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# Iridium-Catalyzed Direct C−H Sulfamidation of Aryl Nitrones with Sulfonyl Azides at Room Temperature

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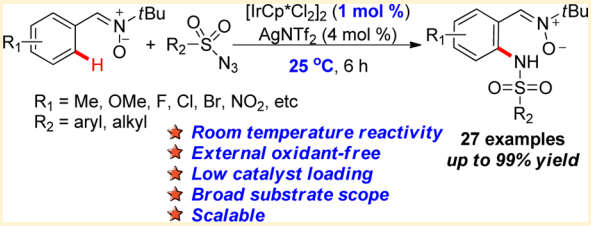
Supporting Information

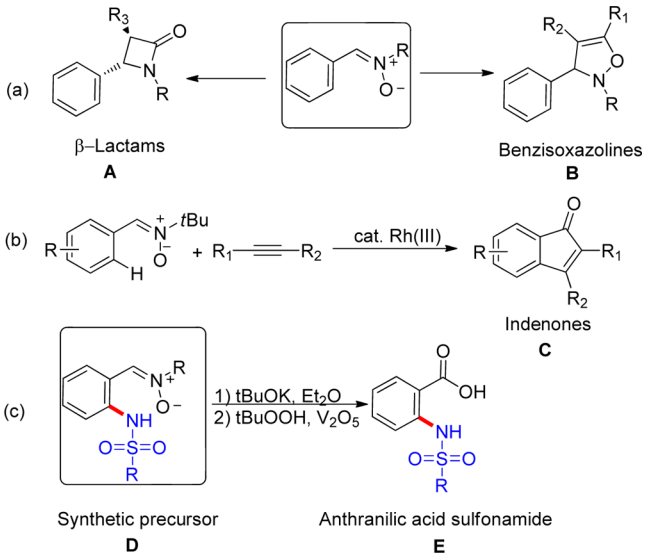
**ABSTRACT:** Ir(III)-catalyzed direct C−H sulfamidation of aryl nitrones has been developed to synthesize various sulfamidated nitrones in moderate to excellent yields with excellent regioselectivity and broad functional group tolerance. This transformation could proceed smoothly at room temperature with low catalyst loading in the absence of external oxidants, acids, or bases. Molecular nitrogen was released as the sole byproduct, thus providing an environmentally benign sulfamidation process. And this protocol could efficiently apply to synthesize the substituted benzisoxazoline via one-step transformation from the product.




## INTRODUCTION

Arylnitrone scaffold is of great importance in organic synthesis and can be easily converted into various heterocycles via diverse transformation.[1] For instance, substituted $\beta$-lactams (**A**) and benzisoxazolines (**B**, Scheme 1a) directly obtained from nitrones are important synthetic building blocks and have been found in a number of biological molecules.[2] Indenone (**C**, Scheme 1b), a useful skeleton in synthetic chemistry, pharmaceuticals, and material science, could be accessed by rhodium-catalyzed C−H annulation of nitrones with internal alkynes.[3] In particular, 2-aminoaryl nitrones containing dual functional groups of amino and nitrone groups are especially valuable because they are readily modifiable. Anthranilic acid sulfonamides (**E**, Scheme 1c), accessed from compound **D**, have been evaluated as human MetAP2 inhibitors with potent activities against the enzyme and against HMVEC proliferation.[4,5] Therefore, the development of a practical approach to introduce amine groups into the nitrone motif is highly important and desirable.

**Scheme 1. Examples Illustrating the Importance of Nitrones**




Employing copper mediators for the activation of aryl (pseudo)halides to react with amine as initiated by Ullmann and Goldberg has been developed.[6] Later, Buchwald and Hartwig independently developed the Pd- and Cu-catalyzed amination starting from (hetero)aryl halides or their pseudos.[7] Recently, a direct C−N bond formation based on transition-metal-catalyzed C−H bond activation has been developed.[8] However, stoichiometric or excessive external oxidants are required in most cases. To avoid the external oxidants, preactivated amino precursors have been employed as the starting materials.[9] However, an additional step is needed to prepare the amine reagent, and stoichiometric byproducts are still generated. To overcome the current limitations, an environmentally benign direct C−H amidation has led chemists to search for alternative approaches. As a consequence, organic azides have been developed as an amino source and internal oxidant by N−$N_2$ bond cleavage, providing environmentally benign methods for the direct C−H amination[10−12] (Scheme 2a). Transition-metal-catalyzed directed C−H amination by chelating groups has been successfully developed.[10−12] In

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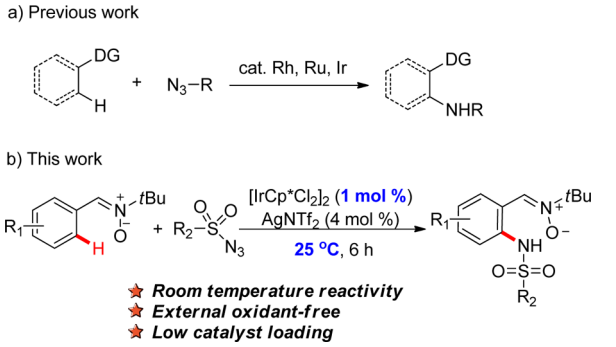
**Scheme 2. Transition-Metal-Catalyzed C−H Amination from Organic Azides**

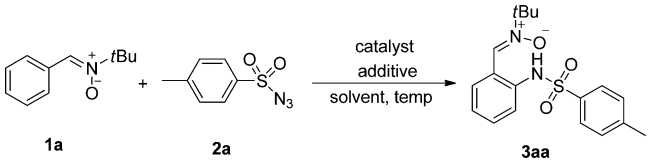



particular, Chang and co-workers have extensively studied the Ir-catalyzed amidation reactions under mild reaction conditions.[12] However, the directing groups reported in the literature were not easily removed or modified. This shortcoming can be attenuated if the chelation groups are converted into other desired functional groups of the synthetic target after the C−H functionalization step. We have developed quinoline *N*-oxides as internal oxidants and utilized a redox process with ferrocene,[13] avoiding external oxidants. As part of our continuing work, we herein embarked on the development of a highly efficient and selective iridium-catalyzed direct C−H sulfamidation of aryl nitrones using sulfonyl azides as the starting materials and avoiding external oxidants (Scheme 2b). Importantly, this transformation could proceed smoothly at room temperature with low catalyst loading, which would make it a potential application in industry.

