JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

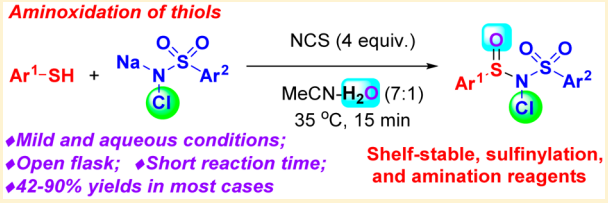
Aminoxidation of Arenethiols to *N*-Chloro-*N*-sulfonyl Sulfinamides

Zhanhui Yang, Wei Xu, Qiuyue Wu, and Jiaxi Xu*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Supporting Information

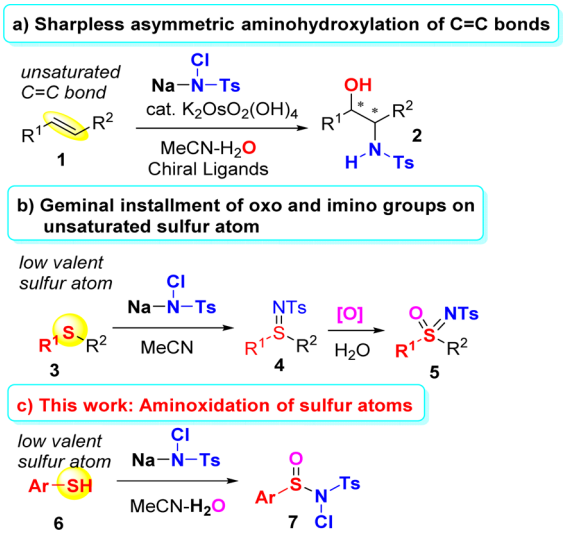
ABSTRACT: A simple and efficient method to synthesize *N*-chloro-*N*-sulfonylsulfinamides by the direct aminoxidation of arenethiols under aqueous and mild conditions is disclosed, geminally installing the oxo and amino groups on the sulfur atom of arenethiols. The products have been primarily developed as sulfinylation reagents to convert Grignard reagents into sulfoxides, and as amination reagents to convert secondary amines into hydrazine derivatives.



For quite a long time, the oxidative amination of unsaturated carbon−carbon bonds, especially the C=C double bond, has received much attention in the synthetic community,[1] because such a strategy provides an excellent arena to easily synthesize important amine intermediates, with one or two C−N bond(s) formed. As a result, a large number of exquisite transformations have been established,[1,2] including the Sharpless asymmetric aminohydroxylation.[3] Placed in this context, as part of our continuing interest in organosulfur chemistry,[4,5] we wondered whether the electron-rich and low valent sulfur(II) in thiols or sulfides could undergo a similar oxidative amination. We thought that the realization of such chemistry could provide a convenient tool to construct a S−N bond.

To initiate the study on the oxidative amination of low valent sulfur atoms, we referred to the Sharpless asymmetric aminohydroxylation, which installs discrete hydroxyl and amino groups across a C=C double bond (vicinal installment) in one single step (Scheme 1a).[3] We hypothesized that the oxygen and nitrogen atoms should probably be installed simultaneously on the low valent sulfur(II) atom of sulfides or thiols (geminal installment) in one single step under modified Sharpless conditions, even though the mechanisms may be significantly different. A literature survey revealed that the geminal *oxo and imino* installment on the low valent sulfur atom had been realized stepwise, with the first imino installment giving sulfilimines **4**, and the subsequent oxo installment giving sulfoximides **5** (Scheme 1b).[6] This report not only encouraged us to initiate the current study but also directed us to the oxidative amination of thiols. Finally, we discovered that the oxidative amination of arenethiols **6** installed *an oxo and a substituted amino* to the sulfur atom to give *N*-chloro-*N*-sulfonylsulfinamides **7** as the major products, providing an efficient method to introduce sulfinyl groups from thiols in a one-pot procedure under mild and aqueous conditions (Scheme 1c). To accurately describe the transformation, we coined the term "aminoxidation".

Scheme 1. Aminohydroxylation of Unsaturated C=C Bonds and Aminoxidation of Thiols



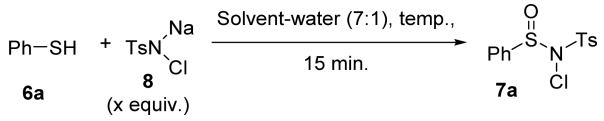
The reaction optimization commenced with the aminoxidation of thiophenol (**6a**) with chloramine-T (**8**) (Table 1). The reaction occurred very fast in the absence of the catalyst $K_2OsO_2(OH)_4$. When 5 equiv of chloramine-T was used, the yields of *N*-chloro-*N*-sulfonylsulfinamide **7a** were 38% at 15 °C and 70% at 35 °C, respectively (Table 1, entries 1 and 2). Solvent screening (entries 3−6) indicated that acetonitrile was optimal, with a yield of 70% (entry 2). Decreasing the amount of chloramine-T to 4 equiv (entry 7) or increasing the temperature to reflux (entry 8) led to decreased yields of 35% and 60%, respectively.

A mechanism was proposed and is shown in Scheme 2. First, thiol **6** is converted into sulfenyl chloride **A** by the positive

Received: February 4, 2016
Published: March 8, 2016

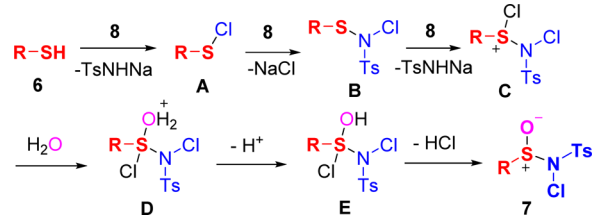
DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057

Table 1. Initial Condition Optimization of the Aminoxidation of Thiophenol with Chloramine-T



entry	conditions	yield (%)
1	x = 5, MeCN−water, 15 °C	38
2	x = 5, MeCN−water, 35 °C	70
3	x = 5, EtOH−water, 35 °C	34
4	x = 5, acetone−water, 35 °C	48
5	x = 5, MeOH−water, 35 °C,	<5
6	x = 5, water, 35 °C,	50
7	x = 4, MeCN−water, 35 °C	35
8	x = 5, MeCN−water, reflux, 5 min	60

