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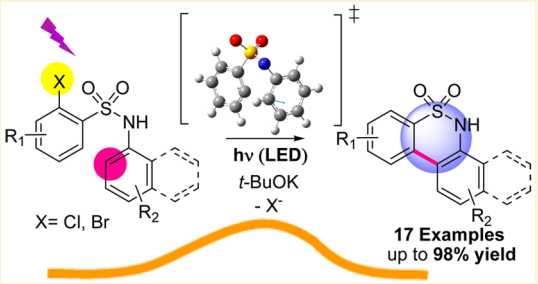
Synthesis of Dibenzosultams by "Transition-Metal-Free" Photoinduced Intramolecular Arylation of *N*-Aryl-2-halobenzenesulfonamides

Walter D. Guerra, Roberto A. Rossi, Adriana B. Pierini,* and Silvia M. Barolo*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

Supporting Information

ABSTRACT: A new and general synthetic route to prepare dibenzosultams is here reported. This approach involves the synthesis of *N*-aryl-2-halobenzenesulfonamides (**3**), followed by intramolecular C−C photoinduced arylation under soft conditions without the use of "Transition Metal". The photostimulated reactions exhibit very good tolerance to different substituent groups with good to excellent isolated yields (42−98%) of products. Moreover, it is shown that LED (λ = 395 nm) is an efficient light energy source to initiate efficiently the reactions. Theoretical inspection of the mechanism was made to probe the involvement of the radical-anion $S_{RN}1$ process.



INTRODUCTION

Sulfonamides and their derivatives are known as "sulfa drugs" and are widely used in medicine.[1] This group is an important organic structure within the drug discovery field. Compounds with benzothiazine dioxide or benzosultam core exhibit versatile inhibitory properties against a diverse array of enzymes such as COX-2,[2] HIV integrase,[3] or Calpain-1.[4] Also, benzothiazine dioxide derivatives have been found to play an active role in nuclear factor-κappaB (NFκB) down regulation.[5]

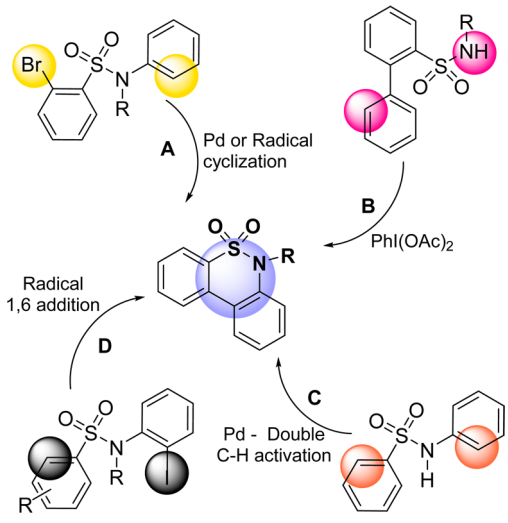
Because of the remarkable importance of benzosultams across medicinal chemistry, many synthetic approaches have been developed.[6] For dibenzosultams, the synthetic approaches are less known and are represented in Scheme 1. These protocols include intramolecular radical cyclization[7] or palladium-catalyzed intramolecular arylation[8] of 2-bromo-*N*-alkyl-*N*-arylbenzenesulfonamides (**A**), intramolecular oxidative amination of 2-arylbenzenesulfonamides under "Transition-Metal-Free" conditions (**B**),[9] double C(sp_2)−H palladium-catalyzed intramolecular oxidative coupling of *N*-arylbenzene-sulfonamides (**C**),[10] or 1,6 radical addition of *N*-(2-iodo-phenyl)-*N*-methyl-benzenesulfonamide (**D**)[11] (Scheme 1).

Radical nucleophilic substitution involving electron-transfer (ET) steps ($S_{RN}1$)[12] is a cyclic process with radicals and radical anions as intermediates. In the $S_{RN}1$ reactions, carbanions and anions derived from heteroatoms can be used as nucleophiles to form new C−C or C−heteroatom bonds. This mechanism has proven to be an important synthetic strategy in heterocycle chemistry.

The intramolecular $S_{RN}1$ has been successfully developed to obtain different annulated systems bearing between 5 and 9 members with broad substitution tolerance.[13] In this context, the reaction of 2-iodobenzenesulfonamide with aliphatic ketone enolates to afford 3-substituted benzothiazines has been reported.[14] However, the reactivity of *N*-aryl-2-halobenzene-sulfonamides under $S_{RN}1$ conditions to obtain dibenzosultams has not been studied yet.

It is important to notice that, despite that useful synthetic protocols have been investigated to prepare dibenzosultams, still several limitations remain like the use of "Transition Metal" (Pd), activated substrates like iodide or bromide aromatic precursors, harsh conditions, or time-consuming reactions which need to be overcome.

Scheme 1. Strategies To Synthesize Dibenzosultams



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In this context, we developed a novel protocol to synthesize dibenzosultams by intramolecular C−C photoinduced arylation of 2-halo-arylsulfonamides. This protocol involves chloride precursors easily prepared from commercial sources. Besides, the heterocycle could be obtained with a free N-H group that is easily functionalized. Furthermore, the utility of this method is fully demonstrated by exploring the scope toward a broad family of dibenzosultams and greener methodologies. This is a new contribution within our efforts devoted to the synthesis of heterocyclic compounds by "Transition-Metal-Free" intramolecular photoinduced arylation reactions.[13a]

RESULTS AND DISCUSSION

Initially, we investigated different alternatives to obtain *N*-aryl-2-halobenzenesulfonamides **3** (Scheme 2). The first strategy involves copper-catalyzed *N*-arylation of 2-chlorobenzenesulfonamide (**1**) with aryl halides **2**[15] (Method A). Under our optimized conditions,[16] the reaction of **1** with iodobenzene (**2a**) gave the coupling product *N*-phenyl-2-chlorobenzenesulfonamide (**3a**, Ar = Ph, X = Cl) in 78% isolated yield. This protocol was extended to different aryl halides, obtaining good to very good isolated yields (50−78%) of the corresponding *N*-aryl-2-chloroarylsulfonamides (**3b−f**, **m−n**, X = Cl) (Scheme 2).

The other strategy to afford the corresponding sulfonamides **3** involves a known reaction between substituted benzenesulfonyl chlorides **4** and different arylamines **5** with pyridine in DCM (CH_2Cl_2) at room temperature (Method B).[17] With this methodology, we synthesized sulfonamides **3g−l**, **o−r** with a range of isolated yields from moderate to excellent depending on the corresponding amine (30−97%) (Scheme 2).[18]

N-Phenyl-2-chlorobenzenesulfonamide (**3a**) was chosen as a model substrate to attempt the intramolecular arylation using *t*-BuOK in DMSO. In this basic medium, the initially neutral **3a** (λ_{max} = 279 and 281 nm) undergoes an acid−base reaction to give the corresponding anion **3a**$^-$ (continuum absorption spectrum until 370 nm; see the SI).[19]

After 3 h of irradiation (HPI-T metal iodide lamps (400 W)), the reaction of **3a** in DMSO with 2 equiv of *t*-BuOK afforded the desired product, 6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (**6a**) in 27% yield, together with 45% of the starting material (entry 1, Table 1). Encouraged by this result, various combinations of irradiation times and equivalents of base were screened (entries 2−5), finding that 3 equiv of *t*-BuOK and 3 h of irradiation gave the best result (97% (86% isolated yield)).[20]

Scheme 2. Synthesis of *N*-Aryl-2-haloarylsulfonamides

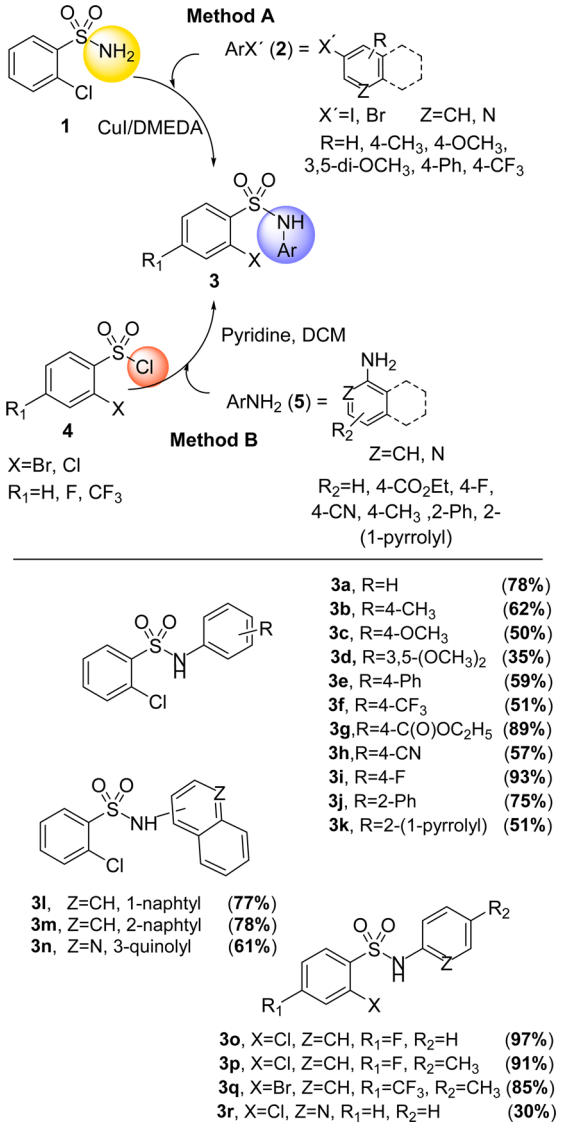
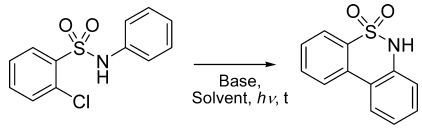


