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# Regiospecific Cleavage of S-N Bonds in Sulfonyl Azides: Sulfonyl Donors

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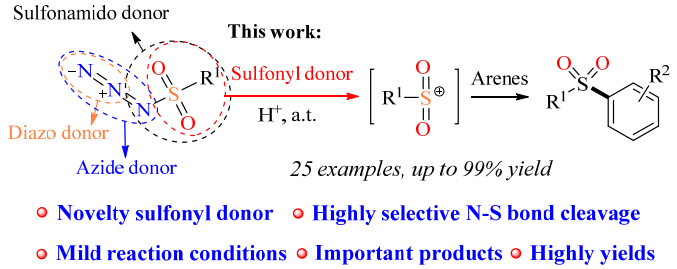


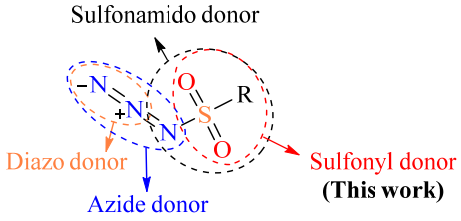

**Abstract:** Sulfonyl azides have been widely used as sulfonamido, diazo, and azido donors, as well as all-nitrogen 1,3-dipoles donors in synthetic chemistry. Here, the sulfonyl azides were used as efficient sulfonyl donors, which is very unusual. Trifluoromethanesulfonic acid-induced formation of the sulfonyl cation reactive species from sulfonyl azides was developed and used for the first time to couple various inactivated arenes to prepare sulfones at ambient temperature.

**Keywords**: sulfonyl azides; S-N bond cleavage; arylsulfonyl compounds; cross-coupling; sulfonation; sulfones

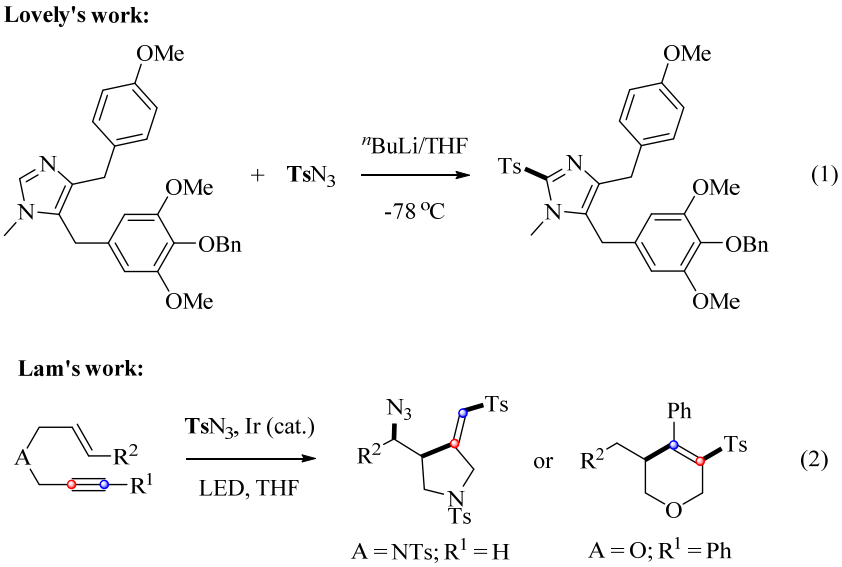
## INTRODUCTION

Sulfonyl azides are very important organic compounds that are widely used as sulfonamido group donors,[1] diazo group donors,[2] and all-nitrogen 1,3-dipoles donors in [3+2] cycloaddition reactions leading to 1,2,3-triazoles,[3] as well as azide group sources[4] in organic synthetic chemistry (Scheme 1).

However, there are few reports[5] where the sulfonyl azides were sulfonyl donors in sulfonylation reactions via highly selective S-N bond cleavage reactions. In 2010, Lovely and co-workers[5a] found that a tosyl derivative was the only substitution product when they treated a methylimidazole derivative with $^{n}$BuLi and $TsN_3$ in one step of the total synthesis of *Naamidine H* natural product. Harsh conditions such as a strong base ($^{n}$BuLi) and low temperatures (–78 °C) were used, and a large amount of starting material was recovered. The authors reported: "This was a somewhat surprising result since we and others have used this approach for the azidation of imidazole C2 position".[5a] However, it is unfortunate that no systematic expansion of this strategy to other aromatic compounds has been reported (Eq. 1). Very recently, Lam et al.[5b] reported the generation of sulfonyl radicals from sulfonyl azides using visible light and a photoactive iridium complex in tetrahydrofuran (THF), which were used to promote sulfonylative and azido sulfonylative cyclizations of enynes to give several classes of highly functionalized oxacycles and azacycles. It is noteworthy that the alkyne moiety of the enyne reagents served as the acceptor of the sulfonyl radicals, whereas the arenes have not been explored in the conversion (Eq. 2). Thus, the development of a new, mild, and regiospecific S-N bond cleavage reaction of the sulfonyl azides for incorporating a sulfonyl group into simple arenes, which extends beyond traditional sulfonylation method, remains unexplored. Therefore, a trifluoromethanesulfonic acid (TfOH)-promoted Friedel–Crafts type sulfonylation reaction was performed here for rapid access to a series of sulfone derivatives, with inactivated arenes serving as the electrophilic receptor and the sulfonyl azides serving as the sulfonyl group donor, via a regiospecific S-N bond cleavage reaction at ambient temperature (AT) (Scheme 2).




