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Photo-Fries rearrangement of *N*-arylsulfonamides to aminoaryl sulfone derivatives

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Abstract—Photochemical reaction of variously substituted *p*-toluenesulfonanilides was studied. The reaction gives rearranged products, *o*- and *p*-amino-substituted diaryl sulfones with the combined yields of 38–72%: the *p*-isomer is more favored over the *o*-isomer with the selectivity ratio of 1.1–4.3 depending on the substituents. *N*-Alkylation of the sulfonanilides increases the yields of the rearranged products, and *e*-withdrawing substituents on the *N*-phenyl ring does not lower the yields drastically. This study provides simple methodology for the synthesis of *o*- and *p*-aminoaryl sulfones which are otherwise not easily accessible.

1. Introduction

Aminoaryl sulfone derivatives are important class of compounds since they show interesting biological and pharmacological properties such as inhibitory effect on *Escherichia coli* dihydropteroate synthase and anti-inflammatory activity.[1–6] The aminoaryl sulfones have usually been prepared by reduction of the corresponding nitroaryl sulfones.[1,2] The nitroaryl sulfones are obtained either from sulfonylation of arenes using nitroaryl sulfonyl chloride in the presence of Lewis acid[1] or from oxidation of nitroaryl sulfides which are prepared from the reaction of chloronitrobenzene with thiophenol derivatives.[2] These procedures have their own drawbacks: the sulfonylation approach suffers from inefficiency with arenes bearing strongly electron-withdrawing substituents, and the oxidation process is limited by the availability of sulfides.

The aminoaryl sulfones have also been prepared via rearrangement of *N*-arylsulfonamide derivatives either chemically[7–12] or photochemically,[12–15] but the studies are rather limited. Moreover, *p*-aminoaryl sulfones were not obtained by chemically induced rearrangement of the sulfonamides.[7–12] Also, the product selectivities of the photochemical reactions of *N*-aryl sulfonamides are widely different among the reports.[12–16] Nozaki et al.[13] reported that irradiation of arenesulfonanilides yielded exclusively *p*-amino-substituted diaryl sulfones without formation of *o*-amino-substituted products, while Hellwinkel et al.[12] later described that *N*-*p*-tolyl-benzenesulfonamides rearrange photolytically to *o*-aminophenyl sulfones. On the other hand, Weiss and co-workers reported the formation of the both, *o*- and *p*-rearranged products,[14] while Badr et al. could not observe the isomeric aminophenyl phenyl sulfones from the photolysis of *N*-arylarenesulfonamides.[16] There is also a report that photolysis of benzenesulfonanilide gave only 4-aminodiphenyl sulfone in isotropic media, but 2-amino-diphenyl sulfone is obtained exclusively upon cyclodextrin encapsulation.[15] On the other hand, Henning et al. reported that *N*-tosyl-β-aminovinyl phenyl ketones rearrange photochemically to α-tosyl-β-aminovinyl phenyl ketones.[17]

In this paper, we carried out a systematic study on the photochemical reaction of *N*-arylsulfonamides using a wide range of variously substituted *N*-aryl-*p*-toluenesulfonamides to find out the scope of the reaction and to exploit the reaction as a methodology for the synthesis of aminoarylsulfones.

2. Results and discussion

Various *N*-aryl-*p*-toluenesulfonamides were easily prepared in almost quantitative yields by tosylation of aniline derivatives with tosyl chloride in the presence of pyridine in CH_2Cl_2. *N*-Alkyl-*N*-aryl-*p*-toluenesulfonamides were obtained in more than 90% yields by alkylation of *N*-aryl-*p*-toluenesulfonamides with alkyl halide in the presence of potassium carbonate in DMF solvent. Figure 1 depicts the various *p*-toluenesulfonanilides prepared and used in this study.

To check the scope and feasibility of the reaction, we first studied the photoreaction of *p*-toluenesulfonamide of

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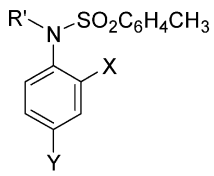
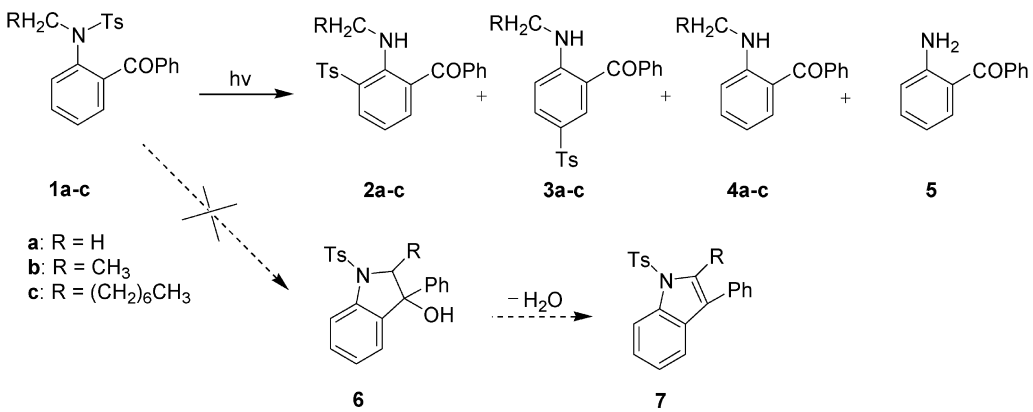


1a-l

a: X = COPh; Y = H; R' = CH_3
b: X = COPh; Y = H; R' = CH_2CH_3
c: X = COPh; Y = H; R' = $(CH_2)_7CH_3$
d: X = H; Y = H; R' = H
e: X = H; Y = H; R' = CH_3
f: X = H; Y = OCH_3; R' = H
g: X = H; Y = OCH_3; R' = CH_3
h: X = OCH_3; Y = H; R' = H
i: X = H; Y = Cl; R' = H
j: X = Cl; Y = H; R' = H
k: X = H; Y = F; R' = H
l: X = F; Y = H; R' = H

Figure 1. *p*-Toluenesulfonanilide derivatives prepared and used in the present study.



