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Walter Damian Guerra, Roberto Arturo Rossi, Adriana Beatriz Pierini, and Silvia Maricel Barolo

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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\*

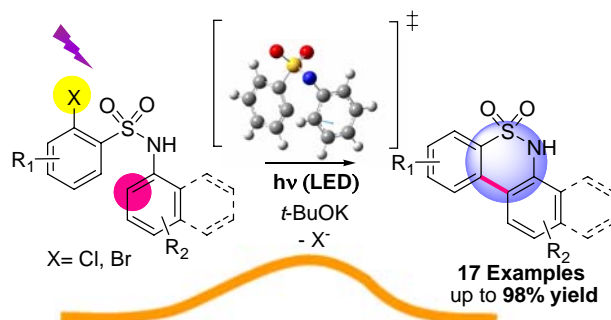
INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.

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CORRESPONDING AUTHOR FOOTNOTE (Phone number: (+54) 351-5353867, e-mail:

[adriana@fcq.unc.edu.ar](mailto:adriana@fcq.unc.edu.ar) and [sbarolo@fcq.unc.edu.ar](mailto:sbarolo@fcq.unc.edu.ar)

TITLE RUNNING HEAD: Synthesis of Dibenzosultams by Photoinduced Arylation

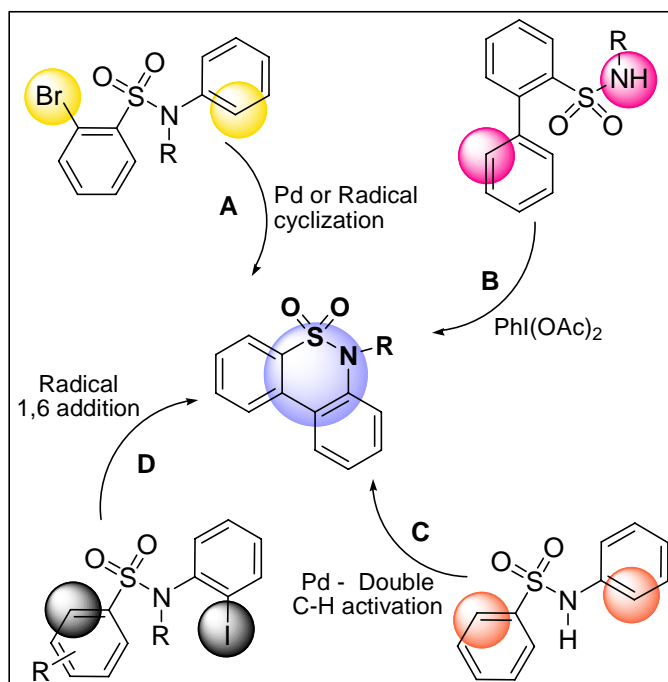


**ABSTRACT:** A new and general synthetic route to prepare dibenzosultams is here reported. This approach involves the synthesis of *N*-aryl-2-halobenzenesulfonamides (**3**) followed by intramolecular C-C photoinduced arylation under soft conditions without the use of “Transition-Metal”. The photostimulated 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 ( $\lambda=395$  nm) is an efficient light energy source to initiate efficiently the reactions. Theoretical inspection about 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.<sup>1</sup> 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,<sup>2</sup> HIV integrase<sup>3</sup> or Calpain-1.<sup>4</sup> Also, benzothiazine dioxide derivatives have been found to play an active role in nuclear factor-kappaB (NFκB) down regulation.<sup>5</sup>

Due to the remarkable importance of benzosultams across medicinal chemistry many synthetic approaches have been developed.<sup>6</sup> For dibenzosultams the synthetic approaches are less known and are represented in Scheme 1. These protocols include intramolecular radical cyclization<sup>7</sup> or palladium-catalyzed intramolecular arylation<sup>8</sup> of 2-bromo-*N*-arylbenzenesulfonamides (**A**), intramolecular oxidative amination of 2-arylbenzenesulfonamides under “Transition-Metal Free” condition (**B**),<sup>9</sup> double C(sp<sup>2</sup>)-H palladium-catalyzed intramolecular oxidative coupling of *N*-arylbenzenesulfonamides (**C**)<sup>10</sup> or 1,6 radical addition of *N*-(2-iodophenyl)-*N*-methyl-benzenesulfonamide (**D**)<sup>11</sup> (Scheme 1).



**Scheme 1.** Strategies to synthesize dibenzosultams

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3 Radical nucleophilic substitution involving electron-transfer (ET) steps ( $S_{RN}1$ )<sup>12</sup> is a cyclic  
4 process with radicals and radical anions as intermediates. In the  $S_{RN}1$  reactions carbanions and  
5 anions derived from heteroatoms can be used as nucleophiles to form new C-C or C-heteroatom  
6 bonds. This mechanism has proven to be an important synthetic strategy in heterocycle chemistry.  
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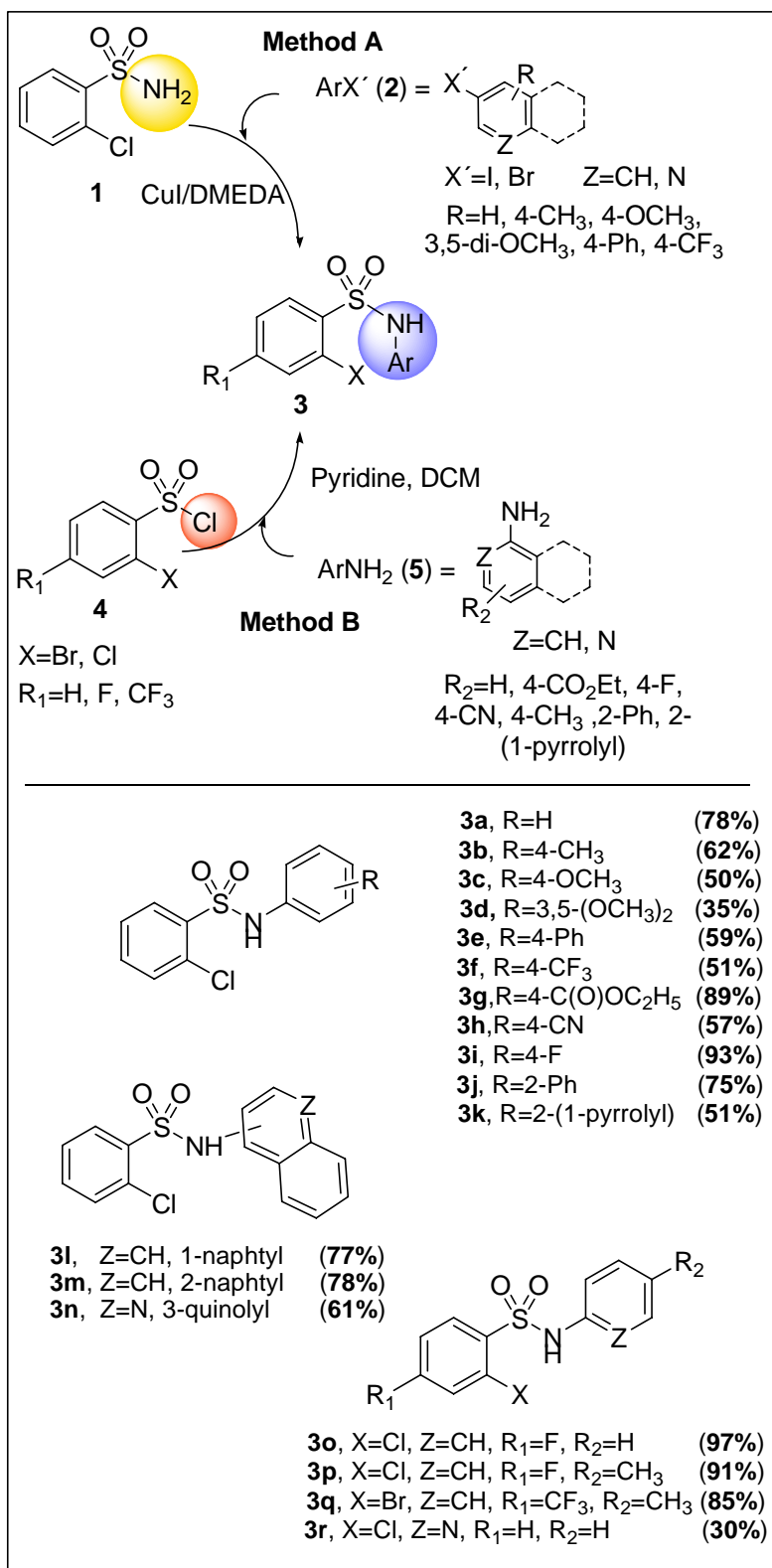
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10 The intramolecular  $S_{RN}1$  has been successfully developed to obtain different annulated  
11 systems bearing between 5 to 9 members with broad substitution tolerance.<sup>13</sup> In this context, the  
12 reaction of 2-iodobenzenesulfonamide with aliphatic ketone enolates to afford 3-substituted  
13 benzothiazines has been reported.<sup>14</sup> However, the reactivity of *N*-aryl-2-halobenzenesulfonamides  
14 under  $S_{RN}1$  conditions to obtain dibenzosultams has not been studied yet.  
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18 It is important to notice that despite useful synthetic protocols have been investigated to  
19 prepare dibenzosultams, still several limitations remain like the use of “Transition-Metal” (Pd),  
20 activated substrates like iodide or bromide aromatic precursors, harsh conditions or time-  
21 consuming reactions which need to be overcome.  
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25 In this context, we developed a novel protocol to synthesize dibenzosultams by  
26 intramolecular C-C photoinduced arylation of 2-halo-arylsulfonamides. This protocol involves  
27 chloride precursors easily prepared from commercial sources. Besides, the heterocycle could be  
28 obtained with a free N-H group that is easily functionalized. Furthermore, the utility of this method  
29 is fully demonstrated by exploring the scope toward a broad family of dibenzosultams and greener  
30 methodologies. This is a new contribution within our efforts devoted to the synthesis of  
31 heterocyclic compounds by “Transition-Metal-free” intramolecular photoinduced arylation  
32 reactions.<sup>13a</sup>  
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## 43 Results and Discussion

