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Selective N═S Coupling Reactions of *N*-Methoxy Arylamides and Sulfoxides Catalyzed by Iron Salt

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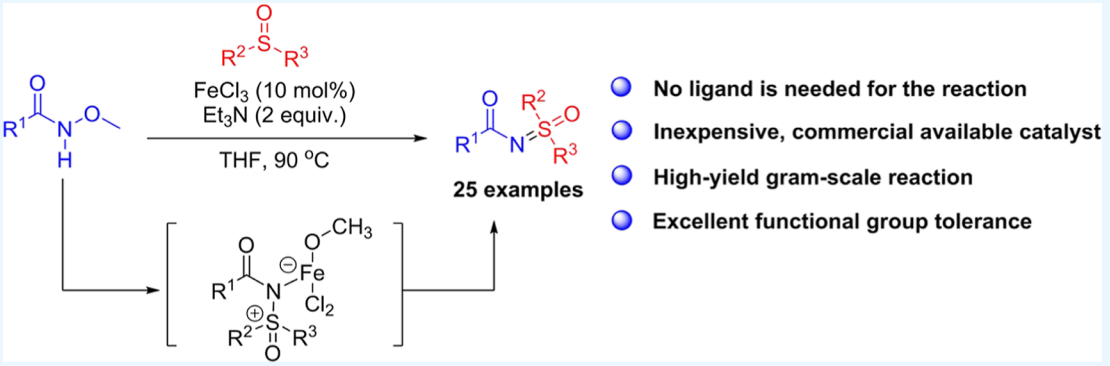

ABSTRACT: An iron-catalyzed selective N═S coupling of *N*-methoxy amides and sulfoxides has been developed and was found to be a highly efficient method for the synthesis of *N*-acyl sulfoximines. Electron-donating as well as electron-withdrawing groups on the phenyl ring are tolerated, and even sensitive substituents are compatible. The current catalytic transformation was conducted under an air atmosphere and can be easily scaled up to a gram scale with a catalyst loading of only 1 mol %. In this case, both coupling partners are used in their native forms, thus obviating prior functionalization and activation.

1. INTRODUCTION

Sulfur-containing functional groups are pervasive across disciplines from materials science to pharmaceutical chemistry.[1,2] Sulfoximines, the monoaza N═S variants of sulfones, have frequently been found in the frameworks of diverse pharmaceuticals, agrochemicals, organocatalysts, and ligands.[3−5] For example, the growing interest in the physicochemical properties of sulfoximines has resulted in a significant surge in their utilization for enhancing pharmacokinetic and pharmacodynamic characteristics during lead optimization studies.[6,7] Recently, the sulfoximines can be synthesized through various strategies, including sulfur imidation, sulfilimine oxidation, and nitrene-transfer reactions.[8−12] However, despite the proliferation of methodologies for accessing sulfonimidoyl-containing compounds, there has been limited progress in the direct synthesis of *N*-acyl sulfoximine derivatives. For a long time, the synthesis of *N*-acyl sulfoximines has been traditionally achieved through oxidation of sulfilimines or N−H acylation of sulfoximines (Scheme 1a).[13−17] Nevertheless, the N═S bond existed in the starting materials required to be presynthesized, limiting the availability of the raw materials.

As a versatile synthon, acyl nitrene is widely applied in the reactions such as C−H bond insertion, aziridination, and nitrene/alkyne metalation, incorporating nitrogen-containing building blocks into complex structural motifs.[18−20] A series of well-documented nitrene precursors, including dioxazole, hydroxylamines, azides, etc., have been developed so far.[21,22] Surprisingly, the construction of *N*-acyl sulfoximines via the acyl nitrene intermediate appears to be rare (Scheme 1b). Dioxazolones can serve as acyl nitrene precursors, undergoing N═S bond coupling with dimethyl sulfoxide (DMSO) at 150 °C under harsh conditions.[23] An alternative transformation pathway from dioxazolone to *N*-acyl sulfoximines is transition metal-catalyzed imidization of sulfoxides combined with light-induced chemical reaction, which necessitates an inert atmosphere and anhydrous solvent conditions.[24,25] Recently, the Xia group developed *N*-pivaloyloxybenzamide as the *N*-acyl nitrene precursor to efficiently construct the *N*-acyl sulfoximines through the nitrene-transfer reaction, while a divalent iron catalyst and the L-phenylalanine ligand are crucial for the reaction.[26] Simultaneously, the Qiu group also utilized *N*-pivaloyloxybenzamide as a highly active acyl nitrene precursor under photoredox/iron dual catalysis and inves-

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Scheme 1. Strategies for the Synthesis of *N*-Acyl Sulfoximines

