有机化学 DOI: 10.6023/cjoc201807033 研究论文
Chinese Journal of Organic Chemistry ARTICLE

通过硝基苯与磺酰氯水相反应直接合成磺酰胺

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摘要 报道了一种简单实用的磺酰胺绿色合成方法, 以硝基苯和磺酰氯为原料, 铁粉为唯一还原剂, 纯水作为溶剂. 该反应具有反应成本低, 溶剂环境友好, 反应条件温和, 底物适用性广的优点.
关键词 水; 绿色有机合成; 磺酰胺; 磺酰氯; 铁粉

Direct Synthesis Sulfonamides from Nitroarenes and Sulfonyl Chlorides in Water

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Abstract A simple and practical route for construction of various sulfonamides from nitroarenes and sulfonyl chlorides with iron powder as the sole reductant in water (green solvent) under open-air conditions was developed. The protocol features low-cost, environmentally benign solvent, mild reaction conditions and wide broad substrate scope.
Keywords water; green organic synthesis; sulfonamides; sulfonyl chlorides; iron power

1 Introduction

As one of the most important structural moieties, sulfonamides are frequently found in various natural bioactive compounds as well as synthetic drugs.[1] Consequently, extensive efforts have been dedicated toward constructing sulfonamides over the past decades.[2] In most synthetic methods for such motifs, anilines were used as the nitrogen sources,[3] which are odorous and potentially toxic. Moreover, anilines are often prepared from the corresponding nitroarenes through hydrogenation reduction. Compared to anilines, nitroarenes are much cheaper, more abundant and more readily accessible. Thus, a direct synthesis of sulfonamides from nitroarenes would be a better fitted and an eco-friendly industrial application. In 2015, Luo *et al.*[4] reported an elegant work for iron salts/trans-*N*,*N*'-dimethyl-1,2-diaminocyclohexane (DMDACH) synergetic catalyzed construction of *N*-arylsulfonamide from sodium arylsulfinates with nitroarenes by using of $NaHSO_3$ as the reductant and hydrogen source (Scheme 1a). In 2016, Deng and co-workers developed a $Pd(OH)_2$-cata- lyzed method for the synthesis of *N*-arylsulfonamide from arylsulfonyl hydrazides and nitroarenes via the hydrogen transfer strategy (Scheme 1b).[5] Both well developed reactions, although effective, but suffer from the limited commercial availability of sulfonating reagents that are too expensive for larger-scale synthesis. Arylsulfonyl hydrazides and sodium arylsulfinates are usually prepared from the corresponding sulfonyl chlorides in the presence of hazardous sulfinate salts and strong bases[6] or dangerous

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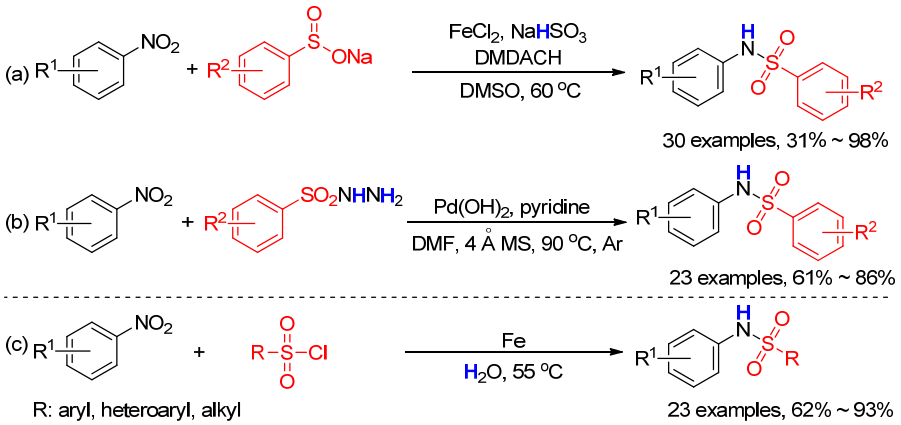
Received July 21, 2018; revised August 31, 2018; published online September 17, 2018.
Project supported by the International Cooperation Project of Qinghai Province (Nos. 2018-HZ-806, 2017-HZ-806), the Qinghai Key Laboratory of Tibetan Medicine Research (No. 2017-ZJ-Y11), the Natural Science Foundation of Shandong Province (Nos. ZR2018MB009, ZR2016JL012), and the National Natural Science Foundation of China (Nos. 21302109, 21302110, 21601106).
青海省国际科技合作专项基金(Nos. 2018-HZ-806, 2017-HZ-806)、青海省藏药重点实验室(Nos. 2017-ZJ-Y11)、山东省自然科学基金(Nos. ZR2018MB009, ZR2016JL012)、国家自然科学基金(Nos. 21302109, 21302110, 21601106)资助项目.