## RESULTS AND DISCUSSION

The condensation of *N*-*tert*-butyl-*α*-phenylnitrone (**1a**) with *p*-toluenesulfonyl azide (**2a**) was initially chosen as a model reaction to screen various reaction parameters (Table 1). To our great delight, the desired product **3aa** was isolated in 75% yield in the presence of $[IrCp^*Cl_2]_2$ (2 mol %) in 1,2-DCE (1,2-dichloroethane) using $AgNTf_2$ as an additive after 12 h at 50 °C (entry 1), the molecular structure of the product **3aa** was further confirmed by single-crystal X-ray diffraction analysis,[14] and the configuration is shown in Figure 1 in the Supporting Information. The yield decreased slightly in the presence of PivOH (entry 2). The procedure was shut down using NaOAc as an additive (entry 3). When the reaction time was decreased to 6 h, the yield was improved to 86% (entry 4). In view of the fact that high temperature might lead to decomposition of the product, the reaction temperature was decreased from 50 to 25 °C, affording a higher yield of 96% (entry 5). Among various silver salts tested, $AgNTf_2$ gave the best yield (entries 5−7). We then examined the nonpolar or polar solvents and found that this reaction did not work in DMF (*N*,*N*-dimethylformamide), acetonitrile, or methanol, but 1,2-DCE gave the highest yield (entries 8−13). A similar yield (95%) could be obtained with as low as 1 mol % catalyst loading (entry 14). Further reducing the loading of catalyst or shortening the reaction time led to lower efficiencies (entries 15 and 16). $Pd(OAc)_2$ showed almost no catalytic activity in this reaction (entry 17). No desired product was detected in the presence of $[RhCp^*Cl_2]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ with copper at 25 °C (entries 18 and 19, Table 1). Elevating the reaction temperature to 80 °C and prolonging the reaction time to 12 h resulted in 82% and 70%

**Table 1. Optimization of the Reaction Conditions**[a]




| entry | catalyst | solvent | *T* (°C) | time (h) | yield (%) |
|---|---|---|---|---|---|
| 1 | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 50 | 12 | 75 |
| 2[b] | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 50 | 12 | 60 |
| 3[c] | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 50 | 12 | n.r. |
| 4 | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 50 | 6 | 86 |
| 5 | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 25 | 6 | 96 |
| 6 | $[IrCp^*Cl_2]_2/AgSbF_6$ | 1,2-DCE | 25 | 6 | 79 |
| 7 | $[IrCp^*Cl_2]_2/AgBF_4$ | 1,2-DCE | 25 | 6 | 67 |
| 8 | $[IrCp^*Cl_2]_2/AgNTf_2$ | toluene | 25 | 6 | 26 |
| 9 | $[IrCp^*Cl_2]_2/AgNTf_2$ | THF | 25 | 6 | 40 |
| 10 | $[IrCp^*Cl_2]_2/AgNTf_2$ | $CH_3CN$ | 25 | 6 | n.r. |
| 11 | $[IrCp^*Cl_2]_2/AgNTf_2$ | $CH_3OH$ | 25 | 6 | n.r. |
| 12 | $[IrCp^*Cl_2]_2/AgNTf_2$ | DMF | 25 | 6 | n.r. |
| 13 | $[IrCp^*Cl_2]_2/AgNTf_2$ | DME | 25 | 6 | 80 |
| 14[d] | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 25 | 6 | 95 |
| 15[e] | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 25 | 6 | 55 |
| 16 | $[IrCp^*Cl_2]_2/AgNTf_2$ | 1,2-DCE | 25 | 3 | 85 |
| 17[f] | $Pd(OAc)_2$ | 1,2-DCE | 80 | 12 | n.r. |
| 18[g] | $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$ | 1,2-DCE | 25 | 6 | n.r. |
| 19 | $[RhCp^*Cl_2]_2/AgSbF_6$ | 1,2-DCE | 25 | 6 | n.r. |
| 20 | $[RhCp^*Cl_2]_2/AgSbF_6$ | 1,2-DCE | 80 | 12 | 82 |
| 21[g] | $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$ | 1,2-DCE | 80 | 12 | 70 |
| 22 | $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$ | 1,2-DCE | 80 | 12 | n.r. |

[a] **1a** (0.2 mmol), **2a** (0.22 mmol), $[IrCp^*Cl_2]_2$ (2 mol %), $AgNTf_2$ (8 mol %), additive (0.3 equiv), solvent (1.0 mL), under air. [b] PivOH as additive. [c] NaOAc as additive. [d] $[IrCp^*Cl_2]_2$ (1 mol %), $AgNTf_2$ (4 mol %). [e] $[IrCp^*Cl_2]_2$ (0.5 mol %), $AgNTf_2$ (2 mol %). [f] 2 equiv of $K_2S_2O_8$ was used. [g] $Cu(OAc)_2$ as additive (0.3 equiv).

yields, respectively (entries 20 and 21, Table 1). $[Ru(p\text{-cymene})Cl_2]_2$ did not work without copper, even under higher temperature and longer reaction time (entry 22). Finally, the optimized reaction conditions were identified as follows: 1 mol % of $[IrCp^*Cl_2]_2$, 4 mol % of $AgNTf_2$, and 1.1 equiv of *p*-toluenesulfonyl azide **2a** in 1,2-DCE under air at 25 °C for 6 h.

With the optimized reaction conditions, the scope of sulfonyl azides was then examined in the sulfamidation of *N*-*tert*-butyl-*α*-phenylnitrone (Scheme 3). It was found that the electron density of arensulfonyl azides did not have significantly influence on this transformation, and the bisamidated products were not detected. Aromatic rings substituted with electron-donating and electron-withdrawing groups were readily sulfamidated at the *ortho*-position and provided the desired products in excellent yields for all most cases (**3aa**−**ai**). Moderate product yield was obtained for 4-nitrobenzenesulfonyl azide (**3aj**). In addition, broad functional groups were also tolerated. For instance, arensulfonyl azides bearing fluoro (**3ae**), chloro (**3af**), bromo (**3ag**), or ketone (**3ai**) groups were smoothly sulfamidated in excellent yields. Aliphatic sulfonyl azides also worked well. Ethylsulfonyl azide and benzylsulfonyl azide afforded the corresponding products **3ak** and **3al** in 94% yields, respectively. Naphthalene-2-sulfonyl azide was a suitable substrate and gave the corresponding sulfamidated product