Scheme 2. Proposed Mechanism for the Aminoxidation

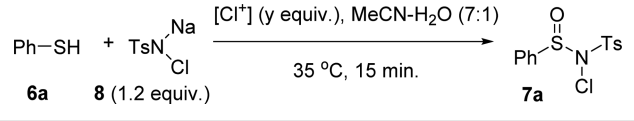


chlorine atom in chloramine-T (**8**).[7] The chlorine atom in **A** acts as a good leaving group; thus the displacement between **A** and the negative nitrogen atom of **8** occurs readily, giving *N*-chloro-*N*-sulfenyl sulfonimide **B**.[8] The oxidation of **B** at their sulfenylmoiety by **8** gives intermediate sulfonium ion **C**, which is attacked by water to form **D**. Subsequent deprotonation and elimination of HCl delivers *N*-chloro-*N*-sulfonylsulfinamide **7**. The oxygen atom in product **7** comes from water.[9]

In the optimized reaction in entry 2 in Table 1, the use of excess chloramine-T (**8**) not only decreased the atom economy of the aminoxidation but also made the purification process tedious, because a large amount of the water-insoluble byproduct *p*-toluenesulfonamide was generated. The mechanism indicates that 1 equiv of chloramine-T acts as nucleophile, while the rest acts as a chloronium [Cl^+] oxidant. Thus, we envisioned that the reaction could be further optimized by introducing other chloronium [Cl^+] oxidants, of which the reduced products were required to be easily soluble in water. Commercially accessible and cheap *N*-chlorosuccinimide (NCS), trichloroisocyanuric acid (TCCA), and sodium chlorite ($NaClO_2$) were tried (entries 1−3 in Table 2),[10] and NCS gave the best result. The combination of 4 equiv of NCS and 1.2 equiv of chloramine-T gave a satisfactory yield of 78% (entry 4 in Table 2).

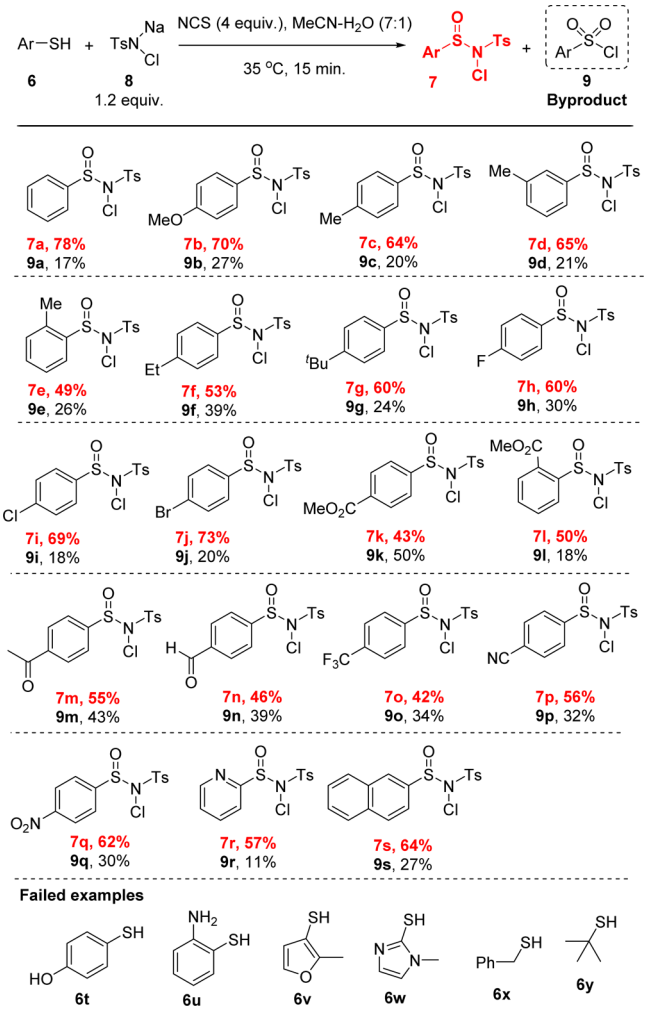
With these new conditions, a series of *N*-chloro-*N*-sulfonylsulfinamides **7** were prepared. The results are summarized in Table 3. Although the byproduct arenesulfonyl chlorides were not avoidable, the desired sulfinamides **7** were obtained in satisfactory to good yields varying from 42% to 78% via one single manipulation. 4-Methoxybenzenethiol (**6b**) readily underwent the aminoxidation to give the corresponding product **7b** in 70% yield, with the electron-rich aryl ring not chlorinated. The substituted arenethiols **6c**, **6d**, and **6e** underwent the aminoxidation, and the corresponding *N*-chloro-*N*-sulfonylsulfinamides **7c**, **7d**, and **7e** were isolated in 64%, 65%, and 49% yields, respectively. Subsequently, the

Table 2. Further Condition Optimization of the Aminoxidation of Thiophenol with Chloramine-T



entry	[Cl^+]	y (equiv)	yield (%)
1	NCS	3	59
2	TCCA	3	12
3	$NaClO_2$	3	33
4	NCS	4	78

Table 3. Aminoxidation of Arenethiols 6 with NCS and Chloramine-T[a]



[a]Reactions of **6k** and **6m**−**p** were performed on a 1 mmol scale, while the others were performed on a 2 mmol scale.

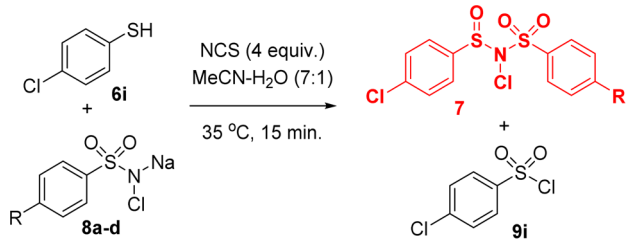
functionality tolerance was screened by subjecting a variety of 4-substituted benzenethiols to the optimal conditions. The ethyl group in **6f** and the *tert*-butyl group in **6g** were well tolerated, with the products **7f** and **7g** obtained in 53% and 60% yields, respectively, although the benzylic position is quite sensitive under oxidative conditions. Also well tolerated were halogen atoms, as exemplified by the reactions of **6h**, **6i**, and **6j** to produce **7h**, **7i**, and **7j** in 60%, 69%, and 73% yields, respectively. The introduction of halogen atoms, especially bromine atom, allows further potential installment of other

