JOC The Journal of Organic Chemistry

Article

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Iron-Catalyzed *N*-Arylsulfonamide Formation through Directly Using Nitroarenes as Nitrogen Sources

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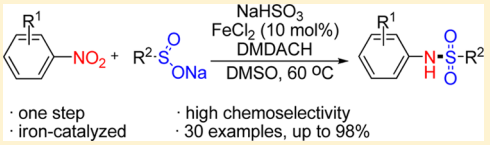
Supporting Information

ABSTRACT: One-step, catalytic synthesis of *N*-arylsulfonamides via the construction of N−S bonds from the direct coupling of sodium arylsulfinates with nitroarenes was realized in the presence of $FeCl_2$ and $NaHSO_3$ under mild conditions. In this process, stable and readily available nitroarenes were used as nitrogen sources, and $NaHSO_3$ acted as a reductant to provide *N*-arylsulfonamides in good to excellent yields. A broad range of functional groups were very well-tolerated in this reaction system. In addition, mechanistic studies indicated that the N−S bond might be generated through direct coupling of nitroarene with sodium arylsulfinate prior to the reduction of nitroarenes by $NaHSO_3$. Accordingly, a reaction mechanism involving *N*-aryl-*N*-arenesulfonylhydroxylamine as an intermediate was proposed.

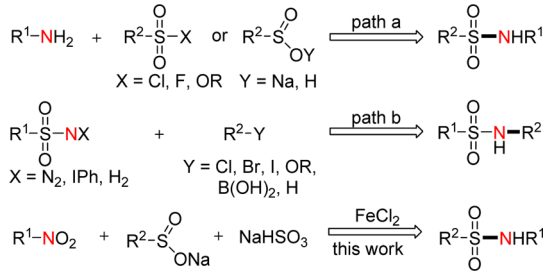


INTRODUCTION

N-Arylsulfonamides are ubiquitous functional scaffolds among medicinally interesting molecules.[1] Over 30 drugs containing this moiety are widely used in clinical therapy.[2] As such, significant efforts have been made toward the development of efficient methods for their preparation.

To date, one of the most conventional routes to *N*-arylsulfonamides involve the direct N−S bond formation (Scheme 1, path a).[3,4] While generally effective, this approach often suffers from the use of aromatic amines as nitrogen sources, which are genotoxic and are undesired potential impurities in the synthesis of active pharamaceutial ingredients.[5] To obviate this drawback, the construction of *N*-arylsulfonamides via metal-catalyzed C−N bond formation has been extensively studied in the past few years (Scheme 1, path b). Such an approach includes the reactions of sulfonamides as nitrogen-based nucleophiles with aryl halides,[6] alcohols,[7] activated esters[8] or arylboronic acids,[9] and the aminosulfonation of hydrocarbons.[10] This alternative route offers a straightforward strategy for the preparation of *N*-arylsulfonamides without the use of anilines; however, it is limited by the harsh conditions, requirement of additional bases and/or ligands, and comparatively complicated starting materials which must be first synthesized. It is highly desirable in this area to develop shortcut approaches to *N*-arylsulfonamides from simple, inexpensive, and stable nitrogen sources. In this regard, readily available nitroarenes are a potential target for reactivity investigations. As abundant nitrogen sources, nitroarenes have been directly converted to a wide range of useful nitrogen-containing compounds, such as *N*-alkylated amines,[11] imines,[12] amides,[13] and aza heterocycles,[14] without prior reduction into anilines as in most traditional approaches.[15] Hence, the facile assembly of *N*-arylsulfonamides directly from nitroarenes would be highly attractive.

Scheme 1. Methods for the Synthesis of Sulfonamides



RESULTS AND DISCUSSION

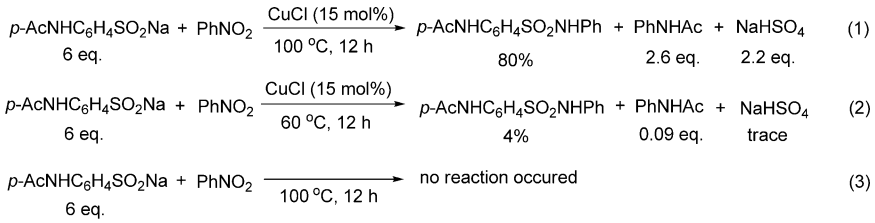
When conducting the catalytic homocoupling of sodium arylsulfinate containing nitro groups,[16] we accidentally noticed the formation of trace amounts of sulfonamide. Further exploration revealed that 91% yield of sulfonamide could be obtained under the optimized conditions (see Supporting Information, Table S1). To our disappointment, harsh conditions (e.g., above 100 °C and 6 equiv of sodium arylsulfinates) were indispensable to this reaction, which limited its practical application. During our investigation of this reaction, a similar situation was reported in a patent by others.[17] Moreover, how this unexpected reaction occurred is not clear yet.

Being curious about the mechanism of this reaction, we then performed controlled reactions between nitrobenzene and sodium *p*-acetaminobenzenesulfinate hoping to obtain some insights into its mechanism (Scheme 2). Surprisingly, in addition to the expected sulfonamide product, acetanilide and $NaHSO_4$ were obtained as well (Scheme 2, eq 1). After 12 h at

Received: January 19, 2015
Published: March 5, 2015

DOI: 10.1021/acs.joc.5b00130
J. Org. Chem. 2015, 80, 3504−3511

Scheme 2. Control Experiments on the Reaction of Sodium *p*-Acetaminobenzenesulfinate with Nitrobenzene