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47 Initially, we investigated different alternative to obtain *N*-aryl-2-halobenzenesulfonamides **3**  
48 (Scheme 2). The first strategy involves copper-catalyzed *N*-arylation of 2-  
49 chlorobenzenesulfonamide (**1**) with aryl halides **2**<sup>15</sup> (Method A). Under our optimized conditions,<sup>16</sup>  
50 the reaction of **1** with iodobenzene (**2a**) gave the coupling product *N*-phenyl-2-  
51 chlorobenzenesulfonamide (**3a**, Ar=Ph, X=Cl) in 78% isolated yield. This protocol was extended to  
52 different aryl halides obtaining good to very good isolated yields (50-84%) of the corresponding *N*-  
53 aryl-2-chloroarylsulfonamides (**3b-f**, **m-n** X=Cl) (Scheme 2).  
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**Scheme 2.** Synthesis of *N*-aryl-2-haloarylsulfonamides

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 at room temperature (Method B).<sup>17</sup> With this methodology we synthesized sulfonamides **3g-l, o-r**

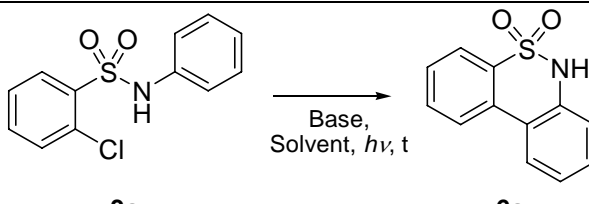
with a range of isolated yields from moderate to excellent depending on the corresponding amine (30 – 97%) (Scheme 2).<sup>18</sup>

*N*-phenyl-2-chlorobenzenesulfonamide (**3a**) was chosen as model substrate to attempt the intramolecular arylation using *t*-BuOK in DMSO. In this basic medium the initially neutral **3a** ( $\lambda_{\text{max}}$ =279 and 281 nm) undergoes an acid-base reaction to give the corresponding anion **3a<sup>-</sup>** (continuum absorption spectrum until 370 nm, see SI).<sup>19</sup>

After 3 hours 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 equivalents of *t*-BuOK and 3 hours of irradiation gave the best result (97% (86% isolated yield)).<sup>20</sup>

The other solvents tested were NH<sub>3</sub>(liq), CH<sub>3</sub>CN and THF. Similar results were obtained in liquid ammonia (-33 °C) (entry 6, Table 1), in CH<sub>3</sub>CN the reaction gave a very good yield (72 %) and THF proved to be ineffective for the reaction (entries 7-8, respectively, Table 1).

**Table 1.** Optimization of the Reaction Conditions<sup>a</sup>

			
Entry	Conditions	Yields (%) <sup>b</sup>	
	Solvent/ Base (Equiv)/ $h\nu$ , t (h)	<b>3a<sup>c</sup></b>	<b>6a</b>
1	DMSO/ <i>t</i> -BuOK (2)/ $h\nu$ , 3h	45	27
2	DMSO/ <i>t</i> -BuOK (2)/ $h\nu$ , 4h	27	53
3	DMSO/ <i>t</i> -BuOK (2)/ $h\nu$ , 6h	23	57
4	DMSO/ <i>t</i> -BuOK (3)/ $h\nu$ , 2h	13	75
5	<b>DMSO/ <i>t</i>-BuOK (3)/ <math>h\nu</math>, 3h</b>	<b>0</b>	<b>97 (86)</b>

6 <sup>d</sup>	NH <sub>3</sub> / <i>t</i> -BuOK (3)/ hν, 3h	4	95 (84)
7 <sup>e</sup>	THF/ <i>t</i> -BuOK (3)/ hν, 3 h	75	15
8 <sup>e</sup>	CH <sub>3</sub> CN/ <i>t</i> -BuOK (3)/ hν, 3 h	18	72
9	DMSO/ NaH (3)/ hν, 3 h	0	75
10	DMSO/ <i>t</i> -BuOK (3)/ hν, 1.5 h	21	64
11 <sup>f</sup>	DMSO/ <i>t</i> -BuOK (3)/ hν, 1.5 h	0	92
12	DMSO/ <i>t</i> -BuOK (3)/ dark, 3h	91	0
13 <sup>g</sup>	DMSO/ <i>t</i> -BuOK (3)/ hν, 1.5 h	97	0
14 <sup>h</sup>	DMSO/ <i>t</i> -BuOK (3)/ hν, 1.5 h	79	13

<sup>a</sup>The reactions were run in 5 mL of solvent with 0.03 M of **3a** and 0.09M 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 of (air and water refrigerated). <sup>b</sup>Yields were determined by CG (internal standard method). Isolated yields are given in parentheses. <sup>c</sup>Substrate **3a** recovered. <sup>d</sup>The reaction of liquid ammonia (NH<sub>3(lig)</sub>) was run in 200 ml (-33°C), with 0.75 mM of **3a** and 2.25 mM of *t*-BuOK. <sup>e</sup>The reactions in THF or CH<sub>3</sub>CN were run in 5 mL. <sup>f</sup>1 equiv of pinacolone was added with respect to the substrate. <sup>g</sup>0.3 equiv of *m*-DNB was added with respect to the substrate. <sup>h</sup>1 equiv of TEMPO was added with respect to the substrate.

