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A One - Pot Cascade Reaction Combining NH-sulfoximines with thiophenols under mild conditions

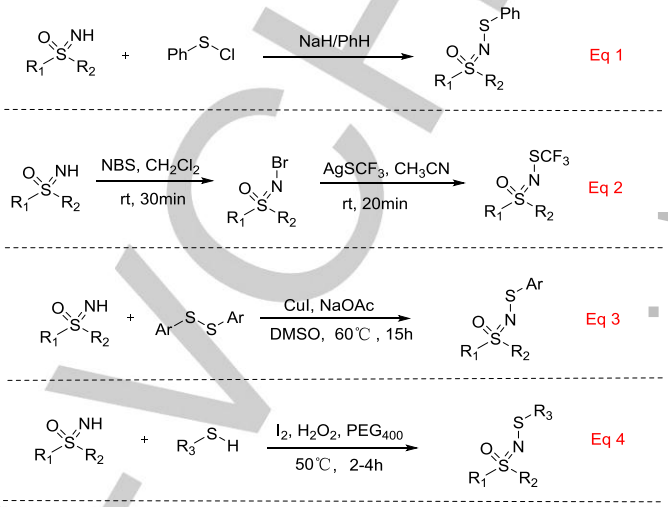
Yao Peng,[a] Yan Lin,[a] Ruifang Nie,[a] Yang Zheng,[a] Yanzhao Liu,[a] Li Guo, *[a] and Yong Wu *[a]

Abstract: A general protocol for the N-thioetherification of NH-sulfoximines was developed. Catalyzed by $[Cu(DMAP)_4I]I$, N-sulfenyl sulfoximines were synthesized by a one-pot cascade reaction using commercially available thiophenols as the sulfur sources at room temperature. The protocol we described was found to be react mild and operationally simple, afforded the corresponding products with good yields and excellent tolerance of the functional groups.

Introduction

Sulfoximines, which were found in early 1950s[1], have been widely applied in organic chemistry, medicinal chemistry and agriculture.[2] In drug development, sulfoximines are associated with a wide variety of biological activities such as antiarrhythmic, polyvalent spasmolytic, antiasthmatic and antiviral activity.[3] For organic synthesis, sulfoximines also could be utilized as chiral auxiliaries[4], chiral ligands[5], organocatalysts[6], and directing group in transition metal-catalyzed C-H functionalizations[7]. Due to their biological activities and the importance in organic chemistry, the processes concerning the synthesis of sulfoximine derivatives have received much consideration. Within the past few decades, many studies focusd on N-H bond modification of sulfoximines have been reported. For instance, iron or copper-catalyzed N-alkylations[8], copper or potassium fluoride -catalyzed N-arylation[9], copper-catalyzed cross-coupling of sulfoximines and alkynes[10], direct N-acylations with carboxylic acids[11] and so on were established. However, to the best of our knowledge, compared with the well-developed formation of N-C bond, the constructions of N-S bond were rarely reported.

In 1984, Shigeru OAE and co-workers reported a construction protocol of N-sulfenyl sulfoximines and arylsulfonyl chloride was needed (eqn (1), Scheme 1).[12] This procedure is not widely used due to the agents' high toxicity and harsh reaction condition. With new techniques for organic synthesis developing, alternative strategy for the construction of N-sulfenyl sulfoximines were reported. In 2015, the N-trifluoromethylthiolated of sulfoximines was established by Bolm through two steps (eqn (2), Scheme 1).[13] Cheng and Yu described a copper-catalyzed N-thioetherification of sulfoximines with disulfides as the sulfur source (eqn (3), Scheme 1).[14] More recently, an odide/oxidant-assisted N–H/S–H dehydrocoupling reaction was reported by Qingle Zeng (eqn (4), Scheme 1).[15] It was the first example of a direct intermolecular dehydrocoupling reaction to construct N-sulfenylsulfoximines. Those protocols



Scheme 1. Sulfoximines based construction of the N-S bond.

enriched the synthesis routes of N-S substituted sulfoximine derivatives. However, they are limited by the multiple-step reactions or the need of heating. Consequently, it is still necessary to develop new accesses for directly synthesis of N-sulfenylation sulfoximine derivatives under mild conditions.

Since the formation of N-C bond of sulfoximines were well-developed,[8-11] it is worth noting that copper showed highly reaction activity in those synthesis strategies. On the other hand, copper also plays an important role in the formation of N–S bond for many compounds.[16] Those reactions were agreed with the "Ullmann-type" reactions which include copper-catalyzed nucleophilic aromatic substitution between various nucleophiles and electrophiles. Furthermore, many copper catalysts were applied as oxidizing agents in organic synthesis.[17] Based on the highly reactivity of copper in the modification of sulfoximine and the formation of N–S bond, we hypothesized copper catalysts may also contribute to the constructions of N–S bond for sulfoximines. In addition, disulfides, which were synthesized from thiophenol, were successfully used in the synthesis of N-sulfenyl sulfoximines as previously reported.[14] Therefore, in this study, we developed a simple and rapidly copper catalyzed N-sulfenyl sulfoximines synthesis under mild conditions.

