Synthesis M. Muneeswara et al. Paper

Iron-Catalyzed One-Pot *N*-Aroylation of *NH*-Sulfoximines with Methylarenes through Benzylic C–H Bond Oxidation

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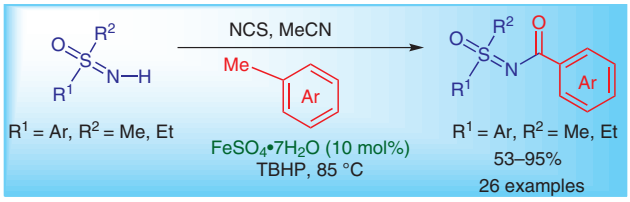

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Abstract An efficient catalytic method has been developed for the synthesis of *N*-aroylated sulfoximines from readily available toluenes (methylarenes) as source of the aroyl coupling partner and *NH*-sulfoximines, employing an environmentally benign iron catalyst. This protocol involves oxidation of benzylic C–H bonds of toluenes to generate aroyl radical intermediates followed by oxidative coupling with *NH*-sulfoximines to form *N*-aroylated sulfoximines in good to excellent yields. The intermediate aroyl radical is successfully trapped with TEMPO to prove the radical pathway of the reaction.

Key words iron, oxidation, amides, cross-coupling, radical reaction

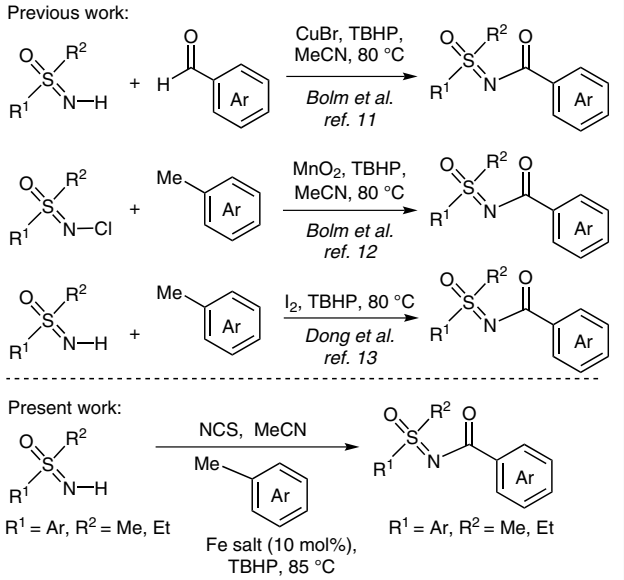
Compounds containing a sulfoximine moiety have attracted significant attention of chemists due to their numerous use in medicinal and agricultural chemistry.[1] *N*-Acylated sulfoximines represent one of the important classes of sulfoximine derivatives, which have found wide application in both biology and synthesis.[2] For instance, recently *N*-acylatesulfoximines were introduced in few important bioactive pseudopeptides to provide unique secondary structures.[3] From the synthetic standpoint, sulfoximines derivatives are being used in asymmetric synthesis as ligands and chiral auxiliaries.[4] Likewise, *N*-acylated sulfoximines are utilized as a directing group for C–H bond activation.[5] These potential applications increased the interest of several research groups to develop new, efficient, and practical synthetic methods for the synthesis of sulfoximines and their derivatives.

Cross coupling reactions that involves direct functionalization of unactivated C–H bonds to form C–C or C–heteroatom bonds have become a very efficient strategy in organic synthesis with high atom and step economy.[6] Over the past few decades, great progress has been made in the area of oxidative coupling of C(sp)–H and C(sp^2)–H bonds for the construction of various C–N bonds.[7] However, for the functionalization of benzylic bonds to form C(sp^2)–N bonds, there are relatively few methods available. Hydrocarbons such as toluenes are the cheapest and most readily available raw materials for the chemical industry. A successful development of cross-coupling of toluenes could lead to various synthetically useful compounds. For example, an oxidative carbon–heteroatom bond forming strategy has been successfully applied to the esterification, cyanation, and amidation of toluenes.[8]

Traditionally, *N*-acylsulfoximines are prepared from sulfoximines and pre-activated coupling partners such as acyl chlorides,[5a,9] aliphatic carboxylic acids,[10] anhydrides,[5d,e] and benzaldehydes.[11] Recently, a MnO_2-mediated aroylation of *N*-chlorosulfoximines employing methylarenes as the source of the aroyl coupling partner was described by Bolm and co-workers (Scheme 1).[12] The reaction failed in the case of methylarenes bearing electron-donating groups at *para* and *ortho* hindered substrates.[12] Very recently, Dong et al.[13a] and Zhao et al.[13b] described a transition-metal-free and an iron-catalyzed aroylation of *NH*-sulfoximines with methylarenes, respectively.

Iron, a nontoxic, readily available, and inexpensive transition metal, has been successfully used as catalyst for benzylic C(sp^3)–H bond cross-coupling with N–H bond.[14] As part of our ongoing effort in developing an iron-catalyzed organic transformations,[15] we recently developed an iron-catalyzed synthesis of amides from toluenes.[16] Inspired by previous results, herein we report a new route for the synthesis of *N*-aroylsulfoximines by iron catalysis using methylarenes as aroyl precursors (Scheme 1).

