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Copper-Catalyzed Denitrogenative *N*-Arylation of Sulfoximines and Sulfonamides with Arylhydrazines

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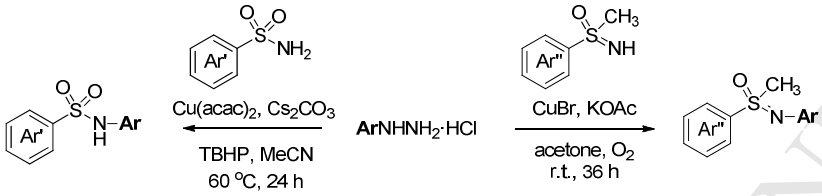

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ABSTRACT

A Cu-mediated ligand-free arylation of *NH*-sulfoximines and sulfonamides by arylhydrazine hydrochlorides was herein demonstrated. The oxidative transformation provided an easy access towards *N*-aryl sulfoximines and sulfonamides in high yields (up to 93% yields) with broad functional groups tolerance (up to 36 examples). The protocol was proposed to take place through the free radical pathway based on the results of control reactions and EPR analysis.

Introduction

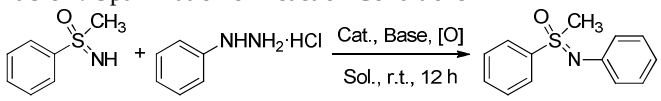
NH-Sulfoximines and sulfonamides, which took possession of analogous structures, have attracted widespread research interests for the unique architectures, as well as for extensive applications in the pharmaceutical and organic synthetic communities.[1] Great development has been broadly witnessed for the past decade and different methodologies have been widely documented for the *N*-functionalization of the useful building blocks. For example, straightforward *N*-arylation of sulfoximines has been successfully achieved, using aryl halides,[2] aryl triflates,[3] aryl boronic acids,[4] aryl siloxanes,[5] diaryl iodonium salts,[6] arynes[7] and *etc*.[8] as the aryl donors, while direct *N*-aryl sulfonamides have been prepared with the employments of aryl halides,[9] aryl boronic acids,[10] aryl siloxanes,[11] aryl nonaflates,[12] cyclohexanones[13] and *etc*[14] as the aryl sacrifices in the system. However, novel transformations towards *N*-aryl sulfoximines and sulfonamides are still severely demanded as the intrinsic requirement for the development of the chemistry discipline. Arylhydrazines,[15] which came into our visual field, have been regarded as an excellent arylation reagent through the C-N bond cleavage, releasing N_2 as the byproduct. Despite of the limited substrate scope, arylhydrazines still remained attractive in the field of the synthetic chemistry, for they are able to undergo the oxidative conditions for the generations of the aryl radicals through SET (single electron transfer) process *via* highly unstable aryldiazene intermediates, even under the molecular oxygen atmosphere. Along this line, methods for the preparations of diaryls and *N*-aryl amines, have been successfully achieved in the presence of different transition metallic catalysts through the denitrogenation pathway.[16-19] Inspired by the fruitful results and the denitrogenation protocols[20] for the formations of arylated anilines (Co/Cu-cocatalyzed system), and successful desulfitative arylation of *NH*-sulfoximines and sulfonamides from our group,[21] we wished to disclosed another practical and facile transformation toward *N*-aryl sulfoximines and sulfonamides mediated by copper-catalysts under oxidative conditions, in which arylhydrazines participated as an efficient aryl donor in the system.

Results and Discussion

The investigation began with the optimization of the conditions for the arylation protocol with *S*-phenyl-*S*-methyl sulfoximine (**1a**) and phenylhydrazine hydrochloride (**2a**) as model substrates, which were summarized in the Table 1. To our satisfaction, $Cu(OAc)_2$ was capable to make the reaction take place in the presence of Cs_2CO_3 as the base in acetonitrile in the dioxygen atmosphere, providing **3aa** in 37% yield at room temperature for 12 hours (entry 1). Other inorganic bases, including K_2CO_3 (entry 2), Na_2CO_3 (entry 3), KOAc (potassium acetate for entry 4), K_3PO_4 (entry 5) rendered the arylation protocol occur at room temperature, giving the desired *N*-phenyl sulfoximine (**3aa**) in yields from 20% to 48%. But oppositely, organic bases including pyridine (entry 6), 1,8-

diazabicyclo[5.4.0]undec-7-ene (DBU for entry 7) and triethyl amine (entry 8) showed negative effects to the transformation and only trace of **3aa** was detected at room temperature for 36 hours. Other cupric catalysts, such as $Cu(TFA)_2$ (TFA for trifluoroacetate, entry 9), $CuSO_4$ (entry 10), $Cu(OTf)_2$ (entry 11), $CuCl_2$ (entry 12) and $CuBr_2$ (entry 13), $Cu(acac)_2$ (entry 14) all performed positively in the system for the generation of **3aa**, but without significant improvement to the transformation.