When the reaction was carried out without *t*-BuOK (NaH as base) it proceeded completely which indicates that anion **3a**<sup>-</sup> 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)<sup>12c</sup> and equimolecular quantities of TEMPO could partially inhibit the reaction (entry 14 versus entry 10, Table 1). These results exclude a benzyne

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3 and other polar mechanisms and evidence an Electron Transfer (ET) process with formation of  
4 radicals. We propose a radical-anion type mechanism ( $S_{RN}1$ ) to be in play.  
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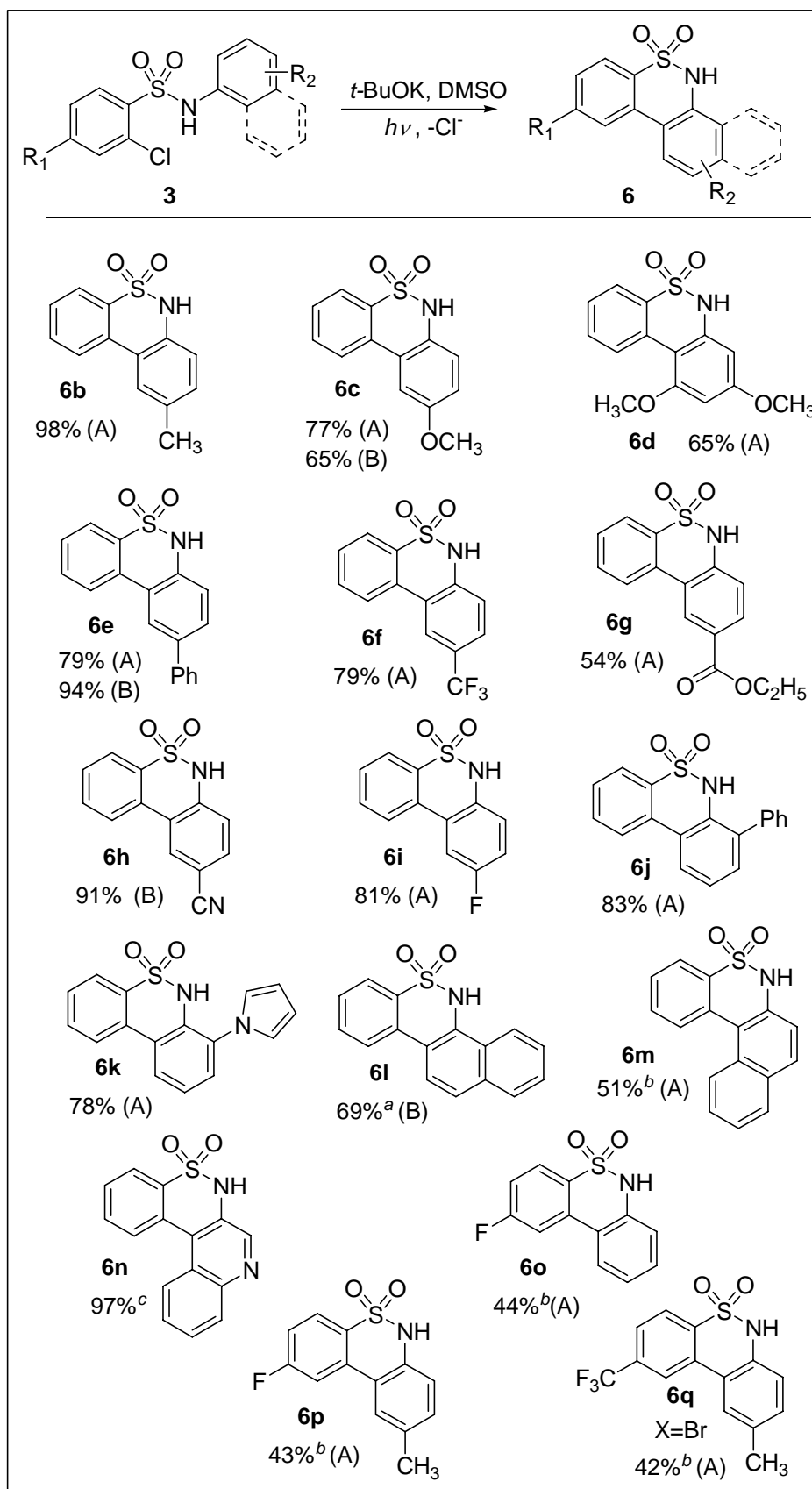
7 To extend the scope of the cyclization reaction, sulfonamides previously synthesized were  
8 submitted to the *t*-BuOK/DMSO/h $\nu$  system, the results being shown in Scheme 3. Modifying the  
9 R-substituent in the NH-phenyl moiety of the sulfonamides, with EWG or EDG, **3b-k**, led to full  
10 conversion of the substrate after 5h of irradiation providing products **6b-k** in good to excellent  
11 isolated yields (54 – 98%). This reveals broad substitution tolerance (CH<sub>3</sub>, OCH<sub>3</sub>, *di*-OCH<sub>3</sub>, CF<sub>3</sub>, F,  
12 CN, C(O)OC<sub>2</sub>H<sub>5</sub>, Ph) and low steric hindrance (tolerate *o*-substitution, **6j-k**).  
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17 The strategy was extended successfully to obtain fused dibensultams after longer irradiation  
18 times. *5H*-Benzo[*e*]naphtho[1,2-*c*][1,2]thiazine 6,6-dioxide (**6n**) and *6H*-benzo[5,6][1,2]thiazino-  
19 [3,4-*c*]quinoline 5,5-dioxide (**6l**) were obtained after 6h with 97% and 69% yields, respectively.  
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30 The effect of modifying the R-substituent in the sulfonyl-phenyl system was also examined.  
31 Substrates with a EWG like F or CF<sub>3</sub> (**3o-q**) were prepared. In these cases the reaction underwent  
32 partially without full conversion after 8h to afford the corresponding dibenzosultams **6o-q** with  
33 moderate yields (~45%).  
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35 Finally, we attempted the reaction of 2-chloro-*N*-(pyridin-2-yl)benzenesulfonamide (**3r**) as  
36 substrate, with a pyridine system, but it was unreactive under our experimental conditions.  
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A=Conventional “work-up” and purification. B= Direct filtration and recrystallization.

<sup>a</sup>Reaction time=6h. <sup>b</sup>Reaction time= 8h. <sup>c</sup>Acid extraction as “work-up” without further purification.

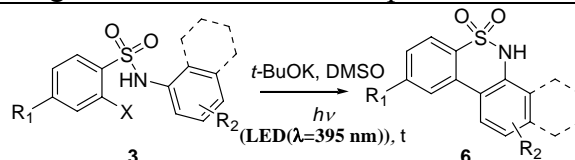
**Scheme 3.** Scope of the Intramolecular Photoinduced Arylation to synthesize 6*H*-dibenzothiazines 5,5-dioxide **6**.

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.<sup>21</sup>

The results under visible LED light are summarized in Table 2. Employing a Violet LED light ( $\lambda_{\text{max}}=395$  nm) the reaction undergo full conversion obtaining 82% yields of **6a** (entry 1, Table 2).<sup>22</sup> 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).