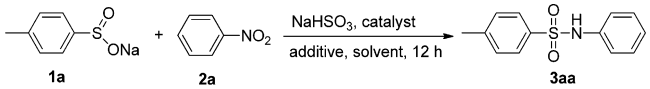
60 °C, only a small amount of products was generated (Scheme 2, eq 2), and no reaction took place in the absence of CuCl even at 100 °C after 12 h (Scheme 2, eq 3). These results indicated that the desulfitative reaction of sodium arylsulfinates occurred in the presence of CuCl at elevated temperature, which is consistent with the reported observation,[18] and the released sulfur dioxide was oxidized to $NaHSO_4$ even under argon atmosphere. The generation of $NaHSO_4$ suggested that $NaHSO_3$ which could be *in situ* generated from the desulfitative reaction of a large excess amount of sodium arylsulfinates and water in solvents might function as a reductant in the sulfonamide formation process.[19] It was then reasonable to envision that if $NaHSO_3$ was added to replace the *in situ* generated $NaHSO_3$ that this unexpected direct sulfonylation of nitroarenes with sodium arylsulfinates might proceed at much lower temperature and without the need of a large excess amount of sodium arylsulfinates.

Then the coupling of sodium *p*-toluenesulfinate (**1a**) and nitrobenzene (**2a**) at 60 °C was selected as a platform to evaluate the proposed chemistry (Table 1). As we anticipated, the desired product could be formed in 43% yield in DMSO (Table 1, entries 1 and 2), while $NaHSO_3$ was used as a reductant. As the amount of $NaHSO_3$ increased, the yield decreased possibly due to the side reaction between nitrobenzene and $NaHSO_3$, which is known as the Piria reaction (Table 1, entry 3).[20] We next explored the reaction in other solvents (Table 1, entries 4−7), and DMSO was found to be the best choice (Table 1, entry 1).

Remarkably, during the study of catalysts (Table 1, entries 8−13), we noticed that the addition of $FeCl_2$ to the reaction system led to a significant increase in yields of the isolated product (Table 1, entry 13). $Cu(OAc)_2$ and $FeCl_3$ also promoted the reaction with slightly lower efficiency (Table 1, entries 10 and 12). With $Cu(OAc)_2$ as the catalyst, the biaryl side product generated from the desulfitative homocoupling of sodium arylsulfinates was also detected (Table 1, entry 10). Other metal salts were not active and gave poor yields. The influence of the amount of $FeCl_2$ on the reactions was investigated (Table 1, entries 14 and 15), and the results showed that a $FeCl_2$ loading of 10 mol % gave the best product yield. The reaction temperature was also screened (Table 1, entries 16 and 17), and 60 °C was found to be an appropriate choice. We observed that the combination of $FeCl_2$ and *trans*-*N,N′*-dimethyl-1,2-diaminocyclohexane (DMDACH) showed the best efficiency (Table 1, entry 21), while $FeCl_2$ plus *N,N′*-dimethylethane-1,2-diamine (DMEDA) or cyclohexane-1,2-diamine (DACH) gave a lower reaction yield (Table 1, entries 18 and 20). Meanwhile, the addition of tetramethylethylenediamine (TMEDA) just led to a decrease in yield (Table 1, entry 19).

With the optimized reaction conditions in hand, we then evaluated the scope of the reactions of *p*-toluenesulfinate (**1a**) with various nitroarenes. As shown in Table 2, most of the substrates with a variety of substituents afforded the products in good to excellent yields under the optimum reaction conditions. Nitroarenes both bearing electron-donating methyl, methoxy, amido, and electron-withdrawing chloro, cyano, trifluoromethyl, carbonyl, ester, and carboxylic acid groups generated the desired products in good to excellent yields. Because of the steric hindrance, *ortho*-nitrotoluene **2d** gave a slightly lower reaction yield (Table 2, entry 4) compared to its para and meta isomers (Table 2, entries 2 and 3). A similar trend was also observed in the reactions of **1a** with methyl nitrobenzoates **2e**−**2g** (Table 2, entries 5−7). A further increase in the steric bulk on the nitroarene **2h** was accompanied by a reduction in the product yield (Table 2, entry 8). It has been reported that aryl sulfones could be

Table 1. Optimization of the Reaction Conditions[a]

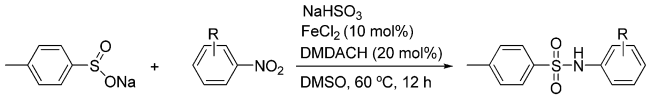


entry	catalyst (mol %)	solvent	additive	yield[b] (%)
1		DMSO		43
2[c]		DMSO		36
3[d]		DMSO		35
4		DMF		12
5		NMP		7
6		THF		n.r.
7		Dioxane		n.r.
8	$ZnCl_2$ (10)	DMSO		44
9	CuCl (10)	DMSO		38
10	$Cu(OAc)_2$ (10)	DMSO		75
11	FeS (10)	DMSO		40
12	$FeCl_3$ (10)	DMSO		79
13	$FeCl_2$ (10)	DMSO		81
14	$FeCl_2$ (5)	DMSO		76
15	$FeCl_2$ (20)	DMSO		80
16[e]	$FeCl_2$ (10)	DMSO		71
17[f]	$FeCl_2$ (10)	DMSO		80
18	$FeCl_2$ (10)	DMSO	DMEDA	84
19	$FeCl_2$ (10)	DMSO	TMEDA	71
20	$FeCl_2$ (10)	DMSO	DACH	85
21	**$FeCl_2$ (10)**	**DMSO**	**DMDACH**	**90**
22	$FeCl_3$ (10)	DMSO	DMDACH	86
23	$Cu(OAc)_2$ (10)	DMSO	DMDACH	83