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3aa**

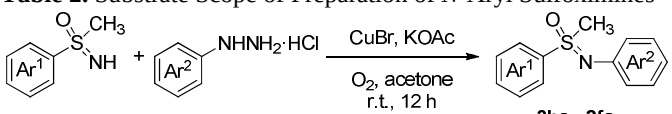
Entry	Cat.	Base	[O]	Sol.	Yield[b]
1	$Cu(OAc)_2$	Cs_2CO_3	O_2	CH_3CN	37%
2	$Cu(OAc)_2$	K_2CO_3	O_2	CH_3CN	42%
3	$Cu(OAc)_2$	Na_2CO_3	O_2	CH_3CN	30%
4	$Cu(OAc)_2$	KOAc	O_2	CH_3CN	48%
5	$Cu(OAc)_2$	K_3PO_4	O_2	CH_3CN	20%
6	$Cu(OAc)_2$	Pyridine	O_2	CH_3CN	trace
7	$Cu(OAc)_2$	DBU	O_2	CH_3CN	trace
8	$Cu(OAc)_2$	NEt_3	O_2	CH_3CN	trace
9	$Cu(TFA)_2$	KOAc	O_2	CH_3CN	30%
10	$CuSO_4$	KOAc	O_2	CH_3CN	32%
11	$Cu(OTf)_2$	KOAc	O_2	CH_3CN	58%
12	$CuCl_2$	KOAc	O_2	CH_3CN	37%
13	$CuBr_2$	KOAc	O_2	CH_3CN	30%
14	$Cu(acac)_2$	KOAc	O_2	CH_3CN	40%
15	CuCl	KOAc	O_2	CH_3CN	58%
16	CuBr	KOAc	O_2	CH_3CN	70%
17	CuI	KOAc	O_2	CH_3CN	62%
18	CuBr	KOAc	O_2	THF	trace
19[c]	**CuBr**	**KOAc**	O_2	**acetone**	**92%**
20	CuBr	KOAc	O_2	DMF	trace
21	CuBr	KOAc	O_2	DMSO	n.d.[d]
22[e]	CuBr	KOAc	TBHP	acetone	70%
23	CuBr	KOAc	DTBP	acetone	trace
24[e]	CuBr	KOAc	$PhI(OAc)_2$	acetone	72%
25[e]	CuBr	KOAc	IBX	acetone	58%
26	-	KOAc	O_2	acetone	n.d.

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Cat. (20 mol%), [O] (0.6 mmol), Base (0.6 mmol) under air in Sol. (1.5 mL) at room temperature for 12 h. [b]Isolated yields. [c]the optimal conditions. [d]for not detected. [e]the reaction finished in 2 hours according to TLC analysis.

Cuprous salts, like CuCl (entry 15), CuBr (entry 16) and CuI (entry 17) offered noteworthy increase in the efficiency of the protocol for the yields of **3aa** were obtained up to 70% (by CuBr for entry 16). Screening on the suitable solvent were subsequently embarked and acetone (entry 19) distinguished from the other solvents tested, such as tetrahydrofuran (THF for entry 18), *N*,*N*-dimethyl formamide (DMF for entry 20) and dimethyl sulfoxide (DMSO for entry 21), because the highest 92% yield of **3aa** was successfully separated when the reaction was conducted in acetone. Effect of external oxidants was also examined under the argon atmosphere. Surprisingly, the reaction between **1a** and **2a** finished in 2 hours in the presence of TBHP (70% in decane), furnishing **3aa** in 70% yield (entry 22). But di-*tert*-butyl peroxide (entry 23) gave only trace **3aa** while $PhI(OAc)_2$ (entry 24) and 2-iodoxybenzoic acid (IBX for entry 25) furnished **3aa** in medium yields within 2 hours. The key role of the cupper catalyst in the reaction was proved when the reaction was carried out in the absence of the catalyst and no reaction was detected (entry 26).

