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One-Pot Synthesis of Aryl Sulfones from Organometallic Reagents and Iodonium Salts

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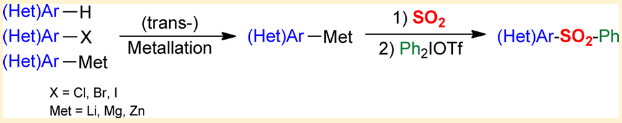
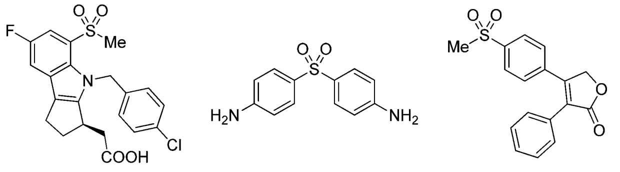
Ⓢ *Supporting Information*

ABSTRACT: A transition-metal-free arylation of lithium, magnesium, and zinc sulfinates with diaryliodonium salts is described. The sulfinic acid salts were prepared from the reaction of the corresponding organometallic reagents and sulfur dioxide. Combination of the three single steps (preparation of the organometallic compound, sulfinate formation, and arylation) leads to a one-pot sequence for the synthesis of aryl sulfones from simple starting materials. The chemoselectivity of unsymmetrical diaryliodonium salts has been investigated. Potential and limitations of this method will be discussed.



■ INTRODUCTION

The sulfonyl moiety is an important motif in organic synthesis[1,2] and especially in medicinal chemistry.[3] Aryl sulfones are useful building blocks and found in many drugs, such as the antibacterial Dapsone,[4] Laropiprant,[5] a prostaglandin D_2 antagonist, or the COX-2 inhibitor Vioxx (Figure 1).[6] Furthermore, diaryl sulfones have shown promising antitumor and antifungal activities or inhibition of the HIV-1 reverse transcriptase.[7]



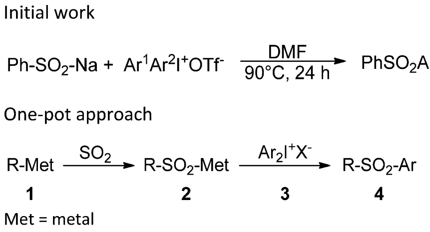
Laropiprant Dapsone Vioxx

Figure 1. Biologically active aryl sulfones.

Due to this importance, numerous strategies for synthesis have been reported. The most common are the oxidation of sulfides[1,2] and the sulfonylation of arenes in the presence of strong acids.[1,2] In recent years efficient routes based on transition-metal-catalyzed[8,9] and transition-metal-free[10] coupling reactions of sodium sulfinates have been introduced. In the course of our investigations toward new methods for the synthesis of sulfonyl-group-containing molecules, we were able to develop a mild, transition-metal-free protocol based on the reaction between arylsulfinic acid sodium salts and diaryliodonium salts (Scheme 1).[11,12]

Although various diaryliodonium salts are commercially available or can be prepared easily,[13,14] the access to aryl sulfinic acid sodium salts is rather limited.[15−17] Therefore, we developed a method based on the in situ generation of arylsulfinic acid lithium salts from the corresponding organolithium reagents.[18,19] This method allows the direct transformation of readily availbale (hetero)aromatic halides and (hetero)arenes into diaryl sulfones. Herein report the extension of this method to the arylation of magnesium and zinc sulfinates and the corresponding one-pot protocols as well as the scope and limitations of these methods.

Scheme 1. Routes to Aryl Sulfones Based on Diaryliodonium Salts



■ RESULTS AND DISCUSSION

Aryl Sulfones from Organolithium Reagents. In preliminary studies, we investigated the reaction of diphenyliodonium triflate **3a** and benzenesulfinic acid lithium salt **2a**, prepared in quantitative yield from phenyllithium and sulfur dioxide (Table 1).[18] The best results were achieved in aprotic polar solvents such as DMF, DMSO, and NMP (entries 1−3). Aprotic nonpolar solvents such as THF or dioxane gave lower yields (entries 4 and 5). The arylation reaction is insensitive to air and moisture and can be performed with commercial grade solvents without an inert atmosphere in similar yields (entries 6 and 7). The nature of the diphenyliodonium counterion X^- has a marked effect on the yield. While similar yields were obtained with non-nucleophilic counterions (OTf^-, PF_6^-, or BF_4^-) (entries 7−9), a significant decrease of the yield was observed for more nucleophilic counterions, such as OTs^- or Cl^- (entries 10 and 11).[20] To our delight, it was possible to merge the two single steps, generation of the lithium sulfinate

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Table 1. Survey of Solvents and Influence of the Counterion[a]

$$\underset{\mathbf{1a}}{\text{Ph-Li}} \xrightarrow{SO_2} \underset{\mathbf{2a}}{\text{Ph-SO}_2\text{-Li}} + \underset{\mathbf{3}}{Ph_2I^+X^-} \xrightarrow[90\ °C,\ 24\ h]{\text{solvent}} \underset{\mathbf{4}}{PhSO_2Ph}$$

entry	solvent	salt	X⁻	yield (%)[b]
1	DMF	**3a**	OTf⁻	84
2	DMSO	**3a**	OTf⁻	80
3	NMP	**3a**	OTf⁻	83
4	1,4-dioxane	**3a**	OTf⁻	47
5	THF	**3a**	OTf⁻	26
6[c]	DMSO	**3a**	OTf⁻	79
7[c]	DMF	**3a**	OTf⁻	86
8	DMF	**3b**	PF_6^-	86
9	DMF	**3c**	BF_4^-	91
10	DMF	**3d**	OTs⁻	65
11	DMF	**3e**	Cl⁻	60
12[d]	DMF	**3a**	OTf⁻	83

[a] Reaction conditions: 1.5 equiv of **2a** and 1.0 equiv of **3** in 1.0 mL of solvent at 90 °C for 24 h. [b] Isolated yield. [c] Reaction run without exclusion of air or moisture. [d] Performed as one-pot-reaction/without isolating the sulfinic acid salt.

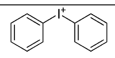
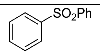
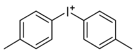
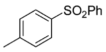
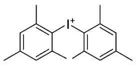
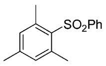
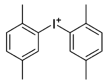
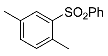
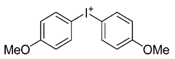
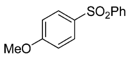
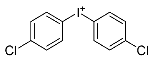
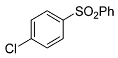
and arylation with an iodonium salt, into a one-pot sequence. Thus, the reaction of PhLi with sulfur dioxide followed by removal of solvents and excess SO_2 and subsequent reaction of the crude sulfinate with Ph_2IOTf furnished the desired sulfone **4a** in comparable 83% yield (compare entries 1 and 12).[21]

With the optimized conditions in hand, we started to investigate the scope of this reaction. First we performed the reaction between benzenesulfinic lithium salt (**2a**) and various symmetrical diaryliodonium salts **3** (Table 2). Good to excellent yields were obtained in all cases (entries 1−6).

Two of the most common procedures for the preparation of organolithium reagents are the lithium−halogen exchange and the direct deprotonation/lithiation of acidic C−H groups.[22] To our delight, both procedures are compatible with our direct arylation approach. The combination of a lithiation reaction with our arylation protocol leads to a four-step, one-pot reaction sequence for the synthesis of aryl sulfones. This sequence consists of the following: (1) generation of the organolithium reagent via exchange or deprotonation; (2) reaction of the lithium reagent with liquid SO_2; (3) removal of excess SO_2 and solvent exchange; (4) treatment of the obtained crude lithium sulfinate with diaryliodonium salts. Using this protocol we were able to transform various (hetero)arenes **5** and (hetero)aromatic halides **6** directly into the corresponding diaryl sulfones **4** (Table 3).[23] Thus, benzene **5a** can be transformed directly into diaryl sulfone **4a** in 52% yield (entry 1). Diaryl sulfone **4g** could be obtained either via direct deprotonation of dimethoxybenzene **5b** or from the corresponding iodoarene **6a** in similar yields (entries 2 and 3). Several anisole derivatives could be functionalized in a similar manner (entries 4−8). Generation of the organolithium reagent via deprotonation or lithium−halogen exchange can be used as complementary methods. Depending on the efficiency of both methods, either similar results are obtained (entries 2 and 3) or one procedure leads to higher yields (entries 4 and 5). Similar results were observed for the lithium-exchange protocol with different halogenated arenes. In the case of aryl sulfone **4e** better results were obtained with the corresponding aryl bromide **6d** (entires 7 and 8). For aryl sulfone **4k**, the reaction with the aryl iodide **6h** furnished the product in higher yield (entries 10 and 11). Arenes bearing "directed metalation groups" (DMG),[24] such as a carbamate **5d** and amide **5e**, could be successfully transformed directly into the diaryl sulfones **4l** and **4m** (entries 12 and 13). More importantly, different heteroarenes, such as thiophene (**5f**), *N*-methylpyrrole (**5g**), pyridines **5h** and **6i**, or ferrocene (**5i**), could be functionalized in a similar manner (entries 14−18).

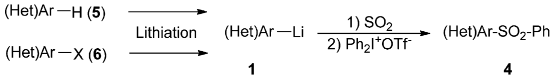
Table 2. Arylation of Benzenesulfinic Acid Lithium Salt 2a[a]

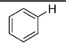
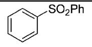
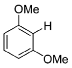
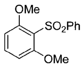
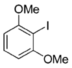
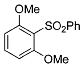
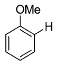
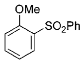
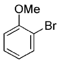
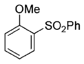
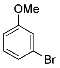
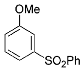
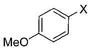
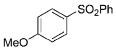
$$\underset{\mathbf{2a}}{\text{Ph-SO}_2\text{-Li}} + \underset{\mathbf{3}}{Ar^1Ar^2I^+OTf^-} \xrightarrow[90°C,\ 24\ h]{\text{DMF}} \underset{\mathbf{4}}{PhSO_2Ar}$$

entry	$Ar^1Ar^2I^+$	product	yield (%)[b]
1	 **3a**	 **4a**	84
2	 **3f**	 **4b**	80
3	 **3g**	 **4c**	67
4	 **3h**	 **4d**	76
5[c]	 **3i**	 **4e**	74
6	 **3j**	 **4f**	78

[a] Reaction conditions: 1.5 equiv of **2a** and 1.0 equiv of **3** in 1.0 mL of DMF for 24 h at 90 °C at a 0.5 mmol scale. [b] Isolated yield. [c] Tosylate as counterion.

Table 3. Direct Lithiation Approach to Diaryl Sulfones[a]



entry	(Het)Ar-H/X	lithiation reagent	product	yield (%)[b]
1[c]	 **5a**	*n*BuLi, TMEDA	 **4a**	52
2[c]	 **5b**	*n*BuLi	 **4g**	79
3[d]	 **6a**	*n*BuLi	 **4g**	74
4[c]	 **5c**	*n*BuLi, TMEDA	 **4h**	61
5[d]	 **6b**	*n*BuLi	 **4h**	97
6[d]	 **6c**	*n*BuLi	 **4i**	92
7[d]	 **6d**: X = Br	*n*BuLi	 **4e**	78
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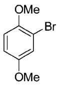
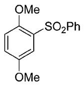
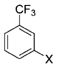
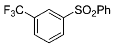
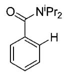
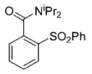
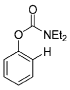
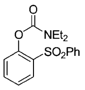
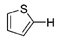
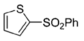
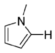
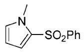
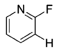
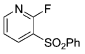
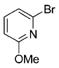
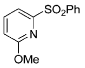
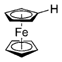
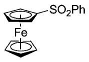
9[d]	 **6f**	*n*BuLi	 **4j**	42
10[d]	 **6g**: X = Br	*n*BuLi	 **4k**	74
11[d]	**6h**: X = I			83
12[c]	 **5d**	*s*BuLi, TMEDA	 **4l**	68
13[c]	 **5e**	*s*BuLi, TMEDA	 **4m**	47
14[c]	 **5f**	*n*BuLi	 **4n**	85
15[c]	 **5g**	*n*BuLi, TMEDA	 **4o**	51
16[c]	 **5h**	LDA	 **4p**	55
17[d]	 **6i**	*t*BuLi	 **4q**	36
18[c]	 **5i**	*t*BuLi	 **4r**	42

[a] Reaction conditions: sulfinate **2** (prepared from 1.5 equiv of **5** or **6**) and 1.0 equiv of **3a** in 1.0 mL of DMF for 24 h at 90 °C at a 0.5 mmol scale. [b] Isolated yield. [c] Organolithium compound was prepared via deprotonation. [d] Organolithium compound was prepared via halogen−metal exchange.