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057

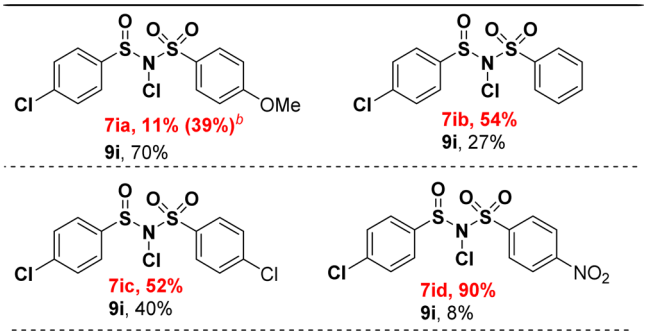
functional groups via coupling reactions. Other functional groups, such as methoxycarbonyl (**6k** and **6l**), acetyl (**6m**), and formyl (**6n**) could also survive from the aminoxidation conditions, delivering the corresponding products **7k**, **7l**, **7m**, and **7n** in 43%, 50%, 55%, and 46% yields, respectively. *N*-Chloro-*N*-sulfonylsulfinamides with other strongly electron-withdrawing groups, for example, **7o**, **7p**, and **7q**, were synthesized in 42%, 56%, and 62% yields, respectively, from the corresponding 4-trifluoromethyl, 4-cyano, and 4-nitrobenzenethiols **6o**, **6p**, and **6q**. Pyridine-2-thiol (**6r**) and naphthalene-2-thiol (**6s**) were also susceptible to the aminoxidation, with **7r** and **7s** being obtained in 57% and 64% yields, respectively. However, arenethiols with strong electron-donating and active amino or hydroxyl groups (**6t** and **6u**) and electron-rich heteroarenethiols (**6v** and **6w**) failed to undergo the aminoxidation, and complex mixtures with no identified structures were isolated. Alkanethiols, such as phenylmethanethiol (**6x**) and *tert*-butanethiol (**6y**), were completely converted into the corresponding sulfonyl chlorides **9x** and **9y**, respectively.

The reactivity of other different sodium *N*-chloroarenesulfonamides (chloramine-Ts) **8a**−**d** in the aminoxidation was also studied, by reacting them with 4-chlorobenzenethiol (**6i**). The results are presented in Table 4. Under the standard conditions,

Table 4. Aminoxidation of 4-Chlorobenzenethiol with NCS and Different Chloramine-Ts[a]



R = MeO, **8a**, R = H, **8b**, R = Cl, **8c**; R = NO_2, **8d**.

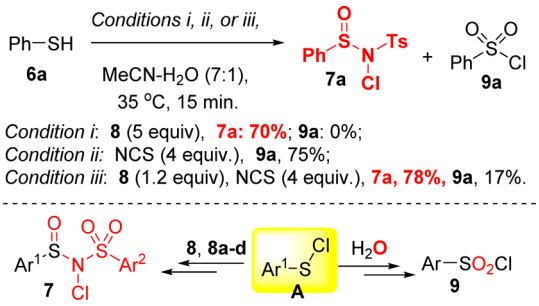


[a]Reactions were performed on a 1 mmol scale. [b]39% yield was obtained when 3 equiv of **8a** was used.

sodium *N*-chloro-4-methoxybenzenesulfonamide (**8a**) showed low reactivity, giving the desired product **7ia** in a low 11% yield. The reactions of sodium *N*-chloroarenesulfonamides **8b** and **8c** delivered the corresponding products **7ib** and **7ic** in higher 54% and 52% yields, respectively. Sodium *N*-chloro-4-nitrobenzenesulfonamide (**8d**) exhibited the highest reactivity, and it reacted with 4-chlorobenzenethiol (**6i**) to give *N*-chloro-*N*-sulfonylsulfinamide **7id** in 90% yield.

In all cases, arenesulfonyl chlorides were obtained as byproducts in varying yields. To understand how they were generated, we conducted the control experiments shown in Scheme 3. When thiophenol (**6a**) was exposed to 5 equiv of chloramine T (**8**), only *N*-chloro-*N*-sulfonylsulfinamide **7a**

Scheme 3. Control Experiments and Two Competitive Processes



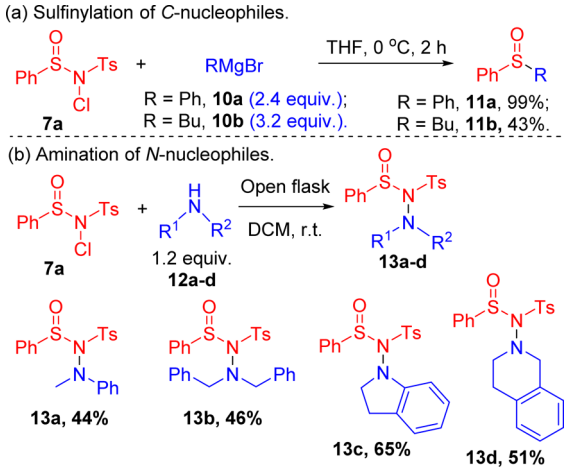
formed in 70% yield, with no benzenesulfonyl chloride (**9a**) isolated (condition i). However, when **6a** was exposed to 4 equiv of NCS, benzenesulfonyl chloride (**9a**) was obtained in 75% yield (condition ii). Thus, it appears that arenesulfonyl chloride byproducts are generated as oxidative chlorination products of thiols with NCS. The present aminoxidation and the oxidative chlorination are the two competitive processes under the standard conditions (condition iii). Under the reaction conditions, the easily generated sulfenyl chlorides **A** can be first attacked by *N*-nucleophilic chloramines (**8**, **8a**−**d**) to initiate the aminoxidation to form *N*-chloro-*N*-sulfonylsulfinamides **7**, or be first attacked by *O*-nucleophilic H_2O to initiate the oxidative chlorination to form sulfonyl chlorides **9**. The substituents of arenethiols can influence the competitive aminoxidation and oxidative chlorination simultaneously, but not sufficiently to eliminate byproduct formation in the current case. However, the substituent effect of the aryl group (Ar^2) of the chloramine-Ts decides the selectivity between **7** and **9**. When different chloramine-Ts such as **8** and **8a**−**d** were employed, the ones with electron-withdrawing groups, such as the nitro group (**8d**), gave better yields, because the corresponding negative amide anions are more stable and the aminoxidation is greatly favored.

The aminoxidation of thiols provides a simple method to introduce a sulfinyl group to the nitrogen atom; in other words, it represents a simple construction of the sulfinamide moiety. It has been well-known that sulfinamides and their derivatives play an important role in synthetic chemistry, serving as chiral auxiliaries and catalysts,[11] good amino protecting groups,[12] and important building blocks.[12d,13]Therefore, a number of routes to sulfinamides are available, including (1) the coupling of amines with sulfinic acids[14] or their derivatives (sodium salts,[15] sulfinyl halides,[16] sulfinylphthalimides,[17] sulfinates,[18] thiosulfinates,[8e] and sulfinylazides),[19] (2) the addition of Grignard reagents to sulfinyl amines RN═S═O,[20] (3) the reductive dearylation of *S*-diarylsulfoximides **4** with elemental sulfur in liquid ammonia,[21] (4) the reductive sulfinamidation of sulfonyl chlorides with amines in the presence of PPh_3,[22] and (5) others.[23,24]Our current method provides a mild, aqueous, and facile method to synthesize *N*-chlorosulfinosulfonimides.