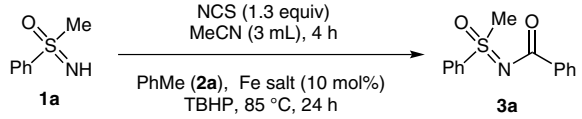
The initial study was carried out by treating *S*-methyl-*S*-phenylsulfoximine (**1a**; 1 equiv) with *N*-chlorosuccinimide (NCS) (1.3 equiv) in acetonitrile at room temperature for 4 hours. The resulting *N*-chlorosulfoximine was treated with



Scheme 1 *N*-Aroylation of sulfoximines

$Fe(OAc)_2$ (10 mol%), toluene (**2a**; 10 equiv), and *tert*-butyl hydroperoxide (TBHP, 10 equiv in decane, 5–6 M) at 85 °C for 24 hours, in one-pot. To our delight, *N*-benzoylsulfoximine **3a** was isolated in 84% yield (Table 1, entry 1). In order to increase the efficiency of the oxidative cross coupling reaction, different parameters like catalysts, reaction temperature, and oxidants were screened. Among the various iron slats examined, $FeSO_4{\cdot}7H_2O$ gave the higher yield of **3a** (entries 2–9). Next, the use of $FeSO_4{\cdot}7H_2O$ and TBHP (8 equiv) led to a maximum yield of 91% at 85 °C in MeCN (entry 10). When the same reaction was carried out with aqueous TBHP, the yield of **3a** was decreased to 45% (entry 11). In this reaction, more benzoic acid (1:2) was isolated compared with the reaction using TBHP in decane (entry 10). This suggests that TBHP in water may facilitate the overoxidation of benzaldehyde to benzoic acid. A sequential increase (90 °C and 100 °C) or decrease (70 °C and 60 °C) of reaction temperatures provided lower yield of **3a**. Other solvents like CH_2Cl_2, DCE, TCE, THF, and 1,4-dioxane were found to be inferior compared to acetonitrile. In the absence of either Fe-catalyst or oxidant, the reaction failed to give the product **3a**. This indicates that the iron catalyst and the oxidant are essential for this reaction. Similarly, the desired product **3a** was not formed in the absence of NCS, which evidences the possible involvement of *N*-chlorosulfoximine in the reaction process (entry 20). When NBS was used instead of NCS, the yield was reduced to 57% (entry 21). Other oxidants such as di-*tert*-butyl peroxide (DTBP) and $PhI(OAc)_2$ failed to yield the product **3a**. Interestingly, 87% of *N*-aroylated product **3a** was isolated when all reagents are added at the same time under optimized conditions (entry 24).

Table 1 Optimization of Reaction Conditions



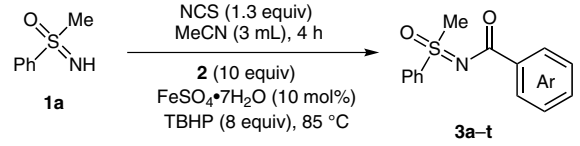
Entry	Fe salt (10 mol%)	**2a** (equiv)	TBHP (equiv)	Yield (%)
1	$Fe(OAc)_2$	10	10	84
2	$FeCl_2$	10	10	80
3	$FeBr_2$	10	10	78
4	$FeSO_4{\cdot}7H_2O$	10	10	90
5	$FeC_2O_4{\cdot}2H_2O$	10	10	81
6	$FeCl_3$	10	10	86
7	$Fe(acac)_3$	10	10	59
8	$FeNO_3{\cdot}9H_2O$	10	10	70
9	$FeSO_4{\cdot}nH_2O$	10	10	73
10	**$FeSO_4{\cdot}7H_2O$**	**10**	**8**	**91**
11	$FeSO_4{\cdot}7H_2O$	10	8	45[a]
12	$FeSO_4{\cdot}7H_2O$	10	6	74
13	$FeSO_4{\cdot}7H_2O$	8	8	70
14	$FeSO_4{\cdot}7H_2O$	10	8	70[b]
15	$FeSO_4{\cdot}7H_2O$	10	8	80[c]
16	$FeSO_4{\cdot}7H_2O$	10	8	45[d]
17	$FeSO_4{\cdot}7H_2O$	10	8	80[e]
18	–	10	8	nd[f]
19	$FeSO_4{\cdot}7H_2O$	10	–	nd
20	$FeSO_4{\cdot}7H_2O$	10	8	nd[g]
21	$FeSO_4{\cdot}7H_2O$	10	8	57[h]
22	$FeSO_4{\cdot}7H_2O$	10	–	nd[i]
23	$FeSO_4{\cdot}7H_2O$	10	–	nd[j]
24	$FeSO_4{\cdot}7H_2O$	10	8	87[k]

[a] Reaction with aq TBHP (70% in H_2O).
[b] Reaction with 5 mol% of Fe salt.
[c] Reaction with 20 mol% of Fe salt.
[d] Reaction at 60 °C.
[e] Reaction at 100 °C.
[f] nd: Not detected.
[g] Reaction without NCS.
[h] Reaction with NBS.
[i] Reaction with DTBP.
[j] Reaction with $PhI(OAc)_2$.
[k] All reagents were added at the same time.

Subsequently, a wide range of methylarenes were examined under the optimized reaction conditions and the results are summarized in Table 2. Halogen-substituted methylarenes at the 3- or 4-position worked notably well and gave the corresponding *N*-aroylsulfoximines in good to excellent yields (76–95%, **3f**–**k**). Methylarenes containing methyl, methoxy, and nitro groups also gave products in good yields (**3b**–**e** and **3o**–**r**). Sterically crowded *ortho*-substituted (methyl or halo groups) methylarenes also successfully gave the corresponding *N*-aroylsulfoximines **3l**–**o** in

good yields. Methylarenes containing two or more methyl groups were selectively monoaroylated to **3o–r** in good yields.[17]