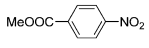
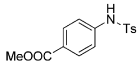
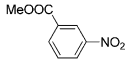
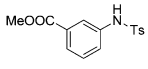
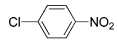
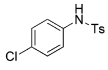
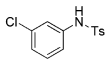
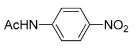
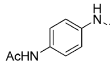
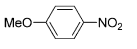
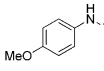
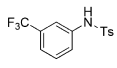
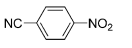
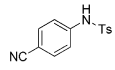
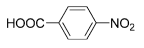
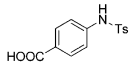
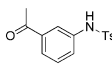
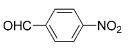
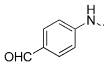
[a]Reaction conditions (unless otherwise stated): nitrobezene (0.5 mmol), sodium *p*-toluenesulfinate (0.75 mmol), $NaHSO_3$ (1.5 mmol), catalyst (0.05 mmol), additive (0.1 mmol), solvent (2.0 mL), 60 °C, 12 h, under argon. DMEDA = *N,N′*-dimethylethane-1,2-diamine. TMEDA = tetramethylethylenediamine. DACH = cyclohexane-1,2-diamine. DMDACH = *trans*-*N,N′*-dimethyl-1,2-diaminocyclohexane. [b]Yield based on **2a**. [c]$NaHSO_3$ (1.0 mmol). [d]$NaHSO_3$ (2.0 mmol). [e]Reaction temperature: 50 °C. [f]Reaction temperature: 70 °C. n.r. = no reaction.

DOI: 10.1021/acs.joc.5b00130
J. Org. Chem. 2015, 80, 3504−3511

Table 2. Reaction of 1a with Various Nitroarenes[a]



1a 2 3

Entry	Nitroarene		Product		Yield (%)[b]
1		**2a**		**3aa**	90
2		**2b**		**3ab**	88
3		**2c**		**3ac**	85
4		**2d**		**3ad**	82
5[c]		**2e**		**3ae**	86
6[c]		**2f**		**3af**	95
7[c]		**2g**		**3ag**	80
8[d]		**2h**		**3ah**	57
9		**2i**		**3ai**	93(85)[e]
10		**2j**		**3aj**	96
11		**2k**		**3ak**	90
12		**2l**		**3al**	85
13[d]		**2m**		**3am**	98
14[d]		**2n**		**3an**	97
15[d]		**2o**		**3ao**	78
16[c]		**2p**		**3ap**	84
17[d]		**2q**		**3aq**	75
18		**2r**		**3ar**	51
19[d]		**2s**		**3as**	93
20	$MeNO_2$	**2t**			n.r.

[a]Reaction conditions: **1a** (0.75 mmol), **2** (0.5 mmol), $NaHSO_3$ (1.5 mmol), $FeCl_2$ (10 mol %), DMDACH (20 mol %), DMSO (2 mL), 12 h, Ar. DMDACH = *trans*-*N*,*N*′-dimethyl-1,2-diaminocyclohexane. [b]Yield based on nitroarene. [c]Reaction time: 16 h. [d]Reaction time: 20 h. [e]20 mmol of **2i** was added, and the reaction time was 20 h. n.r. = no reaction.

formed through a S_NAr-based reaction of sodium arylsulfinates with aryl chloride in some reaction systems.[21] With the present protocol, it is noteworthy that when *p*-nitrochlorobenzene (**2i**) and *m*-nitrochlorobenzene (**2j**) were employed as substrates, **1a** reacted exclusively with the nitro group to give the products **3ai** and **3aj** in 93% and 96% yield, respectively (Table 2, entries 9 and 10), demonstrating good selectivity. Ketone and aldehyde were also well tolerated to afford the corresponding products **3ap** and **3aq** in good yields (Table 2, entries 16 and 17). Possibly due to steric hindrance and side reaction of 1-nitronaphthalene (**2r**) with $NaHSO_3$,[22] the reaction of **1a** with **2r** afforded corresponding **3ar** in a moderate yield of 51% (Table 2, entry 18). Finally, the reaction of 3-nitropyridine (**2s**) also proceeded smoothly to give sulfonamide **3as** in 93% yield (Table 2, entry 19). When nitromethane (**2t**) was conducted under standard conditions, no desired product was detected.

Subsequently, a range of sodium sulfinates was reacted with nitrobenzene, and the results are listed in Table 3. The reaction

Table 3. Reaction of Nitroarenes with Various Sodium Sulfinates[a]

1 2 3

Entry	Sodium sulfinate		Product		Yield[b] (%)
1		**1b**		**3ba**	93
2		**1b**		**3bb**	86
3		**1b**		**3bi**	91
4		**1c**		**3ca**	92
5[c]		**1d**		**3da**	31
6[c]		**1e**		**3ea**	85
7[c]		**1f**		**3fa**	89
8[c]		**1g**		**3ga**	91
9[d]		**1h**		**3ha**	84
10[c]		**1i**		**3ia**	94
11		**1i**		**3is**	81
12		**1j**			n.r.

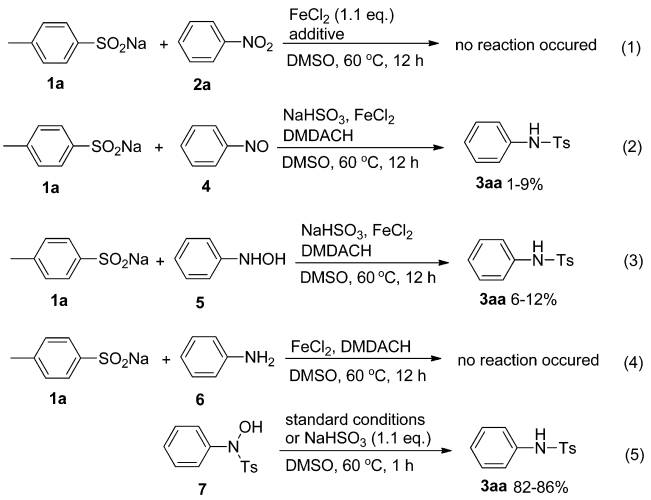
[a]Reaction conditions: **1** (0.75 mmol), **2** (0.5 mmol), $NaHSO_3$ (1.5 mmol), $FeCl_2$ (10 mol %), DMDACH (20 mol %), DMSO (2 mL), 12 h, Ar. n.r. = no reaction. DMDACH = *trans*-*N*,*N*′-dimethyl-1,2-diaminocyclohexane. [b]Yield based on nitroarene. [c]Reaction time: 20 h. [d]Na_2CO_3 (0.75 mmol) was added.