To our delight, this method is not limited to (hetero)-aryllithium reagents, as in the case of the corresponding sodium sulfinates. By using primary, secondary, or tertiary alkyllithium reagents **1b**−**e**, the desired alkyl aryl sulfones **7a**−**d** are obtained in excellent yields (Scheme 2).

Scheme 2. Synthesis of Alkyl Aryl Sulfones

$$\underset{\mathbf{1}}{\text{Alkyl-Li}} \xrightarrow[\text{2) Ph}_2\text{IOTf}]{\text{1) SO}_2} \underset{\mathbf{7}}{\text{Alkyl-SO}_2\text{-Ph}}$$

1b:	MeLi	**7a:**	84 %
1c:	*n*BuLi	**7b:**	89 %
1d:	*t*BuLi	**7c:**	76 %
1e:	*s*BuLi	**7d:**	93 %

Aryl Sulfones from Organomagnesium Reagents. The lithiation approach is inherently limited by the low functional group tolerance of organolithium reagents. As shown in Table 3, the direct functionalization of sensitive heteroaromatics, such as the pyridine derivatives **5h** or **6i**, leads to the desired heteroaryl sulfones in low to moderate yields. Therefore, we investigated similar reactions with organomagnesium reagents. Various procedures for the synthesis of these Grignard reagents exist. In addition, highly functionalized organomagnesium reagents, bearing various sensitive groups, can be prepared efficiently.[25,26] We envisioned that the higher functional group compatibility of Grignard reagents should lead to a broader scope of our one-pot sequence.[27]

In initial investigations with different phenyl magnesium sulfinates we observed a pronounced effect of the Grignard counterion. We started our experiments with a study of the influence of different solvents and counterions (Table 4). As model system, we chose the reaction between benzenesulfinic acid magnesium salts **2b**−**e**, prepared from different phenylmagnesium halides, and diphenyliodonium triflate (**3a**). For the reaction with the benzenesulfinic acid magnesium salt **2b** best results were obtained with DMSO as solvent (entry 3). Other polar aprotic solvents, such as NMP or DMF, lead to lower yield (entries 1 and 2). Unfortunately, the yield decreases for sulfinates prepared from other "Knochel"-type phenyl-Grignards.[28] The presence of additional LiCl in the reaction mixture leads to a slightly lower yield (entry 4). Changing the Grignard counterion from chloride to bromide or iodide, has a marked effect on the reaction yield. In the case of the sulfinate prepared from PhMgI·LiCl the yield drops to 22%. Analysis of the reaction mixture via GC/MS shows the formation of considerable amounts of halobenzenes **6**. These side-products can be formed in a competing arylation of the halide counterions.[29] Considering this side-reaction, a decreased yield in the presence of more nucleophilic counterions or excess lithium chloride should be expected. Unfortunately, various additives or cosolvents could not suppress this side-reaction and improve the overall yield. The only option to enhance the yield of the desired sulfone, is the use of a 3-fold excess of the iodonium reagent. By employing a great excess of the iodonium salt, the yield can be increased considerably for all types of Grignard reagent (entries 8−10).

With the insights gained from the optimization study, we investigated the reaction of benzenesulfinic acid magnesium chloride salt **2f** with various symmetrical diaryliodonium salts **3** (Table 5). In some cases good yields were obtained using slight excess of the magnesium sulfinate (entries 1−3). In other cases the yield of the desired sulfone could be increased dramatically by employing a 3-fold excess of the iodonium salt (entries 4−6).

As mentioned previously, Grignard reagents can be prepared by various protocols (see above). To our delight, two of those methods, the direct insertion of magnesium into organic halides (in the presence or absence of lithium chloride)[28] and the magnesium−halogen exchange[30] are compatible with our arylation protocol. Therefore, we were able to develop a similar one-pot, four-step synthesis of arylsufones via in situ-generated organomagnesium reagents. Generation of the organomagnesium species followed by the reaction of the Grignard reagent with SO_2, removal of excess SO_2, solvent exchange, and treatment of the obtained crude magnesium sulfinate with a diaryliodonium salt leads to the desired aryl sulfones (Table 6). Various aryl chlorides and bromides can be transformed rapidly into the corresponding diaryl sulfones (entries 1 and 2). Especially the halogen−magnesium exchange with *i*PrMgCl·LiCl[30] is well suited for a combination with our arylation procedure. It enables the in situ preparation of the (hetero)arylmagnesium chlorides even from the corresponding bromo- or iodo(hetero)arenes, thus avoiding the formation of more nucleophilic counterions.[31] Using the halogen−magnesium exchange reaction even aryl iodides bearing sensitive functional groups, such as an ester or cyano group, can be transformed directly into the desired aryl sulfones (entries 4 and 5). In general, higher yields were obtained with an excess of

Table 4. Survey of Solvents and Influence of the Grignard Counterion[a]

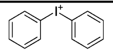
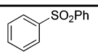
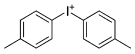
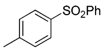
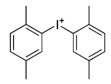
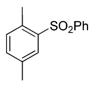
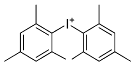
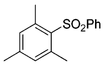
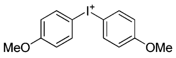
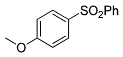
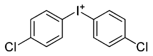
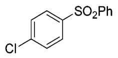
$$\underset{\mathbf{2}}{\text{Ph-SO}_2\text{-MgX}} + \underset{\mathbf{3a}}{\text{Ph}_2\text{I}^+\text{OTf}^-} \xrightarrow[90\ ^\circ\text{C, t}]{\text{solvent}} \underset{\mathbf{4}}{\text{ArSO}_2\text{Ph}}\ \ \underset{\mathbf{6}}{(+\ \text{Ph-X})}$$

entry	X	sulfinate	equiv of $PhSO_2MgX$	equiv of Ph_2IOTf	solvent	*t* (h)	yield (%)[b]
1	Cl	**2b**	1.3	1.0	DMF	24	31
2	Cl	**2b**	1.3	1.0	NMP	24	22
3	Cl	**2b**	1.3	1.0	DMSO	24	75 (57)[c]
4	Cl·LiCl	**2c**	1.3	1.0	DMSO	24	62
5	Br·LiCl	**2d**	1.3	1.0	DMSO	24	31
6	I·LiCl	**2e**	1.3	1.0	DMSO	24	22
7	Cl	**2b**	1.0	3.0	DMSO	24	90
8	Cl·LiCl	**2c**	1.0	3.0	DMSO	24	81
9	Br·LiCl	**2d**	1.0	3.0	DMSO	24	40
10	I·LiCl	**2e**	1.0	3.0	DMSO	24	37

[a] Reaction conditions: equiv of reagents as indicated in 1.0 mL of solvent for 24 h at 90 °C at a 0.5 mmol scale. [b] Isolated yield. [c] Reaction run without exclusion air or moisture.

Table 5. Arylation of Benezesulfinic Acid Magnesium Salt **2b**[a]

$$\underset{\textbf{2b}}{\text{Ph-SO}_2\text{-MgCl}} + \underset{\textbf{3}}{\text{Ar}^1\text{Ar}^2\text{I}^+\text{OTf}^-} \xrightarrow[90\ °\text{C},\ 24\ \text{h}]{\text{DMSO}} \underset{\textbf{4}}{\text{Ar}^1\text{SO}_2\text{Ph}}$$

entry	$Ar^1Ar^2I^+OTf^-$	Ar^1SO_2Ph	yield [%][b]
1	 **3a**	 **4a**	75
2	 **3f**	 **4b**	62
3	 **3h**	 **4c**	56
4	 **3g**	 **4d**	25 (80)[c]
5[d]	 **3i**	 **4e**	27 (62)[c]
6	 **3j**	 **4f**	52 (74)[c]

[a] Reaction conditions: 1.5 equiv of benzenesulfinic acid salt **2b**, 1.0 equiv of iodonium salt **3** in 1.0 mL of DMSO at 90 °C for 24 h at a 0.5 mmol scale. [b] Isolated yields. [c] 1.0 equiv of salt **2b** and 3.0 equiv of salt **3**. [d] Tosylate as counterion.

the iodonium salt (compare entries 3, 5–8). In some cases the yield could be doubled by reversing the reaction stoichiometry (entries 3, 5, 7, and 8). This method is not limited to aryl Grignard reagents. The reaction of alkyl organomagnesium reagents, prepared either in situ or obtained from commercial sources, leads to the desired alkyl aryl sulfones in 17–72% yield (entries 9–11).

The deprotonation of acidic C–H-bonds with suitable magnesium amide bases is another very efficient approach for the synthesis of Grignard reagents.[32] Unfortunately, this procedure is not compatible with our arylation approach. Although thiophene could be transformed into the desired sulfone in 50% overall yield, the direct functionalization of several other heterocycles, such as furan or several nitrogen heterocycles, with tmpMgCl·LiCl was not successful (Scheme 3).

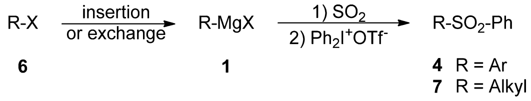
Aryl Sulfones from Organozinc Compounds. Next we turned our attention to reactions with organozinc compounds. Organozinc reagents are known for their exceptional functional group compatibility and can be prepared via various efficient procedures.[25,26,33,34] Therefore, one could expect a broader scope for our one-pot aryl sulfone synthesis. We started our investigations with the reaction between benzenesulfinic acid zinc salt and various diaryliodonium salts (Table 7). The zinc sulfinate was prepared from phenylmagnesium chloride via transmetalation with $ZnCl_2$ and subsequent reaction with sulfur dioxide. Although this procedure leads to the formation of stoichiometric amounts of halide ions, our optimized conditions from the corresponding transformation with Grignard reagents (DMSO, 1.5 equiv of RSO_2Met, 1.0 equiv of Ar_2IOTf) proved to be suitable for reactions with the benzenesulfinic acid zinc salt. The desired diaryl sulfones were obtained in very good yields (entries 1–3, 5, and 6).

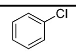
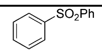
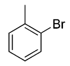
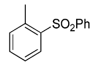
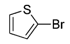
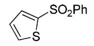
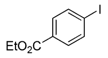
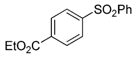
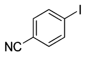
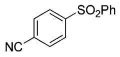
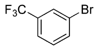
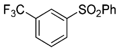
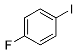
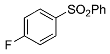
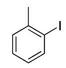
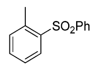
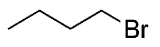
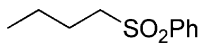
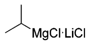
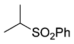
We next examined the scope of our one-pot aryl sulfone synthesis with different organozinc reagents obtained via transmetalation or direct zinc insertion in the presence of LiCl.[35] Unfortunately, the above-mentioned reactions conditions for benzenesulfinic acid zinc salt proved unsuitable for various other aryl and alkyl zinc reagents. Therefore, we decided to investigate the reaction of the zinc sulfinate **2g** in more detail. The ester-substituted zinc sulfinate **2g** was prepared from the corresponding aryl iodide via magnesium–halogen exchange with *i*PrMgCl·LiCl, transmetalation with $ZnCl_2$, and subsequent reaction with SO_2. With this specific synthesis of the zinc sulfinate, we were able to examine *worst case* reaction conditions in the presence of a great excess of halide ions (Table 8). Indeed the reaction of 1.5 equiv of the sulfinic acid zinc salt with 1.0 equiv of diphenyliodonium triflate in different polar aprotic solvents furnished the desired sulfone in low yields (entries 1–3). Performing the reaction in DMSO with 3.0 equiv of the iodonium salt did not affect the yield (entry 4). However, the yield could be improved dramatically by performing the reaction in NMP or DMF and employing a 3-fold excess of the iodonium salt (entries 5 and 6).

With these optimized reaction conditions, various organozinc reagents could be transformed into the corresponding aryl sulfones (Table 9). Several highly functionalized aryl sulfones or heteroaryl sulfones could be prepared in high yields (entries 2–6 and 8). The organozinc reagents were obtained via transmetalation from the corresponding organomagensium compounds (entries 1–8) or from direct zinc insertion in the presence of LiCl (entries 9–11). The latter procedures allow the direct synthesis of aryl alkyl sulfones from functionalized alkyl iodides (entries 10 and 11).