Table 2 Substrate Scope of Methylarenes



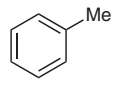
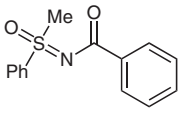
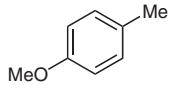
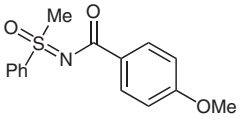
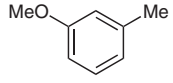
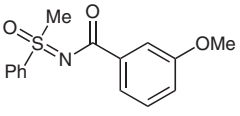
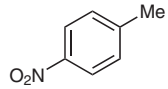
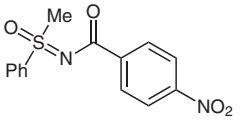
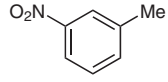
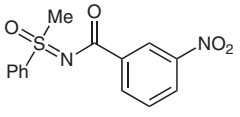
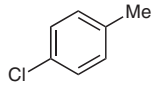
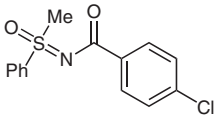
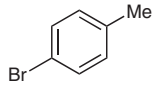
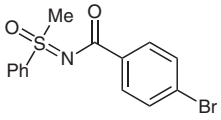
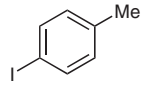
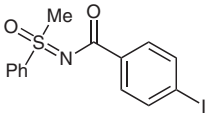
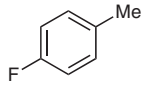
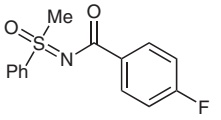
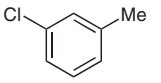
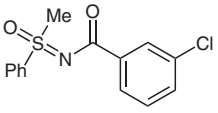
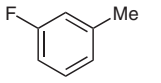
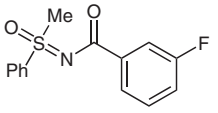
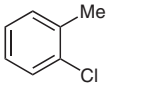
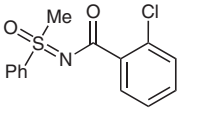
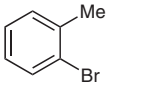
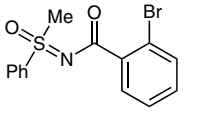
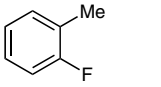
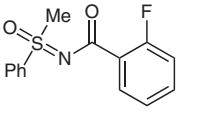
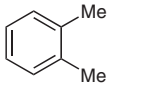
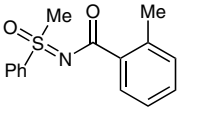
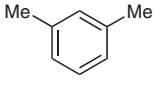
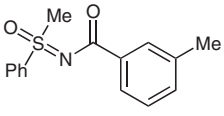
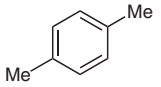
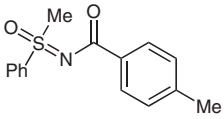
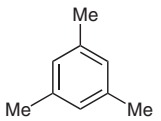
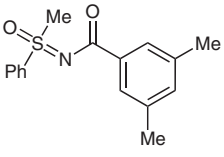
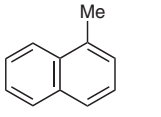
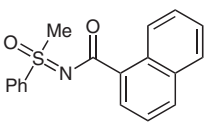
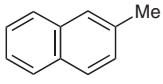
Entry	2	Product 3	Time (h)	Yield (%)
1		**3a** 	24	91
2		**3b** 	18	60
3		**3c** 	24	69
4		**3d** 	36	70
5		**3e** 	24	73
6		**3f** 	24	95
7		**3g** 	24	80
8		**3h** 	24	78
9		**3i** 	24	76

Table 2 (continued)

Entry	2	Product 3	Time (h)	Yield (%)
10		**3j** 	24	80
11		**3k** 	24	80
12		**3l** 	24	64
13		**3m** 	48	62
14		**3n** 	24	53
15		**3o** 	24	61
16		**3p** 	18	76[a]
17		**3q** 	24	85[a]
18		**3r** 	24	63[a]
19		**3s** 	24	66
20		**3t**	24	77

[a] Methylarene (2 mL) was used.

When methylheteroarenes such as methylfuran, methylthiophene and methylpyridine were used as the aroylating reagents under optimized conditions, unfortunately none of them gave the corresponding *N*-aroylsulfoximines. Methylnaphthalenes under the optimized conditions successfully afforded the corresponding products **3s** and **3t** in 66% and 77% yield, respectively.

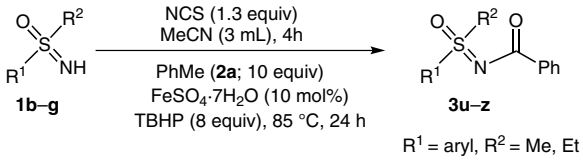
The substrate scope of the sulfoximine moiety was also investigated under the standard reaction conditions with toluene (Table 3). *S*-Methyl-*S*-arylsulfoximines having bromo, nitro, methyl, and methoxy groups **1b**–**f** were aroylated in good yields (69–84%, Table 3, **3u**–**y**). *S*-Ethyl-*S*-phenylsulfoximine also gave corresponding aroylated product **3z** in 63% yield.