Scheme 1. Photoreaction of *p*-toluenesulfonamides **1a**–**c** of *o*-(*N*-alkylamino)benzophenones.

o-(*N*-alkylamino)benzophenone **1a**–**c** considering the following two points. One is that it is generally known that in the photo-Fries rearrangement of aryl esters the presence of electron-withdrawing substituents (for instance acyl groups) in the phenolic ring inhibits the rearrangement.[18,19] The other is that the compounds **1a**–**c** could lead to photocyclized products (vide infra).

1 mM solution of **1a**–**c** in a quartz vessel was irradiated with 254 nm lamps for 4 h under a nitrogen atmosphere. Separation of the reaction mixture by column chromatography gave *o*- and *p*-rearranged products, **2a**–**c** and **3a**–**c**, together with the detosylated compounds **4a**–**c** (Scheme 1). The detosylated and dealkylated product **5** was obtained in less than 5% yield. The compound **6** and/or **7**, which would be formed if photocyclization reaction via δ-hydrogen abstraction[20–22] had occurred, were not detected.

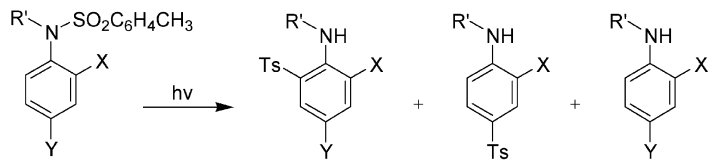
Photoirradiation of **1a**–**c** was also carried out using 350 nm lamps instead of 254 nm since it was reported that near UV irradiation of *o*-benzoyl *N*-alkylanilinium ions and β-aminovinyl phenyl ketones leads to the photocyclized products[20,21] and also the photocyclization reaction of *o*-alkoxybenzophenones to benzofuran derivatives proceeds effectively with 350 nm light.[22] After 4 h, the reaction mixture showed very low conversion of the starting material and the cyclized products were not detected. This is reminiscent of a report[23] that *o*-(*N*-alkylacylamino)benzophenones undergo primarily photolytic deacylation and dealkylation without formation of indoles. It was suggested that photodeacylation occurs from the π,π^* excited state of the acylamino ketone and dealkylation proceeds via intramolecular δ-hydrogen abstraction occurring in the charge-transfer state from the n,π^* excited state.[23]

Table 1 summarizes the yields and the products distribution obtained in the photoreaction of **1a** under various conditions. It shows that the conversion rate of the starting material is slowest in benzene[24] and getting faster in the order of acetonitrile, *t*-butanol, and then methanol solvent: almost all the starting material disappeared in methanol, *t*-butanol, and acetonitrile solvents after 4 h of irradiation

Table 1. Yields and product distribution obtained after photoirradiation of 1 mM solution of **1a** for 4 h

Solvent	λ (nm)	Recovered **1a** (%)	Yield (%)				
			2a	**3a**	**4a**	**5**	**2a**+**3a**
Benzene	254	27	15	19	23	nd	34(47)[a]
	350	86	nd	nd	6	2	nd
MeOH	254	nd	16	18	22	2	34
	350	66	3	5	5	2	8(24)[a]
CH3CN	254	3	21	30	17	nd	51(53)[a]
	350	78	3	2	4	nd	5(23)[a]
t-BuOH	254	nd	22	26	23		48
	350	72	5	2	9	1	7(25)[a]

The yields are isolated yields. nd: not detected.
[a] The yields in parentheses are calculated on the consumed **1a**.



d: X = H; Y = H; R' = H
e: X = H; Y = H; R' = CH_3
f: X = H; Y = OCH_3; R' = H
g: X = H; Y = OCH_3; R' = CH_3
h: X = OCH_3; Y = H; R' = H
i: X = H; Y = Cl; R' = H
j: X = Cl; Y = H; R' = H
k: X = H; Y = F; R' = H
l: X = F; Y = H; R' = H

Scheme 2. Photoreaction of *p*-toluenesulfonamides **1d–l** of various aniline derivatives.

with 254 nm lamps. The combined yields of the rearranged products, *o*- and *p*-aminosulfones based on the consumed **1a** are ca. 50% except in methanol solvent where the yield is 34%. It would be worth mentioning that though it is generally believed that polar solvents such as methanol favor the rearrangement in the photo-Fries rearrangement of phenyl esters,[26] Pitchumani et al.[27] found little difference in the yields of the rearranged products in methanol and benzene. Table 1 also shows that formation of *p*-isomer is a little more favored than *o*-isomer in all the solvents employed here and the selectivity is greatest in acetonitrile solvent as 1.4. The detosylated product **4a** is obtained in ca. 20% yield and the detosylated and dealkylated product **5** is produced in less than 5% yield. The photoreaction of **1a** with 350 nm lamps results in very low conversion and gave small amounts of **2a** and **3a** except in benzene where the rearranged products were not detected. Similar results were obtained with the sulfonamides **1b** and **1c**: the reactions were slowest in benzene and the combined yields of the rearranged products and the ratios of the *p*- to *o*-aminoarylsulfones were highest in acetonitrile solvent.

Since we found that the photoirradiation of the sulfonamides **1a–c** with highly electron-withdrawing substituents with 254 nm light gives *o*- and *p*-amino-substituted arylsulfone derivatives with modest yields, we proceeded with the photoreaction using variously substituted sulfonamides **1d–l** to find out the substituent effects and the scope of the reaction. 5 mM solutions of various sulfonamides **1d–l** were irradiated with 254 nm lamps in acetonitrile solvent and the products were separated to provide the amino-arylsulfones **2d–l** and/or **3d–l** (Scheme 2). The detosylated compounds **4d–l** were obtained with less than 3% yields, which is in contrast to ca. 20% yields of **4a–c** from **1a–c**. The yields of the rearranged products, *o*- and *p*-amino-arylsulfones are listed in Table 2, where the data obtained from **1a–c** are also included for comparison.

