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Oxidative Sulfonylation of Hydrazones Enabled by Synergistic Copper/Silver Catalysis

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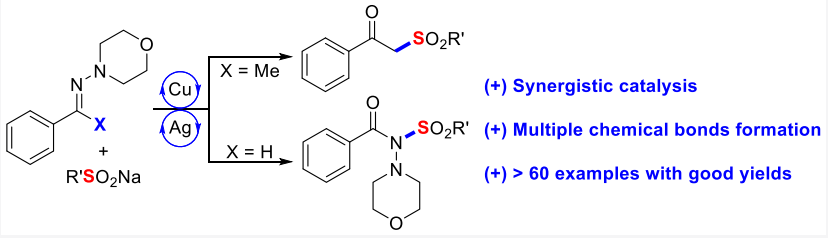

ABSTRACT: A copper/silver-cocatalyzed protocol for oxidative sulfonylation of hydrazones is demonstrated. A wide range of β-ketosulfones and *N*-acylsulfonamides are directly synthesized in moderate to good yields. Our work provides a viable method for scalable preparation of β-ketosulfone derivatives that have found wide applications in the pharmaceutical industry.

INTRODUCTION

Over the past decade, transition-metal-catalyzed C−H functionalization has become a powerful synthetic strategy for the selective assembly of important organic compounds.[1] In particular, synergistic catalysis has received much attention from the organic community because of its ability to improve the selectivity and efficacy of organic transformations.[2] Synergistic catalysts consisting of two catalysts or one catalyst with two or more active sites have been widely employed for catalysis. The combination of multifunctional active species can facilitate many organic transformations that would otherwise not be possible with a single active species. For example, Loh et al. in 2015 reported a synergistic copper/cobalt-catalyzed direct coupling of sp^3 α-carbon of alcohols with alkenes and hydroperoxides.[2e] Recently, Li and co-workers demonstrated a synergistic relay process involving olefin isomerization and umpolung hydrazone addition, which enabled redox-neutral α-alkylations of olefinic alcohols through ruthenium(II) catalysis.[2g]

Sulfonyl compounds are important for organic synthesis and biological medicine (Figure 1).[3] For example, β-ketosulfones are a prerequisite to the synthesis of heterocyclic or vinyl sulfones, β-hydroxysulfones, polyfunctionalized 4*H*-pyrans, quinoxalines, quinolines, allenes, and many others.[4] Therefore, considerable research efforts have been devoted to β-ketosulfone synthesis via various pathways, including the dehalogenative coupling of α-haloketones with sulfinates,[5] reactions of diazo sulfones with aldehydes,[6] oxidation of β-hydroxysulfones or β-ketosulfides,[7] oxidative difunctionalization of alkenes or alkynes,[8] and oxidative coupling of ketones with sulfonylation reagents,[9] as well as electrochemical synthesis.[10] In addition, *N*-acylsulfonamides also are the core structures for a variety of marketed pharmaceuticals.[11] In sharp contrast to approaches for the synthesis of β-ketosulfones, the formation of *N*-acylsulfonamides through oxo-sulfonylation of hydrazones continues to be scarce, with recent progress achieved with the aid of an aerobic oxidative coupling strategy.[12] Despite the progress achieved to date, each reported catalytic system is applicable exclusively to a specific type of substrate, and the generation of different products using single catalytic systems remains challenging.[13] A universal catalytic system for the synthesis of different products could significantly boost synthetic efficiency, benefiting the development of mass-production techniques for practical applications.

Hydrazones are essential and versatile intermediates in organic synthesis due to diverse reactivity profiles of the C=N−N structure. They are commonly employed as substrates for functional group transformation, especially for the functionalization of carbonyl compounds and nitrogen-containing compounds.[14] On the other hand, our previous work demonstrates that the cheap copper salts are effective catalysts for C−S cross-coupling since such metals have multiple oxidation states, which can catalyze reactions via both the oxidative addition/reductive elimination mechanism and the single-electron-transfer process.[15] In addition, the combination of catalytic silver salts and persulfates has proven effective for the generation of sulfonyl radicals from sodium

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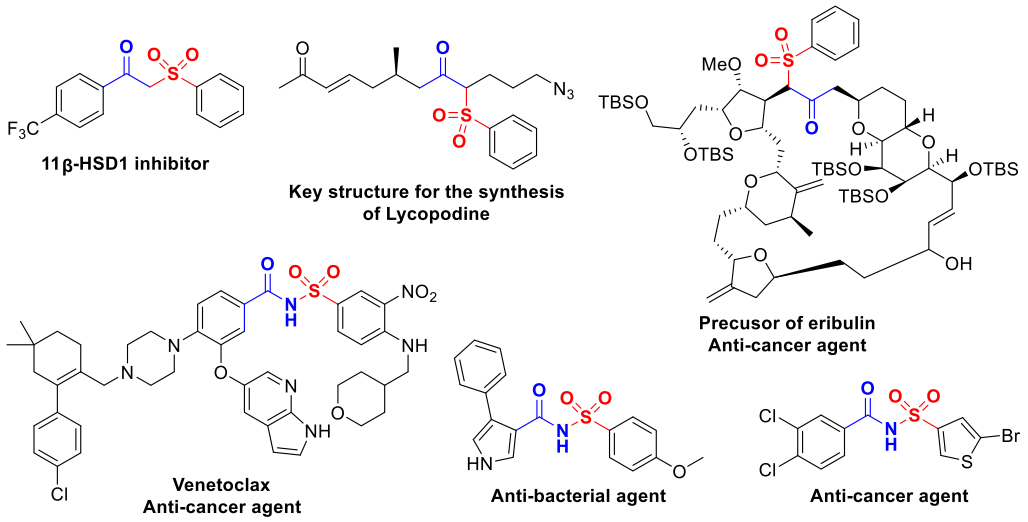
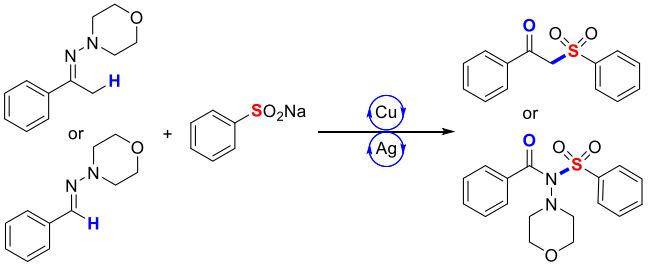


Figure 1. Examples of *β*-ketosulfone- or *N*-acylsulfonamide-based bioactive molecules.

sulfinates in the oxidative sulfonylation.[16] In that regard, we reason that it is possible to achieve the oxidative sulfonylation of hydrazones through synergistic copper/silver cocatalysis. In this study, we demonstrate a one-pot protocol for the synthesis of *β*-ketosulfone by employing ketone hydrazone and sodium benzenesulfinate as starting materials. Moreover, this cocatalytic system also allows direct oxo-sulfonylation of aldehyde hydrazones, giving the corresponding *N*-acylsulfonamides in moderate to good yields (Scheme 1).

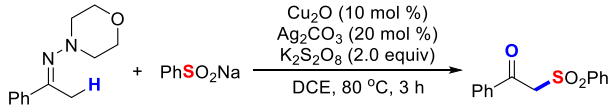
Scheme 1. Copper/Silver-Cocatalyzed Oxidative Sulfonylation of Hydrazones



RESULTS AND DISCUSSION

At the outset, the auxiliary groups for oxidative sulfonylation were tested in MeCN using CuCl as the catalyst (Scheme S1). Results reveal that acetophenone hydrazone (**1a**) gives the highest yield. We thus selected *N*-aminomorpholine as the auxiliary group for further investigation. Subsequently, reaction conditions of oxidative sulfonylation of acetophenone hydrazone (**1a**) with sodium benzenesulfinate (**2a**) were optimized by changing metal catalysts, silver cocatalysts, oxidants, solvents, reaction time, and temperatures (Table 1 and Tables S1−S6). The target product (**3a**) was obtained in 85% yield under standard reaction conditions (Table 1, entry 1). It should be noted that no corresponding product was generated in the absence of Cu_2O (Table 1, entry 2). Only 15% and 18% yields of the product were obtained without Ag_2CO_3 or $K_2S_2O_8$, respectively (Table 1, entries 3 and 4). These results imply that the synergistic action of Ag_2CO_3 and $K_2S_2O_8$ determines organic transformation. Furthermore, no reaction occurred when Cu_2O was replaced with CuO (Table 1, entry 5), and changes in solvent and reaction time did not improve the product yield (Table 1, entries 6 and 7).

Table 1. Optimization of Oxidative Sulfonylation of Acetophenone Hydrazones[a,b]



1a 2a 3a

entry	deviation from initial conditions	yield (%)[b]
1	none	85
2	no Cu_2O	0
3	no Ag_2CO_3	15
4	no $K_2S_2O_8$	18
5	Cu_2O was replaced with CuO	trace
6	DCE was replaced with acetone	73
7	extended reaction time (12 h)	83

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 equiv), DCE (1.0 mL), 80 °C, 3 h, air. [b]Isolated yields. DCE = 1,2-dichloroethane.

With optimal reaction conditions in hand, we next explored the substrate scope of ketone hydrazones for oxidative sulfonylation. The sulfonylation of sodium benzenesulfinate (**2a**) with acetophenone hydrazones, bearing substituent groups at the *ortho*-, *meta*-, or *para*-position, both electron-donating and electron-withdrawing groups, afforded the corresponding *β*-ketosulfones (**3a**−**n**) in 62−85% yields (Table 2). Since such transformations proceeded through a single-electron-transfer pathway, we assumed that benzene *π*-system would likely disperse the electron to stabilize the radical intermediate, and the electronic effect of substituents on the benzene ring has little influence on this process. The molecular structure of *β*-ketosulfone **3g** was confirmed by X-ray crystallographic analysis (CCDC NO. 1902707). As the fluorine atom has a great impact on the physical and biological properties of organic compounds,[17] we also tested acetophenone hydrazones containing several fluorine groups and isolated corresponding products (**3o**−**3q**) in good yields. In addition, heterocyclic ketone and *α*-substituted acetophenone hydrazones were converted to corresponding products (**3r**−**v**)

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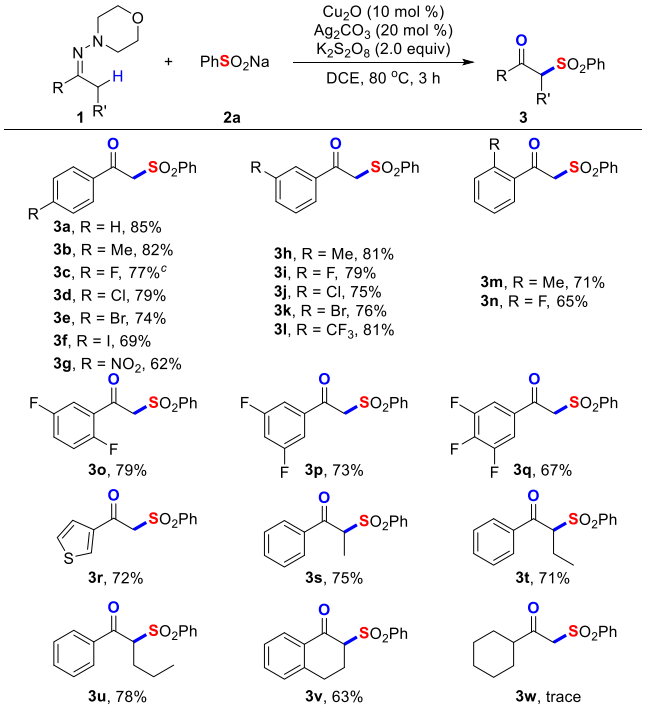
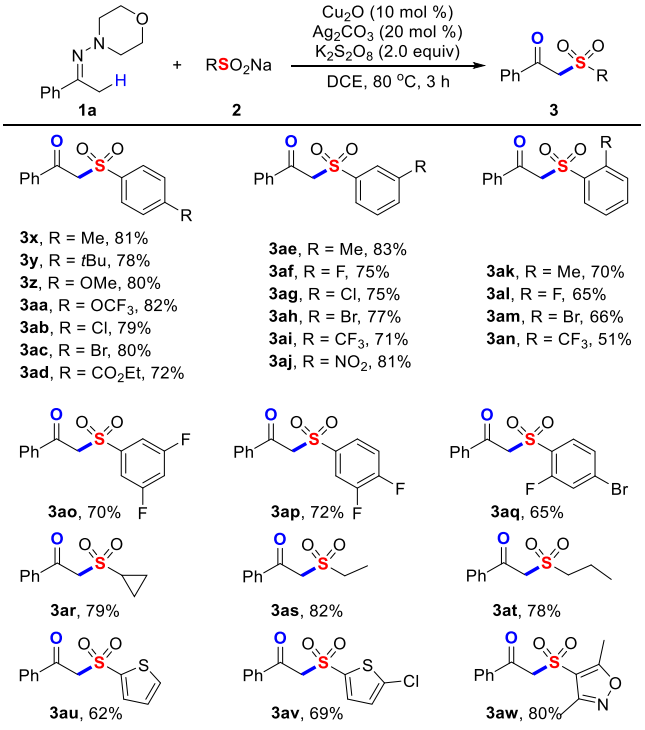
Table 2. Substrate Scope of Ketone Hydrazones[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 equiv), DCE (1.0 mL), 80 °C, 3 h, air. [b]Isolated yields. [c]Reaction was performed on a 1 mmol scale.

