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Copper-Catalyzed *N*-Arylation of Sulfoximines with Arylboronic Acids under Mild Conditions

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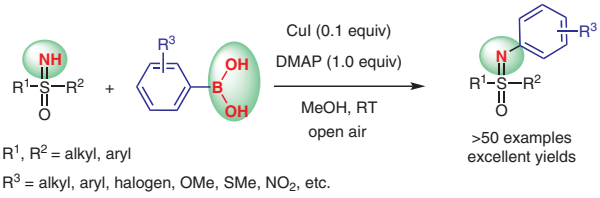

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Abstract *N*-Arylation of sulfoximines with different arylboronic acids, including sterically hindered boronic acids, is achieved using copper(I) iodide and 4-DMAP at room temperature. Moreover, *N*-arylation of biologically relevant L-methionine sulfoximine is demonstrated for the first time. All these reactions provided the desired products in excellent yields within a short span of time. The optimized reaction conditions are well suited to the task of *N*-vinylation of sulfoximine with *trans*-2-phenylvinylboronic acid.

Key words arylation, boronic acid, sulfoximine, catalysis, copper

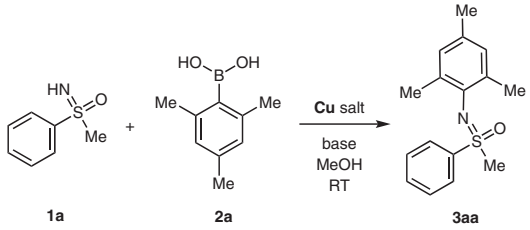
Sulfoximines are mono-aza analogues of sulfones that have been of considerable interest in chemistry and biology.[1] It has been noticed that functionalization of sulfoximines at the nitrogen center displays interesting biological and chemical properties. In this context, *N*-arylsulfoximines have been explored as efficient chiral ligands in asymmetric catalysis.[2a–e] On the other hand, Gnamm et al. have recently reported that *N*-arylsulfoximines exhibit interesting physicochemical and in vitro properties that are significant for drug discovery.[1c] *N*-Arylation of sulfoximine can be achieved with numerous aryl donors[3] such as aryl halides,[4] arylboronic acids,[5] aryl sulfonates,[6] aryl siloxanes,[7] arynes,[8] diaryliodonium salt,[9] etc.,[10] in the presence of Cu, Pd, Fe, and Ni catalysts.

Among them, Bolm's copper-mediated Chan–Lam[11] coupling of sulfoximine with arylboronic acids was found to be more advantageous from a synthetic perspective.[5] This is because the *N*-arylation takes place at room temperature in the presence of catalytic amount of copper(II) acetate under mild reaction conditions. Moreover, arylboronic acids are cheap and more accessible and can be easily stored and handled. Despite having many advantages, this method also has some limitations. For example, *N*-arylation of sulfoximine failed with sterically hindered 2,4,6-trimethylphenylboronic acid. Moreover, this method also requires excess amount of arylboronic acids and longer reaction time.

It is well known that the nitrogen atom in the sulfoximine possesses poor nucleophilicity when compared with alkyl secondary amines,[12] which usually necessitates different reaction conditions for different *N*-functionalization reactions. In this context, we have envisioned that optimizing the reaction conditions with different copper salts in the presence of ligands/bases might lead to delightful results with respect to sterically hindered arylboronic acids. In continuation of our previous work on sulfoximine chemistry,[13] here we disclose an efficient method for the *N*-arylation of sulfoximines with sterically hindered arylboronic acids in the presence of copper(I) iodide and 4-DMAP at room temperature.

At the outset, optimization of the reaction conditions was investigated with *S*-methyl-*S*-phenylsulfoximine (**1a**) and sterically hindered 2,4,6-trimethylphenylboronic acid (**2a**) in the presence of various copper(I) and copper(II) salts (10 mol%) in methanol (Table 1, entries 1–5). The desired product was not observed even after 24 hours at room temperature with $Cu(OAc)_2$, $CuSO_4$, CuCl, CuBr, and CuI. It is well known that ligands and bases play an important role in cross-coupling reactions particularly if the substrates are poorly reactive or sterically hindered.[14] Recently, Phukan and co-workers disclosed the reaction of copper(I) iodide with 4-DMAP, which provides $Cu[(DMAP)_4I]I$ complex in DMSO.[14e] This complex shows excellent catalytic activity in Chan–Lam reactions.[14e] In fact, we have recently demonstrated *N*-alkylation of sulfoximines with alkylboronic acids in the presence of copper(II) acetate and pyridine.[13] In light of this, *N*-arylation was performed with copper(II) acetate in the presence of pyridine as well as 4-DMAP in methanol.

Table 1 Optimization of the Reaction Conditions[a]



1a 2a 3aa

Entry	Catalyst (10 mol%)	Base (1 equiv)	Time (h)	Yield (%)[b]
1	$Cu(OAc)_2$	–	24	n.r
2	$CuSO_4$	–	24	n.r
3	CuCl	–	24	n.r
4	CuBr	–	24	n.r
5	CuI	–	24	n.r
6	$Cu(OAc)_2$	Py	12	59
7	$Cu(OAc)_2$	4-DMAP	12	77
8	$Cu(OAc)_2$	DABCO	12	n.r
9	$Cu(OAc)_2$	DBU	12	n.r
10	$Cu(OAc)_2$	Et_3N	12	57
11	$Cu(OAc)_2$	2,2′-bipy	12	n.r
12	$Cu(OAc)_2$	K_2CO_3	12	n.r
13	$CuSO_4$	4-DMAP	12	20
14	CuCl	4-DMAP	12	60
15	CuBr	4-DMAP	12	69
16	CuI	4-DMAP	4	89
17	$NiCl_2{\cdot}6H_2O$	4-DMAP	12	n.r
18	$Ni(OAc)_2{\cdot}4H_2O$	4-DMAP	12	n.r
19	$NiCl_2{\cdot}6H_2O$	2,2′-bipy/DBU	12	n.r[c]
20	$Ni(OAc)_2{\cdot}4H_2O$	DBU	12	n.r[d]

[a] Reaction conditions: **1a** (155 mg, 1.0 mmol), **2a** (1.5 equiv), copper salt (0.1 equiv), and base (1.0 equiv) were stirred in MeOH (2 mL) under open air.
[b] Isolated yield; n.r. = no reaction.
[c] Reaction was carried out in MeCN.
[d] Reaction was carried out in DMSO.

To our delight, the *N*-arylation proceeded smoothly, and *N*-(2,4,6-trimethyl)phenyl-*S*-methyl-*S*-phenylsulfoximine (**3aa**) was obtained in 59% and 77% yield, respectively (entries 6 and 7).

The reaction was further investigated with various organic and inorganic bases such as DABCO, DBU, Et_3N, 2,2′-bipyridine and K_2CO_3 (Table 1, entries 8–12). Unfortunately, reactions did not proceed well with these additives. Hence, optimization was further investigated with different copper salts in the presence of 4-DMAP in methanol at room temperature (entries 13–16). Among all, copper(I) iodide/4-DMAP system gave the desired product **3aa** in high yield (89%) within 4 hours under open air (entry 16). Furthermore, *N*-arylation was investigated with nickel salts such as $NiCl_2$ and $Ni(OAc)_2$ in the presence of different additives, which was previously explored in Chan–Lam coupling reactions (entries 17–20).[15] These reactions did not provide the desired product even after 12 hours at room temperature.

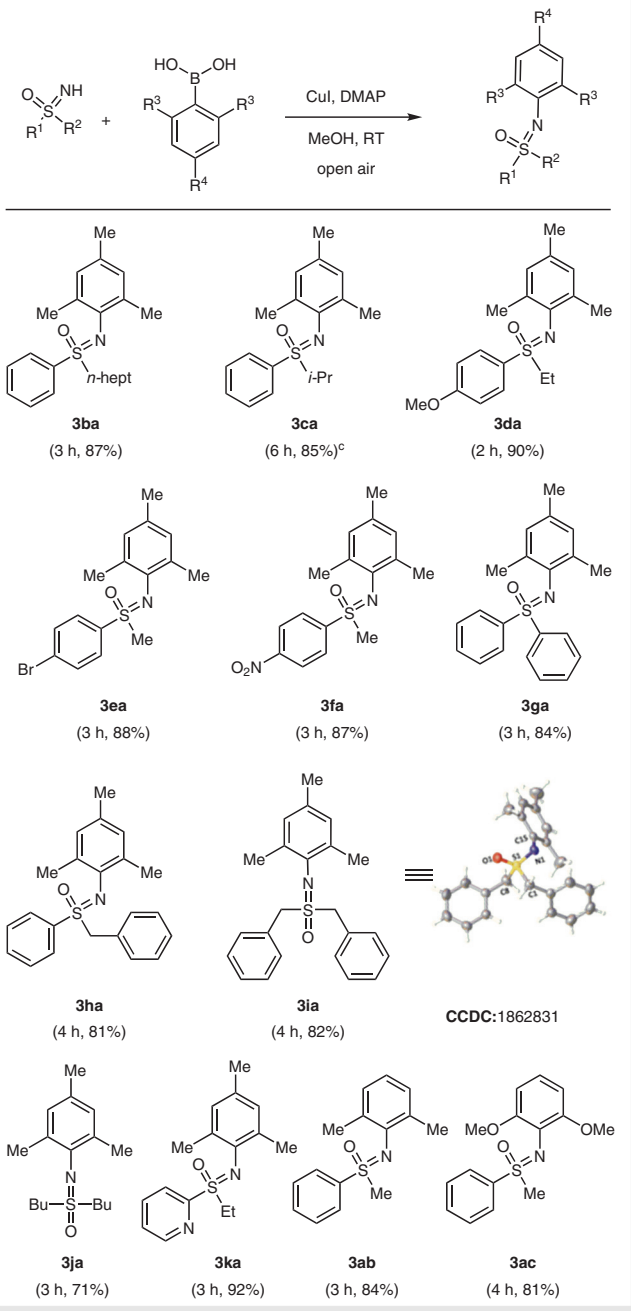
Having established the optimized conditions, *N*-arylation of different sulfoximines with 2,4,6-trimethylphenylboronic acid (**2a**) was investigated (Scheme 1). To our delight, the substrates bearing linear and branched alkyl chains underwent *N*-arylation smoothly and provided the desired products **3ba** and **3ca** in 85–87% yields. It is worth noting that the sterically hindered *S*-isopropyl-*S*-phenylsulfoximine also participated in the coupling reaction with equal efficiency (Scheme 1, **3ca**). Moreover, the substitutions on the aryl ring of the sulfoximine (electron-donating or -withdrawing) did not affect the progress of the reaction significantly (**3da–fa**). Encouraged, we further attempted the *N*-arylation of *S*,*S*-diphenyl, *S*-benzyl-*S*-phenyl, *S*,*S*-dibenzyl, and *S*,*S*-dialkyl sulfoximines as well as heterocyclic sulfoximine with 2,4,6-trimethylphenylboronic acid. To our delight, all these substrates underwent *N*-arylation smoothly in 71–92% yields (**3ga–ka**). Likewise, other sterically hindered *ortho*-substituted arylboronic acids such as 2,6-dimethyl- and 2,6-dimethoxyphenylboronic acids also gave *N*-arylated products **3ab** and **3ac** in 84% and 81% yield, respectively, in 3–4 hours.

