

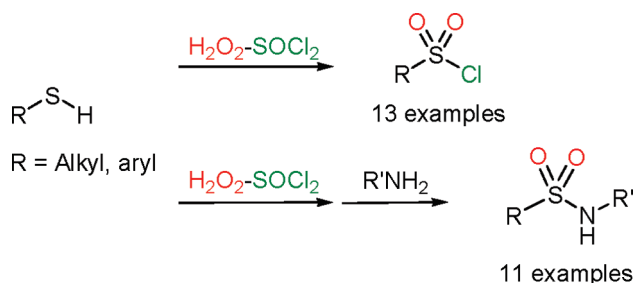
## Direct Conversion of Thiols to Sulfonyl Chlorides and Sulfonamides

Kiumars Bahrami,<sup>\*,†,‡</sup> Mohammad M. Khodaei,<sup>\*,†,‡</sup> and Mehdi Soheilzad<sup>†</sup>

<sup>†</sup>Department of Chemistry, Razi University, Kermanshah 67149, Iran, and <sup>‡</sup>Nanoscience and Nanotechnology Research Center (NNRC), Razi University, Kermanshah 67149, Iran

kbahrami2@hotmail.com; mmkhoda@razi.ac.ir

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$\text{H}_2\text{O}_2$  in combination with  $\text{SOCl}_2$  proved to be a highly reactive reagent for the direct oxidative conversion of thiol derivatives to the corresponding sulfonyl chlorides with high purity through oxidative chlorination. Upon reaction with amines, the corresponding sulfonamides were obtained in excellent yields and in very short reaction times.

### Introduction

The development of simple, versatile, and environmentally friendly processes or methodologies for widely used organic compounds from readily available reagents is one of the major challenges for chemists in organic synthesis. Organic sulfur compounds are widespread in numerous natural products and widely used as various artificial chemicals. Sulfonyl chlorides, in particular, are precursors with extensive uses in organic synthesis.<sup>1</sup> The most typical method for the preparation of sulfonyl chlorides is the oxidative chlorination of sulfur compounds, thiols, sulfides, thioacetates, and thiocarbamates, with aqueous chlorine.<sup>2</sup> Although

other methods are available to do this transformation,<sup>3–7</sup> attention is moving toward newer and more selective methods for this purpose. However, in spite of their potential utility, many of these methods involve various drawbacks such as the use of expensive or less easily available reagents, vigorous reaction conditions, long reaction time, tedious manipulations in the isolation of the pure products, and side reactions. Therefore, the discovery of milder and practical routes for the synthesis of sulfonyl chlorides is highly desirable.

Thionyl chloride ( $\text{SOCl}_2$ ) is a reactive chemical reagent. It is mainly used in the industrial production of organochlorine compounds, which are often intermediates in pharmaceuticals and agrichemicals, but it has not been studied as promoter in the conversion of thiols to sulfonyl chlorides until now.

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is also an attractive and inexpensive oxidant widely used in laboratory and industry synthesis. From the viewpoint of green chemistry,  $\text{H}_2\text{O}_2$  has

\*To whom correspondence should be addressed. Fax: +98(831)4274559 (K.B.).

(1) (a) Hoyle, J. In *The Chemistry of Sulfonic Acids, Esters and their Derivatives (The Chemistry of Functional Groups)*; Patai, S., Rapport, Z., Eds.; John Wiley & Sons: New York, 1991; Chapter 10, p 351. (b) Tanaka, K. In *The Chemistry of Sulfonic Acids, Esters and their Derivatives (The Chemistry of Functional Groups)*; Patai, S., Rapport, Z., Eds.; John Wiley & Sons: New York, 1991; Chapter 11, p 401. (c) Moore, J. D.; Herpel, R. H.; Lichtsinn, J. R.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2003**, *5*, 105. (d) Dubbaka, S. R.; Vogel, P. *J. Am. Chem. Soc.* **2003**, *125*, 15292. (e) Kværnø, L.; Werder, M.; Hauser, H.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 1145. (f) Lassalle, G.; Galtier, D.; Galli, F. European Patent 643047, **1995**. (g) Lezina, O. M.; Kuchin, A. V.; Rubtsova, S. A. Russian Patent 2289574, **2006**.