Table 3. Substrate Scope of Sodium Sulfinates[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 equiv), DCE (1.0 mL), 80 °C, 3 h, air. [b]Isolated yields.

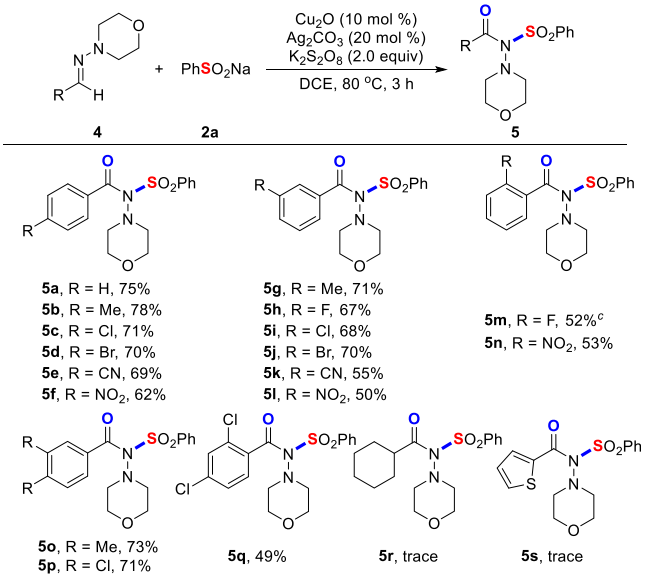
in 63−78% yields. However, the current catalytic system does not tolerate aliphatic ketone hydrazone (**3w**).

We next investigated a wide range of sodium sulfinates. Functionalized sodium sulfinates are well compatible with our catalytic system, affording corresponding products in moderate to good yields (Table 3). Specifically, benzene sodium sulfinates containing either electron-donating or electron-withdrawing groups, at the *ortho*-, *meta*-, or *para*-position, gave corresponding *β*-ketosulfones (**3x−aq**) in 51−83% yields. Reactions of acetophenone hydrazones (**1a**) with both aliphatic and heterocyclic sodium sulfinates proceeded successfully as well, providing corresponding products (**3ar−aw**) in 62−82% yields.

To expand the application scope, we applied the present catalytic system to oxidative sulfonylation of aldehyde hydrazones (**4**) with sodium benzenesulfinate (**2a**). A series of substituted benzaldehyde hydrazones were tested, and the corresponding products (**5a−q**) were obtained in 49−78% yields (Table 4). Notably, aliphatic and heterocyclic aldehyde hydrazones and functionalized benzene sodium sulfinates could not undergo the reaction under standard conditions. NMR data suggest that the morpholine moiety is retained, and the sulfonylation of the aryl group does not occur. The product likely comprises a carbonyl group. The molecular structure of the product was further confirmed by infrared spectroscopy, high-resolution mass spectroscopy, and the single-crystal X-ray crystallographic analysis of **5n** (CCDC no. 2032258).

To demonstrate the scalability of transformation, we carried out gram-scale oxidative sulfonylation of hydrazones, with yields of 79% and 68% for **3a** and **5a**, respectively (Scheme 2a). The potent and selective inhibitor of 11*β*-hydroxysteroiddehydrogenase type 1 (11*β*-HSD1) was also successfully synthesized in 75% yield according to the copper/silver-

Table 4. Substrate Scope of Aldehyde Hydrazones[a,b]



[a]Reaction conditions: **4** (0.2 mmol), **2a** (2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 equiv), DCE (1.0 mL), 80 °C, 3 h, air. [b]Isolated yields. [c]Reaction was performed on a 1 mmol scale.

cocatalyzed protocol (Scheme 2b).[18] Since *β*-ketosulfones are commonly employed as synthons in organic synthesis, further transformations were performed (Scheme 2c). Several organic compounds (**7a−d**) were obtained in good yields using *β*-ketosulfone **3u** as the starting material.

We next performed a series of control experiments in order to understand reaction mechanisms. *β*-Ketosulfone could not

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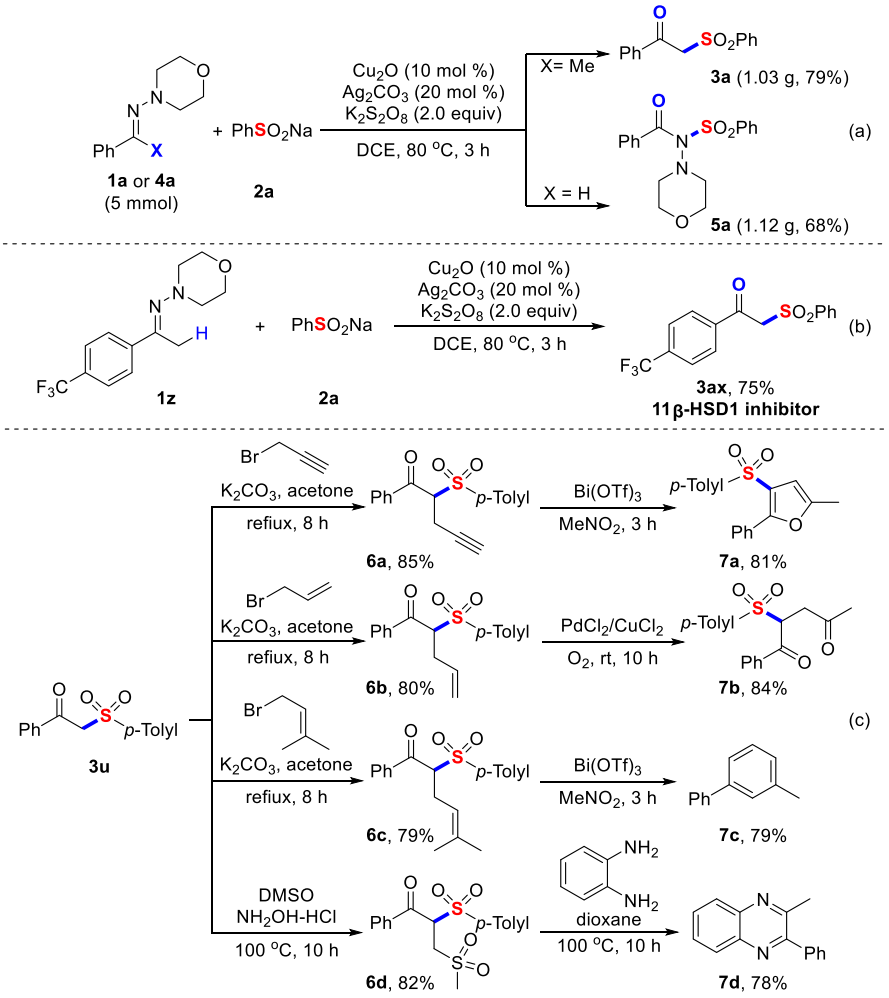
Scheme 2. Gram-Scale Preparation and Further Synthetic Utilization



be obtained without the *N*-aminomorpholine group, indicating the indispensable role of *N*-aminomorpholine in transformation (Scheme 3a). According to literature methods,[9a,19] *N*-aminomorpholine might act as an auxiliary group to generation iminium ions, which is important for C−H functionalization at the *β*-position of acetophenone derivatives. When two equivalents of radical scavengers 2,2,6,6-tetramethylpiperidine-1-oxyl were added to the catalytic system, the oxidative sulfonylation reactions were inhibited (Scheme 3b). Furthermore, the sulfonyl radical was captured in the presence or absence of hydrazones using 1,1-diphenylethylene as the radical collecting reagent (Scheme 3c). These results clearly demonstrate that a radical pathway is involved in these two reactions. The ^{18}O-labeling experiments were performed by adding $H_2{}^{18}O$ to the two reactions, and the only ^{18}O-labeling product of **3a** was obtained. This result indicates that moisture in the reaction may be responsible for the generation of carbonyl of *β*-ketosulfone (Scheme S2). We further studied the level of water content. The enamine (**E**) was isolated in 82% yield for the reaction performed in super dry DCE. These two reactions were further carried out under a nitrogen atmosphere: product **3a** was obtained in 81% yield, and product **5a** was not generated. These results imply that O_2 participates in oxidative sulfonylation of aldehyde hydrazones (Scheme S3). The ^{18}O-labeling product of **5a** was detected when the reaction was performed under an $^{18}O_2$ atmosphere, confirming that the presence of O_2 is responsible for the generation of carbonyl groups. The reaction was also monitored by electron paramagnetic resonance (EPR). When the reaction was performed for 5 min, the EPR signal of Cu(II) appears, suggesting its formation in the reaction mixture (Figure S1).[20]

In light of control experiments and previous literature, we proposed plausible mechanisms for these two reactions in Scheme 4. For oxidative sulfonylation of ketone hydrazones, starting with a single-electron-transfer process between ketone hydrazone **1a** and two molecules of Cu(I), a copper-imine intermediate **B** is obtained with a Cu(II) species.[9a,19a] The obtained Cu(II) species oxidizes sodium sulfinate **2a** to sulfonyl radical **A** with concomitant generation of a Cu(I) species.[19b] Meanwhile, the copper-imine intermediate **B** is transformed to enamine intermediate **C**. Synergistic action of silver salt and oxidant generates main sulfonyl radical **A**, which subsequently attacks the intermediate **C** to produce intermediate **D**.[16a] Afterward, an intramolecular single-electron-transfer process converts intermediate **D** to intermediate **E**. Target product **3a** can be obtained through hydrolysis of intermediate **E**. For oxidative sulfonylation of aldehyde hydrazones, a sulfonyl radical is first generated from sodium benzenesulfinate (**2a**) in the presence of silver salts and oxidants. The addition of the radical to the C═N double bond gives a carbon radical **F**, which interacts with O_2 to give a

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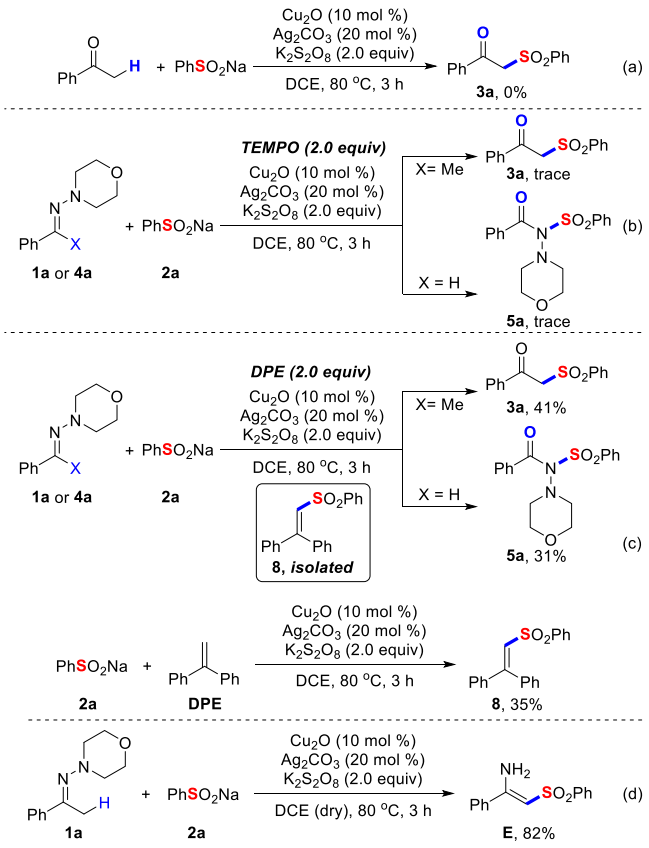
Scheme 3. Control Experiments for Determination of the Reaction Mechanism



peroxy radical, **G**. Subsequent coordination of the peroxy radical **G** with Cu(I) species affords intermediate **H**, which undergoes an elimination process to provide final product **5a** and Cu(II) species.[8b] The obtained Cu(II) species oxidizes sodium sulfinate **2a** to sulfonyl radical **A** with concomitant generation of a Cu(I) species.[19b]

CONCLUSIONS

In summary, we have developed a robust and efficient approach for oxidative sulfonylation of hydrazones via copper/silver synergistic catalysis. Control experiments revealed that a radical pathway is involved in these reactions. A broad range of β-ketosulfones and *N*-acylsulfonamides were generated in good yields, which could be employed as useful synthetic building blocks for the construction of value-added fine chemicals.