With the optimal conditions in hands, evaluation for the substrate scope and limitations of the protocol was then carried out as shown in Table 2. For *NH*-sulfoximines, *S*-tolyl-*S*-methyl sulfoximines were all compatible well in the system and positions of the methyl group had slight influence on the efficiency of the transformation, for *S*-(2-tolyl)-*S*-methyl-*N*-phenyl sulfoximine (**3ba**) were obtained in 75% yield (entry 1), while *S*-(3-tolyl)-*S*-methyl-*N*-phenyl sulfoximine (**3ca**) and *S*-(4-tolyl)-*S*-methyl-*N*-phenyl sulfoximine (**3da**) were furnished in 85% and 90% yields, respectively (entries 2 and 3). Similarly, *S*-(4-methoxypheny)-*S*-methyl-*N*-phenyl sulfoximine (**3ea**) was isolated in 88% yield after 12 h (entry 4). However, *S*-(4-chlorophenyl)-*S*-methyl-*N*-phenyl sulfoximine (**3fa**) was also provided in 93% yield, higher than electron-sufficient phenyl substituted *NH*-sulfoximines (entry 5). Then, exploration for the scope of arylhydrazines was conducted in the CuBr-mediated system under the mild conditions. Satisfyingly, 2-tolyl hydrazine hydrochloride (**2b**) coupled with sulfoximine **1a** successfully, forming the corresponding *N*-aryl sulfoximine **3ab** in 76% yield (entry 6). However, 4-tolyl hydrazine hydrochloride (**2c**) allowed the formation of **3ac** in 90% yield (entry 7), while 4-*tert*-butylphenyl (**2d**) and 4-methoxyphenyl (**2e**) hydrazine hydrochloride reacted with **1a** smoothly, giving the desired *N*-arylated product **3ad** and **3ae** in 82% and 79% yields, separately (entries 8 and 9). Halo substituted arylhydrazines were also tolerated in the system. 4-Fluoro- (entry 10), 2-chloro- (entry 11), 3-chloro- (entry 12), 4-chloro- (entry 13), 2-bromo- (entry 14), 3-bromo- (entry 15), 4-bromo- (entry 16) and 4-iodo- (entry 17) phenyl hydrazine hydrochlorides coupled with 1a successfully, furnishing the desired products **3af** – **3am** in yields from 73% - 89%. It was noteworthy that the positions of the halo groups did not affect the efficiency of the transformation significantly by the comparison between entries 11 – 13 and entries 14 – 16. Electron-deficient arylhydrazine hydrochlorides, which were exemplified by 4-cyanophenyl (**2n** for entry 18) and 4-trifluoromethylphenyl (**2o** for entry 19) underwent the arylation protocol, forming **3an** and **3ao** in 90% and 82% yields, respectively. Polyaryl, such as 2-naphthylhydrazine hydrochloride (**2p**) rendered the formation of **3ap** in 88% yield (entry 20).

Table 2. Substrate Scope of Preparation of *N*-Aryl Sulfoximines[a]



1b -1f **2a - 2p** **3ba - 3fa** **3ab - 3ap**

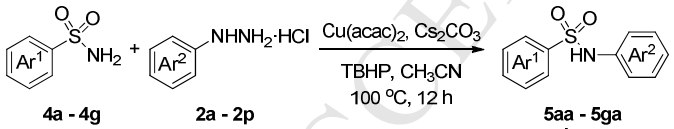
Entry	Ar^1 (**1**)	Ar^2 (**2**)	**3**	Yield[b]
1	2-$CH_3C_6H_4$ (**1b**)	Ph (**2a**)	**3ba**	75%
2	3-$CH_3C_6H_4$ (**1c**)	Ph (**2a**)	**3ca**	85%

3	4-$CH_3C_6H_4$ (**1d**)	Ph (**2a**)	**3da**	90%
4	4-$CH_3OC_6H_4$ (**1e**)	Ph (**2a**)	**3ea**	88%
5	4-ClC_6H_4 (**1f**)	Ph (**2a**)	**3fa**	93%
6	C_6H_5 (**1a**)	2-$CH_3C_6H_4$ (**2b**)	**3ab**	76%
7	C_6H_5 (**1a**)	4-$CH_3C_6H_4$ (**2c**)	**3ac**	90%
8	C_6H_5 (**1a**)	4-*t*BuC_6H_4 (**2d**)	**3ad**	82%
9	C_6H_5 (**1a**)	4-$CH_3OC_6H_4$ (**2e**)	**3ae**	79%
10	C_6H_5 (**1a**)	4-FC_6H_4 (**2f**)	**3af**	81%
11	C_6H_5 (**1a**)	2-ClC_6H_4 (**2g**)	**3ag**	73%
12	C_6H_5 (**1a**)	3-ClC_6H_4 (**2h**)	**3ah**	85%
13	C_6H_5 (**1a**)	4-ClC_6H_4 (**2i**)	**3ai**	87%
14	C_6H_5 (**1a**)	2-BrC_6H_4 (**2j**)	**3aj**	75%
15	C_6H_5 (**1a**)	3-BrC_6H_4 (**2k**)	**3ak**	82%
16	C_6H_5 (**1a**)	4-BrC_6H_4 (**2l**)	**3al**	89%
17	C_6H_5 (**1a**)	4-IC_6H_4 (**2m**)	**3am**	86%
18	C_6H_5 (**1a**)	4-CNC_6H_4 (**2n**)	**3an**	90%
19	C_6H_5 (**1a**)	4-$CF_3C_6H_4$ (**2o**)	**3ao**	82%
20	C_6H_5 (**1a**)	2-Naphthyl (**2p**)	**3ap**	88%

