene, and mesitylene) were commercially available and used as received, except for furan, which was freshly distilled before use. Compounds **3**, **9**, **10**, and **11f** have been characterized by comparison with authentic samples, and their yields calculated by means of GC calibration curves. The reaction course was followed by means of TLC and HPLC analyses (C18 column; eluant: MeOH/water mixture). ^{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. Ion chromatography analyses were performed by means of an instrument equipped with a conductometric detector and an electrochemical suppressor by using the following conditions: eluant, NaHCO$_3$ 0.8 mM + Na$_2$CO$_3$ 4.5 mM; flux, 1 mL min^{-1}; current imposed at detector, 50 mA.

General Procedure for the Synthesis of Arylazo Sulfones 1a–h. Diazonium salts were synthesized by following a known procedure[28] and purified by dissolving in acetone and precipitation by adding cold diethyl ether before use. For the synthesis of **1a–h** we adapted a procedure previously described.[9h] To a cooled (0 °C) suspension of the appropriate diazonium salt (1 equiv, 0.3 M) in CH$_2$Cl$_2$ 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 evaporated. The raw solid was purified by dissolution in cold CH$_2$Cl$_2$ and precipitation by adding *n*-hexane.

*4-Cyanophenylazo mesylate (**1a**):* from 840 mg (3.87 mmol) of 4-cyanobenzenediazonium tetrafluoroborate[29] and 395 mg (3.87 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (13 mL). Compound **1a** was obtained in 52% yield (421 mg, yellow crystalline solid, mp 114.5–115.6 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.08–7.90 (AA′BB′, 4H), 3.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 150.6, 133.6 (CH), 124.6 (CH), 118.0, 117.2, 34.9 (CH$_3$). IR (KBr, ν cm^{-1}): 2922, 2232, 1344, 1334, 1169, 1145, 957. Anal. Calcd for C$_8$H$_7$N$_3$O$_2$S: C, 45.92; H, 3.37; N, 20.08. Found: C, 46.1; H, 3.1; N, 19.8.

*4-Acetylphenylazo mesylate (**1b**):* from 1 g (4.27 mmol) of 4-acetylbenzenediazonium tetrafluoroborate[30] and 436 mg (4.27 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (14 mL). Compound **1b** was obtained in 87% yield (840 mg, orange crystalline solid, mp 120.5–120.9 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.18–8.02 (AA′BB′, 4H), 3.27 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 196.6, 151.1, 141.4, 129.5 (CH), 124.4 (CH), 34.8 (CH$_3$), 26.8 (CH$_3$). IR (KBr, ν cm^{-1}): 1688. Anal. Calcd for C$_9$H$_{10}$N$_2$O$_3$S: C, 47.78; H, 4.45; N, 12.38. Found: C, 47.9; H, 4.4; N, 12.5.

*4-Chlorophenylazo mesylate (**1c**):* from 1.2 g (5.30 mmol) of 4-chlorobenzenediazonium tetrafluoroborate[31] and 541 mg (5.30 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (17.5 mL). Compound **1c** was obtained in 50% yield (577 mg, yellow solid, mp 120.1–120.4 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.92–7.55 (AA′BB′, 4H), 3.22 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 147.2, 141.7, 130.0 (CH), 125.7 (CH), 34.8 (CH$_3$). IR (KBr, ν cm^{-1}): 3052, 2950, 1489, 1345, 1265, 954. Anal. Calcd for C$_7$H$_7$ClN$_2$O$_2$S: C, 38.45; H, 3.23; N, 12.81. Found: C, 38.4; H, 3.1; N, 12.7.

*Phenylazo mesylate (**1d**):* from 1.2 g (6.25 mmol) of benzenediazonium tetrafluoroborate[29] and 638 mg (6.25 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (21 mL). Compound **1d** was obtained in 55% yield (633 mg, orange solid, mp 72.7–73.1 °C dec).[32] ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.00–7.95 (m, 2H), 7.70–7.65 (m, 1H), 7.60–7.55 (m, 2H), 3.24 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 148.9, 135.1 (CH), 129.6 (CH), 124.5 (CH), 34.6 (CH$_3$). IR (KBr, ν cm^{-1}): 3057, 1345, 1266, 1146, 905. Anal. Calcd for C$_7$H$_8$N$_2$O$_2$S: C, 45.64; H, 4.38; N, 15.21. Found: C, 45.5; H, 4.2; N, 15.1.