**Scheme 1. Versatile building blocks of sulfonyl azides.**



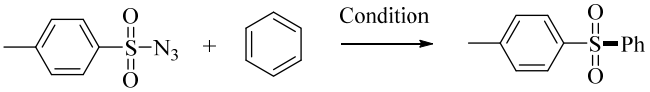

To date, various sulfonyl-containing organic/inorganic compounds including sulfonyl chlorides,[6] sulfonic acids,[7] sulfonic anhydrides,[8] sulphonate,[9] sulfonamides,[10] sulfohydrazide,[11] dimethylsulfoxide (DMSO),[12] DABSO,[13] $K_2S_2O_8$,[14] $SO_2$[15], and $SO_3$,[16] deliver their sulfonyl moiety to an electrophilic receptor. They then produced sulfone derivatives in the presence of a metal-catalyst or under metal-free oxidation reactions.[17] In addition, oxidation of the sulfides can also be used to derive sulfones.[18] Despite these effective methods, the development of a new environmentally benign sulfonylation reagent under simple and mild reaction conditions remains a highly desirable, challenging goal. Sulfonyl azides **1** can react with a strong acid to produce hydrogen azide ($HN_3$) and a reactive sulfonyl cation might be involved. Accordingly, the sulfonyl cation generated in situ may be quickly captured by an arene electrophilic receptor, which would produce an arylsulfonyl compound.

## RESULTS AND DISCUSSION

From the synthesis of *N*-containing heterocycles in the presence of brønsted acid,[19] the reaction conditions were optimized for the sulfonyl delivery reaction of 4-methylbenzenesulfonyl azide (**1a**) with benzene (**2a**). Treatment of starting materials **1a** (1.0 equiv.) and **2a** (1.2 equiv.) with trifluoromethanesulfonic acid (TfOH, 3 equiv) in dichloromethane (DCM, 0.5 mL) at ambient temperature produced the desired 1-methyl-4-(phenylsulfonyl)benzene (**3a**) as a white solid in a 92% yield after 3 h. The structure of **3a** was identified with $^1$H NMR, $^{13}$C NMR, high-resolution mass

spectrometry (HRMS), and MS (Table 1, entry 1). However, a lower yield of **3a** along with recovered **1a** was obtained if the amount of TfOH was decreased (Table 1, entries 2 and 3). Other brønsted acids including methanesulfonic acid (MSA), 4-methylbenzenesulfonic acid (TsOH), $H_2SO_4$, $HNO_3$, and AcOH were ineffective for the reaction (Table 1, entries 4–8). Further investigation of this intermolecular cross-coupling reaction with different solvents indicated that 1,4-dioxane, THF, methanol, diethyl ether, and DMSO did not yield the desired compound **3a** (Table 1, entries 9–13).

**Table 1. Survey of the reaction conditions.**[a]




**1a** **2a** **3a**

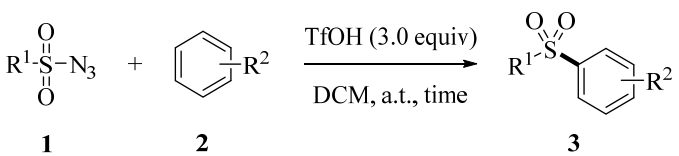
| Entry | Acid (equiv) | Solvent | Time/h | Yield of **3a**/% | Recovered **1a**/% |
|---|---|---|---|---|---|
| 1 | TfOH (3.0) | DCM | 3 | 92 | 0 |
| 2 | TfOH (2.0) | DCM | 3 | 79 | 16 |
| 3 | TfOH (1.0) | DCM | 5 | 50 | 47 |
| 4 | MSA (3.0) | DCM | 5 | NR | 80 |
| 5 | TsOH (3.0) | DCM | 5 | NR | 82 |
| 6 | $H_2SO_4$ (3.0) | DCM | 5 | NR | 72 |
| 7 | $HNO_3$ (3.0) | DCM | 5 | NR | 74 |
| 8 | AcOH (3.0) | DCM | 5 | NR | 97 |
| 9 | TfOH (3.0) | 1,4-Dioxane | 5 | NR | 93 |
| 10 | TfOH (3.0) | THF | 5 | NR | 87 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | TfOH (3.0) | Methanol | 5 | NR | 96 |
| 12 | TfOH (3.0) | Diethyl ether | 5 | NR | 95 |
| 13 | TfOH (3.0) | DMSO | 5 | 8 | 85 |

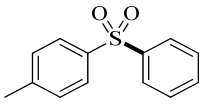
[a] Unless otherwise indicated, all reactions were carried out with **1a** (1.0 mmol), **2a** (1.2 equiv) in 0.5 mL anhydrous solvents at ambient temperature.