[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), CuBr (20 mol%), KOAc (1.0 mmol) under O_2 atmosphere in acetone (4.0 mL) at room temperature for 12 h. [b]Isolated yields.

Inspired by the broad substrate scope and high efficiency of the arylation protocol between *NH*-sulfoximines and arylhydrazine hydrochlorides, investigation of the transformation was further extended on sulfonamides, which possessed analogous structure with *NH*-sulfoximines (Table 3). However, simple transferring the conditions onto the arylation of sulfonamides failed, and the participation of $Cu(acac)_2$ as the catalyst, Cs_2CO_3 as the base, CH_3CN as the solvent was proved crucial to the transformation. Moreover, elevated temperature (100 °C) was also important for the completion of the reaction.

Table 3. Substrate Scope of Preparation of *N*-Aryl Sulfonamides[a]



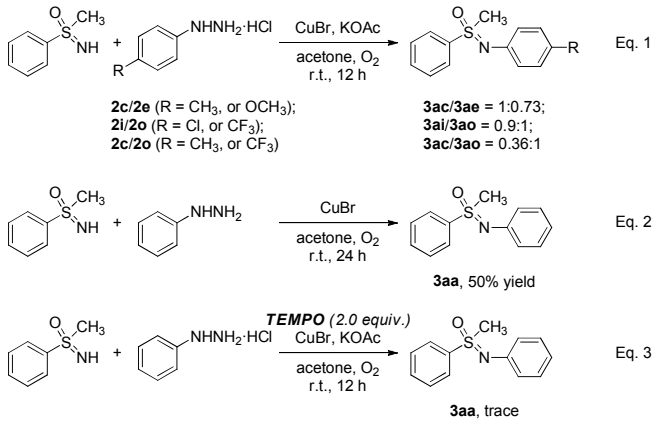
4a - 4g **2a - 2p** **5aa - 5ga** **5ab - 5ap**

Entry	Ar^1 (**4**)	Ar^2 (**2**)	**5**	Yield[b]
1	C_6H_5 (**4a**)	C_6H_5 (**2a**)	**5aa**	68%
2	2-$CH_3C_6H_4$ (**4b**)	C_6H_5 (**2a**)	**5ba**	62%
3	3-$CH_3C_6H_4$ (**4c**)	C_6H_5 (**2a**)	**5ca**	65%
4	4-FC_6H_4 (**4d**)	C_6H_5 (**2a**)	**5da**	70%
5	4-ClC_6H_4 (**4e**)	C_6H_5 (**2a**)	**5ea**	75%
6	4-BrC_6H_4 (**4f**)	C_6H_5 (**2a**)	**5fa**	78%
7	4-$CF_3C_6H_5$ (**4g**)	C_6H_5 (**2a**)	**5ga**	69%
8	C_6H_5 (**4a**)	2-$CH_3C_6H_4$ (**2b**)	**5ab**	62%
9	C_6H_5 (**4a**)	4- $CH_3C_6H_4$ (**2c**)	**5ac**	66%
10	C_6H_5 (**4a**)	4-$CH_3OC_6H_4$ (**2e**)	**5ae**	58%
11	C_6H_5 (**4a**)	4-FC_6H_4 (**2f**)	**5af**	72%
12	C_6H_5 (**4a**)	4-ClC_6H_4 (**2i**)	**5ai**	65%
13	C_6H_5 (**4a**)	4-BrC_6H_4 (**2l**)	**5al**	60%
14	C_6H_5 (**4a**)	4-CNC_6H_4 (**2n**)	**5an**	62%
15	C_6H_5 (**4a**)	2-Naphthyl (**2p**)	**5ap**	69%

[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $Cu(acac)_2$ (20 mol%), TBHP (1.0 mmol), Cs_2CO_3 (1.0 mmol) in sealed tube under air in CH_3CN (4.0 mL) at 100 °C for 12 h. [b]Isolated yields.