SO_2 Surrogates. SO_2 is a toxic and corrosive gas, which requires careful handling and the appropriate equipment and safety procedures. Although the proper handling of sulfur dioxide should cause no problems for a well-trained chemist, the replacement of gaseous sulfur dioxide with solid SO_2 surrogates should lead to a simpler process. Therefore, we performed our one-pot sequence with two common SO_2 surrogates, the DMAP·SO_2 complex from Vogel[36] and the

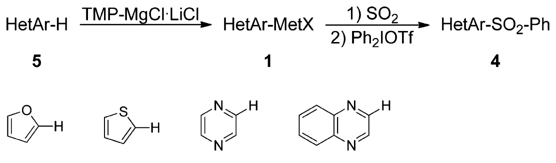
Table 6. Direct Magnesiation Approach to Diaryl Sulfones[a]



entry	R-X or R-MgX	Metallation reagents	$PhSO_2Ar$	Yield [%][b]
1[c]	 **6j**	Mg	 **4a**	75
2[c]	 **6k**	Mg, LiCl	 **4s**	(21)[e]
3[d]	 **6l**	*i*PrMgCl·LiCl	 **4n**	33 (73)[e]
4[d]	 **6m**	*i*PrMgCl·LiCl	 **4t**	46 (34)[e]
5[d]	 **6n**	*i*PrMgCl·LiCl	 **4u**	25 (49)[e]
6[d]	 **6g**	*i*PrMgCl·LiCl	 **4k**	24 (38)[e]
7[d]	 **6o**	*i*PrMgCl·LiCl	 **4v**	30 (66)[e]
8[d]	 **6p**	*i*PrMgCl·LiCl	 **4s**	20 (49)[e]
9[c]	 **8a**	Mg	 **7b**	17
10	Me–MgCl **1e**	-	Me–SO_2Ph **7a**	51
11	 **1g**	-	 **7e**	72

[a]Reaction conditions: 1.5 equiv of aryl halide and 1.0 equiv of Ph_2IOTf in 1.0 mL of DMSO for 24 h at 90 °C at a 0.5 mmol scale. [b]Isolated yield. [c]Grignard reagent was prepared by halogen−metal exchange with iPrMgCl·LiCl. [d]Grignard reagent was prepared by insertion of magnesium. [e]1.0 equiv of aryl halide, 3.0 equiv of Ph_2IOTf in 1.0 mL of DMSO for 24 h at 90 °C at a 0.5 mmol scale.

Scheme 3. Direct Metalation Approach by Deprotonation with tmpMgCl·LiCl



5j, 0% **5f**, 50% **5k**, 0% **5l**, 0%

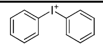
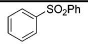
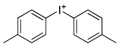
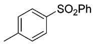
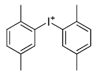
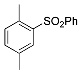
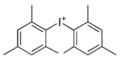
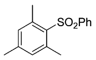
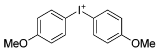
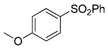
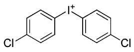
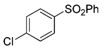
DABSO reagent pioneered by Willis.[17] Unfortunately, the yield decreased considerably to 54% with DABSO and 37% with DMAP·SO_2 (Scheme 4). We assume, that the nucleophilic nitrogen bases DABCO and DMAP can undergo a competing side-reaction with diaryliodonium salt.[37] These results show that gaseous sulfur dioxide is the optimal SO_2 source for this one-pot sequence.

Selectivity Studies. During our initial investigations with sodium sulfinates, we observed a highly chemoselective transfer of one aryl moiety from unsymmetrical diaryliodonium salts.[11] Since the preparation of symmetrical diaryliodonium salts can be difficult or expensive, unsymmetrical salts offer an attractive alternative.[13,14] Therefore, we investigated the chemoselectivity of several selected diaryliodonium salts in reactions with different benzenesulfinic acids salts (Table 10). In the case of the iodonium salt **3m** bearing an electron-rich 4-methoxyphenyl and an electron-poor 3-trifluoromethylphenyl group, a highly selective transfer of the electron-poor aryl moiety was observed for reactions with the lithium and zinc sulfinate (selectivity >12:1) (entries 3-1 and 3-3). Interestingly, reaction of the benzenesulfinic acid magnesium salt delivered the sulfone **4m** with the highest degree of selectivity (entry 3-2). Next, we performed reactions with unsymmetrical iodonium salts **3k** and **3l**, containing one phenyl group and one aryl group with substituents in the ortho positions. In all cases the bulky ortho-substituted aryl moiety was transferred selectively (entries 1 and 2).[38]

The chemoselectivity of unsymmetrical diaryliodonium salts with different steric bulk in the ortho positions was further investigated with the model substrate (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium triflate **3n** (Scheme 5). In the reaction of **3n** with benezenesulfinic acid lithium salt (**2a**) a mixture of the two diaryl sulfones **4c** and **4v** was obtained, with the sterically more demanding mesityl group being transferred

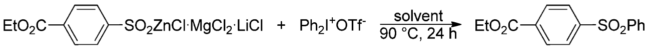
Table 7. Arylation of Benzenesulfinic Acid Zinc Salt 2f[a]

$$\underset{\mathbf{1}}{\text{Ph-MgCl}} \xrightarrow[\text{2) SO}_2]{\text{1) ZnCl}_2} \underset{\mathbf{2f}}{\text{Ph-SO}_2\text{-ZnCl·MgCl}_2} + \underset{\mathbf{3}}{\text{Ar}^1\text{Ar}^2\text{I}^+\text{OTf}^-} \xrightarrow[\text{90 °C, 24 h}]{\text{DMSO}} \underset{\mathbf{4}}{\text{Ar}^1\text{SO}_2\text{Ph}}$$

entry	$Ar^1Ar^2I^+OTf^-$	Ar^1SO_2Ph	yield [%][b]
1	 **3a**	 **4a**	67
2	 **3f**	 **4b**	74
3	 **3g**	 **4d**	74
4	 **3h**	 **4c**	32
5[c]	 **3i**	 **4e**	70
6	 **3j**	 **4f**	64

[a] Reaction conditions: 1.5 equiv of benzenesulfinic acid salt **2f**, 1.0 equiv of salt **3** in 1.0 mL of DMSO at 90 °C for 24 h at a 0.5 mmol scale. [b] Isolated yields. [c] OTs as counterion.

Table 8. Survey of Solvents and Influence of Stoichiometry[a]



2g **3a** **4t**

entry	equiv of Ar-SO_2-ZnX[b]	equiv of $Ph_2I^+OTf^-$	solvent	yield (%)[c]
1	1.5	1.0	DMSO	37
2	1.5	1.0	NMP	8
3	1.5	1.0	DMF	15
4	1.0	3.0	DMSO	43
5	1.0	3.0	NMP	75
6	1.0	3.0	DMF	85

[a] Reaction conditions: equiv of reagents as indicated in 1.0 mL of solvent for 24 h at 90 °C at a 0.5 mmol scale. [b] Preformed organozinc reagent. [c] Isolated yields.

preferentially (selectivity 3.3:1). Interestingly, the chemoselectivity can be reversed by the addition of a transition-metal catalyst. Performing the reaction in the presence of catalytic amounts of CuI leads to a preferential transfer of the less bulky *o*-tolyl moiety (selectivity 2.6:1).[39]

■ CONCLUSION

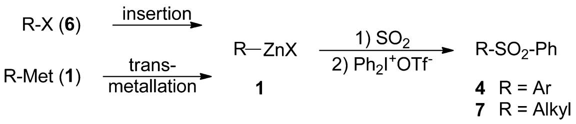
In summary, we have developed a synthesis of aryl sulfones from sulfinic acid lithium, magnesium, and zinc salts. This reaction has a very broad scope, and both aryl and alkyl sulfinates can be arylated in an efficient manner. Reactions with unsymmetrical diaryliodonium salts show high chemoselectivity. On the basis of these reactions, we could develop a practical one-pot-protocol for the direct transformation of (hetero)-aromatic and aliphatic halides as well as (hetero)arenes into aryl sulfones. This protocol consists of the following: (1) generation of the organometallic reagent via metal−halogen exchange, and direct metal insertion or deprotonation; (2) reaction of the organometallic reagent with sulfur dioxide; (3) removal of excess sulfur dioxide; (4) treatment of the formed crude sulfinate with a diaryliodonium salt. Various aryl- and heteroaryl sulfones can be prepared using this straightforward procedure. Reactions with magnesium and zinc sulfintes are inherently limited due to side-reactions of their halide counterions with the iodonium salts. This limitation can be avoided by the employment of an excess of the iodonium salt.

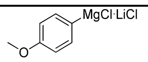
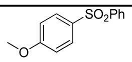
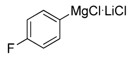
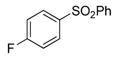
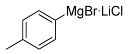
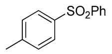
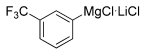
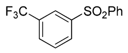
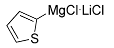
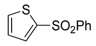
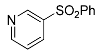
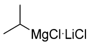
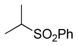
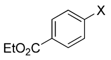
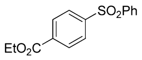
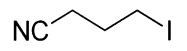
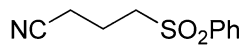
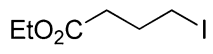
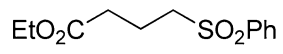
■ EXPERIMENTAL SECTION

General Considerations. All anhydrous solvents were purchased from commercial suppliers and stored over MS4A under an atmosphere of argon. Solvents for column chromatography were technical standard. All starting materials, which were purchased from commercial sources, were used without further purification. SO_2 (sulfur dioxide 3.8) was used directly without further purification. Commercially available diphenyliodonium salts were purchased. Following diaryliodonium salts were synthesized according to literature: Bis(4-methylphenyl)iodonium triflate (**3f**), bis(2,4,6-trimethylphenyl)iodonium triflate (**3g**),[14d] bis(2,4-dimethylphenyl)-iodonium triflate (**3h**),[14d] bis(4-methoxyphenyl)iodonium tosylate (**3i**),[14b] bis(4-chlorophenyl)iodonium triflate (**3j**),[14d] (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (**3k**),[14d] (2,4,6-triisopropylphenyl)-(phenyl)iodonium triflate (**3l**),[20a] (3-trifluoromethylphenyl)(4-methoxyphenyl)iodonium tosylate (**3m**).[14]Chromatography column chromatography was performed with silica 0.04−0.063 mm/230−400 mesh. Thin layer chromatography was performed using aluminum plates coated with SiO_2. The spots were visualized by ultraviolet light. NMR spectroscopy ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz and 101 or 126 MHz, respectively. Chemical shifts are reported as δ-values relative to the residual $CDCl_3$ peak (δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C). Coupling constants (*J*) are given in hertz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet; dd = doublet of doublets; dt = doublet of triplets. Mass spectrometry spectra (MS) were measured using ESI (electrospray ionization) techniques. High resolution mass spectra (MALDI-HRMS) were measured using MALDI (matrix-assisted laser desorption/ionization) techniques. Melting points are uncorrected.

Reactions All reactions were carried out under an inert atmosphere in dried glassware unless otherwise noted. All yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H NMR. **Working with SO_2: SO_2 is a toxic and corrosive gas! It**

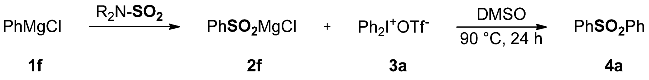
Table 9. Zincation Approach to Diaryl Sulfones[a]



entry	R-X	R-SO_2Ph	yield [%][b]
1[c,d]	 **1h**	 **4e**	44
2[d]	 **1i**	 **4v**	68
3[c,d]	 **1j**	 **4b**	65
4[d]	 **1k**	 **4m**	74
5	 **1l**	 **4n**	59
6	 **1m**	 **4w**	51
7[d]	 **1g**	 **7e**	64
8[d]	 **1n:** X = MgCl·LiCl	 **4v**	85
9	**6m:** X =I		41
10	 **8b**	 **7f**	64
11	 **8c**	 **7g**	84

[a]Reaction conditions: 1.0 equiv of (hetero)aryl halide, 3.0 equiv of Ph_2IOTf in 1.0 mL of DMF for 24 h at 90 °C. [b]Isolated yield. [c]1.5 equiv of (hetero)aryl halide, 1.0 equiv of Ph_2IOTf. [d]Reaction carried out in DMSO.