Scheme 1 Synthesis of sulphonamides from nitroarenes

hydrazine hydrate[7] under relatively harsh reaction conditions. Tedious multistep operations might limit their wide applications in the field of organic synthesis and pharmaceutical chemistry. Therefore, the development of a simple, direct, economic and especially, environmentally friendly method for synthesis of sulfonamides from nitroarenes and readily available sulfonyl chlorides is still highly desirable.

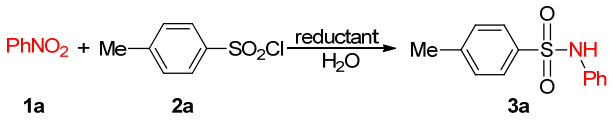
On the other hand, water is not only environmentally friendly reaction media,[8] but it also a "green" hydrogen source for reduction reaction. Over the past decades, considerable efforts have been made in the development of sustainable and economical chemical transformation with water as the hydrogen source.[9] Up to date, there is still no report for the aqueous synthesis of sulfonamides with water as the terminal hydrogen source. Following our interest in environmentally friendly synthesis,[10] herein we report a sustainable, step-economical and practical method for the construction of sulfonamides from sulfonyl chlorides and nitroarenes with water as the reaction media as well as the hydrogen source (Scheme 1c).

2 Results and discussion

At the start of our investigations, we attempted the sulfonamidation of nitrobenzene (**1a%**) and tosyl chloride (**2a**) (1.5 equiv.) with zinc dust (3 equiv.) as the reductant in water (0.5 mL) under ultrasound irradiation (USI). An 18% yield of the desired sulfonamidation product **3a** was formed (Table 1, Entry 1). In addition, a trace amount of *p*-toluenesulfonic acid was observed. This can possibly be attributed to the side reactions of hydrolysis of **2a**. Considering a large amount of **1a** remained completely unconsumed, the reaction outcome of zinc loading was next performed. On increasing the reductant loading to 3.5 and 4 equiv., the **3a** was obtained with the same yields (Table1, Entries 2 and 3). Therefore, the loading of zinc duct was optimized at 3.5 equiv. using iron powder instead of zinc dust led to an increase in the yield of **3a** (Table 1, Entry 4). Adjusting the amount of **2a** to 2 equiv. resulted in the desired product **3a** with 55% yield (Table 1, Entry 5). Further increasing the loading of **2a** did not provide improved the yield of the desired product **3a** (Table 1, Entry 6). The results revealed that ultrasound irradiation was not appropriate for this present reaction. Choosing the best ultrasound irradiation conditions (Table 1, Entry 5), this transformation was further optimized under traditional heating conditions. To our delight, traditional heating used under the same reaction parameters led to 68% yield (Table 1, Entry 7). Further investigations on the effect of reaction temperature suggested that 55 ℃ was ideal temperature for this reaction (Table 1, Entries 8～10). Thus, the optimal reaction conditions are nitrobenzene (**1a**), 2 equiv. of tosyl chloride (**2a**), 3.5 equiv. of Fe powder and water.