Results and Discussion

In our exploration, we first screened reaction conditions with diphenyl sulfoximine (**3a**) and thiophenol (**1a**) as the model substrates. Initially, different copper (I) and copper (II) salts, were tested and no N-thioetherification product was detected (entries 1–4, Table 1). Unfortunately, some previously reported copper complex catalysts such as copper(I) thiophene-2-carboxylate(Tc-Cu)[18], $[Cu(OH)TMEDA]_2Cl_2$[19] and $[Cu(MeCN)_4BF_4]$[20] were also inactive for the coupling (entries 5–7, Table 1). Inspired by Cheng and Yu's work[14], CuI with

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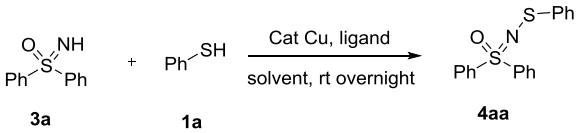
Table 1. Screening of optimal conditions[a].



3a **1a** **4aa**

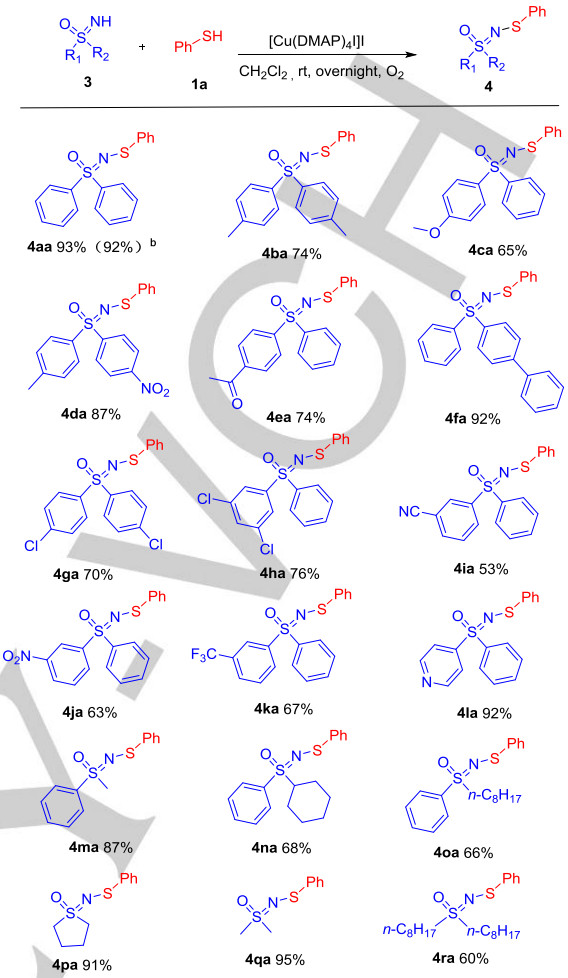
Entry	Cat Cu	ligand	solvent	yield (%)
1	CuI	—	CH_2Cl_2	0
2	CuBr	—	CH_2Cl_2	0
3	$CuSO_4$	—	CH_2Cl_2	0
4	$Cu(OAc)_2$	—	CH_2Cl_2	0
5	Tc-Cu	—	CH_2Cl_2	0
6	$[Cu(OH)TMEDA]_2Cl_2$	—	CH_2Cl_2	0
7	$[Cu(MeCN)_4]BF_4$	—	CH_2Cl_2	0
8	CuI	1,10-phen	CH_2Cl_2	15
9	CuI	DMAP	CH_2Cl_2	71
10	CuI	C_5H_5N	CH_2Cl_2	0
11	$Cu(OAc)_2$	DMAP	CH_2Cl_2	trace
12	Cu_2O	DMAP	CH_2Cl_2	10
13	$CuSO_4$	DMAP	CH_2Cl_2	0
14	**$[Cu(DMAP)_4I]I$**	**—**	**CH_2Cl_2**	**93**

[a] Reaction condition: **3a** (0.23 mmol), **1a** (0.46 mmol), cat Cu (0.069 mmol, 30 mol%), ligand (0.276 mmol) in solvent (3 ml) rt overnight under O_2. Isolated yields.

different ligands were tried in the reaction (entries 8-10, Table 1). We are delight to find that N-sulfenyl sulfoximine (**4aa**) was successfully obtained in 71% yield when catalyzed by CuI and DMAP. Besides, other different sources of copper with DMAP as ligand were tested, and compared with them, CuI with DMAP showed the best catalytic activity (entries 9, 11-13, Table 1). Meanwhile, a square pyramidal copper complex – $[Cu(DMAP)_4I]I$ had been developed for C–N and C–S cross coupling and the complex was synthesized via a disproportionation reaction of CuI and DMAP.[21] We applied this catalyst to our coupling. Catalyzed by $[Cu(DMAP)_4I]I$, N-sulfenyl sulfoximine (**4aa**) was obtained at room temperature and the yield was increased from 71% to 93% (entries 9,14, Table 1). We then optimized the reaction conditions with respect to solvent, the dosage of the catalyst and thiophenol (see supporting information). Overall, we achieved the optimal conditions for the $[Cu(DMAP)_4I]I$-catalyzed N–S bond coupling reaction of sulfoximines and thiophenols (1 equiv. of NH-sulfoximines, 2 equiv. of thiophenols, 20 mol% of $[Cu(DMAP)_4I]I$, CH_2Cl_2, room temperature overnight).