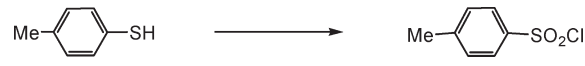
(2) (a) Watson, R. J.; Batty, D.; Baxter, A. D.; Hannah, D. R.; Owen, D. A.; Montana, J. G. *Tetrahedron Lett.* **2002**, *43*, 683. (b) Percec, V.; Bera, T. K.; De, B. B.; Sanai, Y.; Smith, J.; Holerca, M. N.; Barboiu, B.; Grubbs, B. B. B.; Fréchet, J. M. J. *J. Org. Chem.* **2001**, *66*, 2104. (c) Chen, Z.; Demuth, T. P., Jr.; Wireko, F. C. *Bioorg. Med. Chem. Lett.* **2002**, *11*, 2111.

(3) (a) Gareau, Y.; Pellicelli, J.; Laliberté, S.; Gauvreau, D. *Tetrahedron Lett.* **2003**, *44*, 7821. (b) Norris, T. J. *Chem. Soc., Perkin Trans. 1* **1978**, 1378. (c) Barbero, M.; Cadamuro, S.; Degani, I.; Fochi, R.; Regondi, V. *Synthesis* **1989**, 957.

(4) Blotny, G. *Tetrahedron Lett.* **2003**, *44*, 1499.  
(5) Meinzer, A.; Breckel, A.; Thaher, B. A.; Manicone, N.; Otto, H.-H. *Helv. Chim. Acta* **2004**, *87*, 90.

(6) Nishiguchi, A.; Maeda, K.; Miki, S. *Synthesis* **2006**, 4131.  
(7) Prakash, G. K. S.; Mathew, T.; Panja, C.; Olah, G. A. *J. Org. Chem.* **2007**, *72*, 5847.

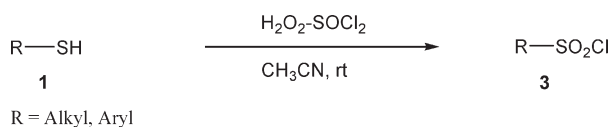
**TABLE 1.** Effect of Increasing Amount of H<sub>2</sub>O<sub>2</sub> and SOCl<sub>2</sub> on Oxidative Chlorination of 4-Methylthiophenol<sup>a</sup>



entry	SOCl <sub>2</sub> (mmol)	30% H <sub>2</sub> O <sub>2</sub> (mmol)	yield % <sup>b</sup>
1	0.25	4	35
2	0.5	4	50
3	0.75	4	70
4	1	2	85
5	1	3	97
6	1	4	97

<sup>a</sup>Reaction conditions: the reactions were performed with 4-methylthiophenol (1 mmol) for 1 min, at 25 °C. <sup>b</sup>Isolated yields.

### SCHEME 1



become more and more popular with regard to the formation of water as a sole byproduct.

In continuation of our interest in the use of hydrogen peroxide in organic synthesis,<sup>8</sup> we report herein for the first time H<sub>2</sub>O<sub>2</sub>–SOCl<sub>2</sub> as a valuable reagent system for the direct oxidative chlorination of thiol derivatives to the corresponding sulfonyl chlorides (Scheme 1).

### Results and Discussion

To evaluate the solvent effect, the oxidative chlorination of 4-methylthiophenol was carried out under similar reaction conditions using various organic solvents. Among various solvents like chloroform, dichloromethane, toluene, acetonitrile, and 1,4-dioxane used for this transformation, acetonitrile and 1,4-dioxane were the solvents of choice as best results were obtained with them.

To optimize the reaction conditions, the reaction of 4-methylthiophenol was selected as model substrate to examine the effects of different amount of H<sub>2</sub>O<sub>2</sub> and SOCl<sub>2</sub> in acetonitrile at room temperature. As can be seen from Table 1, the best result in 97% yield was obtained by carrying out the reaction with 1:3 mol ratios of thiol to H<sub>2</sub>O<sub>2</sub> in the presence of 1 mmol SOCl<sub>2</sub> for 1 min.