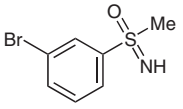
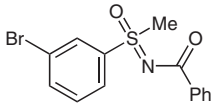
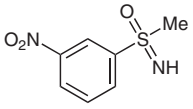
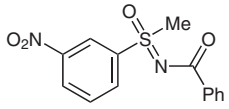
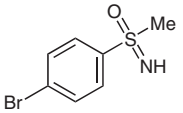
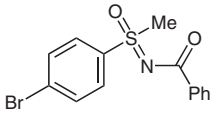
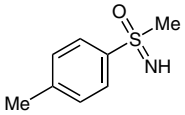
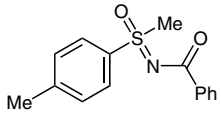
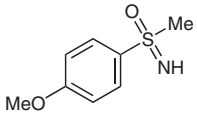
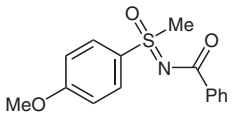
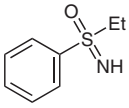
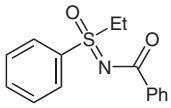
In this one-pot reaction, all three benzylic bonds of the tolyl methyl group are activated by $FeSO_4{\cdot}7H_2O$ catalyst. Initially, two of the benzylic bonds of the tolyl methyl group are converted to C=O group and the third benzylic bond is utilized for the generation of C(sp^2)–N bond.

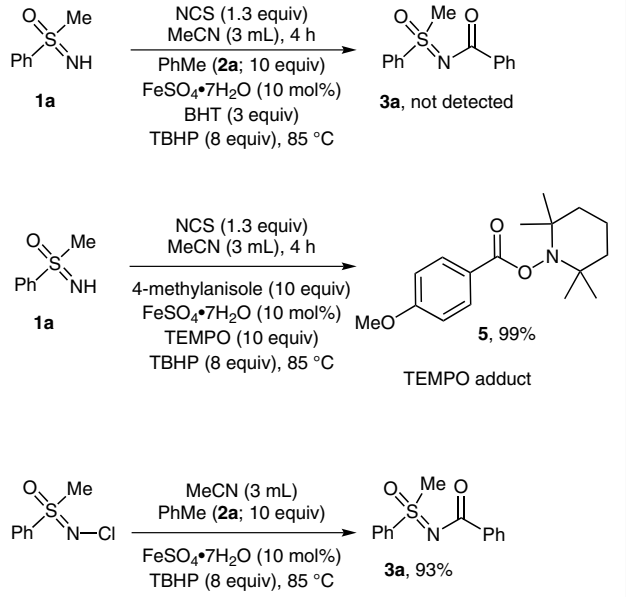
Next, control experiments were conducted to get insights into the reaction mechanism. First, the standard reaction was carried out in the presence of radical-scavenger BHT (3,5-di-*tert*-butyl-4-hydroxytoluene, 3 equiv) and TEMPO (10 equiv). In both reactions, no *N*-aroylated product **3a** was formed, however, aroyl-TEMPO adduct **5** was isolated in 99% yield in the latter reaction (Scheme 2). When the optimization reaction was carried out in the presence of *N*-chlorosulfoximine, instead of sulfoximine and NCS, formation of 93% of *N*-aroylated product **3a** was observed, which evidences the involvement of *N*-chlorosulfoximine in the reaction process.

Based on the above experimental results a plausible mechanism is proposed as shown in Scheme 3. Toluene (**2a**) is likely to be oxidized to benzaldehyde **9** followed by formation of aroyl radical **10** with Fe/TBHP.[16,18] *N*-Chlorosulfoximine **12**, generated from *NH*-sulfoximine by NCS, may generate an amino radical by N–Cl bond cleavage.[19] The re-

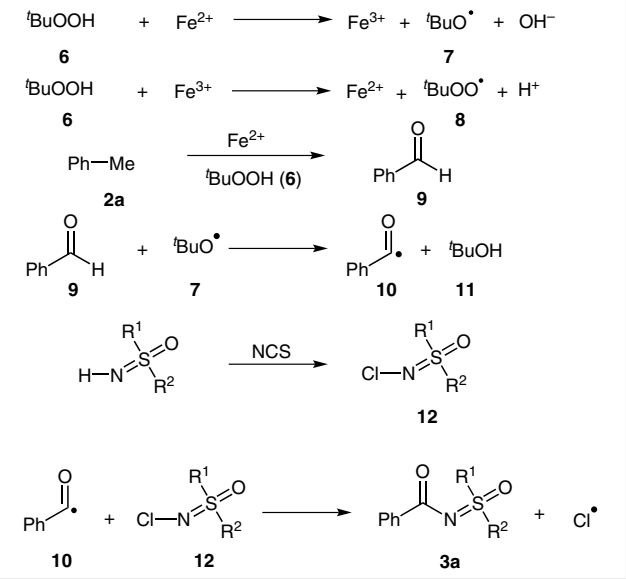
Table 3 Substrate Scope for Sulfoximines



Entry	1	Product 3		Yield (%)
1	**1b**		**3u**		82
2	**1c**		**3v**		69
3	**1d**		**3w**		84
4	**1e**		**3x**		70
5	**1f**		**3y**		77
6	**1g**		**3z**		63



Scheme 2 Control experiments



Scheme 3 Plausible mechanism

action of aroyl radical **10** with the amino radical would give the *N*-aroylated sulfoximine **3a**.[12,13a]

In conclusion, we have developed a one-pot additive- and base-free method for the *N*-aroylation of *NH*-sulfoximines using iron-catalyzed oxidative cross coupling with methylarenes. Electron-rich and sterically hindered methylarenes were successfully converted to the corresponding products. Furthermore, the aroyl radical intermediate was trapped with TEMPO and an aroyl-TEMPO adduct was isolated to understand the radical pathway of the reaction.