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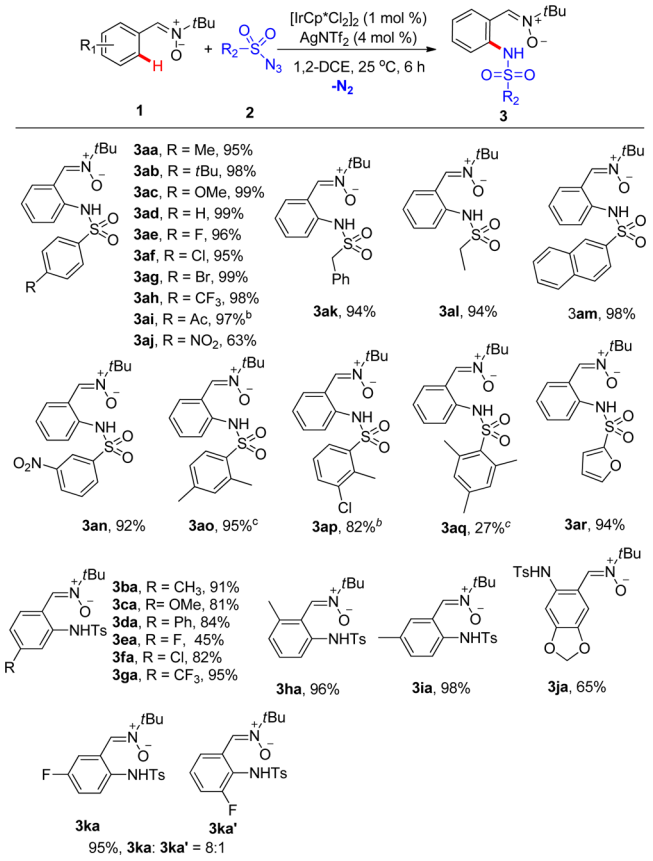
**Scheme 3. Scope of Substrates**[a]



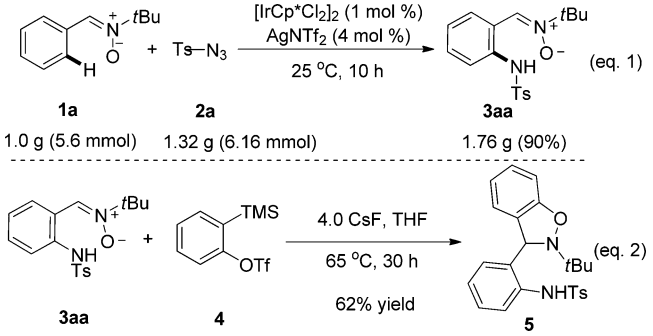

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.22 mmol), $[IrCp^*Cl_2]_2$ (1 mol %), $AgNTf_2$ (4 mol %) in DCE (1.0 mL) at 25 °C for 6 h under air. [b]At 50 °C. [c]At 50 °C for 10 h.

**3am** in 98% yield. Arensulfonyl azide bearing a nitro group at *meta*-position could readily participate in the sulfamidation reaction, providing product **3an** in 92% yield. Arensulfonyl azide with *o*-methyl group slightly decreased the reactivity, presumably due to steric hindrance. When the reaction temperature was raised to 50 °C, the desired products **3ao** and **3ap** were obtained in 95% and 82% yields, respectively. 2,4,6-Trimethylbenzenesulfonyl azide delivered the desired product **3aq** in only 27% yield, even performed at 50 °C. In addition, thiophene-2-sulfonyl azide afforded the corresponding product **3ar** in 94% yield. Trace amounts of desired product were detected when benzoyl azide was employed as a substrate under the standard reaction conditions.

We next investigated a range of aryl nitrones to react with *p*-toluenesulfonyl azide (**2a**) under the optimized conditions (Scheme 3). *Ortho*-sulfamidated products with electron-donating substituents, such as methyl (**3ba**) or methoxy (**3ca**), were obtained in 91% and 81% yields, respectively. *N*-*tert*-Butyl-α-phenyl nitrone substituted with 4-phenyl could also be employed for this conversion and smoothly provided the target product (**3da**) in 84% yield. In addition, substrates bearing electron-withdrawing groups, such as fluoro (**3ea**), chloro (**3fa**), or trifluoromethyl (**3ga**) groups were all sulfamidated in good yields. Excitingly, C−H sulfamidation of aryl nitrones substituted with methyl group at the *ortho* (**3ha**) or *meta* position (**3ia**) occurred selectively at the position with lower steric hindance in excellent yield. *N*-*tert*-Butyl-α-piperonyl nitrone gave the corresponding product (**3ja**) in 65% yield. For aryl nitrone with a smaller F group at the *meta*-position, C−H sulfamidation occurred at two sites, giving the major product (**3ka**) and the minor product (**3ka′**) in 95% total yield with a ratio of 8:1. No reaction was observed for pyridyl nitrone, furyl nitrone, and thienyl nitrone under the standard reaction conditions.

To demonstrate the synthetic potential application of the present method, the sulfamidation of **1a** on a gram scale was attempted. The sulfamidated nitrone **3aa** was obtained with 90% yield (eq 1, Scheme 4). Substituted benzisoxazoline **5**

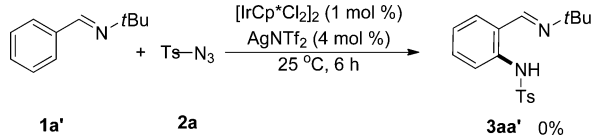
**Scheme 4. Gram-Scale Sulfamidation of 1a and Transformation of Amidated Product**




could be synthesized by the [3 + 2] cycloaddition of arynes **4** and sulfamidated nitrones **3aa** obtained from our methodology, providing 62% yield (eq 2, Scheme 4). In comparison with traditional methods, the current reaction provided an easier, more direct, and step-economic method to various benzisoxazoline derivatives with important biological and pharmacological activities.[15]

To gain insight into the mechanism of this transformation, the controlled experiments were carried out. The desired product was not obtained when the condensation of *N*-benzylidene-2-methylpropan-2-amine (**1a′**) with *p*-toluenesulfonyl azide (**2a**) was processed under the standard conditions, which indicated that iridacycle intermedium was formed by the coordination of the iridium atom with the O atom rather than N atom, and the *N*-oxide moiety was necessary for this transformation (Scheme 5).

**Scheme 5. Control Experiment**




On the basis of the above experimental results and literature results,[12,16] the reaction mechanism was proposed as shown in Scheme 6. First, the dimeric precursor $[IrCp^*Cl_2]_2$ was converted into a cationic species with the aid of silver salt. The six-membered iridacycle **I**[3,17] with one vacant accessible site was formed by the coordination of the iridium atom with the O atom and subsequently electrophilically attacked at the *ortho*-position C atom. Then, intermediate **II** was prepared by azide interacting with the cationic metal center. It was proposed that an iridium nitrenoid species **III** from complex **II** occurs in an oxidative manner to release $N_2$ molecule.[18] A new C−N bond of **IV** was formed by insertion of the nitrenoid species



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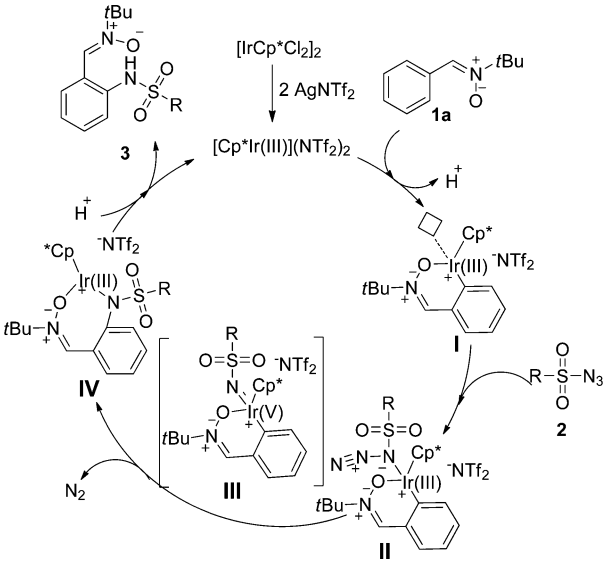
**Scheme 6. Proposed Reaction Mechanism**




into iridacycle. Finally, compound **IV** was protodemetalated to deliver the sulfamidated product **3**.