To our delight, phenyl sulfonamide (**4a**) reacted with **2a** successfully, giving the phenylated product **5aa** in 68% yield (entry 1). Tolyl sulfonamides, exemplified by 2-tolyl (**4b** for entry 2) and 3-tolyl (**4c** for entry 3) sulfonamides were also easily arylated in the $Cu(acac)_2$-mediated system and positions of the methyl group on the substrates showed slight effects on the produce of **5ba** and **5ca** in similar yields. Halophenyl sulfonamides, such as 4-fluorophenyl sulfonamide (**4d**), 4-chlorophenyl sulfonamide (**4e**) and 4-bromophenyl sulfonamide (**4f**) with phenylhydrazine hydrochloride (**2a**), constructing the desired products **5da** – **5fa** in yields from 70% to 78% (entries 4 – 6). Electron-deficient sulfonamide, like 4-trifloromethylphenyl sulfonamide (**4g**) coupled with **2a** and **5ga** was readily isolated in 69% yield (entry 7). In a similar pattern, compatibilities of the substituted arylhydrazines hydrochlorides were also explored in the $Cu(acac)_2$-catalyzed practice. At elevated temperature, good tolerance was witnessed and 2- or 3-methyl- (**2b** and **2c** for entries 8 and 9), 4-methoxy- (**2d** for entry 10), 4-fluoro- (**2f** for entry 11), 4-chloro- (**2i** for entry 12), 4-bromo- (**2l** for entry 13) and 4-cyano- (**2n** for entry 14) and 2-naphthyl- (**2p** for entry 15) hydrazine hydrochlorides reacted with sulfonamide **4a** favorably, forming the desired arylated sulfonamides in yields from 58% to 72%.

To have a deeper insight into the arylation protocol, competitive reactions were conducted for distinguishing the reactivities of arylhydrazine hydrochloride bearing different functional groups, as shown in Scheme 1.



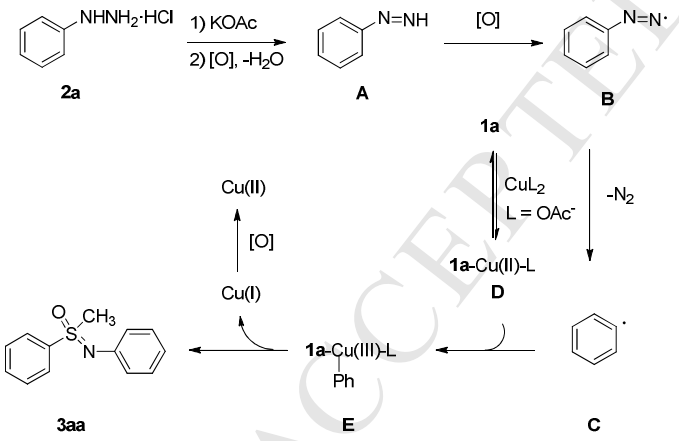
Scheme 1. Competitive and Control Reactions

For instance, a mixture of *p*-tolyl hydrazine hydrochloride (**2c**) and p-methoxyphenylhydrazine hydrochloride (**2e**) reacted with *NH*-sulfoximine **1a** smoothly for 12 hours, forming a mixture of **3ac** and **3ae** in 1:0.73 ratio according to crude ^{1}H-NMR (Eq. 1). In a same manner, a mixture of **2i** and **2o** coupled with **1a** successfully, offering the corresponding arylated sulfoximines **3ai** and **3ao** in 0.9:1 ratio. However, the difference between electron-sufficient and electron-deficient arylhydrazines was declared by the employment of **2c** and **2o**, for formation of a mixture of **3ac** and **3ao** was isolated successfully after 12 hours, in 0.36:1 ratio. It assumed that the electron-deficient substrates

offered higher performance which probably due to the electron effect.

Subsequently, the reaction between **1a** and phenylhydrazine was conducted for clearance of the role of KOAc in the protocol (Eq. 2). However, the reaction completed within 24 hours on the consumption of the hydrazine, furnishing the desired aryl sulfoximine **3aa** in ca. 50% yields, probably due to the homocoupling of **2a**. Addition of radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine-1-oxide) depressed the formation of **3aa** dramatically, for only trace **3aa** were checked aftere 12 hours (Eq. 3). This indicated the denitrogenative transformation might take place through a free radical pathway.