Scheme 4. SO_2 Surrogates



R_2N-SO_2 =		
	DABCO·2SO_2	54 %
	DMAP·2SO_2	37 %
	SO_2 (l)	75 %

should be handled with care only in a well-ventilated fume-hood with the necessary precaution! It is possible to obtain the crude magnesium or zinc sulfinates by passing a stream of sulfur dioxide through the solution of the organometallic reagent. However, with this technique a great excess of SO_2 is introduced into the reaction and has to be removed afterward. In general, better and more reproducible yields were obtained by using a defined amount of liquid SO_2. Therefore, SO_2 was condensed into a dry and Ar-filled Schlenk-flask, cooled to −78 °C. Because of its high heat of evaporation, liquid and cooled SO_2 can be easily handled, measured, and transferred with syringes. For small scale reactions, we recommend this procedure.

For the removal of excess SO_2, we employed the two following procedures. (For the removal of excess SO_2 (gaseous or liquid), appropriate measures to trap and destroy SO_2 should be taken, e.g., passing the SO_2 stream through an aq NaOH solution.)

Procedure A. After warming the reaction mixture to 25 °C within 90 min, the solvents and excess SO_2 were removed under reduced pressure. The residue was coevaporated with CH_2Cl_2 (1.5 mL). This procedure was used for all experiments.

Procedure B. Excess SO_2 was removed by passing Ar through the solution for 30 min. Diaryliodonium salt **3** and solvent (1.0 mL) were added directly to the remaining solution/suspension. The flask was charged with a small distillation head and heated to 90 °C. After the lower boiling solvents (THF or Et_2O) were distilled off (typically within 1 h), the flask was capped with a rubber septum and heated for the remaining time. (As an alternative, the flask can be capped directly with a rubber septum pierced with a 20G needle and heated to 90 °C for 24 h. Low boiling solvents are evaporated directly into the atmosphere! This should be performed only in a closed, well-ventilated fume-hood!).

*Preparation of Benzenesulfinic Lithium Salt **2a**.* A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenyllithium (**1a**) (32.2 mL, 50 mmol, 1.55 M solution in Et_2O, 1.0 equiv) and cooled to −40 °C. At this temperature, liquid SO_2 (1.1 mL, 55 mmol, 1.1 equiv) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with CH_2Cl_2 (150 mL) to afford the solid benzenesulfinic lithium salt (**2a**) (11.32 g). Note: The theoretical amount of lithium salt **2a** (formula weight: 148.11 g/mol) from 32.3 mL of phenyllithium (**1a**) is 7.41 g. The material obtained (11.32 g) should therefore contain 65% of **2a** (assuming 100% conversion). A purity of 65% of this material was thus assumed in later calculations.

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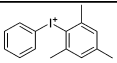
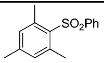
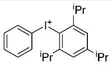
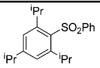
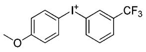
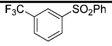
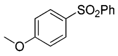
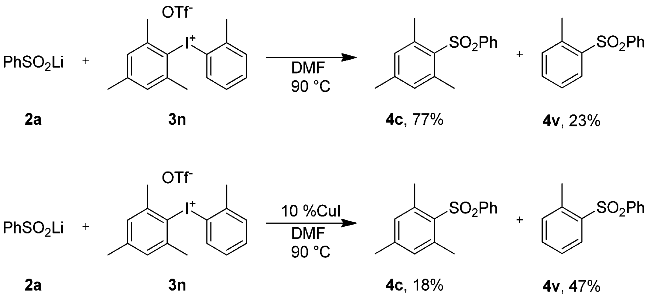
Table 10. Selectivity Studies with Sterically Different Demanding Aryl Substituents[a]

$$\underset{\mathbf{2a}}{\text{Ph-SO}_2\text{-Li}} + \underset{\mathbf{3}}{\text{Ar}^1\text{Ar}^2\text{I}^+\text{OTf}^-} \xrightarrow[90°\text{C, 24 h}]{\text{DMF}} \underset{\mathbf{4}}{\text{Ar}_1\text{SO}_2\text{Ph} + \text{Ar}^2\text{SO}_2\text{Ph}}$$

entry	$Ar^1Ar^2I^+OTf^-$	Ar^1SO_2Ph Ar^2SO_2Ph		Met=[b] Li	Mg	Zn
1	 **3k**		**4c**	73%	80%	59%
		$PhSO_2Ph$	**4a**	-	-	-
2	 **3l**		**4x**	81%	98%	46%
		$PhSO_2Ph$	**4a**	-	-	-
3	 **3m**		**4m**	76%	81%	76%
			**4e**	6%	<2%	5%

[a]Reaction conditions: 1.5 equiv of **2** and 1.0 equiv of **3** in 1.0 mL of DMF for 24 h at 90 °C at a 0.5 mmol scale. [b]Isolated yield.

Scheme 5. Selectivity Studies



*Preparation of Benzenesulfinic Magnesium Chloride Salt **2b**.* A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenylmagnesium chloride (**1f**) (70 mL, 74.2 mmol, 1.06 M solution in 1.0 equiv) and cooled to −40 °C. At this temperature, liquid SO_2 (2.0 mL, 90 mmol, 1.2 equiv) was added, and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with 150 mL of CH_2Cl_2 to afford the solid benzenesulfinic magnesium chloride salt (**2b**) (21.18 g). Note: The theoretical amount of magnesium chloride salt **2b** (formula weight: 200.93 g/mol) from 74.2 mL of phenylmagnesium chloride (**1f**) is 14.9 g. The material obtained (21.18 g) should therefore contain 70% of **2b** (assuming 100% conversion). A purity of 70% of this material was thus assumed in later calculations.

TP 1: Typical Procedure for the Preparation of Sulfones from Benzenesulfinic Lithium Salt (Table 2). A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with benzenesulfinic acid lithium salt **2a** (1.5 equiv), aryliodonium salt **3** (1.0 equiv), and DMF (2.0 mL/mmol iodonium salt, 0.5 M). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc) afforded the analytically pure product.

TP 2: Typical Procedure for the Preparation of Sulfones from Alkyllithium Reagents (Scheme 2). A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with alkyllithium **1** (1.5 equiv) cooled to −78 °C, liquid SO_2 (10 equiv) was added, and the mixture was warmed to 25 °C within 90 min. After removal of SO_2 and solvents according to procedure A, diphenyliodonium triflate (**3a**) and 1.0 equiv and DMF (2.0 mL/mmol iodonium salt, 0.5 M) were added. The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc) afforded the analytically pure product.

*TP 3: Typical Procedure for the Preparation of Sulfones from Benzenesulfinic Acid Magnesium Chloride Salt (**2b**) (Table 5).* A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with benzenesulfinic acid magnesium chloride salt (**2b**) (1.5 equiv or 1.0 equiv), diaryliodonium salt **3** (1.0 equiv or 3.0 equiv, respectively) and DMSO (2.0 mL/mmol iodonium salt, 0.5 M). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc) afforded the analytically pure product.

TP 4: Typical Procedure for the Preparation of Sulfones from Grignard Reagents (Table 6). A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with a corresponding Grignard reagent (**1**)[29] (solution in THF) in THF (total volume 1.5 mL) and cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) and DMSO (2.0 mL/mmol limiting factor, 0.5 M) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc) afforded the analytically pure product.

*TP 5: Typical Procedure for the Preparation of Sulfones from in Situ-Generated Benzenesulfinic Acid Zinc Salt (**2f**) (Table 7).* A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenylmagnesium chloride (**1f**) (0.53 M in THF, 1.4 mL, 0.75 mmol, 0.5 equiv), and zinc chloride (0.7 M in THF, 1.1 mL, 0.8 mmol, 1.6 equiv) was added dropwise. After stirring at 25 °C for 30 min, the mixture was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents from the crude benzenesulfinic zinc salt (**2k**), diaryliodonium salt **3** (1.0 equiv) and DMSO (2.0 mL/mmol iodonium salt, 0.5 M) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the

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aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc) afforded the analytically pure product.

TP 6: Typical Procedure for the Preparation of Sulfones from Organozinc Reagents (Table 9). A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with a corresponding organozinc reagent (**1**)[35] (solution in THF, 0.5 mmol, 1.0 equiv) in THF (total volume 1.5 mL) and cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMF (2.0 mL/mmol organozinc reagent, 0.5 M) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc) afforded the analytically pure product.

4a:[18] Table 2, entry 1. **4a** was prepared from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (91.3 mg, 84%). Table 3, entry 1: To a solution of *n*BuLi (0.34 mL, 2.45 M in hexanes, 0.80 mmol, 1.6 equiv) and TMEDA (0.11 mL, 0.75 mmol, 1.5 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added benzene (**5a**) (67 μL, 0.75 mmol, 1.5 equiv) (lithiation according to ref 22b). The mixture was stirred at 25 °C for 90 min. After removal of excess SO_2 and solvents by procedure A, diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless solid (56.6 mg, 52%). Tables 5 and 6, entry 1: According to TP 3 **4a** was synthesized from benzenesulfinic acid magnesium chloride salt (**2b**) (70 wt %, 215.3 mg, 0.75 mmol) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (82.0 mg, 75%). Table 7, entry 1: According to TP 4, **4a** was prepared from crude benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (72.8 mg, 67%). mp: 123−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00−7.90 (m, 4H), 7.60−7.53 (m, 2H), 7.53−7.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 133.3, 129.4, 127.8. MS: *m*/*z*: calcd for $C_{12}H_{10}O_2S+Na^+$ 241.03, found 241.08. IR (cm^{-1}): 3070 (w), 2923 (w), 1581 (w), 1477 (w), 1447 (m), 1308 (s, -SO_2-), 1294 (s). 1181 (m), 1151 (s, -SO_2-), 1103 (s), 1068 (m), 1023 (m), 997 (m), 935 (w), 759 (s), 726 (s), 682 (s), 582 (s), 557 (s), 427 (w). R_f (hexanes:EtOAc 9:1): 0.19.

4b:[18] Table 2, entry 2. **4b** was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and bis(4-methylphenyl)iodonium triflate (**3f**) (229.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (93.3 mg, 80%). Table 5, entry 2: According to TP 3, **4b** was synthesized from benzenesulfinic acid magnesium chloride salt (**2b**) (70 wt %, 215.3 mg, 0.75 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (**3f**) (229.1 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (72.2 mg, 62%). Table 8, entry 2: **4b** was also synthesized according to TP 4 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(2,4-dimethylphenyl)-iodonium triflate (**3f**) (229.1 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (86.6 mg, 75%). Table 9, entry 3: To a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum charged with tolylmagnesium bromide·LiCl (**1j**) (0.9 M in THF, 0.85 mL; 0.75 mmol, 1.5 equiv) was added $ZnCl_2$ (0.7 M in THF, 1.1 mL, 0.83 mmol, 1.65 equiv) and stirred at 25 °C for 30 min. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) afforded the analytically pure product as a colorless solid (76.0 mg, 65%). mp: 126−128 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95−7.91 (m, 2H), 7.84−7.81 (m, 2H), 7.56−7.52 (m, 1H), 7.51−7.47 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 142.1, 138.8, 133.1, 130.0, 129.4, 127.9, 127.6, 21.7. MS: *m*/*z*: calcd for $C_{13}H_{12}O_2S+Na^+$ 255.05, found 255.10. IR (cm^{-1}): 1592 (w), 1447 (m), 1305 (m, -SO_2-), 1293 (m), 1152 (s, -SO_2-), 1105 (s), 1070 (m), 1043 (w), 1018 (w), 997 (w), 815 (m), 757 (w), 724 (s), 703 (m), 686 (s), 650 (s), 573 (s), 545 (s), 487 (m), 445 (w). R_f (hexanes:EtOAc 9:1):0.19.