Further, we have investigated the *N*-arylation of different sulfoximines with sterically less hindered arylboronic acids (Scheme 2). 4-Methylphenylboronic acid was chosen as a common aryl donor and was employed in the coupling reaction with a variety of sulfoximines under optimized conditions. To our delight, all these reactions proceeded smoothly with excellent yields within 2 hours (Scheme 2, **3ad–nd**).

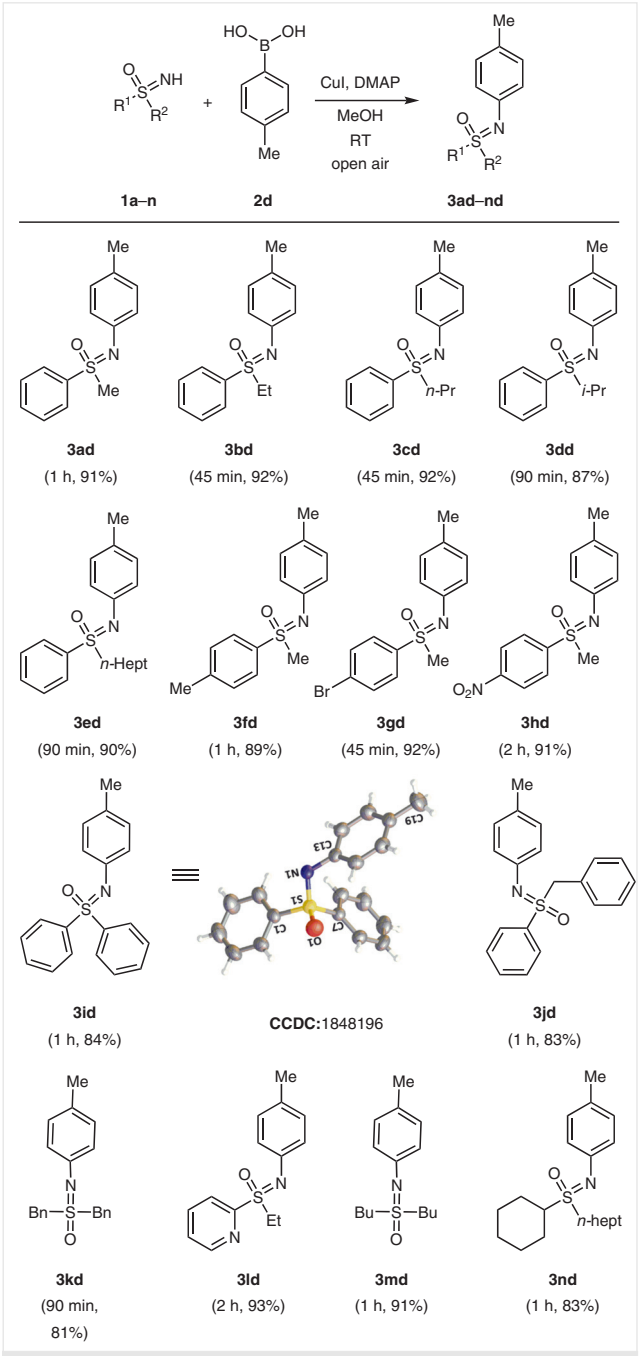
Having explored the substrate scope with different sulfoximines, *N*-arylation with different boronic acids was investigated (Scheme 3). In this context, *S*-methyl-*S*-phenylsulfoximine (**1a**) was subjected to the coupling reaction with arylboronic acids bearing different functional groups under optimized conditions and the results are summarized in Scheme 3. Arylboronic acids having electron-donating (e.g., Et, OMe, and SMe) and -withdrawing groups (F, Cl, Br, and NO_2) at the *para* or *meta* positions were successfully coupled with sulfoximine **1a** in 78–91% yields (Scheme 3, **3ae–an**). Further, to investigate the versatility of the developed methodology, arylboronic acids bearing sensitive functional groups such as vinyl, formyl, acyl, and nitrile were employed for *N*-arylation reactions. To our delight, the coupling reactions preceded smoothly, giving 40–82% yields under optimized reaction conditions (**3ao–ar**). Likewise, more conjugated arylboronic acids such as naphthyl- and biphenylboronic acids also participated in coupling re-

action efficiently (**3as–au**). Similarly, *N*-arylation of dialkylsulfoximines was achieved in excellent yields (**3me** and **3mk**).

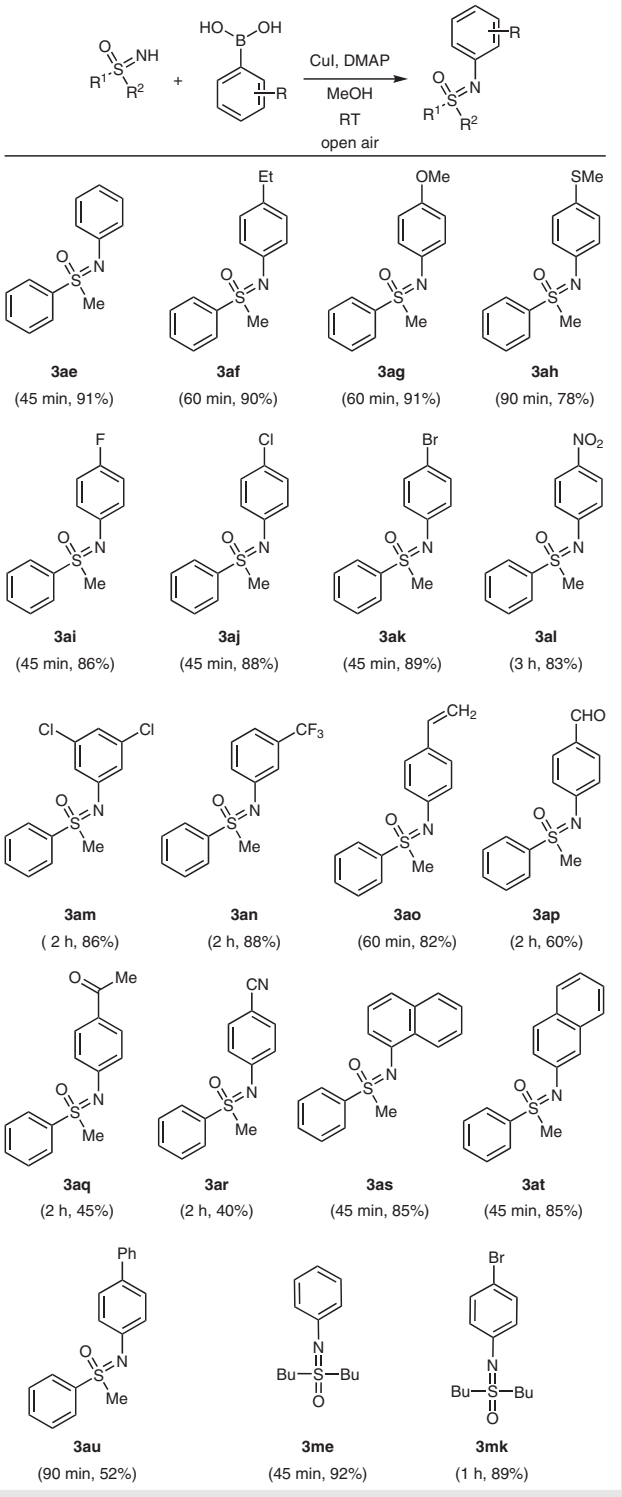
Methionine sulfoximine (MSO) is a biologically relevant sulfoximine that plays an important role in drug discovery.[16] It is noteworthy that so far no method has been developed for the *N*-arylation of methionine sulfoximine. In this context, protected L-methionine sulfoximine was subjected to *N*-arylation with simple as well as sterically hindered arylboronic acids (Scheme 4). To our delight, *N*-arylated L-methionine sulfoximines were obtained in 78–91% yield



Scheme 1 *N*-Arylation of sulfoximine **1a** using sterically hindered arylboronic acids. *Reagents and conditions*: Sulfoximine (150 mg, 1 equiv), arylboronic acid (1.5 equiv), CuI (0.1 equiv), and DMAP (1.0 equiv) were stirred in MeOH (2 mL) under open air. Isolated yields are shown. For **3ac**, arylboronic acid (2.4 equiv) and CuI (0.2 equiv) were used.