Table 1. Optimization of the Reaction Conditions[a]



3a 6a

	conditions	yields (%)[b]	
entry	solvent/base (equiv)/hν, *t* (h)	3a[c]	6a
1	DMSO/*t*-BuOK (2)/hν, 3 h	45	27
2	DMSO/*t*-BuOK (2)/hν, 4 h	27	53
3	DMSO/*t*-BuOK (2)/hν, 6 h	23	57
4	DMSO/*t*-BuOK (3)/hν, 2 h	13	75
5	**DMSO/*t*-BuOK (3)/hν, 3 h**	**0**	**97 (86)**
6[d]	NH_3/*t*-BuOK (3)/hν, 3 h	4	95 (84)
7[e]	THF/*t*-BuOK (3)/hν, 3 h	75	15
8[e]	CH_3CN/*t*-BuOK (3)/hν, 3 h	18	72
9	DMSO/NaH (3)/hν, 3 h	0	75
10	DMSO/*t*-BuOK (3)/hν, 1.5 h	21	64
11[f]	DMSO/*t*-BuOK (3)/hν, 1.5 h	0	92
12	DMSO/*t*-BuOK (3)/dark, 3 h	91	0
13[g]	DMSO/*t*-BuOK (3)/hν, 1.5 h	97	0
14[h]	DMSO/*t*-BuOK (3)/hν, 1.5 h	79	13

[a]The reactions were run in 5 mL of solvent with 0.03 M of **3a** and 0.09 M of *t*-BuOK and irradiated for the specific time. Irradiation was conducted in a photochemical reactor equipped with two Philips metal iodide HPI-T 400 W lamps (air and water refrigerated). [b]Yields were determined by GC (internal standard method). Isolated yields are given in parentheses. [c]Substrate **3a** recovered. [d]The reaction of liquid ammonia ($NH_{3(liq)}$) was run in 200 mL (−33 °C), with 0.75 mM of **3a** and 2.25 mM of *t*-BuOK. [e]The reactions in THF or CH_3CN were run in 5 mL. [f]1 equiv of pinacolone was added with respect to the substrate. [g]0.3 equiv of *m*-DNB was added with respect to the substrate. [h]1 equiv of TEMPO was added with respect to the substrate.

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The other solvents tested were $NH_{3(liq)}$, CH_3CN, and THF. Similar results were obtained in liquid ammonia (−33 °C) (entry 6, Table 1). In CH_3CN, the reaction gave a very good yield (72%), and THF proved to be ineffective for the reaction (entries 7 and 8, respectively, Table 1).

When the reaction was carried out without *t*-BuOK (NaH as base), it proceeded completely, which indicates that anion **3a**$^-$ could initiate the reaction (entry 9, Table 1). Also, the reaction time could be shortened under entrainment conditions such as in the presence of pinacolone enolate ions (entry 11 versus entry 10, Table 1).

Mechanistically, it is important to notice that there was no reaction under dark conditions (entry 12, Table 1). The photostimulated reaction was completely inhibited by *m*-dinitrobenzene (*m*-DNB) (entry 13 versus entry 10, Table 1),[12c] and equimolecular quantities of TEMPO could partially inhibit the reaction (entry 14 versus entry 10, Table 1). These results exclude a benzyne and other polar mechanisms and evidence an electron transfer (ET) process with formation of radicals. We propose a radical-anion type mechanism ($S_{RN}1$) to be in play.

To extend the scope of the cyclization reaction, sulfonamides previously synthesized were submitted to the *t*-BuOK/DMSO/*hν* system, the results being shown in Scheme 3. Modifying the R-substituent in the *N*H-phenyl moiety of the sulfonamides, with EWG or EDG, **3b−k**, led to full conversion of the substrate after 5 h of irradiation, providing products **6b−k** in good to excellent isolated yields (54−98%). This reveals broad substitution tolerance (CH_3, OCH_3, *di*-OCH_3, CF_3, F, CN, $C(O)OC_2H_5$, Ph) and low steric hindrance (tolerate *o*-substitution, **6j−k**).

The strategy was extended successfully to obtain fused dibenzosultams after longer irradiation times. 5*H*-Benzo[*e*]-naphtho[1,2-*c*][1,2]thiazine 6,6-dioxide (**6n**) and 6*H*-benzo-[5,6][1,2]thiazino[3,4-*c*]quinoline 5,5-dioxide (**6l**) were obtained after 6 h with 97% and 69% yields, respectively. 6*H*-Benzo[*e*]naphtho[2,1-*c*][1,2]thiazine 5,5-dioxide (**6m**) was obtained in good yield (51%) after 8 h of irradiation without full conversion of the substrate.

The effect of modifying the R-substituent in the sulfonyl-phenyl system was also examined. Substrates with an EWG like F or CF_3 (**3o−q**) were prepared. In these cases, the reaction underwent partially without full conversion after 8 h to afford the corresponding dibenzosultams **6o−q** with moderate yields (∼45%).

Finally, we attempted the reaction of 2-chloro-*N*-(pyridin-2-yl)benzenesulfonamide (**3r**) as substrate, with a pyridine system, but it was unreactive under our experimental conditions.

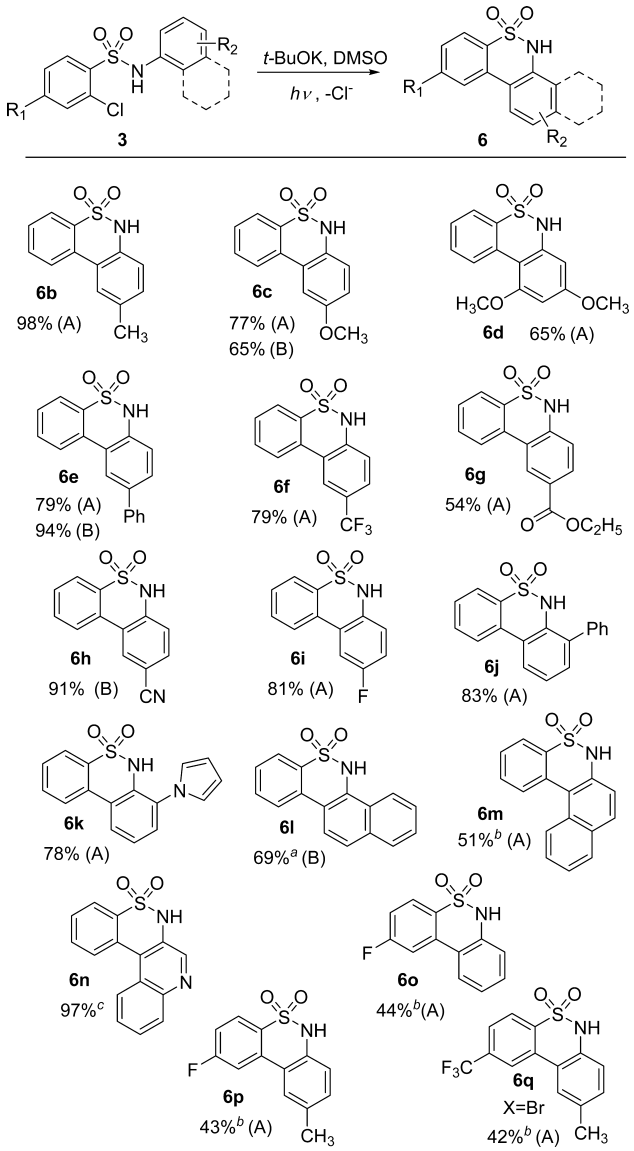
In order to accomplish the goal of sustainable chemistry, we changed the conventional "workup" and purification processes to direct filtration and recrystallization, which led to a reduction in wastes and in the use of solvents. With this methodology, we synthesized dibenzosultams **6c,e,h,l**, with a range of isolated yields from moderate to excellent (Scheme 3).