Preliminary studies on the application of *N*-chlorosulfinosulfonimides **7** as sulfinylation and amination reagents were conducted. As shown in Scheme 4a, sulfinylation of the *C*-nucleophilic Grignard reagents **10a** and **10b** with **7a** produced the corresponding sulfoxides **11a** and **11b** in 99% and 43% yields, respectively. Scheme 4b represents the utilization of **7a**

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057

Scheme 4. Application of *N*-Chlorosulfinosulfonimides as Sulfination and Amination Reagents



as an amination reagent to convert secondary amines **12a–d** into the corresponding hydrazine derivatives **13a–d** in 44–65% yields. All the amination reactions were conducted under very mild conditions, for example, in open flasks at room temperature.

In conclusion, we have developed a simple method to synthesize *N*-chloro-*N*-sulfonylsulfinamides by direct amino-xidation of arenethiols. Compared with the previous methods to construct the sulfinamide moieties, the present method excels with the following advantages: readily available starting materials and reagents, aqueous mild reaction conditions, and simple single manipulation. The current method allows the preparation of *N*-chloro-*N*-sulfonylsulfinamides directly from thiols in one single step under aqueous conditions, *geminally installing the oxo and amino groups on the low valent sulfur atom* of arenethiols in one single operation. Further applications of *N*-chloro-*N*-sulfonylsulfinamides as sulfinylation and amination reagents have been realized in the preparation of sulfoxides and hydrazine derivatives.

EXPERIMENTAL SECTION

General Information. All solvents and reagents were used as commercially received, if not otherwise stated. Melting points were obtained on a melting point apparatus and are uncorrected. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). For ^{19}F NMR spectra, boron trifluoride ether complex was applied as an external standard. The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on an FTIR spectrometer. HRMS measurements were carried out on an LC/MSD TOF mass spectrometer. Elemental analyses were obtained on a elemental analyzer. TLC separations were performed on silica gel GF_{254} plates, and the plates were visualized with UV light.

Thiols **6f**, **6n**, and **6o** were prepared on a 5 mmol scale by Chae's procedure;[25] thiol **6k** was prepared by Winssinger and co-workers' procedure;[26] thiols **6m** and **6p** were prepared by Lees's procedure.[27] Sodium chloro(arenesulfonyl)amides **8a–d** were prepared by Khoramabadi-zad's procedure.[28]

All arenesulfonyl chlorides **9a–s** are reported compounds. Their analytical data and NMR spectra (^{1}H and ^{13}C) are identical with those reported.

General Procedure for the Aminoxidation of Thiols. A 25 mL pear-shaped flask was charged with chloramine-T (2.4 mmol, 0.546 g), NCS (1.068 g, 8 mmol), MeCN (4 mL), and water (0.7 mL). The resultant mixture was vigorously stirred and slowly became a colorless clear solution. Then a solution of arenethiol **6** (2 mmol) in MeCN (1 mL) was added dropwise during 2 min. Upon addition, the mixture was allowed to stand for 15 min at 35 °C in a water bath. After removal of acetonitrile at reduced pressure, a sticky oil or solid was obtained. Then ethyl acetate (15 mL) was added to dissolve the product, and the solid was filtered off. The filtrate was washed with brine (15 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was submitted to column chromatography with petroleum ether (PE) and ethyl acetate (EA) as eluent (v/v = 3:1) to afford the desired products. Products in higher purity could be obtained by a further recrystallization with petroleum ether and ethyl acetate as the solvent.

For the 1 mmol scale reactions, half amounts of the solvents and reagents were used, with the same workup processes.

*N-Chloro-N-(4-methylbenzenesulfonyl)benzenesulfinamide (**7a**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 88–90 °C. Yield: 513 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.78–7.74 (m, 1H), 7.66–7.57 (m, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.5, 142.4, 138.2, 135.6, 129.8, 129.6, 127.3, 126.7, 21.5. IR (film, KBr): ν cm^{-1} 1340, 1288, 1163, 1115, 1087. ESI-HRMS [M + H]$^{+}$ calcd for $C_{13}H_{13}ClNO_3S_2$ 330.0020, found 330.0021.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-methoxybenzenesulfinamide (**7b**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 87–89 °C. Yield: 503 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.3, 144.3, 138.4, 133.5, 129.6, 129.5, 127.4, 114.9, 56.1, 21.6. IR (film, KBr): ν cm^{-1} 1337, 1271, 1164, 1108, 1086. ESI-HRMS [M + H]$^{+}$ calcd for $C_{14}H_{15}ClNO_4S_2$ 360.0126, found 360.0130.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-methylbenzenesulfinamide (**7c**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 58–60 °C. Yield: 439 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.47 (s, 3H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.4, 144.4, 139.6, 138.3, 130.3, 129.6, 127.3, 126.8, 21.7, 21.6. IR (film, KBr): ν cm^{-1} 1341, 1285, 1165, 1112, 1088. ESI-HRMS [M + H]$^{+}$ calcd for $C_{14}H_{15}ClNO_3S_2$ 344.0176, found 344.0181.

*N-Chloro-N-(4-methylbenzenesulfonyl)-3-methylbenzenesulfinamide (**7d**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 75 °C. Yield: 446 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.2 Hz, 2H), 7.86–7.84 (m, 2H), 7.57–7.44 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.47 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.4, 142.5, 140.5, 138.4, 136.4, 129.7, 129.6, 127.5, 126.9, 124.0, 21.7, 21.4. IR (film, KBr): ν cm^{-1} 1342, 1287, 1165, 1112, 1088. ESI-HRMS [M + H]$^{+}$ calcd for $C_{14}H_{15}ClNO_3S_2$ 344.0176, found 344.0182.