DOI: 10.1021/acs.joc.5b00130
J. Org. Chem. 2015, 80, 3504−3511

of sodium bezenesulfinate (**1b**) with nitrobenzene, *p*-nitrotoluene, and *p*-chloronitrobenzene gave the desired products **3ba**, **3bb**, and **3bi** in excellent yields (Table 3, entries 1−3). The reaction of sodium 4-methoxybenzenesulfinate (**1c**) with nitrobenzene furnished **3ca** in 92% yield (Table 3, entry 4). When the 2,4,6 positions of sodium benzenesulfinate were substituted with methyl groups (**1d**), the yield was reduced dramatically to 31%, probably due to the steric hindrance (Table 3, entry 5). Meanwhile, this reaction is also tolerant with bromo, chloro, and fluoro substituents on the aromatic rings of sodium arylsulfinates, and the corresponding target products **3ea**−**3ga** were obtained in excellent yields (85−91%; Table 3, entries 6−8). When sodium sulfinate with an amino group (**1h**) was subjected to this transformation, the desired product **3ha** could be obtained directly in 84% yield with the amino group unaffected (Table 3, entry 9). It is noteworthy that this kind of structural moiety in which the amino group is at the para position of arylsulfonamides is decisive for the antibacterial action,[23] and can only be prepared through multistep synthetic processes by the traditional methods.[24] The protocol was also applied to the synthesis of thiophene sulfonamide, giving the desired product **3ia** and **3is** in 94% and 81% yield, respectively (Table 3, entries 10 and 11). However, sodium alkylsulfinate (**1j**) was not a suitable substrate for this transformation (Table 3, entry 12).

To gain some understanding of the mechanism for this reaction, some control experiments were tentatively examined (for details, see Supporting Information). Release of $NaHSO_4$ was first detected under standard conditions (for details, see Supporting Information). Subsequently, **1a** and **2a** were subjected to the conditions in the presence of 1.1 equiv amount of $FeCl_2$; however, no reaction was detected in the absence of $NaHSO_3$ (Scheme 3, eq 1). This evidence indicated

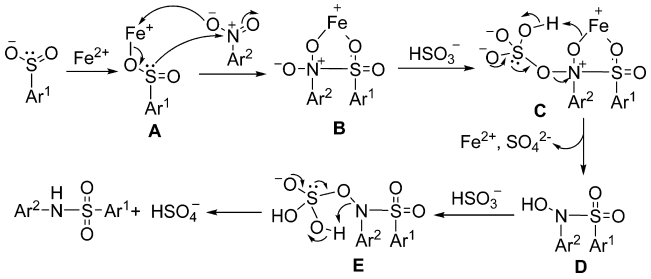
Scheme 3. Control Experiments



that $FeCl_2$ or sodium sulfinate could not act as the reductant and replace the role of $NaHSO_3$ in this transformation. Nitrosobenzene (**4**) and *N*-phenylhydroxylamine (**5**), which are thought to be the intermediates in the reduction of nitroarenes by $NaHSO_3$ in the Piria reaction,[20,22,25] were then tested under the standard conditions (Scheme 3, eqs 2 and 3). The yields of sulfonamide **3aa** were very low. The reaction between sodium *p*-toluenesulfinate (**1a**) and aniline (**6**) did not occur at all (Scheme 3, eq 4). These results suggested that the N−S bond of the sulfonamide might not be formed through the reaction of **1a** with nitrosobenzene (**4**), *N*-phenylhydroxylamine (**5**), or aniline (**6**). That is, in this reaction nitroarenes might not be reduced to nitrosobenzene, *N*-phenylhydroxylamine, or aniline as in the Piria reaction. It was more reasonable to assume that the N−S bond was generated through direct coupling of nitroarene with sodium sulfinate prior to the Piria reaction. The direct coupling of nitroarene with sodium sulfinate implied that *N*-phenyl-*N*-tosylhydroxylamine (**7**) might be involved as an intermediate in the reaction. Consequently, *N*-phenyl-*N*-tosylhydroxylamine (**7**) was prepared following the literature procedure[26] and treated with $NaHSO_3$ to furnish the sulfonamide **3aa** in 86% yield (Scheme 3, eq 5).

On the basis of the above observations, a plausible mechanism for this reaction is proposed in Scheme 4. The

Scheme 4. Proposed Mechanism



reaction starts from the coordination between sodium arylsulfinate and Fe^{2+} to form the arylsulfinic acid salt **A**. Subsequently, complexation and nucleophilic addition of **A** to the nitro group of nitroarene lead to the cyclic five-membered intermediate **B**, which is then attacked by bisulfite to afford intermediate **C**. Release of Fe^{2+} and SO_4^{2-} from intermediate **C** produces *N*-aryl-*N*-arenesulfonylhydroxylamine **D**. Addition of **D** to the bisulfite gives intermediate **E**. Finally, intermediate **E** decomposes to the corresponding *N*-arylsulfonamide and bisulfate which accounts for the acidity of the reaction mixture (for details, see Supporting Information). The reductions of intermediate **B** by bisulfite to *N*-aryl-*N*-arenesulfonylhydroxylamine **D** and **D** to the final product *N*-arylsulfonamide are mechanistically similar to the reductions occurring in the Piria reaction.[20b]

■ CONCLUSIONS

In summary, an efficient and convenient $FeCl_2$-catalyzed system for the construction of sulfonamide directly from nitroarenes and sodium arylsulfinates under mild conditions has been developed. The important feature of this method is using stable and readily available nitroarenes as nitrogen source and inexpensive sodium bisulfite as reductant, which makes it efficient and practical. The process also exhibits significant functional group tolerance and allows for the preparation of a number of *N*-arylsulfonamides in good to excellent yields. The importance of the sulfonamide scaffold would render this protocol attractive for both synthetic and medicinal chemistry. Meanwhile, based on the experimental observations, a novel and interesting mechanism for this reaction is proposed.