**Table 2.** Use of Visible-LED lights in the Intramolecular photoinduced arylation<sup>a</sup>



Entry	3 (%) <sup>b</sup>	t (h)	Products	
			6	Yields (%) <sup>c</sup>
1	<b>3a</b> (---)	3h	<b>6a</b>	82
2	<b>3b</b> (---)	5h	<b>6b</b>	84
3	<b>3i</b> (23)	5h	<b>6i</b>	71
4	<b>3j</b> (15)	5h	<b>6j</b>	80
5	<b>3l</b> (12)	6h	<b>6l</b>	84
6	<b>3m</b> (8)	8h	<b>6m</b>	76

7	<b>3o</b> (---)	5h	<b>6o</b>	94
8	<b>3p</b> (10)	8h	<b>6p</b>	87

<sup>a</sup>The reactions were run in 5 mL of DMSO with **3** (0.03 M) and 0.09M of *t*-BuOK. Irradiation was performed for the specific time with Violet LED (LEDs ( $\lambda = 395 \pm 15$  nm), 3 W, 700 mA). <sup>b</sup>Substrate **3** recovered. <sup>c</sup>Yields were determined by CG (internal standard method).

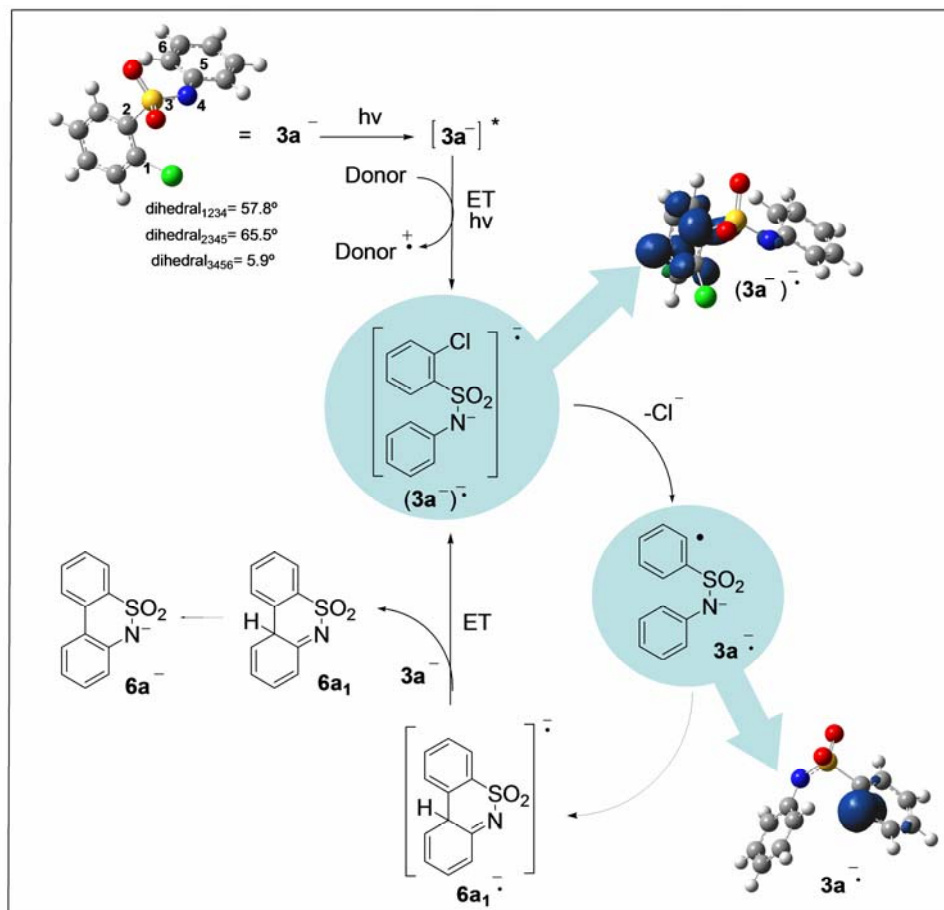
To support our experimental evidences of a radical-anion type mechanism ( $S_{RN}1$ ), we performed a computational study of key mechanistic intermediates and reactive pathways with anion **3a<sup>-</sup>** as model. The results are summarized in Scheme 4. The computational data were obtained with M06-2X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

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

The (**3a<sup>-•</sup>**) formed bears the unpaired spin density at the  $\pi$  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 **3a<sup>-•</sup>** through a transition state characterized by a C-Cl bending transition vector. As known, a  $\sigma(C-Cl)-\pi$  overlap is required for this  $\pi-\sigma$  intramolecular dissociative ET to take place.<sup>27</sup>

After C-Cl fragmentation, the distonic radical anion intermediate **3a<sup>-•</sup>**, represented in Scheme 4, could afford the cyclic radical anion **6a<sub>1</sub><sup>-•</sup>**. 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 **6a<sub>1</sub><sup>-•</sup>** is 24 kcal/mol more stable than the distonic radical anion **3a<sup>-•</sup>** and this difference could be the driving force of the reaction.

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3 Finally,  $6a_1$  and  $(3a^-)^{\bullet}$  could be formed after an ET from  $6a_1^{\bullet}$  to  $3a^-$ . The latter ET  
4 propagates the reaction cycle. Under the basic media  $6a_1$  generate  $6a^-$  and upon reaction work up,  
5 product  $6a$  was formed.  
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41 **Scheme 4.** Proposed Mechanism. The spin density is shown for  $(3a^-)^{\bullet}$  and  $3a^-$  (isodensity =  
42 0.004).  
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## 48 Conclusions

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51 To conclude, we described an efficient route to synthesize dibenzosultams under “Transition-  
52 Metal-Free” conditions starting from *N*-aryl-2-halobenzenesulfonamides easily prepared by two  
53 different procedures. The cyclization reactions are promoted by *t*-BuOK and occur in DMSO at  
54 room temperature. Many functional groups are tolerated, giving access to a wide range of  
55 synthetically relevant heterocycles. Other solvents such as NH<sub>3</sub> and CH<sub>3</sub>CN seem promising to  
56 perform the reactions. We also explored the use of visible LED light improving some yields of  
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3 challenging substrates. Finally, DFT calculations were performed to inspect the energetic and thus  
4 confirm our proposal of the radical-anion type  $S_{RN}1$  mechanism.  
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## 8 9 **Experimental Section**