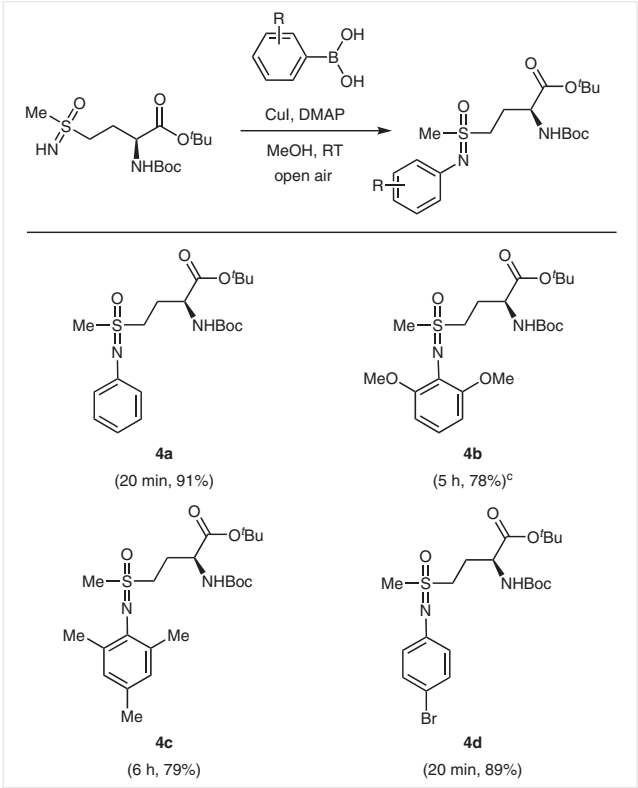


Scheme 2 *N*-Arylation of various sulfoximines using 4-methylphenylboronic acid. *Reagents and conditions*: Sulfoximine (150 mg, 1 equiv), 4-methylphenylboronic acid (1.5 equiv), CuI (0.1 equiv), and 4-DMAP (1.0 equiv) were stirred in MeOH (2 mL) under open air. Isolated yields are shown.



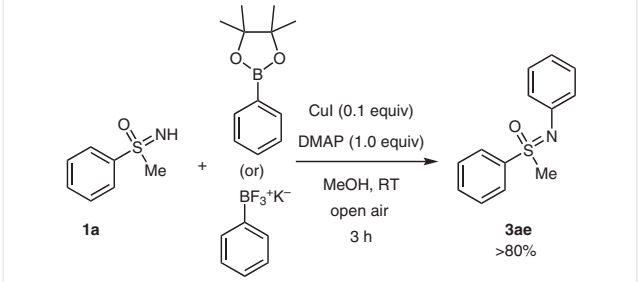
Scheme 3 *N*-Arylation of *S*-methyl-*S*-phenylsulfoximine (**1a**) using various arylboronic acids. *Reagents and conditions*: Sulfoximine (150 mg, 1 equiv), arylboronic acid (1.5 equiv), CuI (0.1 equiv), and 4-DMAP (1.0 equiv) were stirred in MeOH (2 mL) at RT under open air. Isolated yields are shown.

under optimized conditions (Scheme 4, 4a–d), which reveals a great versatility of the developed protocol.



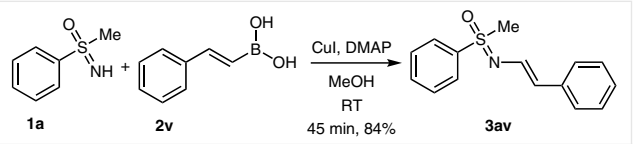
Scheme 4 *N*-Arylation of bioactive L-methionine sulfoximine with arylboronic acids. *Reagents and conditions*: Sulfoximine (150 mg, 1 equiv), arylboronic acid (1.5 equiv), CuI (0.018 g, 0.1 equiv), DMAP (0.118 g, 1.0 equiv), and MeOH (2 mL) were stirred at RT under open air. Isolated yields are shown. For **4b**, arylboronic acid (2.4 equiv) and CuI (0.2 equiv) were used.

It is also noteworthy that the arylboronic acid surrogates such as phenylboronic acid pinacol ester and potassium phenyltrifluoroborate also participated in the coupling reaction efficiently (Scheme 5). Further, we have attempted to prepare the *N*-vinylsulfoximines[17] using vinylboronic



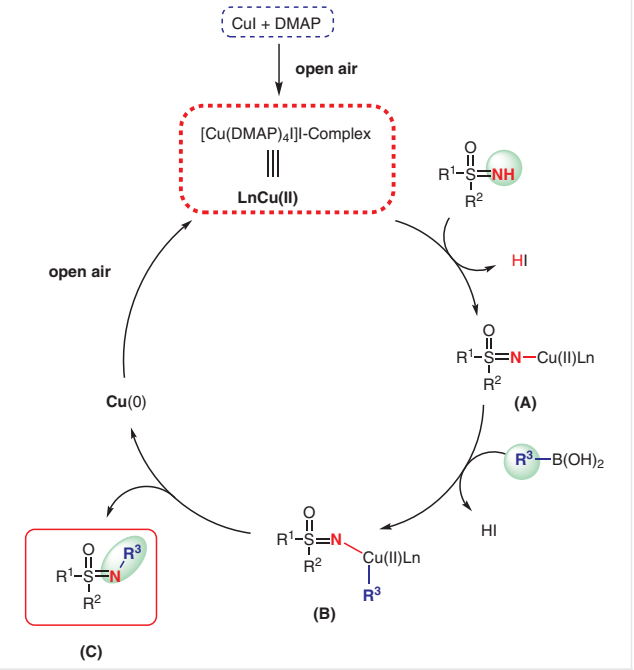
Scheme 5 *N*-Arylation with phenylboronic acid surrogates

acid. In this context, the optimized reaction conditions were well suited to the task with *N*-vinyl-*S*-methyl-*S*-phenylsulfoximine being obtained in 84% yield within 45 minutes at room temperature (Scheme 6, **3av**).



Scheme 6 *N*-Vinylation with vinylboronic acid **2v**

The mechanism of Chan–Lam coupling reaction is well documented in the literature. However, the role of 4-DMAP in the *N*-arylation of sulfoximine with sterically hindered arylboronic acid is not clear to us. Based on the previous reports,[14] a plausible mechanism has been proposed for *N*-arylation of sulfoximine using arylboronic acids (Scheme 7). First, CuI and 4-DMAP provides Cu(II)-complex in situ under open air.[14e] This Cu(II) complex undergoes ligand exchange with sulfoximine to give the intermediate **A**. Subsequently, arylboronic acid undergoes *trans*-metalation with the complex **A** and forms the intermediate **B**. Finally, the reductive elimination of **B** provides the desired *N*-arylated product and copper(0) species. Under open air, the reduced Cu(0) catalyst was re-oxidized to Cu(II) species and the catalytic cycle is resumed.



Scheme 7 Proposed mechanism for *N*-arylation of sulfoximine with arylboronic acid

In conclusion, *N*-arylation of sulfoximines with arylboronic acid was demonstrated using a catalytic amount of copper(I) iodide and 4-DMAP in methanol at room temperature. A wide range of aryl, alkyl, diaryl, arylbenzyl, dibenzyl, and dialkyl sulfoximines were *N*-arylated with sterically hindered arylboronic acids as well as library of other substituted arylboronic acids. All reactions took place at room temperature and provided good to excellent yields of *N*-arylsulfoximines in a short span of time. For the first time, we have also demonstrated the *N*-arylation of biologically relevant L-methionine sulfoximine with different arylboronic acids at room temperature. Surprisingly, the optimized reaction was well suited to the task of *N*-arylation of sulfoximine with arylboronic acid surrogates and *N*-vinylation of sulfoximine with *trans*-2-phenylvinylboronic acid. Overall, the current methodology appears to be more general from a synthetic point of view, and thereby promises to find wide applications in organic synthesis.

Starting materials were prepared using either literature procedures or modified literature procedures.[18] Boronic acids were purchased from Aldrich and Alfa Aesar chemicals. All reactions were performed in round-bottomed flasks under open air. Solvents and other chemicals were purchased from commercial sources and used without further purification. TLC was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV), and then further analyzed by using an I_2 chamber or ninhydrin strain. Column chromatography (cc) was performed on silica gel (60–120 mesh) using an EtOAc/hexane mixture as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer and mass spectra were measured on a Waters Quattro Micro V 4.1.

