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Nanosized CdS as a Reusable Photocatalyst: The Study of Different Reaction Pathways between Tertiary Amines and Aryl Sulfonyl Chlorides through Visible-Light-Induced N-Dealkylation and C−H Activation Processes

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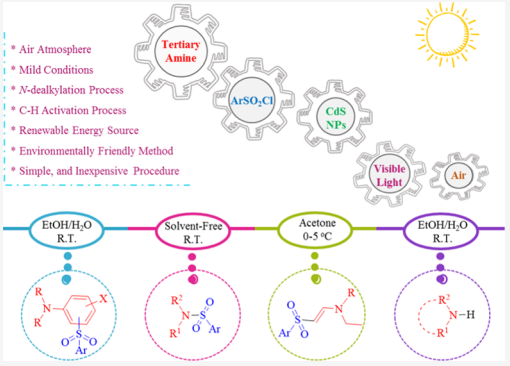
ABSTRACT: It has been found that the final products of the reaction of sulfonyl chlorides and tertiary amines in the presence of cadmium sulfide nanoparticles under visible light irradiation are highly dependent on the applied reaction conditions. Interestingly, with the change of a reaction condition, different pathways were conducted (visible-light-induced N-dealkylation or sp^3 and sp^2 C−H activation) that lead to different products such as secondary amines and various sulfonyl compounds. Remarkably, all of these reactions were performed under visible light irradiation and an air atmosphere without any additive or oxidant in benign solvents or under solvent-free conditions. During this study, the CdS nanoparticles as affordable, heterogeneous, and recyclable photocatalysts were designed, successfully synthesized, and fully characterized and applied for these protocols. During these studies, intermediates resulting from the oxidation of tertiary amines are trapped during the photoinduced electron transfer (PET) process. The reaction was carried out efficiently with a variety of substrates to give the corresponding products at relatively short times in good to excellent yields in parallel with the use of the visible light irradiation as a renewable energy source. Most of these processes are novel or are superior in terms of cost-effectiveness, safety, and simplicity to published reports.



INTRODUCTION

During the past decade, increasing awareness about the rising energy demand and environmental pollution caused by coal and oil encouraged scientists to use clean and renewable energy resources. Accordingly, the application of solar energy as the motive potency in organic synthesis starts to come alive.[1] The sunlight as a safe, plentiful, and easily accessible energy resource is the best candidate for the design of more environmentally benign organic transformations.[2] Another important advantage of the use of sunlight in organic synthesis is the avoidance of thermally induced side reactions due to the conduction of reactions at room temperature. However, most ordinary organic molecules absorb only ultraviolet light, which is only 5% of the solar spectrum, and are restricted to the presence of specific vessels for the conduction of the reaction.[3]

One of the best methods to overcome this problem is the application of visible light photocatalysts as a bridging media for the energy transfer between visible light and the substrates. In the photocatalysis process, the irradiation of a passive precatalyst creates a photoexcited state that could activate one or more substrates and reacts with them.[4] Up to now, five different types of photocatalysts have been designed and used in organic reactions, which include the homogeneous metal complexes of Ru and Ir,[5] organic dyes,[6] heterogeneous semiconductors,[7] plasmonic-metal nanoparticles,[8] and other novel photoelectric materials.[9]

The cadmium sulfide nanoparticles (CdS NPs) as heterogeneous semiconductors are interesting due to their nontoxicity, biocompatibility, and also their broad diversity of applications in photocatalysis, photodevices, and logic circuits.[10] The high surface area and suitable band gap that effectively absorb solar light are two important characteristics of CdS NPs that make them eligible candidates for the application as effective and efficient photocatalysts in sunlight-induced organic transformations.[11] There are few reports about the successful applications of these photocatalysts in different sunlight-induced organic reactions.[12]

Undoubtedly, N-dealkylation is an attractive chemical transformation and a momentous intermediate to the

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pharmaceutical industry as well as the synthesis of synthetic opiates.[13] Hitherto, several general procedures have been reported for the N-demethylation of tertiary amines. The Von Braun reaction is a traditional method for the N-demethylation of tertiary amines in the presence of cyanogen bromide (BrCN). This reaction is approximately replaced by the use of chloroformate reagents due to the high toxicity of BrCN.[14] However, the very high price of chloroformate reagents has limited their usage. One of the most important N-dealkylation reactions is the preparation of secondary amines from tertiary amines, which is reported in the presence of dialkyl azodicarboxylates,[15] cytochrome P-450 enzyme,[16] strong oxidants such as *meta*-chloroperoxybenzoic acid (*m*-CPBA)[13a] and H_2O_2,[13c,d] iron(II) reagents,[17] palladium(II),[18] and ruthenium complexes.[19] Furthermore, photochemical[13e] and biochemical[20] methods have been used for the N-demethylation reaction. However, many of these methods are not very satisfactory because of limited efficiencies, lack of chemoselectivity, toxicity, expensive and unavailable reagents, or vigorous reaction conditions. The restriction to certain substrates is another problem that can be mentioned. To the best of our knowledge, only one photochemical approach is previously enlightened for the N-demethylation of *N*,*N*-dialkyanilines in the presence of Ir complexes and 1,4-diazabicyclo[2.2.2]octane (DABCO) that suffer from some disadvantages such as high toxicity of Ir, application of expensive materials, and difficulty in the synthesis of Ir complexes.[21] This is noteworthy that during the pharmacological evolvements, metabolic studies, and most importantly drug design, the replacement or removal of *N*-alkyl substituents is an often needed synthetic stage. Thus, the need to provide new and simpler methods is strongly felt.

Sulfonamides are the first drugs systematically and largely used as chemotherapeutic and preventive agents against different illnesses.[22] Nowadays, more than 30 drugs containing the sulfonamide functionality are in clinical consumption as antihypertensive,[23] antibacterial,[24] antiprotozoal,[25] antifungal,[26] anti-inflammatory,[27] nonpeptidic vasopressin receptor antagonists,[28] translation initiation inhibitors,[29] anticancer,[30] antiviral human immunodeficiency virus (HIV) protease inhibitor,[31] and anti-Alzheimer.[32] Besides, sulfonamides show other biological activities such as diuretic, antithyroid, and hypoglycemics.[33] Also, sulfonamides are widely used as intermediates in the manufacture of agrochemicals[34] and some frequently used pesticides, including asulam, oryzalin, fomesafen, halosafen, and sulfentrazone (Figure 1).[35]

All of these widespread applications highlight the considerable demands for efficient, cheap, and environmentally friendly manners for the synthesis of these valorous compounds. The utmost common synthetic pathway for the synthesis of sulfonamides is the nucleophilic addition of primary or secondary amines to the sulfonyl chlorides. Another frequently used pathway is the oxidation of sulfides or sulfoxides. Unfortunately, these methods have several limitations, such as the utilization of strong oxidants that are discordant with many functional groups and late-stage functionalization.[36] The coupling between aryl sulfonates with different substrates, such as aryne, aryl boronic acids, aryl halides, diaryliodonium salts, arene diazonium salts, etc., is another procedure used for the preparation of diaryl sulfones.[37,38] The major difficulties of these synthetic routes are the usage of toxic heavy metal catalysts, long reaction times, low yields of desired products, multiple synthetic steps, the formation of isomeric products, etc.[38]

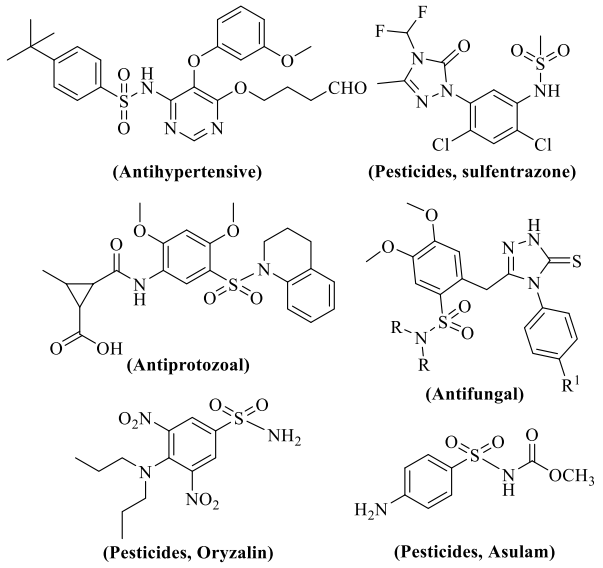

Figure 1. Chemical structures of some biologically active sulfonamide compounds.

One of the newest methods for the synthesis of sulfonamides is conducted through the dealkylation of tertiary amines.[39] Cleavage of the *N*-alkyl group from tertiary amine creates a difficult challenge for organic chemists due to the stability of the *N*-alkyl group. There are several known methods for this important transformation, but they are frequently undesirable due to low efficiency, the toxicity of applied reagents, and lack of chemoselectivity[40] or use of certain substrates.[41] Therefore, the extension of modern strategies for the N-dealkylation process has considerable importance due to the potential and impact of its application for the preparation of agrochemical and pharmaceutical molecules. Due to the strong nucleophilicity of secondary amines, during the synthesis of sulfonamides from the secondary amines, other sensitive functional groups presented at the substrate have to be protected before the sulfonamide synthesis step. To eliminate the need for the protection steps, tertiary amines can be used instead of secondary amines and the desired sulfonamide will be produced by performing an N-dealkylation process.

As far as we know, there is only one report about the synthesis of sulfonamides though the dealkylation of *N*-alkyl tertiary amines in the presence of eosin-Y as a photocatalyst under visible light radiation. This reported method suffers from some crucial drawbacks, such as the use of excess amounts of K_2HPO_4 as an additive, excess amounts of the substrate, and restriction to the O_2 atmosphere, as a special reaction condition may not be accessible in all labs.[42]

Considering the above-mentioned importance of sulfonamides, dealkylation of tertiary amines, and application of photocatalysts in organic synthesis, we herein attempted to study the different reaction pathways between tertiary amines and aryl sulfonyl chloride during the visible-light-induced N-dealkylation and C−H activation processes (Scheme 1).

RESULTS AND DISCUSSION

Two mechanistic pathways can be possible for the production of sulfonamide (**3a**) via the N-dealkylation reaction (Scheme 2). By light collision, CdS NPs as photocatalysts are excited

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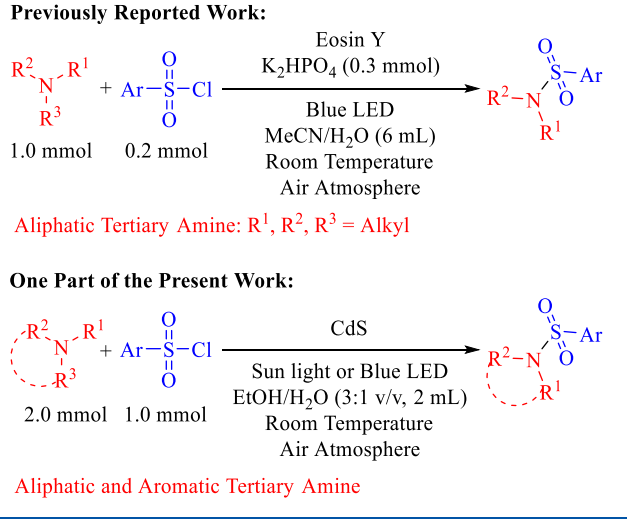
Scheme 1. Photochemical Synthesis of Sulfonamide Derivatives via N-Dealkylation Reaction



and the electron is translocated from the valence band (VB) to the conduction band (CB); hence, the hole and electron pairs will be generated. In fact, due to the lower oxidation potential of tertiary amines (for *N*,*N*-dimethylaniline (DMA), E_{ox} = +0.74 eV vs saturated calomel electrode (SCE) in CH_3CN),[43] they are capable of transferring electrons into the generated hole of CdS NPs (E_{VB} = +1.35 eV vs SCE in CH_3CN).[44] The transfer of an electron from the nitrogen of tertiary amine to the photocatalyst hole creates the tertiary amine radical cation (**A**). On the other hand, oxygen and/or aryl sulfonyl chloride can receive an electron from the conduction band, and subsequently, oxygen radical anion ($O_2^{\bullet-}$) and/or aryl sulfonyl radical (**I**)[42,45] will be produced. This is the beginning of both two paths.