To extend our study, the irradiation source was changed to LED light. Chemical transformations via visible-LED light is one of the emerging strategies to achieve the increasing demand for more sustainable chemical processes due to their ultra-efficient lighting and low cost.[21]

The results under visible-LED light are summarized in Table 2. Employing a Violet LED light (λ_{max} = 395 nm), the reaction undergoes full conversion, obtaining 82% yields of **6a** (entry 1, Table 2).[22] For other studied substrates **3b,i,j,l,m** (entries 2−6, Table 2), the yields obtained were comparable to the classical irradiation source under the same irradiation time. It is interesting to notice that employing this source of irradiation, substrates like **3m,o,p** achieved full conversion with very good yields of dibenzosultams **6m,o,p** (76−94%), showing the efficiency of LED lights (compare Scheme 3 with entries 6−8, Table 2).

To support our experimental evidence of a radical-anion type mechanism ($S_{RN}1$), we performed a computational study of key mechanistic intermediates and reactive pathways with anion **3a**$^-$ as a model. The results are summarized in Scheme 4. The computational data were obtained with the M06-2X DFT functional,[23] the 6-311+G* basis set, and the PCM continuum solvent model.[24]

Scheme 3. Scope of the Intramolecular Photoinduced Arylation To Synthesize 6*H*-Dibenzothiazines 5,5-Dioxide 6[d]



[a]Reaction time = 6 h. [b]Reaction time = 8 h. [c]Acid extraction as "workup" without further purification. [d]A = Conventional "workup" and purification. B = Direct filtration and recrystallization.

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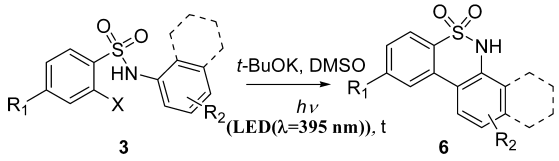
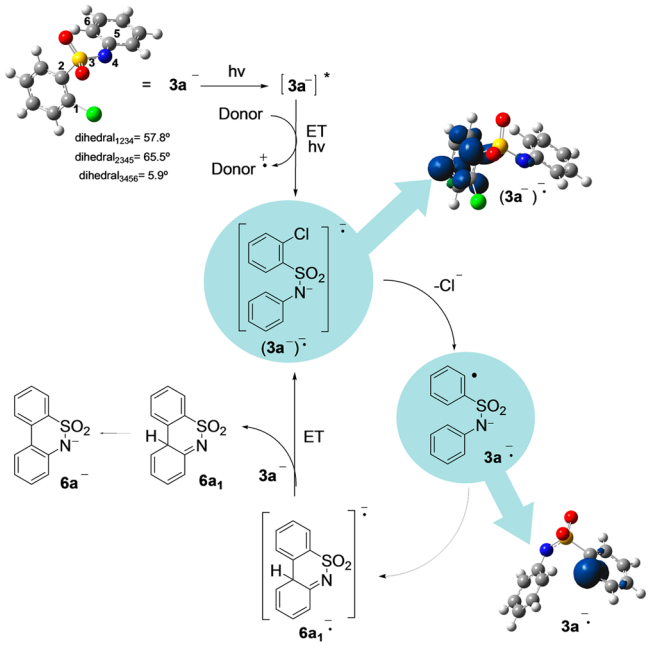
Table 2. Use of Visible-LED Lights in the Intramolecular Photoinduced Arylation[a]



entry	3 (%)[b]	t (h)	products 6	products yields (%)[c]
1	**3a** (---)	3	**6a**	82
2	**3b** (---)	5	**6b**	84
3	**3i** (23)	5	**6i**	71
4	**3j** (15)	5	**6j**	80
5	**3l** (12)	6	**6l**	84
6	**3m** (8)	8	**6m**	76
7	**3o** (---)	5	**6o**	94
8	**3p** (10)	8	**6p**	87

[a]The reactions were run in 5 mL of DMSO with **3** (0.03 M) and 0.09 M of *t*-BuOK. Irradiation was performed for the specific time with Violet LED (LEDs (λ = 395 ± 15 nm), 3 W, 700 mA). [b]Substrate **3** recovered. [c]Yields were determined by GC (internal standard method).

Scheme 4. Proposed Mechanism[a]



[a]The spin density is shown for $(\mathbf{3a}^-)^{\bullet-}$ and $\mathbf{3a}^{\bullet-}$ (isodensity = 0.004).

Initially, we propose that anion $\mathbf{3a}^-$ is formed in the presence of excess *t*-BuO^-. The most stable conformer of $\mathbf{3a}^-$, presented in Scheme 4, could form radical dianion $(\mathbf{3a}^-)^{\bullet-}$ by an ET process. This ET could be achieved from different sources (for example, *t*-BuO^-).[25] In our case, the ET from the base to the excited anion $[\mathbf{3a}^-]^*$ (S_1 state of $\mathbf{3a}^-$ evaluated with TD-DFT) is exothermic and could be responsible for the initiation pathway.[26]

The $(\mathbf{3a}^-)^{\bullet-}$ formed bears the unpaired spin density at the π system of the aryl-Cl moiety (Scheme 4). This intermediate could dissociate with a very low activation energy (0.4 kcal/mol) to afford the distonic radical anion $\mathbf{3a}^{\bullet-}$ through a transition state characterized by a C−Cl bending transition vector. As known, a σ(C−Cl)-π overlap is required for this $\pi-\sigma$ intramolecular dissociative ET to take place.[27]

After C−Cl fragmentation, the distonic radical anion intermediate $\mathbf{3a}^{\bullet-}$, represented in Scheme 4, could afford the cyclic radical anion $\mathbf{6a_1}^{\bullet-}$. In this pathway, the C−C coupling is achieved with an activation energy (E_a) of 9.15 kcal/mol. Also, it is important to emphasize that cyclic radical anion $\mathbf{6a_1}^{\bullet-}$ is 24 kcal/mol more stable than the distonic radical anion $\mathbf{3a}^{\bullet-}$, and this difference could be the driving force of the reaction.

Finally, $\mathbf{6a_1}$ and $(\mathbf{3a}^-)^{\bullet-}$ could be formed after an ET from $\mathbf{6a_1}^{\bullet-}$ to $\mathbf{3a}^-$. The latter ET propagates the reaction cycle. Under the basic media, $\mathbf{6a_1}$ generates $\mathbf{6a}^-$, and upon reaction workup, product **6a** was formed.

CONCLUSIONS

To conclude, we described an efficient route to synthesize dibenzosultams under "Transition-Metal-Free" conditions starting from *N*-aryl-2-halobenzenesulfonamides easily prepared by two different procedures. The cyclization reactions are promoted by *t*-BuOK and occur in DMSO at room temperature. Many functional groups are tolerated, giving access to a wide range of synthetically relevant heterocycles. Other solvents such as NH_3 and CH_3CN seem promising to perform the reactions. We also explored the use of visible-LED light, improving some yields of challenging substrates. Finally, DFT calculations were performed to inspect the energetics and thus confirm our proposal of the radical-anion type $S_{RN}1$ mechanism.

EXPERIMENTAL SECTION

Computational Procedure. All calculations were performed with the Gaussian09 program. The conformers obtained were refined with complete geometry optimization within the M06-2X DFT functional and the 6-311+G* basis set. The geometries thus found were used as starting points for the evaluation of the reaction profiles by using the distinguished reaction coordinate scan. The effect of DMSO as solvent was evaluated through the Tomasi's Polarized Continuum Model (PCM) as implemented in Gaussian09. The inclusion of the solvent in the calculations is a requisite to evaluate valence radical anions. The characterization of stationary points was done by Hessian matrix calculations. The energy informed for TSs, anions, and radical anions includes zero-point corrections. The vertical excited singlet stated (S_1) of anion **3a** was calculated with TD-DTF the M06-2X functional and the 6-311+G* basis set. The energy of S_1 was calculated including the PCM contribution under the StateSpecific approach.

General Considerations. Column chromatography was carried out on silica gel. Melting points were determined using a standard melting point instrument and are uncorrected. Gas chromatographic analyses were performed with a flame-ionization detector, on a 30 m capillary column of a 0.32 mm × 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. GC−MS analyses were performed employing a 25 m × 0.2 mm × 0.33 μm with a 5% phenylpolysiloxane phase column. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a 400.16 MHz in $CDCl_3$, dimethyl sulfoxide-d_6 (CD_3SOCD_3), or acetone-d_6 (CD_3COCD_3) as solvent with TMS as internal standard. Coupling constants are given in Hz, and chemical shifts are reported in δ values in 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. Copies of ^{1}H NMR and ^{13}C NMR spectra are provided.

