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Copper-Promoted Desulfitative *N*-Arylation of Sulfonamides and Sulfoximines with Sodium Arylsulfinates

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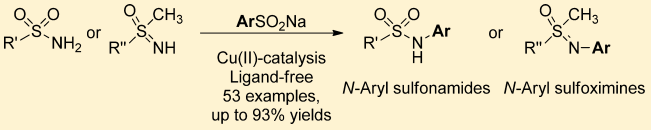
Supporting Information

ABSTRACT: A general and direct *N*-arylation of sulfonamides and NH-sulfoximines by sodium arylsulfinates through a desulfitative pathway was herein demonstrated. The reaction proceeded with catalytic loadings of Cu(II)-catalysts without any external ligands. And the novel arylation protocol featured for high efficiency (up to 93% yields) and good substituent tolerance (up to 53 examples). Moreover, a plausible reaction mechanism was also discussed.

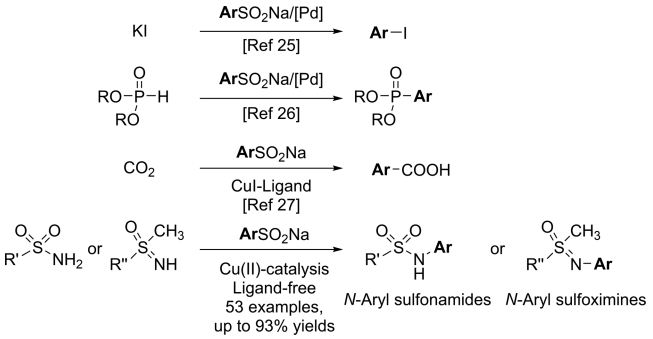


INTRODUCTION

Direct *N*-arylation of sulfonamides and sulfoximines have been widely embarked to enrich the diversity of the significant compounds. Typically, straightforward methods toward *N*-aryl sulfonamides were successfully achieved by using aryl halides,[1] aryl boronic acids,[2] aryl siloxanes,[3] aryl nonaflates,[4] even cyclohexanones[5] and so on[6] under different catalytic systems. While direct arylation of NH-sulfoximines was realized with various aryl donors like aryl halides,[7] aryl triflates,[8] aryl boronic acids,[9] aryl siloxanes,[10] diaryl iodonium salts,[11] arynes,[12] and etc.[13] Recently, based on extensive literature exploration, applications of sodium arylsulfinates, which were frequently used for sulfonylation[14] and sulfuration[15] reactions, have been readily utilized as an efficient aryl reagents through a desulfitative pathway. The methodology offered a significant option for arylation due to the advantages, such as stability and easy-handiness for workup.

Thus far, desulfitative protocols by sodium arylsulfinates have been broadly applied on benzyl chlorides,[16] aldehydes,[17] aryl triflates,[18] polyfluoroarenes,[19] olefins,[20] alkynes,[21] and other heteroaryl compounds,[22] such as thiophenol, indoles, azoles, caffeines, coumarins, and even CuCN[23] for the constructions of C−C bonds.[24] Also, formation of C−I[25] and C−P bonds[26] were well-documented through the desulfitative pathway recently. Generally, expensive palladium catalysts and occasionally copper or silver cocatalysts were crucial to the desulfitative reactions. Thus, for the environmentally benignity, inexpensive transition metal-catalysis was sought for the significant transformation. Inspired by Cheng's description, the desulfitative protocol was realized in the liganded Cu(I)-mediated system for the formation of carboxyl acids.[27] Herein, we preferred to disclose a practical and general method for arylation of sulfonamides and sulfoximines with sodium arylsulfinates by assistance of an inexpensive copper salt without participation of any cocatalysts or external ligands (Scheme 1).

Scheme 1. Desulfitative Arylation Protocols



RESULTS AND DISCUSSION

First, phenyl sulfonamide (**1a**) and sodium phenylsulfinate (**2a**) were chosen as the model substrates for optimization of the conditions, which were summarized in Table 1. To our delight, copper diacetate (50 mol%) rendered the arylation protocol happen with assistance of K_2CO_3 (2.0 equiv) in dry DMSO (dimethyl sulfoxide, 2.0 mL) under air atmosphere (1 atm) at 120 °C for 12 h (entry 1). And the desired *N*,*S*-diphenyl sulfonamide (**3aa**) was isolated in 35% yield. However, $Cu(OTf)_2$, $Cu(TFA)_2$, and CuO failed to make the reaction take place (entries 2−4), while copper halides offered better performance, such as CuI, CuBr, CuCl, $CuBr_2$, and $CuCl_2$, provided the desired product **3aa** in yields from 42% to 76% (entries 5−9). $CuBr_2$ gave a slightly lower yield than $CuCl_2$ did

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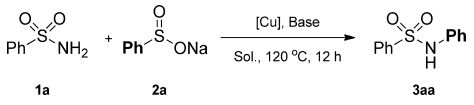
Table 1. Selected Results for Optimization of Conditions[a]



1a 2a 3aa

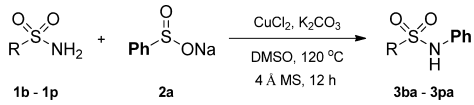
entry	[Cu]	base	sol.	yields (%)[b]
1	$Cu(OAc)_2$	K_2CO_3	DMSO	35%
2	$Cu(OTf)_2$	K_2CO_3	DMSO	trace
3	$Cu(TFA)_2$	K_2CO_3	DMSO	n.d.[c]
4	CuO	K_2CO_3	DMSO	n.d.
5	CuI	K_2CO_3	DMSO	trace
6	CuBr	K_2CO_3	DMSO	42%
7	CuCl	K_2CO_3	DMSO	50%
8	$CuBr_2$	K_2CO_3	DMSO	72%
9	$CuCl_2$	K_2CO_3	DMSO	76%
10[d]	$CuCl_2$	K_2CO_3	DMSO	82 (81)[e]
11	$CuCl_2$	Li_2CO_3	DMSO	trace
12	$CuCl_2$	Na_2CO_3	DMSO	trace
13	$CuCl_2$	$NaHCO_3$	DMSO	52%
14	$CuCl_2$	Cs_2CO_3	DMSO	trace
15	$CuCl_2$	KOAc	DMSO	58%
16	$CuCl_2$	K_3PO_4	DMSO	n.d.
17	$CuCl_2$	KO*t*Bu	DMSO	n.d.
18	$CuCl_2$	K_2HPO_4	DMSO	38%
19	$CuCl_2$	KH_2PO_4	DMSO	20%
20	$CuCl_2$	NEt_3	DMSO	n.d.
21	$CuCl_2$	pyridine	DMSO	n.d.
22	$CuCl_2$	K_2CO_3	C_2H_5OH	n.d.
23	$CuCl_2$	K_2CO_3	DCE	n.d.
24	$CuCl_2$	K_2CO_3	1,4-dioxane	n.d.
25	$CuCl_2$	K_2CO_3	H_2O	n.d.
26	$CuCl_2$	K_2CO_3	DMF	16%
27	$CuCl_2$	K_2CO_3	DMA	22%
28	$CuCl_2$	K_2CO_3	DMSO	62%[f] (48%)[g]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Cu] (0.1 mmol, 50 mol%), Base (0.4 mmol) under air in sol. (2.0 mL) at 120 °C for 12 h. [b]Isolated yields. [c]For not detected. [d]Powdered 4 Å molecular sieves (200 wt%) was added. [e]The yield in the parentheses was obtained at 0.5 mmol (**1a**) scale. [f]The reaction was conducted at 100 °C. [g]The reaction was conducted at 140 °C.

due to the formation of unknown impurities. Surprisingly, the addition of powdered molecular sieves (4 Å, 200 wt%) increased the yield of *N*-phenylated sulfonamide **3aa** to 82% (81% for 0.5 mmol scale for entry 10). Successively, different bases were also screened in the system. Inorganic bases, like Li_2CO_3, Na_2CO_3, Cs_2CO_3, KOAc, K_3PO_4, KO*t*Bu, gave inferior efficiency of the transformation while other bases, such as $NaHCO_3$, K_2HPO_4, and KH_2PO_4, offered the desired product **3aa** in low yields, up to 58% (entries 11−19). Organic bases, such as triethylamine, pyridine, were proven useless to the transformation for no reaction was detected (entries 20 and 21). What's more, the effects of solvents were also tested. Alcoholic solvent (ethanol for entry 22), chlorinated solvent (dichloro ethane, DCE for entry 23), and 1,4-dioxane (entry 24) and water (entry 25) did not make the reaction occur but the participation of DMF (*N*,*N*-dimethylformamide for entry 26) and DMA (*N*,*N*-dimethyl acetylamide for entry 27) gave **3aa** in 16% and 22% yields, respectively. The efficiency of the transformation was depressed at either elevated (140 °C) or decreased (100 °C) reaction temperature (entry 28).