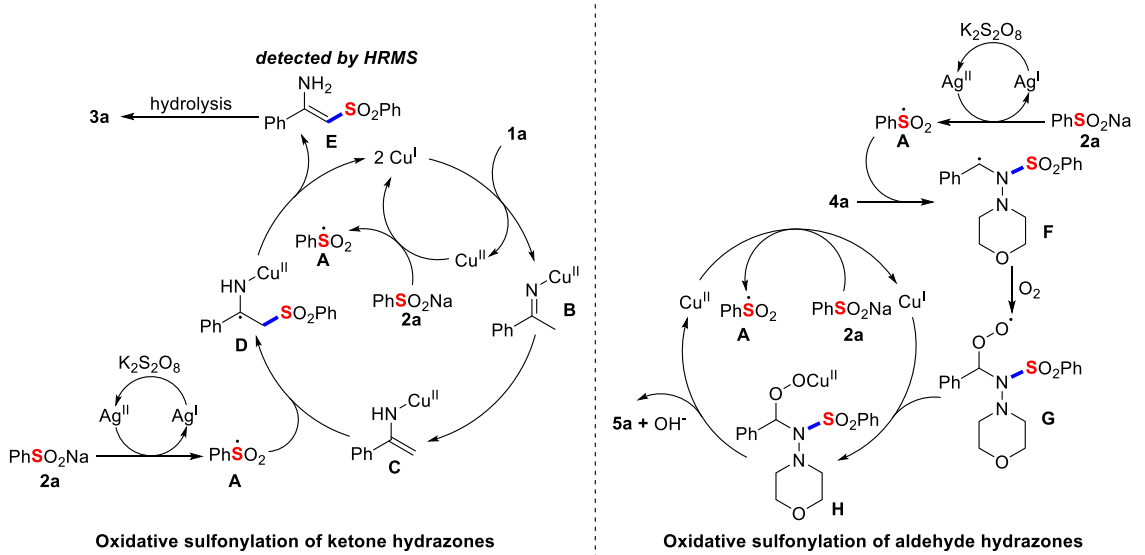
EXPERIMENTAL SECTION

General Information. All reagents and deuterated solvents were commercially available and used without further purification. All sodium sulfinates [(**2a**, **2x**, **2y**, **2aa**−**ac**, **2ai**, **2ar**, **2as**),[16c] (**2aj**, **2au**),[16a] (**2z**, **2ak**−**am**),[24a] (**2ad**, **2an**, **2ap**),[27a] (**2ae**−**ah**, **2ao**, **2aq**, **2at**),[27b] **2av**,[27c] and **2aw**[27d]] are known compounds and prepared as previously described. All aldehyde hydrazones [(**4a**−**g**, **4i**, **4j**, **4m**, **4o**),[28a] (**4h**, **4l**, **4n**, **4q**),[28c] (**4k**, **4p**),[28b] and (**4sr**, **4s**)[28d]] are known compounds and prepared as previously described. All products were separated by silica gel (200−300 mesh) column chromatography with petroleum ether (PE) (60−90 °C) and ethyl acetate (EA). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Advance 500 spectrometer at an ambient temperature with $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive-mode electrospray ionization (ESI) using an Agilent 6530 QTOF mass spectrometer. The crystal structure analysis was performed on a Bruker Smart Apex II diffractometer.

General Procedure for the Synthesis of Ketone Hydrazones (1). A mixture of ketone (5.0 mmol, 1.0 equiv), 4-aminomorpholine (5.5 mmol, 1.1 equiv), acetic acid (5.5 mmol, 1.1 equiv), and EtOH (15.0 mL) in a 25 mL flask was stirred at room temperature for 1 h. After completion of the reaction as indicated by TLC, purified water was added to the mixture to form the precipitate. The precipitate was washed with water and dried *in vacuo* to afford ketone hydrazone.

*N-Morpholino-1-phenylethan-1-imine (**1a**):* white solid (0.97 g, 95% yield), mp 70−71 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (dd, 2H, J = 6.6, 2.7 Hz), 7.38 (dd, 3H, J = 4.9, 1.5 Hz), 3.88 (dd, 4H, J = 5.6, 3.9 Hz), 2.89 (dd, 4H, J = 5.6, 3.9 Hz), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 159.9, 130.2 129.6, 128.3, 126.5, 66.3,

Scheme 4. Plausible Mechanisms underlying Oxidative Sulfonylation



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55.2, 15.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{16}N_2O$ 205.1335, found 205.1356.

*N-Morpholino-1-(p-tolyl)ethan-1-imine (**1b**):* white solid (0.99 g, 91% yield), mp 74−75 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (d, 2H, J = 8.2 Hz), 7.18 (d, 2H, J = 8.0 Hz), 3.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.36 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 163.3, 139.7, 135.9, 129.0, 126.4, 66.3, 55.2, 21.3, 15.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{18}N_2O$ 219.1492, found 219.1508.

*1-(4-Fluorophenyl)-N-morpholinoethan-1-imine (**1c**):* white solid (1.05 g, 95% yield), mp 65−66 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.75 (dd, 2H, J = 8.8, 5.5 Hz), 7.05 (t, 2H, J = 8.7 Hz), 3.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.8 (d, J_{C-F} = 243.2 Hz), 161.0, 134.9 (d, J_{C-F} = 3.8 Hz), 128.4 (d, J_{C-F} = 7.6 Hz), 115.2 (d, J_{C-F} = 21.4 Hz), 66.3, 55.2, 15.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}FN_2O$ 223.1241, found 223.1261.

*1-(4-Chlorophenyl)-N-morpholinoethan-1-imine (**1d**):* white solid (0.91 g, 76% yield), mp 91−92 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (d, 2H, J = 8.6 Hz), 7.34 (d, 2H, J = 8.6 Hz), 3.88 (dd, 4H, J = 5.6, 3.9 Hz), 2.89 (dd, 4H, J = 5.6, 3.9 Hz), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 160.8, 137.1, 131.5, 128.5, 127.8, 66.2, 55.2, 15.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}ClN_2O$ 239.0946, found 239.0953.

*1-(4-Bromophenyl)-N-morpholinoethan-1-imine (**1e**):* white solid (1.35 g, 96% yield), mp 94−95 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (d, 2H, J = 8.6 Hz), 7.34 (d, 2H, J = 8.6 Hz), 3.90−3.82 (m, 4H), 2.90−2.82 (m, 4H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.1, 137.1, 135.6, 128.5, 127.8, 66.3, 55.2, 15.5; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}BrN_2O$ 283.0441, found 283.0446.

*1-(4-Iodophenyl)-N-morpholinoethan-1-imine (**1f**):* yellow solid (1.43 g, 87% yield), mp 99−100 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (d, 2H, J = 8.6 Hz), 7.49 (d, 2H, J = 8.6 Hz), 3.91−3.83 (m, 4H), 2.91−2.82 (m, 4H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.2, 138.2, 137.4, 128.2, 95.9, 66.3, 55.1, 15.5; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}IN_2O$ 331.0302, found 331.0308.

*N-Morpholino-1-(4-nitrophenyl)ethan-1-imine (**1g**).* yellow solid (1.21 g, 97% yield), mp 123−124 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.22 (d, 2H, J = 8.9 Hz), 7.93 (d, 2H, J = 8.9 Hz), 3.92−3.86 (m, 4H), 2.97−2.90 (m, 4H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 160.2, 148.3, 144.5, 127.2, 123.5, 66.2, 55.1, 15.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_3O_3$ 250.1186, found 250.1191.

*N-Morpholino-1-(m-tolyl)ethan-1-imine (**1h**):* white solid (0.89 g, 82% yield), mp 81−82 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.57 (s, 1H), 7.51 (d, 1H, J = 7.7 Hz), 7.25 (d, 1H, J = 7.4 Hz), 7.19 (d, 1H, J = 7.5 Hz), 3.90−3.85 (m, 4H), 2.92−2.82 (m, 4H), 2.38 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 163.8, 138.8, 138.0, 130.4, 128.2, 127.0, 123.7, 66.4, 55.2, 21.5, 15.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{18}N_2O$ 219.1492, found 219.1500.

*1-(3-Fluorophenyl)-N-morpholinoethan-1-imine (**1i**):* white solid (0.92 g, 83% yield), mp 69−70 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.54−7.47 (m, 2H), 7.34 (dd, 1H, J = 8.1, 6.1 Hz), 7.07 (tdd, 1H, J = 8.2, 2.6, 0.8 Hz), 3.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.87 (dd, 4H, J = 5.6, 3.9 Hz), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.8 (d, J_{C-F} = 243.2 Hz), 161.9, 141.0 (d, J_{C-F} = 7.6 Hz), 129.8 (d, J_{C-F} = 7.6 Hz), 122.1 (d, J_{C-F} = 3.8 Hz), 116.4 (d, J_{C-F} = 21.4 Hz), 113.4 (d, J_{C-F} = 21.4 Hz), 66.32, 55.14, 15.69; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}FN_2O$ 223.1241, found 223.1243.

*1-(3-Chlorophenyl)-N-morpholinoethan-1-imine (**1j**):* white solid (1.12 g, 94% yield), mp 98−99 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.76 (s, 1H), 7.61 (d, 1H, J = 7.7 Hz), 7.34 (d, 1H, J = 8.1 Hz), 7.29 (t, 1H, J = 7.8 Hz), 3.90−3.83 (m, 4H), 2.90−2.83 (m, 4H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 160.5, 138.6, 133.5, 132.6, 130.2, 128.3, 125.6, 66.3, 55.1, 15.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}ClN_2O$ 239.0946, found 239.0946.

*1-(3-Bromophenyl)-N-morpholinoethan-1-imine (**1k**):* yellow solid (1.29 g, 91% yield), mp 103−104 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.92 (s, 1H), 7.66 (d, 1H, J = 7.8 Hz), 7.51 (d, 1H, J = 7.9 Hz), 7.26 (s, 1H), 3.89 (dd, 4H, J = 5.6, 3.9 Hz), 2.90 (dd, 4H, J = 5.6, 3.9 Hz), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 160.3, 136.0, 132.5, 129.8, 129.5, 125.1, 122.7, 66.2, 55.1, 15.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}BrN_2O$ 283.0441, found 283.0439.

*N-Morpholino-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1l**):* yellow solid (1.20 g, 88% yield), mp 87−88 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.02 (s, 1H), 7.94 (d, 1H, J = 7.9 Hz), 7.63 (d, 1H, J = 7.8 Hz), 7.49 (t, 1H, J = 7.8 Hz), 3.91−3.84 (m, 4H), 2.93−2.85 (m, 4H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 161.5, 139.5, 130.8 (q, J_{C-F} = 32.8 Hz), 129.7, 128.8, 126.0 (q, J_{C-F} = 3.8 Hz), 124.1 (q, J_{C-F} = 273.4 Hz), 123.3 (q, J_{C-F} = 3.8 Hz), 66.30, 55.14, 15.64; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{15}F_3N_2O$ 273.1209, found 273.1215.

*N-Morpholino-1-(o-tolyl)ethan-1-imine (**1m**):* white solid (0.79 g, 72% yield), mp 90−91 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.22−7.16 (m, 4H), 3.99−3.78 (m, 4H), 2.99−2.82 (m, 4H), 2.32 (d, 6H, J = 22.1 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 167.3, 139.9, 134.9, 130.8, 128.3, 127.5, 125.9, 66.4, 55.0, 25.8, 19.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{18}N_2O$ 219.1492, found 219.1493.