All reactions were carried out in reaction tubes under aerobic atmosphere, unless otherwise mentioned. All the solvents and chemicals were purchased from commercial sources and used without further purification, unless otherwise mentioned. Wherever necessary, solvents were dried by standard literature procedures. Reactions were monitored by TLC using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and analyzed by UV fluorescence quenching using appropriate mixture of EtOAc and hexanes as eluent. Silica gel (particle size 100–200 mesh) purchased from SRL India was used for column chromatography using hexanes and EtOAc mixture as eluent. $FeSO_4{\cdot}7H_2O$, and TBHP were purchased from Sigma-Aldrich. Thioanisoles were purchased from TCI and Sigma-Aldrich. Reactions were carried out in temperature-controlled IKA magnetic stirrers. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 or 500 MHz instrument. ^1H NMR spectra were reported relative to Me_4Si (δ = 0.0) or residual $CHCl_3$ (δ = 7.26). ^{13}C NMR were reported relative to $CDCl_3$ (δ = 77.16). FTIR spectra were recorded on a Nicolet 6700 spectrometer and were reported in frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. All sulfoximines were synthesized according to literature procedures.[5]

Sulfoximines 3a–z; General Procedure

S-Methyl-*S*-arylsulfoximine **1** (1 mmol) and *N*-chlorosuccinimide (174 mg, 1.3 mmol) in MeCN (3 mL) were taken in an oven dried reaction tube. The reaction mixture was stirred at r.t. for 4 h. To this mixture were added $FeSO_4{\cdot}7H_2O$ (10 mol%, 28 mg), the corresponding methylarene **2** (10 mmol), and TBHP (5–6 M in decane, 8 mmol). The reaction mixture was stirred at 85 °C in a preheated oil bath and the reaction was monitored by TLC. After completion of the reaction, the solvent was removed by rotary evaporator. The resulting mixture was washed with sat. aq $Na_2S_2O_3$ (10 mL) followed by sat. aq $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography using hexanes/EtOAc as eluent.

N-Benzoyl-*S*-methyl-*S*-phenylsulfoximine (3a)

Yield: 91% (236 mg); white solid; mp 122–124 °C (Lit.[11] mp 122–123 °C); R_f = 0.35 (30% EtOAc in hexanes).

FTIR (KBr): 1630, 1539, 1448, 1309, 1138, 967 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.47 (s, 3 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.50 (t, *J* = 7.4 Hz, 1 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 8.03–8.09 (m, 2 H), 8.14–8.21 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 127.3, 128.1, 129.6, 129.8, 132.3, 133.9, 135.7, 139.2, 174.4.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO_2S$: 260.0741; found: 260.0740.

N-(4-Methoxylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3b)

Yield: 60% (174 mg); white solid; mp 136–138 °C (Lit.[11] mp 138–139 °C); R_f = 0.36 (40% EtOAc in hexanes).

FTIR (KBr): 1619, 1512, 1421, 1309, 1277, 1159, 983 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 3 H), 3.85 (s, 3 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.57–7.64 (m, 2 H), 7.64–7.72 (m, 1 H), 8.02–8.08 (m, 2 H), 8.12 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4, 55.4, 113.2, 127.2, 128.3, 129.6, 131.5, 133.7, 139.3, 162.9, 173.8.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_3SNa$: 312.0670; found: 312.0671.

***N*-(3-Methoxylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3c)**

Yield: 69% (200 mg); white solid; mp 82–84 °C (Lit.[13a] mp 83–85 °C); R_f = 0.33 (30% EtOAc in hexanes).

FTIR (KBr): 1628, 1527, 1445, 1186, 1119, 1092, 983, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 3 H), 3.83 (s, 3 H), 7.05 (dd, *J* = 8.0, 2.4 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.60 (t, *J* = 7.6 Hz, 2 H), 7.65–7.71 (m, 2 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 55.5, 113.8, 118.9, 122.1, 127.3, 129.1, 129.8, 133.9, 137.1, 139.0, 159.5, 174.2.

HRMS: *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{16}NO_3S$: 290.0843; found: 290.0845.

***N*-(4-Nitrobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3d)**

Yield: 70% (213 mg); pale yellow solid; mp 127–129 °C (Lit.[13a] mp 128–130 °C); R_f = 0.30 (40% EtOAc in hexanes).

FTIR (KBr): 1641, 1512, 1421, 1357, 1186, 1122, 918 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.50 (s, 3 H), 7.64 (t, *J* = 7.6 Hz, 2 H), 7.69–7.75 (m, 1 H), 8.03–8.07 (m, 2 H), 8.23 (d, *J* = 8.8 Hz, 2 H), 8.30 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 123.4, 127.2, 130.0, 130.5, 134.3, 138.5, 141.2, 150.2, 172.2.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}N_2O_4S$: 305.0587; found: 305.0591.

***N*-(3-Nitrobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3e)**

Yield: 73% (222 mg); pale yellow solid; mp 107–109 °C (Lit.[13a] mp 108–110 °C); R_f = 0.30 (40% EtOAc in hexanes).

FTIR (KBr): 1635, 1512, 1421, 1298, 1132, 972, 720 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.50 (s, 3 H), 7.59 (t, *J* = 8.0 Hz, 1 H), 7.62–7.67 (m, 2 H), 7.71 (tt, *J* = 7.6, 1.2 Hz, 1 H), 8.03–8.06 (m, 2 H), 8.34 (dq, *J* = 8.4, 1.2 Hz, 1 H), 8.44 (dt, *J* = 7.6, 1.6 Hz, 1 H), 8.97 (t, *J* = 2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.6, 124.6, 126.7, 127.2, 129.3, 130.0, 134.3, 135.2, 137.5, 138.5, 148.3, 171.9.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}N_2O_4SNa$: 327.0415; found: 327.0415.

***N*-(4-Chlorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3f)**

Yield: 95% (279 mg); pale yellow solid; mp 108–110 °C (Lit.[12] mp 108–110 °C); R_f = 0.36 (30% EtOAc in hexanes).