Next, the scope and limitations of the present protocol were studied under the optimal reaction conditions (Table 2). Arylsulfonyl chlorides bearing with either electron-donating or electron-withdrawing substituents, such as methyl, methoxy, halide (F, Cl and Br), trifluoromethyl, cyan and acetyl groups underwent the sulfonamidation reactions efficiently to afford the desired products in good to excellent yields (**3a**～**3i**). Raised steric hindrances of the substituents of arylsulfonyl chlorides resulted in a low yield of sulfonamide product (**3b** vs. **3k**). Naphthalenesulfonyl and thiophene-2-sulfonyl chloride also displayed good reactivity to afford the corresponding products in good yields (**3l** and **3m**). This method was also extended to aliphatic sulfonyl chlorides, such as methanesulfonyl chloride and butanesulfonyl chloride. These results revealed that aliphatic sulfonyl chlorides were also well tolerated under the standard reaction conditions to deliver the desired products in good yields (**3n** and **3o**). However, no product was afforded when trifluoromathanesulfonyl chloride was utilized as the substrates. Next, the substrate scope of the nitroarenes in this sulfonamidation reaction has also been investigated by the employment of TsCl as a test substrate. Good to excellent yields were generally obtained for nitrobenzenes bearing not only electron-donating but also electron-withdrawing substituents (**3p** ～ **3v**). *β*-Nitronaphthalene could also be transferred into the desired product in good yield (**3w**). No reaction occurred when nitroethane was used as the substrate.

Table 1 Screening the optimal reaction conditions[a]

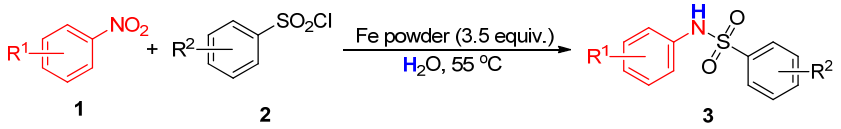


1a 2a 3a

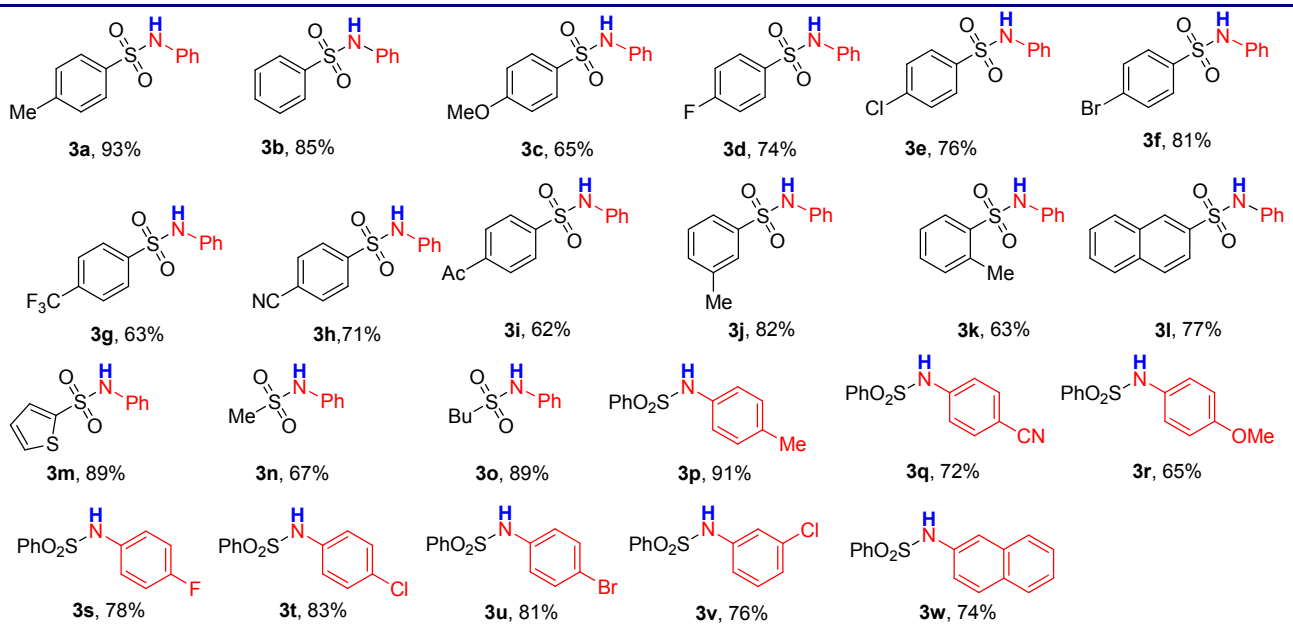
Entry	Reductant (equiv.)	**2a**/equiv.	Conditions	Conv./%	Yield[b]/%
1	Zn dust (3)	1.5	USI, 1.5 h	25	18
2	Zn dust (3.5)	1.5	USI, 1.5 h	33	29
3	Zn dust (4)	1.5	USI, 1.5 h	34	29
4	Fe powder (3.5)	1.5	USI, 1.5 h	48	40
5	Fe powder (3.5)	2	USI, 1.5 h	63	55
6	Fe powder (3.5)	2.5	USI, 1.5 h	61	54
7	Fe powder (3.5)	2	25 ℃, 40 h	75	68
8	Fe powder (3.5)	2	45℃, 40 h	84	76
9	**Fe powder (3.5)**	**2**	**55℃, 40 h**	**100**	**93**
10	Fe powder (3.5)	2	65℃, 40 h	100	84