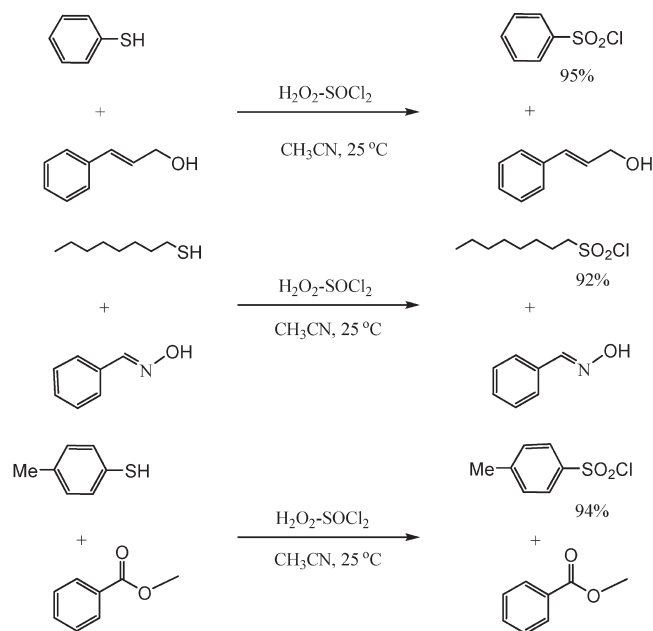
To evaluate the scope of this protocol, the oxidative chlorination of other thiols was further studied (Table 2, entries 1–13). As shown, aromatic thiols having electron-donating and electron-withdrawing groups in the aromatic ring, afforded excellent yields of products with high purity (monitored by NMR spectroscopy). Similarly, heterocyclic thiols, such as 2-mercaptopyrimidine and 2-mercaptobenzimidazole (Table 2, entries 10 and 11), were also investigated. Sulfonyl chlorides such as pyrimidine-2-sulfonyl chloride and benzimidazole-2-sulfonyl chlo-

(8) (a) Bahrami, K. *Tetrahedron Lett.* **2006**, *47*, 2009. (b) Khodaei, M. M.; Bahrami, K.; Khedri, M. *Can. J. Chem.* **2007**, *85*, 7. (c) Khodaei, M. M.; Bahrami, K.; Karimi, A. *Synthesis* **2008**, 1682. (d) Bahrami, K.; Khodaei, M. M.; Kavianinia, I. *Synthesis* **2007**, 547. (e) Bahrami, K.; Khodaei, M. M.; Naali, F. *J. Org. Chem.* **2008**, *73*, 6835. (f) Bahrami, K.; Khodaei, M. M.; Naali, F. *Synlett* **2009**, 569. (g) Bahrami, K.; Khodaei, M. M.; Tirandaz, Y. *Synthesis* **2009**, 369.

(9) Richard, O.; Roblin, O.; James, W. *J. Am. Chem. Soc.* **1950**, *72*, 4890.

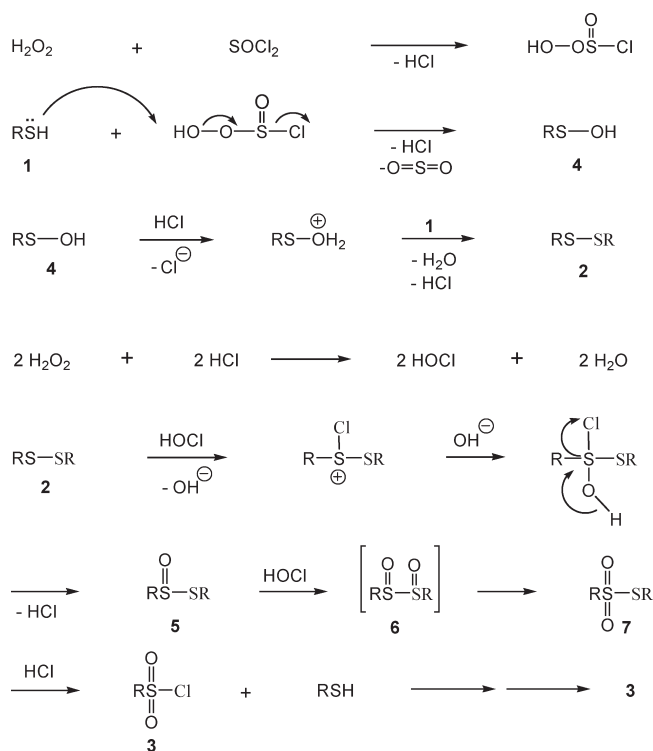
(10) Bornholdt, J.; Fjære, K. W.; Felding, J.; Kristensen, J. L. *Tetrahedron* **2009**, *65*, 9280.