All new products were further characterized by HRMS. HRMS analyses were carried out using a TOF-MS instrument with an ESI source.

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Irradiation was conducted in a reactor equipped with two Philips HPI-T 400 W lamps of metallic iodide (cooled with water) or with LED lights performing at 3W of potency and 700 mV of current.

DMSO as solvent was stored under molecular sieves (4 Å). Anhydrous ethyl ether was stored over Na wire. All solvents were analytical grade. Silica gel (0.063−0.200 mm) was used in column chromatography. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

Representative Procedure for Synthesis of 2-Halo-*N*-phenylbenzenesulfonamides. *Method A.* The cross-coupling copper-catalyzed reaction of 2-chlorobenzenesulfonamide (**1**) with aryl halides was the procedure to synthesize sulfonamides **3a−f/m−n**. A Schlenk tube equipped with a nitrogen inlet and magnetic stirrer was charged with **1** (115.0 mg, 0.6 mmol), copper(I) iodide (11.4 mg, 0.06 mmol), aryl halide (iodobenzene, **2a**) (244.4 mg, 1.2 mmol), K_2CO_3 (381.3 mg, 1.8 mmol), acetonitrile (CH_3CN) (4 mL), and *N*,*N*-dimethylethane-1,2-diamine (DMEDA) (21.6 mg, 0.3 mmol). The tube was then heated to 90 °C for 18 h. The reaction mixture was then cooled to room temperature, and 2 M HCl (10 mL) was added slowly, followed by EtOAc extraction (15 mL × 3). The organic layers were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid of *2-chloro-N-phenylbenzenesulfonamide* (**3a**) was isolated in 78% yield (125.9 mg, 0.468 mmol), mp 145−147 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.00 (dd, *J* = 7.8, 1.4, 1H), 7.49 (dd, *J* = 8.0, 1.6, 1H), 7.45 (td, *J* = 7.6, 1.6, 1H), 7.34−7.30 (m, 1H), 7.23−7.19 (m, 2H), 7.13−7.06 (m, 4H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 136.1, 135.7, 134.1, 132.0, 131.5, 131.3, 129.3, 127.2, 125.7, 121.6. **GC−MS** (EI) *m*/*z* 267 (M^+, 21), 168 (48), 167 (11), 111 (22), 93 (10), 92 (100), 75 (24), 65 (56), 64 (8).[28]

2-Chloro-N-(p-tolyl)benzenesulfonamide (**3b**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 85:15%). A white solid was isolated in 62% yield (104.8 mg, 0.372 mmol), mp 151−152 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 7.96 (dd, *J* = 7.8, 1.4, 1H), 7.49 (dd, *J* = 7.8, 1.4, 1H), 7.44 (td, *J* = 7.7, 1.6, 1H), 7.30 (td, *J* = 7.6, 1.2, 1H), 7.02 (br.s, 1H), 7.00 (br.s, 4H), 2.22 (s, 3H); **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 136.2, 135.8, 133.9, 132.9, 132.0, 131.5, 131.3, 129.9, 127.2, 122.3, 20.8. **GC−MS** (EI) *m*/*z* 281 (M^+, 9), 111 (15), 107 (8), 106 (100), 79 (30), 78 (12), 77 (35), 75 (18), 51 (9). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{12}ClNNaO_2S$ $(M + Na)^+$: 304.0170; Found: 304.0169.

2-Chloro-N-(4-methoxyphenyl)benzenesulfonamide (**3c**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 85:15%). A colorless crystal was isolated in 50% yield (89.1 mg, 0.3 mmol), mp 134−135 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 7.89 (dd, *J* = 7.8, 1.6, 1H), 7.52 (dd, *J* = 8.0, 1.2, 1H), 7.45 (td, *J* = 7.6, 1.6, 1H), 7.29 (td, *J* = 7.6, 1.2, 1H), 7.06−7.02 (m, 2H), 6.95 (br.s, 1H), 6.74−6.7 (m, 2H), 3.71 (s, 3H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 158.1, 136.2, 133.9, 132.0, 131.4, 131.2, 128.1, 127.0, 125.2, 114.4, 55.3. **GC−MS** (EI) *m*/*z* 327 (M^+, 10), 263 (10), 229 (16), 228 (96), 213 (20), 197 (11), 152 (10), 126 (9), 125 (10), 111 (17). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{12}ClNNaO_3S$ $(M + Na)^+$: 320.0119; Found: 320.0106.

2-Chloro-N-(3,5-dimethoxyphenyl)benzenesulfonamide (**3d**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A colorless crystal was isolated in 35% yield (68.7 mg, 0.21 mmol), mp 164−165 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.05 (dd, *J* = 7.8, 1, 1H), 7.51−7.44 (m, 2H), 7.37−7.33 (m, 1H), 7.01 (s, 1H), 6.29 (d, *J* = 2.4, 2H), 6.16 (t, *J* = 2, 1H), 3.69 (s, 6H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 161.2, 136.1, 134.2, 132.1, 131.6, 131.4, 129.1, 127.2, 99.4, 97.6, 55.4. **GC−MS** (EI) *m*/*z* 327 (M^+, 10), 263 (10), 229 (16), 228 (96), 213 (20), 197 (11), 152 (10), 126 (9), 125 (100), 111 (17). **HRMS** (TOF, ESI$^+$): calcd for $C_{14}H_{14}ClNNaO_4S$ $(M + Na)^+$: 350.0224; Found: 350.0227.

N-([1,1′-Biphenyl]-4-yl)-2-chlorobenzenesulfonamide (**3e**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 59% yield (60.9 mg, 0.177 mmol), mp 139−141 °C. **^{1}H NMR** (400.16 MHz, CD_3COCD_3) δ_H: 9.42 (br.s, 1H), 8.14 (d, *J* = 8.0, 1H), 7.60−7.48 (m, 7H), 7.47−7.28 (m, 5H). **^{13}C NMR** (100.62 MHz, CD_3COCD_3) δ_C: 139.8, 137.0, 136.9, 136.4, 134.3, 131.9, 131.7, 131.3, 128.7, 127.4, 127.3, 127.1, 126.4, 120.4. **GC−MS** (EI) *m*/*z* 343 (M^+, 16), 169 (14), 168 (100), 166 (4), 141 (24), 139 (5), 115 (17), 111 (4), 75 (4). **HRMS** (TOF, ESI$^+$): calcd for $C_{18}H_{14}ClNNaO_2S$ $(M + Na)^+$: 366.0326; Found: 366.0329.

2-Chloro-N-(4-(trifluoromethyl)phenyl)benzenesulfonamide (**3f**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 51% yield (102.8 mg, 0.306 mmol), mp 209−211 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.10−8.08 (m, 1H), 7.53−7.36 (m, 6H), 7.22 (d, *J* = 8.4, 2H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 139.1, 135.8, 134.5, 132.0, 131.8, 131.4, 127.4, 127.2 (q, *J* = 33, 1C), 126.7 (q, *J* = 4.0, 1C), 123.8 (q, *J* = 273, 1C), 119.9. **GC−MS** (EI) *m*/*z* 335 (M^+, 16), 236 (41), 177 (16), 175 (43), 160 (21), 140 (27), 114 (14), 113 (51), 111 (100), 75 (48), 63 (14), 50 (14). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_9ClF_3NNaO_2S$ $(M + Na)^+$: 357.9887; Found: 357.9896.

2-Chloro-N-(naphthalen-2-yl)benzenesulfonamide (**3m**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 78% yield (74.4 mg, 0.234 mmol), mp 187−189 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.02 (dd, *J* = 8.0, 1.6, 1H), 7.73−7.68 (m, 3H), 7.57 (d, *J* = 2.0, 1H), 7.45−4.36 (m, 3H), 7.30−7.24 (m, 3H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 136.1, 134.1, 133.5, 133.2, 132.0, 131.5, 131.3, 131.2, 129.4, 127.6, 127.5, 127.2, 126.7, 125.7, 120.9, 118.7. **GC−MS** (EI) *m*/*z* 319 (M^+ + 2, 5), 317 (M^+, 13), 218 (25), 143 (7), 142 (64), 140 (5), 116 (10), 115 (100), 89 (6), 75 (6). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{12}ClNNaO_2S$ $(M + Na)^+$: 340.0170; Found: 340.0164.

