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Transition-Metal-Free and Visible-Light-Mediated Desulfonylation and Dehalogenation Reactions: Hantzsch Ester Anion as Electron and Hydrogen Atom Donor

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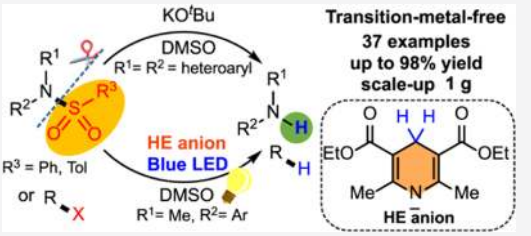
ABSTRACT: Novel approaches for N- and O-desulfonylation under room temperature (rt) and transition-metal-free conditions have been developed. The first methodology involves the transformation of a variety of *N*-sulfonyl heterocycles and phenyl benzenesulfonates to the corresponding desulfonylated products in good to excellent yields using only KO^{t}Bu in dimethyl sulfoxide (DMSO) at rt. Alternately, a visible light method has been used for deprotection of *N*-methyl-*N*-arylsulfonamides with Hantzsch ester (HE) anion serving as the visible-light-absorbing reagent and electron and hydrogen atom donor to promote the desulfonylation reaction. The HE anion can be easily prepared *in situ* by reaction of the corresponding HE with KO^{t}Bu in DMSO at rt. Both protocols were further explored in terms of synthetic scope as well as mechanistic aspects to rationalize key features of desulfonylation processes. Furthermore, the HE anion induces reductive dehalogenation reaction of aryl halides under visible light irradiation.



INTRODUCTION

Many protecting groups were developed for amine functionality and provide desired stability toward acid, basic, reducing, or oxidizing conditions.[1,2] In particular, sulfonamides as nitrogen-protecting groups play an important role in amine chemistry.[3] For instance, benzenesulfonyl or *p*-toluenesulfonyl (tosyl, Ts) groups are easy to introduce, offering extreme robustness and high crystallinity and helping in compound purification.[1] However, drastic conditions are required to remove sulfonyl groups and, consequently, several methodologies to promote desulfonylation reactions have been described. Deprotection methods can be classified into three large families: acidic reductive conditions, reductions in strongly basic media, or electron transfer (ET) cleavage.

The cleavage of N−S bond can be acid-mediated by HBr,[4−6] HCl,[7] H_2SO_4,[7,8] CF_3COOH,[9] CF_3SO_3H,[10] HF-pyridine with anisole,[11] or $CH_3COOH/HClO_4$[12] mostly under very harsh conditions or at high temperatures. Moreover, the N-deprotection method using HBr requires a bromine scavenger such as phenol[4] to avoid monobromination and/or dibromination of the aromatic ring of aniline.

Likewise, many methods using strong bases or nucleophiles are well known, such as NaOH or KOH in MeOH,[13,14] KOH in tetrahydrofuran (THF)/H_2O mixture,[15] NaO^{t}Bu in dioxane,[16] thioglycolate in dimethylformamide (DMF),[17] Cs_2CO_3 in THF/MeOH,[18] $PhMe_2SiLi$ in THF,[19] sodium bis(2-methoxyethoxy)aluminum hydride in benzene or toluene as solvents[20] and *n*-Bu_4NF[21] in dry THF. Despite the large number of N-desulfonylation methodologies in basic media, only a few are useful in industries because long-time reactions and high temperatures are required to obtain the corresponding desulfonylated products. In some cases, a phase-transfer catalyst such as cetyltrimethylammonium bromide is needed due to the low solubility of the amines in the media. The use of MeOH is discouraged by its toxicity and production of toxic methyl *p*-toluenesulfonate as a byproduct, as a consequence of esterification of *p*-toluenesulfonic acid liberated during the reaction. Moreover, Cs_2CO_3 in MeOH produces an *N*-methylated impurity that is difficult to remove during purification processes[18] and also NaOH at reflux in EtOH led to degradation products.[22]

Desulfonylation induced by ET is also widely described. The most common approaches of this type of reductions are promoted by SmI_2,[23−28] Mg/MeOH,[29−33] alkali metals,[34−39] low-valent titanium,[40,41] organic electron donors,[42−44] and electrochemistry.[45−48] In particular, photoinduced ET (PET) has also been applied for desulfonylation reactions.[49] The PET process under UV irradiation using 2-phenyl-*N*,*N*′-dimethylbenzimidazoline as electron and hydrogen donor has been used in tosyl amide deprotection.[50] *N*-sulfonyl indoles

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can be deprotected by a PET reaction with NEt_3 serving as both an electron and proton donor and n-Bu_3SnH serving as a hydrogen atom donor.[51] In 2013, Xiao *et al.* reported N-detosylation of tosyl amides using visible light and iridium as photocatalysts with Hantzsch ester (HE, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate) as electron donor.[52] Moreover, in 2018, Hasegawa and co-workers demonstrated that benzimidazolium naphthoxide betaine and 1,3-dimethyl-2-hydroxynaphthylbenzimidazoline (HONap-BIH) can serve as light-absorbing, electron and hydrogen atom donor for desulfonylation of *N*-sulfonyl-amides and amines.[53,54] Another study of Hasegawa has reported a new visible-light-promoted system for desulfonylation process consisting of benzimidazolium aryloxide betaines (BI^+-ArO^-) and stoichiometric hydride-reducing reagents.[55] More recently, a visible light protocol using Cu complex/HE has just been developed to deprotect N-heterocycles.[56] Finally, an acridine radical as a single-electron reductant has been also used for desulfonylation reactions.[57] However, all of these recent visible light protocols use expensive photocatalysts or even catalysts that are not commercially available.

Over the past few years, Hantzsch esters (HEs) were extensively used in hydrogen transfer reactions.[58] Additionally, with the continuous advances in the visible light photocatalysis field,[59−61] HEs have also been used as an electron donor and a proton source in a large number of photoredox processes.[62] In this sense, a wide range of organic transformations involve the use of transition-metal photocatalysts in combination with HEs as reductants.[63−68] Other recent reports demonstrated the formation of an electron donor−acceptor (EDA) complex between HE and *N*-alkoxyl derivatives, *N*-acyloxyphthalimides, *N*-alkyl-pyridinium salts, or heteroaryl *N*-oxides to undergo PET in the absence of a photocatalyst under visible light irradiation.[69−72] Furthermore, HE in the presence of a base was recently used as a visible-light catalyst to obtain alkenes and diaryl sulfinates.[73,74]

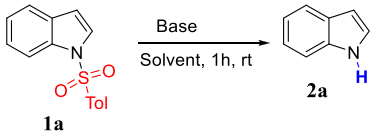
In this context, the development of a convenient, practical, and more economical method to cleavage N−S bonds avoiding the use of high temperatures, harmful solvents, and expensive transition-metal catalysts is highly desired. Herein, we describe two efficient transition-metal-free protocols whose application is related to the nature of the sulfonamide moiety. KO^{t}Bu in dimethyl sulfoxide (DMSO) at room temperature (rt) provides a clean approach for deprotection of *N*-sulfonyl heterocycles and phenyl benzenesulfonates.[53] However, for *N*-methyl-*N*-arylsulfonamides, a stronger reductive method for an effective desulfonylation is needed. Thus, the use of the anion of HE to promote the deprotection of *N*-methyl-*N*-arylsulfonamides under visible light irradiation was explored. In this work, the HE anion is easily prepared *in situ* by reaction of the commercial HE with KO^{t}Bu in DMSO. Additionally, HE anion absorbs light in the visible region; hence, this protocol does not require a transition-metal photocatalyst or an absorbing light complex.

Finally, mechanistic insights were explored to understand the difference in reactivity and the mechanisms involved. The scope of these two methods of N−S (or O−S) cleavage was successfully examined using a large variety of *N*-sulfonyl heterocycles, *N*-sulfonylamines, and even phenyl benzenesulfonates. Furthermore, the use of HE anion as visible-light-absorbing reagent was studied in the reduction of several aryl and heteroaryl halides (RX) including iodide, bromide, and chloride derivatives.