## CONCLUSIONS

In summary, we have developed an iridium-catalyzed direct sulfamidation of aryl nitrones, employing sulfonyl azides as an amino source and internal oxidant. A series of sulfamidated nitrones were prepared in excellent yields with good functional group tolerance at room temperature. In this approach, external oxidants, acids or bases were avoided and $N_2$ was released as the sole byproduct, thus providing an environmentally benign sulfamidation process. The present protocol is anticipated to be an important approach to nitrones, which would be useful to build multitudinous biologically active molecules.

## EXPERIMENTAL SECTION

**General Information.** All catalytic reactions were carried out under air atmosphere. Unless otherwise stated, all reagents were purchased without further purification. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel GF254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). $^1$H NMR spectra were recorded on a 400 MHz spectrometer with deuteraterated chloroform as solutions. The chemical shifts $\delta$ are reported in ppm relative to tetramethylsilane. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, *J*, are reported in hertz (Hz). $^{13}$C {$^1$H} NMR spectra were recorded at 100 MHz spectrometer with deuteraterated chloroform as solutions. The chemical shifts $\delta$ are reported relative to residual $CHCl_3$ ($\delta_c$ = 77.00 ppm). High-resolution mass spectra (HRMS) were obtained on a Q-ToF spectrometer with micromass MS software using electrospray ionization (ESI). X-ray analysis was obtained with an X-ray single-crystal diffractometer. Melting points were measured on a microscopic apparatus and are uncorrected.

**General Procedure for the Preparation of Azide Substrates (2).**[19] To a solution of sodium azide (0.95 g, 15 mmol) in water (5 mL) was added dropwise a solution of sulfonyl chloride (10 mmol) in acetone (5 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Acetone was removed under reduced pressure, and the reaction mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was dried over $Na_2SO_4$, and solvents were removed in vacuo.

**General Procedure for the Preparation of Aryl Nitrones Substrates (1).**[20] Under $N_2$ atmosphere, a round-bottom flask (100 mL) equipped with a magnetic stirrer bar was charged with aldehyde (5 mmol), *N*-methylhydroxylamine hydrochloride (5 mmol), anhydrous $MgSO_4$ (1.0 g), $NaHCO_3$ (0.55 g), and 1,2-dichlorothane (30 mL). The reaction mixture was stirred under reflux for 24 h. After filtration and removal of solvents, the crude product was purified by flash chromatography on silica gel.

**General Procedure for Iridium-Catalyzed C−H Sufamidation of Arylnitrones with Sulfonyl Azides.** Under air atmosphere, a reaction tube (25 mL) equipped with a magnetic stirrer bar was charged with aryl nitrone (**1**, 0.2 mmol), sulfonyl azide (**2**, 0.22 mmol), $[IrCp^*Cl_2]_2$ (1.6 mg, 0.02 mmol, 1 mol %), $AgNTf_2$ (3.1 mg, 0.08 mmol, 4 mol %), and 1,2-dichloroethane (1.0 mL). The reaction mixture was stirred at room temperature for 6 h, filtered through a pad of Celite, and then washed with $CH_2Cl_2$ (10 mL × 3). The solvents were removed under reduced pressure, and the residue was purified by chromatography on silica gel (elute: EtOAc/petroleum ether/$NEt_3$) to give the desired product **3**.

*(Z)-2-Methyl-N-(2-(4-methylphenylsulfonamido)benzylidene)-propan-2-amine oxide (**3aa**):* 65.7 mg, 95%; white solid; mp 151−153 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.54 (br, 1H), 7.59 (d, *J* = 3.5 Hz, 2H), 7.55 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42−7.38 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 4.2 Hz, 2H), 2.38 (s, 3H), 1.55 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.9, 138.0, 137.9, 134.2, 131.6, 131.2, 129.3, 126.8, 124.9, 124.5, 123.6, 71.2, 28.2, 21.5; IR (KBr, cm$^{-1}$): 3430, 3127, 2978, 1600, 1492, 1400, 1326, 1161, 1129, 1092, 925, 890, 845, 802, 775, 723, 665, 548, 434; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_3S^+$ [M + H]$^+$ *m*/*z* 347.1424, found 347.1427.

*(Z)-N-(2-(4-tert-Butylphenylsulfonamido)benzylidene)-2-methyl-propan-2-amine oxide (**3ab**):* 76.1 mg, 98%; white solid; mp 192−195 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.49 (br, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.55 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.45−7.43 (m, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.17−7.15 (m, 2H), 1.52 (s, 9H), 1.3 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 155.8, 137.9, 134.1, 131. 6, 131.0, 130.8, 126.5, 125.6, 125.0, 124. 5, 123.5, 71.0, 35.0, 31.0, 28.1; IR (KBr, cm$^{-1}$) 3421, 3075, 2978, 1571, 1494, 1334, 1167, 1112, 1084, 916, 846, 799, 776, 632, 572, 552, 529; HRMS (ESI) calcd for $C_{21}H_{29}N_2O_3S^+$ [M + H]$^+$ *m*/*z* 389.1893, found 389.1895.

*(Z)-N-(2-(4-Methoxyphenylsulfonamido)benzylidene)-2-methyl-propan-2-amine oxide (**3ac**):* 71.2 mg, 99%; white solid; mp 155 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.50 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.60 (s, 1H), 7.46−7.40 (m, 2H), 7.16−7.14 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.57 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 162.4, 137.9, 134.2, 132.6, 131.5, 131.1, 128.8, 124.6, 124.4, 123.4, 113.8, 71.1, 55.5, 28.1; IR (KBr, cm$^{-1}$) 3423, 3090, 2980, 1596, 1493, 1327, 1259, 1159, 1095, 1027, 924, 890, 835, 805, 774, 667, 568, 550; HRMS (ESI) calcd for $C_{18}H_{22}N_2NaO_4S^+$ [M + Na]$^+$ *m*/*z* 385.1192, found 385.1196.