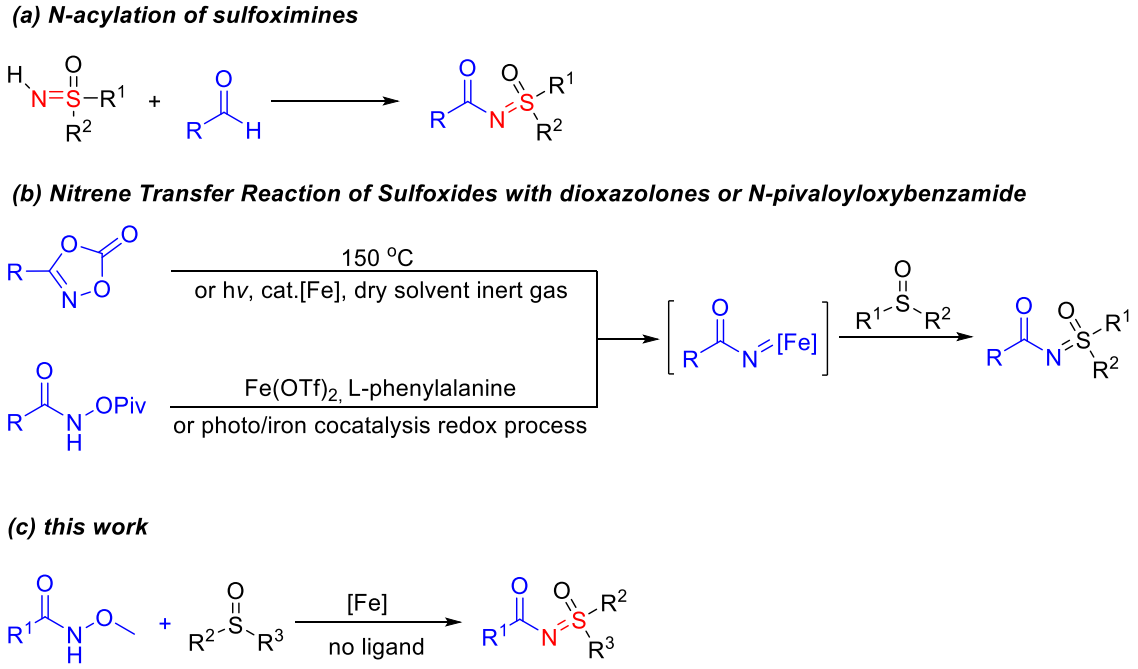
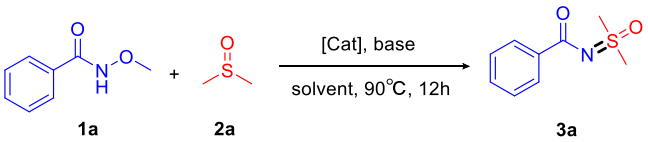


Table 1. Screening of Different Catalysts, Bases, Solvents, and Conditions for the *N*-Methoxybenzamide 1a[ab]



1a 2a 3a

Entry	Catalyst	Base	Solvent(V:V)	Yield (%)
1	-	K_2CO_3	DMSO:THF=1:1	ND
2	$FeCl_3$	-	DMSO:THF=1:1	ND
3	$FeCl_3$	K_2CO_3	DMSO:THF=1:1	56
4	$Fe(acac)_3$	K_2CO_3	DMSO:THF=1:1	23
5	$FeCl_2$	K_2CO_3	DMSO:THF=1:1	41
6	$Fe(OTf)_2$	K_2CO_3	DMSO:THF=1:1	ND
7	$FeCl_3$	Na_2CO_3	DMSO:THF=1:1	<5
8	$FeCl_3$	Cs_2CO_3	DMSO:THF=1:1	ND
9	$FeCl_3$	NaOAc	DMSO:THF=1:1	ND
10	$FeCl_3$	KO*t*-Bu	DMSO:THF=1:1	ND
11	$FeCl_3$	C_2H_3MgBr	DMSO:THF=1:1	74
12	$FeCl_3$	Et_3N	DMSO:THF=1:1	80
13[c]	$FeCl_3$	Et_3N	DMSO:EtOH=1:1	ND
14[c]	$FeCl_3$	Et_3N	DMSO:ACN=1:1	48
15[c]	$FeCl_3$	Et_3N	DMSO:1,4-Dioxane=1:1	27
16[c]	$FeCl_3$	Et_3N	DMSO:Acetone=1:1	25
17[c]	$FeCl_3$	Et_3N	DMSO:*n*-Hexane=1:1	39
18[c]	**$FeCl_3$**	**Et_3N**	**DMSO:THF=1:3**	**95**

[a] Reaction scale: **1a** (0.2 mmol), V_{DMSO}+$V_{Solvent}$=2.0 mL, Catalyst (10 mol%), Base (0.2 mmol), air, 90 °C, 12 h. [b] Isolated yield based on **1a**. [c] 2.0 equiv. Et_3N. ND = Not Detected.