N-Arylation of Sulfoximines with Arylboronic Acids; General Procedure

A mixture of the respective sulfoximine (150 mg, 1 equiv, for **3aa**, **3ba**, **3ja**, **3ab**, **3ac**, **3ad**-**3nd**, **3ae**-**3au**, **3me** and **3mk**) or (200 mg, 1 equiv, for 3ca-3ia and 3ka), CuI (10 mol%), and 4-DMAP (1 equiv) was stirred in MeOH (2 mL) under open air at RT for 5 min. The appropriate arylboronic acid or arylboronic acid surrogate or vinylboronic acid (1.5 equiv) was added to the reaction mixture and allowed to stir at RT. The progress of reaction was monitored by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 and washed with distilled water, aq $NaHCO_3$, and brine. The organic layer was dried (anhyd Na_2SO_4), filtered, and evaporated on a rotary evaporator. The crude product was purified by silica gel column chromatography using EtOAc/hexane as an eluent to obtain the desired products.

N-(2,4,6-Trimethylphenyl)-*S*,*S*-methylphenylsulfoximine (3aa)

Yield: 235 mg (89%); pale yellow oil; cc: 20% EtOAc/hexane; R_f = 0.25.

IR (KBr, film): 1449, 1232, 1221, 749 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.9 Hz, 2 H_{arom}), 7.59 (m, 3 H_{arom}), 6.84 (s, 2 H_{arom}), 3.02 (s, 3 H, CH_3), 2.33 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.4, 138.0, 133.9, 133.1, 132.5, 129.3, 129.2, 128.0, 43.3, 20.8, 20.1.

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{16}H_{20}NOS$: 274.1226; found: 274.1257.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-heptylphenylsulfoximine (3ba)**

Yield: 199 mg (87%); transparent liquid; cc: 10% EtOAc/hexane; R_f = 0.28.

IR (KBr, film): 3280, 2936, 1454, 1218, 1123, 991, 754, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.58 (m, 1 H_{arom}), 7.52 (t, *J* = 7.4 Hz, 2 H_{arom}), 6.78 (s, 2 H_{arom}), 3.30 (m, 1 H, CH_2), 3.05 (m, 1 H, CH_2), 2.30 (s, 6 H, 2 × CH_3), 2.20 (s, 3 H, CH_3), 1.77–1.63 (m, 2 H, CH_2), 1.58–1.44 (m, 1 H, CH_2), 1.23–1.13 (m, 6 H, 3 × CH_2, 1 H, CH_2), 0.83–0.78 (m, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2, 138.3, 133.7, 132.9, 132.1, 129.2, 129.1, 128.6, 56.4, 31.6, 28.8, 28.4, 23.8, 22.6, 20.8, 20.4, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{32}NOS$: 358.2199; found: 358.2195.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-isopropylphenylsulfoximine (3ca)**

Yield: 279 mg (85%); transparent liquid; cc: 10% EtOAc/hexane; R_f = 0.29.

IR (KBr, film): 3024, 2926, 1519, 1279, 1258, 1087, 1069, 1033 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.57–7.41 (m, 3 H_{arom}), 6.72 (s, 2 H_{arom}), 3.53–3.42 (m, 1 H, CH), 2.25 (s, 6 H, 2 × CH_3), 2.16 (s, 3 H, CH_3), 1.42 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.19 (d, *J* = 6.7 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.0, 138.9, 132.9, 132.7, 131.4, 129.2, 129.18, 129.12, 58.3, 20.8, 20.7, 17.4, 16.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{24}NOS$: 302.1573; found: 302.1576.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-ethyl(4-methoxyphenyl)sulfoximine (3da)**

Yield: 286 mg (90%); transparent oil; cc: 20% EtOAc/hexane; R_f = 0.24.

IR (KBr, film): 3025, 2929, 1517, 1296, 1178, 1058, 1031, 1024, 990, 764 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.6 Hz, 2 H_{arom}), 6.98 (d, *J* = 8.8 Hz, 2 H_{arom}), 6.78 (s, 2 H_{arom}), 3.85 (s, 3 H, CH_3), 3.29 (m, 1 H, CH_2), 3.04 (m, 1 H, CH_2), 2.31 (s, 6 H, 2 × CH_3), 2.19 (s, 3 H, CH_3), 1.17 (t, *J* = 7.3 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.3, 138.6, 133.7, 132.0, 131.0, 130.7, 129.1, 114.4, 55.8, 50.8, 20.8, 20.4, 8.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{24}NO_2S$: 318.1522; found: 318.1523.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-(4-bromophenyl)methylsulfoximine (3ea)**

Yield: 264 mg (88%); transparent oil; cc: 10% EtOAc/hexane; R_f = 0.25.

IR (KBr, film): 3036, 2928, 1586, 1474, 1289, 1214, 1181, 1093, 1033 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.68 (d, *J* = 8.5 Hz, 2 H_{arom}), 6.82 (s, 2 H_{arom}), 3.02 (s, 3 H, CH_3), 2.29 (s, 6 H, 2 × CH_3), 2.22 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.6, 137.8, 133.8, 132.7, 132.6, 129.7, 129.3, 128.3, 43.6, 20.8, 20.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}BrNOS$: 352.0365; found: 352.0367.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-methyl(4-nitrophenyl)sulfoximine (3fa)**

Yield: 276 mg (87%); yellow oil; cc: 5–10% EtOAc/hexane; R_f = 0.32.

IR (KBr, film): 3088, 3022, 2998, 2912, 1696, 1518, 1352, 1289, 1098, 1057 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.9 Hz, 2 H_{arom}), 8.29 (d, *J* = 8.9 Hz, 2 H_{arom}), 6.82 (s, 2 H_{arom}), 3.12 (s, 3 H, CH_3), 2.27 (s, 6 H, 2 × CH_3), 2.22 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.6, 148.2, 137.2, 133.6, 133.1, 129.4, 127.1, 124.6, 43.80, 20.8, 20.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}N_2O_3S$: 319.1111; found: 319.1111.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-diphenylsulfoximine (3ga)**

Yield: 259 mg (84%); transparent oil; cc: 10% EtOAc/hexane; R_f = 0.31.

IR (KBr, film): 3089, 2913, 2874, 2380, 2342, 1461, 1274, 1218, 1138, 1109, 1091, 954, 746 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.88 (m, 4 H_{arom}), 7.49–7.48 (m, 2 H_{arom}), 7.45–7.40 (m, 4 H_{arom}), 6.72 (s, 2 H_{arom}), 2.20 (s, 6 H, 2 × CH_3), 2.16 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.4, 137.9, 133.7, 132.4, 132.1, 129.15, 129.10, 128.1, 20.82, 20.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{22}NOS$: 336.1417; found: 336.1419.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-benzylphenylsulfoximine (3ha)**

Yield: 260 mg (81%); transparent oil; cc: 5% EtOAc/hexane; R_f = 0.24.

IR (KBr, film): 3053, 2914, 2838, 2352, 2334, 1445, 1286, 1219, 1134, 1123, 1086, 961, 741 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.4 Hz, 2 H_{arom}), 7.56 (t, *J* = 7.6 Hz, 1 H_{arom}), 7.43 (t, *J* = 7.9 Hz, 2 H_{arom}), 7.22 (d, *J* = 7.0 Hz, 1 H_{arom}), 7.15 (t, *J* = 7.4 Hz, 2 H_{arom}), 6.89 (d, *J* = 7.7 Hz, 2 H_{arom}), 6.84 (s, 2 H_{arom}), 4.48–4.16 (ABq, *J* = 13.5 Hz, 4 H, 2 × CH_2), 2.36 (s, 6 H, 2 × CH_3), 2.24 (s, 3 H, CH_3).

NMR (125 MHz, $CDCl_3$): δ = 138.6, 138.2, 133.9, 133.2, 132.4, 131.1, 129.7, 129.4, 129.3, 128.9, 128.43, 128.40, 62.8, 20.8, 20.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}NOS$: 350.1573; found: 350.1567.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-dibenzylsulfoximine (3ia)**

Yield: 274 mg (82%); white solid; mp 131 °C; cc: 5% EtOAc/hexane; R_f = 0.26.

IR (KBr, film): 3274, 3111, 3058, 3012, 2986, 2976, 1514, 1445, 1418, 1232, 1125, 1071, 1067, 761, 691, 585 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.34 (s, 10 H_{arom}), 6.76 (s, 2 H_{arom}), 4.25–4.17 (ABq, *J* = 12.5 Hz, 4 H, 2 × CH_2), 2.19 (s, 3 H, CH_3), 2.07 (s, 6 H, 2 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.1, 134.0, 132.5, 131.5, 129.3, 129.1, 128.8, 58.5, 20.8, 19.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{26}NOS$: 364.1730; found: 364.1732.

***N*-(2,4,6-Trimethylphenyl)-*S*,*S*-dibutylsulfoximine (3ja)**

Yield: 177 mg (71%); pale yellow viscous oil; cc: 10% EtOAc/hexane; R_f = 0.34.

IR (KBr, film): 3272, 2960, 1724, 1466, 1380, 1242, 1101, 1016, 807, 729 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.79 (s, 2 H), 3.07–2.97 (m, 4 H), 2.27 (s, 6 H), 2.20 (s, 3 H), 1.84–1.78 (m, 4 H), 1.43–1.39 (m, 4 H), 0.92 (t, *J* = 7.3 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.6, 133.8, 132.1, 129.0, 52.9, 25.7, 22.1, 20.8, 19.9, 13.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{30}NOS$: 296.2048; found: 296.2078.

N-(2,4,6-Trimethylphenyl)-*S*,*S*-ethyl(2-pyridyl)sulfoximine (3ka)

Yield: 311 mg (92%); transparent liquid; cc: 10% EtOAc/hexane; R_f = 0.30.