RESULTS

N-Tosylated indole **1a** was selected as a model substrate to optimize our N-desulfonylation reaction conditions. As summarized in Table 1, **2a** was obtained in 49% yield when

Table 1. N-Desulfonylation Reaction of *N*-Indole 1a[a]



1a **2a**

entry	conditions[a]	yields **2a**[b]
1	3 equiv KO^{t}Bu, DMF	49
2	3 equiv KO^{t}Bu, DMSO	96 (91)[c]
3	3 equiv KO^{t}Bu, THF	26
4	3 equiv KO^{t}Bu, EtOH	<5
5	1.1 equiv KO^{t}Bu, DMSO	48
6	3 equiv K_2CO_3, DMSO	–
7	3 equiv Cs_2CO_3, DMSO	–
8	3 equiv KOH, DMSO	–
9	3 equiv KOH, 65 °C, DMSO	12
10	3 equiv NaH, DMSO	21
11	3 equiv NaO^{t}Bu, DMSO	84

[a]The reaction was carried out under N_2 atmosphere using **1a** (1 equiv, 0.1 mmol) and base in 1 mL of solvent, and the mixture was protected from light with aluminum foil. [b]Yields were quantified by gas chromatography (GC) using internal standard method. [c]Isolated yield.

the reaction was carried out in DMF for 1 h, using three equivalents of KO^{t}Bu at rt (Table 1, entry 1). Notably, yield was increased to 96% when DMSO was employed as a solvent (entry 2). A variety of solvents revealed that the reaction media had a significant impact on the reaction efficiency. THF and ethanol did not work well for this desulfonylation process, and **2a** was obtained in 26% yield and traces, respectively, after 1 h (entries 3 and 4). Incomplete conversion was observed when the amount of KO^{t}Bu was lowered (entry 5). Base effect was also examined (entries 6−11), showing that the reaction did not work using K_2CO_3, Cs_2CO_3 or KOH at rt and only 12% yield of **2a** was obtained when the reaction was carried out with KOH at 65 °C.[13] Moreover, 21 and 84% yields of **2a** were obtained when other bases such as NaH and NaO^{t}Bu were employed. This environmentally friendly methodology avoided the use of transition-metal[56] or phase-transfer catalysts,[15] toxic solvents, and high-temperature conditions.[13]

Once optimal reaction conditions were determined, several heterocycles were deprotected using only KO^{t}Bu in DMSO at rt. The results are shown in Table 2. A complete N-desulfonylation of *N*-tosyl 7-azaindole (**1b**), benzotriazole (**1c**), and pyrrole (**1d**) was achieved after 1 h (entries 1−3), whereas only 47% yield of carbazole was obtained under identical conditions (entry 4). Other sulfonyl-protecting groups were tested, such as benzenesulfonyl, 2-chlorobenzenesulfonyl and 2-nitrobenzenesulfonyl (*o*-Ns) groups (substrates **1f−h**), and desulfonylated product **2a** was also obtained in very good yields (entries 5−7). Additionally, desulfonylation reaction of compound **1f** was carried out at higher concentrations to demonstrate the practical utility of this methodology. Product **2a** was successfully obtained without a decrease in the isolated yield when 0.5 mmol of

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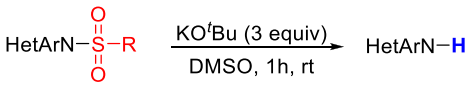
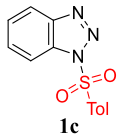
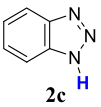
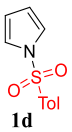
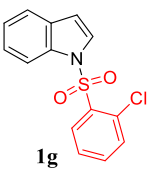
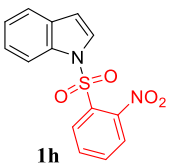
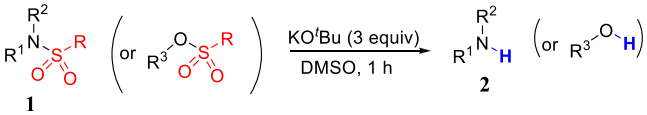
Table 2. N-Desulfonylation of Indoles and Related Heterocycles[a]

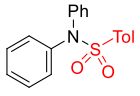
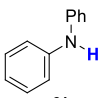
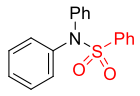
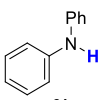
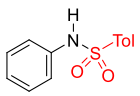
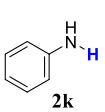
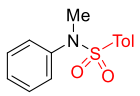
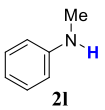
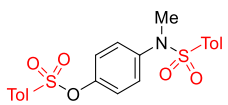
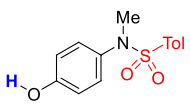
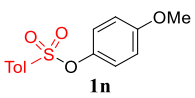
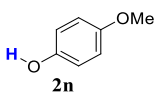
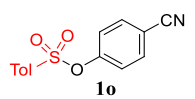
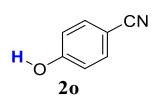
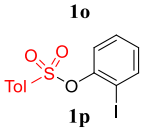
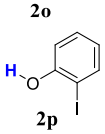
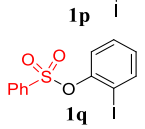
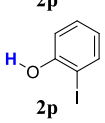


Entry	Substrate	Product	Yield (%)[b]
1	 1b	 2b	87
2	 1c	 2c	67
3	 1d	 2d	99
4	 1e	 2e	47 (1 h) 48 (3 h)[c]
5	 1f	 2a	91, 88,[d] 86[e]
6	 1g	 2a	88
7	 1h	 2a	93

[a]The reaction was carried out under N_2 atmosphere using **1** (1 equiv, 0.1 mmol) and KO^{t}Bu (3 equiv) in DMSO (1 mL), and the mixture was protected from light with aluminum foil. [b]Isolated yields after column chromatography. [c]*N*-Tosylcarbazole (**1e**) was recuperated in 50% yield. [d]Reaction carried out 5 times more concentrated (0.5 mmol of **1f** in 1 mL of DMSO). [e]Reaction carried out starting from 1 g of **1f** in 7.8 mL.

Table 3. N-Detosylation of Amino and Sulfonate Moieties[a]



Entry	Substrate	Product	Yield (%)[b]
1	 1i	 2i	72
2	 1j	 2i	--
3	 1k	 2k	--
4	 1l	 2l	10
5[c]	 1m	 2m	44[c,d]
6	 1n	 2n	74 (75)[c]
7	 1o	 2o	89 (90)[c]
8	 1p	 2p	88 (93)[c]
9	 1q	 2p	80

[a]The reaction was carried out under N_2 atmosphere using **1** (1 equiv, 0.1 mmol) and KO^{t}Bu (3 equiv) in DMSO (1 mL), and the mixture was protected from light with aluminum foil. [b]Yields were quantified by GC using internal standard method. [c]Isolated yield. [d]Using 5 equiv of KO^{t}Bu for 3 h.

1f in DMSO was employed or even when the reaction was scaled up to 1 g (3.9 mmol, entry 5).

Next, our attention was focused on the scope of this desulfonylation process to deprotect different *N*-arylsulfonamides and phenyl benzenesulfonates. For instance, *N*,*N*-diphenyl tosylamine (**1i**) was chosen as a representative derivative of aromatic *p*-toluenesulfonamides, giving the desufonylted product **2i** in 72% yield (Table 3, entry 1). However, *N*,*N*-diphenyl benzenesulfonamide (**1j**) and unsubstituted or *N*-methylsubstituted aromatic sulfonamides (**1k** and **1l**) did not give the corresponding products **2i**, **2k**, or **2l** (Table 3, entries 2–4). These results led us to explore the possibility of carrying out selectively the removal of *p*-toluenesulfonyl group. In this way, the polytosylated substrate **1m** was tested and benzenesulfonate moiety could be selectively deprotected in the presence of *p*-toluenesulfonamide moiety, giving **2m** in moderate isolated yield (entry 5). There are a few examples of removing sulfonyl groups from sulfonates, such as KOH in refluxing MeOH,[75] KOH with ^{t}BuOH in toluene at 100 °C,[76] *n*-PrSLi in hexamethylphosphoramide (HMPA) at 180 °C,[77] or using photochemical process via PET.[78,79] Thus, other benzenesulfonate substrates

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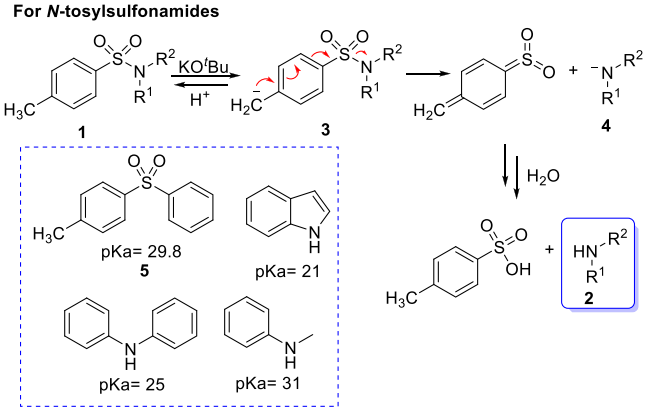
were studied following our protocol, such as 4-methoxyphenyl 4-methylbenzenesulfonate (**1n**), 4-cyanophenyl 4-methylbenzenesulfonate (**1o**), 2-iodophenyl 4-methylbenzenesulfonate (**1p**), and 2-iodophenyl benzenesulfonate (**1q**), giving the corresponding phenols **2n**–**p** in very good yields (74–89%) and using only KO^{t}Bu in DMSO at rt.