With the optimal conditions in hand, the scope and limitations of the substrates were evaluated (Table 2). *p*-Tolyl

Table 2. Substrate Scope of Sulfonamides[a]



1b - 1p 2a 3ba - 3pa

entry	R	3	yield (%)[b]
1	4-$CH_3C_6H_4$	**3ba**	74
2	2-$CH_3C_6H_4$	**3ca**	71
3	4-$CH_3OC_6H_4$	**3da**	73
4	4-*n*-BuC_6H_4	**3ea**	76
5	4-FC_6H_4	**3fa**	79
6	4-ClC_6H_4	**3ga**	85
7	2-ClC_6H_4	**3ha**	65
8	4-BrC_6H_4	**3ia**	88
9	4-$CF_3C_6H_4$	**3ja**	81
10	4-$NO_2C_6H_4$	**3ka**	69
11	2-Naphthyl	**3la**	78
12	2-Thiophenyl	**3ma**	75
13	3-Pyridinyl	**3na**	68
14	CH_3	**3oa**	64
15	CH_3CH_2	**3pa**	62

[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), $CuCl_2$ (0.25 mmol, 50 mol%), K_2CO_3 (2.0 mmol), 4 Å MS (powdered, 200 mg) in dry DMSO (3.0 mL) at 120 °C for 12 h. [b]Isolated yields.

sulfonamide (**1b**) reacted with sodium phenylsulfinate (**2a**) smoothly in the Cu(II)-mediated system, providing the corresponding *N*-phenylated product **3ba** in 74% yield (entry 1). While *o*-tolyl sulfonamide (**1c**) coupled with **2a** readily, and *N*-arylated sulfonamide **3ca** was furnished in a slightly lower yield (71% for entry 2). Electron-sufficient aryl sulfonamides, such as 4-methoxyphenyl sulfonamide **1d** and 4-*n*-butylphenyl sulfonamide **1e**, were successfully arylated by **2a** in medium yields (entries 3 and 4). To our delight, halo groups were also compatible in the system. 4-Fluorophenyl sulfonamide (**1f**), 4-chorophenyl sulfonamide (**1g**), 2-chorophenyl sulfonamide (**1h**), 4-bromophenyl sulfonamide (**1i**) coupled with sodium phenylsulfinate (**2a**) and functionalized *N*-phenyl sulfonamides **3fa**−**3ia** were allowed to form in yields from 65−88% (entries 5−8). The position of the halo group on phenyl group changed the yield of the transformation significantly for 4-chlorophenyl sulfonamide (**1g**) offering the desired products in 85% yield (entry 6), while *N*-phenyl 2-chlorophenyl sulfonamide (**3ha**) was synthesized in only 65% yield (entry 7). Other electon-withdrawing groups, such as trifluoromethyl (**1j**) and nitro (**1k**) substituted phenyl sulfonamides, furnished the desired *N*-arylated products in 81% and 69% yields, respectively (entries 9 and 10). It was pleasing to mention that polyaryl and heteroaryl substituted sulfonamides were also phenylated in the copper catalysis. For example, 2-naphthyl (**1l**), 2-thiophenyl (**1m**), and 3-pyridinyl (**1n**) sulfonamides reacted with **2a**, offering the desired *N*-aryl sulfonamides **3la**−**3na** in a range of 68 to 78% yields (entries 11−13). Beyond our expectations, aliphatic sulfonamides, such as methyl sulfonamide (**1o**) and ethyl sulfonamide (**1p**), underwent the *N*-arylation protocol, leading to the formation of **3oa** and **3pa** in acceptable yields (entries 14 and 15).

In the same manner, the limitations and scope on sodium arylsulfinates were also checked in the reaction, as summarized in Table 3. The incorporation of the methyl group on *para*- or *ortho*- positions of the sodium phenylsulfinates did not exhibit significant influence over the efficiency of the arylation

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Table 3. Substrate Scope of Sodium Arylsulfinates[a]

1a 2a-2t 3ab - 3ar

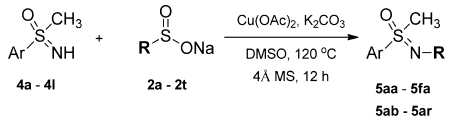
entry	R (2)	3	yield (%)[b]
1	2-$CH_3C_6H_4$ (**2b**)	**3ab**	70
2	4-$CH_3C_6H_4$ (**2c**)	**3ac**	73
3	4-*t*BuC_6H_4 (**2d**)	**3ad**	n.d.[c]
4	4-$CH_3OC_6H_4$ (**2e**)	**3ae**	72[d]
5	4-FC_6H_4 (**2f**)	**3af**	78
6	2-ClC_6H_4 (**2g**)	**3ag**	72
7	3-ClC_6H_4 (**2h**)	**3ah**	70
8	4-ClC_6H_4 (**2i**)	**3ai**	82
9	2-BrC_6H_4 (**2j**)	**3aj**	73
10	3-BrC_6H_4 (**2k**)	**3ak**	70
11	4-BrC_6H_4 (**2l**)	**3al**	81
12	4-IC_6H_4 (**2m**)	**3am**	trace[e]
13	4-$NO_2C_6H_4$ (**2n**)	**3an**	n.d.[c]
14	4-CNC_6H_4 (**2o**)	**3ao**	76
15	4-$CF_3C_6H_4$ (**2p**)	**3ap**	77
16	4-$CH_3C(O)C_6H_4$ (**2q**)	**3aq**	82
17	2-Naphthyl (**2r**)	**3ar**	75
18	2-thiophenyl (**2s**)	**3as**	n.d.[c]
19	CH_3CH_2 (**2t**)	**3at**	n.d.[c]

[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), $CuCl_2$ (0.25 mmol, 50 mol%), K_2CO_3 (2.0 mmol), 4 Å MS (powdered, 200 wt%) in dry DMSO (3.0 mL) at 120 °C for 12 h. [b]Isolated yields. [c]For not detected. [d]$Cu(OAc)_2$ (50 mol%) was used instead of $CuCl_2$ (50 mol %). [e]Detected by GC-MS.

protocol, for *N*-(*o*-tolyl) (**3ab**) and *N*-(*p*-tolyl) phenylsulfonamide (**3ac**) were smoothly generated in similar yields, 70% and 73%, separately (entries 1 and 2). However, sodium (4-*tert*-butylphenyl) sulfinate (**2d**) failed to couple with **1a**, for no product (**3ad**) was detected after 12 h (entry 3). Similarly, *N*-(4-methoxyphenyl)-*S*-phenyl sulfonamide (**3ae**) was successfully furnished in 72% yields with assistance of $Cu(OAc)_2$ (50 mol%) other than $CuCl_2$ (50 mol%) (entry 4). Successively, the trends over the electron-withdrawing aryl-decorated substrates were also observed in the system. For example, sodium (4-fluorophenyl)sulfinate (**2f**), sodium (2-chlorophenyl)sulfinate (**2g**), sodium (3-chlorophenyl)sulfinate (**2h**), sodium (4-chlorophenyl)sulfinate (**2i**), sodium (2-bromophenyl)sulfinate (**2j**), sodium (3-bromophenyl)sulfinate (**2k**), and sodium (4-bromophenyl)sulfinate (**2l**) reacted with **1a** successfully and exhibited good efficiency in the arylation system except sodium (4-iodophenyl)sulfinate (**2m**). The corresponding *N*-arylated sulfonamides **3af**–**3al** were obtained smoothly in yields ranging from 70 to 82% (entries 5–11) while only trace *N*-(4-iodophenyl)-*S*-phenyl sulfonamide (**3am**) was observed by GC-MS detection (entry 12). Sodium (4-nitrophenyl)sulfinate (**2n**) was found ineffective for the arylation protocol for no reaction was detected after 12 h (entry 13). But other electron-withdrawing aryl groups, such as 4-cyanophenyl, 4-trifluoromethylphenyl 4-acetylphenyl fused sodium sulfinates, reacted with **1a** readily and offered the desired products **3ao**–**3aq** in 76–82% yields, respectively (entries 14–16). Moreover, *N*-2-naphthylation of **1a** was also achieved from the copper-assisted transformation and *N*-(2-naphthyl)-*S*-phenyl sulfonamide (**3ar**) was provided in 75% yield (entry 17). But disappointingly, *N*-2-thiophenylation of **1a** failed in the system for no reaction was detected after 12 h (entry 18) and the same result was detected on sodium ethyl sulfinate (**2t** for entry 19).

Inspired by the good tolerance on substituted aryl sulfonamides, the scope of the arylation protocol was further extended onto NH-sulfoximines, as summarized in Table 4. Use

Table 4. Substrate Scope for Arylation of Sulfoximines[a]



4a - 4l 2a - 2t 5aa - 5fa 5ab - 5ar

entry	Ar (4)	R (2)	5	yield (%)[b]
1	C_6H_5 (**4a**)	C_6H_5 (**2a**)	**5aa**	85
2	2-$CH_3C_6H_4$ (**4b**)	C_6H_5 (**2a**)	**5ba**	76
3	3-$CH_3C_6H_4$ (**4c**)	C_6H_5 (**2a**)	**5ca**	80
4	4-$CH_3C_6H_4$ (**4d**)	C_6H_5 (**2a**)	**5da**	82
5	4-$CH_3OC_6H_4$ (**4e**)	C_6H_5 (**2a**)	**5ea**	80
6	4-ClC_6H_4 (**4f**)	C_6H_5 (**2a**)	**5fa**	90
7	C_6H_5 (**4a**)	2-$CH_3C_6H_4$ (**2b**)	**5ab**	77
8	C_6H_5 (**4a**)	4-$CH_3C_6H_4$ (**2c**)	**5ac**	82
9	C_6H_5 (**4a**)	4-*t*BuC_6H_4 (**2d**)	**5ad**	78
10	C_6H_5 (**4a**)	4-$CH_3OC_6H_4$ (**2e**)	**5ae**	76
11	C_6H_5 (**4a**)	4-FC_6H_4 (**2f**)	**5af**	91
12	C_6H_5 (**4a**)	2-ClC_6H_4 (**2g**)	**5ag**	62
13	C_6H_5 (**4a**)	3-ClC_6H_4 (**2h**)	**5ah**	80
14	C_6H_5 (**4a**)	4-ClC_6H_4 (**2i**)	**5ai**	93
15	C_6H_5 (**4a**)	2-BrC_6H_4 (**2j**)	**5aj**	74
16	C_6H_5 (**4a**)	3-BrC_6H_4 (**2k**)	**5ak**	82
17	C_6H_5 (**4a**)	4-BrC_6H_4 (**2l**)	**5al**	89
18	C_6H_5 (**4a**)	4-IC_6H_4 (**2m**)	**5am**	85
19	C_6H_5 (**4a**)	4-$NO_2C_6H_4$ (**2n**)	**5an**	74
20	C_6H_5 (**4a**)	4-CNC_6H_4 (**2o**)	**5ao**	88
21	C_6H_5 (**4a**)	4-$CF_3C_6H_4$ (**2p**)	**5ap**	83
22	C_6H_5 (**4a**)	4-$CH_3C(O)C_6H_4$ (**2q**)	**5aq**	67
23	C_6H_5 (**4a**)	2-naphthyl (**2r**)	**5ar**	79
24	C_6H_5 (**4a**)	2-thiophenyl (**2s**)	**5as**	trace[c]
25	C_6H_5 (**4a**)	CH_3CH_2 (**2t**)	**5at**	n.d.[d]