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14 **Computational Procedure.** All calculations were performed with the Gaussian09 program. The  
15 conformers obtained were refined with complete geometry optimization within the M06-2X DFT  
16 functional and the 6-311+G\* basis set. The geometries thus found were used as starting points for  
17 the evaluation of the reaction profiles by using the distinguished reaction coordinate scan. The  
18 effect of DMSO as solvent was evaluated through the Tomasi's Polarized Continuum Model  
19 (PCM) as implemented in Gaussian09. The inclusion of the solvent in the calculations is a requisite  
20 to evaluate valence radical anions. The characterization of stationary points was done by Hessian  
21 matrix calculations. The energy informed for TSs, anions and radical anions includes zero-point  
22 corrections. The vertical excited singlet stated ( $S_1$ ) of anion **3a** was calculated with TD-DTF the  
23 M06-2X functional and the 6-311+G\* basis set. The energy of  $S_1$  was calculated including the  
24 PCM contribution under the StateSpecific approach.  
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33 **General Considerations.** Column chromatography was carried out on silica gel. Melting points  
34 were determined using a standard melting point instrument and are uncorrected. Gas  
35 chromatographic analyses were performed with a flame-ionization detector, on 30 m capillary  
36 column of a 0.32 mm x 0.25  $\mu$ m film thickness, with a 5% phenylpolysiloxane phase. GC-MS  
37 analyses were performed employing a 25 m x 0.2 mm x 0.33  $\mu$ m with a 5% phenylpolysiloxane  
38 phase column.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a 400.16 MHz in  $\text{CDCl}_3$ ,  
39 Dimethyl sulfoxide- $d_6$  ( $\text{CD}_3\text{SOCD}_3$ ) or acetone- $d_6$  ( $\text{CD}_3\text{COCD}_3$ ) as solvent with TMS as internal  
40 standard. Coupling constants are given in Hz and chemical shifts are reported in  $\delta$  values in ppm.  
41 Data are reported as followed: chemical shift, multiplicity (s = singlet, s br = broad singlet, d =  
42 doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m =  
43 multiplet), coupling constants (Hz), and integration. Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are  
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54 All new products were further characterized by HRMS. HRMS analyses were carried out  
55 using a TOF-MS instrument with an ESI source.  
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58 Irradiation was conducted in a reactor equipped with two Philips HPI-T 400 W lamps of  
59 metallic iodide (cooled with water) or with LED lights performing at 3W of potency and 700 mV  
60 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 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 stirred 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<sub>2</sub>CO<sub>3</sub> (381.3 mg, 1.8 mmol), acetonitrile (CH<sub>3</sub>CN) (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, 2M HCl (10 mL) was added slowly, followed by EtOAc extraction (15 mL x 3). The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, 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 %). White solid of 2-Chloro-*N*-phenylbenzenesulfonamide (**3a**) was isolated in 78% yield (125.9 mg, 0.468 mmol), m.p. 145-147°C. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 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). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 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<sup>+</sup>, 21), 168 (48), 167 (11), 111 (22), 93 (10), 92 (100), 75 (24), 65 (56), 64 (8).<sup>28</sup>

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 %). White solid was isolated in 62% yield (104.8 mg, 0.372 mmol), m.p. 151-152 °C. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 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); <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 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<sup>+</sup>, 9), 111 (15), 107 (8), 106 (100), 79 (30), 78 (12), 77 (35), 75 (18), 51 (9). **HRMS** (TOF, ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>12</sub>CINNaO<sub>2</sub>S (M+Na)<sup>+</sup>: 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 %). Colorless crystal was isolated in 50% yield (89.1 mg, 0.3 mmol), m.p. 134-135 °C. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 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).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+$ , 10), 263 (10), 229 (16), 228 (96), 213 (20), 197 (11), 152 (10), 126 (9), 125 (10), 111 (17). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{13}\text{H}_{12}\text{ClNNaO}_3\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 320.0119; Found: 320.0106.

*2-Chloro-N-(3,5-di-methoxyphenyl)benzenesulfonamide (3d)*. The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  70:30 %). Colorless crystal was isolated in 35% yield (68.7 mg, 0.21 mmol), m.p. 164-165  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 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).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+$ , 10), 263 (10), 229 (16), 228 (96), 213 (20), 197 (11), 152 (10), 126 (9), 125 (100), 111 (17). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{14}\text{H}_{14}\text{ClNNaO}_4\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 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  $\rightarrow$  80:20 %). White solid was isolated in 59% yield (60.9 mg, 0.177 mmol), m.p. 139-141  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400.16 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{H}}$ : 9.42 (br.s, 1H), 8.14 (d,  $J = 8.0$ , 1H), 7.60-7.48 (m, 7H), 7.47-7.28 (m, 5H).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+$ , 16), 169 (14), 168 (100), 166 (4), 141 (24), 139 (5), 115 (17), 111 (4), 75 (4). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{18}\text{H}_{14}\text{ClNNaO}_2\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 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  $\rightarrow$  80:20 %). White solid was isolated in 51% yield (102.8 mg, 0.306 mmol), m.p. 209-211 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 8.10-8.08 (m, 1H), 7.53-7.36 (m, 6H), 7.22 (d,  $J = 8.4$ , 2H).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+$ , 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,  $\text{ESI}^+$ ): calcd for  $\text{C}_{13}\text{H}_9\text{ClF}_3\text{NNaO}_2\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 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  $\rightarrow$  70:30 %). White solid was isolated in 78% yield (74.4 mg, 0.234 mmol), m.p. 187-189 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 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).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 136.1, 134.1, 133.5, 133.2, 132.0, 131.5, 131.3,

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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  
4 ( $M^{+}$ , 13), 218 (25), 143 (7), 142 (64), 140 (5), 116 (10), 115 (100), 89 (6), 75 (6). **HRMS** (TOF,  
5  $ESI^{+}$ ): calcd for  $C_{16}H_{12}ClNNaO_2S$  ( $M+Na$ ) $^{+}$ : 340.0170; Found: 340.0164.

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8 **2-Chloro-N-(quinolin-3-yl)benzenesulfonamide (3n)**. The product was purified by column  
9 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  50:50 %). Light yellow solid  
10 was isolated in 61% yield (116.6 mg, 0.366 mmol), m.p. 166-167  $^{\circ}C$ .  $^1H$  **NMR** (400.16 MHz,  
11  $CDCl_3$ )  $\delta_H$ : 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  
12 (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  $^{13}C$  **NMR** (100.62 MHz,  $CDCl_3$ )  $\delta_C$ : 145.9, 145.3, 135.9, 134.5, 132.0, 131.8, 131.3, 129.5, 129.2,  
14 129.1, 127.8, 127.6, 127.5, 127.4, 126.7. **GC-MS** (EI)  $m/z$  320 ( $M^{+}+2$ , 10), 318 ( $M^{+}$ , 25), 144 (11),  
15 143 (100), 116 (94), 115 (10), 111 (20), 89 (53), 75 (22), 63 (18). **HRMS** (TOF,  $ESI^{+}$ ): calcd for  
16  $C_{15}H_{12}ClN_2O_2S$  ( $M+H$ ) $^{+}$ : 319.0302; Found: 319.0303.

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19 **Method B:** Sulfonamides **3g-l/o-r** were synthesized by sulfonylation of the corresponding aniline.  
20 The aniline (0.72 mmol) was dissolved in dry  $CH_2Cl_2$  (1.2 mL), and the solution was treated with  
21 the corresponding 2-halobenzene-1-sulfonyl chloride (0.6 mmol) and pyridine (0.142 g, 1.8 mmol).  
22 The mixture was stirred at room temperature for 18 h, diluted with  $H_2O$  (15 mL) and extracted with  
23  $CH_2Cl_2$  (3 x 25 mL). The combined organic layers were washed with 1M HCl, brine, dried over  
24  $Na_2SO_4$ , and concentrated in vacuum. After removal of volatile components from the filtrate, the  
25 resulting crude product was purified by column chromatography on silica gel. Ethyl 4-(2-  
26 chlorophenylsulfonamido)benzoate (**3g**) was synthesized from 2-chlorobenzene-1-sulfonyl chloride  
27 (**4a**) and ethyl 4-aminobenzoate and purified eluting with pentane/ EtOAc (100:0  $\rightarrow$  70:30 %).  
28 Light yellow solid was isolated in 89% yield (181.4 mg, 0.534 mmol), m.p. 191-193  $^{\circ}C$ .  $^1H$  **NMR**  
29 (400.16 MHz,  $CD_3SOCD_3$ )  $\delta_H$ : 11.22 (br.s, 1H), 8.13 (d,  $J = 7.6$ , 1H), 7.81 (d,  $J = 8.8$ , 2H), 7.67-  
30 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).  $^{13}C$   
31 **NMR** (100.62 MHz,  $CD_3SOCD_3$ )  $\delta_C$ : 165.1, 141.6, 136.0, 135.0, 132.0, 131.7, 130.7, 130.5, 127.8,  
32 124.6, 117.6, 60.5, 14.1. **GC-MS** (EI)  $m/z$  339 ( $M^{+}$ , 60), 294 (41), 240 (30), 212 (21), 175 (21), 168  
33 (25), 164 (67), 136 (25), 119 (48), 113 (22), 111 (66), 108 (100), 92 (55), 91 (47), 90 (18), 65 (22),  
34 64 (33), 63 (26). **HRMS** (TOF,  $ESI^{+}$ ): calcd for  $C_{15}H_{14}ClNNaO_4S$  ( $M+Na$ ) $^{+}$ : 362.0224; Found:  
35 362.0228.