■ EXPERIMENTAL SECTION

General. All commercial reagents were used without further purification. Sodium arylsulfinate[27] and *N*-phenyl-*N*-tosylhydroxyl-

DOI: 10.1021/acs.joc.5b00130
J. Org. Chem. 2015, 80, 3504−3511

amine (**6**)[26] were prepared according to previous literature. Melting points were determined on a melting point apparatus and were uncorrected. Column chromatography was performed with silica gel. Thin layer chromatography was carried out using silica gel plates. High-resolution mass spectra (HRMS) were obtained with a Q-TOF-Premier (ESI). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz instrument. Spectra were reported relative to Me_4Si (δ 0.0 ppm), $CDCl_3$ (δ 7.26 ppm), and DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR spectra were reported relative to $CDCl_3$ (δ 77.0 ppm) and DMSO-d_6 (δ 39.5 ppm). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, etc. Products were characterized by comparison of ^{1}H and ^{13}C NMR spectroscopic data with those available in the literature. pH was recorded on a pH meter.

Control Experiments on the Reaction of Sodium *p*-Acetaminobenzenesulfinate with Nitrobenzene. Sodium 4-acetamidobenzenesulfinate (663 mg, 3 mmol), nitrobenzene (0.051 mL, 0.5 mmol), and CuCl (7.42 mg, 0.075 mmol) were added in DMSO (2 mL). The pH of the mixture was about 8.3 by the pH meter. The mixture was allowed to react in a sealed tube at 100 °C under argon for 12 h. After cooling to room temperature, the pH of the resulting mixture was reduced to 3.4, indicating the production of H^+. The mixture was then extracted with dichloromethane (3 × 10 mL). Saturated aqueous $BaCl_2$ was added to the aqueous solution (0.5 mL), and there formed white precipitates which were not dissolved in aqueous HCl (1 M), indicating the formation of $BaSO_4$.[28] The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed. Product and acetanilide were separated by short flash chromatography on a silica gel column. Isolated yield was based on nitrobenzene.

Determination of $NaHSO_4$ Released from Standard Reaction Conditions. *p*-Toluenesulfinate (133.5 mg, 0.75 mmol), nitrobenzene (0.051 mL, 0.5 mmol), $NaHSO_3$ (156 mg, 1.5 mmol), $FeCl_2$ (6.3 mg, 10 mol %), and *trans-N,N′*-dimethyl-1,2-diaminocyclohexane (14.2 mg, 20 mol %) were dissolved in DMSO (2 mL). The pH of the mixture was about 9.6 by a pH meter. Then the mixture was stirred at 60 °C for 12 h in a sealed tube under argon atmosphere. After cooling to room temperature, the pH of the resulting mixture was reduced to 3.0. The mixture was then extracted with dichloromethane (3 × 10 mL). Saturated aqueous $BaCl_2$ was added to the aqueous solution (0.5 mL), and there formed white precipitates, which were not dissolved in aqueous HCl (1 M), indicating the formation of $BaSO_4$.[19]

General Procedure for the Synthesis of Sulfonamides. A mixture of sodium arylsulfinates (0.75 mmol), nitroarenes (0.051 mL, 0.5 mmol), $NaHSO_3$ (156 mg, 1.5 mmol), $FeCl_2$ (6.3 mg, 10 mol %), and *trans-N,N′*-dimethyl-1,2-diaminocyclohexane (14.2 mg, 20 mol %) in DMSO (2 mL) were stirred at 60 °C for 12 h in a sealed tube under argon atmosphere. After cooling to room temperature, water (8 mL) was added, the aqueous solution was extracted with dichloromethane (3 × 10 mL), and the combined extract was dried with anhydrous Na_2SO_4. The solvent was removed, and the crude product was separated by a short flash chromatography on a silica gel column to afford the pure product.

*4-Methyl-N-phenyl-benzenesulfonamide (**3aa**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3aa** as a white solid in 90% yield (111 mg). m.p.: 104−105 °C (lit.: 104−105 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70−7.68 (m, 2H), 7.40−7.20 (m, 4H), 7.10−7.07 (m, 4H), 2.36 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 143.9, 136.6, 136.0, 129.7, 129.3, 127.3, 125.3, 121.5, 21.6 ppm. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}NO_2S$ $[M + H]^+$: 248.0745; found, 248.0741.

*4-Methyl-N-(p-tolyl)benzenesulfonamide (**3ab**).*[8b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3ab** as a white solid in 88% yield (115 mg). m.p.: 116−117 °C (lit.: 118−118.7 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.04 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.02−6.96 (m, 4H), 2.32 (s, 3H), 2.17 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 143.0, 136.7, 135.1, 133.2, 129.6, 129.5, 126.7, 120.4, 20.9, 20.2 ppm. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$, 262.0902; found, 262.0901.

*4-Methyl-N-(m-tolyl)benzenesulfonamide (**3ac**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3ac** as a white solid in 85% yield (111 mg). m.p.: 114−115 °C (lit.: 115 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), (6.67 (s, 1H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 143.8, 139.4, 136.4, 136.2, 129.6, 129.1, 127.3, 126.1, 122.2, 118.4, 21.5, 21.3 ppm. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$, 262.0902; found, 262.0904.