[a]Reaction conditions: **4** (0.5 mmol), **2** (1.0 mmol), $Cu(OAc)_2$ (0.1 mmol, 20 mol%), K_2CO_3 (2.0 mmol), 4 Å MS (powdered, 200 wt%) in dry DMSO (3.0 mL) at 120 °C for 12 h. [b]Isolated yields. [c]Detected by GC-MS. [d]For not detected.

of $Cu(OAc)_2$ (20 mol%), instead of $CuCl_2$ (50 mol%), made the reaction take place smoothly. Generally, NH-sulfoximines exhibited higher efficiency than sulfonamides probably due to the different fickleness of the N–H bonds.[28] Analogously, *N*,*S*-diphenyl-*S*-methyl sulfoximine (**5aa**) was favoringly provided in good yield, up to 85% (entry 1). *S*-2-methylphenyl (**4b**), *S*-3-methylphenyl (**4c**), and *S*-4-methylphenyl (**4d**) sulfoximines were readily arylated by sodium phenylsulfinate (**2a**) and the desired products **5ba**–**5da** were furnished in yields from 76 to 82% (entries 2–4). The compatibilities of electron-donating and electron-withdrawing substituents-fused NH-sulfoximines were checked, as illustrated by the formations of *N*-phenyl-*S*-(4-methoxyphenyl)-*S*-methyl sulfoximine (**5ea**) and *N*-phenyl-*S*-(4-chlorophenyl)-*S*-methyl sulfoximine (**5fa**) in 80% and 90% yields, respectively (entries 5 and 6). Moreover, the compatibilities of different substituents-decorated sodium sulfinates were also evaluated in the system. In the same manner, *N*-(*o*-tolyl) sulfoximine (**5ab**) and *N*-(*p*-tolyl) sulfoximine (**5ac**) were provided in 77 and 82% yields, separately (entries 7 and 8) while *N*-(4-*tert*butylphenyl)

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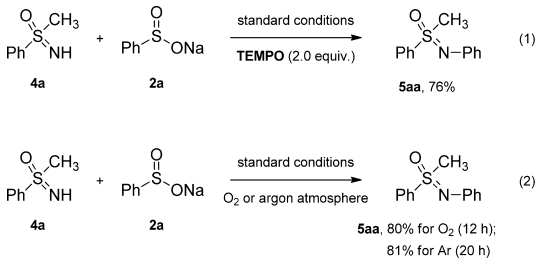
sulfoximine (**5ad**) and *N*-(4-methoxyphenyl) sulfoximine (**5ae**) were isolated in 78 and 76% yields (entries 9 and 10). It was worthy to be mentioned that halo groups were also well-tolerated in the transformation for *N*-(4-fluorophenyl)-(**5af**), *N*-(2-chlorophenyl)-(**5ag**), *N*-(3-chlorophenyl)-(**5ah**), *N*-(4-chlorophenyl)-(**5ai**), *N*-(2-bromophenyl)-(**5aj**), *N*-(3-bromophenyl)-(**5ak**), *N*-(4-bromophenyl)-(**5al**), and *N*-(4-iodophenyl)-(**5am**) sulfoximines were produced in yields of 62 to 93% range (entries 11−18). Successively, *N*-(4-nitrophenyl)-(**5an**), *N*-(4-cyanophenyl)-(**5ao**), *N*-(4-trifluoromethylphenyl)-(**5ap**), and *N*-(4-acetylphenyl)-(**5aq**) sulfoximines were favorably prepared in 67 to 88% yields (entries 19−22). Similarly, *N*-(2-naphthylation) was achieved in the system by using sodium (2-naphthyl) sulfinate (**2r**) in 79% yield (entry 23). However, 2-thiophenylation and ethylation of **4a** with sodium sulfinate failed in the system for trace product (**5as** by GC-MS detection) or even no reaction (**5at**) was observed after 12 h (entries 24 and 25).

Control reactions between NH-sulfoximine (**4a**) and sodium phenylsulfinate (**2a**) were carried out to take a deeper insight into the transformation, as shown in Scheme 2. The efficiency

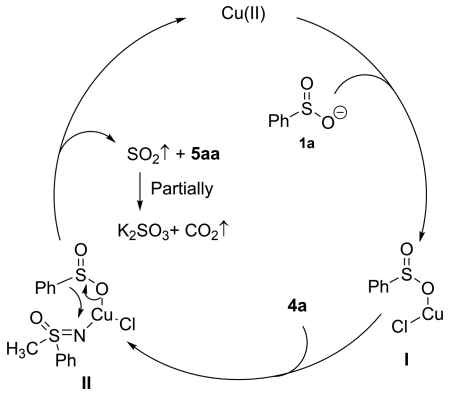
Scheme 2. Control Reactions



of the reaction was not affected by the addition of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl, 76% for Scheme 2, eq 1). The results indicated that the reaction might not proceed via radical particles. Then, the efficiency of the reaction under different inner atmosphere including O_2 and argon was also checked. And the yields of **5aa** obtained under different atmosphere were approximately same, 80 and 81%, respectively (Scheme 1, eq 2).

Based on the results of the control reactions and literature investigations,[16−28] the possible mechanism of the desulfitative reaction was proposed on the reaction between NH-sulfoximine (**4a**) and sodium sulfinate (**2a**) as shown in Scheme 3. First, Cu(II) coupled with sodium phenylsulfinate by

Scheme 3. Proposed Mechanism



anion exchange interaction, forming a new intermediate **I**. Then, NH-sulfoximine (**4a**) coordinated with Cu(II)-core of the intermediate **I**, affording another Cu(II)-centered intermediate **II**. Finally, *N*-phenyl sulfoximine **5aa** was formed, releasing a molecule of SO_2, which was partially basified with K_2CO_3. And Cu(II) entered another cycle of the reaction.

CONCLUSIONS

In summary, we have demonstrated a novel and practical protocol toward *N*-aryl sulfonamides and sulfoximines from sodium arylsulfinates. The transformation was achieved by a Cu(II)-mediated catalysis without participation of any ligands. The efficient and compatible protocol offers a promising avenue toward the molecules of great significance.

EXPERIMENTAL SECTION

General Information. All product mixtures were analyzed by thin layer chromatography glass-backed silica TLC plates with a fluorescent indicator from Branch of Qingdao Haiyang Chemical CO. Ltd. UV-active compounds were detected with a UV lamp (λ = 254 nm). For flash column chromatography, silica gel (200−300 mesh) was used as stationary phase and a mixture of petroleum and ethyl acetate was used as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 in deuterated chloroform at 25 °C with residue solvent peaks as internal standards (δ = 7.26 ppm for ^{1}H NMR and δ = 77.16 ppm for ^{13}C NMR). Chemical shifts δ are reported in ppm, and spin−spin coupling constants (J) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet) and some C−P couplings were ignored due to complexity. Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and high-resolution mass spectra (HRMS) were recorded on Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

General Procedure for the Arylation Reaction. A Schlenk tube (35 mL) equipped with a magnetic bar was loaded with the sulfonamide **1** or sulfoximine **4** (0.5 mmol), $CuCl_2$ (33.5 mg, 0.25 mmol) or $Cu(OAc)_2$ (18.1 mg, 0.1 mmol), and K_2CO_3 (2.0 equiv) in dry DMSO (3.0 mL), then sodium arylsulfinate **2** (1.0 mmol, 2.0 equiv) and 4 Å MS (powdered, 200 mg) were added and the reaction mixture was allowed to stir at 120 °C under air atmosphere (1 atm) for 12 h. After the completion of the reaction (monitored by TLC), the mixture was washed with brine (15 mL) and then extracted with dichloromethane (15 mL × 3). The organic phase was combined and then concentrated. The oily crude product was purified by column chromatography using silica gel (200−300 mesh) as stationary phase and a mixture of petroleum and ethyl acetate as eluent to give the desired product in noted yields.

*N,S-Diphenyl Sulfonamide (**3aa**).* White solid (94.4 mg, 81%), m.p.: 106−107 °C. R_f = 0.17 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 6.81 (br.s, NH) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 136.4, 133.18, 129.5, 129.2, 127.3, 125.7, 122.0 (ppm). IR (in KBr): ν = 3257, 2961, 2362, 1727, 1599, 1496, 1463, 1410, 1337, 1264, 1158, 1094, 1022, 921, 803, 754, 697, 631, 599, 561 cm^{-1}. MS (EI) m/z (%): 233.0, 168.0, 141.0, 92.0, 77.0, 65.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}NO_2S$: 233.0510; Found 233.0505.

*N-Phenyl-S-4-methylphenyl Sulfonamide (**3ba**).* White solid (91.4 mg, 74%), m.p.: 102−103 °C. R_f = 0.15 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 7.9 Hz, 2H), 7.41 (s, 1H), 7.22 (t, J = 7.5 Hz, 4H), 7.11−7.06 (m, 3H), 2.36 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 136.7, 136.1, 129.8, 129.4, 127.4, 125.3, 121.5, 21.6 (ppm). IR (in KBr): ν = 3264, 3226, 2956, 2361,1917, 1645, 1572, 1469, 1383, 1327, 1275, 1221, 1151, 1097, 1024, 921, 810, 757, 652, 603, 576, 546 cm^{-1}. MS (EI) m/z (%):

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247.0, 182.0, 155.0, 91.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2S$: 248.0740; Found 248.0745.

*N-Phenyl-S-2-methylphenyl Sulfonamide (**3ca**).* White solid (87.7 mg, 71%), m.p.: 126−127 °C. R_f = 0.23 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.2 Hz, 1H), 7.41−7.30 (m, 2H), 7.24−7.20 (m, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 8.1 Hz, 3H), 2.62 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.44, 137.37, 136.6, 133.2, 132.7, 130.1, 129.4, 126.4, 124.9, 120.4, 20.5 (ppm). IR (in KBr): ν = 3282, 3064, 2960, 2922, 2856, 2362, 1732, 1633, 1595, 1490, 1467, 1405, 1264, 1216, 1159, 1091, 1025, 967, 915, 804, 755, 696, 626, 588, 540 cm^{-1}. MS (EI) m/z (%): 247.0, 182.0, 155.0, 91.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2S$: 248.0740; Found 248.0748.