4c:[18] Table 2, entry 3. **4c** was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and bis(2,4,6-trimethylphenyl)iodonium triflate (**3g**) (257.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (87.3 mg, 67%). Table 5, entry 4: **4c** was prepared according to TP 3 from benzenesulfinic acid magnesium chloride salt (**2b**) (55 wt %, 182.7 mg, 0.5 mmol) and bis(2,4,6-trimethylphenyl)iodonium triflate (**3g**) (771.5 mg, 1.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (104.0 mg, 80%). Table 7, entry 3: **4c** was also prepared according to TP 4 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(2,4,6-trimethylphenyl)-iodonium triflate (**3g**) (257.2 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (44.6 mg, 34%). Table 10, entry 1: Li: **4c** was synthesized according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (**3k**) (236.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 →9:1) yielded the product as a colorless solid (94.5 mg, 73%). Mg: **4c** was prepared according to TP 3 from benzenesulfinic acid magnesium chloride salt (**2b**) (55 wt %, 182.7 mg, 0.5 mmol) and bis(2,4,6-trimethylphenyl)iodonium triflate (**3k**) (771.5 mg, 1.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (104.0 mg, 80%). Zn: **4c** was prepared according to TP 4 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(2,4,6-trimethylphenyl)iodonium triflate (**3k**) (257.2 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (76.7 mg, 59%). mp: 82−84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.75 (m, 2H), 7.57−7.51 (m, 1H), 7.50−7.44 (m, 2H), 6.94 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.5, 140.2, 133.9, 132.7, 132.3, 129.0, 126.4, 23.0.95, 21.2. MS: *m*/*z*: calcd for $C_{15}H_{16}O_2S+Na^+$ 283.08, found 283.13. IR (cm^{-1}): 1600 (m), 1447 (s), 1348 (m), 1290 (s), 1145 (s), 1093 (s), 1072 (m), 1050 (m), 1030 (s), 999 (m), 855 (s), 761 (s), 645 (s), 585 (s), 572 (s), 530 (s) 495 (m). R_f (hexanes:EtOAc 9:1): 0.30.

4d:[18] Table 2, entry 4. **4d** was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (**3h**) (243.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (94.2 mg, 76%). Table 5, entry 3: According to TP 3, **4d** was synthesized from benzenesulfinic acid magnesium chloride salt (**2b**) (70 wt %, 215.3 mg, 0.75 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (**3h**) (243.2 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (68.5 mg, 56%). Table 7, entry 4: According to TP 2, **4d** was prepared from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (**3h**) (243.2 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (90.6 mg, 74%). mp: 110−111 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.88−7.82 (m, 2H), 7.60−7.54 (m, 1H), 7.53−7.46 (m, 2H), 7.28 (dd, J = 7.7, 1.3 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 138.5, 136.6, 134.9, 134.5, 133.1, 132.7, 129.9, 129.1, 127.7, 21.0, 19.8. MS: m/z: calcd for $C_{14}H_{14}O_2S{+}Na^+$ 269.06, found 269.11. IR (cm^{-1}): 3096 (w), 2923 (w), 1490 (w), 1450 (m), 1292 (s, -SO_2-), 1201 (w), 1154 (s, -SO_2-), 1143 (s, -SO_2-), 1092 (m), 1055 (m), 999 (w), 900 (w), 884 (w), 821 (m), 764 (m), 723 (s), 693 (m), 595 (s), 579 (s), 523 (s), 494 (m), 472 (w), 457 (m), 435 (w). R_f (hexanes:EtOAc 9:1): 0.27.

4e:[18] Table 2, entry 5. **4e** was synthesized from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**3i**) (256.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 9:1 → 1:1) yielded the product as a colorless solid (91.5 mg, 74%). Table 3, entry 7: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 4-bromoanisole (**6d**) (0.1 mL, 1.5 equiv, 0.75 mmol) in dry THF (1.0 mL) and cooled to −78 °C, and then *n*BuLi (0.38 mL, 2.13 M in hexanes, 0.80 mmol, 1.6 equiv) was added dropwise (lithiation according to ref 40). The mixture was stirred at this temperature for 2 h before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (96.9 mg, 78%). Table 3, entry 8: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 4-iodoanisole (**6e**) (175.5 mg, 1.5 equiv, 0.75 mmol) in dry THF (1.0 mL) and cooled to −78 °C, and then *t*BuLi (0.48 mL, 1.64 M in pentane, 0.8 mmol, 1.6 equiv) was added dropwise (lithiation according to ref 41). The mixture was allowed to warm to −50 °C within 2 h before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (65.2 mg, 53%). Table 5, entry 5: **4e** was prepared according to TP 3 from benzenesulfinic acid magnesium chloride salt (**2b**) (55 wt %, 91.3 mg, 0.25 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**3i**) (380.1 mg, 0.75 mmol) in DMSO (0.5 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (38.4 mg, 62%). Table 7, entry 5: **4e** was prepared according to TP 4 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**3i**) (256.2 mg, 0.5 mmol) in DMSO (0.5 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (86.0 mg, 70%). Table 9, entry 1: To a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum charged with bromo(4-methoxyphenyl)magnesium·LiCl[6] (**1h**) (0.9 M in THF, 0.85 mL; 0.75 mmol, 1.5 equiv) was added $ZnCl_2$ (0.7 M in THF, 1.1 mL, 0.80 mmol, 1.6 equiv) and stirred at 25 °C for 30 min. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless solid (55.1 mg, 44%). mp: 90−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H), 7.90−7.86 (m, 2H), 7.57−7.51 (m, 1H), 7.51−7.45 (m, 2H), 6.99−6.93 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 142.5, 133.2, 133.0, 130.0, 129.3, 127.4, 114.6, 55.8. MS: m/z: calcd for $C_{13}H_{12}O_3S{+}Na^+$ 271.04, found 271.09. IR (cm^{-1}): 1590 (s), 1576 (s), 1496 (s), 1464 (m), 1445 (s), 1315 (s, -SO_2-), 1297 (s), 1260 (s), 1185 (m), 1147 (s, -SO_2-), 1104 (s), 1071 (s), 1019 (s), 998 (s), 832 (s), 802 (s), 755 (m), 728 (s), 709 (s), 686 (s), 628 (m), 576 (s), 552 (s), 453 (m). R_f (hexanes:EtOAc 9:1): 0.22.

4f:[18] Table 2, entry 6. **4f** was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and bis(4-chlorophenyl)iodonium triflate (**3j**) (249.5 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (98.2 mg, 78%). Table 5, entry 6: **4f** was prepared according to TP 3 from benzenesulfinic acid magnesium chloride salt (**2b**) (55 wt %, 182.7 mg, 0.5 mmol) and bis(4-chlorophenyl)iodonium triflate (**3j**) (748.6 mg, 1.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (110.3 mg, 74%). Table 7, entry 6: **4f** was prepared according to TP 4 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and bis(4-chlorophenyl)iodonium triflate (**3j**) (249.5 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (80.5 mg, 64%). mp: 94−96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96−7.91 (m, 2H), 7.91−7.86 (m, 2H), 7.61−7.56 (m, 1H), 7.54−7.49 (m, 2H), 7.49−7.45 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 140.3, 140.0, 133.6, 129.8, 129.6, 129.3, 127.8. MS: m/z: calcd for $C_{12}H_9ClO_2S{+}Na^+$ 274.99, found 275.04. IR (cm^{-1}): 1575 (m); 1474 (m), 1447 (m), 1391 (m), 1311 (s, -SO_2-), 1280 (m), 1177 (w), 1152 (s, -SO_2-), 1107 (s), 1085 (s), 1070 (s), 1028 (w), 10017 (m), 998 (m), 827 (m), 764 (s), 748 (s), 718 (s), 700 (m), 685 (s), 608 (s), 531 (s), 493 (s), 468 (m), 436 (m). R_f (hexanes:EtOAc 9:1): 0.22.

4g[18] (Table 3, entry 2): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 1,3-dimethoxybenzene (**5b**) (0.1 mL, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) and cooled to 0 °C with an ice-bath. At this temperature, *n*BuLi (0.34 mL, 2.45 M solution in hexane, 0.83 mmol, 1.65 eqiuv) was added dropwise and the mixture was stirred at 25 °C for 3.5 h (lithiation according to ref 42). Then it was recooled to −30 °C, and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added at once. The mixture was allowed to warm to 25 °C within 60 min, and then excess SO_2 was removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5

mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 1:1) yielded the product as a colorless solid (110.3 mg, 79%). Table 3, entry 3: To a solution of 2-iodo-1,3-dimethoxybenzene (**6h**) (198.1 mg, 0.75 mmol, 1.5 equiv) in dry hexanes (3.5 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.40 mL, 2.13 M in hexane, 0.85 mmol, 1.65 equiv) and the mixture stirred at 25 °C for 16 h (lithiation according to ref 43). After cooling to −78 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents according to procedure A, to the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 4:1 → 1:1) yielded the product as a colorless solid (103.0 mg, 74%). mp: 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 2H), 7.55−7.42 (m, 3H), 7.39 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.6, 144.6, 135.1, 132.4, 128.3, 127.4, 118.1, 105.4, 56.6. MS: *m*/*z*: calcd for $C_{14}H_{14}O_4S+Na^+$ 301.05, found 301.30. IR (cm^{-1}): 2977 (w), 2945 (w), 1577 (s),1476 (s), 1427 (s), 1318 (m, -SO_2-), 1305 (s, -SO_2-), 1290 (m), 1254 (s), 1188 (w), 1150 (s, -SO_2-), 1107 (s), 1088 (s), 1043 (m), 1023 (m), 780 (s), 754 (s), 713 (m), 695 (s), 649 (m), 612 (m), 572 (s), 560 (s), 496 (m), 472 (m). R_f (cyclohexane:EtOAc 9:1): 0.05.

4h[18] (Table 3, entry 4): To a solution of anisole (**5c**) (0.82 mL, 0.75 mmol, 1.5 equiv) and TMEDA (0.22 mL, 1.5 mmol, 3.0 equiv) in dry Et_2O (1.0 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.61 mL, 2.45 M in hexanes, 1.5 mmol, 3.0 equiv) dropwise (lithiation according to ref 44). The mixture was stirred at 25 °C for 30 min and then cooled to −78 °C, and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed by procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (75.7 mg, 61%). Table 3, entry 5: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.33 mL, 2.45 M in hexanes, 0.80 mmol, 1.6 equiv) and cooled to −78 °C. Then 2-bromoanisole (**6b**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise, and the reaction mixture stirred at this temperature for 1 h (lithiation according to ref 40) before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The mixture was allowed to warm to 25 °C within 90 min, and then excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (120.2 mg, 97%). mp: 142−145 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.00−7.94 (m, 2H), 7.58−7.52 (m, 2H), 7.51−7.45 (m, 2H), 7.13−7.08 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.2, 141.7, 135.6, 133.0, 130.0, 129.2, 128.6, 125.4, 120.7, 112.6, 56.00. MS: *m*/*z*: calcd for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.40. IR (cm^{-1}): 1584 (m), 1479 (m), 1466 (m), 1452 (m), 1434 (m), 1304 (s, -SO_2-), 1280 (s), 1243 (m), 1180 (w), 1147 (s, -SO_2-), 1091 (s), 1059 (m), 1034 (m), 1014 (m), 799 (m), 164 (s), 733 (s), 717 (s), 692 (s), 584 (s), 559 (s), 537 (s), 509 (s), 469 (w), 448 (w). R_f (cyclohexane:EtOAc 9:1): 0.09.

4i[18] (Table 3, entry 6): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.33 mL, 2.45 M in hexanes, 0.8 mmol, 1.6 equiv) and cooled to −70 °C. Then 3-bromoanisole (**6c**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise, and the reaction mixture stirred at this temperature for 1 h (lithiation according to ref 40) before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The mixture was allowed to warm to 25 °C within 90 min, and then excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (114.7 mg, 92%). mp: 89−91 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.98−7.91 (m, 2H), 7.59−7.54 (m, 1H), 7.53−7.48 (m, 3H), 7.46−7.43 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.07 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.2, 142.8, 141.7, 133.3, 130.5, 129.4, 127.8, 120.1, 119.7, 112.4, 55.8. MS: *m*/*z*: calcd for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.13. IR (cm^{-1}): 1592 (m), 1474 (m), 1447 (s), 1421 (m), 1298 (s, -SO_2-), 1245 (s), 1181 (m), 1148 (s, -SO_2-), 1099 (s), 1069 (m), 1026 (s), 992 (m), 925 (w), 865 (m), 842 (w), 790 (s), 755 (w), 723 (s), 678 (s), 609 (s), 571 (s), 526 (s), 471 (m); 458 (m), 421 (w). R_f (cyclohexane:EtOAc 9:1): 0.15.