Table 2 shows that photoirradiation of **1d** gives both *o*-aminophenyl tolyl sulfone **2d** and *p*-aminophenyl tolyl sulfone **3d** with 15 and 32% isolated yields, respectively, in contrast to the previous reports of the formation of only the *p*-isomer with 7% isolated yield (25% yield based on the consumed starting material)[13] and the formation of both

Table 2. Yields of *o*- and *p*-aminoaryl sulfones obtained from the photoirradiation of various *p*-toluenesulfonanilides in CH_3CN using 254 nm lamps

Entry	Starting material, **1**	X	Y	R′	Reaction time (h)	Yield of aminoaryl sulfones (%)		
						o-isomer, **2**	*p*-isomer, **3**	**2**+**3**
1	**1a**	COPh	H	CH_3	4	21	30	51
2	**1b**	COPh	H	Et	4	22	30	52
3	**1c**	COPh	H	C_8H_{17}	4	14	24	38
4	**1d**	H	H	H	4	15	32	47
5[a]	**1d**	H	H	H	10	nd	7(25)[b]	7(25)[b]
6[c]	**1d**	H	H	H	Not given	6	13	19
7	**1e**	H	H	CH_3	4	26	26	52
8	**1f**	H	OCH_3	H	5	59	nd	59
9	**1g**	H	OCH_3	CH_3	4	72	nd	72
10	**1h**	OCH_3	H	H	4	25	27	52
11	**1i**	H	Cl	H	0.5[d]	20(39)[b]	nd	20(39)[b]
12	**1i**	H	Cl	H	2[e]	28(30)[b]	12[f](13)[b]	40(43)[b]
13	**1i**	H	Cl	H	5	25[g]	16[f]	41
14	**1j**	Cl	H	H	4	18(5)[h]	32	55
15	**1k**	H	F	H	4	39	nd	39
16	**1l**	F	H	H	5	18	29	47

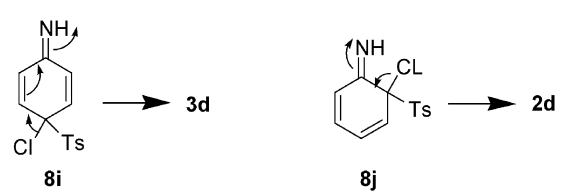
5 mM solution was irradiated except for **1a–c** where 1 mM solution was used. The yields are isolated yields. nd: not detected.
[a] From Ref. 13: solvent was *n*-butanol.
[b] The yields in parentheses are calculated on the consumed starting materials.
[c] From Ref. 14: solvent was diethyl ether and the reaction time was not mentioned.
[d] 49% of the starting material was recovered.
[e] 6% of the starting material was recovered.
[f] Dechlorinated *p*-rearranged product, **3d** was obtained.
[g] 1:1 mixture of **2i** and **2d**.
[h] 5% of the dechlorinated *o*-rearranged product, **2d** was obtained together with 18% yield of **2j**.

isomers with the combined yield of less than 20%.[14] Table 2 also shows that both *o*- and *p*-aminoarylsulfones are formed from all the arylsulfonamides studied here (see entries 1–4, 7, 10, 14, and 16) unless the corresponding positions are already occupied with substituents, and the formation of the *p*-isomer is always favored over the *o*-isomer. The *para* to *ortho* selectivity ratio varies from 1.1 for **1h** (entry 10) to 4.3 for **1d** (entry 4): when two *o*-positions of the starting material are unsubstituted, the selectivity ratio is twice the ratio of the yields. Clarification of the origin for this selectivity is beyond the scope of this work, but it might be worth to mention that the photo-Fries rearrangements of phenyl esters show no general trend of the selectivity.[15,18,27–29]

The combined yields of the rearranged products, **2** and **3** vary from ca. 40% (entries 3, 12, 13, and 15) to 72% (entry 9). Table 2 indicates that *N*-alkylation of sulfonanilides increases the yields of the sulfones (see entry 4 vs 7 and entry 8 vs 9). Introduction of electron-donating substituents often gives higher yields of the rearrangement products (compare entries 7 and 9, and also entries 4, 8, 10, 13, and 15), but the trend is not always hold (compare entries 1 and 7, and also entries 4 and 16).

Table 2 also shows that dechlorinated products are formed in the photoreaction of **1i** and **1j**: only 2-amino-5-chlorophenyl *p*-tolyl sulfone **2i** was detected from irradiation of *N*-*p*-chlorophenylsulfonamide **1i** for 0.5 h (entry 11), but dechlorinated products, *o*- and *p*-aminophenylsulfones, **2d** and **3d** are formed after longer irradiation (entries 12 and 13). *N*-*o*-Chlorophenylsulfonamide **1j** also gives small amount of dechlorinated product, *o*-aminophenylsulfone **2d** in addition to the simply rearranged products **2j** and **3j**. Similar to this, dechlorinated products have been reported in the photo-Fries reaction of phenyl benzoates.[18,30] The dechlorinated products **2d** and **3d** could be formed either via the diene intermediates **8j** and **8i**, respectively, or via initial dechlorination from the starting *N*-chlorophenylsulfonamides **1i–j** followed by rearrangement of the sulfonyl group: irradiation of the rearranged sulfones **2i** and **2j** under the same conditions for the photochemical reaction of **1i** and **1j** gave no appreciable amounts of the dechlorinated products (Scheme 3).

Finally, we would like to mention that the structures of *ortho*- and *para*-aminophenyl sulfones are clearly differentiated by their NMR data, especially the chemical shifts of amino protons, which are listed in Table 3. The table shows that the amine proton(s) of *o*-aminophenylsulfone derivatives absorb at lower field ($\Delta\delta$ is ca. 1 ppm) than the amine proton(s) of the corresponding *p*-isomers (entries 4, 5, 8, 10, and 12), which is well expected since the hydrogen bonding between the amine hydrogen and sulfonyl oxygen atom is



Scheme 3.

Table 3. ^{1}H chemical shifts (δ) of the amine protons of *o*- and *p*-aminoaryl sulfones in $CDCl_3$ solvent

Entry	Compound	X	Y	R′	δ value of amine protons	
					o-isomer, **2**	*p*-isomer, **3**
1	**a**	COPh	H	CH_3	6.65	8.94
2	**b**	COPh	H	Et	6.30	8.93
3	**c**	COPh	H	C_8H_{17}	6.37	9.02
4	**d**	H	H	H	5.12	4.17
5	**e**	H	H	CH_3	6.31	4.38
6	**f**	H	OCH_3	H	4.79	–
7	**g**	H	OCH_3	CH_3	5.94	–
8	**h**	OCH_3	H	H	5.37	4.30
9	**i**	H	Cl	H	5.13	–
10	**j**	Cl	H	H	5.61	4.57
11	**k**	H	F	H	4.98	–
12	**l**	F	H	H	5.22	4.27

possible in the *o*-isomers. However, the situation is reversed in the aminoarylsulfones substituted with *o*-benzoyl group (entries 1–3): the amine proton of 2-amino-3-benzoylphenyl sulfones **2a–c** appear at δ 6.3–6.7, while those of the corresponding *p*-amino isomers **3a–c** are in the range of δ 8.9–9.0. This suggests that when the amine group is located at *ortho* position both to the benzoyl group and sulfonyl group, the amine hydrogen is hydrogen-bonded to the sulfonyl oxygen rather than to the carbonyl oxygen atom: the chemical shifts of the amine protons of **2a–c** are in the same range with those observed in other *o*-aminoaryl sulfones (compare entries 1–3 with entries 5 and 7), while the chemical shifts of the amine protons of **3a–c** are in the similar range with other *o*-aminobenzophenone compounds such as **4a–c** whose chemical shifts are δ 8.5–8.6 (Section 4).