*(Z)-2-Methyl-N-(2-(phenylsulfonamido)benzylidene)propan-2-amine oxide (**3ad**):* 65.8 mg, 99%; white solid; mp 144−145 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.61 (br, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.54 (s, 1H), 7.50−7.47 (m, 2H), 7.45−7.38 (m, 3H), 7.19−7.13 (m, 2H), 1.54 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 140.7, 137.7, 134.1, 132.1, 131.6, 131.1, 128.7, 126.7, 125.0, 124.6, 123.6, 71.1, 28.1; IR (KBr, cm$^{-1}$) 3429, 3129, 2980, 1570, 1497, 1400, 1321, 1239, 1165, 1095, 956, 904, 837, 759, 692, 575, 543; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3S^+$ [M + H]$^+$ *m*/*z* 333.1267, found 333.1271.

*(Z)-N-(2-(4-Fluorophenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ae**):* 67.3 mg, 96%; white solid; mp 150−151 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.78 (br, 1H), 7.73 (dd, $J_1$ = 8.7 Hz, $J_2$ = 5.2 Hz, 2H), 7.62 (s, 1H), 7.44−7.42 (m, 2H), 7.18−7.16 (m, 2H), 7.11−7.06 (m, 2H), 1.57 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 164.7 (d, $J_{C-F}$ = 249.1 Hz), 137.6, 136.9 (d, $J_{C-F}$ = 3.8 Hz), 134.2, 131.5 (d, $J_{C-F}$ = 44.4 Hz), 129.4, 129.3, 124.6, 124.4, 123.4, 115.8 (d, $J_{C-F}$ = 22.4 Hz), 71.2, 28.2; IR (KBr, cm$^{-1}$) 3423, 3066, 2985, 2922, 1590, 1492, 1353, 1326, 1233, 1168, 1093, 842, 778, 665, 565, 544; HRMS (ESI) calcd for $C_{17}H_{19}FN_2NaO_3S^+$ [M + Na]$^+$ *m*/*z* 373.0993, found 373.0996.

*(Z)-N-(2-(4-Chlorophenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3af**):* 69.7 mg, 95%; white solid; mp 145−146 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.90 (br, 1H), 7.62 (s, 1H), 7.61



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(d, $J$ = 7.7 Hz, 2H), 7.46−7.40 (m, 2H), 7.37 (d, $J$ = 8.6 Hz, 2H), 7.20−7.15 (m, 2H), 1.55 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 139.3, 138.6, 137.4, 134.3, 131.7, 131.4, 128.9, 128.1, 124.7, 124.5, 123.4, 71.2, 28.1. IR (KBr, cm$^{-1}$) 3430, 3092, 1570, 1398, 1332, 1278, 1164, 1129, 1089, 925, 890, 832, 800, 774, 612, 550, 480; HRMS (ESI) calcd for $C_{17}H_{20}ClN_2O_3S^+$ $[M + H]^+$ $m/z$ 367.0878, found 367.0881.

*(Z)-N-(2-(4-Bromophenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ag**):* 81.4 mg, 99%; white solid; mp 140 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.86 (s, 1H), 7.62 (s, 1H), 7.58 (d, $J$ = 8.6 Hz, 2H), 7.54 (d, $J$ = 8.7 Hz, 2H), 7.44−7.43 (m, 2H), 7.18−7.17 (m, 2H), 1.57 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 138.8, 137.4, 134.3, 131.9, 131.7, 131.4, 128.2, 127.0, 124.7, 124.5, 123.4, 71.2, 28.1; IR (KBr, cm$^{-1}$) 3426, 3144, 2985, 1571, 1400, 1359, 1274, 1164, 1129, 1069, 925, 804, 780, 736, 599, 543; HRMS (ESI) calcd for $C_{17}H_{19}BrN_2NaO_3S^+$ $[M + Na]^+$ $m/z$ 433.0192, found 433.0197.

*(Z)-2-Methyl-N-(2-(4-(trifluoromethyl)phenylsulfonamido)-benzylidene)propan-2-amine oxide (**3ah**):* 78.5 mg, 98%; white solid; mp 142−143 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.07 (br, 1H), 7.84 (d, $J$ = 8.2 Hz, 2H), 7.68 (d, $J$ = 8.3 Hz, 2H), 7.60 (s, 1H), 7.45−7.44 (m, 2H), 7.20−7.18 (m, 2H), 1.55 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 137.4, 134.3, 133.9 (q, $J_{C-F}$ = 32.8 Hz), 131.8, 131.4, 127.2, 125.8 (q, $J_{C-F}$ = 271.5 Hz), 125.8 (q, $J_{C-F}$ = 3.7 Hz), 124.8, 124.5, 123.4, 71.3, 28.1; IR (KBr, cm$^{-1}$) 3429, 3129, 1609, 1402, 1325, 1167, 1128, 603, 542; HRMS (ESI) calcd for $C_{18}H_{20}F_3N_2O_3S^+$ $[M + H]^+$ $m/z$ 401.1141, found 401.1149.

*(Z)-N-(2-(4-Acetylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ai**).* 72.7 mg, 97%; white solid; mp 137−138 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.04 (br, 1H), 7.97 (d, $J$ = 8.3 Hz, 2H), 7.83−7.80 (m, 2H), 7.61 (s, 1H), 7.44−7.43 (m, 2H), 7.17−7.16 (m, 2H), 2.62 (s, 9H), 1.59 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 196.7, 144.8, 139.6, 137.5, 134.3, 131.8, 131.4, 128.5, 127.0, 124.6, 124.2, 123.3, 71.3, 28.1, 26.7; IR (KBr, cm$^{-1}$) 3426, 2978, 2926, 1690, 1357, 1262, 1163, 807, 637, 589, 542; HRMS (ESI) calcd for $C_{19}H_{23}N_2O_4S^+$ $[M + H]^+$ $m/z$ 375.1373, found 375.1376.

*(Z)-2-Methyl-N-(2-(4-nitrophenylsulfonamido)benzylidene)-propan-2-amine oxide (**3aj**):* 47.6 mg, 63%; yellow solid; mp 191−192 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.43 (br, 1H), 8.27 (d, $J$ = 8.7 Hz, 2H), 7.94 (d, $J$ = 8.7 Hz, 2H), 7.68 (s, 1H), 7.46−7.41 (m, 2H), 7.21−7.19 (m, 2H), 1.59 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.7, 146.8, 137.3, 134.6, 132.0, 131.6, 128.0, 124.8, 124.0, 123.8, 123.0, 71.4, 28.2; IR (KBr, cm$^{-1}$) 3422, 2981, 2921, 1530, 1351, 1164, 850, 806, 780, 735, 681, 617, 599, 542, 465; HRMS (ESI) calcd for $C_{17}H_{19}N_3NaO_5S^+$ $[M + Na]^+$ $m/z$ 400.0938, found 400.0952.