IR (KBr, film): 3353, 3034, 2888, 2779, 2364, 2028, 1574, 1477, 1378, 1259, 1181, 1094, 983, 814 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 4.5 Hz, 1 H_{arom}), 7.78 (d, *J* = 7.8 Hz, 1 H_{arom}), 7.73 (t, *J* = 7.6 Hz, 1 H_{arom}), 7.37 (dd, *J* = 7.4, 4.8 Hz, 1 H_{arom}), 6.68 (s, 2 H_{arom}), 3.85 (m, 1 H, CH_2), 3.63 (m, 1 H, CH_2), 2.14 (s, 3 H, CH_3), 2.08 (s, 6 H, 2 × CH_3), 1.37 (t, *J* = 7.3 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 149.7, 137.8, 137.6, 134.0, 132.1, 128.7, 126.3, 122.3, 46.7, 20.7, 19.5, 7.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{21}N_2OS$: 289.1369; found: 289.1366.

N-(2,6-Dimethylphenyl)-*S*,*S*-methylphenylsulfoximine (3ab)

Yield: 210 mg (84%); yellow oil; cc: 20% EtOAc/hexane; R_f = 0.48.

IR (KBr, film): 1474, 1272, 1089, 756, 733 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.5 Hz, 2 H_{arom}), 7.59 (m, 3 H_{arom}), 7.01 (d, *J* = 7.4 Hz, 2 H_{arom}), 6.87 (t, *J* = 7.4 Hz, 1 H_{arom}), 3.03 (s, 3 H, CH_3), 2.36 (s, 6 H, 2 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.4, 140.9, 134.2, 133.2, 129.4, 128.4, 128.0, 123.3, 43.6, 20.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NOS$: 260.1104; found: 260.1093.

N-(2,6-Dimethoxyphenyl)-*S*,*S*-methylphenylsulfoximine (3ac)

Yield: 228 mg (81%); yellow oil; cc: 40% EtOAc/hexane; R_f = 0.38.

IR (KBr, film): 1449, 1284, 1079, 765 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.7 Hz, 2 H_{arom}), 7.52 (m, 3 H_{arom}), 6.87 (t, *J* = 8.3 Hz, 1 H_{arom}), 6.51 (d, *J* = 8.3 Hz, 2 H_{arom}), 3.70 (s, 6 H, 2 × CH_3), 3.15 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 143.1, 132.5, 129.1, 127.9, 122.6, 122.5, 105.2, 56.1, 45.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{19}NO_3S$: 292.1002; found: 292.0991.

N-(4-Methylphenyl)-*S*,*S*-methylphenylsulfoximine (3ad)

Yield: 215 mg (91%); white solid; mp 112–114 °C; cc: 30% EtOAc/hexane; R_f = 0.18.

IR (KBr, film): 3020, 2923, 1498, 1504, 1287, 1263, 1091, 1069, 1034 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.52 (m, 3 H_{arom}), 6.90 (s, 4 H_{arom}), 3.20 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.3, 139.6, 133.3, 131.2, 129.7, 129.6, 128.8, 123.3, 46.0, 20.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{16}NOS$: 246.0953; found: 246.0940.

N-(4-Methylphenyl)-*S*,*S*-ethylphenylsulfoximine (3bd)

Yield: 230 mg (92%); brown solid; mp 86 °C; cc: 30% EtOAc/hexane; R_f = 0.24.

IR (KBr, film): 3369, 3057, 2929, 2786, 2359, 2048, 1594, 1487, 1394, 1265, 1193, 1093 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.52 (m, 3 H_{arom}), 6.90 (s, 4 H_{arom}), 3.30 (m, 2 H, CH_2), 2.18 (s, 3 H, CH_3), 1.27 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5, 137.6, 133.2, 130.9, 129.7, 129.6, 129.5, 123.3, 51.9, 20.8, 7.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NOS$: 260.1109; found: 260.1102.

N-(4-Methylphenyl)-*S*,*S*-phenylpropylsulfoximine (3cd)

Yield: 243 mg (92%); white solid; mp 110 °C; cc: 30% EtOAc/hexane; R_f = 0.22.

IR (KBr, film): 3020, 2923, 1505, 1287, 1263, 1094, 1069, 1034 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.6 Hz, 2 H_{arom}), 7.51 (m, 3 H_{arom}), 6.89 (s, 4 H_{arom}), 3.28 (m, 1 H, CH_2), 3.23–3.16 (m, 1 H, CH_2), 2.17 (s, 3 H, CH_3), 1.76 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5, 140.6, 138.3, 133.2, 130.8, 129.7, 129.5, 123.3, 59.2, 20.8, 16.7, 12.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{20}NOS$: 274.1266; found: 274.1283.

N-(4-Methylphenyl)-*S*,*S*-isopropylphenylsulfoximine (3dd)

Yield: 230 mg (87%); pale yellow oil; cc: 20% EtOAc/hexane; R_f = 0.34.

IR (KBr, film): 3020, 2923, 1505, 1287, 1263, 1094, 1069, 1034 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.5 Hz, 2 H_{arom}), 7.54 (t, *J* = 7.2 Hz, 1 H_{arom}), 7.47 (t, *J* = 7.4 Hz, 2 H_{arom}), 6.89 (s, 4 H_{arom}), 3.39 (m, 1 H, CH), 2.17 (s, 3 H, CH_3), 1.40 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.26 (d, *J* = 6.6 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.9, 136.2, 133.1, 130.58, 130.55, 129.6, 129.3, 123.2, 57.0, 20.8, 16.4, 15.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}NOSNa$: 296.1085; found: 296.1097.

N-(4-Methylphenyl)-*S*,*S*-heptylphenylsulfoximine (3ed)

Yield: 186 mg (90%); white solid; mp 76 °C; cc: 10% EtOAc/hexane; R_f = 0.50.

IR (KBr, film): 3272, 2927, 1445, 1223, 1110, 991, 752, 689 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.1 Hz, 2 H_{arom}), 7.54–7.46 (m, 3 H_{arom}), 6.90 (s, 4 H_{arom}), 3.34–3.28 (m, 1 H, CH_2), 3.24–3.18 (m, 1 H, CH_2), 2.17 (s, 3 H, CH_3), 1.79–1.78 (m, 1 H, CH_2), 1.67–1.65 (m, 1 H, CH_2), 1.33–1.15 (m, 8 H, 4 × CH_2), 0.83 (t, *J* = 6.8 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5, 138.3, 133.1, 130.8, 130.1, 129.6, 129.52, 129.50, 123.3, 115.4, 57.6, 31.5, 28.8, 28.2, 22.8, 22.6, 20.8, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}NOS$: 330.1886; found: 330.1889.

***N*-(4-Methylphenyl)-*S*,*S*-(4-methylphenyl)methylsulfoximine (3fd)**

Yield: 204 mg (89%); pale yellow viscous oil; cc: 20% EtOAc/hexane; R_f = 0.40.

IR (KBr, film): 3021, 2922, 1505, 1288, 1197, 1093, 1033, 1013 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2 H_{arom}), 7.28 (d, *J* = 7.9 Hz, 2 H_{arom}), 6.90 (s, 4 H_{arom}), 3.18 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.1, 142.5, 136.6, 131.0, 130.3, 129.7, 128.8, 123.3, 46.2, 21.7, 20.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{18}NOS$: 260.1109; found: 260.1149.

***N*-(4-Methylphenyl)-*S*,*S*-(4-bromophenyl)methylsulfoximine (3gd)**

Yield: 191 mg (92%); white solid; mp 150 °C; cc: 30% EtOAc/hexane; R_f = 0.36.

IR (KBr, film): 3026, 2926, 1588, 1486, 1288, 1201, 1094, 1030 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.3 Hz, 2 H_{arom}), 7.62 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.91 (d, *J* = 8.1 Hz, 2 H_{arom}), 6.87 (d, *J* = 8.0 Hz, 2 H_{arom}), 3.20 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.9, 138.6, 132.9, 131.5, 130.4, 129.8, 128.6, 123.3, 46.1, 20.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{15}BrNOS$: 324.0058; found: 324.0056.

***N*-(4-Methylphenyl)-*S*,*S*-methyl-(4-nitrophenyl)sulfoximine (3hd)**

Yield: 198 mg (91%); yellow solid; mp 85 °C; cc: 20% EtOAc/hexane; R_f = 0.28.

IR (KBr, film): 3094, 3029, 2932, 1529, 1348, 1294, 1089, 1041 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.5 Hz, 2 H_{arom}), 8.13 (d, *J* = 8.5 Hz, 2 H_{arom}), 6.92 (d, *J* = 8.1 Hz, 2 H_{arom}), 6.86 (d, *J* = 8.0 Hz, 2 H_{arom}), 3.27 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.7, 145.9, 141.3, 132.1, 130.3, 130.0, 124.8, 123.4, 45.8, 20.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{15}N_2O_3S$: 291.0803; found: 291.0804.

***N*-(4-Methylphenyl)-*S*,*S*-diphenylsulfoximine (3id)**

Yield: 178 mg (84%); white solid; mp 171 °C; cc: 20% EtOAc/hexane; R_f = 0.52.

IR (KBr, film): 3083, 2905, 2877, 2381, 2341, 1467, 1286, 1208, 1119, 1104, 1093, 748 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.6 Hz, 4 H_{arom}), 7.50–7.41 (m, 6 H_{arom}), 7.04 (d, *J* = 8.0 Hz, 2 H_{arom}), 6.93 (d, *J* = 7.9 Hz, 2 H_{arom}), 2.19 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.0, 141.1, 132.7, 131.1, 129.7, 129.4, 128.7, 123.7, 20.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}NOS$: 308.1109; found: 308.1100.