4j[18] (Table 3, entry 9): To a solution of 1-bromo-2,4-dimethoxybenzene (**6f**) (0.11 mL, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.56 mL, 1.2 mmol, 2.4 equiv) dropwise at 25 °C and then stirred for 2 h (lithiation according to ref 45). After cooling to −78 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 1:1) yielded the product as a colorless solid (58.4 mg, 42%). mp: 107−109 °C. ^1H NMR: (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.8 Hz, 1H), 7.96−7.92 (m, 2H), 7.56−7.51 (m, 1H), 7.49−7.44 (m, 2H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H). ^{13}C NMR: (101 MHz, $CDCl_3$): δ = 165.8, 158.8, 142.3, 132.7, 131.9, 128.6, 128.2, 121.5, 104.8, 99.6, 556.00, 55.9. MS: *m*/*z*: calcd for $C_{14}H_{14}O_4S$ $+Na^+$ 301.05, found 302.30. HRMS: *m*/*z*: calcd for $C_{14}H_{14}O_4S+H^+$ 279.06856, found 279.06858. IR (cm^{-1}): 1578 (m), 1489 (w), 1458 (m), 1432 (w), 1408 (w), 1321 (m, -SO_2-), 1299 (S, -SO_2-), 1251 (m), 1210 (s), 1144 (s), 1145 (s, -SO_2-), 1091 (s), 1064 (s), 1020 (s), 938 (w), 920 (m), 840 (w), 829 (m), 813 (w), 792 (w), 765 (m), 733 (s), 708 (m), 691 (s), 658 (m), 641 (m), 592 (s), 555 (s), 528 (s), 470 (w), 454 (m). R_f (cyclohexane:EtOAc 9:1): 0.08.

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4k[18] (Table 3, entry 10): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.38 mL, 2.13 M in hexanes, 0.8 mmol, 1.6 equiv) in dry Et_2O (1.0 mL) and cooled to 0 °C. At this temperature, 3-bromobenzotrifluoride (**6g**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture stirred for 1 h at 0 °C (lithiation according to ref 46). Then it was cooled to −78 °C, and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (106.3 mg, 74%). Table 3, entry 11: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.38 mL, 2.13 M in hexanes, 0.8 mmol, 1.6 equiv) in dry Et_2O (1.0 mL) and cooled to −78 °C. At this temperature, 3-iodobenzotrifluoride (**6h**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture stirred for 1 h at −78 °C (lithiation according to ref 47). Then liquid SO_2 (0.1 mL, 5.0 mmol, 10 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (118.9 mg, 83%). Table 6, entry 6: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *i*PrMgCl·LiCl in THF (in total 1.5 mL solvent) (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) and cooled to −20 °C. Then 3-bromobenzotrifluoride (**6g**) (72 μL, 0.50 mmol, 1.0 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 30 min. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1) afforded the analytically pure product as a colorless solid (53.3 mg, 38%). Table 9, entry 4: To a solution of *i*PrMgCl·LiCl in THF (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) cooled to −20 °C was added 3-iodobenzotrifluoride (**6h**) (72 μL, 0.5 mmol, 1.0 equiv). After stirring 30 min at this temperature, $ZnCl_2$ (0.7 M in THF, 0.79 mL, 0.55 mmol, 1.1 equiv) was added and the mixture was allowed to warm to 25 °C. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the product as a colorless solid (105.8 mg, 74%). mp: 82−84 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.00−7.95 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.64−7.60 (m, 1H), 7.57−7.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 140.8, 133.9, 132.2 (q, *J* = 33.6 Hz), 130.3, 130.0 (q, *J* = 3.5 Hz), 129.7, 128.0, 124.8 (q, *J* = 3.9 Hz), 123.2 (q, *J* = 273.0 Hz). MS: *m/z*: calcd for $C_{13}H_9F_3O_2S+Na^+$ 309.02, found 309.07. IR (cm^{-1}): 3064 (w), 1737 (w), 1609 (w), 1586 (w), 1480 (w), 1449 (w), 1432 (w), 1323 (s, -SO_2-), 1306 (s, -SO_2-), 1180 (m), 1155 (s, -SO_2-), 1124 (s, -SO_2-), 1109 (s), 1067 (s), 998 (w), 930 (m), 842 (w), 821 (w), 803 (m), 757 (m), 731 (s), 686 (s), 649 (m), 634 (m), 584 (s), 553 (s), 500 (m), 459 (w), 424 (w), 407 (w). R_f (hexanes:EtOAc 9:1): 0.16.

4l[18] (Table 3, entry 12): To a solution of *s*BuLi (0.70 mL, 1.2 M in cyclohexane, 0.83 mmol, 1.65 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *N*,*N*-diisopropylbenzamide (**5d**) (154.0 mg, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) at −78 °C (lithiation according to ref 48). The mixture was stirred for 1 h at this temperature, and then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure B, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL) were added and the reaction was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 4:1) yielded the product as a colorless solid (117.5 mg, 68%). mp: 198−200 °C. ^1H NMR (400 MHz, CDCl3): δ = 8.11−8.07 (m, 2H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.58−7.44 (m, 5H), 7.22 (d, *J* = 6.8 Hz, 1H), 3.68−3.50 (m, 2H), 1.69 (d, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9, 141.7, 138.5, 137.7, 133.6, 133.3, 130.4, 129.1, 129.0, 128.5, 127.0, 51.5, 46.0, 20.6, 20.5, 19.9, 19.6. MS: *m/z*: calcd for $C_{19}H_{23}NO_3S+Na^+$ 368.13, found 368.30. HRMS: *m/z*: calcd for $C_{19}H_{23}NO_3S+H^+$ 346.14714, found 346.14703. IR (cm^{-1}): 1628 (s), 1476 (w), 1442 (m), 1371 (m), 1340 (m, -SO_2-), 1317 (s, -SO_2-), 1297 (w), 1212 (w), 1186 (w), 1153 (s, -SO_2-), 1130 (m, -SO_2-), 1105 (m), 1090 (w), 1058 (w), 1035 (w), 782 (m), 759 (m), 730 (m), 710 (m), 688 (m), 656 (w), 590 (s), 568 (s), 533 (w), 502 (w).R_f (cyclohexane:EtOAc 9:1): 0.07

4m[18] (Table 3, entry 13): To a solution of *s*BuLi (0.70 mL, 1.2 M in cyclohexane, 0.83 mmol, 1.65 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added phenyl diethylcarbamate (**5e**) (154.0 mg, 0.75 mmol, 1.5 equiv) at −78 °C (lithiation according to ref 49). The mixture was stirred for 1 h at this temperature, and then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure A, to the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL) and the reaction was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 50:1 → 9:1) yielded the product as a colorless solid (77.8 mg, 47%). mp: 92−93 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.88−7.80 (m, 2H), 7.65−7.52 (m, 2H), 7.52−7.42 (m, 2H), 7.37 (td, *J* = 7.8, 1.1 Hz, 1H), 7.21 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.43 (q, *J* = 7.1 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4, 149.4, 141.5, 134.9, 133.3, 132.7, 130.1, 129.0, 127.4, 125.5, 125.1, 42.2, 41.9, 14.3, 13.3. MS: *m/z*: calcd for $C_{17}H_{19}NO_4S+H^+$ 334.10, found 334.45. HRMS: *m/z*: calcd for $C_{17}H_{19}NO_4S+K^+$ 372.06664, found 372.06664. IR (cm^{-1}): 2983 (w), 1723 (s), 1468 (w), 1448 (w), 1410 (m), 1382 (w), 1321 (s, -SO_2-), 1257 (s), 1201 (s), 1141 (s, -SO_2-), 1093 (s), 1060 (m), 1040 (w), 999 (w), 950 (m), 838 (w), 824 (w), 788 (w), 771 (m), 750 (w), 731 (s), 718 (m), 691 (s), 586 (s), 567 (s), 507 (m). R_f (cyclohexane:EtOAc 4:1): 0.17.

4n[18] (Table 3, entry 14): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.34 mL, 2.45 M in hexanes, 0.83 mmol, 1.5 equiv) and cooled to −78 °C. Then thiophene (**5f**) (0.06 mL, 0.75 mmol, 1.5 equiv) was added dropwise, and the mixture was allowed to warm to 0 °C and stirred at this temperature for 2 h (lithiation according to ref 22b). Then it was recooled to −78 °C, and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed by procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (95.6 mg, 85%). Table 6, entry 3: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *i*PrMgCl·LiCl in THF (in total 1.5 mL solvent) (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) and cooled to −20 °C. Then 2-bromothiophene (**6l**) (48 μL, 0.50 mmol, 1.0 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 30 min. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1) afforded the analytically pure product as a colorless solid (81.3 mg, 73%). Scheme 3: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with thiophene (**5f**) in THF (0.5 mL) (59 μL, 0.75 mmol, 1.5 equiv), and then TMP-MgCl·LiCl (0.95 mL, 0.83 mmol, 1.65 equiv) was added dropwise. After complete addition, the mixture was stirred at 25 °C for 24 h. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless solid (51.5 mg, 50%). Table 9, entry 5: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *i*PrMgCl·LiCl in THF (in total 1.5 mL solvent) (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) and cooled to −20 °C. Then 2-bromothiophene (**6l**) (48 μL, 0.50 mmol, 1.0 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 30 min, then $ZnCl_2$ (0.7 M in THF, 0.9 mL, 0.55 mmol, 1.1 equiv) was added and the mixture was allowed to warm to 25 °C. After recooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1) afforded the analytically pure product as a colorless solid (66.4 mg, 59%). mp: 122−123 °C. ^1H NMR 500 MHz, $CDCl_3$) δ 8.02−7.96 (m, 2H), 7.70 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.60−7.56 (m, 1H), 7.54−7.50 (m, *J* = 10.4, 4.7 Hz, 2H), 7.08 (dd, *J* = 4.9, 3.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.2, 134.0, 133.5, 133.4, 129.5, 128.07.99, 127.5. MS: *m*/*z*: calcd for $C_{10}H_{18}O_2S_2$+Na^+ 246.99, found 247.03. IR (cm^{-1}): 3093 (w), 1503 (w), 1445 (m), 1398 (m), 1343 (w, -SO_2-), 1314 (s, -SO_2-), 1302 (s), 1228 (m), 1147 (s, -SO_2-), 1002 (m), 1081 (m), 11067 (m), 1014 (s), 998 (m), 923 (w), 855 (m), 753 (m), 722 (s), 682 (s), 660 (s), 590 (s), 567 (s), 451 (w), 437 (m). R_f (hexanes:EtOAc 9:1): 0.17.

4o[18] (Table 3, entry 15): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *N*-methylpyrrole (**5g**) (66 μL, 0.75 mmol, 1.5 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv), and then *n*BuLi (0.34 mL, 2.45 M in hexanes, 0.83 mmol, 1.65 equiv) was added dropwise and the mixture was heated to 55 °C for 15 min (lithiation according to ref 50). The mixture was then cooled to −78 °C, and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a pale pink solid (55.9 mg, 51%). mp: 79−81 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91−7.86 (m, 2H), 7.58−7.54 (m, 1H), 7.53−7.48 (m, 2H), 7.04 (dd, *J* = 4.0, 1.9 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 1H), 6.17 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.3, 133.0, 129.8, 129.3, 128.0, 127.3, 119.0, 108.5, 35.8. MS: *m*/*z*: calcd for $C_{11}H_{11}NO_2S$+H^+ 222.06, found 222.80. HRMS: *m*/*z*: calcd for $C_{11}H_{11}NO_2S$+H^+ 222.05833, found 222.05796. IR (cm^{-1}): 3122 (w), 2969 (w), 1513 (w), 1468 (w), 1441 (m), 1396 (w), 1326 (m, -SO_2-), 1297 (s, -SO_2-), 1155 (s, -SO_2-), 1128 (s, -SO_2-), 1098 (m), 1051 (m), 1014 (m), 998 (m), 952 (w), 766 (s), 752 (s), 725 (s), 688(s), 631 (s), 595 (s), 566 (m), 546 (s), 486 (m). R_f (cyclohexane:EtOAc 9:1): 0.18**4p**[18] (Table 3, entry 16): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum, charged with diisopropylamine (0.12 mL, 0.85 mmol, 1.65 equiv) in dry THF (1.0 mL), was cooled to −78 °C, and then *n*BuLi (0.35 mL, 2.45 M in hexanes, 0.85 mmol, 1.65 equiv) was added dropwise. After stirring for 15 min at this temperature, the mixture was stirred for another 15 min at 0 °C. After recooling the in situ-prepared LDA to −70 °C, 2-fluoropyridine (**5h**) (65 μL, 0.75 mmol, 1.5 equiv) was added dropwise and stirred at this temperature for 4 h (lithiation according to ref 51). Then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt were added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 4:1 → 1:1) yielded the product as a colorless solid (65.3 mg, 55%). mp: 90−92 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.56−8.51 (m, 1H), 8.43−8.38 (m, 1H), 8.05−8.00 (m, 2H), 7.68−7.64 (m, 1H), 7.59−7.54 (m, 2H), 7.43−7.39 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.9 (d, *J* = 245.4 Hz), 152.9 (d, *J* = 15.1 Hz), 141.0, 139.7, 134.4, 129.5, 128.6, 125.4 (d, *J* = 30.3 Hz), 122.2 (d, *J* = 4.7 Hz). MS: *m*/*z*:

calcd for $C_{11}H_8FNO_2S+Na^+$ 260.02, found 260.50. HRMS: *m/z*: calcd for $C_{11}H_8FNO_2S+H^+$ 238.03325, found 238.03340. IR (cm^{-1}): 1586 (m), 1568 (w), 1448 (m), 1420 (m), 1326 (m, -SO_2-), 1300 (m), 1228 (w), 1177 (w), 1156 (s, -SO_2-), 1134 (m, -SO_2-), 1091 (m), 1067 (m), 1044 (w), 995 (w), 852 (m), 812 (w), 750 (m), 725 (s), 681 (s), 567 (m), 558 (s), 537 (s), 512 (m), 468 (w), 441 (m). R_f (cyclohexane:EtOAc 9:1): 0.15.