During path I, the tertiary amine radical cation (**A**) converts to an unstable immonium ion (**D**) that will convert to the corresponding secondary amine (**5a**) in the presence of H_2O.[21,42,45] Then, the condensation reaction between the secondary amine and aryl sulfonyl chloride occurs and the desired sulfonamide (**3a**) will be produced. Therefore, briefly, during path I, the tertiary amine converts to the corresponding secondary amine.

During path II, the tertiary amine radical cation (**A**) and aryl sulfonyl radical (**I**) couple together. Subsequently, by a nucleophilic attack, the desired product will produce through intermediate **J**.

Scheme 2. Proposed Mechanism for the Synthesis of *N*-Methyl-*N*-phenylbenzenesulfonamide (3a) via an N-Demethylation Reaction Using CdS NPs

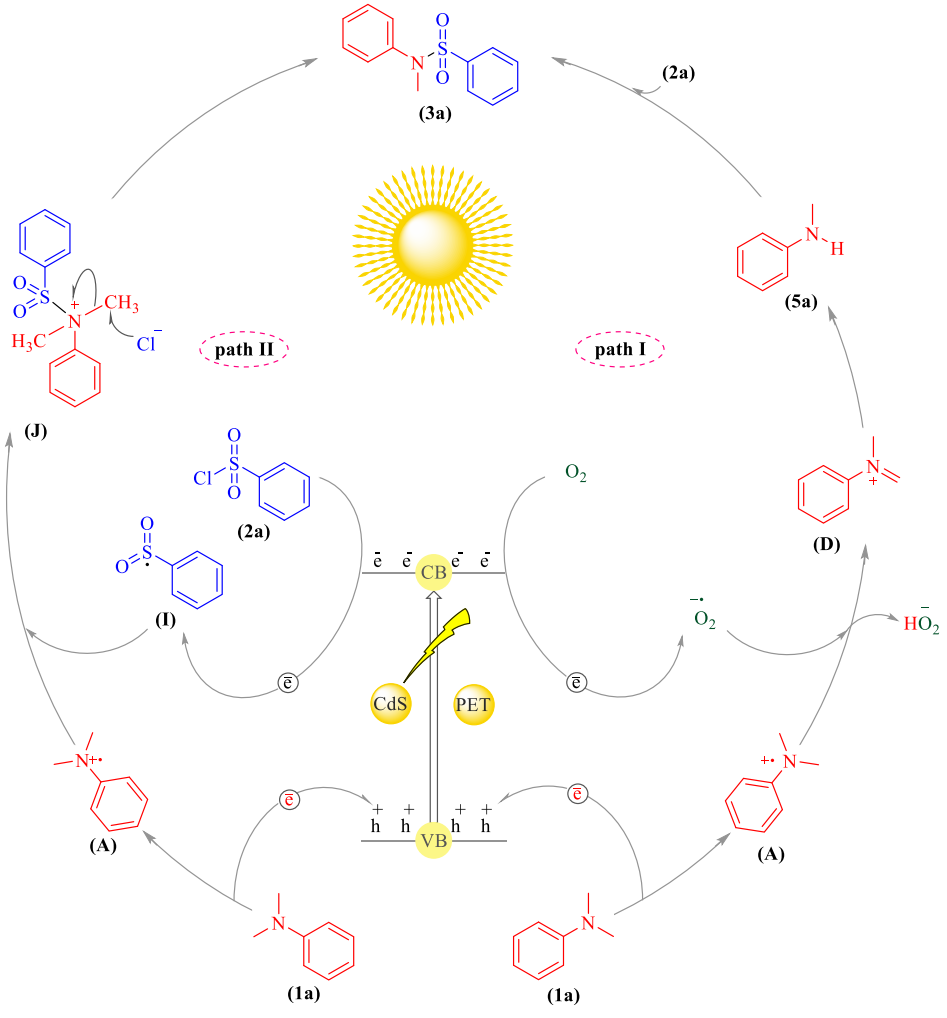


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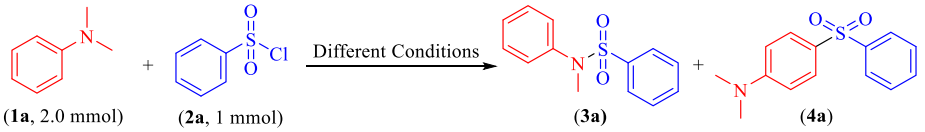
Table 1. Effect of Various Solvents (2 mL) and Different Amounts of K_2HPO_4 on the Synthesis of *N*-Methyl-*N*-phenylbenzenesulfonamide (3a)[a]



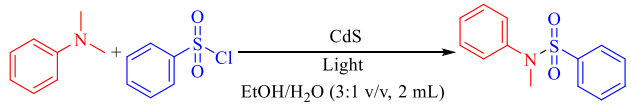
(**1a**, 2.0 mmol) (**2a**, 1 mmol) (**3a**) (**4a**)

entry	solvent (2 mL)	additive	time (h)	yield of **3a** (%)[b]	yield of **4a** (%)[b]
1[c]	H_2O		3.0	5	0
2	EtOH (96%)		0.5	83	0
3[c]	EtOH (absolute)		3.0	36	19
4	EtOH/H_2O (3:1 v/v)		0.5	92	0
5	CH_3CN		0.5	48	36
6[c]	CH_3CN (dry)		3.0	25	44
7[c]	CH_3CN/H_2O (3:1 v/v)		3.0	54	26
8[c]	acetone		3.0	2	0
9[c]	EtOAc		3.0	trace	trace
10[c]	$CHCl_3$		3.0	trace	trace
11[c]	CH_2Cl_2		3.0	7	trace
12[c]	DMSO		3.0	trace	trace
13	DMF		3.0	trace	0
14[c]	solvent-free		3.0	12	64
15[c,d]	CH_3CN/H_2O (1:1 v/v)	K_2HPO_4	3.0	52	29
16[c,d]	EtOH/H_2O (3:1 v/v)	K_2HPO_4	3.0	88	0

[a]Reaction conditions: *N*,*N*-dimethylaniline (2.0 mmol), benzenesulfonyl chloride (1.0 mmol), CdS NPs (0.1 mmol), and solvent (2 mL) under the white light-emitting diode (LED) 12 W lamp irradiation at room temperature (25−28 °C) in an air atmosphere. [b]Isolated yields were calculated relative to benzenesulfonyl chloride consumption. [c]Most of the precursors remained intact. [d]K_2HPO_4 (1.5 mmol) as an additive was added.

According to the results obtained by control experiments (Scheme S1, Supporting Information) and the obtained results of optimization reactions (Tables 1 and 2), we concluded that pathway I is more suitable in an aqueous media, and pathway II is more suitable under solvent-free conditions, or under an argon atmosphere, and with dry solvents.

Table 2. Reaction of *N*,*N*-Dimethylaniline (1a, 2.0 mmol) and Benzenesulfonyl Chloride (2a, 1 mmol) in EtOH/H_2O (3:1 v/v, 2 mL) at 25−28 °C in the Presence of Different Amounts of CdS and Various Light Irradiation under Different Atmospheres[a]



(**1a**, 2.0 mmol) (**2a**, 1 mmol) (**3a**)

entry	CdS (mmol)	light	time (min)	yield (%)[b]
1		white	60	
2	0.05	white	40	83
3	0.1	white	30	94
4	0.15	white	30	95
5	0.1	dark	60	trace
6	0.1	blue	10	95
7	0.1	green	60	66
8	0.1	red	60	41
9	0.1	sun	10	96
10[c]	0.1	blue	10	94
11[d]	0.1	blue	60	22

[a]Reaction conditions: *N*,*N*-dimethylaniline (2.0 mmol), benzenesulfonyl chloride (1.0 mmol), CdS, different irradiation LED 12 W lamps, EtOH/H_2O (3:1 v/v, 2 mL) as a solvent at room temperature. [b]Isolated yields were calculated relative to benzenesulfonyl chloride consumption. [c]Oxygen balloon. [d]Argon balloon.

Therefore, according to the proposed mechanistic pathways in Scheme 2, *N*,*N*-dimethylaniline (**1a**, 2 mmol) was treated with benzenesulfonyl chloride (**2a**, 1 mmol) in the presence of CdS NPs (0.1 mmol, 0.014 g) under white light radiation and an air atmosphere, in CH_3CN (2 mL) as a solvent to achieve product (**3a**). The progress of the reaction was monitored by thin-layer chromatography (TLC), and after a short time (5 min), the products appeared. After the completion of the reaction (30 min), the major products were separated and analyzed by ^1H NMR and $^{13}C\{H\}$ NMR. The results of analyzing surprised us, *N*-methyl-*N*-phenylbenzenesulfonamide (**3a**) and an unexpected product *N*,*N*-dimethyl-4-(phenylsulfonyl)aniline (**4a**) have been taken (Scheme 3).

To justify these products and according to our previous knowledge, we reviewed the behavior of the tertiary amines.

Tertiary amines are potent electron donors owing to low oxidation potential in the photoinduced electron transfer (PET) processes. There are several reports about the single electron transfer (SET) from tertiary amines to appropriate acceptors and the generation of tertiary amine radical cations.[46] As it is demonstrated in Scheme 4, the tertiary amine radical cation (**A**) can convert to the α-aminoalkyl radical (**C**) by the loss of a proton and an electron exchange (Scheme 4, path a). The α-aminoalkyl radical (**C**) can either react as a nucleophile with a suitable substrate or undergo further one-electron oxidation to form an iminium ion (**D**) (this occurs due to the reduced ionization potential of α-aminoalkyl radical (**C**)) and then serve as an electrophile. Another way to create an iminium ion (**D**) is through the removal of hydrogen from the tertiary amine radical cation (**A**) (Scheme 4, path b).[46a] The iminium ion (**D**) converts to a more stable tautomer (**E**) (enamine) and can then serve as an

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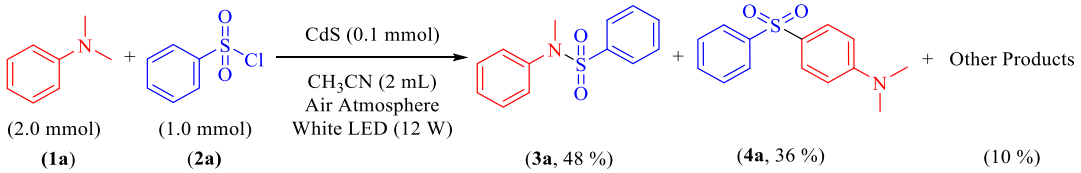
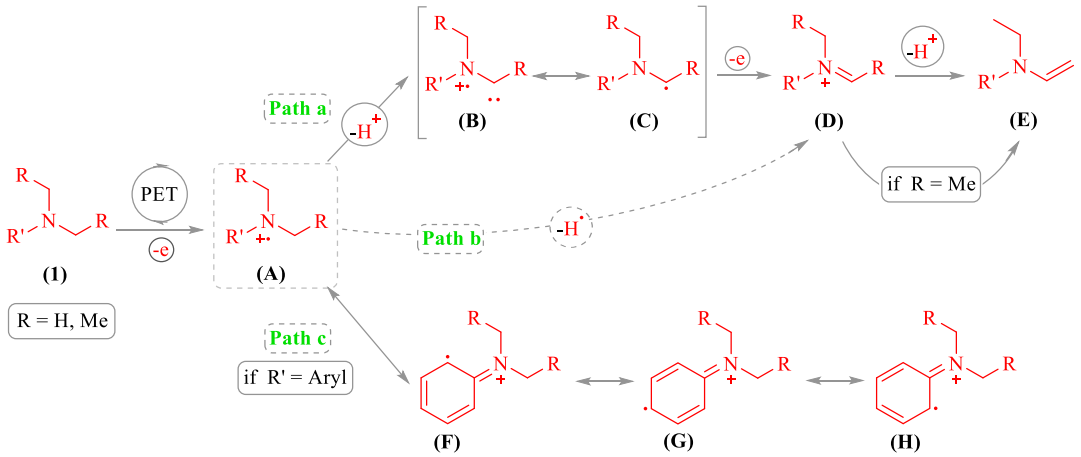
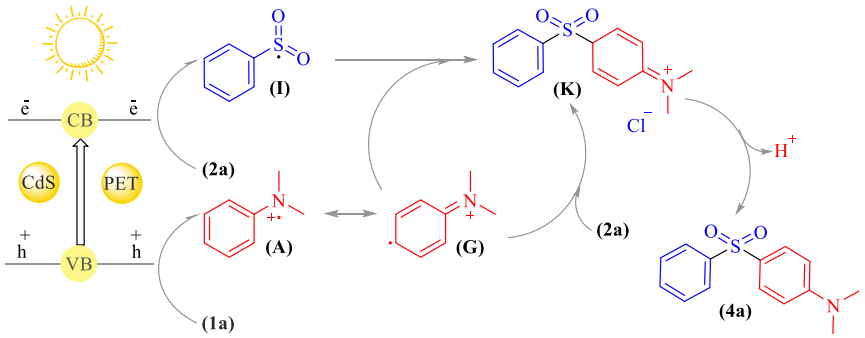
Scheme 3. Reaction between *N,N*-Dimethylaniline (1a) and Benzenesulfonyl Chloride (2a)