*1-(2-Fluorophenyl)-N-morpholinoethan-1-imine (**1n**):* white solid (0.89 g, 80% yield), mp 86−87 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.50 (ddd, 2H, J = 4.6, 2.4, 1.1 Hz,), 7.32 (dd, 1H, J = 8.1, 2.2 Hz), 7.06 (tdd, 1H, J = 8.3, 2.6, 0.9 Hz,), 3.87−3.85 (m, 4H), 2.88−2.86 (m, 4H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.8 (d, J_{C-F} = 245.7 Hz), 161.9 (d, J_{C-F} = 2.5 Hz), 141.5 (d, J_{C-F} = 7.6 Hz), 129.8, (d, J_{C-F} = 7.6 Hz), 122.1 (d, J_{C-F} = 2.5 Hz), 116.4, (d, J_{C-F} = 21.4 Hz), 113.3 (d, J_{C-F} = 21.4 Hz), 66.3, 55.1, 15.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{15}FN_2O$ 223.1241, found 223.1245.

*1-(2,5-Difluorophenyl)-N-morpholinoethan-1-imine (**1o**):* white solid (0.87 g, 73% yield), mp 83−84 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.33−7.28 (m, 1H), 7.05−7.00 (m, 2H), 3.90−3.85 (m, 4H), 2.93−2.85 (m, 4H), 2.37 (d, 3H, J = 3.2 Hz,); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 160.9, 158.5 (d, J_{C-F} = 243.2 Hz), 156.7 (d, J_{C-F} = 245.7 Hz), 128.8 (dd, J_{C-F} = 7.6, 6.3 Hz), 117.3 (dd, J_{C-F} = 10.1, 7.6 Hz), 117.1 (dd, J_{C-F} = 10.1, 7.6 Hz), 115.8 (dd, J_{C-F} = 25.2, 3.8 Hz), 66.3, 54.9, 18.6 (d, J_{C-F} = 6.3 Hz); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{14}F_2N_2O$ 241.1147, found 241.1159.

*1-(3,5-Difluorophenyl)-N-morpholinoethan-1-imine (**1p**):* white solid (0.91 g, 76% yield), mp 92−93 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, 2H, J = 8.7, 2.0 Hz), 6.82 (tt, 1H, J = 8.6, 2.3 Hz), 3.92−3.83 (m, 4H), 2.93−2.83 (m, 4H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 163.0 (d, J_{C-F} = 248.2 Hz), 162.9 (d, J_{C-F} = 248.2 Hz), 160.5, 109.4 (dd, J_{C-F} = 20.2, 6.3 Hz), 104.7 (t, J_{C-F} = 20.2 Hz), 66.24, 55.12, 15.63; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{14}F_2N_2O$ 241.1147, found 241.1161.

*N-Morpholino-1-(3,4,5-trifluorophenyl)ethan-1-imine (**1q**):* yellow solid (1.11 g, 86% yield), mp 101−102 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.43 (dd, 2H, J = 9.0, 6.7 Hz), 3.91−3.84 (m, 4H), 2.89 (s, 4H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 161.2 (m), 110.6 (m), 66.21, 55.15, 15.30; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{13}F_3N_2O$ 259.1053, found 259.1053.

*N-Morpholino-1-(thiophen-3-yl)ethan-1-imine (**1r**):* white solid (0.75 g, 71% yield), mp 122−123 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, 2H, J = 4.6 Hz,), 7.30−7.27 (m, 1H), 3.88−3.84 (m, 4H), 2.84 (s, 4H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 159.5, 141.8, 126.0, 125.7, 124.6, 66.3, 55.2, 16.0; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{10}H_{14}N_2OS$ 211.0900, found 211.0912.

*N-Morpholino-1-phenylpropan-1-imine (**1s**):* white solid (0.92 g, 84% yield), mp 81−82 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.67 (dd, 2H, J = 6.4, 2.8 Hz), 7.40−7.36 (m, 3H), 3.88 (s, 4H), 2.94 (d, 2H, J = 7.3 Hz), 2.85 (s, 4H), 1.08 (t, 3H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 171.1, 137.4, 129.6, 128.4, 127.1, 66.3, 55.8, 22.1, 12.0; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{18}N_2O$ 219.1492, found 219.1490.

*N-Morpholino-1-phenylbutan-1-imine (**1t**):* white solid (0.83 g, 72% yield), mp 87−88 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (dd, 2H, J = 6.5, 2.9 Hz), 7.40−7.33 (m, 3H), 3.92−3.81 (m, 4H), 2.91−

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2.85 (m, 2H), 2.84−2.74 (m, 4H), 1.48 (dd, 2H, J = 15.3, 7.6 Hz), 0.93 (t, 3H, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 170.1, 137.9, 129.4, 128.4, 127.1, 66.3, 55.7, 30.7, 20.7, 14.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{14}H_{20}N_2O$ 233.1648, found 233.1656.

*N-Morpholino-1-phenylpentan-1-imine (**1u**):* white solid (1.10 g, 89% yield), mp 95−96 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (dd, 2H, J = 6.6, 3.0 Hz), 7.40−7.34 (m, 3H), 3.91−3.81 (m, 4H), 2.93−2.87 (m, 2H), 2.85−2.75 (m, 4H), 1.46−1.40 (m, 2H), 1.35 (dd, 2H, J = 14.5, 7.3 Hz,), 0.90 (t, 3H, J = 7.2 Hz,); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 170.3, 137.9, 129.4, 128.4, 127.1, 66.4, 55.7, 29.4, 28.4, 22.8, 13.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{22}N_2O$ 247.1805, found 247.1800.

*N-Morpholino-3,4-dihydronaphthalen-1(2H)-imine (**1v**):* white solid (0.99 g, 86% yield), mp 107−108 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.17 (d, 1H, J = 7.8 Hz), 7.30 (dd, 1H, J = 14.8, 7.4 Hz), 7.20 (t, 1H, J = 7.5 Hz), 7.13 (d, 1H, J = 7.5 Hz), 3.86 (s, 4H), 2.95−2.73 (m, 8H), 1.98−1.87 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 162.4, 144.5, 140.0, 133.4, 128.7, 126.3, 125.2, 66.4, 55.1, 39.2, 29.8, 22.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{14}H_{18}N_2O$ 231.1492, found 231.1500.

General Procedure for Oxidative Sulfonylation of Ketone Hydrazones. A mixture of ketone hydrazone (**1**) (0.2 mmol, 1.0 equiv), sodium sulfinate (**2**) (0.4 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv), and DCE (1.0 mL) in a 15 mL tube was stirred at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for the Synthesis of Product 3c on 1 mmol Scale. A mixture of ketone hydrazone (**1h**) (1.0 mmol, 1.0 equiv), sodium sulfinate (**2**) (2.0 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 mmol, 2.0 equiv), and DCE (5.0 mL) in a 15 mL tube was stirred at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for Gram-Scale Sulfonylation of Acetophenone Hydrazone. A mixture of acetophenone phenylhydrazone (**1a**) (5.0 mmol, 1.0 equiv), sodium benzenesulfinate (**2a**) (10.0 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (10.0 mmol, 2.0 equiv), and DCE (25 mL) was stirred in a 100 mL flask at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

*1-Phenyl-2-(phenylsulfonyl)ethan-1-one (**3a**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 85% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 8.2 Hz), 7.90 (d, 2H, J = 8.2 Hz), 7.66 (t, 1H, J = 7.5 Hz), 7.62 (t, 1H, J = 7.4 Hz), 7.55 (t, 2H, J = 7.7 Hz), 7.48 (t, 2H, J = 7.7 Hz), 4.74 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.0, 139.0, 135.7, 134.4, 134.3, 129.3, 129.2, 128.9, 128.6, 63.5.

*2-(Phenylsulfonyl)-1-(p-tolyl)ethan-1-one (**3b**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (45 mg, 82% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.82 (dd, 2H, J = 8.3, 1.1 Hz), 7.77 (d, 2H, J = 8.3 Hz), 7.59 (t, 1H, J = 7.5 Hz,), 7.48 (t, 2H, J = 7.8 Hz,), 7.21 (d, 2H, J = 8.0 Hz), 4.64 (s, 2H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.5, 145.7, 138.77, 134.2, 133.3, 129.6, 129.5, 129.2, 128.6, 63.5, 21.8.

*1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3c**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (214 mg, 77% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.00 (dd, 2H, J = 8.8, 5.3 Hz), 7.93−7.85 (m, 2H), 7.68 (t, 1H, J = 7.5 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.16 (t, 2H, J = 8.5 Hz), 4.70 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.4, 166.5 (d, J_{C-F} = 258.3 Hz), 138.6, 134.4, 132.3 (d, J_{C-F} = 10.1 Hz), 132.2, 129.3, 128.6, 116.2 (d, J_{C-F} = 21.4 Hz), 63.6. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −102.3.

*1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3d**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (46 mg, 79% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.89 (dd, 4H, J = 13.9, 5.0 Hz), 7.69 (t, 1H, J = 7.5 Hz), 7.57 (t, 2H, J = 7.8 Hz), 7.47 (d, 2H, J = 8.6 Hz), 4.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.9, 141.2, 138.5, 134.4, 134.0, 130.8, 129.3, 129.3, 128.6, 63.6.

*1-(4-Bromophenyl)-2-(phenylsulfonyl)ethan-1-one (**3e**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (50 mg, 74% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.89 (t, 4H, J = 7.9 Hz), 7.68 (t, 1H, J = 7.5 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.46 (d, 2H, J = 8.6 Hz), 4.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.9, 141.2, 138.6, 134.4, 134.1, 130.8, 129.3, 129.3, 128.6, 63.6.

*1-(4-Iodophenyl)-2-(phenylsulfonyl)ethan-1-one (**3f**):*[8d] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (53 mg, 69% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.91−7.82 (m, 4H), 7.69−7.63 (m, 3H), 7.56 (t, 2H, J = 7.7 Hz), 4.70 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.5, 138.3, 134.9, 134.4, 131.5, 130.6, 129.3, 128.6, 103.2, 63.5.

*1-(4-Nitrophenyl)-2-(phenylsulfonyl)ethan-1-one (**3g**):*[8c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (38 mg, 62% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.33 (d, 2H, J = 8.6 Hz), 8.15 (d, 2H, J = 8.6 Hz), 7.89 (d, 2H, J = 7.6 Hz), 7.71 (t, 1H, J = 7.4 Hz), 7.59 (t, 2H, J = 7.7 Hz), 4.80 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.9, 150.9, 139.9, 138.3, 134.7, 130.5, 129.5, 128.5, 124.0, 63.9.

*2-(Phenylsulfonyl)-1-(m-tolyl)ethan-1-one (**3h**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 81% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, 2H, J = 7.6 Hz), 7.73 (d, 2H, J = 11.2 Hz), 7.67 (t, 1H, J = 7.3 Hz), 7.55 (t, 2H, J = 7.7 Hz), 7.43 (d, 1H, J = 7.5 Hz), 7.37 (t, 1H, J = 7.6 Hz), 4.73 (s, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.1, 138.8, 138.8, 135.8, 135.2, 134.2, 129.7, 129.2, 128.8, 128.6, 126.6, 63.5, 21.3.

*1-(3-Fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3i**):*[19a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 79% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.90 (dd, 2H, J = 8.4, 1.1 Hz), 7.77−7.73 (m, 1H), 7.68 (dd, 1H, J = 10.7, 4.3 Hz), 7.63−7.60 (m, 1H), 7.57 (t, 2H, J = 7.8 Hz), 7.48 (td, 1H, J = 8.0, 5.5 Hz), 7.33 (tdd, 1H, J = 8.2, 2.6, 0.7 Hz), 4.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.9, 162.8 (d, J_{C-F} = 249.5 Hz), 138.6, 137.7 (d, J_{C-F} = 6.3 Hz), 134.4, 130.6 (d, J_{C-F} = 7.6 Hz), 129.3, 128.6, 125.3 (d, J_{C-F} = 2.5 Hz), 121.6 (d, J_{C-F} = 21.4 Hz), 115.8 (d, J_{C-F} = 22.7 Hz), 63.6. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −110.9.

*1-(3-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3j**):*[19b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 75% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.91−7.82 (m, 4H), 7.69 (t, 1H, J = 7.5 Hz), 7.60−7.55 (m, 3H), 7.44 (t, 1H, J = 7.9 Hz), 4.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.9, 138.5, 137.2, 135.3, 134.5, 134.4, 130.2, 129.4, 129.2, 128.6, 127.6, 63.5.