2-Chloro-N-(quinolin-3-yl)benzenesulfonamide (**3n**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 50:50%). A light yellow solid was isolated in 61% yield (116.6 mg, 0.366 mmol), mp 166−167 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.68 (d, *J* = 2.8, 1H), 8.04−8.00 (3H, m), 7.94 (br.s, 1H), 7.73 (d, *J* = 8.4, 1.2, 1H), 7.64 (ddd, *J* = 8.3, 7.1, 1.2, 1H), 7.54−7.49 (m, 2H), 7.44 (td, *J* = 7.8, 1.6, 1H), 7.29 (td, J = 7.6, 1.6, 1H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 145.9, 145.3, 135.9, 134.5, 132.0, 131.8, 131.3, 129.5, 129.2, 129.1, 127.8, 127.6, 127.5, 127.4, 126.7. **GC−MS** (EI) *m*/*z* 320 (M^+ + 2, 10), 318 (M^+, 25), 144 (11), 143 (100), 116 (94), 115 (10), 111 (20), 89 (53), 75 (22), 63 (18). **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{12}ClN_2O_2S$ $(M + H)^+$: 319.0302; Found: 319.0303.

Method B. Sulfonamides **3g−l/o−r** were synthesized by sulfonylation of the corresponding aniline. The aniline (0.72 mmol) was dissolved in dry CH_2Cl_2 (1.2 mL), and the solution was treated with the corresponding 2-halobenzene-1-sulfonyl chloride (0.6 mmol) and pyridine (0.142 g, 1.8 mmol). The mixture was stirred at room temperature for 18 h, diluted with H_2O (15 mL), and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with 1 M HCl and brine, dried over Na_2SO_4, and concentrated in vacuum. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel. Ethyl 4-(2-chlorophenylsulfonamido)benzoate (**3g**) was synthesized from 2-chlorobenzene-1-sulfonyl chloride (**4a**) and ethyl 4-aminobenzoate and purified eluting with pentane/EtOAc (100:0 → 70:30%). A light yellow solid was isolated in 89% yield (181.4 mg, 0.534 mmol), mp 191−193 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.22 (br.s, 1H), 8.13 (d, *J* = 7.6, 1H), 7.81 (d, *J* = 8.8, 2H), 7.67−7.63 (m, 2H), 7.57−7.53 (m, 1H), 7.20 (d, *J* = 8.4, 2H), 4.25−4.20 (m, 2H), 1.27−1.23 (m, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 165.1, 141.6, 136.0, 135.0, 132.0, 131.7, 130.7, 130.5, 127.8, 124.6, 117.6, 60.5, 14.1. **GC−MS** (EI) *m*/*z* 339 (M^+, 60), 294 (41), 240 (30), 212 (21), 175 (21), 168 (25), 164 (67), 136 (25), 119 (48), 113 (22), 111 (66), 108 (100), 92 (55), 91 (47), 90 (18), 65 (22), 64 (33), 63 (26). **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{14}ClNNaO_4S$ $(M + Na)^+$: 362.0224; Found: 362.0228.

2-Chloro-N-(4-cyanophenyl)benzenesulfonamide (**3h**). The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A light yellow solid was isolated

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in 57% yield (100.2 mg, 0.342 mmol), mp 199−201 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.41 (br.s, 1H), 8.16−8.14 (m, 1H), 7.70−7.55 (m, 5H), 7.21 (d, J = 8.8, 2H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 141.6, 135.9, 135.2, 133.7, 132.1, 131.7, 130.7, 128.0, 118.6, 117.9, 105.3. **GC−MS** (EI) m/z 294 (M^+ + 1, 14), 292 (M^+, 33), 277 (19), 193 (22), 177 (27), 175 (69), 117 (17), 113 (32), 111 (100), 90 (29), 75 (40), 64 (12), 63 (13). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_9ClN_2NaO_2S$ $(M + Na)^+$: 314.9966; Found: 314.9966.

*2-Chloro-N-(4-fluorophenyl)benzenesulfonamide (**3i**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 93% yield (159.4 mg, 0.558 mmol), mp 214−215 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 10.59 (br.s, 1H), 8.00−7.98 (m, 1H), 7.64−7.47 (m, 3H), 7.13−7.04 (m, 4H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 158.9 (d, J = 240, 1C), 136.3, 134.7, 133.2 (d, J = 3, 1C), 131.8, 131.6, 130.7, 127.7, 121.9 (d, J = 8, 1C), 115.9 (d, J = 23, 1C). **GC−MS** (EI) m/z 287 (M^+ + 2, 7), 285 (M^+, 18), 186 (9), 111 (15), 110 (100), 83 (34), 75 (10), 57 (7). **HRMS** (TOF, ESI$^+$): calcd for $C_{12}H_9ClFNNaO_2S$ $(M + Na)^+$: 307.9909; Found: 307.9919.

*N-([1,1′-Biphenyl]-2-yl)-2-chlorobenzenesulfonamide (**3j**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 75% yield (154.8 mg, 0.45 mmol), mp 159−161 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 9.72 (br.s, 1H), 7.67 (dd, J = 7.9, 1.5, 1H), 7.59−7.54 (m, 1H), 7.51 (dd, J = 8.0, 1.3, 1H), 7.41−7.23 (m, 9H), 7.01 (dd, J = 7.6, 1.3, 1H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 139.7, 138.4, 138.2, 133.9, 132.8, 131.8, 130.9, 130.7, 130.2, 129.0, 128.2, 128.0, 128.0, 127.4, 127.4, 127.0. **GC−MS** (EI) m/z 343 (M^+, 8), 169 (12), 168 (100), 167 (72), 140 (5), 139 (8), 115 (5), 111 (4), 75 (4). **HRMS** (TOF, ESI$^+$): calcd for $C_{18}H_{14}ClNNaO_2S$ $(M + Na)^+$: 366.0326; Found: 366.0322.

*N-(2-(1H-Pyrrol-1-yl)phenyl)-2-chlorobenzenesulfonamide (**3k**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 90:10%). An amber crystal was isolated in 51% yield (100.2 mg, 0.306 mmol), mp 122−124 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.10 (dd, J = 8.0, 1.6, 1H), 7.56 (dd, J = 8.4, 1.2, 1H), 7.48 (ddd, J = 8.0, 7.2, 1.6, 1H), 7.43 (dd, J = 7.8, 1.4, 1H), 7.24 (1H, ddd, J = 8.3, 7.3, 1.6, 1H), 7.20−7.17 (m, 2H), 7.08 (td, J = 7.6, 1.2, 1H), 6.66 (t, J = 2.2, 2H), 6.37 (t, J = 2.2, 2H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 136.2, 134.2, 132.2, 131.1, 131.8, 131.8, 131.1, 128.7, 127.7, 127.0, 124.5, 121.9, 119.0, 110.9. **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{13}ClN_2NaO_2S$ $(M + Na)^+$: 355.0278; Found: 355.0266.

*2-Chloro-N-(naphthalen-1-yl)benzenesulfonamide (**3l**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A brown crystal was isolated in 77% yield (146.8 mg, 0.462 mmol), mp 166−167 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.16 (d, J = 8.4, 1H), 7.91 (dd, J = 8.0, 1.6, 1H), 7.81 (d, J = 7.6, 1H), 7.69 (d, J = 8.4, 1H), 7.56−7.44 (m, 4H), 7.30−7.21 (m, 4H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 136.9, 134.3, 134.0, 131.8, 131.7, 131.5, 131.0, 129.3, 128.3, 127.5, 127.2, 126.8, 126.5, 125.2, 122.0, 121.9. **GC−MS** (EI) m/z 317 (M^+, 14), 218 (8), 143 (12), 142 (100), 140 (6), 116 (9), 115 (87), 89 (6), 75 (7). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{12}ClNNaO_2S$ $(M + Na)^+$: 340.0170; Found: 340.0161.

*2-Chloro-4-fluoro-N-phenylbenzenesulfonamide (**3o**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 97% yield (166.2 mg, 0.582 mmol), mp 109−110 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.01 (dd, J = 8.8, 6.0, 1H), 7.26−7.20 (m, 3H), 7.12−7.09 (m, 3H), 7.06 (br.s, 1H), 7.02 (ddd, J = 8.8, 7.6, 2.4, 1H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 164.7 (d, J = 257, 1C), 135.5, 134.1 (d, J = 10, 1C), 133.1 (d, J = 11, 1C), 132.4 (d, J = 4, 1C), 129.4, 125.9, 121.6, 119.2 (d, J = 25, 1C), 114.5 (d, J = 21, 1C). **GC−MS** (EI) m/z 287 (M^+ + 2, 6), 285 (M^+, 18), 186 (26), 185 (6), 131 (5), 129 (17), 109 (7), 94 (6), 93 (14), 92 (100), 65 (49), 64 (8), 63 (8). **HRMS** (TOF, ESI$^+$): calcd for $C_{12}H_9ClFNNaO_2S$ $(M + Na)^+$: 307.9919; Found: 307.9919.