FTIR (KBr): 1631, 1599, 1563, 1399, 1280, 1167, 1137, 1014, 981, 761 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.62 (t, *J* = 8.0 Hz, 2 H), 7.69 (t, *J* = 7.6 Hz, 1 H), 8.01–8.13 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 127.3, 128.4, 129.9, 131.0, 133.9, 134.2, 138.6, 139.0, 173.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}ClNO_2SNa$: 316.0175; found: 316.0176.

***N*-(4-Bromobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3g)**

Yield: 80% (270 mg); white solid; mp 117–119 °C (Lit.[12] mp 119–121 °C); R_f = 0.51 (30% EtOAc in hexanes).

FTIR (KBr): 1619, 1587, 1464, 1298, 1223, 1127, 742 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.51–7.56 (m, 2 H), 7.60–7.65 (m, 1 H), 7.44 (tt, *J* = 7.2, 1.2 Hz, 1 H), 8.00–8.05 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 127.3, 127.3, 129.9, 131.2, 131.4, 134.4, 134.6, 138.9, 173.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}BrNO_2SNa$: 359.9670; found: 359.9674.

***N*-(4-Iodobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3h)**

Yield: 78% (300 mg); pale yellow solid; mp 121–123 °C (Lit.[13a] mp 123–125 °C); R_f = 0.31 (20% EtOAc in hexanes).

FTIR (KBr): 1619, 1582, 1480, 1378, 1138, 1010, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 3 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.69 (t, *J* = 7.6 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 8.03 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 99.9, 127.3, 129.9, 131.2, 134.0, 135.3, 137.4, 139.0, 173.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}INO_2S$: 385.9705; found: 385.9706.

***N*-(4-Fluorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3i)**

Yield: 76% (211 mg); white solid; mp 112–114 °C (Lit.[11] mp 110–112 °C); R_f = 0.42 (30% EtOAc in hexanes).

FTIR (KBr): 1628, 1599, 1526, 1477, 1311, 1148, 1137, 1091, 980 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.06 (t, *J* = 8.8 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.67–7.73 (m, 1 H), 8.02–8.08 (m, 2 H), 8.13–8.21 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 115.1 (*J* = 21.5 Hz), 127.3, 129.8, 132.0, 132.1, 134.0, 139.1, 165.6 (*J* = 250.6 Hz), 173.2.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}FNO_2S$: 278.0644; found: 278.0644.

***N*-(3-Chlorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3j)**

Yield: 80% (235 mg); white solid; mp 108–110 °C (Lit.[11] mp 110–112 °C); R_f = 0.41 (30% EtOAc in hexanes).

FTIR (KBr): 1650, 1568, 1422, 1295, 1146, 1093, 982, 748 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1 H), 7.62 (t, *J* = 7.7 Hz, 2 H), 7.69 (tt, *J* = 7.2, 1.2 Hz, 1 H), 8.01–8.07 (m, 3 H) 8.14 (t, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 127.3, 127.6, 129.5, 129.7, 129.9, 132.2, 134.1, 134.3, 137.6, 138.9, 173.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}ClNO_2SNa$: 316.0715; found: 316.0717.

***N*-(3-Fluorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3k)**

Yield: 80% (222 mg); white solid; mp 80–82 °C (Lit.[13a] mp 80–82 °C); R_f = 0.40 (30% EtOAc in hexanes).

FTIR (KBr): 1627, 1477, 1441, 1287, 1152, 1070, 985 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.19 (td, *J* = 8.0, 2.4 Hz, 1 H), 7.37 (td, *J* = 8.0, 5.6 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 2 H), 7.69 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.79 (dt, *J* = 8.0, 1.2 Hz, 1 H), 7.83 (ddd, *J* = 9.6, 2.8, 1.6 Hz, 1 H), 8.02–8.07 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 116.4 (*J* = 22.4 Hz), 119.2 (*J* = 21.3 Hz), 125.2 (*J* = 3.1 Hz), 127.3, 129.7 (*J* = 7.5 Hz), 129.9, 134.1, 138.2, 138.9, 162.7 (*J* = 224.6 Hz), 173.1.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}FNO_2S$: 278.0644; found: 278.0646.

***N*-(2-Chlorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3l)**

Yield: 64% (188 mg); pale yellow solid; mp 88–90 °C; R_f = 0.30 (30% EtOAc in hexanes).

FTIR (KBr): 1624, 1464, 1427, 1298, 1223, 1138, 742 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 7.29 (ddd, *J* = 14.0, 6.4, 2.0 Hz, 2 H), 7.33 (dd, *J* = 7.2, 1.6 Hz, 1 H), 7.39 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.59–7.69 (m, 3 H), 7.69 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.83 (dd, *J* = 7.2, 1.6 Hz, 1 H), 8.07–8.11 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4, 126.6, 127.4, 129.8, 130.7, 130.9, 131.3, 132.3, 134.1, 136.3, 138.5, 174.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}ClNO_2SNa$: 316.0715; found: 316.0717.

***N*-(2-Bromobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3m)**

Yield: 62% (210 mg); pale yellow solid; mp 83–85 °C; R_f = 0.29 (30% EtOAc in hexanes).

FTIR (KBr): 1638, 1586, 1563, 1460, 1299, 1220, 1044, 979 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.56–7.65 (m, 3 H), 7.66–7.72 (m, 1 H), 7.79 (dd, *J* = 8.0, 2.0 Hz, 1 H), 8.08–8.13 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4, 120.5, 127.2, 127.4, 129.8, 130.7, 131.3, 133.8, 134.2, 138.4, 138.4, 175.1.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}BrNO_2SNa$: 359.9670; found: 359.9670.

***N*-(2-Fluorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3n)**

Yield: 53% (147 mg); white solid; mp 109–111 °C; R_f = 0.29 (30% EtOAc in hexanes).