Under optimized conditions (Table 1, entry 1), the scope of this Friedel–Crafts type sulfonylation reaction was examined (Scheme 2). Various sulfonyl azides (**1**) with different aryl groups ($R^1$) were investigated first. The starting materials **1a**–**c** bearing the methyl group (-Me) at the *ortho*-, *meta*-, and *para*-positions, **1d** with a methoxyl group (-OMe) at the *para*-position, and benzenesulfonyl azide (**1e**) smoothly reacted with benzene (**2a**), and yielded (84%–92%) the desired sulfones **2a**–**e** at ambient temperatures. Naphthalene-2-sulfonyl azide (**1f**) under the same conditions coupled with **2a** to achieve an excellent yield of **3f** (97%). When *para*-chloro and *para*-trifluoromethyl-substituted benzenesulfonyl azides **1g** and **1h** were employed as substrates, the corresponding sulfonylated products **3g** (90%) and **3h** (97%) were obtained exclusively. Furthermore, the arylsulfonyl azides **1i** and **1j** with electron withdrawing groups, including -$CO_2$Et or -$NO_2$ groups at the *para*-position of the benzene ring, were used for the sulfonylation reaction, and yielded sulfonylated products **3i** and **3j** (83% and 94%, respectively) at 60 °C. This type of diaryl sulfone derivative generally cannot be synthesized with sulfonylation reagents and arenes bearing the EWG(s) on the aryl ring because of limitations of the Friedel–Crafts reaction. These results thus indicated the practicality and flexibility of the present strategy.

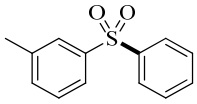
**Scheme 2. Extension of the reaction scope** [a]



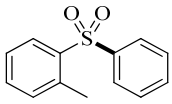

**1** **2** **3**



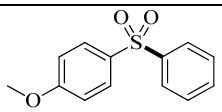
**3a**: 3 h, 92%



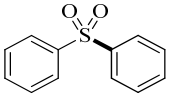
**3b**: 3 h, 91%



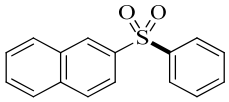
**3c**: 3 h, 92%



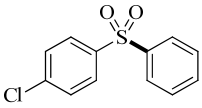
**3d**: 3 h, 84%



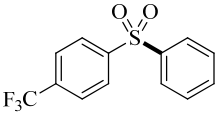
**3e**: 3 h, 86%



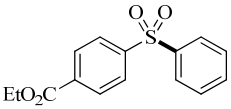
**3f**: 3 h, 97%



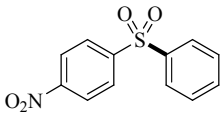
**3g**: 3 h, 90%



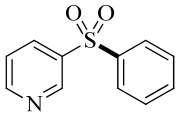
**3h**: 24 h, 97%



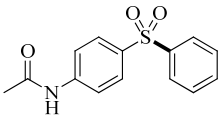
**3i**: 5 h, 83%[b]



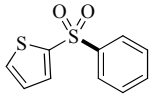
**3j**: 24 h, 94%[b]



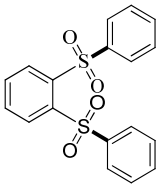
**3k**: 5 h, NR[c]



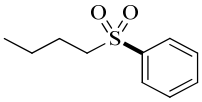
**3l**: 5 h, 98%[b]



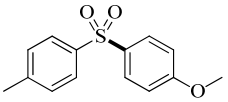
**3m**: 3 h, 89%



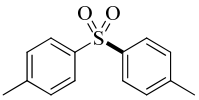
**3n**: 5 h, 45%[d]



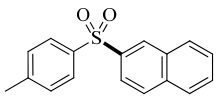
**3o**: 3 h, 80%



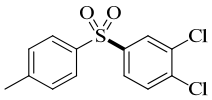
**3p**: 3 h, 67%[e]



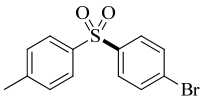
**3q**: 3 h, 78%[f]



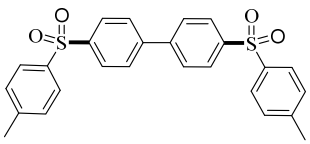
**3r**: 3 h, 59%[g]



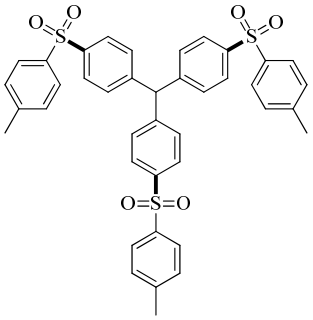
**3s**: 5 h, 75%



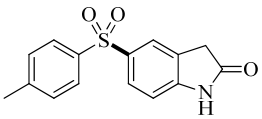
**3t**: 5 h, 93%



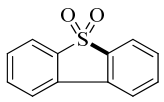
**3u**: 3 h, 95%[h]



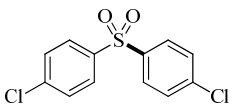
**3v**: 5 h, 91%[i]



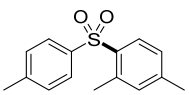
**3w**: 3 h, 58%



**3x**: 3 h, 99%



**3y:** 3 h, 81%



**3z**: 3 h, 93%

[a] Unless otherwise indicated, all reactions were carried out with **1** (1.0 mmol), **2** (1.2 equiv), and TfOH (3.0 equiv) in anhydrous DCM (0.5 mL) at ambient temperature.

[b] Reaction was performed at 60 °C.

[c] 85% of **1k** was recovered.

[d] 2.4 equiv of **2a** was used.

[e] 30% of *ortho*-sulfonylated product 1-methoxy-2-tosylbenzene (**3p'**) was obtained.

[f] 9% of *ortho*-sulfonylated product 1-methyl-2-tosylbenzene (**3q'**) was obtained.

[g] 37% of α-sulfonylated product 1-tosylnaphthalene **3r'** was obtained.

[h] 3.0 equiv of **1a** was used.

[i] 5.0 equiv of **1a** was used.