With the optimal conditions established, the scope and limitation of this reaction were studied. First, we evaluated the reactivity of thiophenol towards various sulfoximines. The results were summarized in Table 2. In the model reaction, diphenyl sulfoximine reacted well with thiophenol given the product **4aa** in 93% yield (**4aa**, Table 2). Diphenyl sulfoximines with either electron-donating or electron-withdrawing substituents reacted smoothly and afforded the desired products in good yields (**4ba–4ka**, Table 2). In addition, S-phenyl-S-pyridyl-sulfoximine was efficiently coupled with thiophenol yielding **4la** (92%, Table 2). Furthermore, treating thiophenol with alkyl sulfoximines also resulted in moderate to excellent yield (**4ma** – **4ra**, 60%-95%, Table 2). The practicability of this procedure was evaluated with **3a** (1.086g, 5 mmol), giving the product **4aa** in 92% yield.

Table 2. Reaction of thiophenol with sulfoximines[a]

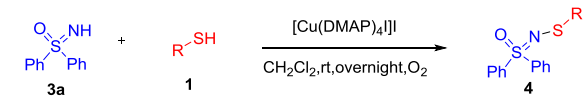


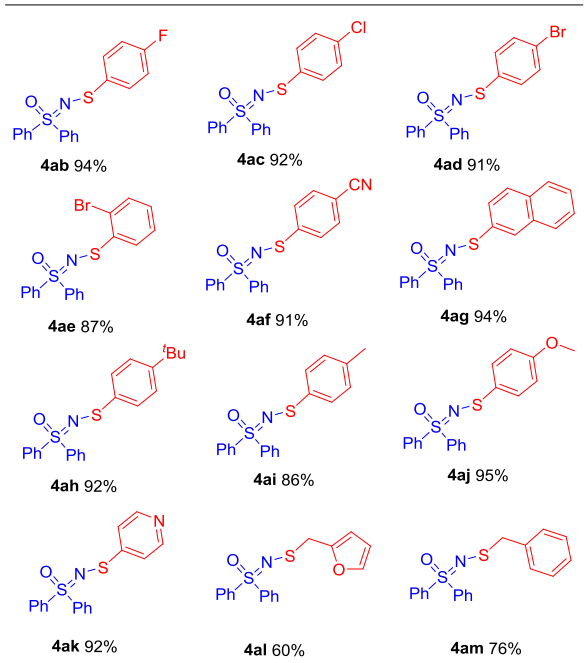
[a] Conditions: **3** (0.4 mmol), **1a** (0.8 mmol), $[Cu(DMAP)_4I]I$ (20 mol%),in CH_2Cl_2 (5 mL) , rt overnight. Isolated yield. [b] Isolated yield at 5 mmol scale reaction.

Next, the different thiols were investigated as shown in Table 3. The thiophenols with halogen substituents on the para or ortho position were well-tolerated in the reaction, affording the expected products in excellent yields (**4ab–4ae**, Table 3). Thiophenols with other substituents such as cyan, naphthyl, alkyl and methoxy also reacted well with diphenyl sulfoximine yielding corresponding N-sulfenylsulfoximines (**4af–4aj**, Table 3). Notably, 4-Mercaptopyridine successfully transformed to the product in high yield, while furfuryl mercaptan, benzyl mercaptane gave lower yield of the corresponding N-sulfenyl sulfoximines products (**4ak–4am**, Table 3). We also tried 1-mercaptooctane, 1-dodecanethiol and both of them reacted with diphenyl sulfoximine (**3a**). Unfortunately, we were unable to get the pure product perhaps because of the instability of target products.

During our research, we found that at the beginning of this reaction thiophenols were quickly coupled into diphenyl sulfides under the optimal conditions, and next, the desired prouducts N-sulfenyl sulfoximines were generated. So, the reaction progress was further explored. As shown in Table 4, catalyzed by [Cu(DMAP)4I]I, both of substituted thiophenols and benzyl mercaptane were quickly transformed into disulphides with high

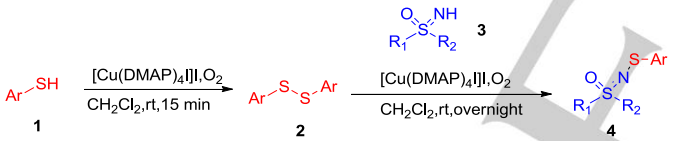
Table 3. Reaction of diphenyl sulfoximine with thiols[a]

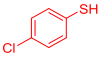
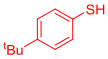
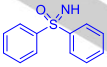
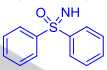
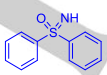
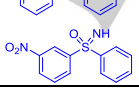




[a] Conditions: **3** (0.4 mmol), **1a** (0.8 mmol), $[Cu(DMAP)_4I]I$ (20 mol%), in CH_2Cl_2 (5 mL), rt overnight. Isolated yield.