The fact that the amine hydrogen is not hydrogen-bonded to CO in the compounds **2a–c** is also manifested in their IR spectra: the carbonyl absorption bands of **2a–c** (1646–1661 cm^{-1}) appear at 21–34 cm^{-1} higher wavenumbers than the corresponding **3a–c** (1622–1627 cm^{-1}) where internal hydrogen bonding between the amine hydrogen and carbonyl group shifts the carbonyl absorption to lower wavenumbers.

Energy calculation provided further support for the presence of the hydrogen bonding between NH and SO rather than between NH and CO. The energy-minimized structures of **2a** by MM2 modelling suggested that two conformations with different distances between the amine hydrogen and the oxygen atoms are energetically feasible. In one form, the distance between the amine hydrogen and the sulfonyl oxygen atom is 1.79 Å, while the distance between the hydrogen and the carbonyl oxygen atom is 4.68 Å. In the other form, the corresponding distances are 4.42 and 1.84 Å, respectively. The former appeared to be more stable than the latter by 3.5 kcal/mol. This is consistent with NMR and IR results.

3. Conclusions

We have shown that photochemical reaction of variously substituted *p*-toluenesulfonanilides provides moderate yields of *o*- and *p*-aminophenyl sulfone derivatives with

the *para* to *ortho* selectivity ratio of 1.1–4.3 depending on the substituents. *N*-Alkylation of the sulfonanilides increases the yields of the rearranged products, and electron-withdrawing substituents on the *N*-phenyl ring does not lower the yields drastically. The results presented here would provide a simple route for the synthesis of *o*- and *p*-aminoarylsulfones which are not easily accessible by other methods.

4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were obtained using tetramethylsilane as an internal standard. The molecular modelling calculations were carried out with MM2 force field provided by Cambridgesoft. Melting points are uncorrected.

4.2. General procedure for the synthesis of *N*-aryl-*p*-toluenesulfonamides 1a–l

To a mixture of aniline derivative (30 mmol) and pyridine (15 ml, 180 mmol) in dichloromethane (100 ml) was added slowly *p*-toluenesulfonyl chloride (6.86 g, 36 mmol). The reaction mixture was stirred at room temperature for 16 h for *o*-aminobenzophenone or 0.5 h for other aniline derivatives. The reaction mixture was concentrated to ca. 50 ml, and then washed with 5% HCl. The organic layer was dried over sodium sulfate, filtered, and evaporated to afford a residue. Purification of the residue by silica gel column chromatography provided the corresponding *N*-aryl-*p*-toluenesulfonamide **1d**, **1f**, or **1h–l** in 90–100% yields.

For preparation of *N*-alkyl-*N*-aryl-*p*-toluenesulfonamides **1a–c**, **1e**, and **1g**, appropriate alkyl halide (7.5–10 mmol) was added slowly to a reaction mixture of *N*-aryl-*p*-toluenesulfonamide (5 mmol) and potassium carbonate (4.15 g, 30 mmol) in 20 ml of DMF and stirred: reaction temp and reaction time are room temperature and 1 h for the reaction with methyl iodide, room temperature and 15 h for ethyl iodide, and 70°C and 20 h for octyl bromide. After concentrating the reaction mixture, dichloromethane (20 ml) was added to the residue and washed with distilled water. The organic layer was dried over sodium sulfate, filtered, and evaporated to afford a residue. Purification of the residue by silica gel column chromatography provided the corresponding *N*-alkyl-*N*-aryl-*p*-toluenesulfonamide in more than 90% yield.

4.2.1. Compound 1a. R_f 0.25 (hexane–ethyl acetate, 5:1); mp 131–132°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, 2H, J=8 Hz), 7.57 (t, 1H, J=8 Hz), 7.49–7.39 (m, 7H), 7.15 (d, 2H, J=8 Hz), 6.97 (d, 1H, J=8 Hz), 3.09 (s, 3H), 2.37 (s, 3H). IR (KBr): 1670, 1593, 1446, 1342, 1159, 709 cm^{-1}. UV (CH_3CN): λ_{max} (ε) 238 nm (22000). Anal. calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83; S, 8.77. Found: C, 69.30; H, 5.23; N, 3.61; S, 8.81.

4.2.2. Compound 1b. R_f 0.45 (dichloromethane–hexane, 5:1); mp 129–131°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, 2H, J=8 Hz), 7.56 (t, 1H, J=7 Hz),7.48–7.37 (m, 7H), 7.14 (d, 1H, J=8 Hz), 7.09 (d, 2H, J=8 Hz), 3.67 (q, 2H, J=7 Hz), 2.31 (s, 3H), 1.16 (t, 3H, J=7 Hz). IR (KBr): 1660, 1595, 1328, 1168, 1146, 711 cm^{-1}. UV (CH_3CN): λ_{max} (ε) 242 nm (23000). Anal. calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 70.01; H, 5.62; N, 3.43; S, 8.12.

4.2.3. Compound 1c. R_f 0.58 (hexane–ethyl acetate, 4:1); oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78–7.75 (m, 2H), 7.56 (t, 1H, J=7 Hz), 7.48–7.35 (m, 7H), 7.16 (d, 1H, J=8 Hz), 7.08 (d, 2H, J=8 Hz), 3.56 (t, 2H, J=8 Hz), 2.31 (s, 3H), 1.56 (br s, 2H), 1.30–1.16 (m, 10H), 0.86 (t, 3H, J=7 Hz). IR (KBr): 1668, 1597, 1346, 1159, 753 cm^{-1}. UV (CH_3CN): λ_{max} (ε) 241 nm (24000). Anal. calcd for $C_{28}H_{33}NO_3S$: C, 72.54; H, 7.17; N, 3.02; S, 6.92. Found: C, 72.87; H, 7.28; N, 3.07; S, 6.68.