*(Z)-2-Methyl-N-(2-(phenylmethylsulfonamido)benzylidene)-propan-2-amine oxide (**3ak**):* 65.1 mg, 94%; white solid; mp 143−144 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.53 (br, 1H), 7.76 (s, 1H), 7.40−7.36 (m, 1H), 7.33−7.26 (m, 6H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.16−7.12 (m, 1H), 4.33 (s, 2H), 1.52 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 138.4, 134.7, 131.7, 131.4, 130.8, 130.5, 129.3, 128.5, 128.4, 123.9, 122.5, 71.1, 58.9, 28.0; IR (KBr, cm$^{-1}$) 3428, 3130, 1602, 1491, 1452, 1401, 1328, 1160, 1129, 1075, 515; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_3S^+$ $[M + H]^+$ $m/z$ 347.1424, found 347.1422.

*(Z)-N-(2-(Ethylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3al**):* 53.5 mg, 94%; white solid; mp 83−86 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.53 (br, 1H), 7.92 (s, 1H), 7.55 (d, $J$ = 8.2 Hz, 2H), 7.48−7.43 (m, 1H), 7.29−7.27 (m, 1H), 7.19−7.15 (m, 1H), 3.12 (q, $J$ = 7.4 Hz, 2H), 1.64 (s, 9H), 1.38 (d, $J$ = 7.4 Hz, 3H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 138.9, 135.2, 132.2, 132.2, 124.4, 123.2, 120.7, 71.2, 47.7, 28.7, 8.8; IR (KBr, cm$^{-1}$) 3099, 2984, 1635, 1599, 1568, 1491, 1405, 1326, 1268, 1189, 1075, 919, 886, 843, 804, 777, 729, 704, 527, 476, 404; HRMS (ESI) calcd for $C_{13}H_{20}N_2NaO_3S^+$ $[M + Na]^+$ $m/z$ 307.1087, found 307.1090.

*(Z)-2-Methyl-N-(2-(naphthalene-2-sulfonamido)benzylidene)-propan-2-amine oxide (**3am**):* 75.0 mg, 98%; white solid; mp 121−124 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.54 (br, 0.4H), 8.25 (s, 1H), 7.86−7.80 (m, 3H), 7.62−7.55 (m, 3H), 7.52 (d, $J$ = 8.4 Hz, 1H), 7.44−7.38 (m, 2H), 7.17−7.11 (m, 2H), 1.45 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 138.2, 135.0, 134.7, 132.4, 132.1, 131.7, 129.5, 129.3, 129.0, 128.2, 128.1, 127.9, 125.6, 125.2, 124.3, 124.0, 122.8, 71.6, 28.5; IR (KBr, cm$^{-1}$) 2977, 1567, 1493, 1452, 1403, 1347, 1159, 1128, 1074, 959, 907, 861, 821, 751, 658, 616, 541, 504, 480; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3S^+$ $[M + H]^+$ $m/z$ 383.1424, found 383.1429.

*(Z)-2-Methyl-N-(2-(3-nitrophenylsulfonamido)benzylidene)-propan-2-amine oxide (**3an**):* 69.4 mg, 92%; yellow solid; mp 181−183 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.38 (s, 1H), 8.55−8.53 (m, 1H), 8.36−8.33 (m, 1H), 8.06 (d, $J$ = 7.8 Hz, 2H), 7.67 (s, 1H), 7.63 (t, $J$ = 8.0 Hz, 1H), 7.49−7.45 (m, 2H), 7.19−7.18 (m, 2H), 1.59 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 148.0, 143.1, 137.2, 134.4, 132.4, 132.0, 131.6, 130.1, 126.6, 124.9, 124.1, 123.2, 121.8, 71.5, 28.1; IR (KBr, cm$^{-1}$) 3090, 2981, 1603, 1535, 1492, 1403, 1358, 1275, 1174, 1127, 1069, 944, 878, 849, 810, 782, 753, 670, 584, 408; HRMS (ESI) calcd for $C_{17}H_{19}N_3Na\ O_5S^+$ $[M + Na]^+$ $m/z$ 400.0938, found 400.0946.

*(Z)-N-(2-(2,4-Dimethylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ao**):* 68.5 mg, 95%; white solid; mp 116−118 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta\delta$ 10.78 (s, 1H), 7.86 (d, $J$ = 8.8 Hz, 1H), 7.82 (s, 1H), 7.32−7.28 (m, 1H), 7.19 (m, 2H), 7.10−7.06 (m, 3H), 2.59 (s, 3H), 2.34 (s, 3H), 1.62 (s, 9H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.9, 138.3, 137.2, 136.5, 134.8, 133.1, 131.4, 131.3, 129.1, 126.6, 123.6, 122.6, 122.4, 71.1, 28.2, 21.1, 20.0; IR (KBr, cm$^{-1}$) 2982, 2922, 1599, 1571, 1492, 1445, 1401, 1324, 1234, 1172, 1143, 1060, 939, 906, 828, 56, 655, 624, 573, 544, 524, 412; HRMS (ESI) calcd for $C_{19}H_{24}N_2NaO_3S^+$ $[M + Na]^+$ $m/z$ 383.1400, found 383.1402.

*(Z)-N-(2-(3-Chloro-2-methylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ap**):* 62.5 mg, 82%; white solid; mp 175 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.24 (br, 1H), 7.96 (d, $J$ = 7.9 Hz, 1H), 7.87 (s, 1H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.35−7.30 (m, 1H), 7.24−7.21 (m, 2H), 7.17 (d, $J$ = 8.2 Hz, 1H), 7.11 (t, $J$ = 7.6 Hz, 1H), 2.71 (s, 3H), 1.63 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 141.6, 138.1, 136.8, 135.4, 135.0, 133.3, 131.6, 131.5, 127.5, 126.5, 123.8, 122.5, 122.3, 71.2, 28.2, 16.7; IR (KBr, cm$^{-1}$) 2979, 2931, 1570, 1495, 1434, 1329, 1151, 1089, 756, 702, 614, 561; HRMS (ESI) calcd for $C_{18}H_{21}ClN_2NaO_3S^+$ $[M + Na]^+$ $m/z$ 403.0854, found 403.0867.