The extension of the reaction scope revealed that compound **1k** was not a viable substrate for the reaction for sulfone **3k** formation, even at 60 °C. In contrast, starting material **1l** with a weak basic amide group on the benzene yielded the sulfonylated product **3l** (98%) at 60 °C. These observations indicated that it was largely caused by a salt-forming reaction of alkaline pyridine (**1k**) with the strong acid TfOH. Moreover, thiophene-2-sulfonyl azide (**1m**) also reacted smoothly with **2a** to give the desired product **3m** in an 89% yield. Benzene-1,2-disulfonyl diazide (**1n**) could also be subjected to the sulfonylation reaction to give the desired product **3n** in a 45% yield, regardless of steric hindrance. The source of the sulfonyl moiety was not limited to an arylsulfonyl group. *n*-Butyl-substituted sulfonyl azide **1o** could also be applied as a sulfonyl donor, and the sulfonylation reaction between **1o** and **2a** proceeded smoothly at ambient temperature to produce target compound **3o** in a 80% isolated yield.

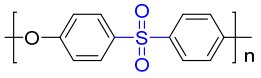
Various arenes were tried for reaction with **1a**. Beyond benzene (**2a**) used for **3a**–**o**, other substituted benzenes, including anisole (**2b**), toluene (**2c**), naphthalene (**2d**), 1,2-dichlorobenzene (**2e**), and bromobenzene (**2f**) were viable substrates. However, in the cases of **2b**–**d**, they produced not only *para*-sulfonylated products **3p**–**t** (37%–93%), but also an *ortho*-substituted isomer **3p**–**r**. In addition,

biphenyl (**2g**) and triphenylmethane (**2h**) worked as well; the corresponding di- and trisulfonylated products **3p** and **3q** were isolated in 95% and 91% yields, respectively. 5-tosylindolin-2-one (**3w**) was obtained in a 58% yield when **1a** reacted with benzoheterocyclic compound indolin-2-one (**2i**). In conjunction with the product **3l**, this selectable bond-formation reaction demonstrated the practicality and flexibility of the protocol. The sulfonylation strategy could occur not only in an intermolecular reaction, but also in an intramolecular reaction. The sulfonylation of [1,1'-biphenyl]-2-sulfonyl azide (**1x**) was also feasible, resulting in an almost quantitative yield of **3x** (99%) via an intramolecular annulation reaction. Starting material *m*-xylene also proceed well with **1a**. The cross-coupling reaction occurred specifically at the *para*-position of the methyl of *m*-xylene, gave the desired product **3z** in 93% yield after 3 h under optimized conditions. We also reacted some heterocycles starting materials with **1a**, including indole, benzo[*d*]oxazole, 1*H*-benzo[*d*]imidazole, and benzofuran. They did not afford the desired products **3**. Some unidentified complex mixture was observed in the case of indole and benzofuran. Some starting materials was recovered in the case of benzo[*d*]oxazole and 1*H*-benzo[*d*]imidazole.

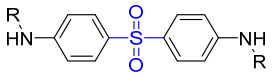
The sulfonyl group is an important moiety that frequently appears in biological molecules, pharmaceuticals, pesticides, and polymers. They distinctly enhance certain features, such as benzobicylon, thiamphemcol, and HDACI.[20] It can also serve as a protecting group for functional groups,[21] or a "baton" that adds to and then leaves from an intermediate in organic synthetic reactions.[5a, 22] These benefits contribute to the diversity of their synthetic methods. With this strategy, the reaction of **1g** with chlorobenzene could be easily performed at ambient temperature affording **3y** in 81% yield after 3 h. This valuable molecule (**3y**) now is a commercial reagent and could be used for the synthesis of poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene),[23] Acedapsone,[24] Dapsone,[14] and other useful valuable derivatives[14] via a simple derivatization reaction (Scheme 3). Acedapsone and Dapsone are antibiotics commonly used in combination with rifampicin and clofazimine for the treatment of leprosy, acne,[25] dermatitis herpetiformis, and various other skin conditions.[26] To further demonstrate the

practicality of the reaction, a large-scale synthesis was examined. For example, the reactions of **1a** (1.2 g, 6 mmol) with **2a** (7.2 mmol) were conducted. It gave **3a** (1.342 g) in 97% yield after 18 h.

**Scheme 3. Representative sulfonyl-containing molecules.**



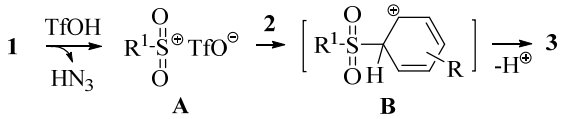
Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)



**Dapsone:** R = H
**Acedapsone**: R = Ac

From the experimental results and proposed mechanisms reported elsewhere,[10a, 27] a probable pathway for the Friedel–Crafts-type cross-coupling of inactivated arenes and sulfonyl azides to prepare diaryl sulfone derivatives is given in Scheme 4. Initially, the acylation donor sulfonyl azides **1** reacted with TfOH to produce hydrogen azide ($HN_3$) and the sulfonyl cation **A** with $TfO^-$ anion as the counterion. This is a potential agent for the Friedel–Crafts sulfonylation. Subsequently, the arene was activated by the electrophilic sulfonyl cation **A** to form the desired sulfonylation product **2** by deprotonation.[28b,29]