*2-Chloro-4-fluoro-N-(p-tolyl)benzenesulfonamide (**3p**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A light yellow solid was isolated in 91% yield (163.6 mg, 0.546 mmol), mp 110−112 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 7.97 (dd, J = 9.0, 5.8, 1H), 7.24 (dd, J = 8, 2.4, 1H), 7.03−7.00 (6H, m), 2.24 (s, 3H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 164.7 (d, J = 257, 1C), 136.1, 134.1 (d, J = 8, 1C), 133.1 (d, J = 11, 1C), 132.8, 132.5, 130.0, 122.3, 119.2 (d, J = 26, 1C), 114.5 (d, J = 22, 1C), 20.8. **GC−MS** (EI) m/z 301 (M^+ + 2, 7), 299 (M^+, 19), 129 (7), 107 (9), 106 (100), 79 (25), 78 (8), 77 (24), 52 (4), 51 (4). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{11}ClFNNaO_2S$ $(M + Na)^+$: 322.0075; Found: 322.0069.

*2-Bromo-N-(p-tolyl)-4-(trifluoromethyl)benzenesulfonamide (**3q**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A colorless solid was isolated in 85% yield (200.1 mg, 0.51 mmol), mp 129−130 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 10.70 (br.s, 1H), 8.23 (d, J = 0.8, 1H), 8.19 (d, J = 8.0, 1H), 7.94 (dt, J = 8.2, 0.8, 1H), 7.04 (d, J = 8.4, 2H), 7.00−6.98 (2H, m), 2.16 (s, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 142.4, 133.9, 133.7 (q, J = 33, 1C), 133.7, 132.5, 132.2 (q, J = 4, 1C), 129.7, 125.3 (q, J = 4, 1C), 122.4 (q, J = 272, 1C), 120.2, 118.3, 20.2. **GC−MS** (EI) m/z 395 (M^+ + 2, 11), 393 (M^+, 11), 223 (4), 144 (12), 125 (4), 107 (8), 106 (100), 79 (25), 78 (10), 77 (27), 52 (4). **HRMS** (TOF, ESI$^+$): calcd for $C_{14}H_{11}BrF_3NNaO_2S$ $(M + Na)^+$: 415.9538; Found: 415.9531.

*2-Chloro-N-(pyridin-2-yl)benzenesulfonamide (**3r**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 30% yield (24.2 mg, 0.09 mmol), mp 212−213 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 14.5 (br.s, 1H), 8.37−8.28 (m, 2H), 7.65 (ddd, J = 9.1, 7.1, 2.0, 1H), 7.45−7.40 (m, 3H), 7.31 (d, J = 8.8, 1H), 6.77 (t, J = 6.4, 1H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 155.5, 142.9, 139.4, 139.2, 132.9, 132.1, 131.9, 131.1, 126.7, 115.5, 113.2. **GC−MS** (EI) m/z 270 (M^+ + 2, 2), 268 (M^+, 47), 266 (100), 264 (74), 172 (22), 168 (16), 133 (22), 124 (30), 121 (24), 118 (15), 109 (32), 98 (17), 79 (16), 78 (16), 62 (14). **HRMS** (TOF, ESI$^+$): calcd for $C_{11}H_9ClN_2NaO_2S$ $(M + Na)^+$: 290.9966; Found: 290.9965.

Representative Procedure for Photostimulated Reactions. Reactions in DMSO (THF or CH_3CN). The following procedure is representative of all of these reactions. The reaction was carried out in a Schlenk tube equipped with a nitrogen inlet and magnetic stirrer at r.t. DMSO (5 mL) was dried and deoxygenated. Then, *t*-BuOK (3.0 equiv, 50.5 mg, 0.45 mmol) was added, and after 5 min, the corresponding 2-halo-*N*-phenylbenzenesulfonamide (1 equiv, 0.15 mmol) was added and the reaction mixture was irradiated for the corresponding time. In case the 2-halo-*N*-phenylbenzenesulfonamide was an oil, it was added dissolved in anhydrous ethyl ether. The reaction was quenched with ammonium nitrate in excess. The "workup" of the reaction could have two processes. "**Workup A**": The residue was extracted with ethyl acetate (EtOAc) (3 × 30 mL), and the organic extracted was washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude products. The products were purified by chromatography on silica gel or quantified by GC using the internal standard method. "**Workup B**": The residue was filtrated over a bed of silica gel with 300 mL of pentane/EtOAc 70:30%. The solvent was removed under reduced pressure, and the crude obtained was then recrystallized.

Reaction in Liquid Ammonia. Liquid ammonia (150 mL), previously dried over Na metal, was distilled into a 250 mL three-neck, round-bottomed flask equipped with a cold-finger condenser and a magnetic stirrer under a nitrogen atmosphere. The base *t*-BuOK (3.0 equiv, 50.5 mg, 0.45 mmol) and then the corresponding 2-halo-*N*-phenylbenzenesulfonamides (1 equiv, 0.15 mmol) were added to the liquid ammonia. After 180 min of irradiation, the reaction was quenched by addition of NH_4NO_3 in excess, and the ammonia was allowed to evaporate. Water (50 mL) was added to the residue, and the mixture was extracted with ethyl acetate (3 × 30 mL). The organic extract was dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to leave the crude products. The products were purified by chromatography on silica gel or quantified by GC using the internal standard method.

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Isolation and Identification of Products. *6H-Dibenzo[c,e][1,2]-thiazine 5,5-Dioxide (**6a**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 75:25%). A white solid was isolated in 86% yield (29.6 mg, 0.128 mmol), mp 195−197 °C (lit.[10] 194−195 °C). **^{1}H NMR** (400.16 MHz, CD_3COCD_3) δ_H: 9.89 (br.s, 1H), 8.24−8.19 (m, 2H), 7.89 (dd, J = 7.8, 1.0, 1H), 7.84−7.80 (m, 1H), 7.68 (td, J = 7.6, 0.8, 1H), 7.49 (td, J = 7.6, 1.2, 1H), 7.36−7.31 (m, 2H). **^{13}C NMR** (100.62 MHz, CD_3COCD_3) δ_C: 136.8, 135.5, 132.4, 132.3, 130.2, 128.2, 125.4, 125.2, 124.1, 122.4, 121.3, 119.9. **GC−MS** (EI) m/z 232 (M^+ + 1, 13), 231 (M^+, 91), 168 (14), 167 (100), 166 (56), 140 (29), 139 (39), 115 (9), 113 (10), 89 (8), 84 (10), 70 (11), 69 (10), 63 (14).

*9-Methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6b**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 98% yield (36.1 mg, 0.147 mmol). This solid was recrystallized from acetone/pentane as a white crystal, mp 217−219 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.19 (br.s, 1H), 8.23 (d, J = 8.0, 1H), 8.02 (s, 1H), 7.96 (dd, J = 7.8, 1.0, 1H), 7.82−7.78 (m, 1H), 7.65 (t, J = 7.4, 1H), 7.28 (dd, J = 8.2, 1.0, 1H), 7.11 (d, J = 8.0, 1H), 2.369 (s, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 134.6, 134.1, 133.2, 132.4, 131.8, 131.1, 128.4, 125.5, 125.4, 121.4, 121.1, 119.8, 20.6. **GC−MS** (EI) m/z 246 (M^+ + 1, 9), 245 (M^+, 69), 181 (21), 180 (100), 178 (9), 153 (6), 152 (17), 151 (7), 127 (5), 90 (9), 89 (5), 77 (11), 76 (7), 75 (5), 63 (6), 51 (5). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{11}NNaO_2S$ (M + Na)$^+$: 268.0403; Found: 268.0400.

*9-Methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6c**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 60:40%). A white solid was isolated in 77% yield (30.2 mg, 0.115 mmol). This solid was recrystallized from acetone/pentane as a light yellow crystal, mp 209−210 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.0 (br.s, 1H), 8.29 (d, J = 8.0, 1H), 7.92 (dd, J = 7.8, 1.0, 1H), 7.82−7.78 (m, 1H), 7.70 (d, J = 2.8, 1H), 7.67 (td, J = 7.6, 0.8, 1H), 7.16 (d, J = 8.8, 1H), 7.09 (dd, J = 8.8, 2.8, 1H), 3.86 (s, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 156.1, 134.8, 132.4, 131.7, 129.7, 128.7, 126.0, 123.1, 121.8, 121.2, 117.1, 109.5, 55.6. **GC−MS** (EI) m/z 262 (M^+ + 1,11), 261 (M^+, 69), 183 (14), 182 (100), 155 (8), 154 (70), 153 (14), 128 (23), 127 (30), 126 (12), 77 (10), 75 (8), 51 (8). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{11}NNaO_3S$ (M + Na)$^+$: 284.0352; Found: 284.0357.