*1-(3-Bromophenyl)-2-(phenylsulfonyl)ethan-1-one (**3k**):*[21c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (51 mg, 76% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03 (t, 1H, J = 1.8 Hz), 7.89 (d, 3H, J = 7.4 Hz), 7.74 (dd, 1H, J = 8.0, 0.9 Hz), 7.69 (t, 1H, J = 7.5 Hz), 7.57 (t, 2H, J = 7.9 Hz), 7.38 (t, 1H, J = 7.9 Hz), 4.70 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 186.8, 138.5, 137.4, 137.2, 134.5, 132.1, 130.4, 129.3, 128.6, 128.0, 123.3, 63.5.

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*2-(Phenylsulfonyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (**3l**).* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (53 mg, 81% yield), mp 110−111 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.17 (d, 2H, J = 9.2 Hz), 7.93−7.85 (m, 3H), 7.71−7.63 (m, 2H), 7.57 (t, 2H, J = 7.8 Hz), 4.76 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 186.9, 138.5, 136.2, 134.5, 132.6, 131.6 (q, J_{C-F} = 32.8 Hz), 130.7 (q, J_{C-F} = 3.8 Hz), 129.6, 129.4, 128.6, 126.0 (q, J_{C-F} = 3.8 Hz), 123.4 (q, J_{C-F} = 273.42 Hz), 63.6. ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) δ −62.9; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{11}F_3O_3S$ 351.0273, found 351.0264.

*2-(Phenylsulfonyl)-1-(o-tolyl)ethan-1-one (**3m**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (39 mg, 71% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, 2H, J = 7.5 Hz), 7.73 (d, 2H, J = 11.2 Hz), 7.67 (t, 1H, J = 7.4 Hz), 7.55 (t, 2H, J = 7.8 Hz), 7.43 (d, 1H, J = 7.5 Hz), 7.36 (t, 1H, J = 7.6 Hz), 4.73 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 188.2, 138.8, 138.7, 135.7, 135.3, 134.3, 129.7, 129.2, 128.8, 128.6, 126.6, 63.4, 21.4.

*1-(2-Fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3n**):*[8d] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (36 mg, 65% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, 2H, J = 7.5 Hz), 7.81 (td, 1H, J = 7.7, 1.7 Hz), 7.65 (t, 1H, J = 7.5 Hz), 7.55 (dt, 3H, J = 15.7, 7.9 Hz), 7.24 (d, 1H, J = 7.7 Hz), 7.11 (dd, 1H, J = 11.4, 8.4 Hz), 4.81 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 186.0 (d, J_{C-F} = 2.5 Hz), 161.9 (d, J_{C-F} = 255.8 Hz), 139.1, 136.2 (d, J_{C-F} = 8.8 Hz), 134.2, 131.2 (d, J_{C-F} = 1.3 Hz), 129.2, 128.6, 124.9 (d, J_{C-F} = 2.5 Hz), 124.5 (d, J_{C-F} = 11.3 Hz), 116.9 (d, J_{C-F} = 23.9 Hz), 67.1 (d, J_{C-F} = 8.8 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) δ −109.2.

*1-(2,5-Difluorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3o**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (47 mg, 79% yield), mp 120−121 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, 2H, J = 7.4 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.48 (ddd, 1H, J = 8.5, 5.5, 3.3 Hz), 7.28−7.24 (m, 1H), 7.15−7.09 (m, 1H), 4.80 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 184.9 (dd, J_{C-F} = 3.4, 1.5 Hz), 158.7 (dd, J_{C-F} = 247.0, 2.5 Hz), 157.9 (dd, J_{C-F} = 252.0, 2.5 Hz), 139.0, 134.3, 129.3, 128.6, 125.4 (dd, J_{C-F} = 13.8, 6.7 Hz), 123.0 (dd, J_{C-F} = 24.6, 9.8 Hz), 118.5 (dd, J_{C-F} = 27.1, 8.0 Hz), 116.9 (dd, J_{C-F} = 25.2, 2.5 Hz); 66.8 (d, J_{C-F} = 9.1 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) δ −114.5 (d, J_{F-F} = 18.4 Hz), −116.5 (d, J_{F-F} = 18.5 Hz); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{14}H_{10}F_2O_3S$ 319.0211, found 319.0221.

*1-(3,5-Difluorophenyl)-2-(phenylsulfonyl)ethan-1-one (**3p**):*[25c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (43 mg, 73% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (dd, 2H, J = 8.4, 1.1 Hz), 7.63 (dd, 1H, J = 10.7, 4.2 Hz), 7.51 (t, 2H, J = 7.8 Hz), 7.40 (dd, 2H, J = 7.6, 2.2 Hz), 7.01 (ddd, 1H, J = 8.3, 5.3, 2.3 Hz), 4.60 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 185.8, 163.1 (dd, J_{C-F} = 252.0, 11.3 Hz), 138.4 (t, J_{C-F} = 7.7 Hz), 138.4, 134.6, 129.4, 128.6, 112.4 (dd, J_{C-F} = 20.2, 6.6 Hz), 109.8 (t, J_{C-F} = 25.2 Hz), 63.7. ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) δ −106.9.

*2-(Phenylsulfonyl)-1-(3,4,5-trifluorophenyl)ethan-1-one (**3q**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (42 mg, 67% yield), mp 124−125 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, 2H, J = 7.5 Hz), 7.71 (t, 1H, J = 7.5 Hz), 7.64 (t, 2H, J = 7.0 Hz), 7.59 (t, 2H, J = 7.8 Hz), 4.66 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 184.9, 151.3 (ddd, J_{C-F} = 254.8, 21.4, 3.2 Hz), 144.0 (dt, J_{C-F} = 283.5, 15.1 Hz), 138.2, 134.7, 131.3 (dd, J_{C-F} = 10.3, 6.0 Hz), 129.5, 128.5, 114.2 (dd, J_{C-F} = 16.9, 5.5 Hz), 63.6. ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) δ −131.0 (d, J_{F-F} = 18.8 Hz), −149.4; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{14}H_9F_3O_3S$ 337.0117, found 337.0102.

*2-(Phenylsulfonyl)-1-(thiophen-3-yl)ethan-1-one (**3r**):*[22a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (38 mg, 72% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.22−8.16 (m, 1H), 7.89 (d, 2H, J = 7.4 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.55 (t, 2H, J = 7.8 Hz), 7.52 (dd, 1H, J = 5.1, 1.1 Hz), 7.33 (dd, 1H, J = 5.1, 2.8 Hz), 4.62 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 181.5, 141.1, 138.6, 135.6, 134.3, 129.3, 128.6, 127.2, 127.0, 65.2.

*1-Phenyl-2-(phenylsulfonyl)propan-1-one (**3s**):*[8b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (41 mg, 75% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, 2H, J = 7.5 Hz), 7.79 (d, 2H, J = 7.4 Hz), 7.65 (t, 1H, J = 7.5 Hz), 7.61 (t, 1H, J = 7.4 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.48 (t, 2H, J = 7.8 Hz), 5.17 (q, 1H, J = 6.9 Hz), 1.58 (d, 3H, J = 6.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 192.5, 136.2, 136.1, 134.2, 134.1, 129.8, 129.2, 128.9, 128.8, 65.0, 13.2.

*1-Phenyl-2-(phenylsulfonyl)butan-1-one (**3t**):*[9b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (41 mg, 71% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90−7.86 (m, 2H), 7.73−7.68 (m, 2H), 7.54 (ddd, 2H, J = 15.1, 8.0, 1.1 Hz), 7.41 (dt, 4H, J = 15.7, 7.8 Hz), 4.94 (dd, 1H, J = 10.8, 3.7 Hz,), 2.14−2.05 (m, 1H), 2.04−1.95 (m, 1H), 0.81 (t, 3H, J = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 192.7, 137.4, 136.5, 134.2, 134.1, 129.8, 129.0, 128.9, 128.8, 71.4, 22.0, 11.5.

*1-Phenyl-2-(phenylsulfonyl)pentan-1-one (**3u**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (47 mg, 78% yield), mp 132−133 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (dd, 2H, J = 8.4, 1.2 Hz), 7.70 (dd, 2H, J = 8.4, 1.2 Hz), 7.58−7.54 (m, 1H), 7.53 (dd, 1H, J = 10.5, 4.3 Hz), 7.44 (t, 2H, J = 7.8 Hz), 7.40 (t, 2H, J = 7.8 Hz), 5.02 (dd, 1H, J = 10.3, 4.2 Hz), 2.04−1.93 (m, 2H), 1.21−1.16 (m, 2H), 0.78 (t, 3H, J = 7.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 192.7, 137.2, 136.5, 134.2, 134.1, 129.8, 128.94, 128.9, 128.8, 69.8, 30.3, 20.4, 13.8; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{17}H_{18}O_3S$ 325.0869, found 325.0879.

*2-(Phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-one (**3v**):*[9b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (36 mg, 63% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, 1H, J = 7.9 Hz), 7.85 (dd, 2H, J = 8.5, 0.9 Hz), 7.60 (t, 1H, J = 7.5 Hz), 7.50 (t, 2H, J = 7.8 Hz), 7.44 (t, 1H, J = 8.1 Hz), 7.24 (t, 1H, J = 7.6 Hz), 7.20 (d, 1H, J = 7.6 Hz), 4.05 (t, 1H, J = 5.7 Hz), 3.44 (ddd, 1H, J = 16.8, 9.6, 4.6 Hz), 2.92 (dt, 1H, J = 17.0, 5.5 Hz), 2.79 (ddd, 1H, J = 17.0, 10.9, 6.1 Hz), 2.59 (ddd, 1H, J = 14.7, 10.0, 5.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 188.7, 143.6, 139.0, 134.6, 134.0, 131.7, 129.12, 129.0, 129.0, 128.0, 127.1, 69.7, 26.6, 23.6.

*1-Phenyl-2-tosylethan-1-one (**3x**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 81% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (dd, 2H, J = 8.4, 1.1 Hz), 7.76 (d, 2H, J = 8.3 Hz), 7.62 (t, 1H, J = 7.4 Hz), 7.48 (dd, 2H, J = 8.0, 7.6 Hz), 7.33 (d, 2H, J = 8.0 Hz), 4.72 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 188.2, 145.4, 135.8, 135.7, 134.4, 129.9, 129.4, 128.9, 128.6, 63.6, 21.8.

*2-((4-(tert-Butyl)phenyl)sulfonyl)-1-phenylethan-1-one (**3y**):*[22b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 78% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (dd, 2H, J = 8.3, 1.1 Hz), 7.81 (d, 2H, J = 8.6 Hz), 7.61 (t, 1H, J = 7.4 Hz), 7.53 (d, 2H, J = 8.6 Hz), 7.47 (t, 2H, J = 7.8 Hz), 4.72 (s, 2H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 188.1, 158.3, 135.9, 135.8, 134.3, 129.3, 128.8, 128.5, 126.2, 63.5, 35.3, 31.0.

*2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one (**3z**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (46 mg, 80% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, 2H, J = 8.3 Hz), 7.81 (dd, 2H, J = 8.8, 0.7 Hz), 7.62 (td, 1H, J = 7.6, 1.1 Hz), 7.49 (t, 2H, J = 7.5 Hz), 6.99 (dd, 2H, J = 8.8, 0.7 Hz), 4.72 (s, 2H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 188.3, 164.2, 135.8, 134.4, 130.9, 130.2, 129.4, 128.9, 114.4, 63.8, 55.7.

*1-Phenyl-2-((4-(trifluoromethoxy)phenyl)sulfonyl)ethan-1-one (**3aa**):*[22c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (58 mg, 82% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, 2H, J = 8.9 Hz), 7.94−7.90 (m, 2H), 7.64 (t, 1H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.8 Hz), 7.36 (d, 2H, J = 8.2 Hz), 4.76 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 187.9,

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153.4, 136.8, 135.6, 134.6, 131.1, 129.2, 129.0, 120.8, 120.2 (q, J_{C-F} = 260.8 Hz), 63.3; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −57.6.

*2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**3ab**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (46 mg, 79% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 7.4 Hz,), 7.84 (d, 2H, J = 8.6 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.51 (dd, 4H, J = 16.0, 8.1 Hz), 4.75 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.9, 141.2, 137.0, 135.6, 134.6, 130.2, 129.6, 129.3, 129.0, 63.3.

*2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one (**3ac**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (54 mg, 80% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 7.5 Hz), 7.76 (d, 2H, J = 8.5 Hz), 7.70 (d, 2H, J = 8.6 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.8 Hz), 4.74 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.9, 137.6, 135.6, 134.6, 132.6, 130.3, 129.8, 129.3, 120.0, 63.3.