Successively, EPR (Electron Paramagnetic Resonance) analysis was conducted to find more information on the possible radical protocol, as exemplified by the reaction between **1a** and **2a**.[22] To our satisfaction, **2a** gave expected signal in the presence of KOAc (2.0 equiv.) under O_2 atmosphere in acetone, giving a g_e factor as 2.00237 (in a range of 2.0020 - 2.0025 for aryl radicals). (P185) Based on the EPR analysis and literature explorations, mechanism of the newly-developed method was proposed by the reaction between **1a** and **2a**, *via* an aryl radical intermediate, which probably was generated in situ from arylhydrazine hydrochloride in the dioxygen atmosphere (Scheme 3). In the presence of KOAc, phenylhydrazine was easily generated in situ. And successive oxidation step took place on the phenylhydrazine, offering another key intermediate phenyldiazene (**A**) with a release of H_2O. Upon the interaction with molecular oxygen, the intermediate **B** was transformed quickly into phenyldiazene radical **C**. Along the emission of nitrogen gas, phenyl radical **D** was formed, which could couple with sulfoximine (**1a**)-liganded Cu(II) complex easily to afford another key Cu(III)-cored intermediate **E**. Then the desired product **3aa** was formed along with an elimination step, giving Cu(I) species, which could be reoxidized into another Cu(II) under the oxidative atmosphere for the next circle.



Scheme 3. Plausible Mechanism

In conclusion, we have disclosed a practical and facile *N*-arylation of sulfoximines and sulfonamides using arylhydrazine hydrochlorides with assistance of a Cu(II)-catalyst under oxidative conditions. The method provided a general methodology towards various *N*-aryl sulfoximines and sulfonamides of great significance with high efficiency.

General Remarks

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 *n*-hexane 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). 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 towards *N*-aryl sulfoximines 3

Under the oxygen atmosphere, a Schlenk tube (35 mL) equipped with a magnetic bar was loaded with the *NH*-sulfoximine **1** (0.5 mmo), arylhydrazine chloride (2.0 equiv.), $Cu(OAc)_2$ (20 mol%), KOAc (2.0 equiv.) in dry acetone (4.0 mL). Then the mixture was allowed to stir at room temperature for 12 hours. After the completion of the reaction, as monitored by TLC analysis, the mixture was filtered through a short celite pad and washed with dichloromethane (15 mL × 3). The filtrate was concentrated, and the oily crude product was purified by column chromatography using silica gel (200 – 300 mesh) as stationary phase and a mixture of *n*-hexane and ethyl acetate (2:1) as eluent to give the corresponding arylated products **3** or **5** (**R_f** = ca.0.3 otherwise noted).

General procedure towards *N*-aryl sulfonamides 5

Under the air atmosphere, a Schlenk tube (35 mL) equipped with a magnetic bar was loaded with the sulfonamide **4** (0.5 mmol), $Cu(acac)_2$ (20 mol%), TBHP (70% in water, 2.0 equiv.), Cs_2CO_3 (2.0 equiv.) in dry solvent MeCN (4.0 mL). Then the reaction mixture was allowed to stir at 60 °C for 12 hours. After the completion of the reaction, as monitored by TLC analysis, the mixture was filtered through a short celite pad and washed with dichloromethane (15 mL × 3). The filtrate was concentrated, and the oily crude product was purified by column chromatography using silica gel (200 – 300 mesh) as stationary phase and a mixture of *n*-hexane and ethyl acetate (2:1) as eluent to give the corresponding arylated products **5** (**R_f** = ca.0.3 otherwise noted).

*N,S-Diphenyl-S-methyl sulfoximine (**3aa**)*: white solid (72.8 mg, 92% yield), m.p. 95 - 96 °C. ^{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 (100MHz, $CDCl_3$): δ = 145.1, 139.6, 133.3, 129.6, 129.1, 128.7, 123.4, 121.8, 46.1 (ppm). IR (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 (ESI): 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 232.0789.

*N-Phenyl-S-(2-methylphenyl)-S-methyl Sulfoximine (**3ba**)*: Colorless thick oil (55.1 mg, 75% yield). ^{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 (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 (ESI): 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. 246.0950.

N-Phenyl-S-(3-methylphenyl)-S-methyl Sulfoximine (***3ca***): Colorless thick oil (62.5 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): 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 (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 (***3da***): Colorless thick oil (66.1 mg, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.7Hz, 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 (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 (ESI): 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: 246.0949.