### SCHEME 2<sup>a</sup>



<sup>a</sup>Reagents and conditions: molar ratio of substrates to H<sub>2</sub>O<sub>2</sub> to SOCl<sub>2</sub> (1:1:3:1), CH<sub>3</sub>CN, 25 °C.

### SCHEME 3. Proposed Mechanism for the Oxidative Chlorination with H<sub>2</sub>O<sub>2</sub>–SOCl<sub>2</sub> Reagent System



ride are unstable at room temperature.<sup>9–11</sup> Pyrimidine-2-sulfonyl chloride rapidly decomposes to 2-chloropyrimidine<sup>10</sup> and, in the case of benzimidazole-2-sulfonyl chloride, byproducts are 2-chlorobenzimidazole and 2-hydroxybenzimidazole<sup>11</sup>

(11) Wright, S. W.; Hallstrom, K. N. *J. Org. Chem.* **2006**, *71*, 1080.

(12) Fries, K.; Eyselbertz, E. *Justus Liebigs Ann. Chem.* **1915**, 407, 194.

TABLE 2. Oxidative Chlorination of Thiol Derivatives

R—SH $\xrightarrow{\hspace{2cm}}$ R—SO <sub>2</sub> Cl					
Entry	Thiol (1)	Sulfonyl chloride (3) <sup>a</sup>	Time (min)	Yield (%) <sup>b</sup>	Ref
1			1	99	4
2			1	97	4
3			1	98	7
4			1	97	7
5			1	98	7
6			1	97	12
7			1	98	3b
8			1	96	4
9			1	98	3c
10			1	0	9
11			1	0	11
12			1	98	6
13	<i>n</i> -Octyl—SH	<i>n</i> -Octyl—SO <sub>2</sub> Cl	1	97	3c

<sup>a</sup>The purified products were characterized by mp, <sup>1</sup>H and <sup>13</sup>C NMR. <sup>b</sup>Yields refer to pure isolated products.

by comparison to commercial samples. Furthermore, cyclohexanethiol and 1-octanethiol, aliphatic thiols, afforded the sulfonyl chlorides in excellent yields (Table 2, entries 12 and 13).

To study the chemoselectivity of this reagent system, we studied the oxidative chlorination of thiols in the presence of carbon-carbon double bond, alcohol, oxime, and ester. The results are depicted in Scheme 2. These studies clearly reveal that this method can be applied for the chemoselective oxidative chlorination of thiol derivatives in the presence of the above-mentioned functional groups in multifunctional molecules.

An investigation of the mechanistic aspects of oxidative chlorination of thiols (1) showed the corresponding disulfide (2) is the main intermediate in this transformation. When the reaction of 4-methylthiophenol was carried out with 1:1 mol ratios of thiol to H<sub>2</sub>O<sub>2</sub> in the presence of 1 mmol SOCl<sub>2</sub> for 5 min the desired disulfide was obtained as major product. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4-methylphenyl disulfide are available as Supporting Information.

The possible mechanism for this transformation is shown in Scheme 3. It is acceptable to assume that the nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on SOCl<sub>2</sub> makes oxygen atoms more electrophilic. Therefore, the mechanism proceeds through hydroxylation of thiol (1) leads to the formation of sulfenic acid (4),

which gives the corresponding symmetric disulfide (2). Then the successive oxidation of both sulfur atoms of the disulfide molecule by hypochlorous acid produces the intermediate (6) that undergoes rapid isomerization to the thiosulfonate (7), which can easily furnish sulfonyl chloride (3). Conversion of 6 to 7 has been well documented and recognized.<sup>13</sup>

Sulfonamides have long been the subject of pharmaceutical interest as a result of their potent biological activities.<sup>14</sup> Examples for recently approved drugs with a sulfonamide structure are the antihypertensive agent bosentan,<sup>15</sup> the