*N-Phenyl-S-4-methoxyphenyl Sulfonamide (**3da**).* White solid (96.0 mg, 73%), m.p.: 108−109 °C. R_f = 0.22 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.8 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.14−7.03 (m, 3H), 6.87 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H) (ppm).^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.3, 136.7, 130.8, 129.6, 129.5, 125.5, 121.8, 114.3, 55.7 (ppm). IR (in KBr): ν = 3256, 3073, 3023, 2923, 2849, 2803, 2362, 1902,1734, 1654, 1598, 1495, 1408, 1336, 1265, 1220, 1157, 1094, 1018, 894, 832, 803, 755, 697, 632, 559 cm^{-1}. MS (EI) m/z (%): 263.0, 198.0, 171.0, 107.0, 91.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_3S$: 264.0689; Found. 264.0699.

*N-Phenyl-S-4-tert-butylphenyl Sulfonamide (**3ea**).* White solid (109.8 mg, 76%), mp: 118−119 °C. R_f = 0.27 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 7.7 Hz, 3H), 1.29 (s, 9H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.9, 136.8, 136.3, 129.4, 127.2, 126.2, 125.2, 121.4, 35.3, 31.1 (ppm). IR (in KBr): ν = 3242, 3087, 2965, 2871, 1911, 1661, 1591, 1486, 1449, 1390, 1332, 1293, 1263, 1217, 1161, 1087, 1013, 908, 817, 755, 699, 643, 575, 547 cm^{-1}. MS (EI) m/z (%): 289.0, 168.0, 133.0, 92.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{20}NO_2S$: 290.1209; Found. 290.1217.

*N-Phenyl-S-4-fluorophenyl Sulfonamide (**3fa**).* White solid (99.2 mg, 79%), mp: 109−111 °C. R_f = 0.17 (petroleum:EtOAc = 5:1).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (dd, J = 8.3, 3.7 Hz, 2H), 7.33−7.26 (m, 2H), 7.18−7.07 (m, 5H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.4 (J_{C-F} = 254.0 Hz), 136.3, 135.1, 130.1(J_{C-F} = 9.4 Hz), 129.6, 125.9, 122.1, 116.4 (J_{C-F} = 22.6 Hz) (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −104.5 (ppm). IR (in KBr): ν = 3215, 3047, 2923, 2858, 2797, 1912, 1592, 1494, 1464, 1408, 1337, 1302, 1231, 1154, 1092, 1019, 938, 906, 841, 760, 712, 601, 543 cm^{-1}. MS (EI) m/z (%): 251.0, 168.0, 159.0, 95.0, 92.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}FNO_2S$: 252.0489; Found. 252.0481.

*N-Phenyl-S-4-chlorophenyl Sulfonamide (**3ga**).* White solid (113.5 mg, 85%), mp: 103−105 °C. R_f = 0.19 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.9 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.8, 137.6, 136.1, 129.6, 129.5, 128.8, 126.0, 122.1 (ppm). IR (in KBr): = 3254, 3089, 3044, 2961, 2927, 2865, 1913, 1724, 1651, 1584, 1470, 1401, 1336, 1276, 1217, 1157, 1089, 1017, 925, 894, 825, 755, 699, 614, 545 cm^{-1}. MS (EI) m/z (%): 267.0, 168.0, 111.0, 92.0(100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClNO_2S$: 268.0194; Found. 268.0200.

*N-Phenyl-S-2-chlorophenyl Sulfonamide (**3ha**).* White solid (86.8 mg, 65%), mp: 146−148 °C. R_f = 0.18 (petroleum:EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, J = 7.9 Hz, 1H), 7.47 (dd, J = 17.8, 11.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.09 (dd, J = 18.7, 7.6 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.3, 135.9, 134.2, 132.2, 131.7, 131.5, 129.5, 127.4, 125.9, 121.8 (ppm). IR (in KBr): ν = 3302, 3086, 3066, 2960, 1599, 1575, 1493, 1454, 1434, 1412, 1340, 1284, 1259, 1219, 1159, 1113, 1043, 918, 804, 756, 708, 694, 586 cm^{-1}. MS (EI) m/z (%): 267.0, 168.0, 149.0,111.0, 92.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClNO_2S$: 268.0194; Found. 268.0191.

*N-Phenyl-S-4-bromophenyl Sulfonamide (**3ia**).* White solid (137.3 mg, 88%), mp: 117−118 °C. R_f = 0.20 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.12−7.06 (m, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.1, 136.1, 132.5, 129.6, 128.9, 128.2, 126.0, 122.1 (ppm). IR (in KBr):ν= 3253, 3087, 2925, 2865, 2804, 2362, 1912, 1726, 1647, 1570, 1468, 1401, 1336, 1275, 1217, 1157, 1071, 1008, 925, 894, 821, 748, 697, 605, 544 cm^{-1}. MS (EI) m/z (%): 312.0, 168.1, 155.0, 92.1(100), 65.1. HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{12}H_{11}BrNO_2S$: 311.9688; Found.311.9695.

*N-Phenyl-S-4-trifluoromethylphenyl Sulfonamide (**3ja**).* White solid (121.9 mg, 81%), mp: 121−123 °C. R_f = 0.29 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.7 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.7, 135.9,134.8 (J_{C-F} = 33.0 Hz), 129.7, 127.9, 126.3 (J_{C-F} = 3.6 Hz), 126.2, 123.3 (J_{C-F} = 271.4 Hz),122.2 (ppm). ^{19}F NMR (376 MHz, CDCl3) δ = −63.2 (ppm). IR (in KBr):ν = 3107, 3056, 2960, 2923, 2873, 2808, 1934, 1593, 1493, 1470, 1404, 1332, 1329, 1165, 1128, 1107, 1092, 1064, 1016, 899, 845, 798, 717, 694, 606, 544 cm^{-1}. MS (EI) m/z (%): 301.0, 236.0, 218.0, 145.0, 92.1(100), 65.1. HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{13}H_{11}F_3NO_2S$: 302.0457; Found. 302.0451.

*N-Phenyl-S-4-nitrophenyl Sulfonamide (**3ka**).* White solid (95.9 mg, 69%), mp: 135−136 °C. R_f = 0.16 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 7.2 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.8 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.4, 144.8, 135.5, 129.8, 128.7, 126.6, 124.4, 122.6 (ppm). IR (in KBr): ν = 3277, 3130, 2923, 2857, 2363, 1917, 1645, 1601, 1523, 1398, 1341, 1306, 1207, 1161, 1093, 1014, 925, 892, 851, 808, 744, 700, 670, 613, 544 cm^{-1}. MS (EI) m/z (%): 278.0, 149.0, 92.0 (100), 84.0, 66.0. HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{12}H_{11}N_2O_4S$: 279.0434; Found. 279.0430.

*N-Phenyl-S-2-naphthyl Sulfonamide (**3la**).* White solid (110.4 mg, 78%), mp: 151−153 °C. R_f = 0.24 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.88 (t, J = 8.5 Hz, 3H), 7.75 (d, J = 8.7 Hz, 1H), 7.64−7.55 (m, 2H), 7.21 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 7.5 Hz, 3H), 6.88 (s, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.5, 136.1, 135.1, 132.2, 129.5, 129.5, 129.4, 129.1, 129.0, 128.0, 127.7, 125.7, 122.4, 122.0 (ppm). IR (in KBr): ν = 3257, 3057, 2962, 2926, 2850, 1716, 1599, 1497, 1414, 1335, 1301, 1221, 1157, 1132, 1074, 1032, 953, 922, 858, 816, 748, 698, 658, 617, 557 cm^{-1}. MS (EI) m/z (%): 283.0, 218.0, 191.0, 127.1 (100), 156.0, 92.1, 65.1 HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{14}NO_2S$: 284.0740; Found. 284.0747.

*N-Phenyl-S-2-thiophenyl Sulfonamide (**3ma**).* White solid (89.6 mg, 75%), mp: 81−83 °C. R_f = 0.26 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50−7.46 (m, 2H), 7.23 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 7.2 Hz, 3H), 6.96 (t, J = 4.3 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.6, 136.4, 133.0, 132.5, 129.5, 127.4, 125.9, 122.1 (ppm). IR (in KBr):ν = 3259, 3097, 2964, 2902, 1599, 1495, 1404, 1344, 1265, 1227, 1155, 1092, 1018, 924, 848, 800, 696, 669, 588, 542 cm^{-1}. MS (EI) m/z (%): 239.0, 162.0, 156.0, 92.0 (100), 83.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}NO_2S_2$: 240.0147; Found: 240.0138.

*N-Phenyl-S-3-pyridinyl Sulfonamide (**3na**).* White solid (79.6 mg, 68%), mp: 141−143 °C. R_f = 0.15 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.95 (s, 1H), 8.73 (d, J = 4.6 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.43−7.33 (m, 2H), 7.23 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.3 Hz, 1H), 7.08 (d, J = 8.1 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 148.1, 136.0, 135.8, 135.1, 129.7, 126.3, 123.8, 122.4 (ppm). IR (in KBr): ν = 3061, 3015, 2945, 2868, 2810, 2753, 2692, 1932, 1860, 1782, 1582, 1491, 1420, 1335, 1225, 1165, 1115, 1031, 999, 942, 814, 742, 693, 626, 586, 550 cm^{-1}. MS (EI) m/z (%): 234.0,169.1, 92.1 (100), 78.0, 65.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}N_2O_2S$: 235.0536; Found. 235.0550.