*N-Chloro-N-(4-methylbenzenesulfonyl)-2-methylbenzenesulfinamide (**7e**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 72–73 °C. Yield: 336 mg, 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.61 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 7.42–7.39 (m, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.71 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.4, 140.7, 138.4, 138.3, 135.5, 133.9, 129.6, 128.4, 127.4, 126.8, 21.6, 20.3. IR (film, KBr): ν cm^{-1} 1342, 1287, 1165, 1112, 1088. ESI-HRMS [M + H]$^{+}$ calcd for $C_{14}H_{15}ClNO_3S_2$ 344.0176, found 344.0180.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-ethylbenzenesulfinamide (**7f**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 76–78 °C. Yield: 378 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.77 (q, J = 7.6 Hz, 2H), 2.44 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.4, 144.4, 139.8, 138.4, 129.6, 129.2, 127.5, 127.0, 29.0, 21.6, 14.9. IR (film, KBr): ν cm^{-1} 1343, 1286, 1167, 1116, 1088. ESI-HRMS [M + H]$^{+}$ calcd for $C_{15}H_{17}ClNO_3S_2$ 358.0333, found 358.0333.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-tert-butylbenzenesulfinamide (**7g**).* The product was prepared on a 2 mmol scale. Colorless sticky oil. Yield: 462 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051–3057

(d, J = 8.0 Hz, 4H), 7.60 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.2, 144.4, 139.5, 138.5, 129.6, 129.6, 127.4, 126.82, 126.79, 35.6, 30.9, 21.6. IR (film, KBr): ν cm^{-1} 1343, 1286, 1166, 1124, 1087. ESI-HRMS $[M + H]^+$ calcd for $C_{17}H_{21}ClNO_3S_2$ 386.0646, found 386.0650.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-fluorobenzenesulfinamide (**7h**).* The product was prepared on a 2 mmol scale. Colorless sticky oil. Yield: 416 mg, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, J = 9.1, 4.7 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.29 (dd, J = 9.2, 8.4 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.6 (d, J_{C-F} = 261.1 Hz), 144.6, 138.3 (d, J_{C-F} = 3.2 Hz), 138.1, 130.1 (d, J_{C-F} = 10.2 Hz), 129.7, 127.4, 117.3 (d, J_{C-F} = 23.4 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −98.56. IR (film, KBr): ν cm^{-1} 1343, 1286, 1167, 1116, 1088. ESI-HRMS $[M + H]^+$ calcd for $C_{13}H_{12}ClFNO_3S_2$347.9926, found 347.9929.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-chlorobenzenesulfinamide (**7i**).* The product was prepared on a 2 mmol scale. Colorless sticky oil. Yield: 501 mg, 69%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01−7.98 (m, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.61−7.55 (m, 1H), 7.36 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 144.7, 140.8, 138.1, 130.1, 129.7, 128.3, 127.4, 21.6. IR (film, KBr): ν cm^{-1} 1343, 1280, 1166, 1119, 1086. ESI-HRMS $[M + H]^+$ calcd for $C_{13}H_{12}Cl_2NO_3S_2$363.9630, found 363.9635.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-bromobenzenesulfinamide (**7j**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 105 °C. Yield: 593 mg, 73%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.7, 141.5, 138.2, 133.1, 131.4, 129.7, 128.3, 127.5, 21.7. IR (film, KBr): ν cm^{-1} 1341, 1278, 1165, 1118, 1088. ESI-HRMS $[M + H]^+$calcd for $C_{13}H_{12}BrClNO_3S_2$ 407.9125, found 407.9126.

*Methyl 4-[(N-chloro-4-methylbenzenesulfonamido)sulfinyl]-benzoate (**7k**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 134−135 °C. Yield: 166 mg, 43%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 3.99 (s, 3H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.7, 145.9, 144.7, 138.1, 136.3, 130.9, 129.8, 127.5, 126.9, 53.0, 21.7. IR (film, KBr): ν cm^{-1} 1725, 1340, 1282, 1162, 1107, 1087. ESI-HRMS $[M + H]^+$ calcd for $C_{15}H_{15}ClNO_5S_2$ 388.0075, found 388.0081.

*Methyl 2-[(N-chloro-4-methylbenzenesulfonamido)sulfinyl]-benzoate (**7l**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 55 °C. Yield: 387 mg, 50%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.83−7.76 (m, 1H), 7.71 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 3.92 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.7, 144.6, 139.4, 138.2, 135.4, 132.5, 131.3, 130.4, 129.6, 128.4, 127.4, 53.3, 21.6. IR (film, KBr): ν cm^{-1} 1733, 1342, 1294, 1165, 1112, 1086. ESI-HRMS $[M + H]^+$ calcd for $C_{15}H_{15}ClNO_5S_2$ 388.0075, found 388.0076.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-acetylbenzenesulfinamide (**7m**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 108−110 °C. Yield: 204 mg, 55%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 4H), 7.96 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.68 (s, 3H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 196.0, 145.7, 144.8, 142.0, 138.1, 129.8, 129.5, 127.5, 127.3, 27.0, 21.7. IR (film, KBr): ν cm^{-1} 1736, 1694, 1342, 1289, 1165, 1118, 1088. ESI-HRMS $[M + H]^+$ calcd for $C_{15}H_{15}ClNO_4S_2$ 372.0126, found 372.0126.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-formylbenzenesulfinamide (**7n**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 145−147 °C. Yield: 164 mg, 46%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.9, 146.7, 144.8, 140.5, 138.0, 130.5, 129.8, 127.7, 127.5, 21.7. IR (film, KBr): ν cm^{-1} 1711, 1343, 1287, 1165, 1116, 1087. ESI-HRMS $[M + H]^+$ calcd for $C_{14}H_{13}ClNO_4S_2$357.9969, found 357.9973.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-trifluoromethylbenzenesulfinamide (**7o**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 81−82 °C. Yield: 166 mg, 42%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.7, 144.8, 137.00 (q, J_{C-F} = 33.7 Hz), 138.1, 129.8, 127.55, 127.49, 127.04 (q, J_{C-F} = 3.6 Hz), 122.58 (q, J_{C-F} = 273.6 Hz), 21.7. ^{19}F NMR (400 MHz, $CDCl_3$): δ −63.4. IR (film, KBr): ν cm^{-1} 1345, 1322, 1291, 1167, 1139, 1088, 1063. ESI-HRMS $[M + H]^+$ calcd for $C_{14}H_{12}ClF_3NO_3S_2$397.9894, found 397.9890.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-cyanobenzenesulfinamide (**7p**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 131−132 °C. Yield: 199 mg, 56%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0, 145.0, 137.9, 133.5, 129.8, 127.6, 127.5, 119.2, 116.3, 21.7. IR (film, KBr): ν cm^{-1} 2237, 1339, 1286, 1162, 1118, 1088. ESI-HRMS $[M + Na]^+$ calcd for $C_{14}H_{11}ClN_2NaO_3S_2$376.9792, found 376.9794.