A plausible mechanism for the desulfonylation reaction, which is consistent with the observations described above, is shown in Scheme 1. Although the pK_a (methyl group) of

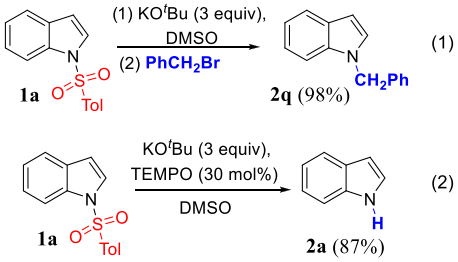
Scheme 1. Possible Mechanism of N-Detosylation Reactions in Basic Medium



toluenesulfonamide is unknown, it can be approximated to that of 1-methyl-4-(phenylsulfonyl)benzene (**5**), whose pK_a is 29.8[80] in DMSO. Therefore, the *N*-tosylsulfonamide forms the corresponding anion **3** in the presence of KO^{t}Bu (^{t}BuOH, pK_a = 32.2),[81] which was indicated by the observation that the solution turned blue. The N–S bond of anion **3** could fragment to produce amide anion **4**, which after protonation finally gives the deprotected product **2**. This fragmentation is thermodynamically controlled by the acidity (pK_a value) of the final deprotected product **2**. Since the conjugate base of compound **5** is more basic than those of indole (pK_a = 21.0 in DMSO)[82] and diphenylamine (pK_a = 25.0 in DMSO),[83] this process is favored for *N*-tosyl indole (**1a**) and diphenyl *N*-tosylamine (**1i**). Meanwhile, for *N*-methyl-*N*-phenyltosylamine (**1l**), this fragmentation does not take place due to the higher pK_a value for *N*-methyl-*N*-phenylamine (pK_a = 30.6 for aniline in DMSO).[83]

A different mechanism for the deprotection of *N*-benzenesulfonamides is proposed, involving a direct attack of the base to the sulfur atom (Scheme 2). This behavior explains the reactivity of **1f**–**h** with phenyl, 2-chlorophenyl, and 2-nitrophenyl as substituents. This mechanism could also explain the lack of reactivity for *N*,*N*-diphenyl benzenesulfonamide (**1j**) due to a high steric hindrance for the nucleophilic attack of the base.

To demonstrate the presence of a polar mechanism, the reaction of **1a** was quenched with benzyl bromide and benzyl indole (**2q**) was obtained in quantitative isolated yield (eq 1). In addition, the reaction of **1a** with KO^{t}Bu was carried out in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical-trapping agent, and a similar yield of **2a** was obtained (87% yield), indicating the absence of radicals as intermediates (eq 2).



Regarding the lack of reactivity of **1j** and **1l** substrates under the proposed polar mechanism (Table 3, entries 2 and 4), we decided to explore PET for N-desulfonylation reactions. As dimsyl anion is able to form aryl and alkyl radicals from RX under visible light irradiation,[84,85] we carried out the reaction for substrate **1j** with KO^{t}Bu in DMSO under irradiation using UV–vis lamps (λ > 350 nm) for 3 h giving the desulfonylation product **2i** in 65% yield (Table 4, entry 1). Moreover, product **2i** was obtained in 88% yield when UV–vis lamps were replaced by using 3 W blue light-emitting diodes (LEDs) (entry 2). To rule out homolytic fragmentation, a photoinduced reaction was performed in the absence of base and substrate **1j** was recovered in quantitative yield (entry 3). When the same conditions were applied to substrate **1r**, the desulfonylated product **2l** was given in only 20% yield (entry 4). Probably, the reduction potential of the excited dimsyl anion (unknown) could not achieve the ET to initiate the reaction. As some anions of substituted dihydro ethyl benzoates and quinoline previously prepared in liquid ammonia have been used as hydrogen donors in reductive reactions,[86,87] we proposed HE anion as both an electron and hydrogen atom donor to promote the desulfonylation reaction of *N*-methyl-*N*-arylsulfonamides as an alternative strategy to [Ir(ppy)$_2$(dtb-bpy)PF$_6$]/HE[52] and Cu complex/HE.[55]

Therefore, the reaction of **1r** with 1 equiv of HE and 1.1 equiv of KO^{t}Bu for 17 h using blue LED afforded product **2l** in 46% yield (Table 4, entry 5). Furthermore, a higher yield was observed when the reaction was carried out employing 2.2 equiv of KO^{t}Bu (73% of **2l**, entry 6). Notably, the yield was increased to 79 and 88% when higher amounts of HE (1.3 and 1.5 equiv) were used (entries 7 and 8). Finally, product **1r** was obtained in 98% yield when 2 equiv of HE were employed (entry 9). No reaction is detected under dark conditions (entry 10) discarding a spontaneous ET or polar mechanism. Moreover, a similar yield of **2l** was given when the reaction was carried out in 1 h, reducing considerably the reaction time (entry 11). No product **2l** was obtained in the absence of base (entry 12) or when other bases and reducing reagents such as NEt$_3$ or *N*-ethyldiisopropylamine (DIPEA)

Scheme 2. Possible Reaction Mechanism for Deprotection of *N*-Benzenesulfonamides

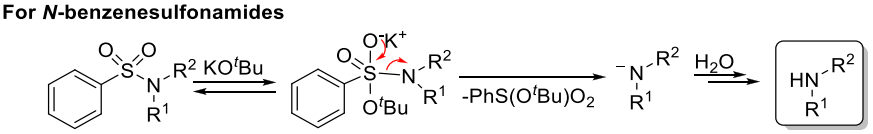


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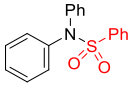
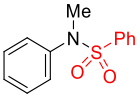
Table 4. Photodesulfonylation of 1j and 1r in DMSO[a]

Entry	Substrate	Conditions	Time (h)	Yield[b]
1[c]	 **1j**	hν (λ> 350 nm), KO^{t}Bu (3 equiv)	3	**2i**, 65
2	**1j**	KO^{t}Bu (3 equiv)	3	**2i**, 88
3	**1j**	Without base	3	**2i**, --
4	 **1r**	KO^{t}Bu (3 equiv)	1	**2l**, 20
5	**1r**	HE (1 equiv) , KO^{t}Bu (1.1 equiv)	17	**2l**, 46
6	**1r**	HE (1 equiv) , KO^{t}Bu (2.2 equiv)	17	**2l**, 73
7	**1r**	HE (1.3 equiv) , KO^{t}Bu (2.2 equiv)	17	**2l**, 79
8	**1r**	HE (1.5 equiv) , KO^{t}Bu (2.2 equiv)	17	**2l**, 88
9	**1r**	HE (2 equiv) , KO^{t}Bu (2.2 equiv)	17	**2l**, 98 (95)[d]
10	**1r**	Dark, HE (2 equiv) , KO^{t}Bu (2.2 equiv)	17	**2l**, --
11	**1r**	HE (2 equiv) , KO^{t}Bu (2.2 equiv)	1	**2l**, 98
12	**1r**	HE (2 equiv)	1	**2l**, --
13	**1r**	DIPEA (2 equiv)	1	**2l**, --
14	**1r**	NEt_3 (2 equiv)	1	**2l**, --
15	**1r**	1,1-diphenylethene (0.5 equiv), HE (2 equiv), KO^{t}Bu (2.2 equiv)	1	**2l**, 77
16	**1r**	TEMPO (30 mol%), HE (2 equiv), KO^{t}Bu (2.2 equiv)	1	**2l**, 68

[a]Unless otherwise noted, the photostimulated reaction conditions were established under N_2 atmosphere using **1** (1 equiv, 0.1 mmol), base, and/or additive in DMSO (1 mL) with blue LED (3 W) in a sealed tube. [b]Yields were quantified by GC using the internal standard method. [c]Irradiation was conducted in a photochemical reactor equipped with two HPIT 400 W lamps (λ ≥ 350 nm). [d]Isolated yield.

were used as control experiments (entries 13 and 14). Finally, the desulfonylation was carried out in the presence of TEMPO and 1,1-diphenylethylene as radical scavengers and the reaction was partially inhibited (entries 15 and 16). We suggest that radical formation could be involved in the key step of this mechanism (Scheme 3).