*N-Phenyl-S-methyl Sulfonamide (**3oa**).* White solid (54.7 mg, 64%), mp: 98−100 °C. R_f = 0.17 (petroleum:EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 2.94 (s, 3H) (ppm). ^{13}C NMR (100

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MHz, $CDCl_3$) δ = 137.0, 129.8, 125.5, 120.9, 39.3 (ppm). IR (in KBr): ν = 3257, 3054, 3018, 2966, 2931, 2360, 1597, 1471, 1394, 1323, 1304, 1157, 1076, 1028, 978, 960, 920, 773, 756, 694, 667, 528, 515 cm^{-1}. MS (EI) m/z (%): 171.0, 156.0, 94.0, 92.0 (100), 65.0, 15.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_7H_{10}NO_2S$: 172.0427; Found. 172.0421.

*N-Phenyl-S-ethyl Sulfonamide (**3pa**)*. White solid (57.4 mg, 62%), mp: 56−58 °C. R_f = 0.21 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.34 (t, J = 7.7 Hz, 2H), 7.24 (s, 1H), 7.17 (t, J = 7.3 Hz, 1H), 3.15 (q, J = 7.4 Hz, 2H), 1.37 (t, J = 7.4 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.1, 129.8, 125.2, 120.5, 46.0, 8.3 (ppm). IR (in KBr):ν = 3084, 3053, 2978, 2943, 2883, 2497, 1952, 1871, 1801, 1601, 1495 1456, 1417, 1221, 1140, 1078, 1051,1032, 922, 621, 523 cm^{-1}. MS (EI) m/z (%): 185.0, 156.0, 108.0,94.0, 92.0 (100), 65.0, 29.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{12}NO_2S$: 186.0583; Found. 186.0589.

*N-(o-Tolyl)-S-phenyl Sulfonamide (**3ab**)*. White solid (86.5 mg, 70%), mp: 121−123 °C. R_f = 0.19 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 7.8 Hz, 1H), 7.17−7.11 (m, 1H), 7.08 (d, J = 4.4 Hz, 2H), 6.42(br.s, NH), 1.98 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.8, 134.5, 133.1, 131.7, 130.9, 129.1, 127.3, 127.1, 126.6, 124.7, 17.6 (ppm). IR (in KBr):ν = 3359, 3224, 3062, 2922, 2361, 1908, 1638, 1449, 1406, 1328, 1256, 1153, 1092, 962, 909, 790, 755, 687, 594, 543 cm^{-1}. MS (EI) m/z (%): 247.0, 168.0, 141.0, 106.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2S$: 248.0740; Found. 248.0764.

*N-(p-Tolyl)-S-phenyl Sulfonamide (**3ac**)*. White solid (90.2 mg, 73%), mp: 118−120 °C. R_f = 0.25 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.53(br.s, NH), 2.27 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.2, 135.8, 133.7, 133.0, 130.0, 129.1, 127.4, 122.8, 21.0 (ppm). IR (in KBr): ν = 3435, 3244, 2923, 2362, 1629, 1512, 1449, 1389, 1327, 1266, 1221, 1161, 1092, 1027, 914, 812, 757, 726, 689, 640, 584, 527 cm^{-1}. MS (EI) m/z (%): 247.0, 168.0, 141.0, 106.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2S$: 248.0740; Found. 248.0733.

*N-(4-Methoxyphenyl)-S-phenylsulfonamide (**3ae**)*. White solid (94.7 mg, 72%), mp: 87−88 °C, R_f = 0.29 (petroleum:EtOAc = 4:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.3 Hz, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 139.1, 133.0, 129.1, 128.8, 127.4, 125.7, 114.6, 55.5 ppm. IR(in KBr): ν = 3257, 3013, 2965, 2841, 1888, 1609, 1513, 1454, 1332, 1253, 1159, 1095, 911, 822, 726, 630, 538 cm^{-1}. MS (EI) m/z: 263.0, 122.0 (100). HRMS(ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_3S$: 264.0689; Found. 264.0682.

*N-(4-Fluorophenyl)-S-phenyl Sulfonamide (**3af**)*. White solid (97.7 mg, 78%), mp: 110−111 °C. R_f = 0.17 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.07 (m, 2H), 6.90 (t, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7 (J_{C-F} = 243.8 Hz), 138.6, 133.3, 132.3, 129.2, 127.4, 124.7 (J_{C-F} = 8.3 Hz), 116.2 (J_{C-F} = 22.7 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −116.2 (ppm). IR (in KBr): = 3259, 3066, 2933, 2862, 1618, 1520, 1466, 1448, 1400, 1327, 1294, 1234, 1163, 1117, 1091, 1070, 1016, 922, 841, 754, 733, 687, 655, 586, 561 cm^{-1}. MS (EI) m/z (%): 251.0, 168.0, 141.0, 110.0, 91.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}FNO_2S$: 252.0489; Found. 252.0495.

*N-(2-Chlorophenyl)-S-phenylsulfonamide (**3ag**)*. White solid (96.2 mg, 72%), mp: 148−149 °C, R_f = 0.39 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.0 Hz, 2H), 7.04 (t, J = 7.7 Hz, 1H), 7.00 (br.s, NH) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.9, 133.4, 129.5, 129.2, 128.1, 127.4, 126.2, 125.4, 122.8 (ppm). IR (in KBr): ν = 3245, 3074, 2996, 2955, 1563, 1468, 1447, 1332, 1259, 1160, 1088, 903, 788, 753, 712, 677, 574 cm^{-1}. MS (EI) m/z: 267.0 (100), 168.1, 141.0, 126.0, 77.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{10}ClNO_2S$: 267.0121; Found. 267.0115.

*N-(3-Chlorophenyl)-S-phenylsulfonamide (**3ah**)*. White solid (93.5 mg, 70%), mp: 117−118 °C, R_f = 0.35 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.18−7.12 (m, 2H), 7.07 (d, J = 7.9 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.9, 137.8, 135.1, 133.5, 130.5, 129.4, 127.3, 125.6, 121.4, 119.3 (ppm). IR(in KBr): ν = 3205, 2905, 2963, 2923, 2848, 1589, 1465, 1314, 1161, 1092, 801, 730, 677, 583, 454 cm^{-1}. MS (EI) m/z: 267.0, 168.1, 141.0, 126.0, 77.0 (100). HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{12}H_{14}ClN_2O_2S$: 285.0459; Found. 285.0430.

*N-(4-Chlorophenyl)-S-phenyl Sulfonamide (**3ai**)*. White solid (109.5 mg, 82%), mp: 120−122 °C. R_f = 0.22 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 135.2, 133.4, 131.2, 129.6, 129.3, 127.3, 123.2 (ppm). IR (in KBr): ν = 3257, 3101, 3068, 2964, 2926, 2852, 1896, 1597, 1491, 1448, 1390, 1329, 1292, 1225, 1161, 1090, 1014, 916, 825, 754, 727, 631, 565, 688, 586, 505 cm^{-1}. MS (EI) m/z (%): 267.0, 168.0, 141.0, 126.0, 91.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClNO_2S$: 268.0194; Found. 268.0186.

*N-(2-Bromophenyl)-S-phenyl Sulfonamide(**3aj**)*. White solid (113.9 mg, 73%), mp: 131−132 °C. R_f = 0.21 (petroleum:EtOAc = 6:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.38 (dd, J = 12.3, 7.7 Hz, 3H), 7.23 (d, J = 7.9 Hz, 1H), 6.94 (t, J = 7.7 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.9, 134.7, 133.5, 132.7, 129.2, 128.8, 127.4, 126.6, 123.1, 116.1 (ppm). IR (in KBr):ν = 3257, 3084, 3054, 3004, 2964, 1583, 1473, 1448, 1400, 1335, 1263, 1170, 1159, 1092, 1026, 904, 798, 756, 723, 687, 586 cm^{-1}. MS (EI) m/z (%): 312.0, 168.0, 141.0, 171.0, 91.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}BrNO_2S$: 311.9688; Found. 311.9683.

*N-(3-Bromophenyl)-S-phenyl Sulfonamide (**3ak**)*. White solid (109.2 mg, 70%), mp: 120−121 °C, R_f = 0.43 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.30 (s, 1H), 7.20 (d, J = 6.3 Hz, 1H), 7.10−7.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.7, 138.0, 133.5, 130.7, 129.3,128.3, 127.3, 124.0, 122.9, 119.6 ppm. IR (in KBr): ν = 3210, 2842, 1585, 1463, 1313, 1161, 1090, 933, 733, 687, 584, 545 cm^{-1}. MS (EI) m/z: 312.0 (100), 170.0, 168.1, 141.0, 91.1, 77.0. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{12}H_{14}BrN_2O_2S$: 328.9954; Found. 328.9963.

*N-(4-Bromophenyl)-S-phenyl Sulfonamide (**3al**)*. White solid (126.4 mg, 81%), mp: 132−134 °C. R_f = 0.18 (petroleum:EtOAc = 6:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 7.1 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.9, 135.7, 133.4, 132.5, 129.3, 127.3, 123.5, 118.9 (ppm). IR (in KBr): ν = 3234, 3089, 3068, 2922, 2848, 1905, 1587, 1489, 1448, 1389, 1325, 1292, 1221, 1159, 1092, 1072, 1012, 914, 810, 727, 688, 561, 501 cm^{-1}. MS (EI) m/z (%): 312.0, 168.0, 141.0, 171.0, 91.0 (100), 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}BrNO_2S$: 311.9688; Found. 311.9681.

*N-(4-cyanophenyl)-S-phenyl Sulfonamide (**3ao**)*. Yellow solid (98.0 mg, 76%), mp: 148−149 °C, R_f = 0.17 (petroleum:EtOAc = 4:1).^1H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.54−7.48 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.0, 138.7, 133.9, 133.8, 129.6, 127.3, 119.6, 118.5, 108.1 (ppm). IR (in KBr): ν = 3253, 2964, 2221, 1610, 1508, 1332, 1159, 1092, 922, 812, 585 cm^{-1}. MS (EI) m/z: 258.0, 141.0, 77.0 (100). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O_2S$: 259.0536; Found. 259.0542.