4.2.4. Compound 1d. R_f 0.59 (hexane–ethyl acetate, 2:1); mp 104–105°C (lit.[31] 103–104°C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, 2H, J=8 Hz), 7.25 (br s, 1H, –NH), 7.23–7.20 (m, 4H), 7.10–7.06 (m, 3H), 2.36 (s, 3H). UV (CH_3CN): λ_{max} (ε) 221 nm (16000).

4.2.5. Compound 1e. R_f 0.70 (hexane–ethyl acetate, 2:1); mp 95–97°C (lit.[32] 93–95°C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (d, 2H, J=8 Hz), 7.32–7.22 (m, 5H), 7.11–7.07 (m, 2H), 3.16 (s, 3H), 2.42 (s, 3H). UV (CH_3CN): λ_{max} (ε) 227 nm (11000).

4.2.6. Compound 1f. R_f 0.51 (hexane–ethyl acetate, 2:1); mp 114.7–115.5°C (lit.[33] 114.5–115°C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, 2H, J=8 Hz), 7.20 (d, 2H, J=8 Hz), 6.99 (d, 2H, J=9 Hz), 6.80 (s, 1H, –NH), 6.75 (d, 2H, J=9 Hz), 3.74 (s, 3H), 2.37 (s, 3H). UV (CH_3CN): λ_{max} (ε) 225 nm (18000).

4.2.7. Compound 1g. R_f 0.67 (hexane–ethyl acetate, 2:1); mp 62–64°C (lit.[11] 61–62°C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (d, 2H, J=8 Hz), 7.24 (d, 2H, J=8 Hz), 7.01–6.95 (m, 2H), 6.83–6.78 (m, 2H), 3.79 (s, 3H), 3.13 (s, 3H), 2.42 (s, 3H). UV (CH_3CN): λ_{max} (ε) 227 nm (18000).

4.2.8. Compound 1h. R_f 0.48 (hexane–ethyl acetate, 2:1); mp 130.4–131.6°C (lit.[34] 146–147°C; lit.[35] 128.5–129.5°C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, 2H, J=8 Hz), 7.51 (d, 1H, J=8 Hz), 7.18 (d, 2H, J=8 Hz), 7.02 (t, 1H, J=8 Hz), 7.00 (s, 1H, –NH), 6.88 (t, 1H, J=8 Hz), 6.73 (d, 1H, J=8 Hz), 3.63 (s, 3H), 2.35 (s, 3H). IR (KBr): 3333, 1595, 1500, 1335, 1159, 754, 661 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 60.41; H, 5.45; N, 4.75; S, 11.52. UV (CH_3CN): λ_{max} (ε) 221 nm (16000), 277 nm (3300).

4.2.9. Compound 1i. R_f 0.58 (hexane–ethyl acetate, 2:1); mp 97.4–98.8°C (lit.[33] 94–95°C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (d, 2H, J=8 Hz), 7.32 (s, 1H, –NH), 7.23 (d, 2H, J=8 Hz), 7.21–7.15 (m, 2H), 7.06–7.00 (m, 2H), 2.38 (s, 3H). UV (CH_3CN): λ_{max} (ε) 227 nm (18000).

4.2.10. Compound 1j. R_f 0.41 (hexane–ethyl acetate, 5:1); mp 109.5–110.2°C (lit.[36] 102°C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (d, 3H, J=8 Hz), 7.26–7.19 (m, 4H), 7.02 (t, 1H, J=8 Hz), 6.98 (s, 1H, –NH), 2.37 (s, 3H). IR

(KBr): 3263, 1593, 1482, 1397, 1334, 1167, 903, 750 cm^{-1}. UV (CH_3CN): λ_{max} (ε) 221 nm (sh, 15000). Anal. calcd for $C_{13}H_{12}NO_2ClS$: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.31; H, 4.46; N, 4.79; S, 11.20.

4.2.11. Compound 1k. R_f 0.58 (hexane–ethyl acetate, 2:1); mp 80–82°C (lit.[37] 80°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, 2H, J=8 Hz), 7.22 (d, 2H, J=8 Hz), 7.11 (br s, 1H, –NH), 7.05 (dd, 2H, J=9, 5 Hz), 6.91 (t, 2H, J=8 Hz), 2.38 (s, 3H). UV (CH_3CN): λ_{max} (ε) 221 nm (14000).

4.2.12. Compound 1l. R_f 0.51 (hexane–ethyl acetate, 2:1); mp 107.8–110.4°C (lit.[38] 108–109°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, 2H, J=8 Hz), 7.58 (dt, 1H, J=8, 2 Hz), 7.21 (d, 2H, J=8 Hz), 7.10–7.02 (m, 2H), 6.97–6.91 (m, 1H), 6.80 (br s, 1H, –NH), 2.37 (s, 3H). UV (CH_3CN): λ_{max} (ε) 221 nm (15000).

4.3. Photoreaction of *N*-aryl-*p*-toluenesulfonamides 1a–l

1 or 5 mM solution (700 ml) of **1a–l** contained in a quartz vessel was purged with nitrogen for 1 h and then irradiated under nitrogen with 254 nm mercury lamp using RPR-100 photochemical reactor (Southern New England Ultraviolet Company) for desired period. The solvent was removed under reduced pressure and the residue was separated by silica gel column chromatography. Irradiation experiments with 350 nm lamps were carried out similarly for compounds **1a–c**. The yields of the products are listed in Tables 1 and 2, and characterization data of the products are given below.