A proposed mechanism for photoinduced N-desulfonylation reaction in the presence of HE anion is shown in Scheme 3. HE anion is easily prepared *in situ* by reaction of HE with KO^{t}Bu in DMSO as a solvent. Anion formation is rapidly detected due to the color of the solution (orange), indicating that the HE anion is the visible-light-absorbing reagent (λ_{max} = 475 nm).[88] After irradiation, ET occurs between the photoexcited HE anion and *N*-methylarylsulfonylamine **1**, forming the corresponding radical anion of the substrate (initial step) and HE radical. The N−S bond cleavage in these radical anions can generate either N-centered anions or radicals depending on the nature of the N-substituent. It is known that *N*-tosyl-*N*,*N*-phenylamine (**1i**) and *N*-benzyl-*N*-phenyl *p*-toluenesulfonamide fragments to give aminyl radicals ($Ph_2N^•$ and $Ph(Bn)N^•$)[43,53] and sulfonate anions ($TolSO_2^-$) (step 1). A fast hydrogen transfer from the HE anion to aminyl radical affords product **2** and the HE radical anion. Alternatively, sulfonate anion can deprotonate HE radical to give the corresponding HE radical anion and sulfonic acid. The driving force for this reaction is the rearomatization of the HE anion (or HE radical) to give the HE radical anion (step 2). Following, ET from the HE radical anion to **1** gives a pyridine derivative and *N*-methylarylsulfonylamides radical anion to continue the radical chain process (step 3). Finally, the intermediate aminyl radical can generate the reductive product **2**, removing a hydrogen from the HE radical (final step).

Next, several *N*-methyl-*N*-arylsulfonamides (**1l** and **1s**−**ab**) were examined under the same photoinduced conditions in the presence of HE anion (Table 5). Desulfonylation reaction exhibited high functional group tolerance and yields. For ortho- or para-substituted sulfonamides with electron-donat-

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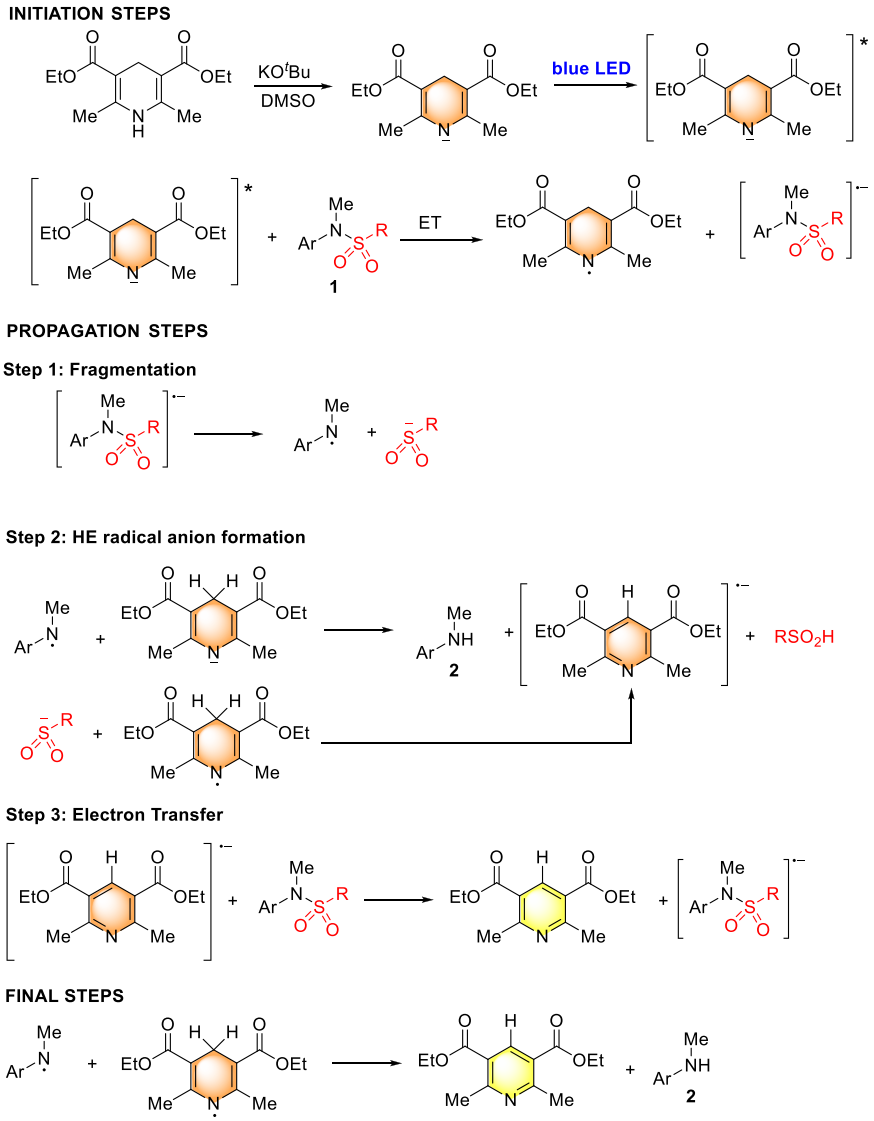
Scheme 3. Proposed Photodesulfonylation Reaction Mechanism Using HE Anion as Visible-Light-Absorbing Reagent and Electron and Hydrogen Atom Donor



ing and electron-withdrawing groups, the reaction gives the desired products in regular to excellent yields (37−98% yields, entries 1−11). Furthermore, similar yields were also obtained if tosyl- or benzenesulfonyl-protecting groups were used.

For *N*-(4-iodophenyl)-*N*-methylbenzenesulfonamide (**1aa**, Table 5, entry 10), the dehalogented product **2l** was obtained as the main product. Regarding this result and the mechanism presented in Scheme 4, the formation of radical anion **1aa**$^{\bullet-}$ as an intermediate is proposed (Scheme 4). This radical anion has two possible reaction pathways. First, a C−I bond fragmentation may occur to give radical **6**, which after reduction affords intermediate **7** (path A). This intermediate can also react with HE anion under photostimulated conditions to finally yield the product **2l**. The other possibility is a N−S bond fragmentation to give anion **8**, which finally provides product **9** with retention of iodine atom (path B). In this case, path B was discarded because **9** was not detected. This result suggests that C−I fragmentation rate giving radical **6** is faster than N−S fragmentation to give **9**. Furthermore, it confirms the presence of radical anions as intermediates in the proposed photoinduced reaction (Scheme 3). Otherwise, C−I fragmentation was not observed for substrates **1p** and **1q** in the first approach (KO^{t}Bu in DMSO at rt; Table 3, entries 8 and 9), showing an important difference between both examined mechanisms.