Table 4. The application of catalyst[a]



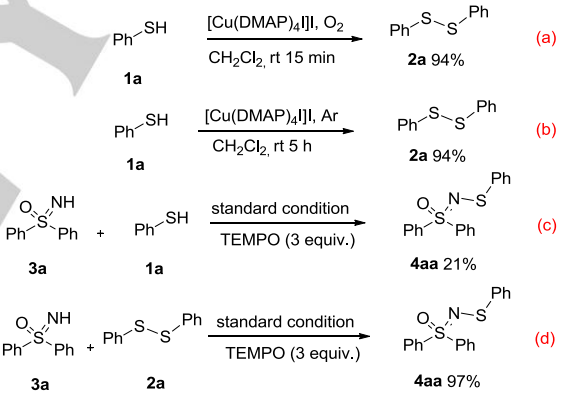
Entry	1	Yield 2[b] (%)	3	Yield 4[c] (%)
1		94		97
2		85		93
3		94		88
4		82		60
5		97		69
6		94		65

[a] Conditions: **1** (0.9 mmol), $[Cu(DMAP)_4I]I$ (20 mol%), in CH_2Cl_2 (5 ml), RT 20min under O_2. [b] Isolate yield. Then **2** (0.4 mmol), **3** (0.4 mmol), $[Cu(DMAP)_4I]I$ (20 mol%) in CH_2Cl_2 (5 ml), rt overnight under O_2. [c] Isolated yield.

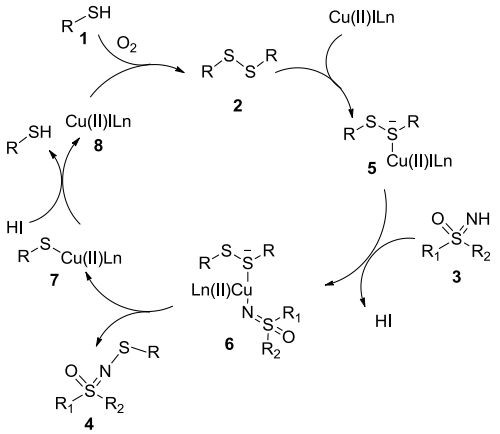
yield at room temperature. Subsequently, sulfoximines could separately react with disulphides affording N-sulfenyl sulfoximines in moderate yields. The results revealed that N-thioetherification of sulfoximines were synthesized via a one-pot cascade reaction.

In order to better understand the mechanism, some control experiments were conducted. Under oxygen atmosphere, thiophenol could be converted into diphenyl sulfide within 20 minutes in excellent yield, while the process needed more than 5 hours under argon (path a, b, Scheme 2), which indicating oxygen can promote the dimerazation process. Further experiments were carried out using 2, 2, 6, 6-tetramethylpiperidine N-oxide (TEMPO) as radical scavenger. Firstly, 3 equiv. of TEMPO was added to the reaction of diphenyl sulfoximine and thiophenol, the reaction process was remarkably inhibited (path c, Scheme 2). On the other hand, diphenyl sulfoximine reacting with diphenyl sulfide was not affected by TEMPO (path d, Scheme 2). This outcome revealed that there is a free radical mechanism in dimerization process that can be blocked by radical scavengers whereas the next N-S conjugation is not affected.

Based on the above experimental results and earlier reported literature[14,15, 22], we postulated a most likely mechanism as shown in Scheme 3. Firstly, thiophenols are dimerized to disulphides, which interact with Cu (II) species leading to the formation of intermediate **5.** Then **5** is subsequently attacked by the nucleophilic sulfoximines to afford intermediate **6** with HI released. The resulting intermediate **6** degradate to the N-sulfenylsulfoximines product and the PhSCu(II) species . With HI, PhSCu(II) is then transformed to Cu(II)ILn and thiophenols to resume the catalytic cycle.



Scheme 2. Mechanistic studies.



Scheme 3. Possible mechanism.

Conclusions

In summary, we have developed a one-pot cascade N-S bond formation method to direct prepare N-sulfenyl sulfoximines with thiophenols and the desired products were obtained in moderate to excellent yields. This reaction proceeded under mild conditions. Moreover, a variety of sulfoximines and thiol substrates are well-compatible. In view of the good functional-group tolerance and the mild reaction conditions, this reaction provides a straightforward and practical way to prepare N-sulfenyl sulfoximine derivatives.

Experimental Section

All substrates and reagents were commercially available and used without further purification. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm). Column chromatography characterization was performed with silica gel (100-200 mesh). ^{1}H NMR spectra were recorded at 400 or 600 MHz and ^{13}C NMR spectra were recorded at 100 or 150 MHz. Chemical shifts are reported in ppm downfield from DMSO-d_6 (δ = 2.50 ppm) for ^{1}H NMR and relative to the central DMSO-d_6 resonance (δ = 39.5 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. ^{19}F NMR spectra were recorded at 376 MHz. Infrared (IR) spectra were recorded on PerkinElmer Spectrum Two instrument. Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). High resolution mass spectroscopy data of the products were recorded on a Waters Q-TOF Premier. The [Cu(DMAP)$_4$I]I was prepared according to reported procedure.[21] The sulfoximines were prepared according to reported procedure. [23]

General Procedure for the Synthesis of N-Sulfenyl sulfoximines (4aa-4am): To a 25 ml round-bottom flask equipped with a magnetic stir bar, sulfoximines (0.23 mmol, 1.00 equiv.) and [Cu(DMAP)$_4$I]I (20% mol) were added. The mixture was purged with oxygen, and then CH_2Cl_2 (5 ml), thiophenols (0.46 mmol, 2.00 equiv.) were added. The reaction mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the solvent was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel with petroleum ether−ethyl acetate and 0.3% trimethylamine as the eluent to afford the N-sulfenyl sulfoximines product.