Scheme 4. Photochemical Different Modes of Reactivity of *N,N*-Dialkylaniline and Trialkylamine Radical Cations (as Tertiary Amine Radical Cations)



Scheme 5. Suggested Mechanism for the Formation of *N,N*-Dimethyl-4-(phenylsulfonyl)aniline (4a)



electrophile or a nucleophile.[42] In the case of tertiary arylamines, the single electron resonances with the aryl moiety to create intermediates **F**–**H** (Scheme 4, path c).

According to the fact that α-aminoalkyl radical (**A**) could be generated from tertiary amine through the PET processes in the presence of CdS NPs under light irradiation, the trapping of these intermediates (**C**–**H**) by aryl sulfonyl chlorides was investigated.

Therefore, the production of compound (**4a**) could be described as shown in Scheme 5. The immonium ion radical (**G**) and aryl sulfonyl radical (**I**) could be coupled together and, finally, benzenesulfonyl-*N,N*-dimethylaniline (**4a**) will be obtained through the intermediate (**K**) by losing a proton (Scheme 5).

Based on these pieces of knowledge, it has been decided to investigate the N-dealkylation of tertiary amines using aryl sulfonyl chlorides and CdS NPs. To find the best reaction conditions, the reaction of *N,N*-dimethylaniline (**1a**) and benzenesulfonyl chloride (**2a**) was selected as a model and the reaction parameters were optimized (Tables 1 and 2).

Different solvents and solvent-free conditions were checked (Table 1, entries 1–16). The product (**3a**) was obtained without any by-products in a mixture of water and ethanol (3:1 v/v) (Table 1, entry 4). Both products (**3a**) and (**4a**) were obtained in CH_3CN (Table 1, entry 5). Interestingly, in dry CH_3CN, the product **4a** was generated more than **3a** (Table 1, entry 6). Under solvent-free conditions, *N,N*-dimethyl-4-(phenylsulfonyl)aniline (**4a**) was obtained as a major product (Table 1, entry 14). The increase of K_2HPO_4 as an additive does not make a significant difference in reaction efficiency (Table 1, entries 15 and 16).

Next, the amount of catalyst was optimized by the choice of water and ethanol (3:1 v/v) as a solvent (Table 2, entries 1–4).

Based on the obtained results, there is no product in the absence of CdS NPs (Table 2, entry 1) and decreasing the amount of CdS NPs leads to an increase in the reaction time (Table 2, entry 2). The reaction was also checked in the presence of more than 0.1 mmol of CdS NPs, but no considerable change of reactivity was observed (Table 2, entry 4). Afterward, to study the effect of light, the model reaction

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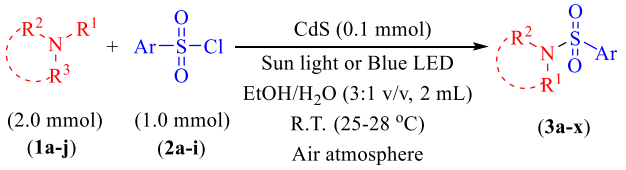
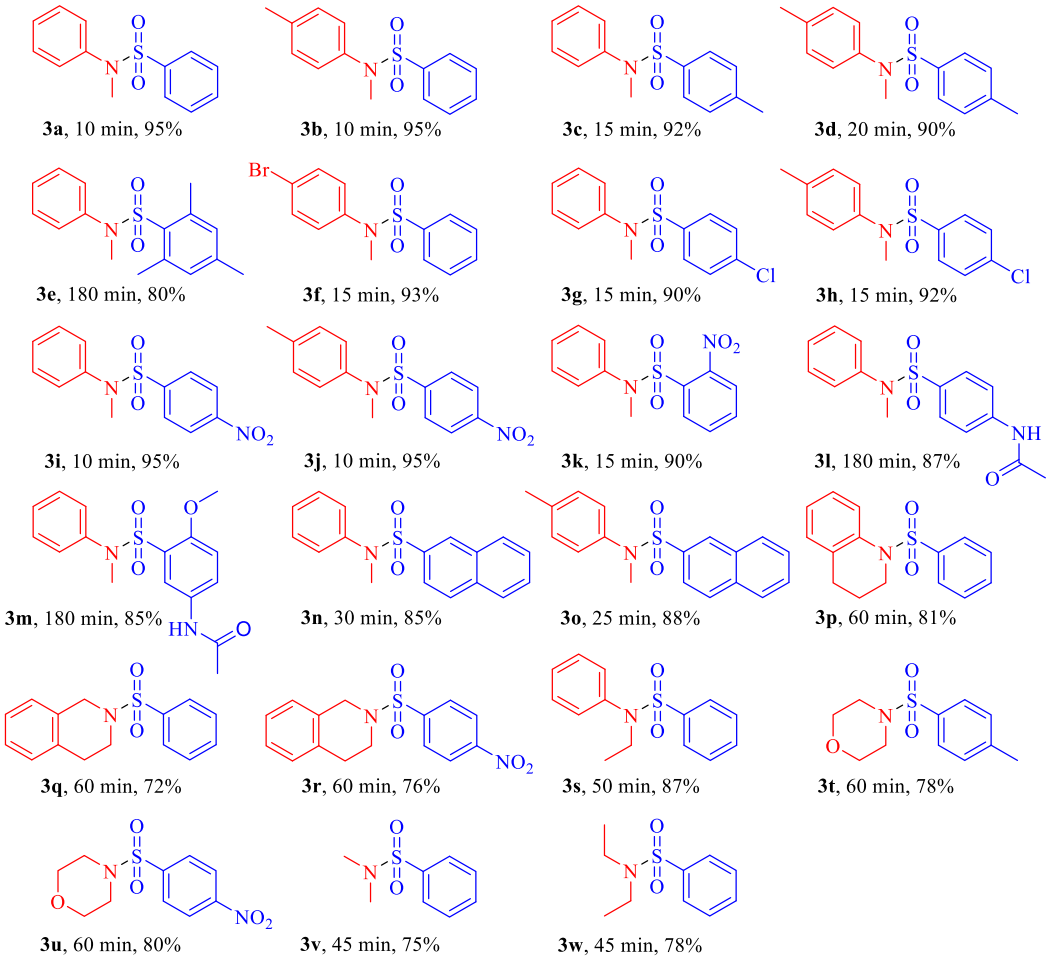
Table 3. Synthesis of *N*-Alkyl-*N*-alkyl(aryl)aryl Sulfonamide Derivatives via N-Dealkylation Reaction[a]





[a]Reaction conditions: tertiary amine (2.0 mmol), aryl sulfonyl chlorides (1.0 mmol), and CdS NPs (0.1 mmol) under blue LED 12 W lamp irradiation, EtOH/H_2O (3:1 v/v, 2 mL) as a solvent, at room temperature (25−28 °C) under an air atmosphere. Isolated yields were calculated relative to benzenesulfonyl chloride consumption.

was studied without light (Table 2, entry 5). Besides, between sunlight, white, blue, green, and red LEDs (Table 2, entries 3, 6−9), the sunlight and blue LEDs provide similar results (Table 2, entries 6, 9). The results of these experiences confirm the act of CdS NPs as photocatalysts for this procedure. The identical results were obtained under an air atmosphere and pure oxygen (Table 2, entries 10, 11); however, there was no remarkable product under an argon atmosphere (Table 2, entry 11). Thus, the sunlight or blue LED irradiation and an air atmosphere using CdS NPs (0.1 mmol) were chosen as the optimum conditions.

To determine the scope of the reaction and the versatility of the applied photocatalyst, the condensation of different aliphatic and aromatic tertiary amines with various aryl sulfonyl chloride under optimized reaction conditions were studied, which are displayed in Table 3. Different aryl sulfonyl chlorides bearing electron-withdrawing and electron-releasing groups on various positions of the aromatic ring and different *N*,*N*-dialkylanilines bearing electron-withdrawing and electron-releasing groups on the para-position of their aromatic rings were applied.

According to Table 1, entry 14, the model reaction mainly produces the *N*,*N*-dimethyl-4-(phenylsulfonyl)aniline (**4a**) in 64% yield under solvent-free conditions. Generally, sulfonyl groups are the main backbone of many biologically active and pharmaceutical compounds, agrochemicals, and polymer materials.[47] In addition, they have a prominent role and numerous applications in organic and medicinal chemistry. Between various kinds of sulfone compounds (aryl, heteroaryl, and alkenyl sulfones), diaryl sulfones occupied a special place because of their unique biological[48] and interesting chemical properties.[49] The chemical structures of some biologically active aryl sulfone compounds are illustrated in Figure 2.[50]

Concerning the importance of diaryl sulfones, diverse synthetic strategies have been exerted for the synthesis of these compounds.[51] In 2018, a photochemical report for the

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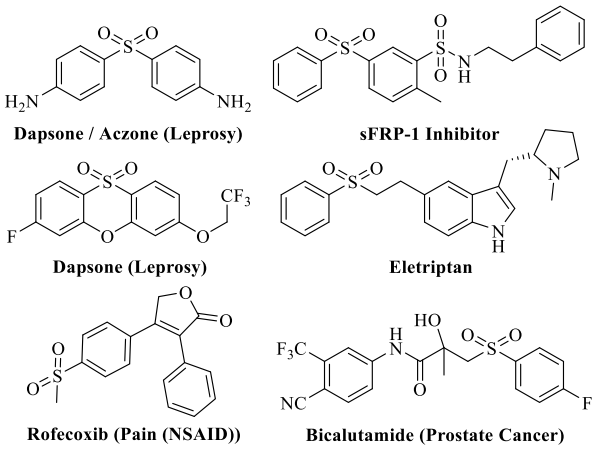


Figure 2. Chemical structures of some biologically active aryl sulfone compounds.