*8,10-Dimethoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6d**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 60:40%). A light yellow solid was isolated in 65% yield (28.4 mg, 0.0975 mmol), mp 229−231 °C. **^{1}H NMR** (400.16 MHz, CD_3COCD_3) δ_H: 9.70 (br.s, 1H), 8.59 (d, J = 8.4, 1H), 7.90 (dd, J = 7.8, 1.0, 1H), 7.66 (td, J = 7.8, 1.2, 1H), 7.52 (td, J = 7.6, 0.8, 1H), 6.56 (d, J = 2.4, 1H), 6.49 (d, J = 2.4, 1H), 4.00 (s, 3H), 3.87 (s, 3H). **^{13}C NMR** (100.62 MHz, CD_3COCD) δ_C: 161.5, 159.6, 139.4, 134.7, 131.4, 131.3, 128.7, 126.4, 120.8, 105.5, 96.5, 95.0, 55.5, 55.0. **GC−MS** (EI) m/z 292 (M^+ + 1, 29), 291 (M^+, 100), 290 (12), 227 (17), 226 (9), 212 (11), 185 (9), 136 (9), 127 (14), 114 (9), 113 (9). **HRMS** (TOF, ESI$^+$): calcd for $C_{14}H_{13}NNaO_4S$ (M + Na)$^+$: 314.0457; Found: 314.0469.

*9-Phenyl-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6e**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (70:30%). A white solid was isolated in 94% yield (43.3 mg, 0.141 mmol). This solid was recrystallized from EtOAc/pentane as colorless flakes, mp 235−236 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.50 (br.s, 1H), 8.47 (d, J = 8.4, 1H), 8.45 (d, J = 2.0, 1H), 7.96 (d, J = 7.2, 1H), 7.85−7.77 (m, 4H), 7.70 (t, J = 7.6, 1H), 7.50 (t, J = 7.6, 2H), 7.39 (t, J = 7.6, 1H), 7.30 (d, J = 8.4, 1H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 139.4, 136.0, 135.9, 134.5, 132.6, 131.7, 128.9, 128.8, 128.7, 127.5, 126.8, 126.1, 123.5, 121.8, 121.1, 120.2. **HRMS** (TOF, ESI$^+$): calcd for $C_{18}H_{13}NNaO_2S$ (M + Na)$^+$: 330.0559; Found: 330.0551.

*9-(Trifluoromethyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6f**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 60:40%). A white solid was isolated in 79% yield (35.5 mg, 0.118 mmol). This solid was recrystallized from ethyl ether/pentane as a white crystal, mp 234−236 °C. **^{1}H NMR** (400.16 MHz, CD_3COCD_3) δ_H: 10.48 (br.s, 1H), 8.56 (s, 1H), 8.42−8.40 (m, 1H), 8.04 (dd, J = 7.8, 1.0, 1H), 7.89 (ddd, J = 8.0, 7.6, 1.2, 1H), 7.84−7.81 (m, 1H), 7.77 (1H, td, J = 7.6, 1.2, 1H), 7.52 (d, J = 8.4, 1H). **^{13}C NMR** (100.62 MHz, CD_3COCD_3) δ_C: 140.0, 135.4, 132.7, 131.1, 129.3, 126.8 (q, J = 4, 1C), 126.1, 125.5 (q, J = 33, 1C), 124.3 (q, J = 270, 1C), 122.7 (q, J = 4, 1C), 122.3, 121.5, 120.2. **GC−MS** (EI) m/z 300 (M^+ + 1, 26), 299 (M^+, 100), 281 (22), 236 (15), 235 (61), 234 (17), 216 (29), 207 (53), 204 (13), 185 (28), 166 (23), 140 (14), 139 (17), 93 (15), 69 (16), 58 (74), 57 (18). (26). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_8F_3NNaO_2S$ (M + Na)$^+$: 322.0120; Found: 322.0120.

*Ethyl 6H-Dibenzo[c,e][1,2]thiazine-9-carboxylate 5,5-Dioxide (**6g**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 50:50%). A light yellow solid was isolated in 54% yield (24.6 mg, 0.081 mmol). This solid was recrystallized from acetone/pentane as a small white solid, mp 263−264 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 12.0 (br.s, 1H), 8.71 (s, 1H), 8.30 (d, J = 8.1, 1H), 8.03 (d, J = 8.4, 1H), 7.97 (d, J = 7.8, 1H), 7.87−7.83 (m, 1H), 7.72 (t, J = 7.6, 1H), 7.29 (d, J = 8.3, 1H), 4.36 (q, J = 7.1, 2H), 1.36 (t, J = 7.1, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 165.2, 142.2, 134.0, 132.5, 131.0, 130.7, 128.9, 126.2, 125.4, 124.0, 121.4, 120.3, 119.8, 60.7, 14.2. **GC−MS** (EI) m/z 304 (M^+ + 1, 13), 303 (M^+, 70), 275 (35), 259 (18), 258 (100), 211 (9), 194 (17), 167 (10), 166 (36), 165 (9), 164 (13), 140 (21), 139 (46), 138 (9). **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{13}NNaO_4S$ (M + Na)$^+$: 326.0458; Found: 326.0454.

*6H-Dibenzo[c,e][1,2]thiazine-9-carbonitrile 5,5-Dioxide (**6h**).* The product was filtrated over a bed of silica gel with 300 mL of pentane/EtOAc 70:30%. The solvent was removed under reduced pressure and then was recrystallized from acetone/pentane. A light yellow solid was isolated in 91% yield (35.0 mg, 0.136 mmol), mp decomposed over 213 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 12.16 (br.s, 1H), 8.80 (d, J = 1.6, 1H), 8.40 (d, J = 8.0, 1H), 7.99 (dd, J = 7.8, 1.0, 1H), 7.91−7.85 (m, 2H), 7.77−7.73 (m, 1H), 7.33 (d, J = 8.4, 1H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 140.4, 134.0, 133.6, 132.9, 130.2, 130.1, 129.6, 126.2, 121.4, 121.2, 120.0, 118.6, 106.0. **GC−MS** (EI) m/z 257 (M^+ + 1, 20), 256 (M^+, 85), 193 (17), 192 (100), 191 (39), 165 (36), 164 (49), 144 (15), 139 (11), 138 (19), 89 (9), 83 (10), 75 (12), 63 (13), 50 (9). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_8N_2NaO_2S$ (M + Na)$^+$: 279.0199 ; Found: 279.0190.

*9-Fluoro-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6i**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 60:40%). A white solid was isolated in 81% yield (30.0 mg, 0.121 mmol). This solid was recrystallized from EtOAc/pentane as a white crystal, mp 214−215 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.41 (br.s, 1H), 8.28 (d, J = 7.9, 1H), 8.13 (dd, J = 10.2, 2.8, 1H), 7.95 (dd, J = 7.8, 1.1, 1H), 7.85−7.81 (m, 1H), 7.71 (td, J = 7.6, 1.0, 1H), 7.36 (td, J = 8.6, 2.8, 1H), 7.24 (dd, J = 8.8, 5.2, 1H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 158.7 (d, J = 238, 1C), 134.5, 132.9, 132.6, 130.9, 129.3, 126.1, 123.3 (d, J = 9, 1C), 121.8 (d, J = 8, 1C), 121.2, 117.5 (d, J = 23, 1C), 111.8 (d, J = 24, 1C). **HRMS** (TOF, ESI$^+$): calcd for $C_{12}H_8FNNaO_2S$ (M + Na)$^+$: 272.0152; Found: 272.0153

*7-Phenyl-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6j**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 83% yield (38.3 mg, 0.124 mmol). This solid was recrystallized from EtOAc/pentane as small white needles, mp 221−222 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 10.2 (br.s, 1H), 8.27 (d, J = 8.0, 1H), 8.23 (dd, J = 7.8, 1.4, 1H), 7.91 (dd, J = 7.6, 0.8, 1H), 7.85−7.80 (m, 1H), 7.70−7.67 (m, 1H), 7.58−7.41 (m, 7H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 138.0, 137.0, 135.7, 133.1, 132.6, 132.4, 131.6, 129.5, 128.9, 128.4, 127.6, 126.5, 126.2, 125.0, 121.6. **HRMS** (TOF, ESI$^+$): calcd for $C_{18}H_{13}NNaO_2S$ (M + Na)$^+$: 330.0559; Found: 330.0554.