PET also provides an alternative route for dehalogenation reactions. In recent years, Pd,[89] Ir,[90] Cu,[91] Pt complex,[92] and Ni supported on carbon nitride[89] have been used to undergo reductions of aryl halides under visible light irradiation. Particularly, dehalogenation and aryl radical generation could also be achieved using many visible light organic photoreductants[93−95] or photocatalyts.[96−102] To further explore our visible-light-promoted method, reduction reaction of aryl or heteroaryl halides in the presence of HE anion was studied. As shown in Table 6, aryl chloride, bromide, and iodide derivatives are dehalogenated (entries 1−10) in good to excellent yields under visible light irradiation using HE anion as electron and hydrogen atom donor. We finally suggest that the oxidation potential of the photoexcited HE anion ($E_{oxHE}{}^*/_{HE}{}^{\bullet-}$ = −2.490 V)[103] is higher than that of the photoexcited dimsyl anion, which does not effectively reduce aryl bromides or chlorides.[84,85]

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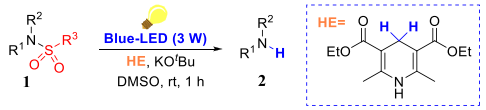
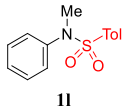
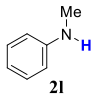
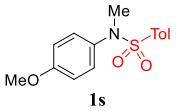
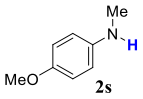
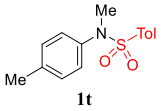
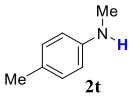
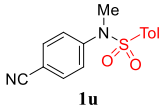
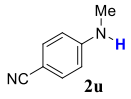
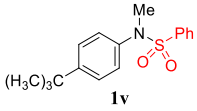
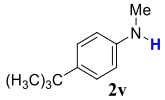
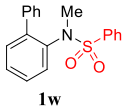
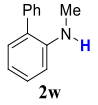
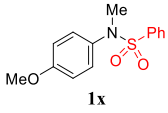
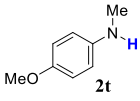
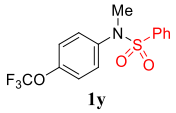
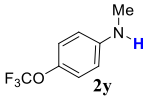
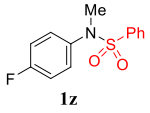
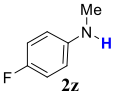
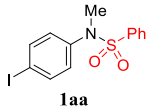
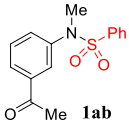
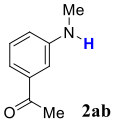
Table 5. Substrate Scope Examination of Photodesulfonylation Reaction[a]



Entry	Substrate	Product	Yield[b]
1	 **1l**	 **2l**	51
2	 **1s**	 **2s**	95(80)[c]
3	 **1t**	 **2t**	98
4	 **1u**	 **2u**	93[c]
5	 **1v**	 **2v**	97 (80)[c]
6	 **1w**	 **2w**	98 (90)[c]
7	 **1x**	 **2t**	64
8	 **1y**	 **2y**	58[c]
9	 **1z**	 **2z**	85
10	 **1aa**	 **2l**	37
11	 **1ab**	 **2ab**	90 (85)[c]

[a]The photostimulated reaction was carried out under N_2 atmosphere using **1** (1 equiv, 0.1 mmol), HE (2 equiv), and KO^{t}Bu (2.2 equiv) in DMSO (1 mL) using 3 W blue LED, at rt in a sealed tube. [b]Yields were quantified by GC using internal standard method. [c]Isolated yields.

CONCLUSIONS

To summarize, in this work, we presented two green synthetic methodologies toward the desulfonylation process under transition-metal-free and rt conditions. The first methodology proceeds under mild reaction conditions using only KO^{t}Bu in DMSO at rt, where a variety of *N*-sulfonyl heterocycles and phenyl benzenesulfonates were effectively deprotected. This strategy involves a polar mechanism very sensitive to both electronic and steric effects. The second methodology involves a visible-light-promoted method utilizing HE anion as electron and hydrogen atom donor and blue LED as a light source. In this way, several *N*-methyl-*N*-arylsulfonamides have given the corresponding products in good to excellent yields. Furthermore, the reaction was highly tolerant to a variety of functional groups and was successfully scaled up to 1 g. Moreover, this methodology was also expanded to aryl halides substrates and it is noteworthy that even the ArCl reacts giving ArH with good yields. HE anion as visible-light-absorbing reagent does not require previous preparation and is a convenient alternative to expensive transition-metal photocatalysts.

EXPERIMENTAL SECTION

General Methods. Purification of desired compounds was done by column chromatography on silica gel. Gas chromatographic (GC) analysis was performed with a flame ionization detector, on a 30 m capillary column of film thickness 0.32 mm × 0.25 μm, with a 5% phenylpolysiloxane phase. Gas chromatography/mass spectroscopy (GC/MS) analysis was performed employing an electronic impact (EI) ionization method and a 25 m × 0.2 mm × 0.33 μm column with a 5% phenylpolysiloxane phase. ^{1}H NMR and ^{13}C NMR{^{1}H} spectra were recorded on 400 and 500 MHz in spectrometers with $CDCl_3$ or acetone-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Additional ^{19}F NMR spectra were recorded for fluorinated compounds using a 377 MHz spectrometer, with $CDCl_3$, acetone-d_6 (CD_3COCD_3), or DMSO-d_6 ($CD_3S(O)CD_3$) as solvents. Coupling constants are given in hertz (Hz), and chemical shifts are reported in δ values in parts per million (ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. All new products were further characterized by two-dimensional (2D) NMR techniques (^{1}H/^{1}H correlation spectroscopy (COSY), ^{1}H/^{13}C heteronuclear single-quantum coherence (HSQC), and ^{1}H/^{13}C heteronuclear multiple-bond correlation spectroscopy (HMBC)) and high-resolution mass spectrometry (HRMS). HRMS analyses were carried out using a time-of-flight mass spectrometry (TOF-MS) instrument with an electrospray ionization (ESI) source. Photoinduced reactions were conducted with blue LED (λ = 465 ± 20 nm) at 3 W of potency and 700 mV of current emission spectra (Figure S1) and HPIT 400 W lamps ($\lambda \geq$ 350 nm, Figure S2). The apparatus and irradiation setup are shown in Figure S3.

Materials. 1*H*-Indole (**2a**), 1*H*-pyrrolo[2,3-*b*]pyridine (**2b**), 1*H*-benzo[*d*][1,2,3]triazole (**2c**), 1*H*-pyrrole (**2d**), 9*H*-carbazole (**2e**), *N*,*N*-diphenylamine (**2i**), 4-methoxyphenol (**2n**), 4-hydroxybenzonitrile (**2o**), 2-iodophenol (**2p**), aniline, benzyl bromide, 4-methoxyaniline, 4-methylaniline, 4-aminobenzonitrile, 4-(*tert*-butyl)-aniline, [1,1′-biphenyl]-2-amine, 4-(trifluoromethoxy)aniline, 4-fluoroaniline, 4-iodoaniline, 4-aminophenol, 3-aminoacetophenone, benzenesulfonyl chloride, 2-chlorobenzenesulfonyl chloride, 2-nitrobenzenesulfonyl chloride, 2-iodonaphthalene (**10a**), 1-bromonaphthalene (**10b**), 1-chloronaphthalene (**10c**), 9-bromoanthracene (**10d**), 9-bromophenanthrene (**10e**), 4-bromo-1,1′-biphenyl (**10f**), 3-iodopyridine (**10g**), 2-chloropyridine (**10h**), 4-bromobenzonitrile (**10i**), 4-chlorobenzonitrile (**10j**), naphthalene (**11a**), anthracene (**11d**), phenanthrene (**11e**), biphenyl (**11f**), pyridine (**11g**), cyanobenzene (**11i**), KO^{t}Bu, NaO^{t}Bu, K_2CO_3, Cs_2CO_3, KOH, NaOH, NaH (60% in mineral oil),

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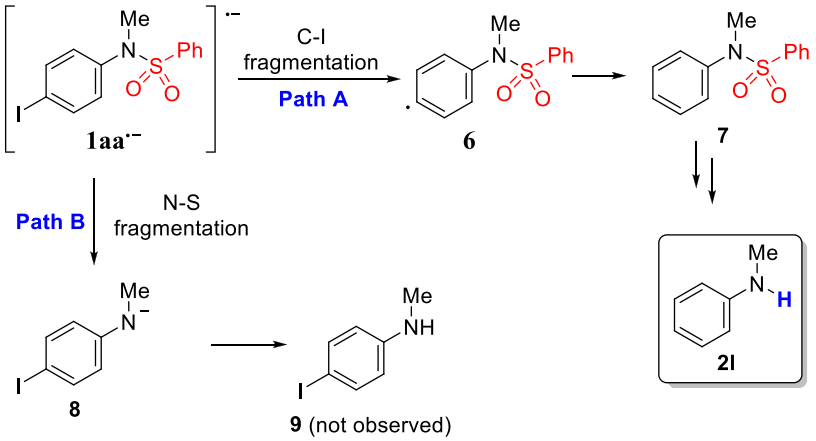
Scheme 4. Possible Fragmentations of Radical Anion 1aa$^{\bullet-}$



NH_4NO_3, NH_4Cl, tetrabutylammonium hydrogen sulfate, Na_2SO_4, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), Hantzsch ester, NEt_3, DIPEA, 1,1-diphenyl ethene, and pyridine were purchased from commercial suppliers and used without further purification. DMSO, DMF, THF, CH_2Cl_2, and toluene were distilled and dried under molecular sieves (3 Å). All solvents were of analytical grade. The silica used in column chromatography corresponds to silica gel 60 (0.063−0.200 mm).