*4-Methyl-N-(o-tolyl)benzenesulfonamide (**3ad**).*[8b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3ad** as a white solid in 82% yield (107 mg). m.p.: 105−107 °C (lit.: 108−109 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13−7.06 (m, 3H), 6.61 (s, 1H), 2.38 (s, 3H), 2.01 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 143.8, 136.7, 134.5, 131.4, 130.8, 129.6, 127.2, 126.9, 126.2, 124.3, 21.6, 17.6 ppm. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$, 262.0902; found, 262.0905.

*Methyl-4-(4-methylphenylsulfonamido)benzoate (**3ae**).*[9c] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2, v/v) afforded **3ae** as a white solid in 86% yield (131 mg). m.p.: 166−168 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.80 (s, 1H), 7.83 (d, *J* = 8.8 Hz 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 165.6, 143.7, 142.4, 136.3, 130.6, 129.8, 126.7, 124.3, 118.1, 51.9, 20.9 ppm. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{16}NO_4S$ $[M + H]^+$, 306.0800; found, 306.0803.

*Methyl-3-(4-methylphenylsulfonamido)benzoate (**3af**).*[29] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2, v/v) afforded **3af** as a white solid in 95% yield (145 mg). m.p.: 152−154 °C (lit.: 152−154 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.50 (s, 1H), 7.73 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62−7.60 (m, 1H), 7.41−7.34 (m, 4H), 3.82 (s, 3H), 2.32 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 165.6, 143.5, 138.3, 136.3, 130.5, 129.8, 129.7, 126.6, 124.5, 124.2, 120.0, 52.2, 20.9 ppm. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{16}NO_4S$ $[M + H]^+$, 306.0800; found, 306.0805.

*Methyl-2-(4-methylphenylsulfonamido)benzoate (**3ag**).*[30] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ag** as a white solid in 80% yield (122 mg). m.p.: 110−112 °C (lit.: 115−116 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.43 (s, 1H), 7.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.57 (td, *J* = 7.8, 1.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.16 (td, *J* = 7.6, 0.8 Hz, 1H), 3.83 (s, 3H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 167.6, 144.0, 138.8, 135.7, 134.4, 131.0, 129.8, 126.9, 123.8, 119.7, 117.6, 52.6, 20.9 ppm. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{16}NO_4S$ $[M + H]^+$, 306.0800; found, 306.0801.

*N-Mesityl-4-methylbenzenesulfonamide (**3ah**).*[31] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3ah** as a white solid in 57% yield (82 mg). m.p.: 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 6.85 (s, 2H), 5.93 (s, 1H), 2.45 (s, 3H), 2.27 (s, 3H), 2.02 (s, 6H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 143.5, 137.9, 137.6, 137.5, 130.0, 129.6, 129.5, 127.2, 21.6, 20.9, 18.6 ppm. HRMS (ESI): *m*/*z* calcd for $C_{16}H_20NO_2S$ $[M + H]^+$, 290.1215; found, 290.1213.

*N-(4-Chlorophenyl)-4-methylbenzenesulfonamide (**3ai**).*[32] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3ai** as a white solid in 93% yield (131 mg). m.p.: 118−119 °C (lit.: 118−119 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.40 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 143.4, 136.8, 136.2, 129.7, 129.1, 128.0, 126.7, 121.4, 20.9 ppm. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{13}ClNO_2S$ $[M + H]^+$, 282.0356; found, 282.0355.

The reaction was also carried out on a larger scale following the general procedure. A mixture of sodium *p*-toluenesulfinate (**1a**) (5.34 g, 0.03 mol), *p*-nitrochlorobenzene (**2i**) (3.151 g, 0.02 mol), $NaHSO_3$

DOI: 10.1021/acs.joc.5b00130
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(6.24 g, 0.06 mol), $FeCl_2$ (0.253g, 10 mol %), and *trans-N,N′*-dimethyl-1,2-diaminocyclohexane (0.568 g, 20 mol %) in DMSO (50 mL) were stirred at 60 °C for 20 h in a sealed tube under argon atmosphere. After purification by the general procedure, the product was obtained in 85% yield (4.789 g).

*N-(3-Chlorophenyl)-4-methylbenzenesulfonamide (**3aj**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3aj** as a white solid in 96% yield (135 mg). m.p.: 135−137 °C (lit.: 135−137 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.17−6.89 (m, 5H), 2.39 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 144.3, 137.8, 135.8, 134.9, 130.3, 129.8, 127.3, 125.3, 121.0, 119.0, 21.6 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{13}ClNO_2S$ $[M + H]^+$, 282.0356; found, 282.0356.

*N-(4-(4-Methylphenylsulfonamido)phenyl)acetamide (**3ak**).*[33] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) afforded **3ak** as a white solid in 90% yield (137 mg). m.p.: 184−185 °C (lit.: 184 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.98 (s, 1H), 9.83 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 2.32 (s, 3H), 1.98 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 168.0, 143.0, 136.6, 135.9, 132.5, 129.5, 126.7, 121.4, 119.7, 23.8, 20.9 ppm. HRMS (ESI): m/z calcd for $C_{15}H_{17}N_2O_3S$ $[M + H]^+$, 305.0960; found, 305.0959.

*N-(4-Methoxyphenyl)-4-methylbenzenesulfonamide (**3al**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3al** as a white solid in 85% yield (118 mg). m.p.: 114−116 °C (lit.: 114.5−115 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.97 (dd, J = 6.8, 2.0 Hz, 2H), 6.77 (dd, J = 6.8, 2.4 Hz, 2H), 6.33 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 157.9, 143.7, 136.0, 129.6, 129.0, 127.3, 125.4, 114.4, 55.4, 21.5 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{16}NO_3S$ $[M + H]^+$, 278.0851; found, 278.0854.