***S, S*-diphenyl-N-phenylthiosulfoximine (4aa):** White solid, m.p 99-101 ^{o}C (Lit.[14] 105-107 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.02 (d, *J* = 7.7 Hz, 4H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 4H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.1, 139.3, 133.7, 129.8, 128.5, 128.1, 124.7, 122.6; IR v: 3053, 2918, 2847, 1578, 1475, 1445, 1212, 1087, 968, 741, 731, 681, 576, 539, 470 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{15}NOS_2$ Na [M + Na]$^+$ 348.0487, found 348.0500.

***S, S*-di(4-methylphenyl)-N-phenylthiosulfoximine (4ba):** Yellow solid, m.p 97-99 ^{o}C (Lit.[14] 108-110 ^{o}C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8.3 Hz, 4H), 7.41 (d, *J* = 8.2 Hz, 4H), 7.33 – 7.25 (m, 4H), 7.07 (t, *J* = 7.0 Hz, 1H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.2, 142.4, 136.7, 130.2, 128.5, 128.0, 124.5, 122.4, 20.9; IR v: 3052, 2958, 2920, 2849, 1592, 1577, 1475, 1218, 1208, 1086, 959, 815, 738, 669, 568, 471 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{19}NOS_2$ Na [M + Na]$^+$ 376.0800, found 376.0810.

***S*-phenyl-*S*-(4-methoxyphenyl)-N-phenylthiosulfoximine (4ca):** Yellow solid, m.p 92-95 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 – 7.93 (m, 4H), 7.67 – 7.61 (m, 3H), 7.31 – 7.28 (m, 4H), 7.15– 7.14 (m, 2H), 7.08 – 7.04 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.3, 142.4, 140.1, 133.4, 130.5, 130.2, 129.8, 128.5, 127.9, 124.6, 122.5, 115.1, 55.9; IR v: 3058, 2952, 2845, 1579, 1492, 1474, 1437, 1265, 1215, 1089, 964, 831, 737, 685, 555 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{17}NO_2S_2$ Na [M + Na]$^+$ 378.0593, found 378.0614.

***S*-(4-methylphenyl)-*S*-(4-nitrophenyl)-N-phenylthiosulfoximine (4da):** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 – 8.60 (m, 1H), 8.49 – 8.47 (m, 1H), 8.42 – 8.38 (m, 1H), 8.00 – 7.97 (m, 2H), 7.93 – 7.86 (m, 1H), 7.48 – 7.47 (m, 2H), 7.35 – 7.26 (m, 4H), 7.13 – 7.07 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.6, 145.8, 141.9, 135.4, 134.5, 132.3, 131.0, 129.1, 128.7, 125.5, 123.3,123.2, 21.5; IR v: 3065, 2923, 2852, 1579, 1529, 1475, 1438, 1347, 1220, 1091, 1002, 973, 874, 810, 731, 689, 672, 574, 540, 469 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{16}N_2O_3S_2Na$ [M + Na]$^+$ 407.0495, found 407.0508.

***S*-phenyl-*S*-(4-acetylphenyl)-*N*-phenylthiosulfoximine (4ea):** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 – 8.13 (m, 4H), 8.07– 8.06 (m, 2H), 7.76 – 7.62 (m, 3H), 7.36 – 7.26 (m, 4H), 7.13 – 7.05 (m, 1H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.3, 143.1, 141.8, 140.3, 138.7, 134.2, 123.0, 129.4, 128.6, 128.38, 124.8, 122.7, 27.1; IR v: 3059, 2962, 2923, 2855, 1688, 1579, 1475, 1445, 1438, 1394, 1257, 1216, 1090, 964, 733, 684, 591, 507 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{17}NO_2S_2$ Na [M + Na]$^+$ 390.0593, found 390.0601.

***S*-phenyl-*S*-(1,1'-biphenyl)-*N*-phenylthiosulfoximine (4fa):** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 – 8.05 (m, 4H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.63 (m, 5H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.3, 142.2, 139.4, 138.2, 138.0, 133.8, 129.9, 129.2, 128.9, 128.8, 128.6, 128.2, 128.0, 127.2, 124.7, 122.6; IR v: 3058, 2923, 2855, 1579, 1475, 1444, 1213, 1089, 967, 734, 685, 581 cm^{-1}; HRMS (ESI): calcd for $C_{24}H_{19}NOS_2$ Na [M + Na]$^+$ 424.0800, found 424.0793.

***S, S*-di(4-chlorophenyl)-*N*-phenylthiosulfoximine (4ga):** White solid, m.p 114-116 ^{o}C (Lit.[14] 120-122 ^{o}C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 7.6 Hz, 4H), 7.72 (d, *J* = 7.6 Hz, 4H), 7.33 – 7.27 (m, 4H), 7.10 (t, *J* = 6.5 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 141.5, 139.2, 137.7, 130.2, 130.0, 128.6, 124.9, 122.7; IR v: 3062, 3049, 1572, 1473, 1393, 1219, 1083, 962, 824, 761, 737, 688, 617, 566, 497, 447 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{13}Cl_2NOS_2Na$ [M + Na]$^+$ 415.9708, found 415.9741.

***S*-phenyl-*S*-(3,5-dicyanphenyl-*N*-phenylthiosulfoximine (4ha):** Yellow solid, m.p 122-124 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 7.4 Hz, 2H), 7.99 – 7.98(m, 3H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.11 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.8, 141.3, 137.9, 135.5, 134.5, 133.5, 130.0, 128.7, 126.7, 125.1, 123.0; IR v: 3064, 2962, 1578, 1564, 1474, 1444, 1226, 1145, 1089, 1006, 980, 802, 734, 660, 582, 565, 486 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{13}Cl_2NOS_2$ Na [M + Na]$^+$ 415.9708, found 415.9719.