N-Phenyl-S-(4-methoxyphenyl)-S-methyl Sulfoximine (***3ea***): Colorless oil (68.9 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.9 Hz, 2H), 7.12 (t, *J* = 7.8Hz, 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 (100 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 (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 (***3fa***): Yellowish oil (73.9 mg, 93%). ^{1}H NMR(400 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* = 7.4Hz, 1H), 3.23 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$): δ =144.7, 140.0, 138.0, 130.3, 129.9 129.2, 123.4, 122.1, 46.2 (ppm). IR (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 (***3ab***): White solid (55.9 mg, 76%), m.p. 62 - 63 °C. ^{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 (100 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 (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 (ESI): 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. (***3ac***): White solid (66.2 mg, 90%), m.p. 108 - 109 °C. ^{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 (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 (ESI): 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 (***3ad***): Yellowish oil (70.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.3Hz, 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 (100 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 (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 (ESI): 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 (***3ae***): White solid (61.9 mg, 79%), m.p. 102 - 103 °C. ^{1}H NMR (400 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 (100 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 (KBr): ν =3026, 3002, 2967, 2929, 2833, 1910, 1503, 1444, 1325, 1263, 1237, 1042, 1006, 976, 826, 746, 635, 535 (cm^{-1}). MS (ESI): 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 (***3af***): White solid (113.3 mg, 91%), m.p. 82 - 83 °C. ^{1}H NMR (400 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 (100 MHz, $CDCl_3$): δ = 158.4 ($J_{C\text{-}F}$ = 238.5 Hz), 141.0, 139.2, 133.4, 129.7, 128.7, 124.5 ($J_{C\text{-}F}$ = 7.8 Hz), 115.6 ($J_{C\text{-}F}$= 22.0 Hz), 46.0 (ppm). ^{19}F NMR (370 MHz, $CDCl_3$): δ = -122.3 (ppm). IR (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 (ESI): 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 (***3ag***): White solid (58 mg, 79%), m.p. 61 - 62 °C, ^{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 (KBr): ν = 3012, 2922, 1639, 1477, 1308, 1198, 1098, 1027, 747, 683, 519(cm^{-1}). MS (ESI): 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 (***3ah***): White solid (67.4 mg, 85%), m.p. 57 - 58 °C. 1H 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 (KBr): ν = 3061, 3021, 2926, 1640, 1589, 1474, 1318, 1275, 1192, 1094, 1029, 785, 685, 522 (cm^{-1}). MS (ESI): 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 (**3ai**)*: White solid (69.1 mg, 87%), m.p. 82 - 83 °C. ^{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 (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 (**3aj**)*: Light brown solid (69.5 mg, 75%), m.p. 64 - 65 °C. ^{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 (KBr): ν = 3011, 2920, 1577, 1197, 1124, 684 (cm^{-1}). MS (ESI): 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 (**3ak**)*: White solid (65.2 mg, 82%), m.p. 85 - 86 °C. ^{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 (KBr): ν = 3156, 2917, 1637, 1486, 1359, 1306, 1115, 964, 896, 617, 444 (cm^{-1}). MS (ESI): 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 (**3al**)*: White solid (82.5 mg, 89%), m.p. 111 - 112 °C. ^{1}H NMR (400 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 (100 MHz, $CDCl_3$): δ = 144.3, 138.9, 133.5, 132.0, 129.7, 128.7, 125.0, 114.4, 46.2 (ppm). IR (KBr): ν = 3063, 3017, 2958, 2928, 2359, 1907, 1570, 1483, 1318, 1289, 1206, 1095, 1023, 994, 826, 753, 631, 532 (cm^{-1}). MS (ESI): 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 (**3am**)*: Yellowish solid (92.1 mg, 86%), m.p. 99 - 100 °C. 1H NMR (400 MHz, CDCl3) 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 (100 MHz, $CDCl_3$) δ = 145.1, 139.0, 137.9, 133.6, 129.7, 128.7, 125.5, 84.8, 46.2 (ppm). IR (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-Cyanophenyl)-S-methyl-S-phenyl sulfoximine (**3an**)*: White solid (69.1 mg, 90%), m.p. 108 - 109 °C. ^{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 (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(**3ao**)*: Brownish thick oil (73.6 mg, 82%). ^{1}H NMR (400 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 (100 MHz, $CDCl_3$): δ = 148.8, 138.9, 133.8, 129.9, 128.6, 126.3 (J_{C-F} = 3.7 Hz), 124.5(J_{C-F} = 311.9 Hz), 123.6 (J_{C-F} = 10.2 Hz), 122.9, 46.4 (ppm). ^{19}F NMR (370 MHz, $CDCl_3$): δ = -61.7 (ppm). IR (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 (ESI): 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-(2-Naphthyl)-S-methyl-S-phenylsulfoximine (**3ap**)*: Yellow solid (74.1 mg, 88%), m.p. 91 - 92 °C. ^{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(100 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 (KBr): ν = 3014, 2963, 2918, 2852, 1622, 1588, 1456, 1266, 1195, 1093, 973, 743, 688, 512 (cm^{-1}). MS (ESI): m/z (%) = 281.1 (100), 218.1, 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.