4q[18] (Table 3, entry 17): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 2-bromo-6-methoxypyridine (**6i**) (141.0 mg, 0.75 mmol, 1.5 equiv) in dry THF (2.0 mL) and cooled to −78 °C. At this temperature, *t*BuLi (0.91 mL, 1.64 M in pentane, 1.5 mmol, 3.0 equiv) was added dropwise and the mixture stirred for 15 min (lithiation according to ref 52). Then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (44.3 mg, 36%). mp: 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12−8.06 (m, 2H), 7.79−7.76 (m, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.65−7.58 (m, 1H), 7.57−7.50 (m, 2H), 6.86 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.2, 155.8, 139.8, 139.1, 133.7, 129.2, 129.0, 115.6, 115.0, 54.1. MS: *m/z*: calcd for $C_{12}H_{11}NO_3S+Na^+$ 272.04, found 272.20. HRMS: *m/z*: calcd for $C_{12}H_{11}NO_3S+H^+$ 250.05324, found 250.05344. IR (cm^{-1}): 3016 (w), 2954 (w), 1601 (w), 1586 (w), 1554 (w), 1469 (m), 1149 (w), 1413 (m), 1330 (w, -SO_2-), 1306 (s, -SO_2-), 1292 (m), 1270 (m), 1162 (s, -SO_2-), 1141 (s, -SO_2-), 1129 (s, -SO_2-), 1079 (m), 1067 (m), 1024 (m), 999 (w), 984 (m), 816 (m), 761 (w), 727 (s), 687 (s), 643 (m), 582 (s), 539 (s). R_f (cyclohexane:EtOAc 9:1): 0.21..

4r[18] (Table 3, entry 18): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with ferrocene (**5i**) (153.2 mg, 0.83 mmol, 1.65 equiv) in dry THF (1.0 mL) and cooled to 0 °C. At this temperature, *t*BuLi (0.46 mL, 1.64 M in pentane, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture was stirred for 15 min (lithiation according to ref 53). After warming to 25 °C, the mixture was recooled to −78 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction mixture was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure B, diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added. The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as an orange solid (68.8 mg, 42%). mp: 140−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.5 Hz, 2H), 7.54−7.47 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 4.69 (s, 2H), 4.51 (s, 5H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 132.7, 129.1, 126.8, 90.4, 71.3, 70.9, 69.4. MS: *m/z*: calcd for $C_{16}H_{14}FeO_2S+Na^+$ 349.00, found 349.20. IR (cm^{-1}): 2921 (w), 1581 (w), 1448 (m), 1411 (w), 1299 (s, -SO_2-), 1184 (m), 1152 (s, -SO_2-), 1140 (s, -SO_2-), 1104 (m), 1084 (m), 1071 (m), 1019 (m), 998 (m), 819 (m), 761 (s), 723 (s), 687 (s), 638 (w), 611 (m), 585 (s), 560 (s), 545 (s), 494 (m), 478 (s), 451 (m). R_f (cyclohexane:EtOAc 9:1): 0.26.

4s[11] (Table 6, entry 2): **4v** was synthesized according to TP 5 from bromo(2-methylphenyl)magnesium·LiCl[29] (0.9 M in THF, 0.85 mL, 0.75 mmol, 1.5 equiv) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1) afforded the analytically pure product as a colorless solid (24.8 mg, 21%). Table 6, entry 8: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *i*PrMgCl·LiCl in THF (in total 1.5 mL solvent) (1.04 M in THF, 0.77 mL, 0.8 mmol, 1.6 equiv) and cooled to 0 °C. Then 2-iodotoluene (**6p**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 1 h. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexane-s:EtOAc 9:1) afforded the analytically pure product as a colorless solid (57.7 mg, 49%). mp: 74−75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (dd, 1H), 7.91−7.83 (m, 2H), 7.61−7.54 (m, 1H), 7.53−7.45 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 139.0, 138.2, 133.8, 133.2, 132.8, 129.6, 129.2, 127.8, 126.6, 20.3. MS: *m/z*: $C_{13}H_{12}O_2S$ calcd for 233.06+H$^+$, found 232.80. IR (cm^{-1}): 3061 (w), 1472 (m), 1446 (m), 1386 (w), 1305 (s, -SO_2-), 1203 (w), 1155 (s, -SO_2-), 1137 (s, -SO_2-), 1091 (m), 1058 (m), 1043 (m), 997 (m), 934 (w), 806 (m), 760 (m), 723 (s), 702 (s), 688 (s), 591 (s), 567 (s), 540 (s), 497 (m), 474 (w), 458 (m), 428 (m). R_f (cyclohexane:EtOAc 9:1): 0.22.

4t (Table 6, entry 4): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *i*PrMgCl·LiCl in THF (in total 1.5 mL) (1.04 M in THF, 0.59 mL, 0.72 mmol, 1.43 equiv) and cooled to −20 °C. Then ethyl 4-iodobenzoate (**6m**) (109 μL, 0.65 mmol, 1.3 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 30 min. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 20:1 → 4:1) afforded the analytically pure product as a colorless solid (67.0 mg, 46%). Table 9, entry 8: To a solution of *i*PrMgCl·LiCl in THF (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) cooled to −20 °C was added ethyl 4-iodobenzoate (**6m**) (83 μL, 0.5 mmol, 1.0 equiv). After stirring 30 min at this temperature, $ZnCl_2$ (0.7 M in THF, 0.79 mL, 0.55 mmol, 1.1 equiv) was added and the mixture was allowed to warm to 25 °C. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. Aftre cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexaness:EtOAc 9:1 → 4:1) afforded the product as a colorless solid (123.4 mg, 85%). Table 9, entry 9: According to TP 6 **4t** was prepared from [4-(ethoxycarbonyl)phenyl]iodo-zinc·LiCl[8] (**1n**) (0.87 M in THF, 0.56 mL) and diphenyliodonium triflate (**3a**) in DMSO. Purification by column chromatography (hexaness:EtOAc 9:1 → 4:1) afforded the product as a colorless solid (62.5 mg, 43%). mp: 92−94 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19−8.11 (m, 2H), 8.07−7.88 (m, 4H), 7.63−7.48 (m, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 145.5, 141.0, 134.8, 133.7, 130.5, 129.6, 128.0, 127.8, 61.9, 14.4. MS: *m/z*: calcd for

$C_{15}H_{14}O_4S$+Na^+ 331.05, found 313.10. HRMS: *m*/*z*: calcd for $C_{15}H_{14}O_4S$+$2H^+$ 292.07176, found 292.07193 IR (cm^{-1}): 3024 (w), 3009 (w), 2925 (w), 1712 (s), 1474 (w), 1402 (m), 1367 (m), 1312 (s, $-SO_2-$), 1269 (s), 1155 (s, $-SO_2-$), 1110 (s), 1088 (s), 1020 (s), 980 (s), 962 (s), 878 (m), 865 (m), 783 (s), 754 (s), 730 (m), 719 (m), 689 (s), 562 (s), 528 (s), 507 (s), 460 (m), 431 (s). R_f (hexanes:EtOAc 9:1): 0.19.

4u[54] (Table 6, entry 5): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 4-iodobenzonitrile (114.5 mg, 0.5 mmol, 1.0 equiv) in THF (1.0 mL) and cooled to −10 °C. Then *i*PrMgCl·LiCl (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 1 h. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1) afforded the analytically pure product as a colorless solid (59.1 mg, 49%). mp: 123−125 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07−8.04 (m, 2H), 7.97−7.94 (m, 2H), 7.82−7.78 (m, 2H), 7.65−7.61 (m, 1H), 7.57−7.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 140.3, 134.2, 133.2, 129.8, 128.4, 128.2, 117.3, 117.1. MS: *m*/*z*: calcd for $C_9H_{12}O_2S$ +H^+ 244.04, found 244.12. IR (cm^{-1}): 2237 (w), 1447 (m), 1396 (m), 1322 (s, $-SO_2-$), 1311 (s, $-SO_2-$), 1290 (s), 1150 (s, $-SO_2-$), 1100 (s), 1070 (s), 1015 (m), 998 (s), 851 (s), 840 (s), 801 (m), 786 (m), 756 (s), 729 (s), 707 (s), 687 (s), 623 (s), 570 (s), 540 (s), 519 (s), 471 (m), 401 (w). R_f (cyclohexane:EtOAc 4:1): 0.30.

4v[11] (Table 6, entry 7): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with iPrMgCl·LiCl in THF (in total 1.5 mL solvent) (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) and cooled to 0 °C. Then 1-fluoro-4-iodobenzene (**6o**) (58 μL, 0.50 mmol, 1.0 equiv) was added dropwise. After complete addition, the mixture was stirred at this temperature for 1 h. Then it was cooled to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added, and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (643.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless solid (78.1 mg, 66%). Table 9, entry 2: To a solution of *i*PrMgCl·LiCl in THF (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) cooled to 0 °C was added 1-fluoro-4-iodobenzene (**6o**) (58 μL, 0.5 mmol, 1.0 equiv). After stirring 1 h at this temperature, $ZnCl_2$ (0.7 M in THF, 0.79 mL, 0.55 mmol, 1.1 equiv) was added and the mixture was allowed to warm to 25 °C. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the product as a colorless solid (75.1 mg, 63%). mp: 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00−7.90 (m, 4H), 7.61−7.55 (m, 2H), 7.54−7.47 (m, 2H), 7.22−7.14 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (d, *J* = 255.9 Hz), 141.6, 137.8 (d, *J* = 3.2 Hz), 133.5, 130.6 (d, *J* = 9.6 Hz), 129.5, 127.7, 116.8 (d, *J* = 22.7 Hz). MS: *m*/*z*: calcd for $C_{12}H_9FO_2S$+Na^+ 259.07, found 259.07. IR (cm^{-1}): 1585 (m), 1491 (m), 1447 (m), 1315 (m, $-SO_2-$), 1291 (s), 1233 (s), 1150 (s, $-SO_2-$), 1101 (s), 1068 (m), 1012 (w), 998 (w), 955 (w), 838 (s), 817 (m), 756 (m), 728 (s), 709 (m), 686 (s), 653 (s), 570 (s), 543 (s), 474 (w), 453 (w), 406 (w). R_f (hexanes:EtOAc 9:1): 0.20.