*(Z)-2-Methyl-N-(2-(thiophene-2-sulfonamido)benzylidene)-propan-2-amine oxide (**3ar**):* 63.6 mg, 94%; white solid; mp 155−157 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.21 (s, 1H), 7.96 (dd, $J_1$ = 8.5 Hz, $J_2$ = 1.0 Hz, 1H), 7.86 (s, 1H), 7.54 (dd, $J_1$ = 8.0 Hz, $J_2$ = 0.9 Hz, 1H), 7.35−7.31 (m, 1H), 7.23 (t, $J$ = 8.1 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 1H), 7.11 (m, 1H), 2.71 (s, 3H), 1.63 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.0, 137.8, 134.7, 132.2, 131.9, 131.7, 131.7, 127.4, 126.2, 125.7, 124.6, 71.7, 28.6; IR (KBr, cm$^{-1}$) 3102, 1598, 1495, 1452, 1401, 1333, 1284, 1227, 1075, 1017, 844, 759, 731, 666, 630, 585, 540; HRMS (ESI) calcd for $C_{15}H_{19}N_2O_3S_2^+$ $[M + H]^+$ $m/z$ 339.0832, found 339.0835.

*(Z)-2-Methyl-N-(4-methyl-2-(4-methylphenylsulfonamido)-benzylidene)propan-2-amine oxide (**3ba**):* 65.6 mg, 91%; white solid; mp 161−162 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.73 (s, 1H), 7.57 (d, $J$ = 8.1 Hz, 2H), 7.49 (s, 1H), 7.30 (s, 1H), 7.18 (d, $J$ = 8.0 Hz, 2H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.96 (d, $J$ = 7.9 Hz, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 1.53 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.7, 142.4, 138.0, 137.8, 134.1, 131.0, 129.1, 126.7, 125.5, 125.4, 120.8, 70.7, 28.1, 21.4, 21.3; IR (KBr, cm$^{-1}$) 3423, 2988, 2923, 1613, 1323, 1161, 1091, 843, 814, 662, 561, 544; HRMS (ESI) calcd for $C_{19}H_{24}N_2NaO_3S^+$ $[M + Na]^+$ $m/z$ 383.1400, found 383.1403.

*(Z)-N-(4-Methoxy-2-(4-methylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ca**):* 61.0 mg, 81%; white solid; mp 149 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.46 (s, 1H), 7.62 (d, $J$ = 7.9 Hz, 2H), 7.48 (s, 1H), 7.19 (d, $J$ = 7.9 Hz, 2H), 7.03 (d, $J$ = 8.7 Hz, 1H), 7.00−6.98 (m, 1H), 6.68−6.65 (m, 1H), 3.77 (s, 3H), 2.37 (s, 3H), 1.54 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 162.5, 142.9, 140.0, 138.0, 134.4, 132. 8, 129.3, 126.8, 115.4, 111.5, 108.2, 70.5, 55.5, 28.2, 21.4; IR (KBr, cm$^{-1}$) 3419, 3092, 2965, 2923, 1611, 1568, 1508, 1325, 1301, 1159, 1144, 1089, 868, 808, 739, 714, 663, 557, 547; HRMS (ESI) calcd for $C_{19}H_{25}N_2O_4S^+$ $[M + H]^+$ $m/z$ 377.1530, found 377.1531.

*(Z)-2-Methyl-N-((3-(4-methylphenylsulfonamido)-[1,1′-biphenyl]-4-yl)methylene)propan-2-amine oxide (**3da**):* 71.0 mg, 84%; white



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solid; mp 147−149 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.74 (br, 1H), 7.73 (s, 1H), 7.62 (d, $J$ = 7.8 Hz, 2H), 7.59−7.54 (m, 3H), 7.46−7.38 (m, 4H), 7.23−7.19 (m, 3H), 2.38 (s, 3H), 1.56 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 144.3, 143.0, 139.3, 138.3, 138.0, 134.0, 131.7, 129.3, 128.9, 128.2, 127.1, 126.9, 123.3, 123.1, 122.3, 71.1, 28.2, 21.4; IR (KBr, cm$^{-1}$) 3428, 3128, 1610, 1401, 1329, 1157, 764, 658, 569, 546; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_3S^+$ [M + H]$^+$ $m/z$ 423.1737, found 423.1739.

*(Z)-N-(4-Fluoro-2-(4-methylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ea**):* 32.8 mg, 45%; white solid; mp 165 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.16 (s, 1H), 7.67 (d, $J$ = 8.2 Hz, 2H), 7.61 (s, 1H), 7.23 (d, $J$ = 8.2 Hz, 2H), 7.17 (dd, $J_{H-F}$ = 10.5 Hz, $J_2$ = 2.5 Hz, 1H), 7.13 (dd, $J$ = 8.8 Hz, $J_{H-F}$ = 6.0 Hz, 1H), 6.85−6.80 (m, 1H), 2.39 (s, 3H), 1.58 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 164.7 (d, $J_{C-F}$ = 250.8 Hz), 143.3, 140.4 (d, $J_{C-F}$ = 11.6 Hz), 137.7, 134.0, 133.1 (d, $J_{C-F}$ = 10.3 Hz), 129.5, 126.8, 118.7 (d, $J_{C-F}$ = 2.9 Hz), 111.4 (d, $J_{C-F}$ = 22.5 Hz), 110.4 (d, $J_{C-F}$ = 25.1 Hz), 71.2, 28.2, 21.5; IR (KBr, cm$^{-1}$) 3406, 3094, 2975, 2924, 1605, 1579, 1504, 1407, 1327, 1160, 1118, 1090, 995, 869, 814, 742, 712, 664, 560, 544; HRMS (ESI) calcd for $C_{18}H_{22}FN_2O_3S^+$ [M + H]$^+$ $m/z$ 365.1330, found 365.1332.

*(Z)-N-(4-Chloro-2-(4-methylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3fa**):* 62.5 mg, 82%; white solid; mp 180 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.19 (br, 1H), 7.65 (d, $J$ = 8.1 Hz, 2H), 7.58 (s, 1H), 7.48−7.47 (m, 1H), 7.23 (d, $J$ = 8.0 Hz, 2H), 7.12−7.06 (m, 2H), 2.40 (s, 3H), 1.57 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 143.3, 139.1, 137.7, 137.6, 133.6, 132.2, 129.5, 126.8, 124.5, 124.0, 121.5, 71.4, 28.2, 21.5; IR (KBr, cm$^{-1}$) 3423, 2978, 2924, 1592, 1328, 1162, 949, 813, 657, 563, 544; HRMS (ESI) calculated for $C_{18}H_{22}ClN_2O_3S^+$ [M + H]$^+$ $m/z$ 381.1034, found381.1036.