[a]Reaction scale: **1a** (0.2 mmol), V_{DMSO} + $V_{solvent}$ = 2.0 mL, catalyst (10 mol %), base (0.2 mmol), air, 90 °C, 12 h. [b]Isolated yield based on **1a**. [c]2.0 equiv of Et_3N. ND = not detected.

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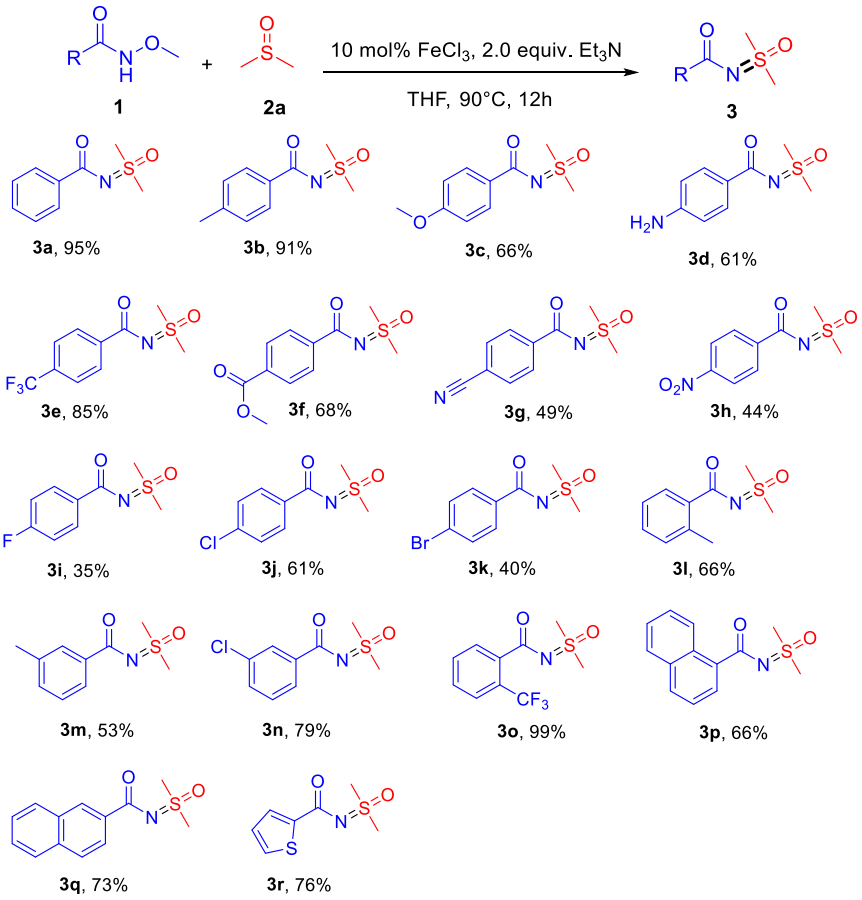
Scheme 2. Scope of the *N*-Methoxy-Substituted Amides 1 in Iron(III)-Catalyzed N═S Cross-Coupling[ab]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.5 mL), $FeCl_3$ (10 mol %), Et_3N(2.0 equiv), THF (1.5 mL), air, 90 °C, 12 h. [b]Isolated yield based on **1**.

tigated one example of the N═S coupling with (methylsulfinyl)benzene.[27] Although dioxazolone and *N*-pivaloyloxybenzamide could be compatible for N═S bond coupling, exploring simple acyl nitrene precursors to promote further transformation of acyl nitrene and sulfoxide under facile and manipulable conditions remains a challenging pursuit in the synthesis of *N*-acyl sulfoximines.

N-Methoxy arylamides, which can be easily prepared from acyl chlorides and methoxyamine, are widely used as the directing group in the transition metal-catalyzed C−H activation reactions and play an extremely important role in the construction of C−N or C−O bonds.[28−33] To the best of our knowledge, the wealth of literature in which *N*-methoxy arylamides serve as acyl nitrene precursors to construct N═S bonds is not observed. On the basis of our previous works on the *N*-arylation of *N*-methoxy benzamides[34,35] and iron-catalyzed oxidative cross-couplings,[36−39] and inspired by the mechanism investigation on the generation of the ferric acyl nitrene intermediate,[19,20,40,41] we questioned whether the amide group that is linked to a methoxy substituent could be strategically employed to accomplish N═S bond cross-coupling. To our delight, an envisioned N═S coupling of *N*-methoxy amides with sulfoxides proceeded smoothly in the presence of an iron salt (Scheme 1c).