4.3.1. Compound 2a. R_f 0.28 (hexane–ethyl acetate, 5:1); mp 141–143°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06 (dd, 1H, J=8, 1 Hz), 7.82 (dd, 2H, J=8, 1 Hz), 7.77 (d, 2H, J=9 Hz), 7.58 (t, 1H, J=8 Hz), 7.44 (t, 2H, J=8 Hz), 7.37 (dd, 1H, J=8, 2 Hz), 7.30 (d, 2H, J=8 Hz), 6.79 (t, 1H, J=8 Hz), 6.65 (q, 1H, J=5 Hz, –NH), 2.54 (d, 3H, J=5 Hz, $-NCH_3$), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.54, 34.71, 115.45, 124.79, 125.92, 126.91, 128.54, 129.80, 130.11, 132.73, 133.35, 136.75, 137.19, 138.52, 144.30, 147.69, 195.93. IR (KBr): 3391, 1648, 1587, 1517, 1398, 1321, 1246, 1144 cm^{-1}. Anal. calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83; S, 8.77. Found: C, 68.93; H, 5.14; N, 3.52; S, 8.46.

4.3.2. Compound 3a. R_f 0.13 (hexane–ethyl acetate, 5:1); mp 180–182°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.94 (br s, 1H, –NH), 8.09 (d, 1H, J=2 Hz), 7.85 (dd, 1H, J=9, 2 Hz), 7.71 (d, 2H, J=8 Hz), 7.60–7.53 (m, 3H), 7.47 (t, 2H, J=8 Hz), 7.26 (d, 2H, J=8 Hz), 6.77 (d, 1H, J=9 Hz), 2.98 (d, 3H, J=5 Hz, $-NCH_3$), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.46, 29.53, 111.57, 116.30, 125.83, 127.02, 128.36, 129.21, 129.74, 131.77, 133.13, 135.76, 139.04, 139.82, 143.45, 154.86, 198.38. IR (KBr): 3308, 1627, 1599, 1303, 1263, 1165, 1098 cm^{-1}. Anal. calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83; S, 8.77. Found: C, 69.18; H, 5.53; N, 3.45; S, 8.76.

4.3.3. Compound 4a. R_f 0.65 (hexane–ethyl acetate, 5:1); mp 65–67°C (lit.[39] 66–67°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.54 (br s, 1H, –NH), 7.60–7.57 (m, 2H), 7.52–7.37 (m, 5H), 6.75 (d, 1H, J=8 Hz), 6.53 (t, 1H, J=8 Hz), 2.96 (d, 3H, J=5 Hz).

4.3.4. Compound 2b. R_f 0.29 (hexane–ethyl acetate, 5:1); mp 162–164°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.10 (dd, 1H, J=8, 2 Hz), 7.80 (dd, 2H, J=8, 2 Hz), 7.77 (d, 2H, J=8 Hz), 7.58 (t, 1H, J=7 Hz), 7.44 (t, 2H, J=7 Hz), 7.37 (dd, 1H, J=8, 1 Hz), 7.30 (d, 2H, J=8 Hz), 6.80 (t, 1H, J=8 Hz), 6.30 (br s, 1H, –NH), 2.70–2.65 (m, 2H), 2.42 (s, 3H), 0.98 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.48, 21.55, 42.89, 115.59, 124.81, 126.37, 127.08, 128.54, 129.72, 130.09, 132.84, 133.35, 136.75, 136.98, 138.41, 144.27, 146.46, 196.02. IR (KBr): 3390, 1646, 1588, 1459, 1322, 1255, 1146, 954 cm^{-1}. Anal. calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 69.93; H, 5.52; N, 3.42; S, 8.15.

4.3.5. Compound 3b. R_f 0.15 (hexane–ethyl acetate, 5:1); mp 121–123°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.93 (br s, 1H, –NH), 8.09 (d, 1H, J=2 Hz), 7.82 (dd, 1H, J=9, 2 Hz), 7.71 (d, 2H, J=8 Hz), 7.58–7.54 (m, 3H), 7.47 (t, 2H, J=8 Hz), 7.26 (d, 2H, J=8 Hz), 6.78 (d, 1H, J=9 Hz), 3.36–3.27 (m, 2H), 2.38 (s, 3H), 1.34 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.12, 21.46, 37.51, 111.90, 116.05, 125.65, 127.02, 128.36, 129.23, 129.73, 131.78, 133.07, 135.90, 139.09, 139.84, 143.43, 153.92, 198.38. IR (KBr): 3297, 1622, 1316, 1257, 1140, 1092 cm^{-1}. Anal. calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 69.60; H, 5.64; N, 3.57; S, 8.38.

4.3.6. Compound 4b. R_f 0.66 (hexane–ethyl acetate, 5:1); oil (lit.[40] 34.5–35.5°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.51 (br s, 1H, –NH), 7.59 (d, 2H, J=8 Hz), 7.50–7.34 (m, 5H), 6.76 (d, 1H, J=9 Hz), 6.51 (t, 1H, J=8 Hz), 3.35–3.25 (m, 2H), 1.35 (t, 3H, J=7 Hz). IR (KBr): 3326, 1618, 1572, 1518, 1257, 1216, 1165, 758 cm^{-1}. Anal. calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.91; H, 6.80; N, 6.29.

4.3.7. Compound 2c. R_f 0.28 (hexane–ethyl acetate, 9:1); oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (dd, 1H, J=8, 2 Hz), 7.81–7.73 (m, 4H), 7.57 (t, 1H, J=7 Hz), 7.43 (t, 2H, J=7 Hz), 7.38 (dd, 1H, J=8, 2 Hz), 7.29 (d, 2H, J=9 Hz), 6.80 (t, 1H, J=8 Hz), 6.37 (t, 1H, J=5 Hz, –NH), 2.65–2.59 (m, 2H), 2.42 (s, 3H), 1.34–1.06 (m, 12H), 0.86 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.04, 21.54, 22.56, 26.54, 28.99, 29.03, 30.24, 31.68, 48.23, 115.44, 124.52, 126.34, 127.00, 128.53, 129.72, 130.05, 132.91, 133.30, 136.79, 137.02, 138.53, 144.21, 146.74, 196.04. IR (KBr): 3373, 1661, 1592, 1456, 1318, 1249, 1150 cm^{-1}. Anal. calcd for $C_{28}H_{33}NO_3S$: C, 72.54; H, 7.17; N, 3.02; S, 6.92. Found: C, 72.35; H, 7.24; N, 2.86; S, 6.85.