***N*-(4-Methylphenyl)-*S*,*S*-benzylphenylsulfoximine (3jd)**

Yield: 173 mg (83%); pale yellow solid; mp 148–151 °C; cc: 20% EtOAc/hexane; R_f = 0.46.

IR (KBr, film): 3054, 2917, 2847, 2364, 2333, 1454, 1298, 1218, 1136, 1101, 1096 743 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.49 (t, *J* = 7.4 Hz, 1 H_{arom}), 7.35 (t, *J* = 7.6 Hz, 2 H_{arom}), 7.26 (t, *J* = 7.4 Hz, 1 H_{arom}), 7.18 (t, *J* = 7.5 Hz, 2 H_{arom}), 6.99–6.91 (m, 6 H_{arom}), 4.51 (ABq, *J* = 13.7 Hz, 2 H, CH_2), 2.20 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5, 136.7, 133.2, 131.4, 131.0, 129.9, 129.8, 129.0, 128.8, 128.6, 128.4, 123.4, 63.3, 20.8.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{19}NOSNa$: 344.1085; found: 344.1070.

***N*-(4-Methylphenyl)-*S*,*S*-dibenzylsulfoximine (3kd)**

Yield: 169 mg (81%); pale yellow solid; mp 86 °C; cc: 20% EtOAc/hexane; R_f = 0.44.

IR (KBr, film): 3275, 3105, 3062, 3010, 2996, 2908, 1504, 1438, 1406, 1242, 1116, 1063, 1037, 760, 698, 580 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 6.2 Hz, 10 H_{arom}), 7.02–6.96 (m, 4 H_{arom}), 4.31–4.25 (ABq, *J* = 14.0 Hz, 4 H, 2 × CH_2), 2.26 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.7, 131.4, 129.9, 129.0, 128.9, 128.7, 123.4, 120.8, 57.5, 20.9.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{22}NOS$: 336.1422; found: 336.1408.

***N*-(4-Methylphenyl)-*S*,*S*-ethyl(2-pyridyl)sulfoximine (3ld)**

Yield: 213 mg (93%); pale yellow solid; mp 165 °C; cc: 20–30% EtOAc/hexane; R_f = 0.46.

IR (KBr, film): 3364, 3047, 2898, 2781, 2354, 2038, 1589, 1483, 1388, 1261, 1184, 1091,973, 814, 757 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.2 Hz, 1 H_{arom}), 8.08 (d, *J* = 7.8 Hz, 1 H_{arom}), 7.84 (t, *J* = 7.7 Hz, 1 H_{arom}), 7.45–7.40 (m, 1 H_{arom}), 6.94–6.86 (m, 4 H_{arom}), 3.65 (dq, *J* = 14.7, 7.4 Hz, 1 H, CH_2), 3.55 (dq, *J* = 14.7, 7.5 Hz, 1 H, CH_2), 2.17 (s, 3 H, CH_3), 1.28 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 150.5, 142.1, 137.9, 131.3, 129.6, 126.8, 124.6, 123.5, 47.9, 20.8, 7.2.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{17}N_2OS$: 261.1062; found: 261.1073.

***N*-(4-Methylphenyl)-*S*,*S*-dibutylsulfoximine (3md)**

Yield: 205 mg (91%); transparent oil; cc: 10% EtOAc/hexane; R_f = 0.38.

IR (KBr, film): 3272, 3018, 2940, 1724, 1486, 1380, 1242, 1101, 1071, 1036, 807, 729 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.95 (d, *J* = 8.3 Hz, 2 H_{arom}), 3.17–3.03 (m, 4 H, 2 × CH_2), 2.25 (s, 3 H, CH_3), 1.82–1.76 (m, 4 H, 2 × CH_2), 1.44–1.36 (m, 4 H, 2 × CH_2), 0.83 (t, *J* = 7.4 Hz, 6 H, 2 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.8, 131.2, 129.8, 123.6, 51.7, 25.3, 21.9, 20.9, 13.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{26}NOS$: 268.1735; found: 268.1755.

***N*-(4-Methylphenyl)-*S*,*S*-cyclohexylheptylsulfoximine (3nd)**

Yield: 170 mg (83%); yellow oil; cc: 15% EtOAc/hexane; R_f = 0.24.

IR (KBr, film): 3310, 2920, 2875, 2814, 2313, 1981, 1504, 1644, 1450, 1277, 1129, 1094, 1034, 958, 849, 773, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.97 (s, 4 H_{arom}), 3.10–3.04 (m, 2 H, CH_2), 3.02–2.96 (m, 1 H, CH_2), 2.33–2.15 (m, 1 H, CH_2, 2 H, CH_2), 2.24 (s, 3 H, CH_3), 1.91–1.89 (m, 2 H, CH_2), 1.81–1.75 (m, 2 H, CH_2), 1.69 (d, *J* = 12.2 Hz, 1 H, CH_2), 1.64–1.48 (m, 2 H, CH_2), 1.33–1.23 (m, 10 H, 5 × CH_2), 0.84 (t, *J* = 6.8 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 130.9, 130.1, 129.7, 123.6, 115.3, 61.7, 48.8, 31.6, 28.9, 28.7, 26.4, 26.0, 25.7, 25.6, 25.3, 22.8, 22.7, 20.9, 14.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{35}NOS$: 336.2356; found: 336.2351.

N-Phenyl-*S*,*S*-methylphenylsulfoximine (3ae)

Yield: 203 mg (91%); white solid; mp 100–101 °C; cc: 30% EtOAc/hexane; R_f = 0.22.

IR (KBr, film): 3044, 2089, 1614, 1486, 1267, 1202, 1093, 1040 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.88 (m, 2 H_{arom}), 7.48 (m, 3 H_{arom}), 7.05 (t, *J* = 7.8 Hz, 2 H_{arom}), 6.94 (d, *J* = 7.5 Hz, 2 H_{arom}), 6.80 (t, *J* = 7.3 Hz, 1 H_{arom}), 3.17 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.1, 139.7, 133.4, 129.7, 129.2, 128.8, 123.5, 121.9, 46.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{14}NOS$: 232.0796; found: 232.0778.

N-(4-Ethylphenyl)-*S*,*S*-methylphenylsulfoximine (3af)

Yield: 225 mg (90%); pale yellow oil; cc: 30% EtOAc/hexane; R_f = 0.28.

IR (KBr, film): 3299, 1615, 1517, 1286, 1225, 1090, 1010, 833 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.7 Hz, 2 H_{arom}), 7.53 (m, 3 H_{arom}), 6.94 (d, *J* = 8.4 Hz, 2 H_{arom}), 6.91 (d, *J* = 8.4 Hz, 2 H_{arom}), 3.20 (s, 3 H), 2.49 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.12 (t, *J* = 7.6 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.4, 139.7, 137.6, 133.3, 129.6, 128.8, 128.5, 123.3, 46.1, 28.2, 15.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NOS$: 260.1109; found: 260.1100.

N-(4-Methoxyphenyl)-*S*,*S*-methylphenylsulfoximine (3ag)

Yield: 229 mg (91%); white solid; mp 102–106 °C; cc: 40% EtOAc/hexane; R_f = 0.18.

IR (KBr, film): 3012, 2930, 2833, 1513, 1444, 1263, 1239, 1042 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.90 (m, 2 H_{arom}), 7.58–7.47 (m, 3 H_{arom}), 6.93 (d, *J* = 9.0 Hz, 2 H_{arom}), 6.66 (d, *J* = 9.0 Hz, 2 H_{arom}), 3.67 (s, 3 H, CH_3), 3.19 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0, 139.7, 138.1, 133.3, 129.6, 128.9, 124.5, 114.5, 55.5, 45.8.

HRMS (ESI-TOF): *m*/*z* [M+ H]$^+$ calcd for $C_{14}H_{16}NO_2S$: 262.0902; found: 262.0887.

N-(4-Thiomethylphenyl)-*S*,*S*-methylphenylsulfoximine (3ah)

Yield: 209 mg (78%); yellow oil; cc: 20% EtOAc/hexane; R_f = 0.42.

IR (KBr, film): 3012, 2930, 2833, 1513, 1444, 1263, 1239, 1042 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.56 (t, *J* = 7.2 Hz, 1 H_{arom}), 7.50 (t, *J* = 7.6 Hz, 2 H_{arom}), 7.04 (d, *J* = 8.4 Hz, 2 H_{arom}), 6.92 (d, *J* = 8.4 Hz, 2 H_{arom}), 3.21 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.1, 139.3, 133.4, 130.1, 129.7, 128.9, 128.7, 123.9, 46.1, 17.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{16}NOS_2$: 278.0673; found: 278.0693.

N-(4-Fluorophenyl)-*S*,*S*-methylphenylsulfoximine (3ai)

Yield: 207 mg (86%); white solid; mp 82–86 °C; cc: 40% EtOAc/hexane; R_f = 0.28.

IR (KBr, film): 3053, 3002, 2928, 1445, 1281, 1263, 1208, 1093, 1032, 821, 745, 679 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.7 Hz, 2 H_{arom}), 7.48 (m, 3 H_{arom}), 6.88 (d, *J* = 8.7, 2 H_{arom}), 6.72 (d, *J* = 8.7 Hz, 2 H_{arom}), 3.15 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3 (d, $J_{C,F}$ = 239.0), 141.0 (d, $J_{C,F}$ = 2.6), 139.1, 133.3, 129.6, 128.6, 124.4 (d, $J_{C,F}$ = 7.7 Hz), 115.5 (d, $J_{C,F}$ = 22.1 Hz), 46.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}FNOS$: 250.0702; found: 250.0687.