***S*-phenyl-*S*-(3-cyanphenyl)-*N*-phenylthiosulfoximine (4ia):** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.31 – 8.29 (m, 1H), 8.17 – 8.11 (m, 3H), 7.82 – 7.66 (m, 4H), 7.32 – 7.29 (m, 4H), 7.11 – 7.09 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.5, 140.8, 138.2, 137.3, 134.3, 132.7, 132.0, 131.2, 130.0, 128.6(d, *J* = 3.5 Hz), 125.0, 122.9, 117.2, 113.1; IR v: 3062, 2923, 2233, 1579, 1473, 1445, 1219, 1086, 972, 734, 684, 580, 552, 524 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{14}N_2OS_2$ Na [M + Na]$^+$ 373.0440, found 373.0448.

***S*-phenyl-*S*-(3-nitrophenyl)-*N*-phenylthiosulfoximine (4ja):** Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 2H), 7.91 (t, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.2, 141.3, 141.1, 138.0, 134.4, 134.2, 131.9, 130.1, 128.6(d, *J* = 7.5Hz), 125.1, 122.9(d, *J* = 7.5Hz); IR v: 3069, 2923, 2874, 1601, 1579, 1529, 1475, 1445, 1348, 1219, 1089, 1065, 972, 874, 732,

683, 577, 540, 469 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{14}N_2O_3S_2$ Na [M + Na]$^+$ 393.0338, found 393.0344.

***S*-phenyl-*S*-(3- trifluoromethyl)-*N*-phenylthiosulfoximine (4ka)：** Yellow oil;^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, *J* = 7.9 Hz, 1H), 8.24 (s, 1H), 8.19 – 8.02 (m, 3H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.10 (t, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.5, 140.8, 138.3, 134.3, 132.5, 131.5, 130.6(d, *J* = 3.3 Hz), 130.3(d, *J* = 32.9Hz), 130.1(q, *J* = 34.8Hz), 130.0, 128.6(d, *J* = 11.1 Hz), 124.9, 124.5 (d, *J* = 4.17 Hz), 122.8, 121.8; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.43; IR v: 3063, 2962, 2326, 1580, 1476, 1446, 1323, 1129, 1096, 1006, 974 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{14}F_3NOS_2$ Na [M + Na]$^+$ 416.0361, found 416.0370.

***S*-phenyl-*S*- pyridyl-*N*-phenylthiosulfoximine (4la)：** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 – 9.16 (m, 1H), 8.87 – 8.86 (m, 1H), 8.40– 8.39 (m, 1H), 8.14 – 8.08 (m, 2H), 7.74 – 7.67 (m, 4H), 7.36 – 7.27 (m, 4H), 7.14 – 7.07 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.1, 148.6, 141.5, 138.5, 136.2 (d, *J*=32.2Hz), 134.2, 130.0, 128.6, 128.4, 124.8 (d, *J*=22.1 Hz), 122.7; IR v: 3055, 3001, 2965, 1577, 1565, 1475, 1443, 1211, 1088, 971, 735, 679, 578, 541, 470 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{14}N_2OS_2$ Na [M + Na]$^+$ 349.0440, found 349.0446.

***S*-methyl-*S*-phenyl-*N*-phenylthiosulfoximine (4ma)：** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 – 7.88 (m, 2H), 7.78 – 7.70 (m, 1H), 7.69 – 7.61 (m, 2H), 7.30 – 7.24 (m, 4H), 7.00 – 7.03 (m, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.7, 138.7, 133.7, 129.5, 128.4, 128.1, 124.4, 122.3, 42.8; IR v: 3020, 2997, 2916, 1468, 1444, 1220, 1082, 974, 953, 806, 787, 684, 525, 505, 486 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{13}NOS_2$ Na [M + Na]$^+$ 286.0331, found 286.0332.

***S*-cyclohexyl-*S*-phenyl-N-phenylthiosulfoximine (4na)：** White solid, m.p 104-108 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73– 7.67(m, 3), 7.60 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 4.2 Hz, 4H), 6.98 (m, 1H), 3.3 (t, *J* = 10.4 Hz, 1H), 2.23 (d, *J* = 11.9 Hz, 1H), 1.78– 1.66 (m, 3H), 1.53 (d, *J* = 12.7 Hz, 1H), 1.42 – 1.12 (m, 4H), 1.06 – 1.00 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.2, 135.3, 133.8, 129.5, 129.4, 128.3, 124.2, 122.1, 62.4, 26.0, 25.1, 24.7, 24.4, 24.3; IR v:3060, 2926, 2851, 1728, 1578,1475, 1438, 1259, 1219, 1191, 1082, 1021, 960, 894, 853 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}NOS_2$ Na [M + Na]$^+$ 354.0957, found 354.0968.