4.3.8. Compound 3c. R_f 0.21 (hexane–ethyl acetate, 9:1); oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.02 (t, 1H, J=5 Hz, –NH), 8.09 (d, 1H, J=2 Hz), 7.82 (dd, 1H, J=9, 2 Hz), 7.71 (d, 2H, J=8 Hz), 7.60–7.54 (m, 3H), 7.47 (t, 2H, J=7 Hz), 7.26 (d, 2H, J=8 Hz), 6.78 (d, 1H, J=9 Hz), 3.28–3.23 (m, 2H), 2.39 (s, 3H), 1.70 (quintet, 2H, J=7 Hz), 1.43 (quintet, 2H, J=7 Hz), 1.38–1.22 (m, 8H), 0.87 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.04, 21.47, 22.58, 27.03, 28.76, 29.10, 29.21, 31.74, 42.90, 111.96, 116.01, 125.54, 127.03, 128.37, 129.23, 129.74, 131.77, 133.06, 135.98,

139.12, 139.89, 143.42, 154.13, 198.42. IR (KBr): 3304, 1627, 1599, 1568, 1319, 1259, 1157, 1102 cm^{-1}. Anal. calcd for $C_{28}H_{33}NO_3S$: C, 72.54; H, 7.17; N, 3.02; S, 6.92. Found: C, 72.52; H, 7.08; N, 2.70; S, 6.63.

4.3.9. Compound 4c. R_f 0.70 (hexane–ethyl acetate, 9:1); oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.62 (br s, 1H, –NH), 7.61–7.58 (m, 2H), 7.51–7.34 (m, 5H), 6.76 (d, 1H, J=8 Hz), 6.50 (t, 1H, J=8 Hz), 3.27–3.22 (m, 2H), 1.72 (quintet, 2H, J=7 Hz), 1.46 (quintet, 2H, J=7 Hz), 1.40–1.22 (m, 8H), 0.88 (t, 3H, J=7 Hz). IR (KBr): 3321, 1621, 1576, 1518, 1258, 1216, 754 cm^{-1}. Anal. calcd for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.85; H, 8.93; N, 4.34.

4.3.10. Compound 2d. R_f 0.46 (hexane–ethyl acetate, 2:1); mp 119.2–119.9°C (lit.[41] 119°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84–7.78 (m, 3H), 7.28–7.23 (m, 3H), 6.77 (t, 1H, J=8 Hz), 6.63 (d, 1H, J=8 Hz), 5.12 (br s, 2H, $-NH_2$), 2.37 (s, 3H)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.56, 117.54, 117.63, 122.14, 126.81, 129.51, 129.62, 134.68, 138.67, 143.82, 145.93.

4.3.11. Compound 3d. R_f 0.15 (hexane–ethyl acetate, 2:1); mp 188.8–189.2°C (lit.[42] 189–193°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 2H, J=8 Hz), 7.70–7.66 (m, 2H), 7.25 (d, 2H, J=8 Hz), 6.66–6.61 (m, 2H), 4.17 (s, 2H, $-NH_2$), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.55, 114.07, 127.02, 129.58, 129.61, 129.74, 139.89, 143.19, 150.76.

4.3.12. Compound 2e. R_f 0.68 (hexane–ethyl acetate, 2:1); mp 142.4–144.3°C (lit.[12] 137°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84 (dd, 1H, J=8, 2 Hz), 7.76 (d, 2H, J=8 Hz), 7.36 (t, 1H, J=8 Hz), 7.24 (d, 2H, J=8 Hz), 6.71 (t, 1H, J=8 Hz), 6.62 (d, 1H, J=8 Hz), 6.31 (br s, 1H, –NH), 2.82 (d, 3H, J=5 Hz), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.56, 30.07, 111.61, 115.72, 121.37, 126.67, 129.48, 130.10, 135.08, 138.85, 143.67, 147.63. IR (KBr): 3408, 1605, 1565, 1518, 1468, 1331, 1288, 1143 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 63.54; H, 5.72; N, 5.05; S, 12.19.

4.3.13. Compound 3e. R_f 0.29 (hexane–ethyl acetate, 2:1); mp 147–149°C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.74 (d, 2H, J=8 Hz), 7.66 (d, 2H, J=8 Hz), 7.21 (d, 2H, J=8 Hz), 6.51 (d, 2H, J=8 Hz), 4.38 (br s, 1H, –NH), 2.80 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.40, 29.92, 111.41, 126.91, 127.81, 129.46, 129.59, 140.27, 143.04, 152.77. IR (KBr): 3400, 1601, 1522, 1350, 1286, 1145, 1106 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 64.02; H, 5.82; N, 5.07; S, 12.02.

4.3.14. Compound 2f. R_f 0.55 (hexane–ethyl acetate, 2:1); mp 155.1–156.3°C (lit.[8] 147.5–148.5°C); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.82 (d, 2H, J=8 Hz), 7.36 (d, 1H, J=3 Hz), 7.28 (d, 2H, J=8 Hz), 6.92 (dd, 1H, J=9, 3 Hz), 6.60 (d, 1H, J=9 Hz), 4.79 (br s, 2H, $-NH_2$), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.60, 55.96, 112.03, 119.28, 122.36, 123.19, 126.88, 129.52, 138.41, 140.10, 143.92, 151.56. IR (KBr): 3426, 3347, 1497, 1304, 1284, 1142 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 60.75; H, 5.48; N, 4.75; S, 11.47.

4.3.15. Compound 2g. R_f 0.63 (hexane–ethyl acetate, 2:1); mp 153.5–154.8°C (lit.[11] 150–151°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, 2H, J=8 Hz), 7.43 (d, 1H, J=3 Hz), 7.25 (d, 2H, J=8 Hz), 7.03 (dd, 1H, J=9, 3 Hz), 6.60 (d, 1H, J=9 Hz), 5.94 (br s, 1H, –NH), 3.77 (s, 3H), 2.79 (d, 3H, J=5 Hz), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.55, 30.49, 56.06, 113.21, 113.43, 121.45, 123.00, 126.71, 129.45, 138.53, 142.51, 143.76, 150.17.

4.3.16. Compound 2h. R_f 0.48 (hexane–ethyl acetate, 2:1); mp 98–99°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, 2H, J=8 Hz), 7.42 (d, 1H, J=8 Hz), 7.24 (d, 2H, J=8 Hz), 6.83 (d, 1H, J=8 Hz), 6.91 (t, 1H, J=8 Hz), 5.37 (br s, 2H, $-NH_2$), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.54, 55.89, 113.62, 116.19, 120.70, 121.51, 126.76, 129.46, 137.08, 138.86, 143.71, 147.29. IR (KBr): 3488, 3384, 1487, 1301, 1217, 1141 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 60.48; H, 5.54; N, 4.82; S, 11.67.