*Ethyl 4-((2-Oxo-2-phenylethyl)sulfonyl)benzoate (**3ad**):*[26a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (48 mg, 72% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.21 (d, 2H, J = 8.4 Hz), 7.98 (d, 2H, J = 8.4 Hz), 7.94 (dd, 2H, J = 8.3, 1.0 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.8 Hz), 4.77 (s, 2H), 4.43 (q, 2H, J = 7.1 Hz), 1.42 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 164.9, 142.2, 135.6, 135.6, 134.6, 130.3, 129.3, 129.0, 128.8, 63.3, 61.9, 14.3.

*1-Phenyl-2-(m-tolylsulfonyl)ethan-1-one (**3ae**):*[23a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (45 mg, 83% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (dd, 2H, J = 8.3, 1.0 Hz), 7.69 (d, 2H, J = 1.6 Hz), 7.62 (t, 1H, J = 7.4 Hz), 7.51−7.42 (m, 4H), 4.73 (s, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.0, 139.6, 138.6, 135.8, 135.1, 134.4, 129.3, 129.1, 128.9, 128.8, 125.7, 63.6, 21.3.

*2-((3-Fluorophenyl)sulfonyl)-1-phenylethan-1-one (**3af**):*[9c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (42 mg, 75% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98−7.88 (m, 2H), 7.71 (d, 1H, J = 7.8 Hz), 7.63 (dd, 2H, J = 15.7, 8.1 Hz), 7.58−7.53 (m, 1H), 7.51 (dd, 2H, J = 14.7, 6.6 Hz), 7.37 (td, 1H, J = 8.2, 2.1 Hz), 4.75 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 162.3 (d, J_{C-F} = 238.1 Hz), 135.6, 134.6, 131.1 (d, J_{C-F} = 7.6 Hz), 129.3, 120.0, 124.5 (d, J_{C-F} = 2.5 Hz), 121.6 (d, J_{C-F} = 21.4 Hz), 116.1 (d, J_{C-F} = 25.2 Hz), 100.1 (d, J_{C-F} = 13.8 Hz), 63.3. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −108.9.

*2-((3-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**3ag**):*[22c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (44 mg, 75% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 7.5 Hz), 7.90 (s, 1H), 7.80 (d, 1H, J = 7.8 Hz), 7.65 (t, 2H, J = 7.5 Hz), 7.51 (t, 3H, J = 7.8 Hz), 4.76 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 140.3, 135.6, 135.5, 134.6, 134.5, 130.5, 129.3, 129.0, 128.7, 126.9, 63.3.

*2-((3-Bromophenyl)sulfonyl)-1-phenylethan-1-one (**3ah**):*[23b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (52 mg, 77% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.04 (t, 1H, J = 1.8 Hz), 7.93 (dd, 2H, J = 8.3, 1.1 Hz), 7.84 (d, 1H, J = 7.9 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.8 Hz), 7.43 (t, 1H, J = 7.9 Hz), 4.75 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 140.5, 137.3, 135.6, 134.6, 131.5, 130.7, 129.3, 129.0, 127.3, 123.2, 63.3.

*1-Phenyl-2-((3-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (**3ai**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (47 mg, 71% yield), mp 115−116 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.17 (s, 1H), 8.12 (d, 1H, J = 7.9 Hz), 7.94−7.89 (m, 3H), 7.71 (t, 1H, J = 7.9 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.8 Hz), 4.79 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 139.9, 135.5, 134.7, 132.2, 131.9 (q, J_{C-F} = 34.0 Hz), 130.9 (q, J_{C-F} = 3.8 Hz), 130.0, 129.2, 129.0, 125.9 (q, J_{C-F} = 3.8 Hz), 123.0 (q, J_{C-F} = 273.4 Hz), 63.2. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −62.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{11}F_3O_3S$ 329.0454, found 329.0444.

*2-((3-Nitrophenyl)sulfonyl)-1-phenylethan-1-one (**3aj**):*[23c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 81% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.76 (t, 1H, J = 1.9 Hz), 8.53 (dd, 1H, J = 8.2, 1.2 Hz), 8.26 (d, 1H, J = 7.8 Hz), 7.97−7.92 (m, 2H), 7.80 (t, 1H, J = 8.0 Hz), 7.66 (t, 1H, J = 7.4 Hz), 7.52 (t, 2H, J = 7.8 Hz), 4.83 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 148.3, 140.7, 135.4, 134.9, 134.5, 130.6, 129.2, 129.1, 128.7, 124.2, 62.9.

*1-Phenyl-2-(o-tolylsulfonyl)ethan-1-one (**3ak**):*[22a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (38 mg, 70% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.99−7.93 (m, 2H), 7.89 (d, 1H, J = 7.9 Hz), 7.62 (t, 1H, J = 7.4 Hz), 7.52 (t, 1H, J = 7.0 Hz), 7.48 (t, 2H, J = 7.8 Hz), 7.33 (dd, 2H, J = 14.5, 7.4 Hz), 4.76 (s, 2H), 2.73 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.0, 138.4, 137.0, 135.9, 134.4, 134.3, 132.8, 130.6, 129.4, 128.9, 126.6, 63.0, 20.6.

*2-((2-Fluorophenyl)sulfonyl)-1-phenylethan-1-one (**3al**):*[24a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (36 mg, 65% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, 2H, J = 7.5 Hz), 7.88 (t, 1H, J = 7.4 Hz), 7.73−7.61 (m, 2H), 7.50 (t, 2H, J = 7.7 Hz), 7.33 (t, 1H, J = 7.6 Hz), 7.26 (s, 1H), 4.93 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 159.7 (d, J_{C-F} = 255.8 Hz), 136.7 (d, J_{C-F} = 8.8 Hz), 135.7, 134.6, 130.8, 129.2, 129.0, 126.7 (d, J_{C-F} = 15.1 Hz), 124.8 (d, J_{C-F} = 3.8 Hz), 117.2 (d, J_{C-F} = 21.4 Hz), 62.2 (d, J_{C-F} = 2.5 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −107.7.

*2-((2-Bromophenyl)sulfonyl)-1-phenylethan-1-one (**3am**):*[21b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (45 mg, 66% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09 (dd, 1H, J = 6.1, 3.5 Hz), 7.97−7.92 (m, 2H), 7.79 (dd, 1H, J = 5.5, 3.6 Hz), 7.62 (dd, 1H, J = 10.8, 4.1 Hz), 7.49 (dt, 4H, J = 11.6, 4.4 Hz), 5.09 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 138.2, 135.8, 135.4, 135.1, 134.5, 132.5, 129.2, 128.9, 128.1, 120.9, 60.5.

*1-Phenyl-2-((2-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (**3an**):*[22c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (33 mg, 51% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.18 (d, 1H, J = 7.8 Hz), 7.94 (d, 3H, J = 8.3 Hz), 7.80 (t, 1H, J = 7.6 Hz), 7.74 (t, 1H, J = 7.6 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.8 Hz), 4.91 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.9, 153.1, 137.5 (q, J_{C-F} = 31.5 Hz), 135.7, 134.6, 134.3, 133.8, 132.5, 129.2, 129.0, 128.5 (q, J_{C-F} = 6.3 Hz), 122.8 (q, J_{C-F} = 273.4 Hz), 63.3. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −56.7.

*2-((3,5-Difluorophenyl)sulfonyl)-1-phenylethan-1-one (**3ao**):*[24b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (41 mg, 70% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97−7.90 (m, 2H), 7.66 (t, 1H, J = 7.0 Hz), 7.51 (t, 2H, J = 7.7 Hz), 7.49−7.41 (m, 2H), 7.14−7.09 (m, 1H), 4.77 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.5, 162.8 (dd, J_{C-F} = 255.8, 11.3 Hz), 141.8, 135.4, 134.8, 129.2, 129.1, 112.8 (dd, J_{C-F} = 21.4, 7.6 Hz), 110.0 (t, J_{C-F} = 25.2 Hz), 63.0. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −104.8.

*2-((3,4-Difluorophenyl)sulfonyl)-1-phenylethan-1-one (**3ap**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (43 mg, 72% yield), mp 127−128 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.96−7.91 (m, 2H), 7.76 (ddd, 1H, J = 9.2, 7.2, 2.2 Hz), 7.72−7.68 (m, 1H), 7.67−7.62 (m, 1H), 7.51 (t, 2H, J = 7.8 Hz), 7.35 (td, 1H, J = 9.0, 7.3 Hz), 4.76 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 154.3 (dd, J_{C-F} = 260.8, 12.6 Hz), 150.2 (dd, J_{C-F} = 255.8, 13.9 Hz), 135.5, 135.3 (t, J_{C-F} = 3.8 Hz), 134.7, 129.2, 129.0, 126.2 (dd, J_{C-F} = 7.9, 4.1 Hz), 118.9 (dd, J_{C-F} = 20.0, 2.0 Hz), 118.4 (d, J_{C-F} = 18.6 Hz), 63.2. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −126.6 (d, J_{F-F} = 23.6 Hz), −132.9 (d, J_{F-F} = 18.8 Hz); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}F_2O_3S$ 319.0211, found 319.0199.

*2-((4-Bromo-2-fluorophenyl)sulfonyl)-1-phenylethan-1-one (**3aq**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (46 mg, 65% yield), mp 134−135 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (dd, 2H, J = 8.4, 1.1 Hz), 7.76−7.71 (m, 1H), 7.67−7.62 (m, 1H), 7.53−7.45 (m, 4H), 4.90 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 159.2 (d, J_{C-F} = 260.8 Hz), 135.5, 134.7, 131.8, 130.5 (d, J_{C-F} = 8.8 Hz), 129.2, 129.0,

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128.4 (d, J_{C-F} = 3.8 Hz), 125.9 (d, J_{C-F} = 13.9 Hz), 120.9 (d, J_{C-F} = 25.2 Hz), 62.1. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −106.6; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}BrFO_3S$ 378.9410, found 378.9415.

*2-(Cyclopropylsulfonyl)-1-phenylethan-1-one (**3ar**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (35 mg, 79% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03 (dd, 2H, J = 8.4, 1.2 Hz), 7.68−7.63 (m, 1H), 7.53 (t, 2H, J = 7.8 Hz), 4.64 (s, 2H), 2.76 (tt, 1H, J = 8.0, 4.8 Hz), 1.29−1.27 (m, 2H), 1.12−1.08 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.9, 135.8, 134.6, 129.3, 129.0, 61.1, 30.9, 5.5.

*2-(Ethylsulfonyl)-1-phenylethan-1-one (**3as**):*[9a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (35 mg, 82% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.06−7.99 (m, 2H), 7.66 (t, 1H, J = 7.4 Hz), 7.53 (t, 2H, J = 7.8 Hz,), 4.57 (s, 2H), 3.29 (q, 2H, J = 7.4 Hz), 1.47 (t, 3H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 189.3, 135.8, 134.7, 129.3, 129.0, 58.8, 48.2, 6.7.

*1-Phenyl-2-(propylsulfonyl)ethan-1-one (**3at**):*[24b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (35 mg, 78% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98−7.92 (m, 2H), 7.59 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.8 Hz), 4.49 (s, 2H), 3.20−3.13 (m, 2H), 1.88 (dq, 2H, J = 15.1, 7.5 Hz), 1.05 (t, 3H, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 189.3, 135.8, 134.7, 129.3, 129.0, 59.6, 55.4, 15.8, 13.1.

*1-Phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one (**3au**):*[21a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (33 mg, 62% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97−7.92 (m, 2H), 7.73 (dd, 1H, J = 4.9, 1.1 Hz), 7.69 (dd, 1H, J = 3.8, 1.1 Hz), 7.63 (dd, 1H, J = 10.7, 4.2 Hz), 7.49 (t, 2H, J = 7.6 Hz), 7.13 (dd, 1H, J = 4.9, 3.9 Hz), 4.82 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 139.4, 135.7, 135.5, 135.0, 134.5, 129.3, 128.9, 128.0, 64.4.

*2-((5-Chlorothiophen-2-yl)sulfonyl)-1-phenylethan-1-one (**3av**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (41 mg, 69% yield); mp 132−133 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, 2H, J = 7.3 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.42 (dd, 3H, J = 9.8, 5.9 Hz), 6.88 (d, 1H, J = 4.1 Hz), 4.75 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.8, 140.7, 137.2, 135.5, 135.2, 134.6, 129.2, 129.0, 127.4, 64.0; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_9ClO_3S_2$ 322.9574, found 322.9574.