FTIR (KBr): 1624, 1485, 1459, 1309, 1213, 1100, 977 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 7.09 (t, *J* = 8.4 Hz, 1 H), 7.13–7.19 (m, 1 H), 7.40–7.48 (m, 1 H), 7.65–7.72 (m, 2 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 8.00 (td, *J* = 7.6, 2.0 Hz, 1 H), 8.06–8.11 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.5, 116.8 (*J* = 22.6 Hz), 123.8 (*J* = 3.8 Hz), 124.5 (*J* = 9.4 Hz), 127.4, 129.8, 132.2, 133.4 (*J* = 8.8 Hz), 134.1, 138.7, 161.8 (*J* = 256.1 Hz), 172.3 (*J* = 3.6 Hz).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}FNO_2S$: 278.0644; found: 278.0646.

***N*-(2-Methylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3o)**

Yield: 61% (167 mg); white solid; mp 88–90 °C (Lit.[13a] mp 89–91 °C); R_f = 0.36 (30% EtOAc in hexanes).

FTIR (KBr): 1630, 1539, 1448, 1261, 1226, 1095, 972 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H), 3.42 (s, 3 H), 7.21 (dd, *J* = 12.8, 7.6 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.60 (t, *J* = 8.4 Hz, 2 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 8.02–8.11 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 44.5, 125.4, 127.2, 129.7, 130.6, 130.9, 131.5, 133.7, 135.3, 139.2, 139.3, 176.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_2SNa$: 296.0721; found: 296.0721.

***N*-(3-Methylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3p)**

Yield: 76% (208 mg); white solid; mp 57–59 °C (Lit.[13a] mp 57–59 °C); R_f = 0.31 (30% EtOAc in hexanes).

FTIR (KBr): 1624, 1578, 1288, 1121, 1085, 978, 753 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.38 (s, 3 H), 7.22–7.24 (m, 2 H), 7.52 (t, *J* = 8.0 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.90–7.88 (m, 2 H), 7.93–8.02 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 44.4, 126.6, 127.2, 128.0, 129.7, 130.0, 133.0, 133.8, 135.6, 137.7, 139.1, 174.5.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NO_2S$: 274.0894; found: 274.0896.

***N*-(4-Methylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3q)**

Yield: 85% (232 mg); white solid; mp 150–152 °C (Lit.[13a] mp 148–150 °C); R_f = 0.43 (30% EtOAc in hexanes).

FTIR (KBr): 1614, 1581, 1312, 1281, 1134, 1093, 980, 782 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.46 (s, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.57–7.64 (m, 2 H), 7.67 (tt, *J* = 7.2, 1.2 Hz, 1 H), 8.03–8.09 (m, 2 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 44.6, 127.4, 129.0, 129.8, 129.9, 133.2, 134.0, 139.5, 142.9, 174.5.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NO_2S$: 274.0894; found: 274.0896.

***N*-(3,5-Dimethylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3r)**

Yield: 63% (181 mg); white solid; mp 114–116 °C (Lit.[13a] mp 114–116 °C); R_f = 0.40 (30% EtOAc in hexanes).

FTIR (KBr): 1624, 1582, 1448, 1314, 1213 1127, 967 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 3.45 (s, 3 H), 7.14 (s, 1 H), 7.57–7.64 (m, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.77 (s, *J* = 7.7 Hz, 2 H), 8.02–8.07 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 44.3, 127.2, 129.4, 129.7, 133.7, 133.9, 135.5, 137.6, 139.2, 174.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}NO_2S$: 288.1051; found: 288.1051.

***N*-(1-Naphthoyl)-*S*-methyl-*S*-phenylsulfoximine (3s)**

Yield: 66% (204 mg); pale yellow oil; R_f = 0.45 (30% EtOAc in hexanes).

FTIR (film): 1620, 1556, 1456, 1360, 1240, 1180, 1060, 960, 760 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.44–7.50 (m, 2 H), 7.50–7.55 (m, 1 H), 7.55–7.60 (m, 2 H), 7.61–7.68 (m, 1 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 7.95 (d, *J* = 8.5 Hz, 1 H), 8.10 (d, *J* = 7.0 Hz, 2 H), 8.35 (d, *J* = 7.3 Hz, 1 H), 9.05 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.5, 124.6, 125.9, 126.4, 127.1, 127.2, 128.3, 129.8, 129.8, 131.3, 132.4, 132.9, 133.8, 133.9, 133.9, 138.9, 176.6.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{15}NO_2SNa$: 332.0721; found: 332.0720.

***N*-(2-Naphthoyl)-*S*-methyl-*S*-phenylsulfoximine (3t)**

Yield: 77% (238 mg); white solid; mp 120–122 °C (Lit.[13a] mp 120–122 °C); R_f = 0.49 (30% EtOAc in hexanes).

FTIR (KBr): 1627, 1560, 1440, 1320, 1260, 1120, 980, 762 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.51 (s, 3 H), 7.53 (dt, *J* = 7.0, 15.0 Hz, 2 H), 7.63 (t, *J* = 7.2 Hz, 2 H), 7.70 (t, *J* = 7.0 Hz, 1 H), 7.82–7.791 (m, 2 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 2 H), 8.20 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.5, 125.7, 126.4, 127.3, 127.8, 127.8, 127.9, 129.5, 129.8, 130.7, 132.7, 133.0, 133.9, 135.5, 139.2, 174.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{15}NO_2SNa$: 332.0721; found: 332.0755.

***N*-Benzoyl-*S*-methyl-*S*-(3-bromophenyl)sulfoximine (3u)**

Yield: 82% (277 mg); pale yellow solid; mp 146–148 °C (Lit.[12] mp 147–149 °C); R_f = 0.49 (30% EtOAc in hexanes).