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38 **2-Chloro-N-(4-cyanophenyl)benzenesulfonamide (3h)**. The product was purified by column  
39 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  70:30 %). Light yellow solid  
40 was isolated in 57% yield (100.2 mg, 0.342 mmol), m.p. 199-201  $^{\circ}C$ .  $^1H$  **NMR** (400.16 MHz,  
41  $CD_3SOCD_3$ )  $\delta_H$ : 11.41 (br.s, 1H), 8.16-8.14 (m, 1H), 7.70-7.55 (m, 5H), 7.21 (d,  $J = 8.8$ , 2H).  $^{13}C$   
42 **NMR** (100.62 MHz,  $CD_3SOCD_3$ )  $\delta_C$ : 141.6, 135.9, 135.2, 133.7, 132.1, 131.7, 130.7, 128.0, 118.6,  
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3 117.9, 105.3. **GC-MS** (EI)  $m/z$  294 ( $M^+ +1$ , 14), 292 ( $M^+$ , 33), 277 (19), 193 (22), 177 (27), 175  
4 (69), 117 (17), 113 (32), 111 (100), 90 (29), 75 (40), 64 (12), 63 (13). **HRMS** (TOF,  $ESI^+$ ): calcd  
5 for  $C_{13}H_9ClN_2NaO_2S$  ( $M+Na$ ) $^+$ : 314.9966; Found: 314.9966.

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

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18 **N-([1,1'-Biphenyl]-2-yl)-2-chlorobenzenesulfonamide (3j)**. The product was purified by column  
19 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  80:20 %). White solid was  
20 isolated in 75% yield (154.8 mg, 0.45 mmol), m.p. 159-161 °C.  $^1H$  **NMR** (400.16 MHz,  
21  $CD_3SOCD_3$ )  $\delta_H$ : 9.72 (br.s, 1H), 7.67 (dd,  $J = 7.9$ , 1.5, 1H), 7.59-7.54 (m, 1H), 7.51 (dd,  $J = 8.0$ ,  
22 1.3, 1H), 7.41-7.23 (m, 9H), 7.01 (dd,  $J = 7.6$ , 1.3, 1H).  $^{13}C$  **NMR** (100.62 MHz,  $CD_3SOCD_3$ )  $\delta_C$ :  
23 139.7, 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,  
24 127.4, 127.0. **GC-MS** (EI)  $m/z$  343 ( $M^+$ , 8), 169 (12), 168 (100), 167 (72), 140 (5), 139 (8), 115  
25 (5), 111 (4), 75 (4). **HRMS** (TOF,  $ESI^+$ ): calcd for  $C_{18}H_{14}ClNNaO_2S$  ( $M+Na$ ) $^+$ : 366.0326; Found:  
26 366.0322.

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29 **N-(2-(1H-Pyrrol-1-yl)phenyl)-2-chlorobenzenesulfonamide (3k)**. The product was purified by  
30 column chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  90:10 %). Amber  
31 crystal was isolated in 51% yield (100.2 mg, 0.306 mmol), m.p. 122-124 °C.  $^1H$  **NMR** (400.16  
32 MHz,  $CDCl_3$ )  $\delta_H$ : 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,  
33 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,  $J$   
34 = 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,  $CDCl_3$ )  $\delta_C$ :  
35 136.2, 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.  
36 **HRMS** (TOF,  $ESI^+$ ): calcd for  $C_{16}H_{13}ClN_2NaO_2S$  ( $M+Na$ ) $^+$ : 355.0278; Found: 355.0266.

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39 **2-Chloro-N-(naphthalen-1-yl)benzenesulfonamide (3l)**. The product was purified by column  
40 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  80:20 %). Brown crystal was  
41 isolated in 77% yield (146.8 mg, 0.462 mmol), m.p. 166-167 °C.  $^1H$  **NMR** (400.16 MHz,  $CDCl_3$ )  
42  $\delta_H$ : 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),  
43 7.56-7.44 (m, 4H), 7.30-7.21 (m, 4H).  $^{13}C$  **NMR** (100.62 MHz,  $CDCl_3$ )  $\delta_C$ : 136.9, 134.3, 134.0,  
44 131.8, 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**  
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(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  $\rightarrow$  80:20 %). White solid was isolated in 97% yield (166.2 mg, 0.582 mmol), m.p. 109-110 °C.  $^1H$  NMR (400.16 MHz,  $CDCl_3$ )  $\delta_H$ : 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,  $CDCl_3$ )  $\delta_C$ : 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  $\rightarrow$  80:20 %). Light yellow solid was isolated in 91% yield (163.6 mg, 0.546 mmol), m.p. 110-112 °C.  $^1H$  NMR (400.16 MHz,  $CDCl_3$ )  $\delta_H$ : 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,  $CDCl_3$ )  $\delta_C$ : 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  $\rightarrow$  80:20 %). Colorless solid was isolated in 85% yield (200.1 mg, 0.51 mmol), m.p. 129-130 °C.  $^1H$  NMR (400.16 MHz,  $CD_3SOCD_3$ )  $\delta_H$ : 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,  $CD_3SOCD_3$ )  $\delta_C$ : 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  $\rightarrow$  70:30 %). White solid was isolated in 30% yield (24.2 mg, 0.09 mmol), m.p. 212-213 °C.  $^1H$  NMR (400.16 MHz,  $CDCl_3$ )  $\delta_H$ : 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,  $CDCl_3$ )  $\delta_C$ : 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

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3 (100), 264 (74), 172 (22), 168 (16), 133 (22), 124 (30), 121 (24), 118 (15), 109 (32), 98 (17), 79  
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5 (16), 78 (16), 62 (14). **HRMS** (TOF, ESI<sup>+</sup>): calcd for C<sub>11</sub>H<sub>9</sub>ClN<sub>2</sub>NaO<sub>2</sub>S (M+Na)<sup>+</sup>: 290.9966;  
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7 Found: 290.9965.

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9 **Representative Procedure for Photostimulated Reactions. Reactions in DMSO (THF or**  
10 **CH<sub>3</sub>CN).** The following procedure is representative of all these reactions. The reaction was carried  
11 out in a Schlenk tube equipped with a nitrogen inlet and magnetic stirred at r.t. DMSO (5 ml) was  
12 dried and deoxygenated, then *t*-BuOK (3.0 equiv, 50.5 mg, 0.45 mmol) was added and after 5 min  
13 the corresponding 2-halo-*N*-phenylbenzenesulfonamide (1 equiv, 0.15 mmol) was added and the  
14 reaction mixture was irradiated for the corresponding time. In case the 2-halo-*N*-  
15 phenylbenzenesulfonamide was an oil, it was added dissolved in anhydrous ethyl ether. The  
16 reaction was quenched with ammonium nitrate in excess. The “work-up” of the reaction could have  
17 two processes. “**Work-up A**” the residue was extracted with ethyl acetate (EtOAc) (3 x 30 ml) and  
18 the organic extracted was washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was  
19 removed under reduced pressure to give the crude products. The products were purified by  
20 chromatography on silica gel or quantified by GC using the internal standard method. Or “**Work-**  
21 **up B**” the residue was filtrate over a bed of silica gel with 300 ml of pentane/ EtOAc 70:30 %. The  
22 solvent was removed under reduced pressure and the crude obtained was then recrystallized.