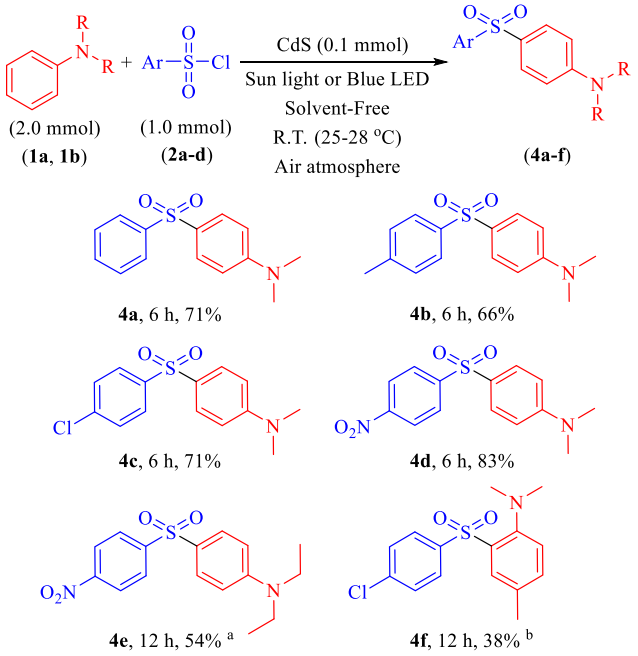
synthesis of diaryl sulfones via the cross-coupling of sodium 4-methylbenzenesulfinate with aryl halides in the presence of merging the Ir complex with $NiCl_2$·glyme catalysis (dual catalysis) and additive in dimethylformamide (DMF) was published.[52] After that, other cross-coupling for the preparation of diaryl sulfones was reported by photochemical methods.[53] To the best of our knowledge, there is not any report for the synthesis of aryl sulfonyl-*N*,*N*-dialkylanilines through the reaction between aryl sulfonyl chlorides and *N*,*N*-dialkylanilines under visible light irradiation or under the nonphotochemical conditions.

Therefore, to illustrate the generality of the method, the reaction of different aryl sulfonyl chlorides and *N*,*N*-dialkylanilines was examined under solvent-free conditions (Table 4). The outcomes represented that all reactions proceeded effectively, and the desired aryl sulfonyl-*N*,*N*-dialkylanilines were obtained in good to excellent yields. The *N*,*N*-diethylaniline relative to *N*,*N*-dimethylaniline provides the corresponding aryl sulfonyl-*N*,*N*-diethylanilines in lower yields (**4e**). While the aryl sulfonyl moiety was connected to the ortho-position in the 4-methyl-*N*,*N*-dimethylaniline compound (**1b**) due to the occupation of the para-position by a methyl group, the steric factors reduce the efficiency (**4f**). In another study, *N*-phenylpyrrolidin (an amine not bearing acyclic alkyl substituent, 2 mmol) was treated with benzenesulfonyl chloride (1 mmol) under the optimized reaction conditions, and unfortunately, a mixture of unknown products was obtained even after a long time (24 h).

According to path I of the proposed mechanism in Scheme 2, it has been speculated that tertiary amine (**1a**) may be converted to the corresponding secondary amine (**5a**) in the presence of CdS NPs and light. To check the possibility of this conversion, the reaction of *N*,*N*-dimethylanilines in the optimal conditions (see the subtitle of Table 3) was examined without the benzenesulfonyl chloride. After 24 h, 35% of *N*-methylanilines (**5a**) was observed. This result first proves the proposed mechanism and also made us think about examining the synthesis of secondary amines from tertiary amines.

The synthesis of amines has long been an important topic of organic synthesis. The secondary amino groups are present in various molecular catalysts, agrochemicals, and pharmaceuticals as substantial structures.[54] Many studies have been devoted to the improvement of the new catalytic synthesis of secondary amines. One of the oldest and most common

Table 4. Synthesis of Aryl Sulfonyl-*N*,*N*-dialkylaniline Derivatives via C−H Activation Reaction[c]



[a]The sulfonamide was formed (20%). [b]The sulfonamide was formed (40%). [c]Reaction conditions: *N*,*N*-dialkylaniline (2.0 mmol), aryl sulfonyl chloride derivatives (1.0 mmol), and CdS nanoparticles (0.1 mmol) under blue LED 12 W lamps and solvent-free conditions at room temperature (25−28 °C) under an air atmosphere. Isolated yields were calculated relative to benzenesulfonyl chloride consumption. In all cases, the sulfonamide was formed as a minor by-product and some of the precursors remained intact.

procedures for the preparation of secondary amines is the N-alkylation of primary amines by alkylating reagents. These methods generally suffer from polyalkylation problem. The intermolecular self-condensation of primary amines can lead to the production of symmetric secondary amines.[55] One of the most interesting procedures for the preparation of secondary amines is the N-dealkylation reaction from tertiary amines. So far, only one photochemical report for the N-dealkylation reaction from tertiary amines has been published. We focused on finding the optimal conditions for the preparation of secondary amines from tertiary amines using CdS NPs as photocatalysts via the N-dealkylation reaction (Table 5).

Rueping's research group used 1,4-diazabicyclo[2.2.2]octane (DABCO) as an effective additive for N-demethylation of *N*,*N*-dialkyanilines in the presence of Ir complexes.[21] Inspired by this work and having in mind the efficiencies of EtOH/H_2O and CH_3CN/H_2O as solvents for the synthesis of benzenesulfonamide (**3a**), we aimed to examine the effect of DABCO (0.1 mol %) in these solvents (Table 5, entry 3, 4). The EtOH/H_2O in the presence of DABCO proved to be the most efficient solvent, giving 65% yield after 24 h (Table 5, entry 3). To examine the role of the water content in the efficiency of the reaction, the model reaction was examined in the presence of different amounts of water (Table 5, entry 3, 5, 6). The reduction of the water content increased the yield to 81% (Table 5, entry 6). It may be due to the role of water in facilitating the iminium hydrolysis process. Moreover, the effectiveness of the application of Cs_2CO_3 and K_2CO_3 instead of DABCO (Table 5, entry 8, 9) was examined, and based on

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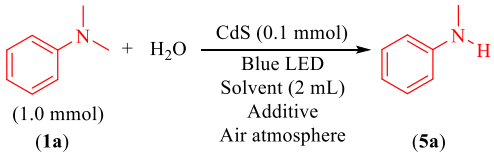
Table 5. Model Reaction without the Presence of Benzenesulfonyl Chloride under Various Conditions for the Synthesis of *N*-Methylaniline (5a)[a]



entry	solvent (2 mL)	additive (0.1 mmol)	yield (%)[b]
1	EtOH/H_2O (3:1 v/v)		trace[c]
2	EtOH/H_2O (3:1 v/v)		35
3	EtOH/H_2O (3:1 v/v)	DABCO	65
4	CH_3CN/H_2O (3:1 v/v)	DABCO	52
5	EtOH	DABCO	74[d]
6	EtOH	DABCO	80[e]
7	CH_3CN	DABCO	60[e]
8	EtOH	Cs_2CO_3	70[e]
9	EtOH	K_2CO_3	70[e]
10	EtOH	DABCO	0[e,f]

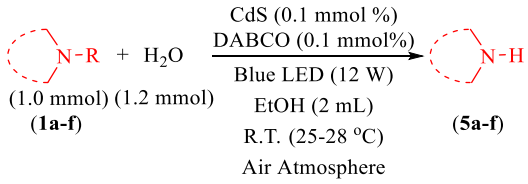
[a]Reaction conditions: *N*,*N*-dimethylaniline (1.0 mmol), CdS NPs (0.1 mmol), additive (0.1 mmol), and solvent (2 mL) under blue LED 12 W lamp irradiation for 24 h at room temperature (25−28 °C) under an air atmosphere. [b]Isolated yields were calculated relative to benzenesulfonyl chloride consumption. [c]Yield was reported after 10 min. [d]Water (0.5 mmol) was added. [e]Water (1.2 mmol) was added. [f]The reaction yield in the absence of light (dark).

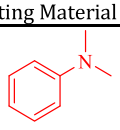
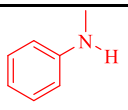
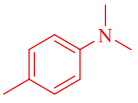
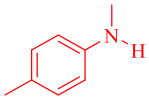
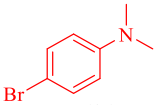
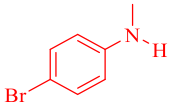
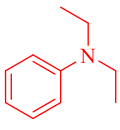
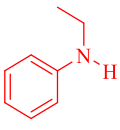
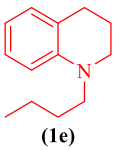
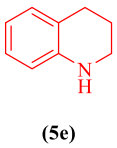
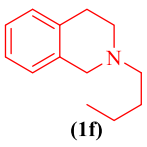
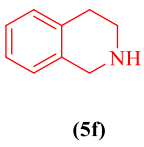
the obtained results, DABCO was superior to other applied bases for this transformation. Henceforth, the model reaction was tested in the absence of light and the obtained results indicate that the presence of light to excite CdS NPs followed by the radical cation tertiary amine formation is necessary for this reaction (Table 5, entry 10).

Based on these findings, the best conditions for the synthesis of secondary amines from tertiary amines was 0.1 mmol of CdS NPs, 0.1 mmol of DABCO, and 1.2 mmol of water under sunlight or blue light irradiation and an air atmosphere, using ethanol as a solvent at room temperature (25−28 °C). To investigate the substrate scope, the N-dealkylation of a variety of tertiary amines was studied under optimized reaction conditions. The outcomes of these experiments are provided in Table 6.

In continuance of these achievements, we attempted the synthesis of vinyl sulfones by changing the reaction conditions. Vinyl sulfones are significant precursors and intermediates for the organic synthesis,[56] some of these compounds are potent inhibitors of enzymes such as SrtA (a transpeptidase required for virulence in *Staphylococcus aureus* and cell wall protein anchoring),[57] sortase,[58] or cysteine proteases.[59] Besides, the *β*-functionalization of unactivated substrates is a very attractive and challenging topic in organic synthesis. Some notable reactions could be realized with the use of transition metal catalysts or strong oxidants[60] and merging photoredox catalysis with organocatalysis.[61] In 2014, Zheng and co-workers presented the preparation of vinyl sulfones via *β*-aryl sulfonylation in the presence of a ruthenium complex for the first time.[45] Followed by in 2017, Zhang and co-workers exploited from this manner in the presence of eosin-Y.[42] In both of these reports, only the aliphatic tertiary amines were studied. Therefore, according to Scheme 4, it has been tried to find a way for the synthesis of vinyl sulfones via trapping enamine (**E**).

Table 6. Synthesis of Secondary Amine Derivatives from Tertiary Amine Derivatives via the N-Dealkylation Reaction[b]



Entry	Starting Material	Product	Yield (%)[a]
1	 (1a)	 (5a)	80
2	 (1b)	 (5b)	85
3	 (1c)	 (5c)	78
4	 (1d)	 (5d)	75
5	 (1e)	 (5e)	72
6	 (1f)	 (5f)	65

[a]Isolated yield. [b]Reaction conditions: tertiary amines (1.0 mmol), CdS NPs (0.1 mmol), DABCO (0.1 mmol), and H_2O (1.2 mmol) in ethanol (2.0 mL) under sunlight or blue light irradiation at room temperature (25−28 °C) under an air atmosphere for 24 h.

As mentioned in Scheme 4, the tertiary amine radical cation (**A**) (derived from transmission of tertiary amine electron to the photocatalyst hole) converts to an unstable immonium ion (**D**) that will convert to the corresponding enamine (**E**). On the other hand, aryl sulfonyl chloride could receive an electron from the conduction band, and subsequently, aryl sulfonyl radical (**I**) produces. The attack of aryl sulfonyl radical (**I**) to the enamine (**E**) occurs and produces the intermediate (**K**). The intermediate (**K**) undergoes the oxidation (**L**) (electron transfer to an electron acceptor such as aryl sulfonyl chloride), deprotonation, and an elimination reaction that provides the favorable vinyl sulfone (**6a**) (Scheme 6).