**Scheme 4. Proposed mechanism.**



**A** **B**

## ■ CONCLUSION

In summary, a trifluoromethanesulfonic acid (TfOH)-promoted regiospecific N-S bond cleavage reaction of sulfonyl azides was developed. It coupled with various inactivated arenes and led to a series of sulfones in good to excellent yields at ambient temperature via Friedel–Crafts type cross-coupling reactions. The procedure was very different from previous aromatic sulfonation reactions performed with sulfonyl chlorides, sulfonic acids, sulphonate, and sulfohydrazide. Here, the cross-coupling method proceeded with readily available sulfonyl azides, without high temperature, additives, metal catalysts, and or complex execution. More importantly, the sulfonyl azides served as a donor of sulfonyl groups, rather than a sulfonamido group donor, a diazo group donor, an all-nitrogen 1,3-dipoles donor, and an azide group source. This will largely broaden application ranges. Furthermore,

the synthetic potential of the products makes this novel intramolecular cyclization very attractive. Application of this Friedel–Crafts sulfonylation to other systems, especially other heterocycles, is currently under investigation.

## ■ EXPERIMENTAL SECTION

**General Remarks.** All reactions were carried out at 25 ºC, unless otherwise indicated. All other reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Starting materials **1** was synthesized following the known literatures.[30] Petroleum ether (PE) used here refers to the 60-90 ºC boiling point fraction of petroleum. Ethyl acetate is abbreviated as EA. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance/600 ($^{1}H$: 600 MHz, $^{13}C\{^{1}H\}$: 150 MHz at 25 ºC) or Bruker Avance/400 ($^{1}H$: 400 MHz, $^{13}C\{^{1}H\}$: 100 MHz at 25 ºC) with tetramethylsilane as the internal standard. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, and m = multiplet), and coupling constants in Hertz (Hz). All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization orthogonal acceleration time-of-flight (ESI-oa-TOF), and the purity of all samples used for HRMS (>95%) was confirmed by $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectroscopic analysis. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All reactions were monitored by thin-layer chromatography (TLC) with GF254 silica gel-coated plates, and in general, it was designated as the end of the reaction when the starting material **1** was consumed 1 h later. Flash chromatography was carried out on $SiO_2$ (silica gel 200−300 mesh).

The general procedure for the synthesis of **3** (**3a** as example): In a round-bottomed flask (25 mL) equipped with a magnetic stirrer, a solution of $CH_2Cl_2$ (0.5 mL) and benzenesulfonyl azide (**1a**) (183 mg, 1.0 mmol) was prepared. Benzene (**2a**) (0.107 mL, 1.2 mmol) was added to the solution and the reaction mixture was stirred magnetically. Then TfOH (0.25 mL, 3.0 mmol) was added. The mixture was well-stirred for 3 h at ambient temperature. After complete conversion, as indicated by thin-layer

chromatography, the reaction was quenched by water and extracted with dichloromethane (3 × 5 mL). The combined filtrate was washed with saturated brine (2 × 5 mL), and dried over anhydrous $Mg_2SO_4$. The residue was purified by column chromatography on a silica gel with ethyl acetate: petroleum ether (2:45) to provide the desired product **3a** as a white solid (213 mg, 92%).

***1-Methyl-4-(phenylsulfonyl)benzene (3a).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (214 mg, 92%): mp: 123-124 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.93 (d, $J$ = 7.8 Hz, 2H), 7.83 (d, $J$ = 7.2 Hz, 2H), 7.54 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 7.5 Hz, 2H), 7.30 (d, $J$ = 7.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 144.1, 142.0, 138.7, 133.0, 129.9, 129.2, 127.7, 127.5, 21.6. HRMS (ESI), *m/z* calcd. for $C_{13}H_{13}O_2S$ ($[M+H]^+$) 233.0631, found: 233.0630.

***1-Methyl-3-(phenylsulfonyl)benzene (3b).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (212 mg, 91%): mp: 119-120 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.94 (d, $J$ = 7.2 Hz, 2H), 7.75 (d, $J$ = 7.8 Hz, 2H), 7.56 (t, $J$ = 7.2 Hz, 1H), 7.50 (t, $J$ = 7.5 Hz, 2H), 7.38 (dd, $J$ = 18.0, 7.8, 2H), 2.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 141.8, 141.4, 139.5, 134.0, 133.1, 129.2, 129.1, 127.9, 127.6, 124.8, 21.3. HRMS (ESI), *m/z* calcd. for $C_{13}H_{12}NaO_2S$ ($[M+Na]^+$) 255.0450, found: 255.0450.

***1-Methyl-2-(phenylsulfonyl)benzene (3c).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (214 mg, 92%): mp: 79-81 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.22 (d, $J$ = 7.8 Hz, 1H), 7.87 (d, $J$ = 7.8 Hz, 2H), 7.57 (t, $J$ = 6.9 Hz, 1H), 7.49 (dd, $J$ = 16.8, 8.4 Hz, 3H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.23 (d, $J$ = 7.2 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 141.3, 138.8, 138.0, 133.6, 133.0, 132.7, 129.4, 129.0, 127.7, 126.5, 20.2. HRMS (ESI), *m/z* calcd. for $C_{13}H_{12}NaO_2S$ ($[M+Na]^+$) 255.0450, found: 255.0449.