[a] Reaction conditions: **1a** (0.2 mmol) and **2a** (0.6 mmol), reductant (3～4 equiv.), solvent (1.5 mL), temperature (25～65 ℃), reaction time (1.5～40 h). [b] Isolated yields based on **1a**.

Table 2 Reaction scope[a]



1 2 3

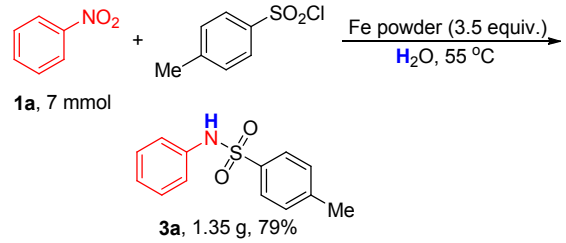


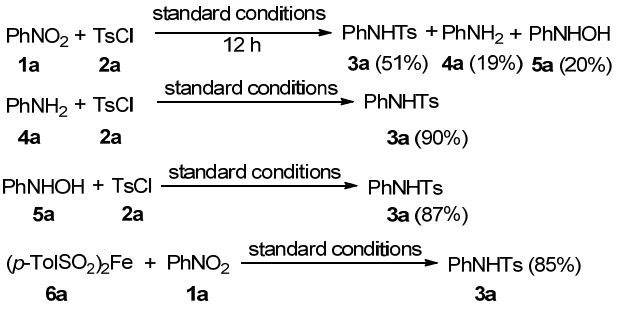
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), iron powder (1.15 mmol), water (1.5 mL).

To demonstrate the practicality and reliability of the present synthetic method, the gram-scale experiment was performed under the standard reaction conditions, furnishing the desired products **3a** in 79% isolated yield (Eq. 1). However, decreasing the loading of TsCl and iron powder leads to a significant decrease in the yield of the desired product **3a**.

To understand the reaction mechanism of the present sulfonamidation reaction, some control experiments were carried out, as shown in Scheme 2. When the reaction of nitrobenzene (**1a**) with tosyl chloride (**2a**) was stopped after 12 h, it was found that in addition to the sulfonamidation product **3a**, unexpectedly, both aniline (**4a**) and *N*-phenylhy- droxylamine (**5a**) were observed. When **4a** and **5a** were subjected to the optimal reaction conditions, the desired product **3a** was obtained in 90% and 87% NMR yields, respectively. These experimental results suggested that this present reaction might involve **4a** and **5a** as the reactive intermediate. Treatment of iron(II) 4-methylbenzene-sulfinate **6a**[11] with **1a** or **4a** under the optimal reaction conditions gave the desired product **3a** in 85% NMR yield, which indicates that **6a** might also be the reac-

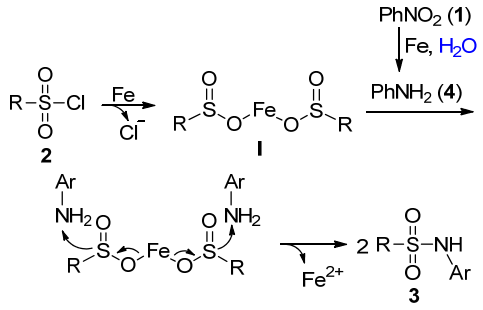
tion intermediate .





Scheme 2 Control experiments

The sulfonamidation reaction may follow a similar reaction pathway to that of the sulfonation of quinoline *N*-oxides with sulfonyl chlorides reported by He *et al.*,[12] with the difference being aniline instead of quinoline *N*-oxides (Scheme 3). First, the nitrobenzene **1** was deep reduced with iron powder to generate aniline **4**. Meanwhile, the sulfonyl chloride **2** was reduced by iron powder into an iron bis-sulphinate compound **I**. Subsequently, the intermediate **I** reacted with aniline **4** to produce the desired product sulfonamide **3** with release of the Fe^{2+}.