*N-(4-Trifluoromethylphenyl)-S-phenyl Sulfonamide (**3ap**)*. White solid (115.9 mg, 77%), mp: 101−102 °C. R_f = 0.22 (petroleum:EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.51−7.45 (m, 4H), 7.21 (d, J = 8.3 Hz, 2H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.0, 138.8, 133.6, 129.5,

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127.3, 126.9 (J_{C-F} = 33.0 Hz), 126.8 (J_{C-F} = 5.5 Hz), 124.0 (J_{C-F} = 270.1 Hz), 119.9 (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −63.2 (ppm). IR (in KBr):ν = 3282, 3070, 2929, 2858, 1920, 1618, 1520, 1471, 1404, 1327, 1229, 1164, 1113, 1014, 914, 848, 755, 723, 600, 559, 506 cm^{-1}. MS (EI) m/z (%): 301.0, 141.0, 77.0 (100), 51.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}F_3NO_2S$: 302.0457; Found. 302.0432.

*N-(4-Acetylphenyl)-S-phenylsulfonamide (**3aq**).* Yellow solid (112.8 mg, 82%), mp: 127−128 °C, R_f = 0.22 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88−7.82 (m, 4H), 7.68 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 2.53 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.1, 141.3, 139.0, 133.6, 133.4, 130.1, 129.4, 127.3, 119.2, 26.6 (ppm). IR(in KBr): ν = 3222, 2928, 2359, 1665, 1595, 1352, 1272, 1166, 1094, 914, 812, 590 cm^{-1}. MS (EI) m/z: 275.1, 260.0 (100), 119.0, 106.1, 77.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_3S$: 276.0689; Found.276.0680.

*N-(2-Naphthyl)-S-phenyl Sulfonamide (**3ar**).* White solid (106.1 mg, 75%), mp: 97−98 °C. R_f = 0.15 (petroleum:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 7.8 Hz, 2H), 7.78−7.67 (m, 3H), 7.55 (s, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.47−7.36 (m, 4H), 7.24 (d, J = 8.8 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 134.0, 133.7, 133.2, 131.3, 129.5, 129.2, 127.8, 127.7, 127.4, 126.8, 125.7, 121.3, 118.8 (ppm). IR (in KBr):ν = 3261, 3057, 2923, 1633, 1600, 1514, 1446, 1416, 1354, 1308, 1157, 1092, 968, 928, 858, 814, 752, 729, 687, 646, 575, 525 cm^{-1}. MS (EI) m/z (%): 283.0, 168.0, 142.0 (100), 115.0, 91.0, 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}NO_2S$: 284.0740; Found. 284.0747.

*N,S-Diphenyl-S-methyl Sulfoximine (**5aa**).* White solid (90.2 mg, 88%), mp: 95−96 °C. R_f = 0.38 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 7.3 Hz, 2H), 7.60−7.55 (m, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.12 (t, J = 7.7 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 6.87 (t, J = 7.2 Hz, 1H), 3.23 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 139.6, 133.3, 129.6, 129.1, 128.7, 123.4, 121.8, 46.1 (ppm). IR (in KBr): ν = 3057, 3015, 2970, 2914, 2342, 1930, 1594, 1486, 1415, 1354, 1267, 1202, 1093, 1040, 973, 830, 756, 672, 623, 550 cm^{-1}. MS (EI) m/z: 231.0, 140.0, 138.0, 91.0, 77.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NOS$: 232.0791; Found. 232.0795.

*N-Phenyl-S-(2-methylphenyl)-S-methyl Sulfoximine (**5ba**).* Colorless oil (93.6 mg, 76%). R_f = 0.42 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.09 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 7.6 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 3.26 (s, 3H), 2.66 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.3, 137.8, 137.7, 133.4, 133.2, 131.4, 129.1, 127.0, 122.7, 121.6, 44.8, 20.7 (ppm). IR (in KBr): ν = 3057, 3027, 2954, 2930, 2340, 1914, 1594, 1488, 1432, 1309, 1266, 1204, 1069, 1034, 1009, 989, 956, 832, 731, 685, 601, 549 cm^{-1}. MS (EI) m/z (%): 245.1 (100), 182.1, 167.1, 154.0, 107.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947; Found. 246.0952.

*N-Phenyl-S-(3-methyl)phenyl-S-methyl Sulfoximine (**5ca**).* Colorless oil (98.0 mg, 80%). R_f = 0.43 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, CDCl3) δ = 7.80 (s, 1H), 7.76 (d, J = 6.2 Hz, 1H), 7.42−7.36 (m, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 6.87 (t, J = 7.3 Hz, 1H), 3.22 (s, 3H), 2.41 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 139.9, 139.5, 134.2, 129.5, 129.1, 129.1, 125.8, 123.4, 121.8, 46.1, 21.5 (ppm). IR (in KBr): ν = 3078, 3026, 2978, 2926, 2312, 1924, 1594, 1487, 1436, 1301, 1291, 1266, 1094, 1040, 980, 954, 833, 745, 840, 610, 544 cm^{-1}. MS (ESI) m/z (%): 246.1, 139.1,108.1, 92.1 (100). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947; Found. 246.0945.

*N-Phenyl-S-(4-methylphenyl)-S-methyl Sulfoximine (**5da**).* Colorless oil (100.5 mg, 82%). R_f = 0.39 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, J = 7.5 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 7.11 (t, J = 7.4 Hz, 2H), 7.00 (d, J = 7.7 Hz, 2H), 6.86 (t, J = 7.3 Hz, 1H), 3.22 (s, 3H), 2.40 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.3, 144.3, 136.5, 130.3, 129.1, 128.8, 123.4, 121.7, 46.3, 21.7 (ppm). IR (in KBr): ν = 3074, 3026, 2956, 2925, 2359, 1908, 1594, 1487, 1449, 1315, 1266, 1204, 1199, 1093, 1012, 995, 826, 749, 688, 605, 521 cm^{-1}. MS (EI) m/z (%): 245.1 (100), 182.1, 167.1, 138.1, 91.1, 65.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947; Found. 246.0941.

*N-Phenyl-S-(4-methoxyphenyl)-S-methyl Sulfoximine (**5ea**).* Colorless oil (104.4 mg, 80%). R_f = 0.29 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.9 Hz, 2H), 7.12 (t, J = 7.8 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.87 (t, J = 7.3 Hz, 1H), 3.84 (s, 3H), 3.22 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.5, 145.3, 130.9, 130.7, 129.1, 123.4, 121.7, 114.9, 55.7, 46.6 (ppm). IR (in KBr): ν = 3016, 2960, 2928, 2842, 1589, 1481, 1439, 1291, 1260, 1187, 1095, 1036, 869, 812, 740, 685, 647, 611, 549 cm^{-1}. MS (ESI) m/z: 262.1 (100), 118.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NO_2S$: 262.0896; Found. 262.0895.

*N-Phenyl-S-(4-chlorophenyl)-S-methyl Sulfoximine (**5fa**).* Yellowish oil (119.6 mg, 90%). R_f = 0.52 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.13 (t, J = 7.9 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 3.23 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.7, 140.0, 138.0, 130.3, 129.9 129.2, 123.4, 122.1, 46.2 (ppm). IR (in KBr): ν = 3081, 3027, 2967, 2927, 2360, 1904, 1578, 1485, 1324, 1290, 1267, 1090, 1084, 1041, 1015, 995, 962, 831, 749, 680, 611, 535 cm^{-1}. MS (ESI) m/z: 266.0 (100), 218.1, 157.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}ClNOS$: 266.0401; Found. 266.0405.

*N-(2-Methylphenyl)-S-methyl-S-phenyl Sulfoximine (**5ab**).* White solid (94.3 mg, 77%), mp: 62−63 °C. R_f = 0.45 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 7.1 Hz, 1H), 7.01 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 3.22 (s, 3H), 2.38 (s, 3H) (ppm).^{13}C NMR (125 MHz, $CDCl_3$) δ = 143.6, 140.1, 133.2, 132.4, 130.5, 129.6, 128.5, 126.4, 122.0, 121.9, 45.7, 18.8 (ppm). IR (in KBr): ν = 3014, 2970, 2926, 2360, 1900, 1571, 1486, 1405, 1315, 1266, 1210, 1118, 1092, 1050, 1030, 1011, 960, 748, 691, 640, 538 cm^{-1}. MS (EI) m/z: 245.0 (100), 167.0, 140.0, 104.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947; Found. 246.0951.

*N-(4-Methylphenyl)-S-methyl-S-phenyl Sulfoximine (**5ac**).* White solid (100.5 mg, 82%), mp: 108−109 °C. R_f = 0.38 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.3 Hz, 2H), 6.92 (s, 4H), 3.22 (s, 3H), 2.20 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.3, 139.7, 133.2, 131.2, 129.7, 129.6, 128.8, 123.3, 46.0, 20.8 (ppm). IR (in KBr): ν = 3020, 2961, 2923, 2360, 1905, 1573, 1505, 1446, 1318, 1287, 1263, 1203, 1094, 1069, 1034, 1012, 994, 824, 746, 688, 612, 532 cm^{-1}. MS (EI) m/z: 245.1 (100), 141.0, 118.1, 106.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947; Found. 246.0944.

*N-(4-(tert-Butylphenyl)-S-methyl-S-phenyl Sulfoximine(**5ad**).* Yellowish solid (111.9 mg, 78%). R_f = 0.50 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.21 (s, 3H), 1.23 (s, 9H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.4, 142.1, 139.9, 133.2, 129.6, 128.7, 125.9, 122.8, 46.1, 34.1, 31.5 (ppm). IR (in KBr): ν = 3029, 2961, 2925, 2364, 1901, 1605, 1578, 1505, 1446, 1317, 1291, 1204, 1095, 1036, 1019, 969, 825, 690, 603, 521 cm^{-1}. MS (EI) m/z: 287.1, 272.1 (100), 180.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}NOS$: 288.1417; Found. 288.1421.