4w[55] (Table 9, entry 6): To a solution of *i*PrMgCl·LiCl in THF (1.04 M in THF, 0.53 mL, 0.55 mmol, 1.1 equiv) at 25 °C was added 3-bromopyridine (**6r**) (49 μL, 0.5 mmol, 1.0 equiv). After stirring 30 min at this temperature, $ZnCl_2$ (0.7 M in THF, 0.79 mL, 0.55 mmol, 1.1 equiv) was added and the mixture stirred another 30 min. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 4:1 → 1:1) afforded the product as a colorless solid (56.0 mg, 51%). mp:120−122 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.2 Hz, 1H), 8.79 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.27−8.22 (m, 1H), 7.99−7.94 (m, 2H), 7.64−7.60 (m, 1H), 7.57−7.53 (m, *J* = 10.6, 4.8 Hz, 2H), 7.48 (dd, *J* = 8.1, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 153.3, 148.5, 148.5, 140.7, 138.7, 135.8, 135.8, 134.1, 129.8, 128.0, 124.2. MS: *m*/*z*: calcd for $C_{11}H_9NO_2S$+H^+ 220.04, found 219.80. IR (cm^{-1}): 1570 (m), 1473 (w), 1445 (w), 1417 (m), 1303 (s, $-SO_2-$), 1234 (w), 1197 (m), 1158 (s, $-SO_2-$), 1129 ($-SO_2-$), 1113 (s), 1094 (m), 1074 (m), 1017 (m), 999 (m), 823 (m), 768 (m), 742 (s), 703 (s), 686 (s), 617 (s), 589 (s), 567 (s), 488 (m), 458 (m), 418 (m). R_f (hexanes:EtOAc 4:1): 0.11.

4x[18] (Table 10, entry 2): **4x** was prepared according to TP 5 from in situ-generated benzenesulfinic acid zinc salt (**2f**) (assume 0.75 mmol) and (2,4,6-triisopropylphenyl)(phenyl)iodonium triflate (**3l**) (278.2 mg, 0.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (78.7 mg, 46%). Table 10, entry 2: Li: **4x** was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65 wt %, 170.9 mg, 0.75 mmol) and (2,4,6-triisopropylphenyl)(phenyl)-iodonium triflate (**3l**) (278.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (139.9 mg, 81%). Mg: **4x** was prepared according to TP 3 from benzenesulfinic acid magnesium chloride salt (**2f**) (55 wt %, 182.7 mg, 0.5 mmol) and (2,4,6-triisopropylphenyl)(phenyl)iodonium triflate (**3l**), (834.6 mg, 1.5 mmol) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (169.0 mg, 98%). mp: 121−123 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.82−7.67 (m, 2H), 7.55−7.50 (m, 1H), 7.50−7.43 (m, 2H), 7.16 (s, 2H), 4.18 (hept, *J* = 6.7 Hz, 2H), 2.95−2.86 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 151.4, 145.4, 132.3, 132.3, 129.1, 125.8, 124.2, 34.4, 29.5, 24.7, 23.7. MS: *m*/*z*: calcd for $C_{21}H_{18}O_2S$+Na^+ 367.17, found 367.22. IR (cm^{-1}): 2960 (m), 2929 (m), 2870 (w), 1597 (m), 1464 (m), 1444 (m), 1422 (m), 1384 (w), 1336 (m, $-SO_2-$), 1292 (s, $-SO_2-$), 1256 (m), 1147 (s, $-SO_2-$), 1090 (m), 1072 (m), 1035 (m), 933 (w), 886 (m), 760 (m), 691 (m), 651 (s), 6223 (m), 573 (s), 556 (s), 528 (m). R_f (hexanes:EtOAc 9:1): 0.47.

7a:[18] Scheme 2. **7a** was prepared according to TP 2 from methyllithium (**1b**) (0.63 mL, 1.2 M in Et_2O, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), and diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (65.5 mg, 84%). Table 6, entry 10: **7a** was prepared according to TP 5 from MeMgCl (**1f**) (2.44 M in THF, 0.31 mL, 0.75 mmol, 1.5 equiv) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) in

DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless solid (39.5 mg, 51%). mp: 88−90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97−7.93 (m, 2H), 7.69−7.64 (m, 1H), 7.60−7.56 (m, 2H), 3.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 133.8, 129.5, 127.5, 44.6. MS: *m*/*z*: calcd for $C_9H_{12}O_2S+Na^+$ 179.01, found 179.06. IR (cm^{-1}): 3021 (w), 2928 (w), 1983 (w), 1829 (w), 1584 (w), 1478 (w), 1448 (m), 1408 (w), 1328 (m, -SO_2-), 1283 (s), 1176 (w), 1142 (s, -SO_2-), 1084 (s), 1024 (w), 1000 (w), 961 (m), 931 (m), 851 (w), 757 (m), 744 (s), 687 (s), 525 (s), 448 (m), 411 (w). R_f (hexanes:EtOAc 4:1): 0.22.

7b:[18] Scheme 2. **7b** was prepared according to TP 2 from *n*butyllithium (**1c**) (0.31 mL, 2.45 M in hexanes, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless oil (88.4 mg, 89%). Table 6, entry 11: **7b** was prepared according to TP 5 from *n*butylmagnesium chloride·LiCl[6] (**1c**) (1.5 M in THF, 0.5 mL, 0.75 mmol, 1.5 equiv) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) in DMSO (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the analytically pure product as a colorless oil (16.7 mg, 17%). ^{1}H NMR (400 MHz, CDCl3) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.11−3.05 (m, 2H), 1.73−1.65 (m, 2H), 1.38 (dt, *J* = 14.6, 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 139.4, 133.7, 129.4, 128.2, 56.2, 24.8, 21.7, 13.6. MS: *m*/*z*: calcd for 199.08+H$^+$, found 198.85. IR (cm^{-1}): 2961 (m), 2936 (w), 2874 (w), 1465 (w), 1447 (m), 1406 (w), 1328 (w, -SO_2-), 1298 (s, -SO_2-), 1234 (m), 1184 (m), 1142 (s, -SO_2-), 1085(s), 1024 (w), 999 (w), 916 (w), 798 (m), 747 (s), 728 (s), 688 (s), 590 (s), 560 (s), 531 (s), 488 (m), 470 (m), 436 (m). R_f (hexanes:EtOAc 9:1): 0.15.

7c:[18] Scheme 2. **7c** was prepared according to TP 2 from *t*butyllithium (**1d**) (0.46 mL, 1.64 M in pentane, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), and diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (75.5 mg, 76%). mp: 93−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98−7.84 (m, 2H), 7.71−7.60 (m, 1H), 7.59−7.47 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.5, 133.7, 130.6, 128.8, 59.9, 23.8. MS: *m*/*z*: calcd for $C_{10}H_{14}O_2S+Na^+$ 221.06, found 221.14. IR (cm^{-1}): 3062 (w), 2979 (w), 2923 (w), 2853 (w), 1583 (w), 1476 (w), 1449 (m), 1379 (w, -SO_2-), 1276 (s), 1200 (w), 1156 (w, -SO_2-), 1129 (s, -SO_2-), 1076 (s), 1022 (w), 997 (w), 943 (w), 801 (w), 765 (m), 725 (s), 696 (s), 638 (s), 590 (m), 566 (s), 519 (m), 458 (w). R_f (cyclohexane:EtOAc 9:1): 0.19.

7d:[18] Scheme 2. **7d** was prepared according to TP 2 from *s*butyllithium (**1e**) (0.63 mL, 1.2 M in cyclohexane, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), and diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol) in DMF (1.0 mL). Purification by chromatography (cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless oil (75.3 mg, 76%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.91−7.85 (m, 2H), 7.68−7.62 (m, 1H), 7.60−7.53 (m, 2H), 3.02−2.89 (m, 1H), 2.07−1.95 (m, 1H), 1.50−1.36 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.6, 133.7, 129.2, 129.2, 61.7, 22.6, 12.7, 11.3. MS: *m*/*z*: calcd for $C_{10}H_{14}O_2S+Na^+$ 221.06, found 221.50. IR (cm^{-1}): 2975 (m), 2939 (w), 1440 (m), 1296 (s, -SO_2-), 1263 (m) 1241 (m), 1138 (s, -SO_2-), 1085 (s), 1071 (m), 1060 (m), 1020 (m), 999 (w), 847 (w), 764 (s), 727 (s), 691 (s), 614 (m), 590 (s), 572 (s), 540 (s), 499 (m), 456 (m), 422 (w). R_f (cyclohexane:EtOAc 9:1): 0.21.

7e:[56] Table 6, entry 11. According to TP 4, **7e** was prepared from *i*PrMgCl·LiCl (1.04 M in THF, 0.48 mL, 0.5 mmol, 1.0 equiv) and diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) in DMSO (1.0 mL). Purification by column chromatography (hexane:EtOAc 20:1 → 9:1) afforded the analytically pure product as a colorless oil (66.7 mg, 72%). Table 9, entry 7: To a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum charged with *i*PrMgCl·LiCl (**1g**) (1.04 M in THF, 0.48 mL, 0.5 mmol, 1.1 equiv) was added $ZnCl_2$ (0.7 M in THF, 0.86 mL, 0.6 mmol, 1.2 equiv) and stirred at 25 °C for 30 min. After cooling to −40 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents, diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol, 3.0 equiv) and DMSO (1.0 mL) were added and the reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (10 mL). The combined organic layers were washed with sat. aqueous NaCl solution (10 mL) and dried over Na_2SO_4, and the solvents were removed under reduced pressure. Purification by column chromatography (hexanes:EtOAc 20:1 → 9:1) afforded the analytically pure product as a colorless oil (58.8 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91−7.83 (m, 2H), 7.67−7.62 (m, 1H), 7.59−7.53 (m, 2H), 3.19 (hept, *J* = 6.7 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 133.7, 129.2, 129.2, 55.7, 15.8. MS: *m*/*z*: calcd for $C_9H_{12}O_2S+Na^+$ 207.05, found 207.10. IR (cm^{-1}): 2981 (w), 2939 (w), 1468 (m), 1447 (m), 1389 (w), 1298 (s, -SO_2-), 1261 (s), 1167 (m), 1138 (s -SO_2-), 1086 (s), 1051 (s), 1024 (m), 1000 (m), 876 (m), 793 (m), 764 (s), 728 (s), 690 (s), 581 (s), 568 (s), 534 (s), 514 (s), 477 (w), 447 (m). R_f (hexanes:EtOAc 9:1): 0.13.

7f:[57] Table 9, entry 10. According to TP 6, **7f** was synthesized from (3-cyanopropyl)iodo-zinc·LiCl[35] (1.38 M in THF, 0.38 mL, 0.5 mmol) and diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol) in DMF (1.0 mL). Purification by column chromatography (hexanes:EtOAc 4:1 → 1:1) afforded the product as a colorless solid (66.1 mg, 64%). mp: 70−72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00−7.85 (m, 2H), 7.74−7.67 (m, 1H), 7.66−7.55 (m, 2H), 3.25−3.19 (m, 2H), 2.63−2.56 (m, 2H), 2.18−2.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 134.4, 129.7, 128.2, 118.2, 54.4, 19.2, 16.4, 16.4. MS: *m*/*z*: calcd for $C_{10}H_{11}NO_2S+Na^+$ 232.04, found 232.09. IR (cm^{-1}): 2935 (w), 2247 (m), 1479 (w), 1444 (m), 1426 (m), 1408 (m), 1304 (s, -SO_2-), 1272 (s), 1210 (m), 1154 (m, -SO_2-), 1142 (s, -SO_2-), 1084 (s), 1053 (m), 1024 (s), 1000 (m), 931 (w), 876 (m), 779 (m), 738 (s), 718 (s), 688 (s), 605 (s), 550 (s), 526 (s), 463 (m). R_f (cyclohexane:EtOAc 4:1): 0.1.

7g:[58] Table 9, entry 11. According to TP 6, **7g** was prepared from (4-ethoxy-4-oxobutyl)iodo-zinc·LiCl[35] (0.89 M in THF, 0.56 mL, 0.5 mmol) and diphenyliodonium triflate (**3a**) (645.3 mg, 1.5 mmol) in DMF (1.0 mL). Purification by column chromatography (hexanes:EtOAc 9:1 → 4:1) afforded the product as a colorless oil (107.1 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94−7.88 (m, 2H), 7.69−7.64 (m, 1H), 7.60−7.54 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.20−3.16 (m, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.06−2.00 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 139.1, 134.0, 129.5, 128.2, 60.9, 55.3, 32.4, 18.4, 14.3. MS: *m*/*z*: calcd for$C_{12}H_{16}O_4S+Na^+$ 279.09, found 278.80. IR (cm^{-1}): 3065 (w), 2980 (w), 2931 (w), 1727 (s), 1585 (w), 1569 (w), 1447 (m), 1375 (m), 1354 (s, -SO_2-), 1299 (s), 1237 (s), 1186 (m), 1143 (s, -SO_2-), 1086 (s), 1029 (s), 935 (w), 842 (w), 791 (m), 738 (s), 689 (s), 587 (m), 562 (m), 530 (s), 486 (w), 447 (w). R_f (cyclohexane:EtOAc 4:1): 0.22.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data and copies of ^{1}H and ^{13}C spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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