*N-Chloro-N-(4-methylbenzenesulfonyl)-4-nitrobenzenesulfinamide (**7q**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 84−86 °C. Yield: 232 mg, 62%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.4, 147.2, 145.0, 137.9, 129.9, 128.4, 127.5, 125.0, 21.7. IR (film, KBr): ν cm^{-1} 1535, 1345, 1296, 1166, 1121, 1088. ESI-HRMS $[M + Na]^+$ calcd for $C_{13}H_{11}ClN_2NaO_5S_2$396.9690, found 396.9700.

*N-Chloro-N-(4-methylbenzenesulfonyl)-pyridine-2-sulfinamide (**7r**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 119−121 °C. Yield: 376 mg, 57%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 4.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 8.0, 1.6 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.71 (dd, J = 7.4, 4.6 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.0, 150.7, 144.6, 139.2, 138.1, 129.7, 129.3, 127.4, 122.2, 21.6. IR (film, KBr): ν cm^{-1} 1527, 1301, 1181, 1161, 1098. ESI-HRMS $[M+2H-Cl]^+$ calcd for $C_{12}H_{13}N_2O_3S_2$ 297.0362, found 297.0359.

*N-Chloro-N-(4-methylbenzenesulfonyl)-naphthalene-2-sulfinamide (**7s**).* The product was prepared on a 2 mmol scale. Colorless solid. Mp: 52−54 °C. Yield: 485 mg, 64%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.05−7.97 (m, 6H), 7.78−7.71 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.5, 139.1, 138.4, 135.8, 131.5, 130.7, 130.4, 129.9, 129.7, 129.1, 128.5, 128.1, 127.5, 120.8, 21.5. IR (film, KBr): ν cm^{-1} 1340, 1289, 1165, 1106, 1085. ESI-HRMS $[M + H]^+$ calcd for $C_{17}H_{15}ClNO_3S_2$380.0176, found 380.0178.

*N-Chloro-N-(4-methoxybenzenesulfonyl)-4-chlorobenzenesulfinamide (**7ia**).* The product was prepared on a 1 mmol scale. Colorless oil. Yield: 42 mg, 11%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 9.0 Hz, 2H), 8.00 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.7, 142.7, 140.9, 132.6, 130.1, 129.8, 128.3, 114.3, 55.7. IR (film, KBr): ν cm^{-1} 1342, 1300, 1262, 1160, 1120, 1086, 1071. ESI-HRMS $[M + Na]^+$ calcd for $C_{13}H_{11}Cl_2NNaO_4S_2$401.9399, found 401.9404.

*N-Chloro-N-benzenesulfonyl-4-chlorobenzenesulfinamide (**7ib**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 107−108 °C. Yield: 188 mg, 54%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09−8.07 (m, 2H), 8.00 (d, J = 9.2 Hz, 2H), 7.67−7.63 (m, 1H), 7.60−7.55 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.8, 141.1, 140.8, 133.6, 130.2, 129.1, 128.3, 127.4. IR (film, KBr): ν cm^{-1} 1346, 1278, 1167, 1118, 1086. ESI-HRMS $[M + H]^+$ calcd for $C_{12}H_{10}Cl_2NO_3S_2$349.9474, found 349.9472.

*N-Chloro-N-(4-chlorobenzenesulfonyl)-4-chlorobenzenesulfinamide (**7ic**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 110 °C. Yield: 199 mg, 52%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03−7.98 (m, 4H), 7.62−7.58 (m, 2H), 7.55−7.51 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.0, 140.6, 140.3, 139.6, 130.2, 129.5, 128.9, 128.3. IR (film, KBr): ν cm^{-1} 1349, 1279, 1168, 1120, 1086. Elemental analysis: calcd for $C_{12}H_8Cl_3NO_3S_2$: C, 37.47; H, 2.10; N, 3.64, found: C, 37.84; H, 2.00; N, 3.57.

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057

*N-Chloro-N-(4-nitrobenzenesulfonyl)-4-chlorobenzenesulfinamide (**7id**).* The product was prepared on a 1 mmol scale. Colorless solid. Mp: 144−145 °C. Yield: 355 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.9 Hz, 2H), 8.27 (d, J = 8.9 Hz, 2H), 8.01 (d, J = 8.9 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.5, 146.5, 143.3, 140.2, 130.3, 128.8, 128.2, 124.4. IR (film, KBr): ν cm^{-1} 1531, 1397, 1350, 1302, 1280, 1169, 1115, 1086. Elemental analysis: calcd for $C_{12}H_8Cl_2N_2O_5S_2$: C, 36.47; H, 2.04; N, 7.09, found: C, 36.67; H, 2.19; N, 7.24.

General Procedure for the Arenesulfinylation of Grignard Reagents. *N*-Chloro-*N*-(4-methylbenzenesulfonyl)benzenesulfinamide (**7a**) (0.125 mmol, 41 mg) was placed into a Schlenk tube. The air was evacuated and refilled with nitrogen three times. Then dry THF (1 mL) was added to dissolve **7a**. The solution was cooled to 0 °C, and phenylmagnesium bromide **10a** (0.3 mmol, 3 mol/L, 0.1 mL) or butylmagnesium bromide **10b** (0.4 mmol, 2 mol/L, 0.2 mL) was dropwise added. The resultant mixture was stirred at 0 °C for 2 h and quenched with water. Extraction with dichloromethane (5 mL), drying over $MgSO_4$, removal of the solvent, and purification by column chromatography on silica gel with PE and EA as eluent afforded sulfoxide **11a** and **11b** as the products, respectively.

*Sulfinyldibenzene (**11a**).* Known compound and commercial reagent. CAS No. 945-51-7. Colorless crystals. Mp 68−70 °C. Yield: 25 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.61 (m, 4H), 7.50−7.42 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.6, 131.0, 129.3, 124.8.

*Butanesulfinylbenzene (**11b**).* Known compound.[29] Colorless oil. Yield: 10 mg, 43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.59 (m, 2H), 7.56−7.48 (m, 3H), 2.82 (ddd, J = 13.2, 7.4, 6.4 Hz, 1H), 2.77 (ddd, J = 13.7, 6.4, 7.4 Hz, 1H), 1.81−1.68 (m, 1H), 1.66−1.54 (m, 1H), 1.52−1.36 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.1, 130.9, 129.2, 124.0, 57.1, 24.1, 21.9, 13.6.

General Procedure for the Amination of Secondary Amines. *N*-Chloro-*N*-(4-methylbenzenesulfonyl)benzenesulfinamide (**7a**) (0.125 mmol, 41 mg) and secondary amine **12** (0.15 mmol) were dissolved in 1 mL of dichloromethane in a tube. The mixture was allowed to stand at room temperature for 2 h. Removal of the solvent and purification by column chromatography on silica gel with PE:EA:Et_3N (5:1:0.3) and then PE:DCM:Et_3N (4:1:0.25) as eluent afforded hydrazine **13** as the product.