*N-(4-Methoxyphenyl)-S-phenyl-S-methyl Sulfoximine (**5ae**).* White solid (99.2 mg, 76%), m.p.: 102−103 °C. R_f = 0.28 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.68 (d, J = 8.9 Hz, 2H), 3.70 (s, 3H), 3.21 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.9, 139.6, 138.0, 133.3, 129.6, 128.8, 124.5, 114.5, 55.5, 45.8 (ppm). IR (in KBr): ν = 3026, 3002, 2967, 2929, 2833, 1910, 1503, 1444, 1325, 1263, 1237, 1042, 1006, 976, 826, 746, 635, 535 cm^{-1}. MS (EI) m/z: 261.0, 179.0 (100), 154.0,121.0, 107.0, 91.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NO_2S$: 262.0896; Found. 262.0898.

*N-(4-Fluorophenyl)-S-phenyl-S-methyl Sulfoximine (**5af**).* White solid (113.3 mg, 91%), mp: 82−83 °C. R_f = 0.33 (petroleum:EtOAc =

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2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 6.95 (dd, J = 9.0, 4.9 Hz, 2H), 6.80 (t, J = 8.7 Hz, 2H), 3.22 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.4 (J = 238.5 Hz), 141.0, 139.2, 133.4, 129.7, 128.7, 124.5 (J = 7.8 Hz), 115.6 (J = 22.0 Hz), 46.0 (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −122.3 (ppm). IR (in KBr): ν = 3063, 3024, 2964, 2928, 2365, 1907, 1574, 1445, 1318, 1291, 1263, 1208, 1093, 1032, 1015, 995, 820, 746, 689, 611, 540 cm^{-1}. MS (EI) m/z (%): 249.1 (100), 186.1, 124.1, 109.1, 77.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}FNOS$: 250.0696; Found. 250.0693.

*N-(2-Chlorophenyl)-S-methyl-S-phenyl Sulfoximine (**5ag**).* White solid (82.2 mg, 62%), mp: 61−62 °C, R_f = 0.45 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 7.6 Hz, 2H), 7.61−7.56 (m, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.30 (d, J = 7.9 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 3.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.2, 139.1, 133.5, 129.9, 129.6, 128.6, 127.2, 124.0, 122.8, 45.7 ppm. IR(in KBr): ν = 3012, 2922, 1639, 1477, 1308, 1198, 1098, 1027, 747, 683, 519 cm^{-1}. MS (EI) m/z (%): 265.0, 202.1, 167.1 (100), 124.1, 92.1, 77.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}ClNOS$: 266.0401; Found. 266.0404.

*N-(3-Chlorophenyl)-S-methyl-S-phenylsulfoximine (**5ah**).* White solid (106 mg, 80%), mp: 57−58 °C, R_f = 0.40 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.0 Hz, 1H), 7.46 (t, J = 7.1 Hz, 2H), 6.97−6.90 (m, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 3.16 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.6, 139.0, 134.4, 133.6, 130.0, 129.8, 128.6, 123.4, 121.8, 121.4, 46.2 (ppm). IR(in KBr): ν = 3061, 3021, 2926, 1640, 1589, 1474, 1318, 1275, 1192, 1094, 1029, 785, 685, 522 cm^{-1}. MS (EI) m/z: 265.0, 202.0, 167.0 (100), 124.0, 77.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}ClNOS$: 266.0401; Found. 266.0404.

*N-(4-Chlorophenyl)-S-methyl-S-phenyl Sulfoximine (**5ai**).* White solid (123.3 mg, 93%), mp: 82−83 °C. R_f = 0.42 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.7 Hz, 2H), 7.60−7.54 (m, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 3.22 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.8, 138.9, 133.5, 129.7, 129.0, 128.6, 126.7, 124.5, 46.1 (ppm). IR (in KBr): ν = 3062, 3016, 2963, 2925, 2064, 1890, 1641, 1585, 1484, 1444, 1293, 1258, 1193, 1092, 1023, 869, 808, 737, 683, 652, 620, 541 cm^{-1}. MS (ESI) m/z: 266.0(100), 218.1, 126.0, 118.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}ClNOS$: 266.0401; Found. 266.0412.

*N-(2-Bromophenyl)-S-methyl-S-phenylsulfoximine (**5aj**).* Light brown solid (114.7 mg, 74%), mp: 64−65 °C, R_f = 0.40 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, J = 7.7 Hz, 2H), 7.63−7.58 (m, 1H), 7.58−7.49 (m, 3H), 7.20 (d, J = 7.9 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 3.25 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 139.2, 133.6, 133.1, 129.7, 128.7, 128.0, 123.7, 123.2, 119.5, 45.6 (ppm). IR (in KBr): ν = 3011, 2920, 1577,1197, 1124, 684 cm^{-1}. MS (EI) m/z: 310.1, 215.1, 167.0 (100), 124.0, 77.0. HRMS (ESI-TOF)m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}BrNOS$: 309.9896; Found. 309.9890.

*N-(3-Bromophenyl)-S-methyl-S-phenylsulfoximine (**5ak**).* White solid (127.1 mg, 82%), mp: 85−86 °C, R_f = 0.42 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, J = 7.5 Hz, 2H), 7.62−7.57 (m, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.18 (s, 1H), 7.01−6.90 (m, 3H), 3.23 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 139.0, 133.6, 130.2, 129.7, 128.6, 126.3, 124.7, 122.6, 121.8, 46.2 (ppm). IR (in KBr): ν = 3156, 2917, 1637, 1486, 1359, 1306, 1115, 964, 896, 617, 444, cm^{-1}. MS (EI) m/z: 310.0, 167.1(100), 124.0, 77.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}BrNOS$: 309.9896; Found. 309.9899.

*N-(4-Bromophenyl)-S-phenyl-S-methyl Sulfoximine (**5al**).* White solid (137.5 mg, 89%), m.p.: 111−112 °C. R_f = 0.48 (petroleum:-EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.23 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.3, 138.9, 133.5, 132.0, 129.7, 128.7, 125.0, 114.4, 46.2 (ppm). IR (in KBr): ν = 3063, 3017, 2958, 2928, 2359, 1907, 1570, 1483, 1318, 1289, 1206, 1095, 1023, 994, 826, 753, 631, 532 cm^{-1}. MS (EI) m/z: 310.0, 167.1(100), 124.1, 90.1, 77.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}BrNOS$: 309.9896; Found. 309.9899.

*N-(4-Iodophenyl)-S-methyl-S-phenyl Sulfoximine (**5am**).* Yellowish solid (151.7 mg, 85%), m.p.: 99−100 °C. R_f = 0.43 (petroleum:-EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 3.23 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.1, 139.0, 137.9, 133.6, 129.7, 128.7, 125.5, 84.8, 46.2 (ppm). IR (in KBr): ν = 3068, 3022, 3001, 2962, 2924, 2362, 1903, 1576, 1481, 1444, 1400, 1319, 1288, 1201, 1093, 1037, 1018, 997, 966, 822, 744, 687, 634, 609, 530 cm^{-1}. MS (ESI) m/z (%): 358.0 (100), 232.1, 218.1, 157.0, 79.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}INOS$: 357.9757; Found. 357.9773.

*N-(4-Nitrophenyl)-S-methyl-S-phenylsulfoximine (**5an**).* Yellow solid (102.1 mg, 74%), mp: 152−153 °C. R_f = 0.27 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 7.8 Hz, 2H), 7.94 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.1 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 3.31 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 141.8, 138.4, 134.1, 130.0, 128.5, 125.3, 122.5, 46.7 (ppm). IR(in KBr): ν = 3103, 2963, 2846, 1584, 1493, 1332, 1268, 1217, 1099, 1020, 855, 803, 751, 693, 539, 498 cm^{-1}. MS (EI) m/z: 276.1(100), 167.1, 125.0, 77.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{13}N_2O_3S$: 277.0641; Found. 277.0648.

*N-(4-Cyanophenyl)-S-methyl-S-phenylsulfoximine (**5ao**).* White solid (112.6 mg, 88%), mp: 108−109 °C, R_f = 0.31 (petroleum:EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 3.28 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.3, 138.5, 133.9, 133.3, 130.0, 128.5, 123.3, 119.7, 104.1, 46.6 (ppm). IR (in KBr): ν = 3055, 2963, 2921, 2555, 2221, 1595, 1498, 1279, 1211, 1171, 1095, 1019, 845, 796, 749, 692, 519 cm^{-1}. MS (EI) m/z: 256.1 (100), 167.1, 125.0, 77.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{14}H_{13}N_2OS$: 257.0743; Found. 257.0746.

*N-4-(Trifluoromethylphenyl)-S-methyl-S-phenylsulfoximine (**5ap**).* Brownish oil (124.1 mg, 83%). R_f = 0.39 (petroleum:EtOAc = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H) (ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.8, 138.9, 133.8, 129.9, 128.6, 126.3 (J = 3.7 Hz), 124.5 (J = 311.9 Hz), 123.6 (J = 10.2 Hz), 122.9, 46.4 (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −61.7 (ppm). IR (in KBr): ν = 3029, 2964, 2928, 2360, 1901, 1613, 1574, 1514, 1485, 1326, 1269, 1203, 1096, 1036, 1020, 999, 956, 826, 749, 635, 531 cm^{-1}. MS (EI) m/z: 299.0 (100), 154.0, 145.0, 124.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{14}H_{13}F_3NOS$: 300.0664; Found. 300.0656.

*N-(4-Acetylphenyl)-S-methyl-S-phenylsulfoximine (**5aq**).* Yellow solid (91.5 mg, 67%), mp: 86−87 °C, R_f = 0.34 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, J = 6.1 Hz, 2H), 7.71 (d, J = 6.5 Hz, 2H), 7.62−7.56 (m, 1H), 7.55−7.49 (m, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H), 2.45 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.2, 150.7, 138.8, 133.7, 130.6, 129.9, 129.8, 128.5, 122.5, 46.5, 26.3 (ppm). IR(in KBr): ν = 3006, 2923, 1672, 1593, 1501, 1414, 1355, 1263, 1208, 1096, 1020, 961, 851, 744, 690, 591, 533, 502 cm^{-1}. MS (EI) m/z: 273.1, 258.1 (100), 168.1, 124.0, 77.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{15}H_{16}NO_2S$: 274.0896; Found. 274.0902.