FTIR (KBr): 1627, 1506, 1456, 1399, 1317, 1064, 1017, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 7.38–7.56 (m, 4 H), 7.80 (dq, *J* = 8.0, 0.8 Hz, 1 H), 7.98 (dq, *J* = 8.0, 0.8 Hz, 1 H), 8.13–8.21 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 123.8, 125.9, 128.2, 129.6, 130.3, 131.3, 132.5, 135.4, 137.1, 141.2, 174.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}BrNO_2SNa$: 359.9670; found: 359.9670.

***N*-Benzoyl-*S*-methyl-*S*-(3-nitrophenyl)sulfoximine (3v)**

Yield: 69% (210 mg); pale yellow solid; mp 142–145 °C; R_f = 0.31 (40% EtOAc in hexanes).

FTIR (KBr): 1641, 1581, 1541, 1345, 1070, 974, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.50 (s, 3 H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.50–7.55 (m, 1 H), 7.83 (t, *J* = 8.0 Hz, 1 H), 8.09–8.15 (m, 2 H), 8.34–8.39 (m, 1 H), 8.50 (dq, *J* = 6.4, 1.0 Hz, 1 H), 8.85 (t, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.2, 122.8, 128.3, 128.4, 129.6, 131.3, 132.7, 132.9, 134.9, 141.6, 148.8, 174.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd $C_{14}H_{12}N_2O_4SNa$: 327.0415; found: 327.0413.

***N*-Benzoyl-*S*-methyl-*S*-(4-bromophenyl)sulfoximine (3w)**

Yield: 84% (284 mg); pale yellow solid; mp 146–148 °C (Lit.[12] mp 147–149 °C); R_f = 0.49 (30% EtOAc in hexanes).

FTIR (KBr): 1627, 1621, 1452, 1310, 1224, 1117, 1020, 967 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.44 (s, 3 H), 7.41 (t, *J* = 8.0 Hz, 2 H), 7.48–7.55 (m, 1 H), 7.69–7.78 (m, 2 H), 7.86–7.94 (m, 2 H), 8.10–8.17 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 128.2, 128.9, 129.3, 132.5, 133.1, 135.4, 138.2, 174.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}BrNO_2SNa$: 359.9670; found: 359.9674.

***N*-Benzoyl-*S*-methyl-*S*-(4-methylphenyl)sulfoximine (3x)**

Yield: 70% (191 mg); white solid; mp 93–95 °C (Lit.[13a] mp 92–94 °C); R_f = 0.38 (30% EtOAc in hexanes).

FTIR (KBr): 1629, 1539, 1448, 1226, 1127, 1086, 967, 787 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.45, (s, 3 H), 3.45 (s, 3 H), 7.36–7.44 (m, 4 H), 7.50 (tt, *J* = 1.2, 7.2 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 2 H), 8.16 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 44.6, 127.3, 128.1, 129.5, 130.4, 132.2, 135.8, 136.0, 145.0, 174.4.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_2SNa$: 296.0721; found: 296.0720.

***N*-Benzoyl-*S*-methyl-*S*-(4-methoxylphenyl)sulfoximine (3y)**

Yield: 77% (223 mg); white solid; mp 82–84 °C (Lit.[13a] mp 83–85 °C); R_f = 0.34 (40% EtOAc in hexanes).

FTIR (KBr): 1629, 1512, 1492, 1280, 1210, 1028, 980 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 3 H), 3.88 (s, 3 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 7.40 (t, *J* = 7.6 Hz, 2 H), 7.50 (tt, *J* = 1.2, 8.8 Hz, 1 H), 7.97 (d, *J* = 9.2 Hz, 2 H), 8.17 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.8, 55.9, 115.0, 128.1, 129.5, 129.5, 130.0, 132.2, 135.8, 164.0, 174.4.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_3SNa$: 312.0670; found: 312.0670.

***N*-Benzoyl-*S*-ethyl-*S*-phenylsulfoximine (3z)**

Yield: 63% (173 mg); white solid; mp 118–120 °C (Lit.[13a] mp 118–120 °C); R_f = 0.35 (30% EtOAc in hexanes).

FTIR (KBr): 1570, 1441, 1320, 1260, 1120, 1080, 930, 730 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.2 Hz, 3 H), 3.60 (q, *J* = 7.2 Hz, 2 H), 7.38–7.44 (m, 2 H), 7.50 (tt, *J* = 1.2, 8.8 Hz, 1 H), 7.56–7.63 (m, 2 H), 7.67 (tt, *J* = 1.2, 8.8 Hz, 1 H), 7.95–8.04 (m, 2 H), 8.14–8.22 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.4, 50.7 128.1, 128.1, 129.5, 129.7, 132.2, 133.8, 135.7, 136.5, 174.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_2SNa$: 296.0721; found: 296.0720.

2,2,6,6-Tetramethylpiperidin-1-yl 4-Methoxybenzoate (5)[15]

Yield: 99% (290 mg); yellow oil; R_f = 0.52 (30% EtOAc in hexanes).

FTIR (film): 1167, 2931, 3414 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.09 (s, 6 H), 1.24 (s, 6 H), 1.37–1.47 (m, 1 H), 1.49–1.60 (m, 2 H), 2.60–1.82 (m, 3 H), 3.84 (s, 3 H), 6.90–6.94 (m, 2 H), 7.90–8.03 (m, *J* = 9.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.1, 20.9, 32.0, 39.1, 55.6, 60.4, 113.8, 122.0, 131.7, 163.4, 166.2.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{26}NO_3$: 292.1913; found: 292.1913.

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Supporting Information

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