Scheme 3 Plausible reaction mechanism

3 Conclusions

In summary, we have developed a new and general route for the synthesis of various functionalized sulfonamides from nitroarenes and sulfonyl chlorides in the presence of iron powder as the sole reductant in water (green solvent) under open-air conditions. In the reaction, both starting materials were reduced by inexpensive and nontoxic iron at the same time. From an economic and industrial perspective, this chemical process has the potential for important impact given the single-step sulfonamidation reaction of readily accessible reagents, the mild reaction conditions, and the excellent functional group tolerance of the method. Thus, this strategy would certainly be valuable from both academic research and industry.

4 Experimental section

4.1 General procedure for the synthesis of 3

Sulfonyl chlorides (0.6 mmol), nitroarenes (0.3 mmol) and Fe powder (1.15 mmol) were added in H_2O (1.5 mL). The mixture was allowed to react in a 10 ml round-bottom flask at 55 ℃ under air for 40 h. After cooling to room temperature, the mixture was extracted with dichloromethane (5 mL×3). The combined organic layer was dried with anhydrous $MgSO_4$. The solvent was removed. Products were separated by short flash chromatography on a silica gel column.

4.2 Characterization of the compounds

4-Methyl-*N*-phenylbenzenesulfonamide (**3a**): White solid (68.9 mg, 93% yield), m.p. 104～105 ℃ (lit.[4] 104～105 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J=8.4 Hz, 2H), 7.28 (brs, 1H), 7.23 (d, J=8.8 Hz, 4H), 7.14 (d, J=7.7 Hz, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 136.7, 136.0, 129.7, 129.3, 127.3, 125.3, 121.5, 21.6.

N-Phenylbenzenesulfonamide (**3b**): White solid (59.4 mg, 85%), m.p. 105～106 ℃ (lit.[4] 106～107 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=7.6 Hz, 2H), 7.58 (t, J=7.2 Hz, 1H), 7.50 (t, J=7.6 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 7.20 (t, J=7.2 Hz, 1H), 7.10 (d, J=7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.2, 136.4, 133.2, 129.6, 129.2, 127.4, 125.5, 122.2.

4-Methoxy-*N*-phenylbenzenesulfonamide (**3c**): White solid (51.3 mg, 65% yield), m.p. 108～109 ℃ (lit.[4] 109～110 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (td, J=8.1, 7.5, 3.6 Hz, 2H), 7.22 (q, J=6.7, 5.4 Hz, 2H), 7.16～6.96 (m, 4H), 6.93～6.78 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.2, 136.7, 130.6, 129.5, 129.4, 125.3, 121.6, 114.3, 55.7.

4-Fluoro-*N*-phenylbenzenesulfonamide (**3d**): White solid (55.7 mg, 74% yield), m.p. 109～110 ℃ (lit.[5] 109～110 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (dd, J=8.9, 5.2 Hz, 2H), 7.28～7.24 (m, 2H), 7.15～7.05 (m, 5H), 6.61 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 164.1, 136.2, 135.0, 135.1, 130.2, 130.0, 129.5, 125.8, 121.9, 116.6, 116.3.

4-Chloro-*N*-phenylbenzenesulfonamide (**3e**): White solid (60.9 mg, 76% yield), m.p. 102～103 ℃ (lit.[5] 104～105 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J=8.0 Hz, 2H), 7.46 (d, J=8.4 Hz, 2H), 7.32 (dd, J=14.7, 8.4 Hz, 3H), 7.20 (q, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7, 137.4, 136.2, 129.6, 129.4, 128.8, 125.6, 121.8.

4-Bromo-*N*-phenylbenzenesulfonamide (**3f**): White solid (75.6 mg, 81% yield), m.p. 113～115 ℃ (lit.[5] 116～117 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58～7.52 (m, 4H), 7.24～7.21 (m, 2H), 7.22～7.15 (m, 1H), 7.09～7.04 (m, 2H), 6.61 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.1, 136.1, 132.4, 129.4, 128.7, 128.2, 125.9, 122.4.