*N-(2-Naphthyl)-S-methyl-S-phenylsulfoximine (**5ar**).* Yellow solid (111.0 mg, 79%), mp: 91−92 °C, R_f = 0.27 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 6.7 Hz, 1H), 7.40 (t, J = 7.1 Hz, 2H), 7.31 (s, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.2 Hz, 2H), 3.19 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.0, 139.3, 134.5, 133.4, 129.64, 129.57, 128.8, 128.7, 127.5, 126.9, 126.0, 124.9, 123.8, 118.7, 46.1 (ppm). IR (in KBr): ν = 3014, 2963, 2918, 2852, 1622, 1588, 1456, 1266, 1195, 1093, 973, 743, 688, 512 cm^{-1}. MS (EI) m/z: 281.1 (100), 218.1,

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141.1, 124.1, 77.1. HRMS (ESI-TOF)m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}NOS$: 282.0947; Found. 282.0950.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00633.

^1H and ^{13}C NMR spectra of all the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) He, H.; Wu, Y.-J. *Tetrahedron Lett.* **2003**, *44*, 3385−3386. (b) Cristau, H.-J.; Cellier, P. P.; Spindler, J.-F.; Taillefer, M. *Chem. - Eur. J.* **2004**, *10*, 5607−5622. (c) Deng, W.; Liu, L.; Zhang, C.; Liu, M.; Guo, Q.-X. *Tetrahedron Lett.* **2005**, *46*, 7295−7298. (d) Hosseinzadeh, R.; Tajbakhsh, M.; Mohadjerani, M.; Alikarami, M. *J. Chem. Sci.* **2010**, *122*, 143−148. (e) Teo, Y.-C.; Yong, F.-F. *Synlett* **2011**, *2011*, 837−843. (f) Rosen, B. R.; Ruble, J. C.; Beauchamp, T. J.; Navarro, A. *Org. Lett.* **2011**, *13*, 2564−2567. (g) Teo, Y.-C.; Yong, F.-F.; Ithnin, I. K.; Yio, S.-H. T.; Lin, Z. *Eur. J. Org. Chem.* **2013**, *2013*, 515−524. (h) Khalaj, M.; Ghazanfarpour-Darjani, M.; Talei Bavil Olyai, M. R.; Shamami, S. F. *J. Sulfur Chem.* **2016**, *37*, 211−221.

(2) (a) Kantam, M. L.; Neelima, B.; Reddy, C. V.; Neeraja, V. *J. Mol. Catal. A: Chem.* **2006**, *249*, 201−206. (b) Islam, S. M.; Mondal, S.; Mondal, P.; Roy, A. S.; Tuhina, K.; Mobarok, M. *Inorg. Chem. Commun.* **2011**, *14*, 1352−1357. (c) Nasrollahzadeh, M.; Ehsani, A.; Maham, M. *Synlett* **2014**, *25*, 505−508. (d) Nasrollahzadeh, M.; Rostami-Vartooni, A.; Ehsani, A.; Moghadam, M. *J. Mol. Catal. A: Chem.* **2014**, *387*, 123−129.

(3) Pan, C.; Cheng, J.; Wu, H.; Ding, J.; Liu, M. *Synth. Commun.* **2009**, *39*, 2082−2092.

(4) Shekhar, S.; Dunn, T. B.; Kotecki, B. J.; Montavon, D. K.; Cullen, S. C. *J. Org. Chem.* **2011**, *76*, 4552−4563.

(5) Cao, X.; Bai, Y.; Xie, Y.; Deng, G.-J. *J. Mol. Catal. A: Chem.* **2014**, *383*−*384*, 94−100.

(6) Lavy, S.; Miller, J. J.; Pažický, M.; Rodrigues, A.-S.; Rominger, F.; Jäkel, C.; Serra, D.; Vinokurov, N.; Limbach, M. *Adv. Synth. Catal.* **2010**, *352*, 2993−3000.

(7) (a) Bolm, C.; Hildebrand, J. P. *Tetrahedron Lett.* **1998**, *39*, 5731−5734. (b) Bolm, C.; Hildebrand, J. P. *J. Org. Chem.* **2000**, *65*, 169−175. (c) Harmata, M.; Hong, X.; Ghosh, S. K. *Tetrahedron Lett.* **2004**, *45*, 5233−5236. (d) Cho, G. Y.; Rémy, P.; Jansson, J.; Moessner, C.; Bolm, C. *Org. Lett.* **2004**, *6*, 3293−3296. (e) Sedelmeier, J.; Bolm, C. *J. Org. Chem.* **2005**, *70*, 6904−6906. (f) Correa, A.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 2673−2676. (g) Correa, A.; Bolm, C. *Adv. Synth. Catal.* **2008**, *350*, 391−394. (h) Larsson, P.-F.; Correa, A.; Carril, M.; Norrby, P.-O.; Bolm, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5691−5693. (i) Yongpruksa, N.; Calkins, N. L.; Harmata, M. *Chem. Commun.* **2011**, *47*, 7665−7667.

(8) Bolm, C.; Hildebrand, J. P.; Rudolph, J. *Synthesis* **2000**, *2000*, 911−913.

(9) (a) Moessner, C.; Bolm, C. *Org. Lett.* **2005**, *7*, 2667−2669. (b) Chinnagolla, R. K.; Vijeta, A.; Jeganmohan, M. *Chem. Commun.* **2015**, *51*, 12992−12995.

(10) Kim, J.; Ok, J.; Kim, S.; Choi, W.; Lee, P. H. *Org. Lett.* **2014**, *16*, 4602−4605.

(11) Vaddula, B.; Leazer, J.; Varma, R. S. *Adv. Synth. Catal.* **2012**, *354*, 986−990.

(12) Aithagani, S. K.; Dara, S.; Munagala, G.; Aruri, H.; Yadav, M.; Sharma, S.; Vishwakarma, R. A.; Singh, P. P. *Org. Lett.* **2015**, *17*, 5547−5549.

(13) Zhu, H.; Teng, F.; Pan, C.; Cheng, J.; Yu, J.-T. *Tetrahedron Lett.* **2016**, *57*, 2372−2374.

(14) (a) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466−1474. (b) Shang, M.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 3354−3357. (c) Wei, W.; Liu, C.; Yang, D.; Wen, J.; You, J.; Wang, H. *Adv. Synth. Catal.* **2015**, *357*, 987−992. (d) Lee, W.-C. C.; Shen, Y.; Gutierrez, D. A.; Li, J. J. *Org. Lett.* **2016**, *18*, 2660−2663.

(15) Xiao, F.; Xie, H.; Liu, S.; Deng, G.-J. *Adv. Synth. Catal.* **2014**, *356*, 364−368 and the citations therein..

(16) Zhao, F.; Tan, Q.; Xiao, F.; Zhang, S.; Deng, G.-J. *Org. Lett.* **2013**, *15*, 1520−1523.

(17) Rao, H.; Yang, L.; Shuai, Q.; Li, C.-J. *Adv. Synth. Catal.* **2011**, *353*, 1701−1706.

(18) Zhou, C.; Liu, Q.; Li, Y.; Zhang, R.; Fu, X.; Duan, C. *J. Org. Chem.* **2012**, *77*, 10468−10472.

(19) Miao, T.; Wang, L. *Adv. Synth. Catal.* **2014**, *356*, 429−436.

(20) Zhou, X.; Luo, J.; Liu, J.; Peng, S.; Deng, G.-J. *Org. Lett.* **2011**, *13*, 1432−1435.

(21) (a) Liu, S.; Bai, Y.; Cao, X.; Xiao, F.; Deng, G.-J. *Chem. Commun.* **2013**, *49*, 7501−7503. (b) Xu, Y.; Zhao, J.; Tang, X.; Wu, W.; Jiang, H. *Adv. Synth. Catal.* **2014**, *356*, 2029−2039.

(22) (a) Liu, B.; Guo, Q.; Cheng, Y.; Lan, J.; You, J. *Chem. - Eur. J.* **2011**, *17*, 13415−13419. (b) Zhang, M.; Zhang, S.; Liu, M.; Cheng, J. *Chem. Commun.* **2011**, *47*, 11522−11524. (c) Chen, R.; Liu, S.; Liu, X.; Yang, L.; Deng, G.-J. *Org. Biomol. Chem.* **2011**, *9*, 7675−7679. (d) Wu, M.; Luo, J.; Xiao, F.; Zhang, S.; Deng, G.-J.; Luo, H.-A. *Adv. Synth. Catal.* **2012**, *354*, 335−340. (e) Yu, X.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2012**, *10*, 7479−7482. (f) Jafarpour, F.; Olia, M. B. A.; Hazrati, H. *Adv. Synth. Catal.* **2013**, *355*, 3407−3412. (g) Miao, T.; Li, P.; Wang, G.-W.; Wang, L. *Chem. - Asian J.* **2013**, *8*, 3185−3190. (h) Yuan, K.; Doucet, H. *Chem. Sci.* **2014**, *5*, 392−396.

(23) Chen, J.; Sun, Y.; Liu, B.; Liu, D.; Cheng, J. *Chem. Commun.* **2012**, *48*, 449−451.

(24) Yuan, K.; Soulé, J.-F.; Doucet, H. *ACS Catal.* **2015**, *5*, 978−991.

(25) Liu, S.; Chen, J.; Zhang, R.; Zhao, F.; Deng, G.-J. *Asian J. Org. Chem.* **2014**, *3*, 1150−1153.

(26) (a) Miao, T.; Wang, L. *Adv. Synth. Catal.* **2014**, *356*, 967−971. (b) Li, J.; Bi, X.; Wang, H.; Xiao, J. *RSC Adv.* **2014**, *4*, 19214−19217.

(27) Sun, S.; Yu, J.-T.; Jiang, Y.; Cheng, J. *Adv. Synth. Catal.* **2015**, *357*, 2022−2026.

(28) (a) Lücking, U. *Angew. Chem., Int. Ed.* **2013**, *52*, 9399−9408. (b) Bizet, V.; Kowalczyk, R.; Bolm, C. *Chem. Soc. Rev.* **2014**, *43*, 2426−2438.

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