*4-tert-Butylphenylazo mesylate (**1e**):* from 958 mg (3.99 mmol) of 4-*tert*-butylbenzenediazonium tetrafluoroborate[29] and 407 mg (3.99 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (13 mL). Compound **1e** was obtained in 40% yield (383 mg, orange needles, mp 70.3–71.0 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.92–7.59 (AA′BB′, 4H), 3.22 (s, 3H), 1.39 (s, 9H).^{13}C NMR (75 MHz, CDCl$_3$) δ: 159.7, 146.9, 126.6 (CH), 124.4 (CH), 35.4, 34.6 (CH$_3$), 30.9 (CH$_3$). IR (KBr, ν cm^{-1}): 3055, 2969, 1344, 1265, 1150, 955. Anal. Calcd for C$_{11}$H$_{16}$N$_2$O$_2$S: C, 54.98; H, 6.71; N, 11.66. Found: C, 55.2; H, 6.5; N, 11.4.

*4-Methoxyphenylazo mesylate (**1f**):* from 890 mg (4.01 mmol) of 4-methoxybenzenediazonium tetrafluoroborate[33] and 409 mg (4.01 mmol) of sodium methanesulfinate in CH$_2$Cl$_2$ (14 mL). Compound **1f**[9i] was obtained in 44% yield (378 mg, yellow needles, mp 81.5–82.6 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.97–7.06 (AA′BB′, 4H), 3.96 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 165.6, 143.1, 127.3 (CH), 114.8 (CH), 55.8 (CH$_3$), 34.8 (CH$_3$). IR (KBr, ν cm^{-1}): 3038, 2934, 1603, 1147, 1028. Anal. Calcd for C$_8$H$_{10}$N$_2$O$_3$S: C, 44.85; H, 4.70; N, 13.08. Found: C, 44.7; H, 4.9; N, 13.3.

*3-Cyanophenylazo mesylate (**1g**):* from 960 mg (4.42 mmol) of 3-cyanobenzenediazonium tetrafluoroborate[34] and 496 mg (4.86 mmol, 1.1 equiv) of sodium methanesulfinate in CH$_2$Cl$_2$ (15 mL). Compound **1g** was obtained in 34% yield (314 mg, orange solid, mp 121.9–122.1 °C dec). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.27 (s, 1H), 8.21 (dd, J = 7.9, 1.0 Hz, 1H), 7.97 (dd, J = 7.9, 1.0 Hz, 1H), 7.77 (t, J = 7.9 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 148.9, 137.5 (CH), 130.8 (CH), 128.2 (CH), 127.6 (CH), 116.9, 114.3, 34.9 (CH$_3$). IR (KBr, ν cm^{-1}) 3039, 2229, 1337, 1197, 965.

Anal. Calcd for $C_8H_7N_3O_2S$: C, 45.92; H, 3.37; N, 20.08. Found: C, 45.8; H, 3.4; N, 20.3.

*2-Cyanophenylazo mesylate (**1h**):* from 1.56 g (7.19 mmol) of 2-cyanobenzenediazonium tetrafluoroborate[35] and 808 mg (7.91 mmol, 1.1 equiv) of sodium methanesulfinate in CH_2Cl_2 (24 mL). Compound **1h**[9g] was obtained in 60% yield, (902 mg, orange solid, mp 117.7−118.4 °C dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.02−7.92 (m, 2H), 7.87−7.79 (m, 2H), 3.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.1, 135.0 (CH), 134.0 (CH), 133.8 (CH), 117.2 (CH), 115.9, 115.1, 34.5 (CH_3). IR (KBr, ν cm^{-1}) 3050, 2234, 1341, 1158, 963. Anal. Calcd for $C_8H_7N_3O_2S$: C, 45.92; H, 3.37; N, 20.08. Found: C, 45.7; H, 3.6; N, 20.2.

General Procedure for Solar Light Metal-Free Arylations via Aryl Azosulfones. A solution (5 mL) of the aryl azosulfone (**1**, 0.05−0.1 M) and the (hetero)aromatic (1−2 M) in MeCN−H_2O 9:1 mixture was poured into a glass Pyrex vessel, purged for 10 min with nitrogen, capped, and exposed to solar simulated light (in a Solarbox) or natural sunlight on a window ledge. In some cases, it was found convenient to use LEDs (450 nm, 1 W) or phosphor coated Hg lamps (366 nm ± 20 nm, 15 W) as light sources. After the completion of the reaction (as detected by HPLC analysis), the solvent was removed in vacuo from the photolyzed solution and the end products were isolated by column chromatography (stationary phase, silica gel chromatography; eluant, cyclohexane/ethyl acetate mixture).