N-Phenyl-*S*-4-trifluoromethylphenyl sulfonamide (**3g**): White solid (56.9 mg, 63%), m.p. 120～121 ℃ (lit.[4] 120～122 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=8.4 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.22 (t, J=7.6 Hz, 1H), 7.12 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 136.1, 134.3 (J_{C-F}=33.2 Hz), 129.2, 127.3, 126.5 (J_{C-F}=3.6 Hz), 126.3, 123.5 (J_{C-F}=271.7 Hz), 122.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.4.

4-Cyano-*N*-phenylbenzenesulfonamide (**3h**): White solid (55.0 mg, 71% yield), m.p. 112～113 ℃ (lit.[7] 110～111 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.4 Hz, 2H), 7.68 (d, J=8.4 Hz, 2H), 7.32 (d, J=7.2 Hz, 2H), 7.23 (t, J=7.8 Hz, 1H), 7.08 (d, J=7.6 Hz, 2H), 6.72 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 135.6, 132.6, 129.7, 127.7, 126.7, 122.3, 117.3, 116.8.

4-Acetyl-*N*-phenylbenzenesulfonamide (**3i**): White solid (51.2 mg, 62%), m.p. 98～99 ℃ (lit.[8] 99～102 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J=8.4 Hz, 2H), 7.88 (d, J=8.3 Hz, 2H), 7.45 (brs, 1H), 7.24 (t, J=7.7 Hz, 2H), 7.14～7.09 (m, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.1, 142.8, 140.2, 135.9, 129.5, 128.9, 127.6, 125.9, 121.9, 26.9.

3-Methyl-*N*-phenylbenzenesulfonamide (**3j**): White solid (60.8 mg, 82% yield), m.p. 103～104 ℃ (lit.[4] 101～102 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62～7.53 (m, 2H), 7.36 (d, J=6.4 Hz, 2H), 7.21 (t, J=7.6 Hz, 2H), 7.18 (brs, 1H), 7.12 (d, J=7.6 Hz, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.5, 139.1, 136.6, 133.9, 129.6, 129.1, 127.7, 125.4, 124.5, 121.7, 21.4.

N-Phenyl-*S*-2-methylphenyl sulfonamide (**3k**): White solid (46.7 mg, 63%), m.p. 124～126 ℃ (lit.[4] 126～127 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.4 Hz, 1H), 7.44～7.33 (m, 2H), 7.26～7.21 (m, 2H), 7.23 (t, J=7.2 Hz, 2H), 7.20 (d, J=8.4 Hz, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.5, 137.4, 136.8, 133.2, 132.3, 130.5, 129.8, 126.4, 124.9, 120.1, 20.7.

N-Phenylnaphthalene-2-sulfonamide (**3l**): White solid (65.4 mg, 77% yield), m.p. 131～133 ℃ (lit.[7] 131～133 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (brs, 1H), 7.96～7.74 (m, 4H), 7.61 (dt, J=20.6, 7.2 Hz, 2H), 7.26～7.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4, 136.2, 135.1, 132.1, 129.6, 129.6, 129.4, 129.1, 128.2, 127.6, 125.7, 122.3, 121.8.

N-Phenylthiophene-2-sulfonamide (**3m**): White solid (63.8 mg, 89% yield), m.p. 82～83 ℃ (lit.[7] 81～83 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=4.4 Hz, 2H), 7.31～7.24 (m, 3H), 7.22～7.15 (m, 3H), 6.73 (d, J=4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.3, 136.4, 133.2, 132.8, 129.8, 127.4, 125.5, 122.2.

N-Phenylmethanesulfonamide (**3n**): White solid (34.4 mg, 67% yield), m.p. 98～100 ℃ (lit.[3g] 99～100 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (t, J=7.6 Hz, 2H), 7.21～7.19 (m, 3H), 6.94 (brs, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.8, 129.7, 125.6, 120.9, 39.6.

N-Phenylbutane-1-sulfonamide (**3o**): White solid (56.9 mg, 89% yield), m.p. 108～110 ℃ (lit.[3g] 108～110 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J=8.6 Hz, 2H), 7.23～7.14 (m, 3H), 6.38 (brs, 1H), 3.07 (t, J=8.0 Hz, 2H), 1.85～1.75 (m, 2H), 1.41 (m, 2H), 0.91 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 129.8, 125.3, 120.5, 51.4, 25.6, 21.6, 13.6.