***S*-*n*-octyl-*S*-phenyl-*N*-phenylthiosulfoximine(4oa) ：** Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.28– 7.24 (m, 4H), 7.05 (t, *J* = 6.7 Hz, 1H), 3.67– 3.56 (m, 2H), 1.67 – 1.66 (m, 1H), 1.52 – 1.51 (m, 1H), 1.32 – 1.17 (m, 10 H), 0.84 – 0.81 (m, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.2, 135.3, 133.8, 129.5, 129.4, 128.3, 124.2, 122.1, 62.4, 26.0, 25.1, 24.7, 24.4, 24.3; IR v: 3058, 2924, 2854, 1581, 1476, 1445, 1208, 1090, 974 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{27}NOS_2$ Na [M + Na]$^+$ 384.1426, found 384.1429.

***N*-phenylthiotetrahydrothiophene sulfoximine (4pa) ：** Yellow solid, m.p 82-85 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.29 – 7.28 (m, 4H), 7.08 – 7.07 (m, 1H), 3.42 – 3.38 (m, 2H), 3.23 – 3.19(m, 2H), 2.20 – 2.19 (m, 2H), 2.11 – 2.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.9, 128.6, 124.4, 121.9, 51.5, 23.5; IR v: 2998, 2961, 2937, 1580, 1475, 1438, 1260, 1193, 1085, 953, 903 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{13}NOS_2$ Na [M + Na]$^+$ 250.0331, found 250.0327.

***S, S*- dimethyl-N-phenylthiosulfoximine (4qa)：** Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.27 – 7.26 (m, 4H), 7.09 – 7.02 (m, 1H), 3.23 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.6, 128.5, 124.2, 121.9, 40.2; IR v: 3010, 2922, 1579, 1475, 1437, 1199, 1018, 961, 736, 689, 489 cm^{-1}; HRMS (ESI): calcd for $C_8H_{11}NOS_2$ Na [M + Na]$^+$ 224.0174, found 224.0175.

***S, S*-di-*n*-octyl-N-phenylthiosulfoximine (4ra)：** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (d, *J* = 4.2 Hz, 4H), 7.07 – 7.02 (m, 1H), 3.31 – 3.29 (m, 4H), 1.73 – 1.67 (m, 4H), 1.37 – 1.34 (m, 4H), 1.26 – 1.22 (m, 16H), 0.87– 0.84 (m, 6H);^{13}C NMR (100 MHz, DMSO-d_6) δ 143.6, 128.3, 124.1, 122.0, 50.3, 31.2, 28.4, 27.7, 22.3, 22.1, 13.9; IR v: 2924, 2854, 1728, 1581, 1476, 1466, 1188, 1055, 1026, 1007, 818 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{39}NOS_2$ Na [M + Na]$^+$ 421.2399, found 421.2391.

***S, S*-diphenyl-*N*-(4-fluorophenylthio)sulfoximine (4ab):** Yellow solid, m.p 117-120 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 – 8.00 (m, 4H), 7.70 (t, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 4H), 7.39 – 7.35 (m, 2H), 7.17–7.12 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.1(d, *J* = 240.3 Hz), 139.2, 133.7, 129.8, 128.1, 125.2(d, *J* =7.8 Hz), 115.6, 115.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.20; IR v: 3059, 2962, 2322, 1581, 1487, 1445, 1259, 1086, 1016, 963, 828 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{14}FNOS_2$Na [M + Na]$^+$ 366.0393, found 366.0407.

***S, S*-diphenyl-*N*-(4- chlorophenylthio)sulfoximine (4ac).** Yellow solid, m.p 125-127 ^{o}C (Lit.[14] 121-123 ^{o}C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 7.9 Hz, 4H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 4H), 7.35 – 7.34 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.4, 139.1, 133.9, 129.9, 128.9, 128.4, 128.1, 124.2; IR v: 3062, 1469, 1445, 1386, 1221, 1082, 954, 811, 729, 682, 575, 531, 482 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{14}ClNOS_2$ Na [M + Na]$^+$ 382.0098, found 382.0106.

***S, S*-diphenyl-*N*-(4-bromophenylthio)sulfoximine (4ad)：** Yellow solid, m.p 119-121 ^{o}C (Lit.[14] 122-123 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.02 (d, *J* = 7.7 Hz, 4H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 4H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.0, 139.1, 133.9, 131.3, 129.9, 128.2, 124.5, 117.1; IR v: 3084, 3062, 1466, 1445, 1218, 1087, 1076, 955, 808, 732, 681, 576, 539, 473 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{14}BrNOS_2$ Na [M + Na]$^+$ 425.9592, found 425.9595.

***S, S*-diphenyl-*N*-(2-bromophenylthio)sulfoximine (4ae)：** Yellow solid, m.p 120-123 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, *J* = 7.5 Hz, 4H), 7.75 – 7.62 (m, 7H), 7.48 – 7.46 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 142.6, 139.2, 133.9, 131.7, 129.9, 128.1, 127.8, 125.8, 124.1, 114.9; IR v: 3052, 2921, 2852, 1439, 1424, 1219, 1088, 956, 743, 724, 681, 575, 540, 490 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{14}BrNOS_2$ Na [M + Na]$^+$ 425.9592, found 425.9597.

***S, S*-diphenyl-*N*-(4-cyanphenylthio)sulfoximine (4af)：** White solid, m.p 134-137 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, *J* = 7.5 Hz, 4H), 7.75 – 7.64 (m, 8H), 7.50 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.3 , 138.9, 134.1, 132.1, 130.0, 128.2, 122.3, 119.2, 106.3; IR v: 3075, 3055, 2226, 1590, 1445, 1215, 1080, 971, 729, 683, 576, 536, 458 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{14}N_2OS_2$Na [M + Na]$^+$ 373.0440, found 373.0445.