Typical Procedures for Synthesis of Sulfonamides. *Method A.* The reaction was carried out in a Schlenk tube equipped with an inert N_2 inlet and magnetically stirred at rt. In the Schlenk tube, DMSO (5 mL) was dried and deoxygenated, KO^{t}Bu (1.0 equiv, 112 mg, 1 mmol) was added, and the mixture was protected from light with aluminum foil. Then, the corresponding NH-heterocycle or aniline (1 equiv, 1 mmol) and benzenesulfonyl chloride (1.2 equiv, 1.2 mmol) were added and the reaction mixture was stirred overnight (18 h). After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess and the residue was extracted with EtOAc or CH_2Cl_2 (3 × 30 mL), the organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to leave the crude products. The reaction was analyzed with TLC, GC, and isolated with column chromatography over silica gel.

For details of methods B to E, see the Supporting Information (SI).

Characterization Data of Synthesized Sulfonamides. *1-[(2-Chlorophenyl)sulfonyl]-1H-indole (**1g**).* The title compound was obtained according to method B and was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 80:20). A light yellow solid was isolated in 71% yield (0.71 mmol, 207 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.2, 1.8 Hz, 1H), 7.74 (d, J = 3.7 Hz, 1H), 7.71−7.65 (m, 1H), 7.60−7.54 (m, 1H), 7.51−7.39 (m, 3H), 7.25−7.18 (m, 2H), 6.67 (d, J = 3.7 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 136.4, 134.8, 134.5, 132.9, 132.4, 131.2, 130.6, 127.9, 127.2, 124.3, 123.3, 121.5, 113.0, 107.5. ^{1}H/^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 8.15/7.51−7.39, 7.74/6.67, 7.71−7.65/7.60−7.54, 7.60−7.54/7.25−7.18, 7.51−7.39/7.51−7.39. ^{1}H/^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.15/131.4, 7.74/127.9, 7.71−7.65/113.0, 7.60−7.54/121.5, 7.51−7.39/134.8, 7.51−7.39/132.4, 7.51−7.39/127.2, 7.25−7.18/123.3, 7.25−7.18/124.3, 6.67/107.5. ^{1}H/^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.15/132.9, 8.15/134.8, 7.74/107.5, 7.74/130.6, 7.74/134.5, 7.71−7.65/132.4, 7.71−7.65/130.6, 7.60−7.54/124.3, 7.60−7.54/134.5, 7.51−7.39/127.2, 7.51−7.39/131.2, 7.51−7.39/132.4, 7.51−7.39/132.9, 7.51−7.39/136.4, 7.25−7.18/113.0, 7.25−7.18/121.5, 7.25−7.18/130.6, 7.25−7.18/134.5, 6.67/127.9, 6.67/130.6, 6.67/134.5. GC/MS EI m/z 293 (M^+ + 2, 9), 291 (M^+, 22), 117 (10), 116 (100), 111 (27), 90 (11), 89 (61), 75 (35), 63 (37), 51 (10), 50 (17). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{11}ClNO_2S$ 292.0194; found 292.0189.

Methylation of Synthesized Sulfonamides (Method F). The reaction was carried out in a round-bottom flask equipped with a magnetic stirred bar. KO^{t}Bu was added (1.1 equiv) to a solution of sulfonamide (1 equiv) in DMSO (2 mL); then, iodomethane (3 equiv) was slowly added. The resulting mixture was stirred at rt overnight. Water was added, the crude was extracted with EtOAc (3 × 30 mL), and the layers were separated. The organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to leave the crude products. The reaction was analyzed with thin-layer chromatography (TLC), GC, and isolated with column chromatography over silica gel.

*N-(4-(tert-Butyl)phenyl)-N-methylbenzenesulfonamide (**1v**).* **1v** was obtained from **1v−s** and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20). A colorless oil was isolated in 74% yield (0.73 mmol, 223 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 3.16 (s, 3H), 1.30 (s, 9H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 150.5, 138.8, 136.9, 132.6, 128.7, 127.9, 126.2, 125.8, 38.2, 34.6, 31.3. ^{1}H/^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.59−7.57/7.46, 7.30/7.00, 3.16/3.16, 1.30/1.30. ^{1}H/^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59−7.57/127.9, 7.59−7.54/132.6, 7.46/128.7, 7.30/125.5, 7.00/126.2, 3.16/38.2, 1.30/31.3. ^{1}H/^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59−7.57/127.9, 7.59−7.57/132.6, 7.46/128.7, 7.46/136.9, 7.30/125.8, 7.30/138.8, 7.00/126.2, 7.00/138.8, 7.00/150.5, 3.16/138.8, 1.30/31.3, 1.30/34.6, 1.30/150.5. GC/MS EI m/z 304 (M^+ + 1, 2), 303 (M^+, 14), 288 (20), 162 (45), 147 (24), 146 (25), 141 (11), 132 (21), 118 (12), 91 (21), 78 (11), 77 (100), 51 (42). HRMS (ESI-TOF$^+$) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_2S$: 304.1366; found 304.1383.

*N-([1,1′-Biphenyl]-2-yl)-N-methylbenzenesulfonamide (**1w**).* **1w** was obtained from **1w−s** and was purified by column chromatography on silica gel eluting with pentane/EtOAc (90:10 → 70:30). A brown solid was isolated in 80% yield (1.33 mmol, 431.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.53 (m, 3H), 7.44−7.34 (m, 9H), 7.28−7.23 (m, 1H), 7.01 (d, J = 7.8 Hz, 1H), 2.99 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 142.4, 139.3, 139.1, 138.8, 132.5, 131.5, 129.1, 128.8, 128.4, 128.1, 128.1, 127.8, 127.7, 127.2, 39.2. ^{1}H/^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.60−7.54/7.46−7.35, 7.46−7.35/7.29−7.25, 7.46−7.35/7.00, 7.29−7.25/7.00, 3.00/3.00. ^{1}H/^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.60−7.54/127.8, 7.60−7.54/132.5, 7.46−7.35/127.2, 7.46−7.35/128.1, 7.46−7.35/128.4, 7.46−7.35/128.8, 7.46−7.35/129.1, 7.46−7.35/131.5, 7.29−7.25/128.1, 7.00/127.7, 3.00/39.2. ^{1}H/^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.60−7.54/127.8, 7.60−7.54/132.5, 7.60−7.54/127.8, 7.46−7.35/127.2, 7.45−7.35/127.7, 7.46−7.35/127.8, 7.46−7.35/128.1, 7.46−7.35/128.8, 7.46−7.35/129.1, 7.46−7.35/138.8, 7.46−7.35/139.3, 7.46−7.35/142.4, 7.29−7.25/131.5, 7.29−7.25/139.1, 7.00/128.4, 7.00/142.4, 3.00/139.1. GC/MS EI

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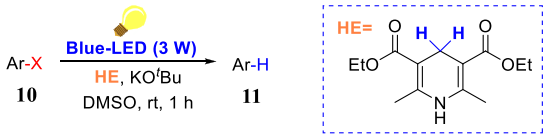
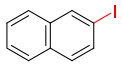
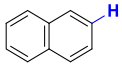
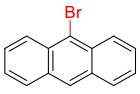
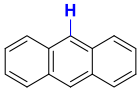
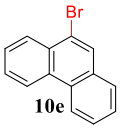
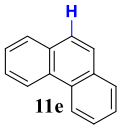
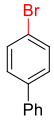
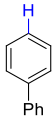
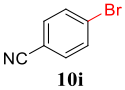
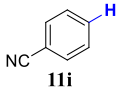
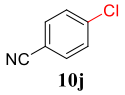
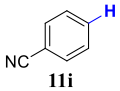
Table 6. Photoinduced Reduction of ArX with HE Anion[a]



Entry	Substrate	Product	Yield[b]
1	 **10a**	 **11a**	81
2	 **10b**	 **11a**	82
3	 **10c**	 **11a**	90
4	 **10d**	 **11d**	89
5	 **10e**	 **11e**	93
6	 **10f**	 **11f**	76
7	 **10g**	 **11g**	59
8	 **10h**	 **11g**	66
9	 **10i**	 **11i**	45
10	 **10j**	 **11i**	40

[a]The photostimulated reaction (1 h) was carried out under N_2 atmosphere using **10** (1 equiv, 0.1 mmol), HE (2 equiv), and KO^{t}Bu (2.2 equiv) in DMSO (1 mL) using 3 W blue LED, at rt in a sealed tube. [b]Yields were quantified by GC using the internal standard method.

m/z 323 (M^+, 1), 182 (66), 181 (26), 180 (28), 167 (85), 166 (14), 152 (15), 115 (11), 77 (100), 51 (54), 50 (11). HRMS (ESI-TOF$^+$) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S$ 324.1053; found 324.1077.