Subsequently, vinyl sulfone derivatives were synthesized by controlling the temperature (0−5 °C) (Table 7). Several side products were observed in very trace amounts that could not be separated and purified. Product (**3**) was formed less than 5% and product (**4**) was not formed (Table 1, entry 8). The aryl sulfonyl chloride was not consumed completely in 5−10

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Scheme 6. Proposed Mechanism for the Synthesis of Vinyl Sulfones (6a) via the sp^3 C−H Activation and the β-Aryl Sulfonylation Reaction in the Presence of CdS NPs as Heterogeneous Photocatalysts

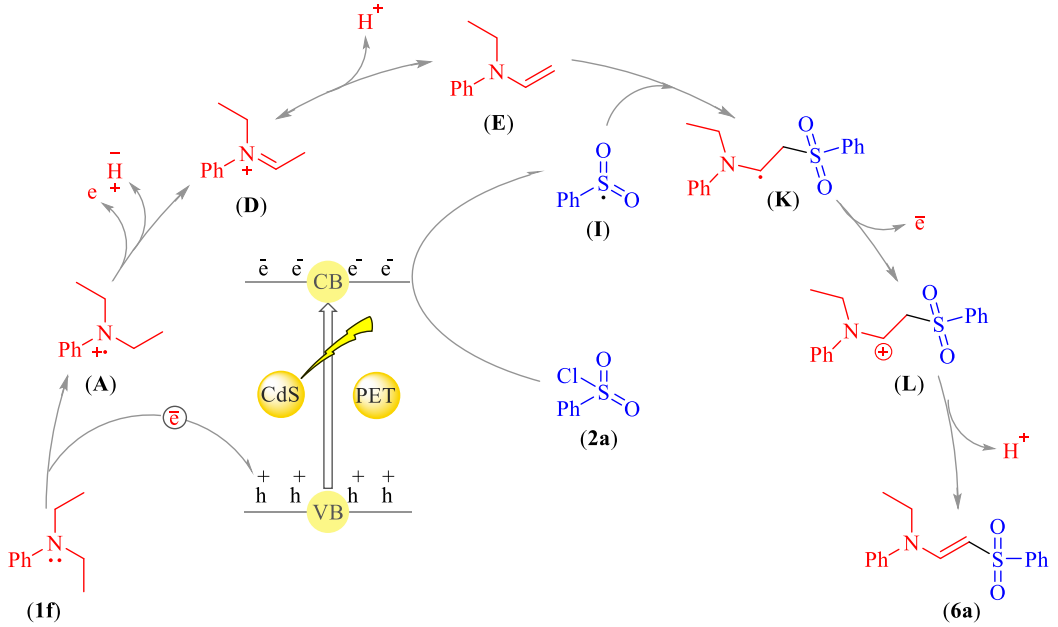
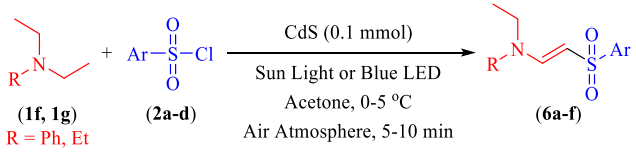
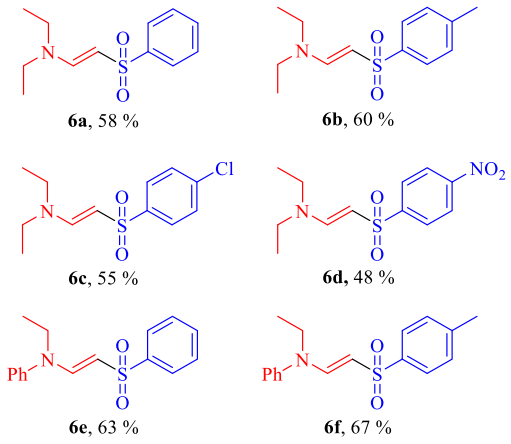


Table 7. Synthesis of Vinyl Sulfones via the sp^3 C−H Activation and the β-Aryl Sulfonylation Reaction[a]





[a]Reaction conditions: triethylamine or *N,N*-diethylanilines (4.0 mmol), aryl sulfonyl chloride derivatives (1.0 mmol), and CdS nanoparticles (0.1 mmol) in acetone under blue LED 12 W lamp irradiation between −5 and 5 °C under an air atmosphere. Isolated yields were calculated relative to benzenesulfonyl chloride consumption.

min. As the reaction time increases, aryl sulfonyl chloride was consumed, but the number of by-products was increased.

The reusability of CdS NPs under optimal conditions for the synthesis of *N*-methyl-*N*-phenylbenzenesulfonamide (**3a**), *N,N*-dimethyl-4-(phenylsulfonyl)aniline (**4a**), *N*-methylaniline (**5a**), and *N,N*-diethyl-2-(phenylsulfonyl)ethen-1-amine (**6a**) was investigated and the obtained results are summarized in Figure 3. Based on the obtained results, recovered CdS NPs could be reused five times with approximately constant efficiencies in all reported reactions (Figure 3). The procedures for the recovery of the applied CdS NPs are separately explained for each conducted reaction in the Experimental Section.

To study the stability of the applied catalyst in all presented reactions in this paper, after the fifth conduction of each reported reaction, the catalyst was separated, washed, dried under reduced pressure, and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and the obtained results are demonstrated in Figure S2. As it is obvious from Figure S2, there are not any differences between the XRD as well as SEM results of recovered catalysts and freshly synthesized catalysts.

CONCLUSIONS

In this study, we presented an overview of the different reaction pathways between tertiary amines and aryl sulfonyl chloride in the presence of CdS NPs as heterogeneous photocatalysts under visible light irradiation. The obtained results expressed the conduction of different reaction pathways with a slight change of reaction conditions, and different products were obtained through N-dealkylation or C−H activation processes.

Meanwhile, this is the first report on the N-dealkylation process of aromatic tertiary amines, leading to the synthesis of sulfonamides, the sp^2 C−H activation reaction for the synthesis of aryl sulfonyl through the reaction between aryl sulfonyl chlorides and *N,N*-dialkylanilines, and the sp^3 C−H activation for the synthesis of vinyl sulfones via the β-aryl sulfonylation reaction of *N,N*-diethylaniline and triethylamine. In other cases, these processes are superior in terms of cost-effectiveness, safety, and simplicity of the procedure compared to the published reports. The common advantages of all of these reactions are the use of visible light irradiation as a renewable energy source under an air atmosphere and the use of CdS NPs as affordable, simple, and inexpensive photo-

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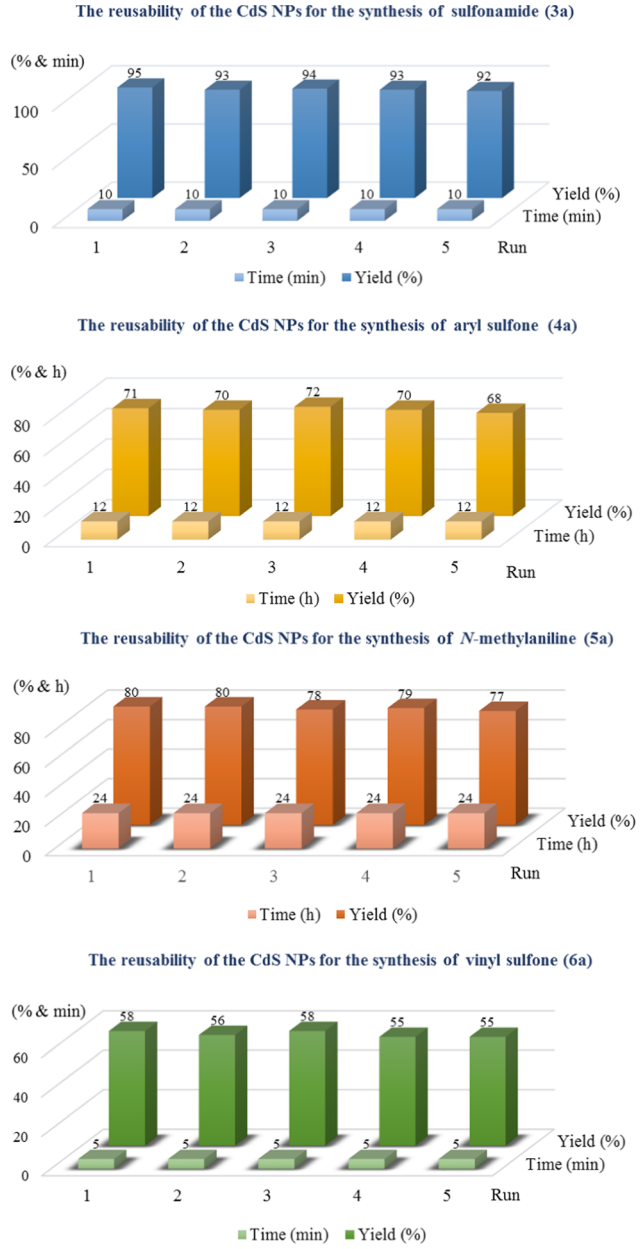

Figure 3. Reusability of CdS NPs under Optimal Conditions for the Synthesis of *N*-Methyl-*N*-phenylbenzenesulfonamide (**3a**), *N*,*N*-Dimethyl-4-(phenylsulfonyl)aniline (**4a**), *N*-Methylaniline (**5a**), and *N*,*N*-Diethyl-2-(phenylsulfonyl)ethen-1-amine (**6a**).

catalysts. All of these advantages make this procedure in good concurrence with some rules of Green Chemistry (Scheme 7).

EXPERIMENTAL SECTION

General Information. Starting materials were obtained from Fluka, Merck, and Sigma-Aldrich companies and used without further purification. All reactions were monitored by TLC, and all yields refer to isolated products. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AVANCE (for ^{1}H NMR 250, 300, and 400 MHz and for ^{13}C{^{1}H} NMR 75 and 100 MHz). The UV−vis diffuse reflectance spectrum was measured with a V_670-JASCO, Japan spectrophotometer. XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel filtered Cu Kα radiation (l = 1.5406 Å). The morphologies of the CdS nanoparticles were determined by SEM using a HITACHI S-4160 instrument. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV.

The light sources used for photochemical experiments were 12 W white LED (wavelength in the range 400−750 nm), 12 W blue LED (wavelength in the range 450−495 nm), 12 W green LED (wavelength in the range 495−570 nm), and 12 W red LED (620−750 nm). Light intensities were strictly the same (0.4 W/cm^2) in each wavelength area. Manufacturer: Iran; model: ED A60; distance from the light source to the irradiation vessel: 5 cm; material of the irradiation vessel: borosilicate glass reaction tube; and any kinds of filters were not used. The room temperature was between 25 and 28 °C. In all cases, the internal temperatures of the reactions were monitored with an internal thermometer and a water bath was used to control the reaction temperature between 25 and 28 °C. In addition to the use of cooling systems, when the reaction temperature increased due to the irradiations of LED lamps, the reaction temperature was reduced with the addition of cold water to the water bath.

General Procedure for the Synthesis of CdS NPs. The CdS NPs were prepared based on the previously presented procedure.[12a] For this, *N*-cetyl *N*,*N*,*N*-trimethylammonium bromide (0.4 g) and sodium sulfide hexahydrate (0.93 g) were mixed in deionized water (300 mL) and stirred until a uniform solution was obtained. Then, the cadmium nitrate tetrahydrate solution (100 mL, 0.045 M) was added drop by drop. The mixture was stirred for 1 h at room temperature and, after this time, was heated to reflux temperature by heating the mantle for 36 h. In the end, insoluble CdS nanoparticles were separated by centrifugation, washed with deionized water (100 mL, three times) and ethanol (100 mL, three times), dried at 50 °C for 24 h, and CdS NPs were obtained as a yellow powder.

General Procedure for the Synthesis of *N*-Alkyl-*N*-alkylaryl Sulfonamide and *N*-Alkyl-*N*-aryl Sulfonamide Derivatives. The CdS NPs (0.1 mmol, 0.014 g) were added to a test tube equipped with a magnetic stir bar. Then, tertiary aromatic or aliphatic amines (2.0 mmol), aryl sulfonyl chloride derivatives (1.0 mmol), and EtOH/H_2O 3:1 v/v (2 mL) were added. The open test tube was located in a water bath under sunlight or blue LED irradiation and stirred at room temperature (25−28 °C) for an appropriate time (Table 3). The reaction advancement was followed by thin-layer chromatography (TLC). After the supplementation of the reaction, the insoluble photocatalyst was separated by centrifugation, washed with ethanol (2 mL, three times), dried at 50 °C for 24 h, and reused. To obtain pure products, the water (1 mL) was added to the separated reaction solution and the obtained mixture was allowed to stand at room temperature for 24 h and during this time, the crystals of pure products were precipitated slowly. In the case of liquid products, column chromatography was used. (Note: the internal temperature of the reactions was monitored with an internal thermometer, and a water bath was used to control the reaction temperature between 25 and 28 °C. When the reaction temperature increased due to the irradiations of LED lamps, the reaction temperature was reduced with the addition of cold water to the water bath.)