*2-((3,5-Dimethylisoxazol-4-yl)sulfonyl)-1-phenylethan-1-one (**3aw**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (45 mg, 80% yield), mp 138−139 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03−7.89 (m, 2H), 7.67 (t, 1H, J = 7.4 Hz), 7.53 (t, 2H, J = 7.8 Hz), 4.70 (s, 2H), 2.56 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 188.0, 176.0, 158.1, 135.4, 134.8, 129.2, 129.1, 115.0, 63.4, 12.7, 10.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{13}H_{13}NO_4S$ 280.0638, found 280.0628.

*2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**3ax**):*[18] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (50 mg, 76% yield); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, 2H, J = 8.2 Hz), 7.97−7.90 (m, 2H), 7.83 (d, 2H, J = 8.3 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.51 (t, 2H, J = 7.8 Hz), 4.78 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 187.7, 142.0, 135.9 (q, J_{C-F} = 32.8 Hz), 135.5, 134.7, 129.4, 129.2, 129.0, 126.4 (q, J_{C-F} = 3.8 Hz), 123.0 (q, J_{C-F} = 273.4 Hz), 63.1. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −63.2.

General Procedure for Oxidative Sulfonylation of Aldehyde Hydrazones. A mixture of aldehyde hydrazone (**4**) (0.2 mmol, 1.0 equiv), sodium benzenesulfinate (**2a**) (0.4 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv), and DCE (1.0 mL) was stirred in a 15 mL tube at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for the Synthesis of Product 5m on a 1 mmol Scale. A mixture of aldehyde hydrazone (**4m**) (1.0 mmol, 1.0 equiv), sodium benzenesulfinate (**2a**) (2.0 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (2.0 mmol, 2.0 equiv), and DCE (5.0 mL) was stirred in a 15 mL tube at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for Gram-Scale Sulfonylation of Benzaldehyde Hydrazone. A mixture of benzaldehyde hydrazone (**4a**) (5.0 mmol, 1.0 equiv), sodium benzenesulfinate (**2a**) (10.0 mmol, 2.0 equiv), Cu_2O (10 mol %), Ag_2CO_3 (20 mol %), $K_2S_2O_8$ (10.0 mmol, 2.0 equiv), and DCE (25 mL) was stirred in a 100 mL flask at 80 °C in an oil bath for 3 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

*N-Morpholino-N-(phenylsulfonyl)benzamide (**5a**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 75% yield), mp 129−130 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, 2H, J = 7.6 Hz), 7.59 (t, 1H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.7 Hz), 7.44−7.38 (m, 3H), 7.35−7.29 (m, 2H), 3.64−3.03 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.4, 136.7, 133.0, 131.9, 129.3, 127.3, 126.7, 125.8, 125.3, 65.2, 51.5; IR (KBr) 2957, 2858, 1682, 1351, 1163 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{18}N_2O_4S$ 369.0879, found 369.0878.

*4-Methyl-N-morpholino-N-(phenylsulfonyl)benzamide (**5b**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (54 mg, 78% yield), mp 136−137 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.11 (d, 2H, J = 8.0 Hz), 7.65 (t, 1H, J = 7.0 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.44 (d, 2H, J = 7.7 Hz), 7.20 (d, 2H, J = 7.7 Hz), 3.59−3.45 (m, 8H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 171.3, 142.1, 138.9, 133.9, 131.9, 129.4, 128.7, 128.5, 128.0, 67.3, 53.6, 21.6; IR (KBr) 2962, 2856, 1681, 1350, 1108 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{20}N_2O_4S$ 383.1036, found 383.1046.

*4-Chloro-N-morpholino-N-(phenylsulfonyl)benzamide (**5c**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (52 mg, 71% yield), mp 142−143 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.13−8.06 (m, 2H), 7.67 (t, 1H, J = 7.4 Hz), 7.58 (t, 2H, J = 7.8 Hz), 7.46 (d, 2H, J = 8.6 Hz), 7.38 (d, 2H, J = 8.6 Hz), 3.59−3.43 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 170.3, 138.6, 137.7, 134.1, 133.3, 129.4, 129.1, 128.8, 128.2, 67.2, 53.6; IR (KBr) 2963, 2856, 1683, 1351, 1167 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}ClN_2O_4S$ 403.0490, found 403.0486.

*4-Bromo-N-morpholino-N-(phenylsulfonyl)benzamide (**5d**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (57 mg, 70% yield), mp 156−157 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.5 Hz), 7.67 (t, 1H, J = 7.4 Hz), 7.58 (t, 2H, J = 7.8 Hz), 7.54 (d, 2H, J = 8.3 Hz), 7.38 (d, 2H, J = 8.4 Hz), 3.60−3.45 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 170.4, 138.6, 134.1, 133.7, 131.2, 129.4, 129.2, 128.8, 126.0, 67.2, 53.6; IR (KBr) 2962, 2852, 1680, 1351, 1109 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{18}BrN_2O_4S$ 448.0063, found 448.0075.

*4-Cyano-N-morpholino-N-(phenylsulfonyl)benzamide (**5e**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 69% yield), mp 138−139 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.13−8.06 (m, 2H), 7.70 (t, 3H, J = 8.1 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.55 (d, 2H, J = 8.4 Hz), 3.43 (dd, 8H, J = 190.8, 45.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.6, 139.5, 138.2, 134.4, 131.8, 129.4, 128.9, 127.5, 117.8, 114.7, 67.2, 53.4; IR

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(KBr) 2966, 2853, 1690, 1352, 1162 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{17}N_3O_4S$ 394.0832, found 394.0822.

*4-Nitro-N-morpholino-N-(phenylsulfonyl)benzamide (**5f**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (46 mg, 62% yield), mp 168−169 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.27 (d, 2H, J = 8.8 Hz), 8.10 (dd, 2H, J = 8.4, 1.0 Hz), 7.71 (t, 1H, J = 7.5 Hz), 7.61 (dt, 4H, J = 7.7, 3.4 Hz), 3.65−3.62 (m, 4H), 3.30−3.21 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.4, 148.9, 141.3, 138.1, 134.5, 129.4, 129.0, 127.8, 123.3, 67.2, 53.4; IR (KBr) 2962, 2856, 1706, 1502, 1327, 1146 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}N_3O_6S$ 414.0730, found 414.0741.

*3-Methyl-N-morpholino-N-(phenylsulfonyl)benzamide (**5g**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 71% yield), mp 139−140 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.15−8.04 (m, 2H), 7.69−7.63 (m, 1H), 7.57 (t, 2H, J = 7.7 Hz), 7.33−7.27 (m, 4H), 3.52 (dd, 8H, J = 41.7, 21.9 Hz), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 171.5, 138.9, 137.7, 134.9, 133.9, 132.1, 129.4, 128.7, 128.1, 127.7, 124.6, 67.3, 53.6, 21.3; IR (KBr) 2958, 2854, 1694, 1352, 1168 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{20}N_2O_4S$ 383.1036, found 383.1023.

*3-Fluoro-N-morpholino-N-(phenylsulfonyl)benzamide (**5h**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (47 mg, 67% yield), mp 128−129 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.11 (d, 2H, J = 7.3 Hz), 7.67 (t, 1H, J = 7.4 Hz), 7.58 (t, 2H, J = 7.8 Hz), 7.38 (td, 1H, J = 7.9, 5.5 Hz), 7.27 (d, 1H, J = 6.7 Hz), 7.18 (ddd, 2H, J = 7.9, 6.7, 2.0 Hz), 3.85−3.15 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.9, 161.9 (d, J_{C-F} = 248.2 Hz), 138.6, 137.0 (d, J_{C-F} = 6.3 Hz), 134.2, 129.7 (d, J_{C-F} = 7.6 Hz), 129.4, 128.8, 123.0 (d, J_{C-F} = 2.5 Hz), 118.2 (d, J_{C-F} = 21.4 Hz), 114.5 (d, J_{C-F} = 23.4 Hz), 67.2, 53.6. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −107.1; IR (KBr) 2959, 2855, 1694, 1354, 1171 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}FN_2O_4S$ 387.0785, found 387.0774.

*3-Chloro-N-morpholino-N-(phenylsulfonyl)benzamide (**5i**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (49 mg, 68% yield), mp 150−151 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.5 Hz), 7.68 (t, 1H, J = 7.4 Hz), 7.58 (t, 2H, J = 7.8 Hz), 7.48−7.43 (m, 2H), 7.39−7.31 (m, 2H), 3.79−3.08 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.8, 138.6, 136.5, 134.2, 133.9, 131.2, 129.4, 129.3, 128.9, 127.5, 125.5, 67.2, 53.6; IR (KBr) 2957, 2853, 1694, 1354, 1167 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}ClN_2O_4S$ 403.0490, found 403.0474.

*3-Bromo-N-morpholino-N-(phenylsulfonyl)benzamide (**5j**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (57 mg, 70% yield), mp 160−161 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.3 Hz), 7.68 (t, 1H, J = 7.4 Hz), 7.59 (dt, 4H, J = 11.0, 8.2 Hz), 7.43 (d, 1H, J = 7.8 Hz), 7.28 (t, 1H, J = 8.7 Hz), 3.82−3.05 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.6, 138.6, 136.7, 134.2, 130.4, 129.7, 129.5, 129.4, 128.9, 126.0, 121.7, 67.2, 53.6; IR (KBr) 2959, 2854, 1694, 1354, 1166 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}BrN_2O_4S$ 446.9985, Found 446.9965.

*3-Cyano-N-morpholino-N-(phenylsulfonyl)benzamide (**5k**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (39 mg, 55% yield), mp 142−143 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.5 Hz), 7.75 (dd, 3H, J = 19.3, 9.4 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.55 (t, 1H, J = 7.8 Hz), 3.80−3.02 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.0, 138.2, 136.3, 134.4, 134.3, 131.4, 130.9, 129.4, 129.0, 128.9, 117.7, 112.4, 67.2, 53.5; IR (KBr) 2960, 2854, 1694, 1355, 1168 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{17}N_3O_4S$ 394.0832, found 394.0818.

*3-Nitro-N-morpholino-N-(phenylsulfonyl)benzamide (**5l**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (37 mg, 50% yield), mp 175−176 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.36 (dd, 2H, J = 8.3, 4.8 Hz), 8.12 (d, 2H, J = 7.5 Hz), 7.87 (d, 1H, J = 7.7 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.62 (dt, 3H, J = 13.8, 6.8 Hz), 3.47 (dd, 8H, J = 158.1, 82.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 168.5, 147.3, 138.3, 136.2, 134.4, 133.6, 129.4, 129.3, 129.0, 125.8, 122.7, 67.2, 53.6; IR (KBr) 2966, 2862, 1683, 1352, 1166 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}N_3O_6S$ 414.0730, found 414.0740.

*2-Fluoro-N-morpholino-N-(phenylsulfonyl)benzamide (**5m**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (181 mg, 52% yield), mp 134−135 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.11 (dd, 2H, J = 8.4, 1.1 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.59 (dd, 2H, J = 11.1, 4.4 Hz), 7.42 (dd, 1H, J = 13.8, 5.5 Hz), 7.28−7.25 (m, 1H), 7.17 (td, 1H, J = 7.5, 0.9 Hz), 7.11−7.05 (m, 1H), 3.65 (d, 4H, J = 4.3 Hz), 3.23−3.09 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 167.9, 158.5 (d, J_{C-F} = 248.2 Hz), 138.5, 134.1, 131.8 (d, J_{C-F} = 7.6 Hz), 129.2, 128.8, 127.8 (d, J_{C-F} = 3.8 Hz), 124.8 (d, J_{C-F} = 17.6 Hz), 124.2 (d, J_{C-F} = 2.5 Hz), 115.2 (d, J_{C-F} = 21.4 Hz), 67.4, 53.6. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) δ −101.3; IR (KBr) 3060, 2851, 1673, 1326, 1145 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}FN_2O_4S$ 387.0785, found 387.0767.

*2-Nitro-N-morpholino-N-(phenylsulfonyl)benzamide (**5n**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (40 mg, 53% yield), mp 179−180 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.15 (d, 1H, J = 7.9 Hz), 8.00 (d, 2H, J = 7.7 Hz), 7.68 (t, 1H, J = 7.0 Hz), 7.63 (t, 1H, J = 7.5 Hz), 7.59−7.49 (m, 3H), 7.34 (dd, 1H, J = 7.6, 1.1 Hz), 3.47−3.06 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 169.2, 138.6, 138.2, 134.2, 132.5, 130.5, 129.3, 128.8, 127.0, 125.9, 117.7, 67.4, 53.3; IR (KBr) 2959, 2851, 1722, 1346, 1160 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}N_3O_6S$ 414.0730, found 414.0737.