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24 **Reaction in Liquid Ammonia.** Liquid ammonia (150 ml), previously dried over Na metal, was  
25 distilled into a 250 mL three-necked, round-bottomed flask equipped with a cold-finger condenser  
26 and a magnetic stirrer under a nitrogen atmosphere. The base *t*-BuOK (3.0 equiv, 50.5 mg, 0.45  
27 mmol) and then the corresponding 2-halo-*N*-phenylbenzenesulfonamides (1 equiv, 0.15 mmol)  
28 were added to the liquid ammonia. After 180 min of irradiation the reaction was quenched by  
29 addition of NH<sub>4</sub>NO<sub>3</sub> in excess, and the ammonia was allowed to evaporate. Water (50 mL) was  
30 added to the residue and the mixture was extracted with ethyl acetate (3 x 30 mL). The organic  
31 extract was dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure to  
32 leave the crude products. The products were purified by chromatography on silica gel or quantified  
33 by GC using the internal standard method.

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35 **Isolation and Identification of Products.** *6H-Dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (6a).* The  
36 product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0  
37 → 75:25 %). White solid was isolated in 86% yield (29.6 mg, 0.128 mmol), m.p. 195-197°C (lit.<sup>10</sup>  
38 194-195°C). **<sup>1</sup>H NMR** (400.16 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ<sub>H</sub>: 9.89 (br.s, 1H), 8.24-8.19 (m, 2H), 7.89 (dd,  
39 *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  
40 (m, 2H). **<sup>13</sup>C NMR** (100.62 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ<sub>C</sub>: 136.8, 135.5, 132.4, 132.3, 130.2, 128.2, 125.4,  
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3 125.2, 124.1, 122.4, 121.3, 119.9. **GC-MS** (EI)  $m/z$  232 ( $M^{+1}$ , 13), 231 ( $M^{+}$ , 91), 168 (14), 167  
4 (100), 166 (56), 140 (29), 139 (39), 115 (9), 113 (10), 89 (8), 84 (10), 70 (11), 69 (10), 63 (14).

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6 *9-Methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (6b)*. The product was purified by column  
7 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  70:30 %). White solid was  
8 isolated in 98% yield (36.1 mg, 0.147 mmol). This solid was recrystallized from acetone/pentane as  
9 white crystal, m.p. 217-219 °C.  **$^1\text{H NMR}$**  (400.16 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{H}}$ : 11.19 (br.s, 1H), 8.23 (d,  
10  $J = 8.0$ , 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  
11 (dd,  $J = 8.2$ , 1.0, 1H), 7.11 (d,  $J = 8.0$ , 1H), 2.369 (s, 3H).  **$^{13}\text{C NMR}$**  (100.62 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{C}}$ :  
12 134.6, 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**  
13 (EI)  $m/z$  246 ( $M^{+1}$ , 9), 245 ( $M^{+}$ , 69), 181 (21), 180 (100), 178 (9), 153 (6), 152 (17), 151 (7), 127  
14 (5), 90 (9), 89 (5), 77 (11), 76 (7), 75 (5), 63 (6), 51 (5). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  
15  $\text{C}_{13}\text{H}_{11}\text{NNaO}_2\text{S}$  ( $M+\text{Na}$ ) $^+$ : 268.0403; Found: 268.0400.

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17 *9-Methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (6c)*. The product was purified by column  
18 chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  60:40 %). White solid was  
19 isolated in 77% yield (30.2 mg, 0.115 mmol). This solid was recrystallized from acetone/pentane as  
20 light yellow crystal, m.p. 209-210 °C.  **$^1\text{H NMR}$**  (400.16 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{H}}$ : 11.0 (br.s, 1H),  
21 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,  $J$   
22 = 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).  **$^{13}\text{C NMR}$**  (100.62  
23 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{C}}$ : 156.1, 134.8, 132.4, 131.7, 129.7, 128.7, 126.0, 123.1, 121.8, 121.2, 117.1,  
24 109.5, 55.6. **GC-MS** (EI)  $m/z$  262 ( $M^{+1}$ , 11), 261 ( $M^{+}$ , 69), 183 (14), 182 (100), 155 (8), 154 (70),  
25 153 (14), 128 (23), 127 (30), 126 (12), 77 (10), 75 (8), 51 (8). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  
26  $\text{C}_{13}\text{H}_{11}\text{NNaO}_3\text{S}$  ( $M+\text{Na}$ ) $^+$ : 284.0352; Found: 284.0357.

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28 *8,10-Di-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (6d)*. The product was purified by  
29 column chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  60:40 %). Light  
30 yellow solid m.p. 229-231 °C was isolated in 65% yield (28.4 mg, 0.0975 mmol)..  **$^1\text{H NMR}$**   
31 (400.16 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{H}}$ : 9.70 (br.s, 1H), 8.59 (d,  $J = 8.4$ , 1H), 7.90 (dd,  $J = 7.8$ , 1.0, 1H),  
32 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),  
33 4.00 (s, 3H), 3.87 (s, 3H).  **$^{13}\text{C NMR}$**  (100.62 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{C}}$ : 161.5, 159.6, 139.4, 134.7,  
34 131.4, 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),  
35 291 ( $M^{+}$ , 100), 290 (12), 227 (17), 226 (9), 212 (11), 185 (9), 136 (9), 127 (14), 114 (9), 113 (9).  
36 **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{14}\text{H}_{13}\text{NNaO}_4\text{S}$  ( $M+\text{Na}$ ) $^+$ : 314.0457; Found: 314.0469.