*(Z)-2-Methyl-N-(2-(4-methylphenylsulfonamido)-4-(trifluoromethyl)benzylidene)propan-2-amine oxide (**3ga**):* 78.7 mg, 95%; white solid; mp 145−148 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.46 (br, 1H), 7.73 (s, 1H), 7.66 (s, 1H), 7.56 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.3 Hz, 2H), 7.30 (d, $J$ = 8.2 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 2.36 (s, 3H), 1.54 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.5, 137.4, 136.5, 132.2, 132.1 (q, $J_{C-F}$ = 32.9 Hz), 130.7, 128.5, 125.9, 122.3 (q, $J_{C-F}$ = 271.1 Hz), 120.2 (q, $J_{C-F}$ = 3.7 Hz), 119.8 (q, $J_{C-F}$ = 3.5 Hz), 71.0, 27.2, 20.5; IR (KBr, cm$^{-1}$) 3126, 1402, 1331, 1263, 1162, 1132, 1090, 959, 892, 819, 667, 564; HRMS (ESI) calcd for $C_{19}H_{22}F_3N_2O_3S^+$ [M + H]$^+$ $m/z$ 415.1298, found 415.1299.

*(Z)-2-Methyl-N-(5-methyl-2-(4-methylphenylsulfonamido)-benzylidene)propan-2-amine oxide (**3ha**):* 69.2 mg, 96%; white solid; mp 190−191 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.27 (s, 1H), 7.54 (d, $J$ = 8.2 Hz, 2H), 7.49 (s, 1H), 7.35 (d, $J$ = 8.3 Hz, 1H), 7.23−7.21 (m, 1H), 7.18 (d, $J$ = 8.0 Hz, 2H), 6.96 (s, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.52 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.7, 135.2, 134.5, 133.9, 132.4, 132.1, 131.1, 129.1, 126.8, 125.4, 123.9, 70.9, 28.1, 21.3, 20.5; IR (KBr, cm$^{-1}$) 3425, 2980, 2925, 1501, 1325, 1160, 1093, 902, 821, 667, 581, 537. HRMS (ESI) calcd for $C_{19}H_{25}N_2O_3S^+$ [M + H]$^+$ $m/z$ 361.1580, found 361.1583.

*(Z)-2-Methyl-N-(2-methyl-6-(4-methylphenylsulfonamido)-benzylidene)propan-2-amine oxide (**3ia**):* 70.7 mg, 98%; white solid; mp 125−126 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.03 (s, 1H), 7.66 (s, 1H), 7.59 (d, $J$ = 8.2 Hz, 2H), 7.30−7.38 (m, 2H), 7.20 (d, $J$ = 8.2 Hz, 2H), 6.99 (d, $J$ = 7.2 Hz, 2H), 2.38 (s, 3H), 2.25 (s, 3H), 1.56 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 142.9, 138.4, 138.2, 133.1, 131.1, 129.3, 126.7, 126.7, 122.6, 122.3, 71.3, 28.1, 21.4, 20.0; IR (KBr, cm$^{-1}$) 3094, 2974, 1599, 1564, 1470, 1399, 1348, 1162, 1095, 1032, 977, 816, 715, 668, 571, 551; HRMS (ESI) calcd for $C_{19}H_{25}N_2O_3S^+$ [M + H]$^+$ $m/z$ 361.1580, found 361.1583.

*(Z)-2-Methyl-N-((6-(4-methylphenylsulfonamido)benzo[d][1,3]-dioxol-5-yl)methylene)propan-2-amine oxide (**3ja**):* 50.8 mg, 65%; yellow solid; mp 166 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.81 (br, 1H), 7.63 (d, $J$ = 8.2 Hz, 2H), 7.55 (s, 1H), 7.22 (d, $J$ = 8.1 Hz, 2H), 6.90 (d, $J$ = 8.2 Hz, 1H), 6.76 (d, $J$ = 8.2 Hz, 1H), 5.95 (s, 2H), 2.41 (s, 3H), 1.50 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 143.3, 139.1, 137.7, 137.6, 133.6, 132.2, 129.5, 126.8, 124.5, 124.0, 121.5, 71.4, 28.2, 21.5; IR (KBr, cm$^{-1}$) 3422, 2975, 2923, 1624, 1470, 1356, 1306, 1272, 1162, 1099, 1074, 966, 857, 810, 762, 692, 544, 521; HRMS (ESI) calcd for $C_{19}H_{23}N_2O_5S^+$ [M + H]$^+$ $m/z$ 391.1322, found 391.1324.

*(Z)-N-(5-Fluoro-2-(4-methylphenylsulfonamido)benzylidene)-2-methylpropan-2-amine oxide (**3ka**):* 62.0 mg, 85%; white solid; mp 121−123 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.11 (br, 1H), 7.85 (s, 1H), 7.68 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 7.8 Hz, 1H), 7.26−7.22 (m, 3H), 7.16 (m, 1H), 2.42 (s, 3H), 1.59 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 158.8 (d, $J_{C-F}$ = 243.3 Hz), 143.2, 137.9, 132.3, 129.2, 127.4, 127.3, 125.7 (d, $J_{C-F}$ = 4.2 Hz), 118.1 (d, $J_{C-F}$ = 20.9 Hz), 71.7, 28.2, 21.5; HRMS (ESI) calcd for $C_{19}H_{23}N_2O_5S^+$ [M + H]$^+$ $m/z$ 365.1330, found 365.1333.

**General Procedure for the Transformation of Sufamidated Product.** Under air atmosphere, a reaction tube (25 mL) equipped with a magnetic stirrer bar was charged with **3aa** (87 mg, 0.25 mmol), *o*-(trimethylsilyl)phenyl triflate **4** (91 $\mu$L, 0.4 mmol), and CsF (152 mg, 1.0 mmol), followed by 2 mL of dry THF. The vial was sealed and placed in an oil bath at 65 °C for about 30 h. The resulting mixture was cooled and concentrated under vacuum to yield the crude product, which was purified by chromatography on silica gel (elute: EtOAc/petroleum ether/$NEt_3$) to give the desired product **5**: 52.4 mg, 62%; white solid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.68 (br, 1H), 7.67 (d, $J$ = 8.2 Hz, 2H), 7.20 (m, 4H), 7.10 (t, $J$ = 6.4 Hz, 1H), 7.01 (t, $J$ = 7.5 Hz, 1H), 6.89 (d, $J$ = 8.1 Hz, 2H), 6.80 (d, $J$ = 8.0 Hz, 1H), 6.68 (t, $J$ = 7.5 Hz, 1H), 6.50 (d, $J$ = 7.6 Hz, 1H), 5.65 (s, 1H), 2.25 (s, 3H), 2.17 (s, 1H), 1.21 (s, 9H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 1155.2, 142.6, 137.1, 136.6, 129.2, 129.0, 128.8, 128.5, 128.2, 127.6, 126.9, 123.4, 121.2, 120.0, 106.9, 68.8, 60.9, 25.2, 21.4.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H and $^{13}$C {$^1$H} NMR spectra of compounds **3** and crystal structure and data of **3aa**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01377.

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### Notes

The authors declare no competing financial interest.

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