*3,4-Dimethyl-N-morpholino-N-(phenylsulfonyl)benzamide (**5o**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (52 mg, 73% yield), mp 154−155 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.11 (dd, 2H, J = 8.3, 0.9 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.56 (t, 2H, J = 7.7 Hz), 7.32−7.27 (m, 2H), 7.15 (d, 1H, J = 7.7 Hz), 3.54−3.33 (m, 8H), 2.30 (s, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 171.4, 140.9, 139.0, 136.2, 133.8, 132.3, 129.4, 129.2, 129.0, 128.7, 125.6, 67.3, 53.6, 19.9, 19.7; IR (KBr) 2958, 2854, 1683, 1352, 1168 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}N_2O_4S$ 397.1192, found 397.1183.

*3,4-Dichloro-N-morpholino-N-(phenylsulfonyl)benzamide (**5p**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (56 mg, 71% yield), mp 171−172 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.4 Hz), 7.59 (dd, 3H, J = 8.8, 6.7 Hz), 7.49 (d, 1H, J = 8.3 Hz), 7.37 (dd, 1H, J = 8.3, 2.0 Hz), 3.66−3.20 (dd, 8H, J = 133.9, 96.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 168.8, 138.5, 135.8, 134.4, 134.3, 132.3, 130.0, 129.7, 129.4, 128.9, 127.0, 67.2, 53.6; IR (KBr) 2941, 2847, 1687, 1360, 1166 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}Cl_2N_2O_4S$ 437.0100, found 437.0110.

*2,4-Dichloro-N-morpholino-N-(phenylsulfonyl)benzamide (**5q**):* purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (39 mg, 49% yield), mp 182−183 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, 2H, J = 7.5 Hz), 7.69 (t, 1H, J = 7.4 Hz), 7.59 (t, 2H, J = 7.8 Hz), 7.41 (d, 1H, J = 1.8 Hz), 7.30 (dd, 1H, J = 8.2, 1.8 Hz), 7.14 (d, 1H, J = 8.2 Hz), 3.55 (dd, 4H, J = 67.7, 9.5 Hz), 3.27−3.15 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 167.8, 138.0, 135.8, 135.0, 134.3, 130.5, 129.3, 129.3, 128.9, 127.0, 126.9, 67.4, 53.2; IR (KBr) 2960, 2855, 1694, 1354, 1167 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}Cl_2N_2O_4S$ 437.0100, found 437.0080.

General Procedure for the Synthesis of Sulphone 7a. K_2CO_3 (3.0 mmol, 3.0 equiv) was added to a solution of **3u** (1.0 mmol, 1.0 equiv) in acetone (10 mL) at room temperature. The reaction mixture was stirred for 10 min. Afterward, propargyl bromide (1.05 mmol, 1.05 equiv) was added to the reaction mixture and stirred at reflux in an oil bath for 8 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM, and the collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the

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obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1) to afford intermediate **6a**. $Bi(OTf)_3$ (2 mol %) and molecular sieves (4 Å, 50 mg) were added to a solution of intermediate **6a** (0.5 mmol, 1.0 equiv) in dry $MeNO_2$ (2 mL) at room temperature. The reaction mixture was stirred for 3 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM, and collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for the Synthesis of Sulphone 7b. K_2CO_3 (2.0 mmol, 2.0 equiv) was added to a solution of **3u** (1.0 mmol, 1.0 equiv) in acetone (10 mL) at room temperature. The reaction mixture was stirred for 10 min, at which time allyl bromide (1.1 mmol, 1.1 equiv) was added to the reaction mixture. The reaction mixture was further stirred at reflux in an oil bath for 16 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1) to afford intermediate **6b**. $PdCl_2$ (10 mmol %) and $CuCl_2$ (0.75 mmol, 1.5 equiv) were added to a mixed solution of THF and MeOH (10 mL; v/v = 9:1) containing intermediate **6b** (0.5 mmol, 1.0 equiv) at room temperature. Oxygen was then bubbled into the mixture for 2 h while stirring for 8 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for the Synthesis of Substituted Diphenyl 7c. K_2CO_3 (3.0 mmol, 3.0 equiv) was added to a solution of **3u** (1.0 mmol, 1.0 equiv) in acetone (10 mL) at room temperature. The reaction mixture was stirred for 10 min, at which time 1,1-dimethyl allyl bromide (1.05 mmol, 1.05 equiv) was added to the reaction mixture. The reaction mixture was further stirred at reflux in an oil bath for 8 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1) to afford intermediate **6c**. $Bi(OTf)_3$ (2 mol %) and molecular sieves (4 Å, 50 mg) were added to intermediate **6c** (0.5 mmol, 1.0 equiv) in dry $MeNO_2$ (2 mL) at room temperature. The reaction mixture was stirred for 3 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1).

General Procedure for the Synthesis of Substituted Quinoxaline 7d. NH_2OH−HCl (1.1 mmol, 1.1 equiv) was added to a stirred solution of **3u** (1.0 mmol, 1.0 equiv) in dimethyl sulfoxide (2 mL) at room temperature and kept for 10 min. Then, the reaction mixture was heated at 100 °C in an oil bath for 10 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 4:1) to afford intermediate **6d**. Compound 1,2-diaminobenzene (0.55 mmol, 1.1 equiv) was added to intermediate **6d** (0.5 mmol, 1.0 equiv) in 1,4-dioxane (15 mL) at room temperature. The reaction mixture was further stirred at 100 °C in an oil bath for 10 h. After completion of the reaction as indicated by TLC, the residue was quenched with water and extracted with DCM. The collected organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1).

1-Phenyl-2-tosylpent-4-yn-1-one (***6a***)*:*[4b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1), white solid (265 mg, 85% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00−7.94 (m, 2H), 7.62 (t, 3H, J = 7.8 Hz), 7.48 (t, 2H, J = 7.8 Hz), 7.30 (d, 2H, J = 8.0 Hz), 5.26 (dd, 1H, J = 8.4, 6.3 Hz), 2.97 (t, 1H, J = 2.4 Hz), 2.95 (d, 1H, J = 2.6 Hz), 2.43 (s, 3H), 1.89 (t, 1H, J = 2.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 190.9, 145.9, 136.9, 134.1, 132.8, 129.8, 129.7, 129.2, 128.8, 78.2, 71.2, 68.2, 21.7, 18.3.

1-Phenyl-2-tosylpent-4-en-1-one (***6b***)*:*[24c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1), white solid (252 mg, 80% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 7.2 Hz), 7.65 (d, 2H, J = 8.3 Hz), 7.60 (t, 1H, J = 7.4 Hz), 7.47 (t, 2H, J = 7.8 Hz), 7.31 (d, 2H, J = 8.1 Hz), 5.58 (ddt, 1H, J = 17.0, 10.1, 6.8 Hz), 5.12 (dd, 1H, J = 10.9, 3.7 Hz), 5.03 (dd, 1H, J = 17.0, 1.4 Hz), 4.97 (dd, 1H, J = 10.2, 1.1 Hz), 2.89−2.73 (m, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 192.0, 145.5, 137.2, 134.0, 133.2, 132.0, 129.9, 129.6, 129.1, 128.8, 119.0, 69.3, 32.5, 21.7.

5-Methyl-1-phenyl-2-tosylhex-4-en-1-one (***6c***)*:*[25a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 5:1), white solid (270 mg, 79% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (dd, 2H, J = 8.3, 1.1 Hz), 7.66 (d, 2H, J = 8.3 Hz), 7.61−7.56 (m, 1H), 7.46 (t, 2H, J = 7.8 Hz), 7.30 (d, 2H, J = 8.0 Hz), 5.02 (dd, 1H, J = 10.2, 4.4 Hz), 4.87 (t, 1H, J = 7.4 Hz), 2.82−2.69 (m, 2H), 2.43 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 192.6, 145.3, 137.4, 136.5, 133.8, 133.6, 129.8, 129.5, 129.0, 128.7, 117.5, 69.7, 27.3, 25.6, 21.7, 17.8.

3-(Methylsulfonyl)-1-phenyl-2-tosylpropan-1-one (***6d***)*:*[4c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 4:1), white solid (300 mg, 82% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93−7.89 (m, 2H), 7.58 (dd, 3H, J = 10.1, 7.9 Hz), 7.44 (t, 2H, J = 7.9 Hz), 7.28 (s, 2H), 5.61 (dd, 1H, J = 11.2, 2.0 Hz), 4.11 (dd, 1H, J = 13.9, 11.2 Hz), 3.76 (dd, 1H, J = 14.0, 1.3 Hz), 2.87 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 190.1, 146.5, 136.0, 134.5, 132.8, 130.0, 129.5, 129.4, 128.8, 64.7, 52.3, 42.7, 21.7.

5-Methyl-2-phenyl-3-tosylfuran (***7a***)*:*[4b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (126 mg, 81% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (dd, 2H, J = 7.3, 2.2 Hz), 7.68 (d, 2H, J = 8.2 Hz), 7.45−7.34 (m, 3H), 7.19 (d, 2H, J = 8.2 Hz), 6.41 (s, 1H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 153.4, 151.6, 144.0, 139.3, 129.6, 129.6, 128.6, 128.5, 128.2, 127.1, 124.5, 108.4, 21.6, 13.4.

1-Phenyl-2-tosylpentane-1,4-dione (***7b***)*:*[24c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), yellowish liquid (139 mg, 84% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (dd, 2H, J = 8.3, 1.1 Hz), 7.56 (dd, 3H, J = 9.8, 7.9 Hz), 7.41 (dd, 2H, J = 8.1, 7.6 Hz), 7.25 (d, 2H, J = 8.0 Hz), 5.51 (dd, 1H, J = 10.8, 2.9 Hz), 3.49 (dd, 1H, J = 18.1, 10.9 Hz), 3.29 (dd, 1H, J = 18.1, 2.9 Hz), 2.40 (s, 3H), 2.16 (s, 3H).

3-Methyl-1,1′-biphenyl (***7c***)*:*[25a] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), colorless liquid (66 mg, 79% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (dd, 2H, J = 8.0, 0.9 Hz), 7.37 (dd, 4H, J = 14.0, 6.2 Hz), 7.28 (t, 2H, J = 7.5 Hz), 7.12 (d, 1H, J = 7.5 Hz), 2.37 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 141.6, 141.4, 138.5, 128.9, 128.8, 128.2, 128.1, 127.4, 127.3, 124.5, 21.7.

2-Methyl-3-phenylquinoxaline (***7d***)*:*[4c] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1), white solid (86 mg, 78% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13−8.08 (m, 1H), 8.05 (dd, 1H, J = 8.2, 1.5 Hz), 7.70 (pd, 2H, J = 7.0, 1.7 Hz), 7.65 (dd, 2H, J = 8.1, 1.3 Hz), 7.49 (ddd, 3H, J = 8.5, 7.8, 6.3 Hz), 2.77 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 154.9, 152.5, 141.2, 141.0, 139.1, 129.7, 129.2, 129.2, 129.0, 128.9, 128.5, 128.3, 24.4.

(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (***8***)*:*[25b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 20:1), yellow liquid (56 mg, 35% yield); ^{1}H NMR ($CDCl_3$, 500

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MHz) δ 7.53−7.48 (m, 2H), 7.41 (t, 1H, J = 7.4 Hz), 7.32−7.18 (m, 9H), 7.14 (d, 2H, J = 7.3 Hz), 7.00 (d, 2H, J = 7.1 Hz).

(Z)-1-Phenyl-2-(phenylsulfonyl)ethen-1-amine (E):[26b] purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), yellow solid (46 mg, 82% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 7.4 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.45 (d, 2H, J = 7.2 Hz), 7.41 (d, 1H, J = 7.1 Hz), 7.36 (t, 2H, J = 7.4 Hz), 5.06 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 156.7, 144.5, 136.8, 132.4, 130.9, 129.0, 128.9, 126.4, 125.9, 91.4.

General Procedure for Sample Preparation and Crystal Measurement. Single crystals of products **3g** and **5n** were prepared by volatilization using a mixture of dichloromethane and diethyl ether as the solvent. Then, a suitable crystal was selected and placed on a CCD area detector diffractometer. The crystal was kept at 296.15 K during data collection. The structure was solved with the Olex2.Solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02249.

Optimization of reaction conditions, mechanism investigation, X-ray crystal data of products **3g** and **5n**, and NMR and HRMS spectra of products (PDF)

Accession Codes

CCDC 1902707 and 2032258 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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