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38 *9-Phenyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (6e)*. The product was purified by column  
39 chromatography on silica gel eluting with pentane/ EtOAc (70:30 %). White solid was isolated in  
40 94% yield (43.3 mg, 0.141 mmol). This solid was recrystallized from EtOAc /pentane as colorless  
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3 flakes, m.p. 235-236 °C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{H}}$ : 11.50 (br.s, 1H), 8.47 (d,  $J = 8.4$ ,  
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,  $J =$   
5 7.6, 2H), 7.39 (t,  $J = 7.6$ , 1H), 7.30 (d,  $J = 8.4$ , 1H).  $^{13}\text{C NMR}$  (100.62 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{C}}$ :  
6 139.4, 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,  
7 121.1, 120.2. **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{NNaO}_2\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 330.0559; Found: 330.0551.  
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10 *9-(Trifluoromethyl)-6H-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (6f)*. The product was purified by  
11 column chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  60:40 %). White solid  
12 was isolated in 79% yield (35.5 mg, 0.118 mmol). This solid was recrystallized from ethyl  
13 ether/pentane as white crystal, m.p. 234-236 °C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{H}}$ : 10.48  
14 (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,  
15 1H), 7.84-7.81 (m, 1H), 7.77 (1H, td,  $J = 7.6$ , 1.2, 1H), 7.52 (d,  $J = 8.4$ , 1H).  $^{13}\text{C NMR}$  (100.62  
16 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{C}}$ : 140.0, 135.4, 132.7, 131.1, 129.3, 126.8 (q,  $J = 4$ , 1C), 126.1, 125.5 (q,  $J =$   
17 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  
18 ( $\text{M}^++1$ , 26), 299 ( $\text{M}^+$ , 100), 281 (22), 236 (15), 235 (61), 234 (17), 216 (29), 207 (53), 204 (13),  
19 185 (28), 166 (23), 140 (14), 139 (17), 93 (15), 69 (16), 58 (74), 57 (18). (26). **HRMS** (TOF,  $\text{ESI}^+$ ):  
20 calcd for  $\text{C}_{13}\text{H}_8\text{F}_3\text{NNaO}_2\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 322.0120; Found: 322.0120.  
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31 *Ethyl 6H-dibenzo[*c,e*][1,2]thiazine-9-carboxylate 5,5-dioxide (6g)*. The product was purified by  
32 column chromatography on silica gel eluting with pentane/ EtOAc (100:0  $\rightarrow$  50:50 %). Light  
33 yellow solid was isolated in 54% yield (24.6 mg, 0.081 mmol). This solid was recrystallized from  
34 acetone/pentane as small white solid, m.p. 263-264 °C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{H}}$ :  
35 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-  
36 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).  
37  $^{13}\text{C NMR}$  (100.62 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{C}}$ : 165.2, 142.2, 134.0, 132.5, 131.0, 130.7, 128.9, 126.2,  
38 125.4, 124.0, 121.4, 120.3, 119.8, 60.7, 14.2. **GC-MS** (EI)  $m/z$  304 ( $\text{M}^++1$ , 13), 303 ( $\text{M}^+$ , 70), 275  
39 (35), 259 (18), 258 (100), 211 (9), 194 (17), 167 (10), 166 (36), 165 (9), 164 (13), 140 (21), 139  
40 (46), 138 (9). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{15}\text{H}_{13}\text{NNaO}_4\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 326.0458; Found:  
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51 *6H-Dibenzo[*c,e*][1,2]thiazine-9-carbonitrile 5,5-dioxide (6h)*. The product was filtrate over a bed  
52 of silica gel with 300 ml of pentane/ EtOAc 70:30 %. The solvent was removed under reduced  
53 pressure and then was recrystallized from acetone/pentane. Light yellow solid was isolated in 91%  
54 yield (35.0 mg, 0.136 mmol), m.p. decomposed over 213°C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CD}_3\text{SOCD}_3$ )  
55  $\delta_{\text{H}}$ : 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-  
56 7.85 (m, 2H), 7.77-7.73 (m, 1H), 7.33 (d,  $J = 8.4$ , 1H).  $^{13}\text{C NMR}$  (100.62 MHz,  $\text{CD}_3\text{SOCD}_3$ )  $\delta_{\text{C}}$ :  
57 140.4, 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**  
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(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  $\rightarrow$  60:40 %). White solid was isolated in 81% yield (30.0 mg, 0.121 mmol). This solid was recrystallized from EtOAc/pentane as white crystal, m.p. 214-215 °C.  **$^1H$  NMR** (400.16 MHz,  $CD_3SOCD_3$ )  $\delta_H$ : 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,  $CD_3SOCD_3$ )  $\delta_C$ : 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  $\rightarrow$  70:30 %). White solid was isolated in 83% yield (38.3 mg, 0.124 mmol). This solid was recrystallized from EtOAc/pentane as small white needles, m.p. 221-222 °C.  **$^1H$  NMR** (400.16 MHz,  $CD_3SOCD_3$ )  $\delta_H$ : 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,  $CD_3SOCD_3$ )  $\delta_C$ : 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  $\rightarrow$  70:30 %). White solid was isolated in 78% yield (34.7 mg, 0.117 mmol). This solid was recrystallized from EtOAc/pentane as light yellow crystal, m.p. 196-197 °C.  **$^1H$  NMR** (400.16 MHz,  $CD_3SOCD_3$ )  $\delta_H$ : 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,  $CD_3SOCD_3$ )  $\delta_C$ : 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 %). Red solid was isolated in 69% yield (29.1 mg, 0.103 mmol). This solid was recrystallized from Acetone/pentane as brown

crystal, m.p. 281-283 °C. **<sup>1</sup>H NMR** (400.16 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>H</sub>: 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). **<sup>13</sup>C NMR** (100.62 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>C</sub>: 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<sup>+</sup>+1, 16), 281 (M<sup>+</sup>, 82), 218 (14), 217 (100), 216 (49), 189 (16), 187 (10), 108 (29), 95 (17), 94 (13). **HRMS** (TOF, ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>11</sub>NNaO<sub>2</sub>S (M+Na)<sup>+</sup>: 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, m.p. decomposed over 223 °C (51 % isolated yield, 21.5 mg, 0.075 mmol). **<sup>1</sup>H NMR** (400.16 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 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<sup>+</sup>+1, 18), 281 (M<sup>+</sup>, 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<sup>+</sup>): calcd for C<sub>16</sub>H<sub>11</sub>NNaO<sub>2</sub>S (M+Na)<sup>+</sup>: 304.0403; Found: 304.0392.

*6H-Benzo[5,6][1,2]thiazino[3,4-c]quinoline 5,5-dioxide (6n)*. An especial procedure was followed to purify this compound. The crude was obtained by extraction from acid media (pH=1, H<sub>2</sub>SO<sub>4</sub>), with EtOAc (3 x 30 ml), the combined organic layers were washed with H<sub>2</sub>O (20 mL) and dried over anhydrous MgSO<sub>4</sub>; the solvent was evaporated under vacuum. Without further purification a yellow solid was obtained in 97% yield (41.1 mg, 0.145 mmol), m.p. decomposed over 185 °C. **<sup>1</sup>H NMR** (400.16 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>H</sub>: 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). **<sup>13</sup>C NMR** (100.62 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>C</sub>: 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<sup>+</sup>): calcd for C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>S (M+H)<sup>+</sup>: 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 %). White solid was isolated in 44% yield (16.5 mg, 0.066 mmol). This solid was recrystallized from EtOAc/pentane as colorless crystal, m.p. 214-216 °C. **<sup>1</sup>H NMR** (400.16 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>H</sub>: 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). **<sup>13</sup>C NMR** (100.62 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) δ<sub>C</sub>: 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<sup>+</sup>): calcd for C<sub>12</sub>H<sub>8</sub>FNNaO<sub>2</sub>S (M+Na)<sup>+</sup>: 272.0152; Found: 272.0164.

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*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 %). White solid was isolated in 43% yield (17.0 mg, 0.065 mmol), m.p. 244-245 °C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{H}}$ : 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).  $^{13}\text{C NMR}$  (100.62 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+ + 1$ , 2), 263 ( $\text{M}^+$ , 75), 199 (22), 198 (100), 196 (6), 170 (13), 151 (6), 99 (9), 89 (6), 86 (7). **HRMS** (TOF,  $\text{ESI}^+$ ): calcd for  $\text{C}_{13}\text{H}_{10}\text{FNNaO}_2\text{S}$  ( $\text{M} + \text{Na}$ ) $^+$ : 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 %). White solid was isolated in 42% yield (19.7 mg, 0.063 mmol), m.p. 244-245 °C.  $^1\text{H NMR}$  (400.16 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 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).  $^{13}\text{C NMR}$  (100.62 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 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 ( $\text{M}^+ + 1$ , 13), 313 ( $\text{M}^+$ , 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,  $\text{ESI}^+$ ): calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NNaO}_2\text{S}$  ( $\text{M} + \text{Na}$ ) $^+$ : 336.0276; Found: 336.0264.

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**Supporting Information Available.** The screening of optimal conditions for *N*-arylation Copper-catalyzed for the synthesis of *N*-phenyl-2-halobenzenesulfonamides and the Uv-vis spectra for **3a** and anion derivative are presented in Supporting Information. Copies of  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra for all substrates and products and theoretical section (xyz of stationary points) are available



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3 in Supporting Information. This material is available free of charge via the Internet at  
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(19) Uv-vis spectra for compounds **3a** (7.4 x 10<sup>-5</sup> M) and anion derivative **3a<sup>-</sup>** are presented in supporting information.

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