2. RESULTS AND DISCUSSION

Our research commenced with the assessment of reliable reaction conditions for the coupling of *N*-methoxybenzamide (**1a**) and DMSO (**2a**) (Table 1). Initially, various catalysts and bases were optimized. The model reaction without either the iron catalyst or the base did not take place (entries 1 and 2). Transition metal or rare-earth catalysts such as Pd(dppf)Cl_2, Ni(dppf)Cl_2, and $CeCl_3{\cdot}7H_2O$ were examined and proved to be ineffective (Table S1, entries 1−5, Supporting Information). When $FeCl_3$ was employed as the catalyst and K_2CO_3 as the base, the reaction conducted at 90 °C provided the N═S coupling product **3a** in moderate yield (entry 3). Screening of various iron catalysts did not give better outcomes (entries 4−6). As we were encouraged by this preliminary result, various bases were tested (entries 7−12). Common inorganic bases such as Na_2CO_3 and Cs_2CO_3 suppressed the reaction, as did NaOAc and KO*t*Bu (entries 7−10). Fortunately, when the organic bases vinylmagnesium bromide and triethylamine were utilized, the reaction was significantly enhanced, affording **3a** in moderate to good yields (entries 11 and 12). Considering the stability and cost, Et_3N was selected as the base. The impact of the amount of iron catalyst and Et_3N on the reaction was examined. It was found that higher catalyst loading did not lead to substantially higher yields, while decreasing the iron loading to 7.5 or 5 mol % was not favorable for the reaction, and the reaction efficiency was suppressed obviously (Table S1, entries 6−8). Gratifyingly, increasing the amount of Et_3N to 2.0 equiv. gave the satisfactory yield (Table S1, entry 9). Interestingly, the solvent system had a significant effect on the reaction. EtOH had a deleterious effect on the N═S bond cross-coupling, while other solvents provided a lower yield of N═S

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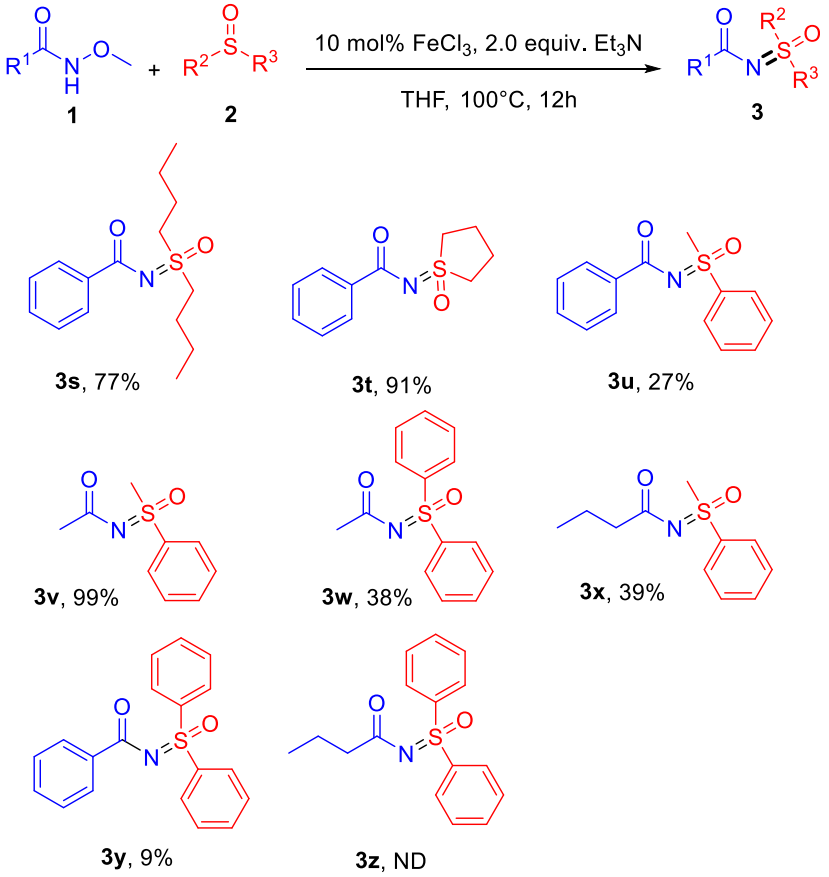
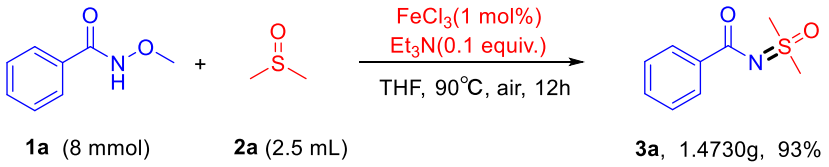
Scheme 3. Scope of the Sulfoxides 2 in Iron(III)-Catalyzed N═S Cross-Coupling of *N*-Methoxy Amides[ab]



[a]Reaction conditions: **1** (0.2 mmol), **2** (2.5 equiv), $FeCl_3$ (0.1 equiv), Et_3N (2.0 equiv), THF (2.0 mL), air, 100 °C, 12 h. [b]Isolated yield based on **1**. ND = not detected.