*4-Methyl-N-(3-(trifluoromethyl)phenyl)benzenesulfonamide (**3am**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) afforded **3am** as a white solid in 98% yield (154 mg). m.p.: 94−95 °C (lit.: 94.5−96.5 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.71 (d, J = 8.0 Hz, 2H), 7.36−7.24 (m, 6H), 7.15 (s, 1H), 2.39 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 144.5, 137.3, 135.6, 131.8 (q, J_{C-F} = 32.5 Hz), 130.0, 129.9, 127.3, 124.9, 123.5 (q, J_{C-F} = 271 Hz), 121.7 (q. J_{C-F} = 3.8 Hz), 117.6 (q, J_{C-F} = 3.8 Hz), 21.5 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{13}F_3NO_2S$ $[M + H]^+$, 316.0619; found, 316.0617.

*N-(4-Cyanophenyl)-4-methylbenzenesulfonamide (**3an**).*[8b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3an** as a white solid in 97% yield (132 mg). m.p.: 183−184 °C (lit.: 180 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 144.9, 141.0, 135.5, 133.6, 130.1, 127.3, 119.3, 118.5, 107.7, 21.6 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{13}N_2O_2S$ $[M + H]^+$, 273.0698; found, 273.0699.

*4-(4-Methylphenylsulfonamido)benzoic Acid (**3ao**).*[34] Purification by column chromatography on silica gel (dichloromethane/methanol = 5/1, v/v) afforded **3ao** as a white solid in 78% yield (113 mg). m.p.: 230−232 °C (lit.: 230−232 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.74 (s, 1H), 10.74 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 166.7, 143.6, 142.0, 136.4, 130.7, 129.8, 126.7, 125.5, 118.0, 20.9 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{14}NO_4S$ $[M + H]^+$, 292.0644; found, 292.0641.

*N-(3-Acetylphenyl)-4-methylbenzenesulfonamide (**3ap**).*[35] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3ap** as a white solid in 84% yield (121 mg). m.p.:129−131 °C (lit.: 129 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.0 Hz, 3H), 7.62 (s, 1H), 7.40−7.33 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.10 (s, 1H), 2.55 (s, 3H), 2.37 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 197.4, 144.2, 138.1, 137.3, 135.9, 129.8, 129.7, 127.3, 125.6, 125.1, 120.7, 26.7, 21.5 ppm. HRMS (ESI): m/z calcd for $C_{15}H_{16}NO_3S$ $[M + H]^+$, 290.0851; found, 290.0853.

*N-(4-Formylphenyl)-4-methylbenzenesulfonamide (**3aq**).*[8b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3aq** as a white solid in 75% yield (103 mg). m.p.: 186−188 °C (lit.: 190.8−191.5 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.95 (s, 1H), 9.81 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 191.5, 143.8, 143.5, 136.3, 131.3, 131.1, 129.9, 126.7, 118.0, 20.93 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{14}NO_3S$ $[M + H]^+$, 276.0694; found, 276.0690.

*4-Methyl-N-(naphthalen-1-yl)benzenesulfonamide (**3ar**).*[36] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3ar** as a white solid in 51% yield (76 mg). m.p.: 143−145 °C (lit.: 143−145 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86−7.79 (m, 2H), 7.71 (d, J = 6.4 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.46−7.33 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 2.33 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 143.8, 136.4, 134.2, 131.5, 129.6, 128.9, 128.4, 127.4, 127.2, 126.6, 126.3, 125.4, 122.7, 121.5, 21.5 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_2S$ $[M + H]^+$, 298.0902; found, 298.0903.

*4-Methyl-N-(pyridin-3-yl)benzenesulfonamide (**3as**).*[8b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3as** as a white solid in 93% yield (115 mg). m.p.: 191−192 °C (lit.: 192−194 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.49 (s, 1H), 8.28−8.24 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.51 (dt, J = 8.4, 2.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 8.4, 4.4 Hz, 1H), 2.34 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 145.2, 143.6, 141.6, 136.2, 134.4, 129.8, 127.2, 126.7, 123.9, 20.9 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{13}N_2O_2S$ $[M + H]^+$, 249.0698; found, 249.0696.

*N-Phenylbenzenesulfonamide (**3ba**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded **3ba** as a white solid in 93% yield (108 mg). m.p.: 105−106 °C (lit.: 110−111 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.0 Hz, 2H), 7.55−7.51 (m, 1H), 7.43 (td, J = 6.8, 1.6 Hz, 2H), 7.24 (td, J = 6.8, 1.6 Hz, 2H), 7.13−7.06 (m, 3H), 6.85 (s, 1H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 139.0, 136.3, 133.0, 129.4, 129.0, 127.2, 125.5, 121.8 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{12}NO_2S$ $[M + H]^+$, 234.0589; found, 234.0591.

*N-(p-Tolyl)benzenesulfonamide (**3bb**).*[37] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3bb** as a white solid in 86% yield (106 mg). m.p.: 116−118 °C (lit.: 118−120 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.12 (s, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.62−7.52 (m, 3H), 7.03−6.95 (m, 4H), 2.18 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 140.0, 135.4, 133.9, 133.2, 130.0, 129.6, 127.1, 121.1 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{14}NO_2S$ $[M + H]^+$, 248.0745; found, 248.0746.

*N-(4-Chlorophenyl)benzenesulfonamide (**3bi**).*[9b] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3bi** as a white solid in 91% yield (121 mg). m.p.: 120−121 °C (lit.: 122−123 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.46 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.64−7.55 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.12−7.10 (d, J = 8.8 Hz, 2H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 144.4, 141.9, 138.3, 134.6, 134.4, 133.4, 131.8, 126.8 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{11}ClNO_2S$ $[M + H]^+$, 268.0199; found, 268.0195.