***1-Methoxy-4-(phenylsulfonyl)benzene (3d).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (209 mg, 84%); mp: 91-93 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.91 (d, $J$ = 7.2 Hz, 2H), 7.88 (d, $J$ = 7.8 Hz, 2H), 7.53 (t, $J$ = 6.9 Hz, 1H), 7.48 (t, $J$ = 7.2 Hz, 2H),

6.96 (d, $J$ = 8.4 Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 163.4, 142.4, 133.1, 132.8, 129.9, 129.2, 127.3, 114.5, 55.6. HRMS (ESI), *m/z* calcd. for $C_{13}H_{13}O_3S$ ($[M+H]^+$) 249.0580, found: 249.0580.

***Sulfonyldibenzene (3e).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (187 mg, 86%): mp: 119-121 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$ = 7.8 Hz, 4H), 7.56 (t, $J$ = 7.2 Hz, 2H), 7.50 (t, $J$ = 7.5 Hz, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 141.6, 133.2, 129.3, 127.7. HRMS (ESI), *m/z* calcd. for $C_{12}H_{10}NaO_2S$ ($[M+Na]^+$) 241.0294, found: 241.0294.

***2-(Phenylsulfonyl)naphthalene (3f).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow solid (260 mg, 97%): mp: 120-122 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.58 (s, 1H), 7.99 (t, $J$ = 7.8 Hz, 3H), 7.93 (d, $J$ = 8.8 Hz, 1H), 7.86 (t, $J$ = 8.2 Hz, 2H), 7.67-7.58 (m, 2H), 7.56 (t, $J$ = 7.2 Hz, 1H), 7.50 (t, $J$ = 7.4 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.7, 138.4, 135.0, 133.2, 132.2, 129.6, 129.4, 129.3, 129.1, 129.09, 127.9, 127.7, 127.6, 122.7. HRMS (ESI), *m/z* calcd. for $C_{16}H_{13}O_2S$ ($[M+H]^+$) 269.0631, found: 269.0631.

***1-Chloro-4-(phenylsulfonyl)benzene (3g).***[32] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (227 mg, 90%): mp: 93-94 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.93 (d, $J$ = 7.8 Hz, 2H), 7.88 (d, $J$ = 7.8 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.52 (t, $J$ = 7.5 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 141.2, 140.1, 139.9, 133.4, 129.6, 129.4, 129.1, 127.6. HRMS (ESI), *m/z* calcd. for $C_{12}H_9ClNaO_2S$ ($[M+Na]^+$) 274.9904, found: 274.9908.

***1-(Phenylsulfonyl)-4-(trifluoromethyl)benzene (3h).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a brown solid (277 mg, 97%): mp: 87-88 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 2H), 7.96 (d, $J$ = 7.2 Hz, 2H), 7.76 (d, $J$ = 8.4 Hz, 2H), 7.61 (t, $J$ = 7.4 Hz, 1H), 7.54 (t, $J$ = 7.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 145.3, 140.6, 134.9 (d, $J$ = 32.9 Hz), 133.8, 129.6, 128.2, 127.9, 126.5 (q, $J$ = 3.7 Hz), 123.11 (d, $J$ = 271.4 Hz). $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -63.2. HRMS (ESI), *m/z* calcd. for $C_{13}H_9F_3NaO_2S$ ($[M+Na]^+$) 309.0168, found: 309.0168.

***Ethyl 4-(phenylsulfonyl)benzoate (3i).***[34] The product was isolated by flash chromatography (eluent:

EA/PE = 1/22) as a yellow oil (242 mg, 83%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 (d, $J$ = 8.4 Hz, 2H), 8.00 (d, $J$ = 8.8 Hz, 2H), 7.94 (d, $J$ = 7.6 Hz, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.51 (t, $J$ = 7.6 Hz, 2H), 4.38 (dd, $J$ = 14.0 Hz,7.2 Hz, 2H), 1.37 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 145.4, 140.9, 134.7, 133.6, 130.4, 129.5, 127.8, 127.7, 61.7, 14.2. HRMS (ESI), *m/z* calcd. for $C_{15}H_{14}NaO_4S$ ($[M+Na]^+$) 313.0505, found: 313.0499.

***1-Nitro-4-(phenylsulfonyl)benzene (3j).***[32] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow solid (247 mg, 94%): mp: 141-142 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.34 (d, $J$ = 8.4 Hz, 2H), 8.13 (d, $J$ = 8.4 Hz, 2H), 7.97 (d, $J$ = 7.2 Hz, 2H), 7.64 (t, $J$ = 7.2 Hz, 1H), 7.56 (t, $J$ = 7.5 Hz, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 150.3, 147.4, 140.0, 134.1, 129.7, 129.0, 128.0, 124.5. HRMS (ESI), *m/z* calcd. for $C_{12}H_9NNaO_4S$ ($[M+Na]^+$) 286.0144, found: 286.0142.

***N-(4-(phenylsulfonyl)phenyl)acetamide (3l).***[31] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (270 mg, 98%): mp: 180-182 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.90 (d, $J$ = 6.6 Hz, 2H), 7.84 (d, $J$ = 7.2 Hz, 2H), 7.81 (s, 1H), 7.65 (d, $J$ = 7.8 Hz, 2H), 7.55 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 6.9 Hz, 2H), 2.17 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 168.9, 142.6, 141.7, 135.9, 133.2, 129.3, 129.0, 127.4, 119.6, 24.7. HRMS (ESI), *m/z* calcd. for $C_{14}H_{13}NNaO_3S$ ($[M+Na]^+$) 298.0508, found: 298.0510.