N-(4-Chlorophenyl)-*S*,*S*-methylphenylsulfoximine (3aj)

Yield: 226 mg (88%); white solid; mp 64–66 °C; cc: 40% EtOAc/hexane; R_f = 0.38.

IR (KBr, film): 3064, 3014, 2926, 1487, 1402, 1371, 1291, 1198, 1091, 738, 681 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.56 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.49 (t, *J* = 7.6 Hz, 2 H_{arom}), 7.02 (d, *J* = 8.6 Hz, 2 H_{arom}), 6.90 (d, *J* = 8.6 Hz, 2 H_{arom}), 3.20 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.8, 139.0, 133.5, 129.7, 129.0, 128.7, 126.8, 124.5, 46.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}ClNOS$: 266.0406; found: 266.0396.

N-(4-Bromophenyl)-*S*,*S*-methylphenylsulfoximine (3ak)

Yield: 266 mg (89%); white solid; mp 109–111 °C; cc: 30% EtOAc/hexane; R_f = 0.44.

IR (KBr, film): 3109, 3026, 2926, 1485, 1401, 1267, 1203, 1007, 821, 732 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.53 (m, 3 H_{arom}), 7.17 (d, *J* = 8.2 Hz, 2 H_{arom}), 6.85 (d, *J* = 8.2 Hz, 2 H_{arom}), 3.21 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.4, 138.9, 133.6, 132.0, 129.7, 128.7, 124.9, 114.4, 46.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}BrNOS$: 309.9901; found: 309.9896.

N-(4-Nitrophenyl)-*S*,*S*-methylphenylsulfoximine (3al)

Yield: 221 mg (83%); yellow solid; mp 149–150 °C; cc: 40% EtOAc/hexane; R_f = 0.22.

IR (KBr, film): 3097, 3020, 2913, 1592, 1294, 1050, 1013 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.7 Hz, 2 H_{arom}), 7.91 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.61 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.53 (t, *J* = 7.6 Hz, 2 H_{arom}), 6.97 (d, *J* = 8.7 Hz, 2 H_{arom}), 3.29 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.3, 152.8, 141.7, 138.2, 134.1, 130.0, 128.5, 126.3, 125.3, 122.5, 115.8, 46.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}N_2O_3S$: 277.0647; found: 277.0637.

N-(3,5-Dichlorophenyl)-*S*,*S*-methylphenylsulfoximine (3am)

Yield: 249 mg (86%); white solid; mp 83 °C; cc: 30% EtOAc/hexane; R_f = 0.40.

IR (KBr, film): 3109, 3026, 2926, 1485, 1401 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.62–7.51 (m, 3 H_{arom}), 6.87 (s, 2 H_{arom}), 6.81 (s, 1 H_{arom}), 3.22 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.5, 138.5, 134.9, 133.9, 129.9, 128.6, 121.8, 121.6, 46.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{12}Cl_2NOS$: 300.0017; found: 300.0011.

N-(3-Trifluoromethylphenyl)-*S*,*S*-methylphenylsulfoximine (3an)

Yield: 254 mg (88%); pale yellow oil; cc: 30% EtOAc/hexane; R_f = 0.28.

IR (KBr, film): 3129, 3016, 2936, 1486, 1401 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.63 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.56 (t, *J* = 7.5 Hz, 2 H_{arom}), 7.28 (d, *J* = 2.9 Hz, 1 H_{arom}), 7.24–7.09 (m, 3 H_{arom}), 3.28 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.8, 138.9, 133.7, 131.4 (q, $J_{C,F}$ = 32 Hz), 129.8, 129.5, 128.7, 126.1, 124.2 (q, $J_{C,F}$ = 272.5 Hz), 120.2 (q, *J* = 3.7 Hz), 118.3 (q, *J* = 3.9 Hz), 46.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}F_3NOS$: 300.0670; found: 300.0656.

N-(4-Vinylphenyl)-*S*,*S*-methylphenylsulfoximine (3ao)

Yield: 203 mg (82%); pale yellow oil; cc: 30% EtOAc/hexane; R_f = 0.16.

IR (KBr, film): 3022, 2910, 2833, 1622, 1513, 1263, 1239, 1042 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.53 (dt, *J* = 32.7, 7.5 Hz, 3 H_{arom}), 7.16 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.95 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.55 (dd, *J* = 17.6, 10.9 Hz, 1 H, CH), 5.53 (d, *J* = 17.6 Hz, 1 H, CH_2), 5.04 (d, *J* = 10.9 Hz, 1 H, CH_2), 3.22 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.0, 139.4, 136.6, 133.4, 131.2, 129.7, 128.7, 127.1, 123.3, 111.6, 46.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NOS$: 258.0953; found: 258.0958.

N-(4-Formylphenyl)-*S*,*S*-methylphenylsulfoximine (3ap)

Yield: 151 mg (60%); pale yellow solid; mp 92–94 °C; cc: 40% EtOAc/hexane; R_f = 0.38.

IR (KBr, film): 3001, 2921, 2836, 1688, 1595 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.75 (s, 1 H_{arom}), 7.93 (d, *J* = 7.8 Hz, 2 H_{arom}), 7.60 (t, *J* = 6.9 Hz, 3 H_{arom}), 7.53 (t, *J* = 7.7 Hz, 2 H_{arom}), 7.05 (d, *J* = 8.4 Hz, 2 H_{arom}), 3.28 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.3, 152.2, 138.7, 133.9, 131.4, 130.2, 130.0, 128.6, 123.0, 116.1, 46.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO_2S$: 260.0745; found: 260.0736.

N-(4-Acetylphenyl)-*S*,*S*-methylphenylsulfoximine (3aq)

Yield: 119 mg (45%); brown solid; mp 86–87 °C; cc: 40% EtOAc/hexane; R_f = 0.22.

IR (KBr, film): 3001, 2911, 2836, 1725, 1597 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.7 Hz, 2 H_{arom}), 7.71 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.59 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.52 (t, *J* = 7.6 Hz, 2 H_{arom}), 6.98 (d, *J* = 8.5 Hz, 2 H_{arom}), 3.26 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.3, 150.7, 138.8, 133.8, 130.7, 130.0, 129.9, 128.6, 122.6, 46.6, 26.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NO_2S$: 274.0902; found: 274.0892.

N-(4-Cyanophenyl)-*S*,*S*-methylphenylsulfoximine (3ar)

Yield: 99 mg (40%); pale yellow oil; cc: 40% EtOAc/hexane; R_f = 0.24.

IR (KBr, film): 3030, 2930, 2217, 1601, 1490, 1298 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.62 (t, *J* = 7.4 Hz, 1 H_{arom}), 7.55 (d, *J* = 7.6 Hz, 2 H_{arom}), 7.35 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.98 (d, *J* = 8.3 Hz, 2 H_{arom}), 3.27 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3, 138.5, 134.0, 133.4, 130.0, 128.6, 123.3, 119.8, 104.1, 46.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}N_2OS$: 257.0749; found: 257.0737.

N-(1-naphthyl)-*S*,*S*-methylphenylsulfoximine (3as)

Yield: 231 mg (85%); brown oil; cc: 30% EtOAc/hexane; R_f = 0.22.

IR (KBr, film): 3065, 3019, 2923, 1511, 1481, 1282, 1191, 1059 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 8.2 Hz, 1 H_{arom}), 7.99 (d, *J* = 7.9 Hz, 2 H_{arom}), 7.74 (d, *J* = 7.9 Hz, 1 H_{arom}), 7.56–7.44 (m, 5 H_{arom}), 7.37 (d, *J* = 8.1 Hz, 1 H_{arom}), 7.16 (t, *J* = 7.8 Hz, 1 H_{arom}), 7.08 (d, *J* = 7.4 Hz, 1 H_{arom}), 3.32 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.7, 139.4, 134.7, 133.4, 130.2, 129.7, 128.6, 127.9, 126.2, 126.0, 125.2, 124.1, 121.7, 116.6, 46.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{16}NOS$: 282.0953; found: 282.0942.

N-(2-Naphthyl)-*S*,*S*-methylphenylsulfoximine (3at)

Yield: 231 mg (85%); brown solid; mp 91–92 °C; cc: 30% EtOAc/hexane; R_f = 0.26.

IR (KBr, film): 3012, 2930, 1521, 1499, 1316, 1298, 1246, 1080, 1013 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.2 Hz, 2 H_{arom}), 7.54–7.31 (m, 6 H_{arom}), 7.24 (s, 1 H_{arom}), 7.17 (t, *J* = 6.9 Hz, 1 H_{arom}), 7.10 (d, *J* = 7.7 Hz, 2 H_{arom}), 3.12 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.0, 139.3, 134.5, 133.4, 129.7, 129.6, 128.86, 128.82, 127.5, 127.0, 126.0, 124.9, 123.8, 118.7, 46.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{16}NOS$: 282.0953; found: 282.0940.

N-(4-Benzylphenyl)-*S*,*S*-methylphenylsulfoximine (3au)

Yield: 154 mg (52%); white solid; mp 140–141 °C; cc: 30% EtOAc/hexane; R_f = 0.14.

IR (KBr, film): 3015, 3019, 2923, 1599, 1511, 1481, 1281, 836 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.6 Hz, 2 H_{arom}), 7.58 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.54–7.47 (m, 4 H_{arom}), 7.38–7.33 (m, 4 H_{arom}), 7.24 (t, *J* = 7.3 Hz, 1 H_{arom}), 7.07 (d, *J* = 8.4 Hz, 2 H_{arom}), 3.24 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.6, 141.0, 139.5, 134.5, 133.4, 129.7, 128.7, 127.8, 126.7, 123.6, 46.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}NOS$: 308.1109; found: 308.1103.