***S, S*-diphenyl-N- naphthylthiosulfoximine (4ag)：** Yellow solid, m.p146-149 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, *J* = 7.8 Hz, 4H), 7.82 (t, *J* = 8.4 Hz, 4H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.66 –7.63 (m, 4H), 7.50 – 7.37 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.0, 139.3, 133.8, 133.3, 131.0, 129.9, 128.3, 128.0, 127.7, 126.8, 126.7, 125.1, 121.7, 119.7; IR v: 3065, 3046, 1618, 1587, 1446, 1211, 1084, 967, 809, 729, 680, 587, 577, 470 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{14}N_2OS_2$Na [M + Na]$^+$ 398.0644, found 398.0653.

***S, S*-diphenyl-*N*-(2- tertiary butylphenylthio)sulfoximine (4ah)：** Yellow solid, m.p 134-136 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, *J* = 7.2 Hz, 4H), 7.70 (t, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 4H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 147.5, 139.4, 138.5, 133.6, 129.7, 128.1, 125.4, 123.1, 34.0, 31.1; IR v: 2953, 2897, 2865, 1495, 1446, 1214, 1086, 956, 821, 729, 684, 640, 575 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{23}NOS_2$Na [M+Na]$^+$ 404.1113, found 404.1133.

***S, S*-diphenyl-*N*-(4-methylphenylthio)sulfoximine (4ai)：** Yellow solid, m.p 105-107 °C (Lit.[14] 110-112 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.8 Hz, 4H), 7.69 (t, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 4H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.4, 138.4, 134.1, 133.7, 129.8, 129.2, 128.1, 123.3, 20.5; IR v: 3068, 3054, 1489, 1443, 1207, 1086, 967, 805, 736, 680, 575, 537, 487 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{17}NOS_2Na$ [M + Na]$^+$ 362.0644, found 362.0647.

***S, S*-diphenyl-*N*-(4- methoxylphenylthio)sulfoximine (4aj)：** Yellow solid, m.p 96-98 °C (Lit.[14] yellow oil); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, *J* = 7.3 Hz, 4H), 7.69 (t, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 4H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 157.8, 139.5, 133.6, 131.8, 129.7, 128.1, 127.1, 114.4, 55.2; IR v: 3062, 2926, 2836, 1588, 1490, 1445, 1231, 1090, 1024, 966, 719, 684, 565, 539 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{17}NOS_2Na$ [M + Na]$^+$ 378.0593, found 378.0596.

***S, S*-diphenyl-*N*- pyridylthiosulfoximine (4ak)：** Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 – 8.27 (m, 2H), 8.05 (d, *J* = 7.6 Hz, 4H), 7.73 (t, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 4H), 7.33 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.9, 150.0, 148.8, 145.7, 138.8, 134.1, 130.0, 128.2, 120.0, 116.6; IR v: 3065, 3036, 1566, 1445, 1404, 1212, 1087, 965, 803, 725, 683, 587, 577,490 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{14}N_2OS_2Na$ [M + Na]$^+$ 349.0440, found 349.0534.

***S, S*-diphenyl-*N*- (2-furfuryl mercaptanthio)sulfoximine (4al)：** Yellow solid, m.p 70-73 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, *J* = 7.2 Hz, 4H), 7.69 – 7.57 (m, 7H), 6.37 – 6.38 (m, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 4.03 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 150.1, 142.4, 139.6, 133.4, 129.6, 128.2, 110.7, 108.4, 37.0; IR v: 3060, 2958, 2916, 1474, 1500, 1445, 1213, 1088, 966, 725, 683, 573, 539 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{15}NO_2S_2Na$ [M + Na]$^+$ 352.0436, found 352.0444.

***S, S*-diphenyl-*N*- benzylthiosulfoximine (4am)：** White solid, m.p 109-111 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.91 (d, *J* = 7.7 Hz, 4H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 4H), 7.29 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 4.00 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.7, 136.8, 133.4, 129.6, 129.3, 128.2, 126.9, 44.7; IR v: 3062, 2936, 1493, 1453, 1444, 1206, 1085, 966, 731, 688, 681, 576, 542, 453 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{17}NOS_2Na$ [M + Na]$^+$ 362.0644, found 362.0656.

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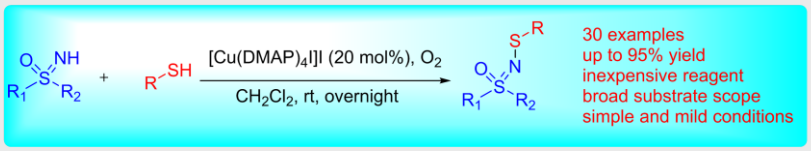

We developed a one-pot cascade N-S bond formation reaction of free NH-sulfoximines with thiophenols to produce diverse N-Sulfenyl Sulfoximines with moderate to excellent yields. Different with previous works, this reaction provides a straightforward, practical way to prepare N-sulfenyl sulfoximine derivatives.

Key Topic*

*Yao Peng, Yan Lin, Ruifang Nie, Yang Zheng, Yanzhao Liu, Li Guo, * and Yong Wu **

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A One-Pot Cascade Reaction Combining NH-sulfoximines with thiophenols under mild condition.