***2-(Phenylsulfonyl)thiophene (3m).***[32] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (200 mg, 89%): mp: 116-118 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 7.2 Hz, 2H), 7.70 (dd, $J$ = 3.6 Hz, 1H), 7.64 (dd, $J$ = 4.8 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.52 (t, $J$ = 7.5 Hz, 2H), 7.08 (dd, $J$ = 4.8, 4.2 Hz, 1H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 143.1, 142.1, 133.9, 133.4, 133.3, 129.3, 127.8, 127.3. HRMS (ESI), *m/z* calcd. for $C_{10}H_9O_2S_2$ ($[M+H]^+$) 225.0038, found: 225.0037.

***1,2-Bis(phenylsulfonyl)benzene (3n).***[37] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow solid (161 mg, 45%): mp: 109-110 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.49 (t, $J$ = 3.9 Hz, 2H), 7.97 (d, $J$ = 7.8 Hz, 4H), 7.84 (t, $J$ = 3.9 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 2H), 7.51 (t,

$J$ = 7.5 Hz, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 141.5, 140.3, 133.9, 133.3, 128.7, 128.0. HRMS (ESI), *m/z* calcd. for $C_{18}H_{14}NaO_4S_2$ ($[M+Na]^+$) 381.0226, found: 381.0235.

***(Butylsulfonyl)benzene (3o).***[38] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow oil (159 mg, 80%); $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.91 (d, $J$ = 7.8 Hz, 2H), 7.65 (t, $J$ = 7.2 Hz, 1H), 7.57 (t, $J$ = 7.8 Hz, 2H), 3.08 (t, $J$ = 7.8 Hz, 2H), 1.73-1.65 (m, 2H), 1.39 (m, 2H), 0.89 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 139.2, 133.6, 129.2, 128.0, 56.1, 24.6, 21.5, 13.5. HRMS (ESI), *m/z* calcd. for $C_{10}H_{14}NaO_2S$ ($[M+Na]^+$) 221.0607, found: 221.0606.

***1-Methoxy-4-tosylbenzene (3p).***[34] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (176 mg, 67%): mp: 157-158 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 7.8 Hz, 2H), 7.79 (d, $J$ = 7.2 Hz, 2H), 7.27 (d, $J$ = 7.8 Hz, 2H), 6.95 (d, $J$ = 7.2 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).$^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 163.1, 156.3, 143.7, 133.8, 129.8, 129.7, 127.4, 114.4, 55.6, 21.5. HRMS (ESI), *m/z* calcd. for $C_{14}H_{14}NaO_3S$ ($[M+Na]^+$) 285.0556, found: 285.0563.

***1-Methoxy-2-tosylbenzene (3p').***[39] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (79 mg, 30%): mp: 105-107 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.14 (d, $J$ = 7.8 Hz, 1H), 7.85 (d, $J$ = 7.8 Hz, 2H), 7.52 (t, $J$ = 7.8 Hz, 1H), 7.27 (d, $J$ = 7.8 Hz, 2H), 7.09 (t, $J$ = 7.5 Hz, 1H), 6.89 (d, $J$ = 7.8 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 157.0, 143.7, 138.6, 135.3, 129.8, 129.3, 129.1, 128.5, 120.5, 112.4, 55.8, 21.6. HRMS (ESI), *m/z* calcd. for $C_{14}H_{14}NaO_3S$ ($[M+Na]^+$) 285.0556, found: 285.0562.

***4,4'-Sulfonylbis(methylbenzene) (3q).***[33] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (192 mg, 78%): mp: 157-158 ºC; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 139.1, 129.9, 127.7, 21.5. HRMS (ESI), *m/z* calcd. for $C_{14}H_{14}NaO_2S$ ($[M+Na]^+$) 269.0607, found: 269.0615.

***1-Methyl-2-tosylbenzene (3q').***[34] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white oil (22 mg, 9%); $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 7.8 Hz, 1H), 7.74 (d, $J$ = 7.8 Hz, 2H), 7.46 (t, $J$ = 7.2 Hz, 1H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.29 (d, $J$ = 7.8 Hz, 2H),

7.22 (d, $J$ = 7.2 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 143.95, 139.20, 138.33, 137.89, 133.44, 132.62, 129.65, 129.29, 127.77, 126.42, 21.58, 20.20. HRMS (ESI), *m/z* calcd. for $C_{14}H_{14}NaO_2S$ ($[M+Na]^+$) 269.0607, found: 269.0613.

Mixture of ***2-Tosylnaphthalene (3r) and 1-Tosylnaphthalene (3r').***[35] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a pink solid (272 mg, 96%); $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.64 (d, $J$ = 8.4 Hz, 1H), 8.56 (s, 1H), 8.49 (d, $J$ = 7.2 Hz, 1H), 8.08 (d, $J$ = 8.4 Hz, 1H), 7.97 (d, $J$ = 7.8 Hz, 1H), 7.83-7.98 (m, 7H), 7.66-7.57 (m, 3H), 7.53 (t, $J$ = 7.2 Hz, 1H), 7.29 (d, $J$ = 7.2 Hz, 2H), 7.25 (s, 1H), 2.38 (s, 3H), 2.36 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.2, 144.0, 138.9, 138.7, 136.2, 135.0, 134.2, 129.9, 129.8, 129.6, 129.4, 129.0, 129.0, 128.8, 128.5, 128.3, 127.9, 127.8, 127.6, 127.5, 126.8, 124.4, 124.4, 122.7, 21.5. HRMS (ESI), *m/z* calcd. for $C_{17}H_{14}NaO_2S$ ($[M+Na]^+$) 305.0607, found: 305.0604.