*4-Methoxy-N-phenylbenzenesulfonamide (**3ca**).*[38] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3ca** as a white solid in 92% yield (121 mg). m.p.: 107−108 °C (lit.: 109−110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.8 Hz, 2H), 7.23 (t, J = 8.0 Hz, 2H), 7.12 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.65 (s, 1H), 3.82 (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 163.1, 136.6, 130.6, 129.4, 129.3, 125.4, 121.7, 114.2, 55.6 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{14}NO_3S$ $[M + H]^+$, 264.0694; found, 264.0694.

*2,4,6-Trimethyl-N-phenylbenzenesulfonamide (**3da**).*[9c] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3da** as a white solid in 31% yield (43 mg).

DOI: 10.1021/acs.joc.5b00130
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m.p.: 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.6 Hz, 2H), 6.91 (s, 2H), 6.76 (s, 1H), 2.60 (s, 6H), 2. Twenty-seven (s, 3H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 142.6, 139.3, 136.5, 133.4, 132.1, 129.3, 125.2, 121.4, 23.0, 21.0 ppm. HRMS (ESI): m/z calcd for $C_{15}H_{18}NO_2S$ [M + H]$^+$, 276.1058; found, 276.1060.

*4-Fluoro-N-phenylbenzenesulfonamide (**3ea**).*[39] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3ea** as a white solid in 85% yield (107 mg). m.p.: 109−111 °C (lit.: 109−111 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10. 30 (s, 1H), 7.83−7.79 (m, 2H), 7.41−7.37 (m, 2H), 7.26−7.22 (m, 2H), 7.10−7.02(m, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 165.5 (d, J_{C-F} = 250 Hz), 137.4, 135.8 (d, J_{C-F} = 3 Hz), 129.7 (d, J_{C-F} = 9.6 Hz), 129.2, 124.3, 120.3, 116.5 (d, J_{C-F} = 22.6 Hz) ppm. HRMS (ESI): m/z calcd for $C_{12}H_{11}FNO_2S$ [M + H]$^+$, 252.0495; found, 252.0496.

*4-Chloro-N-phenylbenzenesulfonamide (**3fa**).*[39] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3fa** as a white solid in 89% yield (119 mg). m.p.: 104−105 °C (lit.: 104−105 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.36 (s, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.10−7.03 (m, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 138.3, 137.7, 137.3, 129.4, 129.2, 128.6, 124.4, 120.4 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{11}ClNO_2S$ [M + H]$^+$, 268.0199; found, 268.0194.

*4-Bromo-N-phenylbenzenesulfonamide (**3ga**).*[39] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded **3ga** as a white solid in 91% yield (142 mg). m.p.: 116−117 °C (lit.: 116−117 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.36 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.6 Hz, 2H), 7.10−7.03 (m, 3H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 138.7, 137.3, 132.3, 129.2, 128.6, 126.7, 124.4, 120.3 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{11}BrNO_2S$ [M + H]$^+$, 311.9694; found, 311.9690.

*4-Amino-N-phenylbenzenesulfonamide (**3ha**).*[40] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ha** as a white solid in 84% yield (104 mg). m.p.: 180−182 °C (lit.: 180−181 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.84 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 8.8 Hz, 2H), 5.95 (s, 2H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 152.8, 138.5, 128.9, 128.7, 124.4, 123.2, 119.4, 112.5 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{13}N_2O_2S$ [M + H]$^+$, 249.0698; found, 249.0701.

*N-Phenylthiophene-2-sulfonamide (**3ia**).*[41] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded **3ia** as a white solid in 94% yield (112 mg). m.p.: 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.50 (dd, J = 3.6, 1.2 Hz, 1H), 7.30 (t, J = 8.0 Hz, 2H), 7.18−7.13 (m, 3H), 7.00 (dd, J = 5.2, 4.0 Hz, 1H), 6.90 (s, 1H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 139.4, 136.1, 132.9, 132.5, 129.4, 127.3, 125.9, 121.9 ppm. HRMS (ESI): m/z calcd for $C_{10}H_{10}NO_2S_2$ [M + H]$^+$, 240.0153; found, 240.0150.

*N-(Pyridin-3-yl)thiophene-2-sulfonamide (**3is**).*[42] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3is** as a white solid in 81% yield (97 mg). m.p.: 182−184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.71 (s, 1H), 8.32 (d, J = 4.8 Hz, 2H), 7.94 ((d, J = 4.8 Hz, 2H), 7.59−7.55 (m, 2H), 7.36 (dd, J = 8.0, 4.4 Hz, 1H), 7.14 (t, J = 4.4 Hz, 1H). ^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6): δ = 146.1, 142.5, 139.8, 134.6, 134.3, 133.3, 128.3, 124.5 ppm. HRMS (ESI): m/z calcd for $C_9H_9N_2O_2S_2$ [M + H]$^+$, 241.0105; found, 241.0101.

*N-Phenyl-N-tosylhydroxylamine (**7**).*[26] m.p.: 138−140 °C (lit.: 142−143 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (t, J = 8.4 Hz, 2H), 7.31−7.22 (m, 5H), 7.29−7.18 (m, 2H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ = 145.0, 141.6, 129.9, 129.0, 128.9, 128.2, 127.4, 123.0, 21.7 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{14}NO_3S$ [M + H]$^+$, 264.0694; found, 264.0690.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of control experiments for the mechanistic investigation and copies of ^{1}H NMR and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (21321061, 21072134, and J1103315/J0104) for financial support and the Comprehensive Training Platform of Specialized Laboratory, College of Chemistry, Sichuan University for NMR and MS measurements.

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DOI: 10.1021/acs.joc.5b00130
J. Org. Chem. 2015, 80, 3504−3511