*N,S-Diphenyl Sulfonamide (**5aa**):*White solid (90.9 mg, 78%), m.p. 106 - 107 °C. ^{1}H NMR (400MHz, $CDCl_3$): 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, NH) (ppm). ^{13}C NMR (100MHz, $CDCl_3$): δ = 139.1, 136.4, 133.18, 129.5, 129.2, 127.3, 125.7, 122.0 (ppm). IR (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 (ESI): m/z (%) = 233.0, 168.0, 141.0, 92.0, 77.0, 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO_2S$ 233.0510; found: 233.0505.

*N-Phenyl-S-2-methylphenyl Sulfonamide (**5ba**)*: White solid (88.9 mg, 72%), m.p. 126 - 127 °C. ^{1}HNMR (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 (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 (ESI): 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-methylphenyl Sulfonamide (**5ca**)*: White solid (92.6 mg, 75%), m.p. 102 - 103 °C. ^{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 (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 (ESI): m/z (%) = 247.0, 182.0, 155.0, 91.0 (100), 65.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_3S$ 248.0740; found: 248.0745.

*N-Phenyl-S-4-fluorophenyl Sulfonamide (**5da**)*: White solid (100.4 mg, 80%), m.p. 109 - 111 °C. ^{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} = 9.4Hz), 129.6, 125.9, 122.1, 116.4 (J_{C-F} = 22.6 Hz) (ppm). ^{19}F NMR (370 MHz, $CDCl_3$) δ = -104.5 (ppm). IR (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 (ESI): 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 (**5ea**)*: White solid (113.5 mg, 85%), m.p. 103 - 105 °C. ^{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 (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 (ESI): 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-4-bromophenyl Sulfonamide (**5fa**)*: White solid (136.8mg, 88%), m.p: 117 - 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0Hz, 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 (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 (ESI): 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 (**5ga**)*: White solid (118.9 mg, 79%), m.p. 121 - 123 °C. ^{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} = 3.6Hz), 126.2, 123.3 (J_{C-F} = 271.4 Hz), 122.2 (ppm). ^{19}F NMR (370 MHz, $CDCl_3$) δ = -63.2 (ppm). IR (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 (ESI): 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-(o-Tolyl)-S-phenyl Sulfonamide (**5ab**)*: White solid (88.9 mg, 72%), m.p. 121 - 123 °C. ^{1}H 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, 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 (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 (ESI): 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(**5ac**)*: White solid (93.9 mg, 76%), m.p. 118 - 120 °C. ^{1}H 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, 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 (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 (ESI): 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 (**5ae**)*: White solid (92.8 mg, 68%), m.p. 87 - 88 °C. ^{1}H 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 (KBr): ν = 3257, 3013, 2965, 2841, 1888, 1609, 1513, 1454, 1332, 1253, 1159, 1095, 911, 822, 726, 630, 538 (cm^{-1}). MS (ESI): 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 (**5af**)*: White solid (102.9 mg, 82%), m.p. 110 - 111 °C. ^{1}H 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 (370 MHz, $CDCl_3$): δ = -116.2 (ppm). IR (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 (ESI): 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-(4-Chlorophenyl)-S-phenyl Sulfonamide (**5ai**)*: White solid (100.5 mg, 75%), m.p. 120 - 122 °C. ^{1}H 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 (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 (ESI): 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-(4-Bromophenyl)-S-phenyl Sulfonamide (**5al**)*: White solid (108.9 mg, 70%), m.p. 132 - 134 °C. ^{1}H 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 (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 (ESI): 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 (**5an**)*: Yellow solid (92.9 mg, 72%), m.p. 148 - 149 °C. ^{1}H 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 (KBr): ν = 3253, 2964, 2221, 1610, 1508, 1332, 1159, 1092, 922, 812, 585 (cm^{-1}). MS (ESI): 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-(2-Naphthyl)-S-phenyl Sulfonamide (**5ap**)*: White solid (111.8 mg, 79%), m.p. 97 - 98 °C. ^{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 (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 (ESI): 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.

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