Scheme 4. Application of the N═S Coupling Reaction for the Gram-Scale Synthesis



coupling product than THF (entries 13−17). Adjusting the ratio of mixed solvents on the reaction was also investigated, and it was discovered that a DMSO/THF ratio of 1:3 was the most suitable solvent system (entry 18 and Table S1, entries 10 and 11). After considerable preliminary experimentation, we defined our best reaction conditions as follows: using 10 mol % $FeCl_3$ and 2 equiv. of Et_3N as the catalyst and base, respectively, the reaction of **1a** (0.2 mmol) with DMSO/THF (1:3, total volume = 2.0 mL) at 90 °C under an air atmosphere for 12 h efficiently delivered the desired *N*-acyl sulfoximine product **3a** in 95% yield (entry 18).

Evaluation of the N═S bond cross-coupling strategy was first examined by screening a range of electronically and sterically distorted *N*-methoxy amides (**1**) (Scheme 2). Substituents with a variety of electron-donating and electron-withdrawing groups including alkyl, methoxyl, amino, ester, cyano, nitro, and halogen at the para-position of the phenyl ring were examined, and a wide range of *N*-acyl sulfoximine products were obtained in yields ranging from 35 to 95% (**3b**−**3k**). The para-substituted electron-donating groups are more beneficial to the N═S coupling of amide substrates than the electron-withdrawing group is. Notably, sensitive functional groups such as trifluoromethyl, ester, cyano, and nitro groups were compatible under the standard conditions, providing synthetic handles for further functionalization (**3e**−**3h**). Moreover, under the present iron-catalyzed coupling conditions, C−X bonds were tolerated, as well (**3i**−**3k**). Especially, when the R group was amino, the corresponding *N*-acyl sulfoximine product **3d** could also be prepared in a 61% yield. The sterically hindered 2- and 3-substituented *N*-methoxy benzamides, as well as the naphthalamides, were able to participate in the reactions successfully to give the corresponding products in moderate to excellent yields (**3l**−**3q**). Interestingly, the introduction of a strong electron-withdrawing trifluoromethyl group in the *ortho*-position led to a surprisingly high yield of up to 99% (**3o**). In addition, heterocyclic substrates were competent substrates for this catalytic system (**3r**).

In addition, various sulfoxides containing bulky alkyl groups or phenyl were tested, and a slight temperature elevation is

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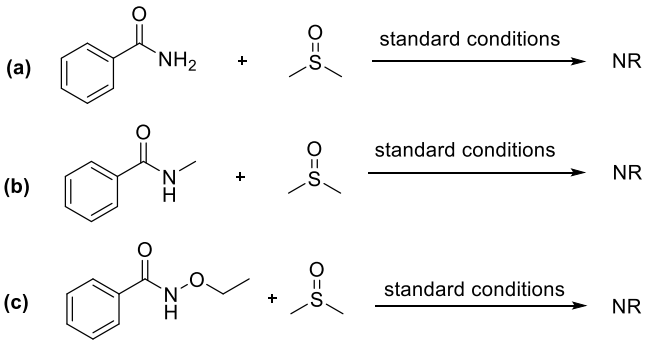
helpful to overcome the high energy barrier caused by increasing spatial hindrance, resulting in the synthetically useful yields of **3s**, **3t**, and **3u** (Scheme 3). Fortunately, attempts to explore the alkylated substrates of the *N*-methoxy amides were also successful (**3v**−**3x**), implying that the reaction was compatible with the alkyl groups as well. However, when both *N*-methoxy amides and sulfoxide were endowed with sterically hindered groups, the yields of the reaction were reduced or even impossible (**3y** and **3z**). The sulfoxide **2a** used previously is liquid, but most of the sulfoxides here are solid; we set the amount of sulfoxide at 2.5 equiv to maximize the yield.

The potential synthetic application of this transformation was subsequently evaluated (Scheme 4). With a catalyst loading as low as 1 mol % and a reduced amount of base to 0.1 equiv, a gram-scale reaction was carried out smoothly, and the *S*,*S*-dimethyl-*N*-benzoylsulfoximine was obtained in 93% yield. This successful example highlights the promising potential of the novel N═S bond coupling method for industrial applications.