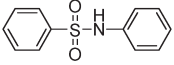
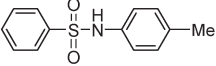
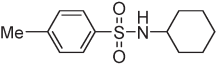
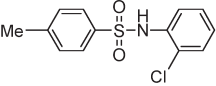
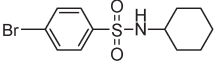
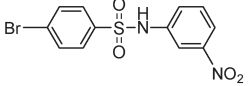
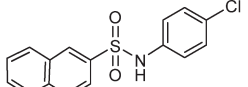
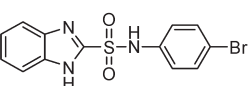
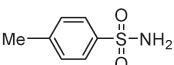
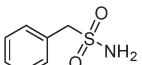
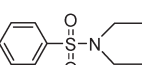
(13) (a) Freeman, F. *Chem. Rev.* **1984**, *84*, 117. (b) Oae, S.; Kim, Y. H.; Takara, T.; Fukushima, D. *Tetrahedron Lett.* **1977**, *18*, 1195. (c) Oae, S.; Takara, T.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2484. (d) Oae, S.; Shinham, K.; Fujimori, K.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 775. (e) Chau, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711.

(14) (a) Harter, W. G.; Albrect, H.; Brady, K.; Caprathe, B.; Dunbar, J.; Gilmore, J.; Hays, S.; Kostlan, C. R.; Lunney, B.; Walker, N. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 809. (b) Reddy, N. S.; Mallireddigari, M. R.; Cosenza, K. G.; Bell, S. C.; Reddy, E. P.; Reddy, M. V. R. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4093. (c) Stranix, B. R.; Lavallee, J.-F.; Sevigny, G.; Yelle, J.; Perron, V.; Leberre, N.; Herbart, D.; Wu, J. J. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3459. (d) Purushottamachar, P.; Khandelwal, A.; Vasaitis, T. S.; Bruno, R. D.; Gediya, L. K.; Njar, V. C. O. *Bioorg. Med. Chem.* **2008**, *16*, 3519.

(15) Wu, C.; Decker, E. R.; Holland, G. W.; Brown, F. D.; Stavros, F. D.; Brock, T. A.; Dixon, R. A. C. *Drugs Today* **2001**, *37*, 441.

TABLE 3. Formation of Sulfonamide Derivatives

$$\text{R-SH} + \text{R}'\text{-NH}_2 \longrightarrow \text{R-SO}_2\text{-NH-R}'$$

Entry	Sulfonamide	Time (min)	Yield (%) <sup>b</sup>	Ref
1		2	97	14d
2		2	96	14d
3		2	98	18c
4		3	94	
5		2	98	
6		3	96	
7		3	95	
8		4	93	
9		2	97	19a
10		3	95	19b
11		2	96	19c

<sup>a</sup>The purified products were characterized by mp, <sup>1</sup>H and <sup>13</sup>C NMR. <sup>b</sup>Yields refer to pure isolated products.

antiviral HIV protease inhibitor amprenavir,<sup>16</sup> and the phosphodiesterase-5 inhibitor sildenafil.<sup>17</sup> Thus synthesis of

(16) De Clercq, E. *Curr. Med. Chem.* **2001**, *8*, 1543.

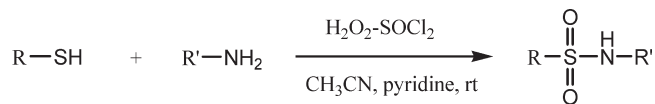
(17) Rotella, D. P. *Nat. Rev. Drug Discovery* **2002**, *1*, 674.