General Procedure for the Synthesis of *N*,*N*-Dialkyl-4-(arylsulfonyl)aniline Derivatives. The CdS NPs (0.1 mmol, 0.014 g) were added to a test tube equipped with a magnetic stir bar. Then, *N*,*N*-dialkylaniline (2.0 mmol) and aryl sulfonyl chloride derivatives (1.0 mmol) were added. The open test tube was located in a water bath under sunlight or blue LED irradiation and stirred at room temperature (25−28 °C) for an appropriate time (12−24 h) under solvent-free conditions. The reaction advancement was followed by thin-layer chromatography (TLC). After the supplementation of the reaction, ethanol (3 mL) was added to the reaction mixture and the insoluble photocatalyst was separated by centrifugation, washed with ethanol (2 mL, three times), dried at 50 °C for 24 h, and reused. The pure *N*,*N*-dialkyl-4-(arylsulfonyl)-aniline products were obtained after the solvent evaporation under reduced pressure and purification by column chromatography. (Note: the internal temperature of the reactions was monitored with an internal thermometer, and a water bath was used to control the reaction temperature between 25 and 28 °C. When the reaction

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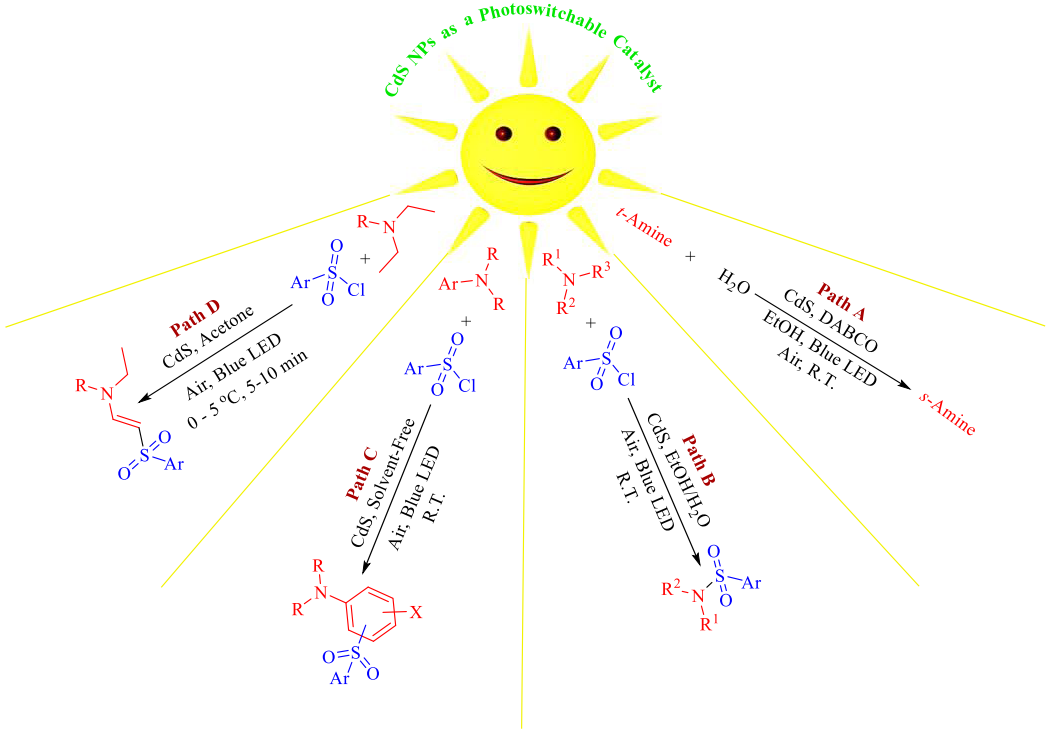
Scheme 7. Different Reaction Pathways between Tertiary Amines and Aryl Sulfonyl Chlorides under Different Conditions via Visible-Light-Induced N-Dealkylation and C−H Activation Reactions in the Presence of CdS NPs as Highly Efficient Reusable Heterogeneous Photocatalysts



temperature increased due to the irradiations of LED lamps, the reaction temperature was reduced with the addition of cold water to the water bath.)

General Procedure for the Synthesis of Secondary Amine Derivatives. The CdS NPs (0.1 mmol, 0.014 g) and DABCO (0.1 mmol, 0.011 g) were added to a test tube equipped with a magnetic stir bar. Then, tertiary aromatic amine derivatives (1.0 mmol), distilled water (1.2 mmol), and EtOH (2 mL) were added. The open test tube was located in a water bath under sunlight or blue LED irradiation and stirred at room temperature (25−28 °C) for an appropriate time (24 h). The reaction advancement was followed by thin-layer chromatography (TLC). After the supplementation of the reaction, the insoluble photocatalyst was separated by centrifugation, washed with ethanol (2 mL, three times), dried at 50 °C for 24 h, and reused. The pure secondary amine products were obtained after the solvent evaporation under reduced pressure and purification by column chromatography. (Note: the internal temperature of the reactions was monitored with an internal thermometer, and a water bath was used to control the reaction temperature between 25 and 28 °C. When the reaction temperature increased due to the irradiations of LED lamps, the reaction temperature was reduced with the addition of cold water to the water bath.)

General Procedure for the Synthesis of Vinyl Sulfone Derivatives. The CdS NPs (10 mol %, 0.014 g), aryl sulfonyl chloride derivatives (1.0 mmol), and acetone (3 mL) were added to a test tube equipped with a magnetic stir bar and then prebathed in ice-salt-water mixtures for 5 min. After that, triethylamine or *N,N*-diethylaniline (4.0 mmol) was added to the mixture. The open test tube was located under sunlight or blue LED irradiation and stirred at 0−5 °C for 5−10 min. The reaction advancement was followed by thin-layer chromatography. Then, the insoluble photocatalyst was separated by centrifugation, washed with ethanol (2 mL, three times), dried at 50 °C for 24 h, and reused. The pure products after the solvent evaporation under reduced pressure and purification by column chromatography was obtained.

Characterization of Compounds. *N-Ethyl-N-phenylbenzenesulfonamide (**3a**).* It was obtained in 95% yield (234.9 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45−7.50 (m, 3H), 7.33−7.40 (m, 2H), 7.18−7.23 (m, 3H), 6.98−7.03 (m, 2H), 3.10 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.6, 134.6, 131.0, 127.1, 126.9, 126.0, 125.5, 124.8, 36.3 ppm; anal. calcd for $C_{13}H_{13}NO_2S$: C 63.14, H 5.30, N 5.66, S 12.96. Found: C 63.21, H 5.49, N 5.75, S 13.12.

*N-Methyl-N-(p-tolyl)benzenesulfonamide (**3b**).* It was obtained in 95% yield (248.2 mg); viscous liquid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.54−7.58 (m, 3H), 7.41−4.48 (m, 2H), 7.09 (dd, 2H, J = 8.0, 0.5 Hz), 6.92−6.98 (m, 2H), 3.15 (s, 3H), 2.33 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.0, 135.5, 130.8, 129.1, 127.7, 126.8, 126.1, 124.7, 36.5, 19.2 ppm; anal. calcd for $C_{14}H_{15}NO_2S$: C 64.34, H 5.79, N 5.36, S 12.27. Found: C 64.30, H 5.84, N 5.29, S 12.42.

*N,4-Dimethyl-N-phenylbenzenesulfonamide (**3c**).* It was obtained in 92% yield (240.4 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.34 (dd, 2H, J = 8.2, 1.2 Hz), 7.13−7.22 (m, 5H), 6.98−7.03 (m, 2H), 3.08 (s, 3H), 2.33 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.6, 141.6, 130.9, 129.3, 128.8, 127.9, 127.3, 126.6, 38.1, 21.6 ppm; anal. calcd for $C_{14}H_{15}NO_2S$: C 64.34, H 5.79, N 5.36, S 12.27. Found: C 64.28, H 5.81, N 5.40, S 12.32.

*N,4-Dimethyl-N-(p-tolyl)benzenesulfonamide (**3d**).* It was obtained in 90% yield (247.8 mg); light yellow liquid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.35 (d, 2H, J = 8.2 Hz), 7.15 (d, 2H, J = 8.2 Hz), 7.00 (d, 2H, J = 8.2 Hz), 6.88 (d, 2H, J = 8.2 Hz), 3.05 (s, 3H), 2.33 (s, 3H), 2.24 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.4, 139.0, 137.2, 133.6, 129.5, 129.3, 127.9, 126.5, 38.2, 21.6, 21.0 ppm; anal. calcd for $C_{15}H_{17}NO_2S$: C 64.43, H 6.22, N 5.09, S 11.64. Found: C 64.51, H 6.17, N 5.13, S 11.56.

*N,2,4,6-Tetramethyl-N-phenylbenzenesulfonamide (**3e**).* It was obtained in 80% yield (231.5 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.13−7.20 (m, 3H), 7.6−7.10 (m, 2H), 6.81 (s, 2H), 3.16 (s, 3H), 2.35 (s, 6H), 2.20 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.5, 140.4, 132.4, 131.8, 130.9, 129.0, 128.8, 127.3, 38.7, 23.8, 23.0

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ppm; anal. calcd for $C_{16}H_{19}NO_2S$: C 66.41, H 6.62, N 4.84, S 11.08. Found: C 66.34, H 6.68, N 4.92, S 10.89.

*N-(4-Bromophenyl)-N-methylbenzenesulfonamide (**3f**).* It was obtained in 93% yield (303.4 mg); light yellow liquid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.51−7.55 (m, 3H), 7.40 (d, 2H, J = 7.2 Hz), 7.34 (d, 2H, J = 8.7 Hz), 6.89 (d, 2H, J = 8.7 Hz), 3.07 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.5, 136.0, 133.0, 132.0, 128.9, 128.8, 128.1, 127.8, 38.0 ppm; anal. calcd for $C_{13}H_{12}BrNO_2S$: C 47.87, H 3.71, N 4.29, S 9.83. Found: C 47.91, H 3.69, N 4.33, S 12.25.

*4-Chloro-N-methyl-N-phenylbenzenesulfonamide (**3g**).* It was obtained in 90% yield (253.5 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.31−7.41 (m, 4H), 7.20−7.24 (m, 3H), 6.99−7.03 (m, 2H), 3.10 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.2, 138.4, 134.0, 128.3, 128.1, 128.1, 126.6, 125.6, 37.2 ppm; anal. calcd for $C_{13}H_{12}ClNO_2S$: C 55.42, H 4.29, N 4.97, S 11.38. Found: C 55.46, H 4.31, N 5.02, S 11.31.

*4-Chloro-N-methyl-N-(p-tolyl)benzenesulfonamide (**3h**).* It was obtained in 92% yield (272.1 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.32−7.43 (m, 4H), 7.02 (dd, 2H, J = 8.2, 0.5 Hz), 6.88 (dd, 2H, J = 8.2, 2.0 Hz), 3.07 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.2, 138.5, 137.6, 135.1, 129.6, 129.3, 21.0, 129.0, 126.5, 38.3 ppm; anal. calcd for $C_{14}H_{14}ClNO_2S$: C 56.85, H 4.77, N 4.74, S 10.84. Found: C 56.93, H 4.73, N 4.79, S 10.76.