*N-Methyl-N-(4-(trifluoromethoxy)phenyl)benzenesulfonamide (**1y**).* **1y** was obtained from **1y–s** and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20). A brown oil was isolated in 70% yield (0.7 mmol, 232 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.45 (m, 5H), 7.16–7.10 (m, 4H), 3.16 (s, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$) δ 147.9, 140.0, 136.2, 133.0, 128.9, 128.0, 127.8, 121.3, 38.1. $^1H/^1H$ COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.61–7.45/7.61–7.45, 7.16–7.10/7.16–7.10, 3.16/3.16. $^1H/^{13}C$ HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.61–7.45/127.8, 7.61–7.45/128.9, 7.61–7.45/133.0, 7.16–7.10/121.3, 7.16–7.10/128.0, 3.16/38.1. $^1H/^{13}C$ HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.61–7.45/127.8, 7.61–7.45/128.9, 7.61–7.45/133.0, 7.61–7.45/136.1, 7.16–7.10/121.3, 7.16–7.10/128.0, 7.16–7.10/139.9, 7.16–7.10/147.9, 3.16/139.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ −58.0. GC/MS EI *m/z* 332 (M^+ + 1, 2), 331 (M^+, 15), 190 (81), 162 (11), 95 (20), 92 (11), 78 (11), 77 (100), 69 (16), 66 (12), 65 (11), 51 (61), 50 (16). HRMS (ESI-TOF$^+$) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{13}F_3NO_3S$ 332.0563; found 332.0572.

One-Pot Synthesis of N-Methyl-N-arylsulfonamides. **1s**, **1t**, **1x**, **1z**, and **1ab** were prepared by a one-pot synthesis starting from the corresponding anilines (2 mmol). First, the sulfonylation reaction was carried out according to methods A–E, and second, without purification, methylation reaction proceeded.

*N-(4-Fluorophenyl)-N-methylbenzenesulfonamide (**1z**).* **1z** was obtained from 4-fluoroaniline according to methods E and methylation reaction and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20). A brown oil was isolated in 79% global yield (1.57 mmol, 416 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.44 (m, 5H). 7.06–6.95 (m, 4H), 3.16 (s, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 248 Hz, 1C), 137.4 (d, *J* = 3, 1C), 136.3, 132.8, 128.8, 128.5 (d, *J* = 9 Hz, 2C), 127.8, 115.7 (d, *J* = 23 Hz, 2C), 38.3. $^1H/^1H$ COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.61–7.44/7.61–7.44, 7.06–6.95/7.06–6.95, 3.16/3.16. $^1H/^{13}C$ HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.61–7.44/127.8, 7.61–7.44/128.8, 7.61–7.44/132.8, 7.06–6.95/115.7, 7.06–6.95/128.5, 3.16/38.3. $^1H/^{13}C$ HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.61–7.44/127.8, 7.61–7.44/128.8, 7.61–7.44/132.8, 7.61–7.44/136.3, 7.06–6.95/115.7, 7.06–6.95/128.5, 7.06–6.95/137.4, 7.06–6.95/161.5, 3.16/137.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.8. GC/MS EI *m/z* 266 (M^+ + 1, 2), 265 (M^+, 17), 124 (100), 122 (14), 97 (26), 96 (29), 95 (41), 77 (80), 75 (21), 57 (13), 51 (51), 50 (15). HRMS (ESI-TOF$^+$) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{13}FNO_2S$ 266.0646; found 266.0654.

*N-(3-Acetylphenyl)-N-methylbenzenesulfonamide (**1ab**).* **1ab** was obtained from 1-(3-amino phenyl)ethan-1-one according to method B and methylation reaction and was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 75:25). An orange oil was isolated in 65% global yield (1.3 mmol, 373.4 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 1H), 7.62–7.37 (m, 8H), 3.20 (s, 3H), 2.56 (s, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$) δ 197.1, 142.0, 137.7, 136.0, 133.0, 131.4, 129.1, 128.8, 127.7, 127.1, 125.7, 37.9, 26.6. $^1H/^1H$ COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.87–7.85/7.62–7.37, 3.20/3.20, 2.56/2.56. $^1H/^{13}C$ HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.87–7.85/121.1, 7.62–7.37/125.7, 7.62–7.37/133.0, 7.62–7.37/127.7, 7.62–7.37/129.1, 7.62–7.37/128.8, 7.62–7.37/131.4. $^1H/^{13}C$ HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.87–7.85/125.7, 7.87–7.85/134.4, 7.87–7.85/197.1, 7.62–7.37/127.1, 7.62–7.37/127.7, 7.62–7.37/128.8, 7.62–7.37/131.4, 7.62–7.37/133.0, 7.62–7.37/136.0, 7.62–7.37/137.7, 7.62–7.37/142.0, 7.62–7.37/197.1, 3.20/142.0, 2.56/197.1. HRMS (ESI-TOF$^+$) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}NO_3S$ 290.0845; found 290.0860.

Desulfonylation Reactions in Dark Conditions. The desulfonylation reaction was carried out in a Schlenk tube equipped with an inert N_2 inlet and magnetically stirred at rt. In the Schlenk tube, DMSO (1 mL) was dried and deoxygenated; then, the corresponding sulfonamide (1 equiv, 0.1 mmol) and KO^{t}Bu (3 equiv, 0.3 mmol) were added and the mixture was protected from light with aluminum foil. After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess and the residue was extracted with EtOAc (3 × 30 mL), and the organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to leave the crude products.

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Yields were quantified by GC employing the internal method using biphenyl as the internal standard.

Photodesulfonylation Reactions under Visible Light Irradiation. The photodesulfonylation reactions were carried out in a vial at rt and under N_2 atmosphere and irradiated with blue LED (3 W) using 1 equiv (0.1 mmol) of sulfonamide, 2.2 equiv of KO^{t}Bu (0.22 mmol), and 2 equiv of Hantzsch ester (0.2 mmol) in DMSO (1 mL of previously dried and deoxygenated). After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess and the residue was extracted with EtOAc (3 × 30 mL), and the organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to leave the crude products. Yields were quantified by GC using the internal method employing 9*H*-carbazole as the internal standard.

*Characterization Data of Desulfonylation Products (**2**).* 1*H*-Indole (**2a**), 1*H*-pyrrolo[2,3-*b*]pyridine (**2b**), 1*H*-benzo[*d*][1,2,3]-triazole (**2c**), 1*H*-pyrrole (**2d**), 9*H*-carbazole (**2e**), diphenylamine (**2i**), aniline (**2k**), 4-methoxyphenol (**2n**), 4-hydroxybenzonitrile (**2o**), 2-iodophenol (**2p**), and 1-benzyl-1*H*-indole (**2q**) were identified by comparing with authentic samples (GC/flame ionization detector (FID) and GC/MS).

*1H-Indole (**2a**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20) in 91% yield (0.091 mmol, 10.6 mg) as a white solid. Starting from 0.5 mmol of substrate, 88% isolated yield (0.44 mmol, 51.5 mg) was obtained. For large-scale reaction, the isolated yield was 86% (3.6 mmol, 423 mg) starting from 1.080 g of substrate.

*1H-Pyrrolo[2,3-b]pyridine (**2b**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20) in 87% yield (0.087 mmol, 10.2 mg) as a white solid.

*1H-Benzo[d][1,2,3]triazole (**2c**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20) in 67% yield (0.067 mmol, 8.0 mg) as a white solid.

*1H-Pyrrole (**2d**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20) in 99% yield (0.099 mmol, 6.6 mg) as a colorless oil.

*9H-Carbazole (**2e**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20) in 47% yield (0.047 mmol, 7.8 mg) as a white solid.