(18) (a) Cremlin, R. *Organosulfur Chemistry: An Introduction*; John Wiley and Sons: New York, 1996. (b) Anderson, K. K. In *Sulfonic Acids and Their Derivatives in Comprehensive Organic Chemistry*, Vol. 3; Barton, D. H. R., Ollis, W. D., Jones, D. N., Eds.; Pergamon Press: Oxford, 1979. (c) Shaabani, A.; Soleimani, E.; Rezayan, A. H. *Tetrahedron Lett.* **2007**, *48*, 2185. (d) Gareau, Y.; Pellicelli, J.; Laliberte, S.; Gauvreau, D. *Tetrahedron Lett.* **2003**, *44*, 7821. (e) Burton, G.; Cao, P.; Li, G.; Rivero, R. *Org. Lett.* **2003**, *5*, 4373. (f) Chantarasriwong, O.; Jang, D. O.; Chavasiri, W. *Tetrahedron Lett.* **2006**, *47*, 7489. (g) Hajipour, A. R.; Mallakpour, S. E.; Najafi, A. R.; Mazlumi, Gh. *Sulfur Lett.* **2000**, *24*, 137. (h) Deng, X.; Mani, N. S. *Green Chem.* **2006**, *8*, 835. (i) Wilden, J. D.; Geldeard, L.; Lee, Ch. C.; Judd, D. B.; Caddick, S. *Chem. Commun.* **2007**, 1074.

these compounds is of continuing interest. There are various synthetic methods for the preparation of sulfonamides.<sup>18</sup> The most commonly used synthetic methods to manipulate sulfonamides involve the nucleophilic attack by ammonia, or primary or secondary amines, with sulfonyl chlorides in the presence of a base. Although this method is efficient, it requires the availability of sulfonyl chlorides, some of which are difficult to store or handle.

(19) (a) Rolla, F. J. *Org. Chem.* **1982**, *47*, 4327. (b) Katohagi, M.; Togo, H. *Tetrahedron* **2001**, *57*, 7481. (c) Gajda, T.; Zwierzak, A. *Synthesis* **1981**, 1005.

## SCHEME 4



R, R' = Alkyl, aryl

We report a practical synthesis of sulfonamides starting from thiols (1 mmol), amines (1 mmol) in the presence of 30% H<sub>2</sub>O<sub>2</sub> (3 mmol), SOCl<sub>2</sub> (1 mmol), and pyridine (0.5 mL). The route for the synthesis of sulfonamides is shown in Scheme 4.

Using optimized reaction conditions, the reaction of structurally and electronically diverse thiols and amines was examined. The results, which are summarized in Table 3, indicate that all the reactions proceeded efficiently and the desired sulfonamides were obtained in excellent yields in fast reaction times with high purity (monitored by NMR spectroscopy). Aryl thiols carrying either electron-donating or electron-withdrawing substituents reacted very well to give the corresponding sulfonamides with equal efficiency. Also, aryl amines appeared to be insensitive to substitution. Primary and secondary alkyl amines and also ammonia undergo this reaction with equal efficiency. For example, *N*-cyclohexyl-4-methylbenzenesulfonamide is produced in 98% yield (Table 3, entry 3), *N,N*-diethylbenzenesulfonamide in 96% yield (Table 3, entry 11), and 4-methylbenzenesulfonamide in 97% yield (Table 3, entry 9). Moreover, the reaction of 2-mercaptobenzimidazole with 4-bromoaniline, contrary to our expectation, gives excellent yield of product (Table 3, entry 8). It is noteworthy that the rapidity of the reaction permits formation of the corresponding heterocyclic sulfonamide.

### Conclusion

In summary, H<sub>2</sub>O<sub>2</sub>-SOCl<sub>2</sub> is an extremely efficient reagent system for the conversion of thiols to sulfonyl chlorides. Furthermore, a novel one-pot conversion of thiols to sulfonamides has been developed. The advantages are excellent yields, the cheapness and availability of the reagents, easy and clean workup, extremely fast reaction, high chemoselectivity, and operation at room temperature. This methodology also overcomes the formation of unwanted byproduct, thus, we believe that the present methodology opens new possibilities for medicinal chemistry and material sciences and could be an important addition to the existing methodologies.

### Experimental Section

**General Procedure for Oxidative Chlorination of Thiols.** A mixture of thiol compound (2 mmol), 30% H<sub>2</sub>O<sub>2</sub> (6 mmol, 0.6 mL), and SOCl<sub>2</sub> (2 mmol, 0.14 mL) was stirred in CH<sub>3</sub>CN at 25 °C for the time indicated in Table 2. After completion of the reaction as indicated by TLC, the reaction mixture was quenched by adding water (10 mL), extracted with ethyl acetate

(4 × 5 mL), and the extract dried with anhydrous MgSO<sub>4</sub>. The filtrate was evaporated under vacuum to afford the analytically pure product. All of the products are known compounds and characterized easily by comparison with authentic samples (<sup>1</sup>H NMR, <sup>13</sup>C NMR, mp).