*4-(Furan-2-yl)benzonitrile (**2a**):* from 105 mg (0.50 mmol) of **1a** and 365 μL (5 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate from 95:5 to 9:1) afforded 59 mg of **2a** (colorless solid, 70% yield, mp 52.5−53.7 °C, lit.[36] 54−56 °C). A 56% yield of **2a** was obtained when exposing a 0.05 M solution of **1a** in the presence of furan (2 M) to natural sunlight for 3 days (8 h a day). The spectroscopic data of **2a** were in accordance with the literature.[13a] Anal. Calcd for $C_{11}H_7NO$: C, 78.09; H, 4.17; N, 8.28. Found: C, 78.1; H, 4.2; N, 8.0.

*2-(4-(Acetyl)phenyl)furan (**2b**):* from 113 mg of **1b** and 365 μL (0.50 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate from 99:1 to 9:1) afforded 58 mg of **2b** (colorless solid, 62% yield, mp 98.8−100.7 °C, lit.[37] 96−98 °C). Compound **2b** was obtained in 87% yield when irradiating a 0.05 M solution of **1a** in the presence of furan (2 M) in MeCN−H_2O 9:1 (5 mL). The spectroscopic data of **2b** were in accordance with the literature.[27a] Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.1; H, 5.2.

*2-(4-Chlorophenyl)furan (**2c**):* from 109 mg (0.50 mmol) of **1c** and 365 μL (5 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate from 99:1 to 9:1) afforded 84 mg of **2c** (94% yield colorless solid, mp 64.8−66.1 °C, lit.[38a] 65−66 °C). The spectroscopic data of **2c** were in accordance with the literature.[38b] Anal. Calcd for $C_{10}H_7ClO$: C, 67.24; H, 3.95. Found: C, 67.1; H, 4.1.

*2-Phenylfuran (**2d**):* from 92 mg (0.5 mmol, 0.1 M) of **1d** and 365 μL (5 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate 99:1) afforded 50.5 mg of **2d** (oil, 70% yield). The spectroscopic data of **2d** were in accordance with the literature.[39] Anal. Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.1; H, 5.3.

*2-(4-(tert-Butyl)phenyl)furan (**2e**):* from 60 mg (0.25 mmol, 0.05 M) of **1e** and 730 μL (10 mmol, 2 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate from 99:1 to 9:1) afforded 35.5 mg of **2e** (oil, 71% yield). The spectroscopic data of **2e** were in accordance with the literature.[40] Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.0; H, 7.9.

*2-(4-Methoxyphenyl)furan (**2f**):* from 54 mg (0.25 mmol., 0.05 M) of **1f** and 730 μL (10 mmol, 2 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate from 99:1 to 9:1) gave 42.8 mg of **2f** (pale gray solid, 96% yield, mp 48.6−49.0 °C, lit.[41a] 49.7−51.2 °C). The spectroscopic data of **2f** were in accordance with the literature.[41b] Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.8; H, 5.4.

*3-(Furan-2-yl)benzonitrile (**2g**):* from 104 mg (0.5 mmol, 0.1M) of **1g** and 365 μL (5 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/ethyl acetate 95:5) afforded 57.5 mg of **2g** (oil, 68% yield) The spectroscopic data of **2g** were in accordance with the literature.[42] Anal. Calcd for $C_{11}H_7NO$: C, 78.09; H, 4.17; N, 8.28. Found: C, 77.8; H, 4.3; N, 8.1.

*2-(Furan-2-yl)benzonitrile (**2h**):* from 104 mg of **1h**, and 365 μL (5 mmol, 1 M) of furan in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 95:5) gave 60 mg of **2i** (oil, 71% yield). The spectroscopic data of **2h** were in accordance with the literature.[43] Anal. Calcd for $C_{11}H_7NO$: C, 78.09; H, 4.17; N, 8.28. Found: C, 78.4; H, 4.5; N, 8.0.