*N-Methyl-4-nitro-N-phenylbenzenesulfonamide (**3i**).* It was obtained in 95% yield (277.7 mg); yellow solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.22 (dt, 2H, J = 9.0, 2.2 Hz), 7.65 (dt, 2H, J = 9.0, 2.2 Hz), 7.22−7.28 (m, 3H), 6.98−7.03 (m, 2H), 3.16 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.1, 142.3, 140.6, 129.3, 129.0, 128.0, 126.6, 124.0, 38.4 ppm; anal. calcd for $C_{13}H_{12}N_2O_4S$: C 53.42, H 4.14, N 9.58, S 10.97. Found: C 53.44, H 4.13, N 9.61, S 11.03.

*N-Methyl-4-nitro-N-(p-tolyl)benzenesulfonamide (**3j**).* It was obtained in 95% yield (291.0 mg); yellow solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.22 (d, 2H, J = 8.7 Hz), 7.66 (d, 2H, J = 8.7 Hz), 7.05 (d, 2H, J = 8.5 Hz), 6.87 (d, 2H, J = 8.5 Hz), 3.13 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.1, 142.4, 138.1, 137.9, 129.9, 129.0, 126.4, 124.0, 38.5, 21.1 ppm; anal. calcd for $C_{14}H_{14}N_2O_4S$: C 54.89, H 4.61, N 9.14, S 10.47. Found: C 54.92, H 4.58, N 9.09, S 10.40.

*N-Methyl-2-nitro-N-phenylbenzenesulfonamide (**3k**).* It was obtained in 90% yield (263.1 mg); yellow solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.13−7.18 (m, 2H), 6.95−7.01 (m, 3H), 6.61 (dd, 2H, J = 8.7, 2.2 Hz), 6.57 (dd, 2H, J = 9.0, 2.0 Hz), 2.85 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.5, 134.8, 132.0, 130.9, 129.2, 128.9, 128.8, 127.9, 126.7, 123.2, 38.3 ppm; anal. calcd for $C_{13}H_{12}N_2O_4S$: C 53.42, H 4.14, N 9.58, S 10.97. Found: C 53.49, H 4.10, N 9.59, S 10.92.

*N-(4-(N-Methyl-N-phenylsulfamoyl)phenyl)acetamide (**3l**).* It was obtained in 87% yield (264.8 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:50 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.53 (d, 2H, J = 8.7 Hz), 7.40 (dt, 2H, J = 8.7, 2.2 Hz), 7.18−7.23 (m, 3H), 6.99−7.03 (m, 2H), 3.10 (s, 3H), 2.14 (s, 3H), 2.11 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/dimethyl sulfoxide (DMSO)-d_6): δ 169.4, 143.4, 141.3, 129.6, 128.6, 128.5, 127.1, 126.32, 118.6, 37.9, 24.2 ppm; anal. calcd for $C_{15}H_{16}N_2O_3S$: C 59.19, H 5.30, N 9.2, S 10.53. Found: C 59.24, H 5.33, N 9.90, S 10.47.

*N-(4-Methoxy-3-(N-methyl-N-phenylsulfamoyl)phenyl)-acetamide (**3m**).* It was obtained in 85% yield (284.2 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:50 v/v); ^{1}H NMR (250 MHz, DMSO-d_6): δ 10.01 (s, 1H), 7.87 (d, 1H, J = 2.7 Hz), 7.77 (dd, 1H, J = 8.8, 2.7 Hz), 7.23−7.30 (m, 2H), 7.11−7.18 (m, 4H), 3.73 (s, 3H), 3.26 (s, 3H), 1.96 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 168.4, 152.1, 141.1, 131.8, 128.8, 126.4, 125.9, 125.4, 125.3, 121.3, 113.1, 56.0, 38.5, 23.6 ppm; anal. calcd for $C_{16}H_{18}N_2O_4S$: C 57.47, H 5.43, N 8.38, S 9.59. Found: C 57.49, H 5.44, N 8.37, S 9.55.

*N-Methyl-N-phenylnaphthalene-2-sulfonamide (**3n**).* It was obtained in 85% yield (252.7 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.07 (d, 1H, J = 1.5 Hz), 7.75−7.81 (m, 3H), 7.48−7.57 (m, 2H), 7.38 (dd, 1H, J = 8.6, 2.0 Hz), 7.16−7.20 (m, 3H), 6.99−7.04 (m, 2H), 3.12 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.4, 133.2, 132.5, 131.3, 130.9, 130.6, 129.4, 128.8, 127.9, 127.0, 125.7, 124.2, 113.1, 113.1, 39.9 ppm; anal. calcd for $C_{17}H_{15}NO_2S$: C 68.66, H 5.08, N 4.71, S 10.78. Found: C 68.71, H 5.12, N 4.67, S 10.74.

*N-Methyl-N-(p-tolyl)naphthalene-2-sulfonamide (**3o**).* It was obtained in 88% yield (274.0 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.81−7.86 (m, 3H), 7.50−7.62 (m, 2H), 7.44 (dt, 1H, J = 8.7, 2.0 Hz), 7.03 (d, 2H, J = 8.2 Hz), 6.92 (dd, 2H, J = 8.5, 2.0 Hz), 3.15 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.9, 137.4, 134.8, 133.8, 132.0, 129.6, 129.2, 129.1, 128.8, 128.8, 127.9, 127.4, 126.7, 123.3, 38.4, 21.1 ppm; anal. calcd for $C_{18}H_{17}NO_2S$: C 69.43, H 5.50, N 4.50, S 10.30. Found: C 69.52, H 5.57, N 4.44, S 10.23.

*1-((4-Nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (**3p**).* It was obtained in 81% yield (221.4 mg); light yellow solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.26 (d, 2H, J = 9.0 Hz), 7.81 (d, 1H, J = 8.4 Hz), 7.77 (d, 2H, J = 9.0 Hz), 7.24 (d, 1H, J = 8.1 Hz), 7.15 (t, 1H, J = 7.6 Hz), 7.05 (d, 1H, J = 7.2 Hz), 3.88 (t, 2H, J = 6.0 Hz), 2.45 (t, 2H, J = 6.6 Hz), 1.63−1.71 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.0, 145.2, 130.9, 129.4, 128.2, 126.9, 125.9, 125.0, 124.2, 46.9, 26.4, 21.8 ppm; anal. calcd for $C_{15}H_{14}N_2O_4S$: C 56.59, H 4.43, N 8.80, S 10.07. Found: C 56.65, H 4.48, N 8.69, S 9.98.

*2-(Phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (**3q**).* It was obtained in 72% yield (229.2 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, 2H, J = 3.6, 1.2 Hz), 7.56−7.60 (m, 3H), 7.14−7.18 (m, 2H), 7.05−7.10 (m, 2H), 4.29 (s, 2H), 3.38−3.41 (m, 2H), 2.95 (t, 2H, J = 4.2) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.4, 133.0, 132.8, 131.5, 129.1, 128.8, 127.7, 126.8, 126.4, 126.3, 47.5, 43.7, 28.8 ppm; anal. calcd for $C_{15}H_{15}NO_2S$: C 65.91, H 5.53, N 5.12, S 11.73. Found: C 65.99, H 5.57, N 5.06, S 11.62.

*2-((4-Nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (**3r**).* It was obtained in 76% yield (241.9 mg); light yellow solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, 2H, J = 7.8 Hz), 8.03 (d, 2H, J = 7.8 Hz), 8.03 (d, 2H, J = 7.8 Hz), 7.16−7.19 (m, 2H), 7.04−7.10 (m, 2H), 4.37 (s, 2H), 3.49 (t, 2H, J = 5.4 Hz), 2.94 (t, 2H, J = 5.4 Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.1, 143.0, 132.7, 130.9, 128.9, 128.7, 127.1, 126.6, 126.2, 124.3, 47.4, 43.7, 28.6 ppm; anal. calcd for $C_{15}H_{14}N_2O_4S$: C 56.59, H 4.43, N 8.80, S 10.07. Found: C 56.73, H 4.41, N 8.78, S 9.97.

*N-Ethyl-N-phenylbenzenesulfonamide (**3s**).* It was obtained in 87% yield (227.3 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:15 v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.46−7.55 (m, 3H), 7.34−7.41 (m, 2H), 7.22−7.25 (m, 3H), 6.94−6.98 (m, 2H), 3.54 (q, 2H, J = 7.2 Hz), 1.00 (t, 3H, J = 7.2 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.7, 132.5, 130.9, 129.0, 128.9, 128.7, 127.9, 127.6, 45.6, 14.0 ppm; anal. calcd for $C_{14}H_{15}NO_2S$: C 64.34, H 5.79, N 5.36, S 12.27. Found: C 64.41, H 5.73, N 5.28, S 12.19.

*4-Tosylmorpholine (**3t**).* It was obtained in 78% yield (188.2 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:10 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 2H, J = 4.5, Hz), 7.35 (d, 2H, J = 4.5, Hz), 3.75 (s, 4H), 2.99 (s, 4H), 2.45 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 132.1, 129.7, 127.9, 66.1, 46.0, 21.5 ppm; anal. calcd for $C_{11}H_{15}NO_3S$: C 54.75, H 6.27, N 5.80, S 13.29. Found: C 54.78, H 6.32, N 5.77, S 13.25.

*4-((4-Nitrophenyl)sulfonyl)morpholine (**3u**).* It was obtained in 80% yield (217.8 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:10 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, 2H, J = 8.7, Hz), 7.97 (d, 2H, J = 8.7, Hz), 3.78 (t, 4H, J = 4.2, Hz), 3.07 (t, 4H, J = 4.2, Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.3, 141.3, 129.0, 124.4, 66.0, 45.9 ppm; anal. calcd for $C_{10}H_{12}N_2O_5S$: C

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44.11, H 4.44, N 10.29, S 11.77. Found: C 44.10, H 4.46, N 10.31, S 11.75.

*N,N-Dimethylbenzenesulfonamide (**3v**).* It was obtained in 75% yield (138.9 mg); brown liquid; TLC (petroleum ether/ethyl acetate, 100:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (dt, 2H, J = 8.4, 1.2 Hz), 7.52 (dd, 1H, J = 7.0, 1.2 Hz), 7.45−7.49 (m, 2H), 2.62 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.4, 132.7, 129.0, 127.7, 37.9 ppm; anal. calcd for $C_8H_{11}NO_2S$: C 51.87, H 5.99, N 7.56, S 17.31. Found: C 51.92, H 6.03, N 7.53, S 17.27.

*N,N-Diethylbenzenesulfonamide (**3w**).* It was obtained in 78% yield (166.4 mg); brown liquid; TLC (petroleum ether/ethyl acetate, 100:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.76 (m, 2H), 7.42−7.49 (m, 3H), 3.17 (q, 4H, J = 7.2 Hz), 1.06 (t, 6H, J = 7.2 Hz) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.4, 132.2, 129.0, 127.0, 42.0, 14.1 ppm; anal. calcd for $C_{10}H_{15}NO_2S$: C 56.31, H 7.09, N 6.57, S 15.03. Found: C 56.25, H 7.13, N 6.61, S 15.11.

*N,N-Dimethyl-4-(phenylsulfonyl)aniline (**4a**).* It was obtained in 71% yield (185.5 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7.63 (m, 3H), 7.44 (t, 2H, J = 7.5 Hz), 7.16 (d, 2H, J = 8.7 Hz), 6.58 (d, 2H, J = 8.4 Hz), 3.02 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 141.0, 133.6, 129.7, 129.3, 127.6, 127.1, 112.2, 40.1 ppm; anal. calcd for $C_{14}H_{15}NO_2S$: C 64.34, H 5.79, N 5.36, S 12.27. Found: C 63.95, H 6.02, N 5.54, S 11.99.

*N,N-Dimethyl-4-tosylaniline (**4b**).* It was obtained in 66% yield (181.7 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 8.1 Hz), 7.06−7.11 (m, 2H), 6.50 (d, 2H, J = 8.4 Hz), 2.93 (s, 6H), 2.35 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 144.2, 140.7, 129.7, 129.3, 127.6, 127.1, 112.2, 40.1, 21.7 ppm; anal. calcd for $C_{15}H_{17}NO_2S$: C 65.43, H 6.22, N 5.09, S 11.64. Found: C 65.50, H 6.31, N 4.97, S 11.59.