*N′,4-Dimethyl-N′-phenyl-N-(benzenesulfinyl)benzenesulfonohydrazide (**13a**).* Colorless oil. Yield: 22 mg, 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.3 Hz, 2H), 7.77−7.70 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.34−7.28 (m, 3H), 7.26 (s, 1H), 7.24 (s, 1H), 7.19−7.12 (m, 2H), 3.29 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.8, 140.8, 140.4, 136.5, 133.5, 129.2, 129.1, 129.0, 128.2, 128.0, 127.7, 126.7, 39.5, 21.5. IR (film, KBr): ν cm^{-1} 1595, 1492, 1447, 1320, 1271, 1155, 1108, 1089, 1074. ESI-HRMS $[M + H]^+$ calcd for $C_{20}H_{21}N_2O_3S_2$ 401.0988, found 401.0993.

*N′,N′-Dibenzyl-4-methyl-N-(benzenesulfinyl)benzenesulfonohydrazide (**13b**).* Colorless oil. Yield: 28 mg, 46%. ^{1}H NMR (400 MHz, CDCl3): δ 7.94−7.82 (m, 4H), 7.58 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.41−7.32 (m, 2H), 7.28−7.24 (m, 2H), 7.21−7.14 (m, 4H), 7.03−6.96 (m, 4H), 4.44 (s, 4H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.7, 140.8, 139.3, 134.6, 133.4, 129.2, 129.1, 128.9, 128.4, 127.9, 127.6, 126.7, 51.0, 21.5. IR (film, KBr): ν cm^{-1} 1599, 1496, 1455, 1447, 1320, 1257, 1155, 1109, 1088, 1074. ESI-HRMS $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_3S_2$ 491.1458, found 491.1460.

*N-(Indolin-1-yl)-4-methyl-N-(benzenesulfinyl)benzenesulfonamide (**13c**).* Colorless oil. Yield: 33 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.85 (dd, J = 8.4, 1.0 Hz, 2H), 7.61−7.53 (m, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.43 (dd, J = 10.8, 4.9 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.14 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 7.0 Hz, 1H), 6.99 (td, J = 7.4, 0.7 Hz, 1H), 4.23−4.12 (m, 1H), 4.05−3.94 (m, 1H), 2.94 (ddd, J = 16.3, 9.7, 6.9 Hz, 1H), 2.84 (ddd, J = 16.3, 9.7, 6.9 Hz, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.9, 141.1, 140.5, 136.6, 133.8, 132.4, 129.193, 129.185, 127.7, 127.1, 126.8, 125.2, 124.5, 115.9, 51.4, 27.8, 21.5. IR (film, KBr): ν cm^{-1} 1600, 1477, 1460, 1322, 1266, 1156, 1112, 1089. ESI-HRMS $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_3S_2$ 413.0988, found 413.0987.

*N-[3,4-Dihydroisoquinolin-2(1H)-yl]-4-methyl-N-(benzenesulfinyl)benzenesulfonamide (**13d**).* Colorless oil. Yield: 27 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96−7.84 (m, 4H), 7.63−7.57 (m, 1H), 7.55−7.47 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.17−7.12 (m, 2H), 7.11−7.03 (m, 1H), 7.03−6.95 (m, 1H), 4.39 (d, J = 15.1 Hz, 1H), 4.33 (d, J = 15.2 Hz, 1H), 3.64 (ddd, J = 11.8, 6.4, 5.1 Hz, 1H), 3.42 (ddd, J = 12.1, 7.3, 4.8 Hz, 1H), 2.96 (ddd, J = 16.3, 6.8, 6.8 Hz, 1H), 2.84 (ddd, J = 16.3, 5.5, 5.5 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.8, 140.6, 136.1, 133.7, 132.9, 131.1, 129.24, 129.17, 128.8, 127.6, 126.9, 126.8, 126.39, 126.33, 47.6, 43.9, 28.5, 21.5. IR (film, KBr): ν cm^{-1} 1446, 1320, 1263, 1156, 1111, 1090, 1076. ESI-HRMS $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_3S_2$ 427.1145, found 427.1145.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00261.

^{1}H, ^{13}C, and ^{19}F NMR spectra of **7**, **11**, and **13** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jxxu@mail.buct.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by the National Basic Research Program of China (No. 2013CB328905), the National Natural Science Foundation of China (Nos. 21372025 and 21572017), and the BUCT Fund for Disciplines Construction and Development (Project No. XK1533).

■ REFERENCES

(1) For selected recent reviews, see: (a) Obora, Y.; Ishii, Y. *Catalysts* **2013**, *3*, 794. (b) Pardo, L. M.; Tellitu, I.; Dominguez, E. *Recent Res. Dev. Org. Chem.* **2012**, *12*, 9. (c) Correa, A.; Bolm, C. *Top. Organomet. Chem.* **2012**, *46*, 55. (d) Zhu, Y.; Cornwall, R. G.; Du, H.; Zhao, B.; Shi, Y. *Acc. Chem. Res.* **2014**, *47*, 3665. (e) Dauban, P.; Darses, B.; Jarvis, A. *Comp. Org. Syn.* **2014**, *7*, 538. (f) Degennaro, L.; Trinchera, P.; Luisi, R. *Chem. Rev.* **2014**, *114*, 7881. (g) Zhu, Y. G.; Wang, Q.; Cornwall, R. G.; Shi, Y. *Chem. Rev.* **2014**, *114*, 8199.

(2) (a) Li, G.; Saibabu Kotti, S. R. S.; Timmons, C. *Eur. J. Org. Chem.* **2007**, *2007*, 2745. (b) Chen, Z.-G.; Wei, J.-F.; Li, R.-T.; Shi, X.-Y.; Zhao, P.-F. *J. Org. Chem.* **2009**, *74*, 1371. (c) Chemler, S. R.; Bovino, M. T. *ACS Catal.* **2013**, *3*, 1076 and the references cited therein..

(3) (a) Li, G.; Chang, H.-T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 451. For reviews, see: (b) Bodkin, J. A.; McLeod, M. D. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2733. (c) Reiser, O. *The Sharpless Asymmetric Aminohydroxylation of Olefins, in Organic Synthesis Highlights III*; Mulzer, J., Waldmann, H., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998. (d) O'Brien, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 326.