4.3.17. Compound 3h. R_f 0.23 (hexane–ethyl acetate, 2:1); mp 158–159°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 2H, J=8 Hz), 7.36 (d, 1H, J=8 Hz), 7.25 (s, 1H), 7.24 (d, 2H, J=8 Hz), 6.66 (d, 1H, J=8 Hz), 4.30 (br s, 2H, $-NH_2$), 3.85 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.47, 55.74, 108.85, 113.12, 122.16, 126.89, 129.13, 129.55, 139.99, 141.19, 143.10, 146.11. IR (KBr): 3498, 3387, 1609, 1511, 1300, 1239, 1145, 1101 cm^{-1}. Anal. calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 60.73; H, 5.55; N, 4.82; S, 11.33.

4.3.18. Compound 2i. R_f 0.46 (hexane–ethyl acetate, 2:1); mp 153–155°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 2H, J=8 Hz), 7.79 (s, 1H), 7.28 (d, 2H, J=8 Hz), 7.19 (dd, 1H, J=8, 2 Hz), 6.58 (d, 1H, J=8 Hz), 5.13 (br s, 2H, $-NH_2$), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.63, 118.98, 122.32, 123.26, 126.96, 128.81, 129.69, 134.66, 138.05, 144.37, 144.46. IR (KBr): 3467, 3370, 1631, 1485, 1311, 1283, 1142 cm^{-1}. Anal. calcd for $C_{13}H_{12}NO_2ClS$: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.34; H, 4.35; N, 4.72; S, 11.33.

4.3.19. Compound 2j. R_f 0.64 (hexane–ethyl acetate, 2:1); mp 114.8–116.9°C (lit.[43] 114°C); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 2H, J=8 Hz), 7.78 (dd, 1H, J=8, 1 Hz), 7.39 (dd, 1H, J=8, 1 Hz), 7.27 (d, 2H, J=8 Hz), 6.71 (t, 1H, J=8 Hz), 5.61 (br, s, 2H, $-NH_2$), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.60, 117.11, 121.05, 123.54, 126.95, 128.46, 129.65, 134.33, 138.11, 142.33, 144.26.

4.3.20. Compound 3j. R_f 0.28 (hexane–ethyl acetate, 2:1); mp 167–168°C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.80 (d, 1H, J=2 Hz), 7.77 (d, 2H, J=8 Hz), 7.59 (dd, 1H, J=9, 2 Hz), 7.27 (d, 2H, J=8 Hz), 6.75 (d, 1H, J=9 Hz), 4.57 (br, s, 2H, $-NH_2$), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.54, 114.74, 118.36, 127.11, 127.50, 129.08, 129.74, 130.38, 139.28, 143.64, 147.15. IR (KBr): 3461, 3363, 1636, 1588, 1499, 1335, 1297, 1147, 1117 cm^{-1}. Anal. calcd for $C_{13}H_{12}NO_2ClS$: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.27; H, 4.35; N, 4.69; S, 11.46.

4.3.21. Compound 2k. R_f 0.45 (hexane–ethyl acetate, 2:1); mp 143–145°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, 2H, J=8 Hz), 7.54 (dd, 1H, J=8, 3 Hz), 7.28 (d, 2H, J=8 Hz), 7.01 (dt, 1H, J=8, 3 Hz), 6.60 (dd, 1H, J=9, 4 Hz), 4.98 (br s, 2H, $-NH_2$), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.61, 115.29 (d, J=25 Hz), 118.95 (d, J=7 Hz), 122.41 (d, J=22 Hz), 122.63 (d, J=6 Hz), 127.00, 129.65, 137.97, 142.39, 144.32, 154.48 (d, J=238 Hz). IR (KBr): 3467, 3365, 1629, 1495, 1305, 1286, 1141 cm^{-1}. Anal. calcd for $C_{13}H_{12}FNO_2S$: C, 58.85; H, 4.56; N, 5.28; S, 12.09. Found: C, 59.04; H, 4.54; N, 5.10; S, 12.27.

4.3.22. Compound 2l. R_f 0.64 (hexane–ethyl acetate, 2:1); mp 113–115°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J=8 Hz), 7.60 (d, 1H, J=8 Hz), 7.28 (d, 2H, J=8 Hz), 7.10 (t, 1H, J=9 Hz), 6.69 (dt, 1H, J=8, 5 Hz), 5.22 (br, s, 2H, $-NH_2$), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.61, 116.40 (d, J=7 Hz), 119.33 (d, J=19 Hz), 124.16 (d, J=2 Hz), 124.81 (d, J=3 Hz), 126.91, 129.67, 135.46 (d, J=15 Hz), 138.33, 144.24, 151.40 (d, J=241 Hz). IR (KBr): 3464, 3372, 1630, 1488, 1300, 1210, 1142 cm^{-1}. Anal. calcd for $C_{13}H_{12}FNO_2S$: C, 58.85; H, 4.56; N, 5.28; S, 12.09. Found: C, 59.01; H, 4.62; N, 5.20; S, 12.40.

4.3.23. Compound 3l. R_f 0.28 (hexane–ethyl acetate, 2:1); mp 155–156°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 2H, J=8 Hz), 7.52–7.48 (m, 2H), 7.26 (d, 2H, J=8 Hz), 6.76 (t, 1H, J=8 Hz), 4.27 (br, s, 2H, $-NH_2$), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.52, 114.83 (d, J=21 Hz), 115.62 (d, J=4 Hz), 124.87 (d, J=3 Hz), 127.10, 129.71, 129.83 (d, J=6 Hz), 139.28, 139.61 (d, J=12 Hz), 143.61, 149.82 (d, J=243 Hz). IR (KBr): 3464, 3374, 1636, 1604, 1515, 1330, 1297, 1212, 1144, 1091 cm^{-1}. Anal. calcd for $C_{13}H_{12}FNO_2S$: C, 58.85; H, 4.56; N, 5.28; S, 12.09. Found: C, 59.03; H, 4.56; N, 4.99; S, 12.26.

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