*4-((4-Chlorophenyl)sulfonyl)-N,N-dimethylaniline (**4c**).* It was obtained in 71% yield (210.0 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 2H, J = 8.7 Hz), 7.49 (d, 2H, J = 8.4 Hz), 7.38 (d, 2H, J = 8.7 Hz), 6.53 (d, 2H, J = 8.4 Hz), 3.01 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 152.3, 140.4, 139.8, 131.4, 129.8, 129.1, 128.6, 112.1, 40.2 ppm; anal. calcd for $C_{14}H_{14}ClNO_2S$: C 56.85, H 4.77, N 4.74, S 10.84. Found: C 56.92, H 4.83, N 4.69, S 10.76.

*N,N-Dimethyl-4-((4-nitrophenyl)sulfonyl)aniline (**4d**).* It was obtained in 83% yield (254.3 mg); yellow solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz), 7.38 (d, 2H, J = 8.4 Hz), 6.61 (d, 2H, J = 8.4 Hz), 2.93 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 153.8, 152.8, 148.8, 129.0, 128.1, 125.4, 124.1, 112.1, 40.1 ppm; anal. calcd for $C_{14}H_{14}N_2O_4S$: C 54.89, H 4.61, N 9.14, S 10.47. Found: C 54.97, H 4.66, N 9.08, S 10.39.

*N,N-Diethyl-4-((4-nitrophenyl)sulfonyl)aniline (**4e**).* It was obtained in 54% yield (180.5 mg); yellow solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz), 7.40 (d, 2H, J = 8.4 Hz), 6.61 (d, 2H, J = 8.4 Hz), 2.92 (q, 4H, J = 7.5 Hz), 1.12 (t, 6H, J = 7.5 Hz) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 153.9, 152.8, 148.9, 129.1, 128.1, 125.4, 124.1, 112.1, 45.1, 12.5 ppm; anal. calcd for $C_{16}H_{18}N_2O_4S$: C 57.47, H 5.43, N 8.38, S 9.59. Found: C 57.38, H 5.47, N 8.42, S 9.64.

*2-((4-Chlorophenyl)sulfonyl)-N,N,4-trimethylaniline (**4f**).* It was obtained in 38% yield (117.7 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, 1H, J = 4.8 Hz), 7.83 (d, 2H, J = 8.4 Hz), 7.36−7.43 (m, 3H), 7.17 (d, 1H, J = 8.7 Hz), 2.99 (s, 6H), 2.38 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 150.9, 140.9, 138.7, 137.1, 135.6, 135.5, 129.7, 129.6, 128.2, 124.3, 45.4, 20.9 ppm; anal. calcd for $C_{15}H_{16}ClNO_2S$: C 58.15, H 5.21, N 4.52, S 10.35. Found: C 58.28, H 5.31, N 4.39, S 10.29.

*N-Methylaniline (**5a**).* It was obtained in 80% yield (85.7 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (t, 2H, J = 7.5 Hz), 6.77 (t, 1H, J = 7.5 Hz), 6.67 (d, 2H, J = 7.8 Hz), 3.7 (s, 1H), 2.88 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.4, 129.2, 117.2, 112.4, 30.7 ppm; anal. calcd for C_7H_9N: C 78.46, H 8.47, N 13.07. Found: C 78.51, H 8.45, N 13.04.

*N,4-Dimethylaniline (**5b**).* It was obtained in 85% yield (103.0 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (dd, 2H, J = 8.1, 0.6 Hz), 6.60 (d, 2H, J = 8.1 Hz), 3.52 (s, 1H), 2.85 (s, 3H), 2.28 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.3, 129.5, 126.3, 112.5, 30.8, 20.1 ppm; anal. calcd for $C_8H_{11}N$: C 79.29, H 9.15, N 11.56. Found: C 79.41, H 9.08, N 11.51.

*4-Bromo-N-methylaniline (**5c**).* It was obtained in 78% yield (145.1 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, 2H, J = 8.4 Hz), 6.48 (d, 2H, J = 8.4 Hz), 3.65 (s, 1H), 2.93 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 148.3, 131.9, 113.9, 108.8, 30.8 ppm; anal. calcd for C_7H_8BrN: C 45.19, H 4.33, N 7.53. Found: C 45.32, H 4.40, N 7.44.

*N-Ethylaniline (**5d**).* It was obtained in 75% yield (90.9 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (t, 2H, J = 7.8 Hz), 6.81 (t, 1H, J = 7.5 Hz), 6.71 (d, 2H, J = 7.5 Hz), 3.57 (s, 1H), 3.46 (t, 3H, J = 7.2 Hz), 3.25 (q, 2H, J = 7.2 Hz) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 148.5, 129.3, 117.2, 112.8, 38.5, 15.0 ppm; anal. calcd for $C_8H_{11}N$: C 79.29, H 9.15, N 11.56. Found: C 79.37, H 9.21, N 11.42.

*1,2,3,4-Tetrahydroquinoline (**5e**).* It was obtained in 72% yield (95.9 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, 2H, J = 7.8 Hz), 6.69 (t, 1H, J = 7.5 Hz), 6.54 (d, 1H, J = 7.5 Hz), 3.85 (s, 1H), 3.361 (t, 2H, J = 6.0 Hz), 2.84 (t, 2H, J = 6.3 Hz), 1.98−2.06 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 144.8, 129.5, 126.8, 121.5, 117.0, 114.2, 42.0, 27.0, 22.2 ppm; anal. calcd for $C_9H_{11}N$: C 81.16, H 8.32, N 10.52. Found: C 81.03, H 8.41, N 10.56.

*1,2,3,4-Tetrahydroisoquinoline (**5f**).* It was obtained in 65% yield (86.6 mg); yellow liquid; TLC (petroleum ether/ethyl acetate, 100:5 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09−7.17 (m, 3H), 7.03 (dd, 1H, J = 8.4, 3.6 Hz), 4.03 (s, 2H), 3.16 (t, 2H, J = 6.0 Hz), 2.82 (t, 2H, J = 6.0 Hz), 1.84 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136.0, 134.8, 129.3, 126.2, 126.0, 125.7, 48.4, 43.9, 29.2 ppm; anal. calcd for $C_9H_{11}N$: C 81.16, H 8.32, N 10.52. Found: C 81.32, H 8.27, N 10.41.

*(E)-N,N-Diethyl-2-(phenylsulfonyl)ethen-1-amine (**6a**).* It was obtained in 58% yield (138.8 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87−7.91 (m, 2H), 7.52−7.54 (m, 3H), 7.36 (d, 1H, J = 12.8 Hz), 4.95 (d, 1H, J = 12.8 Hz), 3.22 (broad doublet, 4H), 1.19 (broad doublet, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.9, 145.2, 131.3, 128.7, 125.9, 91.0, 49.9 (bs), 42.5 (bs), 14.5 (bs), 11.0 (bs) ppm; anal. calcd for $C_{12}H_{17}NO_2S$: C 60.22, H 7.16, N 5.85, S 13.40. Found: C 60.39, H 7.26, N 5.72, S 13.26.

*(E)-N,N-Diethyl-2-tosylethen-1-amine (**6b**).* It was obtained in 60% yield (152.0 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.27 (d, 1H, J = 12.8 Hz), 3.91 (d, 1H, J = 12.8 Hz), 3.18 (broad doublet, 4H), 2.41 (s, 3H), 1.170 (broad singlet, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.1, 142.7, 142.2, 129.1, 126.2, 90.5, 50.1, 42.5 (bs), 21.3 (bs), 14.5 (bs), 11.1 (bs) ppm; anal. calcd for $C_{13}H_{19}NO_2S$: C 61.63, H 7.56, N 5.53, S 12.65. Found: C 61.77, H 7.65, N 5.44, S 12.54.

*(E)-2-((4-Chlorophenyl)sulfonyl)-N,N-diethylethen-1-amine (**6c**).* It was obtained in 55% yield (150.6 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, 2H, J = 8.7 Hz), 7.35 (d, 2H, J = 8.7 Hz), 7.23 (d, 1H, J = 12.6 Hz), 4.80 (d, 1H, J = 12.6 Hz), 3.11 (broad doublet, 4H), 1.08 (broad singlet, 6H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.3, 144.0, 137.7, 129.0, 127.6, 90.9, 50.1 (bs), 42.7 (bs), 14.6 (bs), 11.2 (bs) ppm; anal. calcd for $C_{12}H_{16}ClNO_2S$: C 52.65, H 5.89, N 5.12, S 11.71. Found: C 52.81, H 5.99, N 5.01, S 11.59.

*(E)-N,N-Diethyl-2-((4-nitrophenyl)sulfonyl)ethen-1-amine (**6d**).* It was obtained in 48% yield (136.5 mg); yellow solid; TLC (petroleum

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ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, 3H, J = 7.2 Hz), 1.25 (t, 3H, J = 7.6 Hz), 3.22 (q, 2H, J = 7.2 Hz), 3.48 (q, 2H, J = 7.6 Hz), 4.92 (d, 1H, J = 12.8 Hz), 7.39 (d, 1H, J = 12.8 Hz), 8.05 (d, 2H, J = 8.8 Hz), 8.34 (d, 2H, J = 8.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.2, 150.2, 149.2, 127.3, 124.2, 90.0, 50.4(bs), 42.9(bs), 14.7(bs), 11.1 (bs) ppm; anal. calcd for $C_{12}H_{16}N_2O_4S$: C 50.69, H 5.67, N 9.85, S 11.28. Found: C 50.81, H 5.77, N 9.76, S 11.18.

(E)-N-Ethyl-N-(2-(phenylsulfonyl)vinyl)aniline (**6e**). It was obtained in 63% yield (181.0 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, 2H, J = 7.8 Hz), 7.51−7.62 (m, 3H), 7.43 (d, 1H, J = 12.6 Hz), 7.32 (t, 2H, J = 7.2 Hz), 6.90 (d, 2H, J = 7.2 Hz), 6.78 (t, 1H, J = 7.2 Hz), 4.98 (d, 1H, J = 12.6 Hz), 3.42 (q, 2H, J = 7.8 Hz), 1.21 (t, 3H, J = 7.8 Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.0, 148.5, 145.3, 132.5, 129.2, 129.0, 128.7, 125.9, 121.8, 92.3, 42.8, 14.6 ppm; anal. calcd for $C_{16}H_{17}NO_2S$: C 66.87, H 5.96, N 4.87, S 11.16. Found: C 66.72, H 6.03, N 4.79, S 11.07.

(E)-N-Ethyl-N-(2-tosylvinyl)aniline (**6f**). It was obtained in 67% yield (201.9 mg); white solid; TLC (petroleum ether/ethyl acetate, 100:20 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 8.1 Hz), 7.41 (d, 1H, J = 12.9 Hz), 7.37−7.40 (m, 2H), 7.32 (t, 2H, J = 7.2 Hz), 6.91 (dd, 2H, J = 6.9, 1.8 Hz), 6.80 (t, 1H, J = 7.2 Hz), 5.01 (d, 1H, J = 12.9 Hz), 3.43 (q, 2H, J = 7.5 Hz), 2.42 (s, 3H), 1.22 (t, 3H, J = 7.5 Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.2, 148.9, 142.9, 142.2, 129.1, 128.6, 126.9, 125.6, 122.0, 92.4, 42.9, 21.3, 14.6 ppm; anal. calcd for $C_{17}H_{19}NO_2S$: C 67.75, H 6.35, N 4.65, S 10.64. Found: C 67.92, H 6.22, N 4.71, S 10.53.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02263.

Characterization of catalyst (XRD, UV/vis absorption, SEM, TEM), mechanistic studies, and pictures of ^{1}H NMR and ^{13}C{H} NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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