To gain an insight into the reaction mechanism, a number of control experiments were carried out. Benzamide substrates with different groups at the N atom, including benzamide, *N*-methyl-benzamide, and *N*-ethoxy-benzamide, are not applicable to the iron-catalyzed nitrene-transfer reaction (Scheme 5a−c), which implied that the methoxy group on the nitrogen atom was indispensable.

Scheme 5. Control Experiments of the Iron(III)-Catalyzed N═S Cross-Coupling Reaction



In light of the above results and the previous literature reports,[26,42−44] a plausible reaction mechanism for the iron-catalyzed nitrene-transfer reaction of sulfoxides with *N*-methoxy amides has been proposed (Figure 1). First, *N*-methoxy amide coordinates to an iron(III) catalyst, followed by deprotonation of the N−H bond to form intermediate **A**. Subsequently, it quickly transforms into Fe−nitrenoid complex **B**. **B** is captured by dimethyl sulfoxide to yield species **C** through a nucleophilic addition process. Finally, Fe−N bond cleavage of **C** occurs along with the elimination of the methoxy group to produce the desired *N*-acyl sulfoximine product and to regenerate the iron(III) catalyst.

3. CONCLUSIONS

In conclusion, we have developed a new method for the synthesis of *N*-acyl sulfoximine derivatives. The method involves the iron-catalyzed N═S bond coupling reaction of different substituted *N*-methoxy amides and sulfoxides in the presence under the condition of triethylamine as a base,

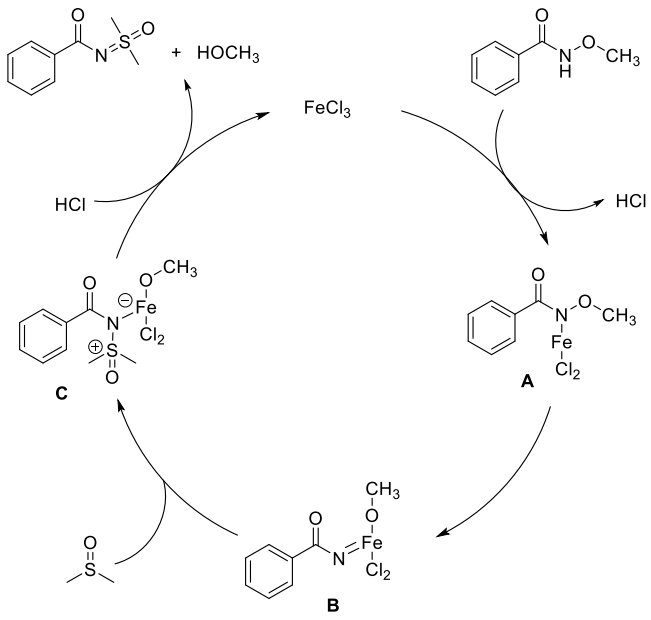


Figure 1. Plausible reaction mechanism of iron(III)-catalyzed N═S cross-coupling.

efficiently affording the *N*-acyl sulfoximines with high functional group tolerance. Featuring readily available starting materials and a cheap and environmentally benign iron(III) catalyst, this method offers operational simplicity and high yield, and at the same time, it is in line with the concept of green chemistry, which opens up a new approach for the preparation and synthesis of sulfoximines.

4. EXPERIMENTAL DETAILS

4.1. General Information. Unless otherwise noted, all of the reagents were purchased from Shanghai Aladdin Bio-Chem Technology (Shanghai, China) and used without purification. Purification of products was conducted by flash chromatography on silica gel (200−300 mesh). Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance III 400 (Bruker, Billerica, MA, USA). The ^{1}H NMR (400 MHz) chemical shifts were obtained relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ 7.26 ppm). The ^{13}C NMR (101 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ 77.16 ppm). The ^{1}H NMR (400 MHz) chemical shifts were obtained relative to DMSO-d_6 as the internal reference (DMSO-d_6: δ 2.50 ppm). The ^{13}C NMR (101 MHz) chemical shifts were given by using DMSO-d_6 as the internal standard (DMSO-d_6: δ 39.9 ppm). Chemical shifts are reported in ppm using tetramethylsilane as the internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet). The model of mass spectrometer used: Thermo Scientific Q Exactive, Orbitrap, USA.

4.2. Subsection General Procedure for the Iron-Catalyzed N═S Coupling of *N*-Methoxy Amides. *N*-methoxy amide **1** (0.2 mmol), sulfoxides **2**, tetrahydrofuran (THF), $FeCl_3$ (10 mol %), and Et_3N (0.4 mmol) were added to a sealed tube. Then, the mixture was stirred at 90 °C in air for 12 h. After the disappearance of the substrate as indicated by the TLC, the reaction mixture was diluted with DCM (10 mL) and washed with water (5 mL × 3). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated

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under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel DCM/MeOH to give the desired product **3**.