*4-(Thiophen-2-yl)benzonitrile (**4a**):* from 52 mg (0.25 mmol, 0.05 M) of **1a** and 800 μL (10 mmol, 2 M) of thiophene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate from 99:1 to 9:1) afforded 34 mg of **4a** (pale yellow solid, 74% yield, mp 88.9−89.3 °C, lit.[44a] 88 °C). Compound **4a** was obtained in 68% yield when exposing the reaction vessel to natural sunlight for 3 days (8 h a day). The spectroscopic data of **4a** were in accordance with the literature.[44b] Anal. Calcd for $C_{11}H_7NS$: C, 71.32; H, 3.81; N, 7.56. Found: C, 71.4; H, 3.7; N, 7.3.

*2-(4-(Acetyl)phenyl)thiophene (**4b**):* from 57 mg of **1b** (0.25 mmol, 0.05 M) and 800 μL (10 mmol, 2 M) of thiophene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate from 99:1 to 9:1) gave 38 mg of **4b** (colorless solid, 75% yield, mp 120.5−120.8 °C, lit.[45a] 120−122 °C). The spectroscopic data of **4b** were in accordance with the literature.[45b] Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.4; H, 5.1.

*2-(4-(tert-Butyl)phenyl)thiophene (**4e**):* from 60 mg of **1e** (0.25 mmol, 0.05 M) and 800 μL (10 mmol, 2 M) of thiophene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate from 99:1 to 9:1) afforded 37 mg of **4e** (oil, 69% yield). Compound **3e** was likewise formed in 27% yield as evaluated on the basis of GC calibration curves. The spectroscopic data of **4e** were in accordance with the literature.[46] Anal. Calcd for $C_{14}H_{16}S$: C, 77.72; H, 7.45. Found: C, 77.7; H, 7.3.

*2-(4-Methoxyphenyl)thiophene (**4f**):* from 54 mg (0.25 mmol, 0.05 M) of **1f** and 800 μL (10 mmol, 2 M) of thiophene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate from 99:1 to 9:1) afforded 27 mg of **4f** (pale yellow solid, 57% yield, mp 99.9−101.1 °C, lit.[47a] 102−103 °C). Compound **3f** was likewise formed in 27% yield as evaluated on the basis of GC calibration curves. The spectroscopic data of **4f** were in accordance with the literature.[47b] Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.30. Found: C, 69.7; H, 5.2.

*4-(5-Methylthiophen-2-yl)benzonitrile (**5a**) and 4-(2-methylthiophen-3-yl)benzonitrile (**5′a**):* from 52 mg (0.25 mmol, 0.05 M) of **1a** and 995 μL (10 mmol, 2 M) of 2-methylthiophene. Purification by column chromatography (eluant: cyclohexane/acetate 95:5) gave 36 mg of a mixture containing **5a**[48a] and **5′a**[48b] in a 3:1 ratio (72% overall yield). **5a** (major isomer): ^{1}H NMR (from the mixture, 300 MHz, $CDCl_3$) δ: 7.64 (s, 4H), 7.19−7.16 (d, *J* = 5.3 Hz, 1H), 6.80−6.78 (m, 1H), 2.58 (s, 3H); ^{13}C NMR (from the mixture, 75 MHz, $CDCl_3$) δ: 142.1, 139.5, 138.8, 132.6 (CH), 126.7 (CH), 125.4 (CH), 125.0 (CH), 118.9, 109.8, 15.4 (CH_3). **5′a** (minor isomer): ^{1}H NMR (from the mixture, 300 MHz, $CDCl_3$) δ: 7.74−7.50 (AA′BB′, 4H), 7.20−7.15 (d, *J* = 3 Hz, 1H), 7.10−7.05 (d, *J* = 3 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (from the mixture, 75 MHz, $CDCl_3$) δ: 147.9, 144.2, 136.6, 135.9, 132.1 (CH), 129.0 (CH), 128.4 (CH), 122.3 (CH), 109.9, 14.1 (CH_3).

*2-(4-Cyanophenyl)pyrrole-1-carboxylic acid tert-butyl ester (**6a**):* from 21 mg (0.1 mmol) of **1a** and 84 μL (0.5 mmol, 0.5 M) of *N*-Boc-pyrrole in MeCN−H_2O 9:1 (1 mL). Purification by column chromatography (eluant: cyclohexane/acetate 9:1) gave 11.5 mg of **6a** (pale yellow solid, 43% yield, mp 98.2−98.5 °C, lit.[49] 110−112 °C). Compound **6a** was obtained in 59% yield exposing the reaction vessel to a 450 nm LED (1W) for 15 h. The spectroscopic data of **6a** were in accordance with the literature.[11] Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.6; H, 6.1; N, 10.2.