**General Procedure for the Synthesis of Sulfonamides.** A mixture of thiol compound (2 mmol), H<sub>2</sub>O<sub>2</sub> (30%, 6 mmol, 0.6 mL), and SOCl<sub>2</sub> (2 mmol, 0.14 mL) was stirred in CH<sub>3</sub>CN at 25 °C for an appropriate time. After completion of the reaction as indicated by TLC, a solution of amine (2 mmol) in pyridine (1 mL) was added to the reaction mixture. The resulting mixture was stirred at room temperature until TLC showed complete disappearance of starting material (Table 3) and then acidified with 2 N HCl solution and extracted with EtOAc. The organic layer was washed with H<sub>2</sub>O and brine and dried over MgSO<sub>4</sub>. The filtrate was evaporated, and the corresponding pure sulfonamide was obtained as a crystalline solid. Recrystallization from a mixture of ethanol and water affords analytically pure product. Spectral and analytical data for new compounds follow.

***N*-2-Chlorophenyl-4-methylbenzenesulfonamide.** mp = 105 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 2.36 (s, 3H), 6.98–7.07 (m, 2H), 7.18–7.26 (m, 4H), 7.63–7.67 (m, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 22, 122.8, 125.5, 126.3, 127.7, 128.3, 129.8, 130.1, 133.9, 136.3, 144.7. Anal. Calcd for C<sub>13</sub>H<sub>12</sub>NSO<sub>2</sub>Cl: C, 55.42; H, 4.26; N, 4.97; S, 11.36. Found: C, 55.06; H, 4.38; N, 4.86; S, 10.85.

***N*-Cyclohexyl-4-bromobenzenesulfonamide.** mp = 100 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 1.15 (m, 5H), 1.53–1.74 (m, 5H), 3.10 (m, 1H), 4.96 (d, 1H, *J* = 7.5 Hz, NH), 7.63 (d, 2H, *J* = 8 Hz), 7.75 (d, 2H, *J* = 8 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 24.6, 25, 33.8, 52.7, 127.3, 128.5, 132.3, 140.6. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>NSO<sub>2</sub>Br: C, 45.28; H, 5.03; N, 4.40; S, 10.06. Found: C, 45.25; H, 5.01; N, 4.23; S, 9.77.

***N*-3-Nitrophenyl-4-bromobenzenesulfonamide.** mp = 118–120 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.17–7.74 (m, 7H), 7.86–8.00 (m, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 115.4, 120.2, 126.4, 128.8, 129.1, 130.6, 132.9, 137.4, 137.6, 148.8. Anal. Calcd for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>SO<sub>2</sub>Br: C, 44.31; H, 2.76; N, 8.61; S, 9.85. Found: C, 43.65; H, 2.68; N, 8.53; S, 9.50.

***N*-4-Chlorophenyl-2-naphthalenesulfonamide.** mp = 115 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.12 (d, 2H, *J* = 8.9 Hz), 7.25 (d, 2H, *J* = 8.9 Hz), 7.57–8.13 (m, 6H), 8.43 (d, 1H, *J* = 1.3 Hz), 10.56 (s, 1H, NH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 122, 122.3, 128.2, 128.3, 128.5, 128.6, 129.5, 129.6, 129.7, 130, 132, 134.7, 136.6, 137.1. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>NSO<sub>2</sub>Cl: C, 60.48; H, 3.78; N, 4.41; S, 10.07. Found: C, 60.31; H, 3.87; N, 4.14; S, 9.88.

***N*-4-Bromophenyl-2-benzimidazolesulfonamide.** mp = 156–158 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.57–7.65 (m, 5H), 8.07 (d, 2H, *J* = 9 Hz), 8.17 (d, 2H, *J* = 9 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 123.6, 123.9, 126.5, 127.2, 132, 132, 142.6, 147.1. Anal. Calcd for C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>SO<sub>2</sub>Br: C, 44.32; H, 2.84; N, 11.93; S, 9.09. Found: C, 44.03; H, 2.51; N, 11.62; S, 8.72.

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**Supporting Information Available:** Complete experimental procedures and relevant spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra) for some compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.