N-(*p*-Tolyl)-*S*-phenyl sulfonamide (**3p**): White solid (67.4 mg, 91%), m.p. 116～117 ℃ (lit.[3g] 116～117 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.6 Hz, 2H), 7.61 (t, J=7.2 Hz, 1H), 7.53 (t, J=7.6 Hz, 2H), 7.07 (d, J=8.2 Hz, 2H), 6.87 (d, J=8.0 Hz, 2H), 6.51 (brs, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.5, 135.2, 133.3, 133.2, 130.4, 129.3, 127.7, 122.4, 21.2.

N-(4-Cyanophenyl)benzenesulfonamide (**3q**): Yellow solid (55.7 mg, 72%), m.p.: 147～149 ℃ (lit.[3g] 147～149 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J=7.8 Hz, 2H), 7.60 (t, J=7.3 Hz, 1 H), 7.54～7.48 (m, 4H), 7.19 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 138.7, 133.9, 133.8,129.6, 127.3, 119.6, 118.5, 108.1.

N-(4-Methoxyphenyl)-*S*-phenylsulfonamide (**3r**): White solid (51.3 mg, 65%), m.p. 87～88 ℃ (lit.[3h] 88～89 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J=7.6 Hz, 2H), 7.53 (t, J=7.4 Hz, 1H), 7.40 (t, J=7.2 Hz, 2H), 7.02 (d, J=8.4 Hz, 2H), 6.72 (d, J=8.4 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 139.6, 133.3, 129.5, 128.3, 127.5, 125.3, 114.5, 55.6.

N-(4-Fluorophenyl)-*S*-phenyl sulfonamide (**3s**): White solid (58.7 mg, 78%), m.p. 111～112 ℃ (lit.[3h] 110～111 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.6 Hz, 2H), 7.47 (t, J=7.2 Hz, 1H), 7.43 (t, J=7.6 Hz, 2H), 7.12 (m, 2H), 6.90 (t, J=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5 (J_{C-F}=243.8 Hz), 138.2, 133.5, 132.7, 129.2, 127.1, 124.9 (J_{C-F}=8.5 Hz), 116.3 (J_{C-F}=22.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −116.5.

N-(4-Chlorophenyl)benzenesulfonamide (**3t**): White solid (66.5 mg, 83% yield), m.p. 104～105 ℃ (lit.[4] 104～105 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J=8.6 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H), 7.28 (d, J=14.8 Hz, 3H), 7.14 (q, J=7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7, 137.4, 136.2, 129.5, 129.5, 128.8, 125.8, 121.9.

N-(4-Bromophenyl)benzenesulfonamide (**3u**): White solid (75.6 mg, 81% yield), m.p. 114～116 ℃ (lit.[4] 116～117 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J=7.6 Hz, 2H), 7.55 (t, J=7.4 Hz, 1H), 7.44 (t, J=7.6 Hz, 2H), 7.34 (d, J=7.8 Hz, 2H), 6.97 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 136.2, 132.6, 129.7, 128.8, 128.2, 126.2, 121.0.

N-(3-Chlorophenyl)-*S*-phenylsulfonamide (**3v**): White solid (60.9 mg, 76%), m.p. 116～117 ℃ (lit.[5] 115～117 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=7.6 Hz, 2H), 7.62 (t, J=7.2 Hz, 1H), 7.44 (t, J=7.2 Hz, 2H), 7.18−7.15 (m, 2H), 7.07 (d, J=8.0 Hz, 1H), 6.93 (d, J=7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 137.7, 135.2, 133.7, 130.2, 129.7, 127.4, 125.6, 121.2, 19.8.

N-(2-Naphthyl)-*S*-phenyl sulfonamide (**3w**): White solid (62.8 mg, 74%), m.p. 97～99 ℃ (lit.[4] 98～99 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=7.8 Hz, 2H),

7.78～7.67 (m, 3H), 7.55 (s, 1H), 7.50 (d, J=7.6 Hz, 1H), 7.47～7.36 (m, 4H), 7.24 (d, J=8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.1, 134.0, 133.7, 133.2, 131.3, 129.5, 129.2, 127.8, 127.7, 127.4, 126.8, 12

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **3a**～**3w**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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