4.3. Characterization Data for Products 3a−3y. The following characterization data are shown in the Supporting Information.

*4.3.1. S,S-Dimethyl-N-benzoylsulfoximine (**3a**).*[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10−8.04 (m, 2H), 7.49−7.43 (m, 1H), 7.36 (t, J = 7.5 Hz, 2H), 3.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.19, 135.45, 132.22, 129.22, 128.10, 41.73.

*4.3.2. 4-Methyl(oxo)-λ^6-sulfaneylidene-4-methylbenzamide (**3b**).*[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04−7.98 (m, 2H), 7.21 (d, J = 7.9 Hz, 2H), 3.39 (s, 6H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.22, 142.78, 132.71, 129.33, 128.81, 41.79, 21.65.

*4.3.3. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-methoxybenzamide (**3c**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.93 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 3.43 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.36, 162.24, 130.78, 128.36, 113.36, 55.40, 41.20.

*4.3.4. 4-Amino-N-(dimethyl(oxo)-λ^6-sulfaneylidene)-benzamide (**3d**).*[45] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.68 (d, J = 8.7 Hz, 2H), 6.50 (d, J = 8.7 Hz, 2H), 5.72 (s, 2H), 3.38 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 173.26, 152.85, 131.15, 123.27, 112.75, 41.77.

*4.3.5. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-(trifluoromethyl)benzamide (**3e**).*[46] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 3.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.80, 138.60, 133.67, 133.35, 129.60, 125.44−124.91 (m), 41.73. ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.83.

*4.3.6. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-[1,1′-biphenyl]-4-carboxamide (**3f**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.10 (d, J = 8.6 Hz, 2H), 8.02 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.49 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.18, 166.29, 140.31, 132.73, 129.47 (d, J = 12.3 Hz), 52.84, 41.45.

*4.3.7. 4-Cyano-N-(dimethyl(oxo)-λ^6-sulfaneylidene)-benzamide (**3g**).*[17] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.12 (dd, J = 7.4, 1.2 Hz, 2H), 7.96−7.92 (m, 2H), 3.50 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 171.51, 140.23, 132.82, 129.75, 118.94, 114.53, 41.42.

*4.3.8. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-nitrobenzamide (**3h**).*[11] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.30 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 170.87, 149.53, 141.41, 130.05, 123.55, 41.00.

*4.3.9. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-fluorobenzamide (**3i**).*[47] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.07−8.01 (m, 2H), 7.30−7.23 (m, 2H), 3.46 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.00, 166.13, 163.65, 132.85 (d, J = 2.7 Hz), 131.83 (d, J = 9.3 Hz), 115.64, 115.43, 41.50. ^{19}F NMR (377 MHz, DMSO) δ: −108.57.

*4.3.10. 4-Chloro-N-(dimethyl(oxo)-λ^6-sulfaneylidene)-benzamide (**3j**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.04−7.92 (m, 2H), 7.52 (dd, J = 8.5, 1.9 Hz, 2H), 3.47 (d, J = 2.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.03, 137.22, 135.11, 131.01, 128.75, 41.47.

*4.3.11. 4-Bromo-N-(dimethyl(oxo)-λ^6-sulfaneylidene)-benzamide (**3k**).*[47] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.93−7.88 (m, 2H), 7.68−7.63 (m, 2H), 3.46 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.18, 135.47, 131.70, 131.21, 126.31, 41.48.

*4.3.12. N-[2-(Methyl)-benzoyl]-S,S-dimethylsulfoximine (**3l**).*[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.0 Hz, 1H), 7.22 (dd, J = 8.8, 4.3 Hz, 1H), 7.12 (t, J = 7.1 Hz, 2H), 3.26 (d, J = 0.7 Hz, 6H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.65, 138.84, 135.32, 131.53, 130.92, 130.38, 125.48, 41.76, 21.66.

*4.3.13. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methylbenzamide (**3m**).*[17] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.85−7.73 (m, 2H), 7.37−7.30 (m, 2H), 3.45 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.82, 137.29, 135.83, 132.48, 129.24, 128.02, 125.92, 41.10, 20.94.

*4.3.14. 3-Chloro-N-(dimethyl(oxo)-λ^6-sulfaneylidene)-benzamide (**3n**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.01−7.87 (m, 2H), 7.63 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 3.49 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 171.13, 137.95, 132.99, 131.70, 130.24, 128.36, 127.23, 41.02.