*Diphenylamine (**2i**).* The title compound was obtained in 72% yield (0.072 mmol, 12.2 mg) as a brown solid.

*4-Methoxyphenol (**2n**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (50:50) in 75% yield (0.075 mmol, 9.3 mg) as a light-pink solid.

*4-Hydroxybenzonitrile (**2o**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (50:50) in 90% yield (0.09 mmol, 10.7 mg) as a white solid.

*2-Iodophenol (**2p**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (50:50) in 93% yield (0.093 mmol, 20.5 mg) as a gray solid.

*1-Benzyl-1H-indole (**2q**).* The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (80:20) in 98% yield (0.098 mmol, 20.3 mg) as a colorless oil.

*N-Methylaniline (**2l**).*[104] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 50:50) in 95% yield (0.095 mmol, 10 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.7 Hz, 2H), 3.64 (s br, 1H), 2.80 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 149.3, 129.1, 117.2, 112.3, 30.6. GC/MS EI m/z 108 (8, M$^+$ + 1), 107 (81 M$^+$), 106 (100), 79 (33), 78 (14), 77 (39), 65 (14), 51 (23), 50 (8).

*N-(4-Hydroxyphenyl)-N,4-dimethylbenzenesulfonamide (**2m**).*[105] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 50:50). A brown oil was isolated in 44% yield (0.014 mmol, 4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.26−7.24 (m, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 5.19 (s br, 1H), 3.12 (s, 3H), 2.42 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 154.9, 143.5, 134.4, 133.6, 129.3, 128.4, 128.0, 115.6, 38.4, 21.5. GC/MS EI m/z 279 (M$^+$ + 2, 1), 278 (M$^+$ + 1, 2), 277 (M$^+$, 10), 123 (7), 122 (100), 94 (19), 91 (11), 65 (18).

*4-Methoxy-N-methylaniline (**2s**).*[106] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 70:30). A light yellow oil was isolated in 80% yield (0.08 mmol, 9.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.82−6.78 (m, 2H), 6.61−6.57 (m, 2H), 3.75 (s, 3H), 2.80 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 152.1, 143.7, 114.9, 113.6, 55.8, 31.6. GC/MS EI m/z 138 (M$^+$ + 1, 4), 137 (M$^+$, 61), 122 (100), 94 (60), 77 (13), 67 (13), 66 (12), 65 (35), 63 (23), 53 (18), 52 (26), 51 (15), 50 (8).

*4-Methyl-N-methylaniline (**2t**).*[104] The title compound was obtained in 98% yield (0.098 mmol, 11.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 8.5 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 3.51 (s br, 1H), 2.80 (s, 3H), 2.24 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 147.2, 129.7, 126.4, 112.6, 31.1, 20.3. GC/MS EI m/z 122 (M$^+$ + 1, 7), 121 (M$^+$, 93), 120 (100), 106 (13), 91 (41), 89 (10), 79 (12), 78 (15), 77 (26), 65 (25), 63 (16), 60 (12), 53 (11), 52 (18), 51 (26), 50 (16).

*4-Cyano-N-methylaniline (**2u**).*[107] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (80:20 → 50:50) as a colorless oil and isolated in 50% yield (0.05 mmol, 6.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.6 Hz, 2H), 6.55 (d, J = 8.6 Hz, 2H), 4.25 (s br, 1H), 2.88 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 152.2, 133.7, 120.4, 111.8, 30.0. GC/MS EI m/z 133 (M$^+$ + 1, 7), 132 (M$^+$, 74), 131 (100), 104 (22), 102 (14), 77 (17), 76 (13), 75 (14), 66 (12), 64 (11), 63 (13), 51 (15), 50 (11).

*4-(tert-Butyl)-N-methylaniline (**2v**).*[106] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20) as a colorless oil and isolated in 80% yield (0.08 mmol, 13.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 3.57 (s br, 1H), 2.82 (s, 3H), 1.28 (s, 9H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 147.0, 140.1, 126.0, 112.2, 33.8, 31.6, 31.0. GC/MS EI m/z 164 (M$^+$ + 1, 3), 163 (M$^+$, 28), 149 (11), 148 (100), 133 (16), 120 (21), 108 (12), 107 (13), 91 (13), 77 (16), 65 (12), 50 (3).

*N-Methyl-[1,1′-biphenyl]-2-amine (**2w**).*[104] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 90:10) as a light yellow oil and isolated in 86% yield (0.086 mmol, 15.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.40 (m, 4H), 7.35−7.32 (m, 2H), 7.08 (dd, J =7.4, 1.2 Hz, 1H), 6.76 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H), 4.09 (s br, 1H), 2.78 (s, 3H).

*4-(Trifluoromethoxy)-N-methylaniline (**2y**).*[107] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 70:30) as a colorless oil and isolated in 58% yield (0.058 mmol, 11.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.8 Hz, 2H), 6.54−6.52 (m, 2H), 3.72 (s br, 1H), 2.8 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 148.1, 140.4, 122.3, 120.8 (q, J = 255 Hz, 1C), 112.5, 30.7. GC/MS EI m/z 192 (M$^+$ + 1, 6), 191 (M$^+$,60), 190 (16), 123 (10), 122 (100), 106 (11), 95 (16), 94 (54), 79 (12), 78 (12), 77 (32), 75 (11), 69 (36), 67 (15), 66 (15), 65 (38), 64 (16), 63 (21), 53 (17), 52 (23), 51 (14).

*4-Fluoro-N-methylaniline (**2z**).*[107] The title compound was obtained in 85% yield (0.085 mmol, 10.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93−6.86 (m, 2H), 6.55−6.51 (m, 2H), 3.32 (s br, 1H), 2.80 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 155.8 (d, J = 234, 1C), 145.7, 115.6 (d, J = 22 Hz, 2C), 113.1 (d, J = 7 Hz, 2C), 31.3. GC/MS EI m/z 126 (M$^+$ + 1, 7), 125 (M$^+$, 89), 124 (100), 97 (32), 96 (20), 95 (20), 83 (23), 77 (17), 75 (18), 62 (15), 57 (12).

*1-(3-(Methylamino)phenyl)ethan-1-one (**2ab**).*[108] The title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 70:30) as a white solid in 85% yield (0.085 mmol, 12.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.26 (m, 2H), 7.20−7.18 (m, 1H), 6−81−6.78 (m, 1H), 3.90 (s br, 1H), 2.88 (s, 3H), 2.58 (s, 3H).

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Photoinduced Reduction of Aryl Halides in Presence of HE. Photostimulated reduction was carried out under N_2 atmosphere using 1 equiv (0.1 mmol) of the corresponding aryl halide, 2 equiv of HE and KO^{t}Bu (2.2 equiv) in DMSO (1 mL), and irradiating with 3 W blue LED at rt. DMSO was previously dried and deoxygenated. After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess. The residue was extracted with EtOAc (3 × 30 mL), and the organic layers were combined, washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to leave the crude products. Yields were quantified by GC using the internal method using 9*H*-carbazole as the internal standard. Naphthalene (**11a**), anthracene (**11d**), phenanthrene (**11e**), biphenyl (**11f**), pyridine (**11g**), and cyanobenzene (**11i**) were identified by comparing with authentic samples (GC/FID and GC/MS).

*Naphthalene (**11a**).* The title compound was obtained in 81% yield (0.081 mmol, 10.4 mg) as a white solid.

*Anthracene (**11d**).* The title compound was obtained in 89% yield (0.089 mmol, 15.9 mg) as a white solid.

*Phenanthrene (**11e**).* The title compound was obtained in 93% yield (0.093 mmol, 16.5 mg) as white solid.

*Biphenyl (**11f**).* The title compound was obtained in 76% yield (0.076 mmol, 11.6 mg) as a white solid.

*Pyridine (**11g**).* The title compound was obtained in 59% yield (0.059 mmol, 4.67 mg) as a colorless oil.

*Cyanobenzene (**11i**).* The title compound was obtained in 45% yield (0.045 mmol, 4.6 mg) as a colorless oil.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01523.

Extra experimental details, UV−vis spectra, ^{1}H NMR and ^{13}C NMR{^{1}H} spectra for substrates and products, emission spectrum for blue LEDs and HPIT 400 W lamps ($\lambda \geq 350$ nm, Figures S1 and S2); UV−vis spectra (Figures S3−S6); light sources (Table S1); sulfonylation (Table S2); and methylation of sulfonamides (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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