*1,1′-Biphenyl-4-carbonitrile (**7a**):* from 52 mg of **1a** (0.25 mmol, 0.05 M), and 890 μL (10 mmol, 2 M) of benzene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate from 99:1 to 9:1) gave 33 mg of **7a** (colorless solid, 74% yield, mp 84.1−85.7 °C, lit.[50a] 83−84 °C). Compound **3a** was likewise formed in 14% yield as evaluated on the basis of GC calibration curves. Compound **7a** was obtained in 70% yield when exposing the reaction vessel to natural sunlight for 3 days (8 h a day). Compound **7a** was isolated in 72% yield when carrying out the reaction in neat benzene. The spectroscopic data of **7a** were in accordance with the literature.[50b] Anal. Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.1; H, 5.1; N, 7.9.

*4-(Acetyl)-1,1′-biphenyl (**7b**):* from 57 mg of **1b** (0.25 mmol, 0.05 M) and 890 μL (10 mmol, 2 M) of benzene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 99:1) afforded 22.5 mg of **7b** (colorless solid, 46% yield, mp 117.7−118.2 °C, lit.[51a] 117−118 °C). Compound **3b** was likewise formed in 43% yield as evaluated on the basis of GC calibration curves. Compound **7b** was found in 52% yield when carrying out the reaction in neat benzene. The spectroscopic data of **7b** were in accordance with the literature.[51b] Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.7; H, 6.3.

*4-(tert-Butyl)-1,1′-biphenyl (**7e**):* from 60 mg of **1e** (0.25 mmol, 0.05 M) and 890 μL (10 mmol, 2 M) of benzene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 99:1) gave 30.5 mg of **7e** (colorless solid, 58% yield, mp 45.1−46.7 °C, lit.[52a] 48−49 °C). Compounds **3e** (21% yield) and **9e** (13% yield) were also determined on the basis of GC calibration curves. Compound **7e** was isolated in 53% yield when carrying out the reaction in neat benzene. The spectroscopic data of **7e** were in accordance with the literature.[52b] Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.5; H, 8.4

*4-Methoxy-1,1′-biphenyl (**7f**):* from 54 mg of **1f** (0.25 mmol, 0.05 M) and 890 μL (10 mmol, 2 M) of benzene in MeCN (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 99:1) afforded 32 mg of **7f** (colorless solid, 70% yield, mp 83.6−85.9 °C, lit.[53a] 84−85 °C). Compound **3f** was likewise formed in 12% yield as evaluated on the basis of GC calibration curves. Compound **7f** was found in 51% yield when carrying out the reaction in neat benzene. The spectroscopic data of **7f** were in accordance with the literature.[53b] Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.8; H, 6.4

*2′,4′,6′-Trimethyl-[1,1′-biphenyl]-4-carbonitrile (**8a**):* from 52 mg of **1a** (0.25 mmol, 0.05 M) and 1390 μL (10 mmol, 2 M) of mesitylene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 99:1) gave 31 mg of **8a** (colorless solid, 56% yield, mp 58.4−59.6 °C). Compound **8a** was likewise formed in 71% yield (as evaluated on the basis of GC calibration curves) by irradiating at 366 nm. The spectroscopic data of **8a** were in accordance with the literature.[54] Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.9; H, 6.5; N, 6.6.

*1-(2′,4′,6′-Trimethyl-[1,1′-biphenyl]-4-yl)ethan-1-one (**8b**):* from 57 mg of **1b** (0.25 mmol, 0.05 M) and 1390 μL (10 mmol, 2 M) of mesitylene in MeCN−H_2O 9:1 (5 mL). Purification by column chromatography (eluant: cyclohexane/acetate 99:1) gave 19 mg of **8b** (colorless solid, 32% yield, mp 96.3−96.8 °C, lit.[55a] 95−96 °C). Compound **8b** was likewise formed in 73% yield (as evaluated on the basis of GC calibration curves) by irradiating at 366 nm. The spectroscopic data of **8b** were in accordance with the literature.[55b] Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.7; H, 7.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01619.

> Full experimental details and characterization of the compounds and selected ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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