*4.3.15. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(trifluoromethyl)benzamide (**3o**).* ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.12 (t, J = 8.0 Hz, 2H), 8.06 (t, J = 7.3 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 3.85 (d, J = 1.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 174.66, 138.42 (d, J = 1.9 Hz), 132.59, 130.23, 129.48, 126.65 (dd, J = 10.5, 5.3 Hz), 126.25, 125.71, 122.99, 42.51, 41.10. ^{19}F NMR (377 MHz, DMSO-d_6) δ: −57.47. HR-MS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{10}H_{10}F_3NO_2S$ + K, 304.0021; found, 304.00159.

*4.3.16. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-naphthamide (**3p**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.85 (dd, J = 8.3, 0.7 Hz, 1H), 8.12−8.02 (m, 2H), 7.96 (d, J = 7.8 Hz, 1H), 7.56 (tdd, J = 15.2, 7.0, 1.5 Hz, 3H), 3.52 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 175.86, 134.88−134.46 (m), 134.07 (d, J = 35.6 Hz), 131.86, 130.88, 129.10, 128.82, 127.35, 126.42 (d, J = 9.3 Hz), 125.22, 41.55.

*4.3.17. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-naphthamide (**3q**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.61 (s, 1H), 8.07 (dd, J = 8.6, 1.6 Hz, 2H), 7.96 (dd, J = 8.1, 4.9 Hz, 2H), 7.60 (ddd, J = 15.4, 10.1, 6.2 Hz, 2H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 173.17, 135.07, 133.70, 132.63, 129.91, 129.64, 128.46−127.97 (m), 127.05, 125.66, 41.59.

*4.3.18. N-(Dimethyl(oxo)-λ^6-sulfaneylidene)thiophene-2-carboxamide (**3r**).*[26] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.76 (dd, J = 5.0, 1.2 Hz, 1H), 7.63 (dd, J = 3.7, 1.2 Hz, 1H), 7.12 (dd, J = 4.9, 3.7 Hz, 1H), 3.45 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 168.25, 141.81, 132.45, 131.79, 128.36, 41.63.

*4.3.19. N-(Dibutyl(oxo)-λ^6-sulfaneylidene)benzamide (**3s**).*[46] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.02 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 6.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 3.66−3.51 (m, 4H), 1.82−1.67 (m, 4H), 1.43 (dd, J = 14.7, 7.4 Hz, 4H), 0.90 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.91, 136.38, 132.26, 129.18, 128.51, 50.85, 23.93, 21.43, 13.88.

*4.3.20. N-(Methyl(oxo)(phenyl)-λ^6-sulfaneylidene)-benzamide (**3t**).*[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (dt, J = 8.5, 1.7 Hz, 2H), 7.53−7.46 (m, 1H), 7.43−7.36 (m, 2H), 3.75−3.65 (m, 2H), 3.33 (ddd, J = 14.4, 7.1, 2.4 Hz, 2H), 2.40−2.25 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.06, 135.23, 132.20, 129.31, 128.07, 52.72, 23.78.

*4.3.21. N-(Methyl(oxo)(phenyl)-λ^6-sulfaneylidene)-benzamide (**3u**).*[46] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.06−8.02 (m, 4H), 7.77 (dd, J = 8.4, 6.3 Hz, 1H), 7.70 (dd, J = 10.3, 4.7 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6

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Hz, 2H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 173.09, 139.20, 136.03, 134.17, 132.63, 130.08, 129.32, 128.70, 127.57, 43.72.

*4.3.22. N-Acetyl Methylphenylsulfoximine (**3v**).*[48] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.95 (d, J = 7.8 Hz, 2H), 7.70 (ddd, J = 15.2, 10.9, 3.9 Hz, 3H), 3.43 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 178.89, 139.15, 133.98, 129.97, 127.48, 43.52, 26.91.

*4.3.23. N-Acetyl Diphenylsulfoximine (**3w**).*[49] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.03−7.98 (m, 4H), 7.69−7.60 (m, 6H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 179.15, 139.80, 134.03, 130.34, 127.74, 27.24.

*4.3.24. N-Butyryl Methylphenylsulfoximine (**3x**).* ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.07−8.01 (m, 2H), 7.30−7.23 (m, 2H), 3.46 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 181.34, 139.34, 134.00 (d, J = 13.6 Hz), 129.91 (d, J = 5.8 Hz), 127.40 (d, J = 8.8 Hz), 43.60, 41.25, 19.05, 14.11. HR-MS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{10}H_{10}F_3NO_2S$ + K, 264.0461; found, 264.04504.

*4.3.25. N-Benzoyl-S,S-diphenyl Sulfoximine (**3y**).*[50] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.13 (dd, J = 21.4, 7.9 Hz, 6H), 7.76−7.60 (m, 7H), 7.52 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 173.16, 139.79, 135.80, 134.24, 132.99, 130.50, 129.54, 128.88, 127.84.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H NMR, ^{13}C NMR, and HRMS for new compounds (PDF)

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Notes

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