(4) (a) He, F. D.; Meng, F. H.; Song, X. Q.; Hu, W. X.; Xu, J. X. *Org. Lett.* **2009**, *11*, 3922. (b) Hu, L. B.; Zhu, H.; Du, D.-M.; Xu, J. X. *J. Org. Chem.* **2007**, *72*, 4543. (c) Kakaei, S.; Chen, N.; Xu, J. X. *Tetrahedron* **2013**, *69*, 302. (d) Kakaei, S.; Xu, J. X. *Tetrahedron* **2013**, *69*, 9068. (e) Hu, G.; Li, P. F.; Xu, J. X. *Org. Lett.* **2014**, *16*, 6036.

(5) (a) Yang, Z. H.; Xu, J. X. *Synthesis* **2013**, *45*, 1675. (b) Yang, Z. H.; Zheng, Y. P.; Xu, J. X. *Synlett* **2013**, *24*, 2165. (c) Yang, Z. H.; Zhou, B. N.; Xu, J. X. *Synthesis* **2014**, *46*, 225. (d) Yang, Z. H.; Xu, J. X. *Org. Syn.* **2014**, *91*, 116 and the references cited therein..

(6) For representative examples, see: (a) Marzinzik, A. L.; Sharpless, B. K. *J. Org. Chem.* **2001**, *66*, 594. (b) Craig, D.; Gore, S. J.; Lansdell,

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057

M. I.; Lewis, S. E.; Mayweg, A. V. W.; White, A. J. P. *Chem. Commun.* **2010**, *46*, 4991.
(7) For formations of sulfenyl chloride, see: (a) Hostier, T.; Ferey, V.; Ricci, G.; Pardo, D. G.; Cossy, J. *Chem. Commun.* **2015**, *51*, 13898. (b) Iwasaki, M.; Fujii, T.; Yamamoto, A.; Nakajima, K.; Nishihara, Y. *Chem. - Asian J.* **2014**, *9*, 58.
(8) For a similar compound, see: Koval, I. V.; Oleinik, T. G.; Kremlev, M. M. *Zh. Org. Khim.* **1979**, *15*, 2319.
(9) When the reaction in entry 2, Table 1, was performed under nitrogen atmosphere, 65% yield was still obtained.
(10) Chlorine (generated *in situ* from NCS and HCl) and hypochlorite were also tested in the condition optimization. The former gave a complex mixture, while the latter gave sulfonyl chloride as the sole product.
(11) For recent reviews, see: (a) Dong, H.-Q.; Xu, M.-H.; Feng, C.-G.; Sun, X.-W.; Lin, G.-Q. *Org. Chem. Front.* **2015**, *2*, 73. (b) Li, Y.; Xu, M.-H. *Chem. Commun.* **2014**, *50*, 3771. (c) Lyzwa, P.; Mikolajczyk, M. *Pure Appl. Chem.* **2010**, *82*, 577. (d) Diner, P.; Sadhukhan, A.; Blomkvist, B. *ChemCatChem* **2014**, *6*, 3063.
(12) (a) Tang, T. P.; Volkman, S. K.; Ellman, J. A. *J. Org. Chem.* **2001**, *66*, 8772. (b) Kells, K. W.; Chong, J. M. *Org. Lett.* **2003**, *5*, 4215. (c) Hannam, J.; Harrison, T.; Heath, F.; Madin, A.; Merchant, K. *Synlett* **2006**, *2006*, 833. (d) Davis, F. A. *J. Org. Chem.* **2006**, *71*, 8993.
(13) Tillett, J. G. Sulphinamides. In *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*; Patai, S., Ed.; Wiley: Chichester, 1990; pp 603−622.
(14) Furukawa, M.; Okawara, T. *Synthesis* **1976**, *1976*, 339.
(15) Billard, T.; Greiner, A.; Langlois, B. R. *Tetrahedron* **1999**, *55*, 7243.
(16) (a) Uchino, M.; Sekiya, M. *Chem. Pharm. Bull.* **1980**, *28*, 126. (b) Wei, J.; Sun, Z. *Org. Lett.* **2015**, *17*, 5396.
(17) Harpp, D. N.; Back, T. G. *Tetrahedron Lett.* **1972**, *13*, 5313. (b) Harpp, D. N.; Back, T. G. *J. Org. Chem.* **1973**, *38*, 4328.
(18) (a) Billard, T.; Greiner, A.; Langlois, B. R. *Tetrahedron* **1999**, *55*, 7243. (b) Davis, F. A.; Zhang, Y.; Andemichael, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem.* **1999**, *64*, 1403. (c) Davis, F. A.; Reddy, R. E.; Szewczyk, J. M.; Reddy, G. V.; Portonovo, P. S.; Zhang, H.; Fanelli, D.; Reddy, R. T.; Zhou, P.; Carroll, P. J. *J. Org. Chem.* **1997**, *62*, 2555. (d) Cogan, D. A.; Liu, G.; Kim, K.; Backes, B. A.; Ellman, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 8011.
(19) Maricich, T. J.; Angeletakis, C. N. *J. Org. Chem.* **1984**, *49*, 1931.
(20) (a) Gilman, H.; Morris, H. L. *J. Am. Chem. Soc.* **1926**, *48*, 2399. (b) Klamann, D.; Sass, C.; Zelenka, M. *Chem. Ber.* **1959**, *92*, 1910.
(21) Sato, R.; Saito, N.; Takikawa, Y.; Takizawa, S.; Saito, M. *Synthesis* **1983**, *1983*, 1045.
(22) Harmata, M.; Zheng, P.; Huang, C.; Gomes, M. G.; Ying, W.; Ranyanil, K.-O.; Balan, G.; Calkins, N. L. *J. Org. Chem.* **2007**, *72*, 683.
(23) Johnson, C. R.; Katekar, G. F. *J. Am. Chem. Soc.* **1970**, *92*, 5753.
(24) Coulomb, J.; Certal, V.; Fensterbank, L.; Lacote, E.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 633.
(25) Liu, Y.; Kim, J.; Seo, H.; Park, S.; Chae, J. *Adv. Synth. Catal.* **2015**, *357*, 2205.
(26) Novoa, A.; Eierhoff, T.; Topin, J.; Varrot, A.; Barluenga, S.; Imberty, A.; Romer, W.; Winssinger, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 8885.
(27) DeCollo, T. V.; Lees, W. J. *J. Org. Chem.* **2001**, *66*, 4244.
(28) Shiri, A.; Khoramabadi-zad, A. *Synthesis* **2009**, *2009*, 2797.
(29) Harpp, D. N.; Vines, S. M.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* **1976**, *41*, 3987.

DOI: 10.1021/acs.joc.6b00261
J. Org. Chem. 2016, 81, 3051−3057