***1,2-Dichloro-4-tosylbenzene (3s).***[36] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (224 mg, 75%): mp: 252-255 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.00 (s, 1H), 7.81 (d, $J$ = 7.2 Hz, 2H), 7.74 (d, $J$ = 7.8 Hz, 1H), 7.56 (d, $J$ = 8.4 Hz, 1H), 7.33 (d, $J$ = 7.2 Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 144.9, 141.9, 138.0, 137.7, 133.9, 131.3, 130.2, 129.4, 127.8, 126.5, 21.6. HRMS (ESI), *m/z* calcd. for $C_{13}H_{10}Cl_2NaO_2S$ ($[M+Na]^+$) 322.9671, found: 322.9676.

***1-Bromo-4-tosylbenzene (3t).***[33] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (288 mg, 93%): mp: 135-136 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.79 (dd, $J$ = 12.9, 8.1 Hz, 4H), 7.62 (d, $J$ = 7.8 Hz, 2H), 7.30 (d, $J$ = 7.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 144.5, 141.1, 138.2, 132.5, 130.0, 129.0, 128.2, 127.7, 21.6. HRMS (ESI), *m/z* calcd. for $C_{13}H_{11}BrNaO_2S$ ($[M+Na]^+$) 332.9555, found: 332.9551.

***4,4'-Ditosyl-1,1'-biphenyl (3u).*** The product was isolated by flash chromatography (eluent: EA/PE = 1/5) as a yellow solid (439 mg, 95%): mp: >300 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.00 (d, $J$ = 8.4 Hz, 2H), 7.85 (d, $J$ = 7.8 Hz, 2H), 7.64 (d, $J$ = 7.8 Hz, 2H), 7.32 (d, $J$ = 7.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C

NMR (150 MHz, $CDCl_3$) $\delta$ 144.5, 143.9, 141.9, 138.4, 130.1, 128.3, 128.2, 127.8, 21.6. HRMS (ESI), *m/z* calcd. for $C_{26}H_{23}O_4S_2$ ($[M+H]^+$) 463.1032, found: 463.1041.

***Tris(4-tosylphenyl)methane (3v).*** The product was isolated by flash chromatography (eluent: EA/PE = 1/2) as a yellow solid (643 mg, 91%): mp: 75-77 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.81 (dd, $J$ = 12.9, 8.1 Hz, 12H), 7.30 (d, $J$ = 7.2 Hz, 6H), 7.10 (d, $J$ = 7.2 Hz, 6H), 5.57 (s, 1H), 2.40 (s, 9H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 146.6, 144.5, 141.2, 138.3, 130.1, 130.0, 128.0, 127.8, 56.1, 21.6. HRMS (ESI), *m/z* calcd. for $C_{40}H_{34}NaO_6S_3$ ($[M+Na]^+$) 729.1410, found: 729.1416.

***5-Tosylindolin-2-one (3w).*** The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow solid (167 mg, 58%): mp: 250-253 °C; $^1$H NMR (400 MHz, DMSO) $\delta$ 10.81 (s, 1H), 7.78 (d, $J$ = 8.4 Hz, 3H), 7.71 (s, 1H), 7.40 (d, $J$ = 8.0 Hz, 2H), 6.96 (d, $J$ = 8.0 Hz, 1H), 3.56 (s, 2H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 176.4, 148.5, 143.8, 139.2, 133.6, 130.0, 128.1, 127.3, 127.0, 123.3, 109.3, 35.5, 20.9. HRMS (ESI), *m/z* calcd. for $C_{15}H_{13}NNaO_3S$ ($[M+Na]^+$) 310.0508, found: 310.0521.

***Dibenzo[b,d]thiophene 5,5-dioxide (3x).***[40] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow solid (214 mg, 99%): mp: 182-183 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.82 (dd, $J$ = 11.6, 7.6 Hz, 2H), 7.65 (td, $J$ = 7.6, 1.1 Hz, 1H), 7.54 (td, $J$ = 7.6, 0.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.8, 133.9, 131.6, 130.4, 122.2, 121.6. HRMS (ESI), *m/z* calcd. for $C_{12}H_9O_2S$ ($[M+H]^+$) 217.0318, found: 217.0325.

***4,4'-Sulfonylbis(chlorobenzene) (3y).***[41] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a white solid (232 mg, 81%): mp: 143-146 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 8.4 Hz, 4H), 7.49 (d, $J$ = 8.4 Hz, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.2, 139.8, 129.8, 129.1. HRMS (ESI), *m/z* calcd. for $C_{12}H_8Cl_2NaO_2S$ ($[M+Na]^+$) 308.9514, found: 308.9511.

***1,3-Dimethyl-5-tosylbenzene (3z)***.[42] The product was isolated by flash chromatography (eluent: EA/PE = 1/22) as a yellow oil (242 mg, 93%); $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 2H), 7.27 (d, $J$ = 8.4 Hz, 2H), 7.17 (d, $J$ = 7.8 Hz, 1H), 7.02 (s, 1H), 2.39 (s, 6H),

2.35 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 144.2, 143.7, 138.7, 137.7, 136.2, 133.3, 129.5, 129.5, 127.6, 127.0, 21.5, 21.3, 20.1. HRMS (ESI), *m/z* calcd. for $C_{15}H_{17}O_2S$ ($[M+H]^+$) 260.0944, found: 260.0956.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Screening of reaction conditions and NMR spectra for compounds (PDF)

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