N-Phenylethynyl-*S*,*S*-methylphenylsulfoximine (3av)

Yield: 209 mg (84%); brown oil; cc: 30% EtOAc/hexane; R_f = 0.36.

IR (KBr, film): 1698, 1636, 1217, 1096, 983, 739, 695 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.3 Hz, 2 H_{arom}), 7.63 (t, *J* = 6.9 Hz, 1 H_{arom}), 7.57 (t, *J* = 7.3 Hz, 2 H_{arom}), 7.16 (m, 4 H_{arom}), 7.04 (m, 1 H_{arom}), 6.90 (d, *J* = 13.6 Hz, 1 H_{arom}), 6.19 (d, *J* = 13.6 Hz, 1 H_{arom}), 3.20 (s, 3 H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.4, 138.0, 133.7, 129.9, 129.8, 128.8, 128.5, 125.7, 125.1, 118.3, 45.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NOS$: 258.0953; found: 258.0930.

N-Phenyl-*S*,*S*-dibutylsulfoximine (3me)

Yield: 197 mg (92%); yellow viscous oil; cc: 10% EtOAc/hexane; R_f = 0.42.

IR (KBr, film): 3048, 2097, 1624, 1573, 1479, 1319, 1274, 1201, 1160, 1079, 943, 841 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 7.8 Hz, 2 H_{arom}), 7.06 (d, *J* = 7.4 Hz, 2 H_{arom}), 6.91 (t, *J* = 7.3 Hz, 1 H_{arom}), 3.17–3.06 (m, 4 H, 2 × CH_2), 1.83–1.76 (m, 4 H, 2 × CH_2), 1.43–1.37 (m, 4 H, 2 × CH_2), 0.91 (t, *J* = 7.3 Hz, 6 H, 2 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.7, 129.2, 123.6, 121.8, 51.8, 25.2, 21.8, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{24}NOS$: 254.1579; found: 254.1571.

N-(4-Bromophenyl)-*S*,*S*-dibutylsulfoximine (3mk)

Yield: 250 mg (89%); pale yellow oil; cc: 40% EtOAc/hexane; R_f = 0.38.

IR (KBr, film): 3272, 3020, 2960, 1726, 1476, 1381, 1262, 1101, 1056, 1002, 807, 729 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.7 Hz, 2 H_{arom}), 6.93 (d, *J* = 8.7 Hz, 2 H_{arom}), 3.16–3.04 (m, 4 H, 2 × CH_2), 1.81–1.76 (m, 4 H, 2 × CH_2), 1.43–1.38 (m, 4 H, 2 × CH_2), 0.91 (t, *J* = 7.3 Hz, 6 H, 2 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.1, 132.1, 125.1, 114.4, 52.0, 25.1, 21.8, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{23}BrNOS$: 332.0684; found: 332.0664.

N-Arylation of an L-Methionine Sulfoximine Derivative with Arylboronic Acids; General Procedure

A mixture of L-methionine sulfoximine derivative (200 mg, 0.59 mmol), CuI (11 mg, 10 mol%), and 4-DMAP (72 mg, 0.59 mmol, 1 equiv) was stirred in MeOH (2 mL) at RT for 5 min under open air. Afterwards, the appropriate arylboronic acid (0.89 mmol, 1.5 equiv) was added and the reaction mixture was allowed to stir at RT until the completion of reaction. The progress of reaction was monitored by TLC using 20–40% EtOAc/hexane as eluent (ninhydrin stain). After completion, the mixture was filtered through a pad of Celite and washed with CH_2Cl_2, and the CH_2Cl_2 solution was evaporated on a rotary evaporator. The crude product was purified by silica gel column chromatography using 10–50% EtOAc/hexane as eluent to obtain the desired product.

tert-Butyl 2-[(*tert*-Butoxycarbonyl)amino]-4-(*S*-methyl-*N*-phenylsulfonimidoyl)butanoate (4a)

Yield: 223 mg (91%); transparent oil; cc: 40% EtOAc/hexane; product spot identified on TLC using ninhydrin stain; R_f = 0.18.

IR (KBr, film): 3845, 3322, 2941, 2817, 2641, 2320, 2082, 1717, 1610, 1529, 1486, 1233, 1202, 1088, 1047, 853, 744 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 6.9 Hz, 2 H_{arom}), 7.04 (t, *J* = 7.0 Hz, 2 H_{arom}), 6.94 (t, *J* = 7.2 Hz, 1 H_{arom}), 5.26 (s, 1 H, CH), 4.22 (s, 1 H, NH), 3.38–3.16 (m, 2 H, SCH_2), 3.03 (s, 3 H, SCH_3), 2.43–2.40 (m, 1 H, CH_2), 2.20–2.10 (m, 1 H, CH_2), 1.41 (d, *J* = 7.4 Hz, 18 H, 6 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 155.5, 145.1, 145.0, 129.44, 129.42, 123.6, 123.5, 122.4, 83.2, 80.4, 52.8, 52.1, 51.1, 50.9, 39.8, 39.7, 28.4, 28.15, 28.11, 27.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{34}N_2O_5S$: 413.2105; found: 413.2104.

tert-Butyl 2-[(*tert*-Butoxycarbonyl)amino]-4-[*N*-(2,6-dimethoxyphenyl)-*S*-methylsulfonimidoyl]butanoate (4b)

Yield: 219 mg (78%); transparent oil; cc: 40% EtOAc/hexane; product spot identified on TLC using ninhydrin stain; R_f = 0.24.

IR (KBr, film): 3842, 3321, 2976, 2941, 2837, 2641, 2320, 2082, 1717, 1529, 1446, 1271, 1223, 1148, 1087, 853, 766, 744 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.91 (t, *J* = 8.2 Hz, 1 H_{arom}), 6.54 (d, *J* = 8.2 Hz, 2 H_{arom}), 5.42–5.19 (m, 1 H, CH), 4.25 (s, 1 H, NH), 3.81 (s, 6 H, 2 × OCH_3), 3.32–3.22 (m, 2 H, SCH_2), 3.05 (d, *J* = 9.0 Hz, 3 H, SCH_3), 2.45 (d, *J* = 5.1 Hz, 1 H, CH_2), 2.27–2.22 (m, 1 H, CH_2), 1.43 (d, *J* = 8.2 Hz, 18 H, 6 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 154.9, 123.1, 105.2, 105.1, 82.6, 80.1, 56.2, 53.0, 41.7, 29.9, 28.5, 28.4, 28.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{38}N_2O_7S$: 473.2316; found: 473.2315.

tert-Butyl 2-[(*tert*-Butoxycarbonyl)amino]-4-(*N*-mesityl-*S*-methylsulfonimidoyl)butanoate (4c)

Yield: 213 mg (79%); transparent oil; cc: 30% EtOAc/hexane; product spot identified on TLC using ninhydrin stain; R_f = 0.24.

IR (KBr, film): 3845, 3322, 2941, 2817, 2641, 2320, 2082, 1717, 1529, 1446, 1223, 1148, 1047, 853, 744 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.80 (s, 2 H_{arom}), 5.27–5.20 (m, 1 H, CH), 4.24 (s, 1 H, NH), 3.33–3.14 (m, 2 H, SCH_2), 2.89 (s, 3 H, SCH_3), 2.49–2.40 (m, 1 H, CH_2), 2.24 (s, 6 H, 2 × ArCH_3-*o*), 2.20 (s, 3 H, ArCH_3-*p*), 2.17–2.11 (m, 1 H, CH_2), 1.44–1.42 (m, 18 H, 6 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 155.6, 138.1, 133.8, 133.7, 132.5, 129.16, 129.14, 83.1, 52.8, 52.3, 51.9, 40.08, 29.8, 28.4, 28.1, 27.4, 20.8, 19.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{40}N_2O_5S$: 455.2574; found: 455.2576.

tert-Butyl (2*S*)-4-[*N*-(4-Bromophenyl)-*S*-methylsulfonimidoyl]-2-[(*tert*-butoxycarbonyl)amino]butanoate (4d)

Yield: 260 mg (89%); transparent liquid; cc: 40% EtOAc/hexane; product spot identified on TLC using ninhydrin stain; R_f = 0.20.

IR (KBr, film): 3845, 3322, 2981, 2856, 2641, 2320, 2082, 1717, 1529, 1476, 1263, 1201, 1142, 1047, 1004, 853, 744 cm^{-1}.

^{1}H NMR (500 MHz, CDCl3): δ = 7.28 (d, *J* = 7.5 Hz, 2 H_{arom}), 6.91 (d, *J* = 7.7 Hz, 2 H_{arom}), 5.26 (s, 1 H, CH), 4.21 (s, 1 H, NH), 3.33–3.17 (m, 2 H, SCH_2), 3.01 (s, 3 H, SCH_3), 2.40–2.35 (m, 1 H, CH_2), 2.13–2.06 (m, 1 H, CH_2), 1.42–1.40 (m, 18 H, 6 × CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 155.5, 144.4, 144.3, 132.3, 132.2, 125.17, 125.14, 115.0, 83.2, 80.4, 52.6, 51.1, 50.9, 39.8, 39.7, 29.8, 28.4, 28.1, 28.0, 27.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{33}BrN_2O_5S$: 491.1210; found: 419.1204.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1612216.

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