*7-(1H-Pyrrol-1-yl)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6k**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 78% yield (34.7 mg, 0.117 mmol). This solid was recrystallized from EtOAc/pentane as a light yellow crystal, mp 196−

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197 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H:10.4 (br.s, 1H), 8.28 (d, J = 8.0, 1H), 8.21 (dd, J = 7.8, 1.4, 1H), 7.94 (dd, J = 7.8, 1.0, 1H), 7.87−7.82 (m, 1H), 7.73−7.70 (m, 1H), 7.55−7.51 (m, 1H), 7.49 (dd, J = 8.0, 1.6, 1H), 7.14 (t, J = 2.0, 2H), 6.31 (t, J = 2.2, 2H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 135.7, 135.6, 132.7, 132.0, 129.8, 129.3, 127.3, 127.0, 126.7, 124.1, 122.1, 121.8, 109.5. **GC−MS** (EI) m/z 297 (M^+ + 1, 12), 296 (M^+, 75), 233 (14), 232 (94), 231 (71), 229 (12), 205 (29), 204 (100), 164 (14), 151 (11), 139 (16), 115 (16), 102 (18). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{12}N_2NaO_2S$ (M + Na)$^+$: 319.0512; Found: 319.0513.

*5H-Benzo[e]naphtho[1,2-c][1,2]thiazine 6,6-Dioxide (**6l**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (70:30%). A red solid was isolated in 69% yield (29.1 mg, 0.103 mmol). This solid was recrystallized from acetone/pentane as a brown crystal, mp 281−283 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.36 (br.s, 1H), 8.41−8.40 (m, 1H), 8.35 (d, J = 8.0, 1H), 8.30 (d, J = 8.8, 1H), 8.04−8.02 (m, 1H), 8.00 (dd, J = 7.6, 1.2, 1H), 7.93 (d, J = 8.8, 1H), 7.88−7.84 (m, 1H), 7.74−7.66 (m, 3H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 134.9, 133.6, 132.6, 132.4, 132.2, 128.6, 128.1, 127.6, 127.0, 126.7, 126.5, 125.1, 123.0, 122.3, 121.4, 119.7. **GC−MS** (EI) m/z 282 (M^+ + 1, 16), 281 (M^+, 82), 218 (14), 217 (100), 216 (49), 189 (16), 187 (10), 108 (29), 95 (17), 94 (13). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{11}NNaO_2S$ (M + Na)$^+$: 304.0403; Found: 304.0392.

*6H-Benzo[e]naphtho[2,1-c][1,2]thiazine 5,5-Dioxide (**6m**).* After evaporation of the solvent, the organic phase was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%), obtaining a mixture of products. After recrystallization of the mixture from acetone/pentane, **6m** was afforded as a colorless solid, mp decomposed over 223 °C (51% isolated yield, 21.5 mg, 0.075 mmol). **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.54 (d, J = 8.4, 1H), 8.27 (d, J = 8, 1H), 8.09 (d, J = 7.2, 1H), 7.92−7.87 (m, 2H), 7.72 (d, J = 7.2, 1H), 7.63−7.59 (m, 2H), 7.52 (d, J = 7.6, 1H), 7.23 (d, J = 8.4, 1H). **GC−MS** (EI) m/z 282 (M^+ + 1, 18), 281 (M^+, 100), 218 (13), 217 (80), 216 (43), 214 (14), 190 (19), 189 (39), 187 (11), 109 (22), 96 (11), 95 (25), 94 (43), 82 (13). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{11}NNaO_2S$ (M + Na)$^+$: 304.0403; Found: 304.0392.

*6H-Benzo[5,6][1,2]thiazino[3,4-c]quinoline 5,5-Dioxide (**6n**).* A special procedure was followed to purify this compound. The crude was obtained by extraction from acid media (pH = 1, H_2SO_4), with EtOAc (3 × 30 mL); the combined organic layers were washed with H_2O (20 mL) and dried over anhydrous $MgSO_4$; and the solvent was evaporated under vacuum. Without further purification, a yellow solid was obtained in 97% yield (41.1 mg, 0.145 mmol), mp decomposed over 185 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 8.94 (s, 1H), 8.63 (d, J = 7.6, 1H), 8.46 (d, J = 7.6, 1H), 8.22−8.14 (m, 2H), 8.00−7.83 (m, 4H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 143.8, 143.7, 136.9, 132.4, 130.6, 130.5, 129.9, 129.2, 128.9, 128.8, 128.6, 125.3, 124.2, 123.4, 121.7. **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{11}N_2O_2S$ (M + H)$^+$: 283.0536; Found: 283.0530.

*2-Fluoro-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6o**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 70:30%). A white solid was isolated in 44% yield (16.5 mg, 0.066 mmol). This solid was recrystallized from EtOAc/pentane as a colorless crystal, mp 214−216 °C. **^{1}H NMR** (400.16 MHz, CD_3SOCD_3) δ_H: 11.5 (br.s, 1H), 8.23 (d, J = 7.2, 1H), 8.15 (dd, J = 10.8, 2.4, 1H), 8.00 (dd, J = 8.8, 5.6, 1H), 7.53−7.48 (m, 2H), 7.31−7.27 (m, 1H), 7.21 (d, J = 8.0, 1H). **^{13}C NMR** (100.62 MHz, CD_3SOCD_3) δ_C: 165.4 (d, J = 248, 1C), 137.1, 134.9 (d, J = 9, 1C), 130.9 (d, J = 2, 1C), 124.4 (d, J = 10, 1C), 120.6 (d, J = 4, 1C), 115.9 (d, J = 23, 1C), 112.3 (d, J = 20, 1C). **HRMS** (TOF, ESI$^+$): calcd for $C_{12}H_8FNNaO_2S$ (M + Na)$^+$: 272.0152; Found: 272.0164.

*2-Fluoro-9-methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6p**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 43% yield (17.0 mg, 0.065 mmol), mp 244−245 °C. **^{1}H NMR** (400.16 MHz, CD_3COCD_3) δ_H: 8.03−7.98 (m, 3H), 7.44 (td, J = 8.5, 2.4, 1H), 7.34 (d, J = 8.4, 1H), 7.21 (d, J = 8.0, 1H), 2.43 (s, 3H). **^{13}C NMR** (100.62 MHz, CD_3COCD_3) δ_C: 164.7 (d, J = 248, 1C), 135.7 (d, J = 9, 1C), 134.8, 134.1, 132.1 (d, J = 3, 1C), 131.8, 125.9, 124.6 (d, J = 10, 1C), 121.7, 120.2, 115.4 (d, J = 23, 1C), 112.1 (d, J = 25, 1C), 20.0. **GC−MS** (EI) m/z 264 (M^+ + 1, 2), 263 (M^+, 75), 199 (22), 198 (100), 196 (6), 170 (13), 151 (6), 99 (9), 89 (6), 86 (7). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{10}FNNaO_2S$ (M + Na)$^+$: 286.0308; Found: 286.0304.

*9-Methyl-2-(trifluoromethyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (**6q**).* The product was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20%). A white solid was isolated in 42% yield (19.7 mg, 0.063 mmol), mp 244−245 °C. **^{1}H NMR** (400.16 MHz, $CDCl_3$) δ_H: 8.21 (s, 1H), 8.11 (d, J = 8, 1H), 7.82−7.79 (m, 2H), 7.30 (d, J = 8, 1H), 7.09 (d, J = 8, 1H), 7.07 (br. s, 1H) 2.48 (s, 3H). **^{13}C NMR** (100.62 MHz, $CDCl_3$) δ_C: 137.7, 135.7, 134.4 (q, J = 33, 1C), 133.5, 133.0, 132.2, 125.8, 124.8 (q, J = 4, 1C), 123.3 (q, J = 271, 1C), 123.2, 122.6 (q, J = 4, 1C), 122.4, 121.2 21.2. **GC−MS** (EI) m/z 314 (M^+ + 1, 13), 313 (M^+, 98), 249 (23), 248 (100), 229 (8), 228 (14), 180 (26), 179 (15), 178 (15), 152 (10), 151 (7), 114 (9), 69 (9). **HRMS** (TOF, ESI$^+$): calcd for $C_{14}H_{10}F_3NNaO_2S$ (M + Na)$^+$: 336.0276; Found: 336.0264.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00330.

The screening of optimal conditions for the copper-catalyzed *N*-arylation for the synthesis of *N*-phenyl-2-halobenzenesulfonamides and the UV−vis spectra for **3a** and anion derivative. Copies of ^{1}H NMR and ^{13}C NMR spectra for all substrates and products and theoretical section (*xyz* of stationary points) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: adriana@fcq.unc.edu.ar. Phone: (+54) 351-5353867 (A.B.P.).

*E-mail: sbarolo@fcq.unc.edu.ar. Phone: (+54) 351-5353867 (S.M.B.).

Notes

The authors declare no competing financial interest.

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